

DISSERTATION

ZUR ERLANGUNG DES GRADES

„DOCTOR RERUM NATURALIUM“ (DR. RER. NAT.)

IM PROMOTIONSFACH CHEMIE

---

**Copolymerization of Dienes:**

**From Mechanistic Insights towards Material**

**Properties of Multiblock Copolymers**

---

vorgelegt von

**Ramona Denise Barent**

geboren am 21.10.1992 in Speyer

Mainz 2023

JOHANNES GUTENBERG  
UNIVERSITÄT MAINZ



Max Planck Graduate Center  
mit der Johannes Gutenberg-Universität

am Fachbereich 09 für Chemie, Pharmazie und Geowissenschaften der

Johannes Gutenberg-Universität Mainz





This thesis was carried out from May 2019 to January 2023 in the research group of Professor Dr. Holger Frey at the Department of Chemistry, Johannes Gutenberg-University, Mainz.

Reviewer 1: Prof. Dr. Holger Frey

Reviewer 2: [REDACTED]

Date of Oral Examination: 22.03.2023

*Referring to §11 of the third section of the Doctoral Degree Regulations (26.04.2009), I hereby declare that I wrote the dissertation submitted without any unauthorized external assistance and used only sources acknowledged in the work. All textual passages which are appropriated verbatim or paraphrased from published and unpublished texts as well as all information obtained from oral sources are duly indicated and listed in accordance with bibliographical rules. In carrying out this research, I complied with the rules of standard scientific practice as formulated in the statutes of Johannes Gutenberg University Mainz to insure standard scientific practice.*



**FÜR MEINE FAMILIE**

“Climb mountains not so the world can see you, but so you can see the world.”

*David McCullough Jr.*

## Danksagungen

Das Gelingen dieser Doktorarbeit haben in den letzten Jahren zahlreiche Menschen durch ihr Mitwirken und ihre Unterstützung ermöglicht, bei denen ich mich von Herzen bedanken möchte.

An erster Stelle gilt besonderer Dank meinem Doktorvater, **Prof. Dr. Holger Frey**, für die Möglichkeit, die vorliegende Dissertation unter seiner Betreuung anfertigen zu dürfen. Durch seine vielseitigen Interessen und Kontakte ermöglichte er diverse Kooperationsprojekte, die ich mit Freuden verfolgte und umsetzte. Ebenso bedanke ich mich für das Vertrauen in theoretischere Projekte und deren Förderung, bei denen ich mich frei verwirklichen konnte. Besonders bedanke ich mich für seine Offenheit und Unterstützung in der letzten Phase der Promotion.

Der Graduiertenschule **Max Planck Graduate Center** (MPGC) möchte ich für die finanzielle Unterstützung sowie die Ermöglichung zahlreicher Fortbildungskurse und Konferenzen bedanken, welche mich nicht nur fachlich, sondern auch persönlich vorangebracht haben. In diesem Zusammenhang möchte ich mich bei [REDACTED] für die Betreuung im Rahmen des MPGC und die Anregung von Kooperationen mit seiner Forschungsgruppe bedanken.

Bei [REDACTED] möchte ich mich für die zahlreichen fachlichen Gespräche und inspirierende Anstöße bedanken. Sein fundamentales Wissen über statistische Copolymerisationen hat mein Verständnis der untersuchten Systeme maßgeblich vorangetrieben.

Die meisten Kapitel dieser Arbeit wären ohne Kooperationspartner nicht möglich gewesen. Ich danke allen für die enge und angenehme Zusammenarbeit. Dank der kritisch-konstruktiven Diskussionen konnte ich wertvolle Einblicke in viele weitere Gebiete erlangen und gemeinsam interessante interdisziplinäre Fragestellungen untersuchen.

[REDACTED] danke ich für seine unermüdliche Untersuchung zum Phasenverhalten der Copolymere. Ohne seine Expertise wäre das Verständnis der Festkörpereigenschaften nicht möglich gewesen. [REDACTED] danke ich für die Einweisung in Zugdehnungsexperimente und seine wertvollen Ratschläge. Großer Dank gilt ebenfalls [REDACTED], die durch rheologische Untersuchungen weitere Einblicke zu dem Temperatureinfluss auf Festkörperstrukturen lieferte.

[REDACTED] möchte ich für die Einführung in das Gebiet gekuppelter Sternarchitekturen danken. Der interessante Abstecher in die Welt nicht-linearer Strukturen eröffnete neue Einsichten in das Erholungsverhalten nach plastischer Verformung.

Spezieller Dank gilt [REDACTED] für die fruchtbare Zusammenarbeit bei der Untersuchung konzentrierter Polymerlösungen. Sein Interesse und seine Motivation, sich mit dem unüblichen System auseinanderzusetzen, haben viele Kapitel diese Arbeit unverkennbar aufgewertet.

Bei [REDACTED], [REDACTED] und [REDACTED] möchte ich mich für die spannende industrierelevante Fragestellung bedanken. In der angenehmen Zusammenarbeit konnte ich wertvolle Einblicke in Forschungs- und Entwicklungsarbeiten eines Unternehmens gewinnen und die produktiven Meetings haben mir interessante Aspekte offenbart.

■■■■■ gilt großer Dank für das Herzstück der Untersuchung verdünnter Polymerlösungen. Sein tatkräftiges Engagement und die anregenden Diskussionen zusammen mit ■■■■■ und ■■■■■ haben diese Arbeit immens bereichert.

Besonderer Dank gilt ■■■■■, durch dessen Fachkenntnisse im Bereich Kernspinresonanz es möglich war, NMR-Copolymerisationsexperimente durchzuführen. Seine Unterstützung und die fachlich wertvollen Gespräche haben mein Verständnis bedeutend geprägt. Weiterhin möchte ich herzlich ■■■■■ des High-Performance-Computing-Teams für seine Geduld und große Hilfsbereitschaft bei der Einführung in die Nutzung des Hochleistungsrechners danken.

Darüber hinaus richtet sich ein besonderer Dank an ■■■■■, ■■■■■, ■■■■■ und ■■■■■, deren Bachelorarbeit beziehungsweise Forschungsmodul ich betreuen durfte. Die Zusammenarbeit mit ihnen hat mir außerordentlich viel Freude bereitet.

Weiterhin danke ich allen ehemaligen sowie aktuellen Mitgliedern des Arbeitskreises. Egal ob im Alltag oder bei unseren jährlichen Hüttenseminaren, Seewochenenden, Ausflügen oder Mittwochabend-Runden, ich hatte stets eine unvergessliche Zeit und schätze die Erinnerungen und daraus entstandenen Freundschaften.

An dieser Stelle möchte ich mich besonders bei ■■■■■ und ■■■■■ bedanken, die mich speziell während meiner Masterarbeit und zu Beginn meiner Promotion mit Rat und Tat unterstützt haben. Ohne sie wäre diese Arbeit nicht möglich gewesen.

Ganz besonderer Dank gilt ebenfalls meinen „Boxnachbarn“ ■■■■■, ■■■■■, ■■■■■ und ■■■■■ für einen stets kurzweiligen Laboralltag. Dank ihnen habe ich mich immer auf einen neuen Arbeitstag gefreut.

Bei ■■■■■, ■■■■■, ■■■■■, ■■■■■ und ■■■■■ möchte ich mich für die tatkräftige Unterstützung im Labor bedanken, insbesondere für die Auftragsmessungen und die Übernahme aller organisatorischen Aufgaben, die im Rahmen des Arbeitskreis-Alltags anfallen. Dank eines so eingespielten Teams funktionieren alle Abläufe reibungslos, weshalb ich mich für die großen, vor allem aber auch für die kleinen Dinge bedanken möchte, von denen wir uns vermutlich nur über einen kleinen Bruchteil im Klaren sind.

Abschließend möchte ich das Wort noch an meine Freunde und Familie richten, die mich während des Studiums begleitet haben. Spezieller Dank gilt ■■■■■ und ■■■■■, die mir immer zugehört, mich aufgebaut, geerdet, abgelenkt oder fokussiert haben. Zuletzt danke ich ■■■■■ für ihre grenzenlose Unterstützung und Rückhalt in jeglicher Hinsicht. Es war nie eine Frage, welche Möglichkeiten sich mir bieten, sondern was ich daraus mache.

## Collaborations

Some chapters were supplemented by contributions by colleagues and scientific collaborators.

Large parts of **Chapter 1** “*Rational Design of Tapered Multiblock Copolymers for Thermoplastic Elastomers*” comply with Chapter 1 of the doctoral thesis of [REDACTED], the first author of this review [REDACTED] was involved eminently reviewing the theoretical background of statistical copolymerizations addressed in the subsections “kinetics of anionic copolymerization”, “*in-situ* monitoring techniques”, “determination of reactivity ratios”, and “copolymerization ‘*in silico*’ - Kinetic Monte Carlo simulation”. Ramona Barent wrote the subsections “commercial application” thematizing compounding, hydrogenation, and selected applications, and “tuning the comonomer gradient profile by the use of modifiers”. In addition, the subsections “choice of monomers”, “microdomain morphologies”, “tapered copolymer blocks – adjusting the phase behavior”, “non-linear chain topologies”, and “kinetics of the anionic copolymerization” were extended by Ramona Barent. Together with [REDACTED] and Prof. Dr. Holger Frey, Ramona Barent was primarily involved in the writing process at review- and editing stage.

[REDACTED] performed and interpreted the small-angle x-ray scattering experiments of **Chapter 3** “*Manipulating the Softness of TPEs by Introducing Flexible End Blocks to Multiblock Copolymers with a Defined or Tapered Interface*”. [REDACTED] characterized selected polymer systems by isochronal rheological measurements. Ramona Barent was responsible for the synthetic parts, the mechanical investigation and writing of the original draft and visualization of the obtained data. All authors were involved in the writing process at review stage.

[REDACTED] performed the mechanical investigation of the linear triblock, linear pentablock and star-shaped multiblock architectures in **Chapter 4** “*Controlling Recovery Properties by the Chain Connectivity Comparing Linear and Star-Shaped Multiblock Copolymers*”. He further synthesized the linear triblock and star-shaped multiblock copolymers, whereas Ramona Barent synthesized the linear pentablock copolymers. Ramona Barent wrote the original draft, while all authors contributed to the writing process at review stage.

[REDACTED] contributed to **Chapter 6** “*Unraveling Different Aggregate Structures in Concentrated Polymer Solutions by Fluorescence Correlation Spectroscopy*” measuring FCS and co-writing the FCS-related parts of the introduction and discussion. In the course of his bachelor thesis, [REDACTED] implemented and optimized the labeling strategy. [REDACTED] was involved in the dynamic light scattering experiments as part of his research module. Ramona Barent was responsible for the polymer synthesis and the transfer of the labeling strategy to the presented multiblocks. Furthermore, Ramona Barent wrote the original draft and visualized the data.

The industrial project with [REDACTED] presented in **Chapter 7** “*Shear-Induced Disassembly of Transient Associative Polymer Networks*” was conceptualized and administered by Prof. Dr. Holger Frey, [REDACTED], and [REDACTED]. Ramona Barent was responsible for the polymer synthesis and the dynamic viscosity measurements, whereas







# Contents

---

|                                 |    |
|---------------------------------|----|
| Motivation and Objectives ..... | 1  |
| Abstract .....                  | 9  |
| Kurzfassung .....               | 14 |
| Graphical Abstract .....        | 20 |

## Chapters:

|            |                                                                                                                                                                                                |     |
|------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Chapter 1. | <i>Introduction to Multiblock Copolymers via Living Anionic Polymerization: Rational Design of Tapered Multiblock Copolymers for Thermoplastic Elastomers .....</i>                            | 24  |
| Chapter 2. | <i>Application Engineering of Soft Multiblock Copolymers: Approaching Performance Requirements for PVC-free Blood Bags .....</i>                                                               | 78  |
| Chapter 3. | <i>Linear (IS)<sub>n</sub>I Multiblock Copolymers: Manipulating the Softness of TPEs by Introducing Flexible End Blocks to Multiblock Copolymers with a Defined or Tapered Interface .....</i> | 97  |
| Chapter 4. | <i>(SIS)<sub>x</sub> Multiblock Copolymers: Controlling Recovery Properties by the Chain Connectivity Comparing Linear and Star-Shaped Multiblock Copolymers .....</i>                         | 140 |
| Chapter 5. | <i>Implementation of Multiblock Copolymers in Solution: Next Generation Viscosity Modifiers .....</i>                                                                                          | 159 |
| Chapter 6. | <i>Fluorescence Labeling of Multiblock Copolymers: Unraveling Different Aggregate Structures in Concentrated Polymer Solutions by Fluorescence Correlation Spectroscopy .....</i>              | 188 |
| Chapter 7. | <i>Viscosity of Concentrated Polymer Solutions: Shear-Induced Disassembly of Transient Associative Polymer Networks .....</i>                                                                  | 227 |
| Chapter 8. | <i>Dilute Solution Properties of Multiblock Copolymers: Conformation Analysis of Sequential and Tapered Multiblock Copolymers in Non-Selective Solvents .....</i>                              | 250 |
| Chapter 9. | <i>Geometric Requirements for Living Anionic Polymerization: Polymerization of Rotationally Constrained 1,3-Dienes .....</i>                                                                   | 276 |

## Appendix:

|                            |                                                                                                                                     |     |
|----------------------------|-------------------------------------------------------------------------------------------------------------------------------------|-----|
| Chapter A1.                | Tapered Multiblock Star Copolymers: Synthesis, Selective Hydrogenation, and Properties .....                                        | 318 |
| Chapter A2.                | In Situ Kinetics Reveal the Influence of Solvents and Monomer Structure on the Anionic Ring-Opening Copolymerization of Epoxides .. | 354 |
| Curriculum Vitae .....     |                                                                                                                                     | 370 |
| List of Publications ..... |                                                                                                                                     | 373 |

## Motivation and Objectives

The self-organization of soft matter is one key paradigm connecting polymer and material science. It dictates essential properties such as mechanics not only in bulk but also in solution, giving access to fascinating classes of materials. Block copolymers are a prime example of soft matter capable of self-assembling into ordered structures.<sup>[1]</sup> A prerequisite for the formation of microphase separated structures in bulk or micellar aggregates in selective solvents is the linkage between chemically dissimilar blocks.<sup>[2]</sup> This quite simple concept renders sheer endless possibilities to customize polymers for vast application fields.

Since the earliest report on “Living Polymers” by Michael Szwarc in 1956,<sup>[3]</sup> the living anionic polymerization, which proceeds without transfer or termination reactions, has been exploited to realize a variety of macromolecular architectures.<sup>[4]</sup> By adjusting the number of blocks, their composition or block profile, and the manner they are linked (e.g., linear or star-shaped architectures), the combination of solely two comonomers offers enormous opportunities to tune the affiliated properties. Along with the high compositional homogeneity, anionically synthesized polymers have not only attracted significant economic interest but are especially appealing to answer fundamental scientific questions correlating structural characteristics with the resulting properties.

Therefore, the purpose of this thesis is to elaborate on the material properties of tailor-made multiblock copolymers based on the two most prominent monomers for living anionic polymerization, isoprene and styrene, against the background of specified scopes of application. The objectives thereof can be divided into the characteristics in bulk and in solution.

### ***Bulk Characteristics***

The excellent elastomeric properties of thermoplastic elastomers are premised on the physical crosslinking of individual vitrified domains, i.e., polystyrene (PS), across the interjacent rubbery phase, i.e., polyisoprene (PI). This is achieved by the localization of at least two PS blocks of one block copolymer chain in different domains formed upon phase separation. Conclusively, a PS-*b*-PI-*b*-PS (short “SIS”) triblock sequence is minimally required for this so-called domain bridging and hence tough materials.<sup>[5]</sup>

With the extension towards multiblock sequences the fraction of bridged chain conformations is increased.<sup>[6]</sup> At the same time the reduced conformational entropy enhances miscibility, this way lowering the order-disorder temperature.<sup>[7]</sup> This offers the potential of further improving the material properties and processability, provided that the structural order mandatory for physical crosslinking is preserved.<sup>[8]</sup> In this manner, extraordinarily tough and resilient materials were realized with implementing (IS)<sub>n</sub> and S(IS)<sub>n</sub> structures.<sup>[6,8,9]</sup> (IS)<sub>n</sub>I type structures have hitherto only been addressed in high impact materials.<sup>[10]</sup> Yet, these structures exhibiting two polyisoprene end blocks offer the possibility to design materials with shorter individual PI blocks compared to a structure with an even block number at constant comonomer ratio,

whose untethered flexible end blocks further restrict the chain conformation of the polystyrene mid blocks by forcing both block junctions to be located at the domain interface.

From the lack of general knowledge about the effect of two soft end blocks in multiblock architectures and a systematic comparison between multiblock copolymers with either a defined or a gradual block profile, the following questions addressed in Chapter 3 of this thesis arise:

*“Can we design a rather soft material of exceptional resilience premised on the combination of a high bridging ratio with flexible end blocks serving as an internal plasticizer? How can mechanical properties and processability be best balanced in dependence of the block profile, block number and molar mass?”*

Apart from this fundamental question, the interest in this topic is intensified by the search for alternative materials to plasticized poly(vinyl chloride) (PVC) used to produce blood bags. PVC is very attractive due to its low price. However, significant amounts of plasticizer have to be added to turn the otherwise brittle and rigid polymer into a flexible but tough material of sufficient impact strength.<sup>[11]</sup> These plasticizers tend to migrate into the blood during storage, which is a double-edged sword.<sup>[12]</sup> While its incorporation into the interior and the erythrocyte membrane is beneficial for cell viability and thus storage time,<sup>[13]</sup> major health concerns related to the commonly used phthalates demand safe alternatives especially for vulnerable patients. Although to date thermoplastic elastomers (TPEs) are comparably expensive, their non-toxicity, sterilizability, and suitability for chemical as well as mechanical recycling render TPEs a promising safe alternative with the potential to contribute to a circular economy.<sup>[14]</sup>

Nonetheless, thermoplastic elastomers face the problem of permanent sets upon large deformations.<sup>[15]</sup> This is explained by the chain pull-out of polystyrene blocks from their domain, in this way overcoming the physical crosslinking by bridged chain conformations.<sup>[16]</sup> A promising strategy to alleviate plastic deformation is the combination of chemical and physical crosslinks, thereby joining the best of both worlds. Multiarm star copolymers maintain the important advantage of facile processing and moreover reprocessability over the elastomeric thermosets, while the covalent core junction results in an improved energy distribution, providing higher strength and minimized irrecoverable set.<sup>[17]</sup> Another advantage of star architectures in comparison to linear analogues is their significantly lower viscosity at similar molar mass, permitting an even more facile processing.<sup>[18]</sup>

The effect of star-architectures has been studied extensively, however, in most cases, the number of arms is not well-defined.<sup>[19]</sup> A work on defined, fully hydrogenated (SI)<sub>6</sub> star-shaped block copolymer architectures covalently linked at the rubbery end revealed faster recovery and also a less permanent set compared to its linear hydrogenated (SI)<sub>2</sub> triblock counterparts, while their toughness was similar.<sup>[20]</sup> Beyond this, (SI)<sub>x</sub> star copolymers with multiple arms were reported to feature higher strengths compared to their linear analogues.<sup>[21]</sup>

Furthermore, (SI<sub>n</sub>)<sub>x</sub> architectures with multiple vitrifying domains per arm, which were linked at the polystyrene end and thus exhibited a glassy core and flexible end blocks, have been reported.<sup>[22]</sup> The materials' properties were governed by viscous flow at moderate temperatures, which was ascribed to the polyisoprene end blocks and the high number of blocks resulting in poor phase segregation.

Concerning star-architectures with an inner polystyrene core, star-shaped (SIS)<sub>x</sub> structures with a glassy core block have also been addressed, comparing their mechanical properties to (SI)<sub>x</sub> architectures with a rubbery core block.<sup>[23]</sup> The vitrification of the covalently linked core block resulted in a significant increase in the tensile shear strength. This is explained by the increased bridging fraction due to the higher amount of vitrifying end blocks in star architectures combined with an impeded backfolding to the domain formed by the dense core.<sup>[24]</sup> However, these structures only featured an average number of arms due to the use of an undefined coupling agent.

These studies motivated us to investigate the mechanical as well as the recovery properties of defined (SIS)<sub>x</sub> structures with a glassy core junction. Comparing the linear (SIS)<sub>1</sub> triblock architectures to the linear (SIS)<sub>2</sub> pentablock and the star-shaped (SIS)<sub>4</sub> multiblock architectures, both principles are accounted for by extending the research question tackled in Chapter 4:

*“How does the domain connectivity passing over from a linear multiblock with two vitrifying end blocks to a star-shaped multiblock architecture with glassy core and end blocks affect the material’s ultimate properties and the recovery?”*

### **Solution Characteristics**

The behavior of block copolymers in solution is primarily governed by the polymer concentration and the block selectivity of the solvent. This was beautifully demonstrated by viscometric investigations for both diluted and concentrated solutions of polystyrene-polybutadiene-polystyrene triblock copolymers in solvents of varying selectivity.<sup>[25]</sup> While in dilute solution, the contribution of the polymer to the viscosity increase is most pronounced in thermodynamically good solvents for both constituent blocks, the viscosity of concentrated solutions exhibits a minimum in the same range. This is explained by the ability of block copolymers to self-assemble into aggregate structures in sufficiently selective solvents.<sup>[26]</sup> In dilute solution, where such phenomena are not present, the viscosity is a function of the polymer coil’s hydrodynamic volume. Since the polymer coil is most expanded if the polymer-solvent interactions are maximized, dilute solutions in non-selective solvents feature the highest viscosity.<sup>[27]</sup> In contrast, the collapse of the solvophobic sequences of block copolymers in selective solvents provokes intermolecular aggregation above a critical concentration, greatly increasing the apparent molar mass and hence the viscosity of the polymer solution.<sup>[28]</sup>

Although the association behavior of diblock and triblock copolymers is widely explored, to date only theoretical approaches have focused on complex polymer architectures with multiple solvophobic blocks per chain<sup>[29]</sup> or tapered block copolymers with a sharp, albeit gradual transition between the comonomers.<sup>[30,31]</sup> Both peculiarities provide special characteristics to the self-assembled structures in selective solvents. Multiblock sequences allow for the formation of larger aggregates with several solvophobic cores, which are expected to be more shear stable due to several junctions per polymer chain. Tapered block-like copolymers further offer the potential to introduce a fine-tuned thermoresponsive behavior due to subtle changes in solubility of the diffuse interface between the solvophilic and solvophobic blocks, which was already reported for amphiphilic gradient copolymers.<sup>[31–33]</sup>

Therefore, implementing multiblock structures with either a sharp or a gradual block profile in selective solvents leads to the following questions, to which Chapter 6 and 7 are dedicated:

*“Which associated structures can be accessed by the concentration-dependent self-organization of multiblock copolymers and how do they operate under shear or at varying temperatures?”*

In this context, Chapter 6 aims at the investigation of the self-organization and diffusion processes at varying concentrations, which is realized by dynamic light scattering (DLS) and fluorescence correlation spectroscopy (FCS). The latter permits to study even highly diluted and concentrated polymer solutions due to its unique single-molecule sensitivity.<sup>[34]</sup> Chapter 7 employs viscometric experiments to study the viscosity at varying shear forces and temperatures, this way detecting probable non-Newtonian behavior.<sup>[35]</sup>

In addition to the fundamental relevance, these topics were further motivated by the potential of multiblock structures for viscosity modification in lubricating oils. Since the viscosity of liquids declines upon temperature increase, polymer additives are employed in order to counteract this adverse effect and maintain proper lubrication.<sup>[36]</sup> However, to date every polymer class implemented features its distinct benefits and drawbacks, thereby confining the performance as viscosity modifier.<sup>[36,37]</sup> Poly(alkyl methacrylates) (PMAs) are the prime example for viscosity modifiers with an unprecedented viscosity-temperature relationship, which is due to their thickening mechanism by coil expansion.<sup>[38,39]</sup> However, there is still room for improvement in terms of thickening efficiency and shear stability.<sup>[40,41]</sup> In contrast, hydrogenated styrene-diene copolymers (HSDs) capable of aggregate formation excel in these tribological parameters, whereas their viscosity improvement with temperature cannot compete with PMAs.<sup>[38,40,42]</sup> By the purpose of unifying both the coil expansion and the association mechanism, HSD multiblock architectures with a gradual block profile represent a promising polymer class. They profit, on one hand, from the easy alignment within the shear flow by partial disassembly and, on the other hand, from a potential coil expansion with increasing temperature due to the enhanced solubility of the diffuse interface between the solvophilic and solvophobic blocks.<sup>[31,32]</sup>

In spite of the continuous attention for such multiblock polymer systems, surprisingly little is known about their dilute solution properties. Yet, understanding the gross conformation of these polymers in solution is the foundation to design multiblock architectures for applications in solution.

Concerning copolymers based on isoprene and styrene in dilute solution, few works reported on their intrinsic viscosity in both good solvents, e.g., toluene, and theta-solvents for polystyrene like cyclohexane and methylisobutyl ketone. At the theta-temperature the long-range forces between the styrene repeating units, which cause a contraction, are balanced by the interaction with the solvent which lead to coil expansion, thus resulting in unperturbed Gaussian dimensions of the polystyrene blocks. SI diblock copolymers were found to behave like unperturbed Gaussian chains in good solvents as well as theta-solvents.<sup>[43]</sup> Extension of the diblock structure towards a SIS triblock copolymer revealed only minor deviations, indicating an almost negligible effect of the heterocontacts on the coil dimension.<sup>[44]</sup> Another study examined the influence of the comonomer ratio on the SI diblock copolymer coil dimension and reported a maximum coil expansion for comonomer ratios close to unity.<sup>[27]</sup> Within this study, a sequential diblock copolymer was further compared to its tapered counterpart,

revealing a similar behavior. However, both polymers differed in their molar mass and comonomer ratio. Furthermore, (IS)<sub>n</sub>I multiblock copolymers ( $\# = (2n+1) = 3, 5, 7 \text{ \& } 9$  at  $M \approx 16 \text{ \& } 160 \text{ kg}\cdot\text{mol}^{-1}$ ) were investigated in toluene, evidencing an increase in the intrinsic viscosity with decreasing block lengths, i.e., increasing block number.<sup>[45]</sup> This chain expansion was accounted to the avoidance of heterocontacts due to the incompatibility of the two constituent blocks.

These experimental results emphasize the complexity of block copolymer solutions, especially upon introducing multiple blocks per polymer chain. This traces back to the balance between, on one hand, minimizing the interface between the constituent blocks and, on the other hand, the interactions between the respective polymer blocks and the solvent.

However, the polymer systems investigated so far exhibited rather narrow molar mass ranges. Furthermore, to date no systematic comparison of tapered and sequential block copolymers was conducted. Due to the uncertain structure-property relationship of such unimers in dilute solution, we ask the fundamental question of Chapter 8:

*“Which impact makes the block profile of multiblock copolymers on the conformation in non-selective solvents or more tangibly spoken on the rigidity of the polymer?”*

### **Mechanistic Insights**

The last chapter of this thesis aims at gaining deeper insight into the polymerization mechanism of the lithium-initiated living carbanionic polymerization mechanism of 1,3-dienes in non-polar media.

Manifold reaction parameters dictate the stereochemistry of polydienes, among them the counterion, which influences the aggregation strength with the living chain end, the polarity of the solvent, and the presence of polar modifiers, which profoundly alters the aggregation itself and thereby the polymerization mechanism.<sup>[46]</sup> The commonly accepted hypothesis for the reaction mechanism in non-polar media comprises an isomerization between the *cisoid* and *transoid* geometry of the ultimate and hence propagating repeating unit,<sup>[47]</sup> whose rate is competitive with the time scale of the monomer addition.<sup>[48]</sup> The monomer addition itself is assumed to proceed via a six-membered coordination of the propagating chain end and the incoming monomer.<sup>[49]</sup> In this way, a high 1,4-stereoselectivity of polydienes is achieved, which is of utmost significance due to the inherent low glass transition temperature enabling a wide temperature range application window.<sup>[50]</sup>

Since the six-membered coordination in the transition state is believed to involve both double bonds of the 1,3-diene, the fundamental question of Chapter 9 arose:

*“Does a prescribed transoid geometry prevent the coordination of the propagating chain end by both double bonds and consequently impede polymerizability?”*

## References

- [1] V. Abetz, *Block Copolymers I*, Springer, Berlin Heidelberg, **2005**.
- [2] a) I. W. Hamley, *The physics of block copolymers*, Oxford University Press, Oxford, **2003**; b) L. Leibler, *Macromolecules* **1980**, *13*, 1602.
- [3] M. Szwarc, *Nature* **1956**, *178*, 1168.
- [4] a) N. Hadjichristidis, H. Iatrou, M. Pitsikalis, J. Mays, *Prog. Polym. Sci.* **2006**, *31*, 1068; b) K. Ntetsikas, V. Ladelta, S. Bhaumik, N. Hadjichristidis, *ACS Polym. Au* **2022**.
- [5] a) K. Karatasos, S. H. Anastasiadis, T. Pakula, H. Watanabe, *Macromolecules* **2000**, *33*, 523; b) K. Rasmussen, E. M. Kober, T. Lookman, A. Saxena, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 104; c) H. Watanabe, Y. Matsumiya, T. Sawada, T. Iwamoto, *Macromolecules* **2007**, *40*, 6885; d) S. S. Tallury, R. J. Spontak, M. A. Pasquinelli, *J. Chem. Phys.* **2014**, *141*, 244911.
- [6] M. O. Tuhin, J. J. Ryan, J. D. Sadler, Z. Han, B. Lee, S. D. Smith, M. A. Pasquinelli, R. J. Spontak, *Macromolecules* **2018**, *51*, 5173.
- [7] a) S.-M. Mai, W. Mingvanish, S. C. Turner, C. Chaibundit, J. P. A. Fairclough, F. Heatley, M. W. Matsen, A. J. Ryan, C. Booth, *Macromolecules* **2000**, *33*, 5124; b) J. T. Koberstein, T. P. Russell, D. J. Walsh, L. Pottick, *Macromolecules* **1990**, *23*, 877; c) M. D. Gehlsen, K. Almdal, F. S. Bates, *Macromolecules* **1992**, *25*, 939; d) A. M. Mayes, M. O. de La Cruz, *J. Chem. Phys.* **1991**, *95*, 4670; e) A. M. Mayes, M. La Olvera de Cruz, *J. Chem. Phys.* **1989**, *91*, 7228; f) H. Nakazawa, T. Ohta, *Macromolecules* **1993**, *26*, 5503.
- [8] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, *51*, 10246.
- [9] R. J. Spontak, S. D. Smith, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 947.
- [10] a) P. Georgopoulos, U. A. Handge, C. Abetz, V. Abetz, *Polymer* **2016**, *104*, 279; b) V. Hirschberg, L. Faust, D. Rodrigue, M. Wilhelm, *Macromolecules* **2020**, *53*, 5572; c) L. Qiao, C. Leibig, S. F. Hahn, K. I. Winey, *Ind. Eng. Chem. Res.* **2006**, *45*, 5598.
- [11] a) K. Sojiphan, A. Iverson, S. Kim, *Materials Selection Analysis: Bag for Viable Blood Storage*, Department of Materials Science and Engineering, Northwestern University, **2004**; b) V. R. Sastri, *Plastics in medical devices. Properties, requirements, and applications*, Elsevier/William Andrew, Amsterdam, **2014**.
- [12] R. J. Jaeger, R. J. Rubin, *N. Engl. J. Med.* **1972**, *287*, 1114.
- [13] C. Mueller-Eckhardt (Ed.), *Transfusionsmedizin*, Springer Berlin Heidelberg, Berlin, Heidelberg, **1996**.
- [14] Ineos Styrolution Group, "Resins for the Healthcare Industry", can be found under [https://www.ineos-styrolution.com/INTERSHOP/static/WFS/Styrolution-Portal-Site/-/Styrolution-Portal/en\\_US/News%20and%20media/download/INEOS\\_Styrolution\\_Healthcare\\_Brochure.pdf](https://www.ineos-styrolution.com/INTERSHOP/static/WFS/Styrolution-Portal-Site/-/Styrolution-Portal/en_US/News%20and%20media/download/INEOS_Styrolution_Healthcare_Brochure.pdf).
- [15] K. K. Indukuri, A. J. Lesser, *Polymer* **2005**, *46*, 7218.
- [16] T. S. Chow in *Adv. Polym. Sci.*, Springer-Verlag, Berlin/Heidelberg, **1992**, pp. 149–190.

- [17] a) L.-K. Bi, L. J. Fetters, *Macromolecules* **1976**, 9, 732; b) D. B. Alward, D. J. Kinning, E. L. Thomas, L. J. Fetters, *Macromolecules* **1986**, 19, 215.
- [18] J. M. Ren, T. G. McKenzie, Q. Fu, E. H. H. Wong, J. Xu, Z. An, S. Shanmugam, T. P. Davis, C. Boyer, G. G. Qiao, *Chem. Rev. (Washington, DC, U. S.)* **2016**, 116, 6743.
- [19] J. S. Shim, J. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, 37, 815.
- [20] A. B. Burns, R. A. Register, *Macromolecules* **2016**, 49, 9521.
- [21] a) L.-K. Bi, L. J. Fetters, *Macromolecules* **1976**, 9, 732; b) V. R. Raju, E. v. Menezes, G. Marin, W. W. Graessley, L. J. Fetters, *Macromolecules* **1981**, 14, 1668.
- [22] C. Wang, Y. Wu, Y. Zhu, H. Ma, M. Zhang, G. Liu, J. He, P. Ni, *Polym. Chem.* **2022**, 13, 3938.
- [23] G. C. Meyer, J. M. Widmaier, *Polym. Eng. Sci.* **1977**, 17, 803.
- [24] R. K. W. Spencer, M. W. Matsen, *Macromolecules* **2017**, 50, 1681.
- [25] D. R. Paul, J. E. St. Lawrence, J. H. Troell, *Polym. Eng. Sci.* **1970**, 10, 70.
- [26] a) C. Lai, W. B. Russel, R. A. Register, *Macromolecules* **2002**, 35, 841; b) J. S. Higgins, J. V. Dawkins, G. G. Maghami, S. A. Shakir, *Polymer* **1986**, 27, 931; c) J. S. Higgins, S. Blake, P. E. Tomlins, S. B. Ross-Murphy, E. Staples, J. Penfold, J. V. Dawkins, *Polymer* **1988**, 29, 1968; d) G. Riess, *Prog. Polym. Sci.* **2003**, 28, 1107.
- [27] D. N. Cramond, J. R. Urwin, *Eur. Polym. J.* **1969**, 5, 35.
- [28] a) Č. Koňák, G. Fleischer, Z. Tuzar, R. Bansil, *J. Polym. Sci., Part B: Polym. Phys.* **2000**, 38, 1312; b) W. Mandema, C. A. Emeis, H. Zeldenrust, *Makromol. Chem.* **1979**, 180, 2163.
- [29] a) J. Zhang, Z.-Y. Lu, Z.-Y. Sun, *Soft Matter* **2013**, 9, 1947; b) V. Hugouvieux, M. A. V. Axelos, M. Kolb, *Macromolecules* **2009**, 42, 392; c) S. Woloszczuk, M. Banaszak, P. Knychala, K. Lewandowski, M. Radosz, *J. Non-Cryst. Solids* **2008**, 354, 4138; d) C. Zhong, D. Liu, *Macromol. Theory Simul.* **2007**, 16, 141; e) V. Hugouvieux, M. A. V. Axelos, M. Kolb, *Soft Matter* **2011**, 7, 2580; f) M. E. Gindy, R. K. Prud'homme, A. Z. Panagiotopoulos, *J. Chem. Phys.* **2008**, 128, 164906.
- [30] a) C. Zheng, *Soft Matter* **2019**, 15, 5357; b) J. Kuldová, P. Košovan, Z. Limpouchová, K. Procházka, *Macromol. Theory Simul.* **2013**, 22, 61; c) G. Pandav, V. Pryamitsyn, K. C. Gallow, Y.-L. Loo, J. Genzer, V. Ganesan, *Soft Matter* **2012**, 8, 6471.
- [31] V. S. Kravchenko, I. I. Potemkin, *J. Phys. Chem. B* **2016**, 120, 12211.
- [32] C. Zheng, H. Huang, T. He, *Macromol. Rapid Commun.* **2014**, 35, 309.
- [33] S. K. Filippov, B. Verbraeken, P. V. Konarev, D. I. Svergun, B. Angelov, N. S. Vishnevetskaya, C. M. Papadakis, S. Rogers, A. Radulescu, T. Courtin et al., *J. Phys. Chem. Lett.* **2017**, 8, 3800.
- [34] K. Koynov, H.-J. Butt, *Curr. Opin. Colloid Interface Sci.* **2012**, 17, 377.
- [35] C. Chassenieux, T. Nicolai, L. Benyahia, *Curr. Opin. Colloid Interface Sci.* **2011**, 16, 18.
- [36] L. R. Rudnick, *Lubricant Additives. Chemistry and Applications, Third Edition*, CRC Press, Portland, **2017**.
- [37] A. Martini, U. S. Ramasamy, M. Len, *Tribol. Lett.* **2018**, 66, 1.



- [38] C. Mary, D. Philippon, L. Lafarge, D. Laurent, F. Rondelez, S. Bair, P. Vergne, *Tribol. Lett.* **2013**, 52, 357.
- [39] M. J. Covitch, K. J. Trickett, *Adv. Chem. Eng. Sci.* **2015**, 05, 134.
- [40] P. Bezot, C. Hesse-Bezot, D. Faure, J. C. Calvez, *Lubr. Sci.* **2000**, 12, 301.
- [41] P. Panwar, E. Schweissinger, S. Maier, S. Hilf, S. Sirak, A. Martini, *J. Mol. Liq.* **2022**, 359, 119215.
- [42] M. J. Covitch in *SAE Tech. Pap. Ser.*, SAE International, **1998**.
- [43] J. Prud'Homme, J. Roovers, S. Bywater, *Eur. Polym. J.* **1972**, 8, 901.
- [44] a) N. Ho-duc, J. Prud'Homme, *Int. J. Polym. Mater.* **1976**, 4, 303; b) J. P. Plante, N. Ho-Duc, J. Prud'Homme, *Eur. Polym. J.* **1973**, 9, 77.
- [45] S. Schlick, M. Levy, *J. Phys. Chem.* **1960**, 64, 883.
- [46] a) R. P. Quirk, *Anionic Polymerization. Principles and Practical Applications*, Taylor and Francis, Boca Raton, **1996**; b) A. H. E. Müller, K. Matyjaszewski, *Controlled and living polymerizations. Methods and materials*, Wiley-VCH, Weinheim, **2009**.
- [47] W. Gebert, J. Hinz, H. Sinn, *Makromol. Chem.* **1971**, 144, 97.
- [48] D. J. Worsfold, S. Bywater, *Macromolecules* **1978**, 11, 582.
- [49] S. Bywater in *Adv. Polym. Sci.*, 4/1 (Eds.: J. D. Ferry, W. Kern, G. Natta, C. G. Overberger, G. V. Schulz, A. J. Staverman, H. A. Stuart), Springer Berlin Heidelberg, Berlin, Heidelberg, **1965**, pp. 66–110.
- [50] a) M. Steube, T. Johann, R. D. Barent, A. H. Müller, H. Frey, *Prog. Polym. Sci.* **2022**, 124, 101488; b) W. Wang, W. Lu, A. Goodwin, H. Wang, P. Yin, N.-G. Kang, K. Hong, J. W. Mays, *Prog. Polym. Sci.* **2019**, 95, 1.

## Abstract

With the groundbreaking work of Hermann Staudinger in 1920, polymer science has evolved tremendously for more than 100 years into manifold directions, impacting countless parts of life. Naming only a few disciplines, polymers find an omnipresent application in the automotive and the construction sector. Their insulating or semiconducting properties are pivotal for electric and electronic devices, whereas membrane technologies rely on their separation capability, and both the medical and the agricultural sector benefit from advanced polymer structures for controlled drug release. Yet, macromolecules played a crucial role long before they were recognized, studied in depth and specialized for targeted applications. For instance, natural rubber has been commercialized for almost the past two centuries, with Charles Goodyear's and Thomas Hancock's vulcanization process providing the basis for stable elastomeric materials. The introduction of synthetic thermoplastic elastomers (TPEs) in the 20<sup>th</sup> century, possessing the processability of thermoplastics and the elasticity of vulcanized rubber, and progress in understanding the chemical nature and the resulting material properties allows for envisioning versatile characteristics. With the living anionic polymerization technique at hand, which is the method of choice for the synthesis of complex but well-defined polymer architectures, new challenges designing materials with tailored physical properties can be met.

The first part of this thesis aspires to elucidate the influence of an (IS)<sub>n</sub>I multiblock architecture on the materials' properties in bulk, whereas the second part evaluates their solution characteristics. At the end of this work a fundamental framework for the living anionic polymerizability in non-polar media is outlined.

**Chapter 1** gives a general introduction to the versatile toolbox of living anionic polymerization against the background of their use as thermoplastic elastomers (TPEs). After a brief outline of the historical background of elastomers and current application fields of TPEs, this review focuses on synthetic approaches tailoring the polymers' and in turn the materials' properties. In particular, inherent mechanical properties are discussed with respect to the phase segregation strength and the resulting microdomain morphologies. The highlighted synthetic strategies focus on lithium initiated living anionic (co)polymerizations of different styrenic and 1,3-diene monomers in hydrocarbons, further emphasizing the influence of modifiers on the block profile in statistical copolymers. In this regard, not only the block profile, but also the influence of the block sequence, the block number, and the polymer chain architecture are elaborated. Furthermore, the benefit of *in situ* monitoring techniques to determine kinetic parameters is demonstrated and expanded on kinetic Monte Carlo simulations, which allow for the calculation of reaction times, greatly facilitating the workflow of multiblock syntheses.

**Chapter 2** reviews the use of plasticized poly(vinyl chloride) for medical devices. In the first part health concerns related to the commonly used plasticizer are discussed within the framework of human exposure and its metabolism. The second and third part evaluate potential solutions by the introduction of different plasticizers and by the replacement of PVC by alternative polymer materials, respectively. For the latter, a project funded by the European Commission addressing the implementation of polyolefins for medical bags and the use of styrenic thermoplastic elastomers for healthcare applications are considered in greater detail.

**Chapter 3** highlights the structural and mechanical investigation of polyisoprene-polystyrene multiblock copolymers with two polyisoprene end blocks. These structures are of interest due to the potential internal plasticizer effect of the flexible end blocks, probably rendering a soft but resilient material. Temperature-dependent small-angle x-ray scattering experiments were implemented to investigate the phase separated morphologies of both sequential and tapered  $(IS)_nI$  multiblock copolymers covering a wide range of molar masses and block numbers. A strong decrease in the segregation strength and hence of the order-disorder temperature was proven, comparing sequential block copolymers with a defined transition between the adjacent blocks with tapered block-like copolymers with a sharp, but gradual comonomer transition in each polyisoprene-polystyrene diblock sequence. This is caused by the reduced enthalpic incompatibility in tapered structures. While the sequential multiblock copolymers exhibited well-ordered lamellar morphologies, the tapered counterparts showed weakly-ordered perforated layers. The viscoelastic responses measured by tensile tests evidenced superior resilience for the sequential structures, while the tapered structures revealed a higher softness and flexibility. The concomitant decrease of the block size by increasing the block number at a given overall molar mass is accompanied by an increased domain bridging, but at the same time a weakened microphase separation. Due to this trade-off, the higher molar mass tapered pentablocks and sequential heptablocks were found to best balance these opposite effects, resulting in a significant mechanical toughness. Interestingly, polymers with the same molar mass per block exhibited comparable domain spacings and hence softness, while the ultimate deformability was found to increase with the extension by a diblock sequence due to an enhanced domain bridging. Comparison with a literature-known analogous structure with two polystyrene end blocks revealed an easier deformability of the structure with two polyisoprene end blocks reasoned in a smaller domain size.

**Chapter 4** further elaborates the mechanical properties of polyisoprene-polystyrene multiblock copolymers with different architectures in terms of chain connectivity. This fundamental research is intriguing due to the potential to minimize the issue of permanent sets upon large deformation while preserving the advantage of easily processable and reprocessable materials. Uniaxial tensile tests as well as recovery measurements were performed comparing linear tapered SIS triblock copolymers with linear  $(SIS)_2$  pentablock and star-shaped  $(SIS)_4$  multiblock copolymers featuring vitrifying core and end blocks. The advanced architectures were synthesized by an “arm-first” approach coupling the  $(SIS)$  arms. For small molar masses per arm, the star-shaped multiblock architectures showed superior ultimate stress and strain at break reflected in a higher toughness, which can be ascribed to their higher bridging fraction. For higher molar masses, the ultimate mechanical properties of the linear pentablock copolymers and the star-shaped structures approached each other reaching a plateau value, showing that at this point the covalent linkage of the star architecture does not provide further resilience. Yet, they still outperformed the simple triblock structure, further emphasizing the importance of large fractions of bridged chain conformations. For polymers with the same overall molar mass, the star-shaped multiblock copolymers could not compete with the linear pentablock copolymers due to an inferior phase segregation and hence facilitated chain pull-out. For three counterparts of equal molar mass per arm, which showed decent phase segregation and comparable ultimate properties, the cyclic strain experiments evidenced striking differences in their recovery behavior. While the star-shaped  $(SIS)_4$  multiblock copolymer showed unprecedented final recovery after 5 minutes of rest, they

exhibited poor initial recovery during receding. In contrast, the linear structures feature superior rapid recovery but smaller final recoveries after resting. These phenomena prove the higher chain flexibility of the linear architectures being responsible for fast restoring, while the even stress distribution in star-shaped architectures with a covalent core junction generates improved shape memory. However, at high stress levels all specimens experienced a permanent set due to substantial restructuring, resulting in converging restoring properties.

**Chapter 5** examines the three most decisive tribological parameters dictating the performance of viscosity modifiers in lubricating oils relating to not only commonly implemented, but also novel polymer classes. Moving metal parts have to be lubricated in order to prevent friction. However, lubricating fluids face a rapid viscosity decrease upon increasing temperature. Therefore, viscosity modifiers are added to attenuate the adverse effects of asperity contact. Yet, optimum performance in all of the three key metrics, i.e., a beneficial viscosity-temperature relationship, thickening efficiency, and shear stability has not been achieved so far. Since these tribological parameters are complexly intercorrelated, their balancing is challenging, which is the reason for the demand for novel lubricant additives. The influence of key polymer characteristics such as molar mass, dispersity, chain composition, and architecture on the hydrodynamic volume and by this on the tribological parameters are accentuated. Furthermore, the chemical nature of the commonly implemented polymer classes comprising poly(alkyl methacrylates), olefinic copolymers, and hydrogenated styrene-diene copolymers is reviewed with respect to their polymerization mechanism and the inherent thickening mechanisms for viscosity improvement. The latter include the coil expansion mechanism prominent in poly(alkyl methacrylate) formulations and association phenomena featured by hydrogenated styrene-diene copolymers. Beyond this, advanced structures aiming at exceeding the current performance limits are discussed. Here, blending approaches and new polymer classes like poly(2-oxazolines) and poly(2-oxazines), but also sophisticated architectures like brush-like, comb-like or linear (tapered) multiblock copolymer structures are emphasized. This promising combination of several benefits gives food for further investigations.

**Chapter 6** addresses the self-organization of multiblock copolymers with both a defined and a gradual block profile in the polyisoprene-selective solvent heptane. Conclusions on the aggregate structures are drawn based on the diffusion behavior at varying concentrations. For this purpose, dilute and concentrated polymer solutions are examined by dynamic light scattering using a cross-correlation approach, which allows to study diffusion processes even in the presence of multiple scattering events. Diverging diffusion coefficients for the triblock and multiblock copolymers at a polymer concentration above 1 wt% proved the formation of non-ergodic systems, i.e., polymer networks, in case of the structures with several solvophobic polystyrene blocks. Complementary fluorescence correlation spectroscopy measurements permitted insights into the self-diffusion of unimers through these polymer networks. These processes were found to be most restricted in networks of sequential multiblock copolymers, which is the consequence of a denser network due to a higher bridging fraction in combination with larger unimer dimensions. The unimer dimensions themselves were studied in highly diluted polymer solutions, where no aggregation phenomena are present. Furthermore, micellar aggregates and their fraction increased going from dilute solutions to higher concentrations, finally adapting the discussed transient polymer networks. In order to enable

fluorescence correlation spectroscopy investigations, a novel post-polymerization protocol for fluorescent dye attachment was established, which stands out by only a marginal alteration in the chemical nature of the labeled polymer.

**Chapter 7** emphasizes the concentration-dependent viscosity-temperature relationship of the (non)-hydrogenated tapered multiblock copolymers in the polyisoprene-selective solvents squalane and a highly isoparaffinic hydrocarbon lubricating oil against the background of the self-assembled structures discussed in Chapter 6. Combining temperature- and frequency-dependent dynamic viscosity measurements with temperature-dependent kinematic viscosity measurements at 40 °C and 100 °C, a clear correlation between the self-organized polymer aggregate structure and the performance as viscosity modifier could be established. At comparably low polymer concentrations, an enhanced viscosity-temperature relationship with increasing overall molar mass, block number, and isoprene content was identified. As an explanation, the formation of loose aggregates with several polystyrene cores and hence extended hydrodynamic volumes in case of multiblock architectures was deduced. Yet at high concentrations, the structures with the shortest individual solvophobic polystyrene blocks faced a deterioration in the investigated tribological key parameters, i.e., the viscosity-temperature relationship and the thickening efficiency. This is explained by the formation of large transient networks, which are more prone to partial disassembly upon shearing. This effect is further intensified by the migration of solvent molecules into the aggregate's cores, which is most pronounced for short polystyrene blocks. The resulting weakened van-der-Waals interactions promote chain pull-out and by this partial disassembly. Comparison of the investigated styrene-diene multiblock copolymers to a commercialized comb-like poly(alkyl methacrylate) displayed a superior performance of the presented structures at low polymer treat rates. This demonstrates the enormous potential of tapered multiblock architectures as advanced viscosity modifiers.

**Chapter 8** aims at understanding the structure-property relationships of multiblock copolymers with a defined or a gradual, albeit sharp block profile in dilute non-selective solution. For this purpose, series of sequential and tapered multiblock copolymers (IS)<sub>n</sub>I with molar masses ranging from 40–400 kg·mol<sup>-1</sup> and block numbers of 3–13 were comprehensively characterized by complementary approaches. Subsequently, dilute solutions in toluene were systematically investigated, implementing classical scaling relationships between the hydrodynamic characteristics derived from analytical ultracentrifugation, intrinsic viscosity, and related experiments. Both rotational and translational diffusion experiments showed subtle differences in the polymer coil dimension and hence rigidity for polymer series with equal block number. For these homologous polymer series, a more rigid and hence expanded chain conformation for the sequential structures was deducible compared to their tapered analogues. Interestingly, the polymer series with different molar masses and block number, whose polymers featured equal degrees of polymerization per polystyrene block, did not comply with the classical scaling relationships. This demonstrates the influence of the block number on the solution properties even in non-selective solvents.

**Chapter 9** studies the polymerizability of rotationally constrained 1,3-dienes with a fixed *cisoid* or *transoid* geometry of the double bonds. Particularly, the reactivity in living anionic polymerization approaches in non-polar media is examined, whose mechanism is proposed to

proceed via a coordinative mechanism. Theoretical simulation approaches of two new 1,3-diene monomers with a rigid, prescribed *cisoid* or *transoid* geometry in cyclohexane as a typical non-polar solvent are combined with synthetic and kinetic studies. Experimental observations correlated with the predicted reactivities and simulated reaction pathways, which showed that a *cisoid* geometry with in-plane double bonds is mandatory for propagation. Indeed, the *cisoid* diene was homo- as well as copolymerizable with isoprene, whereas the *transoid* diene lacked reactivity. The required ring distortion in case of the cyclic *cisoid* diene resulted in higher simulated activation barriers for the propagation step in comparison to the addition of the unrestricted common monomer isoprene. This was experimentally confirmed by real-time  $^1\text{H}$  NMR spectroscopic kinetic investigations, which evinced a gradient formation in statistical copolymerization experiments of the *cisoid* diene with isoprene, whose steepness became flattened upon temperature increase. Additionally, thermal characterization of the statistical copolymers revealed a weakened segregation strength for the tapered diblock copolymers with a smoother gradual distribution of the comonomers along the polymer chain.

**Chapter A1** comprises a complementary examination of the ultimate mechanical properties of the tapered star-shaped polyisoprene-polystyrene multiblock copolymers treated in Chapter 4. Two series of  $(\text{SIS})_4$  multiblock copolymers varying in their comonomer ratio were compared to the linear SIS triblock copolymers representing the corresponding arm structures. While the star-shaped polymers with a lower isoprene content ordered into lamellae and therefore were stiffer and less elastic, the series with a higher isoprene content possessed morphologies with a continuous polyisoprene phase. Irrespective of the formed morphology, the star-shaped  $(\text{SIS})_4$  architectures outperformed the corresponding linear SIS polymers with respect to their toughness and strain at break. Furthermore, selective catalytic hydrogenation of the PI blocks was exemplified for one star-shaped multiblock copolymer and its linear counterpart, this way increasing the segregation strength and decreasing the entanglement molecular weight of the polydiene segments. Interestingly, the influence of hydrogenation on the ultimate properties varied with the polymer architecture. While the linear tapered triblock copolymer experienced a substantial increase in its ultimate properties, the star-shaped multiblock copolymer faced a deteriorated performance. This is explained by differences in the magnitude of strain-hardening improvement in combination with higher amounts of entanglements.

**Chapter A2** focuses on the impact of solvents on the copolymerization kinetics of epoxides via an anionic ring-opening polymerization mechanism. For this purpose, the copolymerization kinetics of ethylene oxide (EO) with glycidyl ethers with varying coordination sites were monitored by *in situ*  $^1\text{H}$  NMR spectroscopy both in tetrahydrofuran (THF) and the highly polar solvent dimethyl sulfoxide (DMSO). The experiments revealed slightly higher reactivities of the glycidyl ethers compared to EO, which lacks in any side group, emphasizing a pronounced chelation effect of the potassium counterion by the side groups of the glycidyl ether monomers about to be added. With allyl glycidyl ether (AGE) featuring one and ethoxy vinyl glycidyl ether (EVGE) possessing two ether-type coordination sites per side group, EVGE showed slightly stronger incorporation preference than AGE. An increase in the disparity of the relative reactivities was found with decreasing solvent polarity, which relies on the degree of solvation of the propagating chain end and its counterion. Density functional theoretical simulation approaches were implemented to illustrate and further justify the pivotal role of the complexation capability of the ether-containing side groups.

## Kurzfassung

Mit der wegweisenden Arbeit von Hermann Staudinger im Jahre 1920 entwickelten sich die Polymerwissenschaften für über 100 Jahre immens in vielfältige Richtungen, die unzählige Bereiche des Lebens beeinflussen. Um nur einige Wissensbereiche zu nennen, Polymere finden allgegenwärtige Anwendung im Automobilbereich und im Bausektor. Ihre isolierenden oder halbleitenden Eigenschaften sind entscheidend für elektrische und elektronische Geräte, wohingegen Membrantechnologien auf ihrem Separationsvermögen aufbauen und sowie der medizinische als auch der Agrarsektor von fortschrittlichen Polymerstrukturen zur kontrollierten Wirkstofffreisetzung profitieren. Doch Makromoleküle spielten bereits lange bevor sie als solche verstanden, im Detail untersucht und für gezielte Anwendungen spezialisiert wurden eine entscheidende Rolle. Beispielsweise wurde Naturkautschuk auf Grundlage des Vulkanisationsprozesses von Charles Goodyear und Thomas Hancock, der die Grundlage für stabile Elastomermaterialien bildete, für annähernd die letzten beiden Jahrhunderte kommerzialisiert. Die Markteinführung synthetischer thermoplastischer Elastomere (TPEs) im 20. Jahrhundert, die die Verarbeitbarkeit von Thermoplasten mit der Elastizität von vulkanisiertem Kautschuk vereinen, sowie der Fortschritt des chemischen Verständnisses und der daraus resultierenden Materialeigenschaften ermöglichen die Konzeption vielseitiger Charakteristika. Mit der lebenden anionischen Polymerisationstechnik, welche die Methode der Wahl zur Synthese komplexer, aber dennoch definierter Polymerarchitekturen ist, können neuen Herausforderungen, Materialien mit maßgeschneiderten physikalischen Eigenschaften zu entwickeln, begegnet werden.

Der erste Teil dieser Dissertationsarbeit strebt die Aufklärung des Einflusses einer  $(IS)_n$ -Multiblockarchitektur auf die Festkörpereigenschaften an, wohingegen der zweite Teil sich mit deren Lösungseigenschaften befasst. Zum Ende dieser Arbeit wird ein grundlegender Zusammenhang für die lebende anionische Polymerisierbarkeit in apolarem Medium umrissen.

**Kapitel 1** leitet die vielseitige Thematik der lebenden anionischen Polymerisation vor dem Hintergrund deren Einsatzes für thermoplastische Elastomere (TPEs) ein. Nach einem kurzen historischen Abriss von Elastomeren und dem gegenwärtigen Anwendungsbereich von TPEs fokussiert sich dieser Review auf synthetische Konzepte zur Anpassung der Polymer- und damit Materialeigenschaften. Insbesondere werden mechanische Eigenschaften hinsichtlich der Segregationsstärke und der resultierenden Mikrodomänen-Morphologien diskutiert. Die hervorgehobenen Synthesestrategien konzentrieren sich auf Lithium-initiierte, lebende anionische (Co)-Polymerisationen von verschiedenen Styrol- und 1,3-Dien-Monomeren in Kohlenwasserstoff-Lösungsmitteln, wobei darüber hinaus der Einfluss von Modifizieren auf das Blockprofil statistischer Copolymere herausgearbeitet wird. In diesem Zusammenhang wird nicht nur der Einfluss des Blockprofils, sondern auch der Blocksequenz, der Blockanzahl und der Polymerarchitektur betrachtet. Weiterhin werden der Nutzen von *in situ* Reaktionsverfolgungsmethoden zur Bestimmung kinetischer Parameter aufgezeigt und kinetische Monte Carlo-Simulationen vertiefend behandelt, welche die Berechnung von Reaktionszeiten ermöglichen und somit ein wertvolles Hilfsmittel zur Optimierung von Arbeitsabläufen der Multiblocksynthese darstellen.

**Kapitel 2** erörtert die Verwendung von Weich-Polyvinylchlorid (PVC) in Medizinprodukten. Im ersten Teil werden Gesundheitsbedenken in Bezug auf den weitläufig eingesetzten

Weichmacher im Rahmen dessen Belastung bei Menschen sowie dessen Metabolismus angesprochen. Im zweiten und dritten Teil werden potentielle Lösungsansätze durch den Einsatz verschiedener Weichmacher beziehungsweise den Ersatz von PVC durch alternative Polymermaterialien evaluiert. In Bezug auf den letzten Teil werden ein von der europäischen Kommission gefördertes Projekt, das die Verwendung von Polyolefinen für medizinische Infusionsbeutel aufgreift, sowie der Einsatz von Styrol-basierten thermoplastischen Elastomeren für medizinische Anwendungen eingehend diskutiert.

**Kapitel 3** beleuchtet die strukturelle und mechanische Untersuchung von Polyisopren-Polystyrol Multiblockcopolymeren mit zwei Polyisopren-Endblöcken. Diese Strukturen sind aufgrund ihres potentiellen intrinsischen Weichmachereffekts durch die flexiblen Endblöcke von Interesse, der zu einem weichen, aber dennoch widerstandsfähigen Material führen könnte. Temperaturabhängige Kleinwinkelstreuung und rheologische Experimente wurden zur Untersuchung der phasenseparierten Morphologien von sowohl sequentiellen als auch verjüngten  $(IS)_n$ -Multiblockcopolymeren herangezogen, die einen großen Bereich an Molekulargewichten und Blockanzahlen umfassen. Der Vergleich von sequentiellen Blockcopolymeren mit einem definierten Übergang zwischen benachbarten Blöcken mit verjüngten blockartigen Copolymeren mit einer scharfen, aber dennoch graduellen Verteilung der Comonomere in jeder Polyisopren-Polystyrol-Diblocksequenz verdeutlichte eine starke Verringerung der Separationsstärke und somit der Übergangstemperatur zwischen einem geordneten und dem ungeordneten Zustand. Die ist auf die verminderte enthalpische Inkompatibilität in verjüngten Strukturen zurückzuführen. Während sequentielle Multiblockcopolymere wohlgeordnete lamellare Morphologien aufwiesen, zeigten die verjüngten Analoga schwachgeordnete perforierte Schichtstrukturen. Die mit Zug-Dehnungsexperimenten untersuchte viskoelastische Reaktion verdeutlichte, dass sequentielle Strukturen widerstandsfähiger sind, während verjüngte Strukturen eine höhere Weichheit und Flexibilität besaßen. Die bei gleichbleibender Molmasse mit zunehmender Blockanzahl einhergehende Abnahme der Blocklänge resultiert in einer erhöhten Domänenüberbrückung, aber gleichzeitig einer schwächeren Mikrophasenseparation. Aufgrund dieses Kompromisses erwies sich das Gleichgewicht zwischen diesen gegensätzlichen Effekten für die verjüngten Pentablock- und sequentiellen Heptablockcopolymere höheren Molekulargewichts am besten eingestellt, was sich in einer beträchtlichen mechanischen Belastbarkeit äußerte. Interessanterweise besaßen Polymere desselben Molekulargewichts pro Block vergleichbare Domänenabstände und somit Weichheit, wohingegen deren Verformbarkeit mit der Erweiterung um eine Diblocksequenz aufgrund der verstärkten Domänenüberbrückung zunahm. Im Vergleich zu literaturbekannten analogen Strukturen mit zwei Polystyrol-Endblöcken zeigen die Strukturen mit zwei Polyisopren-Endblöcken eine einfachere Verformbarkeit, was auf die kleineren Domänengrößen zurückzuführen ist.

**Kapitel 4** erarbeitet ferner die mechanischen Eigenschaften von Polyisopren-Polystyrol-Multiblockcopolymeren mit hinsichtlich ihrer Kettenverknüpfung verschiedenen Architekturen. Diese grundlegende Forschung ist aufgrund der potentiellen Verringerung von permanenten Verformungen bei starker Dehnung spannend, da der Vorteil von einfach prozessierbaren und wiederverarbeitbaren Materialien erhalten bleibt. Lineare verjüngte SIS-Triblockcopolymere wurden anhand von uniaxialen Zug-Dehnungsversuchen sowie Erholungsuntersuchungen mit linearen  $(SIS)_2$ -Pentablock- und sternförmigen  $(SIS)_4$ -



Multiblockcopolymeren, die sich durch starre Kern- und Endblöcke auszeichnen, verglichen. Die erweiterten Architekturen wurden nach einem „*Arm-First*“-Ansatz synthetisiert, bei dem die zunächst hergestellten (SIS)-Arme gekuppelt werden. Für kleine Molmassen pro Arm zeigten die sternförmigen Multiblockarchitekturen bessere Zug- und Dehnungswerte zum Zeitpunkt des Materialbruchs, was einer höheren Belastbarkeit entspricht und auf deren höhere Domänenüberbrückung zurückzuführen ist. Für hohe Molmassen näherten sich die mechanischen Eigenschaften der linearen Pentablockcopolymeren denen der sternförmigen Strukturen an und erreichten einen Plateauwert, was zeigt, dass an diesem Punkt die kovalente Verknüpfung der Sternarchitekturen nicht weiter zur Widerstandsfähigkeit beiträgt. Allerdings übertrafen sie die einfachen Triblockstrukturen, was die Wichtigkeit von hohen Anteilen überbrückender Kettenkonformationen weiter verdeutlicht. Bei Polymeren mit gleichem Gesamtmolekulargewicht konnten die sternförmigen Multiblockcopolymeren nicht mit den linearen Pentablockcopolymeren konkurrieren, da sie eine geringere Phasenseparation und damit ein erleichtertes Herausziehen von Polymerketten aufwiesen. Zyklische Dehnungsexperimente an drei analogen Polymerstrukturen mit demselben Molekulargewicht pro Arm, einer ausreichenden Phasenseparation und vergleichbarer Zugfestigkeit belegten deutliche Unterschiede in deren Formrückgewinnungsverhalten. Während das sternförmige (SIS)<sub>4</sub>-Multiblockcopolymer eine beispiellose finale Rückgewinnung der ursprünglichen Form nach fünfminütiger Ruhephase zeigte, war dessen Anfangserholung während des Zurückfahrens des Probenkopfes in die Ausgangslage gering. Im Gegensatz dazu wiesen die linearen Strukturen eine bessere schnelle Anfangserholung, aber geringere finale Erholungen nach der Ruhephase auf. Diese Beobachtungen belegen, dass die höhere Kettenflexibilität von linearen Architekturen eine schnelle Rückgewinnung bezweckt, wohingegen die gleichmäßigere Spannungsverteilung in sternförmigen Architekturen mit einer kovalenten Kernverbindungsstelle zu einem besseren Formgedächtnis führt. Allerdings unterliegen alle Proben bei hohen Zugwerten einer permanenten Verformung aufgrund von erheblicher Reorganisation, was in konvergierenden Erholungseigenschaften mündet.

**Kapitel 5** befasst sich mit den drei wichtigsten tribologischen Parametern, die die Leistung von Viskositätsmodifizierern in Schmierölen bestimmen, wobei nicht nur auf die im Allgemeinen verwendeten, sondern auch neue Polymerklassen eingegangen wird. Um Reibung vorzubeugen, müssen sich gegeneinander bewegende Metallbauteile geschmiert werden. Allerdings erfahren Schmierflüssigkeiten eine starke Viskositätsabnahme mit steigender Temperatur. Zur Abschwächung der unerwünschten Effekte von Oberflächenkontakt werden deshalb Viskositätsmodifizierer zugesetzt. Dennoch konnte bislang keine optimale Leistungsfähigkeit in allen drei wesentlichen Kennzahlen erreicht werden, welche einen vorteilhaften Zusammenhang zwischen Viskosität und Temperatur, die Verdickungseffizienz und die Scherstabilität umfassen. Die Feinabstimmung dieser tribologischen Parameter ist aufgrund ihrer komplexen Interkorrelation herausfordernd, weshalb neue Schmiermittel-additive notwendig sind. Deshalb wird der Einfluss der wesentlichen Polymercharakteristika wie deren Molmasse, Dispersität, Kettenzusammensetzung und weiterhin deren Architektur auf das hydrodynamische Volumen und somit auf die tribologischen Parameter herausgearbeitet. Darüber hinaus wird die Chemie der meistverwendeten Polymerklassen, zu welchen Polyalkylmethacrylate, olefinische Copolymere und hydrierte Styrol-Dien-Copolymere zählen, hinsichtlich ihres Polymerisationsmechanismus und des inhärenten Verdickungsmechanismus für Viskositätsverbesserung erörtert. Letztere umfassen den

Kettenaufweitungsmechanismus, der bei Polyalkylmethacrylaten vorherrscht, sowie assoziative Phänomene, die bei hydrierten Styrol-Dien-Copolymeren dominieren. Darüber hinaus werden weiterentwickelte Strukturen vorgestellt, die anstreben, die gegenwärtig bestehenden Leistungsgrenzen zu überwinden. Dabei werden Polymerblend-Ansätze und neue Polymerklassen wie Poly(2-oxazoline) und Poly(2-oxazine), aber auch anspruchsvolle Architekturen wie Bürsten-, Kamm- oder lineare (verjüngte) Multiblockcopolymere thematisiert. Diese vielversprechende Kombination mehrerer Vorteile regt zu weiteren Untersuchungen an.

**Kapitel 6** behandelt die Selbstorganisation von Multiblockcopolymeren sowohl mit definiertem als auch mit graduelltem Blockprofil im Polyisopren-selektiven Lösungsmittel Heptan. Die Untersuchung des Diffusionsverhaltens bei unterschiedlichen Konzentrationen erlaubt Rückschlüsse auf die Aggregatstrukturen. Zu diesem Zweck wurden verdünnte und konzentrierte Polymerlösungen mittels dynamischer Lichtstreuung unter Verwendung einer Kreuzkorrelationsmethode ausgewertet, welche die Analyse von Diffusionsprozessen selbst in Gegenwart von Mehrfachstreueignissen gewährleistet. Divergierende Diffusionskoeffizienten der Triblock- und Multiblockcopolymere bei Polymermassenanteilen über 1 % belegten die Ausbildung von nicht-ergodischen Systemen, sprich Polymernetzwerken, im Falle von Strukturen mit mehreren solvophobischen Polystyrolblöcken. Komplementäre fluoreszenzkorrelationsspektroskopische Messungen lieferten Einblicke in Selbstdiffusionsprozesse der Unimere durch diese Polymernetzwerke. Diese Prozesse erwiesen sich als am eingeschränktesten im Falle von Netzwerken aus sequentiellen Multiblockcopolymeren, was auf ein dichteres Netzwerk aufgrund von stärkerer Domänenüberbrückung in Kombination mit größeren Unimerdimensionen zurückzuführen ist. Die Unimerdimensionen wurden in hochverdünnten Polymerlösungen untersucht, in welchen keine Aggregationsphänomene auftreten. Weiterhin wurde eine Zunahme der Micelldimensionen und deren Anteil mit dem Übergang von verdünnten Lösungen hin zu höheren Konzentrationen festgestellt, welche schlussendlich die erwähnten transienten Polymernetzwerke ausbildeten. Um die fluoreszenzkorrelationsspektroskopischen Messungen durchführen zu können wurde ein neues polymeranaloges Syntheseverfahren zur Fluoreszenzfarbstoffmarkierung implementiert, das sich durch eine lediglich geringe Veränderung der chemischen Beschaffenheit der markierten Polymere auszeichnet.

**Kapitel 7** betrachtet den konzentrationsabhängigen Zusammenhang zwischen Viskosität und Temperatur der (un)-hydrierten verjüngten Multiblockcopolymere in den Polyisopren-selektiven Lösungsmitteln Squalane und einem hoch-isoparaffinischen Kohlenwasserstoff-basierten Schmieröl vor dem Hintergrund der selbstorganisierten Strukturen, die in Kapitel 6 thematisiert wurden. Aus temperatur- und frequenzabhängigen dynamischen Viskositätsmessungen sowie kinematischen Viskositätsmessungen bei 40 °C und 100 °C konnte ein klarer Zusammenhang zwischen den selbstorganisierten Polymeraggregatstrukturen und ihrer Effizienz als Viskositätsmodifizierer abgeleitet werden. Bei vergleichsweise niedrigen Polymerkonzentrationen verbesserte sich der Zusammenhang zwischen Viskosität und Temperatur mit steigendem Gesamtmolekulargewicht, Blockanzahl und Isoprenanteil. Grund hierfür war die Ausbildung von losen Aggregaten mit mehreren Polystyrolkernen und somit ausgedehnten hydrodynamischen Volumina im Falle der Multiblockarchitekturen. Hingegen bei hohen Konzentrationen verschlechterten sich die untersuchten tribologischen

Schlüsselparameter, sprich der Zusammenhang zwischen Viskosität mit zunehmender Temperatur und die Verdickungseffizienz, für die Strukturen mit den kürzesten individuellen solvophobischen Polystyrolblöcken. Dies ist auf die Ausbildung großer transienter Netzwerke zurückzuführen, welche unter Scherung stärker zur teilweisen Disassemblierung neigen. Dieser Effekt wird zudem durch die Einlagerung von Lösungsmittelmolekülen in die Aggregatkerne verstärkt, was bei kurzen Polystyrolblöcken am ausgeprägtesten ist. Die resultierenden abgeschwächten van-der-Waals-Wechselwirkungen begünstigen das Herausziehen von Polymerketten und somit eine teilweise Disassemblierung. Der Vergleich der untersuchten Styrol-Dien-Multiblockcopolymeren mit einem kommerzialisierten kammartigen Polyalkylmethacrylat ergab eine verbesserte Leistungsfähigkeit der gezeigten Strukturen bei niedriger Polymerkonzentration. Das verdeutlicht das enorme Potential der verjüngten Multiblockarchitekturen als weiterentwickelte Viskositätsmodifizierer.

**Kapitel 8** bezweckt das Verständnis des Struktur-Eigenschafts-Zusammenhangs von Multiblockcopolymeren mit einem definierten oder einem graduellen, aber dennoch klaren Blockprofil in verdünnter, nicht-selektiver Lösung. Zu diesem Zweck wurden Polymerreihen sequentieller und verjüngter (IS)<sub>n</sub>-Multiblockcopolymeren umfassend mittels komplementärer Methoden charakterisiert, deren Molmassen von 40–400 kg·mol<sup>-1</sup> und deren Blockanzahlen von 3–13 reichten. Anschließend wurden verdünnte Lösungen in Toluol systematisch mittels klassischer Skalierungsverhältnisse zwischen den hydrodynamischen Charakteristika untersucht, die aus analytischen Ultrazentrifugations-, intrinsischen Viskositäts- und verwandten Experimenten abgeleitet wurden. Sowohl Rotations- als auch Translationsdiffusionsexperimente ergaben feine Unterschiede der Polymerkettendimensionen und somit der Steifheit von Polymerreihen identischer Blockanzahl. Für diese homologen Polymerreihen konnte eine steifere und somit stärker aufgeweitete Kettenkonformation im Falle der sequentiellen Strukturen im Vergleich zu den verjüngten Analoga abgeleitet werden. Interessanterweise folgten Polymere unterschiedlicher Molmasse und Blockanzahl, deren Polystyrolblöcke identische Polymerisationsgrade aufwiesen, nicht den klassischen Skalierungsbeziehungen. Dies belegte einen Einfluss der Blockanzahl auf die Lösungseigenschaften selbst in nicht-selektiven Lösungsmitteln.

**Kapitel 9** untersucht die Polymerisierbarkeit von rotationseingeschränkten 1,3-Dienen mit vorgegebener *cis*- oder *trans*-Geometrie der Doppelbindungen. Im Detail wird die Reaktivität in lebenden anionischen Polymerisationen in apolarem Medium analysiert, deren angenommener Mechanismus nach einem koordinativen Mechanismus verläuft. Theoretische Simulationsansätze zweier neuer 1,3-Dien-Monomere mit einer starren, vorgeschriebenen *cis*- oder *trans*-Geometrie in Cyclohexan als typischen unpolares Lösungsmittel wurden mit synthetischen und kinetischen Untersuchungen kombiniert. Die experimentellen Beobachtungen stimmten mit den prognostizierten Reaktivitäten und den simulierten Reaktionspfaden überein, welche die Notwendigkeit einer *cis*-Geometrie der in einer Ebene liegenden Doppelbindungen zum Kettenwachstum aufzeigten. Tatsächlich waren Homo- sowie Copolymerisationsexperimente des *cis*-Diens erfolgreich, wohingegen das *trans*-Dien zu unreaktiv war. Im Vergleich zur Polymerisation des uneingeschränkten geläufigen Monomers Isopren führte die notwendige Ringverzerrung im Falle des cyclischen *cis*-Diens zu höheren simulierten Aktivierungsenergien für dessen Kettenwachstum. Echtzeit-<sup>1</sup>H-kernspinresonanzspektroskopische Kinetikuntersuchungen bestätigten dies experimentell, indem sie die

Gradientenausbildung in statistischen Copolymerisationsexperimenten des *cis*-Diens mit Isopren belegten, wessen Steilheit mit zunehmender Temperatur abflachte. Zusätzlich zeigten thermische Analysen der statistischen Copolymere eine verminderte Segregationsstärke der verjüngten Diblockcopolymere mit einem weichen graduellen Übergang der Comonomere entlang der Polymerkette.

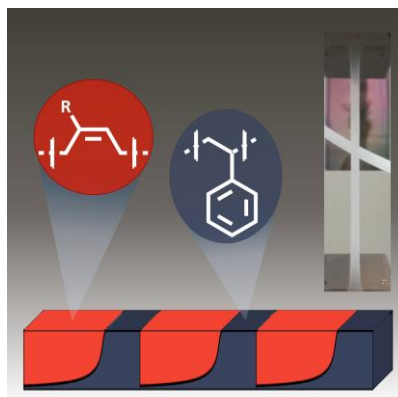
**Kapitel A1** umfasst weiterführende Untersuchungen der mechanischen Eigenschaften der in Kapitel 4 behandelten verjüngten sternförmigen Polyisopren-Polystyrol-Multiblockcopolymere. Zwei Polymerreihen von (SIS)<sub>4</sub>-Multiblockcopolymeren mit unterschiedlichem Comonomerverhältnis wurden mit den linearen SIS-Triblockcopolymeren verglichen, welche die jeweilige Armstruktur widerspiegeln. Während die sternförmigen Polymere geringeren Isoprenanteils geordnete Lamellen ausbildeten und somit steifer und weniger elastisch waren, besaßen die Polymerreihen höheren Isoprenanteils Morphologien mit einer kontinuierlichen Polyisopren-Phase. Ungeachtet der ausgebildeten Morphologie übertrafen die sternförmigen (SIS)<sub>4</sub>-Architekturen die zugehörigen SIS-Polymere hinsichtlich ihrer Belastbarkeit und Dehnbarkeit. Weiterhin wurde die selektive katalytische Hydrierung von PI-Blöcken anhand eines sternförmigen Multiblockcopolymers und seines linearen Gegenparts veranschaulicht, was eine Zunahme der Segregationsstärke und gleichzeitige Abnahme des Verschlaufungsmolekulargewichts der Polydiensegmente bewirkt. Interessanterweise unterschied sich der Einfluss der Hydrierung auf die mechanischen Eigenschaften mit der Polymerarchitektur. Während die mechanischen Eigenschaften der linearen verjüngten Triblockcopolymere erheblich verbessert wurden, verschlechterten sich die Eigenschaften der sternförmigen Multiblockcopolymere. Dies ist auf Unterschiede in der Zug-induzierten Verfestigungszunahme in Zusammenspiel mit verstärkter Verschlaufung zurückzuführen.

**Kapitel A2** fokussiert sich auf den Einfluss von Lösungsmitteln auf Copolymerisationskinetiken von Epoxiden nach einem anionischen Ringöffnungspolymerisationsmechanismus. Dazu wurde die Copolymerisation von Ethylenoxid (EO) mit Glycidylethern unterschiedlicher Koordinierungsstellen mittels *in situ* <sup>1</sup>H-kernspinresonanzspektroskopischen Kinetikuntersuchungen sowohl in Tetrahydrofuran (THF) als auch in Dimethylsulfoxid (DMSO) verfolgt. Die Experimente offenbarten leicht erhöhte Reaktivitäten der Glycidylether im Vergleich zu EO, das über keine Seitengruppe verfügt, was auf einen ausgeprägten Chelateffekt des Kalium-Gegenions durch die Seitengruppen der reagierenden Glycidylether-Monomere hinweist. Ethoxyvinylglycidylether (EVGE), welcher zwei Ether-Koordinationsstellen in der Seitengruppe besitzt, wies einen leicht stärkeren bevorzugten Einbau in die Polymerkette verglichen mit Allylglycidylether (AGE) auf, welcher lediglich über eine Ether-Koordinationsstelle in der Seitengruppe verfügt. Zunehmende Unterschiede in den relativen Reaktivitäten konnten mit abnehmender Polarität des Lösungsmittels festgestellt werden, was aus dem Solvatisierungsgrad des propagierenden Kettenendes und dessen Gegenions resultiert. Dichtefunktionaltheoretische Simulationen wurden zur Visualisierung und weiter zur Belegung der entscheidenden Rolle der Komplexierungsfähigkeit der Ether-beihaltenden Seitengruppen herangezogen.



## Graphical Abstract

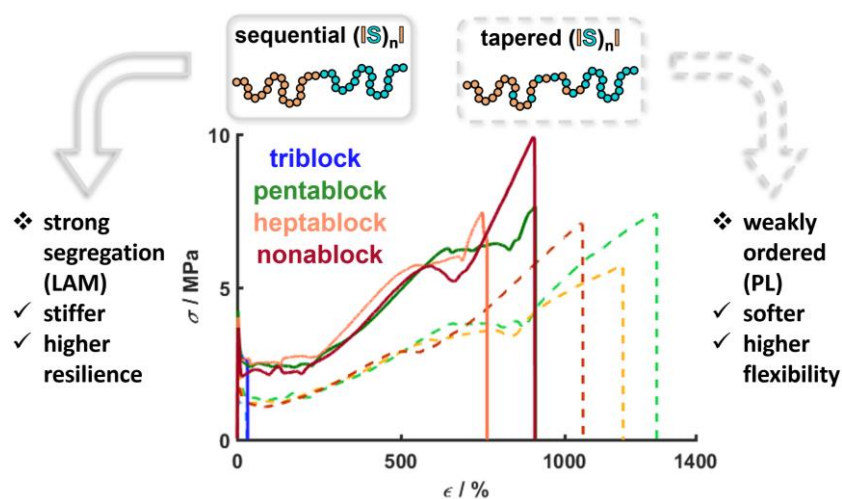
### Chapter 1 | *Introduction to Multiblock Copolymers via Living Anionic Polymerization: Rational Design of Tapered Multiblock Copolymers for Thermoplastic Elastomers*



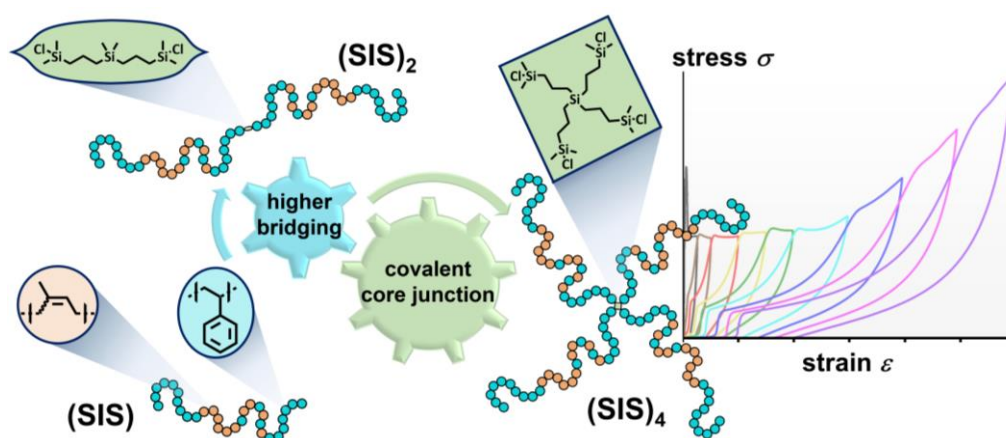
### Chapter 2 | *Application Engineering of Soft Multiblock Copolymers: Approaching Performance Requirements for PVC-free Blood Bags*



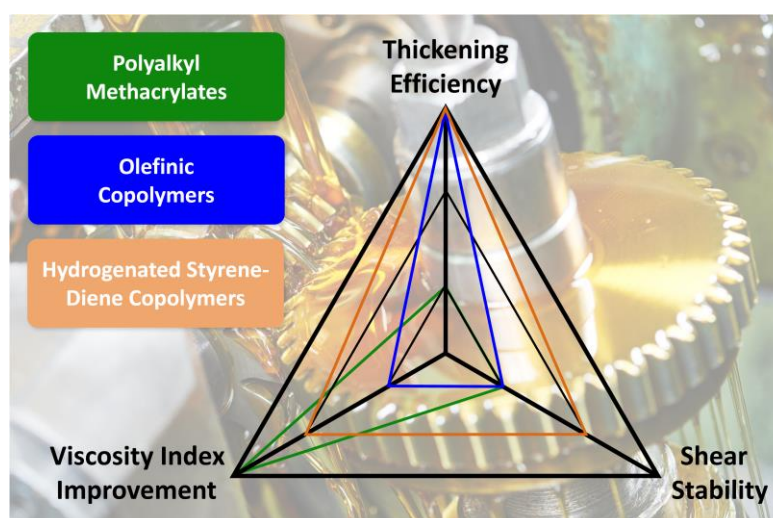
### Chapter 3 | *Linear (IS)<sub>n</sub>I Multiblock Copolymers: Manipulating the Softness of TPEs by Introducing Flexible End Blocks to Multiblock Copolymers with a Defined or Tapered Interface*



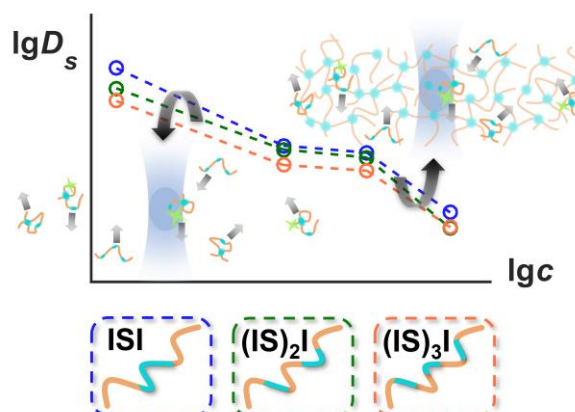
## Chapter 4 | *(SIS)<sub>x</sub> Multiblock Copolymers: Controlling Recovery Properties by the Chain Connectivity Comparing Linear and Star-Shaped Multiblock Copolymers*



## Chapter 5 | *Implementation of Multiblock Copolymers in Solution: Next Generation Viscosity Modifiers*

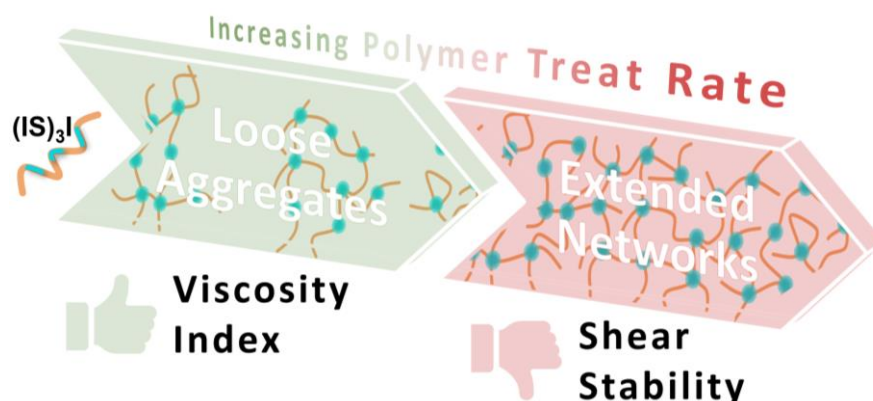


## Chapter 6 | *Fluorescence Labeling of Multiblock Copolymers: Unraveling Different Aggregate Structures in Concentrated Polymer Solutions by Fluorescence Correlation Spectroscopy*

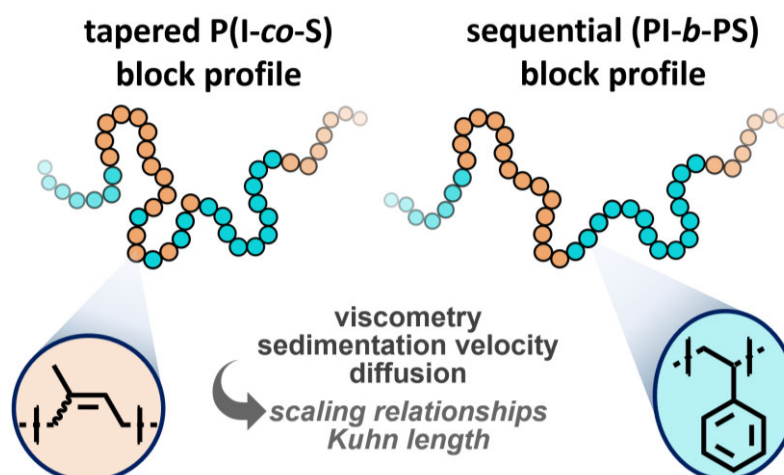




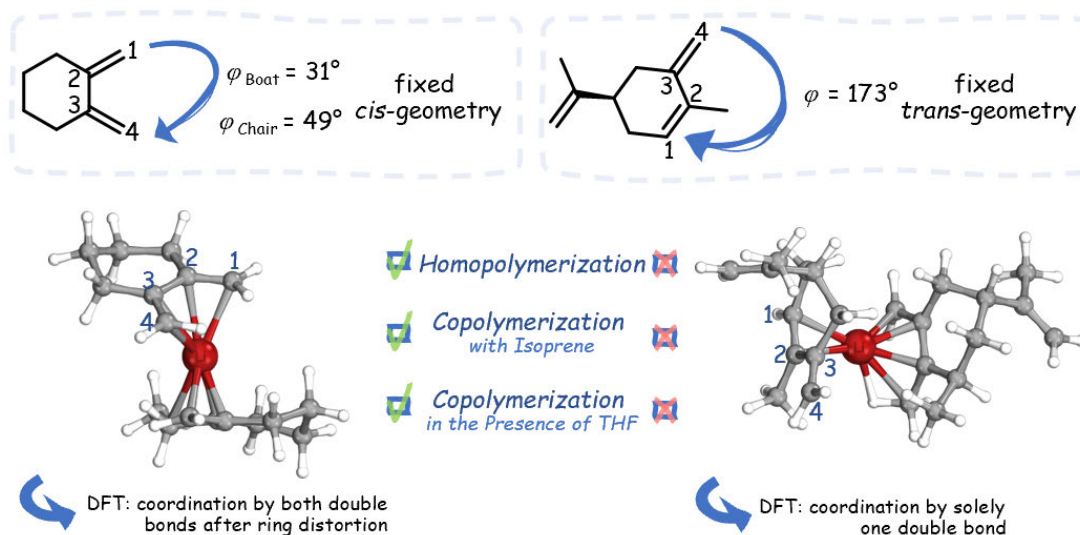
## Chapter 7 | *Viscosity of Concentrated Polymer Solutions: Shear-Induced Disassembly of Transient Associative Polymer Networks*



## Chapter 8 | *Dilute Solution Properties of Multiblock Copolymers: Conformation Analysis of Sequential and Tapered Multiblock Copolymers in Non-Selective Solvents*

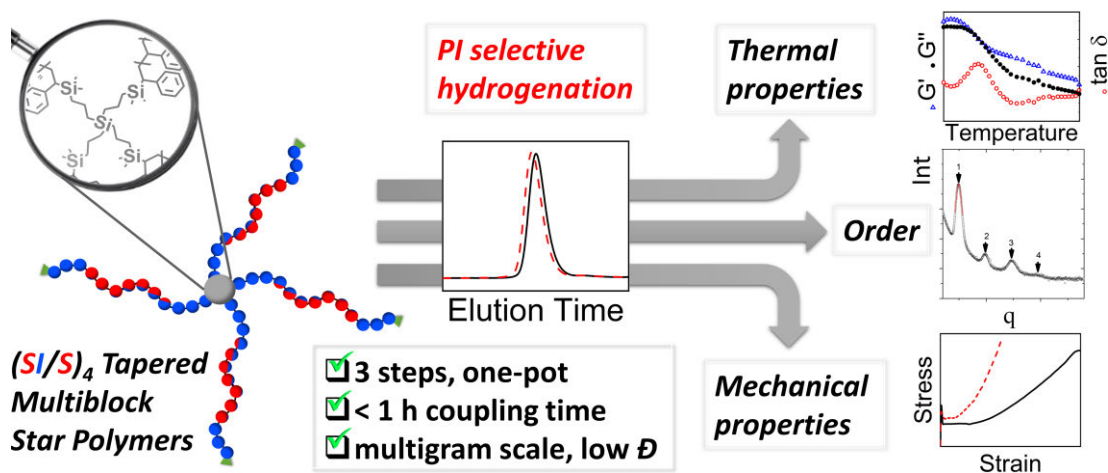


## Chapter 9 | *Geometric Requirements for Living Anionic Polymerization: Polymerization of Rotationally Constrained 1,3-Dienes*

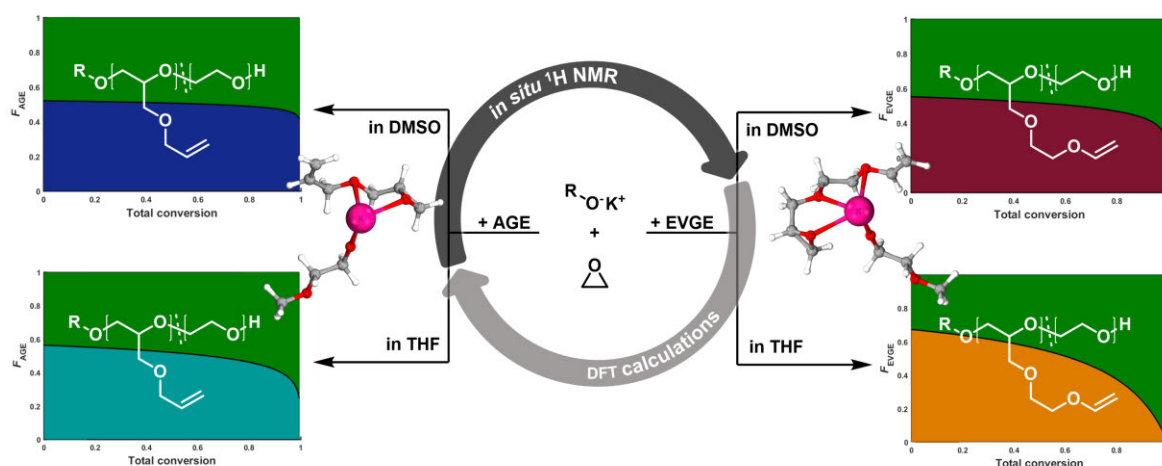




## Chapter A1 | Tapered Multiblock Star Copolymers: Synthesis, Selective Hydrogenation, and Properties



## Chapter A2 | In Situ Kinetics Reveal the Influence of Solvents and Monomer Structure on the Anionic Ring-Opening Copolymerization of Epoxides





---

---

# CHAPTER 1

*Introduction to Living Anionic Polymerization:*  
**Rational Design of Tapered Multiblock Copolymers  
for Thermoplastic Elastomers**

---

---



## CHAPTER 1

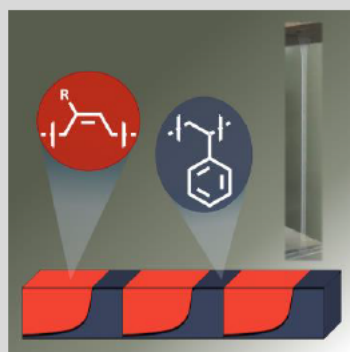
Published in Progress in Polymer Science, 2022. DOI: 10.1016/j.progpolymsci.2021.101488

# ***Introduction to Living Anionic Polymerization: Rational Design of Tapered Multiblock Copolymers for Thermoplastic Elastomers***

Marvin Steube<sup>1</sup>, Tobias Johann<sup>1,2</sup>, Ramona D. Barent<sup>1,2</sup>, Axel H.E. Müller<sup>1\*</sup>, and Holger Frey<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany

<sup>2</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany



Thermoplastic elastomers (TPEs) combine the features of vulcanized thermoset rubbers and thermoplastic materials in their phase-separated microdomain structure. As a consequence, soft, flexible and resilient materials are obtained, which can be high-speed processed from the melt state. In the last decades, a variety of polymerization strategies has been proven successful to synthesize block copolymers for TPE materials on an industrial scale. Motivated by the outstanding properties of natural rubber (*cis*-1,4-polyisoprene), the

alkyllithium initiated anionic polymerization of isoprene and butadiene plays a key role for the flexible block of TPEs. The synthesis of ABA-type triblock copolymers based on styrene and 1,3-dienes leads to phase-segregated systems which do not require chemical crosslinking. The living character of the carbanionic chain end was utilized in numerous studies to synthesize complex, defined comonomer sequences by multi-step synthesis. Systematic variation of numerous parameters, e.g., block size and sequence allowed to correlate the resulting mechanical and morphological properties. In this review the focus is placed on multiblock structures and gradient copolymers, addressing key parameters of the molecular architecture to enable a general concept for the design of TPE materials with tailor-made properties. The choice of monomers, also bio-based diene structures such as  $\beta$ -myrcene or  $\beta$ -farnesene is another parameter. The major focus is put on the direct, i.e., statistical anionic copolymerization kinetics as the method of choice to synthesize rather complex multiblock sequences in a one-pot reaction. On-line spectroscopic methods are presented that enable to monitor the monomer consumption during the copolymerization, which directly translates to the comonomer incorporation and gradient formation. To enable precise insight into the comonomer composition of the formed chains, an overview of the theory of copolymerization and the determination of reactivity ratios is given. Kinetic Monte Carlo simulation (kMC) is a versatile tool. Based on experimentally determined kinetic rate constants, the

copolymerization can be performed *in silico*. This enables access to relevant parameters, as for example the conversion as a function of the time as well as the the composition and monomer sequence in individual chains, which allow rational design and evaluation of synthetic experiments.

## Abbreviations

|                     |                                                                                  |                           |                                                                                      |
|---------------------|----------------------------------------------------------------------------------|---------------------------|--------------------------------------------------------------------------------------|
| $\tilde{\nu}_i$     | Absorption wavenumber of monomer i                                               | PFar                      | Polyfarnesene                                                                        |
| $[M_i]$             | Concentration of monomer i                                                       | PI                        | Polyisoprene                                                                         |
| $^1\text{H-NMR}$    | Proton nuclear magnetic resonance                                                | PI- <i>b</i> -PS          | Polyisoprene- <i>block</i> -polystyrene                                              |
| 4-MS                | 4-methylstyrene                                                                  | PMMA                      | Poly (methyl methacrylate)                                                           |
| $A(\tilde{\nu})$    | Absorption at a certain wavenumber                                               | PMyr                      | Polymyrcene                                                                          |
| $a_A/a_B$           | Ratio of the statistical segment lengths of A and B                              | PPO                       | Poly(phenylene oxide)                                                                |
| AROP                | Anionic ring opening polymerization                                              | PS                        | Polystyrene                                                                          |
| B                   | Butadiene                                                                        | PS- <i>b</i> -PB          | Polystyrene- <i>block</i> -polybutadiene                                             |
| C                   | Cylinders                                                                        | PSCFT                     | Polymer self-consistent field theory                                                 |
| CC-CLD / CoC-CLD    | Chemical composition-chain length distribution                                   | PVC                       | Poly(vinyl chloride)                                                                 |
| $d$                 | Domain spacing                                                                   | $R_g$                     | Radius of gyration                                                                   |
| $\bar{D}$           | Dispersity                                                                       | $r_i$                     | Reactivity ratio of monomer i                                                        |
| DIS                 | Disordered                                                                       | RI                        | Refractive index                                                                     |
| DPE                 | diphenylethene                                                                   | S                         | Spheres with bcc (body centered cubic) lattice (only in the context of morphologies) |
| DTHFP               | 2,2-Di(2-tetrahydrofuryl)propane                                                 | S                         | Styrene                                                                              |
| DVB                 | Divinylbenzene                                                                   | S (cp)                    | Spheres with cp (close packed) lattice                                               |
| $f$                 | Average number of arms (only in the context of star polymers)                    | $S(q)$                    | Structure factor                                                                     |
| Far                 | $\beta$ -Farnesene                                                               | S/B                       | see PS- <i>b</i> -PB                                                                 |
| $f_i$               | volume fraction of component i                                                   | S/I                       | see PI- <i>b</i> -PS                                                                 |
| $F_i$               | instantaneous mole fraction of monomer i incorporated                            | SAXS                      | Small angle X-ray scattering                                                         |
| $F_{V,i}$           | instantaneous volume incorporation of monomer i                                  | SBC                       | Styrenic block copolymers                                                            |
| G                   | gyroid                                                                           | SBR                       | Styrene-butadiene rubber                                                             |
| HPL                 | Hexagonally perforated layers                                                    | SBS                       | Polystyrene- <i>block</i> -polybutadiene- <i>block</i> -polystyrene                  |
| I                   | Isoprene                                                                         | SCFT                      | Self consistent mean-field theory                                                    |
| IS                  | See PI- <i>b</i> -PS                                                             | SEBS                      | Polystyrene- <i>block</i> -poly(ethylene butylene)- <i>block</i> -polystyrene        |
| ISI                 | Polyisoprene- <i>block</i> -polystyrene- <i>block</i> -polyisoprene              | SEC                       | Size exclusion chromatography                                                        |
| $k_{\text{deagg.}}$ | Rate constant for the deaggregation of aggregated chain ends                     | SEPS                      | Polystyrene- <i>block</i> -poly(ethylene propylene)- <i>block</i> -polystyrene       |
| $k_{ii}$            | Homopropagation rate constant of monomer i                                       | SIS                       | Polystyrene- <i>block</i> -polyisoprene- <i>block</i> -polystyrene                   |
| $k_{ij}$            | Crossover reaction rate constant from a chain end bearing monomer i to monomer j | SLD                       | Sequence length distribution                                                         |
| kMC                 | kinetic Monte Carlo simulation                                                   | $T$                       | temperature                                                                          |
| L                   | Lamellae                                                                         | $T_1$                     | Spin-lattice relaxation time in NMR experiments                                      |
| $M$                 | Molecular weight                                                                 | $T_{\text{boiling}}$      | Boiling temperature                                                                  |
| MALDI-ToF           | Matrix-assisted laser desorption/ionization-time of flight                       | TCDMSPS                   | Tetra[3-(chloro-dimethylsilyl)propyl]silane                                          |
| MD                  | Molecular dynamics                                                               | TEA                       | Triethylamine                                                                        |
| MDCBS               | 1,4-Bis(methyldichlorosilyl)butane                                               | TEM                       | transmission electron microscopy                                                     |
| $M_e$               | Entanglement molecular weight                                                    | $T_g$                     | Glass transition temperature                                                         |
| Mid-IR              | Mid-infrared                                                                     | THF                       | Tetrahydrofuran                                                                      |
| $M_n$               | Number average molecular weight                                                  | TMEDA                     | <i>N,N,N',N'</i> -Tetramethylethyldiamine                                            |
| MTBE                | Methyl tert-butyl ether                                                          | $T_{\text{ODT}}$          | Order-disorder transition temperature                                                |
| Myr                 | B-Myrcene                                                                        | TPE                       | Thermoplastic elastomers                                                             |
| $N$                 | total degree of polymerization                                                   | $T_{\text{polym.}}$       | Polymerization reaction temperature                                                  |
| $N$                 | Number of segments per arm (only in the context of star polymers)                | TPU                       | polyurethane based TPEs                                                              |
| $N_{\text{agg}}$    | Aggregation number                                                               | UV                        | Ultraviolet                                                                          |
| NBR                 | Acrylonitrile-butadiene rubber                                                   | $\epsilon_i(\tilde{\nu})$ | Molar attenuation coefficient of monomer or polymer i                                |
| NIR                 | Near-infrared                                                                    | $\lambda_i$               | Absorption wavelength of monomer or polymer i                                        |
| ODT                 | Order-disorder transition                                                        | $\Phi_i$                  | Block volume fraction of component i                                                 |
| PB                  | Polybutadiene                                                                    | $\chi_{AB}$               | Flory-Huggins interaction parameter between A and B                                  |
|                     |                                                                                  | $\chi_{AB,\text{eff}}$    | Effective Flory-Huggins interaction parameter                                        |

Elastomers are typically defined as weakly crosslinked amorphous polymers above their glass transition temperature, named after their outstanding elastic recovery in response to macroscopic deformation.<sup>[1]</sup> The first elastomers relying on covalently crosslinked flexible macromolecules were based on natural rubber, used since 1600 BC by ancient mesoamericans.<sup>[2]</sup> The crosslinking process is essential to generate a soft and permanently form-stable material. In the ancient technology this was achieved by mixing the latex of a the rubber tree (*Castilla elastica*, nowadays harvested from *Hevea brasiliensis*), roughly consisting of *cis*-1,4 polyisoprene (PI), with plant juice (*Ipomoea alba*) to form solid rubber balls.<sup>[2,3]</sup> In 1839 Charles Goodyear developed the hardening of rubbers by the so-called “vulcanization” process, but did not patent his discovery immediately.<sup>[4]</sup> Instead, Thomas Hancock applied for a patent by the end of 1843 – eight weeks before Goodyear.<sup>[5]</sup> It describes the covalent crosslinking of natural rubber by thermal processing with sulfur and white lead ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ). Although Hancock was not the inventor of vulcanizing in the strictest sense of the word, he first showed that sulphur alone is sufficient to effect the change, whereas Goodyear employed other substances in addition. Nowadays, the reaction is known to crosslink linear polyisoprene chains by the intermolecular replacement of C-H bonds by sulfur oligomers and is used on a megaton scale to vulcanize natural rubber.<sup>[6]</sup>

## From Buna to Tapered Triblocks – Brief History of Elastomers

Only one year after the development of the vulcanization process Robert William Thomson presented the first air-filled rubber tire, consequently leading to an increasing demand of natural rubber. In 1860 G. Williams was able to isolate a substance, he named isoprene, from caoutchouc ( $\approx$  *cis* 1,4-PI) as well as guttapercha ( $\approx$  *trans* 1,4-PI).<sup>[7]</sup> In 1910 Matthews made the essential observation of a viscous solid with rubber-like properties by storing isoprene in the presence of sodium metal<sup>[8]</sup> and patented the fabrication of synthetic rubber in Great Britain.<sup>[9]</sup> Only two months later, the German company Bayer registered the same innovation without this knowledge. In 1911 Matthews also acquired a German patent, forcing Bayer to withdraw their registration.<sup>[10]</sup> Not until 15 years later, the alkali metal initiated anionic polymerization became patent-free and immediately was in focus of the company IG Farben.<sup>[11]</sup> Within the next two years the heterogeneous sodium initiated polymerization of butadiene was driven to polybutadienes of different molecular weights, resulting in a variety of synthetic rubbers (Buna 32, Buna 85 and Buna 115), used for tire applications.<sup>[12]</sup> In 1937 also potassium metal was used on technical scale.<sup>[13]</sup> At the same time (1929), Walter Bock invented the radical emulsion polymerization towards styrene-butadiene rubbers (DIN/ISO 1629 SBR) with superior properties for use as tire materials. However, no sodium was involved in the synthetic process, and the product was later commercialized as Buna S by IG Farben. The respective copolymers were of key relevance for the production of tires during the second world war.<sup>[14,15]</sup>

## The Development of Thermoplastic Elastomers (TPEs)

The major drawback of the vulcanization process is the covalent, irreversible crosslinking of chains, which does not allow for recycling (i.e. reshaping of the material) and is also prohibitive for facile thermal processing like injection molding.<sup>[16,17]</sup> Based on the discovery of the living anionic polymerization in 1956 (section 1.2),<sup>[17]</sup> a new fundamental concept for block

copolymer formation by iterative addition of different monomers was introduced.<sup>[18]</sup> With the synthesis and characterization of ABA triblock copolymers based on polystyrene as “hard” segment A (high glass transition temperature) and polyisoprene or polybutadiene as rubbery component B (low glass transition temperature) and its patent registration by Milkovich and Holden of Shell Chemical Company,<sup>[19]</sup> living anionic polymerization gained industrial importance, since triblock copolymers with an elastic mid block component were revealed as an attractive alternative for chemically crosslinked rubber materials.

Motivated by their excellent properties, a fundamental understanding of polymer miscibility and block compatibility finally resulted in the now well-known class of thermoplastic elastomers (TPEs). In these materials, crosslinking is achieved by phase separation of the vitrified high glass transition blocks, such as polystyrene. As a consequence of their immiscibility, the end blocks phase-separate in the bulk state and thereby pin the rubbery mid block. These vitrified hard domains act as crosslinks and allow for thermoreversible melting and reprocessing above the order-disorder temperature. One may regard such structures therefore as “supramolecular elastomers”.

The first fundamental observations were made in the 1930ies by blending liquid plasticized PVC (poly(vinyl chloride)) with NBR (acrylonitrile-butadiene rubber).<sup>[14,20]</sup> As a consequence, elastic materials with rubber-like properties were obtained that did not require vulcanization. The thermal processability allowed fibers to be made by melt extrusion or spinning from solution, while keeping excellent elastic properties of elastomers.<sup>[21]</sup> Polyurethane based structures can be considered as the first thermoplastic elastomers (TPEs) and were obtained by diisocyanate/diol polyaddition.<sup>[22]</sup> Commercial polyurethane based TPEs (also known as “TPUs”) were introduced in the 1960’s by B.F. Goodrich, Mobay, Upjohn, Bayer AG and Elastogran and nowadays still are in the focus of interest.<sup>[14]</sup>

Within the scope of this review, the living anionic polymerization to prepare TPEs shall be in focus. Nevertheless, it ought to be mentioned that the ring-opening polymerization or controlled radical polymerization are alternative methods to realize those structures.<sup>[23–25]</sup>

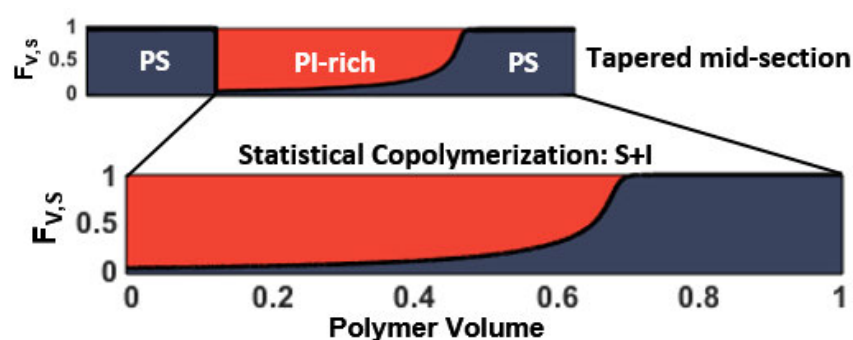
## Living Anionic Polymerization

Another milestone was set by Michael Szwarc, who coined the term “living anionic polymerization” in 1956, realizing that anionic polymerization proceeds without chain termination or transfer reactions.<sup>[17,18]</sup> The living nature of the anionic chain end was concluded, based on the observed increase in viscosity upon consecutive addition of a styrene solution even after completion of the previous step. Although triblock copolymers were synthesized, the sequence of monomer addition steps resulted in the unfavored ISI block sequence (section 2.4). In addition, the bifunctional sodium naphthalenide initiator used by Szwarc required THF as a solvent, resulting in a high content of the 3,4-PI regioisomer with high glass transition temperature.<sup>[26]</sup> Since the research on polyisoprene elastomers via anionic polymerization targeted high *cis* 1,4-PI contents in analogy to the natural rubber structure, the elastomer research groups were not interested in the polar polymerization system used by Szwarc.<sup>[26,27]</sup> Only one year later, Hsieh and Tobolsky reported a method for the homogeneous initiation of isoprene by using *n*-butyllithium.<sup>[28]</sup> They also observed the desired, nearly exclusive formation of the *cis*-1,4 structure, when the reaction was performed in *n*-heptane.



On the other hand an increased content of 3,4-PI in diethyl ether and THF.<sup>[29–31]</sup> Later in that year, Porter combined the principle of alkyllithium initiation and the living nature of monofunctional carbanions to produce SBS block copolymers with the desired high *cis*-1,4 PI content.<sup>[32]</sup> In 1958 Phillips Petroleum Company patented the polymerization of styrene, butadiene and the respective copolymerization.<sup>[26,27,32]</sup> Already at that time, the extent of styrene incorporation was estimated to increase with conversion, leading to so-called “tapered” blocks (shown for P(I-co-S) in Figure 1).<sup>[19]</sup> Similar to PI-*b*-PS block copolymers obtained by consecutive monomer addition and polymerization steps, this structure possesses a block-like character, which enables phase separation. However, instead of a pure polydiene block, a polydiene-rich copolymer block is formed, with gradually increasing styrene content, until finally a pure PS block is obtained. This type of block-like architectures was later found to be attractive for designing the phase behavior of block copolymers in TPEs (section 2.5).<sup>[33,34]</sup> As mentioned in the previous section, subsequently, Holden and Milkovich of Shell Co. produced ABA triblock copolymers relying on both polyisoprene and polybutadiene as the flexible “soft” mid block component amounting to 75-80%<sub>vol</sub> and analyzed their mechanical properties comprehensively.<sup>[19]</sup> They also utilized the copolymerization strategy to produce tapered triblock copolymers (Figure 1) and showed that the non-tapered and tapered triblock architectures of the SBS and SIS type are thermoplastic elastomers. 1965 a series of triblock copolymers was introduced as commercially available products under the trademark “Kraton”.<sup>[35]</sup> These thermoplastic elastomers were named after Kratos, the Greek god of strength and brother of Nike, the god of victory, for their unique strength properties.

These materials can be considered to be the first commercialized TPEs produced by living anionic (co)polymerization.



**Figure 1:** Top: Visualization of a tapered SIS triblock copolymer TPE. Bottom: Highlighted gradient profile (instantaneous styrene volume incorporation  $F_{V,S}$  as a function of the polymer volume) of a tapered block copolymer, obtained by statistical copolymerization (alkyllithium initiation; hydrocarbon solvent).<sup>[36]</sup> Copyright 2020. Adapted with permission American Chemical Society.

In the last decades, the living anionic polymerization has evolved as a powerful tool to control comonomer sequences and to tailor the properties of the resulting materials.<sup>[37]</sup> The “living” nature of the anionic chain ends allows to prepare block sequences by the consecutive addition of different monomers or monomer mixtures, resulting in well-defined molecular weights and narrow molar mass distributions (usually  $\bar{D} < 1.1$ ).

## Commercial Application of TPEs

The manifold accessible structures and beyond that the unlimited possibilities of compounding make TPEs tailorable for a vast variety of applications.<sup>[23,24,38]</sup> Therefore, it is not surprising that the global TPE market size is estimated to be about 20 billion US\$ in 2021 and is expected to grow by around 30% within the next five years.<sup>[39]</sup>

Commonly TPEs benefit from their self-assembling morphologies and hence reinforcing nature of styrenic block copolymers (SBCs) (sections 2.2 & 2.3). This strength is commonly higher than that of most chemically crosslinked elastomers. Together with the scope of compounding, it is possible to customize the material properties.

### Compounding

In plastics engineering compounding denotes the admixture of additives or filler materials. Oftentimes, compounding is necessary to obtain the targeted properties and likewise achieve good processability. One possibility is blending TPEs with other polymers.<sup>[40]</sup> A common way to strengthen TPEs is the addition of impact modifiers (i.e., (hydrogenated) SBS with high styrenic amounts), or end block resins like poly(phenylene oxide) (PPO), typically increasing the end block  $T_g$ . However, oftentimes PS is blended with TPEs to reduce cost, although the mechanical properties are impaired. On the contrary, the addition of end block plasticizers results in an improved flow and a decrease in  $T_g$ . Beyond that, it is possible to improve processability while decreasing the hardness of the material by the addition of oil, which is enriched in the polydiene domains. While in case of SEBS paraffinic oils are the best choice, in case of SBS and SIS naphthenic oils are utilized because of their superior compatibility with the polydienes.<sup>[23]</sup> Furthermore, numerous fillers are commonly added in formulations, which reduces cost, but also permits the properties to be tuned. Among them range antioxidants and antiozonants, UV absorbers and pigments, fire retardants or dispersants. Due to the complexity of these systems, often contour diagrams are generated with the help of statistical design of experiments to determine the optimum formulation.

### Hydrogenation

For many applications, hydrogenation of the polydiene block is necessary. Since the cost doubles in case of mid block hydrogenation, SEBS and SEPS (i.e., hydrogenated SBS or SIS) are preferentially used in high performance technical compounds.<sup>[41,42]</sup> The major advantages are their outstanding stability (i.e., UV and thermal stability) and superior mechanical performance (higher modulus).<sup>[43]</sup> In addition, hydrogenation also affects the processability of the materials. Crosslinking at elevated temperatures, characteristic for PB, as well as chain scission, which is typical for PI, can be prevented. However, one has to be aware of the potential crystallization of hydrogenated 1,4-polybutadiene, which can impede the devised use.<sup>[44,45]</sup> Selective hydrogenation of the PI or PB blocks can be carried out with the Ni/Al catalyst system in a 1:4.25 Ni/Al atomic ratio, at ambient temperature and moderate pressures.<sup>[41,42,45,46]</sup>

### ***Selected Applications***

The development of SBCs for the global market comprises bumpers, fenders, but also weather stripping or sound dampening panels. The latter consist of SIS polymers with high 3,4-PI content, leading to good vibration dampening at room temperature. Modification of bitumen, i.e., roofing and paving, is another large market. Advantage is taken of an improved strength at elevated temperatures, but at the same time reduced fatigue and low temperature cracking due to the increased ductility that prevents water intrusion. For the same reasons, hydrogenated SBCs are used for wire and cable sheathing. In this case flame retardants are added. SBCs also find application as adhesives and sealants, which are mostly solvent based. Since TPEs are able to uniformly dissipate energy throughout the bulk, adhesives benefit from their strength, flexibility and high extendability.

Furthermore, PS-based TPEs find application in the medical sector. Mostly, the compounds are based on hydrogenated SBCs together with polypropylene and oil, resulting in clear and flexible materials that are sterilizable by radiation, ethylene oxide or steam. They are used as tubes, surgical draping or for syringes.<sup>[47]</sup>

Another application field for hydrogenated SBCs that actually drove the commercialization of hydrogenated TPEs is the viscosity index improvement of motor oils, facilitating lubrication at high temperatures while preserving comparably low viscosities at low temperatures. Here, hydrogenated SBCs based on isoprene are preferred, because crystallization of hydrogenated polybutadiene blocks has to be avoided, but at the same time degradation in the engine is undesirable.

Finally, the use of TPEs for footwear has to be mentioned, being the first commercial application of SBCs with the invention of direct injection molding for shoe soles in the 1960ies. It still accounts for a big share of today's applications, benefiting of the good wet grip even at low temperatures.

### **Rational Design of Sequence-Controlled TPEs**

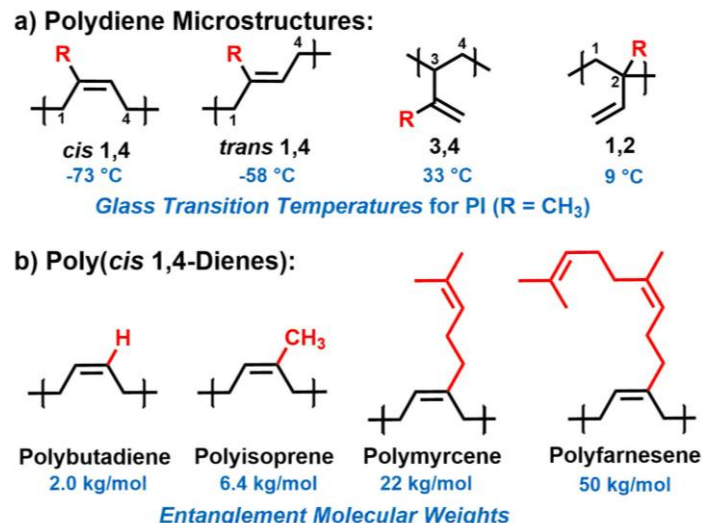
Control of the chain architecture is crucial for the development of macromolecules with defined properties.<sup>[48]</sup> Inspired by nature, the extent of biomimetic approaches increases, since scleroproteins (e.g. proteins like collagen or silk fibroin) with perfectly controlled monomer sequence and secondary and tertiary structure play a key role for the mechanical properties of biological structures in living organisms.<sup>[49]</sup> However, demanding and time-consuming strategies are mandatory for the synthesis of uniform, monodisperse ( $\mathcal{D} = 1$ ) *sequence-defined* macromolecules.<sup>[50]</sup>

In contrast, the synthesis of TPE materials usually relies on rather simple, but straightforward processes, leading to non-uniform, disperse (usually  $1 < \mathcal{D} \leq 1.3$  for chain-growth polymerization techniques), *sequence-controlled* materials.<sup>[51]</sup> For example, in the living anionic polymerization both consecutive monomer addition steps and direct copolymerization reactions are employed to control the block sequence, enabling the resulting properties to be tailored on an industrial scale. Variation of different parameters, e.g., monomer composition, comonomer and block sequence, topology (linear, branched or graft copolymers) lead to a

rather broad range of properties, which can be tailored for the final application. An overview of their consequences for morphologies and mechanical properties will be given in the following sections.

### Choice of Monomers

Although the living anionic polymerization can be utilized to afford acrylate-based TPE materials (e.g., KURARITY® from Kuraray<sup>[52]</sup>), the polymerization of 1,3-dienes (low  $T_g$  component) with styrene derivatives (high  $T_g$  component) is the dominant strategy for TPEs (e.g., Styrolux® or Styroflex® from BASF<sup>[53]</sup>). While the latter typically shows full monomer conversion in the absence of side-reactions ( $T_{\text{polym.}} \approx 20\text{--}80\text{ }^\circ\text{C}$ ; alkylolithium initiation, hydrocarbon solvents),<sup>[54–58]</sup> the polymerization of (meth)acrylic monomers requires specific reaction conditions (low temperatures, less nucleophilic and sterically hindered initiators, Lewis base and/or Lewis acid ligands), depending on the monomer, in order to avoid reaction of the active anions with the carbonyl group.<sup>[59–62]</sup> As the low nucleophilicity of the acrylate-based anionic species impedes the controlled crossover reaction (Figure 16) to styrene or (non-functional) 1,3-dienes, the polymerization of the acrylate has to be initiated by the more reactive polystyryllithium or polydienyllithium species.<sup>[63]</sup> In addition, bifunctional initiators, coupling strategies or macromonomer approaches can be used to widen the scope of accessible block sequences (section 2.4) and chain topologies (section 2.7). However, in terms of the resulting material properties limitations are not only set by the controlled (co)polymerization.



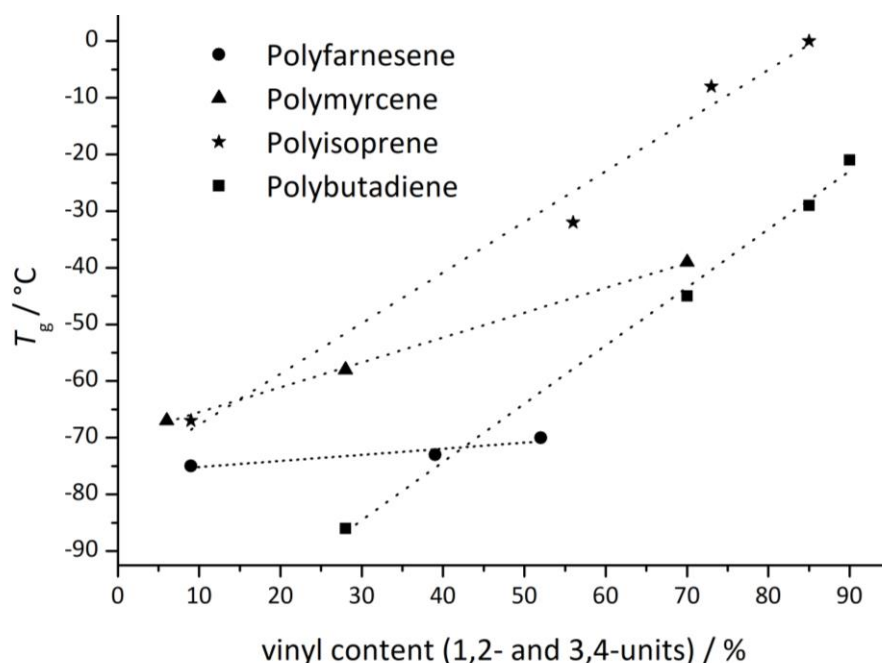
**Figure 2:** a) Stereo- and regioisomers of polydienes. b) Selection of *cis*-1,4-polydienes obtained by living anionic copolymerization and their entanglement molecular weights.<sup>[64,65,66]</sup>

In the polymerization of 1,3-dienes the *cis*-1,4 repeating unit (Figure 2a) is preferred because of the resulting low  $T_g$ , high thermal stability and lower entanglement molecular weight of the respective polydienes. Consequently, functionalized heteronuclear 1,3-dienes are usually avoided, as they tend to coordinate the lithium atom, increasing the side-chain vinyl content and consequently the  $T_g$  (so-called “randomizer effect”; section 2.6). Nevertheless it has to be noted that a high vinyl content is sometimes targeted for further post-polymerization modification reactions<sup>[67]</sup> or to suppress crystallization, which is especially pronounced in hydrogenated 1,4-polybutadiene.<sup>[68]</sup> Cyclic 1,3-dienes (e.g., 1,3-cyclohexadiene<sup>[69]</sup> or

benzofulvene<sup>[70]</sup>) are less attractive as a rubbery component for TPE materials, as the polymerization leads to covalently bridged backbone atoms and consequently a strong increase of the  $T_g$ .<sup>[71]</sup> However, depending on the microstructure composition (i.e. use of hydrocarbon or polar solvents during the polymerization; section 3.1), they can serve as a high- $T_g$  component.<sup>[72]</sup>

Considering these limitations, the choice of 1,3-dienes shown in Figure 2 permits structural variation to adjust the resulting properties.  $\beta$ -Myrcene and  $\beta$ -farnesene are bio-based terpene monomers, that are produced on large scales from turpentine oil<sup>[73]</sup> or sugar cane,<sup>[74]</sup> respectively. The resulting polymers (Figure 2b) have been introduced for instance in tire mixtures.<sup>[75]</sup> Another potential bio-based monomer for carbanionic polymerization represents the 1,2-disubstituted diene  $\beta$ -ocimene, that so far only has been catalytically polymerized.<sup>[76]</sup> By increasing the length of the side-chain from polybutadiene to polyfarnesene, an increase of the entanglement molecular weight from  $M_e = 2.0$  to 50 kg/mol is observed,<sup>[64,65]</sup> which can be explained by an increase in persistence length.<sup>[77]</sup> This shifts the topology stepwise from a linear chain to a graft-type copolymer architecture, also resulting in remarkably different properties (section 2.7).

Furthermore, the  $T_g$  of the resulting polymers depends on the vinyl content to a different extent for distinct dienes (Figure 3). The order of increase in the glass transition temperature correlates to the length of the side chain. In case of PI, the additional side chains of the 1,2- and 3,4-units drastically increase the rotational energy barrier and hence limit the molecular motion, whereas for polymyrcene (PMyr) and polyfarnesene (PFar) the influence of the vinyl content on the free volume is considerably smaller, leading to a weaker dependence of the  $T_g$  on the incorporation mode.<sup>[78,79,80]</sup>



**Figure 3:** Glass transition temperature as a function of vinyl content for polybutadiene, polyisoprene, polymyrcene and polyfarnesene <sup>[80,81]</sup>. <sup>[81]</sup> Copyright 2020. Adapted with permission from American Chemical Society.

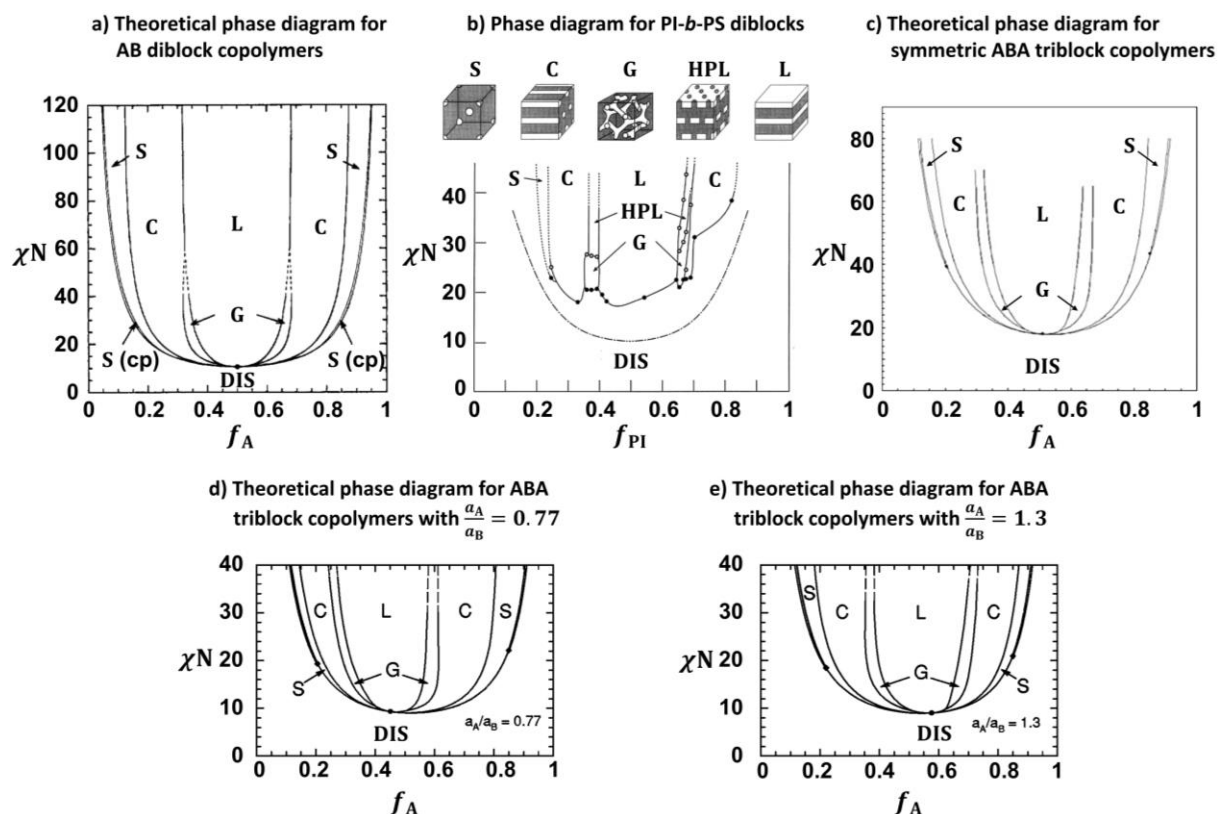
Due to their good accessibility and low entanglement molecular weight, polybutadiene and polyisoprene are by far the most important compounds for synthetic rubbers. Compared to

polyisoprene, the lack of merely one methyl group in butadiene leads to a considerably lower entanglement molecular weight by a factor of more than three.<sup>[65]</sup> However, this also contributes to its difficult handling ( $T_{\text{boiling}} \approx -4\text{ }^{\circ}\text{C}$ ) as well as the undesired crystallization in the hydrogenated state.<sup>[68]</sup> Moreover, due to the growing awareness of the negative impact of fossil resources, the demand for eco-friendly and “green” products has increased within the last years, for which reason manufacturers harness bio-based monomers.<sup>[79,82]</sup>

With respect to the choice of the styrenic monomer, besides styrene only 4-methylstyrene (4-MS) has an industrial relevance for the synthesis of TPEs. However, implementing alkyl-substituted styrene derivatives in copolymers with 1,3-dienes enhances the miscibility (i.e., lower Flory-Huggins parameter) in general, as shown for the poly(4-MS)/PI and the poly(4-*tert*-butylstyrene)/PI systems.<sup>[83,84]</sup> Nevertheless, by targeting high molecular weights, this reduced segregation strength may also be desired to lower the order-disorder transition temperature ( $T_{\text{ODT}}$ ; section 2.2) and moreover, a steeper gradient is formed upon copolymerization in non-polar solvents (section 3.1).<sup>[85]</sup> However, it is important to emphasize that alkyl-substituted styrene derivatives contain acidic benzylic protons, whose participation in chain transfer reactions has to be suppressed. This is achieved when the polymerization temperature is restricted to room temperature or below.<sup>[85–88,89]</sup>

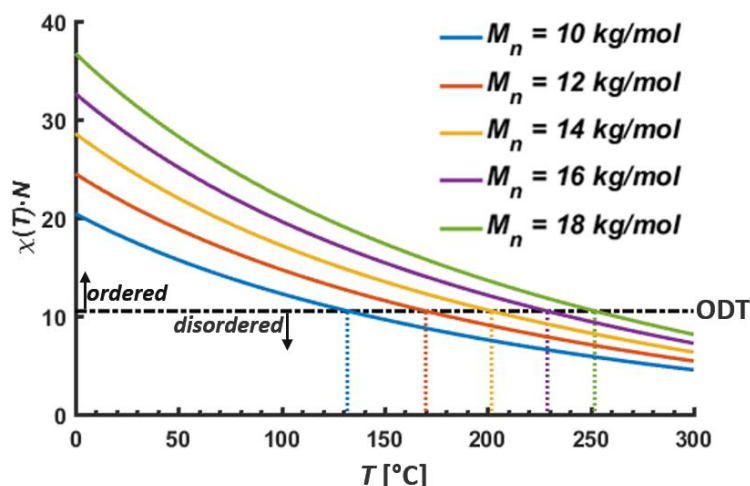
### Effect of Molecular Weight and Physical Limitations

The strong segregation of block copolymers with flexible, low- $T_g$  and high- $T_g$  blocks results in elastomers that are thermoreversibly crosslinked by the vitrified “hard” (low- $T_g$ ) domains. Hence, phase separation is a crucial requirement. Based on Leibler’s self-consistent mean-field theory (SCFT) and de Gennes’ random-phase approximation it is possible to predict the expected phase state for block copolymers (e.g., PI-*b*-PS).<sup>[90,91]</sup> The molecular weight directly affects the segregation strength, which is quantified by the product  $\chi_{\text{AB}}N$ , where  $\chi_{\text{AB}}$  is the Flory-Huggins interaction parameter (i.e., enthalpic interaction for the given repeating units of type A and B) and  $N$  denotes the total degree of polymerization (entropic contributions). For the phase behavior of symmetrical diblock copolymers, the order-disorder transition (ODT) is predicted at  $(\chi_{\text{AB}}N)_{\text{ODT}} = 10.5$ <sup>[90]</sup> (Figure 4a), whereas for symmetric ABA triblock copolymers the minimum value for phase separation is calculated with  $(\chi_{\text{AB}}N)_{\text{ODT}} = 18$ .<sup>[92]</sup> At equal volume fractions (Figure 4c) the minimum ODT is at a volume fraction  $f_A$  of 0.5, while for a ratio of the statistical segment lengths,  $a_A/a_B$ , different from unity, the phase boundaries are shifted (Figure 4d,e).<sup>[93]</sup> Considering asymmetric triblock copolymers, a shift of the order-order phase boundaries (OOT) accompanied by an increase in domain spacing is predicted.<sup>[94]</sup> In general, large molecular weights are desired for phase separation, depending on the magnitude of  $\chi_{\text{AB}}(T)$  (typically,  $M_n \approx 10\text{ kg/mol}$  for symmetric S/I diblock copolymers for a reasonable operating temperature window, Figure 5).<sup>[95]</sup> In addition, high mid block molecular weights exceeding the entanglement molecular weights by far are relevant to provide multiple entanglement per chain, which translates to tough materials.<sup>[96]</sup>



**Figure 4:** Phase diagrams for AB diblock copolymers a) calculated using the mean-field theory<sup>[97]</sup> and b) experimentally determined for PI-*b*-PS.<sup>[57]</sup> Phase diagram for symmetric ABA triblock copolymers with c) equal statistical segment lengths ( $a_A/a_B = 1$ ) or d,e) various ratios calculated with the self-consistent field theory (SCFT).<sup>[92,93]</sup> The phases are denoted as follows: S = bcc spheres ( $\text{Im}\bar{3}\text{m}$ ), S (cp) = close packed spheres, C = cylinders, G = gyroid ( $\text{Ia}\bar{3}\text{d}$ ), HPL = perforated layers (believed to be metastable), L = lamellae, DIS = disordered. The respective experimental morphologies found are illustrated under b). The dashed-dotted line is the mean field prediction for the order-disorder transition (ODT)<sup>[90]</sup>.<sup>[57,92,93,97]</sup> Copyright 1995, 2006, 1999 and 1996. Adapted with permission from American Chemical Society, John Wiley & Sons Inc and American Institute of Physics.

Thermoplastic elastomers are typically processed by high-speed melt extrusion. For this purpose disordered melts are preferred in terms of their lower melt viscosities compared to their phase separated analogues.<sup>[53,61,98]</sup> The vast majority of hydrocarbon polymers exhibits pronounced miscibility at higher temperatures due to the temperature dependence of  $\chi_{AB}(T)$ . The order-disorder transition temperature  $T_{\text{ODT}}$  has to be located above the highest glass transition (or melting) temperature of the copolymer, because phase separation and nanodomain ordering has to occur already in the melt above the glass transitions of both components, where the movement of the chains is unhindered. Otherwise, cooling the materials from the disordered state (i.e.,  $T > T_{\text{ODT}}$  and  $T > T_g$ ) vitrifies the domains (i.e.,  $T \approx T_g$ ), which impedes consecutive self-assembly to macrophase-separated domains at lower temperatures (i.e.,  $T < T_{\text{ODT}}$  but  $T < T_g$ ). Hence, carefully adjusting  $N$  leads to a  $T_{\text{ODT}}$  located above the  $T_g$  ( $T_{\text{ODT}} > T_g$ ) of the high  $T_g$  component, but below the degradation temperature of the polymer.<sup>[95]</sup> For most block copolymers this fits in the range of  $T_{\text{ODT}} \approx 100\text{--}250\text{ }^\circ\text{C}$ .<sup>[65]</sup> Taking a volume-symmetric PS-*b*-PI diblock copolymer as an example ( $\chi_{\text{IS}}(T_{\text{ODT}}) \cdot N = 10.5$ ), the  $T_{\text{ODT}}$  can be calculated in dependence of the molecular weight (Equation Set S1, Supp. Inf.). As visualized in Figure 5, the  $T_{\text{ODTs}}$  (dotted vertical lines) increase from  $T_{\text{ODT}} \approx 130\text{ }^\circ\text{C}$  to  $\approx 250\text{ }^\circ\text{C}$  by increasing  $M_n = 10$  to  $18\text{ kg/mol}$ .



**Figure 5:** Visualization of the phase segregation strength  $\chi_{is}(T) \cdot N$  as a function of the temperature for PI-*b*-PS of different molecular weights ( $M_n \sim N$ ). The dashed-dotted horizontal line is the mean field prediction for the ODT at  $\Phi_{PI} = 0.5$ .<sup>[90]</sup> Order-disorder transition temperatures for  $\chi_{is}(T) \cdot N = 10.5$  are indicated as a dotted vertical line.

As a consequence, the targeted molecular weight must be adjusted carefully to the location of the ODT of the respective morphology and  $\chi_{AB}(T)$  of the respective monomer combination. Of course, the latter is a function of several parameters, as for example the chosen monomer combination, the comonomer sequence (section 2.5) and the polymer topology (e.g., linear- or star-type, section 2.7).

### Microdomain Morphologies

The *block volume fraction* ( $\Phi_A = 1 - \Phi_B$ ) directly determines the formed microdomain morphology in the melt. This is visualized in the phase diagram, which assigns the morphology to  $\Phi_A$  for a given value of  $\chi_{AB}N$  (Figure 4a,b). In general, the ODT shifts to larger values for asymmetric block volume fractions ( $\Phi_A \neq 0.5$ ) beyond the classical lamellar phase.<sup>[57]</sup> Hence, a change of the block volume fraction can also lead to an ODT for similar molecular weights. Usually phases are distributed asymmetrically around  $\Phi_A = 0.5$ , which is explained by differences in the space-filling characteristics (i.e. the conformational asymmetry) that shifts the phases beyond the value anticipated for symmetric diblock copolymers ( $\Phi_{LAM} = 0.5$ ).<sup>[57,99]</sup>

Since the microdomain morphology found in the bulk state dictates the resulting mechanical properties, its alteration offers the potential to combine the properties of the two chemically connected polymers.<sup>[53]</sup> While low- $T_g$  polymers exhibit rubbery properties (i.e., large elongation at break), high- $T_g$  polymers are stiff and hard materials (i.e., high yield point, low strain at break). If a microdomain morphology with one continuous phase is formed, as it is the case for spheres or cylinders, the mechanical properties of the block copolymers are usually governed by the matrix (i.e., the continuous phase).

For example, the elastic deformation in a continuous low  $T_g$ -phase ( $\Phi_{elastic} \gg 0.5$ , e.g.,  $\Phi_{PI} \geq 0.7$  for PI-*b*-PS to reach a cylindrical structure, see Figure 4b) occurs without deformation of the high- $T_g$  phase, which leads to thermoplastic elastomers with a highly reversible elastic deformation, whereas a continuous polystyrene matrix leads to rather brittle thermoplastic materials that stand out with a high modulus and hence impact strength. On the other hand, if a microdomain morphology with two continuous phases is formed (e.g., lamellae), fairly soft

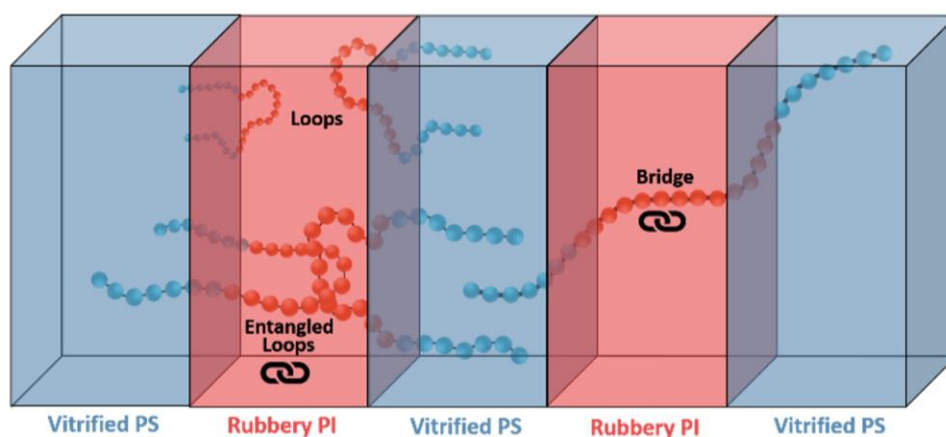


plastomers without pronounced yield point or elastic recovery but extended plastic deformation are obtained. Depending on monomer combination and comonomer sequence, also bicontinuous (non-classical) morphologies are observed (e.g., the gyroid structure, space group  $Ia\bar{3}d$ ).<sup>[57]</sup> For these structures a comparably large elastic modulus is found, which is explained by its bicontinuity, meaning that the interconnected continuous high- $T_g$  phase must deform as well, when the low- $T_g$  matrix is deformed.<sup>[100]</sup>

This wide spectrum of materials with differing characteristics that can be obtained from only two building units, varying polymer architecture has been covered by numerous investigations, showing that increasing the asymmetry in the block volumes enhances curvature of the domains in the melt, which finally leads to phase transitions from lamellar layers via cylinders to spheres (classical morphologies).<sup>[101]</sup>

### Effect of Block Sequence and Multiblock Copolymers

Either *ABA* or *BAB* triblock copolymers are obtained by further increasing the block number from an AB diblock copolymer by one polymer block. This change of the block sequence influences the microphase separation and the affiliated mechanical response. For example, the need to locate two block junctions at the domain interface reduces the conformational entropy. This leads to increased miscibility of an  $A_{n/2}B_mA_{n/2}$  triblock compared to an  $A_nB_m$  diblock copolymer (i.e., similar chain length).<sup>[102,103]</sup> However, compared to an  $A_{n/2}B_m$  diblock obtained by hypothetically snipping the triblock into half, phase separation is facilitated for the triblock copolymer, as revealed in experimental and theoretical studies. This trend follows by further increasing the block numbers to multiblock copolymers (see later in this section).



**Figure 6:** Visualization of conformations described for SIS triblock copolymers. The bridged conformation provides mechanical properties beyond entanglements.

In triblock copolymers, the presence of a mid block enables different chain conformations.<sup>[104]</sup> Whereas in the *bridged conformation* both block junctions are tethered to different interfaces, both end blocks reside in the similar microdomain in the *looped conformation* (Figure 6). The bridging and looping fraction exert a significant influence on the equilibrium morphologies.<sup>[55,105,106]</sup> As shown by Spontak *et al.*, the bridging conformation leads to a comparably larger reduction in the equilibrium domain sizes than the looping conformation.<sup>[106]</sup>

Although changes in the phase behavior are evident, they are less significant in comparison to those observed in the mechanical properties of SIS triblock copolymers<sup>[93,94,96,107]</sup>. Here, the

bridged mid blocks connect the vitrified domains in addition to entanglements and thus enhance the mechanical properties of the copolymers.<sup>[93,102,105,108–110]</sup> As a consequence the fraction of bridged mid blocks ( $\approx 45\%$ ) is of particular interest and has been in the focus of several studies.<sup>[56,105,111]</sup> For example, Bates *et al.* were able to favor the bridged (or looped) conformation in dependence of the applied shear rate and amplitude. This resulted in an orientation of the lamellar domains in the perpendicular or parallel orientation.<sup>[110,112]</sup> Watanabe *et al.* investigated the loops-to-bridges ratio in SIS triblock copolymers in dependence on the sample history. They could show that quenched chain configurations obtained when the samples were not annealed at  $T > T_g^{\text{PS}}$  exhibit smaller number fractions of knotted loops or bridges, which was attributed to the extra constraint for the chain motion of the polyisoprene mid block.<sup>[105]</sup> A comprehensive review on TPE materials emphasizing triblock structures and typical structure property relationships is given by Mays and coworkers.<sup>[24]</sup>

Cohen *et al.* oriented the lamellae of a SBS triblock copolymer with 45%<sub>wt</sub> PS by roll-casting. They investigated the mechanical properties in dependence of the lamellar orientation.<sup>[113]</sup> Stretching the lamellae along their axis (parallel orientation) caused the PS layers to break up and release the rubbery layers. In contrast, the perpendicular orientation folded into a “chevron”-like morphology with diagonal orientations. As a consequence, a comparably larger elastic modulus was observed in case of the parallel orientation.

By comparing SIS with the inverted ISI block sequence, significant differences were found in their elastic and rheological behavior.<sup>[96,107]</sup> The mechanical properties of the SIS architectures show results comparable to PI vulcanizates (SBR rubber), and can be considered as a recyclable, melt-processable alternative.<sup>[114]</sup> In contrast, “crosslinking” in ISI triblock copolymers occurs via flexible, low- $T_g$  end blocks, which undergo chain-pullout in the respective domains.<sup>[26,115]</sup>

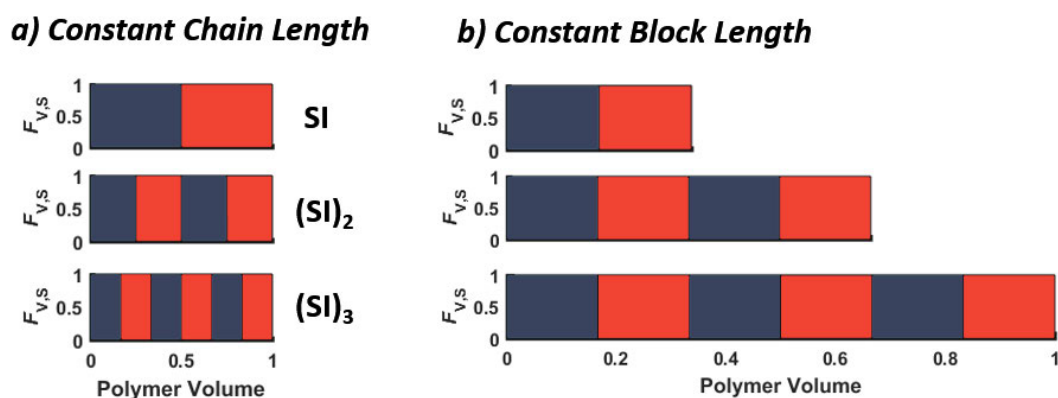
Theoretical results of Matsen *et al.* indicate that even the symmetry of the triblock copolymer (i.e., the relative size of the two end blocks) and the total composition play a crucial role for the morphology (section 2.2, Figure 4).<sup>[93,94]</sup> Comparable experimental results were obtained by Spontak *et al.*, who demonstrated that the  $T_{\text{ODTs}}$  of SIS triblock copolymers are also sensitive to the individual volume fractions of the end blocks for a similar total composition.<sup>[116]</sup>

A reasonable attempt to increase the number of bridges by the design of the molecular architecture is manifested by the so-called *multiblock copolymers*,  $(\text{AB})_n$ . Until the 1990ies almost all multiblock copolymers were synthesized by condensation reactions.<sup>[16]</sup> Unfortunately, the fundamental principle of the step-growth polymerization leads to a high dispersity ( $\mathcal{D} \leq 2$ ) as well as an ill-defined product (mixture of different block numbers), which hampered the systematic investigation of the molecular architecture. Although multiblock copolymer architectures produced by the consecutive multi-step chain-growth polymerization method were already described in 1960, the existing examples are rather rare.<sup>[117]</sup> Synthetic approaches for the implementation of multistep carbanionic polymerizations comprise the break-seal or high-vacuum technique.<sup>[118]</sup> Since the 1990ies Spontak, Bates and others have demonstrated how to capitalize on the living nature of the highly sensitive carbanionic chain end and investigated the phase behavior and the dynamic-mechanical properties of defined  $(\text{AB})_n$  multiblock copolymers based on styrene and isoprene<sup>[56,106,119,120]</sup>. Bates *et al.* found an increased immiscibility for multiblock copolymers with increasing block number and constant block size (i.e. increasing chain length; Figure 7b).<sup>[121]</sup> Spontak *et al.* investigated a series of multiblock copolymers with a similar chain length and a series with constant block length

(Figure 7). Although a contraction of domain sizes is expected for the series with decreasing block sizes (Figure 7a), even the domain sizes of multiblock copolymers with a constant block size were found to decrease with increasing block number (Figure 7b).<sup>[56,106]</sup> This was explained by the increased number of bridged PI blocks caused by the multiblock architecture, which also lead to superior mechanical properties (e.g., an increase of the Young modulus and the strain at break). In the following years, the unique morphological and mechanical behavior of styrene/isoprene based multiblock copolymers was the focus of numerous studies.<sup>[53,110,119,121,122,123,124]</sup>

A commercial product taking advantage of the peculiar property profile inherent in the multiblock structure is Styroflex<sup>®</sup> marketed by BASF (for synthesis: see section 2.6).<sup>[53]</sup> This S/B multiblock copolymer stands out for its high toughness, excellent recovery properties and thermal stability. Furthermore, advantageous features are its high-speed processability appropriate for extrusion and injection molding, and transparency, making Styroflex<sup>®</sup> suitable for palette or food packaging.

In 2018 and 2019 our group introduced the synthesis of tapered multiblock copolymers based on styrene (or 4-methylstyrene) and isoprene by consecutive copolymerization steps (a tapered diblock is visualized in Figure 1).<sup>[54,83,86,125]</sup> This strategy avoids coupling steps as well as demanding fractionation after polymer synthesis. In this case, the multiblock architecture resulted in increased toughness, whereas the “multigradient” comonomer sequence lowered  $\chi_{IS}$  and allowed to reduce the  $T_{ODT}$  in the accessible range for block molecular weights far beyond the entanglement molecular weight (e.g.,  $T_{ODT} \approx 185$  °C for  $P(I-co-S)_3$  with  $M_{n,total} \approx 240$  kg/mol).<sup>[125]</sup>



**Figure 7:** Visualization of sequential  $(AB)_n$  multiblock copolymers with  $n=1-3$ . a) Increasing the number of blocks leads to a decrease of the block length. b) Increasing the number of blocks leads to an increase of the chain molecular weight.

### Tapered Copolymer Blocks – Adjusting the Phase Behavior

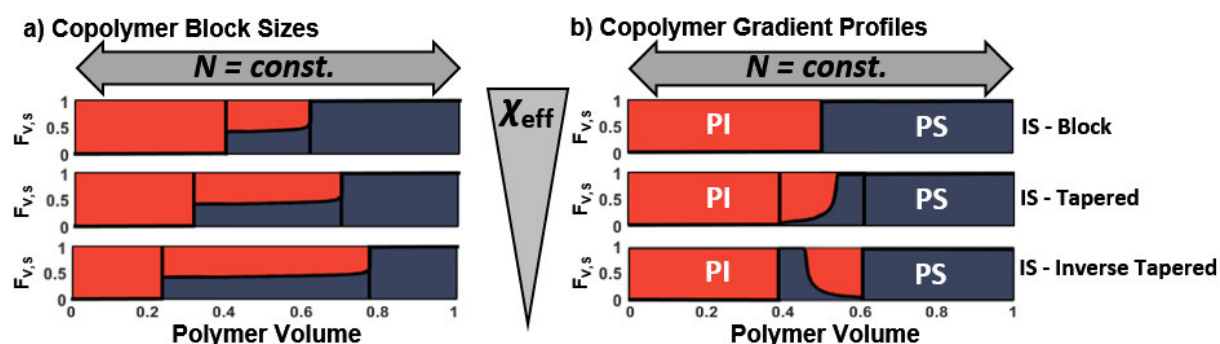
In theory, the consecutive living polymerization of two monomers allows to realize every comonomer sequence by multi-step reactions. In practice, the experimental effort increases with the number of monomer addition steps, the targeted molecular weight and the reaction time, since every monomer addition step bears the risk of chain termination.<sup>[125]</sup> This translates to limitations based on the effort and skill of the synthetic chemist.<sup>[126]</sup> The statistical copolymerization has been proven to offer an excellent tool to design otherwise rather

demanding comonomer sequences in a single step. These are usually classified as block, gradient or alternating copolymers.

Since 1958 up to now the statistical copolymerization of 1,3-dienes with styrene initiated by alkylolithium in hydrocarbons has been of strong industrial and academic interest.<sup>[19,32,127,128]</sup> The resulting “tapered” block structure consists of a polydiene block copolymer containing a small amount of styrene, followed by a steep gradient and a pure polystyrene block.<sup>[129]</sup> The term “tapered block copolymer” was introduced by Geoffrey and Milkovich of Shell Co. to account for both the gradient as well as the block-like sequence (Figure 1).<sup>[19]</sup> In the following years, the copolymerization kinetics and the resulting comonomer sequence were in the focus of several studies.<sup>[127,128,130–132]</sup> Details are given in Section 3.

In extensive work, Kraus *et al.* compared the influence of the comonomer sequence on thermal and dynamic-mechanical properties of block, tapered block and random copolymers and found an increased miscibility (e.g., single  $T_g$ s) for random and tapered copolymers.<sup>[130,133]</sup> The groups of Weidisch and Knoll correlated the mechanical properties of SBS triblock copolymers with differing gradient to their morphology.<sup>[134]</sup> They observed a broadened interface for an asymmetric tapered SBS triblock that led to a lamellar morphology instead of a cylindrical morphology with PB cylinders, that would be the case for the counterpart with a perfect block structure. On the contrary, the triblock with a random S/B mid block showed PS cylinders in a PB matrix. These findings explained the decrease in yield stress with growing gradient and the absence of a pronounced yield point in case of the triblock comprising a random mid block. Cirlin reported that substantial interfacial mixing played a key role during mechanical failure of TPEs.<sup>[135]</sup>

To estimate the degree of segregation and account for the reduction in the enthalpic incompatibility by the polymer composition, the effective Flory-Huggins parameter ( $\chi_{AB,eff}$ ) was introduced according to the binary interaction theory.<sup>[109,136]</sup> This reduction of  $\chi_{AB}$  to  $\chi_{AB,eff}$  was utilized in 1983 by Gronski *et al.*, who synthesized IS diblock copolymers with varying length of random P(I-*ran*-S) copolymer mid blocks (Figure 8a).



**Figure 8:** Parameters that influence the effective Flory-Huggins Parameter ( $\chi_{eff}$ ) for a given monomer pair.  $\chi_{eff}$  was found to decrease with a) increasing copolymer mid block size and b) the copolymer gradient profile.

This allowed the dynamic-mechanical properties to be investigated by systematically increasing the volume fraction of the interphase.<sup>[137–139]</sup> In contrast, Hadjichristidis *et al.* used tapered copolymer mid blocks with the gradient profile visualized in Figure 1. In accordance with the results of Gronski, the size of the copolymer mid block enhanced the compatibility in the system. Furthermore, the stronger reduction of  $\chi_{eff}$  for the inverse tapered systems in comparison to the tapered systems (Figure 8b) was explained by the opposite block sequencing

(i.e., the discontinuity in the gradient profile  $F_{V,S}$  vs. polymer volume; Figure 1). Hence, beyond the mere length, also the gradient profile (i.e. the comonomer sequence) of the copolymer block dictates the phase behavior<sup>[140]</sup> and allows to adjust the resulting thermal and mechanical properties by another independent parameter.

Tapered multiblock copolymers with low dispersity can be formed by repeated addition of a monomer mixture of styrene and isoprene or another diene monomer.<sup>[125]</sup> In this case, mechanical properties are correlated to the thermal and morphological properties of the resulting multiblock copolymers. Repeated addition of a mixture of styrene and isoprene was exploited to generate tapered multiblock copolymer architectures of the  $(AB)_n$  type with up to 10 blocks ( $1 \leq n \leq 5$ ) by our group. Thereby, the polymer chains were subdivided into alternating flexible polyisoprene-rich (PI) domains and rigid polystyrene (PS) segments. All multiblock copolymers exhibited 50 %<sub>mol</sub> of each monomer and therefore a lamellar structure if ordered. The di-, tetra-, hexa-, octa- and decablock copolymers of 80, 240 and 400 kg/mol were investigated. With increasing block number, the block length decreases and segregation becomes weaker. The question was addressed, to which extent the tapered multiblock copolymers are capable of forming ordered, nanosegregated morphologies. Detailed thermal, structural, and rheological investigations showed that the tapered multiblock copolymers with a molecular weight of 240 kg/mol formed ordered phases with the expected lamellar morphology. However, X-ray scattering data and transmission electron microscopy (TEM) images of the octablock and decablock copolymers confirmed weakly ordered structures at ambient temperature. The domain spacing,  $d$ , was found to scale as  $d \sim N^{0.62}$ , where  $N$  is the total degree of polymerization, suggesting stretching of chains and nonideal configurations. Following the structure factor,  $S(q)$ , as a function of temperature revealed that the tapered multiblock copolymers undergo a fluctuation-induced first-order transition at the respective order-disorder transition temperature,  $T_{ODT}$ . The viscoelastic response of the tapered copolymers was controlled by the nanodomain structure, the degree of segregation, nanodomain-bridging configurations of blocks, and also the proximity to the glass temperature of the vitrified PS domains. Interestingly, the tapered hexablock copolymers were found to best combine structural integrity and mechanical toughness, while maintaining a large strain at break (>900%) (Figure 9).

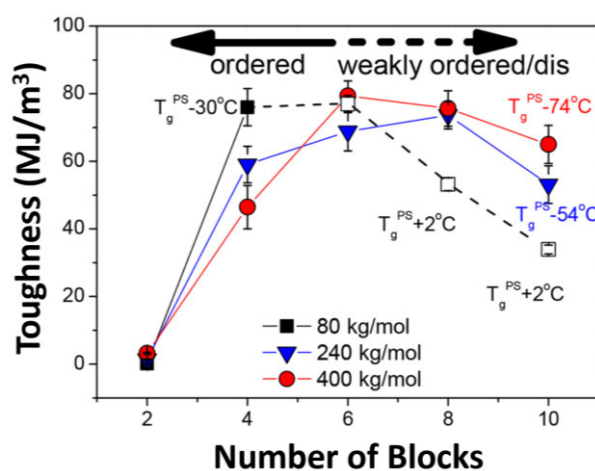
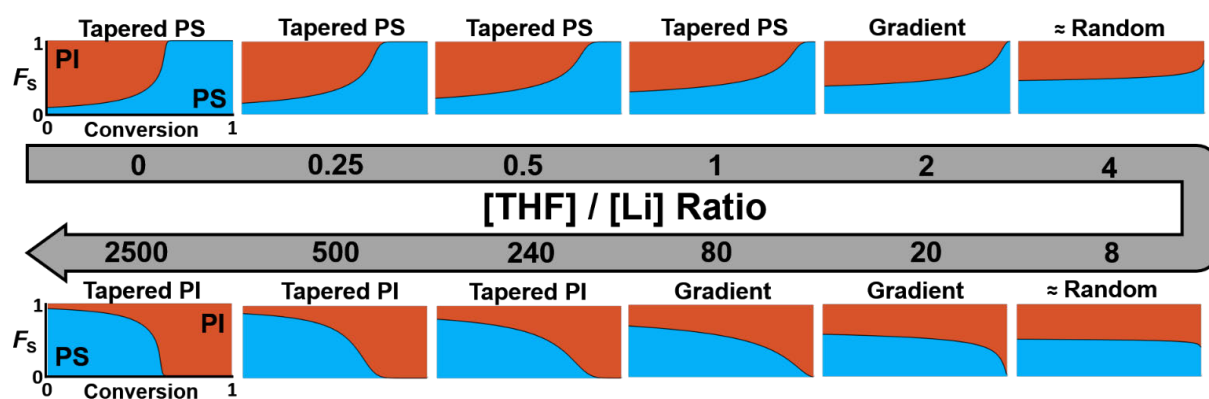


Figure 9: Dependence of toughness on the number of blocks in tapered multiblock copolymers. Solid and dashed arrows indicate ordered and disordered (or weakly ordered) regimes. Open symbols indicate disordered copolymers. Measurements are made at ambient temperature, and the difference to the respective glass transition temperature of the PS block is indicated in the diagram.<sup>[125]</sup> Copyright 2018. Adapted with permission from American Chemical Society.

## Tuning the Comonomer Gradient Profile by the Use of Modifiers

Besides the previously discussed tapered block structure that is characteristic for the statistical copolymerization of 1,3-dienes with styrene initiated with alkyllithium in hydrocarbons, it is possible to tailor the gradient using modifiers, which are sometimes called “randomizers”. Although the underlying concept of affecting the copolymerization kinetics by complex formation (section 3.1, for the proposed mechanism see Figure 17) is known since 1959<sup>[141]</sup> and commonly used in industry,<sup>[53,142]</sup> the use of modifiers is still subject of ongoing research.

Basically, a distinction is made between Lewis bases forming so-called  $\sigma$  complexes (i.e., electron-donors, e.g., amines and ethers), and Lewis acids forming  $\mu$  complexes (i.e., stabilization of the living center through a strong bimetallic complex, e.g. alkoxides), and mixed  $\sigma+\mu$  and  $\sigma-\mu$  complexes, the latter denoting the implementation of two functions within one molecule, e.g. alkoxy alkoxides. The most prominent Lewis bases used are *N,N,N',N'*-tetramethylethyldiamine (TMEDA),<sup>[143]</sup> triethylamine (TEA),<sup>[137–139,144]</sup> tetrahydrofuran (THF),<sup>[36,127,145]</sup> methyl *tert*-butyl ether (MTBE)<sup>[146]</sup> or 2,2-di(2-tetrahydrofuryl)propane (DTHFP),<sup>[145]</sup> while common Lewis acids are alkoxides with lithium,<sup>[147]</sup> sodium<sup>[148]</sup> and potassium counterion<sup>[53]</sup> or compounds with even heavier alkali metals<sup>[149]</sup> as counterion. This was comprehensively reviewed by Carlotti *et al.*<sup>[150]</sup> The effect of Lewis bases on the copolymerization kinetics is detailed in section 3.1 and the effect of varying amounts of THF on the comonomer gradient is shown in Figure 10.



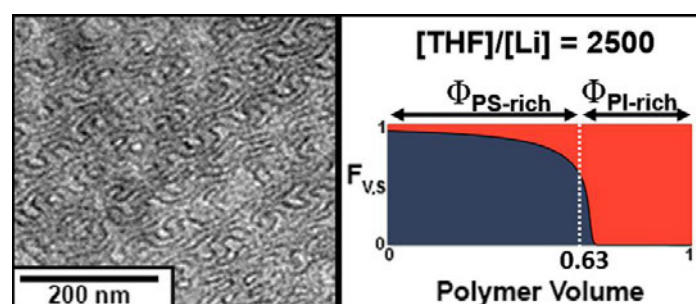
**Figure 10: P(I-co-S) gradient profiles.**  $F_S$ : Instantaneous styrene incorporation. An increase of the [THF]/[Li] ratio, favors styrene incorporation in the early stage of the copolymerization. This finally inverts the gradient from tapered PS block copolymers to tapered PI block copolymers.<sup>[36]</sup> Copyright 2020. Adapted with permission from American Chemical Society.

This nomenclature was first introduced by Teyssié *et al.* for the anionic polymerization of acrylic monomers,<sup>[142,151]</sup> and later adapted to describe the influence of polar modifiers on the anionic polymerization of dienes.<sup>[152]</sup> However, not only the gradient profile is tuned using modifiers, what allows not only to randomize but even invert the monomer incorporation during a statistical copolymerization, but the microstructure is altered. Kozak *et al.* investigated the influence of polar modifiers on the microstructure of polybutadiene and found an enhanced vinyl addition for all types of modifiers but in the following strength:  $\sigma+\mu > \sigma-\mu > \sigma > \mu$ .<sup>[152]</sup> Furthermore, they reported a dependence of the *cis/trans* ratio on the applied complex type, leading to a decreasing ratio from  $\sigma-\mu > \sigma+\mu \approx \mu > \sigma$ . These findings are in line with numerous other investigations.<sup>[153]</sup>



Consequently, the material properties are highly affected by the implementation of such modifiers. As discussed in section 2.5, the increased miscibility (i.e., reduced  $\chi_{\text{eff}}$ ) broadens the interface of the microdomains, which can change the morphology or even inhibit microphase separation: typically, single  $T_g$ s, sometimes even disordered structures show large local composition variations due to the phenomenon of self-concentration and hence two  $T_g$ s are detectable.<sup>[154]</sup> On the other hand, mechanical properties like elasticity and toughness are not only governed by the microdomain morphology, but also by the microstructure (i.e., vinyl content in polydienes, Figure 3), which furthermore affects properties like thermal stability or the operating temperature.

In analogy to the example in the last section, the morphology and the resulting mechanical properties are discussed for styrene-isoprene diblock copolymers with varying amount of THF as a randomizer (Figure 10). All diblock copolymers consist of 50 %<sub>mol</sub> of each monomer, therefore the morphology obtained without randomizer is lamellar. Since no bridging of the PS domains occurs in the tapered diblock copolymers, a rather brittle material is obtained. With a ratio of  $[\text{THF}]/[\text{Li}]=0.5$ , the gradient is flattened and hence the size of the pure PS block is decreased, resulting in hexagonally packed PS cylinders. Due to the change in morphology, the material shows viscoelastic flow beyond the yield point. This is attributed to the isolation of the PS cylinders, which suppresses crack propagation. A further increase in THF content ( $[\text{THF}]/[\text{Li}] = 2$  to 20) leads to disordered states, also displayed in a single glass transition temperature. These polymers lack mechanical properties, meaning that the stretching results in ductile behavior even at low strain. With  $[\text{THF}]/[\text{Li}]=240$ , the gradient is inverted, and PI cylinders are formed. The presence of the continuous PS-rich matrix results in a very hard and brittle material. However, very high THF content does not result in lamellae again, but shows very special structural changes. TEM and SAXS measurements indicate the formation of a bicontinuous morphology (Figure 11). In analogy to the PI-cylinders, the bicontinuous gyroid morphology exhibits a comparably high yield stress and poor toughness.



**Figure 11:** TEM image of P(I-co-S) synthesized at a  $[\text{THF}]/[\text{Li}]$  ratio of 2500 and the respective polymer volume composition profile. The PS-rich phases of the gyroid structure appear electron-opaque (i.e., dark) because the sample was stained with  $\text{RuO}_4$ .<sup>[36]</sup> Copyright 2020. Adapted with permission from American Chemical Society.

Extending this work, the statistical anionic copolymerization of the biobased monomer  $\beta$ -myrcene with styrene in cyclohexane was investigated, focusing on the influence of the modifiers (i.e., Lewis bases) tetrahydrofuran (THF) and 2,2-di(2-tetrahydrofuryl)propane (DTHFP) on the reactivity ratios.<sup>[145]</sup> The bidentate modifier DTHFP affected the reactivity ratios much more than THF: minute amounts (of only 0.35 equivalent relative to Li) are required to randomize the copolymer, and one equivalent to invert the reactivity ratios. Although all copolymers have the same composition (33%<sub>mol</sub> myrcene, corresponding to 39.6%<sub>weight</sub> and 45%<sub>vol</sub>), very similar molecular weights (about 90 kg mol<sup>-1</sup>) and low dispersities (1.06 to 1.10),

different morphologies could be obtained. Lamellar, cylindrical and gyroid structures were identified by TEM and SAXS measurements. In conclusion, the use of modifiers is a versatile tool to tailor the  $T_g$  and hence service temperature, but also material properties in terms of toughness or elasticity.

This may be exemplified by the synthesis of Styroflex<sup>®</sup>,<sup>[53]</sup> a flexible and tough TPE although it contains almost 70% styrene (section 2.4), that features a triblock structure with two PS end blocks and a random P(B-co-S) mid block. THF as randomizer was found to be inappropriate, because the 1,2-vinyl content would rise up to 30% and hence the lower operating temperature would increase significantly. Moreover, hampered thermal stability is often concomitant with high vinyl contents, since gel formation or cross-linking can occur. This was circumvented implementing potassium triethylcarboxide as randomizer in a molar ratio of  $[K]/[Li]=1:30$ , resulting in a random mid block exhibiting a  $T_g$  of approximately -30 °C. Strictly speaking, this random mid block is a multiblock of short PS and PB blocks (Figure 12). This is explained by a change of the degree of aggregation of the organolithium chain ends and an expected exchange of the counterions with the propagating chain ends.<sup>[153]</sup>

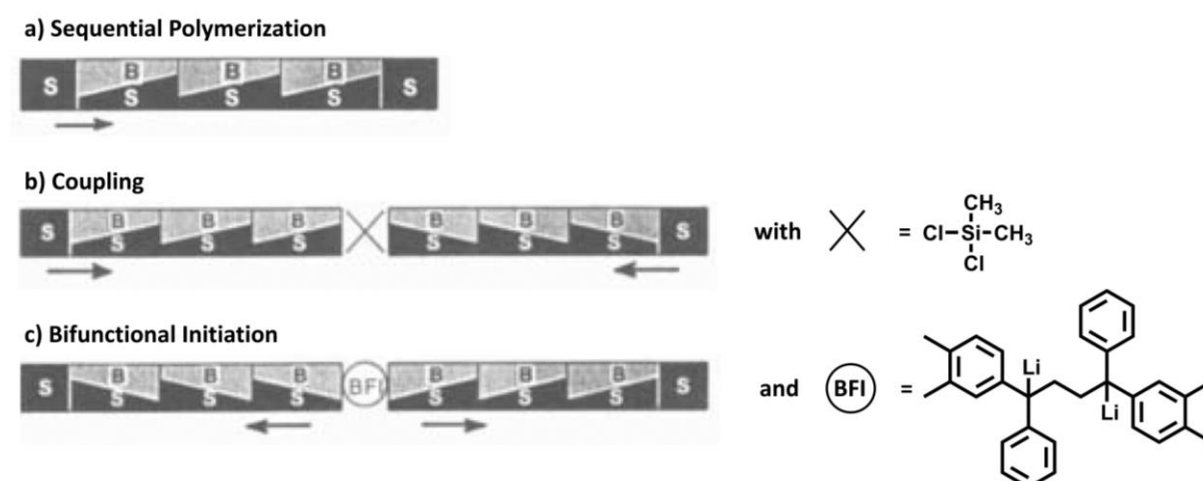


Figure 12: Synthesis routes to Styroflex<sup>®</sup> including a) sequential (co)polymerization of 1<sup>st</sup> styrene, 2<sup>nd</sup> a butadiene-styrene mixture and 3<sup>rd</sup> styrene, b) coupling after sequential (co)polymerization of 1<sup>st</sup> styrene, 2<sup>nd</sup> a butadiene-styrene mixture, and c) bifunctional initiation of a butadiene-styrene mixture and subsequent polymerization of styrene. The bars indicate the chemical composition along the polymer chain.<sup>[53]</sup> Copyright 1998. Adapted with permission from John Wiley & Sons Inc.

## Non-Linear Chain Topologies

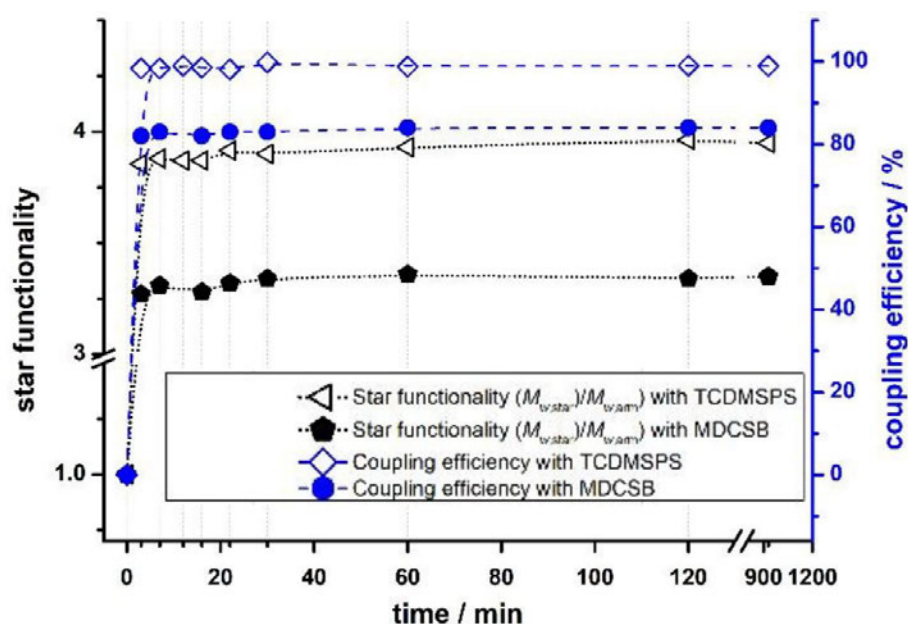
Beyond the classical linear chain topology, also star and brush block copolymers are successfully established TPE materials. These topologies can be obtained by coupling strategies (“arm-first” approach), multifunctional initiators (“core-first” approach) or synthetic approaches relying on macromonomers and can show remarkably different properties.<sup>[59,72,155–157]</sup>

As indicated by the name, the core-first method rests on multifunctional initiators, whose efficiency is often hampered, since retarded initiation of the different arms leads to asymmetric structures. For this strategy, the implementation of controlled radical polymerization is favored over living anionic polymerization, since the latter suffers from strong aggregation phenomena<sup>[155]</sup>. Moreover, usually polar solvents are required to ensure solubility of the initiator, which is



why the microstructure of dienes is affected, namely leading to higher vinyl contents (section 2.6).<sup>[157,158]</sup>

On the contrary, for the synthesis of star polymers via carbanionic polymerization techniques the arm-first method relies on the polymerization of the arms and a final coupling step using electrophilic linking agents or bifunctional monomers.<sup>[156]</sup> In 1962 Morton *et al.* demonstrated the feasibility of this approach.<sup>[159]</sup> The implementation of benzyl halides as coupling agents faces the problem of side reactions, e.g. lithium-halogen exchange.<sup>[160]</sup> This can be circumvented using reagents with multifunctional di- or trichlorosilane moieties<sup>[158,161]</sup> (i.e., reduced nucleophilicity), with a few units of butadiene<sup>[161,162]</sup> or isoprene<sup>[163–165]</sup> (i.e., reduced steric hinderance) or by the reaction with diphenylethene (DPE)<sup>[158]</sup> (i.e., reduced nucleophilicity of the active centers). However, coupling in apolar solvents takes several days and is prone to impurities, which is why often an incomplete coupling is observed. Since this entails demanding purification steps, an acceleration is favorable. This can be achieved by the addition of a small amount of THF<sup>[166]</sup> or the separation of the Si-Cl moieties by spacers.<sup>[158]</sup> Recently, our group applied both principles with the introduction of the tetrafunctional coupling agent tetra[3-(chloro-dimethylsilyl)propyl]silane (TCDMSPS) bearing monochlorosilyl groups, realizing highly efficient coupling of living polystyryl chains within a few minutes (Figure 13).<sup>[167]</sup>

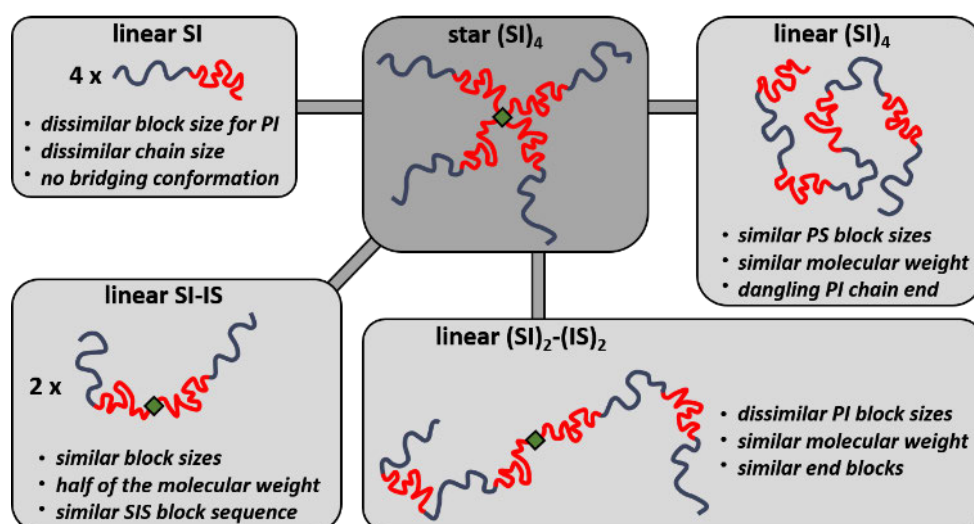


**Figure 13:** Coupling kinetics for the synthesis of PS 4-arm star polymers using the in house-synthesized tetra[3-(chloro-dimethylsilyl)propyl]silane (TCDMSPS) and the commercially available 1,4-bis(methyl-dichlorosilyl)butane (MDCSB). The latter shows a pronounced decrease in star functionality and hence revealed a significantly low molecular weight shoulder arising from uncoupled arms. The coupling efficiency benefits from spatially separated Si-Cl moieties and hence alleviated steric constraints.<sup>[167]</sup> Copyright 2019. Adapted with permission from Royal Society of Chemistry.

Furthermore, a difunctional monomer, e.g., divinylbenzene (DVB), can be used as linking agent, if it is added in latter stages of the polymerization.<sup>[164,168]</sup> Information regarding the number of segments per arm  $N$  and the average number of arms  $f$  can be derived from viscosity measurements, since the radius of gyration  $R_g$  follows the proportionality  $R_g \propto N^{0.6} f^{0.2}$  and  $R_g \propto M^{0.2}$  for constant  $N$ .<sup>[169]</sup> However, the main drawback of this strategy is the ill-defined number of arms, which is why the chlorosilanes are the linking agents of choice in research.

Nevertheless, the use of DVB is technically important, since it can be implemented on large scale and provides the opportunity to produce asymmetric stars.<sup>[170]</sup>

Comparing a *block copolymer* of an  $(AB)_n$  type star with the AB linear arms (cf., structure SI linear and  $(SI)_4$  star in Figure 14), an increased immiscibility has been observed for the star-type architecture in theoretical and experimental studies.<sup>[59,165,171]</sup> Phase diagrams obtained by SCFT calculations show similar microdomain morphologies as found for the diblock analogues.<sup>[57,172]</sup> However, the observed asymmetry in the phase diagram shows a preference for the inner block of the arms to locate inside of the cylindrical or spherical structure.<sup>[59,172]</sup>



**Figure 14:** Comparison of a  $(SI)_4$ -star topology with linear di-, tri- and multiblock analogous structures (grey: PS-chain; red: PI-chain). Symmetries which allow the use of a coupling agent are indicated by a green diamond.

An increase of mechanical properties is observed for this kind of coupling strategies. However, in this case the coupling reaction (i.e., formation of  $(SI)_4$  star) increases the molecular weight and enables bridging of the PI mid block. Hence, the observed toughening cannot be solely attributed to the star architecture but is also a function of the SIS block sequence (section 2.4) and the increased molecular weight (i.e., entanglements; section 2.2).

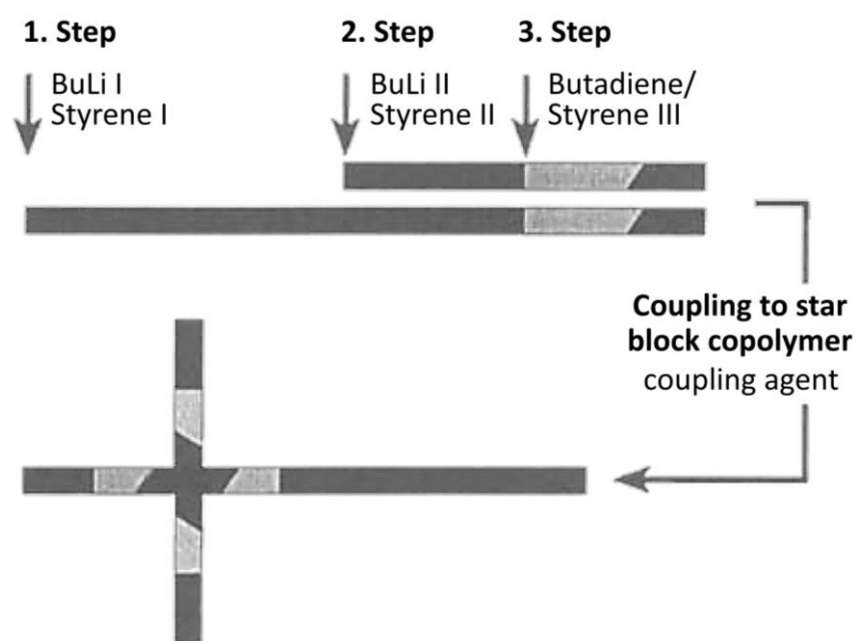
Consequently, the linear coupled analogue ( $(SI-IS)$  linear in Figure 14) serves for a better comparison with the  $(SI)_4$  star. In contrast to theoretical expectations,<sup>[173]</sup> the confined star architecture led to an increased miscibility compared to the linear analogues.<sup>[174]</sup> Fetters *et al.* compared the mechanical characteristics of  $(IS)_n$  star block copolymers with their linear SIS type analogues.<sup>[164]</sup> They found that these star block copolymers had superior tensile properties compared to their linear SIS analogues, saturating when the number of arms is larger than six. The higher tensile strength was attributed to the star topology, leading to an even distribution of stress throughout the network formed by the multiplicity of arms crosslinked at one center (i.e., multiple bridging by a single chain).

Additional studies were performed by our group in collaboration with Register *et al.* by comprehensively comparing the mechanical properties the arms with the coupled 4-arm tapered star copolymers of the type  $[PS-b-P(I-co-S)]_4$ .<sup>[175]</sup> Coupling the triblock copolymers into star copolymers resulted materials outperforming their corresponding linear analogues. This was attributed to an elevated bridging fraction of the rubbery phases and an additional fracture resistance by the bridging chains in the glassy domains. Furthermore, the significant changes

in mechanical behavior are believed to originate in the altered morphology. However, there was no obvious discontinuity going from disordered to ordered copolymers.

These studies support the conclusion that the core junction in multi-arm star topologies acts as a permanent crosslink. An increasing number of arms leads to tough and mechanically stable materials. Similar results are obtained for linear block junctions as present in linear multiblock copolymer architectures (section 2.4).<sup>[55,56,83,125,126]</sup> To the best of our knowledge, a direct comparison of star-block copolymers with the linear multiblock analogues has not been made. However, this is not straightforward, as the mechanical properties are a function of several, usually not independent parameters (phase state, entanglement behavior, molecular conformations), which are difficult to investigate individually (compare (SI)<sub>4</sub> star with (SI)<sub>4</sub> linear and (SI)<sub>2</sub>-(IS)<sub>2</sub> linear in Figure 14). Still, it is peculiar that the increased ultimate toughness and strain at break that are present in the before mentioned [PS-*b*-P(I-co-S)]<sub>4</sub> tapered star copolymers<sup>[175]</sup> are not evident by simply arranging these blocks in a linear multiblock structure.<sup>[125]</sup>

A prominent star-shaped copolymer of industrial relevance is Styrolux® by BASF; a transparent high performance material of exceptional toughness.<sup>[53]</sup> It is used neatly or blended with polystyrene for applications like packaging films and for injection molded parts. This unsymmetric star block copolymer is prepared by sequential anionic polymerization, also involving a second initiator feed to yield a mixture of long and short blocks, and a final coupling step with an oligofunctional coupling agent (often multiepoxides like epoxidized lipids) giving on average unsymmetrical star polymers with four arms (Figure 15).



**Figure 15: Synthesis strategy of Styrolux®, giving unsymmetrical 4-arm tapered star copolymers.** As a first step, a pure PS block is formed adding butyllithium and styrene, followed by further addition of a higher amount of butyllithium and styrene. As a third step, a mixture of styrene and butadiene is copolymerized, leading to a tapered block transition consisting of a short, butadiene-rich and a long, styrene-rich area. These triblock copolymers are finally coupled.<sup>[53]</sup> Copyright 1998. Adapted with permission from John Wiley & Sons Inc.

Beyond star copolymers, graft and brush-like block copolymers are an attractive class of materials to control the physical properties by the conformation of the macromolecular chain.<sup>[176]</sup> Key parameters, such as the length, the density and the entropic and enthalpic

repulsion of the side-chain as well as the length and flexibility of the backbone define the resulting morphological<sup>[177]</sup> and mechanical properties.<sup>[176,178,179,180]</sup>

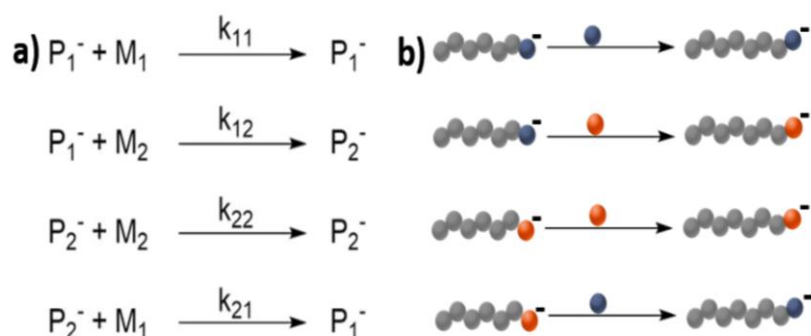
Compared to their linear analogues, the repulsive interactions of the side-chains cause the backbone to stretch.<sup>[181]</sup> Hence, with increasing side-chain length and density the entanglement molecular weight ( $M_e$ ) increases. Interestingly, Hillmyer *et al.* observed that lower graft densities improved mechanical performance. However, this appeared to have less impact on polymers with rigid backbones.<sup>[176]</sup> Relying on this concept, Mays *et al.* combined sufficiently large molecular weights with comparably low grafting densities and observed an increase of mechanical properties in acrylate-based graft block copolymers. These elastic materials showed an excellent high elongation at break ( $\approx 1500\%$ ) and recovery ( $\approx 5\%$  residual strain). In accordance to the results of multi-arm star block copolymers and linear multiblock copolymers, this was explained by the high  $T_g$  poly (methyl methacrylate) (PMMA) side-chains, which allow to pin the structure in multiple vitrified domains (i.e. multiple bridging by single chains).<sup>[182]</sup>

For both star and graft block copolymer architectures a large recovery as well a comparably low melt viscosity is described, underlining the similarities in these highly branched structures.<sup>[176,179,180,182,183]</sup>

This influence of a side-chain is already perceivable to some extent in polyfarnesene (PFar; section 2.1). With the increasing persistence length and hence entanglement molecular weight from PB to PFar, a decrease in toughness, but also a reduced melt and solution viscosity is observable, which is advantageous in high-speed melt extrusion processing.<sup>[184]</sup> In a recent review, polyfarnesene as well as other terpene-based diene monomers have been summarized with a view to their enormous potential for partially biobased TPEs.<sup>[81]</sup>

## Statistical Copolymerization – “*in situ*” Kinetics and “*in silico*” Simulations

In 1944 Mayo and Lewis solved “The Problem of Copolymerization” as they called it.<sup>[185]</sup> In the same year Alfrey and Goldfinger independently developed a similar equation.<sup>[186]</sup> Four fundamental reactions for the formation of copolymers (Figure 16) are proposed for the “terminal copolymerization model”: The homopropagation of either monomer 1 (rate constant  $k_{11}$ ) or monomer 2 ( $k_{22}$ ) and the crossover reaction from a chain end bearing monomer 1 to monomer 2 ( $k_{12}$ ) and vice versa ( $k_{21}$ ). The reactivity ratios are defined by the ratio of homopropagation to crossover rate constant  $r_1 = k_{11}/k_{12}$  and  $r_2 = k_{22}/k_{21}$ .



**Figure 16: Fundamental reactions for the formation of a copolymer via living anionic copolymerization.**<sup>[185,186]</sup>  
 a) Elementary reactions; b) visualization of the terminal model. The reactivity of the last repeating unit (colored) is representative for the polymer chain.

Three years earlier, Wall had introduced a simpler, *non-terminal copolymerization model*, considering that the monomer reactivities are independent of the structure of the chain end ( $k_{11} = k_{21}$ ,  $k_{22} = k_{12}$ ,  $r_1 \cdot r_2 = 1$ ; Equation S7.4, Supp. Inf.).<sup>[187]</sup> Non-terminal copolymerization behavior applies for a range of systems, including the anionic ring-opening polymerization of various epoxides<sup>[188,189,190]</sup> or the monomer-activated AROP,<sup>[189,190]</sup> but also some carbanionic polymerizations.<sup>[145,184,191]</sup>

In subsequent works the copolymerization models were further advanced to also account for the repeating unit adjacent to the chain end (“penultimate copolymerization model”).<sup>[192]</sup>

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (1)$$

For industrial synthesis and final application, the Mayo-Lewis copolymerization equation (Equation 1) has been proven to be of great importance. To run radical batch polymerizations up to high conversion, the polymerization must be performed at the azeotropic point. At this point, the compositional drift shows no significant dependence from the conversion and hence the polymer composition resembles the monomer feed. For living polymerizations (i.e., absence of chain-transfer or irreversible termination reactions) such as the anionic copolymerization of styrene and 1,3-dienes or the controlled radical copolymerization of methyl methacrylate and *n*-butyl acrylate<sup>[193]</sup>, the reactivity ratios directly translate to the resulting comonomer sequence in the polymer backbone (e.g., flat or steep gradient), since all chains are initiated at the same time. Consequently, the compositional heterogeneity found in radical copolymerization is avoided. Although the principle has long been known, the interest in sequence-controlled TPEs is in the focus of present studies, which is also due to the increasingly developed methods for online monitoring of gradient formation (section 3.2).<sup>[125,144,194–196]</sup>

## Kinetics of the Anionic Copolymerization

The (co)polymerization of styrene with dienes in *non-polar, non-coordinating hydrocarbons* is usually performed by alkyllithium initiation, as the lithium counterion leads to a comparably large content of the *cis*-1,4-polydiene microstructure.<sup>[28,197,198]</sup> The initiation of 1,3-dienes and styrene is fast,<sup>[58,199]</sup> which enables chain initiation to be kinetically separated from propagation and to prevent broadening of the molecular weight distribution.<sup>[200]</sup>

Although the propagation rates generally show a first order dependence with respect to the monomer concentration (butadiene,<sup>[197]</sup> isoprene,<sup>[197]</sup> styrene<sup>[201–203][201,204,205,205]</sup>), different dependences are found in respect to the initiator concentration. This is explained by the peculiar reaction mechanism, where lithium-aggregated anionic polymer chain ends are in equilibrium with the respective non-aggregated species. Only the non-aggregated “unimeric” chains are assumed to add monomer.<sup>[33,127,198,206,207]</sup> Related to the aggregation number,  $N_{agg}$  of the respective anionic species, the kinetic order is given by  $1/N_{agg}$ , which enables a facile treatment of the complex aggregation-deaggregation equilibria. For polystyryllithium the formation of dimers ( $N_{agg} = 2$ ) is generally accepted.<sup>[58,203,205,208,209,210]</sup> In case of polybutadienyllithium<sup>[206,209,211–214]</sup> and polyisoprenyllithium,<sup>[60,210–212,214,215]</sup> controversial

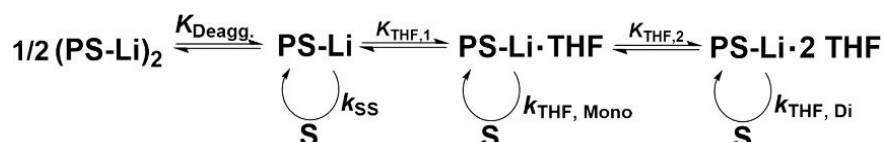
results have been discussed. Worsfold and Bywater observed a gradual change from tetrameric to dimeric PI-Li species as a result of a decreasing chain end concentration.<sup>[195,211]</sup>

The reactivity ratios in the copolymerization of 1,3-dienes with styrene derivatives in apolar solvents are highly disparate,  $r_{\text{diene}} \gg 1$ ,  $r_{\text{S}} \ll 1$  (Table 1). This results in steep gradients, so-called tapered structures (see also sections 1.2 & 2.5).<sup>[54,85,131,191,194,195]</sup> Although the homopropagation of styrene proceeds faster than that of the polydiene, e.g. isoprene ( $k_{\text{SS}} > k_{\text{II}}$ ), the latter is preferentially incorporated (Table 1, entry 1).<sup>[54,128,194,195]</sup> This is explained by the magnitude of the cross-propagation constants, which highly favor polyisoprenyllithium (PI-Li) chain ends ( $k_{\text{SI}} \gg k_{\text{IS}}$ ).<sup>[54]</sup>

Rather polar, coordinating solvents (Lewis bases, section 2.6) dramatically affect the reactivity ratios and thus also the monomer gradient in the respective copolymers (Figure 10). Taking the copolymerization of isoprene and styrene in THF as an example, the reactivity ratios can be adjusted to the same values (Table 1, entry 3) or even inverted (Table 1, entry 4).<sup>[36,216]</sup> This observation is explained by the coordinative interaction of lithium with the Lewis base, exemplified for THF in Figure 17. As a consequence of the coordination, the anionic chain end is further polarized. Hence, less associated chain ends are assumed, which is further supported by the observed first-order dependence of the polymerization rate on the active chain end concentration.<sup>[197,217]</sup>

**Table 1:** Selected copolymerization systems and their reactivity ratios in comonomer systems including the dienes isoprene (I),  $\beta$ -myrcene (Myr) and  $\beta$ -farnesene (Far) in combination with the styrenic monomers styrene (S) and 4-methylstyrene (4-MS). The polymerizations are carried out in cyclohexane with tetrahydrofuran (THF), triethylamine (TEA), *N,N,N',N'*-tetramethylethylene diamine (TMEDA) or 2,2-di(2-tetrahydrofuryl)propane (DTHFP) as polar modifier. The kinetics are examined with either <sup>a</sup> NIR, <sup>b</sup> <sup>1</sup>H-NMR or <sup>c</sup> mid-IR measurements.

| monomer<br>1 | monomer<br>2 | <i>T</i> [°C]   | modifier               | <i>r</i> <sub>1</sub> | <i>r</i> <sub>2</sub> | <i>r</i> <sub>1</sub> · <i>r</i> <sub>2</sub> | ref.  |
|--------------|--------------|-----------------|------------------------|-----------------------|-----------------------|-----------------------------------------------|-------|
| I            | S            | 20 <sup>a</sup> | -                      | 10.03                 | 0.015                 | 0.15                                          | [36]  |
| I            | S            | 60 <sup>a</sup> | -                      | 9.93                  | 0.04                  | 0.39                                          | [54]  |
| I            | 4-MS         | 23 <sup>b</sup> | -                      | 25.4                  | 0.007                 | 0.18                                          | [85]  |
| I            | S            | 20 <sup>a</sup> | [THF]/[BuLi] = 8       | 0.65                  | 0.74                  | 0.47                                          | [36]  |
| I            | S            | 20 <sup>a</sup> | [THF]/[BuLi] = 2500    | 0.012                 | 12.58                 | 0.15                                          | [36]  |
| I            | S            | 40 <sup>c</sup> | 49% <sub>vol</sub> TEA | 0.94                  | 0.76                  | 0.71                                          | [144] |
| Myr          | S            | 23 <sup>b</sup> | -                      | 36                    | 0.028                 | 1                                             | [191] |
| Myr          | S            | 20 <sup>a</sup> | [THF]/[BuLi] = 20      | 0.87                  | 1.15                  | 1                                             | [145] |
| Myr          | S            | 20 <sup>a</sup> | [THF]/[BuLi] = 2500    | 0.10                  | 10.0                  | 1                                             | [145] |
| Myr          | S            | 20 <sup>a</sup> | [DTHFP]/[BuLi] = 1     | 0.067                 | 15.3                  | 1                                             | [145] |
| Myr          | S            | 23 <sup>b</sup> | [TMEDA]/[BuLi] = 1     | 0.15                  | 17.52                 | 1.63                                          | [143] |
| Myr          | 4-MS         | 23 <sup>b</sup> | -                      | 140                   | 0.007                 | 1                                             | [191] |
| Far          | S            | 23 <sup>b</sup> | -                      | 27                    | 0.037                 | 1                                             | [184] |



**Figure 17:** Proposed reaction mechanism of the homopropagation of polystyryllithium in mixtures of a hydrocarbon solvent and THF <sup>[218]</sup>. The chain-ends form inactive dimers in pure non-polar solvent, whereas on the addition of THF, the dimers break up into mono- and dietherate complexes, both being polymerization active.<sup>[36]</sup> Copyright 2020. Adapted with permission from American Chemical Society.

Besides ethers like THF or DTHFP (Table 1, entry 10), amines like TEA or TMEDA are widely used in copolymerizations performed in hydrocarbons to modify the gradient profile.<sup>[123,127,139,141,219,220,221]</sup> A comparable trend is observed upon the exchange of the counterion (i.e., Lewis acid, section 2.6) with its higher homologues (e.g. sodium) or ionic additives (e.g. potassium *tert*-butanolate).<sup>[53,222]</sup> While the replacement of lithium as counterion alters the coordination strength with the propagating chain end and hence the reactivity ratios, the presence of several counterions, as is the case using ionic additives, an exchange of the coordinating cation can take place on the timescale of propagation, leading to varying incorporation preferences throughout chain growth.<sup>[153]</sup>

Care should be taken, as the gradient profile (i.e., reactivity ratios) does not solely depend on the modifier. Further reaction parameters like the [modifier]/[Li] ratio<sup>[36,127]</sup> and the temperature<sup>[54,216]</sup> have to be adjusted as well with respect to the polar modifier to obtain a certain comonomer incorporation.

Moreover, the ionization of the carbon-metal bond remarkably affects the microstructure of the formed polydiene (section 2.6).<sup>[28,30,223,224]</sup> An increase of the vinyl regioisomers (3,4- and 1,2-units; Figure 2) is accompanied by an increase of  $T_g$ .<sup>[29,153,224,225,226]</sup> Therefore, this increase is generally not desired for TPE materials, when utilizing the polydiene as soft, rubbery component.<sup>[53]</sup> However, there are also examples aiming at a high side-chain vinyl content in order to facilitate subsequent post-polymerization reactions (section 2.1).<sup>[227]</sup>

Despite the industrially highly relevant hydrogenation already discussed in section 1.3, which enhances the polymers' stability and increases its flexibility, prominent functionalization reactions include the thiol-ene addition<sup>[228]</sup> or Diels-Alder reactions like the triazolinedione click.<sup>[229]</sup> Furthermore, the epoxidation<sup>[230]</sup> or bromination<sup>[231]</sup> of the double bonds can be implemented to alter the polymer properties, achieving a higher polarity or flame retardant properties, respectively.

### ***In Situ* Monitoring Techniques**

The determination of the polymer composition at different stages of the reaction is a straightforward method to determine the comonomer gradient.<sup>[127,141,219,221,225]</sup> As several batches of a similar copolymerization experiment have to be quenched and analyzed at different conversions, this leads to a comparably high experimental effort and nowadays belongs to the more traditional approaches.

Based on recent developments, on-line methods allow the real-time monitoring of the monomer conversion via NMR,<sup>[85,87,189,232]</sup> near-infrared (NIR),<sup>[54,196,233]</sup> mid-infrared (mid-IR),<sup>[144,194,234]</sup> or ultraviolet (UV) spectroscopy.<sup>[203,205,235]</sup> These methods feature high temporal

resolution and are able to monitor the complete course of the polymerization within one experiment. Thus, high data resolution (depending on the measurement method up to 20,000 data points or more) within only one experiment is achievable. Hence, these on-line experiments are currently the method of choice to monitor and analyze copolymerizations, particularly for living copolymerizations.

In recent years, on-line NMR spectroscopy has been proven to be an efficient tool to track the depletion of individual monomers over time. However, the time resolution is limited by the  $T_1$  times of the signals of interest ( $5T_1 \approx 1$  min), and typically the polymerization conditions must be tailored to be performed within an NMR tube (use of deuterated solvent, adjusted initiator and monomer concentrations, sample preparation in a glove box).

Both issues can be resolved by *in situ* probing the reaction via UV, NIR or mid-IR spectroscopy. The temporal resolution is much higher and since the probe is directly attached to the reaction vessel, the progress of a reaction can be tracked on the very same batch used to investigate material properties.<sup>[54]</sup> This is especially useful for reactions with modifiers, the weighing of which becomes difficult for batch sizes suitable for NMR. Furthermore, the setup becomes important in multi-step reactions (section 2.4), where a defined polymer structure can only be obtained by postponing the monomer addition until the majority of the previous addition step has reacted.<sup>[54]</sup>

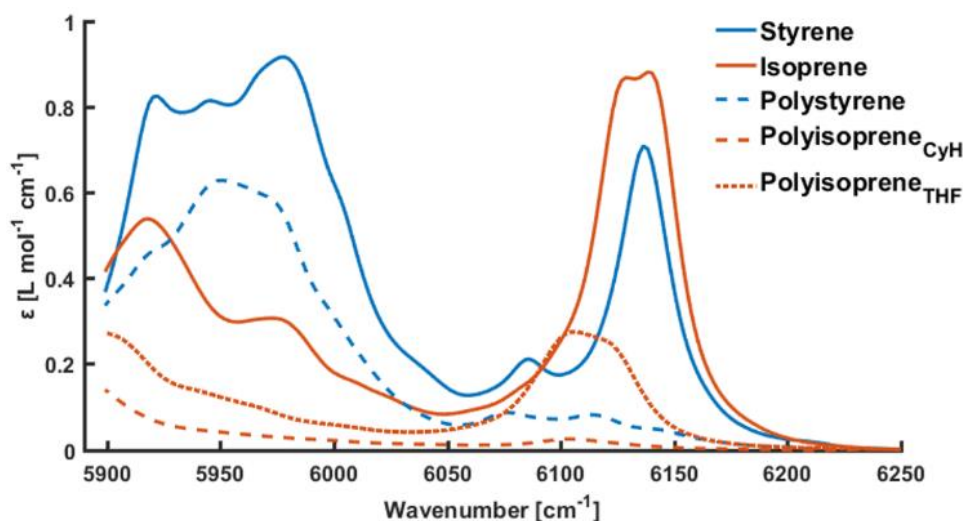
As demonstrated in a seminal publication by Fontanille *et al.*, mid-IR spectroscopy is an efficient method to *in situ* monitor the copolymerization by tracking the depletion of the well resolved monomer absorption peaks ( $\tilde{\nu}_S = 1597 \text{ cm}^{-1}$ ;  $\tilde{\nu}_I = 1630 \text{ cm}^{-1}$ ). Unfortunately, the implementation of mid-IR spectroscopy is technically challenging because the optical fibers require crystalline media, e.g. AgCl, or hollow waveguides resulting in mechanically less robust and expensive conduits, which require permanent installation in a polymerization setup.<sup>[236]</sup>

This issue is solved using *in situ* UV spectroscopy to monitor the absorption of the monomer and the anionic chain ends. Already in 1960 Worsfold *et al.* started to quantify homo- and cross propagation rates of styrene, isoprene and butadiene via *in situ* measurements.<sup>[58,131,203,218,235]</sup> As shown by Fontanille *et al.*, this setup can also be used to probe the homo- and copolymerization of styrene and isoprene.<sup>[194]</sup> As stated by Worsfold,<sup>[131]</sup> it is unfortunate that the absorption band of polybutadienyllithium ( $\lambda_{PB-Li} \approx 275 \text{ nm}$ ) is largely masked by that of styrene ( $\lambda_S \approx 290 \text{ nm}$ ) and of polystyrene ( $\lambda_{PS} \approx 260 \text{ nm}$ ). However, the absorption band of polystyryllithium ( $\lambda_{PS-Li} \approx 330 \text{ nm}$ ) appears at a measurable wavelength. Hence, in on-line UV studies, the determination of cross-propagation rate constants is not achieved by tracking the individual monomer consumption rates during the copolymerization reaction. Instead, they were determined by the respective cross-addition step (i.e., adding isoprene to polystyryllithium ( $k_{SI}$ ) or *vice versa* ( $k_{IS}$ )). Also for this “model reaction”, Fontanille *et al.* stated that the formation of mixed aggregates only allowed an evaluation for the first moments of the crossover reaction.<sup>[194]</sup>

Near-infrared (NIR) spectroscopy also utilizes comparably small wavelengths, enabling a facile setup by using affordable, flexible, mineral glass or polymer based optical fibers.<sup>[54,237]</sup> Long *et al.* experienced the kinetic data evaluation to be hampered by the overlapping absorption bands of styrene, isoprene and the respective repeating units formed during the (co)polymerization.<sup>[196]</sup> In 2019 our group started to utilize differences in the individual molar attenuation coefficients,  $\varepsilon(\tilde{\nu})$ , in a part of the NIR spectrum to access the individual monomer



and polymer concentrations at any time.<sup>[36,54]</sup> For this purpose, the spectra in the range  $\tilde{\nu} = 5900 - 6250 \text{ cm}^{-1}$  at a  $1.9 \text{ cm}^{-1}$  data interval were recorded and used to solve a linear equation system (184 equations) for every spectrum (typically 4 s resolution in up to 12,000 spectra; Figure 18).<sup>[54]</sup> This allows to determine the reactivity ratios of isoprene and styrene in cyclohexane as a function of the temperature ( $T = 10\text{--}60^\circ\text{C}$ ). For the investigation of the effect of ligands, e.g. THF, on the copolymerization kinetics the change of the NIR spectra with increasing THF content has to be taken into account, which is partially due to changes of the polydiene stereostructure.<sup>[36,145]</sup>



**Figure 18: Molar attenuation coefficients of the species present during the living anionic copolymerization of styrene and isoprene.**<sup>[36,54]</sup>

$$A(\tilde{\nu}) = c_I \cdot \varepsilon_I(\tilde{\nu}) + c_S \cdot \varepsilon_S(\tilde{\nu}) + c_{PI_{CyH}} \cdot \varepsilon_{PI_{CyH}}(\tilde{\nu}) + c_{PI_{THF}} \cdot \varepsilon_{PI_{THF}}(\tilde{\nu}) + c_{PS} \cdot \varepsilon_{PS}(\tilde{\nu}) \quad (2)$$

Equation 2 shows the linear equation system for the deconvolution of the combined monomer and polymer absorption bands of the spectra being present during the living anionic copolymerization of isoprene and styrene. The first two terms account for the monomer absorptions, while the latter three terms include the polymer absorptions.

Comparing all methods, NIR spectroscopy combines a facile setup, low cost, and a high temporal resolution. Furthermore, the method enables the determination of homo- and cross-propagation constants (i.e., reactivity ratios, which represent the gradient profile). To get further insight into mechanistic processes, UV-probing can be used to identify the changes of the active anionic species during polymerization.<sup>[238]</sup>

## Determination of Reactivity Ratios

Reactivity ratios are the foundation to understand the copolymerization behavior and determine the comonomer sequence formed during the copolymerization reaction. Incipently, the *terminal* as well as the *non-terminal copolymerization model* and the chain end reactivities associated thereto were discussed (Figure 16). Based on the fundamental importance of these parameters, several methods for the evaluation of reactivity ratios were introduced. At their time of introduction, typically graphical methods (i.e., evaluation with pen and paper) were employed. The first prominent method was reported by Fineman and Ross in 1950 by

linearizing the Mayo-Lewis equation (Equation Set S3).<sup>[239]</sup> The Fineman-Ross formalism enables direct determination of reactivity ratios from the slope and intercept of the linear graph. Kelen and Tüdös further optimized the Fineman-Ross method by eliminating biases introduced by the linearization using a symmetrization factor (Equation Set S4).<sup>[240]</sup> While these methods can be performed by hand without any computer, they rely on the differential copolymerization equation and require both the monomer feed,  $f_1 = [M_1]/([M_1]+[M_2])$ , and the instantaneous mole fraction of each monomer incorporated into the polymer,  $F_1 = d[M_1]/d([M_1]+[M_2])$ , for evaluation (Equation Set S5).

Although *in situ* monitoring techniques enable a comparably high data resolution, the determination of reactivity ratios is still not straightforward. To obtain the instantaneous monomer incorporation mole fraction  $F_1$ , the derivative of the measurement has to be calculated. Unfortunately, this calculation is highly influenced by data noise and thus prone to result in erroneous reactivity ratios. However, this issue can partially be solved using advanced methods for differentiation, such as the total-variation regularization-based numerical differentiation.<sup>[241]</sup>

As an alternative to the differential methods, the integrated form of the Mayo-Lewis equation as reported by Meyer and Lowry can be used (Equation S6).<sup>[242]</sup> Meyer and Lowry analytically integrated the copolymerization equation derived by Skeist.<sup>[243]</sup> In contrast to “old” graphical methods, this equation requires non-linear fitting methods.

In the particular case of an *ideal copolymerization* ( $r_1 r_2 = 1$ , *non-terminal model*) the Jaacks equation (Equation 3, Equation set S7) is most useful since the reactivity ratios  $r_1 = 1/r_2$  are obtained by a linear plot:

$$\ln \frac{[M_1]_0}{[M_1]_t} = r_1 \ln \frac{[M_2]_0}{[M_2]_t} \quad (3)$$

It is directly derived by integration of the differential equations for the comonomer depletion (Equations S7.1-S7.3) given by Wall. Jaacks initially introduced it for copolymerization systems with one monomer being present in excess.<sup>[244]</sup>

Alternatively, the Meyer-Lowry equation can be simplified for the ideal case (“ideal integrated”, Equation S7.5).<sup>[190]</sup> Beckingham, Sanoja and Lynd (BSL) introduced an alternative treatment of data for the non-terminal model.<sup>[190,245]</sup> The BSL Method (Equations S7.6) needs two non-linear fits.

An overview of the various methods to determine reactivity ratios is given in Table S1. Ockham’s razor recommends to use the model with the least number of parameters.<sup>[246]</sup> Thus, for a new copolymerization system it is highly recommended to first check whether it is ideal (non-terminal model) using a Jaacks plot. Only when deviations from linearity are significant one should then use the Meyer-Lowry treatment (terminal model). This prevents overfitting of the data set (see Flow-Scheme S1).

### Copolymerization “*In Silico*” – Kinetic Monte Carlo Simulation

In the last decades computational power has increased remarkably. Hence calculation times have been reduced considerably faster than the experimental time.<sup>[247]</sup> Nowadays, computer-

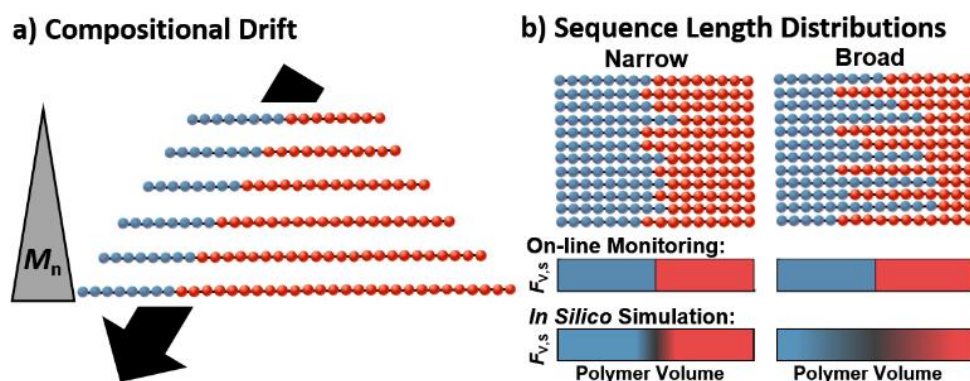
aided prediction and rational selection of experiments can significantly increase the overall scientific throughput and thus scientific progress. Exceptional work has been performed by introducing the Polymer Self-Consistent Field theory (PSCFT) which helped to understand the phase-segregation behavior of block copolymers.<sup>[90]</sup> Molecular dynamics (MD) simulations have been used to predict the behavior of (co)polymer chains in bulk and solution.<sup>[248]</sup> While many works for the prediction of material properties have been reported, nearly all methods are focused on polymer physics and only few methods can be regarded as practical tools for the synthetic polymer chemist. In this context we want to highlight the kinetic Monte Carlo (kMC) simulation.

kMC simulations of copolymerization reactions can be performed using experimentally determined reaction rates (section 3.3, Equation Set S8). If the assumed copolymerization reactions with their specific aggregation numbers (section 3.1) and experimentally determined rate constants are correct, the simulation perfectly represents the experimental outcome. Hence every single computed polymer chain and the corresponding monomer-by-monomer sequence can be obtained and analyzed (e.g., regarding the composition distribution, the segment length distribution as well as their drift within the molecular weight distribution as discussed later in this section). This yields not only valuable information for the prediction of experimental data but can also provide information that is difficult to obtain via experimental methods (e.g., triad composition, length of uninterrupted repeating units).

For living or controlled copolymerization methods the implementation of a kMC model is quite simple, as the nature of the mechanism excludes side reactions (e.g., irreversible termination or chain transfer reactions to monomers) of the polymerization active species, which allows to consider only the fundamental copolymerization equations as shown in Figure 16.

The reported kMC models for controlled and free radical copolymerizations are extremely comprehensive and even specialized methods for, e.g., electrochemically mediated ATRP<sup>[249]</sup> or laser-induced free-radical polymerizations<sup>[250]</sup> have been developed. Complicated features (e.g. branching) were considered by Broadbelt, D’Hooge and others.<sup>[251]</sup> Especially the *chemical composition-chain length distribution* (CC-CLD or CoC-CLD; i.e. the copolymer composition distribution as a function of the chain length) was thoroughly investigated.<sup>[252]</sup>

In contrast to radical copolymerization, comprehensive kMC models for the living anionic copolymerization have rarely been reported to date. To the best of our knowledge, only the chain length distribution of multiblock copolymers prepared via continuous flow,<sup>[124]</sup> the slow crossover reaction from alkynyl-functionalized 1,1-diphenylethylene to styrene,<sup>[253]</sup> and several works in our group have been published up to date.<sup>[85,125,254]</sup> As shown by the following examples, kMC simulations based on the kinetics of the living anionic polymerization of 1,3-dienes and styrene can facilitate synthesis and understanding of TPEs. In contrast to the CC-CLD, the compositional drift resembles the change in the *mean* composition of copolymer chains as a function of the chain length (Figure 19a) and can be experimentally accessed via SEC (e.g., analyzing the responses of RI and UV detector) or MALDI-ToF mass spectrometry.<sup>[88,255]</sup> As an example, in a recent work, the copolymerization of isoprene and styrene derivatives produced a compositional drift in dependence of the molecular weight, resulting in a broadening of the molecular weight distribution. However, a prediction of the molecular weight distribution (and SEC curve) via kMC confirmed that indeed a broadened molecular weight distribution was to be expected (Figure S1).



**Figure 19:** Red and blue spheres represent different monomer units. a) Visualization of a compositional drift for increasing molecular weight ( $M_n$ ). With increasing  $M_n$  the content of red spheres increases. b) Visualization of a narrow (left) and broad (right) sequence length distribution for samples with a similar chain length. The black area in the bars below visualizes the area in the chains where red and blue spheres are present.

Nonetheless, copolymers with a narrow molecular weight distribution and similar composition with respect to the molecular weight can still show different compositions on the per-chain level (Figure 19b). For this purpose, the *sequence length distribution* (SLD) affords the per-chain microstructure, enabling a detailed comparison of the monomer sequence of individual polymer chains. These results are not accessible via conventional experimental methods, where always an average value of multiple chains is obtained. As an example, the degradation products of the ozonolysis of a tapered P(I-co-S) multiblock were predicted via kMC. The SLD of the copolymer accurately described the resulting PS segment distribution after cleavage of all isoprene repeating units and verified the desired tapered multiblock architecture.<sup>[125]</sup> In addition, the kMC model was also used to reduce reaction times in multi-step syntheses (Figure S2).

Both parameters, the CoC-CLD and SLD, precisely reflect the microstructure of copolymers and hence are of great interest for the prediction and evaluation of copolymerization experiments in the rational design of TPEs.<sup>[256]</sup>

## Conclusions

The progress in synthetic polymer chemistry enables to access numerous parameters for copolymerizations. It is a challenge for the synthetic chemist to rationally design and control the monomer sequence resulting from copolymerization statistics to obtain a tailor-made material for a targeted application. Here, we review recent developments in the field of sequence-controlled TPEs to permit an in-depth understanding of the effect of comonomer sequencing on morphological and the corresponding mechanical properties. In recent years, the multi-step living anionic (co)polymerization has been proven to be an efficient tool to design, synthesize and investigate complex tapered block copolymer architectures in a defined manner. The precise quantification of fundamental kinetic processes in the statistical copolymerization is crucial to secure the formation of the desired comonomer gradient along the polymer backbone. On-line monitoring techniques are established as the method of choice to determine rate constants. To generate an in-depth insight into the (co)polymerization behavior, the kinetic Monte Carlo simulation can be used to reproduce the copolymerization *in silico*, based on the experimentally determined rate constants. This allows a precise

calculation of reaction times and a comparison of individual chains in terms of their composition and sequence. Hence, *in situ* measurements and *in silico* simulations have been proven to be an effective combination to understand the statistical living copolymerization, which is employed to directly generate tapered block copolymers and also complex sequences in a single reaction vessel, merely adding suitable monomer mixtures.

## Declaration of Competing Interest

The authors declare that they have no known competing or financial interest or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

We thank both Prof. George Floudas (University of Ioannina, Greece) and Prof. Markus Gallei (Saarland University, Germany) for longstanding collaborations and joint projects in the area of multiblock copolymers and TPEs.

## Supplementary Materials

Supplementary material associated with this article can be found, in the online version, at doi: 10.1016/j.progpolymsci.2021.101488.

## References

- [1] V. Gold, *The IUPAC Compendium of Chemical Terminology*, International Union of Pure and Applied Chemistry, Research Triangle Park, NC, **2019**.
- [2] A. Gumboldt, *Chem. Unserer Zeit* **1967**, 1, 41.
- [3] S. Thomas, *Natural rubber materials. Volume 1: Blends and IPNs*, Royal Society of Chemistry, Cambridge, **2014**.
- [4] C. Slack, *Noble obsession. Charles Goodyear, Thomas Hancock, and the race to unlock the greatest industrial secret of the nineteenth century*, Hyperion, New York, **2002**.
- [5] C. Goodyear, *Improvement in India-Rubber Fabrics*, US3633A, **1844**.
- [6] K. Hübner, *Chem. Unserer Zeit* **2016**, 50, 67.
- [7] B. Erman, J. E. Mark, C. M. Roland (Eds.), *The science and technology of rubber*, Elsevier Academic Press, Amsterdam, Heidelberg, **2013**.
- [8] J. Race, *J. Soc. Chem. Ind.* **1912**, 31, 611.
- [9] F. E. Matthews, E. H. Strange, *Improvements in the Manufacture of Synthetic Caoutchouc and the like*, GB191024790A, **1910**.
- [10] F. E. Matthews, E. H. Strange, *Neuere Arbeiten auf dem Kautschukgebiet*, DE249868, **1911**.

- [11] A. Holt, *Angew. Chem.* **1914**, 27, 153.
- [12] A. Requardt, *Nachr. Chem.* **2016**, 64, 150.
- [13] G. Ebert, P. Orth, R. Heidebroek, *Polymerisation von Butadien*, DE715825C, **1937**.
- [14] J. G. Drobny, *Handbook of thermoplastic elastomers*, Andrew Elsevier, Oxford, **2014**.
- [15] A. Requardt, *Chem. Unserer Zeit* **2020**, 54, 106.
- [16] A. Noshay, J. E. McGrath, *Block Copolymers. Overview and Critical Survey*, Elsevier Science, Burlington, **1977**.
- [17] M. Szwarc, *Nature* **1956**, 178, 1168.
- [18] M. Szwarc, M. Levy, R. Milkovich, *J. Am. Chem. Soc.* **1956**, 78, 2656.
- [19] G. Holden, R. Milkovich, *Block polymers of monovinyl aromatic hydrocarbons and conjugated dienes*, US3265765A, **1962**.
- [20] a) R. E. Christ, W. E. Hanford, *Treatment of polymeric materials*, GB580524A, **1941**; b) R. E. Christ, W. E. Hanford, *Treatment of polyesters and product therefrom*, US2333639A, **1940**; c) W. E. Hanford, D. F. Holmes, *Process for making polymeric products and for modifying polymeric products*, US2284896A, **1939**; d) D. H. Coffey, *Improvements in the manufacture of synthetic polymeric materials*, GB574134A, **1942**.
- [21] a) C. S. Schollenberger, *Simulated vulcanizates of polyurethane elastomers*, US2871218A, **1995**; b) C. S. Schollenberger, H. Scptt, G. R. Moore, *Rubber Chem. Technol.* **1962**, 35, 742.
- [22] O. Bayer, W. Siefken, H. Rinke, L. Orthner, H. Schild, *A process for the production of polyurethanes and polyureas*, DE728981, **1937**.
- [23] G. Holden, H. R. Kricheldorf, R. P. Quirk (Eds.), *Thermoplastic elastomers*, Hanser, Munich, **2004**.
- [24] W. Wang, W. Lu, A. Goodwin, H. Wang, P. Yin, N.-G. Kang, K. Hong, J. W. Mays, *Prog. Polym. Sci.* **2019**, 95, 1.
- [25] K. Parkatzidis, H. S. Wang, N. P. Truong, A. Anastasaki, *Chem* **2020**, 6, 1575.
- [26] N. R. Legge, *Rubber Chem. Technol.* **1987**, 60, 83.
- [27] N. R. Legge, *Rubber Chem. Technol.* **1989**, 62, 529.
- [28] H. Hsieh, A. V. Tobolsky, *J. Polym. Sci.* **1957**, 25, 245.
- [29] H. Hsieh, D. J. Kelley, A. V. Tobolsky, *J. Polym. Sci.* **1957**, 26, 240.
- [30] H. Morita, A. V. Tobolsky, *J. Am. Chem. Soc.* **1957**, 79, 5853.
- [31] L. M. Porter, *Process for preparing block copolymers utilizing organolithium catalysts*, US3149182A, **1957**.
- [32] L. M. Porter, *Block polymers and process for preparation thereof*, GB888624A, **1958**.
- [33] R. E. Cunningham, M. R. Treiber, *J. Appl. Polym. Sci.* **1968**, 12, 23.
- [34] a) Y. Tsukahara, N. Nakamura, T. Hashimoto, H. Kawai, T. Nagaya, Y. Sugimura, S. Tsuge, *Polym. J.* **1980**, 12, 455; b) R. Roy, J. K. Park, W.-S. Young, S. E. Mastroianni, M. S. Tureau, T. H. Epps,

- Macromolecules* **2011**, *44*, 3910; c) A. R. Ashraf, J. J. Ryan, M. M. Satkowski, B. Lee, S. D. Smith, R. J. Spontak, *Macromol. Rapid Commun.* **2017**, *38*.
- [35] "Pioneering Innovation. History 1960s", can be found under <https://kraton.com/company/1960s.php>, **2021**.
- [36] M. Steube, T. Johann, H. Hübner, M. Koch, T. Dinh, M. Gallej, G. Floudas, H. Frey, A. H. E. Müller, *Macromolecules* **2020**, *53*, 5512.
- [37] M. Morton, J. E. McGrath, P. C. Juliano, *J. Polym. Sci., Part C: Polym. Symp.* **1969**, *26*, 99.
- [38] a) K. Matyjaszewski, Y. Gnanou, L. Leibler, *Macromolecular engineering: precise synthesis, materials properties, applications. 4 volume*, Wiley-VCH, Weinheim, **2011**; b) D. L. Handlin, D. R. Hansen, K. J. Wright, S. R. Trenor in Müller, Matyjaszewski (Hg.) *2009 – Controlled and Living Polymerizations*, pp. 555–603; c) G. Scholz, M. Gehringer, *Thermoplastische Elastomere: im Blickfang*, De Gruyter, **2021**.
- [39] MarketsandMarkets Research Private Ltd., "TPE Market by Type (SBC, TPU, TPO, TPV, COPE, PEBA), End Use Industry (Automotive, Building&Construction, Footwear, Wire&Cable, Medical, Engineering), Region (North America, Europe, APAC, South America, MEA) - Global Forecast to 2026", can be found under <https://www.marketsandmarkets.com/Market-Reports/thermoplastic-elastomers-market-1012.html>.
- [40] a) S. Thomas, A. R. Ajitha (Eds.), *Compatibilization of polymer blends. Micro and nano scale phase morphologies, interphase characterization, and properties*, Elsevier, Amsterdam, **2019**; b) L. Kane, D. A. Norman, S. A. White, M. W. Matsen, M. M. Satkowski, S. D. Smith, R. J. Spontak, *Macromol. Rapid Commun.* **2001**, *22*, 281; c) R. J. Spontak, S. D. Smith, A. R. Ashraf, *Macromolecules* **1993**, *26*, 5118; d) L. Kane, D. A. Norman, S. A. White, R. J. Spontak, *MRS Online Proc. Libr.* **1996**, *461*; e) L. Kane, M. M. Satkowski, S. D. Smith, R. J. Spontak, *Macromolecules* **1996**, *29*, 8862; f) R. J. Spontak, S. D. Smith, A. Ashraf, *Macromolecules* **1993**, *26*, 5118.
- [41] M. M. Wald, M. G. Quam, *Selectively Hydrogenated Block Copolymers*, US3700633A, **1972**.
- [42] R. J. A. Eckert, *Hydrogenated Star-Shaped Polymer*, US4116917A, **1978**.
- [43] A. R. Ashraf, J. J. Ryan, M. M. Satkowski, S. D. Smith, R. J. Spontak, *ACS Appl. Mater. Interfaces* **2018**, *10*, 3186.
- [44] J. Schmelz, H. Schmalz, *Polymer* **2012**, *53*, 4333.
- [45] R. Velichkova, V. Toncheva, C. Antonov, V. Alexandrov, S. Pavlova, L. Dubrovina, E. Gladkova, *J. Appl. Polym. Sci.* **1991**, *42*, 3083.
- [46] a) H. J. Baumgartner, J. G. Balas, *Hydrogenation Process*, US3937759, **1976**; b) M. M. Wald, M. G. Quam, *Partially Hydrogenated Block Copolymers*, US3595942, **1971**.
- [47] S. Basak, *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2021**, *58*, 579.
- [48] a) N. Badi, J.-F. Lutz, *Chem. Soc. Rev.* **2009**, *38*, 3383; b) P. Hodrokoukes, G. Floudas, S. Pispas, N. Hadjichristidis, *Macromolecules* **2001**, *34*, 650; c) X. Qiang, R. Chakroun, N. Janoszka, A. H. Gröschel, *Isr. J. Chem.* **2019**, *295*, 2418.
- [49] S. Martens, J. van den Begin, A. Madder, F. E. Du Prez, P. Espeel, *J. Am. Chem. Soc.* **2016**, *138*, 14182.

- [50] a) T. Mori, S. Masukawa, T. Kikkawa, A. Fujimori, A. Satoh, K. Matsumoto, M. Jikei, Y. Oishi, Y. Shibasaki, *RSC Adv.* **2017**, 7, 33812; b) S. K. Varshney, C. Jacobs, J. P. Hautekeer, P. Bayard, R. Jerome, R. Fayt, P. Teyssie, *Macromolecules* **1991**, 24, 4997; c) J. Xu, C. Fu, S. Shanmugam, C. J. Hawker, G. Moad, C. Boyer, *Angew. Chem., Int. Ed. Engl.* **2017**, 56, 8376.
- [51] a) V. P. Beyer, J. Kim, C. R. Becer, *Polym. Chem.* **2020**, 11, 1271; b) J.-F. Lutz (Ed.), *Sequence-controlled polymers*, Wiley-VCH, Weinheim, Germany, **2018**.
- [52] "KURARITY", can be found under <https://www.elastomer.kuraray.com/kurarity/what-is-kuraritytm/>.
- [53] K. Knoll, N. Nießner, *Macromol. Symp.* **1998**, 132, 231.
- [54] M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey, A. H. E. Müller, *Macromolecules* **2019**, 52, 9299.
- [55] S. D. Smith, R. J. Spontak, M. M. Satkowski, A. R. Ashraf, A. K. Heape, J. S. Lin, *Polymer* **1994**, 35, 4527.
- [56] R. J. Spontak, S. D. Smith, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 947.
- [57] A. K. Khandpur, S. Foerster, F. S. Bates, I. W. Hamley, A. J. Ryan, W. Bras, K. Almdal, K. Mortensen, *Macromolecules* **1995**, 28, 8796.
- [58] A. F. Johnson, D. J. Worsfold, *J. Polym. Sci., Part A: Gen. Pap.* **1965**, 3, 449.
- [59] N. Hadjichristidis, G. Floudas, S. Pispas, *Block copolymers. Synthetic strategies, physical properties, and applications*, Wiley-Interscience, Hoboken, N.J., **2003**.
- [60] G. Allen, J. C. Bevington (Eds.), *Comprehensive polymer science. The synthesis, characterization, reactions & applications of polymers*, Pergamon Press, Oxford, **1989**.
- [61] N. Hadjichristidis, H. Iatrou, S. Pispas, M. Pitsikalis, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, 38, 3211.
- [62] R. D. Allen, T. E. Long, J. E. McGrath, *Polym. Bull.* **1986**, 15, 127.
- [63] G. G. Odian, *Principles of polymerization*, Wiley-Interscience, Hoboken, NJ, **2004**.
- [64] C. Iacob, T. Yoo, J. Runt, *Macromolecules* **2018**, 51, 4917.
- [65] J. E. Mark, *Physical properties of polymers handbook*, Springer Science & Business Media, New York, NY, **2007**.
- [66] a) S. Wu, *Polym. Eng. Sci.* **1992**, 32, 823; b) C. A. Bero, C. M. Roland, *Macromolecules* **1996**, 29, 1562.
- [67] a) C. P. Pinazzi, J. C. Soutif, J. C. Brosse, *Eur. Polym. J.* **1975**, 11, 523; b) A. H. Gabor, E. A. Lehner, G. Mao, L. A. Schneggenburger, C. K. Ober, *Chem. Mater.* **1994**, 6, 927; c) B. Ameduri, B. Boutevin, M. Nouri, *J. Polym. Sci., Part A: Polym. Chem.* **1993**, 31, 2069; d) C. Rüttiger, M. Appold, H. Didzoleit, A. Eils, C. Dietz, R. W. Stark, B. Stühn, M. Gallei, *Macromolecules* **2016**, 49, 3415.
- [68] B. Rodgers (Ed.), *Rubber compounding. Chemistry and applications*, CRC Press, Boca Raton, **2021**.



- [69] a) I. Natori, S. Inoue, *Macromolecules* **1998**, *31*, 982; b) K. Hong, J. W. Mays, *Macromolecules* **2001**, *34*, 782; c) K. Bornani, X. Wang, J. L. Davis, X. Wang, W. Wang, J. P. Hinestrosa, J. W. Mays, S. M. Kilbey, *Soft Matter* **2015**, *11*, 6509.
- [70] a) Y. Kosaka, K. Kitazawa, S. Inomata, T. Ishizone, *ACS Macro Lett.* **2013**, *2*, 164; b) Y. Kosaka, R. Goseki, S. Kawauchi, T. Ishizone, *Macromol. Symp.* **2015**, *350*, 55; c) Y. Kosaka, S. Kawauchi, R. Goseki, T. Ishizone, *Macromolecules* **2015**, *48*, 4421.
- [71] a) Y. Cai, J. Lu, D. Zuo, S. Li, D. Cui, B. Han, W. Yang, *Macromol. Rapid Commun.* **2018**, *39*, e1800298; b) A. Nakahara, K. Satoh, M. Kamigaito, *Macromolecules* **2009**, *42*, 620; c) W. Wang, R. Schlegel, B. T. White, K. Williams, D. Voyloy, C. A. Steren, A. Goodwin, E. B. Coughlin, S. Gido, M. Beiner et al., *Macromolecules* **2016**, *49*, 2646; d) S. Riyajan, D.-J. Liaw, Y. Tanaka, J. T. Sakdapipanich, *J. Appl. Polym. Sci.* **2007**, *105*, 664.
- [72] W. Wang, W. Lu, N.-G. Kang, J. Mays, K. Hong, *Elastomers. Thermoplastic Elastomers Based on Block, Graft, and Star Copolymers*, InTech, **2017**.
- [73] A. Behr, L. Johnen, *ChemSusChem* **2009**, *2*, 1072.
- [74] K. R. Benjamin, I. R. Silva, J. P. Cherubim, D. McPhee, C. J. Paddon, *J. Braz. Chem. Soc.* **2016**.
- [75] a) J. Zhang, J. Lu, D. Wang, B. Han, *J. Mater. Sci.* **2020**, *55*, 16544; b) S. Kuwahara, K. Hirata, D. Koda, *Rubber composition and tire*, US8785542B2, **2011**.
- [76] a) D. H. Lamparelli, V. Paradiso, F. Della Monica, A. Proto, S. Guerra, L. Giannini, C. Capacchione, *Macromolecules* **2020**, *53*, 1665; b) M. Naddeo, A. Buonerba, E. Luciano, A. Grassi, A. Proto, C. Capacchione, *Polymer* **2017**, *131*, 151.
- [77] L. J. Fetters, D. J. Lohse, D. Richter, T. A. Witten, A. Zirkel, *Macromolecules* **1994**, *27*, 4639.
- [78] a) C. Wahlen, M. Rauschenbach, J. Blankenburg, E. Kersten, C. P. Ender, H. Frey, *Macromolecules* **2020**, *53*, 9008; b) J. Zhang, J. Lu, K. Su, D. Wang, B. Han, *J. Appl. Polym. Sci.* **2019**, *136*, 48159.
- [79] J. M. Bolton, M. A. Hillmyer, T. R. Hoyer, *ACS Macro Lett.* **2014**, *3*, 717.
- [80] T. Yoo, S. K. Henning, *Rubber Chem. Technol.* **2017**, *90*, 308.
- [81] C. Wahlen, H. Frey, *Macromolecules* **2021**.
- [82] P. Sarkar, A. K. Bhowmick, *J. Appl. Polym. Sci.* **2018**, *135*, 45701.
- [83] E. Galanos, E. Grune, C. Wahlen, A. H. E. Müller, M. Appold, M. Gallei, H. Frey, G. Floudas, *Macromolecules* **2019**, *52*, 1577.
- [84] J. Zhao, M. D. Ediger, Y. Sun, L. Yu, *Macromolecules* **2009**, *42*, 6777.
- [85] E. Grune, T. Johann, M. Appold, C. Wahlen, J. Blankenburg, D. Leibig, A. H. E. Müller, M. Gallei, H. Frey, *Macromolecules* **2018**, *51*, 3527.
- [86] E. Grune, M. Appold, A. H. E. Müller, M. Gallei, H. Frey, *ACS Macro Lett.* **2018**, *7*, 807.
- [87] T. Johann, D. Leibig, E. Grune, A. H. E. Müller, H. Frey, *Macromolecules* **2019**, *52*, 4545.
- [88] P. von Tiedemann, J. Blankenburg, K. Maciol, T. Johann, A. H. E. Müller, H. Frey, *Macromolecules* **2019**, *52*, 796.

- [89] a) A. Natalello, A. Alkan, P. von Tiedemann, F. R. Wurm, H. Frey, *ACS Macro Lett.* **2014**, *3*, 560; b) J. Lal, J. E. Mark (Eds.), *Advances in Elastomers and Rubber Elasticity*, Springer US, Boston, MA, s.l., **1986**; c) J. Chen, L. J. Fetters, *Polym. Bull.* **1981**, *4*.
- [90] L. Leibler, *Macromolecules* **1980**, *13*, 1602.
- [91] P. G. de Gennes, *J. Phys.* **1970**, *31*, 235.
- [92] B. Abu-Sharkh, A. AlSunaidi, *Macromol. Theory Simul.* **2006**, *15*, 507.
- [93] M. W. Matsen, R. B. Thompson, *J. Chem. Phys.* **1999**, *111*, 7139.
- [94] M. W. Matsen, *J. Chem. Phys.* **2000**, *113*, 5539.
- [95] C. Sinturel, F. S. Bates, M. A. Hillmyer, *ACS Macro Lett.* **2015**, *4*, 1044.
- [96] P. Georgopoulos, U. A. Handge, C. Abetz, V. Abetz, *Polymer* **2016**, *104*, 279.
- [97] M. W. Matsen, F. S. Bates, *Macromolecules* **1996**, *29*, 1091.
- [98] E. V. Gouinlock, R. S. Porter, *Polym. Eng. Sci.* **1977**, *17*, 535.
- [99] F. S. Bates, M. F. Schulz, A. K. Khandpur, S. Förster, J. H. Rosedale, K. Almdal, K. Mortensen, *Faraday Discuss.* **1994**, *98*, 7.
- [100] B. J. Dair, C. C. Honeker, D. B. Alward, A. Avgeropoulos, N. Hadjichristidis, L. J. Fetters, M. Capel, E. L. Thomas, *Macromolecules* **1999**, *32*, 8145.
- [101] a) C. D. Han, D. M. Baek, J. K. Kim, T. Ogawa, N. Sakamoto, T. Hashimoto, *Macromolecules* **1995**, *28*, 5043; b) C. Soto-Figueroa, M.-R. Rodríguez-Hidalgo, J.-M. Martínez-Magadán, L. Vicente, *Macromolecules* **2008**, *41*, 3297.
- [102] S.-M. Mai, W. Mingvanish, S. C. Turner, C. Chaibundit, J. P. A. Fairclough, F. Heatley, M. W. Matsen, A. J. Ryan, C. Booth, *Macromolecules* **2000**, *33*, 5124.
- [103] a) J. T. Koberstein, T. P. Russell, D. J. Walsh, L. Pottick, *Macromolecules* **1990**, *23*, 877; b) M. D. Gehlsen, K. Almdal, F. S. Bates, *Macromolecules* **1992**, *25*, 939; c) A. M. Mayes, M. O. de La Cruz, *J. Chem. Phys.* **1991**, *95*, 4670; d) A. M. Mayes, M. La Olvera de Cruz, *J. Chem. Phys.* **1989**, *91*, 7228; e) H. Nakazawa, T. Ohta, *Macromolecules* **1993**, *26*, 5503.
- [104] H. Keskkula, *J. Polym. Sci. C Polym. Lett.* **1989**, *27*, 243.
- [105] K. Karatasos, S. H. Anastasiadis, T. Pakula, H. Watanabe, *Macromolecules* **2000**, *33*, 523.
- [106] R. J. Spontak, J. M. Zielinski, G. G. Lipscomb, *Macromolecules* **1992**, *25*, 6270.
- [107] L. Qiao, C. Leibig, S. F. Hahn, K. I. Winey, *Ind. Eng. Chem. Res.* **2006**, *45*, 5598.
- [108] G. Floudas, S. Paraskeva, N. Hadjichristidis, G. Fytas, B. Chu, A. N. Semenov, *J. Chem. Phys.* **1997**, *107*, 5502.
- [109] H. Watanabe, Y. Matsumiya, T. Sawada, T. Iwamoto, *Macromolecules* **2007**, *40*, 6885.
- [110] L. Wu, T. P. Lodge, F. S. Bates, *Macromolecules* **2004**, *37*, 8184.
- [111] a) F. Drolet, G. H. Fredrickson, *Macromolecules* **2001**, *34*, 5317; b) M. W. Matsen, M. Schick, *Macromolecules* **1994**, *27*, 187; c) H. Watanabe, *Macromolecules* **1995**, *28*, 5006; d) B. Li, E. Ruckenstein, *Macromol. Theory Simul.* **1998**, *7*, 333.
- [112] T. J. Hermel, L. Wu, S. F. Hahn, T. P. Lodge, F. S. Bates, *Macromolecules* **2002**, *35*, 4685.

- [113] Y. Cohen, R. J. Albalak, B. J. Dair, M. S. Capel, E. L. Thomas, *Macromolecules* **2000**, *33*, 6502.
- [114] M. Morton in *Advances in chemistry series, Vol. 99* (Ed.: N. A. J. Platzer), American Chemical Society, Washington, DC, **1971**, pp. 490–509.
- [115] S. Mishra, R. M. Badani Prado, T. E. Lacy, S. Kundu, *Soft Matter* **2018**, *14*, 7958.
- [116] M. W. Hamersky, S. D. Smith, A. O. Gozen, R. J. Spontak, *Phys. Rev. Lett.* **2005**, *95*, 168306.
- [117] a) S. Schlick, M. Levy, *J. Phys. Chem.* **1960**, *64*, 883; b) N. Corbin, J. Prud'Homme, *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1645; c) W. M. Cole, S. Futamura, *Process for producing multiblock copolymer and products produced thereby*, US3937760A, **1974**; d) N. Corbin, J. Prud'Homme, *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1937.
- [118] a) N. Hadjichristidis, H. Iatrou, S. Pispas, M. Pitsikalis, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211; b) N. Hadjichristidis, A. Hirao, *Anionic Polymerization*, Springer Japan, Tokyo, **2015**.
- [119] I. Noda (Ed.) *Studies in Polymer Science*, Elsevier Science, Burlington, **2012**.
- [120] S. D. Smith, R. J. Spontak, M. M. Satkowski, A. R. Ashraf, J. S. Lin, *Phys. Rev. B* **1993**, *47*, 14555.
- [121] L. Wu, E. W. Cochran, T. P. Lodge, F. S. Bates, *Macromolecules* **2004**, *37*, 3360.
- [122] a) Y. Matsushita, Y. Mogi, H. Mukai, J. Watanabe, I. Noda, *Polymer* **1994**, *35*, 246; b) Y. Nagata, J. Masuda, A. Noro, D. Cho, A. Takano, Y. Matsushita, *Macromolecules* **2005**, *38*, 10220; c) M. Ganß, *Struktur-Eigenschafts-Beziehungen in Styrol-Butadien basierten Blockcopolymeren mit statistischen Copolymerblöcken*. Dissertation, **2012**; d) Y. Matsumiya, H. Watanabe, A. Takano, Y. Takahashi, *Macromolecules* **2013**, *46*, 2681; e) Y. Higaki, K. Suzuki, Y. Kiyoshima, T. Toda, M. Nishiura, N. Ohta, H. Masunaga, Z. Hou, A. Takahara, *Macromolecules* **2017**, *50*, 6184; f) M. O. Tuhin, J. J. Ryan, J. D. Sadler, Z. Han, B. Lee, S. D. Smith, M. A. Pasquinelli, R. J. Spontak, *Macromolecules* **2018**, *51*, 5173.
- [123] J. Kelsey, N. Pickering, A. Clough, J. Zhou, J. L. White, *Macromolecules* **2017**, *50*, 7233.
- [124] E. Mastan, J. He, *Macromolecules* **2017**, *50*, 9173.
- [125] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, *51*, 10246.
- [126] M. Appold, E. Grune, H. Frey, M. Gallei, *ACS Appl. Mater. Interfaces* **2018**, *10*, 18202.
- [127] I. Kuntz, *J. Polym. Sci.* **1961**, *54*, 569.
- [128] M. Morton, F. R. Ells, *J. Polym. Sci.* **1962**, *61*, 25.
- [129] A. A. Korotkov, N. N. Chesnokova, *Polym. Sci. U.S.S.R.* **1961**, *2*, 284.
- [130] G. Kraus, C. W. Childers, J. T. Gruver, *J. Appl. Polym. Sci.* **1967**, *11*, 1581.
- [131] A. F. Johnson, D. J. Worsfold, *Makromol. Chem.* **1965**, *85*, 273.
- [132] K. F. O'Driscoll, I. Kuntz, *J. Polym. Sci.* **1962**, *61*, 19.
- [133] a) G. Kraus, K. W. Rollmann, *Angew. Makromol. Chem.* **1971**, *16*, 271; b) L. H. Sperling (Ed.) *Polymer science and technology, Vol. 4*, Plenum Press, New York, NY, **1974**.
- [134] a) R. Adhikari, R. Godehardt, W. Lebek, R. Weidisch, G. H. Michler, K. Knoll, *J. Macromol. Sci., Part B: Phys.* **2001**, *40*, 833; b) U. Staudinger, B. K. Satapathy, M. Thunga, R. Weidisch, A. Janke, K. Knoll, *Eur. Polym. J.* **2007**, *43*, 2750.

- [135] D. H. Kaelble, E. H. Cirlin, *J. Polym. Sci., Part C: Polym. Symp.* **1973**, 43, 131.
- [136] a) G. ten Brinke, F. E. Karasz, W. J. MacKnight, *Macromolecules* **1983**, 16, 1827; b) R.-J. Roe, W.-C. Zin, *Macromolecules* **1980**, 13, 1221; c) D. R. Paul, J. W. Barlow, *Polymer* **1984**, 25, 487.
- [137] F. Annighfer, W. Gronski, *Colloid Polym. Sci.* **1983**, 261, 15.
- [138] F. Annighöfer, W. Gronski, *Makromol. Chem.* **1984**, 185, 2213.
- [139] W. Gronski, F. Annighöfer, R. Stadler, *Makromol. Chem.* **1984**, 6, 141.
- [140] J. R. Brown, S. W. Sides, L. M. Hall, *ACS Macro Lett.* **2013**, 2, 1105.
- [141] D. J. Kelley, A. V. Tobolsky, *J. Am. Chem. Soc.* **1959**, 81, 1597.
- [142] P. Bayard, R. Fayt, P. Teyssie, S. K. Varshney, B. Vuillemin, P. Heim, *System for initiating the anionic polymerization of monomers*, CA2074133C, **1991**.
- [143] L. Shaw, L. R. Hutchings, *Polym. Chem.* **2020**, 11, 7020.
- [144] J. M. Kim, S. B. Chakrapani, B. S. Beckingham, *Macromolecules* **2020**, 53, 3814.
- [145] D. Fuchs, H. Hübner, T. Kraus, B.-J. Niebuur, M. Gallei, H. Frey, A. H. E. Mueller, *Polym. Chem.* **2021**.
- [146] M. C. Iovu, E. Buzdugan, M. Teodorescu, A. G. Britchi, G. Hubca, H. Iovu, *Angew. Makromol. Chem.* **1999**, 271, 18.
- [147] a) H. L. Hsieh, *J. Polym. Sci., Part A-1: Polym. Chem.* **1970**, 8, 533; b) H. S. Makowski, M. Lynn, *J. Macromol. Sci., Part A: Pure Appl. Chem.* **1968**, 2, 683.
- [148] A. A. Arest-Yakubovich, *Macromol. Symp.* **1994**, 85, 279.
- [149] H. L. Hsieh, C. F. Wofford, *J. Polym. Sci., Part A-1: Polym. Chem.* **1969**, 7, 449.
- [150] A. Forens, K. Roos, C. Dire, B. Gadenne, S. Carlotti, *Polymer* **2018**, 153, 103.
- [151] a) J.-S. Wang, R. Jerome, P. Bayard, P. Teyssie, *Macromolecules* **1994**, 27, 4908; b) C. Zune, R. Jérôme, *Prog. Polym. Sci.* **1999**, 24, 631.
- [152] R. Kozak, M. Matlengiewicz, *Int. J. Polym. Anal. Charact.* **2017**, 22, 51.
- [153] R. Quirk in *Handbook of polymer synthesis, characterization, and processing* (Ed.: E. Saldívar-Guerra), Wiley, Hoboken, NJ, **2013**, pp. 127–162.
- [154] T. P. Lodge, T. C. B. McLeish, *Macromolecules* **2000**, 33, 5278.
- [155] N. Hadjichristidis, H. Iatrou, M. Pitsikalis, J. Mays, *Prog. Polym. Sci.* **2006**, 31, 1068.
- [156] A. Hirao, R. Goseki, T. Ishizone, *Macromolecules* **2014**, 47, 1883.
- [157] J. M. Ren, T. G. McKenzie, Q. Fu, E. H. H. Wong, J. Xu, Z. An, S. Shanmugam, T. P. Davis, C. Boyer, G. G. Qiao, *Chem. Rev. (Washington, DC, U. S.)* **2016**, 116, 6743.
- [158] N. Hadjichristidis, M. Pitsikalis, S. Pispas, H. Iatrou, *Chem. Rev. (Washington, DC, U. S.)* **2001**, 101, 3747.
- [159] M. Morton, T. E. Helminiak, S. D. Gadkary, F. Bueche, *J. Polym. Sci.* **1962**, 57, 471.

- [160] a) T. Altares, D. P. Wyman, V. R. Allen, K. Meyersen, *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 4131; b) M. Pitsikalis, S. Sioula, S. Pispas, N. Hadjichristidis, D. C. Cook, J. Li, J. W. Mays, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4337.
- [161] J. Roovers, L. L. Zhou, P. M. Toporowski, M. van der Zwan, H. Iatrou, N. Hadjichristidis, *Macromolecules* **1993**, *26*, 4324.
- [162] a) R. W. Pennisi, L. J. Fetters, *Macromolecules* **1988**, *21*, 1094; b) S. Perny, J. Allgaier, D. Cho, W. Lee, T. Chang, *Macromolecules* **2001**, *34*, 5408.
- [163] N. Hadjichristidis, A. Guyot, L. J. Fetters, *Macromolecules* **1978**, *11*, 668.
- [164] L.-K. Bi, L. J. Fetters, *Macromolecules* **1976**, *9*, 732.
- [165] G. Floudas, S. Pispas, N. Hadjichristidis, T. Pakula, I. Erukhimovich, *Macromolecules* **1996**, *29*, 4142.
- [166] a) S. Park, D. Cho, K. Im, T. Chang, D. Uhrig, J. W. Mays, *Macromolecules* **2003**, *36*, 5834; b) A. B. Burns, R. A. Register, *Macromolecules* **2016**, *49*, 2063.
- [167] P. von Tiedemann, K. Maciol, J. Preis, P. Sajkiewicz, H. Frey, *Polym. Chem.* **2019**, *10*, 1762.
- [168] L. J. Fetters, A. D. Kiss, D. S. Pearson, G. F. Quack, F. J. Vitus, *Macromolecules* **1993**, *26*, 647.
- [169] a) D. Held, A. H. Müller, *Macromol. Symp.* **2000**, *157*, 225; b) M. Daoud, J. P. Cotton, *J. Phys.* **1982**, *43*, 531.
- [170] a) P. Dreypuss, L. J. Fetters, D. R. Hansen, *Rubber Chem. Technol.* **1980**, *53*, 728; b) D. Feldman, *J. Polym. Sci. C Polym. Lett.* **1986**, *24*, 613.
- [171] a) T. Hashimoto, Y. Ijichi, L. J. Fetters, *J. Chem. Phys.* **1988**, *89*, 2463; b) Y. Ijichi, T. Hashimoto, L. J. Fetters, *Macromolecules* **1989**, *22*, 2817.
- [172] M. W. Matsen, M. Schick, *Macromolecules* **1994**, *27*, 6761.
- [173] M. La Olvera de Cruz, I. C. Sanchez, *Macromolecules* **1986**, *19*, 2501.
- [174] a) D. M. A. Buzza, I. W. Hamley, A. H. Fzea, M. Moniruzzaman, J. B. Allgaier, R. N. Young, P. D. Olmsted, T. C. B. McLeish, *Macromolecules* **1999**, *32*, 7483; b) D. M. A. Buzza, A. H. Fzea, J. B. Allgaier, R. N. Young, R. J. Hawkins, I. W. Hamley, T. C. B. McLeish, T. P. Lodge, *Macromolecules* **2000**, *33*, 8399.
- [175] P. von Tiedemann, J. Yan, R. D. Barent, R. J. Spontak, G. Floudas, H. Frey, R. A. Register, *Macromolecules* **2020**, *53*, 4422.
- [176] J. Zhang, D. K. Schneiderman, T. Li, M. A. Hillmyer, F. S. Bates, *Macromolecules* **2016**, *49*, 9108.
- [177] E. B. Zhulina, S. S. Sheiko, A. V. Dobrynin, O. V. Borisov, *Macromolecules* **2020**, *53*, 2582.
- [178] a) S. S. Sheiko, B. S. Sumerlin, K. Matyjaszewski, *Prog. Polym. Sci.* **2008**, *33*, 759; b) S. S. Sheiko, F. C. Sun, A. Randall, D. Shirvanyants, M. Rubinstein, H. Lee, K. Matyjaszewski, *Nature* **2006**, *440*, 191; c) J. Rzaev, *Macromolecules* **2009**, *42*, 2135.
- [179] J. Zhang, T. Li, A. M. Mannion, D. K. Schneiderman, M. A. Hillmyer, F. S. Bates, *ACS Macro Lett.* **2016**, *5*, 407.
- [180] W. F. M. Daniel, J. Burdyńska, M. Vatankhah-Varnoosfaderani, K. Matyjaszewski, J. Paturej, M. Rubinstein, A. V. Dobrynin, S. S. Sheiko, *Nat. Mater.* **2016**, *15*, 183.

- [181] L. Jiang, D. Nykypanchuk, A. E. Ribbe, J. Rzaev, *ACS Macro Lett.* **2018**, *7*, 619.
- [182] W. Lu, A. Goodwin, Y. Wang, P. Yin, W. Wang, J. Zhu, T. Wu, X. Lu, B. Hu, K. Hong et al., *Polym. Chem.* **2018**, *9*, 160.
- [183] A. B. Burns, R. A. Register, *Macromolecules* **2016**, *49*, 9521.
- [184] C. Wahlen, J. Blankenburg, P. von Tiedemann, J. Ewald, P. Sajkiewicz, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2020**, *53*, 10397.
- [185] F. R. Mayo, F. M. Lewis, *J. Am. Chem. Soc.* **1944**, *66*, 1594.
- [186] T. Alfrey, G. Goldfinger, *J. Chem. Phys.* **1944**, *12*, 205.
- [187] F. T. Wall, *J. Am. Chem. Soc.* **1941**, *63*, 1862.
- [188] a) W. Zhang, J. Allgaier, R. Zorn, S. Willbold, *Macromolecules* **2013**, *46*, 3931; b) F. Heatley, G. Yu, C. Booth, T. G. Blease, *Eur. Polym. J.* **1991**, *27*, 573; c) X. Pang, R. Jing, J. Huang, *Polymer* **2008**, *49*, 893; d) A. Lee, P. Lundberg, D. Klinger, B. F. Lee, C. J. Hawker, N. A. Lynd, *Polym. Chem.* **2013**, *4*, 5735.
- [189] J. Herzberger, D. Leibig, J. C. Liermann, H. Frey, *ACS Macro Lett.* **2016**, *5*, 1206.
- [190] J. Blankenburg, E. Kersten, K. Maciol, M. Wagner, S. Zarbakhsh, H. Frey, *Polym. Chem.* **2019**, *10*, 2863.
- [191] E. Grune, J. Bareuther, J. Blankenburg, M. Appold, L. Shaw, A. H. E. Müller, G. Floudas, L. R. Hutchings, M. Gallei, H. Frey, *Polym. Chem.* **2019**, *10*, 1213.
- [192] E. Merz, T. Alfrey, G. Goldfinger, *J. Polym. Sci.* **1946**, *1*, 75.
- [193] a) J. C. Bevington, D. O. Harris, *J. Polym. Sci., Part B: Polym. Lett.* **1967**, *5*, 799; b) N. Grassie, B. Torrance, J. D. Fortune, J. D. Gemmell, *Polymer* **1965**, *6*, 653.
- [194] S. Quinebèche, C. Navarro, Y. Gnanou, M. Fontanille, *Polymer* **2009**, *50*, 1351.
- [195] D. J. Worsfold, *J. Polym. Sci., Part A-1: Polym. Chem.* **1967**, *5*, 2783.
- [196] T. E. Long, H. Y. Liu, B. A. Schell, D. M. Teegarden, D. S. Uerz, *Macromolecules* **1993**, *26*, 6237.
- [197] M. Morton, E. E. Bostick, R. A. Livigni, L. J. Fetters, *J. Polym. Sci., Part A: Gen. Pap.* **1963**, *1*, 1735.
- [198] A. A. Korotkov, N. N. Chesnokova, L. B. Trukhmanova, *Polym. Sci. U.S.S.R.* **1960**, *1*, 10.
- [199] a) H. L. Hsieh, *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 153; b) H. L. Hsieh, *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 163; c) S. Bywater, D. J. Worsfold, *J. Organomet. Chem.* **1967**, *10*, 1; d) J. E. L. Roovers, S. Bywater, *Macromolecules* **1968**, *1*, 328.
- [200] L. Gold, *J. Chem. Phys.* **1958**, *28*, 91.
- [201] F. J. Welch, *J. Am. Chem. Soc.* **1960**, *82*, 6000.
- [202] K. F. O'Driscoll, A. V. Tobolsky, *J. Polym. Sci.* **1959**, *35*, 259.
- [203] D. J. Worsfold, S. Bywater, *Can. J. Chem.* **1960**, *38*, 1891.
- [204] a) K. F. O'Driscoll, A. V. Tobolsky, *J. Polym. Sci.* **1959**, *35*, 259; b) D. J. Worsfold, S. Bywater, *Can. J. Chem.* **1960**, *38*, 1891; c) C. Geacintov, J. Smid, M. Szwarc, *J. Am. Chem. Soc.* **1961**, *83*, 1253.
- [205] R. C. P. Cubbon, D. Margerison, *Proc. R. Soc. London, Ser. A* **1962**, *268*, 260.

- [206] P. Margl, *Can. J. Chem.* **2009**, *87*, 891.
- [207] R. Zelinski, C. W. Childers, *Rubber Chem. Technol.* **1968**, *41*, 161.
- [208] a) M. Morton, L. J. Fetters, E. E. Bostick, *J. Polym. Sci., Part C: Polym. Symp.* **1963**, *1*, 311; b) R. Cubbon, D. Margerison, *Polymer* **1965**, *6*, 102; c) H. L. Hsieh, *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 173.
- [209] L. J. Fetters, N. P. Balsara, J. S. Huang, H. S. Jeon, K. Almdal, M. Y. Lin, *Macromolecules* **1995**, *28*, 4996.
- [210] Y. Zhao, N. Miyamoto, S. Koizumi, T. Hashimoto, *Macromolecules* **2010**, *43*, 2948.
- [211] D. J. Worsfold, S. Bywater, *Macromolecules* **1972**, *5*, 393.
- [212] L. J. Fetters, M. Morton, *Macromolecules* **1974**, *7*, 552.
- [213] H. Watanabe, Y. Oishi, T. Kanaya, H. Kaji, F. Horii, *Macromolecules* **2003**, *36*, 220.
- [214] A. Z. Niu, J. Stellbrink, J. Allgaier, L. Willner, A. Radulescu, D. Richter, B. W. Koenig, R. P. May, L. J. Fetters, *J. Chem. Phys.* **2005**, *122*, 134906.
- [215] S. Bywater, *Macromolecules* **1998**, *31*, 6010.
- [216] Y. L. Spirin, A. A. Arest-Yakubovich, D. K. Polyakov, A. R. Gantmakher, S. S. Medvedev, *J. Polym. Sci.* **1962**, *58*, 1181.
- [217] M. Morton, L. J. Fetters, *J. Polym. Sci., Part A: Gen. Pap.* **1964**, *2*, 3311.
- [218] S. Bywater, D. J. Worsfold, *Can. J. Chem.* **1962**, *40*, 1564.
- [219] T. A. Antkowiak, A. E. Oberster, A. F. Halasa, D. P. Tate, *J. Polym. Sci., Part A-1: Polym. Chem.* **1972**, *10*, 1319.
- [220] a) C. F. Wofford, *Production of random copolymers in organolithium polymerization systems*, US3498960A, **1967**; b) S. Bywater, I. J. Alexander, *J. Polym. Sci., Part A-1: Polym. Chem.* **1968**, *6*, 3407; c) F. Liu, H. Tan, T. Tang, *Chin. J. Polym. Sci.* **2013**, *31*, 1647; d) M. Liao, Q. Wang, N. Wang, L. Xu, C. Li, A. Liang, *Polym. Sci., Ser. B* **2014**, *56*, 753; e) Z. Zhao, H. Shen, K. Sui, G. Wang, *Polymer* **2018**, *137*, 364; f) A. F. Halasa, B. B. Gross, W.-L. Hsu, *Rubber Chem. Technol.* **2010**, *83*, 380; g) G. A. Moczygemba, W. J. Trepka, *Tapered block styrene/butadiene copolymers*, US5227419A, **1990**; h) G. A. Moczygemba, N. R. Knight, W. J. Trepka, N. E. Stacy, *Block copolymers of monovinylarenes and conjugated dienes containing two interior tapered blocks*, US5399628A, **1993**.
- [221] B. Lehong, Y. Shengkang, *J. Appl. Polym. Sci.* **1992**, *44*, 1507.
- [222] a) A. H. E. Müller, K. Matyjaszewski, *Controlled and living polymerizations. Methods and materials*, Wiley-VCH, Weinheim, **2009**; b) J. E. L. Roovers, S. Bywater, *Trans. Faraday Soc.* **1966**, *62*, 701; c) A. Garton, S. Bywater, *Macromolecules* **1975**, *8*, 694; d) K. Sardelis, H. J. Michels, G. Allen, F. R. S, *Polymer* **1984**, *25*, 1011.
- [223] a) S. Bywater, A. F. Johnson, D. J. Worsfold, *Can. J. Chem.* **1964**, *42*, 1255; b) M. Szwarc, *J. Polym. Sci.* **1959**, *40*, 583; c) G. Consiglio, *Angew. Chem.* **1994**, *106*, 1869.
- [224] S. Bywater, Y. Firat, P. E. Black, *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 669.
- [225] A. V. Tobolsky, C. E. Rogers, *J. Polym. Sci.* **1959**, *38*, 205.

- [226] a) A. V. Tobolsky, C. E. Rogers, *J. Polym. Sci.* **1959**, *40*, 73; b) J. M. Widmaier, G. C. Meyer, *Macromolecules* **1981**, *14*, 450.
- [227] K. A. Günay, P. Theato, H.-A. Klok, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 1.
- [228] a) G. E. Serniuk, F. W. Banes, M. W. Swaney, *J. Am. Chem. Soc.* **1948**, *70*, 1804; b) N. ten Brummelhuis, C. Diehl, H. Schlaad, *Macromolecules* **2008**, *41*, 9946.
- [229] a) S. van der Heijden, K. de Bruycker, R. Simal, F. Du Prez, K. de Clerck, *Macromolecules* **2015**, *48*, 6474; b) S. Billiet, K. de Bruycker, F. Driessen, H. Goossens, V. van Speybroeck, J. M. Winne, F. E. Du Prez, *Nat. Chem.* **2014**, *6*, 815.
- [230] a) D. Zuchowska, *Polymer* **1980**, *21*, 514; b) A. Matic, A. Hess, D. Schanzenbach, H. Schlaad, *Polym. Chem.* **2020**, *11*, 1364.
- [231] G. Camino, M. Guaita, A. Priola, *Polym. Degrad. Stab.* **1985**, *12*, 241.
- [232] a) B. Obermeier, F. Wurm, H. Frey, *Macromolecules* **2010**, *43*, 2244; b) A. Natalello, M. Werre, A. Alkan, H. Frey, *Macromolecules* **2013**, *46*, 8467; c) N. D. Dolinski, Z. A. Page, E. H. Discekici, D. Meis, I.-H. Lee, G. R. Jones, R. Whitfield, X. Pan, B. G. McCarthy, S. Shanmugam et al., *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 268; d) S. Dadashi-Silab, I.-H. Lee, A. Anastasaki, F. Lorandi, B. Narupai, N. D. Dolinski, M. L. Allegrezza, M. Fantin, D. Konkolewicz, C. J. Hawker et al., *Macromolecules* **2020**, *53*, 5280.
- [233] J. E. Puskas, T. E. Long, R. F. Storey, S. Shaikh, C. L. Simmons, *In Situ Spectroscopy of Monomer and Polymer Synthesis*, Springer US, Boston, MA, **2003**.
- [234] D. T. Williamson, J. F. Elman, P. H. Madison, A. J. Pasquale, T. E. Long, *Macromolecules* **2001**, *34*, 2108.
- [235] D. J. Worsfold, S. Bywater, *Can. J. Chem.* **1964**, *42*, 2884.
- [236] V. Artyushenko (Ed.), *Advanced Photonics: Speciality in optical fibers. Mid IR-Fiber Optics for Process Spectroscopy and Laser Power Delivery*, Optical Society of America, Washington, D.C., **2014**.
- [237] Y. Takezawa, S. Ohara, *J. Appl. Polym. Sci.* **1993**, *49*, 169.
- [238] S. Bywater, D. J. Worsfold, *Can. J. Chem.* **1967**, *45*, 1821.
- [239] M. Fineman, S. D. Ross, *J. Polym. Sci.* **1950**, *5*, 259.
- [240] T. Kelen, F. Tds, B. Turcsnyi, *Polym. Bull.* **1980**, *2*, 71.
- [241] R. Chartrand, *ISRN Applied Mathematics* **2011**, *2011*, 1.
- [242] V. E. Meyer, G. G. Lowry, *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 2843.
- [243] I. Skeist, *J. Am. Chem. Soc.* **1946**, *68*, 1781.
- [244] a) V. Jaacks, *Angew. Chem.* **1967**, *79*, 419; b) V. Jaacks, *Makromol. Chem.* **1972**, *161*, 161.
- [245] a) B. S. Beckingham, G. E. Sanoja, N. A. Lynd, *Macromolecules* **2015**, *48*, 6922; b) N. A. Lynd, R. C. Ferrier, B. S. Beckingham, *Macromolecules* **2019**, *52*, 2277.
- [246] R. Hoffmann, V. I. Minkin, B. K. Carpenter, *Bull. Soc. Chim. Fr.* **1996**, 117.
- [247] a) M. Smotherman, D. Spicer, *Commun. ACM* **2010**, *53*, 28; b) G. E. Moore, *IEEE Solid-State Circuits Soc. Newsl.* **2006**, *11*, 33.



- [248] a) B. Dünweg, K. Kremer, *J. Chem. Phys.* **1993**, *99*, 6983; b) Y. Seo, J. R. Brown, L. M. Hall, *Macromolecules* **2015**, *48*, 4974.
- [249] D. R. D'hooge, M. Fantin, A. J. D. Magenau, D. Konkolewicz, K. Matyjaszewski, *React. Chem. Eng.* **2018**, *3*, 866.
- [250] Y. W. Marien, P. H. M. van Steenberge, C. Barner-Kowollik, M.-F. Reyniers, G. B. Marin, D. R. D'hooge, *Macromolecules* **2017**, *50*, 1371.
- [251] a) A. S. Cho, L. J. Broadbelt, *Mol. Simul.* **2010**, *36*, 1219; b) D. R. D'hooge, P. H. van Steenberge, M.-F. Reyniers, G. B. Marin, *Prog. Polym. Sci.* **2016**, *58*, 59; c) D. R. D'hooge, *Macromol. Rapid Commun.* **2018**, *39*, e1800057; d) S. Hamzehlou, Y. Reyes, J. R. Leiza, *Macromol. React. Eng.* **2012**, *6*, 319; e) J. Lu, H. Zhang, Y. Yang, *Makromol. Chem., Theory Simul.* **1993**, *2*, 747; f) V. R. Regatte, H. Gao, I. A. Konstantinov, S. G. Arturo, L. J. Broadbelt, *Macromol. Theory Simul.* **2014**, *23*, 564; g) A. A. A. Smith, A. Hall, V. Wu, T. Xu, *ACS Macro Lett.* **2019**, *8*, 36; h) P. H. M. van Steenberge, D. R. D'hooge, Y. Wang, M. Zhong, M.-F. Reyniers, D. Konkolewicz, K. Matyjaszewski, G. B. Marin, *Macromolecules* **2012**, *45*, 8519; i) L. Wang, L. J. Broadbelt, *Macromolecules* **2010**, *43*, 2228; j) Z. Zheng, J. Ling, A. H. E. Müller, *Macromol. Rapid Commun.* **2014**, *35*, 234.
- [252] a) S. Anantawaraskul, J. B. P. Soares, P. M. Wood-Adams, *Macromol. Theory Simul.* **2003**, *12*, 229; b) S. K. Fierens, P. H. M. van Steenberge, M.-F. Reyniers, D. R. D'hooge, G. B. Marin, *React. Chem. Eng.* **2018**, *3*, 128; c) W. H. Stockmayer, *J. Chem. Phys.* **1945**, *13*, 199.
- [253] L. Yang, L. Han, H. Ma, H. Shen, C. Li, S. Zhang, L. Lei, X. Hao, Y. Li, *Eur. Polym. J.* **2019**, *120*, 109212.
- [254] C. Livitsanou, M. Steube, T. Johann, H. Frey, G. Floudas, *Macromolecules* **2020**.
- [255] a) R. X. E. Willemse, A. M. van Herk, *J. Am. Chem. Soc.* **2006**, *128*, 4471; b) R. X. E. Willemse, B. B. P. Staal, E. H. D. Donkers, A. M. van Herk, *Macromolecules* **2004**, *37*, 5717.
- [256] P. van Steenberge, D. R. D'hooge, M.-F. Reyniers, G. B. Marin, *Chem. Eng. Sci.* **2014**, *110*, 185.

## Supporting Information

### Calculation of the Order-Disorder Transition Temperature

According to equation S1.1, the Flory-Huggins interaction parameter,  $\chi$ , can be calculated for a given temperature  $T$ .<sup>[1]</sup> According to Leibler, the order-disorder transition for volume-symmetric diblock copolymers is given by equation S1.2. This enables to calculate the order-disorder transition temperature ( $T_{ODT}$ ) as a function of the degree of polymerization  $N$  (equation S1.3). To calculate the degree of polymerization for a volume-symmetric diblock copolymer (equations S1.4- S1.9), the densities  $\rho$  and the molecular weights  $M$  of the isoprene and styrene repeating units need to be considered.<sup>[2]</sup>

$$M_{PI-unit} = 68.12 \text{ g/mol}; \rho_{PI}(140 \text{ }^{\circ}\text{C}) = 0.830 \text{ g/cm}^3;$$

$$M_{PS-unit} = 104.15 \text{ g/mol}; \rho_{PS}(140 \text{ }^{\circ}\text{C}) = 0.969 \text{ g/cm}^3$$

$$\chi_{IS}(T) = \frac{71.4}{T} - 0.0857 \quad (\text{S1.1})$$

$$\chi_{IS}(T_{ODT}) \cdot N = \left( \frac{71.4}{T_{ODT}} - 0.0857 \right) \cdot N = 10.5 \quad (\text{S1.2})$$

$$T_{ODT} = \frac{71.4}{\frac{10.5}{N} + 0.0857} \quad (\text{S1.3})$$

$$V_{PS} = V_{PI} \quad (\text{S1.4})$$

$$N_{PS} \cdot \frac{M_{PS}}{\rho_{PS}} = N_{PI} \cdot \frac{M_{PI}}{\rho_{PI}} \quad (\text{S1.5})$$

$$\frac{N_{PS}}{N_{PI}} = \frac{\frac{M_{PI}}{\rho_{PI}}}{\frac{M_{PS}}{\rho_{PS}}} = \frac{82.1}{108} \quad (\text{S1.6})$$

$$N = N_{PS} + N_{PI} \quad (\text{S1.7})$$

$$\begin{aligned} M_{average} &= \frac{N_{PS}}{N} \cdot M_{PS-unit} + \frac{N_{PI}}{N} \cdot M_{PI-unit} \\ &= \frac{82.1}{82.1 + 108} \cdot M_{PS-unit} + \frac{108}{82.1 + 108} \cdot M_{PI-unit} = 83.6 \end{aligned} \quad (\text{S1.8})$$

$$N = \frac{M_n}{M_{average}} \quad (\text{S1.9})$$

## Methods for the Determination of Reactivity Ratios

### Terminal model

The Mayo-Lewis equation (Eq. S2.1) as well as its rearranged form (Eq. S2.5) describe the instantaneous monomer incorporation,  $F$ , in dependence of the monomer feed,  $f$ , for the *terminal copolymerization model* [3]. The reactivity ratios  $r_1$  and  $r_2$  can be determined by least square fitting of a corresponding data set.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (\text{S2.1})$$

Introducing the monomer feed,  $f$ , and the instantaneous monomer incorporation  $F$ ,

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad (\text{S2.2})$$

$$f_2 = 1 - f_1 \quad (\text{S2.3})$$

$$F_1 = \frac{d[M_1]}{d([M_1] + [M_2])} \quad (\text{S2.4})$$

leads to

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (\text{S2.5})$$

Fineman and Ross introduced a linearization of the Mayo-Lewis equation. The reactivity ratios can be determined from the intercept ( $r_2$ ) and slope ( $r_1$ ) when  $H$  is plotted versus  $G$ .<sup>[4]</sup>

$$G = \frac{f_1(2F_1 - 1)}{(1 - f_1)F_1} \quad (\text{S3.1})$$

$$H = \frac{f_1^2(1 - F_1)}{(1 - f_1)^2 F_1} \quad (\text{S3.2})$$

$$G = H \cdot r_1 - r_2 \quad (\text{S3.3})$$

Kelen and Tüdös introduced a correction factor  $\alpha$ , which is determined based on the smallest and highest value  $H$  of the Fineman-Ross formalism and used to account for biases introduced by the linearization. The reactivity ratios can be determined from the slope and the intercept when  $\mu$  is plotted versus  $\eta$ .<sup>[5]</sup>

$$\alpha = (H_{\min} \cdot H_{\max})^{0.5} \quad (\text{S4.1})$$

$$\eta = \frac{G}{\alpha + H} \quad (\text{S4.2})$$

$$\mu = \frac{H}{\alpha + H} \quad (\text{S4.3})$$

$$\eta = \left( r_1 + \frac{r_2}{\alpha} \right) \cdot \mu - \frac{r_2}{\alpha} \quad (\text{S4.4})$$

As an alternative to the differential methods, the integrated form of the Mayo-Lewis equation (Equation S6).<sup>[6]</sup> Meyer and Lowry analytically integrated the copolymerization equation derived by Skeist.<sup>[7]</sup> The reactivity ratios  $r_1$  and  $r_2$  can be obtained via least square fitting of this equation to a corresponding data set based on versus  $1 - \text{total monomer conversion } X$  (Equation S5.3).<sup>[6]</sup>

The individual monomer conversions are defined as

$$x_1 = 1 - \frac{[M_1]}{[M_1]_0} \quad (\text{S5.1})$$

$$x_2 = 1 - x_1 \quad (\text{S5.2})$$

and the total monomer conversion is defined as

$$X = 1 - \frac{[M_1] + [M_2]}{[M_1]_0 + [M_2]_0} = 1 - \frac{[M]}{[M]_0} \quad (\text{S5.3})$$

Using the monomer feeds

$$\frac{f_1}{f_{1,0}} = \frac{[M_1]}{[M_1]_0} \cdot \frac{[M_1]_0 + [M_2]_0}{[M_1] + [M_2]} = \frac{1 - x_1}{1 - X} \quad (\text{S5.4})$$

$$\frac{f_2}{f_{2,0}} = \frac{1 - x_2}{1 - X} \quad (\text{S5.5})$$

Meyer and Lowry derived an integrated form of the Mayo-Lewis equation,

$$\frac{[M]}{[M]_0} = \left( \frac{f_1}{f_{1,0}} \right)^{\frac{r_2}{1-r_2}} \cdot \left( \frac{f_2}{f_{2,0}} \right)^{\frac{r_1}{1-r_1}} \cdot \left( \frac{f_{1,0} - \left( \frac{1-r_2}{2-r_1-r_2} \right)}{f_1 - \left( \frac{1-r_2}{2-r_1-r_2} \right)} \right)^{\frac{1-r_1 r_2}{(1-r_1)(1-r_2)}} \quad (\text{S6})$$

where the reactivity ratios can be obtained by non-linear fitting.

### **Non-Terminal Model (Ideal Polymerization)**

For the *non-terminal copolymerization model* we assume that  $k_{11} = k_{21} = k_1$  and  $k_{12} = k_{22} = k_2$ . Then,  $r_1 = k_1/k_2 = 1/r_2$ . By definition, the nature of the active chain end is not relevant, i.e., chain ends  $[M_1^*]$  and  $[M_2^*]$  can be regarded as  $[M^*]$ . The differential equations for the consumption of the comonomers are

$$\frac{d[M_1]}{dt} = k_1 [M^*] [M_1] \quad (\text{S7.1})$$

$$\frac{d[M_2]}{dt} = k_2[M^*][M_2] \quad (S7.2)$$

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \quad (S7.3)$$

This equation was first derived by Wall.<sup>[8]</sup> It is easily linearized by integration:

$$\ln \frac{[M_1]_0}{[M_1]_t} = r_1 \ln \frac{[M_2]_0}{[M_2]_t} \quad (S7.4)$$

Much later, the same equation was derived by Jaacks for the terminal model and the special case that one comonomer is in large excess of the other one.<sup>[9]</sup> The reactivity ratio can be obtained from the slope of the linear fit.

Alternatively, the Meyer-Lowry equation S6 can be simplified by setting  $r_1 \cdot r_2 = 1$ , leading to Eq. S7.5:

$$X = 1 - \left( \frac{f_1}{f_{1,0}} \right)^{\frac{1}{r_1-1}} \left( \frac{1-f_1}{1-f_{1,0}} \right)^{\frac{r_1}{1-r_1}} \quad (S7.5)$$

The Meyer-Lowry treatment for ideal polymerizations is also named “ideal integrated”.<sup>[10]</sup>

Beckingham, Sanoja and Lynd (BSL) introduced an alternative treatment of data for the non-terminal model.<sup>[11]</sup> The BSL Method uses the two equations S7.6 and also needs non-linear fitting.

$$\begin{aligned} X &= 1 - f_{1,0}(1 - x_1) - (1 - f_{1,0})(1 - x_1)^{r_2} \\ X &= 1 - f_{2,0}(1 - x_2)^{r_2} - (1 - f_{2,0})(1 - x_2) \end{aligned} \quad (S7.6)$$

**Table S1: Comparison of the selected methods for evaluation of the reactivity ratios.**

| Formalism                                           | Model        | Data foundation | Prerequisites                | Fitting method | Recommended |
|-----------------------------------------------------|--------------|-----------------|------------------------------|----------------|-------------|
| <b>Mayo-Lewis</b> <sup>[3]</sup>                    | terminal     | differential    | $F_1, f_1$                   | non-linear     | no          |
| <b>Fineman-Ross</b> <sup>[4]</sup>                  | terminal     | differential    | $F_1, f_1$                   | linear         | no          |
| <b>Kelen-Tüdös</b> <sup>[5]</sup>                   | terminal     | differential    | Fineman-Ross                 | linear         | no          |
| <b>Mayer-Lowry (M-L)</b> <sup>[6]</sup>             | terminal     | integrated      | $X, f_1, f_{1,0}$            | non-linear     | yes         |
| <b>Jaacks</b> <sup>[9]</sup>                        | non-terminal | integrated      | $M_1, M_2, M_{1,0}, M_{2,0}$ | linear         | yes         |
| <b>Integrated Ideal (M-L ideal)</b> <sup>[10]</sup> | non-terminal | integrated      | $X, f_1, f_{1,0}$            | non-linear     | yes         |
| <b>BSL</b> <sup>[11]</sup>                          | non-terminal | integrated      | $M_1, M_2, M_{1,0}, M_{2,0}$ | non-linear     | yes         |

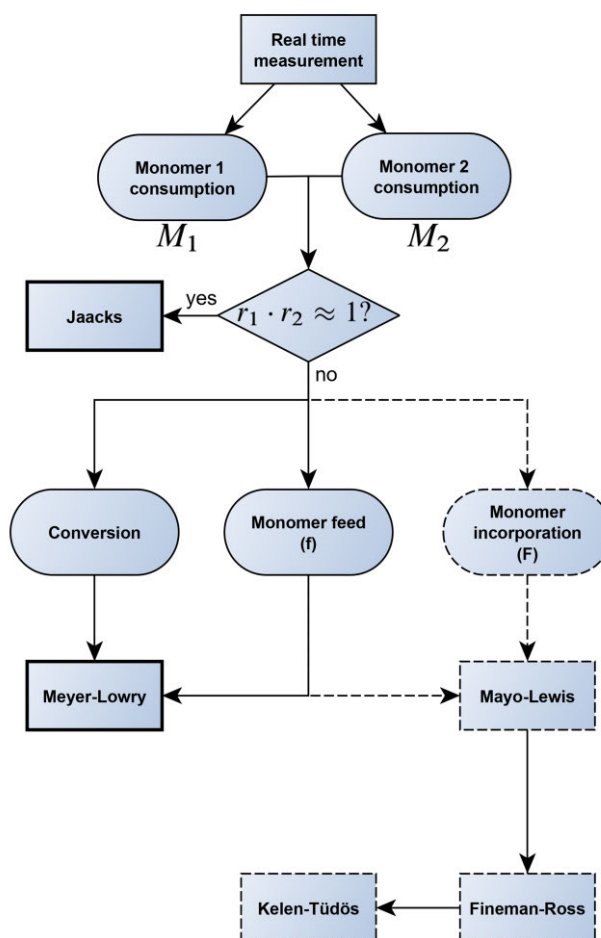


Figure S1: Overview of the common methods for determination of reactivity ratios. Methods based on the differential copolymer equation are marked by dashed lines and are not recommended for evaluation of copolymerization kinetics. Recommend methods are highlighted in bold.

## Kinetic Monte Carlo Simulations

The basic principle of every MC simulation relies on stochastics. While each individual calculation is very simple, and only the available brute-force computational power renders this method suitable to accurately predict copolymerization experiments.

The foundation to perform kMC simulations was built up by Gillespie.<sup>[12]</sup> A typical kMC process is based on the reported equations by Gillespie and the conversion of the continuum-based reaction rates to number-based probabilities. Equation Set S8 summarizes the equations needed to perform a kinetic Monte Carlo (kMC) simulation of a living anionic copolymerization. The homopropagation ( $k_{11}$ ,  $k_{22}$ ) and crosspropagation ( $k_{12}$ ,  $k_{21}$ ) rate constants are transformed to number-based probabilities ( $kMC_{11}$ ,  $kMC_{12}$ ,  $kMC_{22}$ ,  $kMC_{21}$ ) (Equations S8.1-8.4). Here,  $A_1$  and  $A_2$  denote the corresponding aggregation number (e.g., 2 in case of dimers and 4 in case of tetramers). Based on the cumulative probabilities  $P_V$  (Eq. S8.5) and a by a uniformly distributed random number  $rn_1=[0...1]$  (Eq. S8.6), these number-based probabilities are then used to determine which reaction is performed next. The corresponding time step is calculated by a second random number  $rn_2=[0...1]$  (Eq. S8.7). After selection of the reaction step by a random number, the reaction is applied, and the number of residual molecules is adjusted. Then the

process is repeated. Specifically, for the prediction of chain growth polymerizations like a living anionic copolymerization, a virtual flask is created ( $10^{-19}$  L to  $10^{-16}$  L volume), in which chain ends (typically 100 000 or more) are placed and reacted with monomers. The reaction is chosen and simulated based on their reaction probability, which scales with the kinetic rate constants. Like in a real reaction flask, each addition of a monomer to a chain end alters the overall concentration of the monomers.

$$kMC_{11} = \frac{k_{11}}{(NV)^{1/A_1}} \quad (S8.1)$$

$$kMC_{22} = \frac{k_{22}}{(NV)^{1/A_2}} \quad (S8.2)$$

$$kMC_{12} = \frac{k_{12}}{(NV)^{1/A_1}} \quad (S8.3)$$

$$kMC_{21} = \frac{k_{21}}{(NV)^{1/A_2}} \quad (S8.4)$$

$$P_v = \frac{R_v}{\sum_{M=1}^M R_v} \quad (S8.5)$$

$$\sum_{v=1}^{\mu-1} P_v < rn_1 < \sum_{v=1}^{\mu} P_v \quad (S8.6)$$

$$\tau = \frac{1}{\sum_{M=1}^M R_v} \ln \left( \frac{1}{rn_2} \right) \quad (S8.7)$$

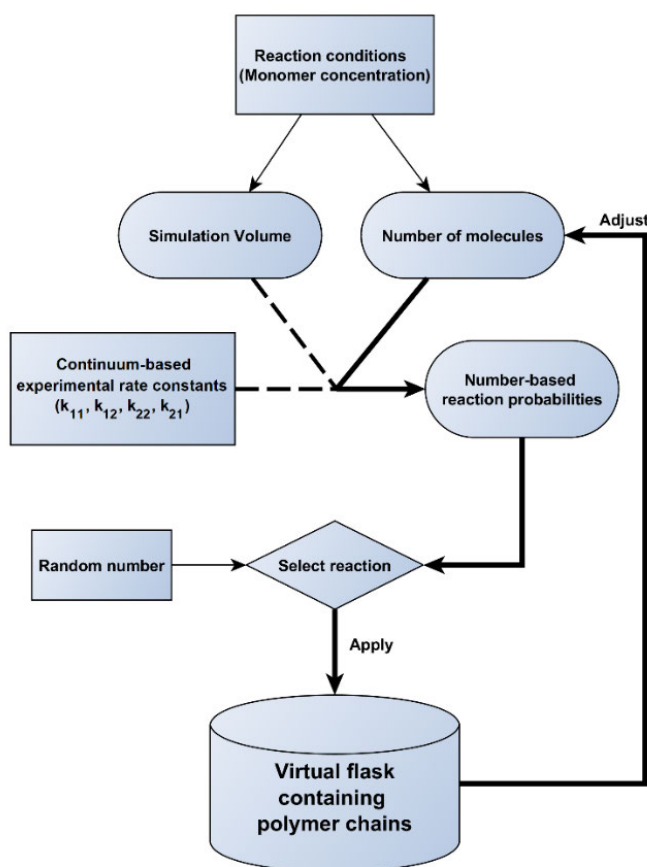


Figure S2: Simplified scheme of the process of performing a kMC simulation.

### kMC Example: SEC Distributions – Failed polymerization or not?

When performing a living anionic polymerization, a monomodal narrow molecular weight distribution is typically expected. Hence, to determine if a copolymerization was successful, typically the molecular weight distribution (e.g., the dispersity) via SEC is used as the first proxy for evaluation. Prediction of the dispersity of homopolymers prepared via living anionic copolymerization is straightforward based on the Poisson distribution ( $\bar{D} = 1 + 1/DP_n - 1/DP_n^2$ ). In contrast, the dispersity of a copolymerization cannot be predicted in a trivial manner.<sup>[13,14]</sup>

In two of our previous works, we synthesized statistical copolymers of styrene derivatives and isoprene.<sup>[13,14]</sup> All low molecular weight polymers ( $< 5000 \text{ g mol}^{-1}$ ) showed broadening of the molecular weight distribution and thus were first regarded as failed polymerizations due to experimental problems. The low molecular weight fraction of the molecular weight distribution was found to exhibit an increased isoprene content. This was ascribed to the rather slow crossover from a PI-Li chain end to 4-methyl styrene (4MS) compared to the homopropagation of 4MS.<sup>[13]</sup> However, a prediction of the molecular weight distribution (and SEC curve) via kMC showed that no experimental error was present, and indeed a broadened molecular weight distribution was to be expected (Figure S1).

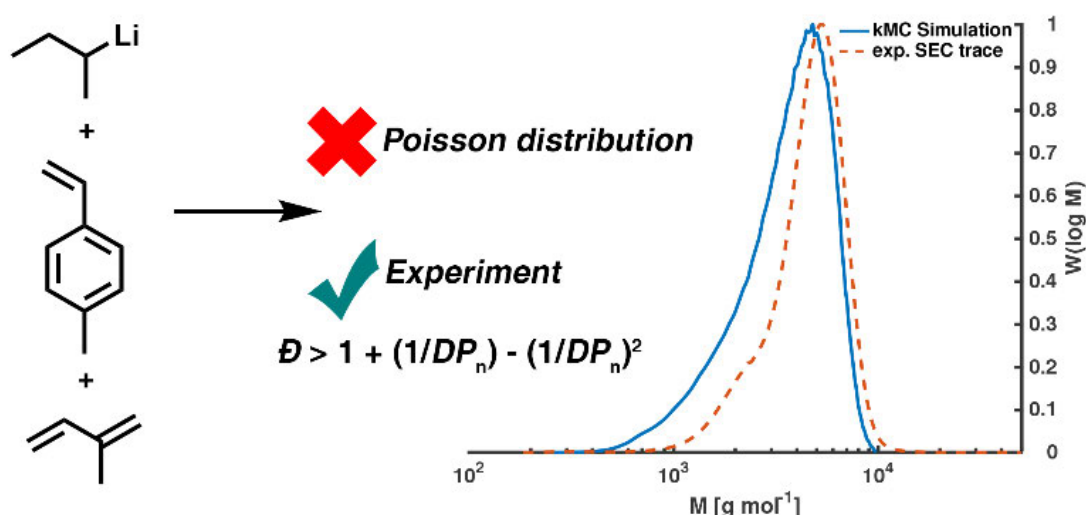


Figure S3: The copolymerization of 4-methyl styrene (4MS) and isoprene to obtain statistical P(I-co-4MS) copolymers leads to a broad molecular weight distribution (red dashed line), exceeding the dispersity of an ideal Poisson distribution. kMC simulation (blue solid line) confirmed that this molecular weight distribution is based on kinetic peculiarities and not on experimental errors.

### kMC example: Optimization of the reaction time<sup>[15]</sup>

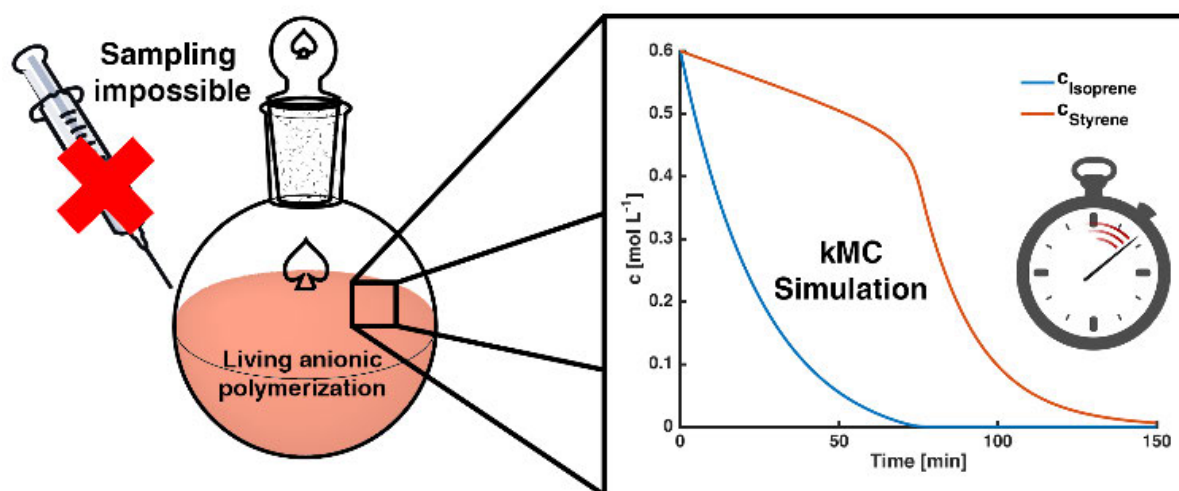
Due to the high sensitivity of the chain ends towards termination by impurities, the polymerization must be contained in a closed system.<sup>[15]</sup> Hence, sampling of the polymerization is exceptionally difficult and comprises the risk of irreversible termination by introducing impurities.

In previous works, we employed the living anionic copolymerization to synthesize tapered multiblock copolymers by multiple additions of a monomer mixture to the living polymer solution.<sup>[15,16]</sup> To obtain defined polymer structures it is crucial to postpone the monomer addition until the majority of the monomer of the previous addition step has reacted. Thus, a



single value parameter such as the reaction time to the desired threshold conversion (e.g., 99.5 %) becomes a crucial parameter in optimizing the polymer synthesis.

By feeding all reaction parameters to the kMC model the time-dependent monomer conversion and reaction time can be predicted within less than one minute of calculation effort. The simulation via kMC also accounts for aggregation effects of the chain ends that are present in the living anionic copolymerization of styrene and isoprene in hydrocarbons. This consideration typically leads to errors, when this calculation is performed via solving the ordinary differential equation set based on the Mayo-Lewis equations. Hence, the overall synthesis throughput is optimized by utilizing kMC simulations by knowing the exact waiting time that is required until the polymerization of added monomers is completed (Figure S2).



**Figure S4:** Illustration of the use of kMC simulations to predict the time-dependent monomer conversion of a living anionic copolymerization of styrene and isoprene. Based on the actual reaction rates, the kMC simulation enables a prediction of the monomer concentration in the flask at any given time.

## References

- [1] a) F. S. Bates, M. F. Schulz, A. K. Khandpur, S. Förster, J. H. Rosedale, K. Almdal, K. Mortensen, *Faraday Discuss.* **1994**, 98, 7; b) A. K. Khandpur, S. Foerster, F. S. Bates, I. W. Hamley, A. J. Ryan, W. Bras, K. Almdal, K. Mortensen, *Macromolecules* **1995**, 28, 8796.
- [2] L. J. Fetters, D. J. Lohse, D. Richter, T. A. Witten, A. Zirkel, *Macromolecules* **1994**, 27, 4639.
- [3] F. R. Mayo, F. M. Lewis, *J. Am. Chem. Soc.* **1944**, 66, 1594.
- [4] M. Fineman, S. D. Ross, *J. Polym. Sci.* **1950**, 5, 259.
- [5] T. Kelen, F. Tds, B. Turcsnyi, *Polym. Bull.* **1980**, 2, 71.
- [6] V. E. Meyer, G. G. Lowry, *J. Polym. Sci., Part A: Gen. Pap.* **1965**, 3, 2843.
- [7] I. Skeist, *J. Am. Chem. Soc.* **1946**, 68, 1781.
- [8] F. T. Wall, *J. Am. Chem. Soc.* **1941**, 63, 1862.
- [9] V. Jaacks, *Angew. Chem.* **1967**, 79, 419.

- [10] J. Blankenburg, E. Kersten, K. Maciol, M. Wagner, S. Zarbakhsh, H. Frey, *Polym. Chem.* **2019**, *10*, 2863.
- [11] B. S. Beckingham, G. E. Sanoja, N. A. Lynd, *Macromolecules* **2015**, *48*, 6922.
- [12] a) D. T. Gillespie, *J. Phys. Chem.* **1977**, *81*, 2340; b) D. T. Gillespie, *J. Comput. Phys.* **1976**, *22*, 403.
- [13] E. Grune, T. Johann, M. Appold, C. Wahlen, J. Blankenburg, D. Leibig, A. H. E. Müller, M. Gallei, H. Frey, *Macromolecules* **2018**, *51*, 3527.
- [14] P. von Tiedemann, J. Blankenburg, K. Maciol, T. Johann, A. H. E. Müller, H. Frey, *Macromolecules* **2019**, *52*, 796.
- [15] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, *51*, 10246.
- [16] E. Galanos, E. Grune, C. Wahlen, A. H. E. Müller, M. Appold, M. Gallei, H. Frey, G. Floudas, *Macromolecules* **2019**, *52*, 1577.





---

---

# CHAPTER 2

*Application Engineering of Soft Multiblock  
Copolymers: Approaching Performance  
Requirements for PVC-free Blood Bags*

---

---



## CHAPTER 2

To be Submitted

# *Application Engineering of Soft Multiblock Copolymers: Approaching Performance Requirements for PVC-free Blood Bags*

Ramona D. Barent<sup>1,2</sup> and Holger Frey<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany

<sup>2</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany



## Introduction

The early days of blood transfusion trace back to the 16th century, however first attempts failed due to the lack of knowledge in angiology.<sup>[1]</sup> With the revolutionary publication of William Harvey's experiments on the blood circulation in 1628, research into blood transfusion became sounder.<sup>[2]</sup> Nonetheless, transfusions involving humans often gave fatal results.

Observing potential agglutination of sera taken from "healthy" humans motivated Karl Landsteiner to examine its agglutination reaction in depth.<sup>[3]</sup> He identified three different

isoagglutinines<sup>[4]</sup> and together with the proof of a fourth blood type without any isoagglutinines,<sup>[5]</sup> the antigen-antibody reaction upon mixing incompatible blood samples could be correlated with the antigen characteristics A, B, AB and O. This deduction is a milestone in history, laying the scientific foundation of blood transfusion, for which Landsteiner was awarded with the Nobel Prize in Physiology and Medicine in 1930. Another breakthrough was achieved in 1940 with the work of Karl Landsteiner, Alexander S. Wiener and Philip Levine discovering the Rhesus blood group system,<sup>[6]</sup> which to that date caused most adverse transfusion reactions.

Around 1950, plastic bags for blood collection replaced the bulky and breakable glass bottles used until then. Two more crucial drawbacks associated with the use of glass bottles are inadequate sterility leading to blood contamination, and potential air bubbles causing embolism during transfusion. Up until the 1980ies, almost all blood bags were fabricated from poly(vinyl chloride) (PVC).<sup>[7]</sup>

PVC is a rather rigid and brittle polymer, for which reason plasticizers have to be added to facilitate processing and to tune the materials' final properties in terms of softness, flexibility, and toughness.<sup>[8]</sup> Usually di-(2-ethylhexyl)phthalate (DEHP) is utilized as plasticizer in large amounts, which accounts for 30-40% by weight for PVC bags for intravenous administration and medical tubings.<sup>[1,8]</sup> Despite the toxicity of DEHP and the awareness of migration of DEHP from medical devices made from PVC resulting in ultimate deposition in tissue (*vide infra*), which is well known since the 1970ies,<sup>[9]</sup> DEHP-plasticized PVC has been hard to replace. DEHP/PVC fulfills all requirements including mechanical (stability in terms of kinking, flexibility and resilience), optical (transparency) and barrier performance criteria, is easily processed and welded and furthermore is suitable for steam sterilization – all this at low cost.<sup>[7,8,10]</sup> Besides all these specific material properties, the major reason to stick with this system is DEHP's stabilizing effect on red blood cells, allowing for a longer storage time of blood reserves.<sup>[1]</sup>

In consequence of the addition of DEHP to the CMR list in the EU (carcinogenic, mutagenic and reproductive toxicant substances), its use in European countries is restricted for most applications, e.g., cosmetics or toys.<sup>[11,12]</sup> Despite emphasizing the risks in medical devices, especially for sensitive patient groups, a general prohibition of DEHP-containing medical devices has not been demanded, which is explained by the necessity to maintain established health and life support.<sup>[13]</sup> Yet, one may evaluate the use of plasticized PVC critically, and it is important to consider alternatives, since the European Union only allows the use of materials when justified in a benefit-risk analysis.<sup>[14]</sup> In 2016, the annual use of plasticized PVC for medical applications in Europe was estimated to approximate  $3 \cdot 10^4$  tons, especially including containers, flexible tubing and medical gloves.<sup>[11]</sup> Still, to date no acceptable alternatives for blood bags intended for red blood cell storage are available. Potential replacement of DEHP or implementation of PVC-free materials will be discussed below.

## Exposure to DEHP

Plasticizers, e.g., DEHP, are not chemically bound to a polymer matrix, for which reason they may leach upon heating or in contact with fluids like blood reserves. The migration into blood depends on temperature, the lipid content, the stabilizer solution and also storage time.<sup>[9,15]</sup> The degree of leaching can vary from 10-15% of the available plasticizer.<sup>[8,16,17]</sup> However,



migration of DEHP and the resulting incorporation into the interior and membrane fractions of erythrocytes also has a stabilizing effect of the erythrocyte membrane due to the reduction of osmotic fragility, thus reducing hemolysis.<sup>[15,18]</sup> As a result, series of studies have identified DEHP and its metabolites in human tissue and sera of patients.

In addition to exposure to DEHP in the medical setting, also environmental sources, e.g., food, lead to an ambient daily exposure. Based on the measurement of primary and secondary excreted DEHP metabolites, the range of the daily body burden can be calculated. In 2016, it has been estimated to 1-3 µg/kg bw/d for adults and 6-17 µg/kg bw/d for infants and children, excluding medical and occupational exposure, with bw/d standing for body weight per day. Depending on the respective medical treatment and its duration, the use of DEHP-plasticized PVC may increase the exposure drastically. Highest extents of exposures for adults as well as infants are 3 orders of magnitude larger than the usual daily exposure (see Table 1). These values exceed the tolerable daily intake (TDI) of DEHP considerably, which is established at 48 µg/kg bw/d.<sup>[11]</sup>

**Table 1: Human exposure to DEHP without medical exposure (entries 1,2) as well as following medical treatment with DEHP/PVC medical devices (entries 3-5). The examples given refer to treatments resulting in the highest extent of exposure. (values taken from <sup>[11]</sup>)**

| Age Group            | Treatment - Time Period                                                      | Exposure in µg/kg body weight per day |
|----------------------|------------------------------------------------------------------------------|---------------------------------------|
| adults               | <i>median exposure in daily life</i>                                         | 1-3                                   |
| infants and children | <i>median exposure in daily life</i>                                         | 6-17                                  |
| adults               | blood transfusion (trauma or ECMO <sup>a</sup> patients) - <i>short term</i> | 8.000-10.000                          |
|                      | hemodialysis - <i>chronic</i>                                                | 2.200                                 |
| neonates             | parenteral nutrition - <i>weeks – months</i>                                 | 6.000                                 |

<sup>a</sup> ECMO: extracorporeal membrane oxygenation

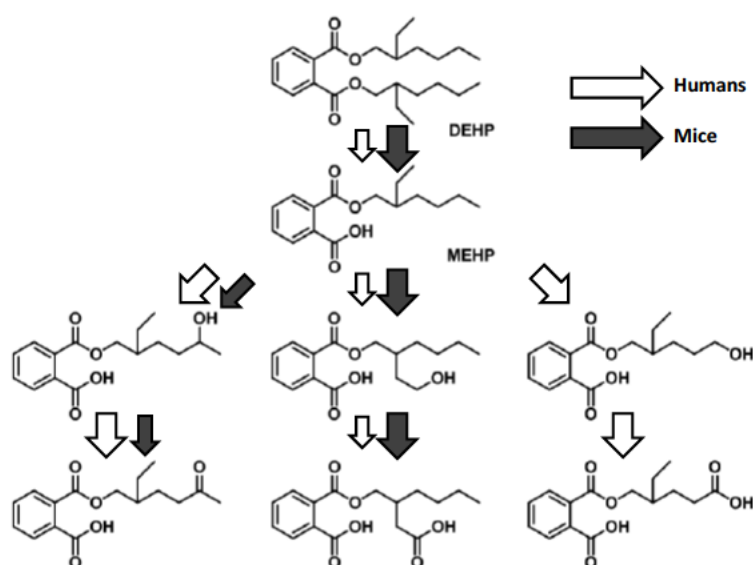
## Metabolism of DEHP

DEHP is classified as a reproductive toxin (category 1B) impairing fertility and its carcinogenicity cannot be ruled out (category 2B). However, the metabolic profile of DEHP differs in humans and animals, such as rats.

At first, DEHP is hydrolyzed in the intestine by lipases to (mono(-2-ethylhexyl) phthalate) (MEHP), which is rapidly absorbed together with DEHP.<sup>[8,19]</sup> This initial metabolism step is qualitatively similar for all species, although hydrolysis is more effective in rodents than in higher mammals or humans because of higher lipase concentrations.<sup>[20]</sup> Once absorbed, the metabolites are distributed throughout the body, above all to fat, the lungs, the gastrointestinal tract, liver, and kidney. This spreading resembles each other across species.<sup>[21]</sup> Besides the intestine, liver, kidney, lungs pancreas and plasma also contain enzymes hydrolyzing DEHP. However, since hydrolysis occurs more readily in the intestinal tract, ingestion may be more hazardous than intravenous exposure.<sup>[22]</sup> Finally, MEHP and other

primary metabolites are further converted in the liver to secondary metabolites.<sup>[23]</sup> The crucial point is, that these pathways differ across species. Rodents largely metabolize via oxidative pathways, while primates and humans predominantly glucuronidate the metabolites before excretion (see Figure 1).<sup>[23,24]</sup>

In conclusion, rats excrete unconjugated forms of DEHP and its metabolites, which are biologically active. On the contrary, humans mostly excrete DEHP as glucuronides not having toxic effects.<sup>[11]</sup> The ratio between the glucuronides and the free, non-conjugated metabolites is 0.13 for rats, but 3.5-5.3 for humans. In other words, while the major part (77.6% in males and 84.2% in females) of DEHP's metabolites are excreted as non-toxic conjugates in case of humans<sup>[25]</sup>, rats excrete only 11.5% of the metabolites in a non-toxic form.<sup>[26]</sup> In particular, alcohol and ketone metabolites are excreted mainly as glucuronic acid conjugates, while carboxylic acid metabolites are only partially glucuronidated.<sup>[23]</sup> This is of high relevance when interpreting toxicological studies.



**Figure 1:** Major metabolic pathways and resulting metabolites of DEHP. White and black arrows assign the probability, which correlates to the arrows' size, of these pathways in mice and humans, respectively. <sup>adapted from [24]</sup>

## DEHP Toxicity and Carcinogenicity

Since the focus of this work lies on alternative polymer materials for blood bags, detailed specification on toxicity and carcinogenicity studies goes beyond the scope. Reviews comprising overviews on mainly rodent animal studies can be found elsewhere.<sup>[8,11]</sup> In the following, most concerning conclusions from animal testings or in *vitro* studies are briefly discussed in the context of human health risks.

Long term DEHP exposure of rodents shows that the plasticizer induces toxicity; most of all in the kidney, liver, and testis. In order to investigate the impact of blood transfusions on primates, rhesus monkeys were subjected to repeated blood transfusions through DEHP/PVC tubing over one year, leading to hepatic dysfunctions and cholestasis.<sup>[17,27]</sup> The reproductive and developmental toxicity is highly species-dependent, with rodents being most susceptible to effects on the testicular function.<sup>[11]</sup> Although the testes of cynomolgus monkeys were not affected after high DEHP exposure<sup>[28]</sup>, *in vitro* studies using human specimens are alarming. For

instance, an *in vitro* study using human adult testis tissue showed a suppressed testosterone production.<sup>[29]</sup> Furthermore, some indication for alteration in fetal germ cells were found.<sup>[30]</sup>

The mode of action for carcinogenicity in rodents is ascribed to peroxisome proliferation, which is mediated by the activation of a certain receptor (PPAP $\alpha$ ).<sup>[11,31]</sup> This mechanism is not considered to be relevant in the human liver because the level of PPAP $\alpha$  expression is lower, thus not exceeding the threshold for this pathway.<sup>[32]</sup> Yet, multiple molecular signals and pathways in several cell types in the liver may be involved in hepatic tumor induction, which is why a potential carcinogenicity of DEHP cannot be ruled out.<sup>[11]</sup>

Besides these results, epidemiological studies can be analyzed for human risk assessment. However, cause-effect deductions are weak, since for instance also a specific diet is associated with many disorders. Furthermore, often single samples representative for a short term exposure are taken and limited number of metabolites are measured. Nonetheless, epidemiological studies associated with DEHP exposure of adult men found a small decrease in testosterone levels in their blood. However, the decrease of this reproductive hormone level is not biologically significant. On the other side, alteration in sperm concentration, morphology and motility indicated a significant deterioration in semen quality.<sup>[33]</sup> Furthermore, a weak association of DEHP with breast tumors was found.<sup>[34]</sup>

Summarizing, it is difficult to extrapolate the toxicity and carcinogenicity from animal studies to humans, because not every tested species can be considered as a suitable model for studies relevant to humans. Moreover, the meaning of studies on human cells has not been elucidated completely, for which reason further investigation is necessary.

Nevertheless, the effects of DEHP and its metabolites shown so far identify male fetuses and male neonates as well as patients with chronic illnesses to be most vulnerable. Consequently, the safest solution would be the use of DEHP/PVC-free medical devices, especially for groups at high risk, and hence the investigation of potential substitutes for PVC should be promoted.

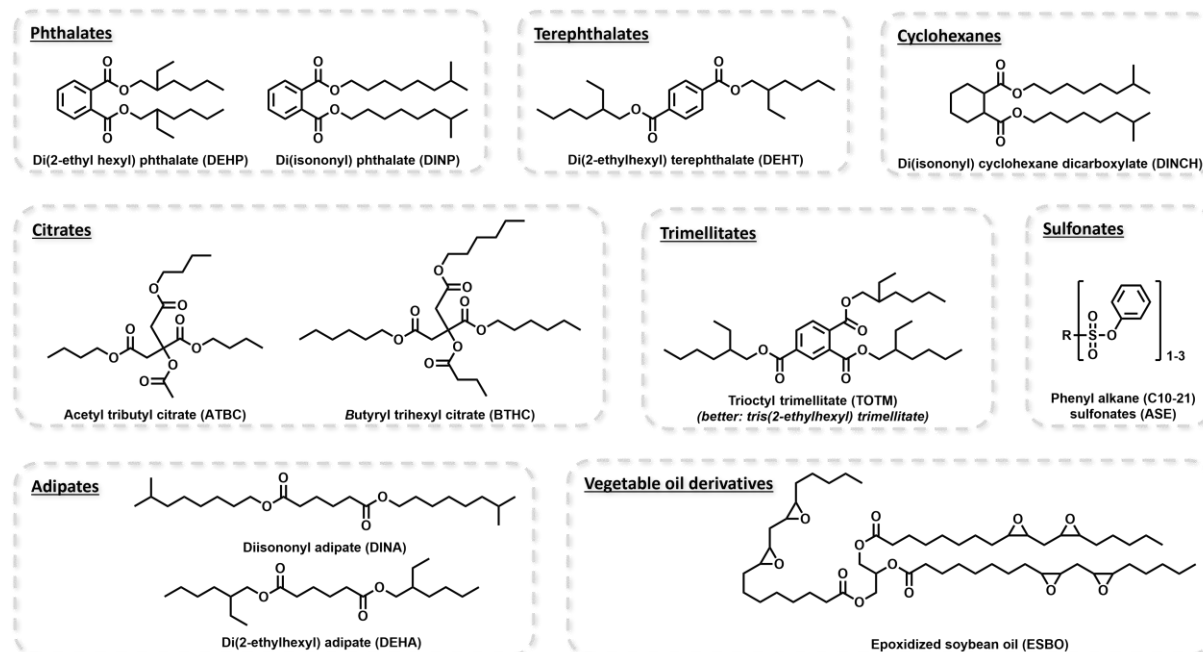
## Alternative Plasticizers

Because of the stabilizing effect of DEHP on erythrocytes and the optimum performance of PVC, one way to address the health problems correlated with DEHP is to find non-toxic plasticizers with similar advantages for storage time of blood reserves.

Huge efforts to classify potential alternative plasticizers for healthcare applications have been made by, e.g., the Danish Environmental Protection Agency (EPA)<sup>[35]</sup> and the Scientific Committee on Emerging and Newly-Identified Health Risks (SCENIHR)<sup>[11]</sup>, who evaluated migration and health effects of 10 and 8 alternative plasticizers, respectively (see Table 2). These potential alternatives include phthalates, terephthalates, citrates, adipates, trimellitates, cyclohexanes, sulfonates and vegetable oil derivatives (for chemical structure and full name see Figure 2).

The first indication for the suitability of a potential substitute is its extent of leaching into liquids used to simulate blood reserves. Oftentimes, human blood is simulated by water/ethanol mixtures. From the plasticizers tested (for explanation of the abbreviations see Figure 2), especially TOTM, DINCH and BTHC showed lower tendency to migration compared to DEHP.

Furthermore, the exposure of patients to DEHP, TOTM and DEHA via plasticized tubings was calculated, showing that the tolerable daily intake (TDI) of DEHP is far overshoot, whereas the critical thresholds for TOTM and DEHA were not exceeded.<sup>[35]</sup>



**Figure 2: Chemical structures of the plasticizers for PVC discussed in this section. The corresponding substance classes are circled.**

Next, health issues caused by the uptake have to be assessed. Detailed information on the toxicity can be found elsewhere.<sup>[36]</sup> Table 2 gives a condensed classification of toxicity obtained from studies with animals. As discussed in the previous sections, deduction from animal studies to human risks should be interpreted with caution because of differing metabolism mechanisms and carcinogenic pathways. Regardless of the validity of the results for human hazards, plasticizers with generally low toxicity would be favorable. From that point of view, DEHT, BTHC and ESBO could be promising alternatives to DEHP. ESBO only shows subchronic toxicity, mostly affecting liver and kidney, which applies to all substances tested.

Another important consideration is the uptake of the plasticizers in the body. For instance, TOTM and DEHT are poorly absorbed via the gastrointestinal tract, however data concerning intravenous uptake are still required.<sup>[36]</sup> For DINCH, a subacute intravenous toxicity study did not indicate irreversible, but reversible effects on hematological parameters.<sup>[37]</sup>

Besides these health aspects, the stabilizing effect for red blood cells is of great interest, since comparable storage times are essential for the use of other plasticizers in PVC blood bags. For this purpose, three characteristic values can be measured over time, namely hemolysis, the 2,3-DPG level (2,3-diphosphoglycerate) and the ATP level (adenosine triphosphate) of the stored blood. Comparisons between studies have to be drawn with caution, since these values depend not only on the plasticizer used, but also on the additive solution implemented or eventual mixing protocols during storage.<sup>[38]</sup> Blood collections are always stabilized with an additive solution, including substances to prevent coagulation (e.g., citrates), a buffer to prevent a pH drop caused by lactic acid produced during anaerobic glycolysis (e.g., phosphate buffers), sugars that can be metabolized (e.g., dextrose, glucose, mannitol), and adenine, which promotes ATP and 2,3-DPG synthesis.<sup>[39]</sup>

**Table 2: Summary of the migration, toxicity and carcinogenicity of alternative plasticizers listed by the Danish EPA<sup>[35]</sup> and SCENIHR<sup>[11]</sup>, adapted from [36]**

| Alternative PVC Plasticizer | Migration compared to DEHP                                                                       | Endocrine Activity | Reproduction Toxicity | (Sub)chronic Toxicity | Carcinogenicity  |
|-----------------------------|--------------------------------------------------------------------------------------------------|--------------------|-----------------------|-----------------------|------------------|
| DEHP                        | reference                                                                                        | ✓                  | ✓                     | ✓                     | ✓                |
| DINP                        | ↓ <sup>[11]</sup>                                                                                | no specific data   | ✓                     | ✓                     | ✓                |
| DEHT                        | ↑ <sup>[11]</sup><br>↔ (in oil and hexane) <sup>[35]</sup><br>↓ (in soapy water) <sup>[35]</sup> | ✗                  | ✗                     | ✓                     | uncertain        |
| ATBC                        | ↑ <sup>[11,35]</sup>                                                                             | ✗                  | ✓                     | ✓                     | ✗                |
| BTHC                        | ↓ <sup>[11]</sup>                                                                                | no specific data   | ✗                     | ✓                     | no specific data |
| DEHA                        | ↓ <sup>[11]</sup><br>↑ <sup>[35]</sup>                                                           | ✗                  | ✓                     | ✓                     | ✓                |
| DINA                        | ↑ <sup>[35]</sup>                                                                                | no specific data   | ✓                     | ✓                     | ✓                |
| TOTM                        | ↓ <sup>a [11]</sup><br>↓ (25-300x) <sup>[35]</sup>                                               | ✗                  | ✓                     | ✓                     | no specific data |
| DINCH                       | ↓ <sup>[11]</sup><br>↓ (3-10x) <sup>[35]</sup>                                                   | ✓                  | ✗                     | ✓                     | ✓                |
| ASE                         | ↑ (in water) <sup>[35]</sup><br>↓ (in ethanol) <sup>[35]</sup>                                   | no specific data   | ✓                     | ✓                     | no specific data |
| ESBO                        | low volatility <sup>[35]</sup>                                                                   | no specific data   | ✗                     | ✓                     | ✗                |

The arrows ↑, ↓, and ↔ indicate a higher, lower, or similar migration of the plasticizer in comparison to DEHP, respectively.

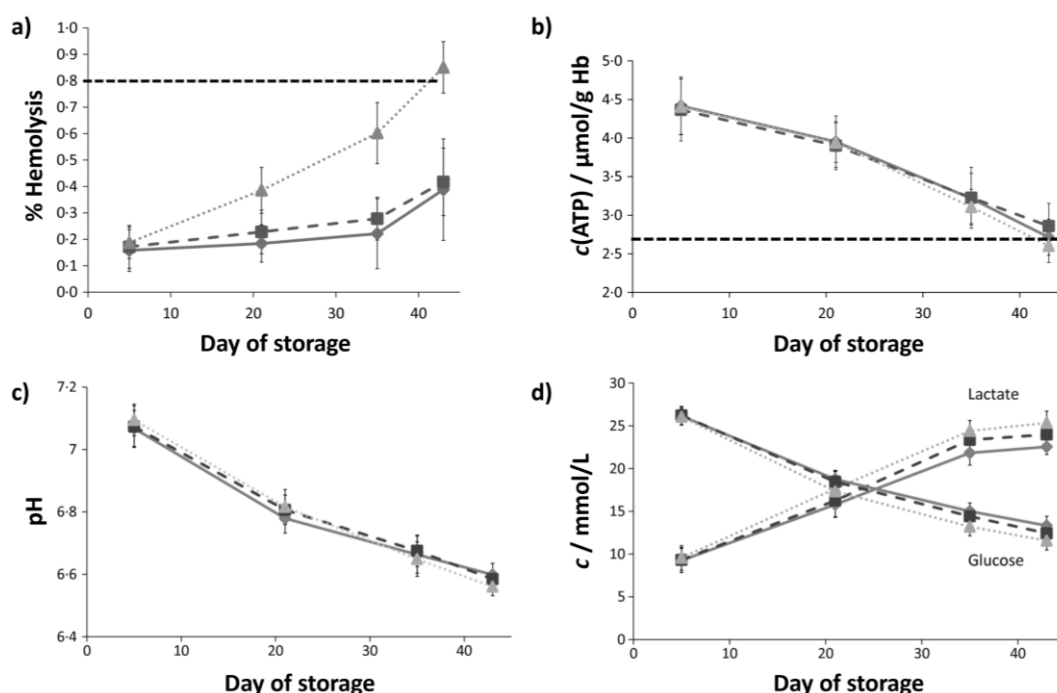
<sup>a</sup> much lower migration was reported, but TOTM-based materials contain significant DEHP and DEHT impurities.

In the following, the red blood cell (RBC) concentrate quality during storage is evaluated for PVC blood bags plasticized with DEHP, DINCH and BTHC.<sup>[40]</sup> The temporal development of the characteristic values for the three different blood bag systems is shown in Figure 3. The concentrates were stabilized with a saline-adenine-glucose-mannitol (SAG-M) additive solution, a hypertonic additive without a buffer, for which reason the pH value can be interpreted as well.

Hemolysis describes the rupturing of red blood cells and can be back calculated from the hemoglobin concentration. The European maximum limit of hemolysis is defined at 0.8%. The amount of hemolysis is significantly higher in BTHC/PVC bags than in DINCH/PVC or DEHP/PVC bags, exceeding the limit on day 43 (Figure 3a).

Besides, the extracellular pH value over time was evaluated, showing a continuous decrease for all three systems, yet remaining above 6.5 until day 43. During the latter half of the storing period, BTHC/PVC bags exhibited the lowest pH (Figure 3c). These alteration in pH are driven by the metabolic changes. Glucose consumption and lactate production correlate with metabolic rates, being highest in BTHC/PVC blood bags (Figure 3d). The rate of 2,3-diphosphoglycerate (2,3-DPG) production, a molecule that can bind to desoxyhemoglobin, is an indicator for the

intracellular red blood cell pH value. The 2,3-DPG concentration decreased for all three systems from day 5 to day 21, with BTHC/PVC bags showing higher values than DEHP/PVC and DINCH/PVC bags. With  $1.1 \pm 0.5$  mol/mol Hb,  $0.5 \pm 0.4$  mol/mol Hb, and  $0.4 \pm 0.4$  mol/mol Hb, respectively, all values are in the same range, giving no additional information.<sup>[40]</sup>



**Figure 3:** a) Percent hemolysis, b) ATP concentration, c) pH values at 22 °C, and d) glucose and lactate concentration in red cell concentrates stored in pediatric bags with SAG-M additive solution. The bags were composed of either DEHP/PVC (solid, grey line/diamonds), DINCH/PVC (dashed, dark grey line/squares), or BTHC/PVC (dotted, light grey line/triangles).<sup>adapted from [40]</sup>

Finally, the concentration of adenosine triphosphate (ATP), an energy-carrying molecule, are compared. ATP levels correlate with *in vivo* recovery. Negative consequences in terms of red blood cell recovery are found below 2-3  $\mu\text{mol/g Hb}$  in 75% of the units tested. The ATP content showed a characteristic decrease, but no significant differences among the three systems investigated could be detected (Figure 3b). Yet, only DINCH met the accepted ATP level of 2.7  $\mu\text{mol/g Hb}$ .<sup>[41]</sup>

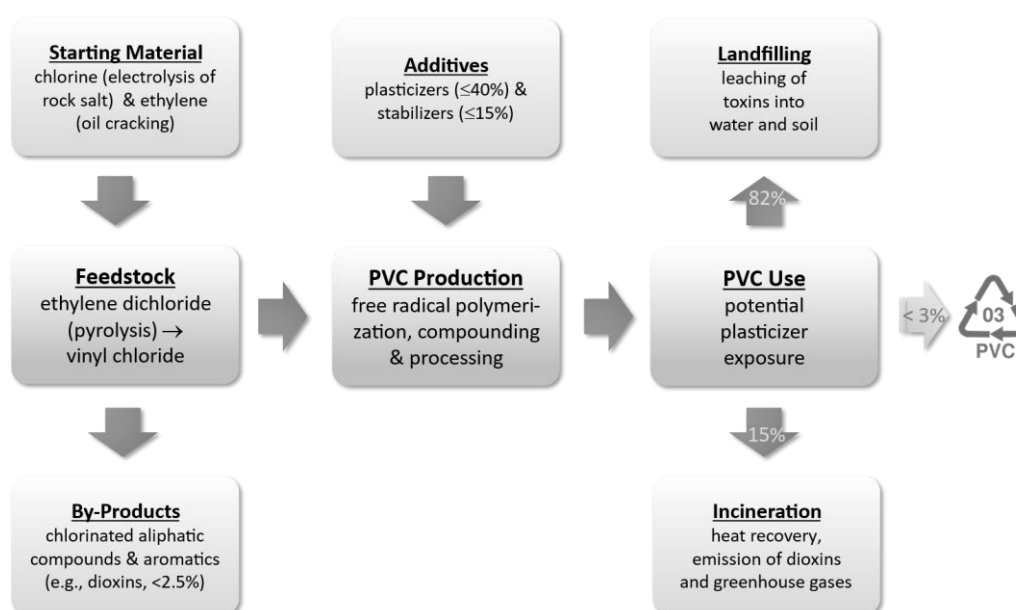
In conclusion, DINCH is a promising alternative for DEHP, whereas the concentrate quality is deteriorated when using BTHC as plasticizer. Since the migration of DEHP is an order of magnitude higher in DEHP/PVC systems than in DINCH/PVC but the characteristic values discussed do not differ remarkably, these results suggest a different interaction of the non-aromatic DINCH with PVC, but also the red blood cell membrane.

Within this framework, it should be mentioned that other plasticizers like BTHC were already introduced for commercial products, especially for platelet storage. Since the storage conditions and material requirements like high oxygen permeability differ from those for red blood cells, on which the focus is laid in this review, their discussion is omitted. Surprisingly, BTHC/PVC bags are FDA approved due to its slower leaching and stated lower toxicity and hence available on the US, Canadian and Scandinavian market.<sup>[7,42]</sup> This is argued with its metabolites hexanol, butyric acid, and citric acid, which are unlikely to accumulate in the body.<sup>[43]</sup> However, due to the higher price, bad smell and skin irritation in some medical employees, BTHC has not been widely adopted.<sup>[7]</sup>

Although most alternative plasticizers show a better toxicological profile with higher margins of safety, missing toxicological data for humans or endocrine activities in animal studies give reason for health concerns. Since these plasticizers are used in other products such as food contact materials and toys as well, future risk assessment is mandatory.

## Lifecycle Impacts of PVC

Another reason for which it would be judicious to consider alternative non-PVC materials are the hazards related to poly(vinyl chloride). Even though mass streams of PVC for healthcare applications are small, with approximately 25% of all plastics, PVC is the most widely used polymer in medical devices.<sup>[10]</sup>



**Figure 4: Lifecycle Hazards of PVC.**

The lifecycle of PVC (see Figure 4) starts with ethylene dichloride (EDC), which is produced by an iron(III) catalyzed reaction of ethylene and chlorine. In 2002, the annual quantity produced was estimated to be nearly 20 million tons.<sup>[44]</sup> EDC is possibly carcinogenic and moreover toxic especially when inhaled, the latter also applying to its starting material chlorine. Approximately 95% of the world's production of EDC is converted to vinyl chloride by thermal decomposition; again, a chemical being toxic and carcinogenic. After polymerization of vinyl chloride, the material properties of PVC are tuned by processing PVC together with additives, e.g., by extrusion or injection molding. Additives comprise plasticizers such as DEHP discussed so far, whose amounts range around 40%.<sup>[45]</sup> On top, the most crucial additives are heat stabilizers, because PVC degrades above 70 °C and is sensitive to light and heat. For rigid PVC, up to 15% of thermal stabilizers need to be added to trap the hydrogen chloride released upon degradation.<sup>[10,45]</sup> Barium-zinc additives are very effective heat stabilizers but restricted for medical applications in some countries, which is why calcium-zinc formulations are often used for healthcare application.<sup>[10,45]</sup> Other additives like fillers, flame retardants, impact modifiers or pigments account for a relatively small proportion.<sup>[45]</sup>

After use, post-consumer waste of PVC is either incinerated or landfilled. The proportion of post-consumer waste PVC recycling is very low around 3%. Although the amount rises steadily,

obstacles concerning methods for separation or reprocessing of mixed PVC waste or composite materials have to be overcome. In contrast, with 80% most pre-consumer waste, i.e., waste generated during production or from the handling or installation of PVC products, is recycled, since it can easily be collected separately in defined qualities.<sup>[45,46]</sup>

Upon incineration, energy can be recovered from the combustion heat, but the gas and liquid effluent have to be treated. Most additives can be burned to form carbon dioxide and water, but the release of heavy metals and emission of dioxins and greenhouse gases cause global problems.<sup>[45,47]</sup> Yet, state-of-the-art technologies for waste incineration are capable of suppressing HCl and dioxin emissions.<sup>[45]</sup> When the waste is landfilled under soil buried conditions, additives like stabilizers and plasticizers are released from PVC, but also dioxins and aromatic hydrocarbons are formed if carbon, chlorine and metal components are present, and leach into the landfill water, contaminating local ground water.<sup>[45,48]</sup>

The recycling processes include mechanical and chemical recycling. For mechanical recycling, first pure fractions of PVC are separated from other materials, which are shredded and finally converted into re-granulates by afterwards using mills and extruders.<sup>[45]</sup> Few high quality mechanical recycling processes exist for single product groups like bottles, pipes or window frames. For example, the Vinylloop® mechanical recycling processes developed by Solvay shows best performance and can already compete with landfilling in terms of costs.<sup>[45]</sup> On the contrary, for chemical recycling of mixed PVC waste, the processes are still in the research phase. Most aim at the production of liquid organics and gases which can replace primary oil- or gas-based resources.<sup>[45]</sup> Nevertheless, recycling processes are still limited and energy recovery by incineration is too low, which is why landfilling dominates. Together with the benefits coming along with the disuse of harmful plasticizers, a successful phase out of PVC would improve environmental pollution and health issues.

## Alternative Polymer Materials

In order to prevent leaching of plasticizers from the polymer material used in medical devices, two approaches are possible. On one hand, the PVC could be co-extruded or non-plasticized PVC could be blended. For the first approach, an inner layer of unplasticized material is used as a barrier.<sup>[7]</sup> Alternatively, non-plasticized PVC itself is blended with another polymer to tailor its properties without facing the issue of plasticizer leaching. For this purpose, especially polyethylene vinyl acetate (EVA) has been used successfully. EVA itself cannot replace PVC due to its tackiness and poor kinking resistance. However, blends of PVC and EVA are appropriate, with higher EVA contents resulting in an increased flexibility, impact strength and transparency.<sup>[49]</sup>

On the other hand, plasticized PVC might be replaced completely by a polymer material with a similar property profile without the addition of plasticizers. Several polymers theoretically fulfilling the basic prerequisites for the use in medical devices have been identified (see Table 3).<sup>[7,13]</sup> The application of plasticized PVC in the construction sector, e.g., for pipes or flooring, is beyond the scope of this review. Criteria which have to be taken into consideration when targeting healthcare applications are not only the physical and mechanical properties, but also chemical and sterilization resistance as well as welding capabilities.<sup>[49]</sup>



**Table 3: Overview of the physical and mechanical properties, transparency, welding capability and sterilization resistance of potential alternative polymer materials to PVC.**<sup>[10,49,50]</sup>

| Alternative Polymer Material                             | Physical and Mechanical Properties                                                                                                                                                                                                                                                  | Transparency                                                     | Welding Capability                                       | Sterilization Resistance                                               |
|----------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------------------------|------------------------------------------------------------------------|
| Poly(vinyl chloride) (PVC)                               | <ul style="list-style-type: none"> <li>- good kinking resistance</li> <li>- wide temperature application window</li> <li>- <i>flexibility, impact strength and toughness achieved using plasticizers</i></li> </ul>                                                                 | transparent                                                      | radio-frequency, and thermal welding                     | EO, steam and radiation sterilization                                  |
| Polyolefins (ethylene-propylene copolymers)              | <ul style="list-style-type: none"> <li>- chemically resistant</li> <li>- flexibility, impact strength and toughness adjustable by comonomer ratio</li> <li>- reduced gas permeability with PP content</li> </ul>                                                                    | transparent, yet dependent on crystallinity                      | ultrasonic, hot gas and friction welding                 | EO sterilization                                                       |
| Hydrogenated styrene-diene copolymers (SEBS / SEPS TPEs) | <ul style="list-style-type: none"> <li>- thermal and oxidative stability after hydrogenation</li> <li>- flexibility, impact strength and toughness adjustable by comonomer ratio</li> <li>- permeability expected due to segmental motion of non-vitrified rubbery phase</li> </ul> | transparent                                                      | ultrasonic and vibration welding                         | EO, gamma, UV and electron beam radiation sterilization                |
| Polyamides                                               | <ul style="list-style-type: none"> <li>- flexibility, impact strength and toughness dependent on the number of methylene units</li> <li>- <i>swelling in water</i> (except PA 12)</li> </ul>                                                                                        | transparent, yet dependent on crystallinity                      | ultrasonic welding                                       | EO sterilization                                                       |
| Polyurethanes (TPUs)                                     | <ul style="list-style-type: none"> <li>- low-temperature flexibility</li> <li>- flexibility, impact strength and toughness, as well as hydrolytic stability dependent on the soft segments</li> <li>- <i>poor kinking resistance</i></li> </ul>                                     | transparent, but brownish discoloration upon high UV irradiation | radio-frequency, ultrasonic and thermal welding          | EO and high-energy radiation sterilization                             |
| Silicones                                                | <ul style="list-style-type: none"> <li>- wide temperature application window</li> <li>- low-temperature flexibility</li> <li>- high gas permeability</li> <li>- high biocompatibility</li> <li>- wide range of hardness</li> <li>- chemically resistant</li> </ul>                  | transparent                                                      | difficult to weld or join, <i>adhesives needed</i>       | EO, steam, autoclave, gamma, and electron beam radiation sterilization |
| Fluoropolymers (PTFE or copolymers with ethylene (ETFE)) | <ul style="list-style-type: none"> <li>- flexibility, impact strength and toughness tunable by copolymerization of TFE with ethylene</li> <li>- permeation resistant</li> <li>- chemically inert, unless exposed to gamma or electron beam radiation</li> </ul>                     | transparent, yet dependent on crystallinity                      | IR welding (PTFE), ultrasonic and hot gas welding (ETFE) | EO, autoclave, and steam sterilization                                 |

|                                                                            |                                                                                                                                                                                                                                                              |                                                   |                                                             |                     |
|----------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|-------------------------------------------------------------|---------------------|
| Copolyesters<br>(e.g.,<br>polyethylene<br>terephthalate<br>glycol (PET-G)) | <ul style="list-style-type: none"> <li>- flexibility, impact strength and toughness tunable by second diol implemented</li> <li>- low-temperature flexibility</li> <li>- low gas permeability</li> <li>- <i>limited by processing constraints</i></li> </ul> | transparent,<br>yet dependent<br>on crystallinity | ultrasonic,<br>laser, and<br>radio-<br>frequency<br>welding | EO<br>sterilization |
|----------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|-------------------------------------------------------------|---------------------|

Disadvantages rendering a material inadequate for complete PVC replacement are highlighted by italic letters.

Besides these general aspects of transparency, weldability and sterilizability, material requirements change with the intended healthcare application. While skin contact devices like wound aids are soft-touch materials with a high flexibility, medical tubes are rather hard materials allowing bending but preventing kinking. Medical bags have to be flexible when they are squeezed (Young's modulus should be less than 0.1 GPa), but at the same time rigid and resilient in order to withstand high g-forces because of centrifugation up to 5000 xg (tensile strength should be greater than 40 MPa).<sup>[51]</sup>

Moreover, medical bags for blood collections face special requirements regarding gas permeability and temperature application window. The collection of the whole blood occurs at physiological temperatures of around 37 °C, but plasma is stored at temperatures of -40 °C, whereas red blood cells are stored at 2-6 °C. On top, the material used for platelet storage must be permeable to gases such as oxygen and carbon dioxide to maintain viability (oxygen flow of 10-20  $\mu\text{mol}\cdot\text{h}^{-1}$ ).<sup>[51]</sup> If oxygen tensions are low, metabolism of glucose by glycolysis is enhanced (Pasteur effect), leading to an increased rate of lactate production and thus a low pH, which impairs viability.<sup>[52]</sup> Consequently, the material has to allow an easy entry of oxygen to favor aerobic metabolism.<sup>[53,54]</sup> Furthermore, the efflux of carbon dioxide is important, since it corrects the pH of the storage medium by shifting the equilibrium of bicarbonate protonation towards the products, namely water and carbon dioxide (Le Chatelier).<sup>[54]</sup>

Among the summarized materials, polyolefins and hydrogenated styrene-diene copolymers should be emphasized, since they are easily processed, sterilized, and can compete with DEHP-plasticized PVC in terms of material performance. For instance, copolymer resins of ethylene and octene with less than 20% of octene show appropriate toughness and elasticity, are transparent and sealable.<sup>[50]</sup> Even though the use of other alternative polymers is limited, oftentimes coextrusion of several non-PVC polymers can solve the issue.

This approach has been tested with polyolefin as a barrier layer, e.g., polypropylene (PP) or linear low-density polyethylene (LLDPE), and a second layer made of polyamides,<sup>[55]</sup> styrenic block copolymers (SEBS),<sup>[56]</sup> ethylene vinyl acetate copolymers (EVA),<sup>[57]</sup> or blends of polyurethanes and polyesters<sup>[58]</sup>. Although these films mostly fulfill the requirements like good physical properties, barrier properties, weldability and in some cases also autoclaving, they are not successfully commercialized because of their high cost.<sup>[50]</sup>

The implementation of polyolefin medical bags for platelet containers and pre-mixed drugs for intravenous injection has progressed a lot now having a considerable market share, since they exhibit improved storage conditions and shelf-life due to their oxygen permeability.<sup>[50,59]</sup>

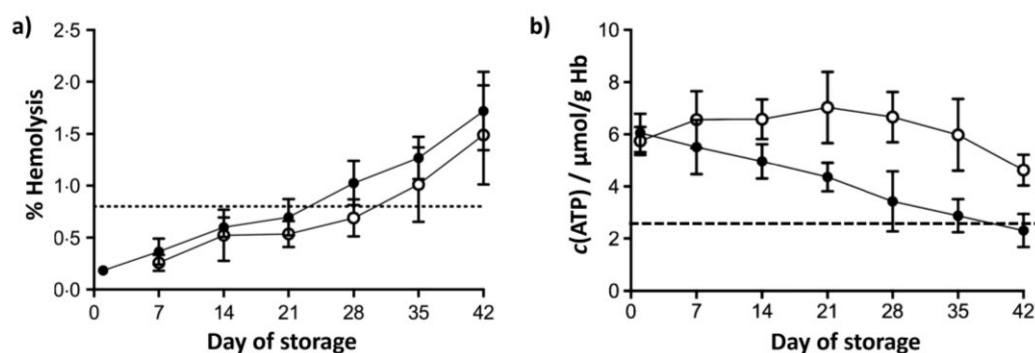
Attempts to use polyolefin blood bags for red blood cell storage have been made as well, however facing opposite effects. The storage of red blood cells stabilized with a saline-adenine-

glucose-mannitol (SAG-M) additive solution with phosphate buffer was compared in the polyolefin blood bags produced by Baxter and DEHP-plasticized PVC blood bags in 2001.<sup>[60]</sup>

The absence of the plasticizer DEHP and the stabilizing effect of the erythrocyte membranes coming along with its migration resulted in a 4 times higher hemolysis in case of the polyolefin bags. Besides, lower ATP concentration were observed in case of the polyolefin bags, while the rates of glucose consumption and lactate formation was comparable. This was attributed to the high gas permeability, leading to higher oxygen partial pressures and lower carbon dioxide partial pressures throughout the whole storage time. High oxygen levels may have caused oxidative stress, whereas the loss of carbon dioxide affected the intracellular buffer system.

A recent project funded by the European Commission evaluated the storage of red blood cells in novel polyolefin blood bags.<sup>[7]</sup> The bags are made of a three-layered film of polypropylene with the inner layer designed for blood contact, the middle layer modified to allow sealing and the outer layer providing a certain durability.<sup>[15]</sup> Red blood cell concentrates were stabilized with either phosphate-adenine-guanosine-glucose-saline-mannitol (PAGGS-M) or phosphate-adenine-guanosine-glucose-sodium gluconate-mannitol (PAGGG-M) additive solutions, which are isotonic and associated with low levels of hemolysis (Figure 5).<sup>[61]</sup>

The extracellular pH decreased during storage for both additive solution, which is less pronounced for PAGGS-M due to a slower glucose consumption and lactate production. However, with pH values of 6.3 and 6.2 for PAGGS-M and PAGGG-M after 6 weeks, respectively, the decrease in pH is much more pronounced in comparison to DEHP-plasticized PVC (see Figure 3,  $\text{pH} > 6.5$ ). Beyond that, increased hemolysis with levels exceeding the European maximum limit of 0.8% were reached even after 3 weeks (Figure 5a), thus not being competitive against DEHP-plasticized PVC (see Figure 3, hemolysis  $< 0.4\%$  after 6 weeks). At least, sufficient ATP levels could be observed for PAGGG-M solutions (Figure 5b), with  $4.6 \mu\text{mol/g Hb}$  even outperforming plasticized PVC (see Figure 3,  $c(\text{ATP}) \approx 2.7 \mu\text{mol/g Hb}$ ).<sup>[15]</sup>



**Figure 5:** a) Percent hemolysis, and b) ATP concentration in red cell concentrates stored in polyolefin bags with PAGGS-M (filled symbols) or PAGGG-M (opened symbols) additive solution. <sup>adapted from [15]</sup>

In conclusion, although ATP levels are superior compared to plasticized PVC or to polyolefin bags tested before,<sup>[60]</sup> the inability to prevent excessive hemolysis does not make them an appropriate PVC-substitute. Above that, technical challenges in meeting the performance standards of PVC still need to be overcome, due to the lower mechanical stability of polyolefin plastics.<sup>[7,10]</sup>

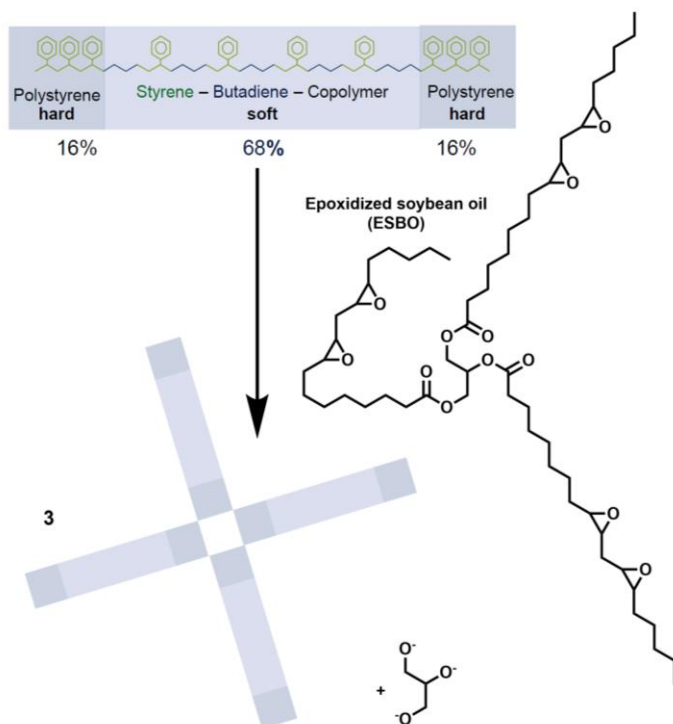
Recent development of styrenic thermoplastic elastomers for healthcare applications was promoted by Ineos Styrolution, centering huge knowledge by the joint venture and later buyout of BASF and the acquisition of a product line from Chevron Phillips.<sup>[62,63]</sup> Their materials

find application for instance for intravenous tubings, bags and drip chambers, but also soft applications like wound aids.<sup>[64]</sup> The underlying concept is based on the coupling of Styroflex® to star-shaped architectures (Figure 6a).<sup>[65]</sup>

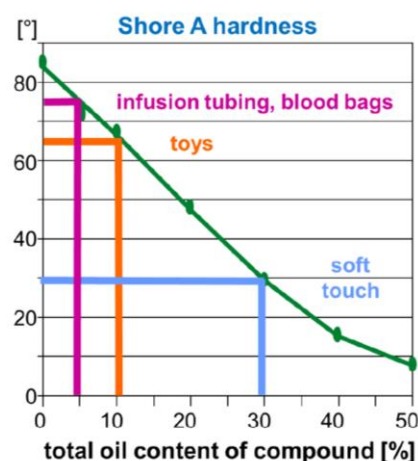
Styroflex® is a flexible and tough TPE featuring a triblock structure with two polystyrene end blocks and a random, hydrogenated butadiene-styrene mid block (Figure 6a, top). The formation of the random mid block is achieved implementing a sterically hindered tertiary alkoxide like potassium triethylcarbinolate as a randomizer.<sup>[66]</sup> Using this randomizer, low 1,2-vinyl contents preserving high thermal stability, and at the same time outstanding material properties (Young's Modulus = 120 MPa and elongation at break > 650%) are achieved.<sup>[62]</sup> Furthermore, Styroflex® is easily processed and exhibits high oxygen permeability.

The hardness of the respective material is fine-tuned by coupling of this triblock copolymer into star-shaped architectures and subsequent plasticizing with food-approved plasticizers, e.g., mixtures of mineral oils and vegetable oils like low-aromatic paraffinic or naphthenic oils and rapeseed oil, respectively.<sup>[63]</sup> Epoxidized soybean oil is preferentially chosen as coupling agent, which gives star-shaped structures with commonly four branches due to two epoxy groups in combination with one ester group, which reacts with two living chain ends. The efficiency of this coupling step ranges around 70% consequently giving also 30% of linear chains, which become terminated during the coupling step.<sup>[63]</sup> Low contents of the plasticizing oil mixture, which is metered in during the extrusion of the star-shaped multiblock copolymer, lead to a rather hard material finding application for tubings and bags, whereas higher contents result in soft-touch materials (see Figure 6b).<sup>[62]</sup>

#### a) Coupling approach to star-shaped architectures



#### b) Fine-tuning of the material's hardness using a plasticizing oil



**Figure 6:** Concept for a control over the hardness of styrenic thermoplastic elastomers. a) Schematic visualization of the block copolymer structure of Styroflex® and the star-shaped architecture obtained by coupling with epoxidized soybean oil. b) Plot of the material's hardness against the content of mixture of a mineral and a vegetable oil used for plasticizing. <sup>adapted from [62]</sup>

In pronounced contrast to plasticized PVC, only small amounts of comparably non-polar plasticizers have to be introduced, which together with the star-shaped architecture results in negligible bleeding.<sup>[63]</sup> Furthermore, drug absorption below levels of plasticized PVC are reported.<sup>[62]</sup> However, studies on the red blood cell quality upon storage in styrenic block copolymer blood bags are currently not accessible.

Currently, TPEs are comparably high priced, but they are available in uniform grades and can easily and rapidly be processed by injection molding or extrusion on standard equipment. Furthermore, TPEs are suitable for chemical and mechanical recycling, thus contributing to a circular economy.<sup>[64]</sup> Market analyses determine the market size of medical styrenic block copolymers to 535.5 million US\$ and anticipate an average annual growth rate of 8%.<sup>[67]</sup> This is reasoned on one side in its material properties with regard to performance (strength, flexibility) and safety (non-allergic, non-toxic, easily sterilizable by ultraviolet radiation) and on the other side due to rapid evolution in medical technologies.

In conclusion, styrenic thermoplastic elastomers are a very promising material class, for which further research has to be pursued in order to identify acceptable alternatives to plasticized PVC for red blood cell storage, so that precautions especially for the treatment of vulnerable patient groups can be taken.

## Conclusions

Every year, 16 million blood bags are used in Europe alone, which equals about 1.7 million kilograms of PVC and 1 million kilograms of phthalate plasticizers, causing a massive burden on the environment.<sup>[7]</sup> Besides blood bags, also other intravenous bags should be manufactured of PVC-free materials in the future, since in the European Union about 150.000 people depend on frequent dialysis, equaling 21 million tons of PVC and over 6 million tons of plasticizer every year.

The amount of this material is one reason to push the replacement of PVC by a material of lower density, which can ideally be recycled in a large proportion. Moreover, the negative impacts of plasticizers on patients but also on the environment is huge. Therefore, the use of alternative plasticizers for PVC might minimize patient exposure to potentially toxic substances. However, it would not solve the environmental problems of PVC itself.

Fortunately, alternative intravenous bags based on polyolefins or styrenic thermoplastic elastomers are available on the market. Both polymer classes are easily processable, sterilizable and possess a similar property profile to DEHP-plasticized PVC. Though, evaluation of the red blood cell viability in blood bags made of polyolefins revealed high hemolysis levels. Concerning the discussed bags made of styrenic thermoplastic elastomers, plasticizers, albeit less polar and not prone to migration, have to be introduced to tune the material's hardness. In addition, studies on the blood quality upon storage are currently not accessible. Therefore, at present no alternative polymer materials to DEHP-plasticized PVC intended for red blood cell storage have been introduced to the market.

In spite of higher cost, especially sensitive groups, should have access to a treatment with medical devices fabricated without harmful substances for precautionary reasons. These include neonates and infants prone to high exposure levels because of their low body weights,

pregnant women, and people with chronic diseases. Furthermore, developing manufacturing processes and gaining market share of materials with a life-cycle perspective offers the opportunity of lowering cost for waste handling and the purification of exhaust gases. Another outcome could be a minor contribution to climate change by the emission of greenhouse gases. In consequence, ongoing research and development of alternatives to plasticized PVC is essential.

## References

- [1] C. Mueller-Eckhardt (Ed.), *Transfusionsmedizin*, Springer Berlin Heidelberg, Berlin, Heidelberg, **1996**.
- [2] W. Harvey, H. de Landau, *Exercitatio anatomica de motu cordis et sanguinis in animalibus*, Sumptibus F. Fitzeri, Francofurti, **1628**.
- [3] K. Landsteiner, *entralbl. Bakteriologie*. **1900**, 27, 357.
- [4] a) K. Landsteiner, *Wien. Klin. Wochenschr.* **1901**, 1132; b) P. Eisenberg, *Wien. Klin. Wochenschr.* **1901**, 1020.
- [5] A. von Decastello, A. Sturli, *Muench. Med. Wochenschr.* **1902**, 1090.
- [6] K. Landsteiner, A. S. Wiener, *Exp. Biol. Med.* **1940**, 43, 223.
- [7] L. Stig, *Blood Bags. A pilot case to stimulate eco-innovation within the healthcare sector*, **2017**.
- [8] J. A. Tickner, T. Schettler, T. Guidotti, M. McCally, M. Rossi, *Am. J. Ind. Med.* **2001**, 39, 100.
- [9] R. J. Jaeger, R. J. Rubin, *N. Engl. J. Med.* **1972**, 287, 1114.
- [10] L. W. McKeen in *Handbook of polymer applications in medicine and medical devices* (Eds.: K. Modjarrad, S. Ebnesajjad), Elsevier/William Andrew, Oxford, UK., **2014**, pp. 21–53.
- [11] Scientific Committee on Emerging and Newly Identified Health Risks, *Opinion on the safety of medical devices containing DEHP plasticized PVC or other plasticizers on neonates and other groups possibly at risk*, European Commission, Luxembourg, **2015**.
- [12] European Chemicals Agency, "Background document for bis(2-ethylhexyl) phthalate (DEHP). Document developed in the context of ECHA's first Recommendation for the inclusion of substances in Annex XIV", can be found under [https://echa.europa.eu/documents/10162/17232/dehp\\_21697\\_en.pdf/eba86104-1e3e-7ce2-ffc2-40950d6a1b9f](https://echa.europa.eu/documents/10162/17232/dehp_21697_en.pdf/eba86104-1e3e-7ce2-ffc2-40950d6a1b9f), **2009**.
- [13] Bundesinstitut für Arzneimittel und Medizinprodukte, "DEHP als Weichmacher in Medizinprodukten aus PVC", can be found under [https://www.bfarm.de/SharedDocs/Risikoinformationen/Medizinprodukte/DE/dehp\\_2006.html](https://www.bfarm.de/SharedDocs/Risikoinformationen/Medizinprodukte/DE/dehp_2006.html), **2006**.
- [14] *Regulation (EU) 2017/745 of the European Parliament and of the Council of 5 April 2017 on medical devices*, **2017**.
- [15] H. Gulliksson, S. Meinke, A. Ravizza, L. Larsson, P. Höglund, *Vox Sang.* **2017**, 112, 33.
- [16] G. Latini, G. B. Avery, *Acta Paediatr.* **1999**, 88, 1174.
- [17] S. V. Kevy, M. S. Jacobson, *Environ. Health Perspect.* **1982**, 45, 57.

- [18] G. Rock, M. Tocchi, P. R. Ganz, E. S. Tackaberry, *Transfusion* **1984**, 24, 493.
- [19] P. W. Albro, S. R. Lavenhar, *Drug Metab. Rev.* **1989**, 21, 13.
- [20] C. Rhodes, T. C. Orton, I. S. Pratt, P. L. Batten, H. Bratt, S. J. Jackson, C. R. Elcombe, *Environ. Health Perspect.* **1986**, 65, 299.
- [21] a) J. W. Daniel, H. Bratt, *Toxicology* **1974**, 2, 51; b) C. C. Peck, P. W. Albro, *Environ. Health Perspect.* **1982**, 45, 11.
- [22] G. M. Pollack, R. C. Li, J. C. Ermer, D. D. Shen, *Toxicol. Appl. Pharmacol.* **1985**, 79, 246.
- [23] M. J. Silva, E. Samandar, J. L. Preau, L. L. Needham, A. M. Calafat, *Toxicology* **2006**, 219, 22.
- [24] Y. Ito, M. Kamijima, C. Hasegawa, M. Tagawa, T. Kawai, M. Miyake, Y. Hayashi, H. Naito, T. Nakajima, *Environ. Health Prev. Med.* **2014**, 19, 117.
- [25] Y. Kurata, N. Shimamura, M. Katoh, *J. Toxicol. Sci.* **2012**, 37, 401.
- [26] Y. Kurata, F. Makinodan, N. Shimamura, M. Katoh, *J. Toxicol. Sci.* **2012**, 37, 33.
- [27] M. S. Jacobson, S. V. Kevy, R. J. Grand, *J. Lab. Clin. Med.* **1977**, 89, 1066.
- [28] G. Pugh, J. S. Isenberg, L. M. Kamendulis, D. C. Ackley, L. J. Clare, R. Brown, A. W. Lington, J. H. Smith, J. E. Klaunig, *Toxicol. Sci.* **2000**, 56, 181.
- [29] C. Desdoits-Lethimonier, O. Albert, B. Le Bizec, E. Perdu, D. Zalko, F. Courant, L. Lesné, F. Guillé, N. Dejucq-Rainsford, B. Jégou, *Hum. Reprod.* **2012**, 27, 1451.
- [30] R. Lambrot, V. Muczynski, C. Lécureuil, G. Angenard, H. Coffigny, C. Pairault, D. Moison, R. Frydman, R. Habert, V. Rouiller-Fabre, *Environ. Health Perspect.* **2009**, 117, 32.
- [31] IARC Working Group on the Evaluation of Carcinogenic Risk to Humans, *Chemical Agents and Related Occupations*, International Agency for Research on Cancer, Lyon, France, **2012**.
- [32] C. R. Elcombe, A. M. Mitchell, *Environ. Health Perspect.* **1986**, 70, 211.
- [33] G. Pan, T. Hanaoka, M. Yoshimura, S. Zhang, P. Wang, H. Tsukino, K. Inoue, H. Nakazawa, S. Tsugane, K. Takahashi, *Environ. Health Perspect.* **2006**, 114, 1643.
- [34] L. López-Carrillo, R. U. Hernández-Ramírez, A. M. Calafat, L. Torres-Sánchez, M. Galván-Portillo, L. L. Needham, R. Ruiz-Ramos, M. E. Cebrián, *Environ. Health Perspect.* **2010**, 118, 539.
- [35] B. S. Nielsen, D. N. Andersen, E. Giovalle, M. Bjergstrøm, P. B. Larsen, *Alternatives to classified phthalates in medical devices*, Miljøstyrelsen, **2014**.
- [36] S. P. den Braver-Sewradj, A. Piersma, E. V. S. Hessel, *Crit. Rev. Toxicol.* **2020**, 50, 650.
- [37] R. M. David, R. D. White, M. J. Larson, J. K. Herman, R. Otter, *Toxicol. Lett.* **2015**, 238, 100.
- [38] K. Radwanski, M. Thill, K. Min, *Vox Sang.* **2014**, 106, 322.
- [39] E. R. Simon, *Blood* **1962**, 20, 485.
- [40] K. Serrano, E. Levin, D. Chen, A. Hansen, T. R. Turner, J. Kurach, A. Reidel, W. F. Boecker, J. P. Acker, D. V. Devine, *Vox Sang.* **2016**, 110, 227.
- [41] P. F. van der Meer, R. N. I. Pietersz, *Vox Sang.* **2007**, 93, 176.
- [42] B. H. Shaz, K. Grima, C. D. Hillyer, *Transfusion* **2011**, 51, 2510.

- [43] C. J. Draper, T. J. Greenwalt, U. J. Dumaswala, *Transfusion* **2002**, 42, 830.
- [44] J. Field, R. Sierra-Alvarez, *Rev. Environ. Sci. Bio/Technol.* **2004**, 3, 185.
- [45] M. Baitz, J. Kreißig, E. Byrne, *Life Cycle Assessment of PVC and of principal competing materials*, **2004**.
- [46] M. Sadat-Shojai, G.-R. Bakhshandeh, *Polym. Degrad. Stab.* **2011**, 96, 404.
- [47] J. Yu, L. Sun, C. Ma, Y. Qiao, H. Yao, *Waste Manag.* **2016**, 48, 300.
- [48] I. Mersiowsky, *Water Res.* **2001**, 35, 3063.
- [49] V. R. Sastri, *Plastics in medical devices. Properties, requirements, and applications*, Elsevier/William Andrew, Amsterdam, **2014**.
- [50] M. Sunny, *Studies on Metallocene Polyolefin and Polyvinyl Chloride for Blood and Blood Component Storage Applications, Dissertation*, Cochin University of Science and Technology, Cochin, **2006**.
- [51] K. Sojiphan, A. Iverson, S. Kim, *Materials Selection Analysis: Bag for Viable Blood Storage*, Department of Materials Science and Engineering, Northwestern University, **2004**.
- [52] R. Carmen, *Transfus. Med. Rev.* **1993**, 7, 1.
- [53] S. Murphy, F. H. Gardner, *Blood* **1975**, 46, 209.
- [54] C. V. Prowse, D. de Korte, J. R. Hess, P. F. van der Meer, *Vox Sang.* **2014**, 106, 1.
- [55] R. H. Kelch, *Polyolefin/copolyamide rf active adhesive film*, WO2001088039A1, **2001**.
- [56] L. A. Rosenbaum, W. Anderson, L. Woo, D. Laurin, A. L. Buan, M. T. K. Ling, Y.-P. S. Ding, D. S. Hayward, J. P. Hoppesch, G. Nebgen et al., *Multi-layered polymer based film structure for medical grade products*, WO1995013918A1, **1995**.
- [57] S. B. Ohlsson, P. de Cambourg, W. J. J. Leysen, *Multi-layer film*, US5399396A, **1995**.
- [58] I. Patel, H. Bowerman, L. Rosenbaum, R. Mennenoh, P. Ryan, *Material for medical grade products and products made therefrom*, WO1993014810A2, **1993**.
- [59] J. de Wildt-Eggen, J. G. Schrijver, H. J. Bouter-Valk, R. Fijnheer, M. Bins, H. C. van Prooijen, *Transfusion* **1997**, 37, 476.
- [60] H. R. Hill, C. K. Oliver, L. E. Lippert, T. J. Greenwalt, J. R. Hess, *Vox Sang.* **2001**, 81, 161.
- [61] J. W. Lagerberg, E. Gouwerok, R. Vlaar, M. Go, D. de Korte, *Transfusion* **2015**, 55, 522.
- [62] M. Verswyvel, K. Knoll, N. Nießner, *Styrenic Thermoplastic Elastomers for Healthcare Applications*, Durham, **2017**.
- [63] M. Verswyvel, N. Nießner, E. Jahnke, D. Wagner, K. Knoll, *Very soft, non-sticky and transparent styrenic thermoplastic elastomer composition*, WO2018/166958 A1, **2018**.
- [64] Ineos Styrolution Group, "Resins for the Healthcare Industry", can be found under [https://www.ineos-styrolution.com/INTERSHOP/static/WFS/Styrolution-Portal-Site/-/Styrolution-Portal/en\\_US/News%20and%20media/download/INEOS\\_Styrolution\\_Healthcare\\_Brochure.pdf](https://www.ineos-styrolution.com/INTERSHOP/static/WFS/Styrolution-Portal-Site/-/Styrolution-Portal/en_US/News%20and%20media/download/INEOS_Styrolution_Healthcare_Brochure.pdf).



- [65] a) J. M. Brown, N. E. Stacy, C. E. Stouffer, J. D. Wilkey, M. A. Smith, *Styrene butadiene block copolymers for film applications*, US9550869B2, **2017**; b) J. J. Zhou, W. H. Pace, D. A. Young, *Styrene-butadiene block copolymers for tubing applications*, US20160264773A1, **2016**; c) J. J. Zhou, *Methods for controlling hardness of styrene-butadiene block copolymers*, US9441090B1, **2016**.
- [66] K. Knoll, N. Nießner, *Macromol. Symp.* **1998**, 132, 231.
- [67] Global Market Insights, "Medical Styrenic Block Copolymer (SBC) Market Size, Share and Industry Analysis Report by Product (SBS, SIBS, SEBS) and Application (Tubing, Medical Bags, Equipment, Packaging & Diagnostics Products, Wound Care), Regional Outlook, Application Development Potential, Competitive Market Share & Forecast, 2021 – 2027", can be found under <https://www.gminsights.com/industry-analysis/medical-styrenic-block-copolymer-market>, **2021**.



---

## CHAPTER 3

***Linear (IS)<sub>n</sub>I Multiblock Copolymers:* Manipulating  
the Softness of TPEs by Introducing Flexible End  
Blocks to Multiblock Copolymers with a Defined or  
Tapered Interface**

---



## CHAPTER 3

To be Submitted

# Linear $(IS)_nI$ Multiblock Copolymers: Manipulating the Softness of TPEs by Introducing Flexible End Blocks to Multiblock Copolymers with a Defined or Tapered Interface

Ramona D. Barent<sup>1,2</sup>, Igor Perevyazko<sup>5</sup>, Nina Mikusheva<sup>5</sup>, George Floudas<sup>3,4\*</sup>, and Holger Frey<sup>1\*</sup>

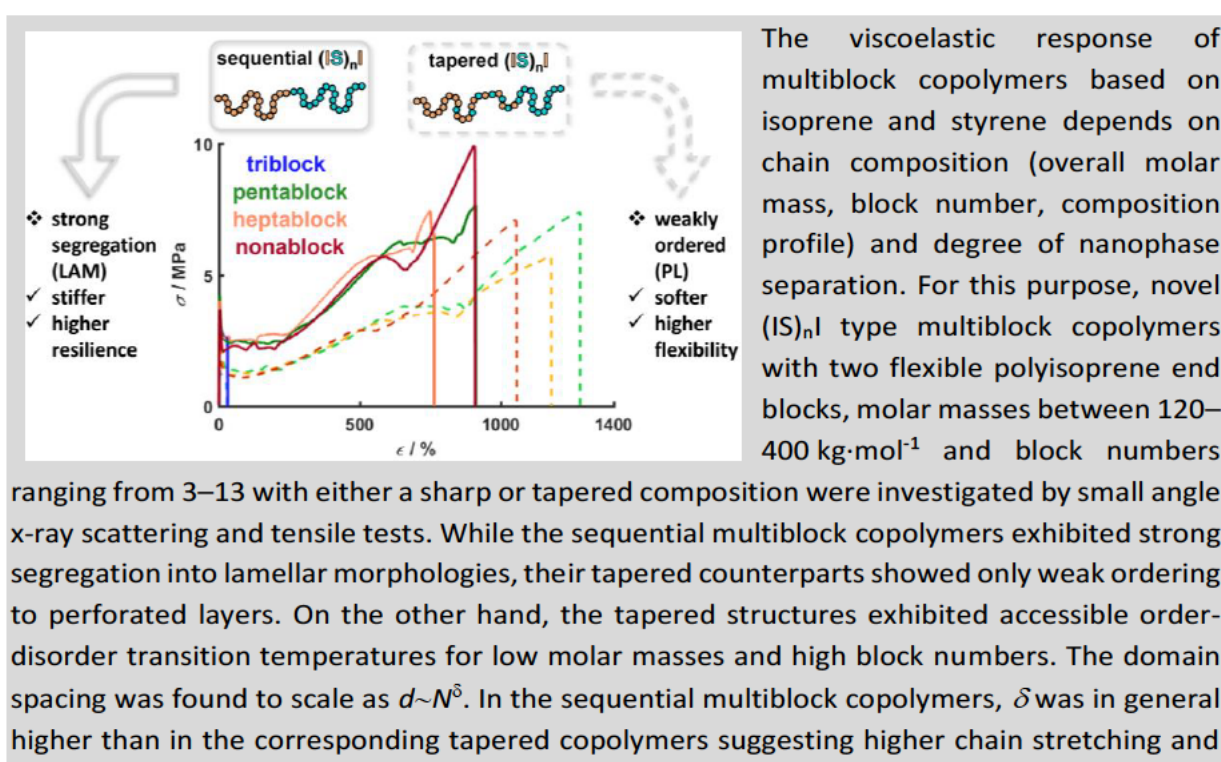
<sup>1</sup> Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany

<sup>2</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany

<sup>3</sup> Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

<sup>4</sup> Department of Physics, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece

<sup>5</sup> Department of Molecular Biophysics and Physics of Polymers, St. Petersburg University, Universitetskaya nab. 7/9, 199034, Saint Petersburg, Russia



non-Gaussian conformations. In addition, the domain spacing was found to scale with the number of blocks in  $(AB)_nA$  type copolymers revealing predominant bridged (looped) chain configurations in the sequential (tapered) multiblock copolymers. Generally, tensile tests revealed high toughness ( $20\text{--}70\text{ MJ}\cdot\text{m}^{-3}$ ) for the multiblock copolymers with at least two rigid, i.e., hard, polystyrene blocks, with the tapered structures being softer and more flexible. Stiffness increased with increasing block number, reflecting their smaller domain sizes. Moreover, the maximum deformation was found to increase with overall molar mass. With their soft, albeit resilient properties, these materials are promising for the replacement of plasticized polymers, e.g., pol(vinyl chloride), avoiding release of plasticizer.

## Introduction

Block copolymers stand out due to the chemical linkage between different polymer chains, which in contrast to blends of homopolymers allows the desired nanophase separation at sufficiently high molar masses.<sup>[1]</sup> This formation of different domains consisting of the individual polymers gives access to “new” materials with optimized mechanical properties which excel the individual components.<sup>[2]</sup>

A common approach is the combination of a rather brittle and stiff polymer exhibiting a high glass-transition temperature (high- $T_g$ ), e.g., polystyrene (PS), with a soft and rubbery polymer with a low glass-transition temperature (low- $T_g$ ), e.g., polyisoprene (PI).<sup>[3]</sup> In this way, either elastically as well as plastically deformable thermoplastic elastomers<sup>[4]</sup> or high impact materials<sup>[5]</sup> with an operating window from roughly  $-65\text{ }^\circ\text{C}$  ( $T_g(\text{PI})$ ) up to  $100\text{ }^\circ\text{C}$  ( $T_g(\text{PS})$ ) are obtained, depending on the ratio of both comonomers. However, a simple AB diblock architecture cannot impart the required mechanical properties. The architecture has to be extended to an ABA triblock structure to ensure high mechanical stability, with A being the high- $T_g$  component forming vitrified domains.<sup>[6]</sup>

Primarily, the properties are governed by the molar mass, the incompatibility, and the volume fraction of the constituent polymers, dictating the morphology formed upon nanophase separation.<sup>[7,8,9]</sup> Beyond this, chain conformation strongly affect the mechanics, with bridged mid blocks mainly being responsible for elasticity.<sup>[10]</sup> With the vitrification of the high- $T_g$  phase, chain pullout is impeded, thus providing resilience. Apart from that, the domain orientation affects the mechanical response, with randomly oriented fingerprint morphologies possessing higher ductility and toughness compared to oriented lamellar morphologies.<sup>[11]</sup> However, without external strain application during processing, defect-free block copolymer phases are improbable.<sup>[12]</sup>

AB diblock as well as ABA triblock copolymers have been investigated most extensively, providing a deep understanding of their bulk behavior.<sup>[3]</sup> Further extension of the block sequences towards multiblock copolymers offers new potential for structure and rheology control. However, most studies focus on the realization of very tough and resilient materials, which is why structures with two polystyrene end blocks  $(\text{SI})_n\text{S}$  (with  $n \geq 1$ ) or multiblock copolymers with an even number of blocks  $(\text{SI})_n$  (with  $n > 1$ ) were emphasized.<sup>[9,13–17]</sup> Regarding structures with two polyisoprene end blocks  $(\text{IS})_n\text{I}$ , only ISI triblock copolymers have been investigated and compared to its SIS and IS counterparts, with most studies focusing on high impact polystyrene.<sup>[7,18,19]</sup>

However, the introduction of two polyisoprene end blocks in tri- and multiblock copolymers shortens the individual PI block length compared to a structure with an even block number at constant comonomer ratio. This can be expected to influence the PI domain sizes. Moreover, the two flexible end block leading to dangling chains might cause an internal plasticizer effect and further restrict the chain conformation of the polystyrene mid blocks by forcing both block junctions to be located at the domain interface.

Apart from the fundamental question of the effect of two flexible end blocks on the materials' properties, the design of the polymers is driven by the intended application for blood bags, leading to a non-bleeding and chlorine-free alternative to plasticized poly(vinyl chloride). The latter causes major concern because of migration of the plasticizer, which is linked to health issues. Besides general aspects like transparency, weldability and sterilizability, special requirements have to be met for a certain medical application. Medical bags need to be flexible when they are squeezed (elastically deformable, Young's modulus  $E_{\text{modulus}} < 100$  MPa), but at the same time have to withstand g-forces because of centrifugation (rigid and resilient, toughness  $U > 40$  MPa).<sup>[20]</sup> With the combination of two flexible end blocks with several polystyrene mid blocks, both high flexibility and resilience are targeted. The development of alternatives to plasticized poly(vinyl chloride) (PVC) is progressing, with Ineos Styrolution providing thermoplastic elastomer-based (TPE) approaches.<sup>[21,22]</sup> Their materials are based on hydrogenated PS-*b*-P(B-*ran*-S)-*b*-PS triblock copolymers,<sup>[23]</sup> which are coupled to star architectures using epoxidized soybean oil.<sup>[24]</sup> However, the TPE's softness is again fine-tuned metering in a plasticizer, endowing properties for intravenous tubings, bags and drip chambers (5% of the plasticizer), but also very soft materials for wound aids (30% of the plasticizer).<sup>[25]</sup> Yet, only small amounts of comparably non-polar, food-approved plasticizers, e.g., mixtures of a of mineral oils and vegetable oils, are sufficient, which in contrast to plasticizers used in PVC do not tend to migrate into the polar medium of the reserve.<sup>[22]</sup>

Within this work, we present the first systematic investigation of (IS)<sub>n</sub>I type multiblock copolymers covering a wide range of molar masses and block numbers. These well-defined structures are synthesized by living carbanionic polymerization, which offers high precision in terms of dispersity, molar mass, compositional and structural homogeneity.<sup>[3,9,26,27]</sup> The influence of the polymer chain structure, i.e., the presence of two flexible polyisoprene end blocks and moreover a systematically varied number of vitrifying polystyrene mid blocks on the mechanical properties will be characterized and discussed in context of the respective morphologies. In addition, for each chain composition polymer structures with varying segregation strength are compared. For this purpose, both tapered and sequential block structures differing in their block profile were synthesized. Tapered block copolymers are gradient copolymers with gradual transition between the polyisoprene and the polystyrene block. This broadened interface increases miscibility and at the same time shortens the effective polystyrene block length by the incorporation of several styrene repeating units within the polyisoprene-rich block.

## Experimental Section

### Materials and General Polymerization Procedure

The solvent cyclohexane (Fisher Science,  $\geq 99.8\%$ ) was dried over sodium with benzophenone as an indicator. Methanol (MeOH, Fisher Science,  $\geq 99.9\%$ ) was used as purchased. The stabilizer of isoprene (I, Acros Organics, 98%) and styrene (S, Acros Organics, 99%) was removed by filtering the monomers through a column containing basic aluminum oxide and purified hereafter by degassing and distillation over calcium hydride (Acros Organics, 93%) and trioctylaluminum (Sigma Aldrich, 25 wt% in hexanes). *Sec*-Butyllithium (*sec*-BuLi, Acros Organics, 1.3 M in cyclohexane/hexane (92/8)) was used as supplied.

All purification and reaction steps were conducted under Schlenk condition, meaning that all glassware was flame-dried three times prior to use and all manipulations were carried out either under high-vacuum ( $1 \cdot 10^{-3}$  mbar) or an argon atmosphere. First, the monomers were dried under reduced pressure and room temperature over ground calcium hydride over night after degassing by three freeze-thaw-cycles. On the next day, the monomers were distilled into a flask containing trioctylaluminum obtained by evaporation of the solvent under reduced pressure. Again, purification was performed over night at room temperature and reduced pressure. Then, the monomers were distilled into a graduated ampoule, which was flooded with argon after thawing. Cyclohexane was freshly distilled under normal pressure and drained into an evacuated glass reactor with a Nd stirring bar. The reaction flask was flushed with argon after cooling cyclohexane to room temperature. The ampoules were mounted to the reaction flask with transition pieces connected to the Schlenk line.

The initiator *sec*-BuLi was added to the solvent in an argon counterflow. Subsequently, the whole glass apparatus was sealed, and the solvent was heated to either 40 °C or 60 °C for the preparation of tapered or sequential block copolymers, respectively. Then, the first monomer feed was added under vigorous stirring. The reaction time for each pure block or tapered diblock was calculated using a kinetic Monte-Carlo simulation. Typical reaction times per block or tapered diblock sequence ranged between 30 min and 5 hours, depending on the concentration and temperature. Details can be found in the Supp. Inf. of previous publications.<sup>[3,26]</sup> To guarantee full monomer conversion, the calculated reaction times were extended by 10%. After all monomer feeds and their consumption, the living chain ends were terminated by addition of methanol in an argon counterflow. The polymers were precipitated pouring the reaction solution into a 5-10-fold excess of methanol, dried at reduced pressure for at least one week and stored in the absence of light at -20 °C under argon atmosphere.

### Small-Angle X-Ray Scattering

SAXS measurements were recorded using CuK $\alpha$  radiation (Rigaku Micro Max 007 x-ray generator, Osmic Confocal Max-Flux curved multilayer optics). 2D diffraction patterns were recorded on an Mar345 image plate detector at a sample-detector distance of 2060 mm. Intensity distributions as a function of the modulus of the total scattering vector,  $q = (4\pi/\lambda) \cdot \sin(2\theta/2)$ , where  $2\theta$  is the scattering angle and  $\lambda = 0.154$  nm is the wavelength, were obtained by radial averaging of the 2D datasets. Samples in the form of films with a thickness



of 0.25-0.45 mm were prepared by slow solvent casting. Temperature-dependent measurements of 1 hour long with 1 hour of equilibration at each temperature were made by heating the films from 303 K–423 K in 30 K steps and subsequent cooling.

### Tensile Testing

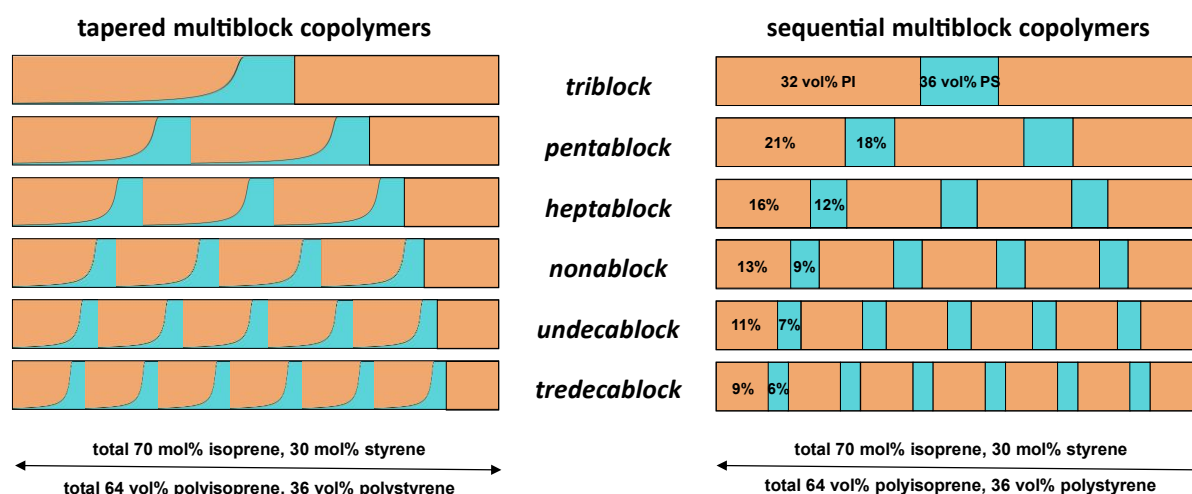
Tensile tests were performed using either an EZ-LX HS universal testing machine (Shimadzu) or a Z005 materials testing machine (Zwick/Roell) both having pneumatic grips (pressure 5-7 bar). All films were prepared by dissolving 1.50 g of the azeotropically dried polymer in 22 mL chloroform with one grain of BHT to prevent crosslinking, casting the solution into a teflon mold, followed by slow evaporation (3-7 days) at room temperature and normal pressure and finally full removal of the solvent under reduced pressure. Dogbone shaped specimens (60 mm full length x 4.5 mm notch width x 0.25-0.45 mm thickness) were stamped out of the films without prior thermal annealing. With this, the thickness is at least 2-3 times the domain spacing ( $d_{\text{max}}=123$  nm), eliminating the probability of a dependence of the elastic moduli on the film thickness.<sup>[28]</sup> The specimens were clamped with a distance of 32 mm and uniaxially stretched with a rate of 10 mm·min<sup>-1</sup> at room temperature. A pre-load of 0.1 N was applied to take sample deflection into account. Characteristic parameters were determined averaging over 3-6 independent experiments.

Some extraordinarily resilient specimens did not rupture but slid out of the grip. Therefore, for the determination of ultimate parameters like stress and strain at break as well as toughness, only ruptured specimens were taken into account. If all measured specimens slid out, the values are marked with an asterisk and are most likely underestimated.

## Results and Discussion

### Polymer Characterization

Various previous works showed that the statistical copolymerization of isoprene and styrene in nonpolar solvents like cyclohexane results in the formation of a tapered diblock structure with a gradual transition from polyisoprene to polystyrene.<sup>[9,29]</sup> Repeating this statistical copolymerization steps permits the synthesis of tapered multiblock copolymers. Figure 1 visualizes the tri- and multiblock copolymers studied in this work exemplified for one overall molar mass. Furthermore, the volume fractions of every polyisoprene and polystyrene block are denoted for the sequential multiblock copolymers. The tapered structures (Figure 1, left) are simulated based on the reactivity ratios of isoprene and styrene at 40 °C in cyclohexane ( $r_I=10.9$  and  $r_S=0.029$ ).<sup>[26]</sup>

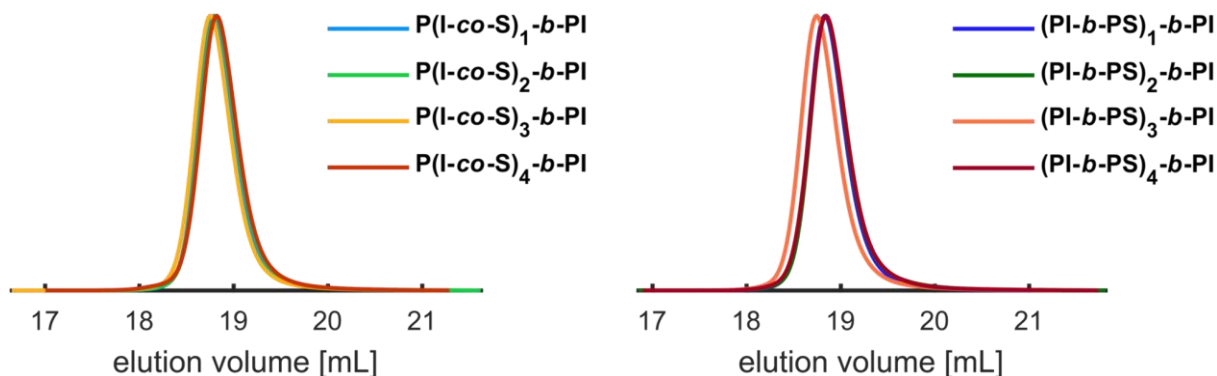


**Figure 1:** Visualization of the distribution of the comonomers isoprene (orange) and styrene (cyan) along the polymer chain exemplified for one molar mass, but varying block number. A molar-based composition diagram is plotted, showing the mean incorporation (y axis) at every conversion (x axis).

Within this work, several polymer series with an odd number of blocks (two polyisoprene end blocks),  $\approx 70$  mol% isoprene and  $\approx 30$  mol% styrene ( $\approx 39$  wt%) are investigated, with the polyisoprene exhibiting almost exclusively 1,4 units ( $\geq 93\%$ ). The polymers differ in their overall molar mass (120, 160, 240, and 320  $\text{kg}\cdot\text{mol}^{-1}$ ) and feature systematically varied block numbers (tri-, penta-, hepta-, nona-, undeca- and tredecablock copolymers). Besides, selected examples of polymers with 400  $\text{kg}\cdot\text{mol}^{-1}$  were synthesized due to the high synthetic effort caused by high viscosities. Moreover, each polymer is synthesized with a tapered and a sequential block structure, implementing repetitive copolymerizations of a mixture of isoprene and styrene, or iterative stepwise polymerizations of isoprene and styrene, respectively. All polymerizations were carried out in cyclohexane and initiated with *sec*-butyllithium, which affords the above visualized tapered block structures (Figure 1, left) due to the highly disparate reactivity ratios and further guarantees a high 1,4-stereoselectivity of polyisoprene. The inherent low glass temperature ( $T_g(1,4\text{-PI}) < -60$  °C) enables a wide temperature range application window.<sup>[30]</sup>

In pronounced contrast to previous works from our group and others,<sup>[9,13–17]</sup> uneven block numbers with two flexible polyisoprene end blocks were synthesized in order to design

comparably soft materials and furthermore to study the effect of flexible end blocks on morphologies and mechanical properties. Well-defined polymers could be obtained. SEC measurements show monomodal, narrow molar mass distributions with low dispersity (Figure 2, Figure S1). The molar masses listed in Table 1 are overestimated because of the use of polystyrene standards.



**Figure 2:** SEC traces (THF, PS calibration standard, RI detector) of the tapered (left) and sequential (right) multiblock copolymers with  $160 \text{ kg}\cdot\text{mol}^{-1}$ . The SEC traces of the other molar mass series are given in Figure S1.

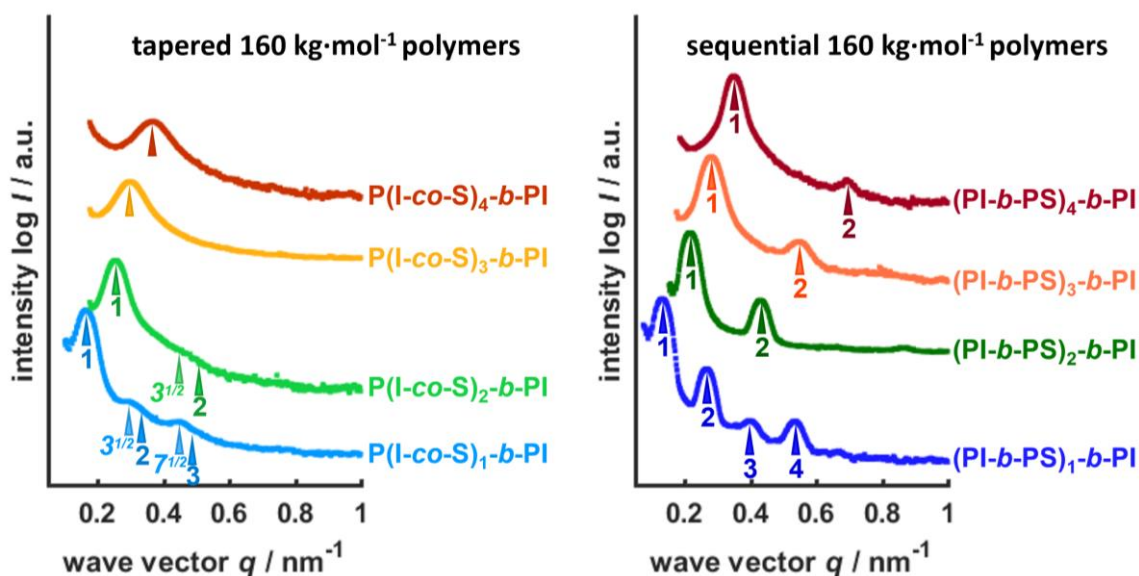
**Table 1:** Number-average molar mass  $M_n$  and dispersity  $\mathcal{D}$  (SEC in THF, PS calibration standard, RI detector) of the tapered multiblock copolymers  $\text{P(I-co-S)}_n\text{-b-PI}$  (tap) and sequentially polymerized multiblock copolymers  $(\text{PI-b-PS})_n\text{-b-PI}$  (seq). For additional information about the molar fraction of the comonomer isoprene  $P_n(\text{I})$  and its 1,4-content  $\omega_{1,4}(\text{I})$ , see Table S1.

| block number<br>#=2n+1 | target $M$<br>[ $\text{kg}\cdot\text{mol}^{-1}$ ] | (IS) <sub>n</sub> I block<br>type | $M_n^a$<br>[ $\text{kg}\cdot\text{mol}^{-1}$ ] | $\mathcal{D}^a$ | (IS) <sub>n</sub> I block<br>type | $M_n^a$<br>[ $\text{kg}\cdot\text{mol}^{-1}$ ] | $\mathcal{D}^a$ |
|------------------------|---------------------------------------------------|-----------------------------------|------------------------------------------------|-----------------|-----------------------------------|------------------------------------------------|-----------------|
| 3                      | 120                                               | tap                               | 133.5                                          | 1.04            | seq                               | 120.9                                          | 1.07            |
| 5                      | 120                                               |                                   | 130.8                                          | 1.04            |                                   | 132.4                                          | 1.09            |
| 7                      | 120                                               |                                   | 131.1                                          | 1.06            |                                   | 136.3                                          | 1.08            |
| 3                      | 160                                               | tap                               | 163.2                                          | 1.07            | seq                               | 155.9                                          | 1.07            |
| 5                      | 160                                               |                                   | 158.9                                          | 1.08            |                                   | 151.0                                          | 1.09            |
| 7                      | 160                                               |                                   | 170.2                                          | 1.08            |                                   | 168.6                                          | 1.09            |
| 9                      | 160                                               |                                   | 158.6                                          | 1.09            |                                   | 151.1                                          | 1.10            |
| 3                      | 240                                               | tap                               | 277.5                                          | 1.08            | seq                               | 268.7                                          | 1.14            |
| 5                      | 240                                               |                                   | 273.9                                          | 1.14            |                                   | 306.1                                          | 1.18            |
| 7                      | 240                                               |                                   | 303.5                                          | 1.14            |                                   | 246.9                                          | 1.06            |
| 9                      | 240                                               |                                   | 324.9                                          | 1.17            |                                   | 304.5                                          | 1.15            |
| 11                     | 240                                               |                                   | 257.9                                          | 1.15            |                                   | 254.8                                          | 1.13            |
| 13                     | 240                                               |                                   | 272.8                                          | 1.17            |                                   | 275.1                                          | 1.14            |
| 3                      | 320                                               | tap                               | 376.1                                          | 1.05            | seq                               | 400.5                                          | 1.06            |
| 5                      | 320                                               |                                   | 361.7                                          | 1.12            |                                   | 387.8                                          | 1.08            |
| 7                      | 320                                               |                                   | 369.9                                          | 1.09            |                                   |                                                |                 |
| 9                      | 320                                               |                                   |                                                |                 |                                   | 373.6                                          | 1.07            |
| 3                      | 400                                               | tap                               | 556.0                                          | 1.07            | seq                               | 558.6                                          | 1.08            |
| 5                      | 400                                               |                                   |                                                |                 |                                   | 476.9                                          | 1.07            |

## Morphological Investigation

The SAXS results for the tapered as well as the sequential multiblock copolymers with a molar mass of  $160 \text{ kg}\cdot\text{mol}^{-1}$  obtained at 363 K are shown in Figure 3. The pattern of the other samples with molar masses ranging between 120 and  $400 \text{ kg}\cdot\text{mol}^{-1}$  can be found in the Supp. Inf. (see Figure S2-S6).

The sequential block copolymers are well ordered and show Bragg reflections with relative  $q$  values of  $1 : 2 : 3 : 4$  relative to the first reflection, corresponding to a lamellar morphology (LAM). In contrast, the tapered  $160 \text{ kg}\cdot\text{mol}^{-1}$  triblock and pentablock copolymers exhibit reflections with relative  $q$  values of  $1 : 3^{1/2} : 2 : 7^{1/2} : 3$  suggesting a weakly ordered cylindrical (CYL) structure in the absence of long-range order. In the case of the tapered heptablock and nonablock copolymers the single peak is very broad indicative of correlation hole scattering in the disordered phase (DIS).<sup>[31]</sup>



**Figure 3:** SAXS patterns of the tapered (left) and sequential (right) multiblock copolymers (blue: triblock, green: pentablock, orange: heptablock, red: nonablock) with a molar mass of  $160 \text{ kg}\cdot\text{mol}^{-1}$  at 363 K (except tap.  $160 \text{ kg}\cdot\text{mol}^{-1}$  nonablock,  $T=333 \text{ K}$ ). The arrows give the positions of the Bragg reflections corresponding to a lamellar (darker color), or a cylindrical (lighter color, italic letters) morphology. The patterns are shifted vertically for clarity.

In order to locate the order-disorder transition temperature  $T_{\text{ODT}}$ , temperature-dependent SAXS measurements were performed in the temperature range of 303–423 K (see Supp. Inf., Figure S7-S41). The inverse intensity of the first Bragg reflection plotted vs. the inverse temperature allows to determine the  $T_{\text{ODT}}$  from the abrupt discontinuity in the structure factor. The obtained order-disorder transition temperatures coincide with the results from independent rheological investigation (see Supporting Information, Figures S42-S44).

Table 2 summarizes the obtained order-disorder transition temperatures and the respective morphologies. The polymers without an assigned  $T_{\text{ODT}}$  did not exhibit an accessible disordered state up to 423 K. Accessible order-disorder temperatures play a key role for processing of the materials, for instance by injection molding.

**Table 2: Morphologies and the order-disorder transition temperatures  $T_{ODT}$ 's of the tapered multiblock copolymers  $P(I-co-S)_n-b-PI$  and analogous sequentially polymerized multiblock copolymers  $(PI-b-PS)_n-b-PI$  determined at 363 K. CYL: cylindrical structure in the absence of long-range order, LAM: lamellar structure, and DIS: disordered state.**

| polymer characteristics |                                         | tapered $P(I-co-S)_n-b-PI$ |                              | sequential $(PI-b-PS)_n-b-PI$ |                              |
|-------------------------|-----------------------------------------|----------------------------|------------------------------|-------------------------------|------------------------------|
| block number<br>$2n+1$  | target $M_n$<br>[ $kg \cdot mol^{-1}$ ] | Morphology <sup>a</sup>    | $T_{ODT}$ <sup>a</sup> / [K] | Morphology <sup>a</sup>       | $T_{ODT}$ <sup>a</sup> / [K] |
| 3                       | 120                                     | CYL/LAM                    | –                            | LAM                           | –                            |
| 5                       | 120                                     | CYL (weak)                 | ~393                         | LAM                           | –                            |
| 7                       | 120                                     | DIS                        | ~363                         | LAM                           | –                            |
| 3                       | 160                                     | CYL                        | –                            | LAM                           | –                            |
| 5                       | 160                                     | CYL/DIS (weak)             | –                            | LAM                           | –                            |
| 7                       | 160                                     | DIS                        | ~423                         | LAM                           | –                            |
| 9                       | 160                                     | DIS                        | ~363                         | LAM                           | ~423                         |
| 3                       | 240                                     | LAM/CYL                    | –                            | LAM                           | –                            |
| 5                       | 240                                     | LAM/CYL                    | –                            | LAM                           | –                            |
| 7                       | 240                                     | LAM/CYL                    | –                            | LAM                           | –                            |
| 9                       | 240                                     | CYL/LAM                    | –                            | CYL/LAM                       | –                            |
| 11                      | 240                                     | LAM                        | –                            | LAM                           | –                            |
| 13                      | 240                                     | DIS                        | 363–393                      | LAM                           | –                            |
| 3                       | 320                                     | CYL/LAM                    | –                            | CYL/LAM                       | –                            |
| 5                       | 320                                     | CYL/LAM                    | –                            |                               |                              |
| 7                       | 320                                     | LAM                        | –                            | LAM                           | –                            |
| 9                       | 320                                     |                            |                              | LAM                           | –                            |
| 3                       | 400                                     | CYL/LAM                    | –                            | LAM                           | –                            |
| 5                       | 400                                     |                            |                              | LAM                           | –                            |

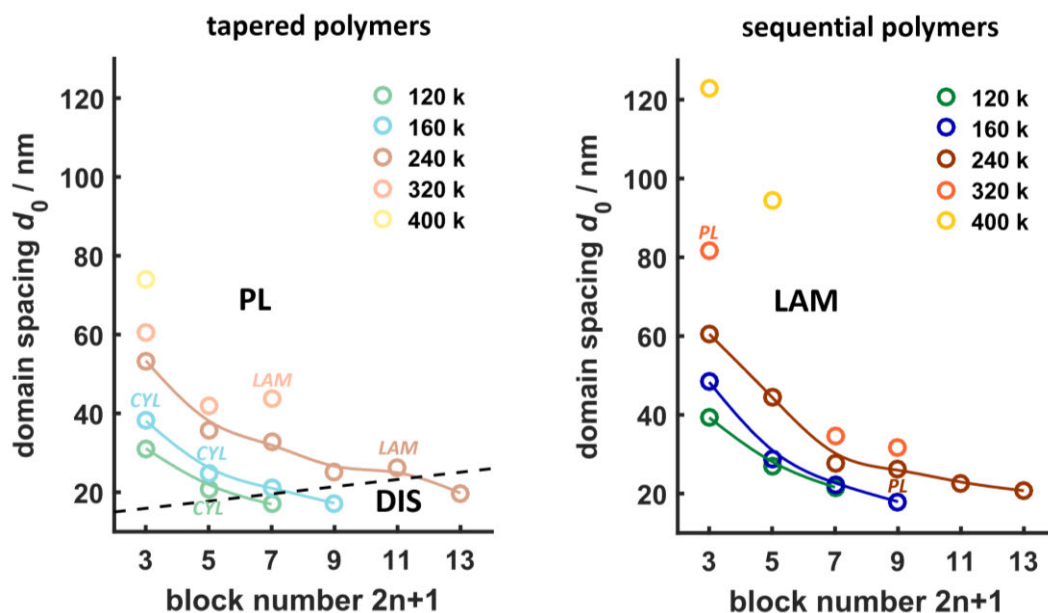
<sup>a</sup> SAXS measurements were performed in a temperature regime between 303–423 K with temperature intervals of 30 K. If no order-disorder transition temperature is assigned,  $T_{ODT}$  ranges higher than 423 K.

For the sequential triblock copolymer, the product of the Flory-Huggins interaction parameter and the degree of polymerization  $\chi N$  can be calculated with the literature known  $\chi$ -parameter of polyisoprene and polystyrene  $\chi_{PIPS}=71.4K/T[K]-0.0857$ .<sup>[32]</sup> For the lowest molar mass triblock copolymer ( $M=120 kg \cdot mol^{-1}$ ,  $N=1520$ ,  $\chi N(363 K)=169$ ), the magnitude of  $\chi N$  at a volume fraction of  $f_A=64\%$  is significantly above the theoretical value for an order-disorder transition.<sup>[33]</sup> This explains the predominance of well-ordered lamellar morphologies in the case of the sequential multiblock copolymers.

In the case of tapered copolymers, the degree of segregation is reduced due to the gradual comonomer transition. In order to account for the reduced enthalpic incompatibility, an effective Flory-Huggins parameter is introduced with  $\chi_{eff} < \chi$ .<sup>[3,34]</sup> Steube *et al.* reported a 10-fold reduction in  $\chi$  for a tapered octablock relative to a sequential diblock.<sup>[9]</sup> Assuming a 10-fold reduction of  $\chi$  for multiblock copolymers with 4 diblock sequences compared to  $\chi$  for triblock copolymers with one diblock sequence, one can get an idea of the order-disorder

transition of the tapered nonablock copolymers. With approximated magnitudes of  $\chi N(363\text{ K})=22$  ( $M=160\text{ kg}\cdot\text{mol}^{-1}$ ,  $N=2026$ ) and  $\chi N(363\text{ K})=34$  ( $M=240\text{ kg}\cdot\text{mol}^{-1}$ ,  $N=3040$ ) for the tapered nonablock copolymers with 160 and 240  $\text{kg}\cdot\text{mol}^{-1}$ , this agrees quite well with the observation of a disordered phase in the case of the nonablock with 160  $\text{kg}\cdot\text{mol}^{-1}$ , but an ordered state for the nonablock with 240  $\text{kg}\cdot\text{mol}^{-1}$ . Since the minimum value for phase separation for symmetric ABA triblock copolymers with identical segment length is simulated to range at  $\chi N=18$  at equal volume fractions  $f_A=f_B$ , an order-disorder transition at slightly higher magnitudes of  $\chi N$  is reasonable and hence validates the assumption with respect to the reduction of the Flory-Huggins interaction parameter.<sup>[35]</sup> The substantial decrease in  $\chi N$  for the tapered structures explains the formation of perforated layers or weakly ordered cylindrical morphologies in case of the tapered structures and also highlights lowering of the order-disorder temperatures for tapered copolymers with low molar masses or high block numbers.<sup>[36]</sup>

The domain spacing  $d_0$  represents the periodicity of the respective morphology. For polymers with a lamellar structure, the domain spacing is calculated from the modulus of the scattering vector  $q^*$  of the first maximum as  $d_{\text{LAM}}=d_0=2\pi/q^*$ . For the polymers exhibiting a cylindrical morphology, the inter-cylinder distance can be further obtained as  $d_{\text{CYL}}=d_0(4/3)^{1/2}$ . Figure 4 presents the domain spacing  $d_0$  at 363 K as a function of the number of blocks for the tapered and sequential multiblock copolymers with molar masses between 120–400  $\text{kg}\cdot\text{mol}^{-1}$ . The dashed line separates the ordered from the disordered (DIS) morphologies. Deviation from the common morphology (tap.: perforated layers (PL), seq.: lamellae (LAM)) are denoted next to the respective polymer in *italic*.



**Figure 4:** Domain spacing  $d_0$  in dependence of the block number  $2n+1$  of the tapered (left) and sequential (right) multiblock copolymers obtained by SAXS measurements at 363 K (except seq. 240k triblock: 393 K, and tap. 160k nonablock: 333 K). The different domain spacings of a copolymer series are connected by a line to guide the eye.

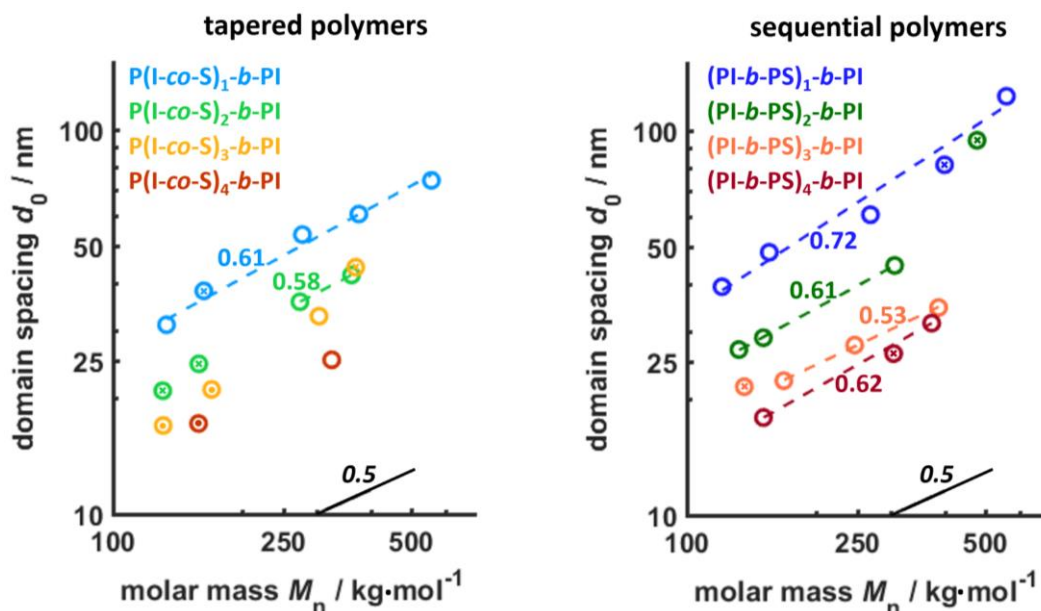
For polymers of the same molar mass series exhibiting the same morphology, the domain spacing decreases with increasing block number of the multiblock copolymers. For both the tapered and the sequential multiblock copolymers, the decrease in  $d_0$  with increasing block number is stronger for higher molar masses (e.g., the decrease in the domain spacings

comparing triblock with pentablock copolymers reveals reductions by  $\omega^{\text{tap. 320k}}=69\%$ ,  $\omega^{\text{tap. 240k}}=67\%$  for the tapered structures, and  $\omega^{\text{seq. 400k}}=77\%$ ,  $\omega^{\text{seq. 240k}}=74\%$ ,  $\omega^{\text{seq. 160k}}=60\%$  in the case of the sequential structures). Interestingly, polymers with the same degree of polymerization  $N$  per polystyrene block exhibit comparable domain spacings (e.g., sequential multiblock copolymers with  $16 \text{ kg}\cdot\text{mol}^{-1}$  per PS block:  $d_0^{160k,5}=29 \text{ nm}$ ,  $d_0^{240k,7}=28 \text{ nm}$ ,  $d_0^{320k,9}=32 \text{ nm}$ ; sequential multiblock copolymers with  $32 \text{ kg}\cdot\text{mol}^{-1}$  per PS block:  $d_0^{120k,7}=22 \text{ nm}$ ,  $d_0^{160k,9}=18 \text{ nm}$ ,  $d_0^{240k,13}=21 \text{ nm}$ ).

In addition, the domain spacing increases with the overall molar mass for identical block numbers. The comparison of the domain spacing of the tapered multiblock copolymers with their sequential counterparts reveals, in general, a higher  $d_0$  for the sequential copolymers, which is very pronounced for the copolymers with the lower block numbers. For the higher block numbers domain spacings become comparable.

Figure 5 depicts the dependence of the domain spacing on the overall number-average molar mass in a double-logarithmic representation. From the scaling of the domain spacing with the overall degree of polymerization  $d_0 \sim N^\delta$ , it is possible to draw conclusions on the chain conformation. In the case of unperturbed, i.e., Gaussian chains,  $\delta=1/2$ , whereas copolymers in the strong segregation limit (SSL, i.e.,  $\chi N \gg 10$ ) with an extended chain conformation exhibit  $\delta \sim 2/3$ .

Note that solely polymers with the same morphology were correlated (tapered: PL, sequential: LAM). In the case of the tapered polymers,  $\delta > 1/2$  ( $\delta^{\text{tri}} = \delta^{\text{penta}} \approx 0.6$ ) indicating an extended chain conformation away from Gaussian coils. This is in line with earlier findings in tapered  $P(\text{I-co-S})_n$  without the PI end block ( $\delta \approx 0.62$ ).<sup>[9]</sup> For the sequential multiblock copolymers,  $\delta$  is, in general, higher than in the corresponding tapered copolymers suggesting higher chain stretching and non-Gaussian conformations. This is more evident for the lower number of block as  $\delta^{\text{tri}} \approx 0.7$ .



**Figure 5:** Domain spacing  $d_0$  in dependence of the number-average molar mass  $M_n$  obtained by SEC measurements of the tapered (left) and sequential (right) multiblock copolymers obtained by SAXS measurements at 363 K in a double-logarithmic representation (except seq. 240k triblock: 393 K, and tap. 160k nonablock: 333 K). Polymers with morphologies deviating from the common ones (tap.: PL, seq.: LAM) are excluded for the linear regression and are marked with a cross or a point (DIS).



The reduced domain spacing with increasing number of blocks in the multiblock copolymers can be discussed with respect to the formation of loops and bridges of the mid blocks. The looping statistics of sequential  $(AB)_n$  multiblock copolymers suggest two extreme conformational cases: fully extended (bridged) chains where the domain spacing scales as  $d_0 \sim n^{-0.66}$ .<sup>[37]</sup> For an average number of loops the predicted scaling is  $d_0 \sim n^{-0.86}$ . We can compare the current multiblock copolymers with respect to their looped/bridged conformations by plotting the domain spacing vs. the number of blocks in the corresponding  $(AB)_n A$  (Figure 6). The domain spacing for the sequential and the tapered multiblock copolymers were found to scale as  $d_0 \sim n^{-0.71}$  and  $d_0 \sim n^{-0.55}$  for the 160 kg·mol<sup>-1</sup> series, respectively. Somewhat lower exponents were found for the 240 kg·mol<sup>-1</sup> series. Nevertheless, results indicate a higher propensity for bridged (looped) configurations in the sequential (tapered) copolymers. Entangled loops in the tapered multiblock copolymers could enhance mechanical strength (*vide infra*).

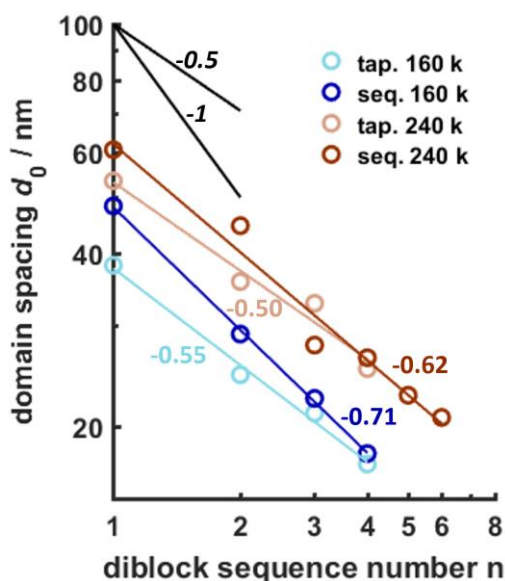


Figure 6: Domain spacing  $d_0$  of ordered specimens in dependence of the number of diblock sequences  $n$  of the  $(IS)_n I$  type tapered and sequential multiblock copolymers with 160 and 240 kg·mol<sup>-1</sup> in a log-log representation. Lines with slopes of -0.5 and -1 are shown for comparison.

## Mechanical Properties

The viscoelastic properties of block copolymers result from the phase separation into different domains of the high- $T_g$  polymer, i.e., polystyrene (PS), and the low- $T_g$  component, i.e., polyisoprene (PI). Crosslinked PI exhibits elastic properties, such as large elongation (high  $\epsilon$ ) but is very ductile (low  $\sigma$ ), whereas PS leads to a certain stiffness resulting in a high yield point (high  $\sigma$ ) but lower elongation (low  $\epsilon$ ). The combined material properties are governed by the fraction of the individual polymers and the arrangement of the blocks along the block copolymer chain, i.e., the block profile. On a molecular level the properties are controlled by (i) the morphology formed upon nanophase separation, (ii) the segregation strength, and (iii) the bridged, looped and entangled conformations of chains. To discuss the mechanical properties measured, the following general trends should be taken into consideration.

- (i) Morphologies with one continuous phase (S, CYL) of the minority polymer feature properties governed by the continuous phase. Consequently, a continuous PI phase leads



to materials which can be deformed elastically to a large extent (high  $\epsilon_{\text{yield point}}$ ). Morphologies with two continuous phases which are interconnected (G, PL) have to deform together under stress, which results in comparably high elastic moduli ( $E_{\text{modulus}}$ ) and comparably high yield stress ( $\sigma_{\text{yield point}}$ ).<sup>[38]</sup> Lamellae also exhibit two continuous phases leading to a certain strength, but they are not interconnected. Without bridging (*vide infra*), this reduces the materials' resilience. Therefore, the elastic recovery of the materials is rather poor, but large plastic deformation due to the displacement along the interfaces are possible.

- (ii) At a given degree of polymerization  $N$ , composition and block number, the segregation strength depends on the Flory-Huggins interaction parameter  $\chi$  between the constituent polymers., whose magnitude is higher for sequential block copolymers than tapered analogous structures due to the broadened interface.<sup>[3]</sup>
- (iii) In general, elasticity and mechanical strength are strongly influenced by chain entanglements until chain pull-out. Entanglement molecular weights of *cis*-1,4-PI ( $5.4 \text{ kg}\cdot\text{mol}^{-1}$ ) and polystyrene ( $13.3 \text{ kg}\cdot\text{mol}^{-1}$ ) are exceeded for all polymers studied (see theoretical values in Table S1,  $M(\text{PI})_{\text{min}}/\text{block} \approx 4 \cdot M_e(\text{PI})$ ;  $M(\text{PS})_{\text{min}}/\text{block} \approx M_e(\text{PS})$ ), however increasing the block number shortens the individual block length.<sup>[39]</sup> Previous works predicted that loops are more favored at higher block numbers.<sup>[37]</sup> As a consequence of an increasing bridging fraction, the microstructural periodicities are also affected by the block number since the stretched bridging block limits the dimension of the PI domain.

Figure 7 shows representative stress-strain curves obtained by uniaxial stretching.

A key objective of this work was the difference between sequential and tapered block copolymers with respect to mechanical properties. The first, most striking difference between the stress-strain curves is that all sequential multiblock copolymers experience stronger strain hardening than their tapered counterparts. This is evidenced by the higher increase in force that is required to achieve the same plastic deformation (see Figure 7,  $\Delta\sigma_{\text{tap}} < \Delta\sigma_{\text{seq}}$ ). The effect is most pronounced for lower molar masses ( $120 \text{ \& } 160 \text{ kg}\cdot\text{mol}^{-1}$ ) or high block numbers ( $240 \text{ kg}\cdot\text{mol}^{-1}$  with  $2n+1=11 \text{ \& } 13$  blocks). This originates directly from the weakened segregation strength in tapered multiblock copolymers, reflecting a more diffuse phase boundary and is most pronounced for the polymers near the order-disorder transition (see Figure 7, note that the denoted phase state corresponds to the data determined by SAXS at 363 K, whereas the tensile tests were performed at ambient temperatures).

Secondly, tapered and sequential block copolymers also differ in their flexibility upon elastic deformation, represented by the Young's moduli (Figure 8). The elastic moduli of the sequential block copolymers are higher, and hence the material is stiffer than the values of tapered block copolymers ( $E_{\text{modulus,tap}} < E_{\text{modulus,seq}}$  resulting from  $\epsilon_{\text{yield point,tap}} > \epsilon_{\text{yield point,seq}}$  but  $\sigma_{\text{yield point,tap}} < \sigma_{\text{yield point,seq}}$ , see Figure S45). The formed nanodomain morphology does not explain the large differences, since both tapered and sequential structures commonly feature a morphology with two continuous phases (PL and LAM). On the contrary, this general observation results from the increased interfacial width especially for the higher number of blocks. The tapered structures exhibit a shortened effective PS block length and an extended effective PI block due to the incorporation of styrene repeating units within the polyisoprene block.

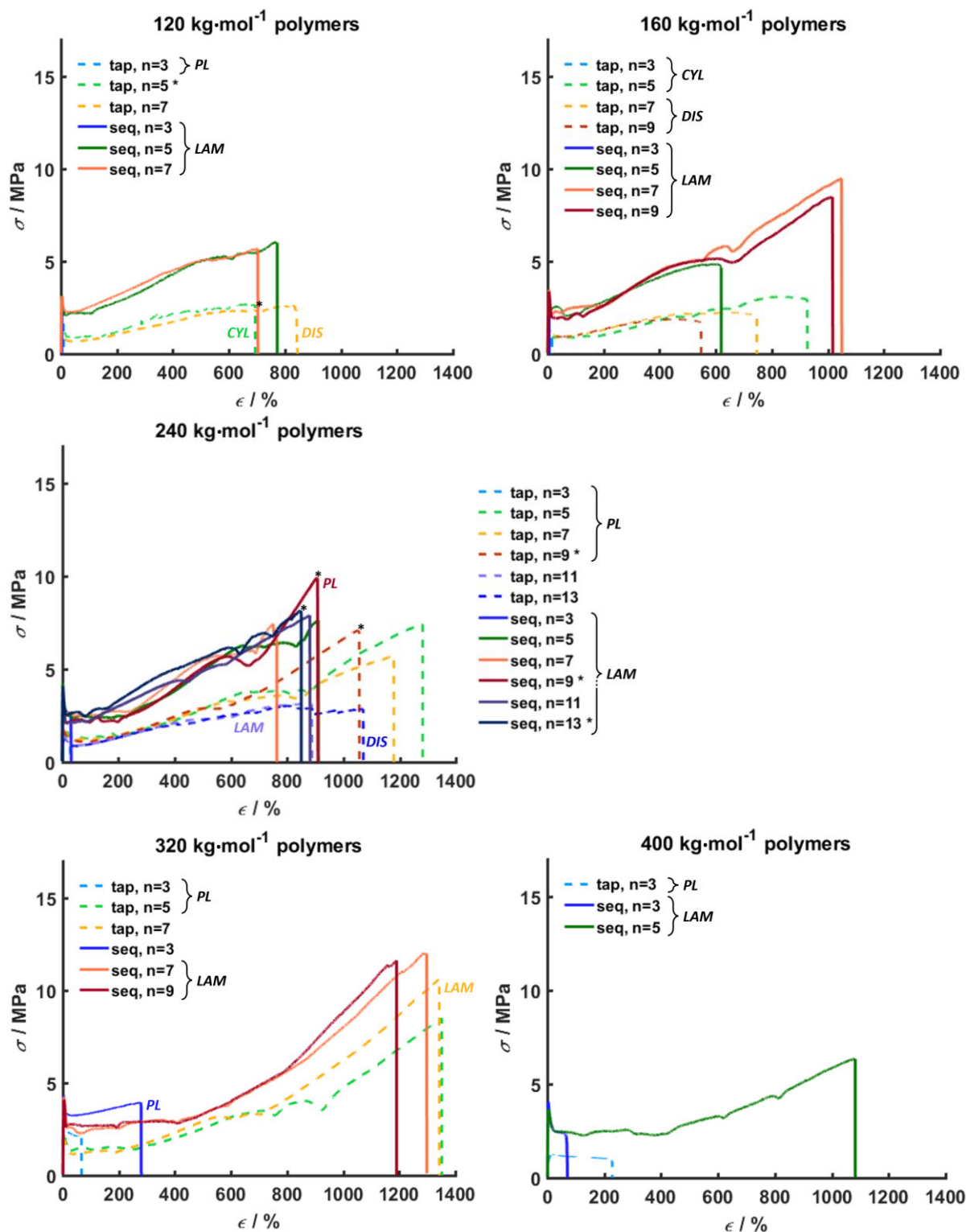
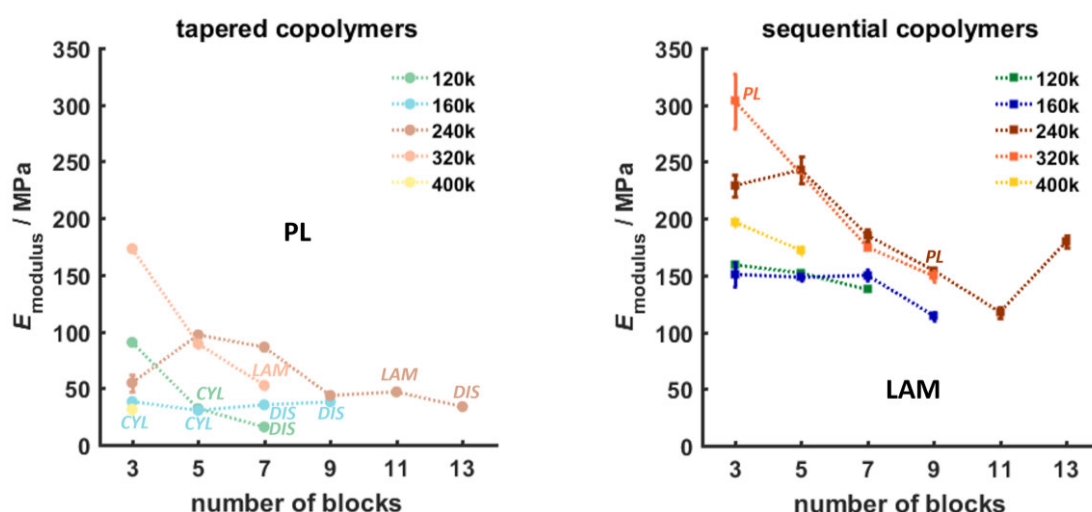


Figure 7: Representative stress-strain ( $\sigma$ - $\epsilon$ ) curves for all polymers investigated, sorted by molar mass (top left: 120, top right: 160, middle: 240, bottom left: 320, bottom right: 400  $\text{kg}\cdot\text{mol}^{-1}$ ). Sequential: solid lines; tapered: dashed lines; curves marked with an asterisk: specimens did not break but slid out of a clamp.

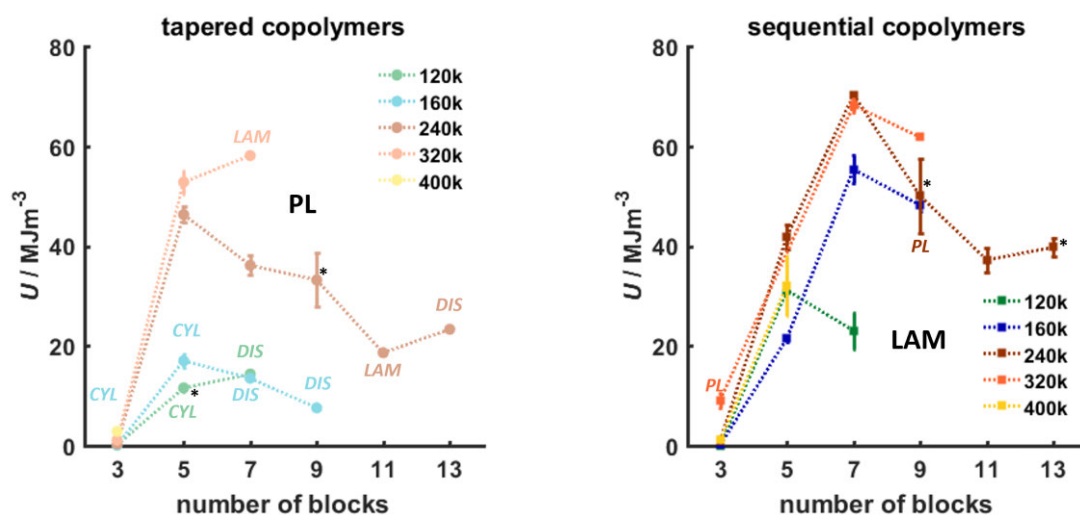
Another key question of the current work is the effect of two flexible end blocks. In comparison to tapered  $(\text{IS})_n$  multiblock copolymers with an odd block number and hence only one polyisoprene end block, the herein presented tapered structures possess drastically decreased elastic moduli (for the 240 & 400  $\text{kg}\cdot\text{mol}^{-1}$  multiblock copolymers  $(\text{IS})_n$  with  $n=1-5$ ,  $E_{\text{modulus}}=300-$

400 MPa).<sup>[9]</sup> This reflects the influence of the molar fraction of isoprene (50 vs. 70 mol% for (IS)<sub>n</sub> and (IS)<sub>n</sub>I, respectively) and maybe also of the two flexible chain ends.



**Figure 8:** Elastic moduli of the tapered (left) and sequential (right) block copolymers in dependence of their block number.

Comparing the ultimate properties of the polymer series with respect to their molar mass (see Supp. Inf., Figure S45 & S46) and number of blocks (see Supp. Inf., Figure S47 & S48), a generally valid difference of triblock copolymers with respect to the other multiblock copolymers is visible. Triblock copolymers break shortly after the yield point, showing a brittle behavior, clearly due to the lack of domain bridging. In contrast, the multiblock copolymers with more than one vitrifying polystyrene block show much higher strain at break.



**Figure 9:** Toughness of the tapered (left) and sequential (right) block copolymers in dependence of their block number. The asterisks mark specimens which slid out of the clamps before rupture.

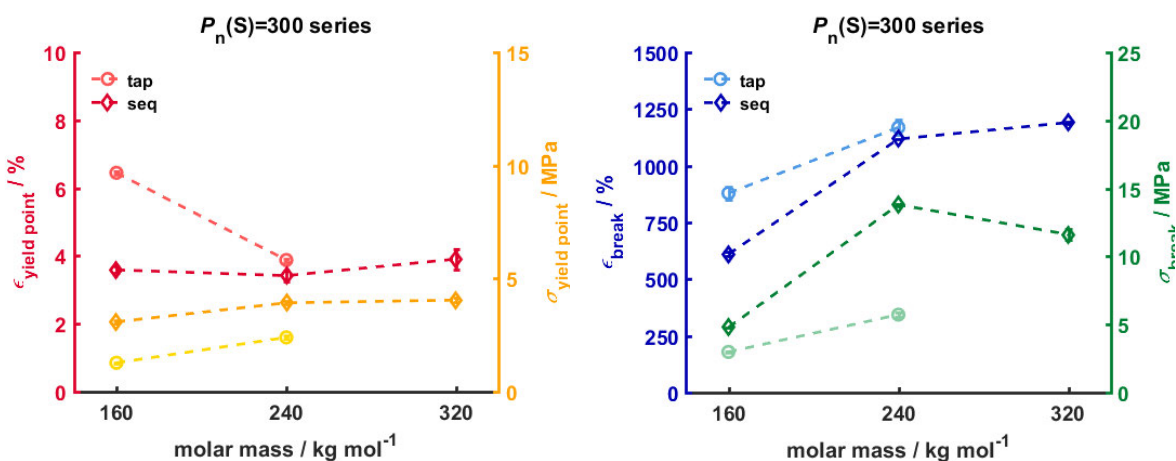
The triblock copolymers of lower molar mass do not even feature a pronounced yield point and hence a separated elastic and viscous region. This indicates that with a molar mass of polyisoprene per block lower than 10 times the entanglement molecular weight (i.e., for the 120 & 160 kg·mol<sup>-1</sup> triblock copolymers), chain entanglements of the two polyisoprene end blocks are not sufficient to provide at least low resilience. Therefore, the materials flow even at low strains. Comparing the ultimate properties ( $\epsilon_{\text{break}}$  &  $\sigma_{\text{break}}$ ) of the sequential triblock copolymers of 320 and 400 kg·mol<sup>-1</sup> (see Figure 7, bottom left and right graph, blue traces),

higher values and hence a higher toughness  $U$  (Figure 9) of the lower molar mass triblock with a perforated layer morphology demonstrate the influence of the nanodomain morphology. Without domain bridging, the interconnectivity present in perforated layers results in a higher resilience compared to a lamellar structure.

While the elastic modulus is a measure of the material's stiffness, toughness describes the ability of the material to absorb deformation energy. Therefore, materials with a combination of strength and ductility exhibit high toughness. Since the toughness equals the area under a tensile curve, this correlates with both the maximum strain and strength. Generally, the maximum elongation at break  $\epsilon_{\text{break}}$  increases with the overall molar mass, while the maximum strain at break  $\sigma_{\text{break}}$  depends only weakly on the molar mass (see Supp. Inf., Figure S46).

Comparing the polymers with respect to their block profile, it is remarkable that the sequential multiblock copolymers exhibit the highest toughness at a block number of 7, whereas tapered structures with 5 blocks are commonly the toughest (Figure 9). As discussed at the beginning of this section, this results from the balance between segregation strength, which decreases with the block number, and the block connectivity, with the bridge/loop ratio (see Figure 6) being higher for sequential copolymers. For this certain composition, the molecular weight of polyisoprene per block approaches the tenfold of the entanglement molecular weight. Therefore, it can be supposed that at that point the chain entanglements of the two polyisoprene end blocks further enhance the material properties.

The observation for the tapered structures indicates that the weaker segregation strength together with reduced entanglements have a stronger impact on the deformability (higher elongation at break  $\epsilon_{\text{break}}$ ) and at the same time toughness ( $U$ ). Weak segregation results in the collapse of the physical crosslinks. For the sequential multiblock copolymers, the stronger segregation compensates the reduced PI entanglements with increasing block number, thus resulting in a higher resilience and maximum toughness ( $U$ ) for the heptablock copolymers.



**Figure 10:** Characteristics of the yield point (left:  $\epsilon_{\text{yield point}}$  – dark red: sequential, red: tapered, and  $\sigma_{\text{yield point}}$  – orange: sequential, yellow: tapered) and the break point (right:  $\epsilon_{\text{break}}$  – dark blue: sequential, blue: tapered, and  $\sigma_{\text{break}}$  – dark green: sequential, pale green: tapered) of the polymers with a degree of polymerization of 300 polystyrene units per PS block in dependence of their overall molar mass (160 kg·mol<sup>-1</sup> pentablock, 240 kg·mol<sup>-1</sup> heptablock, 320 kg·mol<sup>-1</sup> nonablock).

Beyond this, the elongation at break is improved with increasing the molar mass at a given block number, which is explained by the higher individual block length and hence more entanglements (see Supp. Inf., Figure S48). However, after an initial increase of the overall

material properties with the molar mass at a given block number, they approach each other or are even worsened, most probably resulting from an impeded ordering of the long polymer chains.

Finally, polymers with increasing block number and molar mass, but equal block length of the individual polystyrene blocks are compared. While the materials can generally be stretched to a larger extent ( $\epsilon_{\text{break}}$ ) with increasing block number, resulting from increased bridging, the softness ( $\epsilon_{\text{yield point}}$  &  $\sigma_{\text{yield point}}$ ) of the material is almost unaltered (see Figure 10), which originates from the comparable domain spacings (*vide supra*).

Comparison to similar literature-known structures are drawn in order to place these findings into context. Wahlen *et al.* investigated a tapered SIS triblock copolymer (120 kg·mol<sup>-1</sup>, 68 vol% PI, CYL with  $d_0=36.7$  nm) with a similar composition to the tapered 120 kg·mol<sup>-1</sup> ISISI pentablock (CYL with  $d_0=20.9$  nm), both featuring one PI mid block.<sup>[40]</sup> The smaller domain spacing in case of the pentablock copolymer results from the prescribed localization of both polystyrene block ends at the domain interface. Slightly more energy is required to deform the tapered SIS triblock than the tapered ISISI pentablock ( $\sigma_{\text{SIS},600\%}=3.8$  MPa vs.  $\sigma_{\text{ISISI},600\%}=2.5$  MPa), which can tentatively be explained by the higher amount of entanglements in the case of the triblock because of a longer individual PI block.

Furthermore, Winey and coworkers investigated sequential SIS and ISI triblock copolymers ( $\approx 100$  kg·mol<sup>-1</sup>, 38–39 wt% PS), which featured different morphologies in dependence of the solvent they were cast from (SIS(cyclohexane): CYL, SIS(toluene): LAM, ISI(cyclohexane): CYL, ISI(toluene): gyroid).<sup>[19]</sup> Comparison to the sequential ISI triblock and ISISI pentablock copolymers of 120 kg·mol<sup>-1</sup> presented in this work (LAM) evidences considerably higher Young's moduli for the copolymers with a lamellar morphology ( $E_{\text{modulus,SIS,CYL}}=69$  MPa,  $E_{\text{modulus,ISI,CYL}}=34$  MPa &  $E_{\text{modulus,ISI,GYR}}=97$  MPa vs.  $E_{\text{modulus,SIS,LAM}}=138$  MPa,  $E_{\text{modulus,ISI,LAM}}=159$  MPa &  $E_{\text{modulus,ISISI,LAM}}=152$  MPa). Conclusively, the material's stiffness is only weakly affected by the block sequence, but strongly depends on the nanodomain morphology.

## Conclusion

In this work, the mechanical properties of (IS)<sub>n</sub>I type multiblock copolymers covering a broad range of molar masses (120–400 kg·mol<sup>-1</sup>) and block numbers (3–13) with both defined (sequential) and gradient (tapered) block profile have been investigated with respect to segregation into ordered morphologies and resulting mechanical properties. The volume fractions of the constituent polymers were held constant at 64 vol% polyisoprene and 36 vol% polystyrene.

Small angle x-ray scattering (SAXS) experiments revealed strong segregation of the sequential multiblock copolymers into mainly lamellar morphologies, whereas the tapered analogues exhibited weak ordering, commonly in perforated layers. As a result, the tapered copolymers of low molar masses and high block numbers featured accessible order-disorder transition temperatures required for several applications. The domain spacing was found to scale as  $d_0 \sim N^\delta$ . In the sequential multiblock copolymers,  $\delta$  was, in general, higher than in the corresponding tapered copolymers suggesting higher chain stretching and non-Gaussian conformations. This was more evident for the lower number of blocks, where  $\delta^{\text{tri}} \approx 0.7$ . In

addition, the domain spacing of the  $160 \text{ kg}\cdot\text{mol}^{-1}$  multiblock copolymers was found to scale with the number of diblock sequences  $n$  in  $(\text{IS})_n\text{I}$  as  $d_0 \sim n^{-0.71}$  and  $d_0 \sim n^{-0.55}$  for the sequential and tapered multiblock copolymers, respectively. Results suggest a higher propensity for bridged (looped) configurations in the sequential (tapered) copolymers with significance to the mechanical properties.

The viscoelastic responses of the multiblock copolymers are related to composition, segregation strength, the final morphology and the bridged/looped chain conformations of the mid blocks. All triblock copolymers are rather brittle, while the multiblock copolymers with at least two PS blocks forming bridges connecting the different vitrified polystyrene domains, can endure much higher strains. Here, the tapered structures show a weaker strain hardening and a lower elastic modulus due to the lower segregation strength and the broader interface between the polyisoprene and the polystyrene blocks. Polymers close to the order-disorder transition even flow at low strains, meaning that they do not feature separated elastic and viscous regions.

Besides, the toughness is a function of the multiblock structure. In terms of toughness and stiffness, sequential heptablock copolymers of either  $240$  or  $320 \text{ kg}\cdot\text{mol}^{-1}$  best combine bridged chain configurations and segregation strength, which result in superior mechanical properties ( $U=70$  &  $68 \text{ MJ}\cdot\text{m}^{-3}$ , respectively). However, to obtain a material of comparable toughness ( $U=58 \text{ MJ}\cdot\text{m}^{-3}$ ), which is softer and more flexible, the heptablock of  $320 \text{ kg}\cdot\text{mol}^{-1}$  with a tapered interface between the PS and PI diblock sequences is most suitable ( $E_{\text{modulus,tap}}=53 \text{ MPa}$  vs.  $E_{\text{modulus,seq}}=175 \text{ MPa}$ ). In the latter, entangled loops are likely responsible for the improved toughness.

With the potential application as a plasticized PVC substitute for medical bags in mind, the tapered penta- and heptablock of  $320 \text{ kg}\cdot\text{mol}^{-1}$  as well as the tapered pentablock copolymer of  $240 \text{ kg}\cdot\text{mol}^{-1}$  perfectly fulfill the mechanical prerequisites in terms of flexibility ( $E_{\text{modulus}} < 100 \text{ MPa}$ , with the heptablock being softer) and at the same time rigidity as well as resilience, which is necessary to withstand centrifugation forces ( $U > 40 \text{ MJ}\cdot\text{m}^{-3}$ ).<sup>[20]</sup> Furthermore, the implementation of tapered structures is favorable due to the better processability originating from lower order-disorder transition temperatures. With respect to an accessible  $T_{\text{ODT}}$ , the  $240 \text{ kg}\cdot\text{mol}^{-1}$  tapered pentablock appears to be most suitable. Another advantage of the accessible  $T_{\text{ODT}}$  of the  $(\text{IS})_n\text{I}$  multiblock copolymers relates to their recyclability. Multiple “crosslinking” achieved here not by chemical coupling, but by mere physical crosslinks, enhances their reprocessability from the melt state.

## References

- [1] a) R. J. Spontak, S. D. Smith, A. Ashraf, *Macromolecules* **1993**, 26, 5118; b) S. Jangareddy, T. Sun, A. B. Burns, R. A. Register, *Macromolecules* **2021**, 54, 3999.
- [2] J. Yan, R. J. Spontak in *Elastomer Blends and Composites*, Elsevier, **2022**, pp. 353–404.
- [3] M. Steube, T. Johann, R. D. Barent, A. H. Müller, H. Frey, *Prog. Polym. Sci.* **2022**, 124, 101488.
- [4] G. Holden, R. Milkovich, *Block polymers of monovinyl aromatic hydrocarbons and conjugated dienes*, US3265765, **1966**.

- [5] C. F. Fryling, *High impact polystyrene*, US3144420A, **1964**.
- [6] H. Keskkula, *J. Polym. Sci. C Polym. Lett.* **1989**, 27, 243.
- [7] P. Georgopoulos, U. A. Handge, C. Abetz, V. Abetz, *Polymer* **2016**, 104, 279.
- [8] a) N. Singh, M. S. Tureau, T. H. Epps, *Soft Matter* **2009**, 5, 4757; b) P. Hodrokoukes, G. Floudas, S. Pispas, N. Hadjichristidis, *Macromolecules* **2001**, 34, 650; c) M. Thunga, U. Staudinger, B. K. Satapathy, R. Weidisch, M. Abdel-Goad, A. Janke, K. Knoll, *J. Polym. Sci., Part B: Polym. Phys.* **2006**, 44, 2776; d) M. Steube, T. Johann, H. Hübner, M. Koch, T. Dinh, M. Gallei, G. Floudas, H. Frey, A. H. E. Müller, *Macromolecules* **2020**, 53, 5512; e) S. Foerster, A. K. Khandpur, J. Zhao, F. S. Bates, I. W. Hamley, A. J. Ryan, W. Bras, *Macromolecules* **1994**, 27, 6922; f) T. an Huy, H. Le Hai, R. Adhikari, R. Weidisch, G. H. Michler, K. Knoll, *Polymer* **2003**, 44, 1237.
- [9] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, 51, 10246.
- [10] a) K. Karatasos, S. H. Anastasiadis, T. Pakula, H. Watanabe, *Macromolecules* **2000**, 33, 523; b) K. Rasmussen, E. M. Kober, T. Lookman, A. Saxena, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, 41, 104; c) H. Watanabe, Y. Matsumiya, T. Sawada, T. Iwamoto, *Macromolecules* **2007**, 40, 6885; d) S. S. Tallury, R. J. Spontak, M. A. Pasquinielli, *J. Chem. Phys.* **2014**, 141, 244911.
- [11] T. Zhang, N. Wang, R. A. Riggelman, *Macromolecules* **2022**, 55, 10880.
- [12] a) T. Meins, N. Dingenouts, J. Kübel, M. Wilhelm, *Macromolecules* **2012**, 45, 7206; b) L. Schneider, M. Heck, M. Wilhelm, M. Müller, *Macromolecules* **2018**, 51, 4642.
- [13] M. O. Tuhin, J. J. Ryan, J. D. Sadler, Z. Han, B. Lee, S. D. Smith, M. A. Pasquinielli, R. J. Spontak, *Macromolecules* **2018**, 51, 5173.
- [14] R. J. Spontak, S. D. Smith, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 947.
- [15] L. Wu, E. W. Cochran, T. P. Lodge, F. S. Bates, *Macromolecules* **2004**, 37, 3360.
- [16] S. D. Smith, R. J. Spontak, M. M. Satkowski, A. R. Ashraf, A. K. Heape, J. S. Lin, *Polymer* **1994**, 35, 4527.
- [17] J. L. Adams, W. W. Graessley, R. A. Register, *Macromolecules* **1994**, 27, 6026.
- [18] V. Hirschberg, L. Faust, D. Rodrigue, M. Wilhelm, *Macromolecules* **2020**, 53, 5572.
- [19] L. Qiao, C. Leibig, S. F. Hahn, K. I. Winey, *Ind. Eng. Chem. Res.* **2006**, 45, 5598.
- [20] K. Sojiphan, A. Iverson, S. Kim, *Materials Selection Analysis: Bag for Viable Blood Storage*, Department of Materials Science and Engineering, Northwestern University, **2004**.
- [21] M. Verswyvel, K. Knoll, N. Nießner, *Styrenic Thermoplastic Elastomers for Healthcare Applications*, Durham, **2017**.
- [22] M. Verswyvel, N. Nießner, E. Jahnke, D. Wagner, K. Knoll, *Very soft, non-sticky and transparent styrenic thermoplastic elastomer composition*, WO2018/166958 A1, **2018**.
- [23] K. Knoll, N. Nießner, *Macromol. Symp.* **1998**, 132, 231.
- [24] a) J. M. Brown, N. E. Stacy, C. E. Stouffer, J. D. Wilkey, M. A. Smith, *Styrene butadiene block copolymers for film applications*, US9550869B2, **2017**; b) J. J. Zhou, W. H. Pace, D. A. Young, *Styrene-butadiene block copolymers for tubing applications*, US20160264773A1, **2016**; c) J. J.

- Zhou, *Methods for controlling hardness of styrene-butadiene block copolymers*, US9441090B1, **2016**.
- [25] Ineos Styrolution Group, "Resins for the Healthcare Industry", can be found under [https://www.ineos-styrolution.com/INTERSHOP/static/WFS/Styrolution-Portal-Site/-/Styrolution-Portal/en\\_US/News%20and%20media/download/INEOS\\_Styrolution\\_Healthcare\\_Brochure.pdf](https://www.ineos-styrolution.com/INTERSHOP/static/WFS/Styrolution-Portal-Site/-/Styrolution-Portal/en_US/News%20and%20media/download/INEOS_Styrolution_Healthcare_Brochure.pdf).
- [26] M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey, A. H. E. Müller, *Macromolecules* **2019**, *52*, 9299.
- [27] K. Ntetsikas, V. Ladelta, S. Bhaumik, N. Hadjichristidis, *ACS Polym. Au* **2022**.
- [28] M. Saito, K. Ito, H. Yokoyama, *Macromolecules* **2021**, *54*, 8538.
- [29] D. J. Worsfold, *J. Polym. Sci., Part A-1: Polym. Chem.* **1967**, *5*, 2783.
- [30] W. Wang, W. Lu, A. Goodwin, H. Wang, P. Yin, N.-G. Kang, K. Hong, J. W. Mays, *Prog. Polym. Sci.* **2019**, *95*, 1.
- [31] P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY, **1979**.
- [32] A. K. Khandpur, S. Foerster, F. S. Bates, I. W. Hamley, A. J. Ryan, W. Bras, K. Almdal, K. Mortensen, *Macromolecules* **1995**, *28*, 8796.
- [33] M. W. Matsen, R. B. Thompson, *J. Chem. Phys.* **1999**, *111*, 7139.
- [34] R.-J. Roe, W.-C. Zin, *Macromolecules* **1980**, *13*, 1221.
- [35] B. Abu-Sharkh, A. AlSunaidi, *Macromol. Theory Simul.* **2006**, *15*, 507.
- [36] E. Galanos, M. Steube, H.-J. Butt, H. Frey, G. Floudas, *J. Chem. Phys.* **2022**, *156*, 134904.
- [37] R. J. Spontak, J. M. Zielinski, G. G. Lipscomb, *Macromolecules* **1992**, *25*, 6270.
- [38] B. J. Dair, C. C. Honeker, D. B. Alward, A. Avgeropoulos, N. Hadjichristidis, L. J. Fetters, M. Capel, E. L. Thomas, *Macromolecules* **1999**, *32*, 8145.
- [39] L. J. Fetters, D. J. Lohse, D. Richter, T. A. Witten, A. Zirkel, *Macromolecules* **1994**, *27*, 4639.
- [40] C. Wahlen, J. Blankenburg, P. von Tiedemann, J. Ewald, P. Sajkiewicz, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2020**, *53*, 10397.



# Supporting Information

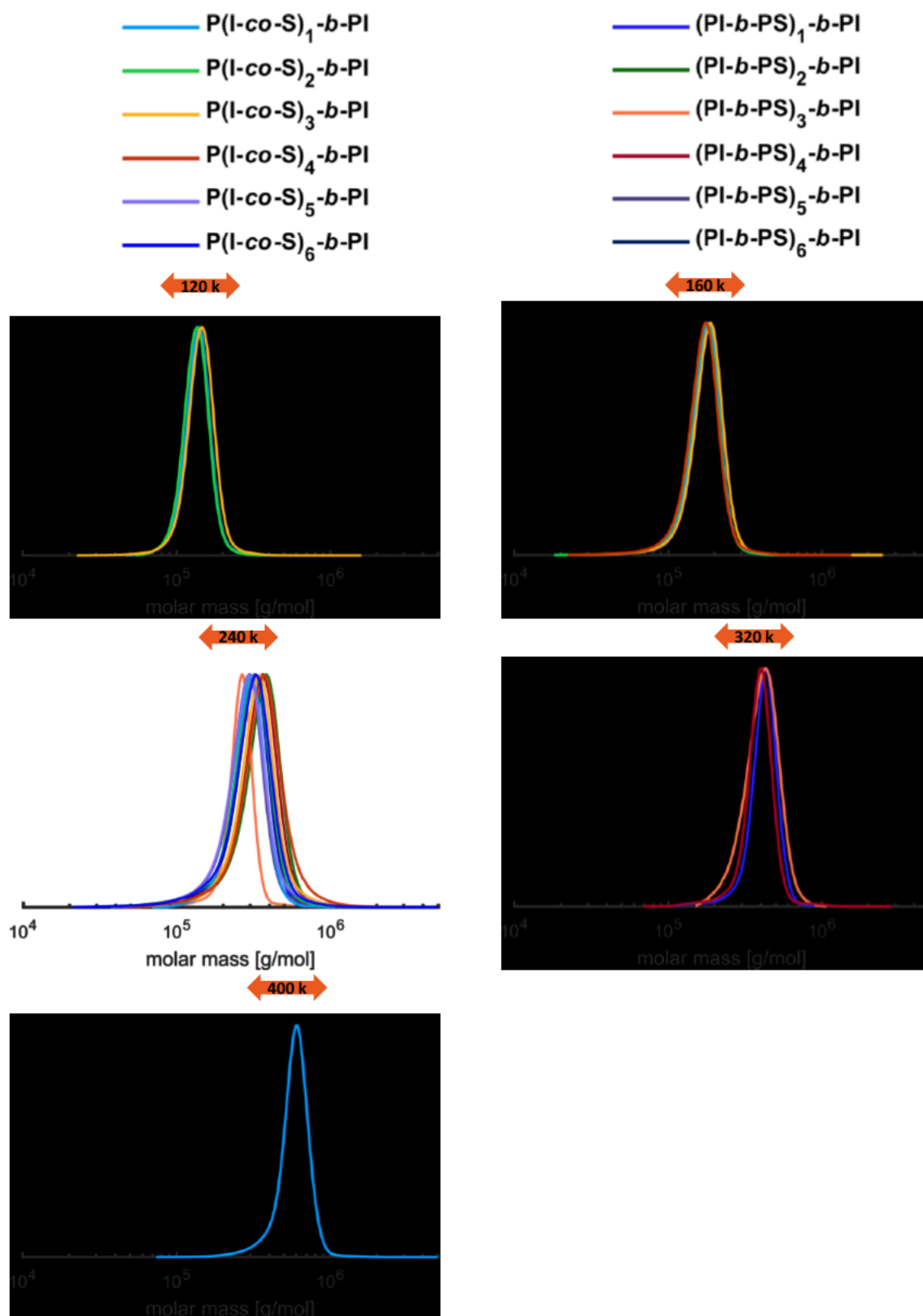


Figure S1: SEC traces (THF, PS calibration standard, RI detector) of the series with different molar masses (top left: 120, top right: 160, middle left: 240, middle right: 300, bottom left: 400 kg·mol<sup>-1</sup>). Derived number average molar masses and dispersities are comprised in Table S1.

**Table S1: Overview of the characteristics of the statistically copolymerized multiblock copolymers P(I-co-S)<sub>n</sub>-b-PI with a tapered interface (tap) and the sequentially polymerized multiblock copolymers (PI-b-PS)<sub>n</sub>-b-PI (seq). The corresponding SEC traces are given in the SI (see Figure S1).**

| (IS) <sub>n</sub><br>block type | block number<br>#=2n+1 | target $M_n$<br>[kg·mol <sup>-1</sup> ] | $M(PI)/\#$<br>[kg·mol <sup>-1</sup> ] | $M(PS)/\#$<br>[kg·mol <sup>-1</sup> ] | $M_n^a$<br>[kg·mol <sup>-1</sup> ] | $\mathcal{D}^a$ | $P_n(I)^b$<br>[%] | $\omega_{1,4}(I)^b$<br>[%] |
|---------------------------------|------------------------|-----------------------------------------|---------------------------------------|---------------------------------------|------------------------------------|-----------------|-------------------|----------------------------|
| tap                             | 3                      | 120                                     | 36                                    | 47                                    | 133.5                              | 1.04            | 68.7              | 94                         |
|                                 | 5                      | 120                                     | 24                                    | 24                                    | 130.8                              | 1.04            | 69.7              | 94                         |
|                                 | 7                      | 120                                     | 18                                    | 16                                    | 131.1                              | 1.06            | 70.4              | 94                         |
| seq                             | 3                      | 120                                     | 36                                    | 47                                    | 120.9                              | 1.07            | 69.0              | 94                         |
|                                 | 5                      | 120                                     | 24                                    | 24                                    | 132.4                              | 1.09            | 69.4              | 94                         |
|                                 | 7                      | 120                                     | 18                                    | 16                                    | 136.3                              | 1.08            | 69.8              | 94                         |
| tap                             | 3                      | 160                                     | 48                                    | 63                                    | 163.2                              | 1.07            | 69.9              | 94                         |
|                                 | 5                      | 160                                     | 32                                    | 32                                    | 158.9                              | 1.08            | 70.9              | 94                         |
|                                 | 7                      | 160                                     | 24                                    | 21                                    | 170.2                              | 1.08            | 70.0              | 95                         |
|                                 | 9                      | 160                                     | 19                                    | 16                                    | 158.6                              | 1.09            | 68.9              | 94                         |
| seq                             | 3                      | 160                                     | 48                                    | 63                                    | 155.9                              | 1.07            | 69.1              | 93                         |
|                                 | 5                      | 160                                     | 32                                    | 32                                    | 151.0                              | 1.09            | 70.2              | 93                         |
|                                 | 7                      | 160                                     | 24                                    | 21                                    | 168.6                              | 1.09            | 70.0              | 93                         |
|                                 | 9                      | 160                                     | 19                                    | 16                                    | 151.1                              | 1.10            | 71.6              | 94                         |
| tap                             | 3                      | 240                                     | 72                                    | 95                                    | 277.5                              | 1.08            | 69.2              | 94                         |
|                                 | 5                      | 240                                     | 48                                    | 47                                    | 273.9                              | 1.14            | 68.7              | 94                         |
|                                 | 7                      | 240                                     | 36                                    | 32                                    | 303.5                              | 1.14            | 68.9              | 94                         |
|                                 | 9                      | 240                                     | 29                                    | 24                                    | 324.9                              | 1.17            | 69.4              | 94                         |
|                                 | 11                     | 240                                     | 24                                    | 19                                    | 257.9                              | 1.15            | 69.4              | 94                         |
|                                 | 13                     | 240                                     | 21                                    | 16                                    | 272.8                              | 1.17            | 69.6              | 94                         |
| seq                             | 3                      | 240                                     | 72                                    | 95                                    | 268.7                              | 1.14            | 69.3              | 94                         |
|                                 | 5                      | 240                                     | 48                                    | 47                                    | 306.1                              | 1.18            | 69.6              | 93                         |
|                                 | 7                      | 240                                     | 36                                    | 32                                    | 246.9                              | 1.06            | 68.9              | 93                         |
|                                 | 9                      | 240                                     | 29                                    | 24                                    | 304.5                              | 1.15            | 70.0              | 93                         |
|                                 | 11                     | 240                                     | 24                                    | 19                                    | 254.8                              | 1.13            | 68.7              | 93                         |
|                                 | 13                     | 240                                     | 21                                    | 16                                    | 275.1                              | 1.14            | 69.2              | 93                         |
| tap                             | 3                      | 320                                     | 97                                    | 127                                   | 376.1                              | 1.05            | 69.8              | 94                         |
|                                 | 5                      | 320                                     | 64                                    | 63                                    | 361.7                              | 1.12            | 68.6              | 95                         |
|                                 | 7                      | 320                                     | 48                                    | 42                                    | 369.9                              | 1.09            | 69.2              | 94                         |
| seq                             | 3                      | 320                                     | 97                                    | 127                                   | 400.5                              | 1.06            | 69.9              | 93                         |
|                                 | 7                      | 320                                     | 48                                    | 42                                    | 387.8                              | 1.08            | 69.1              | 94                         |
|                                 | 9                      | 320                                     | 39                                    | 32                                    | 373.6                              | 1.07            | 68.4              | 93                         |
| tap                             | 3                      | 400                                     | 121                                   | 158                                   | 556.0                              | 1.07            | 70.3              | 94                         |
| seq                             | 3                      | 400                                     | 121                                   | 158                                   | 558.6                              | 1.08            | 70.0              | 94                         |
|                                 | 5                      | 400                                     | 81                                    | 79                                    | 476.9                              | 1.07            | 69.6              | 94                         |

<sup>a</sup> Determined by SEC (THF, PS calibration standard, RI detector). The number average molar masses are overestimated because of the incorporation of 70 mol% isoprene. <sup>b</sup> determined by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) integrating on the 1,4-polyisoprene ( $\delta$ =4.8-5.4 ppm), 3,4-polyisoprene ( $\delta$ =4.5-4.8 ppm), and polystyrene signals ( $\delta$ =6.2-7.4 ppm).

## Small-Angle X-Ray Scattering

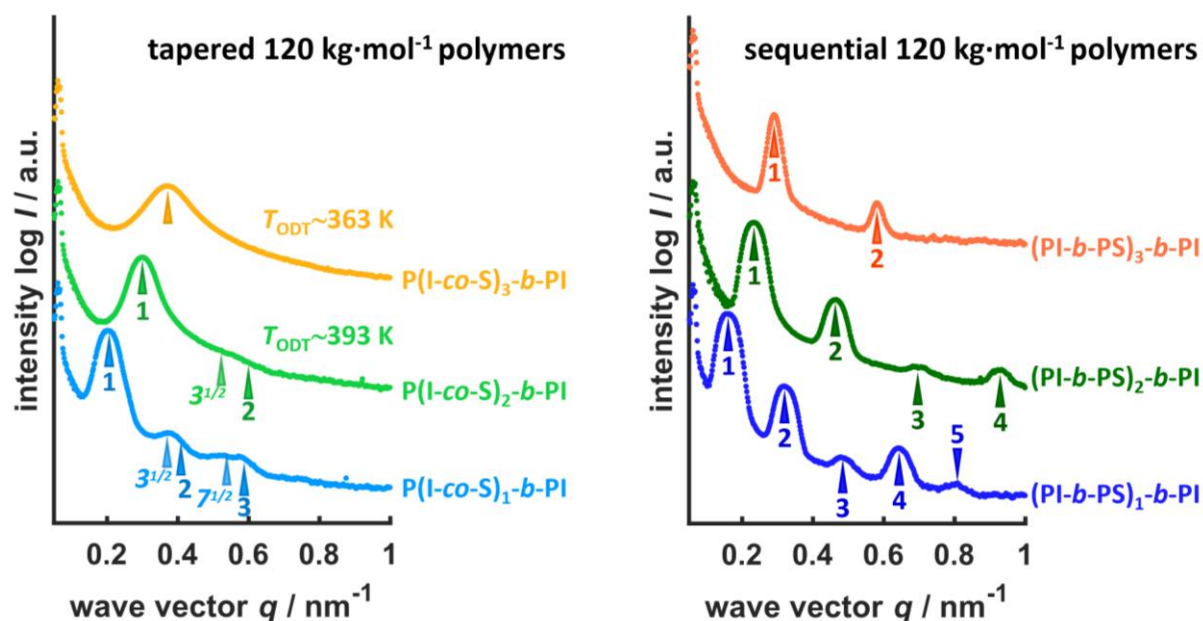


Figure S2: SAXS patterns of the tapered (left) and sequential (right) multiblock copolymers with a molar mass of 120 kg·mol<sup>-1</sup> at 90 °C. The color code denotes the different block numbers (blue: triblock, green: pentablock, orange: heptablock), with the lighter colors corresponding to the tapered structures. The arrows give the positions of the Bragg reflections corresponding to a lamellar (darker color), or a cylindrical (lighter color, italic letters) morphology. The curves are shifted vertically for clarity.

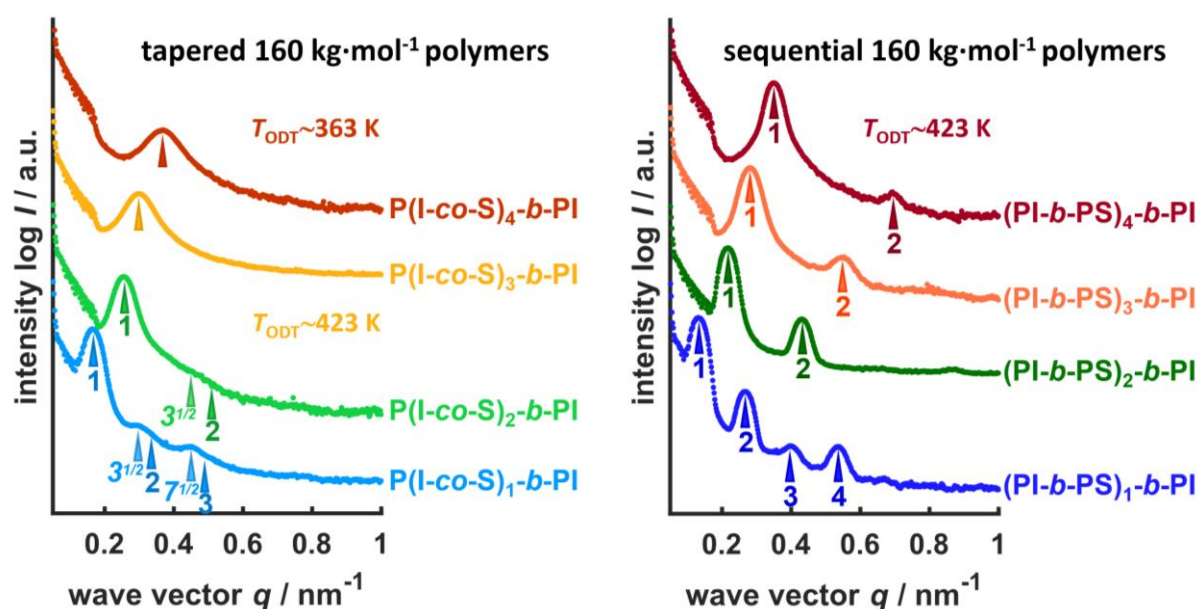


Figure S3: SAXS patterns of the tapered (left) and sequential (right) multiblock copolymers with a molar mass of 160 kg·mol<sup>-1</sup> at 90 °C (except tap. 160 kg·mol<sup>-1</sup> nonablock,  $T=60$  °C). The color code denotes the different block numbers (blue: triblock, green: pentablock, orange: heptablock, red: nonablock), with the lighter colors corresponding to the tapered structures. The arrows give the positions of the Bragg reflections corresponding to a lamellar (darker color), or a cylindrical (lighter color, italic letters) morphology. The curves are shifted vertically for clarity.

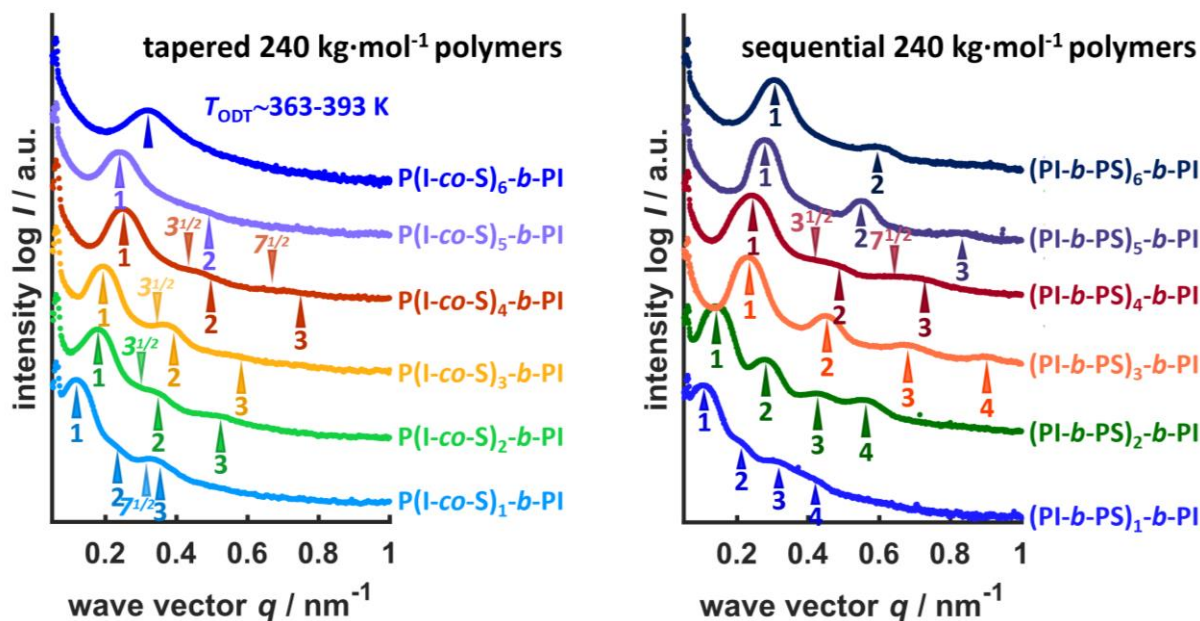


Figure S4: SAXS patterns of the tapered (left) and sequential (right) multiblock copolymers with a molar mass of 240 kg·mol<sup>-1</sup> at 90 °C (except seq. 240 kg·mol<sup>-1</sup> triblock,  $T=120$  °C). The color code denotes the different block numbers (blue: triblock, green: pentablock, orange: heptablock, red: nonablock, violet: undecablock, dark blue: tredecablock), with the lighter colors corresponding to the tapered structures. The arrows give the positions of the Bragg reflections corresponding to a lamellar (darker color), or a cylindrical (lighter color, italic letters) morphology. The curves are shifted vertically for clarity.

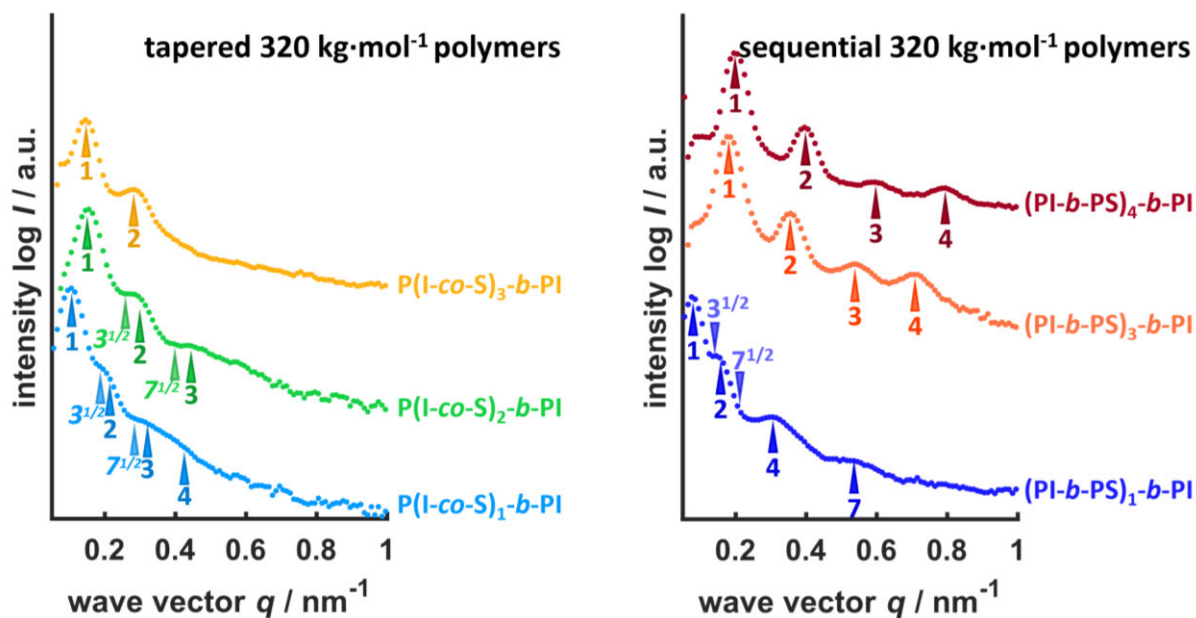


Figure S5: SAXS patterns of the tapered (left) and sequential (right) multiblock copolymers with a molar mass of 320 kg·mol<sup>-1</sup> at 90 °C. The color code denotes the different block numbers (blue: triblock, green: pentablock, orange: heptablock, red: nonablock), with the lighter colors corresponding to the tapered structures. The arrows give the positions of the Bragg reflections corresponding to a lamellar (darker color), or a cylindrical (lighter color, italic letters) morphology. The curves are shifted vertically for clarity.

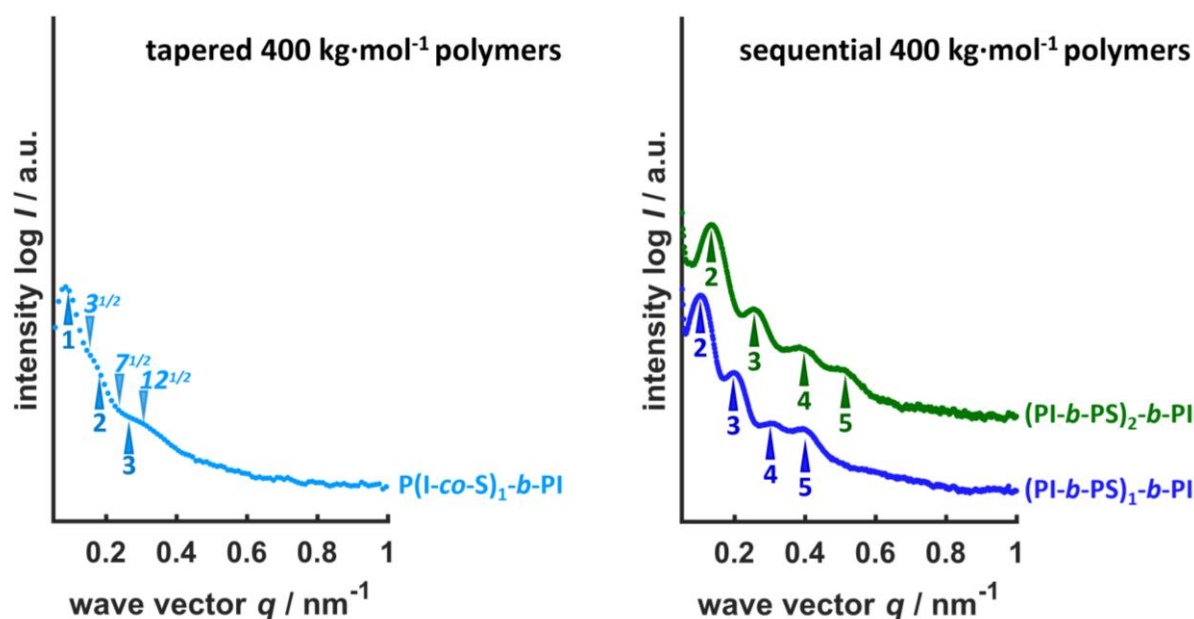


Figure S6: SAXS patterns of the tapered (left) and sequential (right) multiblock copolymers with a molar mass of 400 kg·mol<sup>-1</sup> at 90 °C. The color code denotes the different block numbers (blue: triblock, green: pentablock), with the lighter colors corresponding to the tapered structures. The arrows give the positions of the Bragg reflections corresponding to a lamellar (darker color), or a cylindrical (lighter color, italic letters) morphology. The curves are shifted vertically for clarity.

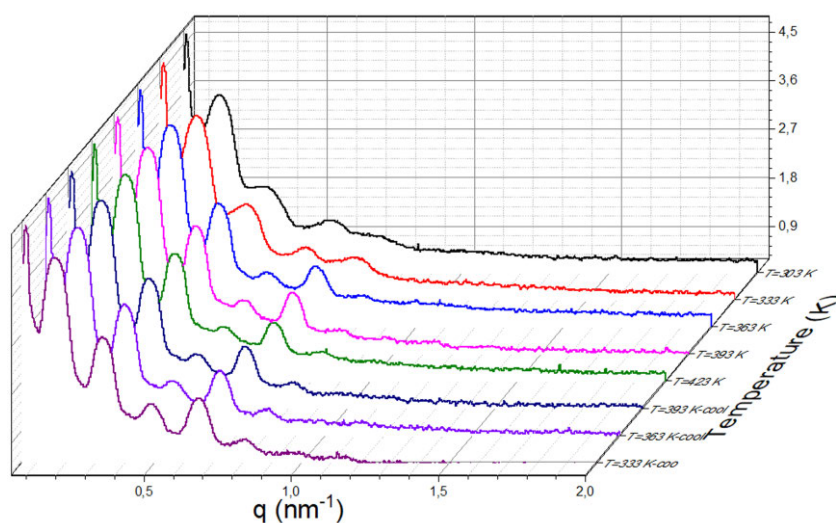


Figure S7: Temperature-dependent SAXS measurements of the sequential triblock with 120 kg·mol<sup>-1</sup>.



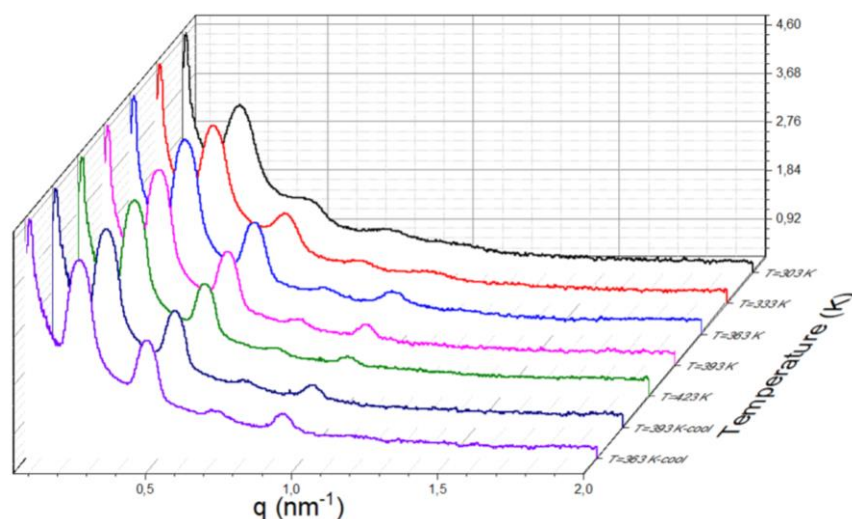


Figure S8: Temperature-dependent SAXS measurements of the sequential pentablock with  $120 \text{ kg} \cdot \text{mol}^{-1}$ .

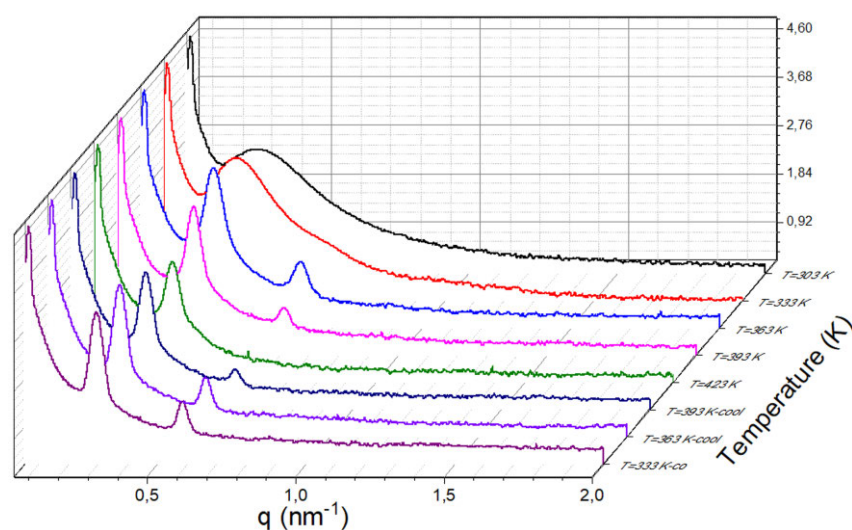


Figure S9: Temperature-dependent SAXS measurements of the sequential heptablock with  $120 \text{ kg} \cdot \text{mol}^{-1}$ .

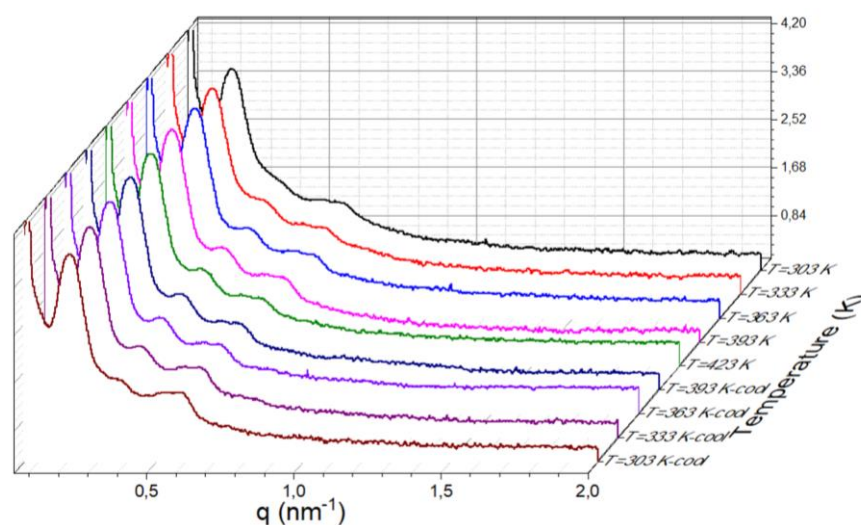


Figure S10: Temperature-dependent SAXS measurements of the tapered triblock with  $120 \text{ kg} \cdot \text{mol}^{-1}$ .

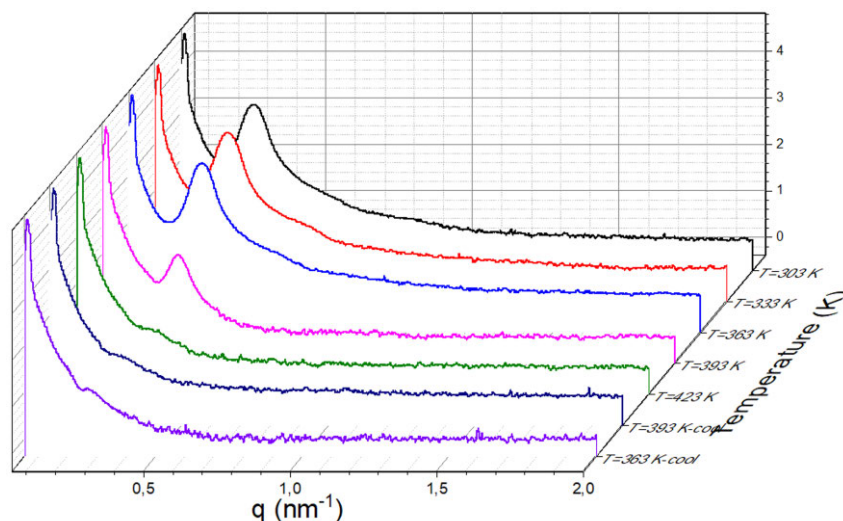


Figure S11: Temperature-dependent SAXS measurements of the tapered pentablock with 120 kg·mol<sup>-1</sup>.

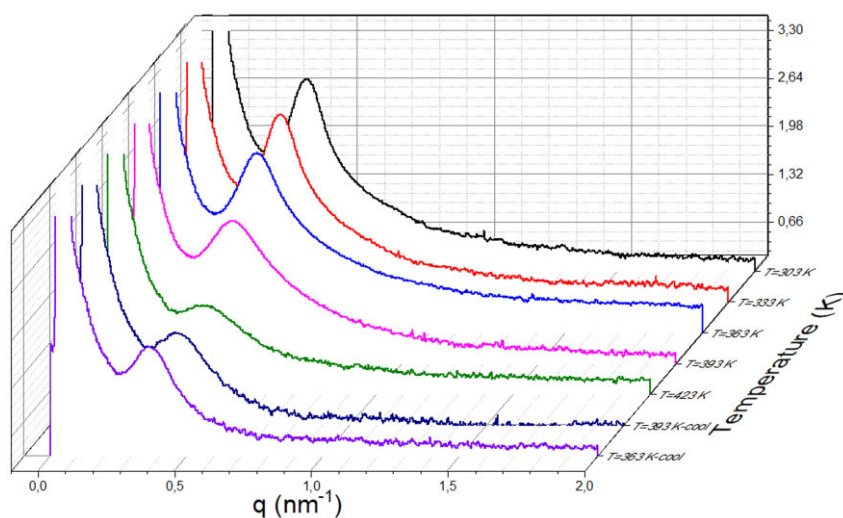


Figure S12: Temperature-dependent SAXS measurements of the tapered heptablock with 120 kg·mol<sup>-1</sup>.

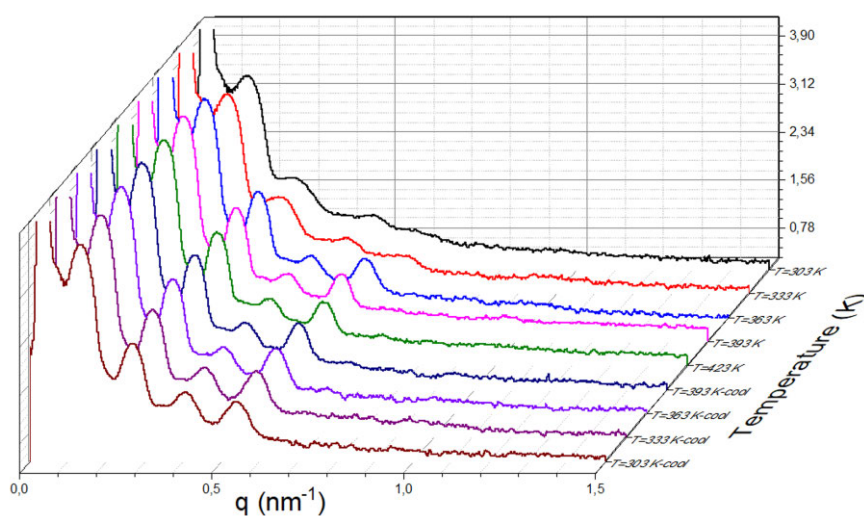


Figure S13: Temperature-dependent SAXS measurements of the sequential triblock with 160 kg·mol<sup>-1</sup>.

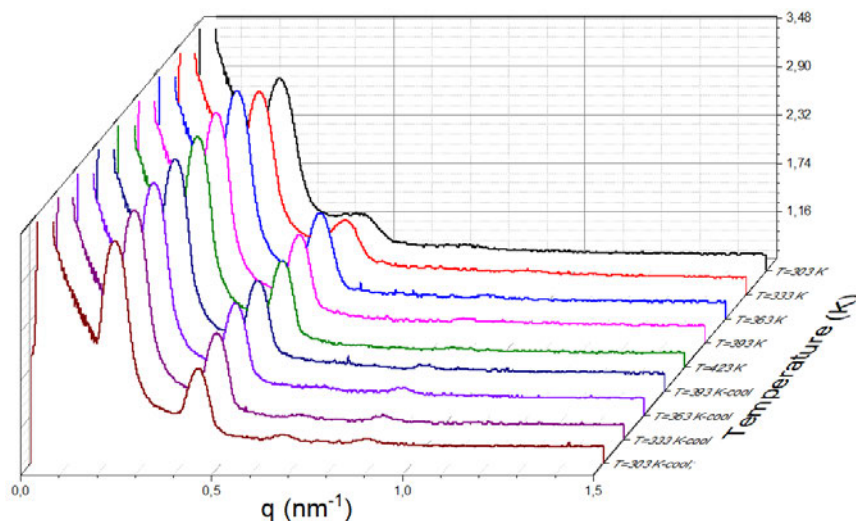


Figure S14: Temperature-dependent SAXS measurements of the sequential pentablock with 160 kg·mol<sup>-1</sup>.

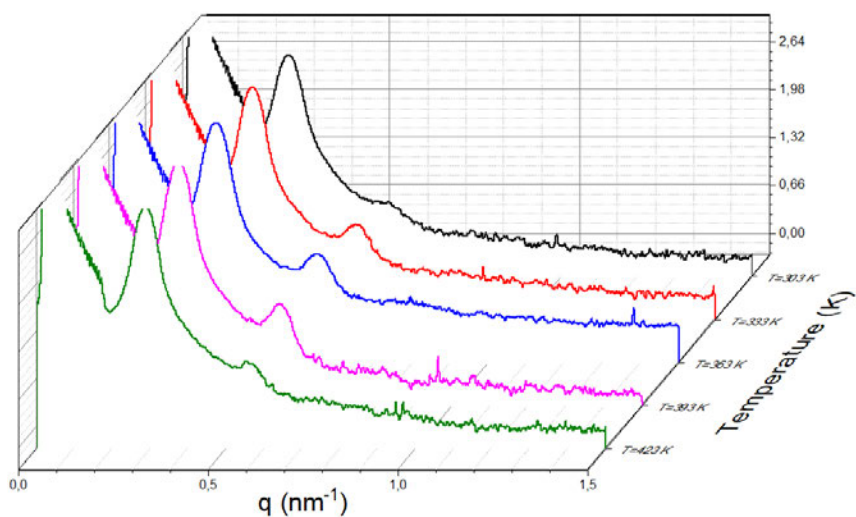


Figure S15: Temperature-dependent SAXS measurements of the sequential heptablock with 160 kg·mol<sup>-1</sup>.

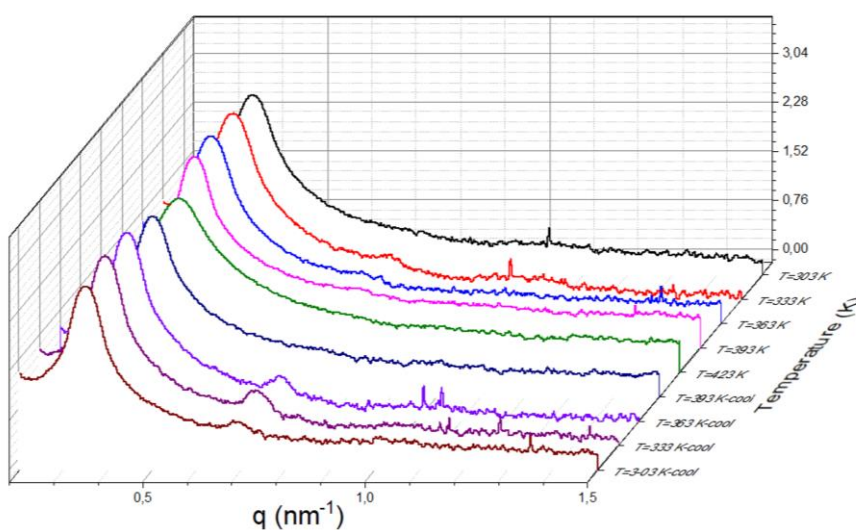


Figure S16: Temperature-dependent SAXS measurements of the sequential nonablock with 160 kg·mol<sup>-1</sup>.



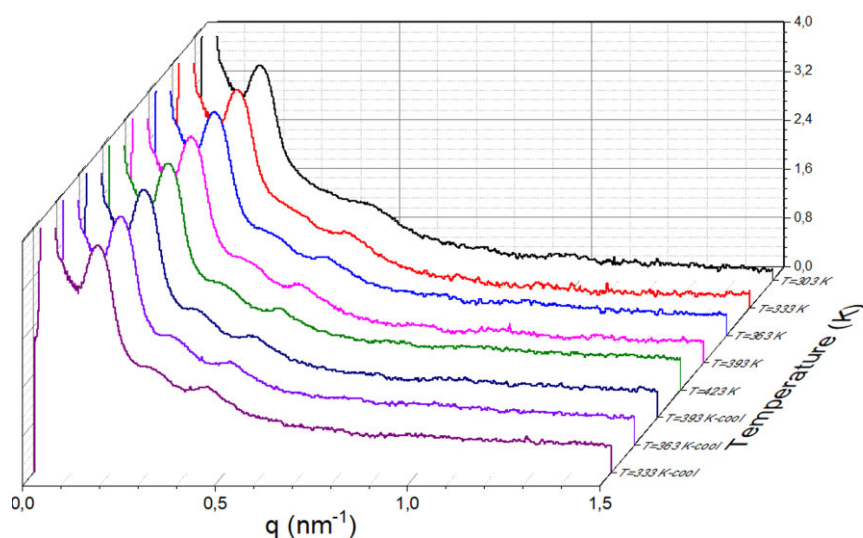


Figure S17: Temperature-dependent SAXS measurements of the tapered triblock with 160 kg·mol<sup>-1</sup>.

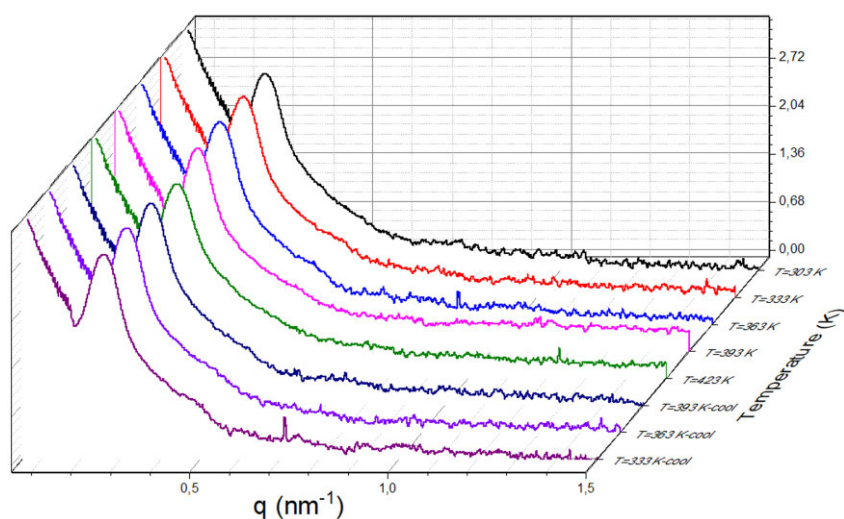


Figure S18: Temperature-dependent SAXS measurements of the tapered pentablock with 160 kg·mol<sup>-1</sup>.

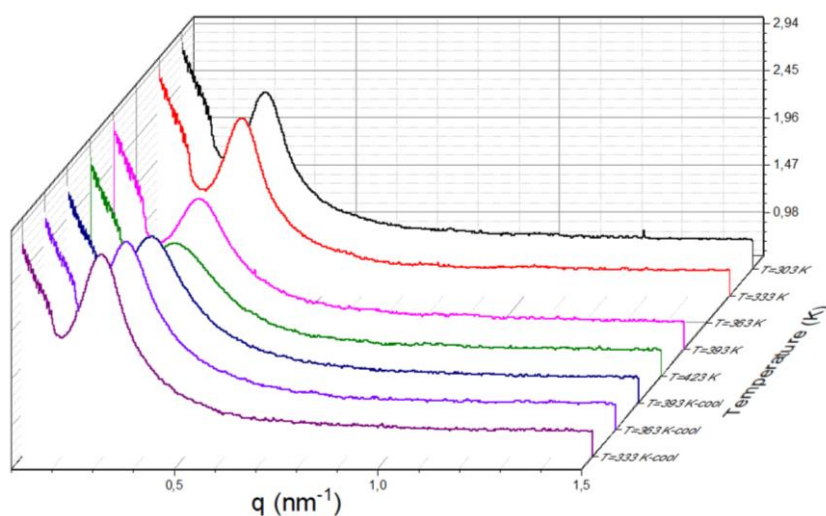


Figure S19: Temperature-dependent SAXS measurements of the tapered heptablock with 160 kg·mol<sup>-1</sup>.

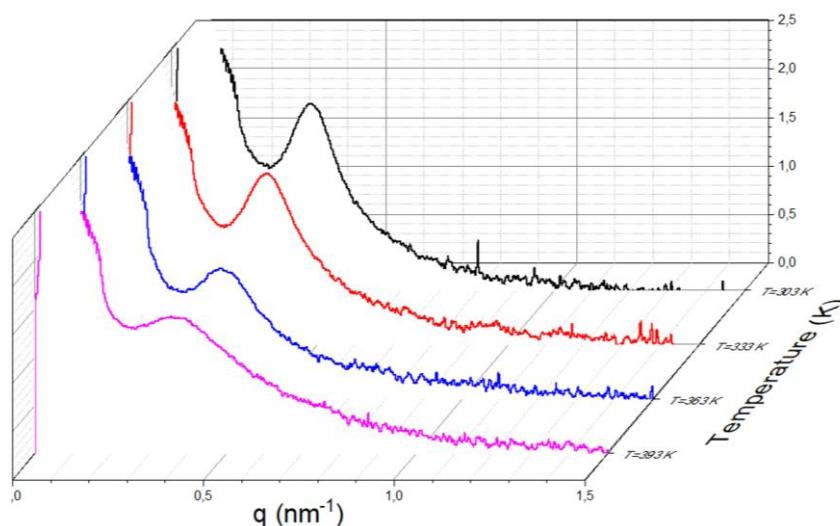


Figure S20: Temperature-dependent SAXS measurements of the tapered nonablock with  $160 \text{ kg}\cdot\text{mol}^{-1}$ .

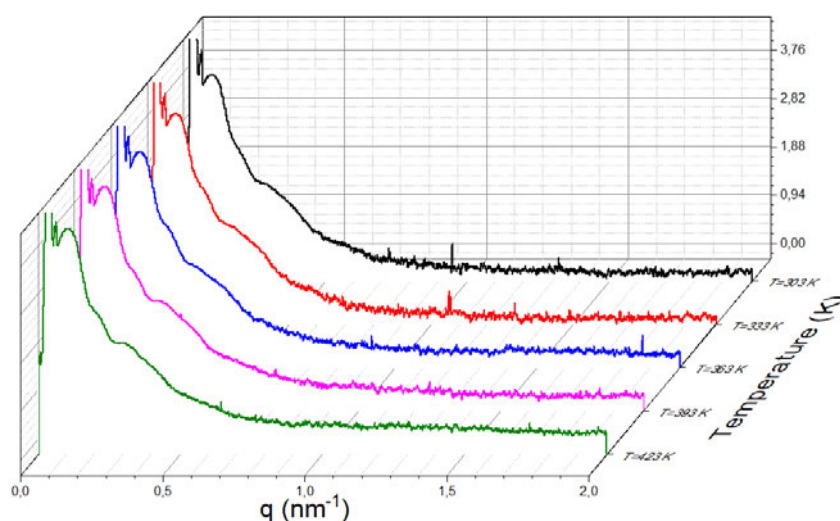


Figure S21: Temperature-dependent SAXS measurements of the sequential triblock with  $240 \text{ kg}\cdot\text{mol}^{-1}$ .

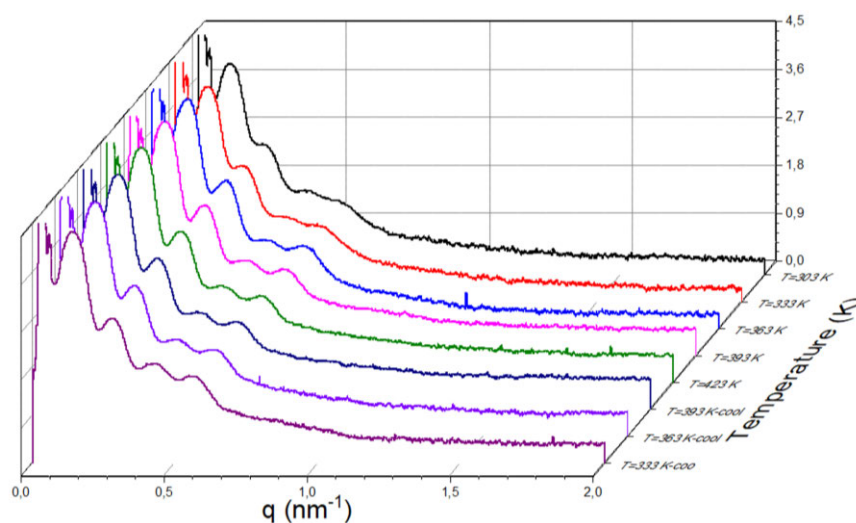


Figure S22: Temperature-dependent SAXS measurements of the sequential pentablock with  $240 \text{ kg}\cdot\text{mol}^{-1}$ .

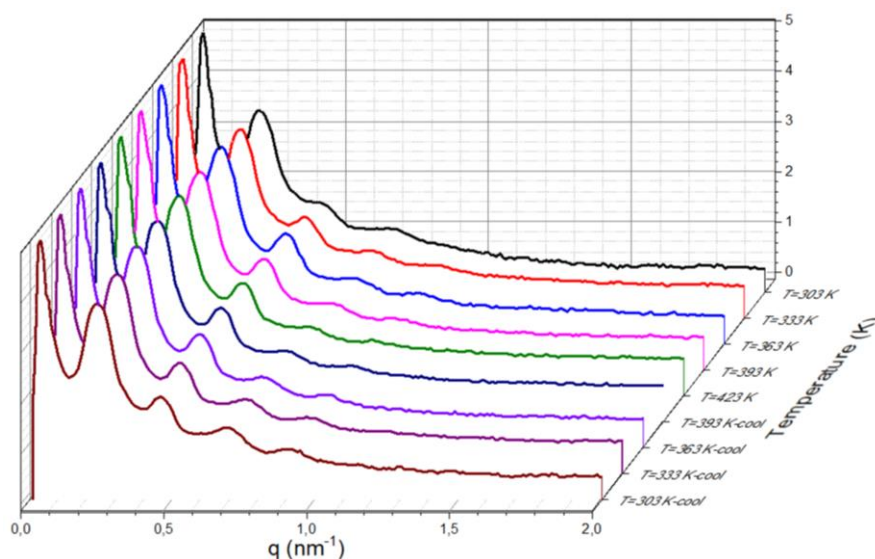


Figure S23: Temperature-dependent SAXS measurements of the sequential heptablock with 240 kg·mol<sup>-1</sup>.

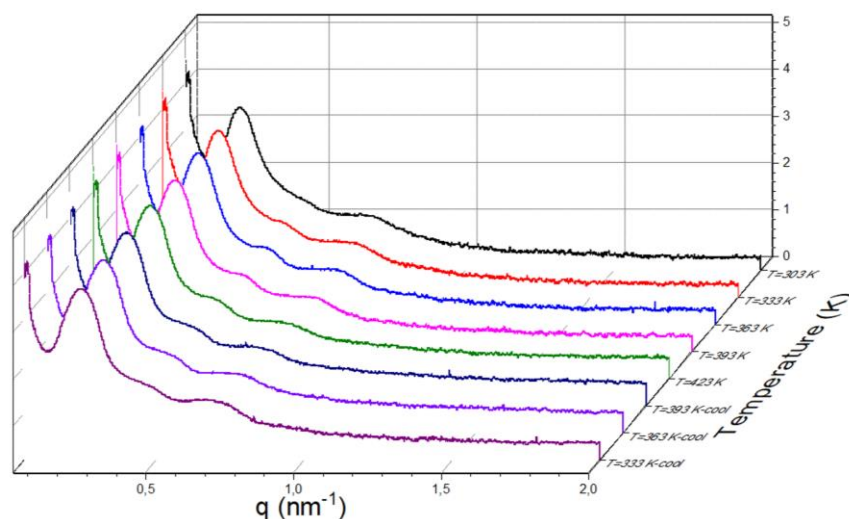


Figure S24: Temperature-dependent SAXS measurements of the sequential nonablock with 240 kg·mol<sup>-1</sup>.

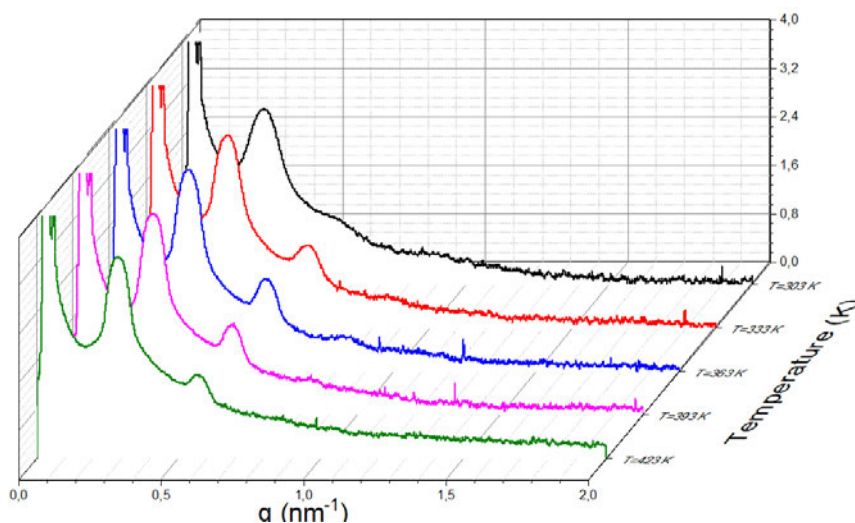


Figure S25: Temperature-dependent SAXS measurements of the sequential undecablock with 240 kg·mol<sup>-1</sup>.

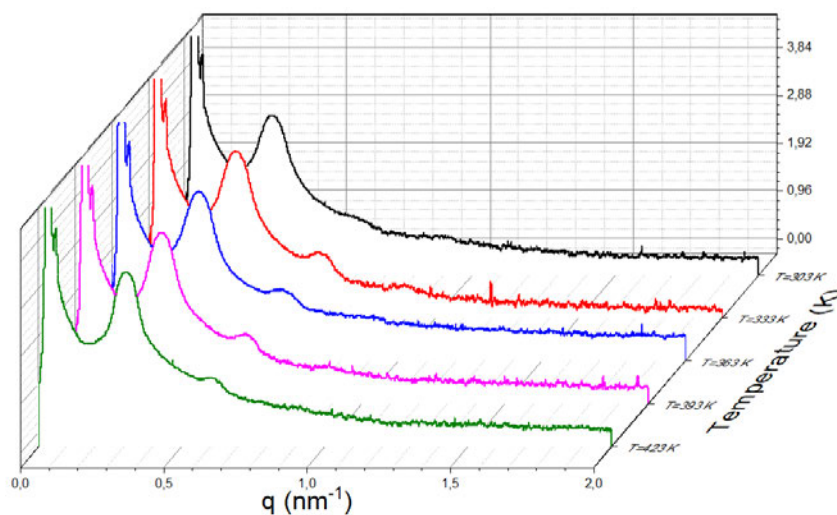


Figure S26: Temperature-dependent SAXS measurements of the sequential tredecablock with  $240 \text{ kg}\cdot\text{mol}^{-1}$ .

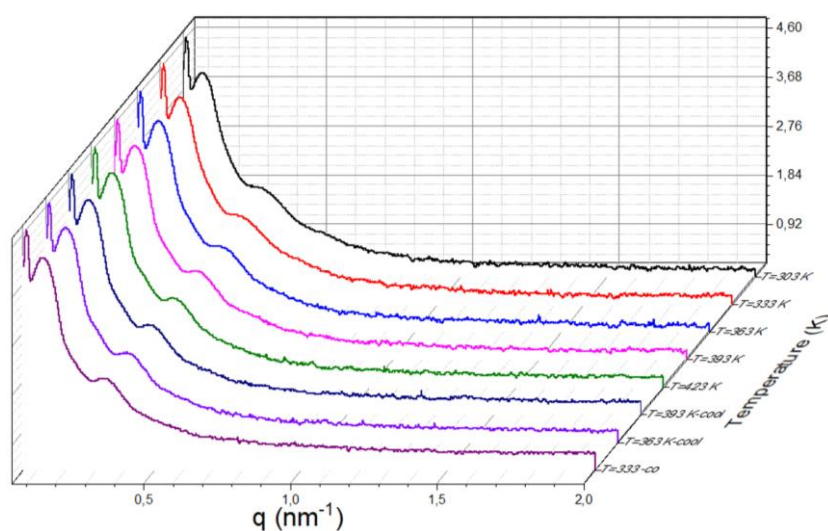


Figure S27: Temperature-dependent SAXS measurements of the tapered triblock with  $240 \text{ kg}\cdot\text{mol}^{-1}$ .

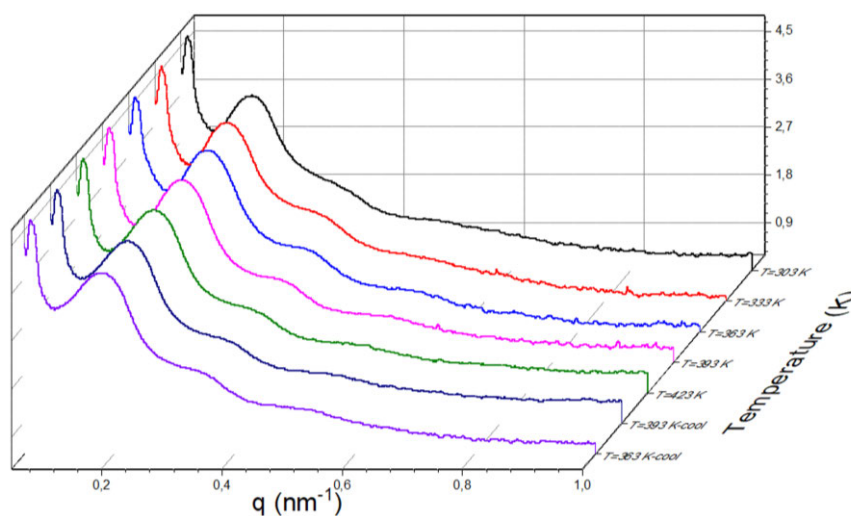


Figure S28: Temperature-dependent SAXS measurements of the tapered pentablock with  $240 \text{ kg}\cdot\text{mol}^{-1}$ .



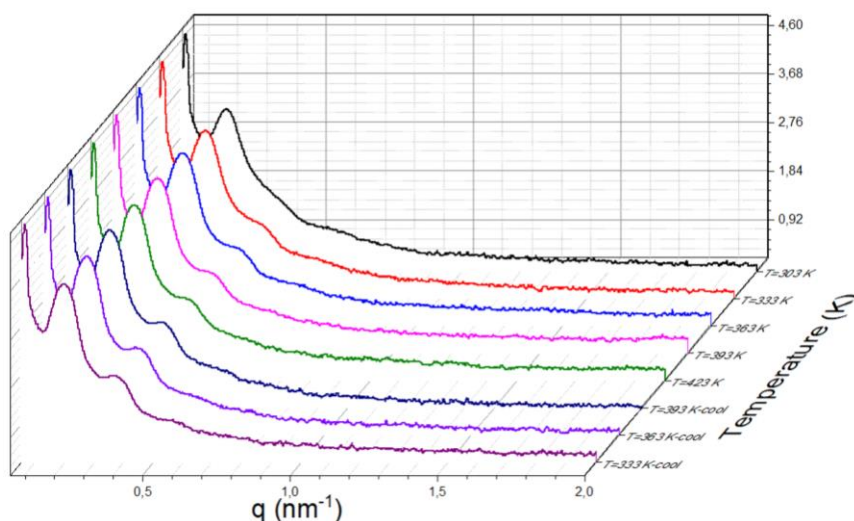


Figure S29: Temperature-dependent SAXS measurements of the tapered heptablock with 240 kg·mol<sup>-1</sup>.

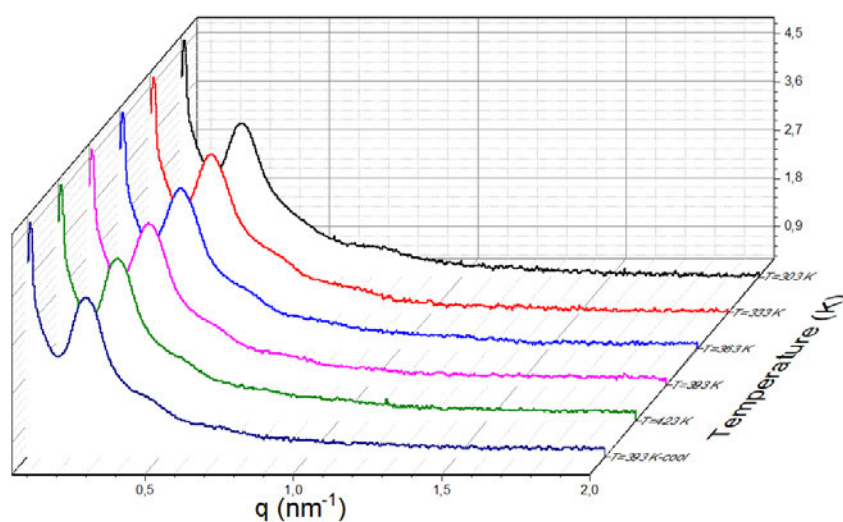


Figure S30: Temperature-dependent SAXS measurements of the tapered nonablock with 240 kg·mol<sup>-1</sup>.

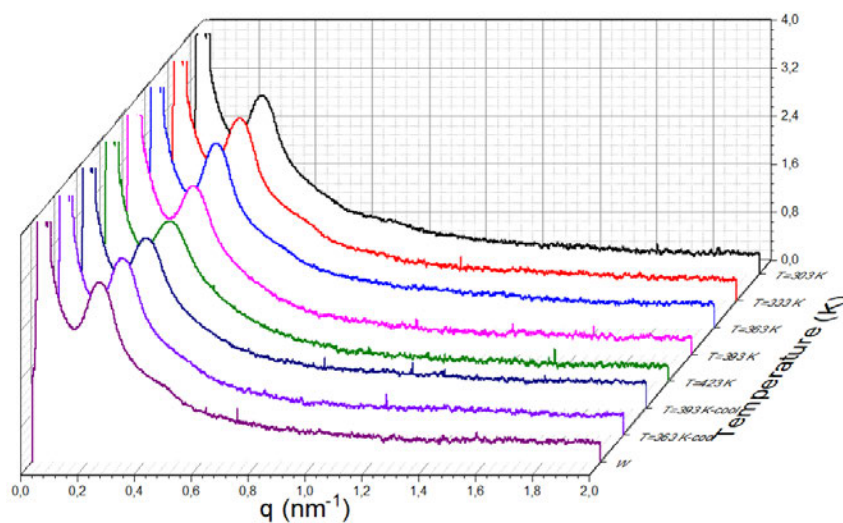


Figure S31: Temperature-dependent SAXS measurements of the tapered undecablock with 240 kg·mol<sup>-1</sup>.

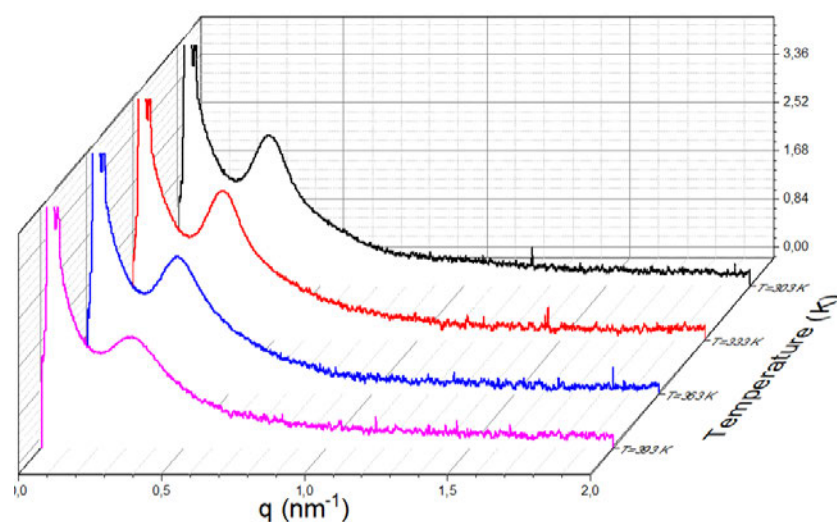


Figure S32: Temperature-dependent SAXS measurements of the tapered tredecablock with 240 kg·mol<sup>-1</sup>.

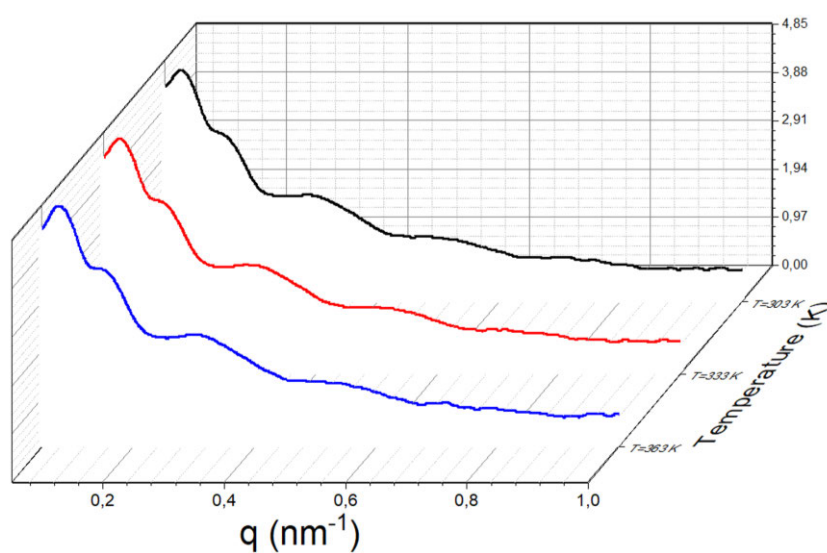


Figure S33: Temperature-dependent SAXS measurements of the sequential triblock with 320 kg·mol<sup>-1</sup>.

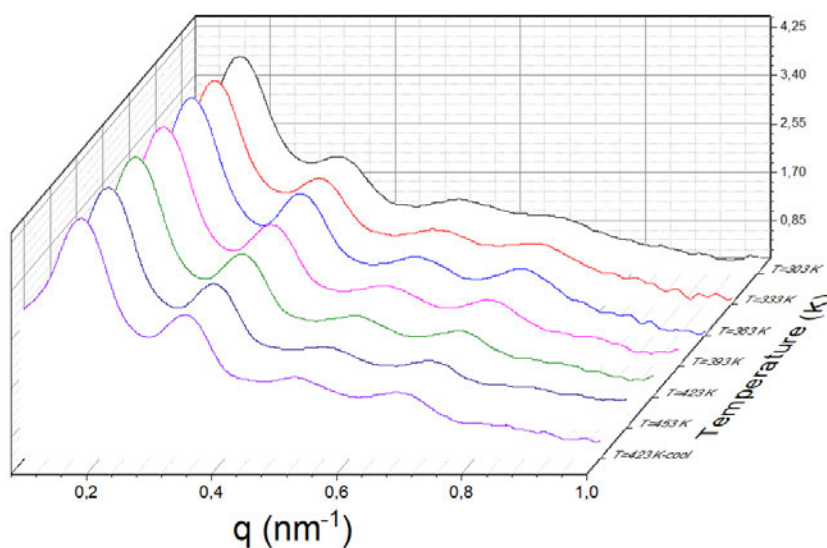


Figure S34: Temperature-dependent SAXS measurements of the sequential heptablock with 320 kg·mol<sup>-1</sup>.

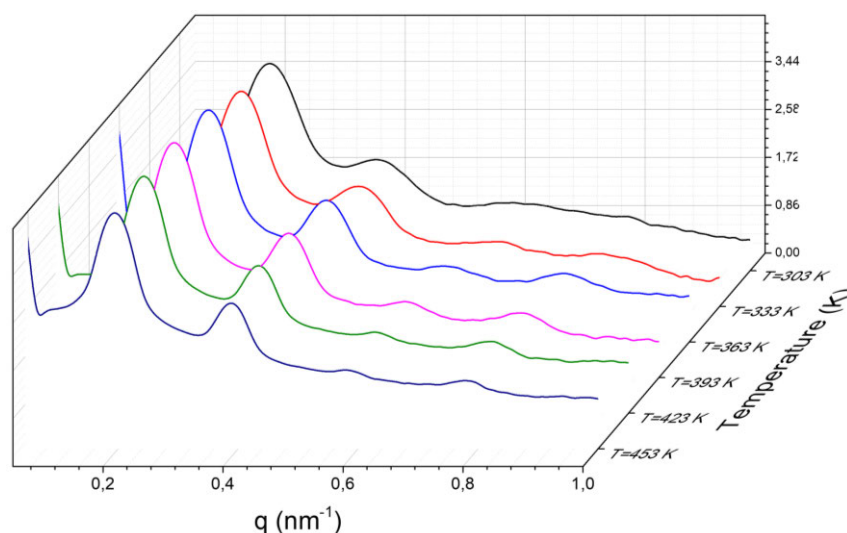


Figure S35: Temperature-dependent SAXS measurements of the sequential nonablock with 320 kg·mol<sup>-1</sup>.

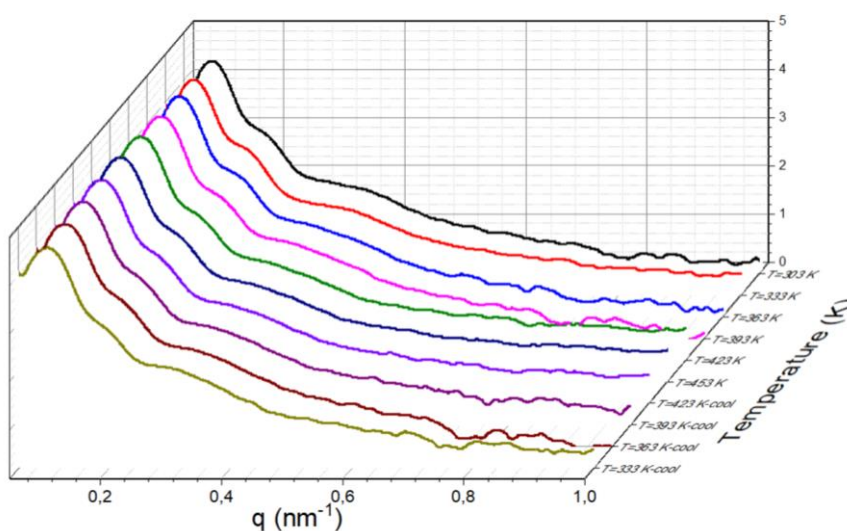


Figure S36: Temperature-dependent SAXS measurements of the tapered triblock with 320 kg·mol<sup>-1</sup>.

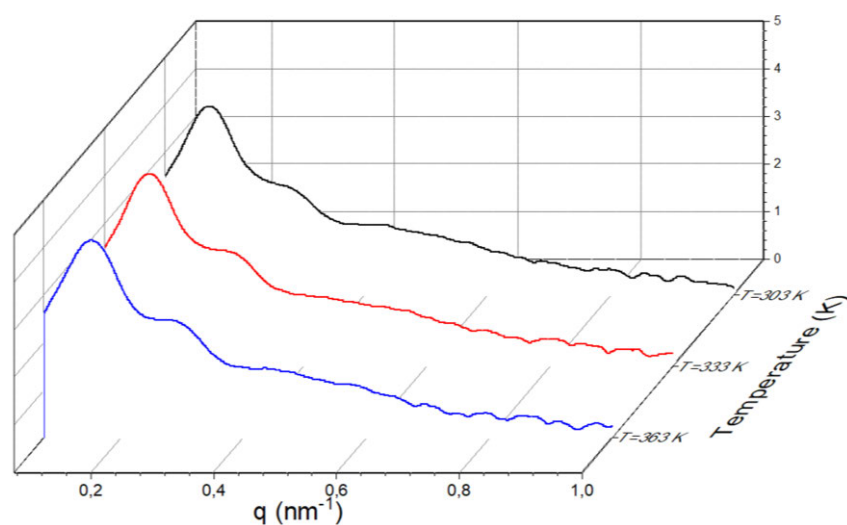


Figure S37: Temperature-dependent SAXS measurements of the tapered pentablock with 320 kg·mol<sup>-1</sup>.

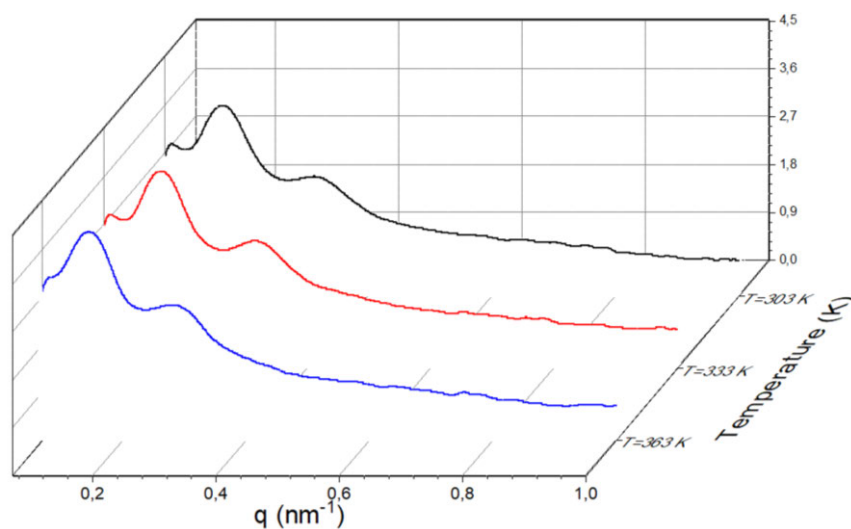


Figure S38: Temperature-dependent SAXS measurements of the tapered heptablock with 320 kg·mol<sup>-1</sup>.

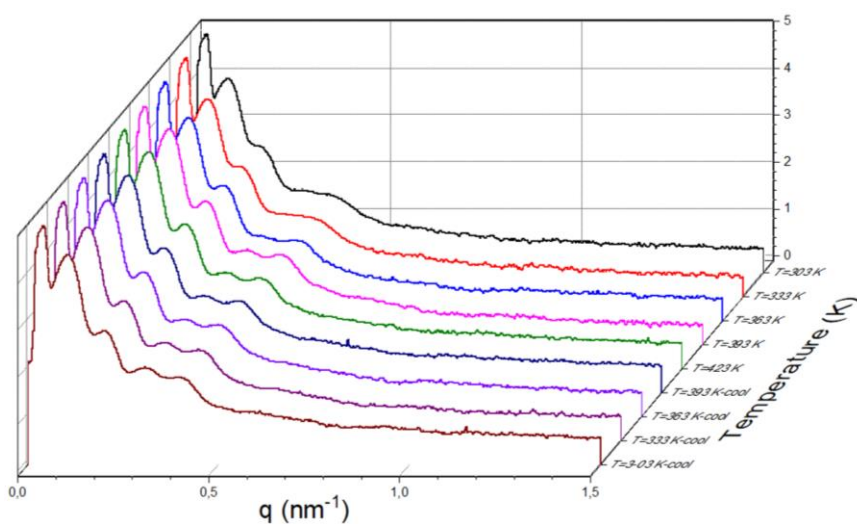


Figure S39: Temperature-dependent SAXS measurements of the sequential triblock with 400 kg·mol<sup>-1</sup>.

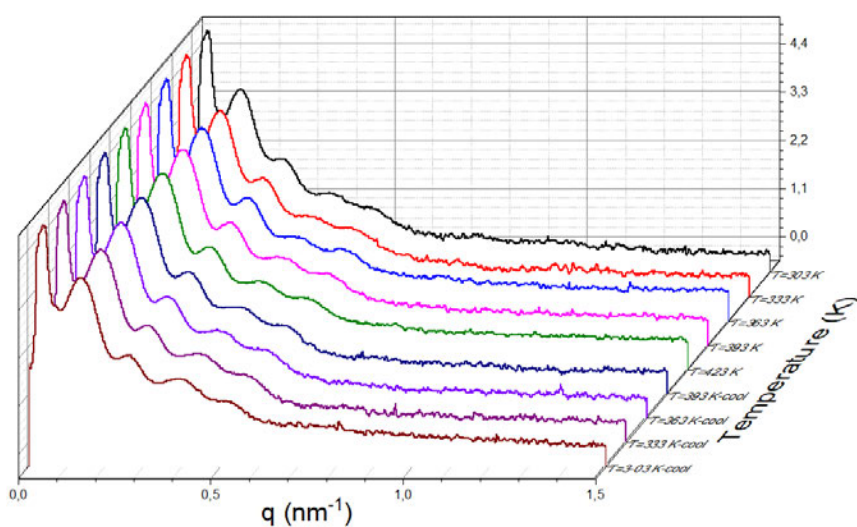


Figure S40: Temperature-dependent SAXS measurements of the sequential pentablock with 400 kg·mol<sup>-1</sup>.



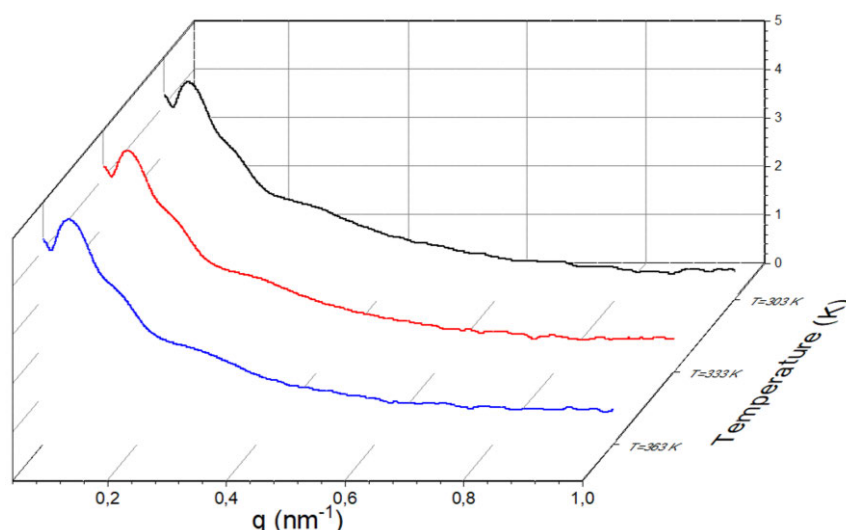


Figure S41: Temperature-dependent SAXS measurements of the tapered triblock with  $400 \text{ kg}\cdot\text{mol}^{-1}$ .

## Rheological Measurements

Dynamic mechanical measurements were performed on rotational rheometer (Modular Compact Rheometer MCR 702e, Anton Paar, Graz, Austria) using parallel plate geometry measuring system with a diameter of 15 mm. The samples were placed on the lower plate of the temperature control device, the upper plate was brought into contact, and the sample was heated to a convenient temperature to form a solid piece. The gap thickness was adjusted at the loading temperature, which was chosen equal to maximum softening temperature. The amplitude sweep test was used to determine the linear viscoelastic region. The constant plateau values at low strain indicate that samples exhibit a primarily solid-like elastic response in this strain range. Subsequent frequency and temperature sweep tests were performed in the linear viscoelastic regime. The temperature sweep tests were recorded at angular frequencies, amplitudes, and heating rates of  $\omega=0.01 \text{ rad}\cdot\text{s}^{-1}$ , 0.01% and  $3 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ , in the case of the polymers with  $160 \text{ kg}\cdot\text{mol}^{-1}$ , and  $\omega=1 \text{ rad}\cdot\text{s}^{-1}$ , 1% and  $5 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  for the polymers with  $120 \text{ kg}\cdot\text{mol}^{-1}$ . The frequency sweep tests were carried out in a temperature regime around the order-disorder temperature  $T_{\text{ODT}}$ , performed in the linear viscoelastic regime. If necessary, a normal force up to  $F=1 \text{ N}$  (0.25 N for soft or liquid samples) was applied to keep the upper plate in contact with the sample during the measurement.

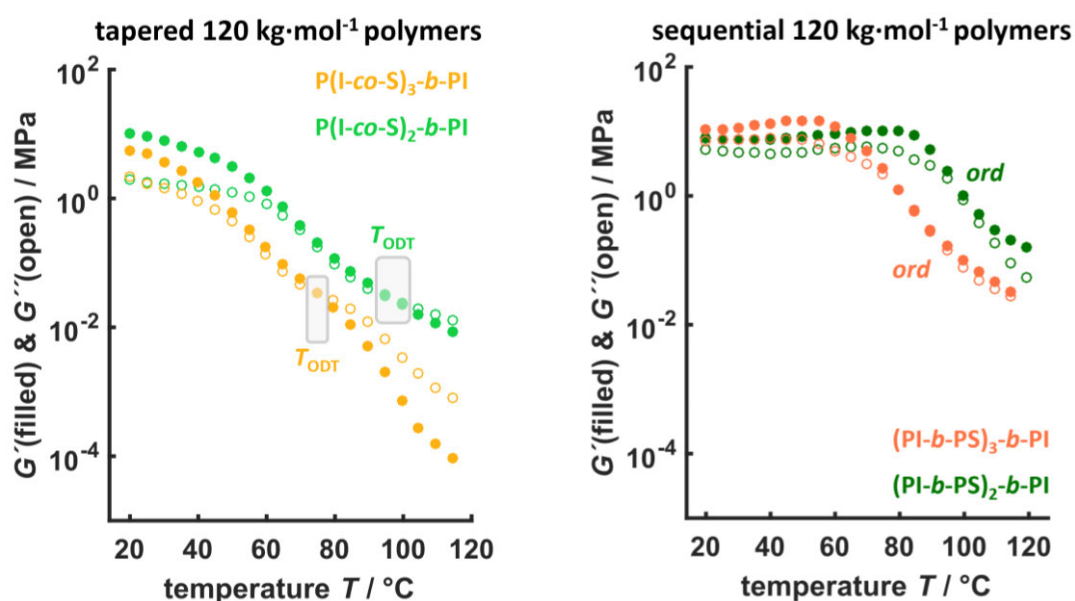
## Rheological Properties

Isochronal measurements of the storage modulus  $G'$  and loss modulus  $G''$  were performed at low frequencies with low strain amplitude by slowly heating the specimens. It is important to note that a normal force of 1 N was applied to keep the upper plate in contact with the specimen.

In general, rheology is a sensitive method to locate the order-disorder as well as order-order transitions between different morphologies.<sup>[1]</sup> Under isochronal conditions, a fluctuation induced first-order transition is evident by the drop in the shear storage modulus  $G'(T)$  at the order-disorder transition temperature  $T_{\text{ODT}}$ . As mentioned above, the applied normal force kept

the upper plate in contact with the specimen, which is why this drop might be less pronounced than expected. Together with the insights gained by temperature-dependent SAXS measurements (see Supp. Inf., Figure S7-41 and in the main paper, Table 2), a rough estimation of the  $T_{\text{ODT}}$ 's is possible. Note that the assigned phase states in Figure S42 and S43 originate from the morphological investigation by SAXS (see main paper) and cannot be concluded from the rheological measurements itself.

Figure S42 shows the isochronal measurements of the storage moduli  $G'$  and loss moduli  $G''$  for the polymers with  $120 \text{ kg}\cdot\text{mol}^{-1}$ . While the sequential penta- and heptablock remain ordered over the temperature range of 20–120 °C, the tapered penta- and heptablock are known from SAXS to undergo a phase transition from an ordered state to the disordered state at 95–100 °C and 75 °C, respectively. Below the order-disorder transition, the copolymers show viscoelastic response. However, the discontinuity in the shear storage modulus  $G'(T)$  is not very pronounced.



**Figure S42:** Rheological measurements of the tapered (left) and sequential (right) multiblock copolymers with an overall molar mass of  $120 \text{ kg}\cdot\text{mol}^{-1}$ . The storage moduli  $G'$  (filled symbols) and the loss moduli  $G''$  (open symbols) are plotted in dependence of the temperature. The strain amplitude was held constant at 1 %, the angular frequency was held constant at  $1 \text{ rad}\cdot\text{s}^{-1}$  and the heat rate was set to  $5 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .

In Figure S43, the storage moduli  $G'$  and loss moduli  $G''$  at isochronal conditions for the polymers with  $160 \text{ kg}\cdot\text{mol}^{-1}$  are depicted as an example. For a high number of blocks, order-disorder transitions can be observed for both the tapered and the sequential multiblock copolymers. Note that the moduli are shifted horizontally for a clarification. Still, the storage and loss moduli of the different polymers range at comparable magnitudes, as can be seen in Figure S44.

The sequential multiblock copolymers are well ordered over the whole temperature range studied up to 150 °C, with the exception of the sequential nonablock, which features a phase transition from an ordered state to the disordered state at 176–179 °C. The tapered tri- and pentablock copolymers remain ordered during the temperature sweep test, while the tapered hepta- and nonablock exhibit order-disorder transitions at 112–115 °C and 75–80 °C, respectively. In the ordered state, all polymers display viscoelastic responses, with the

sequential polymers exhibiting a pronounced plateau, in which the storage modulus  $G'$  is larger than the loss modulus  $G''$ .

Comparing the order-disorder transition temperatures derived from the isochronal rheological measurements with the values deduced from temperature-dependent SAXS measurements (main paper, Table 2) reveals an excellent agreement within the temperature intervals of the measurements.

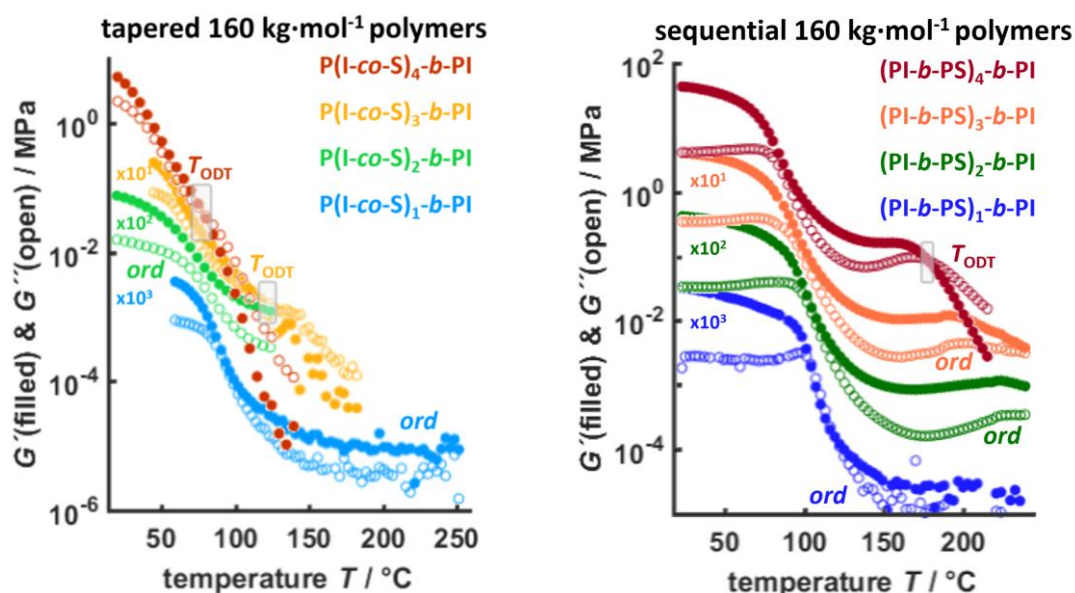


Figure S43: Rheological measurements of the tapered (left) and sequential (right) multiblock copolymers with an overall molar mass of  $160 \text{ kg}\cdot\text{mol}^{-1}$ . The storage moduli  $G'$  (filled symbols) and the loss moduli  $G''$  (open symbols) are plotted in dependence of the temperature. The strain amplitude was held constant at 0.01 %, the angular frequency at  $1 \text{ rad}\cdot\text{s}^{-1}$  and the heat rate was set to  $3 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  or  $5 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .

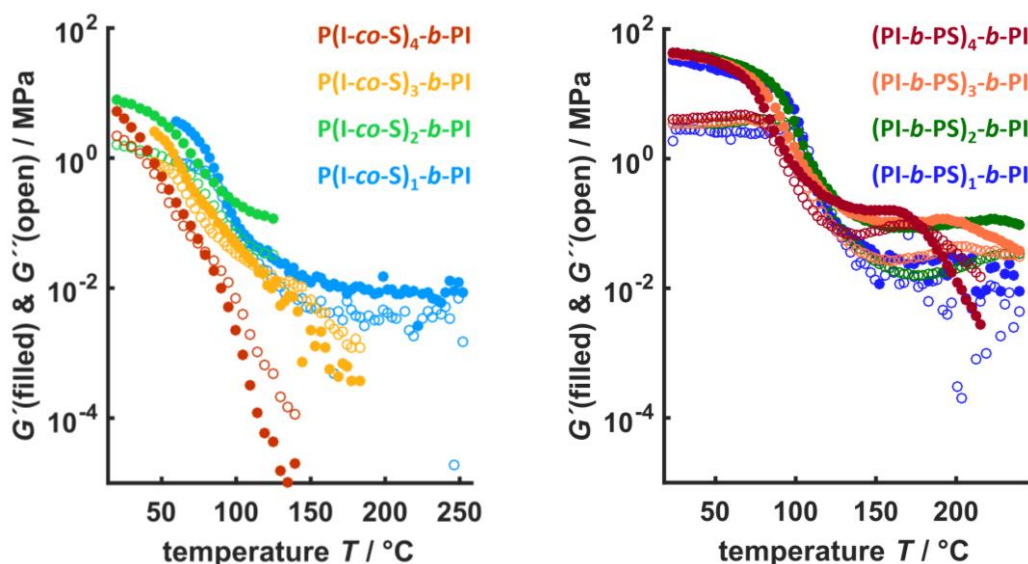


Figure S44: Rheological measurements of the tapered (left) and sequential (right) multiblock copolymers with an overall molar mass of  $160 \text{ kg}\cdot\text{mol}^{-1}$ . The storage moduli  $G'$  (filled symbols) and the loss moduli  $G''$  (open symbols) are plotted in dependence of the temperature. Different colors denote varying block numbers. The color code denotes the different block numbers (blue: triblock, green: pentablock, orange: heptablock, red: nonablock), with the lighter colors corresponding to the tapered structures. The strain amplitude was held constant at 0.01 %, the angular frequency was held constant at  $1 \text{ rad}\cdot\text{s}^{-1}$  and the heat rate was set to  $3 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  or  $5 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .

**Table S2: Mean values and its errors (maximum deviation) based on 3-6 repetitions of uniaxial tensile tests. Young's moduli ( $E_{\text{modulus}}$ ): slope of the initial linear increase; yield point: maximum stress ( $\sigma_{\text{yield point}}$ ) and strain ( $\epsilon_{\text{yield point}}$ ) before permanent deformation (typically, a drop in stress is observed due to necking followed by strain hardening in case of well-separated multiblock copolymers); break point: maximum stress ( $\sigma_{\text{break}}$ ) and strain ( $\epsilon_{\text{break}}$ ); toughness ( $U$ ): integral of the stress-strain curve.**

| (IS) <sub>n</sub> I Copolymer |              |                                            | Young's Modulus            |                                   | Yield Point                         |                                            |                                     |                                            | Toughness                |                                 | Break Point                   |                                      |                               |                                      |
|-------------------------------|--------------|--------------------------------------------|----------------------------|-----------------------------------|-------------------------------------|--------------------------------------------|-------------------------------------|--------------------------------------------|--------------------------|---------------------------------|-------------------------------|--------------------------------------|-------------------------------|--------------------------------------|
| Block type                    | Block number | 2n+1<br>Molar mass [kg·mol <sup>-1</sup> ] | $E_{\text{modulus}}$ [MPa] | $\Delta E_{\text{modulus}}$ [MPa] | $\epsilon_{\text{yield point}}$ [%] | $\Delta \epsilon_{\text{yield point}}$ [%] | $\sigma_{\text{yield point}}$ [MPa] | $\Delta \sigma_{\text{yield point}}$ [MPa] | $U$ [MJ/m <sup>3</sup> ] | $\Delta U$ [MJ/m <sup>3</sup> ] | $\epsilon_{\text{break}}$ [%] | $\Delta \epsilon_{\text{break}}$ [%] | $\sigma_{\text{break}}$ [MPa] | $\Delta \sigma_{\text{break}}$ [MPa] |
| tap                           | 3            | 120                                        | 90.46                      | 1.77                              | -                                   | -                                          | -                                   | -                                          | 0.17                     | 0.02                            | 7.68                          | 0.75                                 | 2.05                          | 0.19                                 |
|                               | 5            | 120                                        | 31.94                      | 0.72                              | 6.39                                | 0.06                                       | 1.39                                | 0.01                                       | 11.56                    | 0.86                            | 667.03                        | 27.22                                | 2.59                          | 0.05                                 |
|                               | 7            | 120                                        | 15.80                      | 0.30                              | 9.52                                | 0.56                                       | 0.78                                | 0.01                                       | 14.35                    | 0.00                            | 836.10                        | 118.55                               | 2.58                          | 0.22                                 |
| seq                           | 3            | 120                                        | 159.29                     | 2.35                              | -                                   | -                                          | -                                   | -                                          | 0.08                     | 0.01                            | 3.76                          | 0.14                                 | 2.66                          | 0.04                                 |
|                               | 5            | 120                                        | 152.13                     | 2.06                              | 2.93                                | 0.08                                       | 3.12                                | 0.05                                       | 31.15                    | 0.00                            | 772.00                        | 0.00                                 | 6.00                          | 0.00                                 |
|                               | 7            | 120                                        | 137.47                     | 0.91                              | 3.23                                | 0.01                                       | 3.06                                | 0.04                                       | 23.03                    | 3.61                            | 607.00                        | 63.47                                | 5.24                          | 0.30                                 |
| tap                           | 3            | 160                                        | 38.20                      | 3.70                              | -                                   | -                                          | -                                   | -                                          | 0.09                     | 0.05                            | 8.78                          | 4.22                                 | 1.10                          | 0.19                                 |
|                               | 5            | 160                                        | 30.44                      | 0.64                              | 6.45                                | 0.04                                       | 1.28                                | 0.02                                       | 17.01                    | 1.40                            | 879.40                        | 29.13                                | 2.99                          | 0.04                                 |
|                               | 7            | 160                                        | 35.38                      | 1.63                              | 5.83                                | 0.15                                       | 1.31                                | 0.01                                       | 13.52                    | 0.61                            | 737.50                        | 10.50                                | 2.15                          | 0.03                                 |
|                               | 9            | 160                                        | 37.91                      | 0.69                              | 6.22                                | 0.05                                       | 1.24                                | 0.02                                       | 7.58                     | 0.54                            | 536.43                        | 17.89                                | 1.60                          | 0.10                                 |
| seq                           | 3            | 160                                        | 150.89                     | 10.25                             | -                                   | -                                          | -                                   | -                                          | 0.14                     | 0.02                            | 6.32                          | 0.84                                 | 2.22                          | 0.24                                 |
|                               | 5            | 160                                        | 148.31                     | 3.01                              | 3.59                                | 0.10                                       | 3.09                                | 0.07                                       | 21.50                    | 0.60                            | 610.57                        | 10.44                                | 4.79                          | 0.01                                 |
|                               | 7            | 160                                        | 150.09                     | 4.71                              | 3.85                                | 0.07                                       | 3.46                                | 0.01                                       | 55.36                    | 2.85                            | 1049.33                       | 29.56                                | 9.49                          | 0.25                                 |
|                               | 9            | 160                                        | 114.44                     | 3.76                              | 4.73                                | 0.04                                       | 3.36                                | 0.02                                       | 48.16                    | 1.13                            | 1019.33                       | 13.78                                | 8.40                          | 0.06                                 |
| tap                           | 3            | 240                                        | 54.77                      | 7.49                              | 3.40                                | 0.17                                       | 1.45                                | 0.18                                       | 0.34                     | 0.06                            | 26.16                         | 3.85                                 | 0.98                          | 0.09                                 |
|                               | 5            | 240                                        | 97.02                      | 2.01                              | 3.80                                | 0.13                                       | 2.51                                | 0.02                                       | 46.30                    | 1.62                            | 1273.75                       | 16.75                                | 7.58                          | 0.38                                 |
|                               | 7            | 240                                        | 86.36                      | 2.94                              | 3.88                                | 0.05                                       | 2.40                                | 0.07                                       | 36.13                    | 1.98                            | 1169.00                       | 34.00                                | 5.73                          | 0.17                                 |
|                               | 9            | 240                                        | 43.60                      | 0.86                              | 6.03                                | 0.12                                       | 1.70                                | 0.01                                       | 33.20                    | 5.36                            | 1031.03                       | 77.96                                | 6.83                          | 0.80                                 |
|                               | 11           | 240                                        | 46.78                      | 1.82                              | 5.08                                | 0.07                                       | 1.53                                | 0.06                                       | 18.62                    | 0.56                            | 883.47                        | 24.29                                | 3.17                          | 0.01                                 |
|                               | 13           | 240                                        | 33.73                      | 1.16                              | 6.61                                | 0.35                                       | 1.22                                | 0.01                                       | 23.32                    | 0.37                            | 1103.00                       | 159.69                               | 2.75                          | 0.08                                 |
|                               | 3            | 240                                        | 229.08                     | 9.88                              | 2.55                                | 0.11                                       | 3.92                                | 0.02                                       | 1.02                     | 0.19                            | 35.54                         | 8.30                                 | 2.48                          | 0.08                                 |
| seq                           | 5            | 240                                        | 242.96                     | 11.62                             | 2.73                                | 0.35                                       | 4.08                                | 0.19                                       | 41.87                    | 2.49                            | 911.92                        | 36.58                                | 7.92                          | 0.32                                 |
|                               | 7            | 240                                        | 185.20                     | 5.48                              | 3.42                                | 0.16                                       | 3.93                                | 0.06                                       | 70.30                    | 0.43                            | 1118.00                       | 0.00                                 | 13.81                         | 0.08                                 |
|                               | 9            | 240                                        | 154.25                     | 2.02                              | 3.76                                | 0.39                                       | 3.75                                | 0.10                                       | 50.01                    | 7.43                            | 962.87                        | 54.70                                | 11.48                         | 1.82                                 |
|                               | 11           | 240                                        | 117.64                     | 4.90                              | 3.58                                | 0.04                                       | 2.78                                | 0.10                                       | 37.21                    | 2.39                            | 826.97                        | 35.89                                | 7.54                          | 0.23                                 |
|                               | 13           | 240                                        | 179.92                     | 5.06                              | 3.31                                | 0.01                                       | 4.18                                | 0.06                                       | 39.75                    | 1.86                            | 805.30                        | 29.07                                | 7.44                          | 0.47                                 |
| tap                           | 3            | 320                                        | 173.11                     | 3.32                              | 3.30                                | 0.07                                       | 3.89                                | 0.14                                       | 1.15                     | 0.27                            | 46.92                         | 12.92                                | 2.15                          | 0.10                                 |
|                               | 5            | 320                                        | 89.17                      | 3.26                              | 3.85                                | 0.07                                       | 2.32                                | 0.03                                       | 52.79                    | 2.31                            | 1384.00                       | 21.33                                | 9.24                          | 0.49                                 |
|                               | 7            | 320                                        | 52.51                      | 3.52                              | 5.60                                | 0.62                                       | 1.92                                | 0.00                                       | 58.12                    | 0.45                            | 1345.00                       | 2.00                                 | 10.58                         | 0.04                                 |
| seq                           | 3            | 320                                        | 303.51                     | 24.13                             | 2.50                                | 0.00                                       | 4.28                                | 0.02                                       | 9.14                     | 1.48                            | 259.07                        | 38.44                                | 3.81                          | 0.16                                 |
|                               | 7            | 320                                        | 174.79                     | 1.10                              | 3.39                                | 0.16                                       | 4.11                                | 0.09                                       | 68.20                    | 1.31                            | 1290.00                       | 9.00                                 | 12.10                         | 0.07                                 |
|                               | 9            | 320                                        | 149.41                     | 4.54                              | 3.91                                | 0.30                                       | 4.05                                | 0.10                                       | 61.77                    | 0.16                            | 1191.00                       | 4.00                                 | 11.62                         | 0.39                                 |

|     |   |     |        |      |      |      |      |      |       |      |        |        |      |      |
|-----|---|-----|--------|------|------|------|------|------|-------|------|--------|--------|------|------|
| tap | 3 | 400 | 31.42  | 4.28 | 8.78 | 1.22 | 1.23 | 0.03 | 2.88  | 0.32 | 238.53 | 33.78  | 1.07 | 0.10 |
| seq | 3 | 400 | 197.04 | 3.97 | 2.89 | 0.21 | 3.94 | 0.09 | 1.12  | 0.44 | 45.41  | 16.65  | 2.34 | 0.03 |
|     | 5 | 400 | 171.85 | 3.62 | 3.27 | 0.19 | 3.61 | 0.04 | 32.10 | 6.17 | 982.65 | 100.35 | 5.51 | 0.82 |

“seq” denotes the sequentially polymerized multiblock copolymers  $(PI-b-PS)_n-b-PI$ ; “tap” denotes the iteratively statistically copolymerized multiblock copolymers  $P(I-co-S)_n-b-PI$  with a tapered interface. The values indicated by an italic front are to be interpreted with caution, because all specimens of this polymer did not break but slid out of one grip. Hence, the maximum deformation and the toughness might be higher than reported. These values are marked in plots with an asterisk. The triblock copolymers of the 120 and 160 kg·mol<sup>-1</sup> series showed a gradual transition from elastic to plastic deformation, which is why no yield point was determined.

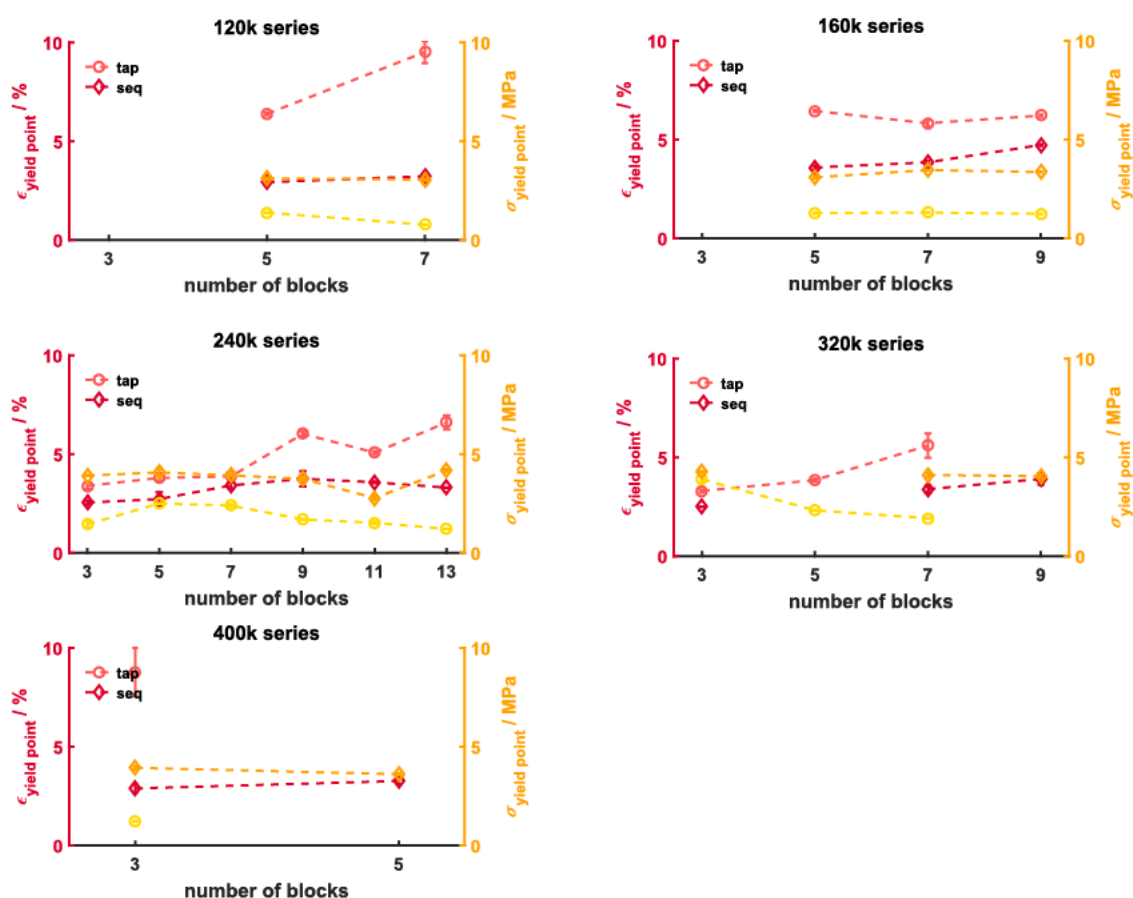
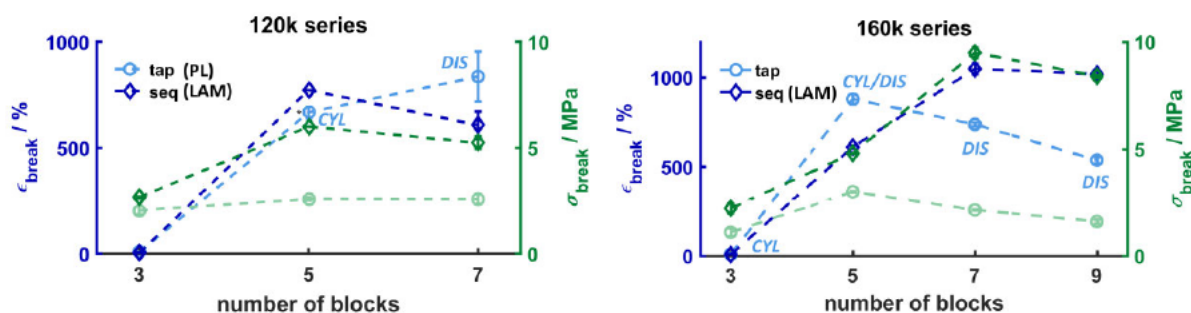


Figure S45: Characteristics of the yield point of the polymers sorted by molar mass (top left: 120, top right: 160, middle left: 240, middle right: 320, bottom left: 400 kg·mol<sup>-1</sup>). Plot of the strain ( $\epsilon_{\text{yield point}}$ ; dark red: sequential, red: tapered) and stress ( $\sigma_{\text{yield point}}$ ; orange: sequential, yellow: tapered) at the yield point in dependence of the block number.



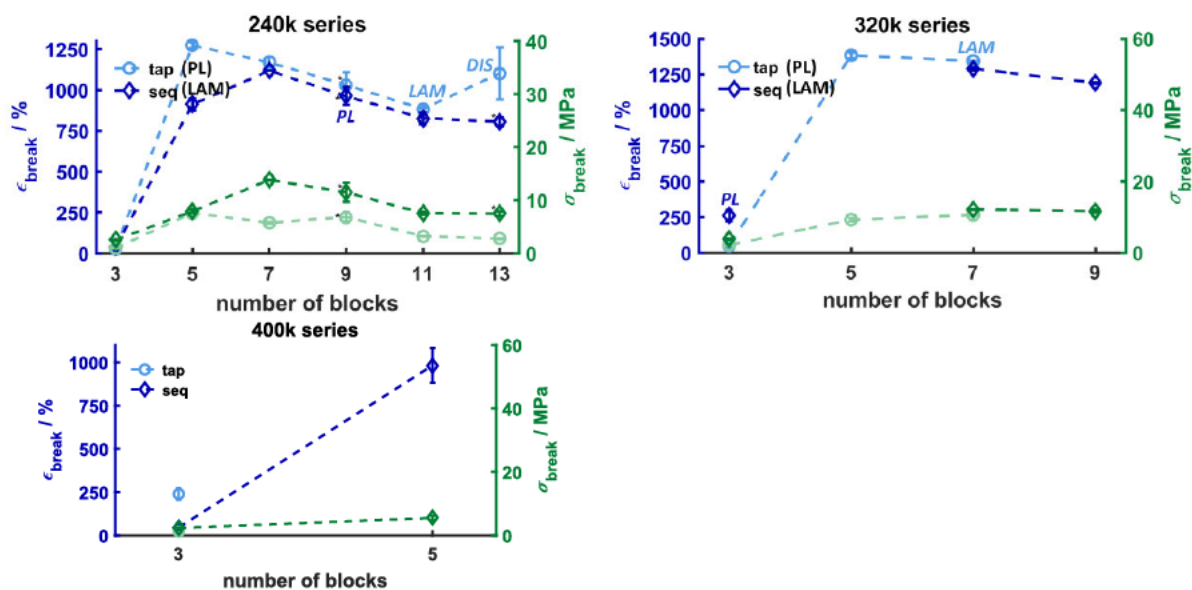


Figure S46: Characteristics of the break point of the multiblock copolymer series of differing molar (top left: 120, top right: 160, middle left: 240, middle right: 320, bottom left: 400 kg·mol<sup>-1</sup>) in dependence of their block number. Strain ( $\epsilon_{\text{break}}$ ; dark blue: sequential, blue: tapered) and stress ( $\sigma_{\text{break}}$ ; dark green: sequential, pale green: tapered) at the break point are plotted with varying block number.

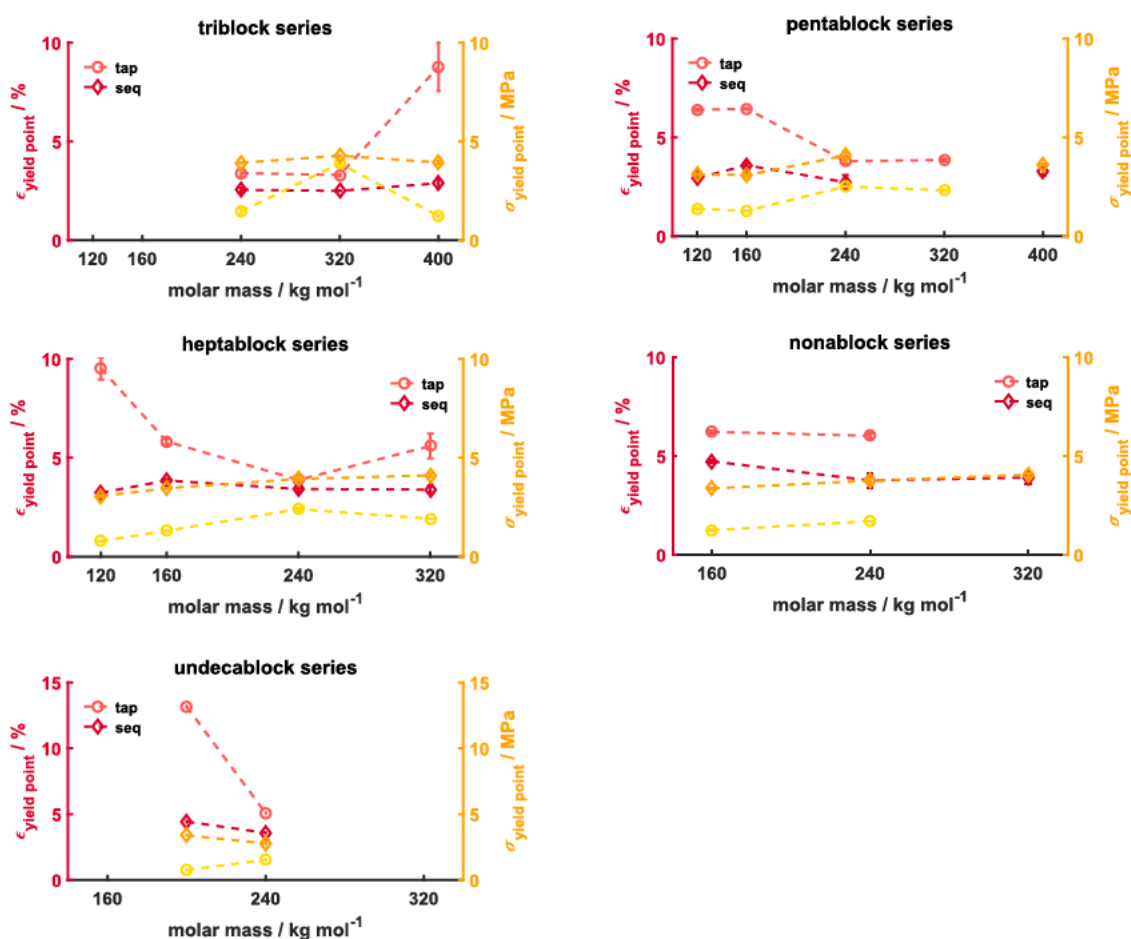


Figure S47: Characteristics of the yield point of the multiblock copolymer series of differing block number (top left: tri-, top right: penta-, middle left: hepta-, middle right: nona-, bottom left: undecablock copolymers) in dependence of their overall molar mass. Plot of the strain ( $\epsilon_{\text{yield point}}$ ; dark red: sequential, red: tapered) and stress ( $\sigma_{\text{yield point}}$ ; orange: sequential, yellow: tapered) at the yield point in dependence of the molar mass.



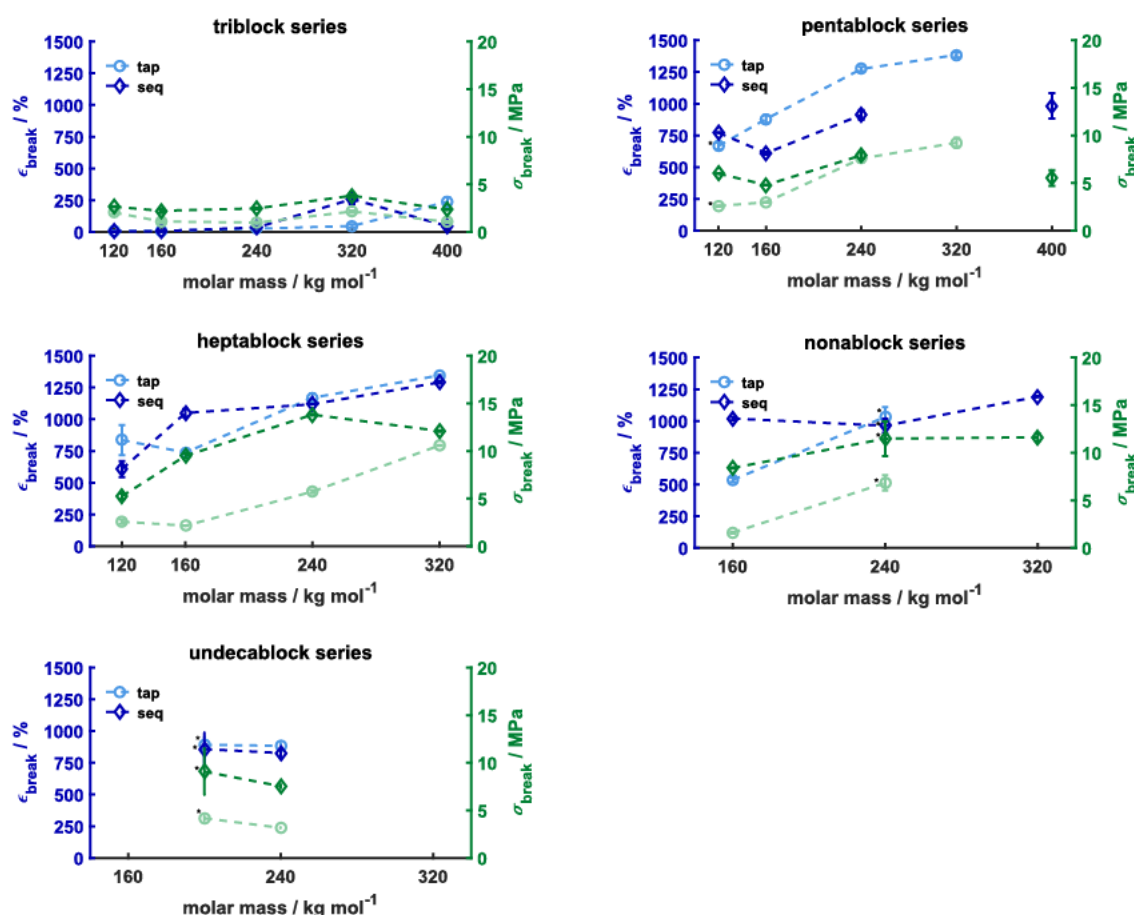


Figure S48: Characteristics of the break point of the multiblock copolymer series of differing block number (top left: tri-, top right: penta-, middle left: hepta-, middle right: nona-, bottom left: undecablock copolymers) in dependence of their overall molar mass. Strain ( $\epsilon_{\text{break}}$ ; dark blue: sequential, blue: tapered) and stress ( $\sigma_{\text{break}}$ ; dark green: sequential, pale green: tapered) at the break point are plotted with varying molar mass.

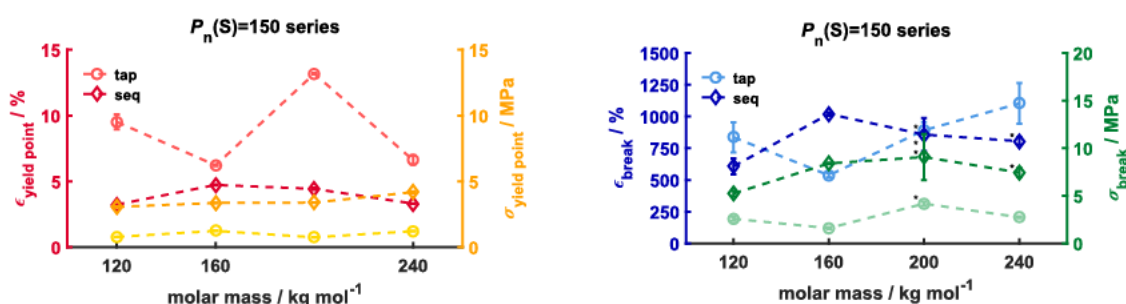


Figure S49: Characteristics of the yield and the break point of the polymers with a degree of polymerization of 150 polystyrene units per PS block in dependence of their overall molar mass (120 kg·mol<sup>-1</sup> heptablock, 160 kg·mol<sup>-1</sup> nonablock, 200 kg·mol<sup>-1</sup> undecablock, 240 kg·mol<sup>-1</sup> tredecablock). Left: Plot of the strain ( $\epsilon_{\text{yield point}}$ ; dark red: sequential, red: tapered) and stress ( $\sigma_{\text{yield point}}$ ; orange: sequential, yellow: tapered) at the yield point for the triblock copolymers with varying molar masses. Right: Plot of the strain ( $\epsilon_{\text{break}}$ ; dark blue: sequential, blue: tapered) and stress ( $\sigma_{\text{break}}$ ; dark green: sequential, pale green: tapered) at the break point for the triblock copolymers with varying molar masses.

- [1] a) M. W. Matsen, F. S. Bates, *J. Chem. Phys.* 1997, 106, 2436; b) N. Hadjichristidis, G. Floudas, S. Pispas, *Block copolymers. Synthetic strategies, physical properties, and applications*, Wiley-Interscience, Hoboken, N.J, 2003.





---

# CHAPTER 4

***(SIS)<sub>x</sub> Multiblock Copolymers: Controlling  
Recovery Properties by the Chain Connectivity  
Comparing Linear and Star-Shaped Multiblock  
Copolymers***

---



## CHAPTER 4

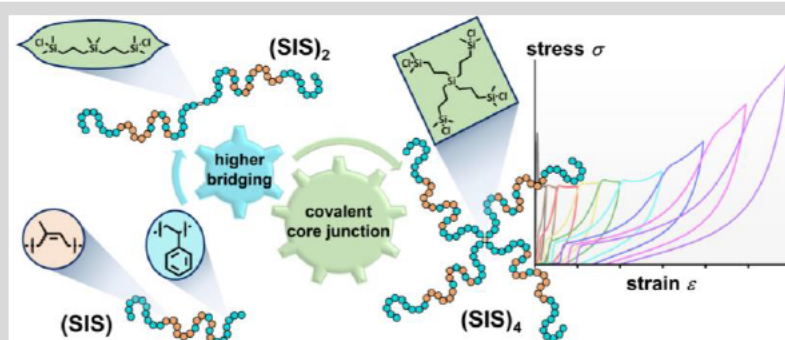
To be Submitted

# *(SIS)<sub>x</sub>* Multiblock Copolymers: Controlling Recovery Properties by the Chain Connectivity Comparing Linear and Star-Shaped Multiblock Copolymers

Ramona D. Barent<sup>1,2</sup>, Philipp von Tiedemann<sup>1,2</sup>, and Holger Frey<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany

<sup>2</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany



The mechanical properties of thermoplastic elastomers are compared for different chain architectures. Tapered polystyrene-*block*-poly(isoprene-*grad*-styrene) (SIS) triblock architectures are compared to linear (SIS)<sub>2</sub> pentablock and star-shaped (SIS)<sub>4</sub> multiblock architectures, which were synthesized by the “arm-first” coupling approach. Targeted molar masses per SIS arm ranged from 20–60 kg·mol<sup>−1</sup>, keeping the polystyrene fraction unaltered at 60 wt%. Uniaxial tension measurements revealed superior toughness for the linear pentablock copolymers and star-shaped multiblock copolymers for equal molar masses per arm, which approached each other for 40 kg·mol<sup>−1</sup> per arm reaching a plateau value of  $U=80\text{--}85\text{ MJ}\cdot\text{m}^{-3}$ . At this point, the covalent linkage of the star architecture does not provide further resilience. Yet, both (SIS)<sub>2</sub> and (SIS)<sub>4</sub> are tougher than SIS due to higher bridging fractions. Cyclic strain experiments showed superior final recovery after 5 minutes of rest for the star-shaped multiblock copolymer, which ranged around 100% for strains  $\leq 100\%$ . However, this structure exhibited poor rapid recovery during receding, whereas the linear architectures performed better due to their higher chain flexibility. For high strains, initial and final recoveries converged for all architectures. These results indicate that the covalent junction of the vitrifying core improves recovery but cannot suppress a permanent set at large deformation.

## Introduction

The term thermoplastic elastomers (TPEs) designates a class of materials, which is unique due to its elastomeric properties at considerable toughness, but in contrast to vulcanized elastomers is also melt-processable.<sup>[1]</sup> These inherent properties are achieved by a smart combination of chemical and physical linkages.<sup>[2]</sup> TPEs are based on block copolymer structures with at least two vitrifying blocks, consisting of a polymer with high glass transition temperature (high- $T_g$ ), e.g., polystyrene (PS).<sup>[2]</sup> The chemical linkage to a soft and rubbery polymer block with a low glass-transition temperature (low- $T_g$ ), e.g., polyisoprene (PI), results in combined mechanical properties upon nanophase separation.<sup>[3]</sup> The latter is crucial, since the segregation results also in bridged chain conformations with the high- $T_g$  blocks of one block copolymer being tethered in neighboring nanodomains.<sup>[4–7]</sup> This physically cross-linked network provides elasticity and mechanical stability.<sup>[2]</sup>

To realize nanophase separation in an accessible temperature range, a certain degree of polymerization has to be employed, which is lower for block copolymers with more pronounced incompatibility of the constituent polymers.<sup>[8]</sup> When the material is heated above the glass-transition temperature of the vitrifying domains ( $T_g(\text{PS})=100\text{ }^\circ\text{C}$ ), both phases behave liquid-like. However, the energy barrier for the flow in the still segregated melts is large, resulting in high viscosities and elasticities. Only upon accessing the order-disorder transition temperature ( $T_{\text{ODT}}$ ), above which the physical crosslinks are broken, the melt is disordered. Therefore, the demand for melt processability of TPEs is an order-disorder transition temperature close to the higher glass transition temperature, allowing for processing at rather low temperatures from the homogeneous melt.<sup>[1,9]</sup>

Therefore, the herein discussed thermoplastic elastomers have the important advantage of a facile processability and moreover reprocessability in comparison to chemically crosslinked elastomers, i.e., vulcanized rubbers. However, the downside of the mere physical crosslinking in TPEs compared to chemically crosslinked rubbers is the permanent set upon plastic deformation of the vitrified domains.<sup>[10]</sup> Attempts to enhance the mechanical properties, such as recovery, focus on chain architectures with multiple physical crosslinks per chain. By increasing the connectivity between the separated domains, an improved energy distribution is expected.<sup>[11]</sup> This can be achieved employing either linear multiblock copolymers or branched chain architectures, the latter exhibiting a covalent junction at the core of the star-shaped architecture. The effect of star-architectures has been studied extensively, however in most cases of star-branched TPEs, the number of arms is not well-defined.<sup>[12]</sup>

Register and coworkers investigated fully hydrogenated styrene-butadiene star-shaped architectures with 6 arms of poly(vinyl cyclohexane)-*block*-poly(ethylene propylene) coupled at the rubbery end (C-EP)<sub>6</sub> and compared its mechanics to the linear counterpart (C-EP)<sub>2</sub> prepared with a bifunctional coupling agent.<sup>[13]</sup> Both polymers had equal molar masses per arm, comparable domain sizes, and expectedly a cylindrical morphology, albeit this could not be verified with absolute certainty due to the lack of well-developed higher order SAXS reflections. Therefore, the authors concluded rather limited long-range order for the samples in question. However, they were able to demonstrate that the star-shaped polymer recovered rapidly and finally to a larger extent than the linear analogues, although the material's toughness was the same. At higher applied strain levels, the recovery values approached each

other. Further studies revealed higher strength for  $(SI)_x$  star copolymers compared to their linear analogues.<sup>[11,14]</sup>

Hillmyer and coworkers focused on sustainable  $(AB)_x$  polyester TPEs with crystalline poly(L-lactide) domains and flexible poly( $\gamma$ -methyl- $\epsilon$ -caprolactone) mid blocks.<sup>[15]</sup> Star-shaped architectures with  $x=4$  and 6 arms were compared to linear analogues ( $x=2$ ), which were prepared using a bifunctional rather than a tetra- or hexafunctional initiator. SAXS measurements revealed either spherical or cylindrical PLLA domains with poor long-range order and comparable domain sizes for the  $(AB)_x$  star-shaped architectures ( $x=4, 6$ ). Furthermore, for constant molar mass per arm, they demonstrated superior tensile strength, toughness, and recovery for the star architectures. Yet, the ultimate properties of the four- and six-armed architectures were comparable.

Concerning star-shaped  $(SIS)_x$  architectures, Meyer and Widmaier investigated these polymer structures with a polystyrene core and PS end chains for various arm numbers and compared their mechanical properties to  $(SI)_x$  star architectures.<sup>[16]</sup> A significant increase in tensile shear strength could be observed when implementing a covalently linked core, which was capable of forming a glassy domain. However, the number of arms per specimen was only given as an average value, since divinylbenzene was used as a coupling agent.

Recently, Wang *et al.* presented an investigation of tapered star-shaped  $(SI_n)_x$  multiblock copolymers with eight arms.<sup>[17]</sup> The arms were synthesized by repetitive (1-3 times) statistical anionic copolymerization of isoprene and styrene, yielding tapered di-, tetra-, and hexablock structures. Coupling of the living polystyryllithium chain ends yielded star-shaped structures with an outer polyisoprene end block. In consequence, bulk properties were governed by viscous flow at moderate temperatures, the transition temperature decreasing with increasing number of tapered blocks per arm.

Herein, we report tensile test and recovery data of linear styrene-isoprene SIS triblock copolymers and analogues with extended architectures. These comprise both linear SIS-SIS pentablock copolymers and star-shaped SIS multiblock copolymers with four arms. The number of arms was precisely defined using recently published chlorosilane coupling agents.<sup>[18]</sup>

## Experimental Section

### Materials and General Polymerization Procedure

The solvents cyclohexane (Fisher Science,  $\geq 99.8\%$ ) and tetrahydrofuran (THF, Fisher Science,  $\geq 99.8\%$ ) were dried over sodium with benzophenone as an indicator. Methanol (MeOH, Fisher Science,  $\geq 99.9\%$ ) was used as purchased but degassed with argon for the termination of living chain ends. The stabilizer of isoprene (I, Acros Organics, 98%) and styrene (S, Acros Organics, 99%) was removed by filtering the monomers through a column containing basic aluminum oxide and purified hereafter by degassing and distillation over calcium hydride (Acros Organics, 93%). *Sec*-Butyllithium (*sec*-BuLi, Acros Organics, 1.3 M in cyclohexane/hexane (92/8)) was used as supplied. The coupled chain architectures were synthesized *via* the “arm-first” approach. As coupling agents chlorosilanes were chosen since they are least prone to side reactions. C3 alkyl spacers between the chlorosilane moieties and the use of monochloro-dimethylsilyl groups for

coupling ensured complete coupling efficiencies due to the less-dense cores compared to the sterically hindered tetrachlorosilane, and subsequent fractionation to isolate the desired polymer was circumvented. Bis-3-(chloro-dimethylsilyl)propyl)dimethylsilane and tetra(3-(chloro-dimethylsilyl)-propyl)-silane were used as bifunctional and tetrafunctional coupling agents, respectively. Furthermore, the coupling agent was dissolved in tetrahydrofuran prior to addition. THF is known to enhance the coupling efficiency due to the shift of the equilibrium of the aggregated chain ends towards solvated ions. Detailed synthesis description can be found elsewhere.<sup>[18]</sup>

All purification and reaction steps were conducted under Schlenk condition, meaning that all glassware was flame-dried three times prior to use and all manipulations were carried out either under high-vacuum ( $1 \cdot 10^{-3}$  mbar) or an argon atmosphere. First, the monomers were dried under reduced pressure and room temperature over ground calcium hydride over night after degassing by three freeze-thaw-cycles. On the next day, the monomers were distilled and transferred into an argon-filled glovebox. Cyclohexane was freshly distilled under normal pressure and drained into an evacuated 250 mL glass reactor sealed with a fluoropolymer stopper.

The initiator *sec*-BuLi was added to the reaction flask containing cyclohexane and styrene inside the glovebox *via* a syringe. The reaction time for full monomer consumption was calculated using a kinetic Monte-Carlo simulation. Details can be found in the Supp. Inf. of previous publications.<sup>[2,19]</sup> To guarantee full monomer conversion, the calculated reaction times were extended by 10%. Subsequently, a mixture of styrene and isoprene was added to the living polystyryllithium solution in order to form the gradient IS diblock sequence.

The quantity of styrene was equal for both addition steps. The concentration of the final monomer/solvent mixture was in the range of 10-15 wt% to guarantee homogeneous mixing. After full monomer consumption, the arms were either terminated with degassed methanol to obtain tapered SIS triblock structures or coupled to pentablock or star architectures. Therefore, 0.5 equivalents for the bifunctional coupling agent or 0.25 equivalents of the tetrafunctional coupling agent were added dropwise as a stock solution in THF. For this purpose, 100 equivalents of THF per equivalent lithium were implemented. The coupling reaction was run until decolorization, which required less than 1 hour. The polymers were precipitated by pouring the reaction solution into a 5-10-fold excess of methanol containing small amounts of the antioxidant BHT (butylated hydroxy toluene), dried at reduced pressure for at least one week and stored in the absence of light at -20 °C under argon atmosphere.

### Size Exclusion Chromatography

SEC measurements of the linear (SIS)<sub>2</sub> pentablock copolymers were carried out in THF on an instrument consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump, a set of three MZ-Gel SDplus columns based on SDV with particle sizes of 5 µm (porosities of 100, 103 and 105 Å for molecular weight areas <3 000, 1 000-40 000 and 10 000-2 000 000 Da, respectively) and RI (35 °C) as well as UV detectors (254 nm). 100 µL of the sample solution were loaded, operating at room temperature at flow rates of 1 mL·min<sup>-1</sup>. Polystyrene (PS) standards used for calibration were provided by Polymer Standards Service GmbH. Number average molar masses  $M_n$  and dispersities  $\bar{D}$  were calculated from the RI signal. Size exclusion

measurements of the star-shaped (SIS)<sub>4</sub> multiblock copolymers were performed using a Waters 515 pump, two 30 cm Polymer Laboratories PLgel Mixed-C columns, a Wyatt Technologies miniDAWN TREOS light-scattering detector (658 nm) and a Wyatt Optilab T-rEX RI detector (25 °C). Weight average molar masses  $M_w$  were calculated from the multiangle laser light-scattering detector signals. For this purpose, the  $dn/dc$  values were weight-fraction-weighted with respect to the PS and PI contents known from NMR analysis. The respective homopolymer  $dn/dc$  values of PS=0.189 mL·g<sup>-1</sup> and PI=0.130 mL·g<sup>-1</sup> were measured at 25 °C and 658 nm. The apparent dispersities  $\bar{D}$  were derived from the RI signal using linear PS standards.

## NMR Spectroscopy

<sup>1</sup>H NMR spectra were using a Bruker Avance II 400 spectrometer with 400 MHz and a 5 mm BBFO-Smart-Probe with z-gradient. The spectra were referenced internally to residual proton signals of deuterated chloroform (CDCl<sub>3</sub>).

## Tensile and Recovery Testing

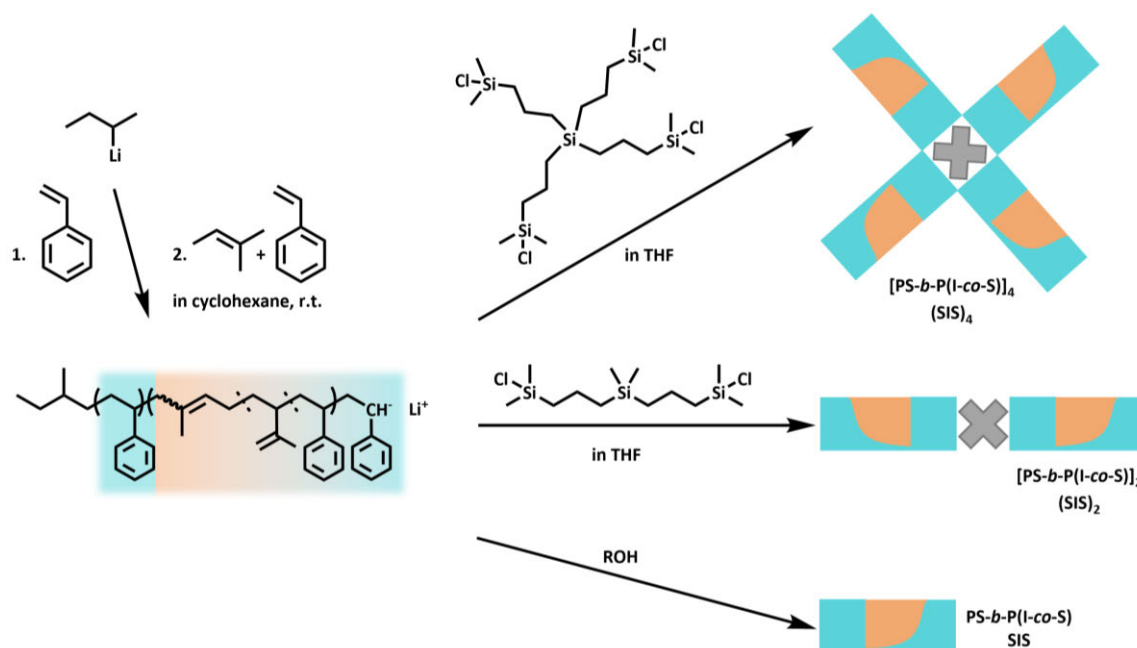
Uniaxial tensile tests as well as initial and final recovery measurements were performed using an Instron 6865 load frame. All films were prepared by dissolving 2.5-3 g of the azeotropically dried polymer in 2 mL chloroform, casting the solution into a glass petri dish, followed by slow evaporation (7 days) at room temperature and normal pressure and finally full removal of the solvent under reduced pressure. Dogbone shaped specimens were stamped out of the films using an ASTM D1708 dogbone die. For all tensile tests, the specimens were uniaxially stretched with a rate of 5.08 cm·min<sup>-1</sup> at room temperature. Characteristic parameters were determined averaging over at least 3 independent experiments. The ultimate strength  $\sigma_{\text{break}}$  and strain at break  $\varepsilon_{\text{break}}$  were extracted from the point of failure. The ultimate toughness  $U$  of the materials was calculated by integration of the stress-strain curve. Recovery measurements were performed applying cyclic strains. The specimens were strained to a preset strain  $\varepsilon_a$  with a crosshead speed of 5.08 cm·min<sup>-1</sup>. After reaching the preset strain, the crosshead was returned to its initial position at the same rate. After the sample was allowed to rest for 5 minutes, the next cyclic strain cycle was started. The prescribed strain was continuously increased, with values of 25, 50, 100, 150, 200, 300, 400, 500 and finally 600%. The initial residual strain  $\varepsilon_s^i$  was taken from the point where the stress reached zero upon unloading. The final residual strain  $\varepsilon_s^f$  corresponds to the strain at which the stress became nonzero in the subsequent advancing cycle. The initial and final recovery was backcalculated using the equation  $R=1-\varepsilon_s/\varepsilon_a$  (see Figure S2 for an exemplified determination of the residual strains).

## Results and Discussion

### Polymer Characterization

In this work, bulk properties of tapered multiblock copolymers are compared for different chain architectures. For this purpose, PS-*b*-P(I-co-S) triblock copolymers (abbreviated as SIS) with equal PS block length, which are capable of mid block bridging, were coupled by a bifunctional and tetrafunctional coupling agent to linear pentablock copolymers (SIS-SIS = (SIS)<sub>2</sub>) and star-shaped copolymers with four triblock arms ((SIS)<sub>4</sub>), respectively (see Figure 1).

The tapered diblock sequence was obtained by the statistical copolymerization of isoprene and styrene in the nonpolar solvent cyclohexane, which features a polyisoprene block with few styrene units, followed by a rather sharp gradient transition to a pure polystyrene block. The block profile of the tapered structures shown in Figure 1 were simulated based on the reactivity ratios of isoprene and styrene at 40 °C in cyclohexane ( $r_I=10.9$  and  $r_S=0.029$ ) for equimolar ratios of the comonomers.<sup>[19]</sup> The polymers synthesized differ in their overall molar masses (40–240 kg·mol<sup>-1</sup>), allowing a systematic comparison of polymers with the same molar mass per arm but varying architecture and hence overall molar mass. Besides, conclusions on the influence of the chain architecture at constant overall molar mass can be drawn.



**Figure 1:** One-pot synthesis routes to tapered SIS triblock copolymers by protic termination (bottom), to linear (SIS)<sub>2</sub> pentablock copolymers via a bifunctional coupling agent (middle), and to star-shaped (SIS)<sub>4</sub> copolymers using a tetrafunctional coupling agent (top). The distribution of the comonomers isoprene (orange) and styrene (cyan) along the chains is visualized by bars showing the molar-based composition diagram, i.e., the mean incorporation (y axis) at every conversion (x axis).

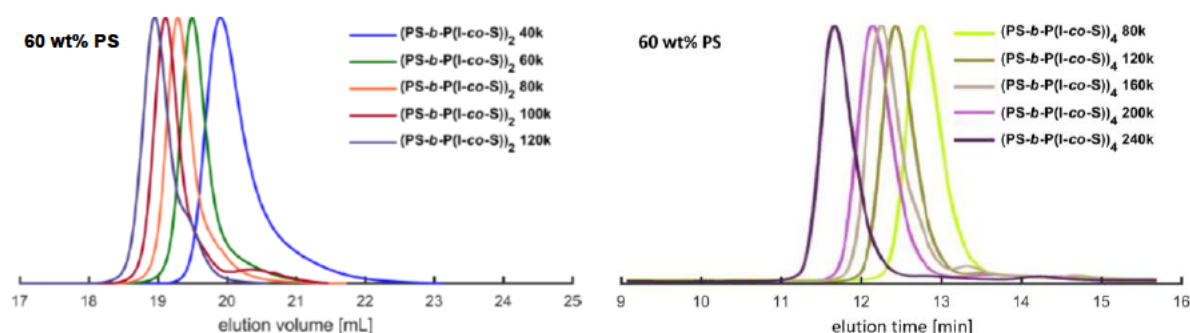
The polymers discussed were synthesized with a monomer ratio of 50 mol% isoprene and 50 mol% styrene. The molecular characteristics of the synthesized polymers are summarized in Table 1. The “arm-first” approach employing chlorosilane coupling agents of high coupling efficiency due to spatially decoupled monochloro-dimethylsilyl coupling agents and the presence of THF allowed for the synthesis of well-defined polymer structures without the necessity of subsequent fractionation.<sup>[18]</sup> The SEC traces (Figure 2) show only minor traces of



lower molar mass side products that are most pronounced for the higher molar mass polymers, which can be assigned to either PS homopolymers resulting from termination upon adding the isoprene-styrene mixture or uncoupled arms.

Based on self-consistent field theory predictions, for polymers with 50 mol% isoprene and 50 mol% styrene ( $\approx 60$  wt%, 57 vol% PS) lamellar (LAM) morphologies are expected for all chain architectures.<sup>[20,21]</sup> In case of the triblock precursors and star-shaped (SIS)<sub>4</sub> multiblock copolymers, this was proven by SAXS measurements published elsewhere.<sup>[22]</sup>

Furthermore, analogous polymers were synthesized with 70 mol% isoprene and 30 mol% styrene ( $\approx 40$  wt%, 36 vol% PS). Since they exhibit different morphologies ((SIS)<sub>1</sub>: hexagonally packed cylinders (CYL), (SIS)<sub>4</sub>: irregular bicontinuous morphology (BIC))<sup>[22]</sup>, a straightforward comparison is not possible. The molecular characteristics and recovery data of these polymers can be found in the Supp. Inf. (see Table S1 and Figure S1 for information on polymer characterization and Figure S3 and S4 for recovery data).



**Figure 2:** SEC traces (THF, PS calibration standard, RI detector) of the 60 wt% PS polymer series (left: linear (SIS)<sub>2</sub> pentablock copolymers, right: star-shaped (SIS)<sub>4</sub> multiblock copolymers). The derived number average molar masses and dispersities are summarized in Table 1.

**Table 1:** Overview of the characteristics of the linear and star-shaped tapered multiblock copolymers obtained by coupling. The corresponding SEC traces are given in the SI (see Figure S1).

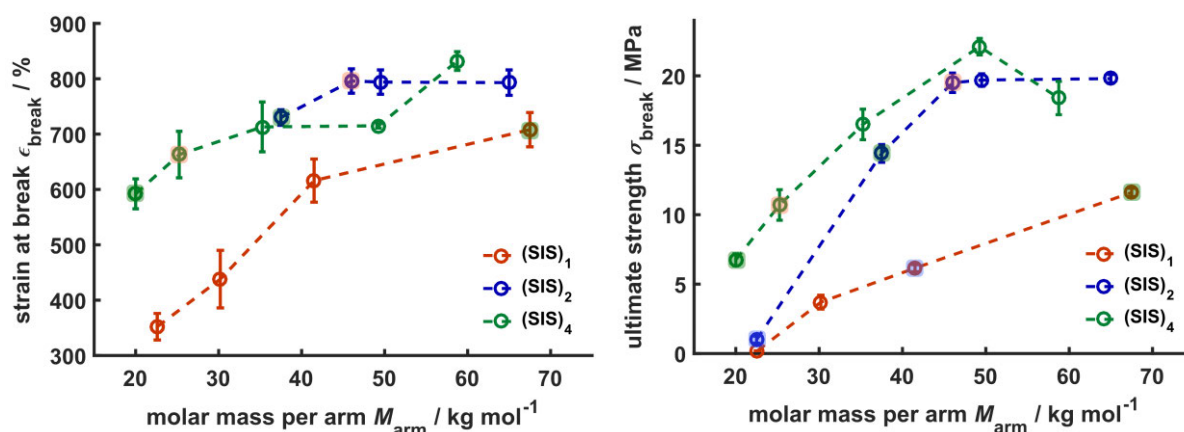
| (SIS) <sub>x</sub><br>block type | target w(S)<br>[%] | target M <sub>n</sub><br>[kg·mol <sup>-1</sup> ] | target M <sub>n</sub> /arm<br>[kg·mol <sup>-1</sup> ] | M <sub>n</sub> <sup>a</sup> or M <sub>w</sub> <sup>b</sup><br>[kg·mol <sup>-1</sup> ] | Đ <sup>a</sup> | w(S) <sup>c</sup><br>[%] |
|----------------------------------|--------------------|--------------------------------------------------|-------------------------------------------------------|---------------------------------------------------------------------------------------|----------------|--------------------------|
| (SIS) <sub>2</sub>               | 60                 | 40                                               | 20                                                    | 45                                                                                    | 1.16           | 57                       |
|                                  | 60                 | 60                                               | 30                                                    | 75                                                                                    | 1.09           | 58                       |
|                                  | 60                 | 80                                               | 40                                                    | 92                                                                                    | 1.09           | 58                       |
|                                  | 60                 | 100                                              | 50                                                    | 99                                                                                    | 1.17           | 57                       |
|                                  | 60                 | 120                                              | 60                                                    | 130                                                                                   | 1.09           | 57                       |
| (SIS) <sub>4</sub>               | 60                 | 80                                               | 20                                                    | 80                                                                                    | 1.05           | 65                       |
|                                  | 60                 | 120                                              | 30                                                    | 101                                                                                   | 1.06           | 63                       |
|                                  | 60                 | 160                                              | 40                                                    | 141                                                                                   | 1.06           | 60                       |
|                                  | 60                 | 200                                              | 50                                                    | 197                                                                                   | 1.09           | 62                       |
|                                  | 60                 | 240                                              | 60                                                    | 235                                                                                   | 1.05           | 58                       |

<sup>a</sup> Determined by SEC (THF, PS calibration standard, RI detector). Number average molar masses are given for the linear (SIS)<sub>2</sub> pentablock copolymers, which are overestimated because of the isoprene incorporation. Dispersities are derived from the RI signal for both linear (SIS)<sub>2</sub> pentablock copolymers and star-shaped (SIS)<sub>4</sub> multiblock copolymers; <sup>b</sup> determined by SEC (THF, MALLS detector for the star-shaped (SIS)<sub>4</sub> multiblock copolymers); <sup>c</sup> determined by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) integrating on the 1,4-polyisoprene ( $\delta=4.8$ -5.4 ppm), 3,4-polyisoprene ( $\delta=4.5$ -4.8 ppm), and polystyrene signals ( $\delta=6.2$ -7.4 ppm).

## Tensile Properties

The viscoelastic properties of block copolymers are ruled by manifold parameters, such the strength of the phase separation into different domains, the morphology formed thereupon, and the chain configurations.<sup>[23,24]</sup> The latter comprise looped, entangled loop and bridged configurations of the polymer chains.<sup>[4–7]</sup> Bridging, i.e., physical connection of adjacent nanodomains by the location of two PS blocks in different domains, contributes most to a material's strength and toughness and can be improved by either employing higher block numbers or going from linear to star-shaped architectures.<sup>[13,24,25]</sup> For this purpose, PS-*b*-P(I-co-S) triblock copolymers (SIS) with equal PS block length, capable of mid block bridging, were coupled by a bifunctional and a tetrafunctional coupling agent into linear pentablock copolymers ((SIS)<sub>2</sub>) and star-shaped copolymers with four triblock arms ((SIS)<sub>4</sub>), respectively.

In the following, the ultimate properties of the tapered multiblock copolymers are compared for these different chain architectures. Figure 3 shows the strain as well as the stress at the point of mechanical failure upon uniaxial deformation for the polymers containing 60 wt% polystyrene and hence lamellar morphologies. For the SIS triblock copolymers (red) it is clearly visible that the materials can be stretched to a larger extent ( $\epsilon_{\text{break}}$ ) with increasing molar mass because they can withstand higher forces ( $\sigma_{\text{break}}$ ) without breaking. This is also reflected in an overall increase in toughness (see Figure 4) with increasing molar masses.

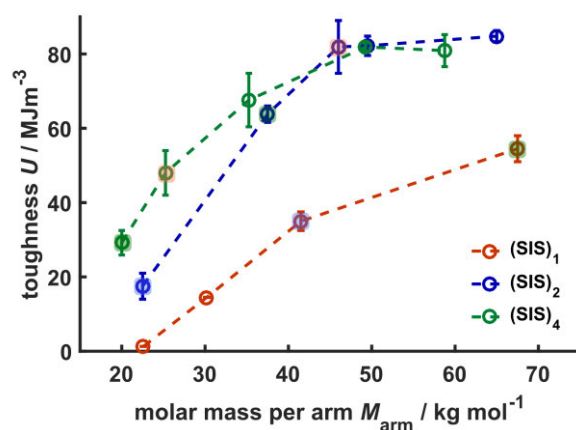


**Figure 3:** Characteristics of the break point (left: strain at break  $\epsilon_{\text{break}}$ , right: ultimate strength  $\sigma_{\text{break}}$ ) of the 60 wt% PS polymer series investigated in dependence on the molar mass per arm. Red: linear triblock copolymers SIS, blue: linear pentablock copolymers (SIS)<sub>2</sub>, green: star-shaped multiblock copolymers (SIS)<sub>4</sub>. Polymers of equal overall molar mass are highlighted by colored boxes (blue: 40 kg·mol<sup>-1</sup>, green: 80 kg·mol<sup>-1</sup>, red: 100 kg·mol<sup>-1</sup>).

This can be explained by their chain conformation. Besides a looped conformation where both PS blocks are located in the same PS domain, the triblock copolymers are capable of bridged chain conformations.<sup>[2,26]</sup> Bridges are formed, when the two PS block junctions reside in different PS domains, enhancing mechanical properties together with entangled loops.<sup>[27]</sup> One factor contributing to the increase in ultimate properties with increasing molar masses is the higher number of entanglements. With entanglement molecular weights of *cis*-1,4-PI (5.4 kg·mol<sup>-1</sup>) and polystyrene (13.3 kg·mol<sup>-1</sup>)<sup>[28]</sup>, for the lowest molar mass of ( $M(\text{SIS})=20 \text{ kg}\cdot\text{mol}^{-1}$ ,  $M(\text{PI})=8 \text{ kg}\cdot\text{mol}^{-1}$  PI), the entanglement molecular weight is not significantly exceeded. On the contrary, for the highest molar mass ( $M(\text{SIS})=80 \text{ kg}\cdot\text{mol}^{-1}$ ,

$M(\text{PI})=32 \text{ kg}\cdot\text{mol}^{-1} \text{ PI}$ ), the PI mid block equals the 6-fold of the entanglement molecular weight, further contributing to the material's toughness.

Another factor is the extent of segregation, which is indispensable for domain bridging and counteracts chain pullout of a PS block, thereby providing resilience. At given volume fractions of the constituent polymers, the segregation strength depends on the product of the degree of polymerization  $N$  and the Flory-Huggins interaction parameter  $\chi$  of these polymers. For triblock copolymers, the product of  $\chi N$  has to exceed 18 for nanophase separation into a lamellar morphology.<sup>[29]</sup> With  $\chi_{\text{PI/PS}}=-0.0419+39T^{-1}$  ( $T$  in K)<sup>[30]</sup>, this theoretical limit is just reached for the lowest molar mass ( $\chi N(20 \text{ kg}\cdot\text{mol}^{-1})_{\text{r.t.}}\approx 20.6$ ), which is why a certain miscibility between the blocks within this weak segregation regime is to be expected. Segregation becomes more pronounced with increasing molar masses ( $\chi N(30 \text{ kg}\cdot\text{mol}^{-1})_{\text{r.t.}}\approx 31$ ,  $\chi N(40 \text{ kg}\cdot\text{mol}^{-1})_{\text{r.t.}}\approx 41$ ,  $\chi N(50 \text{ kg}\cdot\text{mol}^{-1})_{\text{r.t.}}\approx 52$ , and  $\chi N(60 \text{ kg}\cdot\text{mol}^{-1})_{\text{r.t.}}\approx 62$ ), which reduces the probability for PS chain pullout from the PS nanodomains. Together with the increase of chain entanglements, both factors enhance resilience with increasing molar mass.



**Figure 4:** Toughness of the 60 wt% PS polymer series investigated in dependence on the molar mass per arm. Red: linear triblock copolymers SIS, blue: linear pentablock copolymers  $(\text{SIS})_2$ , green: star-shaped multiblock copolymers  $(\text{SIS})_4$ . Polymers of equal overall molar mass are highlighted by colored boxes (blue:  $40 \text{ kg}\cdot\text{mol}^{-1}$ , green:  $80 \text{ kg}\cdot\text{mol}^{-1}$ , red:  $100 \text{ kg}\cdot\text{mol}^{-1}$ ).

The same trend can be observed for the linear  $(\text{SIS})_2$  pentablock copolymers (blue). The overall higher ultimate properties for the pentablock copolymers with the same molar mass per arm result from the doubled overall molar mass by coupling each SIS triblock to generate a  $(\text{SIS})_2$  pentablock architecture. On top of the considerations drawn for the triblock copolymers, the bridging/looping ratio is a dictating parameter. Spontak and coworkers predicted an increase in the bridging fraction with increasing block number from roughly 60% for the triblock to 75% for a pentablock even in bulk.<sup>[25]</sup> The comparison of triblock and pentablock copolymers of the same overall molar mass reveals a higher toughness for the SIS triblock for low molar masses ( $40 \text{ kg}\cdot\text{mol}^{-1}$ , blue boxes), but higher toughness for the  $(\text{SIS})_2$  pentablock for higher molar masses ( $80 \text{ kg}\cdot\text{mol}^{-1}$ , green boxes). This is explained in the following manner: for the  $40 \text{ kg}\cdot\text{mol}^{-1}$  polymers, the individual block lengths of the pentablock result in poor segregation, whereas the triblock exhibits well-defined domains and minor PS chain pullout. Only at higher molar masses, the phase separation of the pentablock is sufficient, thus outperforming the triblock due to the increased bridging.

The star-shaped  $(\text{SIS})_4$  multiblock copolymers (green) presented in this work have been examined and discussed in depth previously.<sup>[22]</sup> Besides the mechanical performance, thermal

and morphological properties have been investigated. DSC measurements of the polymers revealed two glass transition temperatures, the first in the range of  $-33\text{ }^{\circ}\text{C}$  and a second  $T_g$  at roughly  $60\text{ }^{\circ}\text{C}$  for low molar masses, approaching  $100\text{ }^{\circ}\text{C}$  with increasing molar mass. The higher glass transition of the polyisoprene-rich segments (pure PI:  $T_g(\text{PI}) \approx -65\text{ }^{\circ}\text{C}$ ) can be explained by the intrinsic incorporation of styrene units into the PI-rich block due to the tapered microstructure. However, the molar mass dependence of the glass transition of polystyrene (pure PS:  $T_g(\text{PS}) = 100\text{ }^{\circ}\text{C}$ ) is a first indication for a weak phase separation for short individual block lengths, which becomes more pronounced at elevated molar masses. SAXS analysis revealed disordered morphologies for the  $80$  and  $120\text{ kg}\cdot\text{mol}^{-1}$  star copolymers, the latter exhibiting an order-disorder transition when cooled to  $20\text{ }^{\circ}\text{C}$ . High molar mass star copolymers ordered into lamellae at room temperature. The  $160\text{ kg}\cdot\text{mol}^{-1}$  tetra-arm star showed an order-disorder transition at  $125\text{ }^{\circ}\text{C}$ . The  $T_{\text{ODT}}$ 's of the  $200$  and  $240\text{ kg}\cdot\text{mol}^{-1}$  star-shaped multiblock copolymers were not accessible, since they ranged above  $180\text{ }^{\circ}\text{C}$ . These findings are in line with theoretical considerations with regard to phase diagrams of star copolymers, predicting similar phase diagrams for  $(\text{AB})_n$  star block copolymers to those of diblock copolymers.<sup>[20]</sup> Matsen and Schick simulated phase diagrams for three- and five-arm star copolymers, which were topologically equivalent to the diblock copolymers, but showed larger regions of ordered morphologies for small volume fractions and shifted boundaries of the order-order transitions to higher volume fractions of the inner block. Consequently, the observation of two glass transitions for the low molar mass star copolymers is due to the phenomenon of self-concentration.<sup>[31]</sup> Tensile tests again reveal an increase in toughness of the four-arm star with increasing molar mass, however the magnitude of increase becomes smaller at higher molar masses. No obvious discontinuity between disordered and ordered polymers can be found, which might be a result of strain-induced ordering.

Comparing the linear  $(\text{SIS})_2$  pentablock with the star-shaped  $(\text{SIS})_4$  architecture, the values for toughness converge with increasing molar mass, and a plateau value is reached for molar masses of  $40\text{ kg}\cdot\text{mol}^{-1}$  per arm (see Figure 4). In conclusion, at that point the star architecture does not provide further resilience. For lower molar masses per arm, the toughness as well as the ultimate strength (see Figure 3) of the star-shaped  $(\text{SIS})_4$  is higher than the one of the linear  $(\text{SIS})_2$  pentablock copolymers. Since the star-shaped polymers can be considered as two pentablock copolymers chemically joined at their central linkages, bridging becomes more likely. This is reasoned in the core blocks tethered in a PS domain and four PS end blocks capable of forming a bridged chain conformation. Furthermore, backfolding can become less likely because of the denser core.<sup>[32]</sup> Therefore, star-shaped chain architectures exhibit an enhanced resistance to block pullout from the PS domains, which is of key importance for weakly segregated or disordered structures.

Finally, the tensile properties of  $(\text{SIS})_2$  and  $(\text{SIS})_4$  structures of equal molar masses ( $80\text{ kg}\cdot\text{mol}^{-1}$ , green boxes) are compared. The linear pentablock exhibits superior ultimate mechanical properties, because the individual block length is sufficient for strong segregation strength preventing chain pullout, which does not hold true for the star-shaped multiblock with comparably short individual blocks. Therefore, the increased bridging in case of the star-shaped copolymers cannot outweigh the increased PS chain pullout out of the disordered specimen featuring only weak self-concentration.

## Recovery Properties

Within the next section, the materials' recoveries are evaluated. For this purpose, the specimens were strained to a prescribed strain  $\varepsilon_a$ , which was successively increased from 25 to 50, 100, 150, 200, 300, 400, 500 and finally 600%. After attaining the prescribed strain, the crosshead was returned to its initial position at the same rate. Before starting the next stretching with the increased, prescribed strain, the specimen was allowed to rest for 5 minutes.

Figure 5 shows the stress-strain curves obtained for the three polymers with  $60 \text{ kg}\cdot\text{mol}^{-1}$  per arm and 60 wt% polystyrene but differing architecture. Analogous studies of the 40 wt% polystyrene polymers with  $60 \text{ kg}\cdot\text{mol}^{-1}$  per arm are given in the Supp. Inf. (Figures S3 and S4).

As discussed before, for these compositions the toughness of the linear  $(\text{SIS})_2$  pentablock and the star-shaped  $(\text{SIS})_4$  multiblock does not depend on the chain architecture anymore. With a plateau value ranging between  $U=80\text{--}85 \text{ MJ}\cdot\text{m}^{-3}$  (see Figure 4), the energy per unit volume of deformed material which is required for rupture is equal. However, the SIS triblock can absorb less energy ( $U\approx 50 \text{ MJ}\cdot\text{m}^{-3}$ ), which is also visible in the lower engineering stress necessary to reach the prescribed deformation (see Figure 5). Nonetheless, all three polymers ought to exhibit qualitatively similar morphologies, namely lamellae, which is why the recovery capability is solely determined by the chain architecture.

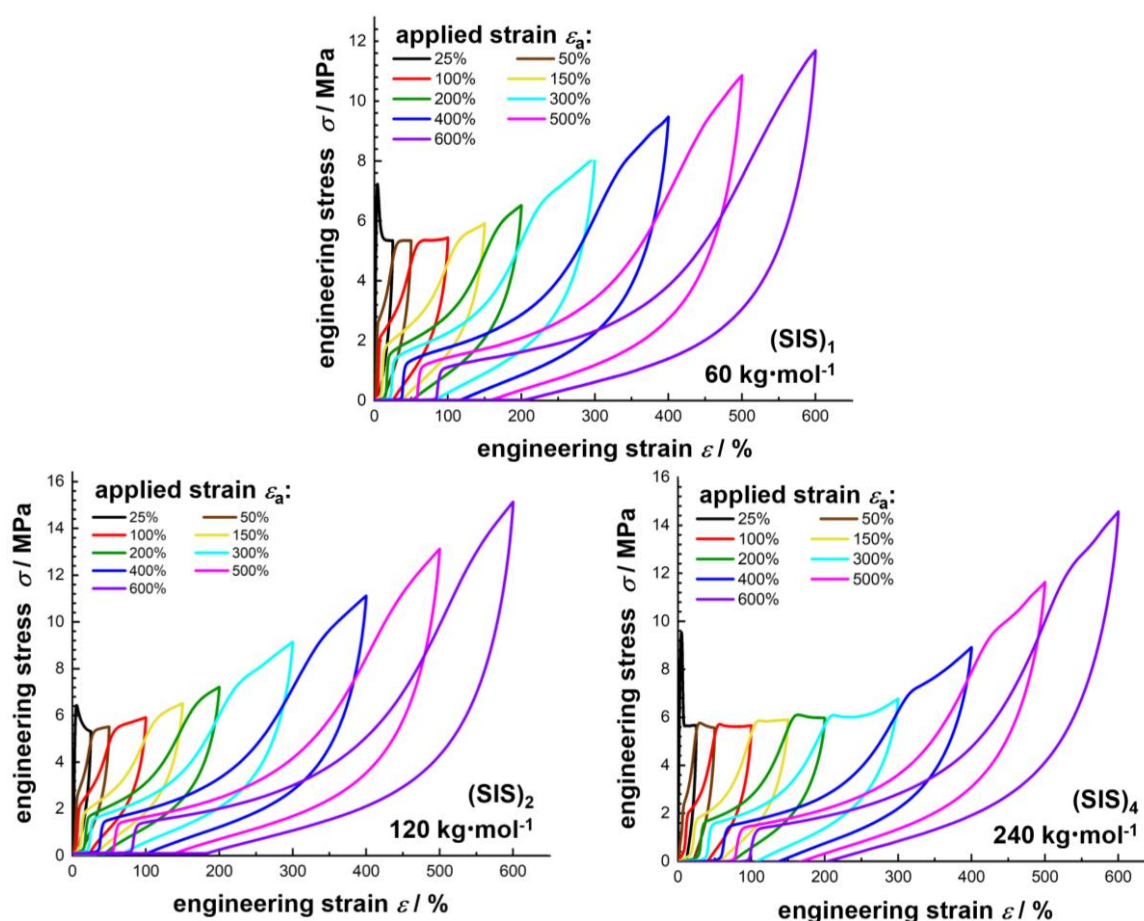
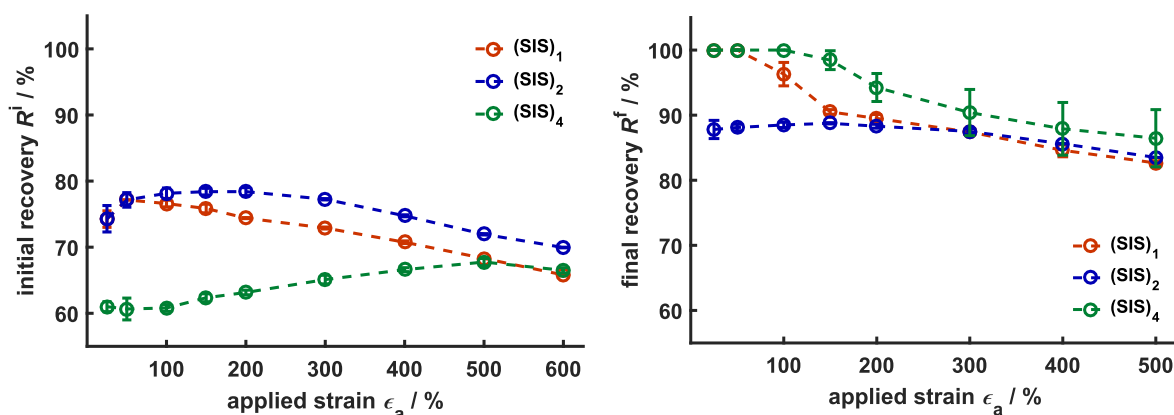


Figure 5: Strain hystereses for the three polymers with an equal molar mass per arm of  $60 \text{ kg}\cdot\text{mol}^{-1}$  and 60 wt% PS. Top: linear SIS triblock copolymer with an overall molar mass of  $60 \text{ kg}\cdot\text{mol}^{-1}$ , bottom left: linear  $(\text{SIS})_2$  pentablock copolymer with an overall molar mass of  $120 \text{ kg}\cdot\text{mol}^{-1}$ , bottom right: star-shaped  $(\text{SIS})_4$  multiblock copolymer with an overall molar mass of  $240 \text{ kg}\cdot\text{mol}^{-1}$ .



To quantify the recovery, the residual strain  $\varepsilon_s$  is measured; once after the stress first dropped to zero while receding the crosshead (initial residual strain  $\varepsilon_s^i$ ) and a second time when the stress became nonzero in the subsequent advancing cycle (final residual strain  $\varepsilon_s^f$ ). The initial and final recovery was calculated by  $R=1-\varepsilon_s \varepsilon_a^{-1}$  (see Figure S2 for an exemplified determination of the residual strains). In Figure 6 the initial recovery  $R^i$  as well as final recovery after 5 minutes of resting in the initial position  $R^f$  are plotted against the applied preset strain  $\varepsilon_a$ .



**Figure 6:** Initial (left,  $R^i$ ) and final recovery (right,  $R^f$ ) in dependence of the applied prescribed strain  $\varepsilon_a$  for the three strain hysteresis shown in Figure 5.

Interestingly, the linear (SIS)<sub>2</sub> pentablock (blue) shows a superior initial recovery ( $R^i$ , Figure 6, left) with up to 78% recovery at modest strain levels ( $\varepsilon_a \leq 300\%$ ), which means that the material recovers rapidly during receding. At high strain levels ( $\varepsilon_a > 300\%$ ), the recovery continuously drops to even 70% initial recovery. However, only an additional recovery of 10-15% can be observed during the 5 minutes rest ( $R^f$ , Figure 6, right).

The linear SIS triblock (red) shows the same initial recoveries as the (SIS)<sub>2</sub> pentablock at low strain levels ( $\varepsilon_a \leq 50\%$ ) and thereafter slightly reduced initial recoveries at higher strain levels, continuously decreasing to finally  $R^i = 66\%$  at 600% strain ( $R^i$ , Figure 6, left). On the contrary, the material recovers strongly during resting, which even resulted in 100% final recovery at low strain levels ( $\varepsilon_a \leq 50\%$ ) ( $R^f$ , Figure 6, right). At higher strain levels, the final recovery decreases rapidly, approaching  $R^f$  values equal to the (SIS)<sub>2</sub> pentablock copolymers at  $\varepsilon_a = 200\%$ .

In pronounced contrast, the star-shaped (SIS)<sub>4</sub> multiblock copolymer (green) features a peculiar recovery behavior. With  $R^i \approx 60-65\%$  the initial recovery is very poor at modest strain levels ( $\varepsilon_a \leq 300\%$ ) ( $R^i$ , Figure 6, left). At high strain levels ( $\varepsilon_a > 300\%$ ), the recovery continuously increases up to 68% initial recovery. Although recovery during receding is minor, the material shows superior final recoveries of  $R^f = 100\%$  at strain levels  $\varepsilon_a \leq 100\%$  ( $R^f$ , Figure 6, right). At higher strain levels, the final recovery decreases slightly, reaching  $R^f$  values of 87% at  $\varepsilon_a = 500\%$ . Hence, additional recoveries of 10-15% at high strain levels and additional recoveries of even 40% for modest strain levels are observed during 5 minutes rest.

This very different behavior can be explained by the covalent junction of the core PS block, which allows to distribute the stress evenly and provides a certain shape memory of the network at moderate strain levels. At higher strain levels, this feature is not able to suppress plastic deformation of the glassy domains anymore, which is why the recovery is worse in this case. On the contrary, the linear analogues exhibit a higher chain flexibility, enabling

comparably fast restoration of the initial state. Since the bridging fraction and also the ultimate toughness of the pentablock are higher than the values of the triblock, the latter shows slightly impaired recovery behavior during receding. Yet, an easier chain diffusion in case of the SIS triblock is a probable explanation for the superior final recovery at low strains. Still, also the linear counterparts face substantial restructuring of the glassy domains at higher strain levels, explaining the permanent set of all specimens upon large deformation.

## Conclusion

Coupling tapered conventional SIS triblock copolymers into either linear  $(\text{SIS})_2$  pentablock copolymers or four-arm star-shaped  $(\text{SIS})_4$  multiblock copolymers has a huge impact on the ultimate tensile properties as well as on the recovery properties. For these three different architectures but same molar mass per SIS triblock arm, the ultimate toughness increased in the order  $\text{SIS} < (\text{SIS})_2 < (\text{SIS})_4$ . This can be explained by the higher bridging fraction in both pentablock copolymers and star-shaped multiblock copolymers and further by the covalent core junction in star architectures. With increasing molar mass per arm, ultimate properties increased for all architectures, which is grounded in a more pronounced phase separation and increasing chain entanglements. Comparing the toughness of SIS,  $(\text{SIS})_2$  and  $(\text{SIS})_4$  for the same overall molar mass of  $80 \text{ kg}\cdot\text{mol}^{-1}$ , the linear pentablock exhibits superior mechanical properties. This originates from increased bridging at sufficient phase separation comparing  $(\text{SIS})_2$  and SIS. On the contrary, phase segregation of  $(\text{SIS})_4$  is insufficient due to the comparably short individual blocks and further potential constraints in the ordering process. Therefore, in this case the star architecture cannot compete with the linear counterpart. The recovery properties for SIS,  $(\text{SIS})_2$  and  $(\text{SIS})_4$  with the same molar mass per SIS triblock arm of  $60 \text{ kg}\cdot\text{mol}^{-1}$  revealed strong dependencies on the chain architectures. The star architecture exhibits superior final recovery compared to the linear analogues, but the recovery during receding is minor. With respect to the initial recovery, the linear pentablock performs best. On increasing the preset strain, the recoveries for all three architectures converge. Conclusively, the implementation of star-shaped architectures is recommendable for applications where small final permanent sets are important, but the material can rest between use. Complementary, linear multiblock architectures are well-suited for applications with quick successive mechanical deformations.

## References

- [1] J. Yan, R. J. Spontak in *Elastomer Blends and Composites*, Elsevier, **2022**, pp. 353–404.
- [2] M. Steube, T. Johann, R. D. Barent, A. H. Müller, H. Frey, *Prog. Polym. Sci.* **2022**, *124*, 101488.
- [3] H.-C. Kim, S.-M. Park, W. D. Hinsberg, *Chemical reviews* **2010**, *110*, 146.
- [4] K. Karatasos, S. H. Anastasiadis, T. Pakula, H. Watanabe, *Macromolecules* **2000**, *33*, 523.
- [5] K. Rasmussen, E. M. Kober, T. Lookman, A. Saxena, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 104.
- [6] H. Watanabe, Y. Matsumiya, T. Sawada, T. Iwamoto, *Macromolecules* **2007**, *40*, 6885.

- [7] S. S. Tallury, R. J. Spontak, M. A. Pasquinelli, *J. Chem. Phys.* **2014**, *141*, 244911.
- [8] a) P. J. Flory, *The Journal of Chemical Physics* **1942**, *10*, 51; b) M. L. Huggins, *J. Phys. Chem.* **1942**, *46*, 151; c) M. L. Huggins, *J. Am. Chem. Soc.* **1942**, *64*, 1712.
- [9] G. Holden, E. T. Bishop, N. R. Legge, *J. Polym. Sci., Part C: Polym. Symp.* **1969**, *26*, 37.
- [10] K. K. Indukuri, A. J. Lesser, *Polymer* **2005**, *46*, 7218.
- [11] L.-K. Bi, L. J. Fetters, *Macromolecules* **1976**, *9*, 732.
- [12] J. S. Shim, J. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 815.
- [13] A. B. Burns, R. A. Register, *Macromolecules* **2016**, *49*, 9521.
- [14] V. R. Raju, E. v. Menezes, G. Marin, W. W. Graessley, L. J. Fetters, *Macromolecules* **1981**, *14*, 1668.
- [15] S. Liffland, M. A. Hillmyer, *Macromolecules* **2021**, *54*, 9327.
- [16] G. C. Meyer, J. M. Widmaier, *Polym. Eng. Sci.* **1977**, *17*, 803.
- [17] C. Wang, Y. Wu, Y. Zhu, H. Ma, M. Zhang, G. Liu, J. He, P. Ni, *Polym. Chem.* **2022**, *13*, 3938.
- [18] P. von Tiedemann, K. Maciol, J. Preis, P. Sajkiewicz, H. Frey, *Polym. Chem.* **2019**, *10*, 1762.
- [19] M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey, A. H. E. Müller, *Macromolecules* **2019**, *52*, 9299.
- [20] M. W. Matsen, M. Schick, *Macromolecules* **1994**, *27*, 6761.
- [21] a) M. W. Matsen, R. B. Thompson, *J. Chem. Phys.* **1999**, *111*, 7139; b) M. W. Matsen, M. Schick, *Macromolecules* **1994**, *27*, 7157; c) L. Chen, Y. Qiang, W. Li, *Macromolecules* **2018**, *51*, 9890.
- [22] P. von Tiedemann, J. Yan, R. D. Barent, R. J. Spontak, G. Floudas, H. Frey, R. A. Register, *Macromolecules* **2020**, *53*, 4422.
- [23] a) P. Georgopoulos, U. A. Handge, C. Abetz, V. Abetz, *Polymer* **2016**, *104*, 279; b) N. Singh, M. S. Tureau, T. H. Epps, *Soft Matter* **2009**, *5*, 4757; c) P. Hodoroukes, G. Floudas, S. Pispas, N. Hadjichristidis, *Macromolecules* **2001**, *34*, 650; d) M. Thunga, U. Staudinger, B. K. Satapathy, R. Weidisch, M. Abdel-Goad, A. Janke, K. Knoll, *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2776; e) M. Steube, T. Johann, H. Hübner, M. Koch, T. Dinh, M. Gallei, G. Floudas, H. Frey, A. H. E. Müller, *Macromolecules* **2020**, *53*, 5512; f) S. Foerster, A. K. Khandpur, J. Zhao, F. S. Bates, I. W. Hamley, A. J. Ryan, W. Bras, *Macromolecules* **1994**, *27*, 6922; g) T. an Huy, H. Le Hai, R. Adhikari, R. Weidisch, G. H. Michler, K. Knoll, *Polymer* **2003**, *44*, 1237.
- [24] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, *51*, 10246.
- [25] M. O. Tuhin, J. J. Ryan, J. D. Sadler, Z. Han, B. Lee, S. D. Smith, M. A. Pasquinelli, R. J. Spontak, *Macromolecules* **2018**, *51*, 5173.
- [26] L. Qiao, C. Leibig, S. F. Hahn, K. I. Winey, *Ind. Eng. Chem. Res.* **2006**, *45*, 5598.
- [27] S. D. Smith, R. J. Spontak, M. M. Satkowski, A. R. Ashraf, A. K. Heape, J. S. Lin, *Polymer* **1994**, *35*, 4527.
- [28] L. J. Fetters, D. J. Lohse, D. Richter, T. A. Witten, A. Zirkel, *Macromolecules* **1994**, *27*, 4639.



- [29] B. Abu-Sharkh, A. AlSunaidi, *Macromol. Theory Simul.* **2006**, *15*, 507.
- [30] J. N. Owens, I. S. Gancarz, J. T. Koberstein, T. P. Russell, *Macromolecules* **1989**, *22*, 3380.
- [31] T. P. Lodge, T. C. B. McLeish, *Macromolecules* **2000**, *33*, 5278.
- [32] R. K. W. Spencer, M. W. Matsen, *Macromolecules* **2017**, *50*, 1681.

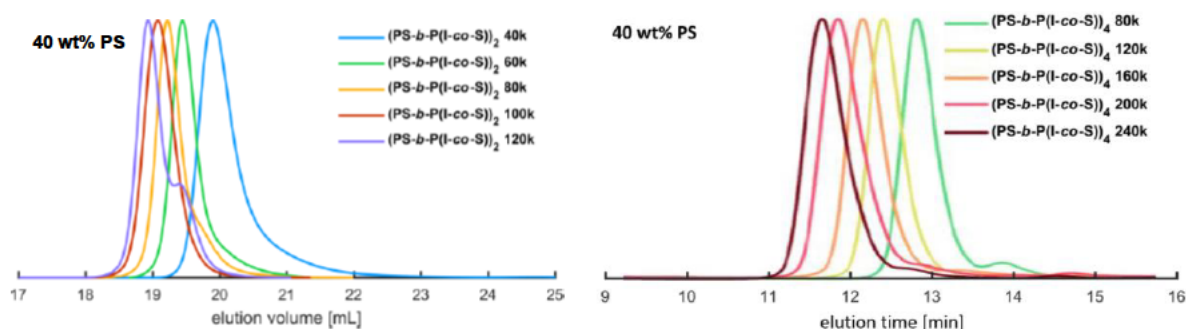
## Supporting Information

### Polymer Characterization

**Table S1:** Overview of the characteristics of the linear and star-shaped tapered multiblock copolymers with 40 wt% polystyrene obtained by coupling. The corresponding SEC traces are given in Figure S1.

| (SIS) <sub>x</sub><br>block type | target <i>w</i> (S)<br>[%] | target <i>M<sub>n</sub></i><br>[kg·mol <sup>-1</sup> ] | target <i>M<sub>n</sub></i> /arm<br>[kg·mol <sup>-1</sup> ] | <i>M<sub>n</sub></i> <sup>a</sup> or <i>M<sub>w</sub></i> <sup>b</sup><br>[kg·mol <sup>-1</sup> ] | <i>Đ</i> <sup>a</sup> | <i>w</i> (S) <sup>c</sup><br>[%] |
|----------------------------------|----------------------------|--------------------------------------------------------|-------------------------------------------------------------|---------------------------------------------------------------------------------------------------|-----------------------|----------------------------------|
| (SIS) <sub>2</sub>               | 40                         | 40                                                     | 20                                                          | 43                                                                                                | 1.23                  | 37                               |
|                                  | 40                         | 60                                                     | 30                                                          | 79                                                                                                | 1.09                  | 38                               |
|                                  | 40                         | 80                                                     | 40                                                          | 97                                                                                                | 1.10                  | 37                               |
|                                  | 40                         | 100                                                    | 50                                                          | 121                                                                                               | 1.07                  | 37                               |
|                                  | 40                         | 120                                                    | 60                                                          | 124                                                                                               | 1.11                  | 37                               |
| (SIS) <sub>4</sub>               | 40                         | 80                                                     | 20                                                          | 69                                                                                                | 1.12                  | 38                               |
|                                  | 40                         | 120                                                    | 30                                                          | 111                                                                                               | 1.04                  | 39                               |
|                                  | 40                         | 160                                                    | 40                                                          | 138                                                                                               | 1.05                  | 39                               |
|                                  | 40                         | 200                                                    | 50                                                          | 188                                                                                               | 1.08                  | 40                               |
|                                  | 40                         | 240                                                    | 60                                                          | 235                                                                                               | 1.09                  | 40                               |

<sup>a</sup> Determined by SEC (THF, PS calibration standard, RI detector). Number average molar masses are given for the linear (SIS)<sub>2</sub> pentablock copolymers, which are overestimated because of the isoprene incorporation. Dispersities are derived from the RI signal for both linear (SIS)<sub>2</sub> pentablock copolymers and star-shaped (SIS)<sub>4</sub> multiblock copolymers; <sup>b</sup> determined by SEC (THF, MALLS detector for the star-shaped (SIS)<sub>4</sub> multiblock copolymers); <sup>c</sup> determined by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) integrating on the 1,4-polyisoprene (δ=4.8-5.4 ppm), 3,4-polyisoprene (δ=4.5-4.8 ppm), and polystyrene signals (δ=6.2-7.4 ppm).



**Figure S1:** SEC traces (THF, PS calibration standard, RI detector) of the 40 wt% PS polymer series (left: linear (SIS)<sub>2</sub> pentablock copolymers, right: star-shaped (SIS)<sub>4</sub> multiblock copolymers). Different colors assign varying molar masses. Derived number average molar masses and dispersities are comprised in Table S1.

## Exemplified Analysis of Recovery Data

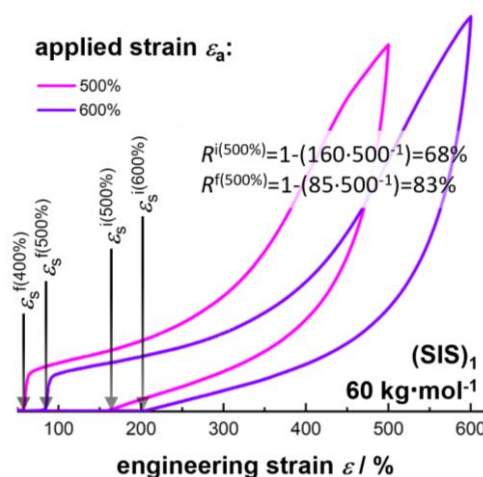


Figure S2: Definition of the initial ( $\epsilon_s^i$ ) and final residual strain ( $\epsilon_s^f$ ), and the calculation of the initial ( $R^i$ ) and final recovery ( $R^f$ ) thereof, exemplified for the raw cyclic strain test data for prescribed strains  $\epsilon_a$  of 500 (pink) and 600% (violet) from the SIS triblock copolymer with 60 kg·mol<sup>-1</sup> and 60 wt% PS.

## Recovery Data of the 40 wt% PS Polymers

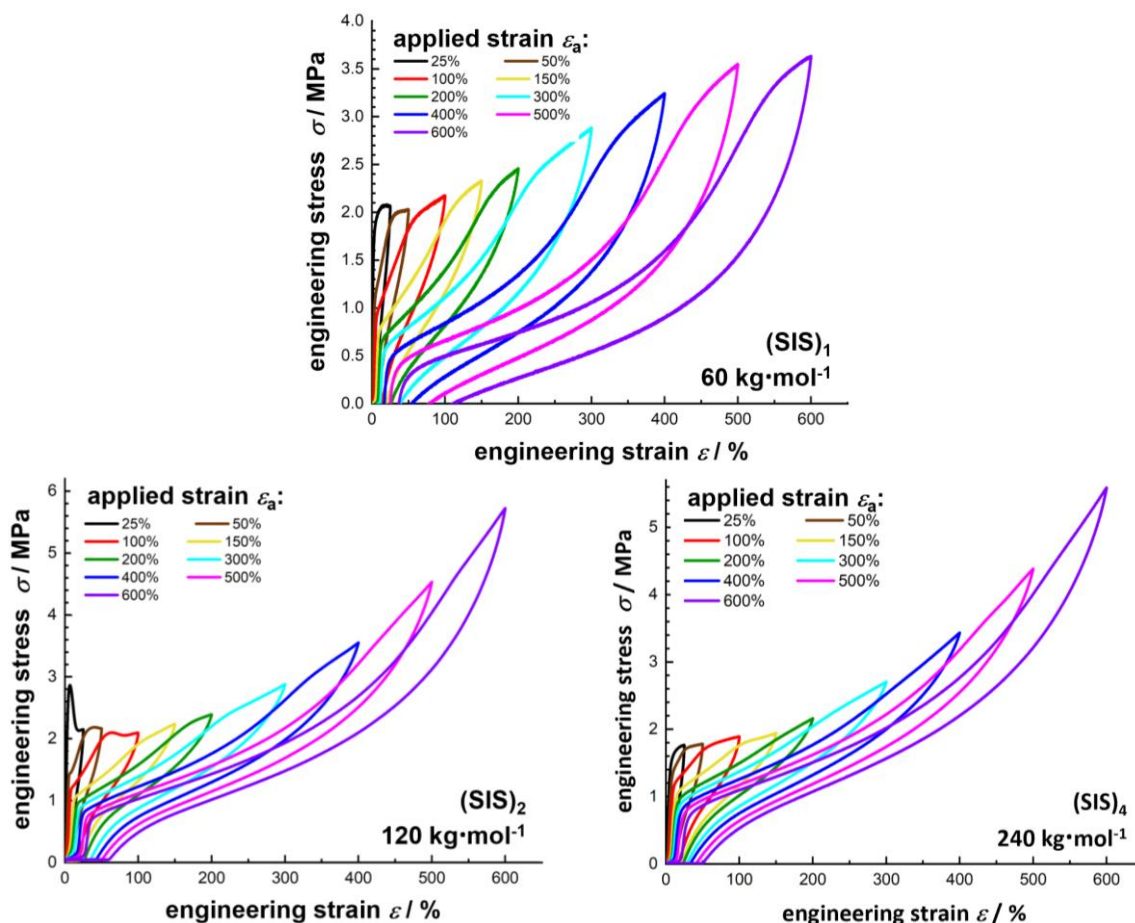
In addition to the polymers with 50 mol% isoprene and 50 mol% styrene ( $\approx 60$  wt%, 57 vol% PS) discussed in the main manuscript, analogous series with varied monomer ratios of 70 mol% isoprene and 30 mol% styrene ( $\approx 40$  wt%, 36 vol% PS) were synthesized. In the following, recovery data for the three polymers with 60 kg·mol<sup>-1</sup> per arm and 40 wt% polystyrene but differing architecture are shown.

However, previous studies revealed hexagonally packed cylinders with an order-disorder transition temperature of 135 °C for the tapered SIS triblock copolymer, but a bicontinuous morphology without accessible order-disorder transition temperature for the star-shaped (SIS)<sub>4</sub> multiblock copolymer.<sup>[22]</sup> The morphology has a huge impact on the material properties. Since cylinders exhibit only one continuous phase of the excess polymer, the material shows dominating properties of the continuous phase (for SIS: polyisoprene, soft and flexible). In bicontinuous morphologies, both phases are continuously interconnected, which is why the polystyrene domain has to be deformed together with the polyisoprene domain, resulting in a less elastic material. Lamellae, which were formed for all the 60 wt% PS polymers, exhibit two continuous phases leading to a certain strength, but since they are not interconnected, poor elastic recovery but large plastic deformations are expected.

In analogy to the previous recovery measurements, the specimens were strained to a prescribed strain  $\epsilon_a$  (25, 50, 100, 150, 200, 300, 400, 500 and finally 600%) and then the crosshead was receded. Before starting the next stretching with the increased prescribed strain, the specimens were allowed to rest for 5 minutes.

Figure S3 shows the stress-strain curves obtained for the 40 wt% PS polymers. The stress-strain curves reveal a significantly decreased tensile strength with 2-3.5 MPa for the SIS triblock (vs. 6-12 MPa for the SIS triblock with 60 wt%, see Figure 5), 2-5.5 MPa for the (SIS)<sub>2</sub> pentablock (vs. 6-15 MPa for the (SIS)<sub>2</sub> pentablock with 60 wt%, see Figure 5), and 1.8-5.5 MPa for the star-

shaped (SIS)<sub>4</sub> multiblock (vs. 6–14 MPa for the star-shaped (SIS)<sub>4</sub> with 60 wt%, see Figure 5). In conclusion, the triblock is less tough compared to the coupled counterparts.



**Figure S3:** Strain hystereses for the three polymers with an equal molar mass per arm of 60 kg·mol<sup>-1</sup> and 40 wt% PS. Top: linear SIS triblock copolymer with an overall molar mass of 60 kg·mol<sup>-1</sup>, bottom left: linear (SIS)<sub>2</sub> pentablock copolymer with an overall molar mass of 120 kg·mol<sup>-1</sup>, bottom right: star-shaped (SIS)<sub>4</sub> multiblock copolymer with an overall molar mass of 240 kg·mol<sup>-1</sup>.

Again, recovery was quantified by the residual strains  $\varepsilon_s$  right after receding and upon subsequent stretching after 5 minutes (see Figure S4). In Figure 6 the initial recovery  $R^i$  as well as final recovery after 5 minutes of resting in the initial position  $R^f$  are plotted against the applied preset strain  $\varepsilon_a$ . In pronounced contrast to the 60 wt% PS polymers with lamellar morphologies, all architectures of the 40 wt% PS series show comparable recoveries, which are significantly higher than the ones of the 60 wt% PS polymers. The linear SIS triblock exhibits highest initial recoveries at modest strain levels ( $\varepsilon_a \leq 200\%$ ). At high strain levels ( $\varepsilon_a > 200\%$ ), the star-shaped polymer recovers best during receding. The final recoveries are also qualitatively equal for all architectures and reach levels higher than 90%  $R^f$ , almost independent of the prescribed strain. On the contrary, the 60 wt% PS polymers with lamellar morphologies exhibited higher recoveries at low strain levels ( $\varepsilon_a \leq 100\%$ ), but a strong dependence on the applied strain resulting in a decrease to 85–90% of final recovery.

This very different behavior might be a result of the formed nanodomain morphology. As discussed in advance, lamellae show poor elastic recovery. The continuous phase and moreover interconnectivity in case of the star-shaped (SIS)<sub>4</sub> with 40 wt% PS provides resistance to plastic

deformation on top to bridging. The latter have a smaller impact on the overall properties, which is why a distinct dependence on the chain architectures cannot be observed.

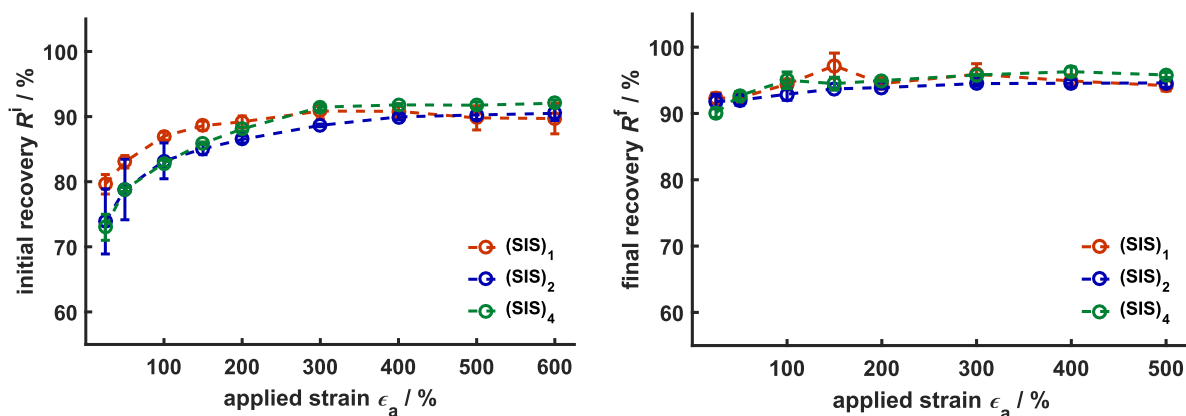


Figure S4: Initial (left,  $R^i$ ) and final recovery (right,  $R^f$ ) in dependence of the applied prescribed strain  $\epsilon_a$  for the three strain hysteresis shown in Figure S3.



---

---

# CHAPTER 5

*Implementation of Multiblock*

*Copolymers in Solution:*

**Next Generation Viscosity Modifiers**

---

---





## CHAPTER 5

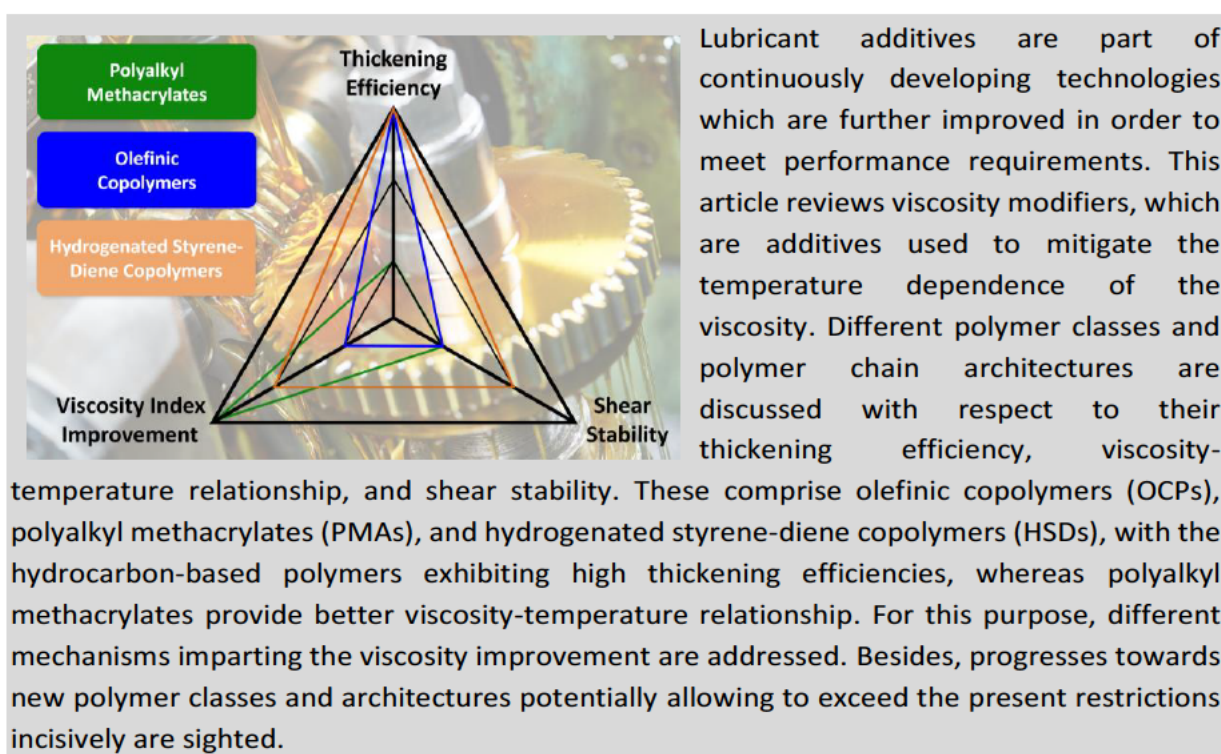
To be Submitted

# *Implementation of Multiblock Copolymers in Solution: Next Generation Viscosity Modifiers*

Ramona D. Barent<sup>1,2</sup> and Holger Frey<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany

<sup>2</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany



## Introduction

For nearly all modern machines, lubrication is necessary since they mostly rely on moving metal parts. Contact of these elements has to be prevented, as friction causes heat generation and wear. While the metal parts of engines are designed to be exposed to minimum contact, gears and bearings experience massive friction.<sup>[1,2]</sup> Therefore, the primary task of lubricants is the minimization of direct metal-to-metal contact by a film between the moving parts.

Furthermore, lubricants dissipate heat, protect surfaces against oxidation or corrosion and ensure smooth operation by suspending deposits. In the special case of hydraulic technologies, lubricants are further implemented for power transfer.<sup>[1]</sup>

Lubricants can be solid, liquid, or gaseous, but fluid-film lubrications are the most common lubricants, which is why within this work, only liquid lubricants will be reviewed.<sup>[1]</sup> Generally, lubricant formulations consist of a non-volatile base oil or mixtures thereof, and different polymer additives. To meet the requirements of an intended application, both the choice of the base oil and the lubricant additives play an important role, since the performance of the different additives varies with the base oil. The specifications of importance for various applications are compiled in Table 1. These comprise not only the already mentioned friction, oxidation, and corrosion control as well as dispersancy, but also performance upon temperature and pressure changes. The latter tribological parameters essentially influence the oil film thickness.<sup>[1]</sup>

**Table 1: Lubricant property requirements for various applications.<sup>[1]</sup>**

| Application                   | Friction Control | Oxidation and Corrosion Control | Dispersancy | Low Temperature Fluidity | Beneficial Viscosity-Temperature Relationship | Beneficial Viscosity-Pressure Relationship |
|-------------------------------|------------------|---------------------------------|-------------|--------------------------|-----------------------------------------------|--------------------------------------------|
| Engine Oils                   | ✓                | ✓                               | ✓           | ✓                        | ✓                                             | ✗                                          |
| Automatic Transmission Fluids | ✓                | ✓                               | ✓           | ✓                        | ✓                                             | ✓                                          |
| Tractor Hydraulic Fluids      | ✓                | ✓                               | ✓           | ✓                        | ✓                                             | ✓                                          |
| Industrial Hydraulic Fluids   | ✓                | ✓                               | ✓           | ✓                        | ✗                                             | ✓                                          |
| Gear Oils                     | ✓                | ✓                               | ✗           | ✓                        | ✓                                             | ✓                                          |
| Industrial or Turbine Oils    | ✓                | ✓                               | ✗           | ✗                        | ✓                                             | ✗                                          |

With 65-98%, the key component of lubricant formulations is the base oil, while the additives account for 0-1% in case of pour point depressants, 0-30% of viscosity modifiers and 2-20% for a general-purpose performance package, which usually is sold separately.<sup>[1]</sup> A performance package itself comprises manifold additives like stabilizers, oxidation and corrosion inhibitors, deposit control agents, or film forming agents. This work outlines the different functional principles of viscosity modifiers and relates them to the polymer classes, touching the chemistry of pour-point depressants as well.

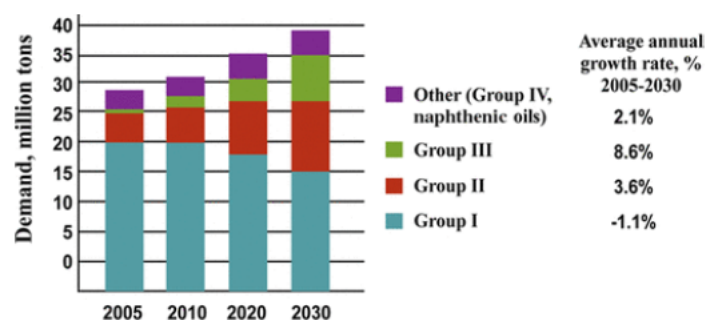
Base oils are categorized by the American Petroleum Institute. Five groups are classified and Table 2 summarizes the key parameters of the groups I, II and III, which are their viscosity index, saturates content, and sulfur level. The viscosity index is a measure of the change in viscosity relative to a temperature change. On top, the classifications group IV comprising poly( $\alpha$ -olefins), which are wax-free, and group V including all other base stocks are defined. Due to cost issues the market develops towards group II and III base oils, where hydrocarbons

can be used, as represented in the change in demand and forecast demand of the different base stocks (see Figure 1).<sup>[2]</sup> This is reasoned in the improved performance characteristics such as superior oxidative stability and by this low friction increase, with the friction being directly related to fuel economy.

**Table 2: Classification of the Base Stocks of Group I-III.**<sup>[3]</sup>

| Base Stock | Amount of Saturates <sup>a</sup> | Amount of Sulfur | Range of the Viscosity Index |
|------------|----------------------------------|------------------|------------------------------|
| Group I    | <90%                             | ≤0.03%           | 80-120                       |
| Group II   | ≥90%                             | ≤0.03%           | 80-120                       |
| Group III  | ≥90%                             | ≤0.03%           | ≥120                         |

<sup>a</sup>During hydrocracking processes, which involve the treatment with hydrogen at high pressures in the presence of a catalyst, olefins are converted into saturates. Furthermore, hydrocracking achieves the conversion of aromatic molecules into naphthenes, larger molecules are cracked to compounds of molar masses suitable for use as base oils, normal paraffins are isomerized to branched alkanes, and sulfur and nitrogen containing compounds are removed.



**Figure 1: Demand for base oils for the period of 2005-2010 as well as the forecast for 2020-2030.** taken from [4]

Regardless of the type of oil, all fluids have a rapid decrease in viscosity upon increasing temperature in common. Since the temperature application window of lubricants usually encompasses a wide temperature range, performance might not be rendered at elevated temperatures facing issues of surface contact. However, the use of a more viscous fluid does not solve the problem because of viscous friction at low temperatures leading to poor efficiencies. Therefore, the implementation of viscosity modifiers in lubricant formulations is important to mitigate this adverse effect and to ensure a sufficient film thickness throughout the whole temperature range.

Within this work, different polymer classes including olefinic copolymers (OCPs), polyalkyl methacrylates (PMAs), and hydrogenated styrene-diene copolymers are presented (see Figure 2). The parameters and mechanisms influencing the viscosity and thus dictating the performance as viscosity modifiers will be discussed.

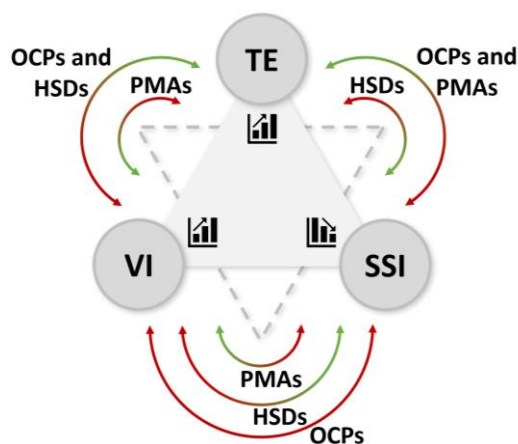


**Figure 2: Polymer classes widely used for viscosity modification.**

Currently, there is no viscosity modifier available that provides optimum performance. Due to the trade-off between the viscosity-temperature relationship quantified by the viscosity index,

the thickening efficiency, and shear stability (see Figure 3), the different viscosity modifiers are suitable for particular applications.<sup>[5]</sup> The viscosity index is a measure of the decrease in viscosity with temperature and is known to be high for polyesters like polyalkyl methacrylates. On the contrary, hydrocarbon-based polymers such as olefinic copolymers and hydrogenated styrene-diene copolymers exhibit high thickening efficiencies, representing low polymer treat rates required to achieve a certain increase in viscosity. Finally, the shear stability index quantifies the resistance to the permanent viscosity loss upon shearing. This parameter is influenced, for instance, by the polymer architecture, but also depends on the dispersity of the polymer.

Therefore, different architectures and chain compositions will be addressed. Furthermore, promising chain architectures not used in the field of lubricant additives so far will be highlighted, giving food for thought for the design of novel viscosity modifiers. This development is required, since effective additives meeting the challenges of lubricant formulation for various applications are of industrial and economic interest. For instance, legislation drives changes to fuel composition and progress towards ultralow-viscosity engine oils for improved fuel efficiency, requiring specialized viscosity modifiers.<sup>[2]</sup>



#### Thickening Efficiency

$$TE = \frac{2}{\ln 2} \frac{1}{c} \ln \left( \frac{v_{\text{tested solution}}^{100^\circ\text{C}}}{v_{\text{base oil}}^{100^\circ\text{C}}} \right)$$

#### Viscosity Index

$$VI = 100 \cdot \left( \frac{v_{\text{reference oil, VI=0}}^{40^\circ\text{C}} - v_{\text{tested solution}}^{40^\circ\text{C}}}{v_{\text{reference oil, VI=0}}^{40^\circ\text{C}} - v_{\text{reference oil, VI=100}}^{40^\circ\text{C}}} \right)$$

#### Shear Stability Index

$$SSI = 100 \cdot \left( \frac{v_{\text{sheared solution}}^{100^\circ\text{C}} - v_{\text{unsheared solution}}^{100^\circ\text{C}}}{v_{\text{unsheared solution}}^{100^\circ\text{C}} - v_{\text{base oil}}^{100^\circ\text{C}}} \right)$$

**Figure 3:** Definition of the viscosity index (VI), the shear stability index (SSI) and the thickening efficiency (TE).  
 $v$ : Kinematic viscosities  $v$  of the base oil, a reference oil of prescribed kinematic viscosity, or the polymer solution at different temperatures or after shearing experiments.

## Viscosity-Temperature Relationship

The viscosity of a polymer solution is enhanced both by high molar masses and the concentration of the dissolved polymer. In the dilute regime, the contribution of a polymer to the viscosity increase is approximated by the Kuhn-Mark-Houwink-Sakurada power law (equation 1), showing the dependence of the intrinsic viscosity of a polymer  $[\eta]$  on the average molar masses  $M$ .  $K$  and  $\alpha$  are constants depending on the polymer and the solvent. The exponent  $\alpha$  adopts 0.5 for an ideal gaussian coil at theta condition, increases for flexible coils dissolved in better solvents to  $0.5 \leq \alpha \leq 0.8$ , and attains values  $>0.8$  for semi-flexible polymers with a maximum of 1.7-2 for a rigid, rodlike molecule.<sup>[5,6]</sup> In contrast to linear polymers,  $\alpha$  can be  $<0.5$  for ring or hyperbranched polymer architectures and further depends on the molar mass in the latter case.<sup>[7]</sup>

$$[\eta] = K \cdot M^\alpha \quad (1)$$

The concentration dependence is described by the Huggins or Kraemer relation (equations 2 and 3, respectively), which allow extrapolation to infinite dilution to experimentally determine intrinsic viscosities. Here, the  $\eta_{sp}$  denotes the specific viscosity and  $\eta_r$  the reduced viscosity. Both can be calculated by the difference in viscosity of a solution to the pure solvent (equation 4). The respective coefficients  $k_H$  and  $k_K$  are constant for a given polymer-solvent system. The advantage of the Kraemer equation is the smaller concentration dependence. However, it is only valid for a Huggins coefficient of  $k_H=1/3$ , which is why in case of doubt the linear fit should be obtained from the Huggins equation.<sup>[8]</sup>

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \quad (2)$$

$$\frac{\ln \eta_r}{c} = [\eta] + k_K [\eta]^2 c \quad (3)$$

$$\eta_{sp} = \frac{\eta - \eta_{solvent}}{\eta_{solvent}} = \eta_r - 1 \quad (4)$$

The intrinsic viscosity is a first indication for the ability of a polymer to increase the viscosity of a solvent and generally, higher molar masses and concentration increase the viscosity. Still, due to the extrapolation to infinite dilution, the intrinsic viscosity is tangibly spoken a reciprocal density of the polymer coil in solution and hence possible changes in the thickening mechanisms (*vide infra*) with varying concentration such as crystallization and association phenomena are not taken into account. Besides, the intrinsic viscosity does not provide any insight into the viscosity-temperature relationship.

For this purpose, the viscosity index (VI) was introduced, which quantifies the temperature dependence and is calculated according to equation 5. Here, the kinematic viscosity at 40 °C of the tested solution is weighted against the kinematic viscosities  $\nu$  at 40 °C of two reference oils with a VI of 0 and 100, which have the same kinematic viscosity at 100 °C as the tested solution. The higher the VI, the lower the temperature dependence of the viscosity of a solution.

$$VI = 100 \cdot \left( \frac{\nu_{reference\ oil, VI=0}^{40\ ^\circ C} - \nu_{tested\ solution}^{40\ ^\circ C}}{\nu_{reference\ oil, VI=0}^{40\ ^\circ C} - \nu_{reference\ oil, VI=100}^{40\ ^\circ C}} \right) \text{ with } \nu_{reference\ oils}^{100\ ^\circ C} = \nu_{tested\ solution}^{100\ ^\circ C} \quad (5)$$

The mechanisms for viscosity index improvement by a polymer additive are discussed in a later section and in the first place depend on the polymer's chemistry. Basically, polyalkyl methacrylates are good viscosity index improvers, since the polymer coil expands with temperature changes contributing increasingly to the solution viscosity, while the coil size of hydrocarbon-based polymers such as olefinic copolymers and hydrogenated styrene-diene copolymers is barely temperature-dependent. Yet, hydrogenated styrene-diene copolymers are able to aggregate, thereby introducing a temperature response of the system's viscosity.

Besides, the viscosity index is weakly correlated to the architecture of polymer chains. For instance, two polymers of the same molar mass in the backbone of the polymer, i.e., the same molar mass share belongs to the side chains, can differ in their radius of gyration and *vice versa*. Here, for similar backbone molar mass the polymer with the larger radius of gyration has the higher viscosity index, whereas for polymers with the same radius of gyration, the polymer with lower molar mass of the backbone is more efficient.<sup>[9]</sup>

Since the mechanisms for viscosity improvement, shear stability and thickening efficiency are complexly intercorrelated, the influence of the polymer's chemistry, chain composition and architecture will be addressed multiple times throughout this work when appropriate.

## Shear Stability

In addition to a beneficial viscosity-temperature relationship, good performance of a viscosity modifier critically depends on its durability. During use, lubricant formulations are subjected to high shear stresses for many applications. This results in both a reversible and a permanent decrease in viscosity.

The shear thinning phenomena are pictured in Figure 4. Before experiencing shear forces, the oil containing a viscosity modifier exhibits a comparably high viscosity which behaves as a Newtonian liquid at low shear stress levels (1<sup>st</sup> Newtonian).

At moderate shear stress levels, the shape of the polymer coils changes from spherical to an elongated configuration and the disassembly of associated chains takes place, leading to a decrease in viscosity until a second plateau of a viscosity independent of the shear stress (2<sup>nd</sup> Newtonian), where the polymer chains are maximally aligned within the flow, and all aggregates are broken up. For this case, the viscosity increases to the initial value when the shear rates are decreased and the polymer coils return to their initial shape and reassemble, which is why this effect is called a temporary or reversible viscosity loss (Figure 4, horizontal shift). Normally, the temporary viscosity loss increases with the molar mass of the polymer.<sup>[2]</sup> The decrease in viscosity upon shearing typically begins at strain levels above  $10^4 \text{ s}^{-1}$ .<sup>[2,10]</sup>

However, at high shear stress levels, where turbulent flows and cavitation become more likely, also chain degradation can take place, leading to a decrease in the molar mass and an increase in dispersity. The homolytic C-C bond cleavage results in free radicals, which are quickly quenched by the oil, antioxidants, or dissolved oxygen molecules.<sup>[2]</sup> Therefore, not the chemical structure but the molar mass and hence the end-to-end distance of the polymer chain are affected. In consequence, the system faces a permanent viscosity loss (Figure 4, vertical shift). Typically, chain scission is notable at strain levels above  $10^6 \text{ s}^{-1}$ <sup>[10]</sup> and statistically occurs near the middle of linear polymer chains.<sup>[11]</sup> As a result, permanent viscosity loss is self-limiting, reaching a plateau when the chains are degraded to a sufficiently low molar mass.<sup>[12]</sup> The permanent shear stability is quantified by the shear stability index SSI (see Figure 3), with higher values indicating a more pronounced viscosity loss. Conclusively, low SSI values are desirable.

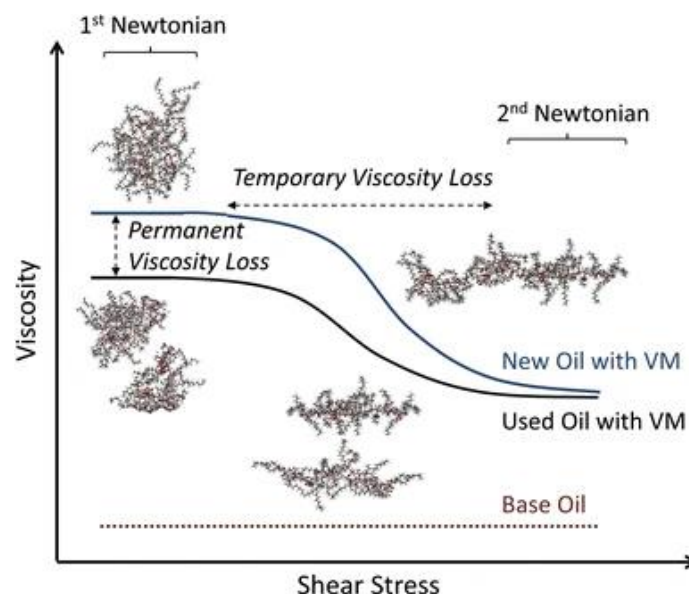
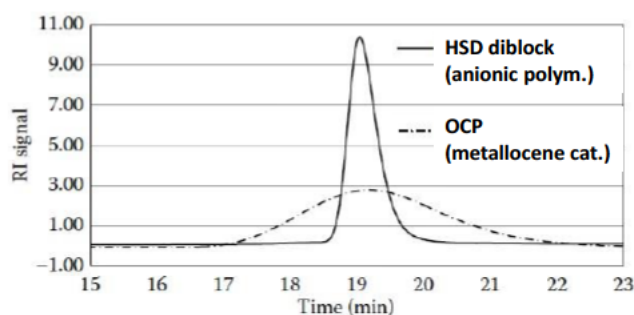


Figure 4: Reversible and permanent shear thinning upon shearing. taken from [5]



In general, lower molar mass polymers are more shear stable because of an easier alignment within the flow. Furthermore, the solubility of the viscosity modifier in the base oil plays a role, since more extended polymer chains take more time to align, rendering chain scission more likely. On the other side, lower molar mass polymers exhibit worse thickening efficiency (*vide infra*) and a detrimental viscosity-temperature relationship, which is why the balancing of the three parameters is challenging.

As a result, the dispersity of a polymer indirectly affects the overall performance. The broader a molar mass distribution, the higher are the shares of comparably long and as well as short chains. On one hand, the longer polymer chains might experience chain degradation and hence reduce the shear stability. On the other hand, the shorter chains contribute little to the viscosity increase. Therefore, narrow molar mass distribution improve the balance between thickening efficiency and shear stability, allowing to target higher molar masses at minimum permanent viscosity loss.<sup>[13]</sup> In consequence, the polymerization mechanism has a strong impact on the performance as viscosity index improver, as exemplified for catalytic and anionic polymerization in Figure 5.



**Figure 5:** SEC traces of a hydrogenated styrene-diene diblock copolymer (HSD), polymerized under living anionic conditions (solid line) and of an olefinic copolymer (OCP) polymerized by metallocene catalysis (dashed line). Both viscosity modifiers exhibit comparable molar masses at the signal maximum. adapted from [2]

Furthermore, the polymer architecture is important for both temporary and permanent shear stability and thus opens up another approach for viscosity modifier improvement.<sup>[5]</sup> Long chain branching results in viscosity modifiers less prone to temporary shear loss.<sup>[11]</sup> Branching can occur during PMA synthesis by chain transfer reactions or in case of OCPs is achieved by implementing a terpolymerization with a non-conjugated diene. However, long chain branching affects the thickening efficiency detrimentally (*vide infra*).

Comparing linear and star-shaped polymers, the more compact structure of star-shaped polymers in solution leads to a higher permanent shear stability at similar molar masses due to faster alignment under shear.<sup>[11]</sup> However, comparing the star-shaped polymers with their linear counterparts whose molar mass equals the molar mass of one arm, the star-shaped polymers are less shear stable and their behavior approaches the one of the linear arm.<sup>[11,14]</sup>

Introducing a block structure into linear polymers enables self-assembly, if one block is sufficiently insoluble. These aggregates are capable of partially disassembling under shear, thereby increasing the temporary shear stability.<sup>[15,16]</sup> However, especially for diblock copolymers, micellization can be restricted by chain scission, particularly disjoining the two covalently linked blocks, this way increasing both permanent and temporary shear induced viscosity loss.<sup>[11]</sup> Consequently, multiblock structures might be beneficial, which will be discussed later when reviewing advanced structures.

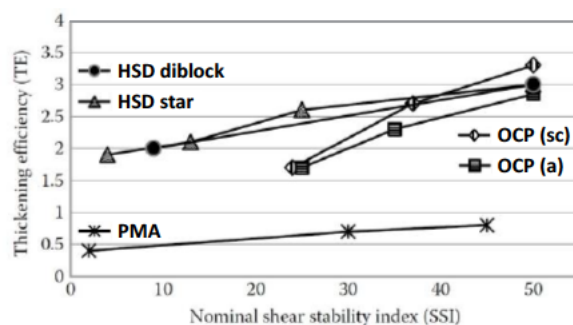
Besides, the intended application determines the demands with respect to shear stability, since the shearing severity a lubricant is subjected to varies with the application. The highest shear forces are experienced in gear oils, followed by hydraulic fluids and automatic transmission fluids, whereas the demands for engine oils are rather low.<sup>[2]</sup>

## Thickening Efficiency

As a third key parameter, the thickening efficiency of a polymer additive is defined, and small values are desirable since it directly translates into lower polymer treat rates sufficient for an adequate lubrication. As discussed above (intrinsic viscosity), the thickening efficiency correlates with the hydrodynamic volume of the polymer coil in solution. The latter scales with the root mean-square end-to-end distance of the polymer as  $V_H \sim r^3$ , which depends in a first approximation on the molar mass and the polymer architecture.

Side chains as present in polyalkyl methacrylates strongly affect the hydrodynamic volume. In this context, thickening efficiency depends linearly on the percentage of the molar mass in the polymer backbone.<sup>[9]</sup> For polyalkyl methacrylates (PMAs), only about 15% of the polymer's molecular weight is in the backbone, whereas the fraction for olefinic copolymers (OCPs) ranges above 80%, resulting in a higher thickening efficiency of OCPs.<sup>[2]</sup> In case of hydrogenated styrene-diene copolymers (HSDs), the methyl side group of 1,4-polyisoprene or the short side groups of 1,2- and 3,4-diene repeating units impair the thickening efficiency only to a minimal extent.<sup>[2]</sup> Besides, long chain branching is associated with a smaller hydrodynamic volume and hence reduced thickening. This also holds true for star-shaped architectures, which form denser structures in solution than their linear counterparts of equal molar mass and therefore exhibit worse thickening efficiency.

Furthermore, the solubility of the viscosity modifier in the base oil and hence its chemistry strongly contribute to the thickening efficiency (see Figure 6). While polyalkyl methacrylates exhibit comparably poor solubility, their thickening efficiency is significantly lower at a given shear stability. The chemical nature of olefinic copolymers and hydrogenated styrene-diene copolymers is similar, resulting in much closer thickening efficiencies, which are higher due to the better solubility.<sup>[2]</sup> Yet, different underlying polymerization mechanisms and hence dispersities render HSDs less prone to a shear induced viscosity loss than OCPs (*vide supra*, Shear Stability). Besides, HSDs are associative thickeners, circumventing a permanent loss by reversible disassembly.



**Figure 6:** Thickening efficiency (TE) and corresponding shear stability index (SSI) for different viscosity modifiers in dependence of their molar mass. Polymer classes: linear diblock as well as star-shaped hydrogenated styrene-diene copolymers (HSD), semicrystalline (sc) as well as amorphous (a) olefinic copolymers (OCP), and polyalkyl methacrylates (PMA). <sup>adapted from [2]</sup>

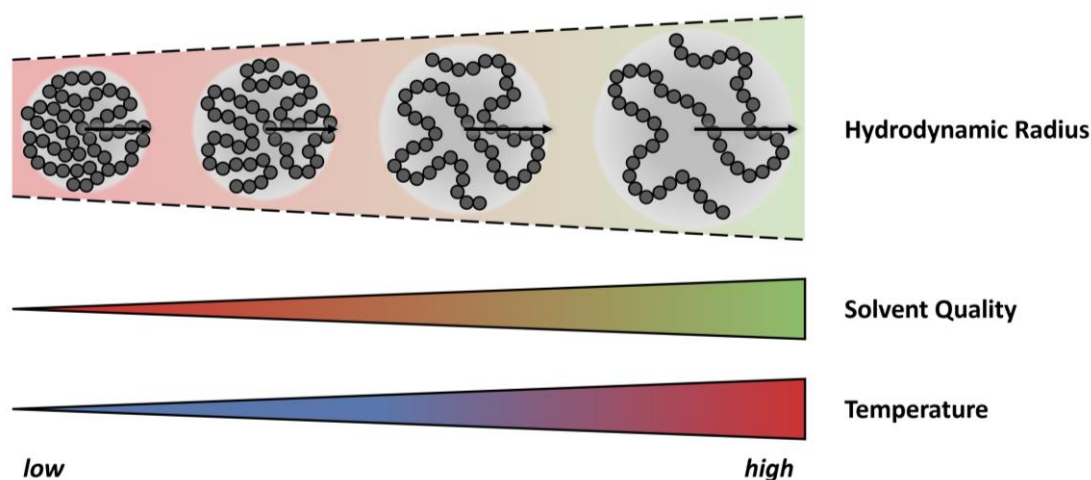


## Mechanisms for Viscosity Improvement

Several mechanisms have been presented to explain the viscosity improvement by the addition of polymeric modifiers. The most prominent concepts are coil expansion with temperature or aggregation phenomena. The polymer coil expansion is the dominant mechanism for the viscosity index improvement of polyalkyl methacrylates (PMAs), whereas the performance of hydrogenated styrene-diene copolymers (HSDs) primary relies on reversible association, which will both be discussed in the ensuing paragraphs.<sup>[17,18]</sup>

### Polymer Coil Expansion

The coil expansion mechanism is based on the change of solubility with temperature. At lower temperatures, the polymer does not precipitate, but forms a rather contracted coil, which contributes only to a small extent to the system's viscosity. With increasing temperature, the solubility increases, and the coils expand (see Figure 7). On a molecular level, this can be explained by altered interaction parameters between the polymer repeating units among themselves relative to the interaction parameters between the polymer repeating units and the solvent molecules. Therefore, especially polar polymer structures like PMAs experience a temperature-dependent coil expansion.<sup>[19]</sup> On the contrary, nonpolar structures like olefinic copolymers that are chemically similar to the solvent are well solvated at all temperatures.<sup>[2]</sup>

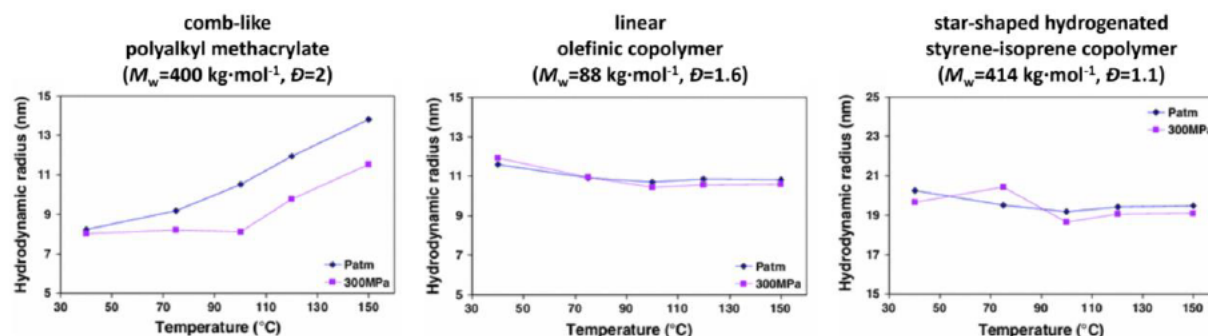


**Figure 7: Polymer coil expansion upon solvent quality or temperature increase.** adapted from [18]

Figure 8 shows the change in the hydrodynamic radius with temperature of the three common polymer classes discussed within this review. Furthermore, normal pressure as well as elevated pressures are investigated. In case of polyalkyl methacrylates (PMAs) the hydrodynamic radius increases with increasing temperature, although the effect is weakened at higher pressures. On the contrary, the hydrodynamic radii of hydrogenated styrene-diene copolymers (HSDs) and olefinic copolymers (OCPs) remain steady over the whole temperature range from 40-150 °C as well as at normal pressure and 300 MPa.<sup>[20,21]</sup>

Since the architecture of a viscosity modifier influences the coil size and hence thickening efficiency (*vide supra*), also coil expansion with temperature depends on the molar mass of the polymer's backbone. The radius of gyration increases faster for linear than branched PMAs with temperature, rendering linear architectures a better viscosity index improver.<sup>[22]</sup>

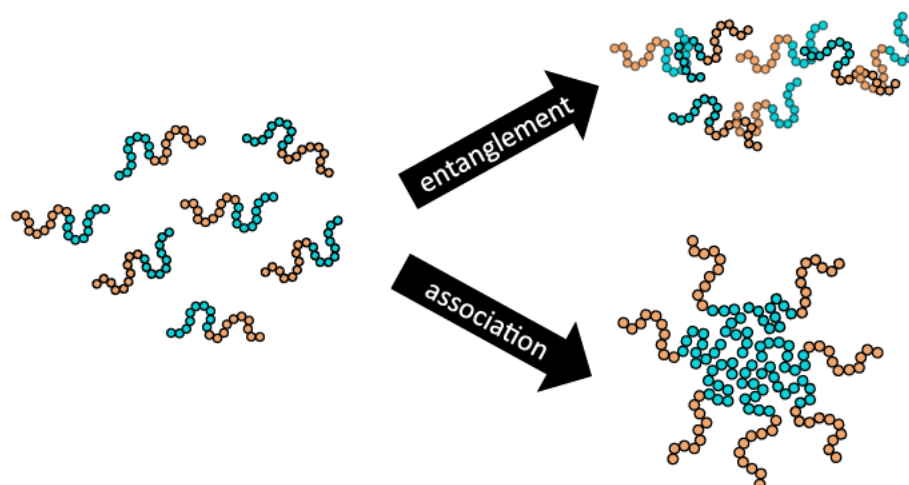
Particularly, the mechanism of polymer coil expansion causes an improved viscosity-temperature relationship and hence is beneficial for a viscosity modifier performance.



**Figure 8:** Influence of temperature and pressure on the hydrodynamic radius of different polymer classes (left: PMAs, middle: OCPs, right: HSDs) used for viscosity index improvement. Set-up: high-pressure falling-ball viscometer, ( $r_h$  are back calculated using Einstein's law for rigid spheres for a dilute suspension). Polymer concentrations: 1.2%<sub>w/w</sub>, solvent: hydrocracked mineral base oil. <sup>adapted from [21]</sup>

## Association

A single flexible polymer chain of a homopolymer is known to form a diffuse coil in a good solvent, whereas in a poor solvent it collapses into a dense globule. The former described polymer chain expansion mechanism for viscosity increase relies on this principle. Going from a homopolymer to a copolymer with a sufficient share of an insoluble block, the collapse of these moieties can also cause a viscosity increase. This association mechanism is caused by the interaction of multiple polymer chains and comprises the entanglement by the interpenetration of polymer chains as well as the self-assembly of polymer chains describing physical cross-linking (see Figure 9), both physically increasing the apparent molar mass and hence viscosity.<sup>[23]</sup> Generally, the viscosity of a solution increases with the viscosity modifier concentration according to equation 2 and 3. If a system is capable of association phenomena, a nonlinearity is observed at critical concentration. These encompass the critical overlap concentration  $c^*$  as well as the critical micelle concentration  $c_{cmc}$ . Above the critical overlap concentration, not a dilute but a semi-dilute solution with interacting polymer chains is obtained, whereas above the critical micelle concentration polymer chains start to aggregate. Both critical concentration are molar mass, solvent and temperature dependent.<sup>[5]</sup>



**Figure 9:** Schematic representation of the viscosity index improvement by polymer entanglement (top) or association (bottom) of unimers due to an apparent molar mass increase.

As stated above, association is predominant in block copolymers in a selective solvent, meaning that the individual blocks differ in their solubility depending on the block size of the insoluble part.<sup>[2]</sup> For example, hydrogenated styrene-diene block copolymers feature oil-insoluble polystyrene segments, which tend to form a core enclosed by a soluble polydiene corona.<sup>[5,24]</sup> Besides, so-called stickers which provide strong physical interaction such as hydrogen bonds can cause the association of chains.<sup>[25]</sup>

The temperature dependence of these aggregates was extensively studied.<sup>[26,27]</sup> Figure 10 demonstrates the change of the intrinsic viscosity with temperature for a block-like linear hydrogenated styrene-butadiene copolymer. The intrinsic viscosity increases non-monotonically with temperature, showing a huge increase between 40 and 60 °C. Above 80 °C, the intrinsic viscosity decreases again. Comparison with the hydrodynamic radii obtained by dynamic light scattering experiments shows micelle formation at low temperatures, which are broken up above 80 °C. Furthermore, below 40 °C the micelle volume does not depend on the temperature.<sup>[28]</sup>

Other studies focused on the concentration dependence of aggregates of polystyrene-*block*-polydiene diblock copolymers<sup>[27,29]</sup> and polystyrene-*block*-polydiene-*block*-polystyrene triblock copolymers<sup>[24,30]</sup> in polydiene-selective solvents, revealing that at high concentration even networks are formed.<sup>[31]</sup>

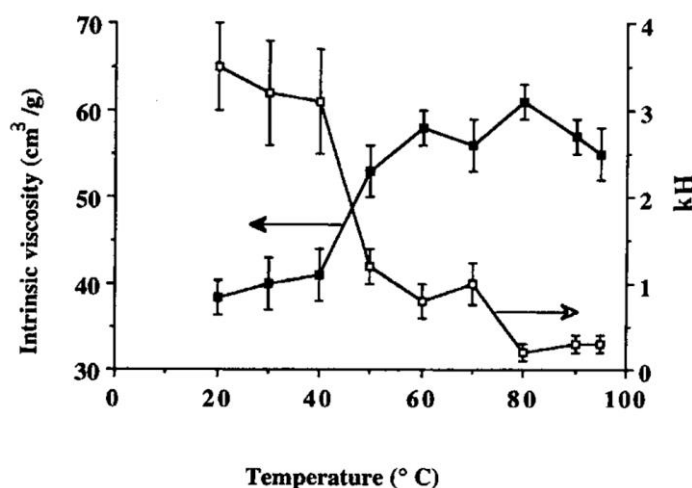


Figure 10: Intrinsic viscosity (filled symbols) and Huggins coefficient (open symbols) of a blocklike hydrogenated styrene-butadiene copolymer ( $M_w=128 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}=1.4$ ) in a base oil as a function of temperature. taken from [28]

## Polymer Classes for Viscosity Improvement

The commonly used polymer classes are shown in Figure 2. Generally, the polymeric hydrocarbons such as the olefinic copolymers (OCPs), polyisobutylene but also hydrogenated styrene-diene copolymers (HSDs) possess high thickening efficiencies, while the polyesters like polyalkyl methacrylates (PMAs) offer a superior viscosity-temperature relationship. In the following, the three polymer classes are discussed against the background of the implemented polymerization techniques and the inherent mechanisms for viscosity improvement.

## Olefinic Copolymers

Olefinic copolymers comprising polyethylene and polypropylene units in the first place are catalytically synthesized using Ziegler-Natta<sup>[32]</sup> or metallocene<sup>[33]</sup> based catalyst systems.<sup>[5]</sup> Due to this, the resulting copolymers synthesized by Ziegler-Natta catalysis exhibit extremely broad molar mass distribution ( $\bar{D} > 5$ ). On the contrary, metallocenes allow for a better control over the molar mass distribution.<sup>[2]</sup> The influence of the dispersity has been elucidated discussing the shear stability (*vide supra*). Generally, narrow molar mass distribution are beneficial for high thickening efficiencies, viscosity index improvements and shear stabilities since higher molar mass polymers can be employed.



Another aspect affecting the overall performance as viscosity modifier is the ratio of both comonomers ethylene and propylene. As a result of the linear structure of polyethylene, high ethylene contents lead to a better solubility in oils and hence a superior thickening efficiency. At the same time, long polyethylene sections are capable of crystallization or strong interaction with the waxes in mineral oils, which cause the reverse effect by the concomitant poor solubility<sup>[34]</sup> and poor flow at low temperatures.<sup>[35]</sup> For ratios of 45-55% polyethylene, an amorphous material which cold-flows at room temperature is obtained. On the contrary, if the polyethylene share is higher than 60%, semicrystalline copolymers which do not flow under ambient conditions are formed.<sup>[2]</sup> For a crystallinity exceeding 25%, the OCPs are unsuitable for viscosity modification. Primarily, this relies on the poor oil solubility because the polyethylene sequences do not longer crystallize into fringed micelles or short bundled structures.<sup>[36]</sup> Beyond this, the hydrodynamic volume of the polymer shrinks with the crystallization. As long as the OCP stays dissolved, the intrinsic viscosity drops and hence the viscosity modifier contributes less to the viscosity at temperatures below the crystallization temperature.

For the crystallization tendency, also the catalyst chosen for polymerization plays a role. Ethylene is more reactive in Ziegler-Natta catalyzed polymerizations, for which reason longer polyethylene sequences are favored.<sup>[2]</sup> Metallocene catalysis stands out not only because of a better control over the composition and the molar mass distribution, but also a high catalyst efficiency. As a result, lesser amounts are needed, which makes their removal redundant.<sup>[2]</sup> Besides, also higher  $\alpha$ -olefins are polymerizable with metallocene catalysis.

Furthermore, oxidative and thermal stability of the copolymers has to be considered, which diminishes for high propylene contents due to the labile tertiary protons of polypropylene.<sup>[2,35]</sup> Conclusively, a random distribution of the comonomer units along the polymer chain allows high polyethylene contents and therefore a maximum thickening efficiency and oxidative stability without facing crystallization issues at low temperatures. However, this does not hold true for multiblock copolymers with comparably short block length (*vide infra*, Advanced Structures).

Oftentimes, terpolymers of ethylene, propylene and a third, nonconjugated diene are employed as viscosity modifiers as well. This way, a cross-linkable moiety is introduced and long-chain branching becomes possible. The main advantages are the reduction of tackiness and an easier handling. However, long-chain branching has detrimental effects on the thickening efficiency (*vide supra*). To date, the correlation between the diene content and the thermal stability has not been proven.<sup>[2]</sup> Further properties additionally to the viscosity



modification can be achieved by the copolymerization with maleic anhydride and subsequent grafting on aromatic or aliphatic nitrogen-containing moieties, providing soot-controlling,<sup>[37]</sup> antioxidant,<sup>[38]</sup> and dispersant<sup>[39]</sup> characteristics.

Still, due to the trade-off between thickening efficiency and shear stability OCPs perform poorly, which makes them unsuitable for most applications. Nevertheless, they are attractive for gasoline and diesel engines since they can be produced at low costs and possess a high thickening efficiency.

### Hydrogenated Styrene-Diene Copolymers

Styrene-diene copolymers are synthesized by the anionic polymerization of styrene and a 1,3-diene, which is normally butadiene or isoprene.<sup>[40]</sup> Afterwards, the polydiene is hydrogenated to guarantee oxidative stability. In case of 1,4-polybutadiene, this results in a polyethylene structure, whereas hydrogenated 1,4-polyisoprene equals poly(ethylene-*alt*-propylene). Living anionic polymerizations are quite demanding, since only traces of impurities like protic species, oxygen or carbon dioxide impair the reaction.<sup>[40]</sup> Nonetheless, highly defined polymers with narrow molar mass distribution ( $\bar{D} \leq 1.1$ ) and manifold chain architectures like multiple block or tapered block-like structures,<sup>[41]</sup> but also star-shaped polymers<sup>[42]</sup> are accessible. A variety of linear diblock copolymers,<sup>[43]</sup> triblock copolymers,<sup>[44,45]</sup> and star-shaped HSDs<sup>[46–48]</sup>, but also tapered block-like structures<sup>[49]</sup> have been introduced to the market. The tapered structures will be outlined in the section treating advanced structures.



The performance of HSDs as viscosity modifier relies on the oil-soluble polydienes, whereas polystyrene is insoluble in oils over most of the relevant temperature range, its solubility increasing at higher temperatures and with shortened block lengths.<sup>[2]</sup> Therefore, a greater polydiene proportion ensures maximum thickening efficiency. Yet, polystyrene is important to improve thermal and oxidative stability and to provide a considerable shear stability. On top, polystyrene results in improved soot handling and piston cleanliness, since the soot surface is largely aromatic and interacts with polystyrene domains.<sup>[2]</sup> In combination with the polydiene part, agglomeration can be prevented by steric hindrance.<sup>[50]</sup> The effect depends on the styrene content and the distribution of polystyrene long the polymer chain, with star architectures contributing less to soot handling.<sup>[2]</sup>

The shear stability of linear HSDs can be attributed to the disassembly of associated chains with a polystyrene core and a polydiene corona. The formed micelles provide the necessary thickening at higher temperatures.<sup>[2]</sup> To maintain good performance at low temperatures, large blocks of hydrogenated 1,4-polybutadiene are to be avoided due to its potential crystallization. Yet, the use of butadiene can be explained by economical means due to the inexpensive monomer butadiene.<sup>[2]</sup> Apart from polystyrene, also polyisoprene or 1,2-butadiene repeating units are capable of disrupting undesired, large linear polyethylene segments, which resemble polybutylene upon hydrogenation. The ratio of the different polydiene microstructures can be adjusted by the reaction conditions, i.e., the choice of the solvent, counterion or the implementation of polar additives.<sup>[51]</sup> The polydiene segments can be selectively hydrogenated using either a heterogeneous or a homogeneous catalyst system. The most prominent

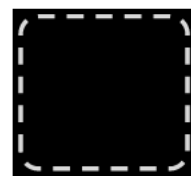
examples for heterogeneous catalysts are nickel on diatomaceous earth or Raney nickel, while the preferred homogeneous catalyst is obtained by the reduction of nickel octoate with triethylaluminum.<sup>[44–48,52]</sup> However, it is noteworthy that the hydrogenation of styrene-diene copolymers with a heterogeneous catalyst system can be very challenging since potential aggregation hampers the contact between the polymer repeating units and the active sites of the catalyst.

Besides aggregation phenomena of linear HSDs, improved shear stability can be realized with star-shaped architectures, however at the expense of worse thickening.<sup>[53]</sup> These structures are easily realized by the reaction of living chains, called arms, with divinyl benzene<sup>[54]</sup> or diisocyanates<sup>[2]</sup>. These approaches typically result in a distribution of arm numbers varying between 10–20.<sup>[46,47,55]</sup> Star-shaped copolymers with homo-polyisoprenyl arms<sup>[47,55]</sup>, or block structures based on styrene, isoprene<sup>[46,56]</sup> and/or butadiene<sup>[57]</sup> as arms are known. For structures with hydrogenated polybutadiene, adverse effects on the low-temperature viscosity due to crystallization could be minimized by polymerizing butadiene at late stages, resulting in polybutadiene segments near the core.<sup>[57]</sup> Comparing a star-shaped HSD with hydrogenated polyisoprene arms with stars of hydrogenated polydiene-polystyrene-polydiene triblock copolymers, the triblock copolymers stand out due to better shear stability and higher viscosity index.<sup>[56]</sup>

Altogether, HSDs excel in thickening efficiency at superior shear stability, which results from the narrow molar mass distribution in combination with the particular shear alignment of aggregates or star-shaped polymers. Due to this profitable balance between thickening efficiency and shear stability (see Figure 6), lower polymer treat rates are sufficient. Their relatively lower contribution to the viscosity at high shear rates at temperatures are beneficial since better fuel efficiency can be achieved, as long as the film thickness still guarantees wear protection.<sup>[2]</sup> Consequently, linear as well as star-shaped HSDs were commercialized for multigrade engine oils and heavy-duty diesel, which replace most of the monograde lubricants. Furthermore, they find application in top-tier formulations of lower viscosity oils for, e.g., transmission fluids. Nonetheless, shear stability demands for many specialized lubricant applications cannot be met.<sup>[12]</sup>

## Polyalkyl Methacrylates

Polyalkyl methacrylates are commonly polymerized using free radical polymerization techniques, resulting in dispersities of minimally 1.5 or 2, for chain termination by recombination or disproportionation, respectively. Besides, chain transfer reactions by hydrogen abstraction at random sites along the polymer chain can cause the formation of branched polymers, impairing the thickening efficiency of the formed polymer.<sup>[2]</sup> Choosing a controlled radical polymerization approach, the dispersity can be lowered ( $\bar{D} \leq 1.3$ ) and gives access to block or star architectures (*vide infra*), however at the expense of higher cost.<sup>[6]</sup>



The most important factor influencing the performance of PMAs as viscosity index improvers is their solubility, which is tuned by the alkyl residue. Therefore, different alkyl methacrylates are usually copolymerized, rendering a wide spectrum of polymers with highly adjustable solubility and flexibility. Short side chains ( $<C_7$ ) are poorly soluble in oils, but have a

considerable impact on the polymer coil size (*vide supra*, Thickening Efficiency), thus tuning the thickening efficiency and the viscosity-temperature relationship.<sup>[5]</sup> Since the solubility increases with side chain length, intermediate chain lengths (C<sub>8</sub>-C<sub>13</sub>) provide solubility in hydrocarbon media. The implementation of long-chain methacrylates (>C<sub>14</sub>) renders a further benefit by the interaction of the side chains with waxes present in many base oils. The pendant side chains have been shown to co-crystallize at the edges of the growing wax plates and in this way sterically hinders the formation of three-dimensional structures, which is summarized under the term “pour point depressancy”. As a result, the operating temperature window is expanded to colder regimes.<sup>[2]</sup> Furthermore, the incorporation of polar monomers containing nitrogen (e.g., diethylaminoethyl methacrylate<sup>[58]</sup>) or oxygen atoms provides dispersant properties, which enable to suspend soot particles and small polar molecules resulting from the oxidation of the oil or fuel.<sup>[2]</sup> Besides, physical adsorption on polar surfaces forms a boundary film, additionally decreasing friction and consequently wear.

However, only free radical copolymerization at the azeotropic monomer ratio will result in a homogeneous material, whereas other monomer combinations result in the stronger depletion of one monomer for comonomer pairs with diverging reactivity ratios. Due to the continuous termination and initiation of polymer chains, a polymer blend with chains greatly varying in composition is formed. Since the reactivity ratios of alkyl methacrylates are similar, this has not to be taken into consideration for the copolymerization of methacrylates with varying side chain length.<sup>[2]</sup> Yet, for the incorporation of polar monomers which do not readily copolymerize with methacrylates, controlled radical polymerization techniques or grafting strategies have to be implemented. This way, non-methacrylates like styrene<sup>[59]</sup> increasing the shear stability, nitrogen-containing monomers (e.g., *N*-vinylpyrrolidone<sup>[60]</sup> and *N*-vinyl imidazole<sup>[61]</sup>) or oxygen-containing monomers (e.g., hydroxyethyl methacrylates<sup>[62]</sup> and ether-containing methacrylates<sup>[63]</sup>) providing dispersant properties can be introduced.

The superior viscosity-temperature relationship of PMAs is based on their temperature-dependent solubility (*vide supra*, Polymer Coil Expansion). At low temperatures, poly methacrylates are poorly soluble in oils, hardly contributing to the systems' viscosity. As the temperature increases, the polymers become more soluble and the coils expand, now increasing the viscosity to a significant extent.<sup>[18]</sup>

Besides, PMAs are attractive due to their stability. Regarding thermal stability, depolymerization and ester pyrolysis only occurs under severe conditions ( $T > 235$  °C and  $T > 250$  °C, respectively).<sup>[2]</sup> Besides, the pendant methyl group of methacrylates shields the ester group from nucleophilic reagents. Furthermore, PMAs are not prone to oxidation reactions since they lack allylic, benzylic, or tertiary hydrogen atoms.

In summary, PMAs lead to an outstanding viscosity index improvement and good low-temperature performance compared to OCPs. The major drawback besides a permanent viscosity loss upon shearing is the low thickening efficiency. Therefore, they find application where high viscosity indices and superior low-temperature properties are required, including hydraulic fluids for instance for aircrafts, gear oils and transmission fluids.<sup>[1,5]</sup> Their use for engine oils is limited, since higher treat rates makes them cost-disadvantageous compared to OCPs. However, in special cases like heavy-duty engine oils, PMAs are utilized due to their concomitant soot control.<sup>[2]</sup>

## Advanced Structures

Besides the discussed common viscosity modifiers, more complex structures uniting the properties of different polymer classes or exceeding the performance limits were tackled in recent developments in this area.

### Advanced Viscosity Modifiers relying on Coil Expansion

As discussed before, especially polar polymer structures like PMAs provide good viscosity-temperature relationships, however facing the issue of high polymer treat rates due to poor thickening efficiencies. One approach to combine both a good viscosity-temperature relationship with high thickening efficiencies is compounding of PMAs and OCPs. To enable blending of these immiscible polymers, compatibilizers have to be introduced, which are grafted structures with roughly 70% PMA and 30% OCP.<sup>[64]</sup> Furthermore, comb-like PMA structures obtained by radical copolymerization of alkyl methacrylates onto polyolefin macromonomers are of interest, since a higher hydrodynamic volume at low temperatures allows for lower polymer treat rates.<sup>[65]</sup> Besides, the viscosity index is improved compared to conventional PMAs, however at the expense of a slightly worsened permanent shear stability.<sup>[66]</sup>

Studies on polymers from 2-oxazolines or 2-oxazines (see Figure 11, left) demonstrate another possibility to improve friction reduction. These polymers, whose solubility can be adjusted in analogy to PMAs by the introduction of various substituents in the side chain, show an improved viscosity at high temperatures and shear rates.<sup>[67]</sup> Although no statements concerning the thickening efficiency have been made, the implementation of polar repeating units with two or three methylene spacers instead of one as in case of poly(alkyl methacrylates) most likely enhances the thickening efficiency, since the fraction of the polymer's molecular weight in the backbone correlates with the thickening efficiency (*vide supra*). Recently, the cationic ring opening method of 2-oxazolines has been developed further towards a combination with controlled radical polymerization techniques allowing for various brush architectures, however at high cost (see Figure 11, right).<sup>[68]</sup>

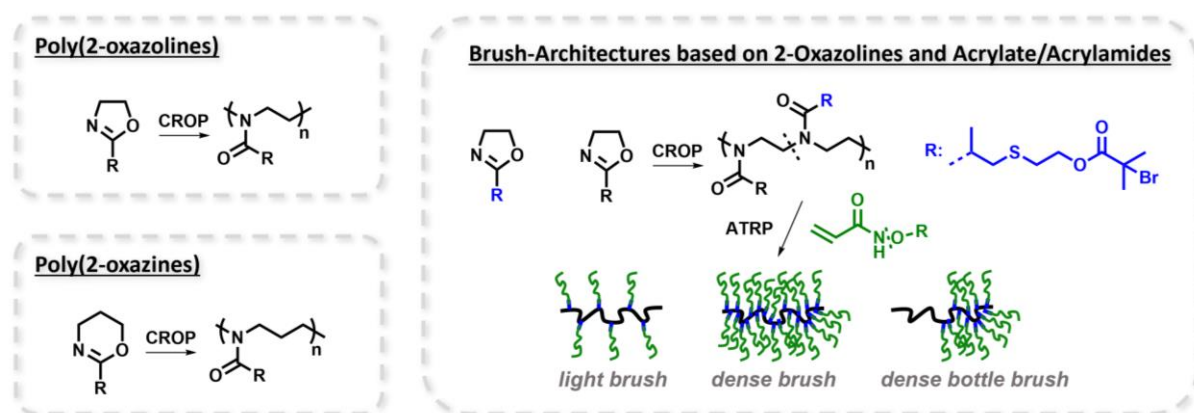


Figure 11: Advanced polymer structures based on 2-oxazolines or 2-oxazines, which can be polymerized by cationic ring opening polymerization (CROP). The polymerization of acrylates or acrylamides in case of the brush-architectures proceeds by controlled radical polymerization techniques, namely atom transfer radical polymerization (ATRP).



As depicted, in a first step, a poly(2-oxazoline) backbone is formed, with some repeating units bearing an initiator function for copper-catalyzed controlled radical polymerization. The distribution of these monomers with an initiator function, so-called inimers, later defines the location and density of the brushes. In a second step, acrylates or acrylamides can be polymerized onto the initiator functions forming the brushes. To date, these structures have not been investigated in the context of lubrication application, but the combination of a higher backbone molar mass compared to PMAs together with the brush- or comb-like architecture appears promising.

### ***Advanced Viscosity Modifiers relying on Association***

The introduction of block structures for viscosity modification has a beneficial effect on permanent shear stability, since the formed aggregates partially disassemble under shear. By this mechanism, chain degradation and hence permanent viscosity loss can be circumvented to a large extent, however the temporary viscosity loss is pronounced at high shear rates.

To counteract this reversible viscosity loss, one approach relies on the extension of the widely used di- and triblock copolymers to multiblock copolymers. Going from diblock to multiblock copolymers, different insoluble blocks of the same polymer chain can participate in the formation of different aggregated domains by intramolecular,<sup>[69]</sup> but also intermolecular association.<sup>[70]</sup> The latter allows for the formation of more extended structures or even a three-dimensional network, i.e., a gel in solution.<sup>[71]</sup> All in all, the association of multiblock copolymers in a selective solvent promises even larger aggregates, which can be expected to thicken the oil to a larger extent and whose disassembly is more gradual, since multiple physical connection per chain exist.

Manifold theoretical approaches have been employed to investigate self-assembled structures of multiblock copolymers in solution. However, most works treat amphiphilic multiblock copolymers, whose hydrophobic blocks oftentimes become less soluble upon temperature increase, because the miscibility is entropy-driven and the hydration becomes weaker with increasing temperature. Therefore, the definition of the temperature influence on the solvent quality has to be examined carefully. Prominent examples are copolymers with poly(*N*-isopropyl acryl amide)<sup>[72]</sup> or poly(propylene oxide)<sup>[73]</sup>.

There are several intrinsic key parameters having a strong effect on the self-assembled structures, such as block number, ratio of solvophilic to solvophobic moieties, and their compatibility as well as rigidity. Besides, also extrinsic parameters like concentration and solvent quality influence the self-assembly of multiblock copolymers. The nature of the collapsed state can further change with time and the probability of chain rearrangement.<sup>[15]</sup> The self-assembly starts with the formation of clusters along the chain, meaning intramolecular chains of micelles, which is rather fast, potentially followed by a coalescence of the clusters and kinetic rearrangement into more compact globules, which can also cause macrophase separation.<sup>[74]</sup> Figure 12 shows the predicted self-assembled structures of an icosablock with a solvophobic ratio of 50% in dilute solution, thereby neglecting intermolecular association account. In a selective solvent, the formation of single flower-like micelles was predicted.<sup>[75]</sup> Furthermore, more extended structures with multiple bridges and higher number of cores were obtained upon simulating multiblock copolymers with soluble A-blocks of higher rigidity.

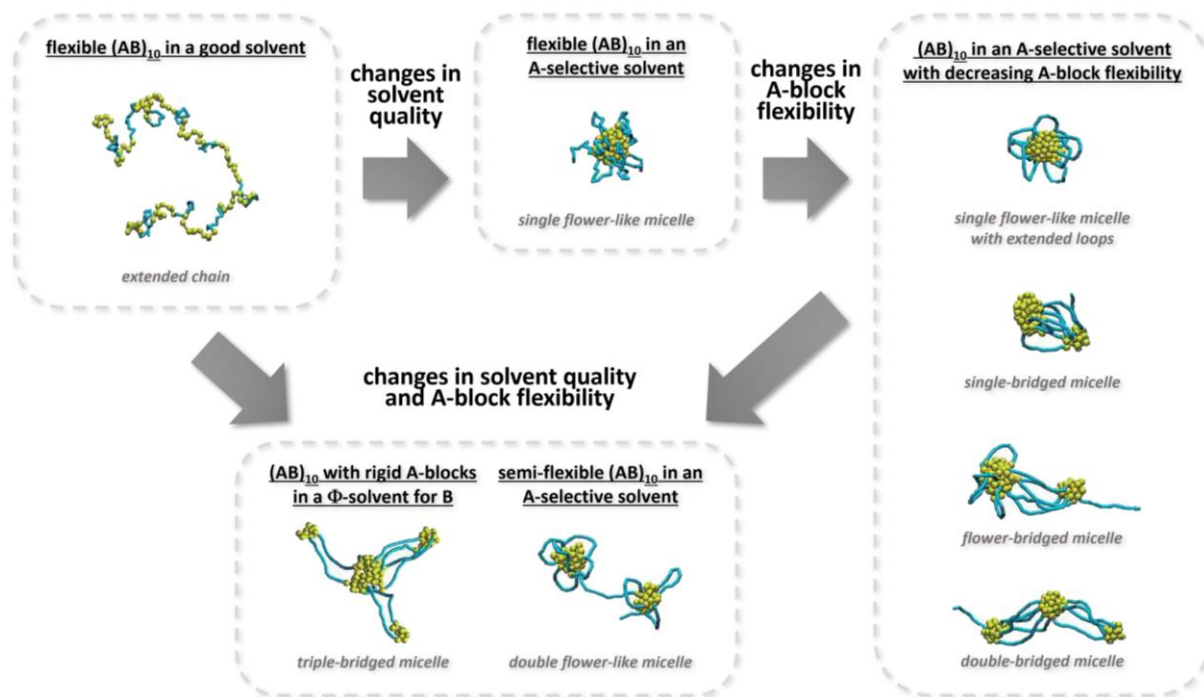


Figure 12: Self-assembled structures of amphiphilic  $(AB)_{10}$  block copolymers with 10 hydrophilic A-blocks (blue) and 10 hydrophobic B-blocks (yellow) in dilute solution, which were predicted by Brownian dynamics simulation. The predicted structures vary due to changes in solvent quality and A-block flexibility. <sup>adapted from [75]</sup>

For even higher block numbers and hence longer polymer chains, a transition from single- to multi-flower-like micelles was identified (see Figure 13). These structures of several flower-like motifs are often referred to as pearl-necklace structures. <sup>[69]</sup>

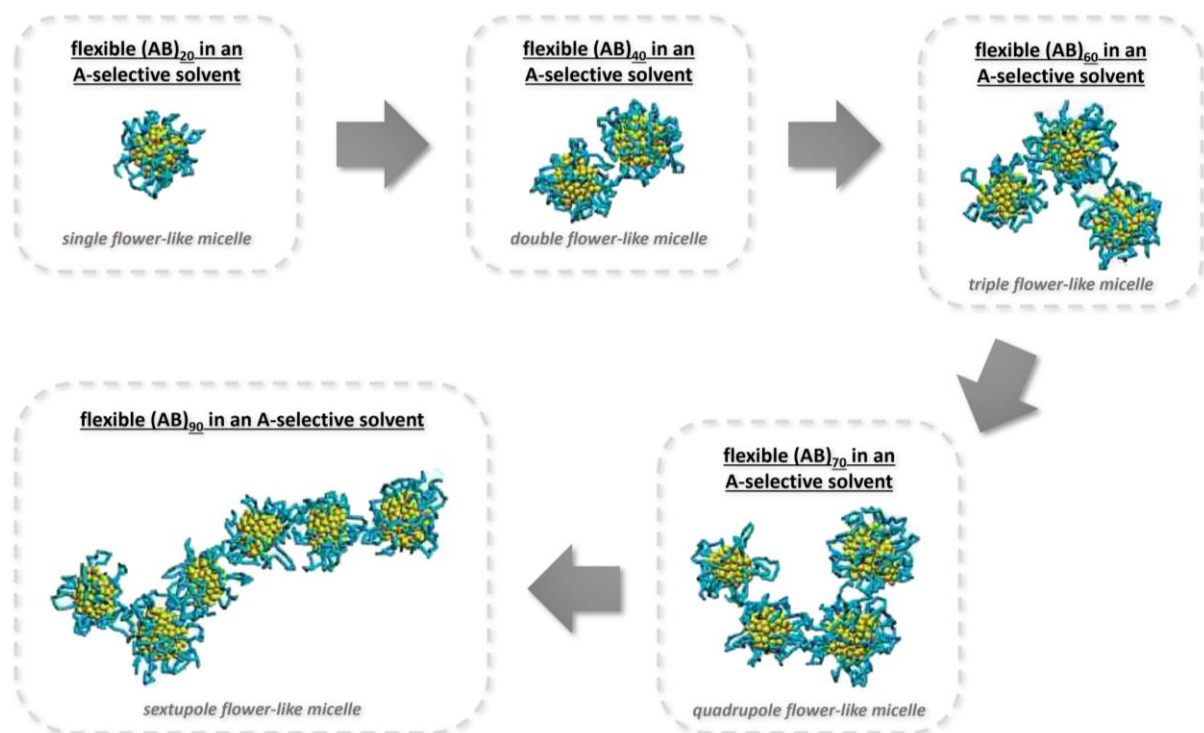
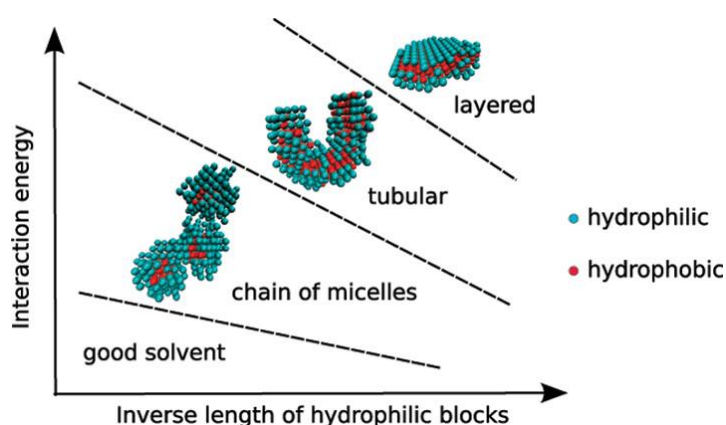


Figure 13: Self-assembled structures of amphiphilic  $(AB)_n$  block copolymers with  $n$  hydrophilic A-blocks (blue) and  $n$  hydrophobic B-blocks (yellow) in dilute solution, which were predicted by Brownian dynamics simulation. The predicted structures vary due to increasing block numbers and hence polymer chain length. <sup>adapted from [75]</sup>

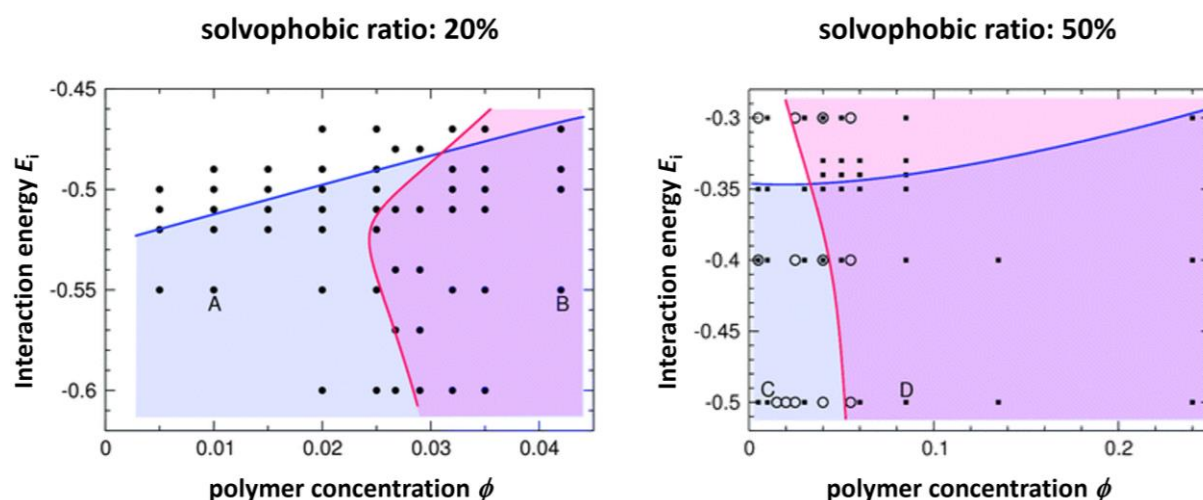
With respect to the ratio of solvophilic to solvophobic moieties, different intramolecular structures were predicted, with the phase boundaries being dependent on the solvent quality. Figure 14 shows that with decreasing solvent quality, a transition from a coil to different intramolecular structures occurs, which are chains of micelles, also referred to as pearl-necklaces<sup>[69]</sup>, tubular and layered structures.<sup>[76,77]</sup> The higher the fraction of solvophobic units, the earlier is the onset of the coil-to-globule transition as well as the change between the collapsed structures. Decreasing solvent quality leads to an increase in core size, while decreasing solvophobic ratio, i.e., increasing length of the solvophilic blocks, reinforces the protective corona and hence tends to decrease the core size. Therefore, an increase of both parameters keeps the structure unchanged.<sup>[76]</sup> In other words, whether micelles of pearl-necklace structures merge depends on the balance between the attractive interaction between the solvophobic blocks, and the excluded volume of looped solvophilic blocks.<sup>[78]</sup> An analogous trend was predicted for varying the compatibility between the two constituent blocks of the multiblock copolymers.<sup>[79]</sup>



**Figure 14:** Phase diagram of multiblock copolymers as a function of the solvophobic ratio (small inverse lengths of the hydrophilic blocks correspond to a small solvophobic ratio) and the interaction energy (higher interaction energies correspond to a worsened solvent quality). taken from [76]

In semi-dilute solution both intra- and intermolecular interaction come into play. Figure 15 recaps the phase diagrams of multiblock copolymers with 10 blocks but differing solvophilic to solvophobic ratios.<sup>[80]</sup> The left phase diagram was simulated for decablock copolymers with overall 20% of solvophobic moieties, while the right phase diagram corresponds to decablock copolymers with 50% of the solvophobic units. Both phase diagrams illustrate the obtained structure in solution as a function of concentration  $\phi$  and interaction energy  $E_i$ , which can also be interpreted as solvent quality. Within the blue area, micelles were predicted, whereas within the red area, gelation occurs.

For both solvophobic ratios, the blue line shows that with increasing interaction strength (i.e., lower interaction energy  $E_i$  values, which correspond to stronger attractive forces between the solvophobic moieties and hence a worse solvent), critical micelle concentration denoting the onset of self-assembly decrease. However, for the polymers of a solvophobic ratio of 50%, micellization occurs already at weaker interaction energies (i.e., high  $E_i$  values, which correspond to better solvents) at a given concentration. The decablock copolymers with 20% of solvophobic units featured spherical micelles, whereas for the decablock copolymers with 50% of solvophobic units, core-shell structure became more elongated (see Figure 14, tubular structure). For both systems, longer chains resulted in the corresponding extended structures, which are pearl-necklace or worm-like structures, respectively.



**Figure 15:** Phase diagrams of multiblock copolymers with 10 blocks simulated with either a short solvophobic block and a long solvophilic block (left) or equal block length (right). The areas denote the formation of micelles (blue) or gels (red) as a function of interaction energy  $E_i$  and concentration  $\phi$ . Within the white area, neither micellization nor gelation takes place. adapted from [80]

The red lines feature distinct behaviors for the multiblock copolymers with either 20% or 50% of solvophobic moieties. For a solvophobic ratio of 20%, the phase diagram reveals a pronounced non-monotonic relationship, with the earliest onset of gelation at a concentration of 2.6% leading to a sol-gel transition followed by a gel-sol transition upon increasing the interaction strength. At lower concentration, no gel formation was simulated. This curvature in the sol-gel phase boundary can be explained by increasing core size with increasing interaction strength, which effectively shortens the chains. This prevents gelation at higher interaction energies.<sup>[80]</sup> For 50% of solvophobic moieties, no maximum, but a slight shift of the boundary to higher concentration with increasing interaction energy was predicted, which is ascribed to this aforementioned increase in core size. Again, remarkably lower concentrations are sufficient to observe gelation, what narrows the window of isolated associated structures at the expense of a large area in which network-structures are formed.

There are few experimental studies proving the before discussed theoretically predicted structures. For instance, for amphiphilic multiblock copolymers based on 2-(dimethylamino)ethyl methacrylate and methyl methacrylate, only a slight increase of the hydrodynamic radii upon extending the triblock towards a pentablock structure with two hydrophilic end blocks was observed, implying backfolding of the chains resulting in flower-like micelles.<sup>[81]</sup> Besides, photoinitiated crosslinking of assembled structures of triblock copolymers with poly(methacryloxyethyl acrylate) end blocks and a poly(ethylene oxide) mid block evidenced flower-like micelles at low concentration and a transient network above a critical concentration.<sup>[82]</sup>

Furthermore, the influence of the block number  $m$  and the degree of polymerization per block  $n$  in  $(A_nB_n)_m$  multiblock copolymers on the phase separation was theoretically studied, revealing a critical ratio, above which macrophase separation takes place.<sup>[83]</sup> Table 3 reveals that for equal degrees of polymerization per block  $n$ , an increase in block number  $m$  and hence overall molar mass favors macrophase separation (data per row). However, for a fixed number of blocks, longer individual blocks reduce the tendency for macroscopic phase separation (data per column).



**Table 3: Microphase separation (i.e., micellization, blue) versus macrophase separation (red) for multiblock copolymers with equal fractions of solvophilic and solvophobic units as a function of degree of polymerization per block and number of blocks per chain.** <sup>adapted from [83]</sup>

| Diblock      | Tetrablock   | Hexablock    | Octablock    | Dodecablock  |
|--------------|--------------|--------------|--------------|--------------|
| $(A_1B_1)_1$ | $(A_1B_1)_2$ | $(A_1B_1)_3$ | $(A_1B_1)_4$ | $(A_1B_1)_6$ |
| $(A_3B_3)_1$ | $(A_3B_3)_2$ | $(A_3B_3)_3$ | $(A_3B_3)_4$ | $(A_3B_3)_6$ |
| $(A_5B_5)_1$ | $(A_5B_5)_2$ | $(A_5B_5)_3$ | $(A_5B_5)_4$ | $(A_5B_5)_6$ |

This dependency of the association behavior was also found experimentally, comparing a hydrogenated triblock based on styrene and butadiene forming flower-like micelles,<sup>[24]</sup> with the polystyrene-polybutadiene pentablock copolymer with comparable degree of polymerization per block and hence a higher overall molar mass, which macrophase separated in heptane within the dilute regime.<sup>[84]</sup>

Another theoretical study focused on the influence of the block number at a constant overall composition and molar mass on the collapse upon cooling.<sup>[74]</sup> For an alternating “multiblock”, the internal energy decreases most pronouncedly at a comparably low temperature, whereas a more gradual decrease of the internal energy with an onset at higher temperatures was predicted as the block number decreased and hence individual block length increased. In terms of chain collapse, the higher the block number, the later is the onset upon cooling. Furthermore, the radius of gyration was calculated, showing that the change in structural dimension is most dramatic for small block sizes, since the intramolecular association of the solvophobic blocks implies a constraint of the solvophilic block.

However, further theoretical or experimental information on the influence of the block number or individual block length has not been reported so far. Moreover, behavior of aggregates of multiblock copolymers under shear is not well studied and, due to this, understood. Yet, two practical examples providing insight into the applicability for viscosity modifiers shall be highlighted.

Regarding olefinic multiblock copolymers, the former company Dow Chemicals patented a metallocene catalysis with different catalysts of opposite reactivity towards the comonomers in combination with a chain shuttling agent transferring the active propagating center from one catalyst to another, leading to the formation of OCP multiblock copolymers.<sup>[85]</sup> The hard blocks comprise 60-95 wt% of polyethylene, while the softer segments have a larger polypropylene fraction (55-75 wt% polyethylene). This way, the crystallinity of the polyethylene moieties could be controlled. It is stated that these multiblock structures enhance both oil solubility and clarity of this class of OCPs. However, since both hard as well as soft blocks are readily soluble in base oils, no improved shear stability could be achieved (SSI=25-50).

Kraton patented multiblock structures of hydrogenated styrene-diene copolymers for improved compounding<sup>[86]</sup> or adhesives<sup>[87]</sup>. Linear multiblock copolymers with two polydiene end blocks and 1-5 polystyrene mid blocks are described. The advantage of multiblock structures lies in good tack, peel strength and shear behavior provided by polydiene end blocks and at least two network-forming blocks. This cannot be achieved using diblock copolymers or

blends thereof, since shear properties such as holding power are detrimental. Nevertheless, to the best of our knowledge no implementation as lubricant additives has been reported. This may be reasoned in an insufficient control over the molar mass distribution, since the synthesis of these multiblock copolymers relies on sequential polymerization and/or coupling. Multiple monomer feeds allow for accessing linear multiblock structures by sequential polymerization, but can result in a blend of various polymers differing in their block number, if the reaction apparatus is not sealed properly or if the monomers are not purified entirely. With respect to coupling strategies, incomplete coupling by the implemented dibromo ethane or nonstoichiometric amounts in analogy lead to undefined products. Although the molar mass distributions are stated to be close to monodisperse, adverse effects on the shear stability might be an obstacle for their use as viscosity modifier.

### ***Advanced Viscosity Modifiers relying on Association and Polymer Coil Expansion***

The ultimate goal for viscosity modification is certainly the invention of structures with an exceptional improvement of the viscosity index, which at the same time exhibit good shear stability and thickening efficiency. For this purpose, both mechanisms of coil expansion and association ought to be unified in polymers with a narrow molar mass distribution. On this aspect, the potential of gradient structures shall be outlined.

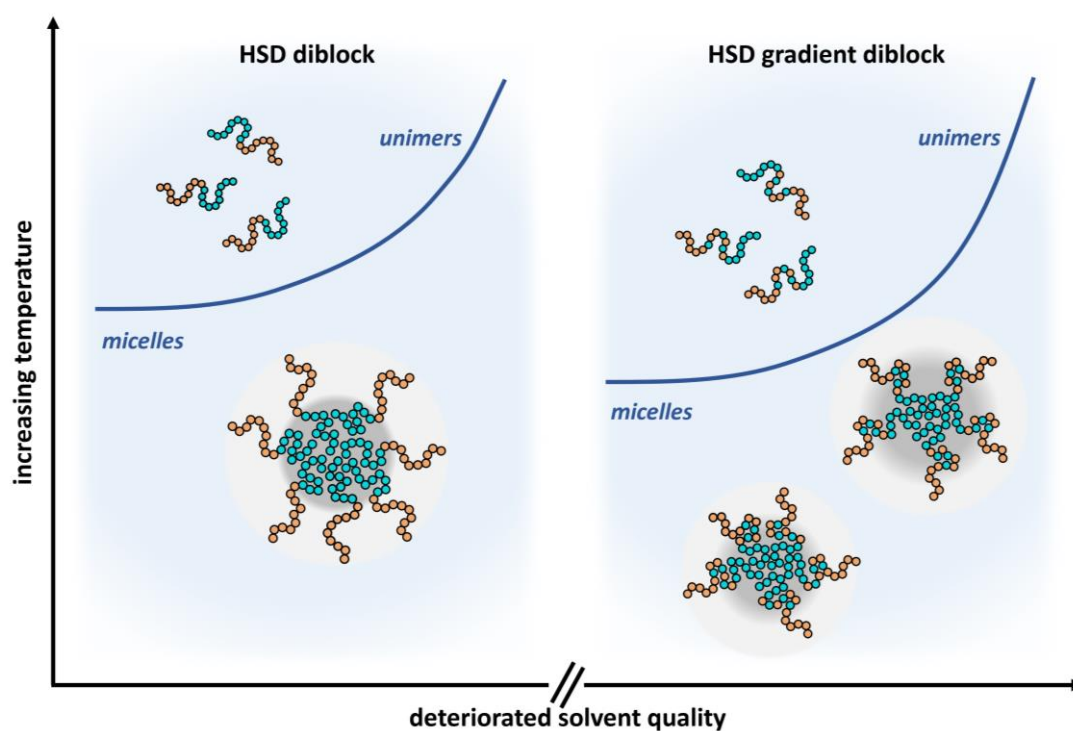
As described before, polymer coil expansion with temperature renders a pronounced viscosity increase, which is well known for poly(alkyl methacrylates), while the molecular dimensions of hydrocarbon-based polymers are constant with temperature.<sup>[20]</sup> The viscosity increase of hydrogenated styrene-diene copolymers only relies on the interaction of multiple polymer chains.<sup>[2]</sup> However, the introduction of gradient structures bears the potential to introduce a temperature responsiveness to the polymer's coil size of hydrogenated styrene-diene copolymers.

Gradient copolymers slightly differ from block copolymers in their chain composition, i.e., block profile. Such structures are formed by the copolymerization of two monomers with highly disparate reactivity ratios. The resulting so-called tapered or gradient copolymers exhibit a block-like structure, but the interface between the two adjacent blocks is diffuse, since the less reactive monomer forming the second block is also incorporated within the first block of the more reactive monomer, yet to a much lesser extent.<sup>[40]</sup> Basically, gradient copolymers show a similar micellization behavior to block copolymers, however few works reported special characteristics, which will be summarized in the following.<sup>[88]</sup>

Upon reaching a critical temperature, concentration, and solvent quality, unimers aggregate into micelles, as depicted in Figure 16. The key difference between block copolymer micelles and gradient copolymer micelles is the interface. While block copolymer micelles exhibit a sharp interface between core and corona, gradient copolymers possess a more diffuse transition between non-solvated core and dissolved corona. This can be explained by the interaction parameters between the polymer's repeating units and the solvent molecules. For the core-forming block, the interaction of the repeating units among themselves is favored over the interaction with the solvent. By the presence of both soluble and insoluble repeating units within the interface between the two blocks, loop formation in the interfacial region due

to association of solvophobic repeating units is likely.<sup>[89]</sup> As a result, the interface of gradient copolymer micelles is swollen by solvent molecules.<sup>[90]</sup>

Three predictions concerning differences between gradient and block copolymer micelles have been made and are also captured in Figure 16: gradient copolymers exhibit a weaker association compared to corresponding block copolymers with the same composition.<sup>[89,91,92]</sup> This is attributed to the shorter effective length of the solvophobic block, leading to better solubility of gradient copolymers. Therefore, the onset of micellization is slower in gradient copolymers. Furthermore, the aggregation number of gradient copolymer micelles is smaller leading to smaller aggregate sizes, which is explained by the larger occupied interface area due to loop formation.<sup>[89,91]</sup> Lastly, the so-called reel-in effect describing the thermoresponsive properties of gradient copolymer micelles is stated.<sup>[89]</sup> It characterizes the reverse stretching or shrinkage of the diffuse interface induced by altering temperature or solvent quality. This effect is reasoned in solubility changes of the solvophobic repeating units, resulting in a dissolution or collapse of the gradual chain segments near the interface.<sup>[93]</sup>



**Figure 16:** Schematic illustration of the structural transitions of block copolymers (left) and gradient block-like copolymers (right) upon micelle formation. The micelles of gradient copolymers are smaller due to a decreased aggregation number and exhibit a diffuse core-corona interface of the gradual chain segments which forms loops, the latter being temperature dependent.

For hydrogenated styrene-diene copolymers, the increasing solubility of polystyrene with increasing temperature leads to the assumption, that gradual chain segments become more drained by solvent with increasing temperature and hence the chains become more stretched, by this means inducing a significant change in hydrodynamic volume and hence viscosity. However, to date, the reel-in effect has only been reported for other, mostly amphiphilic or pH-responsive, gradient copolymer systems.<sup>[94]</sup> Nonetheless, from a theoretical point of view, tapered hydrogenated styrene-diene copolymers are promising candidates for superior viscosity index improvers, for which reason their investigation in solution should be promoted.

## Outlook

On a long term, the development of lubricants aims at better emission control, fuel efficiency and fluid lifetime. While conventional demands such as thermal and oxidative stability are maintained, requirements for the aforementioned objectives are oftentimes contradictory and hence not straightforward to access.<sup>[2]</sup> For instance, the use of lubricants of low overall viscosity is beneficial for an improved fuel efficiency, since it reduces frictional losses. At the same time, film thickness has to be sufficient over the whole application temperature range, which is why high viscosity indices are needed to minimize the viscosity decrease by temperature changes. Furthermore, superior shear stabilities are mandatory to provide reasonable lifetime of these low-viscosity lubricants. Both aspects imply higher treat rates of the viscosity modifier, which is economically unfavored. Besides, for viscosity modifiers used so far, higher treat rates result in higher low-temperature viscosities, which deteriorate cold-cranking performance. All these correlations emphasize the need for further developed viscosity modifiers with enhanced shear stabilities and thickening efficiencies providing outstanding viscosity index improvement. Even if the progress towards engines based on batteries, fuel cells, or hydrogen gas continues, which can lead to a decline in the engine oil demand, their use in hydraulics still represents an important field of application.

## Conclusions

Within this review, the fundamental relationships between the key parameters defining the performance of viscosity modifiers were outlined. These are (i) viscosity index improvement, which designates the viscosity decrease upon increasing temperature, (ii) thickening efficiency, which quantifies the amount of polymer needed to access a certain viscosity-temperature relationship, and (iii) shear stability, which is a measure of the resistance to permanent viscosity loss upon shearing.

To date, three polymer classes are commonly implemented for viscosity modification: poly(alkyl methacrylates) (PMAs) provide a good viscosity index improvement, but rather poor thickening efficiencies and shear stabilities; olefinic copolymers (OCPs) exhibit good thickening efficiencies, but a poor viscosity index improvement and shear stabilities; and hydrogenated styrene-diene copolymers (HSDs) stand out due to their superior shear stability and good thickening efficiency, but cannot compete with PMAs in terms of viscosity index improvement. The latter is reasoned in the mechanism for viscosity increase of HSDs, which relies on the association of the block copolymers, whereas PMAs feature a stronger viscosity index improvement because of polymer coil expansion with temperature.

However, none of the current viscosity modifiers can provide optimum performances in all three of these properties. Therefore, several approaches towards superior additives were addressed. As potential alternatives to PMAs, poly(2-oxazolines) and poly(2-oxazines) were presented, most probably enhancing thickening efficiency by altering the fraction of the molar mass of the polymer within the backbone. For viscosity modifiers with high shear stability, multiblock architectures of HSDs were highlighted, whose self-assembled structures may further enhance shear stability and thickening efficiency due to more extended structures with multiple aggregating blocks per chain. To further optimize HSDs with respect to their viscosity



index improvement, the introduction of HSDs with a tapered interface between the blocks was proposed. The rather diffuse core-corona interface of the formed micelles could provide access to thermoresponsive structures, since solubility of the diffuse interface should be enhanced with increasing temperature, which might lead to chain extension within the corona of the aggregated polymers.

Yet, these advanced structures were not investigated in detail against the background of an application as viscosity modifier. Therefore, this work intends to motivate for a continuing development and tribological characterization of viscosity index improvers.

## References

- [1] S. Q. A. Rizvi, *A comprehensive review of lubricant technology. Selection, and design*, ASTM International, West Conshohocken, PA, **2008**.
- [2] L. R. Rudnick, *Lubricant Additives. Chemistry and Applications, Third Edition*, CRC Press, Portland, **2017**.
- [3] American Petroleum Institute, "APPENDIX E—API BASE OIL INTERCHANGEABILITY GUIDELINES FOR PASSENGER CAR MOTOR OILS AND DIESEL ENGINE OILS", can be found under <https://www.api.org/certification-programs/engine-oil-diesel-exhaust-fluid/~media/files/certification/engine-oil-diesel/publications/appendix-e-rev-09-01-11.ashx>, **2011**.
- [4] Y. Porfiryev, S. Shuvalov, P. Popov, D. Kolybelsky, D. Petrova, E. Ivanov, B. Tonkonogov, V. Vinokurov, *ACS Omega* **2020**, 5, 11946.
- [5] A. Martini, U. S. Ramasamy, M. Len, *Tribol. Lett.* **2018**, 66, 1.
- [6] S. Koltzenburg, R. Mülhaupt, M. Maskos, O. Nuyken, *Polymere: Synthese, Eigenschaften und Anwendungen*, Springer Berlin Heidelberg; Springer Spektrum, Berlin, **2022**.
- [7] Y. Lu, L. An, Z.-G. Wang, *Macromolecules* **2013**, 46, 5731.
- [8] W.-M. Kulicke, C. Clasen, *Viscosimetry of Polymers and Polyelectrolytes*, Springer Berlin Heidelberg, Berlin, Heidelberg, **2004**.
- [9] P. Panwar, E. Schweissinger, S. Maier, S. Hilf, S. Sirak, A. Martini, *J. Mol. Liq.* **2022**, 359, 119215.
- [10] J. Holtzinger, J. Green, G. Lamb, D. Atkinson, H. Spikes, *Tribol. Trans.* **2012**, 55, 631.
- [11] M. J. Covitch in *SAE Tech. Pap. Ser.*, SAE International, **1998**.
- [12] R. M. Mortier (Ed.) *Springer Link Books*, Springer Netherlands, Dordrecht, **2010**.
- [13] P. Bezot, C. Hesse-Bezot, D. Faure, J. C. Calvez, *Lubr. Sci.* **2000**, 12, 301.
- [14] J. Cui, S. Oberoi, I. Goldmints, S. Briggs, *SAE Int. J. Fuels Lubr.* **2014**, 7, 882.
- [15] S.-H. Choi, F. S. Bates, T. P. Lodge, *Macromolecules* **2011**, 44, 3594.
- [16] S.-H. Choi, T. P. Lodge, F. S. Bates, *Phys. Rev. Lett.* **2010**, 104, 47802.
- [17] Y. Tsunashima, M. Hirata, Y. Kawamata, *Macromolecules* **1990**, 23, 1089.
- [18] M. J. Covitch, K. J. Trickett, *Adv. Chem. Eng. Sci.* **2015**, 05, 134.

- [19] U. S. Ramasamy, S. Lichter, A. Martini, *Tribol. Lett.* **2016**, 62.
- [20] D. Lariviere, A.-F. A. Asfour, A. Hage, J. Z. Gao, *Lubr. Sci.* **2000**, 12, 133.
- [21] C. Mary, D. Philippon, L. Lafarge, D. Laurent, F. Rondelez, S. Bair, P. Vergne, *Tribol. Lett.* **2013**, 52, 357.
- [22] B. G. P. van Ravensteijn, R. B. Zerdan, C. J. Hawker, M. E. Helgeson, *Macromolecules* **2021**, 54, 5473.
- [23] M. E. Shivokhin, T. Narita, L. Talini, A. Habicht, S. Seiffert, T. Indei, J. D. Schieber, *J. Rheol.* **2017**, 61, 1231.
- [24] Č. Koňák, G. Fleischer, Z. Tuzar, R. Bansil, *J. Polym. Sci., Part B: Polym. Phys.* **2000**, 38, 1312.
- [25] a) A. Jangizehi, M. Ahmadi, S. Seiffert, *J. Polym. Sci., Part B: Polym. Phys.* **2019**, 57, 1209; b) E. J. Regalado, J. Selb, F. Candau, *Macromolecules* **1999**, 32, 8580.
- [26] a) W. Mandema, H. Zeldenrust, C. A. Emeis, *Makromol. Chem.* **1979**, 180, 1521; b) J. S. Higgins, S. Blake, P. E. Tomlins, S. B. Ross-Murphy, E. Staples, J. Penfold, J. V. Dawkins, *Polymer* **1988**, 29, 1968.
- [27] C. Lai, W. B. Russel, R. A. Register, *Macromolecules* **2002**, 35, 841.
- [28] P. Bezot, C. Hesse–Bezot, B. Elmakoudi, B. Constants, D. Faure, P. Hoornaert, *J. Appl. Polym. Sci.* **1994**, 51, 1715.
- [29] a) S.-H. Choi, F. S. Bates, T. P. Lodge, *Macromolecules* **2014**, 47, 7978; b) S.-H. Choi, F. S. Bates, T. P. Lodge, *J. Phys. Chem. B* **2009**, 113, 13840; c) J. S. Higgins, J. V. Dawkins, G. G. Maghami, S. A. Shakir, *Polymer* **1986**, 27, 931.
- [30] E. Raspaud, D. Lairez, M. Adam, J.-P. Carton, *Macromolecules* **1994**, 27, 2956.
- [31] a) E. Raspaud, D. Lairez, M. Adam, J.-P. Carton, *Macromolecules* **1996**, 29, 1269; b) M. O. Tuhin, J. J. Ryan, J. D. Sadler, Z. Han, B. Lee, S. D. Smith, M. A. Pasquinelli, R. J. Spontak, *Macromolecules* **2018**, 51, 5173.
- [32] H. Hagen, J. Boersma, G. van Koten, *Chem. Soc. Rev.* **2002**, 31, 357.
- [33] J. B. P. Soares, A. E. Hamielec, *Polym. React. Eng.* **1995**, 3, 131.
- [34] I. d. Rubin, A. Sen, *J. Appl. Polym. Sci.* **1990**, 40, 523.
- [35] K. Marsden, *Lubr. Sci.* **1989**, 1, 265.
- [36] J. Minick, A. Moet, A. Hiltner, E. Baer, S. P. Chum, *J. Appl. Polym. Sci.* **1995**, 58, 1371.
- [37] M. K. Mishra, I. d. Rubin, *Multifunctional copolymer and lubricating oil composition*, US5429757A, **1995**.
- [38] M. K. Mishra, R. G. Saxton, *CHEMTECH* **1995**, 25.
- [39] R. Bloch, T. J. McCrary, D. W. Brownwell, *Ethylene copolymer viscosity index improver-dispersant additive useful in oil compositions*, US4517104A, **1985**.
- [40] M. Steube, T. Johann, R. D. Barent, A. H. Müller, H. Frey, *Prog. Polym. Sci.* **2022**, 124, 101488.
- [41] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, 51, 10246.

- [42] P. von Tiedemann, J. Yan, R. D. Barent, R. J. Spontak, G. Floudas, H. Frey, R. A. Register, *Macromolecules* **2020**, *53*, 4422.
- [43] D. Clair, D. Evans, *Lubricating compositions*, US3772196, **1973**.
- [44] D. H. Olson, D. L. Handlin, *Polymeric viscosity index improver and oil composition comprising the same*, US4788361A, **1988**.
- [45] R. B. Rhodes, C. A. Stevens, *Asymmetric triblock copolymer viscosity index improver for oil compositions*, CA2155686A1, **2006**.
- [46] R. B. Rhodes, C. A. Stevens, *Star polymer viscosity index improver for oil lubricating compositions*, CA2152992C, **2006**.
- [47] R. J. A. Eckert, *Hydrogenated Star-Shaped Polymer*, US4116917A, **1978**.
- [48] S. Briggs, C. Chu, *Viscosity index improvers for lubricating oil compositions*, US7163913B2, **2007**.
- [49] G. Holden, R. Milkovich, *Block polymers of monovinyl aromatic hydrocarbons and conjugated dienes*, US3265765A, **1962**.
- [50] A. J. D. Ritchie, J. G. Bansal, J. Emert, G. P. Fetterman, A. Gutierrez, M. D. Irving, C. J. Locke, M. T. Minotti, *EGR equipped diesel engines and lubricating oil compositions*, US6715473B2, **2004**.
- [51] a) A. Forens, K. Roos, C. Dire, B. Gadenne, S. Carlotti, *Polymer* **2018**, *153*, 103; b) M. Steube, T. Johann, H. Hübner, M. Koch, T. Dinh, M. Gallei, G. Floudas, H. Frey, A. H. E. Müller, *Macromolecules* **2020**, *53*, 5512.
- [52] a) S. Schiff, M. M. Johnson, W. L. Streets, *Viscosity index improvers*, US3554911A, **1971**; b) R. C. Jones, *Hydrogenated block copolymers of butadiene and a monovinyl aryl hydrocarbon*, US3431323, **1969**.
- [53] R. J. A. Eckert, D. F. Covey, *Lubr. Sci.* **1988**, *1*, 65.
- [54] N. Hadjichristidis, A. Hirao, *Anionic Polymerization*, Springer Japan, Tokyo, **2015**.
- [55] L. J. Fetters, L.-K. Bi, *Star polymers and process for the preparation thereof*, US3985830, **1976**.
- [56] S. Oberoi, S. Briggs, *Viscosity index improvers for lubricating oil compositions*, US9133413B2, **2015**.
- [57] R. B. Rhodes, D. L. Handlin, C. A. Stevens, *Star polymer viscosity index improver for oil compositions*, US5460739A, **1995**.
- [58] W. E. Catlin, *Lubricating oil compositions containing polymeric additives*, US2737496A, **1956**.
- [59] J. Jarrin, M. Robine, G. Parc, F. Dawans, *Copolymer compositions usable as additives for lubricating oils*, US4756843A, **1988**.
- [60] R. L. Stambaugh, R. D. Bakule, *Lubricating oils and fuels containing graft copolymers*, US3506574A, **1970**.
- [61] E. Koch, U. Schoedel, *Graft copolymeric lubricating oil additives*, US3732334A, **1973**.
- [62] H. G. P. van der Voort, K. Maurits, J. B. Baurdoux, H. van Oosten, *Lubricating composition containing non-ash forming additives*, US3249545A, **1966**.

- [63] N. Bauer Laverne, *Preparation of copolymers useful as dispersants in oils*, US3052648A, **1962**.
- [64] F. Wenzel, U. Schoedel, H. Jost, H. Pilz, *Lubricating oil additives*, US4149984A, **1979**.
- [65] T. Stöhr, B. Eisenberg, M. Müller, *Öllösliche Kammpolymere*, EP1899393B1, **2012**.
- [66] a) T. Stöhr, B. Eisenberg, M. Müller, *SAE Int. J. Fuels Lubr.* **2009**, *1*, 1511; b) B. Eisenberg, T. Stöhr, *Getriebeölformulierung zur Verringerung des Kraftstoffverbrauchs*, WO2014170169A1, **2014**.
- [67] A. Schwarz, M. Hartweg, B. Cattoz, D. J. Phillips, A. Strong, R. Becer, *Lubricating oil additives*, US10876064B2, **2020**.
- [68] V. P. Beyer, B. Cattoz, A. Strong, A. Schwarz, C. R. Becer, *Macromolecules* **2020**, *53*, 2950.
- [69] A. Halperin, *Macromolecules* **1991**, *24*, 1418.
- [70] A. Halperin, E. B. Zhulina, *Europhys. Lett.* **1991**, *16*, 337.
- [71] S. C. Glotzer, R. Bansil, P. D. Gallagher, M. F. Gyure, F. Sciortino, H. Stanley, *Phys. A* **1993**, *201*, 482.
- [72] K. Rikiyama, Y. Sanada, K. Watanabe, M. Aida, Y. Katsumoto, *Macromolecules* **2019**, *52*, 7188.
- [73] T. Horiuchi, T. Sakai, Y. Sanada, K. Watanabe, M. Aida, Y. Katsumoto, *Langmuir* **2017**, *33*, 14649.
- [74] I. R. Cooke, D. R. M. Williams, *Macromolecules* **2003**, *36*, 2149.
- [75] J. Zhang, Z.-Y. Lu, Z.-Y. Sun, *Soft Matter* **2013**, *9*, 1947.
- [76] V. Hugouvieux, M. A. V. Axelos, M. Kolb, *Macromolecules* **2009**, *42*, 392.
- [77] a) S. Woloszczuk, M. Banaszak, P. Knychala, K. Lewandowski, M. Radosz, *J. Non-Cryst. Solids* **2008**, *354*, 4138; b) C. Zhong, D. Liu, *Macromol. Theory Simul.* **2007**, *16*, 141.
- [78] T. Koga, *Eur. Phys. J. E: Soft Matter Biol. Phys.* **2005**, *17*, 381.
- [79] K. Lewandowski, M. Banaszak, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2011**, *84*, 11806.
- [80] V. Hugouvieux, M. A. V. Axelos, M. Kolb, *Soft Matter* **2011**, *7*, 2580.
- [81] N. A. Hadjiantoniou, T. Krasia-Christoforou, E. Loizou, L. Porcar, C. S. Patrickios, *Macromolecules* **2010**, *43*, 2713.
- [82] a) V. Kadam, T. Nicolai, E. Nicol, L. Benyahia, *Macromolecules* **2011**, *44*, 8225; b) V. S. Kadam, E. Nicol, C. Gaillard, *Macromolecules* **2012**, *45*, 410.
- [83] M. E. Gindy, R. K. Prud'homme, A. Z. Panagiotopoulos, *J. Chem. Phys.* **2008**, *128*, 164906.
- [84] H. Nie, M. Li, R. Bansil, Č. Koňák, M. Helmstedt, J. Lal, *Polymer* **2004**, *45*, 8791.
- [85] a) C. L. P. Shan, R. L. Kuhlman, G. L. Rath, P. J. Kenny, M. M. Hughes, R. Cong, *Viscosity index improver for lubricant compositions*, US8486878B2, **2013**; b) C. L. P. Shan, R. L. Kuhlman, G. L. Rath, P. J. Kenny, M. M. Hughes, R. Cong, *Viscosity index improver for lubricant compositions*, US8492322B2, **2013**; c) D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Science* **2006**, *312*, 714.
- [86] K. J. Wright, C. L. Willis, T. Nishi, N. Masuko, D. L. Handlin, R. C. Bening, *Block copolymer compositions*, US7585916B2, **2009**.

- [87] G. R. Himes, *Multiblock hydrogenated polymers for adhesives*, US5627235A, **1997**.
- [88] C. Zheng, *Soft Matter* **2019**, *15*, 5357.
- [89] V. S. Kravchenko, I. I. Potemkin, *J. Phys. Chem. B* **2016**, *120*, 12211.
- [90] S. K. Filippov, B. Verbraeken, P. V. Konarev, D. I. Svergun, B. Angelov, N. S. Vishnevetskaya, C. M. Papadakis, S. Rogers, A. Radulescu, T. Courtin et al., *J. Phys. Chem. Lett.* **2017**, *8*, 3800.
- [91] J. Kuldová, P. Košovan, Z. Limpouchová, K. Procházka, *Macromol. Theory Simul.* **2013**, *22*, 61.
- [92] G. Pandav, V. Pryamitsyn, K. C. Gallow, Y.-L. Loo, J. Genzer, V. Ganesan, *Soft Matter* **2012**, *8*, 6471.
- [93] C. Zheng, H. Huang, T. He, *Macromol. Rapid Commun.* **2014**, *35*, 309.
- [94] a) S. Okabe, K. Seno, S. Kanaoka, S. Aoshima, M. Shibayama, *Polymer* **2006**, *47*, 7572; b) S. Okabe, K. Seno, S. Kanaoka, S. Aoshima, M. Shibayama, *Macromolecules* **2006**, *39*, 1592; c) S. Eggers, T. Eckert, V. Abetz, *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 399; d) C. Zheng, H. Huang, T. He, *Macromol. Rapid Commun.* **2013**, *34*, 1654; e) N. Merlet-Lacroix, E. Di Cola, M. Cloitre, *Soft Matter* **2010**, *6*, 984.



---

# CHAPTER 6

*Fluorescence Labeling of Multiblock Copolymers:*  
**Unraveling Different Aggregate Structures in  
Concentrated Polymer Solutions by Fluorescence  
Correlation Spectroscopy**

---





## CHAPTER 6

To be Submitted

# ***Fluorescence Labeling of Multiblock Copolymers: Unraveling Different Aggregate Structures in Concentrated Polymer Solutions by Fluorescence Correlation Spectroscopy***

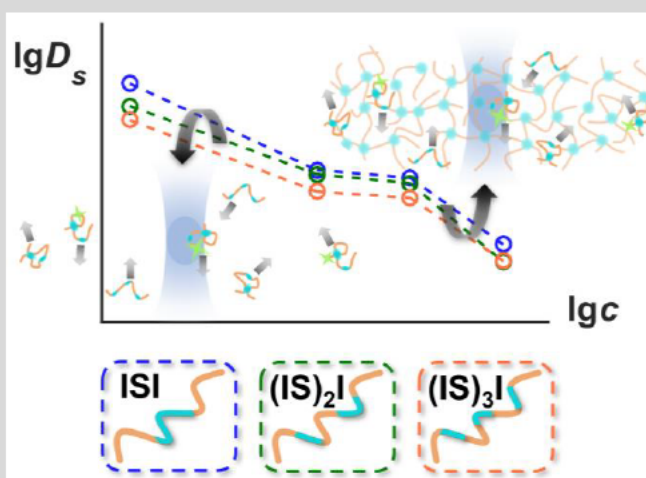
Ramona D. Barent<sup>1,2</sup>, Domenik T. Mundil<sup>1</sup>, Benny Mathes<sup>1</sup>, Kaloian Koynov<sup>3\*</sup>, and Holger Frey<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany

<sup>2</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany

<sup>3</sup> Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

We report a novel strategy to label polymers based on isoprene with a fluorescent dye by a post-polymerization protocol. The subsequent reaction steps comprise bromination, the introduction of an azide functionality and finally a copper-catalyzed 1,3-dipolar cycloaddition. The substantial benefit of this strategy is that only a small amount of a batch can be labeled on small scale, with the labeled polymers exhibiting only a marginally altered chemical nature.



Besides, chain degradation and cross-linking are circumvented. The optimized reaction sequence is implemented labeling sequential and tapered multiblock copolymers consisting of polyisoprene and polystyrene blocks. Here, an odd number of blocks with two polyisoprene end blocks was targeted to ensure solubility in heptane as polyisoprene-selective solvent. Fluorescence correlation spectroscopy reveals a higher tendency for loop formation in case of the tapered structures with more than one solvophobic block. This influences not only the dimension of the unimers, but also of the micellar aggregates. Furthermore, the self-diffusion of unassociated unimers through the gelled polymer matrix is found to be most restricted in case of the sequential multiblock copolymers with more than one polystyrene block, which might result out of a combination of larger unimer dimensions and a higher bridging fraction, the latter reducing the distance between adjacent PS microdomains.

## Introduction

Polymeric micelles possess a vast potential, spanning the range from stabilizers, nanoreactors or drug delivery systems to the application of block copolymers as viscosity modifiers in selective solvents.<sup>[1]</sup> As a result, the self-assembly of block copolymers is studied in depth.<sup>[2]</sup> Yet, the association behavior introducing multiple solvophobic blocks per chain<sup>[3,4]</sup> or tapered block copolymers with a sharp, albeit gradual transition between the comonomers<sup>[5,6,7]</sup> is rather unexplored. Therefore, this work aims at the investigation of the self-organization and dynamics of block as well as tapered block-like copolymers in solution. For this purpose, both sequential and tapered multiblock copolymers of polyisoprene (PI) and polystyrene (PS) with 3, 5 and 7 blocks prepared by living anionic polymerization were studied in a polyisoprene selective solvent.

The dynamics of polymer micelles are of utmost importance, since not only the diffusion behavior, but also the unimer-micelle as well as the association-dissociation equilibration affects the potential application as, e.g., stabilizer of colloids. The kinetics of micellization can be monitored by stopped-flow experiments combined with for instance time-resolved light scattering.<sup>[8]</sup> The exchange rate of unimers between different micelles can be studied by steady-state emission spectroscopy,<sup>[9]</sup> time-resolved small-angle neutron scattering by partial deuterium labeling,<sup>[10,11]</sup> or fluorometry<sup>[12]</sup>. Besides, scattering experiments in general like small angle x-ray or neutron scattering (SAXS and SANS) are effective tools to examine the self-organization or dynamics in polymer solutions. Furthermore, these techniques as well as rheology of polymer solutions can be implemented to monitor the diffusion of copolymers, with the latter allowing to study the viscosity under shear and to reveal non-Newtonian behavior.<sup>[13]</sup>

In order to study the diffusion of macromolecules or colloids in the steady state, the most common methods implemented are diffusion ordered nuclear magnetic resonance spectroscopy (DOSY-NMR), dynamic light scattering (DLS), analytical ultracentrifugation (AUC), and fluorescence correlation spectroscopy (FCS), each having its advantages and drawbacks.<sup>[14]</sup> NMR experiments allow to track rapidly diffusing species, whose scattering might be insufficient for DLS. However, measurable diffusion coefficients are limited by the relaxation times of the excited nuclei. DLS is a very versatile tool as a wide range of diffusion coefficients is accessible, but the concentration range is defined by the signal-to-noise ratio, which becomes too small for low or highly concentrated solutions.<sup>[15]</sup> In the latter case, multiple scattering becomes pronounced rendering invalid results unless advanced approaches like the cross-correlation are used.<sup>[16]</sup> Beyond this, especially for polydisperse samples the signal arising from weakly scattering diffusers may be imperceptible since the scattering intensity depending on the scattering angle differs with the particle size. AUC enables the investigation at very low concentration and the sedimentation profile gives valuable information on the particles size distribution and the density. Yet, one has to be aware that unlike the other methods AUC does not rely on Brownian motion of the species but the sedimentation within a centrifugal field, whose force might affect the reversible association.<sup>[17]</sup> FCS studies provide information on the diffusion of fluorescent species in their immediate surrounding by the autocorrelation analysis of the fluorescence intensity fluctuations. These fluorescent species can be single dye molecules, but also fluorescently labeled polymers or colloids.<sup>[18]</sup> Due to the detection of on

average only one fluorescent species at a time diffusing through the very small observation volume ( $<1\ \mu\text{m}^3$ ), FCS has the unique feature of single molecule sensitivity and is suitable for polymers and colloids with hydrodynamic radii up to 250 nm.

Comparing DOSY-NMR, DLS and AUC to FCS, all these methods have the advantage in common that no fluorescent label attached to the tracked species is necessary. In return, due to the selectivity based on the fluorescence detection, FCS offers the possibility to study the dynamic properties of individual polymer chains dispersed in a matrix of, e.g., unlabeled chains. Therefore, information, whose loss is inherent for the previously discussed techniques due to the simultaneous detection of a large number of molecules, is accessible by FCS experiments. Moreover, the fluorescence of the monitored species is not affected by strong background signals as it is the case for DLS.

In the last two decades, FCS has become an important tool in polymer and colloid science.<sup>[18]</sup> The method was applied to address the dynamics of labeled polymers in solutions at various concentration and obtain information on both self-diffusion<sup>[19,20,21]</sup> and cooperative diffusion<sup>[20]</sup>. Besides, FCS was used to follow the diffusion of fluorescent tracers in polymer solutions<sup>[22]</sup>, gels<sup>[23]</sup> or melts<sup>[24]</sup>.

FCS is also very well suited to monitor the molecular self-assembly of copolymers into aggregates.<sup>[25,26,27]</sup> In this respect, the concentration-dependent determination of diffusion coefficients allows to trace the association of fluorescently labeled copolymers forming micellar structures above the critical micelle concentration ( $c_{\text{CMC}}$ ), with the diffusion coefficients giving access to the dimension of the copolymer chain or aggregate in solution.<sup>[26,27]</sup>

As addressed above, if the traced fluorescent species in FCS experiments are polymers or colloids, the attachment of a fluorescent label is necessary. The photostability and the quantum yield are key features, which have to be considered for the selection of the fluorescent dye used for labeling. Moreover, the chemical nature of the polymers and the envisaged solvent are criteria for the choice of the dye since the molecular behavior of the polymer chains should not be affected. For the investigation of aggregation phenomena in solution, it is further necessary to covalently attach the fluorescent dye to the polymer chains in a defined manner, in order to avoid the problem of fast exchange of the dye between micellar structures in solution. Here, the separation of the dye-labeled polymers of any traces of free dye molecules is crucial in order to minimize the polydispersity of fluorescent species.

Various approaches to prepare polymeric tracers have been developed. In the field of radical polymerization, initiators containing a fluorescent moiety have been used for nitroxide mediated reversible-deactivation radical polymerizations<sup>[28]</sup>, but also functionalized comonomers were introduced to miniemulsion polymerization techniques<sup>[29]</sup>. Concerning living anionic polymerization, labeled styrene and diphenylethylene derivatives have been employed for chain-end<sup>[21]</sup> or in-chain functionalization<sup>[30]</sup>. Furthermore, the post-polymerization modification of quantitatively end-capped living chain ends was reported.<sup>[31]</sup>

Except for the last example, all these strategies have in common, that the labeled polymer itself is synthesized in a separate polymerization reaction batch. As a consequence, the unlabeled analogues required for the matrix in case of more concentrated polymer solutions have to be synthesized on top. Here, the major issue consists in the deviating polymer characteristics, i.e., molar mass or polydispersity. Furthermore, introducing a functionalized monomer to statistical

copolymerization experiments may influence the reactivity ratios and hence the obtained comonomer distribution along the polymer chain.

With respect to post-modification protocols for the introduction of dye labels to diene-based polymers, the copper-catalyzed Huisgen cycloaddition reaction between azides and alkynes is the most promising approach.<sup>[32,33]</sup> This is premised on its low sensitivity to oxygen and water, comparably mild conditions and a high efficiency.<sup>[34]</sup> Moreover, alkyne-functionalized polycyclic aromatic dyes are commercially available, which are most suitable since their non-polarity renders only a small change of the polymer's chemical nature. Another crucial factor is that this cycloaddition reaction does not involve radical species as it is the case for thiol-ene additions, which are prone to cross-linking or chain degradation reactions.<sup>[35]</sup>

Manifold approaches to introduce a dye by an azide-alkyne click reaction have been reported. Zhang *et al.* incorporated a coumarin-dye to azide-functionalized dendrigraft polybutadiene, which was obtained by epoxidation of the polydiene, followed by hydrochlorination and subsequent esterification with 2-bromoisobutyryl bromide, whose bromide was then converted in to an azide.<sup>[36]</sup> Unfortunately, no additional information on the polydispersity of the polymers after functionalization is provided. Abetz and coworkers took the reverse approach, functionalizing a styrene-butadiene triblock in an analogous manner, but implementing an alkyne containing carboxylic acid for the esterification reaction, which was then reacted with an azide-functionalized dye.<sup>[37]</sup> Upon hydrochlorination, only a small increase in lower molar mass fractions could be observed by size exclusion chromatography (SEC), indicating that almost no unfavorable side reactions occurred.

Geiselhart *et al.* reported the introduction of a pyrene moiety by a cascade reaction comprising the bromination with *N*-bromosuccinimide, followed by the nucleophilic attack of THF and the subsequent ring opening of the oxonium intermediate by a carboxylic acid derivative.<sup>[38]</sup>

Tsarevsky and coworkers functionalized polyisoprene with a trifluoro methyl group and a halogen by the reaction with the Togni's reagent II in the presence of thionyl halide and copper(II) salts.<sup>[39]</sup> The later addressed azide moiety was introduced by the nucleophilic substitution of the halide. Due to the already broad distribution of the virgin polymer, degradation or cross-linking reactions cannot be ruled out completely. However, the elimination reaction competing with the substitution of the halide was confirmed, with the concomitant acidic conditions rendering chain scission or cross-linking probable. Besides, cycloaddition reactions between the formed azide and the extremely electron-deficient olefin due to the introduction of the trifluoro methyl moiety were observed.

Wang *et al.* circumvented the substitution reaction of a halide by a one-step introduction of both the trifluoro methyl and the azide group.<sup>[40]</sup> For this purpose, polybutadiene was reacted with the Togni's reagent II and trimethylsilyl azide. Although no intermolecular reactions, i.e., cross-linking or chain degradation, could be observed by SEC, intramolecular radical coupling between adjacent intermediates led to cyclization. Subsequent pyrene labeling proved the addressability of the azide anchoring site.

Albeit that routes towards azide-functionalized polydienes are already implemented, all these examples have an ester or a trifluoro methyl group in common. These polar or solvophobic moieties have a huge potential to alter polymer's chemical nature.

Our motivation for a new post-modification approach is rooted in the synthesis of sequentially polymerized multiblock copolymers or block-like tapered multiblock copolymers by living anionic polymerization techniques.<sup>[41,42]</sup> On one hand, the comprehensive effort in drying and transferring all reagents by trap-to-trap distillations into an all-glass apparatus makes the use of functionalized monomers or end-capping agents inadequate. On the other hand, the costs would rise tremendously as the syntheses of high molar mass polymers imply large scale batches, as small amounts of the initiator are needed. Besides, both labeled and unlabeled polymers, which are mixed to adjust the overall concentration while keeping the tracer concentration at a constant low level, possess the same molar mass, polydispersity and microstructure eliminating altered solution behavior of the multiblock copolymers.

Therefore, within the first part of this work we present a post-modification protocol for fluorescent dye labeling installing solely azide groups by the nucleophilic substitution reaction of halides. The second part is dedicated to the investigation of the self-organization and dynamics of sequential as well as tapered PI-PS multiblock copolymers in heptane, which is a PI-selective solvent. For this purpose, fluorescence correlation spectroscopy was used to monitor the diffusion behavior of labeled PI-PS multiblock copolymers over a wide range of copolymer concentrations.

## Experimental Section

The synthetic routes were optimized modifying a model polyisoprene homopolymer with a comparatively low molar mass. For an easier characterization, not only low degrees of polymerization needed for the dye labeling, but also high degrees of functionalization were targeted. Hereafter, the protocol was transferred to multiblock copolymers with polyisoprene and polystyrene blocks.

A detailed experimental description of the polymer syntheses of multiblock copolymers can be found elsewhere.<sup>[41]</sup> Comprehensive information on the synthesis of polyisoprene as well as its post-polymerization modification reactions including NMR and fluorescence emission spectra can be found in the Supp. Inf.. Furthermore, the autocorrelation functions and the fits of the fluorescence correlation spectroscopy (FCS) measurements (see Figure S14-S19) as well as the size distribution for all concentrations obtained by dynamic light scattering (DLS) (see Figure 20-22) are shown. Besides, details on the instrumentation setup and the data evaluation for FCS and DLS as well as of size exclusion chromatography (SEC), nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), and fluorescence emission are given as well.

### Post-Polymerization Protocol

In the first step, the double bonds of polyisoprene exhibiting 94% of 1,4-repeating units are brominated. Secondly, the halide was replaced by an azide via nucleophilic substitution, which was then reacted with an alkyne functionalized perylene dye in a copper-catalyzed 1,3-dipolar cycloaddition.

### Characterization of the Polymer's Dynamics

*Polymer solution preparation* in heptane was based on the dilution of different stock solutions. After dilution, the solutions were put on a shaker at room temperature for several days. For the preparation of the stock solutions, the desired amount of polymer, which was dried azeotropically with benzene before use, was suspended in heptane. The sealed flask was annealed at 80 °C for at least one hour while stirring to achieve proper dissolution and prevent kinetically trapped structures. For DLS measurements, stock solutions of 1 wt%, 5 wt%, and 10 wt% were prepared and further dissolved with heptane to obtain polymer solutions in the concentration range of 0.1 wt% - 10 wt% (0.1 wt% steps between 0.1 wt% - 1 wt% and 2.5 wt% steps for 1 wt% - 10 wt%). For FCS measurements, a stock solution of 10 wt% of overall polymer concentration with  $10^{-6} \text{ mol}\cdot\text{L}^{-1}$  of the perylene labeled polymer was prepared. For this purpose, the defined amount of the dye-labeled polymer in benzene was transferred into a flask and the solvent was evaporated under high vacuum. Next, the required amount of the unlabeled polymer was weighed in and the solution in heptane was prepared as described above. 1 wt% as well as 0.1 wt% solutions were obtained by dilution, by this decreasing the concentration of the dye-labeled polymer to  $10^{-7}$  and  $10^{-8} \text{ mol}\cdot\text{L}^{-1}$ , respectively. For one polymer (tapered pentablock), also a solution of 1 wt% with  $10^{-6} \text{ mol}\cdot\text{L}^{-1}$  of the labeled polymer was prepared as described. Comparison of the FCS data revealed similar autocorrelation functions, proving that solution preparation by dilution from a stock solution without a repeated annealing does not affect the system. Moreover, 0.001 wt% solutions ( $10^{-7} \text{ mol}\cdot\text{L}^{-1}$ ) of solely the dye-labeled polymer in heptane were prepared analogously.

*DLS measurements* were conducted at 25 °C using the 3D cross-correlation method suppressing multiple light scattering events. Each experiment was repeated 5 times. The obtained autocorrelation functions were analyzed using the CORENN algorithm which is suitable for polydisperse samples.

*FCS measurements* were performed at 23 °C, carrying out an average of 2-3 experiments per sample. The obtained autocorrelation functions at 0.1 and 1 wt% were analyzed using a two-component fit (see Supp. Inf.) with a fixed value for the freely diffusing unimers, which was derived from the measurement of the solution containing only the perylene-labeled polymer at very low concentration ( $c=10^{-7} \text{ mol}\cdot\text{L}^{-1} = 10^{-3} \text{ wt}\%$ ). The autocorrelation function at  $10^{-3} \text{ wt}\%$  itself was fitted by a single-component fit. For the 10 wt% samples, a two-component fit without any fixed value was performed. Here, the temporal fluctuations of the detected fluorescence spectroscopy at longer timescales were analyzed and discussed. The process at comparably short diffusion times can arise from a cooperative network diffusion. As stated by Zettl *et al.*, the formation of a transient network as it is the case for entangled polymers allows not only to observe the self-diffusion of the polymer chains  $D_s$  by FCS, but also the cooperative diffusion  $D_c$ .<sup>[20]</sup> This is reasoned in the effective long-range interaction of the chains through the network, correlating the diffusion of a single polymer chain with the cooperative network diffusion. By the motion of an individual polymer chain, the surrounding polymer chains diffuse coherently. This cooperative motion leads to the temporal fluctuation of the detected fluorescence intensity at short timescales. Due to the complex calibration and the polydisperse nature of the aggregates, the systematic error of the obtained hydrodynamic radii ranges up to 20%.

## Results and Discussion

### Dye-Labeling by Post-Polymerization Modification

The synthetic route for dye-labeled polymers based on isoprene with a high 1,4-PI content is presented in Figure 1. As reported in the experimental section, post-polymerization modification was optimized functionalizing polyisoprene with  $10 \text{ kg} \cdot \text{mol}^{-1}$ , monitoring the individual reactions targeting low as well as high degrees of functionalization.

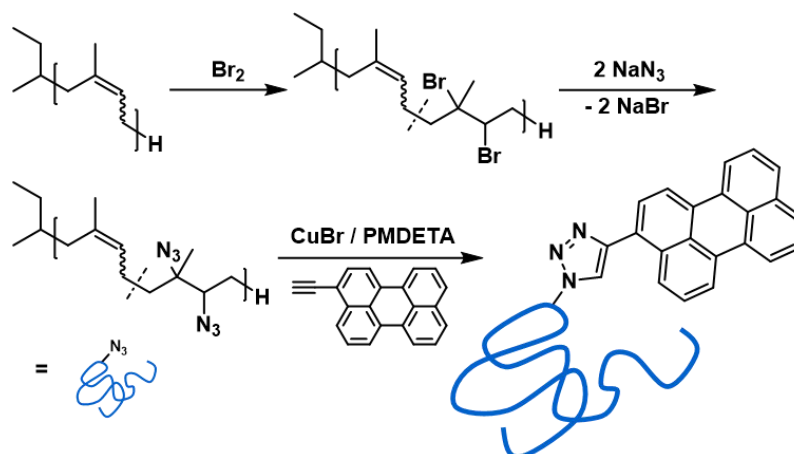


Figure 1: Reaction steps for perylene-labeling of polymers based on isoprene with high 1,4-content content including bromination, azidation and a subsequent copper-catalyzed 1,3-dipolar cycloaddition.

### Bromination

Halogenated polymers tend to eliminate spontaneously, the resulting acidic conditions promoting polymer degradation and cross-linking reactions (Figure 2). To confront this issue, acid scavengers, e.g., alkali metals or epoxides, are added in industry during processing and left in the polymer.<sup>[43]</sup> As these kind of additives could interfere with the subsequent reactions, bromination without the presence of an acid scavenger in combination with an immediate conversion of the brominated polymer has been considered as the most feasible approach.

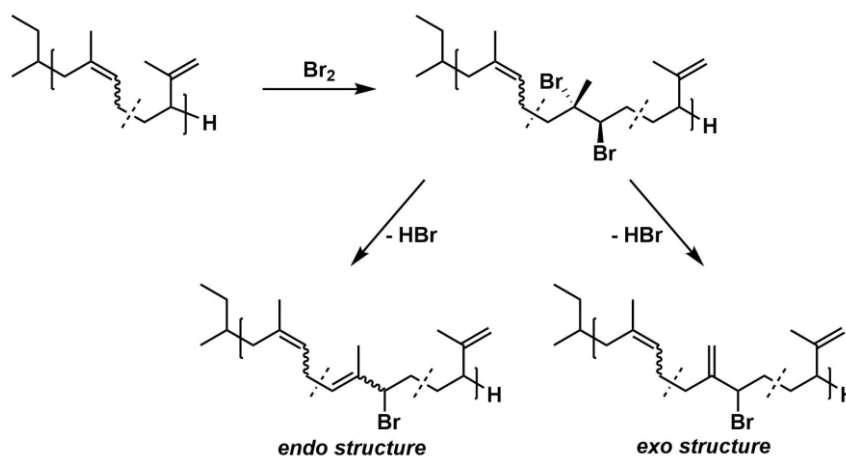
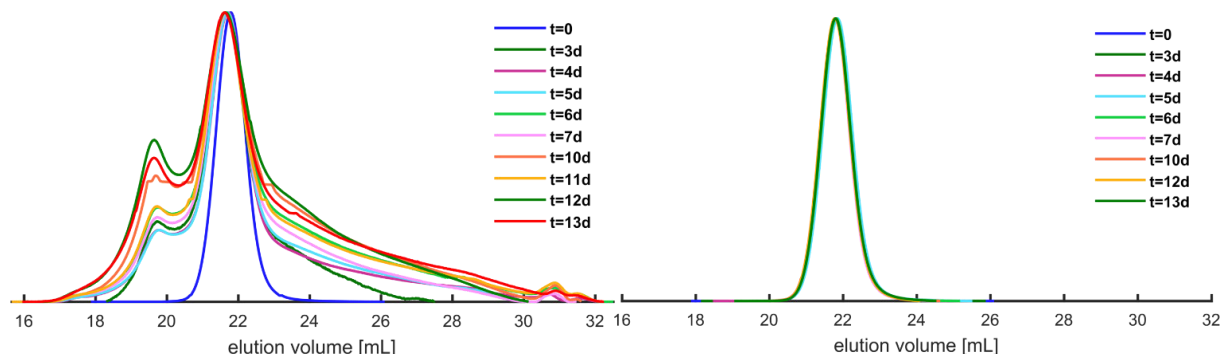


Figure 2: Addition of bromine to polyisoprene and subsequent elimination of HBr, giving the reported *endo* or *exo* structure. The acidic conditions tracing back to the elimination can lead to chain scission and cross-linking.

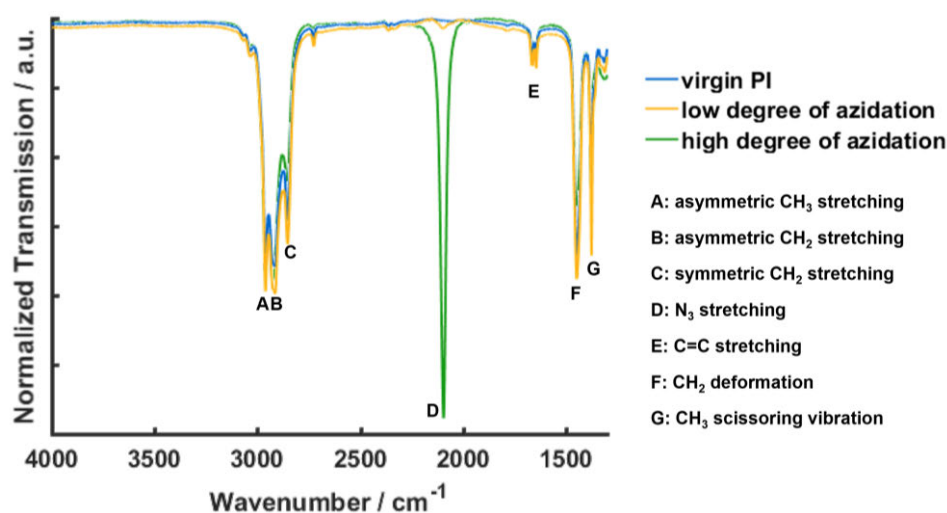
The initial formation of the dibrominated structure was confirmed by 2D NMR experiments (see Figure S6-S10, the chemical shift of the quaternary carbon excludes the formation of unsaturated moieties). Characterization by SEC revealed a unimodal distribution direct after the reaction (Figure 3,  $t=0$ ), indicating that no chain degradation or cross-linking occurred during bromination. However, chain scission upon storage of the brominated polymer in bulk state was monitored over a course of two weeks by SEC (Figure 3, left), showing already large fractions of higher and lower molar mass after a few days. Besides, the formation of an insoluble fraction indicated cross-linking of the polymer. On the contrary, storing the brominated polymer in solution did not lead to a degradation or cross-linking of the polymer (Figure 3, right).



**Figure 3:** SEC traces (eluent: THF, detector: RI) of highly functionalized PI over a period of time of 13 days. Left: Samples stored in bulk state under argon atmosphere at room temperature. The samples consisted of a soluble and hence measured part as well as an insoluble part. Right: Samples stored in THF solution at room temperature ( $1\text{--}2\text{ mg}\cdot\text{mL}^{-1}$ ).

### Azidation

The subsequent substitution of the halide by an azide was conducted in a mixture of THF and DMF. The polar environment promotes a unimolecular substitution, preventing side reactions by cationic intermediates. The ratio of both solvents was adjusted to obtain a proper dissolution of the polymer and the reagent sodium azide. Successful azidation could be validated by infrared spectroscopy, showing the appearance of the azide stretching band (Figure 4).



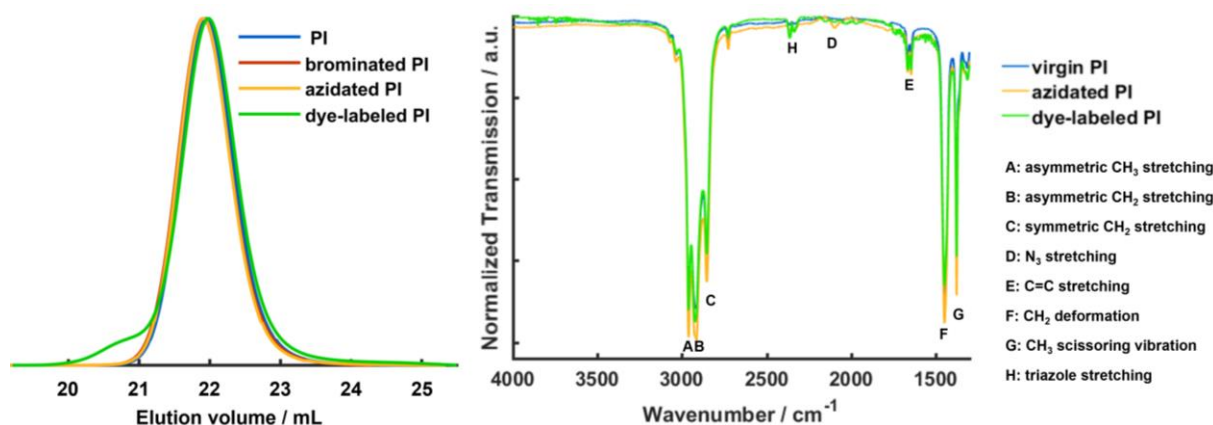
**Figure 4:** FTIR spectra of polyisoprene (blue) and of the azidated polyisoprenes with a low (yellow) as well as a high (green) degree of functionalization.



### Copper-catalyzed 1,3-dipolar cycloaddition

The 1,3-dipolar cycloaddition between the azide moiety of the modified polyisoprene with low degree of functionalization and the alkyne-substituted perylene was conducted in the presence of excess of copper(I)<sup>[33]</sup> with PMDETA as ligand, because a work of Matyjaszewski and coworkers showed the highest rate constants for this tridentate aliphatic amine ligand.<sup>[44]</sup>

Successful labeling of the polyisoprene was validated by <sup>1</sup>H- as well as DOSY-NMR (see Figure S11 and S12). The relative intensities of the aromatic protons of the perylene-moiety to the methylene protons of the polymer backbone revealed an overall functionalization of every tenth polymer chain. The absence of the alkyne proton as well as the unitary diffusion coefficient measured by DOSY evidenced chain functionalization. Further proof is provided by SEC and IR measurements (Figure 5). The SEC trace of the dye-labeled polymer shows a small shoulder at higher molar masses molecular weights, however significant alteration in the molar mass distribution were not observed. The infrared spectrum of the perylene-labeled polyisoprene features a new band belonging to the triazole moiety formed by the 1,3-dipolar cycloaddition, while the band of the azide stretching disappears.



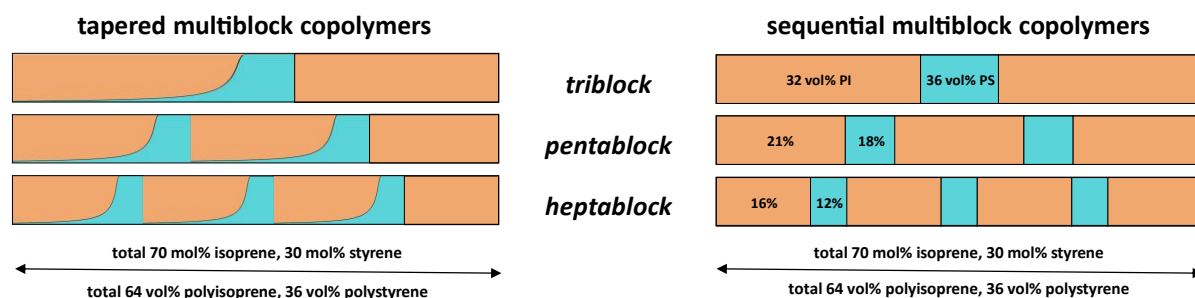
**Figure 5:** Left: SEC traces (eluent: THF, calibration: PI, detector: RI) of PI with a low degree of functionalization. The polymers showed molar masses of 11250, 11510, 11480, 11090 g·mol<sup>-1</sup> and dispersities of 1.05, 1.05, 1.05, 1.11 for the virgin (blue), brominated (red), azidated (yellow) and dye-labeled (light green) PI, respectively. Right: IR spectra of polyisoprene (blue), the azidated polyisoprene with a low degree of functionalization (yellow) as well as the dye-labeled polymer (light green).

Besides, fluorescence emission spectroscopy of the functionalized polyisoprene revealed a clear fluorescence with maxima arising from the perylene moiety (see Figure S13).

### Dye-Labeling of Multiblock Copolymers based on Isoprene and Styrene

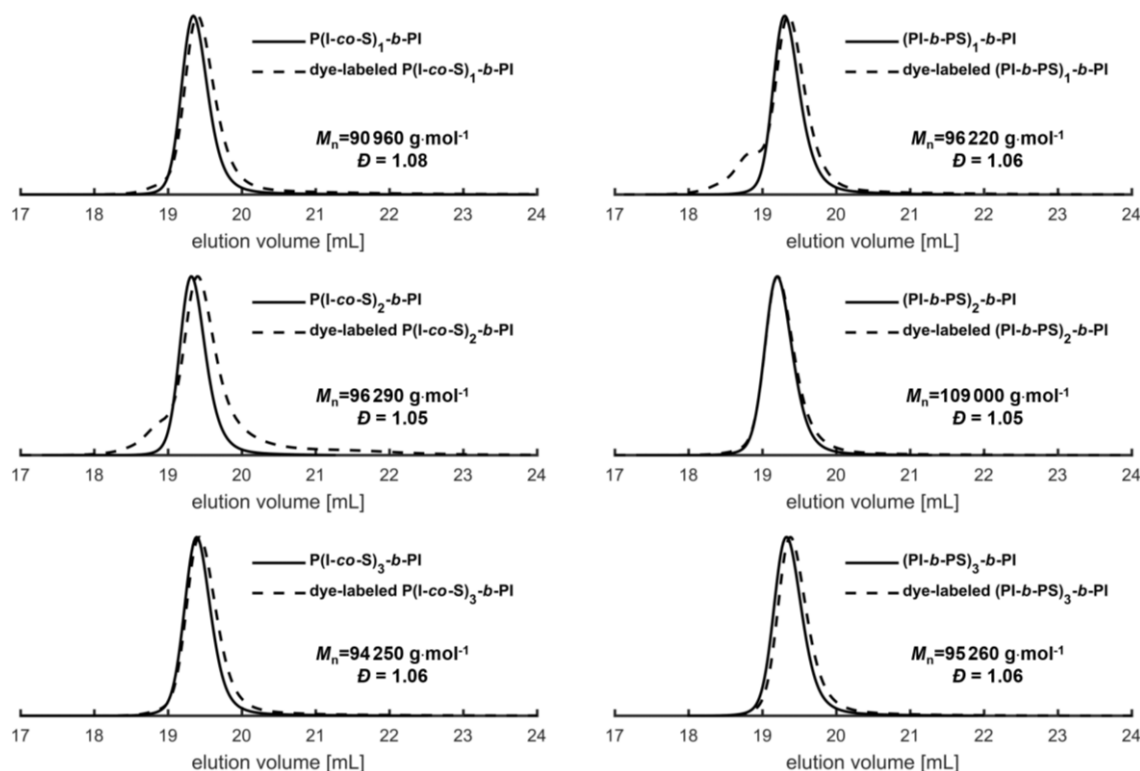
The post-polymerization modification protocol described above was transferred to multiblock copolymers based on isoprene and styrene. All polymers exhibit the same overall molar mass (80 kg·mol<sup>-1</sup>) and comonomer ratio (70 mol% isoprene), but varied in their block number (3, 5 and 7) and gradient profile (tapered vs. sequential). Figure 6 depicts the comonomer distribution of isoprene (orange) and styrene (cyan) along the polymer chain plotting the mean incorporation at every conversion. The tapered structures (Figure 6, left) is simulated based on the reactivity ratios of isoprene and styrene at 40 °C in cyclohexane ( $r_1=10.9$  and  $r_5=0.029$ ).<sup>[45]</sup>

Three tapered block copolymers ( $P(I-co-S)_n-b-PI$  with  $n=1-3$ ) with a gradual transition between polyisoprene and the adjacent polystyrene block were functionalized, which were obtained by statistical copolymerization in cyclohexane.<sup>[41,46]</sup> The analogous block copolymers ( $(PI-b-PS)_n-b-PI$  with  $n=1-3$ ) with a sharp transition between the polyisoprene and polystyrene blocks were prepared by sequential polymerization of the two comonomers in cyclohexane. The polymerization in non-polar media resulted in almost exclusively 1,4-repeating units of polyisoprene ( $\geq 93\%$ ).



**Figure 6:** Distribution visualization of the comonomers isoprene (orange) and styrene (cyan) along the polymer chain. The molar-based composition diagram reflects the mean incorporation (y axis) at every conversion (x axis). The gradient profile of the tapered multiblock copolymers is simulated based on the reactivity ratios of isoprene and styrene at 40 °C in cyclohexane ( $r_1=10.9$  and  $r_2=0.029$ ).<sup>[45]</sup> The volume fractions of the individual blocks are denoted for the sequential structures.

Figure 7 shows the SEC traces of the virgin as well as the perylene-labeled multiblock copolymers. The labeled tapered pentablock as well as the sequential triblock exhibit shoulders at higher molar mass, whereas the other labeled multiblock copolymers showed similar molar mass distributions to their virgin polymers.



**Figure 7:** SEC traces (eluent: THF, detector: RI, calibration: PS) of the tapered multiblock (left) and the sequential multiblock copolymers (right) with varying block number (top: triblock, middle: pentablock, bottom: heptablock copolymers). Solid line: virgin polymers, dashed line: dye-labeled polymers. The number average molar masses and dispersities are given for the virgin copolymers.

## Study of Diffusion Processes in Polymer Solutions

In the following section, solution properties of the tapered multiblock  $P(I-co-S)_n-b-PI$  and sequential multiblock copolymers  $(PI-b-PS)_n-b-PI$  with  $n=1-3$  in heptane accessed by FCS and DLS measurements are interpreted in the context of theoretical studies and experimental results of similar structures reported in literature.

Within the dilute regime, i.e., below the critical overlap concentration, both FCS and DLS experiments yield the diffusion coefficient of single polymer chains or micellar structures, if the critical micelle concentration is exceeded. For freely diffusing micelles in the dilute regime, a lower diffusion coefficient compared to the unimers will be observed due to the apparent increase in molar mass concomitant with aggregation. Within the semi-dilute regime interparticle interaction bias the obtained diffusion coefficient. In that event, FCS experiments yield the self-diffusion coefficient  $D_s$  of one labeled polymer chain relative to its surrounding, whereas DLS experiments give the cooperative diffusion coefficient  $D_c$  of various polymer chains within a density gradient.<sup>[20,47]</sup> The hindrance of the self-diffusion results in an increase of the cooperative diffusion coefficient as well as the decrease of the self-diffusion coefficient.<sup>[20]</sup>

Taking association of multiple polymer chains into networks into account as it is the case for block copolymers in selective solvents, the system becomes more complex. DLS experiments on polymer networks reveal the complexity of the interpretation of non-ergodic systems.<sup>[48,49]</sup> Light scattering results from fluctuations of the refractive index, which is intrinsically related to concentration fluctuations in the sample. In case of a polymer network, two kinds of concentration fluctuations are present. The spatial variation being constant over time represents the gel inhomogeneity and is superimposed by an additional time-dependent variation, the dynamic concentration fluctuation around its local average.<sup>[48]</sup> Therefore, at least two relaxation modes can be found. The fastest mode corresponds to the cooperative chain dynamics of the individual strands and the intermediate slower mode is often assigned to the macroscopic viscoelastic relaxation of the entire network due to density fluctuations on 100 nm scales.<sup>[50]</sup> Here, the fluctuations of the network strands between two adjacent crosslinking junctions is dependent on the scattering vector  $q$ , whereas the network relaxation is  $q$ -independent if the relaxation time lies on similar time scales as the scattering experiment.<sup>[48,50]</sup> Sometimes, a third mode exists, which is correlated with the diffusion of polymer aggregates within the network.

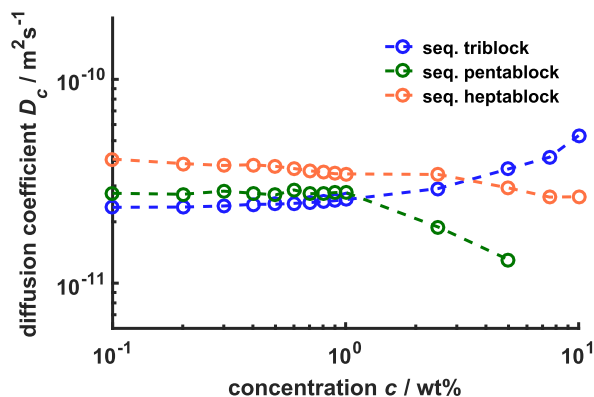
### Dynamic Light Scattering

First, dynamic light scattering experiments are qualitatively evaluated in order to specify the presence of either micellar aggregates or polymer gels and networks. The apparent cooperative diffusion coefficients of the sequential multiblock copolymers obtained by DLS measurements are displayed in Figure 8.

The DLS experiments were conducted in just one volume element of the sample and hence potential local differences due to a speckle pattern as it is the case in polymer gels are neglected. Furthermore, the diffusion coefficients are obtained by the classical Siegert relation.<sup>[51]</sup> This means, that the non-ergodicity of a gel or a network is not taken into account

by partial heterodyne data analysis. Therefore, solely an apparent diffusion coefficient is obtained. Since the intensity fluctuations were measured at only one scattering angle ( $90^\circ$ ), no statements concerning the nature of the concentration fluctuation can be made.

Nonetheless, the non-linearity of the apparent diffusion coefficient with increasing concentration confirms that at concentrations above 1 wt%, the diffusing species start to interact. Consequently, at  $c > 1$  wt%, the apparent cooperative diffusion coefficient  $D_c$  is measured, whereas at concentrations  $c < 1$  wt%, the diffusion coefficient obtained by DLS coincides with the self-diffusion coefficient of aggregates.



**Figure 8:** Apparent cooperative diffusion coefficient  $D_c$  of the sequential multiblock copolymers (blue: triblock, green: pentablock, orange: heptablock) in the concentration regime between 0.1-1 wt% obtained by DLS measurements.

For the sequential triblock (blue),  $D_c$  increases remarkably at concentrations above 1 wt%. This is ascribed to the fastened relaxation of local concentration fluctuations and hence expected for light scattering experiments on concentrated polymer solutions.<sup>[47]</sup>

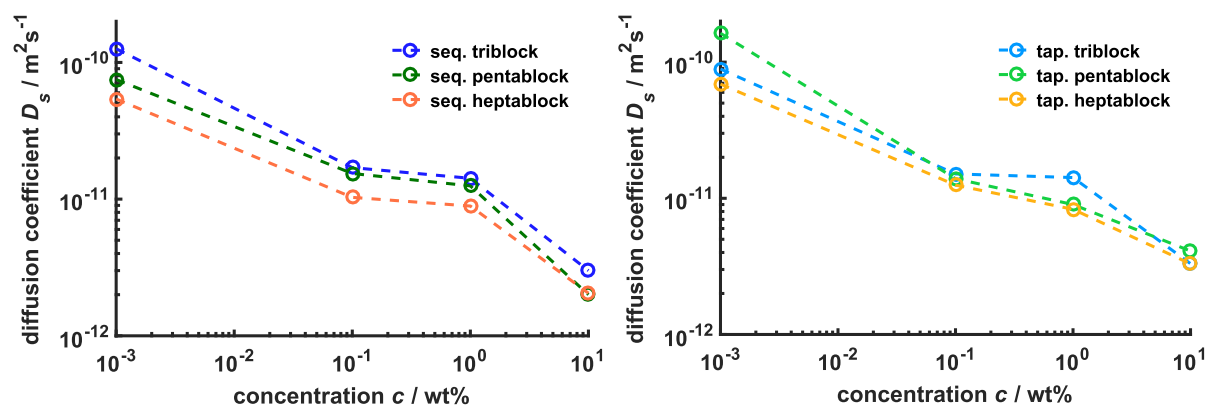
The sequential penta- (green) and heptablock (orange) show a decrease in  $D_c$  above 1 wt%. This indicates network formation. As discussed above, polymer networks feature a fast relaxation mode and an intermediate slower mode, which originate from the cooperative dynamics of the individual network strands between two junctions and from the relaxation of the entire network, respectively. At that point it is noteworthy that the scattering intensity of a particle scales with the square of the refractive index increment.<sup>[15]</sup> With the refractive indices of  $n_D^{20}(\text{PI})=1.52$ <sup>[52]</sup>,  $n_D^{20}(\text{PS})=1.59$ <sup>[52]</sup> and  $n_D^{20}(\text{heptane})=1.39$ <sup>[53]</sup>, polystyrene has a higher scattering contrast. Considering that dynamics of polystyrene blocks contribute to the measured intensity to a higher extent, it is plausible that the network relaxation is the predominant relaxation mode, since the network strands are polyisoprene blocks tethered between collapsed polystyrene domains.

Comparison of the diffusion coefficients at  $c=1$  wt% obtained by DLS and FCS reveals self-diffusion coefficients of the aggregates of the same magnitude ( $D_{\text{DLS}}=(2-4) \cdot 10^{-11} \text{ m}^2\text{s}^{-1}$  vs.  $D_{\text{FCS}}=(1-2) \cdot 10^{-11} \text{ m}^2\text{s}^{-1}$  (*vide infra*)). Surprisingly, an inversed trend in the diffusion coefficient with increasing block number and hence shortened individual block lengths is observed ( $D_{\text{DLS}}^{\text{tri}} < D_{\text{DLS}}^{\text{penta}} < D_{\text{DLS}}^{\text{hepta}}$  vs.  $D_{\text{FCS}}^{\text{tri}} > D_{\text{FCS}}^{\text{penta}} > D_{\text{FCS}}^{\text{hepta}}$ ). One possible explanation is that the autocorrelation of the measured intensity in DLS experiments, which is mainly caused by polystyrene, is maintained for a shorter time in case of multiblock copolymers due to the incoherent relative movement of multiple polystyrene cores within the same loose aggregate (*vide infra*).

### Fluorescence Correlation Spectroscopy

With the information about the different concentration regimes at hand, the solution properties of the sequential and tapered multiblock copolymers  $(P(I-co-S)_n-b-PI)$  &  $(PI-b-PS)_n-b-PI$ ,  $n=1-3$  in heptane accessed by FCS measurements are compared and interpreted in the context of theoretical studies and experimental results of similar structures reported in literature.

The derived self-diffusion coefficients  $D_s$  covering the dilute ( $10^{-3} - 1$  wt%) and semi-dilute regime ( $1 - 10$  wt%) are given in Figure 9. Corresponding autocorrelation functions and fits of the fluorescence correlation spectroscopy measurements can be found in the Supp. Inf. (see Figure S14-S19). Comparing the obtained dependence of  $D_s$  on the polymer concentration  $c$  to non-associating polymers as described above, a discontinuity from the asymptotic behavior approaching infinite dilution is evident. While the trend between  $0.1 - 10$  wt% resembles the one of a non-associating polymer, the change of mobility by increasing the concentration from  $10^{-3}$  to  $10^{-1}$  wt% is massive, thus evidencing that the critical micelle concentration is exceeded, and the self-diffusion of micellar aggregates is measured.



**Figure 9:** Double logarithmic plot of the diffusion coefficients  $D_s$  of the sequential (left) and tapered (right) multiblock copolymers obtained by FCS measurements in heptane at varying concentrations ( $10^{-3} - 10$  wt%).

At the highest concentration investigated of 10 wt%, the macroscopic appearance clearly proved gelation of all samples, whereas dilution to 1 wt% and 0.1 wt% resulted in liquids of comparably low viscosity. Together with the above discussed qualitative results of the DLS measurements, different assumptions were underlaid.

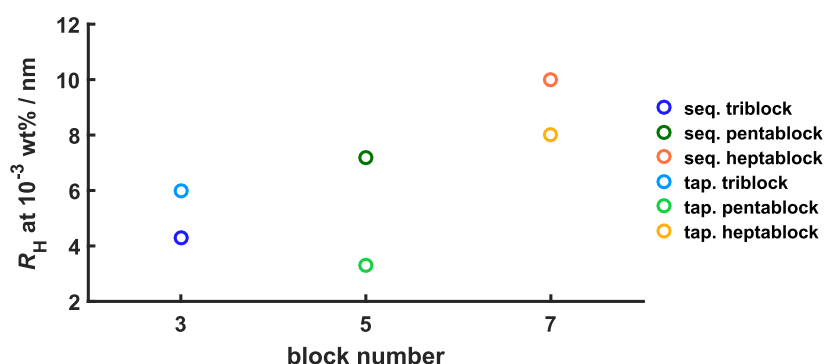
The fits at 1 and 0.1 wt% were performed with a two-component fit appropriate for freely diffusing micelles, which are in equilibrium with non-associated unimers. In the course of this, the first value of the two-component fit was fixed at the size of the corresponding unimers obtained from the measurements at  $10^{-3}$  wt%, while the second value gave the average diffusion coefficient of all aggregated species present.

The autocorrelation functions at 10 wt% were interpreted as unimers with constrained diffusion behavior because of the interpenetrating chains in a gelled matrix. Again, a second diffusion time was observed, which appears at shorter timescales than the self-diffusion time. As discussed above, this can result from the correlation between the cooperative network diffusion and the single chain motion. Therefore, a two-component fit was implemented without specifying any value.

First, the hydrodynamic radii  $R_H$  of the unimers calculated from the self-diffusion coefficients at 0.001% are discussed (Figure 10). Comparing the unimer dimensions of the sequential polymers with differing block number, the hydrodynamic radius increases monotonically with increasing block number (seq.:  $R_H^{\text{tri}} < R_H^{\text{penta}} < R_H^{\text{hepta}}$ ).

This evidences that that partitioning the solvophilic polyisoprene as well as the solvophobic polystyrene domains into more blocks does not lead to a predominant fraction of chain conformations with loop formation, yielding intramolecularly associated collapsed PS blocks called flower-like self-assembled structures, since this would result in smaller dimensions compared to the triblock.<sup>[3]</sup> On the contrary, this suggests that mainly several compact polystyrene cores are formed along a chain of unrestricted mobility.

In contrast to this, the tapered analogues show a nonlinear relation indicating that loop formation plays a role (tap.:  $R_H^{\text{tri}} > R_H^{\text{penta}} << R_H^{\text{hepta}}$ ). With the tapered pentablock exhibiting smaller dimensions than the tapered triblock, the pentablock shows a certain fraction of a looped conformation. The fact that the heptablock has larger dimensions than the tri- and pentablock indicates that at least a certain fraction of the unimers possess a looped conformation, which could also involve only two of the three PS blocks.



**Figure 10:** Hydrodynamic radii  $R_H$  of the multiblock copolymers obtained by FCS measurements in heptane at  $10^{-3}$  wt%.

Wang and Mattice theoretically discussed the tendency for loop formation of a triblock.<sup>[54]</sup> They identified the loss of entropy due to the coronal loop and the interfacial energy gain by favored interactions of the solvophobic moieties to be the major factors affecting the ratio of associated and unassociated unimers.

Comparing the tapered multiblock copolymers with their sequential counterparts shows that the tapered triblock is larger ( $R_H^{\text{tri,tap}} > R_H^{\text{tri,seq}}$ ), whereas the tapered penta- and the heptablock copolymers are smaller ( $R_H^{\text{penta,tap}} < R_H^{\text{penta,seq}}$  &  $R_H^{\text{hepta,tap}} < R_H^{\text{hepta,seq}}$ ). Both could be reasoned in the the larger effective polyisoprene block due to the incorporation of a few styrene repeating units. The increased solvophilic block lengths in case of the triblock copolymers explains the larger overall dimensions. The comparison of the penta- and the heptablock copolymers show that in both cases loop formation occurs to a certain extent for the tapered structures. Again, the longer solvophilic block promotes loop formation because of a lower steric limitations.

The observation for the sequential multiblock copolymers coincides with the results of Lairez and coworkers, who investigated dilute solutions of polystyrene-*block*-polyisoprene-*block*-polystyrene triblock copolymers (SIS,  $M_w=165 \text{ kg}\cdot\text{mol}^{-1}$ , 30 wt% styrene,  $c<1.6 \cdot 10^{-3} \text{ g}\cdot\text{mL}^{-1}$ ) in tetrahydrofuran as good solvent and *n*-heptane as polydiene-selective solvent.<sup>[55]</sup> As they

observed comparable radii in both solvents, they deduced that the unimers adopt an extended chain conformation.

At 0.1 and 1 wt%, both unimers and micellar aggregates are present. The two-component fit (see Supp. Inf., equation S2,  $m=2$ ) of the corresponding FCS autocorrelation curves allows determination of not only the diffusion coefficients, but also the relative fractions  $\omega_{\text{unim}}$  and  $\omega_{\text{mic}}$  ( $\omega_{\text{unim}} + \omega_{\text{mic}} = 1$ ) of these species. The hydrodynamic radii  $R_H$  of the micelles (Figure 11) in terms of an equivalent sphere and their relative fraction  $\omega_{\text{mic}}$  (Figure 12) are discussed in terms of aggregate size and solubility.

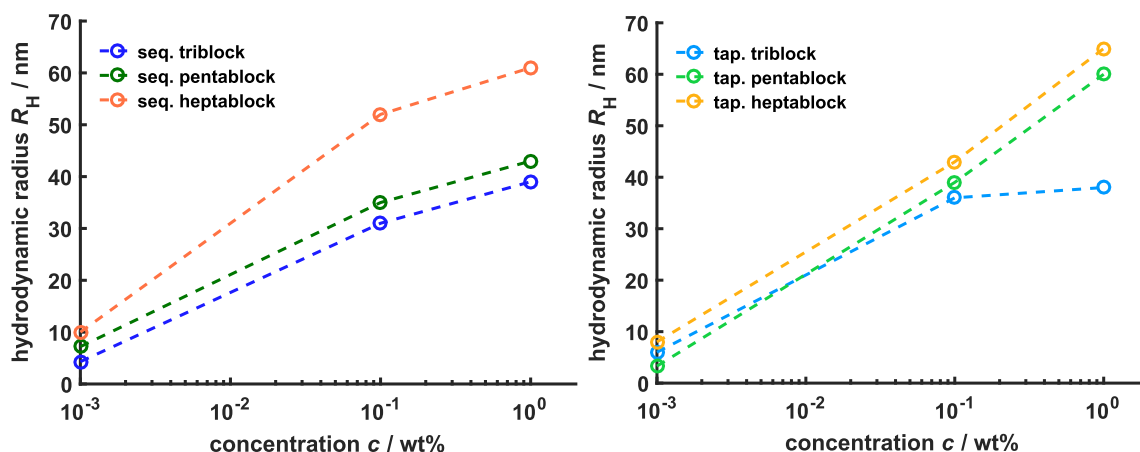


Figure 11: Hydrodynamic radii  $R_H$  of the sequential (left) and tapered (right) multiblock copolymers obtained by FCS measurements in heptane at varying concentrations ( $10^{-3}$ ,  $10^{-1}$  and 1 wt%).

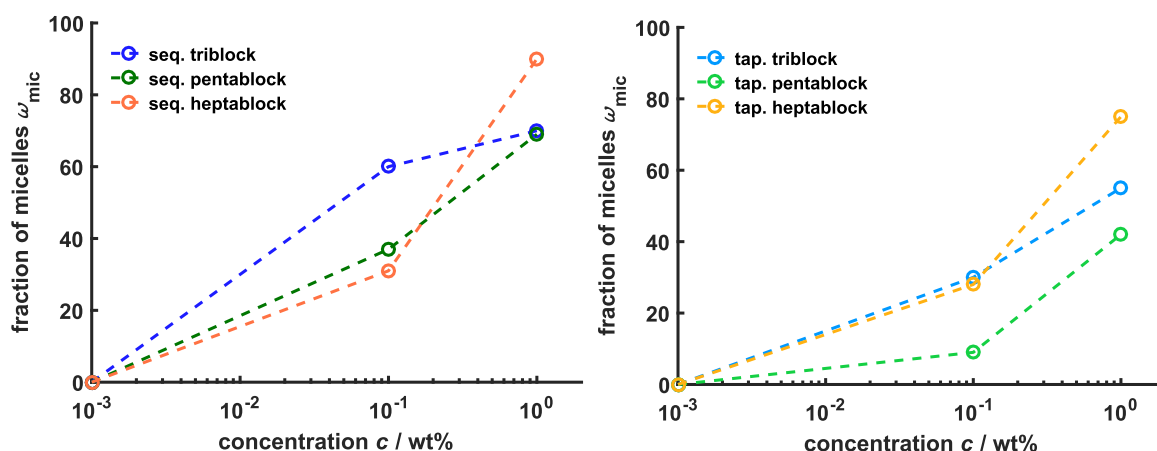


Figure 12: Relative fraction of the micellar structures  $\omega_{\text{mic}}$  of the sequential (left) and tapered (right) multiblock copolymers obtained by FCS measurements in heptane at varying concentrations ( $10^{-3}$ ,  $10^{-1}$  and 1 wt%).

Comparing the relative micellar fractions of the sequential and tapered structures at 0.1%, it is evident that the sequential multiblock copolymers have higher fraction ratios than their tapered counterparts. This reflects the enhanced solubility of the tapered structures due to its shortened pure polystyrene blocks. In case of the sequential structures, the triblock copolymers feature the highest relative fraction of micelles, whereas the penta- and heptablock exhibit a notably smaller micellar fraction ratio ( $\omega_{\text{mic}}^{\text{tri}} \gg \omega_{\text{mic}}^{\text{penta}} > \omega_{\text{mic}}^{\text{hepta}}$ ). This indicates a worsened solubility of the triblock compared to the penta- and heptablock, which can be explained by a longer individual solvophobic PS block length. The tapered structures show a different trend, with the pentablock exhibiting the lowest relative micellar fraction and hence

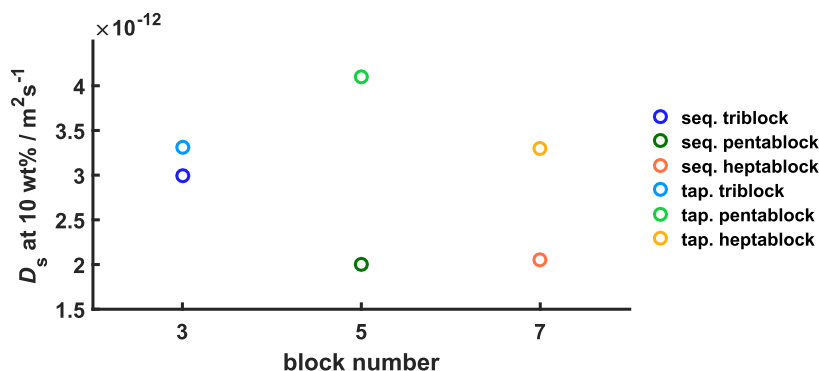


best solubility ( $\omega_{\text{mic}}^{\text{tri}} \approx \omega_{\text{mic}}^{\text{hepta}} \gg \omega_{\text{mic}}^{\text{penta}}$ ). As indicated by its unimer dimension, intramolecular association is most pronounced in case of the tapered pentablock. This might account for the reduced tendency for intermolecular aggregate formation.

The hydrodynamic radii at 0.1 wt% increase with their block number ( $R_{\text{H}}^{\text{tri}} < R_{\text{H}}^{\text{penta}} < R_{\text{H}}^{\text{hepta}}$ ) for both sequential and tapered multiblock copolymers. From a theoretical perspective, polymer chains with several core forming blocks can form a loop as discussed above against the background of the unimeric chain conformation. In case of micellar structures, loop formation results in a larger occupied interfacial area and hence a lower aggregation number and smaller aggregate sizes.<sup>[6,7]</sup> The observed trends indicate that an extended chain conformation is favored over the looped conformation. This is especially pronounced in the considerably larger hydrodynamic radius of the sequential heptablock, implying the formation of loose aggregates with several solvophobic polystyrene cores. Note that the obtained dimensions are averaged over all associated species present, rendering the tendency to form these loose aggregates less distinct in case of the tapered multiblock copolymers.

This is further manifested in the relative micellar fractions and aggregate size at 1 wt%. Especially for the tapered penta- and heptablock,  $R_{\text{H}}$  and  $\omega_{\text{mic}}$  increase remarkably with increasing concentration. This suggests a shift towards larger fractions of loose aggregates. In contrast to this, the sequential penta- and heptablock feature only a minor increase in their micellar dimension, but a pronounced increase of the relative micellar fraction. This indicates that the nature of the aggregates is only slightly altered.

At 10 wt%, all polymer solutions showed gelation, which is why the derived self-diffusion coefficients are interpreted as unimers diffusing through a gelled matrix (Figure 13).



**Figure 13:** Diffusion coefficients  $D$  of the multiblock copolymers obtained by FCS measurements in heptane at 10 wt%.

As discussed above, the diffusion of unimers through a transient network by entangled polymer chains is restricted and can be described by the reptation theory.<sup>[56]</sup> Considering a network formed of associating block copolymers, the attractive force between solvophobic moieties of different polymer chains can further impede the unimer diffusion. Besides, chain exchange can systematically slow down the unimer diffusion and hence distort the diffusion time.

Generally, the activation energy for chain expulsion depends on the interaction between the core-forming repeating unit and the solvent and can be estimated by  $kT\chi N_{\text{core}}$ , with the Boltzmann constant  $k$ , the temperature  $T$ , the Flory-Huggins interaction parameter  $\chi$  and the solvophobic block length  $N_{\text{core}}$ .<sup>[11,57]</sup> Moreover, at temperatures below the glass transition temperature of the core-forming block the chains are kinetically frozen, which impedes chain



exchange. Due to this, the solvent selectively plays a further role for the energy barrier for chain expulsion, since solvent molecules penetrating the micellar core serve as plasticizer, this way decreasing the glass transition temperature and promoting chain movements.<sup>[58,59]</sup> Moreover, chain expulsion is favored for a very compact conformation of the core-forming block, resulting in a more frequent exchange if the chain has a compact conformation near the surface.<sup>[60]</sup>

Lund *et al.* investigated the chain exchange kinetics of polybutadiene-polystyrene diblock copolymers (PB-PS,  $M=20 \text{ kg}\cdot\text{mol}^{-1}$ , 50 wt% PS) and the triblock obtained by coupling of the polystyryl chain ends (PB-PS-PB,  $M=40 \text{ kg}\cdot\text{mol}^{-1}$ , 50 w% polystyrene) in various alkanes being polydiene-selective solvents using time-resolved small-angle neutron scattering (TR-SANS). With increasing length of the solvent (decane < dodecane < tetradecane < hexadecane) they observed higher aggregation numbers ( $N_{\text{agg}}^{\text{diblock}}=85\text{--}110$  in  $\text{C}_{10}\text{H}_{22}$  and  $\text{C}_{16}\text{H}_{34}$ , respectively) and lower solvent fractions in the micellar core ( $\phi_{\text{solv}}^{\text{diblock}}=30\text{--}60$  in  $\text{C}_{16}\text{H}_{34}$  and  $\text{C}_{10}\text{H}_{22}$ , respectively). However, even if the PS core was swollen by only 7% hexadecane, DSC confirmed a lowered glass transition temperature to almost 50 °C. Therefore, they concluded that vitrification does not play a role for the systems investigated. Since they found identical solvent fractions and a halved aggregation number for the triblock, a direct comparison of the exchange kinetics at room temperature was possible. In tetradecane, both di- and triblock showed a logarithmic relaxation curve, which was shifted to longer timescales for the triblock. This evidenced an increased activation energy for the triblock due to the doubled chain length, but further indicated a cooperative chain expulsion mechanism involving several chains for both systems. Still, with roughly 25 min in case of the diblock and 75 min in case of the triblock until half of the chains had exchanged, the kinetics were rather slow. However, in dodecane, the triblock exhibited a logarithmic relaxation, whereas the diblock was close to a single exponential decay, signifying a single chain behavior. The time for 80% of the chains to exchange ranged around 20 min (diblock) and 140 min (triblock), representing the acceleration of the chain exchange. Conclusively, due to the triblock structure with two solvophilic end blocks, topological interaction and the confinement within the core increase the cooperativity for chain expulsion and slows down the chain exchange.

Lodge and coworkers investigated the chain exchange kinetics of hydrogenated polystyrene-polyisoprene ( $M=96 \text{ kg}\cdot\text{mol}^{-1}$ , 27% styrene) by time resolved small-angle neutron scattering (TR-SANS), in solvent mixtures of varying selectivity.<sup>[58]</sup> In pure squalane at 70 °C, which equals the glass transition temperature of the solvent drained PS core block,<sup>[61]</sup> the timescale of chain exchange was in the range of  $10^5$  minutes, i.e., more than two months. An analogous investigation in a mixture with 25% of 1-phenyl dodecane, which is a less polydiene-selective solvent, revealed drastically accelerated exchange kinetics in the range of several minutes. This reflects the favored interaction between PS and the solvent mixture and the decreased glass transition temperature of PS, which was calculated to range around 37 °C, now being located way below the measuring temperature.

Conclusively, plasticization of the polystyrene cores by heptane migrating into it is very likely. Yet, the chain exchange of the multiblock copolymers at room temperature is expected to be negligible on the time scale of the diffusion time of the unimers, which is less than 1 second. Even though the free energy barrier for chain expulsion scales linearly with degree of polymerization per polystyrene block  $N_{\text{core}}$ <sup>[62]</sup> and hence the penalty for chain expulsion is reduced with increasing block number and for tapered structures in terms of a lowered  $N_{\text{core}}$ ,

the two polyisoprene chain ends and several associating blocks per chain in case of the penta- and heptablock copolymers increase the barrier for chain pullout.

With a length of the observation volume of 300 nm, several polystyrene domains are located within the focus. If we assume that either a labeled unassociated chain becomes part of the aggregate or a labeled chain is expelled within the focus, the signal would autocorrelate excessively long. Therefore, we assume that the observed diffusion process mainly arises from unaggregated labeled unimers diffusing through the polymer gel without effectively associating with the aggregate. Yet, potential attractive forces between the polystyrene blocks of the unimer and the aggregate's PS cores are expected to slow down the diffusion.

For the self-diffusion coefficient of the sequential multiblock copolymers, a drastic decrease in mobility is observed going from one PS block to two or three PS blocks (Figure 13,  $D_s^{\text{tri}} < D_s^{\text{penta}} \approx D_s^{\text{hepta}}$ ). This suggests that the neighboring polystyrene microdomains are connected by bridged chain conformation. In consequence, the maximum distance between adjacent PS microdomains is limited by the length of the PI mid blocks. On the contrary, in case of the sequential triblock, the solvophilic PI blocks are longer and chains of different aggregates are less interpenetrated, therefore imposing less topological restrictions on a diffusing unimer.

This is in clear contrast to the self-diffusion of the tapered structures through the polymer gel (Figure 13,  $D_s^{\text{tri}} \approx D_s^{\text{hepta}} < D_s^{\text{penta}}$ ). The clearly enhanced mobility of the pentablock copolymers cannot be explained by connectivity of the matrix. A possible reason can be found in the smaller unimer dimension of the tapered pentablock (*vide supra*, Figure 10). The higher tendency for loop formation in case of the tapered penta- and heptablock might also affect the bridging ratio in the polymer gel, with a lower bridging fraction resulting in a less dense network and hence facilitated unimer diffusion. Furthermore, the intramolecular association of the unimers renders the polystyrene blocks of the unimers less prone to attractive interaction with the matrix.

Comparison of the sequential multiblock copolymers with their tapered analogues shows slower unimer diffusion through the gelled matrix for the sequential structures. This can be explained by the longer solvophilic polyisoprene blocks and an enhanced solubility of the tapered structures, thus together with the intramolecular association assuming for less attractive forces between solvophobic moieties.

Spontak and coworkers provided a theoretical insight into the effect of the number of solvophobic blocks on the chain conformation.<sup>[63]</sup> Molecular conformation of linear sequential  $A(BA)_n$  multiblock copolymers with the same overall molar mass and composition in B-selective solvents were evaluated by dissipative particle dynamics simulations in the framework of network formation. In gels with a polymer fraction of 10%, an overall bridging fraction of 60–65% was predicted for both multiblock copolymers with two and three solvophobic blocks. Although with 20% a significant contribution to the bridging fraction of the structure with three solvophobic cores traces back to structures with two cores connected intramolecularly by two bridges, the extended chain structure with three cores connected intramolecularly by two bridges contributes the largest share.

This supports the interpretation of the huge difference between the self-diffusion coefficients of the sequential triblock and the penta- as well as heptablock explained by the decrease in periodicity due to large amounts of bridged chain conformation.

Higgins *et al.* investigated polystyrene-*block*-poly(ethylene-*alt*-propylene) diblock copolymers ( $100 \text{ kg}\cdot\text{mol}^{-1}$ , 38.5 wt% PS) solutions in dodecane, which were investigated by small-angle neutron scattering (SANS). They reported aggregate formation above 1.4 wt%, with hydrodynamic radii around 125 nm.<sup>[64]</sup> At concentrations above 3-4 wt%, long-range ordering ascribed to a sol-gel transition was observed.<sup>[65]</sup> Due to the shortened individual PI blocks by compartmenting them in two blocks, the smaller micellar dimensions of the triblock copolymers at 0.1 and 1 wt% described within this work fit the expectations. Yet, the comparably late onset of micellization is in pronounced contrast to our observation, especially considering that dodecane is a more PI-selective solvent than heptane.

Koňák *et al.* studied solutions of polystyrene-*block*-poly(ethylene-*alt*-butylene)-*block*-polystyrene triblock copolymers ( $70 \text{ kg}\cdot\text{mol}^{-1}$ , 28 wt% PS) in heptane using dynamic light scattering.<sup>[66]</sup> They found flower-like micelles at concentrations of 0.5 wt%, the presence of also larger bridged clusters between 1.1 – 2.6 wt% and gelation above 4 wt%. In comparison to the pentablock copolymers of this work, the compartment of the solvophilic block into three blocks with two dangling polyisoprene end blocks explains the favored formation of bridged clusters over flower-like micelles, with the higher occupied interfacial area impeding loop formation.

Furthermore, the results for the pentablock can be compared with the observation of Lairez and coworkers, who studied polystyrene-*block*-polyisoprene-*block*-polystyrene triblock copolymer ( $160 \text{ kg}\cdot\text{mol}^{-1}$ , 28 wt% PS) solutions in heptane by static light scattering. They determined a critical micelle concentration of 0.2 wt% and a radius of gyration of 25 nm<sup>[55]</sup>, with aggregates continuously increasing in size until the overlap concentration. The increase in the aggregates' dimension was attributed to bridged clusters. The overlap concentration was assigned to 1.7 wt% due to a successive decrease of the scattered intensity per monomer.<sup>[67]</sup> Conclusively, we observe an earlier onset of micellization and larger aggregates in spite of approximately half the molar mass.

The results of the heptablock copolymers can be set in relation to the  $(\text{PS-}b\text{-PI})_2\text{-}b\text{-PS}$  pentablock copolymers with three solvophobic blocks ( $120 \text{ kg}\cdot\text{mol}^{-1}$ , 35 wt% PS), whose solutions in heptane were investigated by SANS and DLS.<sup>[68]</sup> At concentrations of 1, 2, 4 and 6 wt%, macroscopic phase separation occurred upon cooling the annealed solution. Above the cloud point, no flower-like micelles were observed. At concentrations of 8 and 9 wt%, a transparent gel was obtained, which was stable over the whole temperature range investigated. Conclusively, the higher molar mass and two solvophobic end blocks of the pentablock copolymers impede solubility compared to sequential heptablock discussed in this work exhibiting two dangling polyisoprene end blocks. Besides, the critical concentration for network formation is comparable to the multiblock copolymers investigated in this work.

## Conclusion

This work presents an efficient strategy for fluorescent dye-labeling by post-polymerization modification. Bromination and immediate subsequent azidation allows to install an azide moiety without facing chain degradation or cross-linking issues, which can later be addressed by a copper-catalyzed 1,3-dipolar cycloaddition. In contrast to previous works, no additional moieties further altering the chemical nature of the polymer are introduced.

The optimized dye-labeling protocol was transferred to tapered  $(P(I-co-S)_n-b-PI)$  as well as sequential  $((PI-b-PS)_n-b-PI)$  block copolymers with three, five and seven blocks ( $n=1-3$ ). The dynamic properties of these multiblock copolymers were studied implementing fluorescence correlation spectroscopy in the range of 0.001 – 10 wt%. Prior to that, the semi-dilute concentration regime was specified by dynamic light scattering. Above 1 wt%, deviation from the linear relationship between the cooperative diffusion coefficient and the polymer concentration proved the onset of interparticle interaction.

FCS measurements below the critical micelle concentration rendered smaller hydrodynamic dimensions for the tapered structures with more than one solvophobic polystyrene block, regardless of the longer solvophilic polyisoprene blocks. This proved a higher tendency for loop formation, which is also reflected in smaller aggregate sizes at 0.1 wt%. With increasing concentration, the fraction of larger loose aggregate structures with several solvophobic polystyrene cores increased in case of both sequential and tapered multiblock copolymers. At 10 wt%, gelation was observable for all polymers. The self-diffusion of the unimers in polymer networks was found to be more restricted in case of the sequential multiblock copolymers, which might result of a higher bridging fraction together with the larger unimer sizes. Moreover, less interaction between the unimers and the solvophobic moieties of the matrix are expected for the tapered multiblock copolymers due to their tendency to form intramolecular aggregates.

## References

- [1] a) D. M. Vriezema, M. Comellas Aragonès, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, *Chem. Rev. (Washington, DC, U. S.)* **2005**, 105, 1445; b) K. Kataoka, A. Harada, Y. Nagasaki, *Adv. Drug Delivery Rev.* **2012**, 64, 37; c) A. Martini, U. S. Ramasamy, M. Len, *Tribol. Lett.* **2018**, 66, 1.
- [2] a) G. Riess, *Prog. Polym. Sci.* **2003**, 28, 1107; b) V. Abetz, *Block Copolymers II*, Springer, Berlin Heidelberg, **2005**.
- [3] J. Zhang, Z.-Y. Lu, Z.-Y. Sun, *Soft Matter* **2013**, 9, 1947.
- [4] a) V. Hugouvieux, M. A. V. Axelos, M. Kolb, *Macromolecules* **2009**, 42, 392; b) S. Woloszczuk, M. Banaszak, P. Knychala, K. Lewandowski, M. Radosz, *J. Non-Cryst. Solids* **2008**, 354, 4138; c) C. Zhong, D. Liu, *Macromol. Theory Simul.* **2007**, 16, 141; d) V. Hugouvieux, M. A. V. Axelos, M. Kolb, *Soft Matter* **2011**, 7, 2580; e) M. E. Gindy, R. K. Prud'homme, A. Z. Panagiotopoulos, *J. Chem. Phys.* **2008**, 128, 164906.

- [5] a) C. Zheng, *Soft Matter* **2019**, *15*, 5357; b) S. K. Filippov, B. Verbraeken, P. V. Konarev, D. I. Svergun, B. Angelov, N. S. Vishnevetskaya, C. M. Papadakis, S. Rogers, A. Radulescu, T. Courtin et al., *J. Phys. Chem. Lett.* **2017**, *8*, 3800; c) G. Pandav, V. Pryamitsyn, K. C. Gallow, Y.-L. Loo, J. Genzer, V. Ganesan, *Soft Matter* **2012**, *8*, 6471.
- [6] V. S. Kravchenko, I. I. Potemkin, *J. Phys. Chem. B* **2016**, *120*, 12211.
- [7] J. Kuldová, P. Košovan, Z. Limpouchová, K. Procházka, *Macromol. Theory Simul.* **2013**, *22*, 61.
- [8] a) C. Honda, Y. Hasegawa, R. Hirunuma, T. Nose, *Macromolecules* **1994**, *27*, 7660; b) K. Edwards, M. Almgren, S. Tormod, Z. Tuzar, *Makromol. Chem., Rapid Commun.* **1988**, 785.
- [9] a) S. Creutz, J. van Stam, S. Antoun, F. C. de Schryver, R. Jérôme, *Macromolecules* **1997**, *30*, 4078; b) S. Creutz, J. van Stam, F. C. de Schryver, R. Jérôme, *Macromolecules* **1998**, *31*, 681; c) J. van Stam, S. Creutz, F. C. de Schryver, R. Jérôme, *Macromolecules* **2000**, *33*, 6388.
- [10] a) Y.-Y. Won, H. T. Davis, F. S. Bates, *Macromolecules* **2003**, *36*, 953; b) S.-H. Choi, F. S. Bates, T. P. Lodge, *Macromolecules* **2011**, *44*, 3594; c) R. Lund, L. Willner, D. Richter, H. Iatrou, N. Hadjichristidis, P. Lindner, *J. Appl. Crystallogr.* **2007**, *40*, 327-331.
- [11] S.-H. Choi, T. P. Lodge, F. S. Bates, *Phys. Rev. Lett.* **2010**, *104*, 47802.
- [12] M. Štěpánek, K. Procházka, W. Brown, *Langmuir* **2000**, *16*, 2502.
- [13] C. Chassenieux, T. Nicolai, L. Benyahia, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 18.
- [14] R. Pecora, R. Borsali (Eds.) *Springer reference*, Springer, New York, NY, **2008**.
- [15] W. Schärtl, *Light Scattering from Polymer Solutions and Nanoparticle Dispersions*, Springer Berlin Heidelberg, New York, **2007**.
- [16] I. D. Block, F. Scheffold, *Rev. Sci. Instrum.* **2010**, *81*, 123107.
- [17] K. L. Planken, H. Cölfen, *Nanoscale* **2010**, *2*, 1849.
- [18] K. Koynov, H.-J. Butt, *Curr. Opin. Colloid Interface Sci.* **2012**, *17*, 377.
- [19] a) H. Zettl, W. Häfner, A. Böker, H. Schmalz, M. Lanzendörfer, A. H. E. Müller, G. Krausch, *Macromolecules* **2004**, *37*, 1917; b) H. Zettl, U. Zettl, G. Krausch, J. Enderlein, M. Ballauff, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2007**, *75*, 61804.
- [20] U. Zettl, S. T. Hoffmann, F. Koberling, G. Krausch, J. Enderlein, L. Harnau, M. Ballauff, *Macromolecules* **2009**, *42*, 9537.
- [21] T. Cherdhirankorn, A. Best, K. Koynov, K. Peneva, K. Muellen, G. Fytas, *J. Phys. Chem. B* **2009**, *113*, 3355.
- [22] A. Vagias, R. Raccis, K. Koynov, U. Jonas, H.-J. Butt, G. Fytas, P. Košovan, O. Lenz, C. Holm, *Phys. Rev. Lett.* **2013**, *111*, 88301.
- [23] a) A. Michelman-Ribeiro, H. Boukari, R. Nossal, F. Horkay, *Macromolecules* **2004**, *37*, 10212; b) R. Raccis, R. Roskamp, I. Hopp, B. Menges, K. Koynov, U. Jonas, W. Knoll, H.-J. Butt, G. Fytas, *Soft Matter* **2011**, *7*, 7042.
- [24] T. Cherdhirankorn, V. Harmandaris, A. Juhari, P. Voudouris, G. Fytas, K. Kremer, K. Koynov, *Macromolecules* **2009**, *42*, 4858.

- [25] a) R. Erhardt, A. Böker, H. Zettl, H. Kaya, W. Pyckhout-Hintzen, G. Krausch, V. Abetz, A. H. E. Müller, *Macromolecules* **2001**, *34*, 1069; b) D. Horn, J. Klingler, W. Schorf, K. Graf in *Prog. Colloid Polym. Sci.*, v. *111* (Eds.: H. Rehage, G. Peschel), Steinkopff; Springer, Darmstadt, New York, **1998**, pp. 27–33; c) H. Schuch, J. Klingler, P. Rossmanith, T. Frechen, M. Gerst, J. Feldthusen, A. H. E. Müller, *Macromolecules* **2000**, *33*, 1734.
- [26] T. B. Bonn  , K. L  dtke, R. Jordan, P.   t  p  nek, C. M. Papadakis, *Colloid Polym. Sci.* **2004**, *282*, 833.
- [27] T. B. Bonn  , K. L  dtke, R. Jordan, C. M. Papadakis, *Macromol. Chem. Phys.* **2007**, *208*, 1402.
- [28] a)   . Chmela, J. Koll  r, L. Hr  kov  , *J. Photochem. Photobiol., A* **2015**, *307-308*, 123; b) G. T. Gavrancovic, S. Csihony, N. B. Bowden, C. J. Hawker, R. M. Waymouth, W. E. Moerner, G. G. Fuller, *Macromolecules* **2006**, *39*, 8121; c) N. B. Bowden, K. A. Willets, W. E. Moerner, R. M. Waymouth, *Macromolecules* **2002**, *35*, 8122.
- [29] Y.-J. Jang, C. Naundorf, M. Klapper, K. M  llen, *Macromol. Chem. Phys.* **2005**, *206*, 2027.
- [30] S. Ni, P. Zhang, Y. Wang, M. A. Winnik, *Macromolecules* **1994**, *27*, 5742.
- [31] H. Zettl, W. H  fner, A. B  ker, H. Schmalz, M. Lanzend  rfer, A. H. E. M  ller, G. Krausch, *Macromolecules* **2005**, *38*, 6748.
- [32] R. Huisgen, *J. Org. Chem.* **1968**, *33*, 2291.
- [33] V. O. Rodionov, V. V. Fokin, M. G. Finn, *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 2210.
- [34] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.
- [35] K. A. G  nay, P. Theato, H.-A. Klok, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 1.
- [36] Y. Zhang, K. Shen, F. Guo, Y. Wang, Y. Wang, Y. Wang, Y. Li, *RSC Adv.* **2013**, *3*, 20345.
- [37] E. Wittenberg, V. Abetz, *Polymer* **2017**, *121*, 304.
- [38] S. J. Rowan, C. Barner-Kowollik, B. Klumperman, P. Gaspard, R. B. Grubbs, M. A. Hillmyer, L. R. Hutchings, M. K. Mahanthappa, D. Moatsou, R. K. O'Reilly et al., *ACS Macro Lett.* **2016**, *5*, 1.
- [39] Y. Cao, K. D. Sayala, P. L. Gamage, R. Kumar, N. V. Tsarevsky, *Macromolecules* **2020**, *53*, 8020.
- [40] S. Wang, S. Zhang, C. Feng, G. Lu, P. Theato, X. Huang, *Polym. Chem.* **2021**, *12*, 5589.
- [41] M. Steube, T. Johann, E. Galanos, M. Appold, C. R  ttiger, M. Mezger, M. Gallei, A. H. E. M  ller, G. Floudas, H. Frey, *Macromolecules* **2018**, *51*, 10246.
- [42] E. Grune, M. Appold, A. H. E. M  ller, M. Gallei, H. Frey, *ACS Macro Lett.* **2018**, *7*, 807.
- [43] I. J. Gardner, J. V. Fusco, N. F. Newman, Ronald C. Kowalski, W. M. Davis, *Acid scavenged polymer halogenation*, US5087674, **1990**.
- [44] P. L. Golas, N. V. Tsarevsky, B. S. Sumerlin, K. Matyjaszewski, *Macromolecules* **2006**, *39*, 6451.
- [45] M. Steube, T. Johann, M. Plank, S. Tjabering, A. H. Gr  schel, M. Gallei, H. Frey, A. H. E. M  ller, *Macromolecules* **2019**, *52*, 9299.
- [46] D. J. Worsfold, *J. Polym. Sci., Part A-1: Polym. Chem.* **1967**, *5*, 2783.
- [47] H. Fujita, *Polymer Solutions*, Elsevier Science, Amsterdam, **2014**.
- [48] S. Seiffert, *Prog. Polym. Sci.* **2017**, *66*, 1.

- [49] P. N. Pusey, W. van Megen, *Phys. A* **1989**, 157, 705.
- [50] M. F. Koziol, K. Fischer, S. Seiffert, *Macromolecules* **2021**, 54, 4375.
- [51] A. Siegert, *MIT Radiat. Lab Rep. No 465* **1943**, 28.
- [52] G. Wypych, *Handbook of Polymers (Second Edition)*, ChemTec Publishing, **2016**.
- [53] A. Blanco, A. Gayol, D. Gómez, J. M. Navaza, *Phys. Chem. Liq.* **2013**, 51, 381.
- [54] Y. Wang, W. L. Mattice, D. H. Napper, *Macromolecules* **1992**, 25, 4073.
- [55] E. Raspaud, D. Lairez, M. Adam, J.-P. Carton, *Macromolecules* **1994**, 27, 2956.
- [56] a) T. C. B. McLeish, *Adv. Phys.* **2002**, 51, 1379; b) L. Wu, E. W. Cochran, T. P. Lodge, F. S. Bates, *Macromolecules* **2004**, 37, 3360; c) T. P. Lodge, N. A. Rotstein, S. Prager in *Advances in Chemical Physics*, John Wiley & Sons, Hoboken, NJ, USA, **2007**, pp. 1–132.
- [57] Z. Li, E. E. Dormidontova, *Soft Matter* **2011**, 7, 4179.
- [58] E. Wang, J. Zhu, D. Zhao, S. Xie, F. S. Bates, T. P. Lodge, *Macromolecules* **2020**, 53, 417.
- [59] D. Schaeffel, A. Kreyes, Y. Zhao, K. Landfester, H.-J. Butt, D. Crespy, K. Koynov, *ACS Macro Lett.* **2014**, 3, 428.
- [60] A. G. Denkova, E. Mendes, M.-O. Coppens, *Soft Matter* **2010**, 6, 2351.
- [61] C. Lai, W. B. Russel, R. A. Register, *Macromolecules* **2002**, 35, 841.
- [62] S. C. Seeger, T. P. Lodge, K. D. Dorfman, *Macromolecules* **2022**, 55, 10220.
- [63] M. O. Tuhin, J. J. Ryan, J. D. Sadler, Z. Han, B. Lee, S. D. Smith, M. A. Pasquinelli, R. J. Spontak, *Macromolecules* **2018**, 51, 5173.
- [64] J. S. Higgins, J. V. Dawkins, G. G. Maghami, S. A. Shakir, *Polymer* **1986**, 27, 931.
- [65] J. S. Higgins, S. Blake, P. E. Tomlins, S. B. Ross-Murphy, E. Staples, J. Penfold, J. V. Dawkins, *Polymer* **1988**, 29, 1968.
- [66] Č. Koňák, G. Fleischer, Z. Tuzar, R. Bansil, *J. Polym. Sci., Part B: Polym. Phys.* **2000**, 38, 1312.
- [67] E. Raspaud, D. Lairez, M. Adam, J.-P. Carton, *Macromolecules* **1996**, 29, 1269.
- [68] H. Nie, M. Li, R. Bansil, Č. Koňák, M. Helmstedt, J. Lal, *Polymer* **2004**, 45, 8791.

## Supporting Information

### Materials

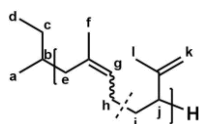
The solvents cyclohexane (Fisher Science,  $\geq 99.8\%$ ) and tetrahydrofuran (THF, Fisher Science,  $\geq 99.8\%$ ) were dried over sodium with benzophenone as an indicator. Dimethylformamide (DMF, Acros Organics, 99.8%, over molecular sieve), methanol (MeOH, Fisher Science,  $\geq 99.9\%$ ), isopropanol (iPrOH, VWR Chemicals, 100%) and benzene (Carl Roth,  $\geq 99.5\%$ ) were used as purchased. Heptane (Sigma Aldrich,  $\geq 99\%$ ) used for the preparation of polymer solutions exhibited spectrophotometric grade.

The stabilizers of isoprene (I, Acros Organics, 98%) and styrene (S, Carl Roth,  $\geq 99.5\%$ ) were removed by filtering the monomers through a column containing basic aluminum oxide and purified hereafter by degassing and distillation over calcium hydride (Acros Organics, 93%) and trioctyl aluminum (Sigma Aldrich, 25 wt% in hexanes). The initiator *sec*-Butyllithium (*sec*-BuLi, Acros Organics, 1.3 M in cyclohexane/hexane (92/8)) was used as supplied. Sodium azide (Acros Organics,  $\geq 99\%$ ) and 3-ethynyl perylene (Lumiprobe,  $>95\%$ ) were weighed into a glass vial and put under inert gas atmosphere by evacuating and flooding with argon three times. Copper(I) bromide (Sigma Aldrich, 98%) was purified stirring a solution with glacial acetic acid for 24 h at room temperature, followed by washing twice with absolute ethanol and twice with diethyl ether. Then, CuBr was dried under vacuum for several days and handled afterwards in a glovebox under argon atmosphere. *N,N,N',N'',N''*-pentamethyl-diethylenetriamine (PMDETA, TCI,  $>99\%$ ) was used without further purification.

### Carbanionic Polymerization

After the above-described drying procedure, the monomers were distilled into a graduated ampoule and cyclohexane was freshly distilled into a Mortom flask glass reactor equipped with a rare earth magnetic stirring bar under normal pressure. The required amount of *sec*-BuLi was added in argon counterflow and the solution was tempered to 40 °C. The living carbanionic polymerization was started via the addition of the desired amount of the monomer or monomer mixture. In case of multiblock syntheses monomer mixtures were added several times. The respective reaction times were calculated using kinetic Monte Carlo simulation. The living chain ends were terminated by addition of methanol. The polymers were precipitated pouring the reaction solution into an 8-fold excess of a methanol-isopropanol mixture, dried at reduced pressure for at least one week and stored in the absence of light at -20 °C.

In the following, the polyisoprene homopolymer (SEC:  $M_n=11250 \text{ g}\cdot\text{mol}^{-1}$ ,  $\bar{D}=1.05$ ) used for the optimization of the labeling protocol is characterized by 2D NMR analysis (Figure S1-S5), revealing a ratio of 1,4- to 3,4-units of 94:6 (NMR:  $M_n$  of  $8030 \text{ g}\cdot\text{mol}^{-1}$ ).



$^1\text{H}$  (850 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$ [ppm] = 5.3 (1H, g), 4.9 (2H, k), 2.2 (2H, h), 2.2 (2H, e<sup>cis</sup>), 2.1 (2H, e<sup>trans</sup>), 2.1 (1H, j), 1.8 (3H, f<sup>cis</sup>), 1.7 (3H, f<sup>trans</sup>), 1.7 (3H, l), 1.5 (2H, i), 0.9 (3H, d), 0.9 (3H, a).

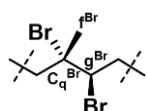


$^{13}\text{C}$  (214 MHz,  $\text{C}_6\text{D}_6$ )  $\delta[\text{ppm}] = 147.6 (\text{C}_q^{3,4})$ ,  $135.3 (\text{C}_q^{1,4})$ ,  $125.4 (\text{G})$ ,  $111.7 (\text{K})$ ,  $48.1 (\text{J})$ ,  $40.1 (\text{E}^{\text{trans}})$ ,  $32.4 (\text{E}^{\text{cis}})$ ,  $31.4 (\text{I})$ ,  $26.7 (\text{H})$ ,  $23.5 (\text{F}^{\text{cis}})$ ,  $18.5 (\text{L})$ ,  $19.2 (\text{A})$ ,  $16.0 (\text{F}^{\text{trans}})$ ,  $11.5 (\text{D})$ .

## Bromination of Polyisoprene

0.1 mmol (1 eq.) of the polymer (1.0 g in case of 10k PI) were transferred into a Schlenk flask and dried azeotropically with benzene. After flushing with argon, a 10 wt% solution in dry cyclohexane (10 g, 12.8 mL) was prepared and 0.1 mmol of bromine (1 eq., 0.2 mL of a  $0.5 \text{ mol}\cdot\text{L}^{-1}$  solution in cyclohexane) were added at room temperature under light exclusion. After one minute of reaction time, 0.4 mL of a  $0.5 \text{ mol}\cdot\text{L}^{-1}$  solution of sodium hydroxide in methanol was added. The polymer was precipitated into a 10-fold excess of methanol, centrifugated (4500 rpm,  $0^\circ\text{C}$ , 10 min) and decanted. Afterwards, the polymer was dissolved in benzene, passed through a  $0.2 \mu\text{m}$  diameter porous filter and directly transferred into a flask sealed with a teflon stopper connected to a Schlenk splitter for further reaction.

To allow an easier characterization of the modified polymers, also a bromination with 50 eq. of bromine (10.0 mL,  $0.5 \text{ mol}\cdot\text{L}^{-1}$  in cyclohexane) was conducted.  $^1\text{H}$  as well as  $^{13}\text{C}$ -JMOD-NMR spectra (Figure S6 and S7) are given for polyisoprene with a low degree of bromination ( $M_n=11510 \text{ g}\cdot\text{mol}^{-1}$ ,  $D=1.05$ ); the characterization by 2D NMR analysis (HSQC, HMBC, COSY, Figure S8-S10) is shown for a high degree of bromination in order to get a significant signal intensity.



$^1\text{H}$  (850 MHz,  $\text{C}_6\text{D}_6$ )  $\delta[\text{ppm}] = 4.2 (1\text{H}, \text{g}^{\text{Br}})$ ,  $1.8 (3\text{H}, \text{f}^{\text{Br}})$ .

$^{13}\text{C}$  (214 MHz,  $\text{C}_6\text{D}_6$ )  $\delta[\text{ppm}] = 74.6 (\text{C}_q^{\text{Br}})$ ,  $66.8 (\text{G}^{\text{Br}})$ ,  $31.4 (\text{F}^{\text{Br}})$ .

## Azidation of Polyisoprene

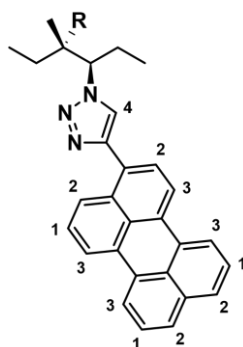
The reaction was carried out in a flask sealed with a teflon stopper connected to a Schlenk splitter, which was also connected to a flask with THF over sodium. 0.1 mmol (1 eq.) of the brominated polymer with the lower degree of functionalization ( $\sim 1.0 \text{ g}$  in case of 10k PI) were dried azeotropically with benzene overnight. 17 mL THF were distilled into the reaction flask by trap-to-trap distillation. 1.0 mmol (10 eq., 65.0 mg) of sodium azide were dissolved in 17 mL dry DMF and added to the polymer solution in THF under argon atmosphere by syringe, resulting in a blueish  $3 \text{ mmol}\cdot\text{L}^{-1}$  solution of the polymer. Here, a concentration of  $0.06 \text{ mmol}\cdot\text{L}^{-1}$  of  $\text{NaN}_3$  in DMF is essential to ensure complete solubility. Moreover, a mixture of THF and DMF at a ratio of 1:1 was used to obtain a solution that is polar enough to solvate the intermediate anions and to prevent micelle formation of PI-PS copolymers with polyisoprene lying in the core of the structure, which would be likely in pure DMF. The reaction was allowed to stir vigorously for 3 days at room temperature. The product was precipitated into a 10-fold excess of methanol, centrifugated (4500 rpm,  $0^\circ\text{C}$ , 10 min) and decanted. Afterwards, the polymer was dissolved in benzene, centrifugated again to sediment the salts, passed through a  $0.2 \mu\text{m}$  diameter porous filter and dried *in vacuo* afterwards.

The azidation of the brominated polymer with a higher degree of functionalization was carried out analogously. 0.02 mmol (1 eq.) of the highly brominated polymer ( $\sim 200$  mg in case of 10k PI) were dissolved in 77 mL THF and reacted with 10.0 mmol (500 eq., 650 mg) of sodium azide in 77 mL DMF, giving a  $1.3 \cdot 10^{-7} \text{ mol} \cdot \text{L}^{-1}$  solution of the polymer. The reaction solution was concentrated before precipitation. However, 2D NMR analysis did not show remarkable alteration in the spectra. Yet, a successful introduction of the azide group was proven by FTIR ( $\tilde{\nu}(\text{N}_3)=2094 \text{ cm}^{-1}$ ). The SEC trace showed no evidence for chain degradation or cross-linking but a slight shift in molar mass ( $M_n=11480 \text{ g} \cdot \text{mol}^{-1}$ ,  $\bar{D}=1.05$ ).

### Copper-catalyzed 1,3-dipolar cycloaddition of Polyisoprene and 3-Ethynyl Perylene

For the synthesis a Schenk splitter connected to three flasks sealed with teflon stoppers and to a flask with THF over sodium was used. 0.016 mmol (1.0 eq.) of the azidated polymer with the lower degree of functionalization ( $\sim 160$  mg in case of 10k PI) was dissolved in benzene, transferred to one of the flasks and dried azeotropically overnight. 10 mL THF were distilled onto the polymer by trap-to-trap distillation. 0.040 mmol (2.5 eq., 5.7 mg) CuBr were weighted into the second flask and 4 mL THF were distilled into this flask afterwards. 0.040 mmol (2.5 eq., 0.008 mL) PMDETA were added via syringe to the CuBr, giving a slightly yellowish solution of the catalyst. 0.008 mmol (0.5 eq.) of 3-ethynyl perylene were dissolved in 2 mL THF, which was distilled into the third flask before. Both the solution of the catalyst and the perylene dye were added to the polymer solution in THF under inert gas by syringe, turning the reaction solution bright yellow. The reaction was allowed to stir vigorously for 7 days at room temperature under light exclusion. The final reaction solution was passed through column with neutral aluminum oxide to remove the copper catalyst, concentrated, dissolved in benzene and precipitated into a 10-fold excess of methanol. The polymer was decanted and dried *in vacuo*. Preparative SEC in chloroform was used to remove residual dye.

The SEC trace ( $M_n=11090 \text{ g} \cdot \text{mol}^{-1}$ ,  $\bar{D}=1.11$ ) revealed a small shoulder at higher molar masses. FTIR showed a disappearance of the azide stretch ( $\tilde{\nu}(\text{N}_3)=2094 \text{ cm}^{-1}$ ), while a new band arising from the formed triazole moiety appeared ( $\tilde{\nu}(\text{triazole})=2350 \text{ cm}^{-1}$ ). Besides, dye-functionalization of the polyisoprene was proven by fluorescence emission spectrometry ( $I_{\text{max}}=471$  &  $497 \text{ nm}$ ).  $^1\text{H}$  as well as  $^1\text{H}$ -DOSY-NMR spectra (Figure S11 and S12) further verified the successful attachment of the perylene dye.



$^1\text{H}$  (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta[\text{ppm}] = 7.42$  (1H, 4),  $7.36$  (4H, 3),  $7.05$  (4H, 2),  $6.96$  (3H, 1).

## Characterization Methods

*Size exclusion chromatography* was carried out in THF on an instrument consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump, a set of three PSS-SDV 5 mL columns ( $10^2$ ,  $10^3$ ,  $10^4$  Å) and RI (35 °C) as well as UV detectors (254 nm). A polyisoprene standard and a polystyrene standard provided by Polymer Standard Service were used for the calibration of polyisoprene and the polyisoprene-polystyrene copolymers, respectively.

$^1\text{H}$  NMR spectra at 850 MHz, 400 MHz and 300 MHz, the  $^{13}\text{C}$  NMR spectra at 214 MHz, 100 MHz and 75 MHz, and the respective 2D NMR spectra were recorded at 23 °C on a Bruker Avance III (5 mm QXI-probe with a z-gradient), a Bruker Avance II (5 mm BBFO-head with z-gradient) and a Bruker Avance III (5 mm BBFO-head with z-gradient), respectively. The spectra were referenced internally to residual proton signals of the deuterated solvent.

*Fourier transform infrared (FTIR) spectroscopy* was used to follow the reaction progress of the functionalization reactions. The measurements in the range of  $650\text{--}4000\text{ cm}^{-1}$  were performed using a Nicolet iS10 FT-IR spectrometer supplied by Thermo Fisher Scientific.

*Fluorescence emission* was recorded using a Cary Eclipse spectrometer supplied by Varian in the range of  $455\text{--}1100\text{ nm}$ . The scanning rate was  $600\text{ nm}\cdot\text{min}^{-1}$  and the spectra were measured with an excitation wavelength of 435 nm and excitation as well as emissions slits of 5 nm. The polymers were dissolved in THF and degassed with argon for 30 min to avoid quenching by oxygen before transferring it into a quartz glass cuvette with a thickness  $d$  of 1 cm.

*FCS measurements* were carried out on a commercial FCS setup (LSM 880, Carl Zeiss, Germany). The perylene dyes were excited by a 405 nm diode laser (LDH-D-C-405, PicoQuant, Berlin, Germany) focused into the studied samples by a Zeiss C-Apochromat  $40\times/1.2\text{ W}$  water-immersion objective. The focus was positioned only 20  $\mu\text{m}$  deep in the studied solutions to minimize aberrations caused by the refractive index mismatch between the immersion liquid (water) and the sample media (e.g., copolymer solutions in heptane). The fluorescent light was detected in the range of  $420\text{--}550\text{ nm}$  with the microscope's inbuilt 32-channel GaAsP photomultiplier array (QUASAR, Carl Zeiss, Jena, Germany) operating in photon counting mode. An Attotfluor steel cell (Invitrogen, Leiden, The Netherlands) with a mounted microscope glass coverslip of 25 mm diameter and 0.15 mm thickness was used as a sample chamber. For each sample, a series of 10 measurements with total duration of 300 s were performed. During FCS measurements, the temperature,  $T$ , was kept constant at 23 °C ( $\Delta T < 0.5\text{ °C}$ ). The time-dependent fluctuations of the fluorescence intensity,  $\delta I(t)$ , were recorded and analyzed by an autocorrelation function  $G(t)$  (equation S1).

$$G(t) = 1 + \frac{\langle \delta I(t') \delta I(t'+t) \rangle}{\langle I(t') \rangle^2} \quad (\text{S1})$$

The experimentally obtained  $G(t)$  was fitted with an equation for an ensemble of  $m$  different types of diffusing species (equation S2):

$$G(t) = 1 + \left[ 1 + \frac{f_T}{1-f_T} e^{-\frac{t}{\tau_T}} \right] \frac{1}{N} \sum_{i=1}^m \frac{f_i}{\left[ 1 + \frac{t}{\tau_{D_i}} \right] \sqrt{1 + \frac{t}{S^2 \tau_{D_i}}}} \quad (\text{S2})$$

where  $N$  is the average number of diffusing fluorescent species in the observation volume,  $f_T$  and  $\tau_T$  are the fraction and the decay time of the triplet state,  $\tau_{Di}$  is the diffusion time of the  $i$ th species,  $f_i$  is the fraction of component  $i$ , and  $S=z_0r_0^{-1}$  is the structure parameter, with  $z_0$  and  $r_0$  being the axial and radial dimensions of the confocal volume, respectively.

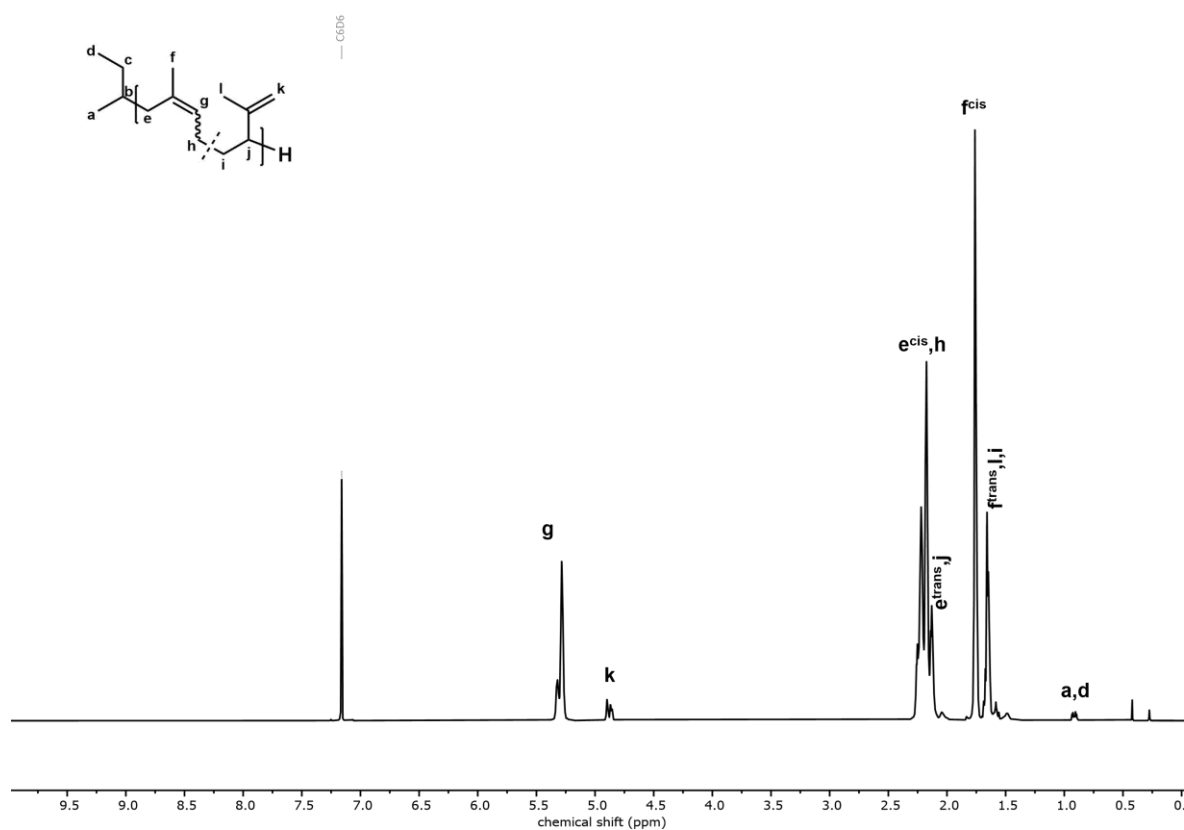
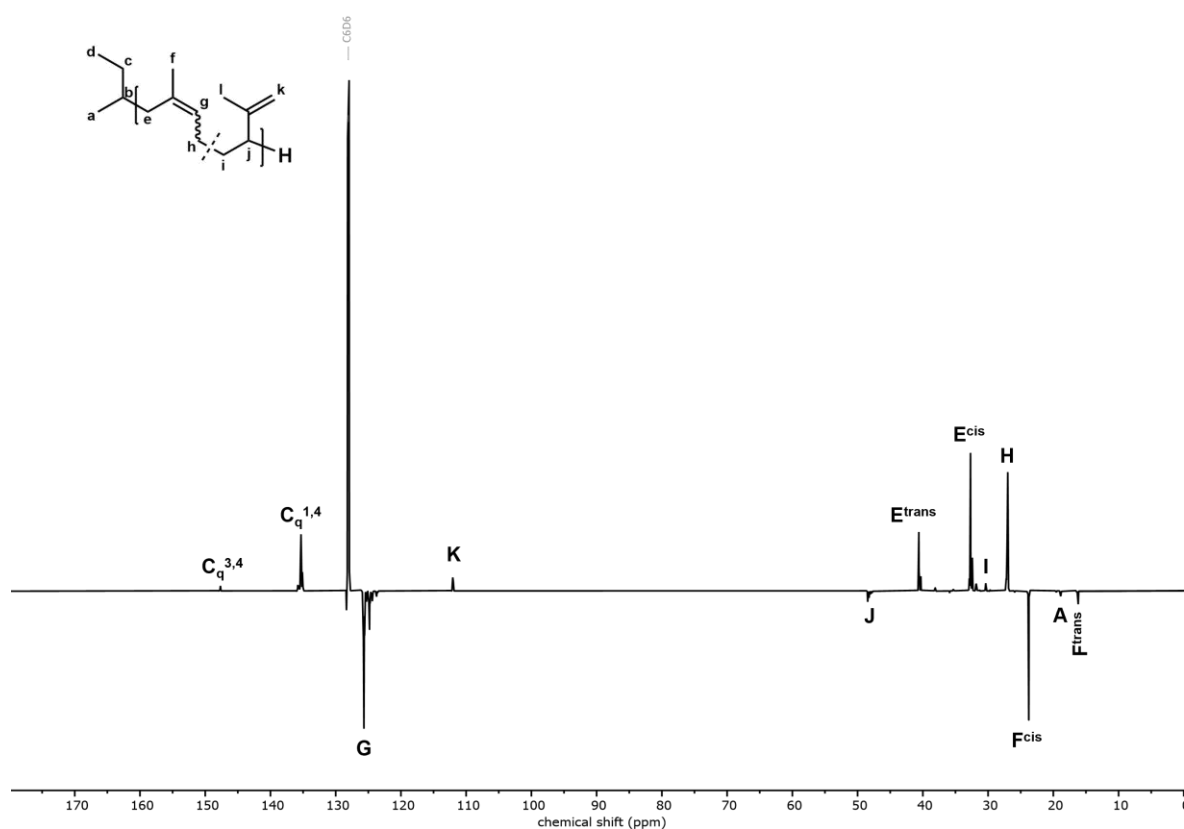
The fits yielded the corresponding diffusion times  $\tau_{Di}$  of the  $i$ th species, which are related to their respective diffusion coefficient  $D_i$  (equation S3).

$$\tau_{Di} = \frac{r_0^2}{4D_i} \quad (S3)$$

However, since the value of  $r_0$  depends strongly on the specific characteristics of the optical setup and the refractive index of the studied sample, a suitable calibration is required. The value of  $r_0$  was estimated from FCS measurements in water assuming similar dimensions of the confocal volume in both media. The overall concentration of the fluorescent polymers in all cases was in the order of  $5 \cdot 10^{-8}$  M.

*Dynamic light scattering* was performed at 25 °C at a scattering angle of 90° and a scattering intensity of 300 kHz using a NanoLab 3D instrument supplied by LS Instruments. 1.5 mL of the polymer solutions were transferred into acrylic glass cuvettes, passing the solutions through a PTFE syringe filter with a pore width of 0.45 mm. For the calculation of the hydrodynamic radii from the diffusion coefficients by the Stokes-Einstein equation, the solvent viscosity and the refractive index of heptane at 25 °C were set to  $\eta=0.39$  mPa·s and  $n_D^{25}=1.39$ , respectively. Each experiment, which was repeated 5 times, comprised a waiting period of 2 min at the prescribed temperature and scattering intensity and a subsequent light scattering measurement of 2 min. For this purpose, the Modulated 3D Cross-Correlation technology was used, which subtracts multiple light scattering events. This is achieved by the performance of two simultaneous light scattering experiments at the same scattering vector, which are temporally separated at frequencies exceeding the timescale of the investigated dynamics in order to avoid the detection of signal arising from second illumination beam. The autocorrelation functions were interpreted using the CORENN (constrain weighted, regularized non-linear, least-squares) algorithm allowing the interpretation of multimodal samples.

## NMR spectra of polyisoprene

Figure S1:  $^1\text{H}$ -NMR spectrum (850 MHz,  $\text{C}_6\text{D}_6$ ) of polyisoprene.Figure S2:  $^{13}\text{C}$ -JMOD-NMR spectrum (214 MHz,  $\text{C}_6\text{D}_6$ ) of polyisoprene.

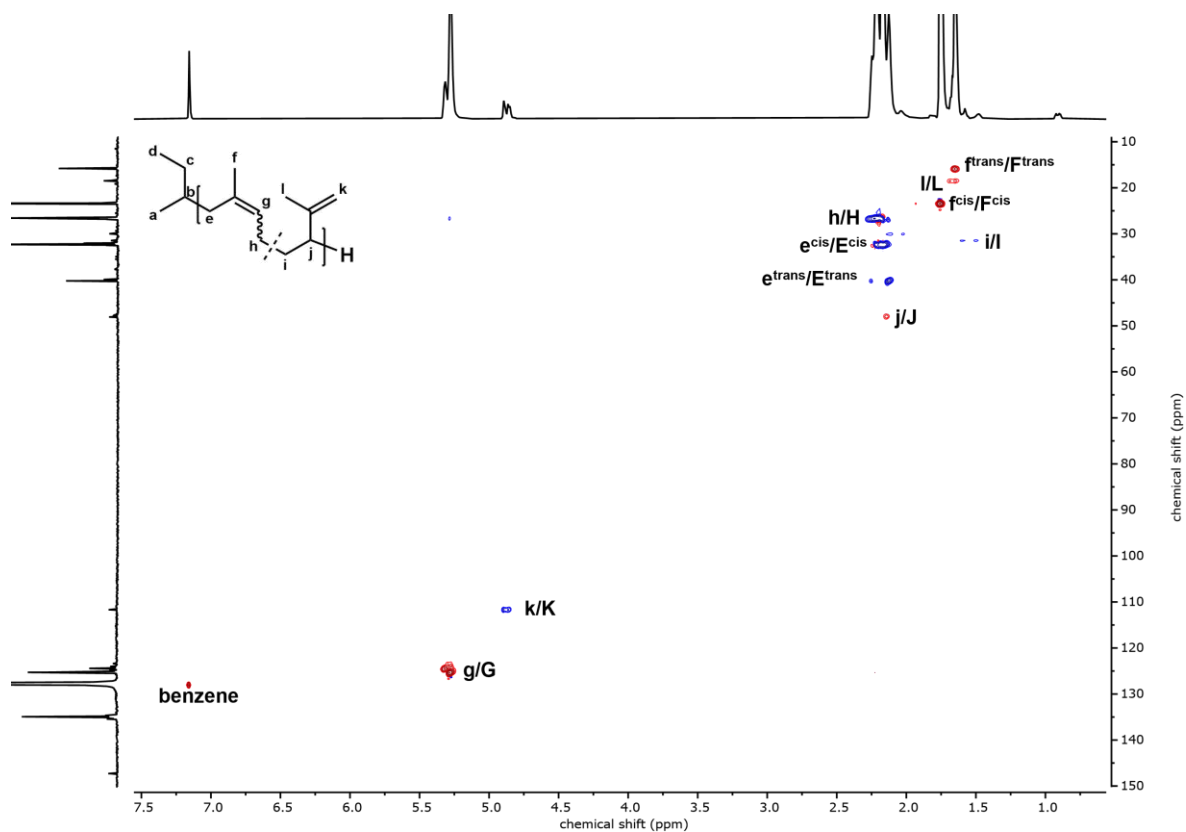


Figure S3:  $^1\text{H}^{13}\text{C}$ -HSQC-NMR spectrum (850/214 MHz,  $\text{C}_6\text{D}_6$ ) of polyisoprene.

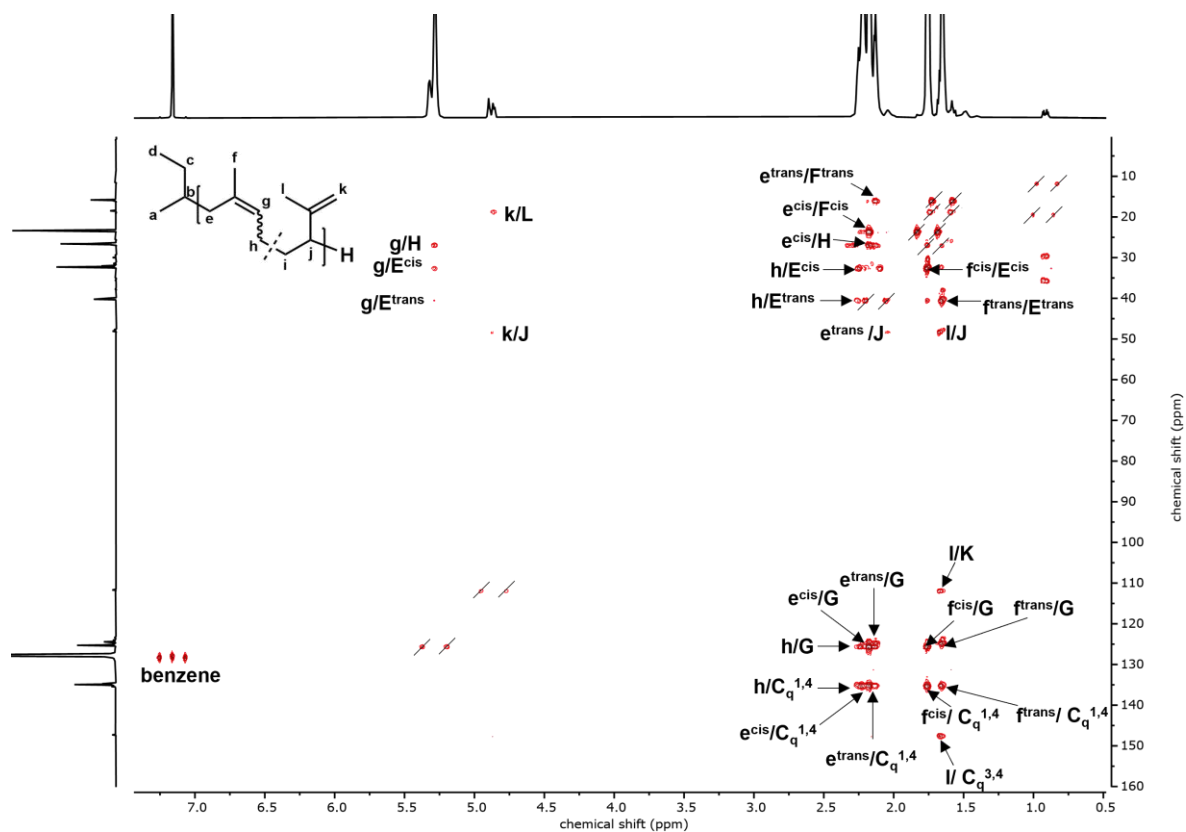


Figure S4:  $^1\text{H}^{13}\text{C}$ -HMBC-NMR spectrum (850/214 MHz,  $\text{C}_6\text{D}_6$ ) of polyisoprene.

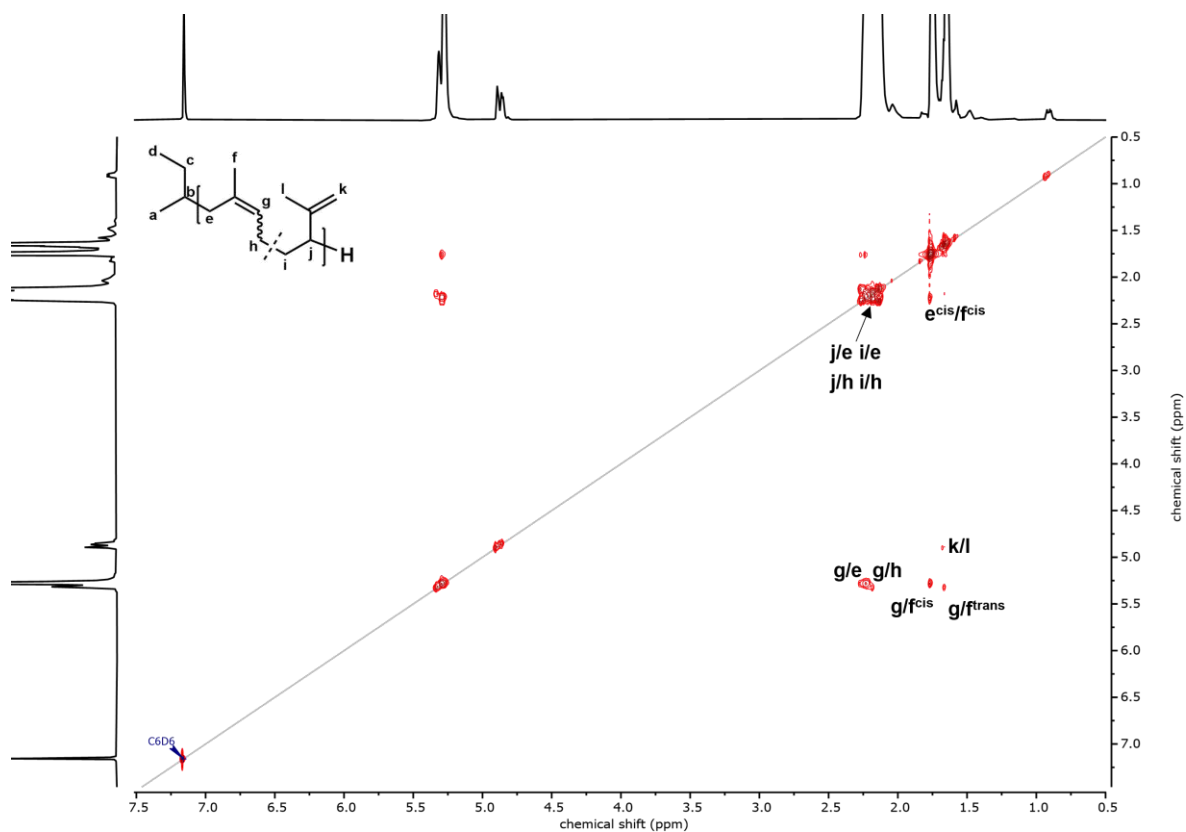


Figure S5:  $^1\text{H}$ - $^1\text{H}$ -COSY-NMR spectrum (850 MHz,  $\text{C}_6\text{D}_6$ ) of polyisoprene.

### NMR spectra of brominated polyisoprene

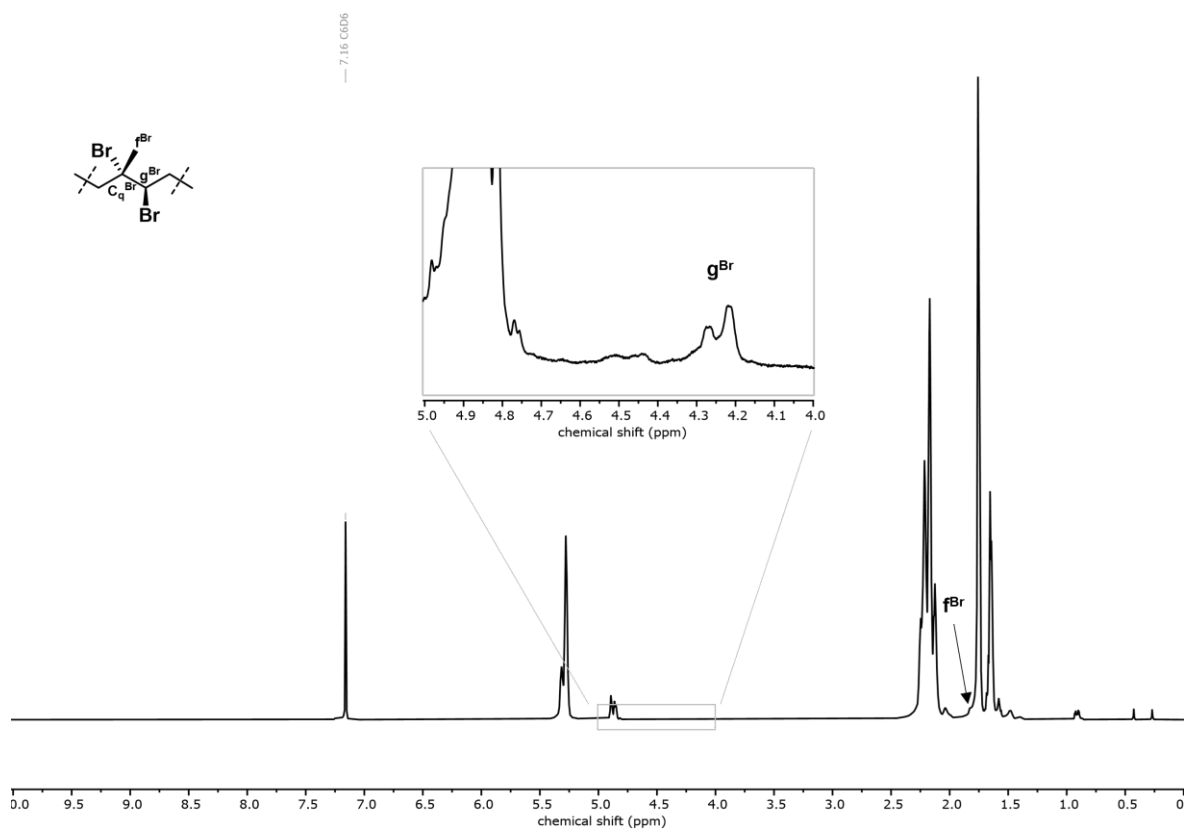


Figure S6:  $^1\text{H}$ -NMR spectrum (850 MHz,  $\text{C}_6\text{D}_6$ ) of brominated polyisoprene.

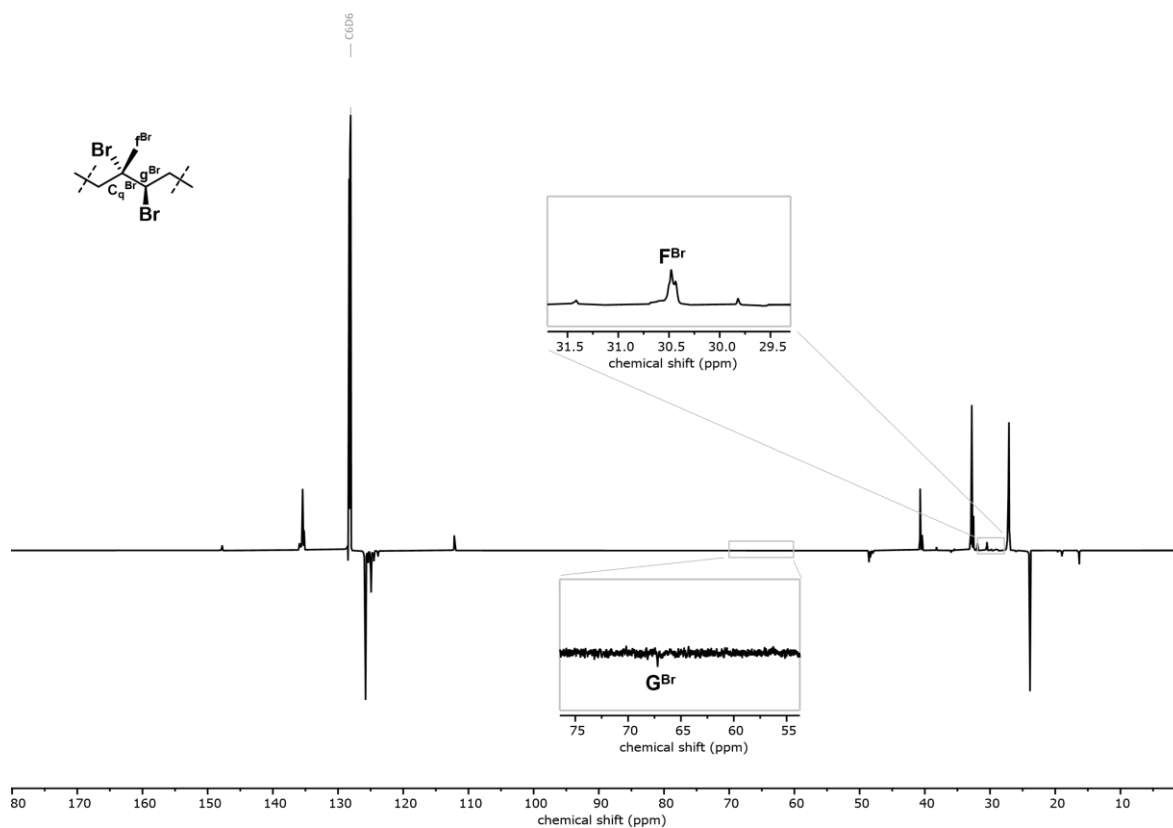


Figure S7:  $^{13}\text{C}$ -JMOD-NMR spectrum (214 MHz,  $\text{C}_6\text{D}_6$ ) of brominated polyisoprene.

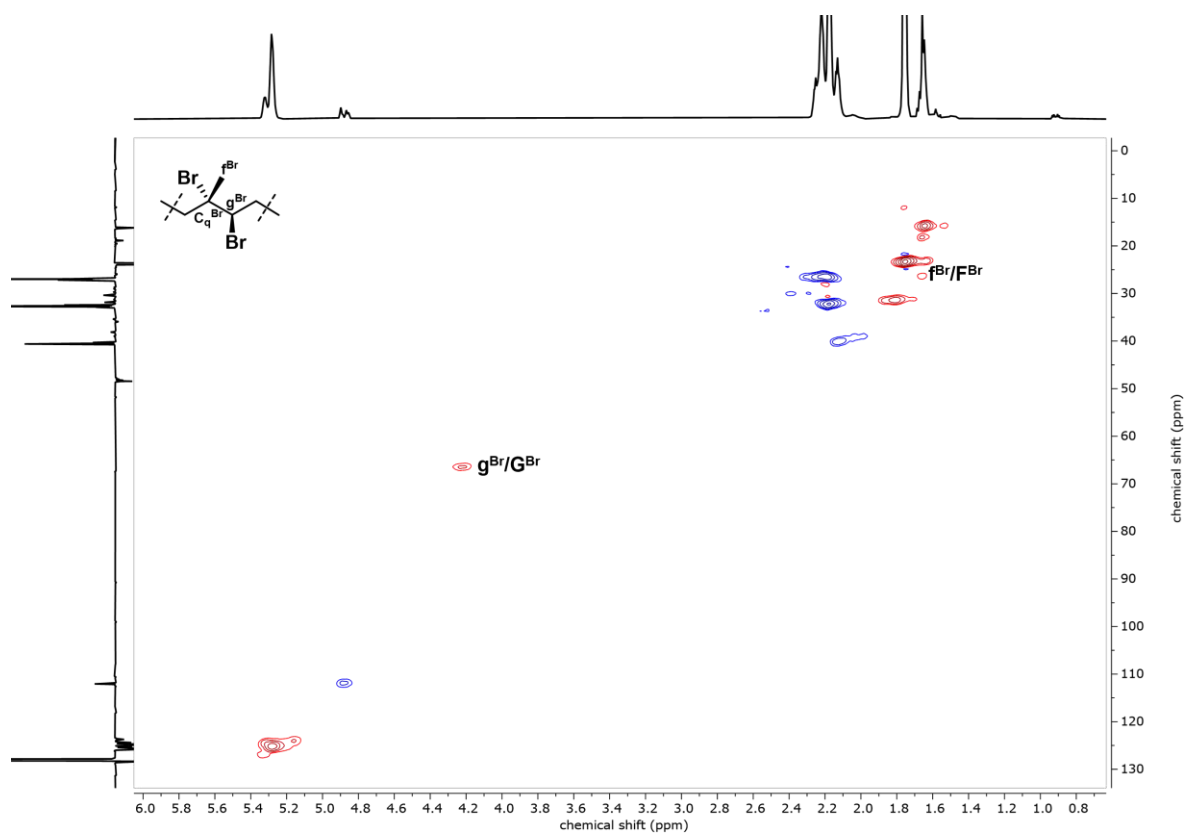


Figure S8:  $^1\text{H}$  $^{13}\text{C}$ -HSQC-NMR spectrum (300/75 MHz,  $\text{C}_6\text{D}_6$ ) of brominated polyisoprene.



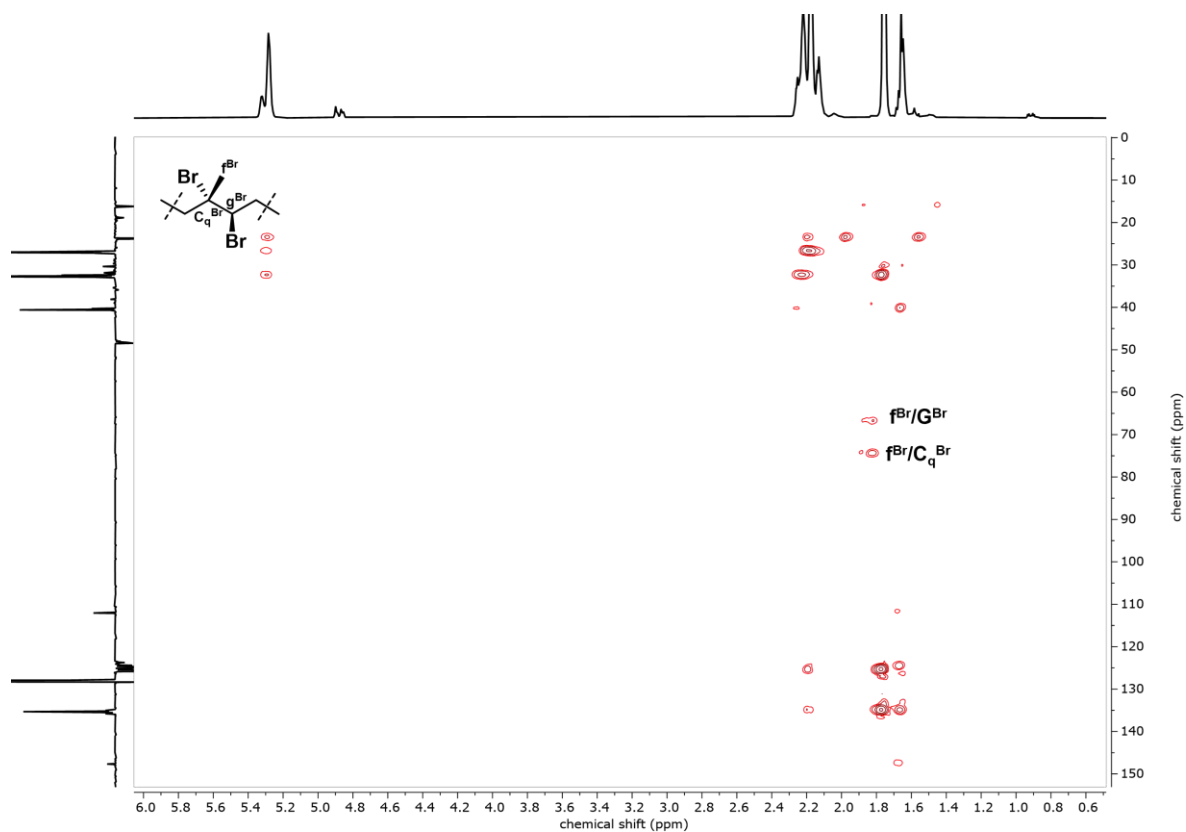


Figure S9:  $^1\text{H}^{13}\text{C}$ -HMBC-NMR spectrum (300/75 MHz,  $\text{C}_6\text{D}_6$ ) of brominated polyisoprene.

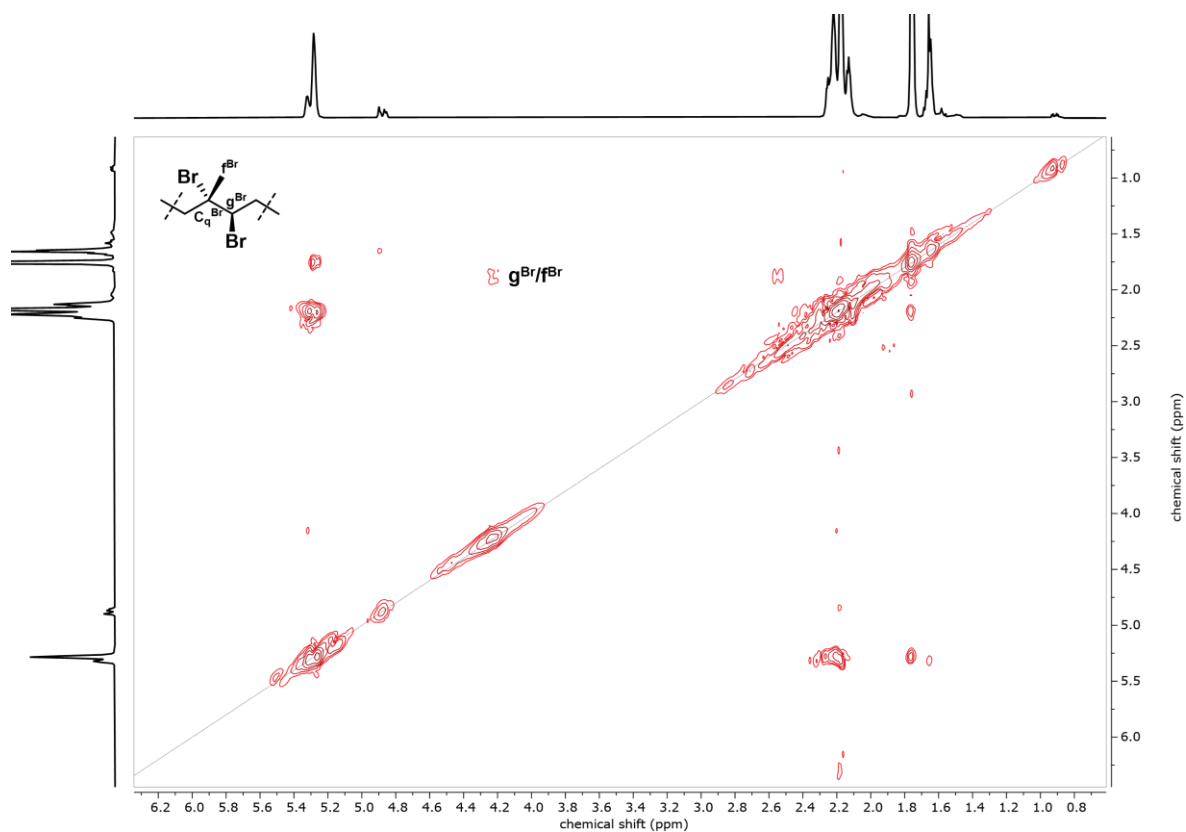
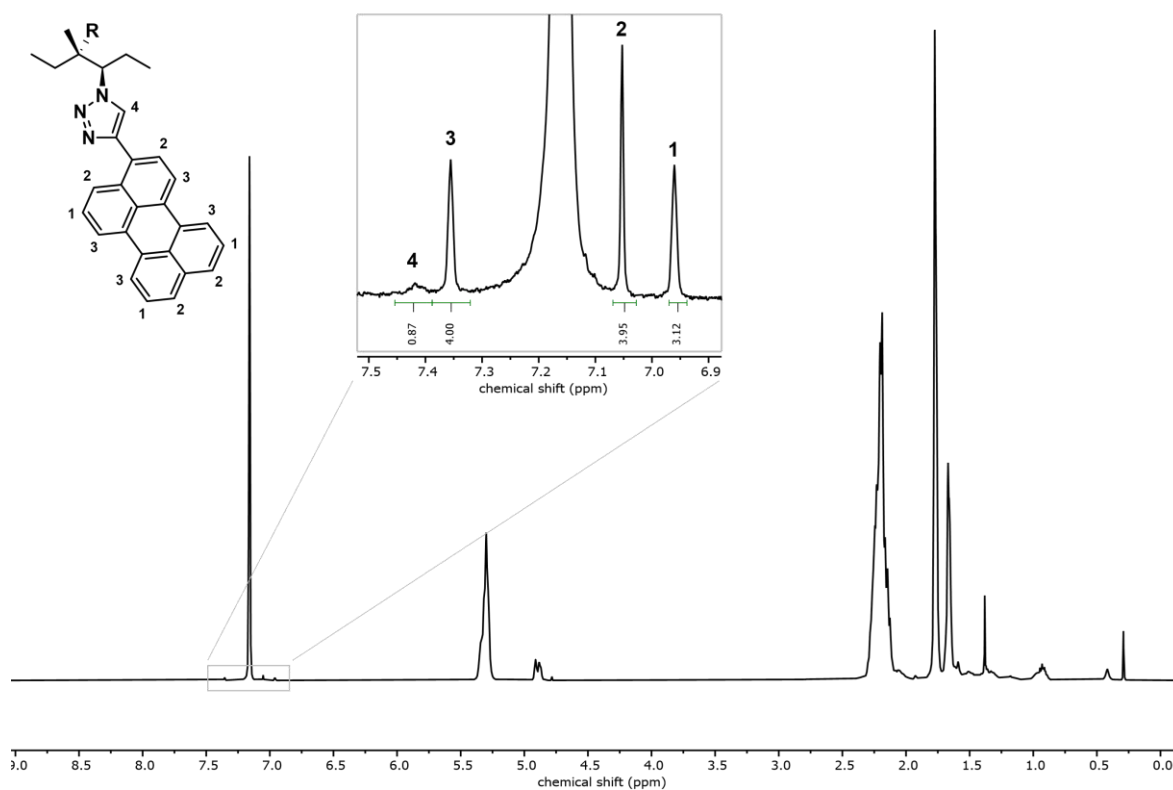
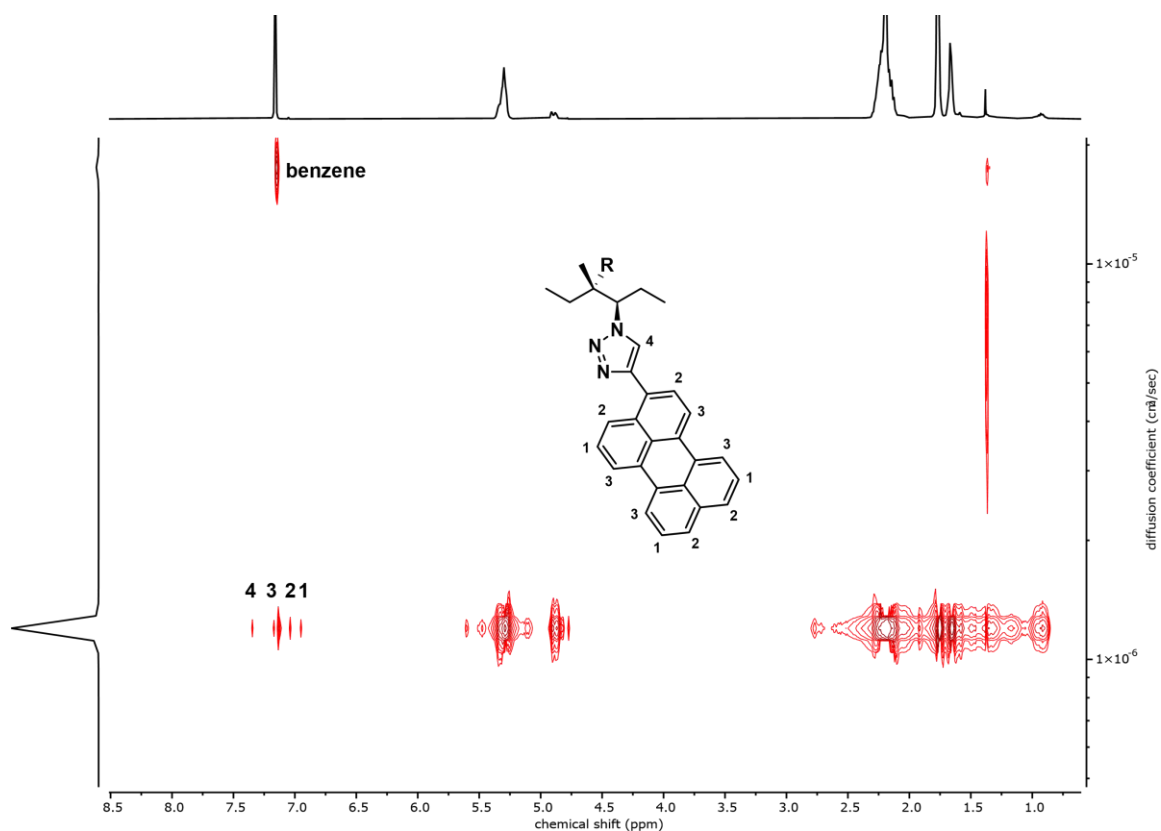


Figure S10:  $^1\text{H}^1\text{H}$ -COSY-NMR spectrum (300 MHz,  $\text{C}_6\text{D}_6$ ) of brominated polyisoprene.

**NMR spectra of perylene-labeled polyisoprene****Figure S11:**  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ ) of perylene-labeled polyisoprene.**Figure S12:**  $^1\text{H}$ -DOSY-NMR spectrum (400 MHz,  $\text{C}_6\text{D}_6$ ) of perylene-labeled polyisoprene.

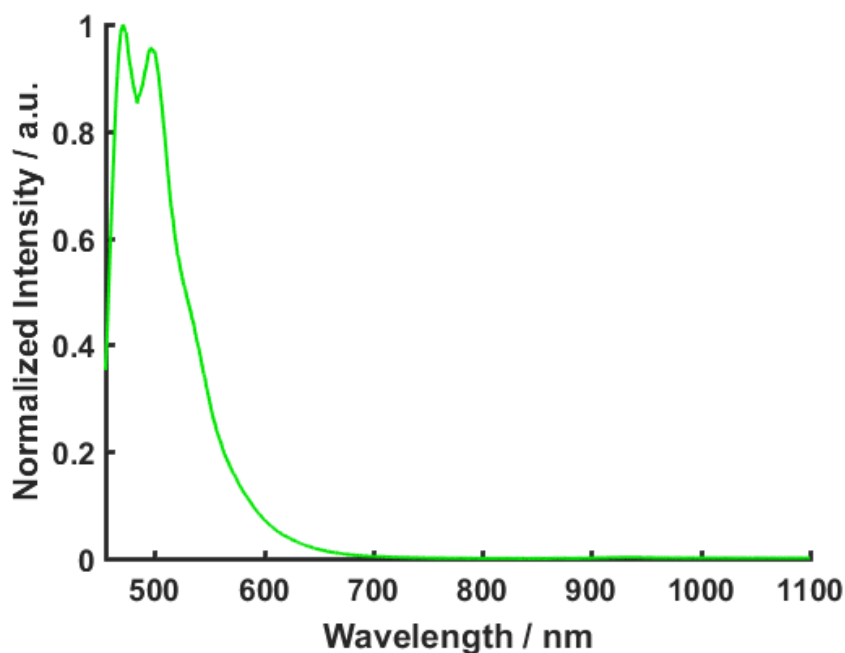


Figure S13: Fluorescence emission spectrum of the perylene-labeled polyisoprene in THF ( $c=0.67 \text{ mol}\cdot\text{L}^{-1}$ ). The maxima at 471 and 497 nm belong to the perylene moiety.

#### Autocorrelation functions obtained by FCS measurements

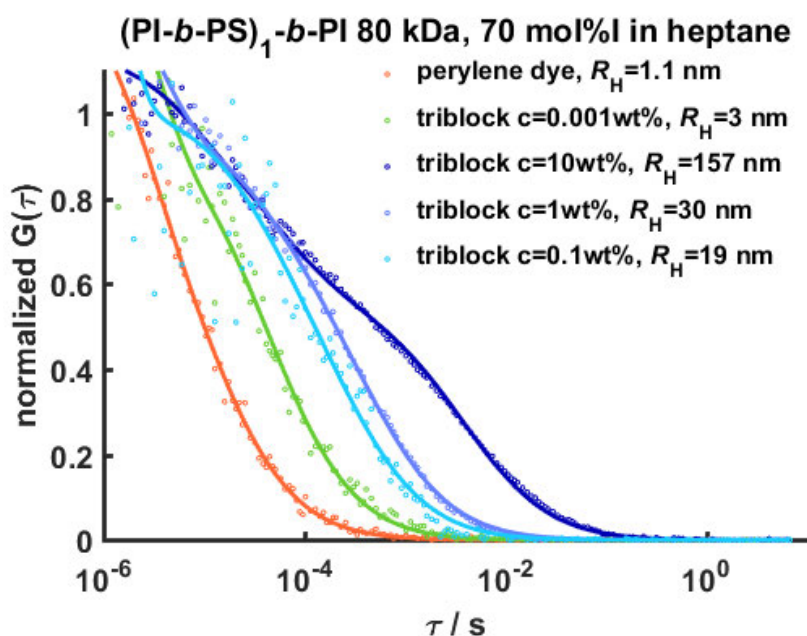


Figure S14: Autocorrelation functions  $G(\tau)$  of the perylene dye molecule (orange), the labeled sequential triblock copolymer at  $10^{-3} \text{ wt}\%$  (green) as well as of mixtures of labeled and unlabeled polymer at overall concentrations of 10 wt% (dark blue), 1 wt% (blue), and 0.1 wt% (light blue) in heptane. The two-component fit curves with a fixed values for the freely diffusing unimers (green) are plotted as solid lines.

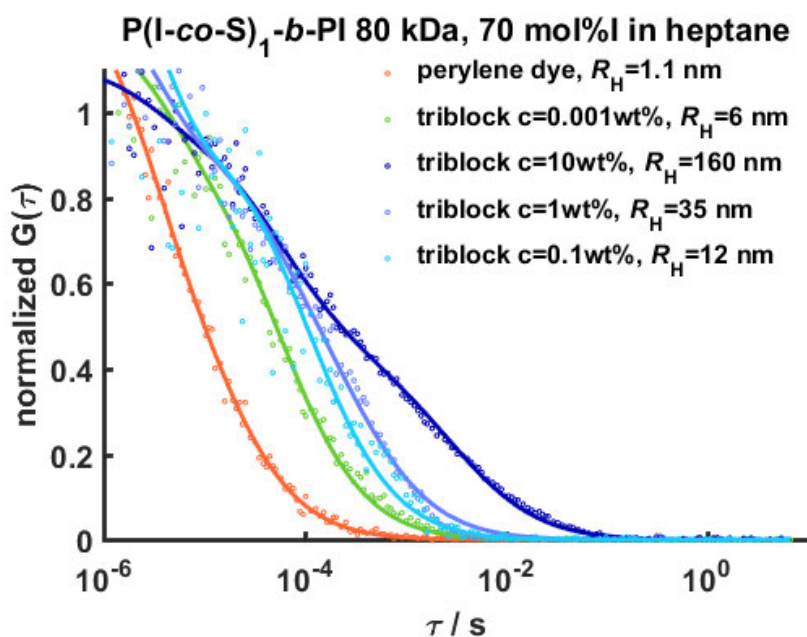


Figure S15: Autocorrelation functions  $G(\tau)$  of the perylene dye molecule (orange), the labeled tapered triblock copolymer at  $10^{-3}$  wt% (green) as well as of mixtures of labeled and unlabeled polymer at overall concentrations of 10 wt% (dark blue), 1 wt% (blue), and 0.1 wt% (light blue) in heptane. The two-component fit curves with a fixed values for the freely diffusing unimers (green) are plotted as solid lines.

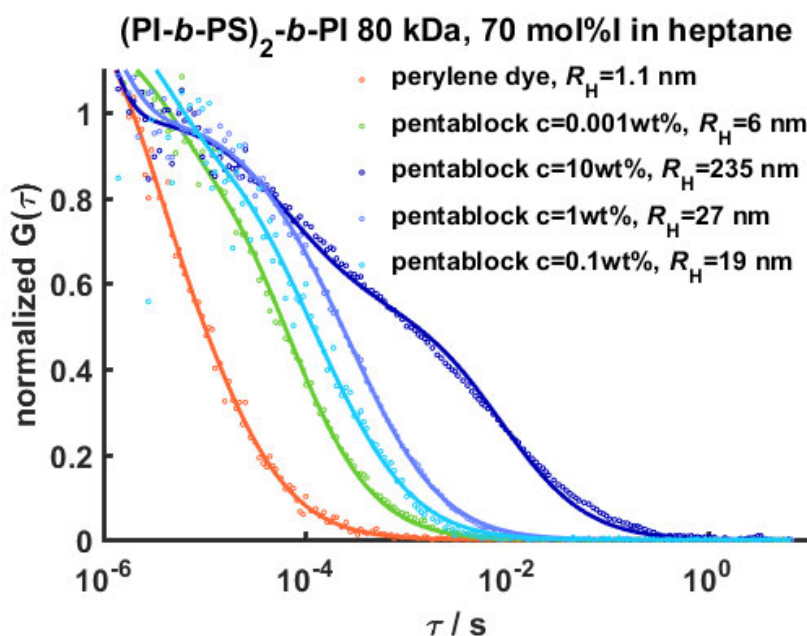


Figure S16: Autocorrelation functions  $G(\tau)$  of the perylene dye molecule (orange), the labeled sequential pentablock copolymer at  $10^{-3}$  wt% (green) as well as of mixtures of labeled and unlabeled polymer at overall concentrations of 10 wt% (dark blue), 1 wt% (blue), and 0.1 wt% (light blue) in heptane. The two-component fit curves with a fixed values for the freely diffusing unimers (green) are plotted as solid lines.

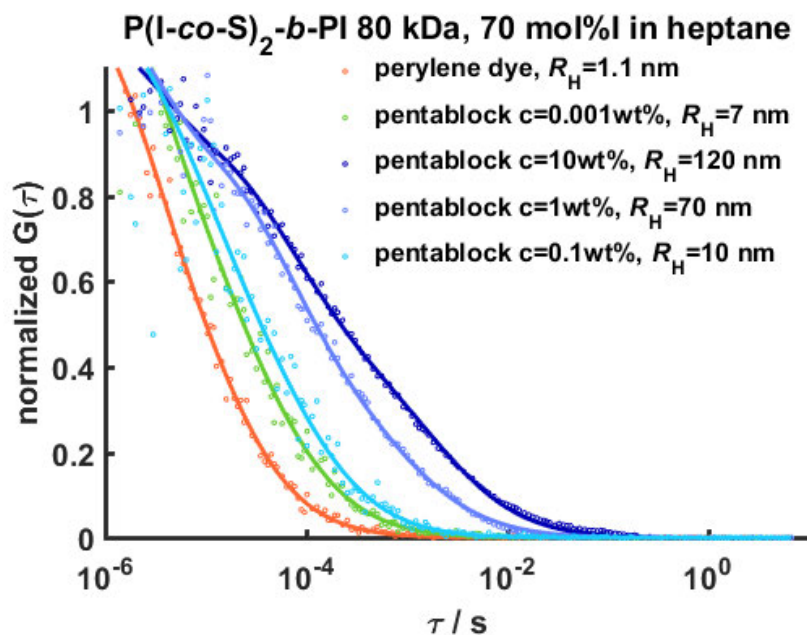


Figure S17: Autocorrelation functions  $G(\tau)$  of the perylene dye molecule (orange), the labeled tapered pentablock copolymer at  $10^{-3} \text{ wt}\%$  (green) as well as of mixtures of labeled and unlabeled polymer at overall concentrations of 10 wt% (dark blue), 1 wt% (blue), and 0.1 wt% (light blue) in heptane. The two-component fit curves with a fixed values for the freely diffusing unimers (green) are plotted as solid lines.

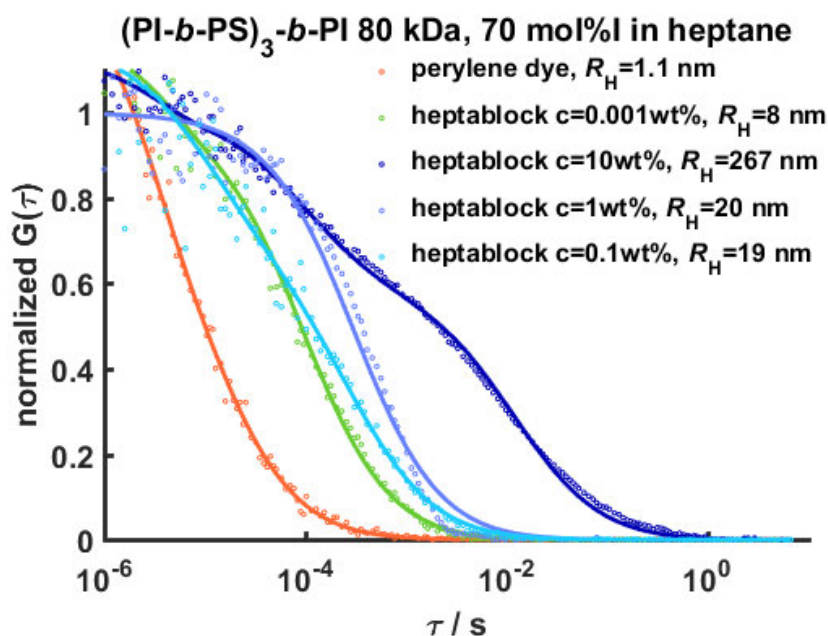


Figure S18: Autocorrelation functions  $G(\tau)$  of the perylene dye molecule (orange), the labeled sequential heptablock copolymer at  $10^{-3} \text{ wt}\%$  (green) as well as of mixtures of labeled and unlabeled polymer at overall concentrations of 10 wt% (dark blue), 1 wt% (blue), and 0.1 wt% (light blue) in heptane. The two-component fit curves with a fixed values for the freely diffusing unimers (green) are plotted as solid lines.

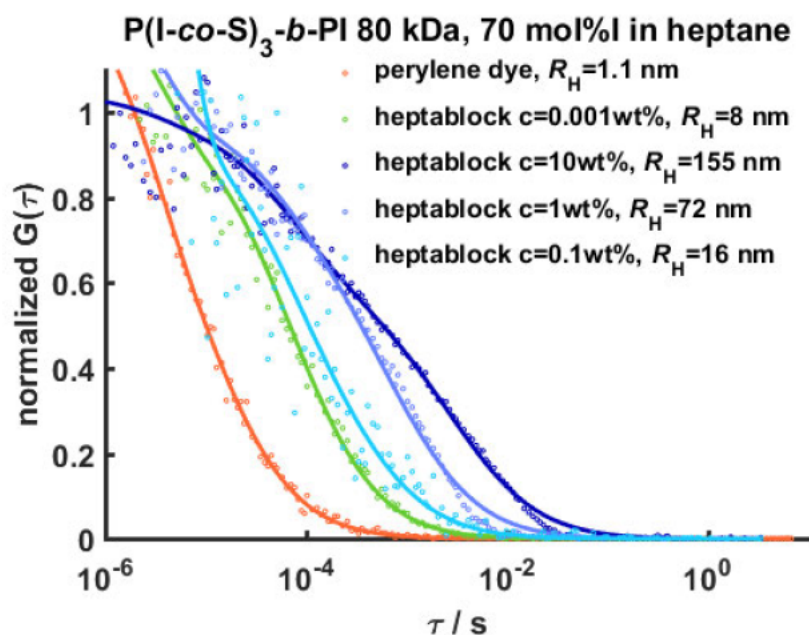


Figure S19: Autocorrelation functions  $G(\tau)$  of the perylene dye molecule (orange), the labeled tapered heptablock copolymer at  $10^{-3}$  wt% (green) as well as of mixtures of labeled and unlabeled polymer at overall concentrations of 10 wt% (dark blue), 1 wt% (blue), and 0.1 wt% (light blue) in heptane. The two-component fit curves with a fixed values for the freely diffusing unimers (green) are plotted as solid lines.

#### Autocorrelation functions obtained by DLS measurements

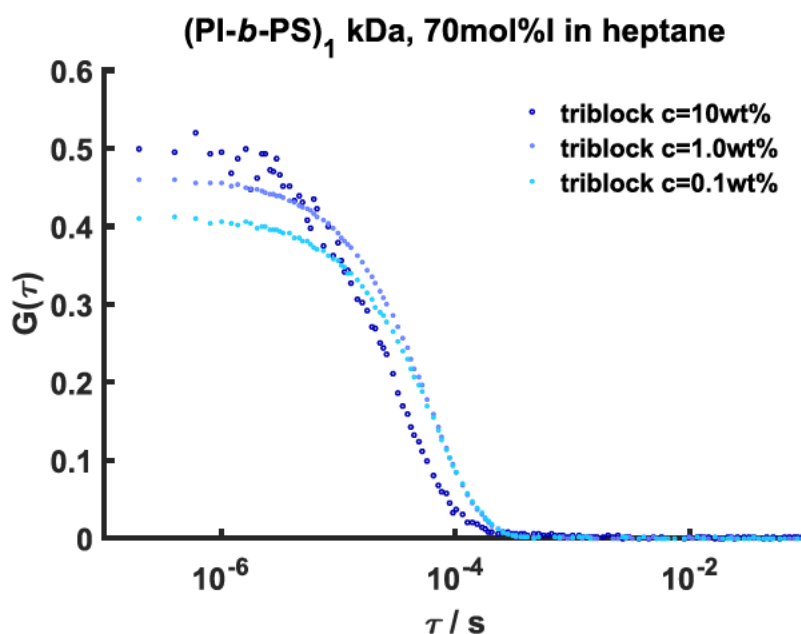


Figure S20: Autocorrelation functions  $G(\tau)$  of the sequential triblock copolymer at 10 wt% (dark blue), 1 wt% (blue), and 0.1 wt% (light blue) in heptane. The data were fitted using the CORENN algorithm.

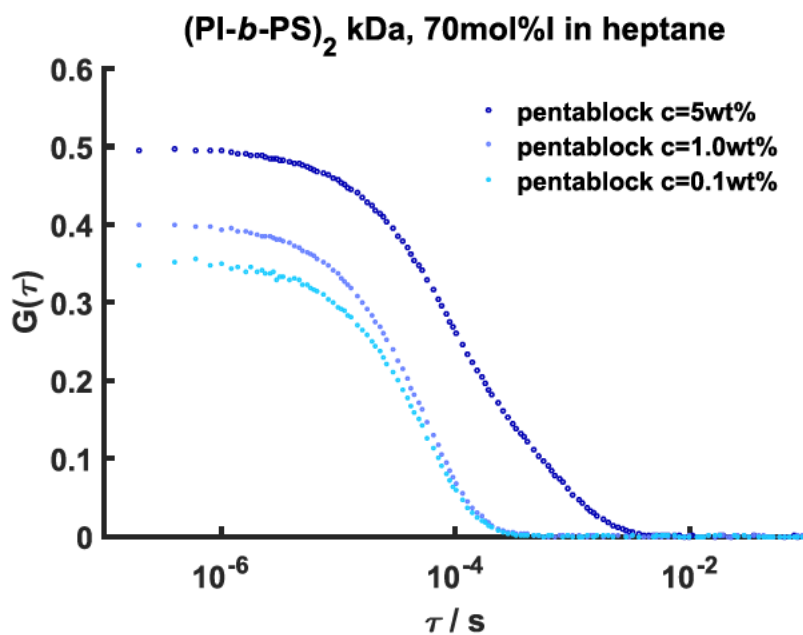


Figure S21: Autocorrelation functions  $G(\tau)$  of the sequential pentablock copolymer at 5 wt% (dark blue), 1 wt% (blue), and 0.1 wt% (light blue) in heptane. The data were fitted using the CORENN algorithm.

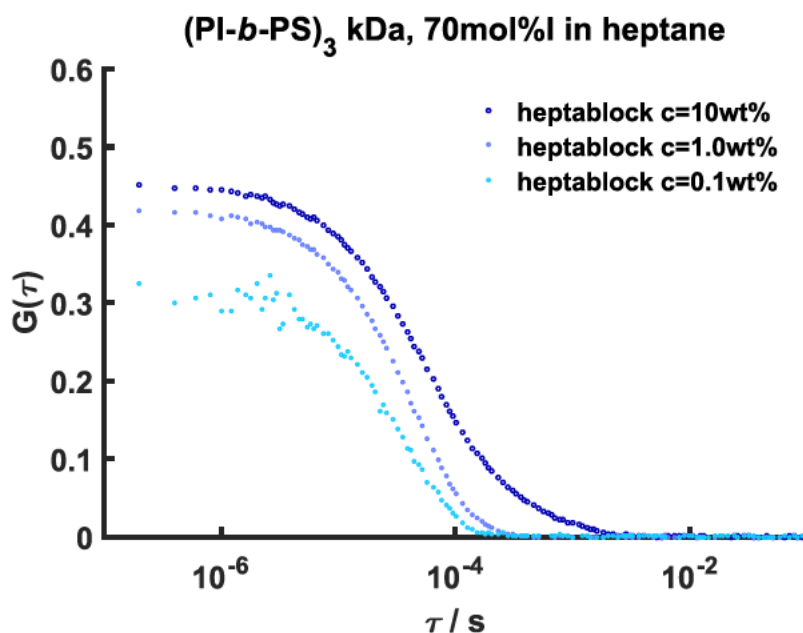


Figure S22: Autocorrelation functions  $G(\tau)$  of the sequential heptablock copolymer at 10 wt% (dark blue), 1 wt% (blue), and 0.1 wt% (light blue) in heptane. The data were fitted using the CORENN algorithm.





---

---

# CHAPTER 7

*Viscosity of Concentrated Polymer Solutions:*  
**Shear-Induced Disassembly of Transient  
Associative Polymer Networks**

---

---



## CHAPTER 7

Results achieved in Collaboration with [REDACTED] subjected to a Non-Disclosure Agreement

# Viscosity of Concentrated Polymer Solutions: Shear-Induced Disassembly of Transient Associative Polymer Networks

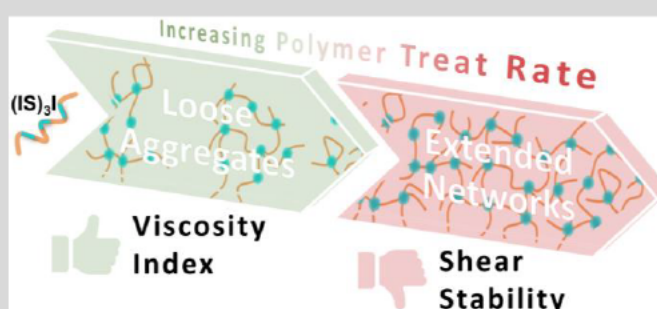
Ramona D. Barent<sup>1,2</sup>, [REDACTED] and Holger Frey<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany

<sup>2</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany

[REDACTED]

The performance of viscosity modifiers, which are additives attenuating the temperature dependence of the viscosity of a lubricant, is governed by both the chemistry and the architecture of the employed polymers. Key metrics to categorize the functionality are the viscosity index, thickening efficiency, and shear stability.



Based on the current state of the art, pros and cons of different polymer classes have to be weighed carefully with respect to the targeted application field. While in general, poly(alkyl methacrylates) (PMAs) exhibit superior viscosity indices, they lack an excellent thickening efficiency or shear stability. In contrast, hydrogenated styrene-diene copolymers (HSDs) commonly stand out due to their exceptional thickening efficiency at reasonable shear stabilities but cannot compete with PMAs in terms of the viscosity-temperature relationship. Within this work, we investigate in the first place the temperature-viscosity relationship of (non)-hydrogenated styrene-isoprene copolymers with multiple solvophobic polystyrene blocks and a tapered interface per diblock sequence. By the combination of [REDACTED] and dynamic viscosity measurements, [REDACTED] as well as the dynamic viscosity indices were calculated. [REDACTED]

[REDACTED]



viscosity index at lower treat rates and acceptable shear stabilities.<sup>[6]</sup> The shear stability, i.e., the permanent loss in viscosity upon shearing, depends on the dispersity as well as the architecture of a polymer and is discussed below.<sup>[1]</sup> Although PMA structures exhibit a superior viscosity-temperature relationship, a comb-like architecture results in a smaller hydrodynamic volume at constant molar mass compared to a linear structure, which directly translates into a lower thickening efficiency. Together with the presumably higher dispersity resulting from the free radical polymerization and, if implemented, a subsequent grafting approach affecting the shear stability of the viscosity modifier, there is still room for improvement.

These drawbacks can be tackled by implementing hydrocarbon-based polymers, which capitalize on high thickening efficiencies. Especially hydrogenated styrene-diene copolymers (HSDs) polymerized under living anionic conditions afford excellent shear stabilities and an effective thickening due to their defined structure. Nevertheless, in terms of a beneficial viscosity-temperature relationship required for most applications, so far HSDs cannot compete with PMAs.

In a first instance, the viscosity of a polymer solution is enhanced with molar masses and concentration.<sup>[2]</sup> Therefore, the intrinsic viscosity is a first indication of the capability of a polymer to increase the viscosity of a certain solvent. Typically, polymers with molar masses ranging from 1–100 kg·mol<sup>-1</sup> are implemented to avoid chain degradation processes (*vide infra*).<sup>[7]</sup> Beyond that, the underlying thickening mechanism affects the viscosity-temperature relationship. For this purpose, the influence of a viscosity modifier at varying temperature is quantified by the viscosity index (*vide infra*, equation 2). On top of the chemistry and hence the thickening mechanism, the viscosity index weakly correlates with the architecture of a polymer. Generally, the larger the radius of gyration of a polymer coil, the more efficient is the increase in viscosity.<sup>[5]</sup>

The shear stability of a viscosity modifier describes its durability when subjected to high shear stresses, which is the case for many applications. Here, it is distinguished between a reversible and a permanent decrease in viscosity upon shear.<sup>[2,5]</sup> Upon shearing, a polymer coil aligns within the flow and hence is elongated. In case of associated polymers (*vide infra*), partial disassembly can take place. In these cases, the viscosity increases to the initial value when the stress is released, as the polymer coils return to their undistorted shape and reassemble. This effect is described by the term reversible or temporary viscosity loss. The decrease in viscosity upon shearing typically begins at strain levels above 10<sup>4</sup> s<sup>-1</sup>.<sup>[1,8]</sup> At even higher stress levels above 10<sup>6</sup> s<sup>-1</sup>, turbulent flows and cavitation can cause chain degradation.<sup>[8]</sup> The concomitant decrease in molar mass causes a permanent viscosity loss, which is self-limiting when the chains are degraded to sufficiently low molar masses, allowing facile alignment within the flow.<sup>[9]</sup> For the same reason, a low dispersity of the polymers is beneficial. The broader a molar mass distribution, the higher is the fraction of long chains prone to degradation and short chains contributing little to the viscosity increase.<sup>[10]</sup> Furthermore, the architecture is important for both the temporary and permanent shear stability. For instance, long chain branched structures are less prone to a reversible viscosity loss, and star-shaped polymers align faster within the flow due to their more compact structure, leading to a higher permanent shear stability.<sup>[11]</sup>

The two main thickening mechanisms discussed in literature comprise the polymer coil expansion mechanism and the association mechanism, applying to PMAs and HSDs,

respectively.<sup>[12]</sup> Polymer coil expansion with temperature relies on a rather low solubility at low temperatures, which continuously increases with the temperature. On a molecular level, the increasing radius of gyration traces back to the altered interaction between the polymers' repeating units and the solvent molecules. Therefore, especially polar polymers like PMAs feature this thickening mechanism.<sup>[13]</sup> In contrast, the dimensions of HSDs remain unaltered over a temperature range from 40-150 °C as well as at normal pressure and 300 MPa.<sup>[14]</sup> The superior thickening efficiency of HSDs relies on the association thickening mechanism. With the solvophobic blocks of the block copolymers promoting aggregation, the apparent molar mass is increased, thus increasing the viscosity to a larger extent.<sup>[15]</sup> Going from polystyrene-*block*-polydiene diblock<sup>[16,17]</sup> to polystyrene-*block*-polydiene-*block*-polystyrene triblock copolymers<sup>[18]</sup> in polydiene-selective solvents, the formation of networks at high polymer concentration can occur.<sup>[19,20]</sup> However, the influence of higher block numbers on the performance as viscosity modifier has not been studied in depth to date.

Consequently, this work aims at the characterization of polystyrene-polyisoprene multiblock copolymers in aliphatic oils by viscosity measurements at systematically varied concentrations, shear rates, and temperatures. For this purpose, linear tapered multiblock structures  $P(I-co-S)_n-b-PI$  with two polyisoprene end blocks were prepared. The two flexible, solvophilic end blocks were designed to ensure good solubility. The polymer characteristics are varied in terms of the overall molar mass, block number and isoprene content. Introducing multiple blocks promises a better viscosity index improvement due to the formation of larger aggregates with a higher apparent molar mass. Yet, the decrease of the glass transition temperature of the solvophobic blocks, which reflects the incorporation of solvent molecules, with decreasing PS block length as well as the reduced overall van-der-Waals interaction tethering the PS blocks within one micellar core promote the tendency to disassemble under shear. Consequently, the shear-induced temporal viscosity loss might be a function of the overall polymer composition. In contrast to sequential block copolymers with a sharp transition between the comonomers, tapered block-like structures feature a more diffuse interface between the non-solvated core and the dissolved corona, which is swollen by solvent molecules.<sup>[21]</sup> The presence of both soluble and insoluble repeating units within the gradual regime between the two blocks can cause loop formation due to the attractive interaction between the solvophobic units.<sup>[22]</sup> This loop formation within the core-corona interface could allow to introduce thermoresponsive properties by the so-called "reel-in effect", describing the reverse stretching of the diffuse interface by increasing the temperature. This is reasoned in changes of the solubility of the solvophobic blocks, resulting in a dissolution of the gradual chain segments near the interface upon temperature increase.<sup>[23]</sup> This way, the contribution to the viscosity increase would rise with temperature, given that no disassembly and hence reduction of the apparent molar mass occurs.

## Experimental Section

### General Polymerization Procedure

The solvent cyclohexane (Fisher Science,  $\geq 99.8\%$ ) was dried over sodium with benzophenone as an indicator. Methanol (MeOH, Fisher Science,  $\geq 99.9\%$ ) was used as purchased. The stabilizer of isoprene (I, Acros Organics, 98%) and styrene (S, Acros Organics, 99%) was removed by filtering the monomers through a column containing basic aluminum oxide and purified hereafter by degassing and distillation over calcium hydride (Acros Organics, 93%) and trioctylaluminium (Sigma Aldrich, 25 wt% in hexanes). *Sec*-Butyllithium (*sec*-BuLi, Acros Organics, 1.3 M in cyclohexane/hexane (92/8)) was used as supplied.

All purification and reaction steps were conducted under Schlenk condition, meaning that all glassware was flame-dried three times prior to use and all manipulations were carried out either under high-vacuum ( $1 \cdot 10^{-3}$  mbar) or an argon atmosphere. Firstly, the monomers were dried under reduced pressure and room temperature over ground calcium hydride over night after degassing by three freeze-thaw-cycles. On the next day, the monomers were distilled into a flask containing trioctylaluminium obtained by evaporation of the solvent under reduced pressure. Again, purification was performed over night at room temperature and reduced pressure. Then, the monomers were distilled into a graduated ampoule, which was flooded with argon after thawing. Cyclohexane was freshly distilled under normal pressure and drained into an evacuated glass reactor with a Nd stirring bar. The reaction flask was flushed with argon after cooling cyclohexane to room temperature. The ampoules were mounted to the reaction flask with transition pieces connected to the Schlenk line.

The initiator *sec*-BuLi was added to the solvent in an argon counterflow. Subsequently, the whole glass apparatus was sealed, and the solvent was heated to 40 °C. Then, the first monomer feed of a mixture of isoprene and styrene was added under vigorous stirring. The reaction time for each tapered diblock was calculated using a kinetic Monte-Carlo simulation. Typical reaction times per block or tapered diblock sequence ranged between 30 min and 3 hours, depending on the concentration and temperature. Details can be found in the Supp. Inf. of previous publications.<sup>[24]</sup> To guarantee full monomer conversion, the calculated reaction times were extended by 10%. After all monomer feeds and their consumption, the living chain ends were terminated by addition of methanol in an argon counterflow. The polymers were precipitated pouring the reaction solution into a 5-10-fold excess of methanol, dried at reduced pressure for at least one week and stored in the absence of light at -20 °C under argon atmosphere.

### Polymer Characterization

Eight tapered copolymers  $P(I-co-S)_n-b-PI$  with a range of overall molar masses (40 and 80 kg·mol<sup>-1</sup>), block number ( $\# = 2n + 1 = 3, 5$  and 7) and isoprene content (70 and 80 mol% isoprene) were prepared, as described above. The characteristics obtained by SEC and NMR measurements are given in Table 1.

*Size exclusion chromatography* was carried out in THF on an instrument consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump, a set of three PSS-SDV 5 mL columns ( $10^2$ ,  $10^3$ ,  $10^4$  Å) and RI (35 °C) as well as UV detectors (254 nm). A polystyrene standard provided by Polymer Standard Service were used for SEC calibration for the polyisoprene-polystyrene copolymers.

$^1\text{H}$  NMR spectra at 400 MHz were recorded at 23 °C on a Bruker Avance II (5 mm BBFO-head with z-gradient). The spectra were referenced internally to residual proton signals of the deuterated solvent.

**Table 1:** Characteristics of the statistically copolymerized multiblock copolymers  $\text{P(I-co-S)}_n\text{-b-PI}$  with a tapered interface. The corresponding SEC traces are given in the Supp. Inf. (see Figure S1).

| block number<br>#=2n+1 | target $M_n$<br>[kg·mol <sup>-1</sup> ] | target<br>$P_n(\text{I})$ [%] | $M(\text{PI})/\#$<br>[kg·mol <sup>-1</sup> ] | $M(\text{PS})/\#$<br>[kg·mol <sup>-1</sup> ] | $M_n^a$<br>[kg·mol <sup>-1</sup> ] | $\bar{D}^a$ | $P_n(\text{I})^b$<br>[%] | $\omega_{1,4}(\text{I})^b$<br>[%] |
|------------------------|-----------------------------------------|-------------------------------|----------------------------------------------|----------------------------------------------|------------------------------------|-------------|--------------------------|-----------------------------------|
| 3                      | 40                                      | 70                            | 12                                           | 16                                           | 52.6                               | 1.14        | 70.3                     | 94                                |
| 5                      | 40                                      | 70                            | 8                                            | 8                                            | 45.9                               | 1.15        | 69.9                     | 94                                |
| 3                      | 80                                      | 70                            | 25                                           | 29                                           | 91.0                               | 1.08        | 72.4                     | 94                                |
| 5                      | 80                                      | 70                            | 17                                           | 15                                           | 96.3                               | 1.05        | 72.8                     | 94                                |
| 7                      | 80                                      | 70                            | 13                                           | 10                                           | 94.3                               | 1.06        | 72.7                     | 94                                |
| 3                      | 80                                      | 80                            | 29                                           | 22                                           | 100.1                              | 1.04        | 80.6                     | 94                                |
| 5                      | 80                                      | 80                            | 19                                           | 11                                           | 102.6                              | 1.06        | 81.5                     | 94                                |
| 7                      | 80                                      | 80                            | 14                                           | 7                                            | 104.0                              | 1.06        | 80.7                     | 94                                |

<sup>a</sup> Determined by SEC (THF, PS calibration standard, RI detector). The number average molar masses are overestimated because of the incorporation of 70 or 80 mol% isoprene. <sup>b</sup> determined by  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) integrating on the 1,4-polyisoprene ( $\delta=4.8\text{--}5.4$  ppm), 3,4-polyisoprene ( $\delta=4.5\text{--}4.8$  ppm), and polystyrene signals ( $\delta=6.2\text{--}7.4$  ppm).

## Selective Hydrogenation

A part of the synthesized polymers was selectively hydrogenated to enhance chemical stability. Hydrogenation was carried out

. The hydrogenated samples were used for the determination of whereas the non-hydrogenated polymers were subjected to the dynamic viscosity measurements in squalane.

## Kinematic Viscosity Measurements

The hydrogenated polymers were dissolved or suspended in



[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

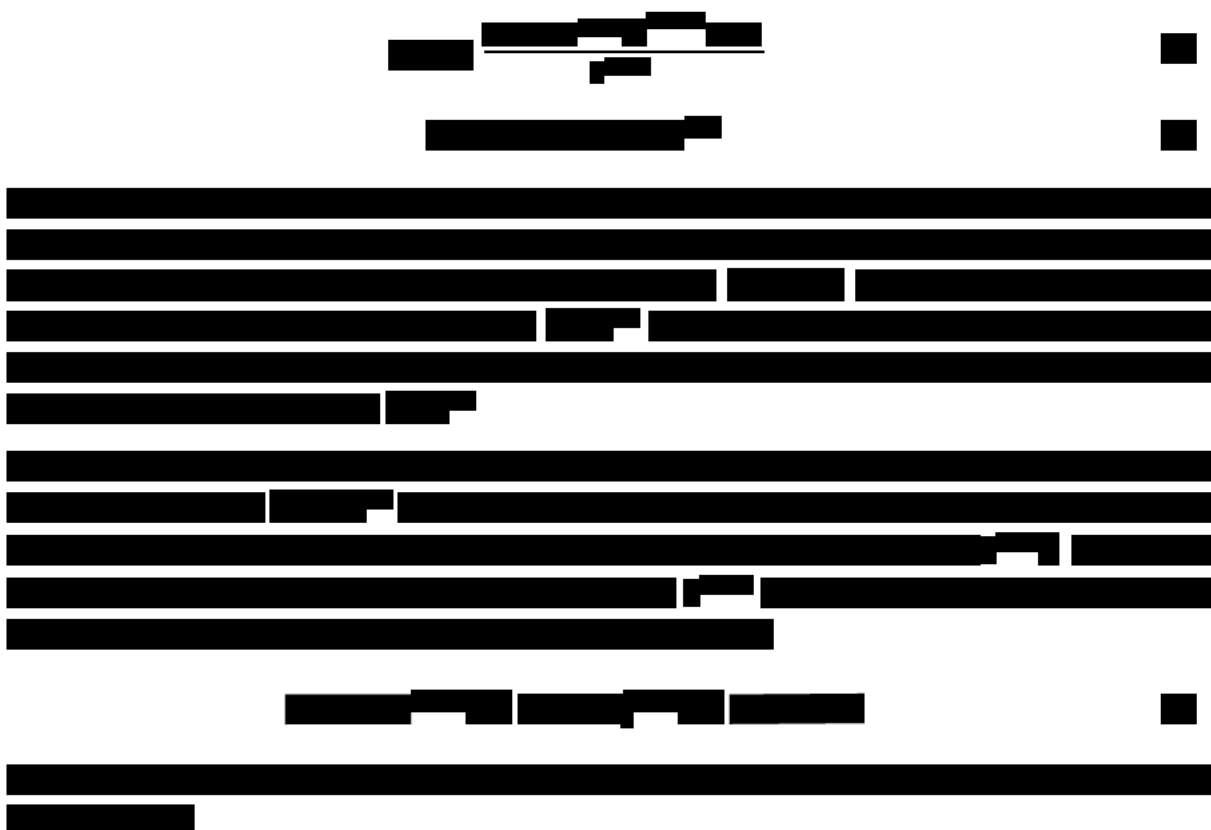
[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]



### Dynamic Viscosity Measurements

The non-hydrogenated polymers were dissolved in squalane (Figure 2, 2,6,10,15,19,23-hexamethyl-tetracosane,  $C_{30}H_{62}$ ) as a model aliphatic isoparaffinic mineral oil. The model oil is characterized by a density of  $\rho_{sq}^{40}=0.796 \text{ g}\cdot\text{mL}^{-1}$  and  $\rho_{sq}^{100}=0.757 \text{ g}\cdot\text{mL}^{-1}$  at 40 °C and 100 °C, respectively.<sup>[35]</sup> The kinematic viscosities range at  $\nu_{sq}^{40}=19.05 \text{ cSt}$  and  $\nu_{sq}^{100}=4.13 \text{ cSt}$  at 40 °C and 100 °C, and the dynamic viscosities are  $\eta_{sq}^{40}=15.16 \text{ mPa}\cdot\text{s}$  and  $\eta_{sq}^{100}=3.13 \text{ mPa}\cdot\text{s}$  at 20 °C and 100 °C, respectively.<sup>[36]</sup>

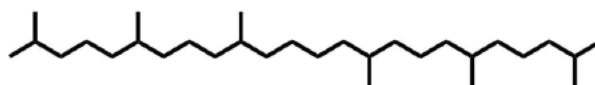


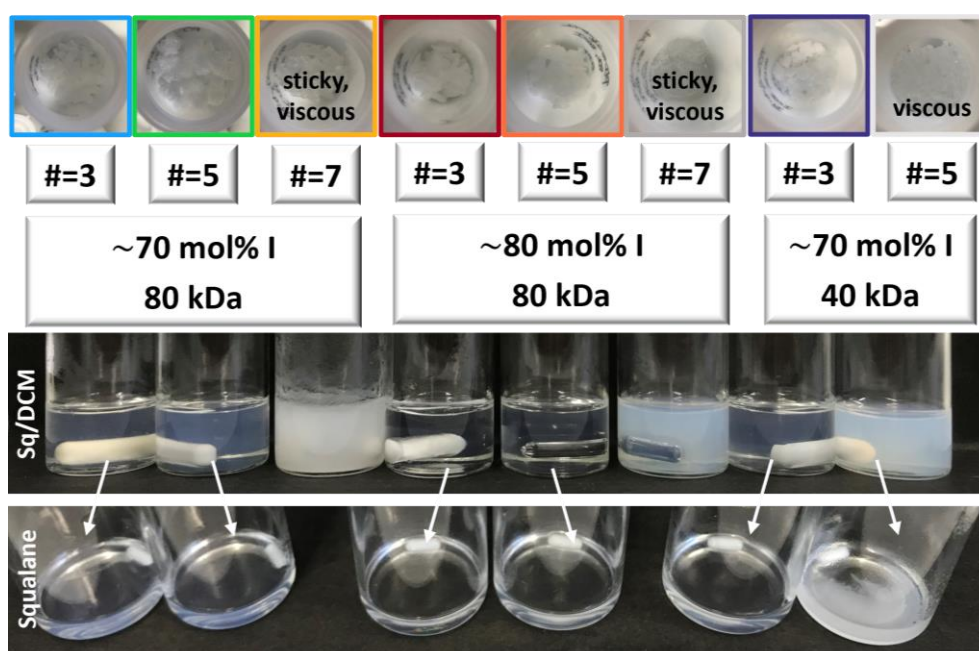
Figure 2: Chemical structure of squalane.

The polymer solutions were prepared by a solvent/cosolvent approach. First, the polymer was weighted in and dissolved in a mixture of squalane (Sq) and dichloromethane (DCM). 10 wt% of the polymer in squalane were targeted. Furthermore, BHT (butylated hydroxytoluene, 2,6-di-*tert*-butyl-4-methylphenol) was added as a stabilizer. The cosolvent was allowed to evaporate at room temperature and normal pressure for 20 days (the DCM evaporation was traced gravimetrically). Afterwards, remaining traces of DCM were removed at room temperature applying a reduced pressure for 2 days. Finally, the polymer solution was annealed at 160 °C for 1 hour and then allowed to cool down to room temperature. The sticky and viscous bulk materials, i.e., the 80 kg·mol<sup>-1</sup> heptablock copolymers and the 40 kg·mol<sup>-1</sup> pentablock, gave opaque solutions in the mixtures of squalane and dichloromethane and precipitated after cosolvent evaporation (see Figure 3). Therefore, only the transparent,

homogeneous polymer solutions (i.e., solutions of the  $80 \text{ kg}\cdot\text{mol}^{-1}$  tri- and pentablock copolymers and the  $40 \text{ kg}\cdot\text{mol}^{-1}$  triblock) were investigated.

Dynamic viscosity measurements  $\eta$  were performed with a rotational viscometer (Anton Paar modular compact rheometer type MCR 302) using a cone-plate geometry (50 mm cone radius and an angle of  $1^\circ$ ). In contrast to a capillary viscometer, a constant shear rate and a constant shear field is realized. A periodic strain was introduced by a sinusoidal deformation. Measurements at constant temperature ( $T=20\text{--}120^\circ\text{C}$  in  $20^\circ\text{C}$  steps) were performed at varying shear rates ( $\dot{\gamma}=0.1\text{--}100 \text{ s}^{-1}$ ).

All measured dynamic viscosities and values calculated thereof can be found in the Supp. Inf. (Table S2).



**Figure 3:** Solubility of the tapered multiblock copolymers in squalane. The sticky and viscous polymers ( $80 \text{ kg}\cdot\text{mol}^{-1}$  heptablock copolymers (70 mol% I: yellow, 80 mol% I: grey) and  $40 \text{ kg}\cdot\text{mol}^{-1}$  pentablock (70 mol% I: light grey)) were insoluble in squalane and hence were not investigated by dynamic viscosity measurements.

## Results and Discussion

In order to quantify the increase in viscosity by the addition of the tapered multiblock copolymers based on isoprene (I) and styrene (S)  $P(I-co-S)_n-b-PI$  (short  $(IS)_nI$ ) and relate it to the polymer characteristics, viscosity measurements of the polymers with varied overall molar mass (40 and 80 kg·mol<sup>-1</sup>), block number ( $\# = 2n + 1 = 3, 5$  and 7) and isoprene content (70 and 80 mol% isoprene) are discussed. For this purpose, [REDACTED]

[REDACTED] Furthermore, the dynamic viscosities of the non-hydrogenated polymers in squalane, a model compound for aliphatic oils, were determined by rheological measurements in dependence of the applied shear rate and are set in relation to the results from the viscosity measurements.

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

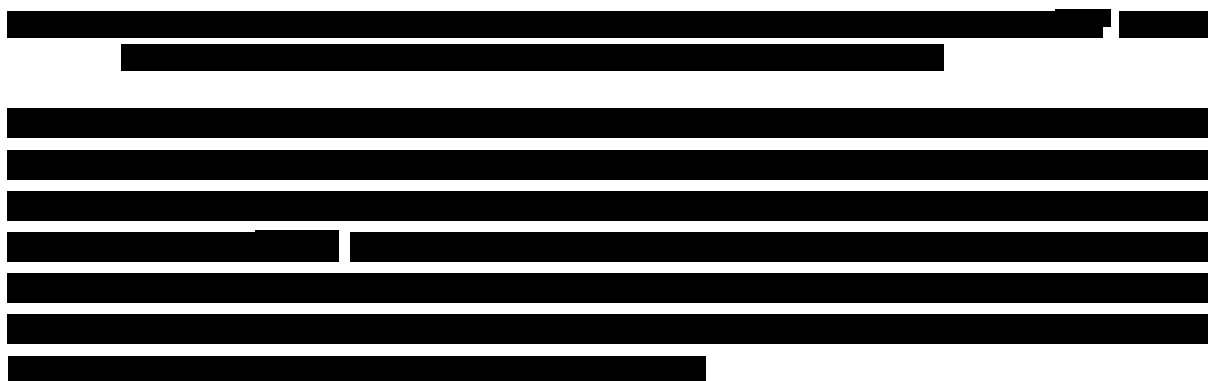
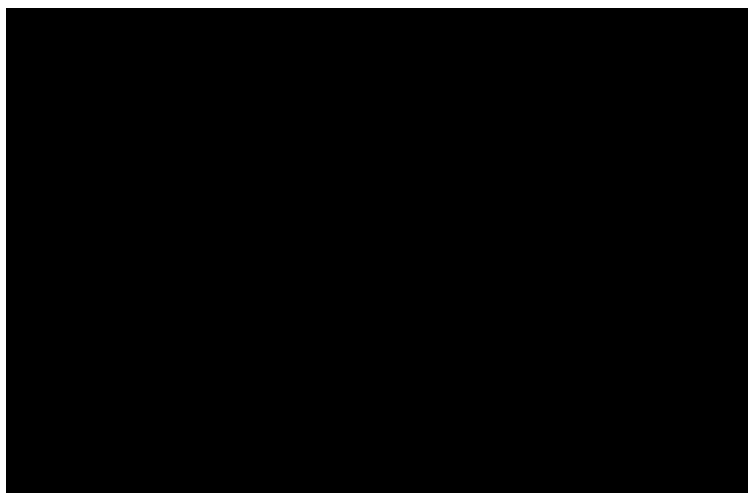
[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]



### Dynamic Viscosities

The dynamic viscosities were measured of 10 wt% polymer solutions in squalane at temperatures between 20–120 °C with shear rates between 0.1–100 s<sup>-1</sup>. At 20 °C, some dynamic viscosities showed a frequency dependence (Figure 7, right), whereas at higher temperatures, the viscosity was constant with varying shear rate.

The average dynamic viscosities are plotted in dependence of the temperature in the left graph of Figure 7. Note, that the above discussed heptablock is not characterized since the cosolvent approach did not yield a transparent, homogeneous polymer solution. Furthermore, the commercial PMA-based oil additive provided by Evonik was not tested, since the thickening mechanism does not rely on association but polymer coil expansion. Therefore, potential non-linear behavior due to partial disassembly is not expected.

With increasing temperature, all fluids have a rapid decrease in dynamic viscosity in common. Between 20–60 °C, the dynamic viscosity increases with molar mass ( $\eta^{\text{tri},40\text{k}} < \eta^{\text{tri},80\text{k}}$ ), block number ( $\eta^{\text{tri}} < \eta^{\text{penta}}$ ) and isoprene content ( $\eta^{70\%} < \eta^{80\%}$ ). Except for the viscosity of the pentablock with 80 kg·mol<sup>-1</sup> and 80 mol% isoprene, these trends are also valid for temperatures up to 120 °C. The 80 kg·mol<sup>-1</sup> 80 mol% isoprene pentablock (orange) shows a more pronounced decrease in viscosity with increasing temperature, dropping below the dynamic viscosity of the analogous triblock (red) at 80 °C and below the dynamic viscosity of the 80 kg·mol<sup>-1</sup> 70 mol% isoprene pentablock (green) above 100 °C.

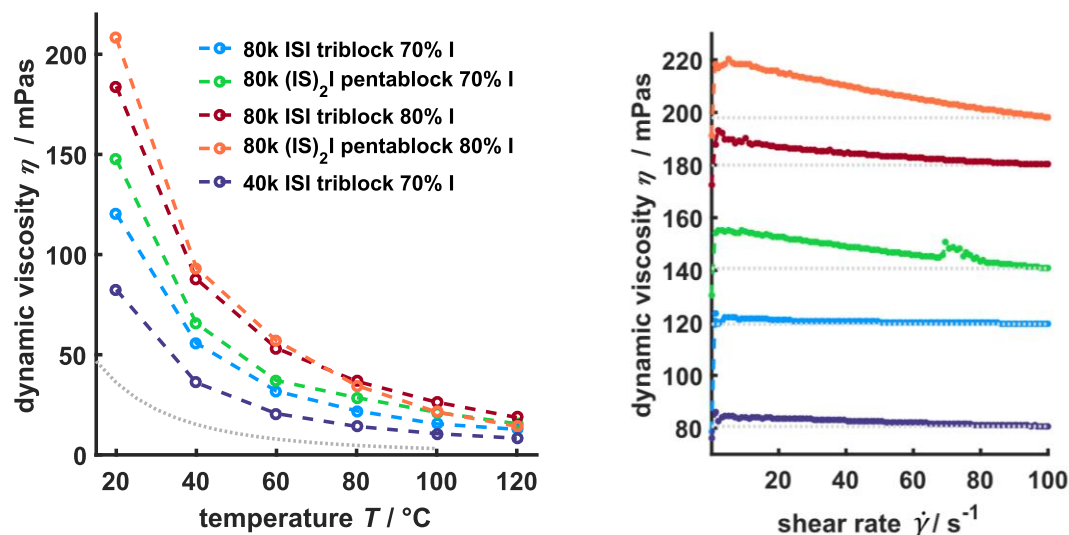


Figure 7: Temperature dependent dynamic viscosities averaged over the shear rate regime of 0.1-100 s<sup>-1</sup> (left) and shear rate dependent dynamic viscosities at 20 °C (right) of the tapered multiblock copolymers at 10 wt% in squalane. Grey dotted line:  $\eta$  (squalane) (left); horizontal line reflecting at  $\eta$  (100 s<sup>-1</sup>) to guide the eye with respect to the shear thinning (right).

Since the 80 kg·mol<sup>-1</sup> 80 mol% isoprene pentablock exhibits the shortest individual polystyrene blocks of the 80 kg·mol<sup>-1</sup> polymers, we suggest that this difference might arise from the most pronounced decrease in the glass transition temperature of the polystyrene domains, which increases with decreasing polystyrene fraction (*vide supra*). This promotes partial disassembly and accelerates chain exchange kinetics.<sup>[37]</sup>

At 20 °C, the dynamic viscosities of the pentablock copolymers (green, orange) and the 80 kg·mol<sup>-1</sup> 80 mol%I triblock (red) show a frequency dependence (Figure 7, right). In case of transient networks, frequency dependent rheological measurements can reveal a decrease of the viscosity at higher shear rates (shear thinning), which is sometimes preceded by an increase in viscosity (shear thickening).<sup>[38]</sup> The shear thinning, non-Newtonian, i.e., non-linear, behavior oftentimes observed for transient networks is thought to be related to a non-Gaussian stretching of the polyisoprene mid blocks connecting different polystyrene domains and a final break-up of the bridges.<sup>[39]</sup> The formation of additional, new bridges due to the reorganization under shear is reflected in a shear thickening behavior, which is observed for the 80 kg·mol<sup>-1</sup> pentablock with 70 mol% isoprene (green).

The viscoelastic response is determined by the amount and the lifetime of the bridges. Besides, also chain entanglements can contribute to the non-Newtonian behavior, as reflected in the weak non-Newtonian behavior of the 80 kg·mol<sup>-1</sup> 80 mol% isoprene triblock (red).

Spontak and coworkers provided theoretical insights into the effect of the number of solvophobic blocks on the amount of bridged chain conformation.<sup>[20]</sup> For this purpose, networks of linear sequential A(BA)<sub>n</sub> multiblock copolymers with the same overall molar mass and composition in B-selective solvents were simulated using the dissipative particle dynamics approach. At a polymer fraction of 10%, an overall bridging fraction of 60-65% was predicted for both multiblock copolymers with two and three solvophobic blocks. Yet, they differed in the amount of solvophobic blocks connected by one polymer chain. In case of the multiblock with three solvophobic blocks, 20% of the bridges connected two cores by two bridges. Still,



the largest amount of the bridging fraction results from the extended chain structure with three cores connected intramolecularly by two bridges.

Since high angular frequencies, i.e., high shear rates, equal fast motions on a short timescale, the observed shear thinning at high shear rates represents the escape of polystyrene blocks from a core upon fast motions, in this way eliminating a bridged conformation. For slower motions (lower shear rates), the system can react by rearrangement or distortion of the network and in this manner maintains the higher viscosity.

In order to quantify the performance of the non-hydrogenated multiblock copolymers based on isoprene and styrene, the Roelands Slope Indices  $RSI$  can be discussed (see Experimental Section, equation 3). Even at first sight, it is evident that the absolute value of the negative slope, i.e., the  $RSI$ , of the pentablock with 80 kg·mol<sup>-1</sup> and 80 mol% isoprene is way higher than the magnitude of the other negative slopes (Figure 8).

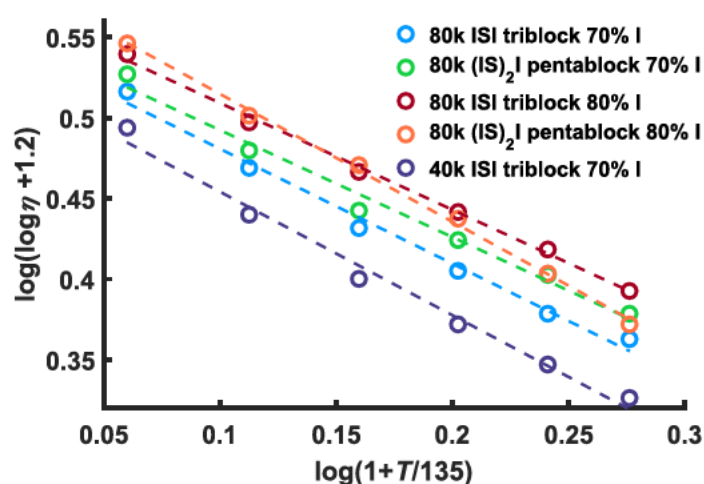


Figure 8: Plots of the dynamic viscosities at 10 wt% in squalane in dependence on the temperature  $T$  according to equation 3. Negative slope: Roelands Viscosity Index ( $RSI$ ).

Furthermore, the  $RSI$  values can be converted into the dynamic viscosity indices  $DVI$  (see Experimental Part, equation 5), now rendering magnitudes comparable to the conventional viscosity index  $VI$  (see Experimental Part, equation 2).

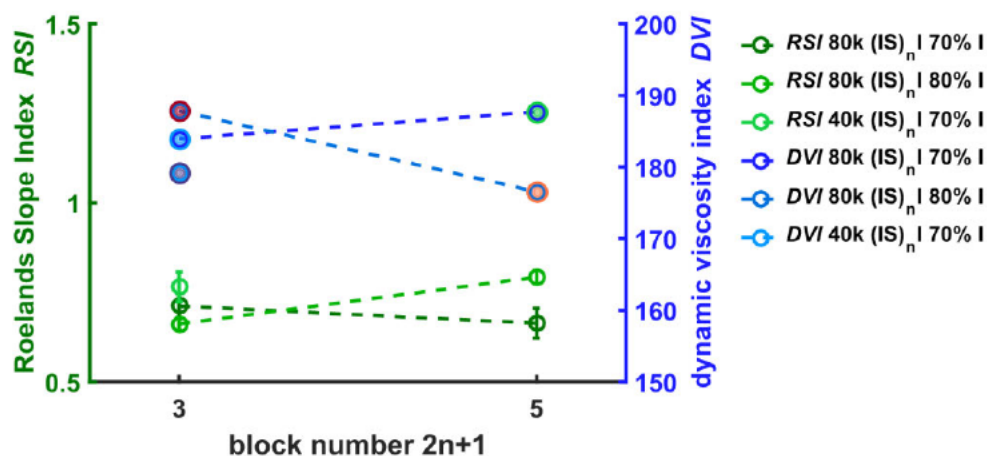


Figure 9: Roeland Slope Indices  $RSI$  (left y-axis, green markers) and dynamic viscosity indices  $DVI$  (right axis, blue markers) in dependence of the block number. The values are derived from the linear regressions shown in Figure 8 according to equation 3 and 5, respectively.

Figure 9 shows the *RSI* as well as the *DVI* values in dependence of the block number. For the triblock copolymers, the *DVI* increases with molar mass ( $DVI^{\text{tri},40k} < DVI^{\text{tri},80k}$ ), and isoprene content ( $DVI^{70\%} < DVI^{80\%}$ ), which is in accordance with

The latter trend can be explained the better solubility upon increasing the solvophilic ratio. Comparing the pentablock copolymers, an inversion of the trend becomes evident, with the 80 mol% isoprene pentablock exhibiting a lower *DVI* ( $DVI^{70\%} > DVI^{80\%}$ ). This is further observable comparing the tri- and pentablock copolymers with the same overall molar mass and isoprene content. While the *DVI* of the 70 mol% isoprene polymers increases as expected with the block number, the *DVI* of the 80 mol% isoprene polymers decreases with the block number. As explained above, this might be reasoned in the most pronounced partial disassembly due to the shortest individual polystyrene blocks. This fact allows solvent molecules to penetrate the micellar cores, this way plasticizing them and facilitating the chain pullout by weakening the overall van-der-Waals interaction.

### Comparison of the obtained Viscosity-Temperature Relationships

As discussed above,

Beyond this, the dynamic viscosity indices *DVI* were calculated from the dynamic viscosity measurements performed with solutions of the non-hydrogenated structures in squalane.

At 10 wt%, and the *DVI* values showed a superior performance of the triblock copolymers compared to their counterparts with higher block numbers ( $PVI^{\text{tri}} > PVI^{\text{penta}} > PVI^{\text{hepta}}$  with constant 70 mol% isoprene;  $DVI^{\text{tri}} > DVI^{\text{penta}}$  with constant 80 mol% isoprene). Only for 70 mol% isoprene, the *DVI* was higher for the pentablock structure ( $DVI^{\text{tri}} < DVI^{\text{penta}}$  with constant 70 mol% isoprene). This leads to the assumption that the extended transient network structures, which are formed in concentrated solutions of polymers with multiple solvophobic polystyrene blocks, are disadvantageous for the shear stability and viscosity-temperature relationship. This is substantiated by the penetration of solvent molecules into the solvophobic polystyrene cores, which becomes more likely with decreasing individual polystyrene block length. The solvent molecules serve as plasticizer, reducing the van-der-Waals interaction and rendering chain pullout and hence partial disassembly probable. The more extended such a transient network is, the more impeded is the alignment of the associated structure within the shear flow. Together with the promoted chain pullout, the extended structures of multiblock copolymers are more prone to disassembly phenomena than the spherical aggregates of triblock copolymers with one solvophobic block.

This is expected, since the apparent molar mass and the dimension of loose aggregates increases with the number of polymer chains associate per aggregate. This indicates that at that point,

[REDACTED] This further speaks in favor of the increase in dimension or fraction of the loose aggregates. [REDACTED]

Conclusively,

This means, that there is an optimum chain composition, which has a limited overall molar mass so that the polymer still does not experience chain scission, and at the same time a certain block number, balancing the tendency to form loose aggregates by and the probability for disassembly phenomena.

## Conclusion

Within this work, we compared the viscosity-temperature relationship for tapered (IS)<sub>n</sub>I multiblock copolymers with varying molar masses, block numbers and isoprene content.

Frequency-dependent rheological measurements of 10 wt% polymer solutions in squalane at various temperatures revealed an increase in the dynamic viscosity with the overall molar mass, with the block number and with the isoprene content, the latter two statements being valid at constant overall molar masses. With shear rates of  $0.1\text{-}100\text{ s}^{-1}$ , the applied forces were very low, and hence the temporary shear-induced viscosity loss marginal, which typically is observable at strain levels above  $10^4\text{ s}^{-1}$ .

Calculations of the dynamic viscosity index *DVI* revealed an enhanced viscosity-temperature relationship for the non-hydrogenated triblock copolymers with increasing overall molar mass and isoprene content. On the contrary, for the pentablock copolymers, the formulation with the oil additive of a higher isoprene content showed a worsened performance. This was explained by the partial disassembly, which is most likely for this structure, as it exhibits the shortest individual solvophobic polystyrene blocks.

[REDACTED]

[REDACTED]

For the application of the discussed styrene-isoprene multiblock copolymers as viscosity modifiers, small decreases in viscosity with increasing temperature, i.e., high viscosity indices, are desired to allow proper lubrication with comparably thin oil films over a large temperature range. Besides, low polymer treat rates are preferable from an economic perspective. The 80 kg·mol<sup>-1</sup> heptablock showed an optimum performance of the investigated polymers, profiting from a high viscosity index at low polymer treat rates.

[REDACTED]

## Conflicts of Interest

This project was financed by [REDACTED] and in the course of the collaboration, the ownership as well as the usage rights are conferred to [REDACTED]. Therefore, the service inventions and gained knowledge are subject to a non-disclosure agreement.

## Author Contributions

[REDACTED] and [REDACTED] elaborated the conceptualization of the project together with Holger Frey (JGU). [REDACTED] further administered the project and was responsible for [REDACTED]. [REDACTED] was responsible for the [REDACTED]. Ramona D. Barent (JGU)

synthesized the polymers, performed the dynamic viscosity measurements and was responsible for writing of the original draft and visualization of the obtained data [REDACTED] and [REDACTED] revised the manuscript. All authors were involved in the writing process at review- and editing stage.

## Acknowledgements

We thank Jürgen Ludwig (JGU) for specialty glassware and Monika Schmelzer (JGU) for the SEC measurements. Furthermore, we gratefully thank [REDACTED] for valuable experimental support optimizing [REDACTED].

## References

- [1] L. R. Rudnick, *Lubricant Additives. Chemistry and Applications, Third Edition*, CRC Press, Portland, 2017.
- [2] A. Martini, U. S. Ramasamy, M. Len, *Tribol. Lett.* **2018**, 66, 1.
- [3] D02 Committee, *Test Method for Apparent Viscosity of Engine Oils and Base Stocks Between 10C and 35C Using Cold-Cranking Simulator*, ASTM International, West Conshohocken, PA.
- [4] G. E. Totten (Ed.) *ASM Handbook, volume 18*, ASM International, Materials Park, Ohio, 2017.
- [5] P. Panwar, E. Schweissinger, S. Maier, S. Hilf, S. Sirak, A. Martini, *J. Mol. Liq.* **2022**, 359, 119215.
- [6] T. Stöhr, B. Eisenberg, M. Müller, *SAE Int. J. Fuels Lubr.* **2009**, 1, 1511.
- [7] G. W. Stachowiak, A. W. Batchelor, *Engineering tribology*, Elsevier Butterworth-Heinemann, Amsterdam, Boston, 2006.
- [8] J. Holtzinger, J. Green, G. Lamb, D. Atkinson, H. Spikes, *Tribol. Trans.* **2012**, 55, 631.
- [9] R. M. Mortier (Ed.) *Springer Link Books*, Springer Netherlands, Dordrecht, 2010.
- [10] P. Bezot, C. Hesse-Bezot, D. Faure, J. C. Calvez, *Lubr. Sci.* **2000**, 12, 301.
- [11] M. J. Covitch in *SAE Tech. Pap. Ser.*, SAE International, 1998.
- [12] a) Y. Tsunashima, M. Hirata, Y. Kawamata, *Macromolecules* **1990**, 23, 1089; b) M. J. Covitch, K. J. Trickett, *Adv. Chem. Eng. Sci.* **2015**, 05, 134.
- [13] U. S. Ramasamy, S. Lichter, A. Martini, *Tribol. Lett.* **2016**, 62.
- [14] a) D. Lariviere, A.-F. A. Asfour, A. Hage, J. Z. Gao, *Lubr. Sci.* **2000**, 12, 133; b) C. Mary, D. Philippon, L. Lafarge, D. Laurent, F. Rondelez, S. Bair, P. Vergne, *Tribol. Lett.* **2013**, 52, 357.
- [15] M. E. Shivokhin, T. Narita, L. Talini, A. Habicht, S. Seiffert, T. Indei, J. D. Schieber, *J. Rheol.* **2017**, 61, 1231.
- [16] a) S.-H. Choi, F. S. Bates, T. P. Lodge, *Macromolecules* **2014**, 47, 7978; b) S.-H. Choi, F. S. Bates, T. P. Lodge, *J. Phys. Chem. B* **2009**, 113, 13840; c) J. S. Higgins, J. V. Dawkins, G. G. Maghami, S. A. Shakir, *Polymer* **1986**, 27, 931.
- [17] C. Lai, W. B. Russel, R. A. Register, *Macromolecules* **2002**, 35, 841.

- [18] a) Č. Koňák, G. Fleischer, Z. Tuzar, R. Bansil, *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 1312; b) E. Raspaud, D. Lairez, M. Adam, J.-P. Carton, *Macromolecules* **1994**, *27*, 2956.
- [19] E. Raspaud, D. Lairez, M. Adam, J.-P. Carton, *Macromolecules* **1996**, *29*, 1269.
- [20] M. O. Tuhin, J. J. Ryan, J. D. Sadler, Z. Han, B. Lee, S. D. Smith, M. A. Pasquinelli, R. J. Spontak, *Macromolecules* **2018**, *51*, 5173.
- [21] S. K. Filippov, B. Verbraeken, P. V. Konarev, D. I. Svergun, B. Angelov, N. S. Vishnevetskaya, C. M. Papadakis, S. Rogers, A. Radulescu, T. Courtin et al., *J. Phys. Chem. Lett.* **2017**, *8*, 3800.
- [22] V. S. Kravchenko, I. I. Potemkin, *J. Phys. Chem. B* **2016**, *120*, 12211.
- [23] C. Zheng, H. Huang, T. He, *Macromol. Rapid Commun.* **2014**, *35*, 309.
- [24] a) M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey, A. H. E. Müller, *Macromolecules* **2019**, *52*, 9299; b) M. Steube, T. Johann, R. D. Barent, A. H. Müller, H. Frey, *Prog. Polym. Sci.* **2022**, *124*, 101488.
- [25] D02 Committee, *Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)*, ASTM International, West Conshohocken, PA.
- [26] ASTM D2270-10, "Standard practice for calculating viscosity index from kinematic viscosity at 40 and 100C. Technical report", can be found under <http://ppapco.ir/wp-content/uploads/2019/07/ASTM-D2270-2016.pdf>, **2016**.
- [27] T. S. Rushing, R. D. Hester, *Rev. Sci. Instrum.* **2003**, *74*, 176.
- [28] D. B. Cunningham, P. H. Doe, S. D. Joshi, A. Moradi - Araghi, *Rev. Sci. Instrum.* **1986**, *57*, 2310.
- [29] TA Instruments, "Rheology Theory and Applications. Boston Rheology Training", can be found under <https://www.tainstruments.com/wp-content/uploads/Boston-Rheology-Training-2019.pdf>, **2019**.
- [30] J. Zakarian, M. E. Webb, B. Hunter in *SAE Tech. Pap. Ser.*, SAE International, **2015**.
- [31] C. J. A. Roelands, *Correlational aspects of the viscosity-temperature-pressure relationship of lubricating oils, Dissertation*, University of Technology, Delft, **1966**.
- [32] J. Zakarian, *SAE Int. J. Fuels Lubr.* **2012**, *5*, 1123.
- [33] R. E. Hersh, E. K. Fisher, M. R. Fenske, *Ind. Eng. Chem.* **1935**, *27*, 1441.
- [34] T. Voglhuber-Brunnmaier, A. O. Niedermayer, B. Jakoby, *Technisches Messen* **2022**, *89*, 4.
- [35] S. K. Mylona, M. J. Assael, M. J. P. Comuñas, X. Paredes, F. M. Gaciño, J. Fernández, J. P. Bazile, C. Boned, J. L. Daridon, G. Galliero et al., *J. Phys. Chem. Ref. Data* **2014**, *43*, 13104.
- [36] M. J. P. Comuñas, X. Paredes, F. M. Gaciño, J. Fernández, J. P. Bazile, C. Boned, J. L. Daridon, G. Galliero, J. Pauly, K. R. Harris et al., *J. Phys. Chem. Ref. Data* **2013**, *42*, 33101.
- [37] E. Wang, J. Zhu, D. Zhao, S. Xie, F. S. Bates, T. P. Lodge, *Macromolecules* **2020**, *53*, 417.
- [38] C. Chassenieux, T. Nicolai, L. Benyahia, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 18.
- [39] D. A. Vega, J. M. Sebastian, Y.-L. Loo, R. A. Register, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 2183.



## Supporting Information

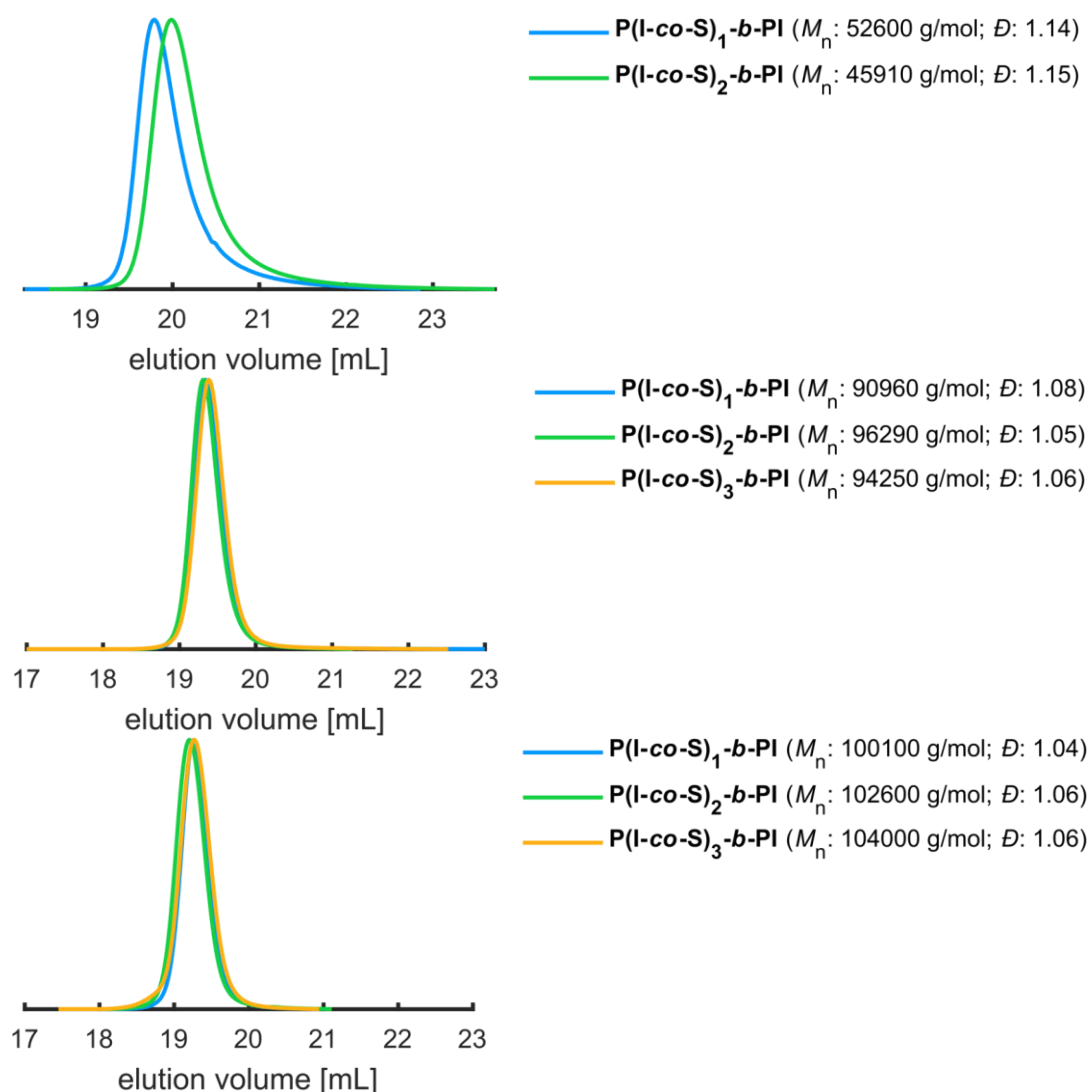


Figure S1: SEC traces (THF, PS calibration standard, RI detector) of the series with 40 kg·mol<sup>-1</sup> and 70 mol% isoprene (top), 80 kg·mol<sup>-1</sup> and 70 mol% isoprene (middle), and 80 kg·mol<sup>-1</sup> and 80 mol% isoprene (bottom). Derived number average molar masses and dispersities are comprised in Table 1.

**Table S1: Overview of the measured kinematic viscosities ( $\nu$ ) and calculated viscosity indices ( $VI$ ), proportional viscosity indices ( $PVI$ ), and apparent polymer treat rates ( $TR_{app}$ ).**

| block number<br>#=2n+1 | target $M_n$<br>[kg·mol <sup>-1</sup> ] | target<br>$P_n(I)$ [%] | $TR$<br>[wt%] | $\nu^{40\text{ °C}}$<br>[cSt] | $\nu^{100\text{ °C}}$<br>[cSt] | $VI$ | $PVI$ | $TR_{app}^a$<br>[wt%] |
|------------------------|-----------------------------------------|------------------------|---------------|-------------------------------|--------------------------------|------|-------|-----------------------|
| 3                      | 80                                      | 70                     | 2.5           | 25.2                          | 5.5                            | 170  | 132,7 | 1,73                  |
|                        |                                         |                        | 5             | 31,1                          | 7,1                            | 204  | 157.6 | 1.7                   |
|                        |                                         |                        | 10            | 109,6                         | 32,3                           | 328  | 431.1 | 0.85                  |
| 5                      | 80                                      | 70                     | 2.5           | 24.8                          | 5.6                            | 174  | 138,5 | 1,61                  |
|                        |                                         |                        | 5             | 31,8                          | 7,4                            | 212  | 163.9 | 1.57                  |
|                        |                                         |                        | 10            | 124,3                         | 25,3                           | 238  | 263.8 | 0.96                  |
| 7                      | 80                                      | 70                     | 2.5           | 27.2                          | 6.3                            | 196  | 150,7 | 1,12                  |
|                        |                                         |                        | 5             | 40,7                          | 9,4                            | 233  | 183.2 | 1.09                  |
|                        |                                         |                        | 10            | 230,6                         | 26,1                           | 145  | 149.0 | 0.95                  |
| 3                      | 80                                      | 80                     | 2.5           | 27.1                          | 6.1                            | 109  | 144,1 | 1,22                  |
|                        |                                         |                        | 5             | 36.0                          | 8,3                            | 216  | 171.9 | 1.3                   |
|                        |                                         |                        | 10            | 173,5                         | 33,5                           | 239  | 287.6 | 0.83                  |
| PMA oil additive       | 50                                      | -                      | 2.5           | 23.4                          | 5.1                            | 154  | 127,7 | 2,5                   |
|                        |                                         |                        | 5             | 27,6                          | 6,1                            | 177  | 141.5 | 2.44                  |
|                        |                                         |                        | 10            | 40,1                          | 8,6                            | 201  | 162.8 | 2.46                  |
|                        |                                         |                        | 20            | 96,5                          | 17,4                           | 198  | 194.1 | 2.44                  |

<sup>a</sup> The apparent polymer treat rates were calculated so that the kinematic viscosity at 100 °C equals the kinematic viscosity of the PMA-based commercial oil additive at a polymer treat rate of 2.5 wt%.



**Table S2: Overview of the measured dynamic viscosities ( $\eta$ ), and calculated Roelands Slope Indices ( $RSI$ ) and dynamic viscosity indices ( $DVI$ ).**

| block number<br>#=2n+1 | target $M_n$<br>[kg·mol <sup>-1</sup> ] | target<br>$P_n(I)$ [%] | $T$<br>[°C] | $\eta$<br>[mPas] | $RSI$ | $d\ RSI$ | $DVI$ |
|------------------------|-----------------------------------------|------------------------|-------------|------------------|-------|----------|-------|
| 3                      | 40                                      | 70                     | 20          | 82.5             | 0.77  | 0.04     | 179.2 |
|                        |                                         |                        | 40          | 36.0             |       |          |       |
|                        |                                         |                        | 60          | 20.6             |       |          |       |
|                        |                                         |                        | 80          | 14.2             |       |          |       |
|                        |                                         |                        | 100         | 10.6             |       |          |       |
|                        |                                         |                        | 120         | 8.3              |       |          |       |
| 3                      | 80                                      | 70                     | 20          | 120.4            | 0.71  | 0.04     | 184.0 |
|                        |                                         |                        | 40          | 55.8             |       |          |       |
|                        |                                         |                        | 60          | 31.8             |       |          |       |
|                        |                                         |                        | 80          | 22.0             |       |          |       |
|                        |                                         |                        | 100         | 15.5             |       |          |       |
|                        |                                         |                        | 120         | 12.8             |       |          |       |
| 5                      | 80                                      | 70                     | 20          | 147.5            | 0.66  | 0.04     | 187.7 |
|                        |                                         |                        | 40          | 65.6             |       |          |       |
|                        |                                         |                        | 60          | 37.1             |       |          |       |
|                        |                                         |                        | 80          | 28.6             |       |          |       |
|                        |                                         |                        | 100         | 21.2             |       |          |       |
|                        |                                         |                        | 120         | 15.5             |       |          |       |
| 3                      | 80                                      | 80                     | 20          | 184.0            | 0.66  | 0.02     | 187.8 |
|                        |                                         |                        | 40          | 87.8             |       |          |       |
|                        |                                         |                        | 60          | 53.2             |       |          |       |
|                        |                                         |                        | 80          | 36.7             |       |          |       |
|                        |                                         |                        | 100         | 26.3             |       |          |       |
|                        |                                         |                        | 120         | 18.7             |       |          |       |
| 5                      | 80                                      | 80                     | 20          | 208.1            | 0.79  | 0.02     | 176.6 |
|                        |                                         |                        | 40          | 93.3             |       |          |       |
|                        |                                         |                        | 60          | 57.0             |       |          |       |
|                        |                                         |                        | 80          | 34.6             |       |          |       |
|                        |                                         |                        | 100         | 21.4             |       |          |       |
|                        |                                         |                        | 120         | 14.3             |       |          |       |



---

---

# CHAPTER 8

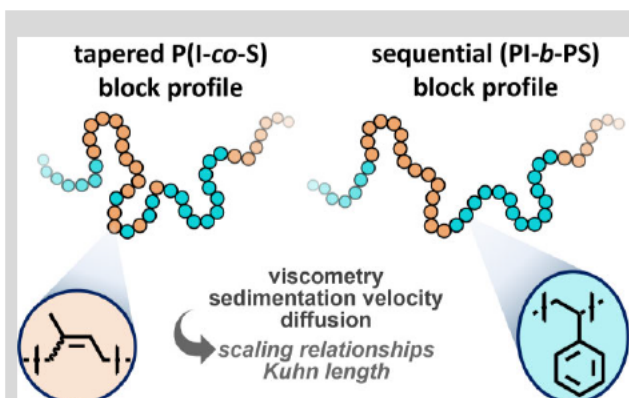
*Dilute Solution Properties of Multiblock  
Copolymers: Conformation Analysis of Sequential  
and Tapered Multiblock Copolymers in Non-  
Selective Solvents*

---



**CHAPTER 8**

To be Submitted

***Dilute Solution Properties of Multiblock Copolymers: Conformation Analysis of Sequential and Tapered Multiblock Copolymers in Non-Selective Solvents***Ramona D. Barent<sup>1,2</sup>, Ilja Anufriev<sup>3</sup>, Ivo Nischang<sup>3,4</sup>, Igor Perevyazko<sup>5\*</sup>, and Holger Frey<sup>1\*</sup><sup>1</sup> Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany<sup>2</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany<sup>3</sup> Laboratory of Organic and Macromolecular Chemistry, Friedrich Schiller University Jena, Humboldtstraße 10, 07743 Jena, Germany<sup>4</sup> Jena Center for Soft Matter, Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany<sup>5</sup> Department of Molecular Biophysics and Physics of Polymers, St. Petersburg University, Universitetskaya nab. 7/9, 199034, Saint Petersburg, Russia

Advances in polymerization techniques provide access to molecular architectures beyond the conventional AB diblock or ABA triblock copolymers, thus offering the opportunity to tailor the resulting properties by the chemical composition. Concerning the potential of an extension to linear multiblock copolymers for bulk materials, progress has been made. However, in spite of the high and continuous

attention to such multiblock polymer systems, little is known about their dilute solution properties and as a consequence regarding basic macromolecular parameters, which determine their conformation and solution behavior. Therefore, this work aims at understanding the structure-property relationships in dilute solution. We present a comprehensive systematic study of sequential and tapered multiblock copolymers (IS)<sub>n</sub>I based on isoprene and styrene in a non-selective solvent. The polymers are characterized by complementary approaches. With this information at hand, the gross conformation in toluene is investigated, implementing the classical scaling relationships between hydrodynamic characteristics derived from analytical ultracentrifugation, intrinsic viscosity, and related

experiments. Furthermore, the statistical segment lengths are estimated by taking excluded volume and draining effects into account. All multiblock copolymers showed the expected behavior of a flexible polymer chain in dilute solution. Yet, for homologous polymer series coinciding in their block number, subtle differences in rigidity for the different block profiles were deducible. Both methods revealed a more rigid and hence expanded chain conformation for the sequential structures compared to their tapered analogues. Polymers which differ in molar mass and block number do not follow the classical scaling relationship with respect to their intrinsic viscosity, evidencing that the solution properties are further influenced by the block number even in non-selective solvents. This conclusion is further underlined by significantly higher magnitudes of the Kuhn segment lengths compared to the homologous tri-, penta- and heptablock copolymer series.

## Introduction

Block copolymers are of great interest due to the chemical connection, i.e., covalent bond between the constituent blocks. In case of incompatible blocks like polydienes and polystyrene spatially limited nanophase separation occurs, combining the inherent properties of each polymer both in bulk and in solution.<sup>[1]</sup> The practical use of nanophase separation in bulk has been widely explored, with thermoplastic elastomers (TPEs) or high impact materials being the most prominent examples of block copolymer-based materials with outstanding mechanical properties.<sup>[2,3]</sup> Concerning the application of polydiene-polystyrene block copolymers in solution, hydrogenated polymers were commercialized as lubricating additives, modifying the temperature impact on the viscosity of the oil.<sup>[4]</sup>

By variation of intrinsic parameters comprising molar mass, number of blocks, ratio of the comonomers but also the block profile, which can be defined in case of sequential block copolymers, gradual in case of tapered block copolymers,<sup>[5]</sup> but also ideally random<sup>[6]</sup> if appropriate randomizers are used, it is possible to specify polymer properties. Furthermore, extrinsic parameters like the choice of the solvent, the temperature and the concentration influence the acquired solution properties. With the progress of the last decades achieved in the field of anionic polymerization techniques, sophisticated block copolymer architectures including high block numbers with well-defined molar masses and narrow distribution ( $\mathcal{D} \leq 1.1$ ) are readily accessible.<sup>[5,7,8]</sup>

A specific peculiarity of block copolymer in solution relies on their ability to self-assemble, which tremendously influences the viscosity of the polymer's solution. This has been demonstrated in an elegant work in the 1970ies by Paul *et al.*, who examined the viscosity of a polystyrene-*block*-polybutadiene-*block*-polystyrene (abbreviated as SBS) solution at low and high concentration and correlated it to the thermodynamic interaction between the polymer and the solvent.<sup>[9]</sup> The latter was quantified by the Hildebrand solubility parameter  $\delta$ , which can be related to the polymer-solvent interaction for non-polar systems, with small differences in  $\delta$  describing a maximized enthalpic miscibility.<sup>[10]</sup> For dilute solutions, they observed a maximized intrinsic viscosity  $[\eta]$  for a solubility parameter of the solvent in the vicinity to the ones of the copolymer, i.e., a thermodynamically good solvent for both constituent blocks. This reflects the most expanded polymer coil conformation due to the favorable polymer-solvent interaction, which results in the highest contribution to the solution's viscosity. In pronounced

contrast to this, the relative viscosity  $\eta_{rel}$  of concentrated solutions exhibits a minimum in the same  $\delta$  range. This evidences the formation of intermolecularly self-assembled structures in solvents with disparate solubility parameters compared to the copolymer, which possess a higher hydrodynamic volume than the unassociated unimeric polymer coils, this way increasing the viscosities of the polymer solutions.<sup>[9]</sup>

Various works are dedicated to the concentration- and temperature-dependent intermolecular aggregate formation<sup>[11]</sup> and numerous simulation studies modeled the self-assembly<sup>[12]</sup>. However, less systematic investigation addressed the unimeric polymer chains at high dilution in non-selective solvents. Since this is the foundation for understanding their behavior at higher concentration or in more selective solvents, the focus of this work lies on their conformational analysis.

For a homopolymer, the chain conformation in a theta-solvent can be described according to the Fixman-Stockmayer equation, which relates the unperturbed Gaussian chain dimension to its intrinsic viscosity.<sup>[13]</sup> Investigations of copolymers based on styrene (S) and methyl methacrylate (MMA) provided insight into the validity for copolymers. In case of statistical copolymers, the polymers did not comply with the Fixman-Stockmayer equation. This was ascribed to the heterocontacts between the repeating units of the different comonomers, which cause a chain extension and hence deviation from a Gaussian distribution.<sup>[14]</sup> On the contrary, diblock copolymers obey this relation in the special case of extremely long blocks, where heterocontacts are minimized and both blocks adopt a Gaussian conformation.<sup>[15]</sup>

Concerning copolymers based on isoprene (I) and styrene (S), analogous results were obtained. In 1972, Prud'homme *et al.* reported diblock copolymers to follow the Fixman-Stockmayer behavior in cyclohexane and even in toluene as a good solvent for both constituent polymers.<sup>[16]</sup> The comparison of the SI diblock with SIS triblock copolymers revealed only minor deviations, indicating that the effect of the heterocontacts on the coil dimension is almost negligible.<sup>[17]</sup> Cramond and Urwin observed a maximum of the polymer expansion for SI diblock copolymers at a comonomer ratio close to unity in toluene, cyclohexane and methylisobutyl ketone.<sup>[18]</sup> Furthermore, in their work from 1977 they compared a sequential diblock to its tapered counterpart with identical comonomer ratio and found a similar behavior. Even for random copolymers and (SI)<sub>3</sub> hexablock copolymers, the evaluation of the intrinsic viscosities in toluene as a good solvent and methylisobutyl ketone as poor solvent only indicated a minor influence of heterocontacts on the chain conformation.<sup>[19]</sup> Schlick and Levy investigated the intrinsic viscosity of (IS)<sub>n</sub>I multiblock copolymers with 3, 5, 7 and 9 blocks at two different overall molar masses in toluene. They found an increase in  $[\eta]$  with decreasing block lengths, i.e., increasing block number.<sup>[20]</sup> They accounted this chain expansion to the avoidance of heterocontacts due to the incompatibility of the two comonomers, which would coincide with the initially described observations for PS-*b*-PMMA diblock copolymers. However, since this literature was published as early as 1960, it is not possible to make a profound statement regarding the precision and dispersity of the two multiblock copolymer series with molar masses of approximately 16 and 160 kg·mol<sup>-1</sup> due to limited analytical possibilities at the time of publication. Yet, turbidimetric analyses indicated decent homogeneities.

Besides these quite early conformational analyses, conclusions on the chain conformation were also drawn from scattering experiments published in the 1990ies. Tsunashima and coworkers investigated dilute solutions of SB diblock copolymers in three non-selective solvents

(tetrahydrofuran, benzene and thiophenol) and in a polydiene-selective solvent (*n*-decane).<sup>[21]</sup> In good solvents highly extended chains were observed, whereas the comparison of the DLS data in the selective solvent revealed collapsed polystyrene segments surrounded by the swollen polydiene block. Lairez and coworkers performed comparable experiments on dilute solutions of SIS triblock copolymers in tetrahydrofuran as a good solvent and *n*-heptane as polydiene-selective solvent.<sup>[22]</sup> They discussed the observed radii of the unimers against the background of the two different chain conformation, which comprise the extended structure with two collapsed end blocks and the looped structure with the two solvophobic end blocks intramolecularly aggregating in one core. From the observation of comparable radii in both solvents they deduced that the unimers adopt an extended chain conformation, since the looped, ring-like conformation would result in a radius being smaller by the factor of  $2^{0.5}$  than linear polymers.<sup>[23]</sup>

Whether a triblock copolymer forms a loop allowing the interaction between the terminal blocks was discussed theoretically by Wang and Mattice.<sup>[24]</sup> They identified the loss of entropy due to the coronal loop and the interfacial energy gain by favored interaction of the solvophobic moieties to be the major factors affecting the ratio of associated and unassociated unimers. By this rather simple consideration of a triblock copolymer, it becomes apparent that extrinsic as well as intrinsic parameters specified at the beginning influence the chain conformation in dilute solution.

By the introduction of multiple blocks per polymer chain, the balance between minimizing the interface between the constituent blocks and the interaction between the solvophobic blocks and the solvent becomes even more complex. Zhang *et al.* predicted the intramolecular self-assembly of multiblock copolymers with 20 blocks, showing that single as well as bridged flower-like micelles are supposed to form, depending on the block flexibility of the solvophilic block and the solvent selectivity.<sup>[25]</sup>

Wołoszczuk *et al.* simulated the chain conformation of multiblock copolymers with 8 blocks in a selective solvent with varying solvent quality and compared these results to a homopolymer of the solvophobic comonomer and a simple diblock.<sup>[26]</sup> For the homopolymer, the diblock and the multiblock, extended chain conformation were predicted if the excluded-volume interaction dominate. In case of the solvophobic homopolymer and the diblock copolymer, a single coil-to-globule transition with a collapsed solvophobic block was predicted upon decreasing solvent quality. Interestingly, no change in the conformation of the solvophilic block of the diblock was observed. In contrast, a two-step transition was proposed for the multiblock with decreasing mean-squared end-to-end distances for both the solvophilic and solvophobic blocks, the latter exhibiting a stronger shrinkage. First, a conformation with individual collapsed solvophobic blocks connected by more swollen solvophilic blocks was simulated (pearl-necklace structure), followed by a compact globular structure. In case of the globular structure, the number of contacts between the solvophobic moieties and the solvent are further reduced, implying that the penalty of loop formation of the solvophilic blocks is overcome at highly worsened solvent qualities for the solvophobic blocks. Furthermore, they compared the onsets of the transition of multiblock copolymers with varying block lengths, showing that the transition to globular state occurs at better solvent qualities for longer individual block lengths.

These experimental results as well as the theoretical consideration emphasize the complexity of block copolymer solutions. In this context, this work aims at elucidating the influence of the



block profile on polymer conformation in toluene as a good solvent, relying on an extended series of systematically varied multiblock copolymer samples.

In the current work, we systematically characterize dilute solutions of  $(IS)_nI$  multiblock copolymers covering a wide range of molar masses ( $40 - 400 \text{ kg}\cdot\text{mol}^{-1}$ ) and block numbers (3 – 13), while keeping the overall ratio of solvophilic to solvophobic units constant. For each chain composition tapered and sequential block structures are introduced, with the tapered copolymers exhibiting a rather sharp, but nevertheless gradual change in comonomer composition along every diblock sequence, while the sequential copolymers evince a pure block structure.

The gross conformation of the polymer chains in toluene as non-selective solvent are deduced, implementing the classical scaling relationships. Further calculation of the Kuhn segment lengths allows to assess information on the rigidity of the different homologous polymer series studied throughout this work.

## Experimental Section

### Materials and General Polymerization Procedure

The solvent cyclohexane (Fisher Science,  $\geq 99.8\%$ ) was dried over sodium with benzophenone as an indicator. Methanol (MeOH, Fisher Science,  $\geq 99.9\%$ ) was used as purchased. The stabilizer of isoprene (I, Acros Organics, 98%) and styrene (S, Acros Organics, 99%) was removed by filtering the monomers through a column containing basic aluminum oxide and purified hereafter by degassing and distillation over calcium hydride (Acros Organics, 93%) and trioctylaluminium (Sigma Aldrich, 25 wt% in hexanes). *Sec*-butyllithium (*sec*-BuLi, Acros Organics, 1.3 M in cyclohexane/hexane (92/8)) was used as supplied.

All purification and reaction steps were conducted under Schlenk condition, meaning that all glassware was flame-dried three times prior to use and all manipulations were carried out either under high-vacuum ( $1\cdot 10^{-3}$  mbar) or an argon atmosphere. First, the monomers were dried under reduced pressure and room temperature over ground calcium hydride over night after degassing by three freeze-thaw-cycles. On the next day, the monomers were distilled into a flask containing trioctylaluminium obtained by evaporation of the solvent under reduced pressure. Again, purification was performed over night at room temperature and reduced pressure. Then, the monomers were distilled into a graduated ampoule, which was flooded with argon after thawing. Cyclohexane was freshly distilled under normal pressure and drained into an evacuated glass reactor with a Nd stirring bar. The reaction flask was flushed with argon after cooling cyclohexane to room temperature. The ampoules were mounted to the reaction flask with transition pieces connected to the Schlenk line.

The initiator *sec*-BuLi was added to the solvent in an argon counterflow. Subsequently, the whole glass apparatus was sealed, and the solvent was heated to either  $40^\circ\text{C}$  or  $60^\circ\text{C}$  for the preparation of tapered or sequential block copolymers, respectively. Then, the first monomer feed was added under vigorous stirring. The reaction time for each pure block or tapered diblock was calculated using a kinetic Monte-Carlo simulation. Typical reaction times per block or tapered diblock sequence ranged between 30 min and 5 hours, depending on the

concentration and temperature. Details can be found in the Supp. Inf. of previous publications.<sup>[2,5]</sup> To guarantee full monomer conversion, the calculated reaction times were extended by 10%. After all monomer feeds and their consumption, the living chain ends were terminated by addition of methanol in an Argon counterflow. The polymers were precipitated pouring the reaction solution into a 5-10-fold excess of methanol, dried at reduced pressure for at least one week and stored in the absence of light at -20 °C under argon atmosphere.

### Viscometry

The intrinsic viscosities  $[\eta]$  were averaged over the values obtained by the Huggins and the Kraemer extrapolation procedures (equations 1 and 2), analyzing the specific or relative viscosities  $\eta_{sp}$  and  $\eta_r$  at varying concentration  $c$ .

$$\frac{\eta_{sp}}{c} = \frac{\eta_r - 1}{c} = [\eta] + k_H[\eta]^2 c \quad (1)$$

$$\frac{\ln \eta_r}{c} = [\eta] + k_K[\eta]^2 c \quad (2)$$

The relative viscosities of the polymer solutions in toluene were recorded using an Anton Paar Automated Microviscometer. The respective flow times of the solvent and the polymer solutions were determined in a measuring system of capillary/ball combination at 20 °C at a tilting angle of 45°. Huggins extrapolation plots exemplified for series 1 are given in the Supp. Inf. (see Figure S2).

### Size Exclusion Chromatography

Size exclusion chromatography (SEC) was performed in THF using a differential refractive index detector coupled with a differential viscometer and a multiangle light scattering (MALLS) detector, yielding the average molar masses ( $M_n$  and  $M_w$ ,  $M_{[\eta]}$  and  $M_{LS}$ ) as well as the intrinsic viscosity  $[\eta]$ . The number- and weight-average molar masses  $M_n$  and  $M_w$  were obtained by the universal calibration method,  $M_{[\eta]}$  corresponds to the molar mass from viscosity detection and  $M_{LS}$  is the weight-average molar mass by MALLS detection. Besides, the refractive index increments  $dn \cdot dc^{-1}$  were determined at 25 °C using an Optilab rEX system with a 658 nm laser supplied by Wyatt.

### Analytical Ultracentrifugation

Sedimentation velocity analysis were performed using a Beckman Coulter ProteomeLab XL-I analytical ultracentrifuge with double-sector aluminum centerpieces with a 12 mm optical path length. The centerpieces were placed in a four-whole rotor (An-60Ti), applying a rotor speed of 40000 to 60000 rpm depending on the sample. Sedimentation was followed by the interference optical detection system. The data were analyzed using the continuous  $c(s)$  analysis in the Sedfit program, which is based on the numerical solutions of the Lamm equation.<sup>[27]</sup>

In the first place, processing the velocity sedimentation data with the modern analytical solutions (Sedfit or others), allows determination of both the sedimentation coefficients (and their distributions) and the translation diffusion coefficients, which in turn leads to the molar mass determination via the Svedberg relationship (equation 3).

$$M_{s,D} = s_0 RT \cdot [D_0(1 - \nu\rho_0)]^{-1} = R \cdot [s] \cdot [D]^{-1} \quad (3)$$

$s_0$  and  $D_0$  denote the sedimentation and the translation diffusion coefficients at infinite dilution, whereas  $[s]$  and  $[D]$  are the intrinsic sedimentation and translation diffusion coefficients.  $R$  is the universal gas constant,  $T$  the absolute temperature,  $\nu$  the partial specific volume of the polymer and  $\rho_0$  the solvent density. The term  $(1 - \nu\rho_0)$  is also called the buoyancy factor.

The translation diffusion coefficients estimated by the  $c(s)$  analysis are initially represented in a form of the frictional ratios ( $f/f_{\text{sph}}$ ), where  $f$  is the translation friction coefficient for a given macromolecule or particle and  $f_{\text{sph}}$  is that of a solid spherical particle having the same mass and density as the given macromolecule or particle. This is a well-known analytical construct in polymer physics (and biophysics) that can be used in particular as a measure of particle asymmetry as well. The  $c(s)$  analysis provides the weight-average frictional ratio of all species in the sample. The values along with the sedimentation coefficients were extrapolated to zero solute concentration  $(f/f_{\text{sph}})_0$  and used to calculate the molar masses via the the modified Svedberg equation (equation 4), with  $N_A$  denoting the Avogadro number.

$$M_{s,f} = 9\pi \cdot 2^{0.5} \cdot N_A \cdot \left( [s] \cdot \left( \frac{f}{f_{\text{sph}}} \right)_0 \right)^{1.5} \cdot \nu^{0.5} \quad (4)$$

The hydrodynamic characteristics, which permit access the gross conformation of polymers in solution, are the intrinsic viscosity  $[\eta]$ , the translation diffusion coefficient at infinite dilution  $D_0$  as well as the sedimentation coefficient at infinite dilution  $s_0$ . According to the equations 5 (Flory-Fox relation), 6 (Stokes-Einstein-Kirkwood relation) and 7 (Svedberg relation), all parameters scale with the hydrodynamic radius of the polymer coil in solution, or to be more precise, the mean-square end-to-end distance of the polymer chain  $\langle h^2 \rangle$ . Since the intrinsic viscosity scales with hydrodynamic size to the power of 3 (equation 5), it is most sensitive to size variation.

$$[\eta] = \Phi \cdot \langle h^2 \rangle^{3/2} \cdot M^{-1} \quad (5)$$

$$D_0 = k_B T \cdot (P \cdot \eta_0 \cdot \langle h^2 \rangle^{1/2})^{-1} \quad (6)$$

$$s_0 = M \cdot (N_A \cdot P \cdot \eta_0 \cdot \langle h^2 \rangle^{1/2})^{-1} \quad (7)$$

$\Phi$  and  $P$  denote Flory hydrodynamic parameters,  $k_B$  is the Boltzmann constant, and  $\eta_0$  the solvent viscosity.

Since these hydrodynamic characteristics are related to the same macromolecular parameters such as molar mass and mean-square end-to-end distance ( $[\eta] \sim \langle h^2 \rangle^{3/2} M^{-1}$ ,  $D_0 \sim \langle h^2 \rangle^{-1/2}$ ,  $s_0 \sim M \langle h^2 \rangle^{-1/2}$ ), the interrelation between these characteristics can be established via the hydrodynamic invariant  $A_0$  (equation 8).<sup>[28,29]</sup> The intrinsic diffusion and sedimentation

coefficients can be calculated by equation 9 and 10, respectively, with the buoyancy factor depending on the polymer's partial specific volume and the solvent density (equation 11).

$$A_0 = (R \cdot [s] \cdot [D]^2 [\eta])^{1/3} = R \cdot [s] \cdot [\eta]^{1/3} \cdot M^{-2/3} \quad (8)$$

$$[D] = D_0 \cdot \eta_0 \cdot T^{-1} \quad (9)$$

$$[s] = s_0 \cdot \eta_0 (1 - v\rho_0)^{-1} \quad (10)$$

## Density Measurements

The partial specific volume  $v$  was determined by density measurements according to the procedure of Kratky *et al.* (equation 11).<sup>[30]</sup>

$$(\rho - \rho_0) = (1 - v\rho_0)c \quad (11)$$

Density measurements were performed with a DMA 5000M density meter supplied by Anton Paar at concentration  $c$  in the range of  $(0.05\text{--}2.3) \cdot 10^{-2} \text{ g} \cdot \text{mL}^{-1}$ . The determination of the required partial specific volume is exemplarily shown for series 1 in the Sup. Inf. (see Figure S3).

## Hydrodynamic Characteristics in Cyclohexane

This work summarizes the in-depth study of the multiblock copolymers' chain conformation in toluene as non-selective solvent. By increasing the solvent quality towards one of the two blocks, the influence of the block profile on the gross conformation of the polymer coils in solution is expected to be prominent as well. Preliminary velocity analyses in cyclohexane at varying temperature are given in the Sup. Inf. (see Hydrodynamic Characteristics in Cyclohexane, Figure S4). Detailed investigation of these complex systems will be subject of upcoming works.

## Results and Discussion

The scope of this work comprises a systematic conformational analysis of dilute solutions of multiblock copolymers with varied block number based on isoprene and styrene in toluene as a good solvent for both constituent comonomers.

For this purpose, (IS)<sub>n</sub>I multiblock copolymers covering a wide range of molar masses (40 – 400 kg·mol<sup>-1</sup>) and block numbers (3 – 13) are investigated, while keeping the overall ratio of solvophilic to solvophobic units (70 mol% isoprene and 30 mol% styrene) constant. On top, for each chain composition tapered and sequential block structures are introduced, with the tapered copolymers exhibiting a rather sharp, but gradual change in comonomer composition along every diblock sequence. Figure 1 visualizes the tri- and multiblock copolymers studied in this work. The tapered structures (Figure 1, right) are simulated based on the reactivity ratios of isoprene and styrene at 40 °C in cyclohexane ( $r_1=10.9$  and  $r_2=0.029$ ).<sup>[5]</sup>

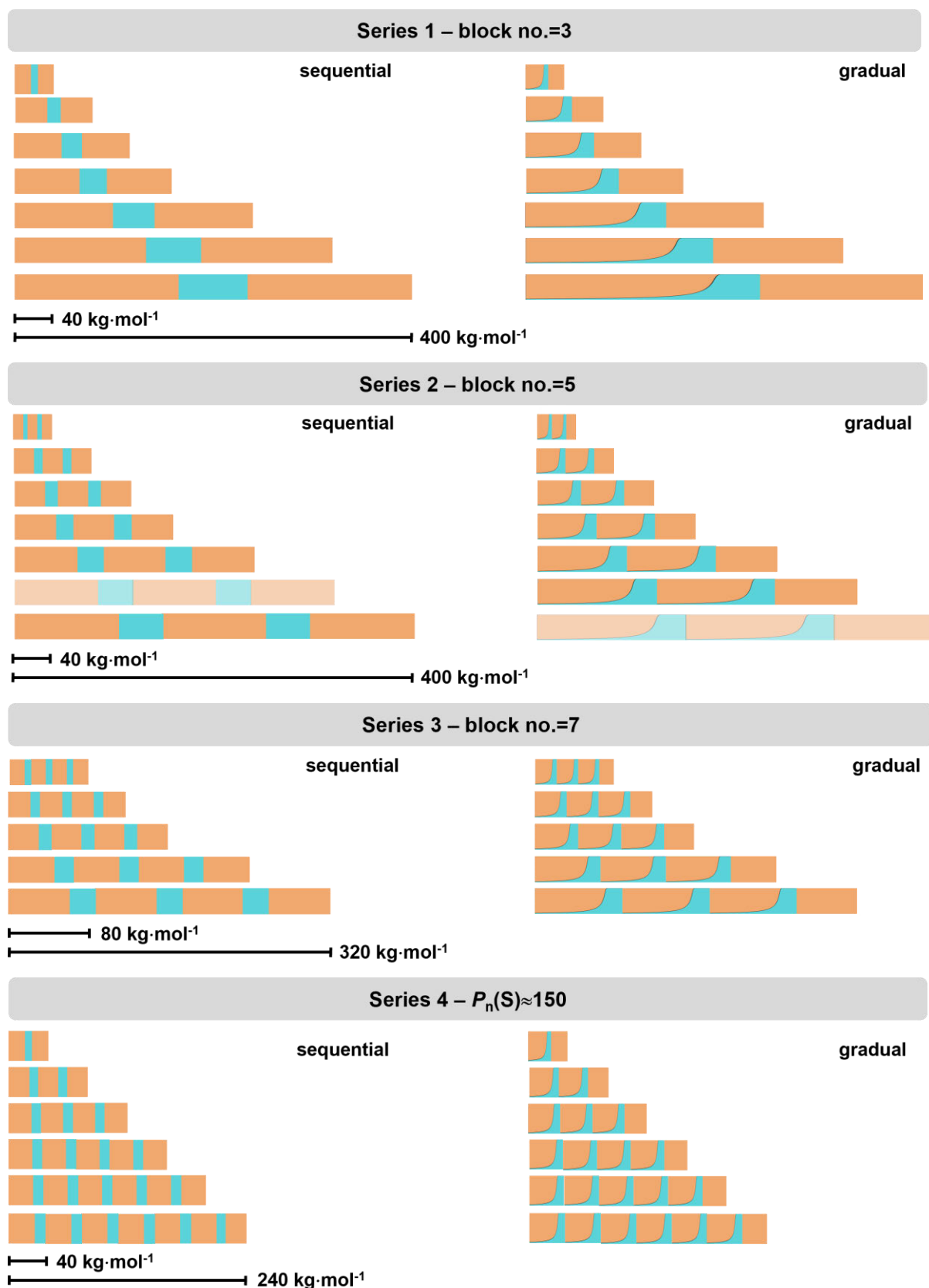


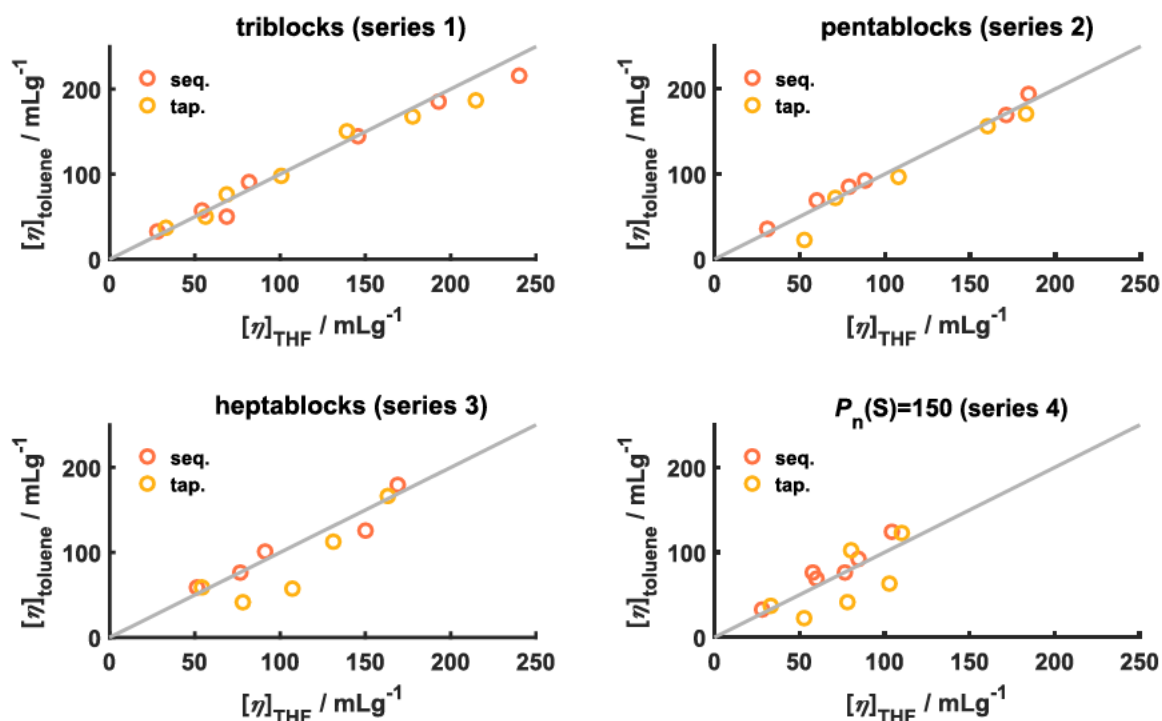
Figure 1: Schematic representation of the polymer series analyzed within this work showing the distribution of the comonomers isoprene (orange) and styrene (cyan) along the polymer chain (molar-based composition diagrams showing the mean incorporation (y axis) at every conversion (x axis)). Lightly colored polymers are missing in the systematic series.

Previous works showed that the statistical copolymerization of isoprene and styrene in nonpolar solvents like cyclohexane results in the formation of a tapered diblock structure with a gradual transition from polyisoprene to polystyrene.<sup>[8,31]</sup> Repeating this statistical copolymerization step allows the synthesis of tapered multiblock copolymers. On the other hand, the sequential block structures were obtained implementing iterative stepwise polymerization of first isoprene and, after full consumption, styrene. For both structures with different block profiles (tapered and sequential), polyisoprene exhibits almost exclusively 1,4-units ( $\geq 93\%$ ) since it is polymerized in cyclohexane. Table S1 summarizes the molecular characteristics of the synthesized polymers. Well-defined polymers could be obtained. SEC measurements show monomodal, narrow molar mass distributions with low dispersity (see Figure S1).

In this work, four systematic polymer series have been investigated (Figure 1) comprising three series of polymers with identical block number, whose individual block lengths vary with the overall molar mass (series 1, 2 and 3 corresponding to the tri-, penta- and heptablock copolymers, respectively). The polymers of series 4 exhibit an identical degree of polymerization per individual polystyrene block and the molar masses within this series increases by chain extension by a diblock sequence.

### Intrinsic Viscosity Determination

The intrinsic viscosities were measured in THF and toluene, using a differential viscometer coupled to SEC and a rolling ball viscometer, respectively.



**Figure 2:** Correlation between the intrinsic viscosities for the triblock (series 1, top left), pentablock (series 2, top right), heptablock copolymers (series 3, bottom left) and copolymers with the same degree of polymerization per PS block (series 4, bottom right). The intrinsic viscosities were obtained by rolling-ball viscometry  $[\eta]_{\text{toluene}}$  and SEC coupled to a differential viscosimeter  $[\eta]_{\text{THF}}$ , measured in toluene and THF, respectively.

Extrapolation to zero concentration according to the Huggins and Kramer relation (equation 1 and 2) gave the intrinsic viscosities, whose magnitudes were averaged out. Both toluene and THF are thermodynamically good solvents for polystyrene and polyisoprene. Figure 2 shows that the intrinsic viscosities in toluene and THF show practically the same values. However, for series 3 and series 4, the intrinsic viscosities of the tapered structures seem to be slightly lower than for the sequential structures. Yet, they correlate among themselves, with the sequential structures exhibiting a slightly better correlation than the tapered structures. This proves the consistency between the measurements in THF and toluene, emphasizing the validity of the below described approach for the estimation of the average molar mass relying on hydrodynamic invariants.

### Molar Mass Determination

A multiplicity of orthogonal experiments was conducted to determine the molar masses. These comprise size exclusion chromatography in THF and velocity sedimentation experiments in toluene, yielding  $M_n$ ,  $M_w$ ,  $M_{[\eta]}$ ,  $M_{LS}$  in THF and  $M_{sf}$  in toluene (see Experimental Part).  $M_{sf}$  is calculated by the modified Svedberg equation (equation 4). All initially obtained values are listed in Table S2. As can be seen, in many cases, a notable discrepancy between the values is in place.

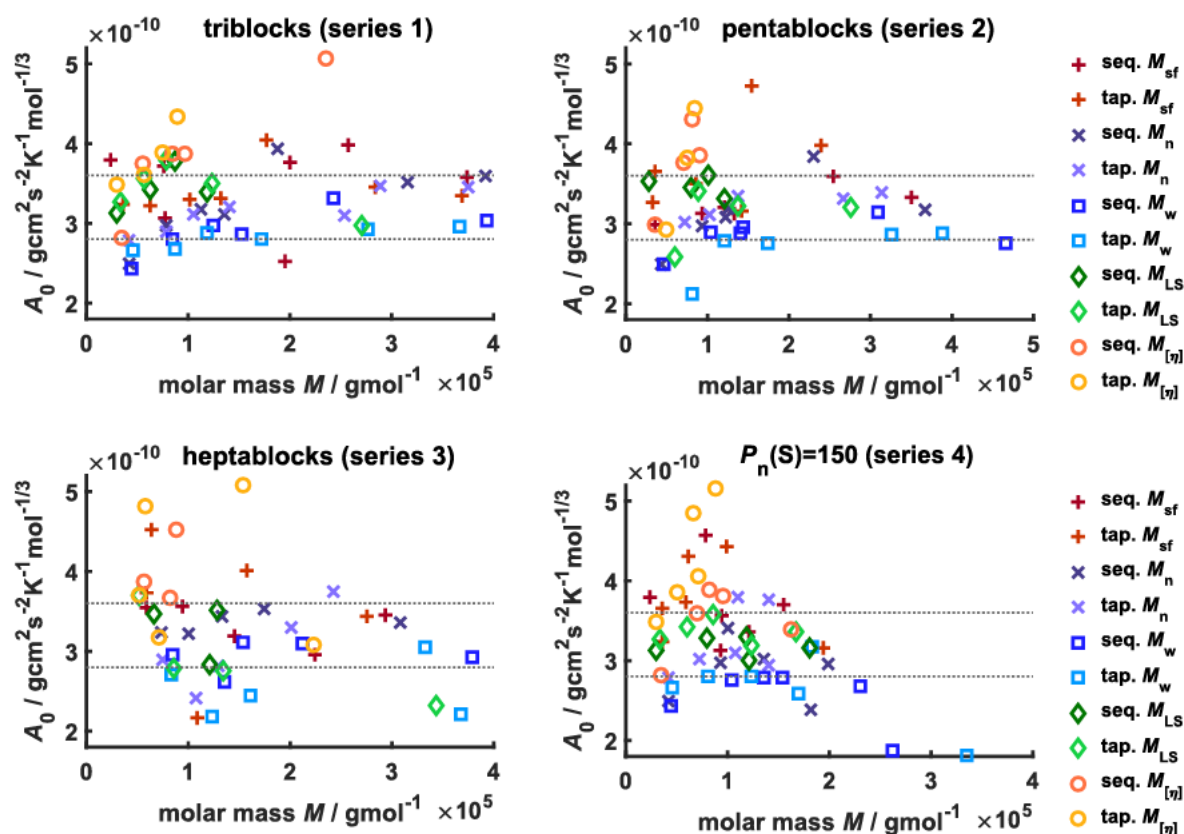


Figure 3: Plot of the hydrodynamic invariants  $A_0$  calculated by equation 8 against the different molar masses for the triblock (series 1, top left), pentablock (series 2, top right), heptablock copolymers (series 3, bottom left) and copolymers with the same degree of polymerization per PS block (series 4, bottom right). The grey lines mark the limits of the range in which the molar masses were used for the calculation of an average molar mass.

In order to operate with the statistically most relevant and physically sound values for a given macromolecular population, the concept of the hydrodynamic invariants  $A_0$  was used.

As described before, the hydrodynamic invariant  $A_0$  expresses the interrelation of the three fundamental solution characteristics, i.e., the intrinsic viscosity  $[\eta]$ , the translation diffusion coefficient  $D_0$ , and the sedimentation coefficient  $s_0$  (equation 8) that are related to the molar mass and the size of the macromolecules.

Theoretically, the limits of the hydrodynamic invariant are  $A_0=2.914$  and  $4.15 \cdot 10^{-10} \text{ g} \cdot \text{cm}^2 \text{s}^{-2} \text{K}^{-1} \text{mol}^{-1/3}$ , corresponding to the lower limit of a solid impermeable spherical conformation and a rigid polymer and therefore an expanded chain conformation, respectively.<sup>[28,29]</sup> Generally, the experimental  $A_0$  values of flexible linear polymers in thermodynamically good solvents are in the range of  $(3.2 \pm 0.2) \cdot 10^{-10} \text{ g} \cdot \text{cm}^2 \text{s}^{-2} \text{K}^{-1} \text{mol}^{-1/3}$ .

Figure 3 shows the distribution of hydrodynamic invariants  $A_0$  for the different molar masses. The grey lines marking the “acceptable” range of  $A_0$  ( $A_0=(3.2 \pm 0.4) \cdot 10^{-10} \text{ g} \cdot \text{cm}^2 \text{s}^{-2} \text{K}^{-1} \text{mol}^{-1/3}$ ) that was applied to select the most relevant molar mass values that were further used for the conformational analysis. The average molar mass values are shown in Table S2.

## Conformation Analysis in Toluene

### Classical Scaling Relationships

In order to access information on the gross conformation of the multiblock copolymers in the non-selective solvent toluene, which is a good solvent for both polyisoprene and polystyrene, classical scaling relationships for the intrinsic viscosity  $[\eta]$ , the diffusion coefficient  $D_0$  at infinite dilution, and the sedimentation coefficient  $s_0$  at infinite dilution are examined. According to equations 12-14, for homopolymers both the hydrodynamic characteristics performed under rotational ( $[\eta]$ ) and translational friction ( $s_0$ ,  $D_0$ ) exhibit power-law dependencies on the molar mass  $M$ .

$$[\eta] \sim M^{b_{[\eta]}} \quad (12)$$

$$D_0 \sim M^{b_{D_0}} \quad (13)$$

$$s_0 \sim M^{b_{s_0}} \quad (14)$$

Figure 4 shows the power-law dependencies for the polymer series investigated. The scaling indices  $b_i$  are derived from the slope of a linear fit of the double logarithmic plot of the hydrodynamic characteristics against the molar mass and compiled in Table 1.

In order to validate and further proceed with the analysis of the scaling indices and gross conformation, their intercorrelation must be fulfilled within the known relationships. (equations 15 and 16). These values are given in Table 1 as well.

$$|b_{D_0}| + b_{s_0} = 1 \quad (15)$$

$$b_{D_0} = (1 + b_{[\eta]})/3 \quad (16)$$



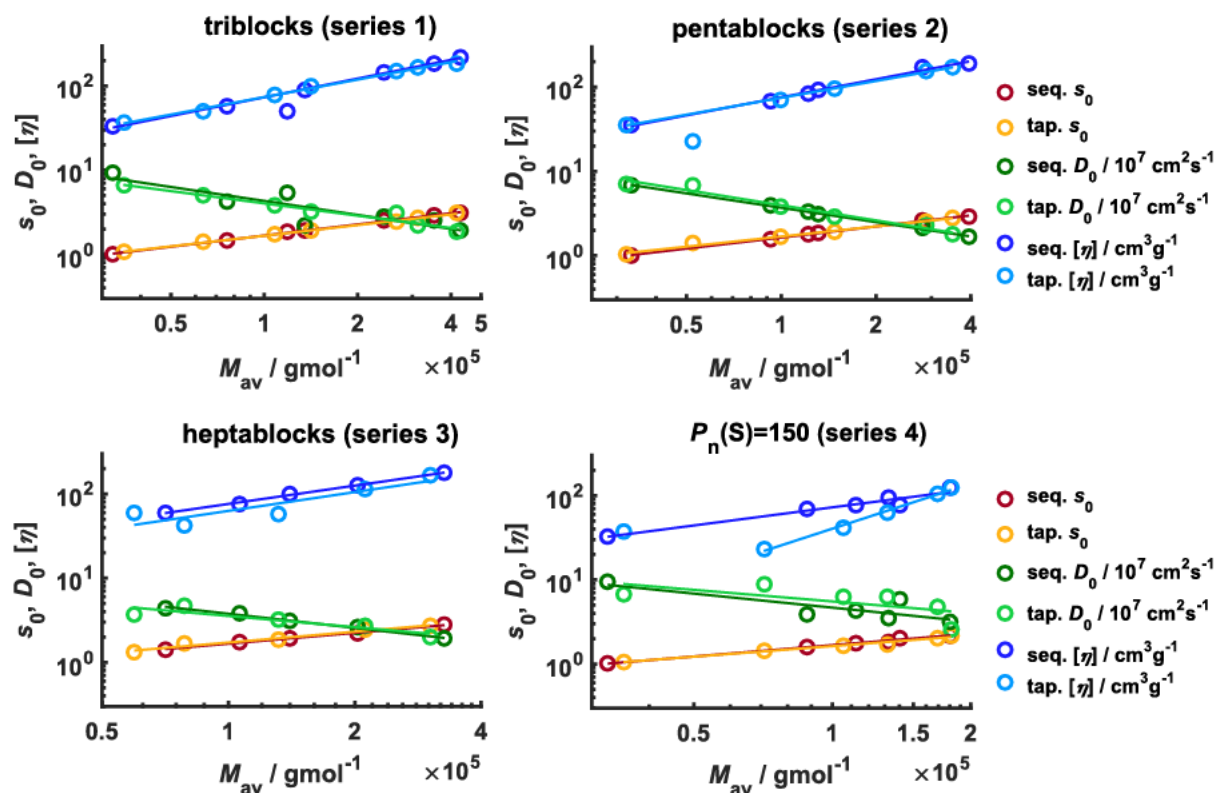


Figure 4: Double logarithmic plot of the sedimentation coefficient  $s_0$  at infinite dilution (red), the diffusion coefficient  $D_0$  at infinite dilution (green) and the intrinsic viscosity  $[\eta]$  (blue) in toluene at 20 °C against the average molar mass  $M_{av}$  of the triblock (series 1, top left), pentablock (series 2, top right), heptablock copolymers (series 3, bottom left) and copolymers with the same degree of polymerization per PS block (series 4, bottom right). The slope of the linear fits corresponds to the scaling indices  $b_i$ .

It should be noted that for polymers with an identical number of blocks (series 1-3), scaling relationships have linear trends and obey the interrelation within the experimental error according to equation 15 and 16, which is typical for homologous polymers. However, in case of multiblock copolymers with the same individual block lengths (series 4), the hydrodynamic characteristics, do not comply with the power-law dependencies on the molar mass  $M$ . This is most pronounced for the intrinsic viscosity  $[\eta]$  because it is most sensitive to changes in the hydrodynamic size. Most likely this can be related to different amounts of heterocontacts, which influence the molecular dimension in solution. Therefore, they cannot be considered as structural homologues.

The magnitude of the scaling indices (series 1-3) refers to a random coil conformation in thermodynamically good solvents. Similar scaling indices were established for the respective homopolymers ( $b_{[\eta]}(\text{PI})^{\text{toluene}, 30\text{ °C}} = 0.728^{[32]}$  and  $b_{[\eta]}(\text{PS})^{\text{toluene}, 25\text{ °C}} = 0.736^{[33]}$ ). Differences in the intrinsic viscosities with increasing block number as noted by Schlick and Levy<sup>[20]</sup> cannot be observed.

Comparing the scaling indices of the intrinsic viscosity for the different block profile structures within the homologous series, the sequential copolymers exhibit higher values than the tapered analogous. From this results from rotational friction experiments, it can be deduced that the sequential copolymer coils adopt a more extended conformation, whereas the tapered copolymers are more flexible.

**Table 1:** Overview of the scaling indices of the the intrinsic viscosity  $b_{[\eta]}$ , diffusion coefficient  $b_{D_0}$ , and sedimentation coefficient  $b_{s_0}$  derived from a linear regression of the double logarithmic plot of the corresponding hydrodynamic characteristic and the molar mass  $M$  (see Figure 4). Besides, the values to evaluate the interrelation according to the equations 14 and 15 are given.

| multiblock series         | (IS) <sub>n</sub> I block type | $b_{[\eta]}$     | $b_{D_0}$         | $b_{s_0}$        | $b_{s_0} +  b_{D_0} $ | $(1 + b_{[\eta]})/3$ |
|---------------------------|--------------------------------|------------------|-------------------|------------------|-----------------------|----------------------|
| triblock copolymers       | tapered                        | 0.690<br>± 0.025 | -0.485<br>± 0.049 | 0.420<br>± 0.010 | 0.90                  | 0.56                 |
|                           | sequential                     | 0.738<br>± 0.010 | -0.531<br>± 0.132 | 0.440<br>± 0.006 | 0.99                  | 0.58                 |
| pentablock copolymers     | tapered                        | 0.664<br>± 0.017 | -0.599<br>± 0.051 | 0.399<br>± 0.025 | 1.00                  | 0.55                 |
|                           | sequential                     | 0.712<br>± 0.023 | -0.566<br>± 0.012 | 0.436<br>± 0.010 | 1.00                  | 0.57                 |
| heptablock copolymers     | tapered                        | 0.741<br>± 0.219 | -0.439<br>± 0.126 | 0.425<br>± 0.043 | 0.86                  | 0.58                 |
|                           | sequential                     | 0.723<br>± 0.028 | -0.558<br>± 0.031 | 0.427<br>± 0.017 | 0.98                  | 0.57                 |
| $P_n(S)/\text{block}=150$ | tapered                        | 1.779<br>± 0.081 | -0.455<br>± 0.260 | 0.416<br>± 0.027 | 0.87                  | 0.93                 |
|                           | sequential                     | 0.714<br>± 0.087 | -0.544<br>± 0.191 | 0.448<br>± 0.015 | 1.00                  | 0.57                 |

### Thermodynamic Rigidity of the Polymer Chains

Further interpretation of the hydrodynamic data is related to the evaluation of the conformational parameters that define the polymer conformation and consequent behavior in solution. The fundamental conformational parameters are the thermodynamic rigidity (Kuhn segment length)  $A$  and the diameter of the polymer chains  $d$ . The rigidity primarily depends on the interaction of the polymer's chain segments among each other as well as with the solvent. With  $1 > b_{[\eta]} > 0.5$  and or  $0.33 < b_{s_0} < 0.5$ , both excluded volume effects and intramolecular draining effects have to be taken into account. Therefore, the Gray-Bloomfield-Hearst theory, which describes translational friction based on a worm-like necklace model, was applied (Equation 17).<sup>[34]</sup> Calculations were performed using the parameter  $\varepsilon$ , which characterizes the deviation of the mean-square end-to-end distance from the ideal Gaussian due to volume swelling effects ( $\langle h^2 \rangle M^{1+\varepsilon}$ ).

$$[s] \cdot P \cdot N_A = \left( \frac{3}{1-\varepsilon} (3 - \varepsilon) \right) \cdot \frac{M_L^{(1+\varepsilon)/2}}{A^{(1-\varepsilon)/2}} M^{(1-\varepsilon)/2} + \frac{PM_L}{3\pi} \cdot \left( \frac{\ln A}{d} - \left( \frac{3A}{d} \right)^{-1} - \varphi(\varepsilon) \right) \quad (17)$$

where  $P$  is the Flory hydrodynamic parameter,  $N_A$  the Avogadro number,  $\varepsilon$  is the hydrodynamic parameter,  $M_L$  the mass per unit lengths of the polymer,  $M$  is the average molar mass of the whole polymer, and  $\varphi(\varepsilon)$  is a function which can approximated by  $\varphi(\varepsilon)=1.431+2.64\varepsilon+4.71\varepsilon^2$ .<sup>[35]</sup> The mass per unit lengths  $M_L$  was averaged over the mass of a isoprene and a styrene repeating

unit and weighted with its molar fraction. The hydrodynamic parameter  $\varepsilon$  is calculated by equation 18.<sup>[36]</sup>

$$\varepsilon = \frac{2b[\eta]^{-1}}{3} = 2 \cdot |b_{D_0}| - 1 = 1 - 2b_{S_0} \quad (18)$$

Figure 5 displays the linear regression according to the Gray-Bloomfield-Hearst theory for the polymer series investigated. For the homologous series with identical block number (series 1-3) good correlation can be found, whereas the values of the polymers which vary in molar mass and block number (series 4) scatter more pronouncedly. The slope of the corresponding dependencies will yield the rigidity parameter, while the hydrodynamic diameter  $d$  can be calculated from the intercept of the linear regression.

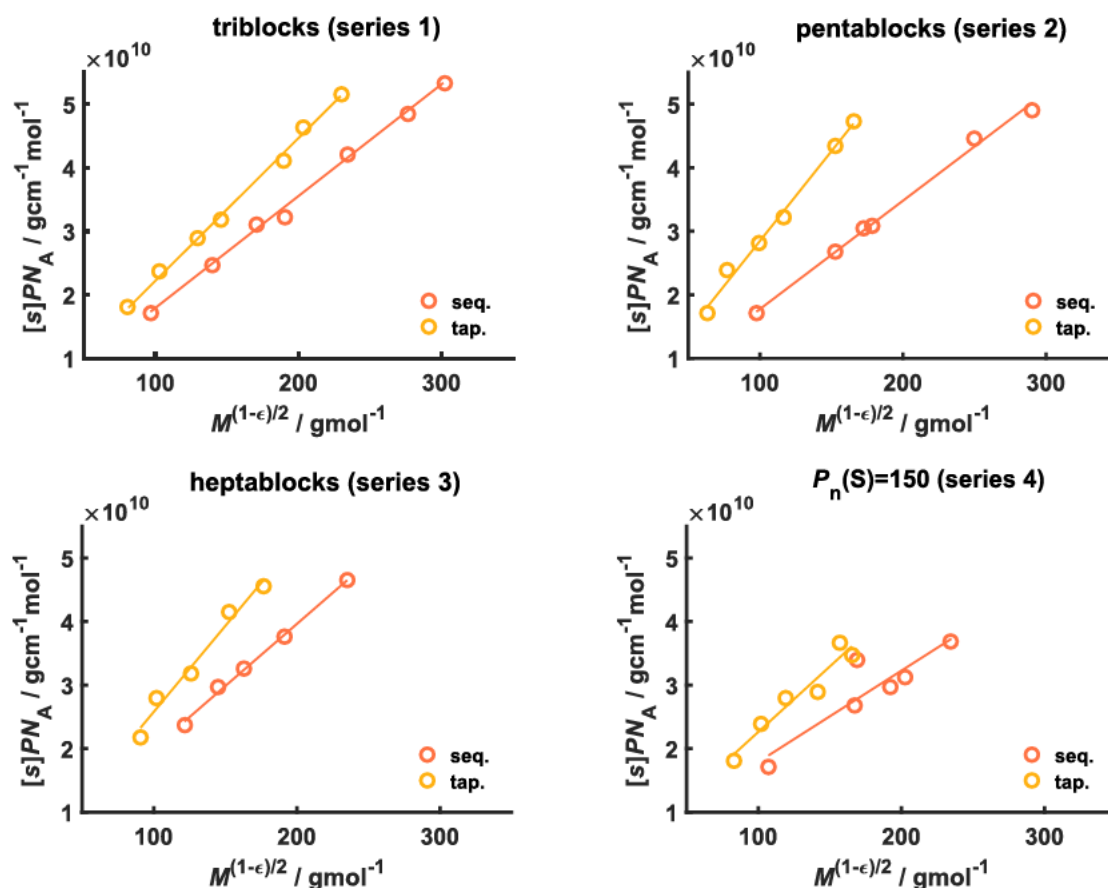


Figure 5: Correlation between the intrinsic diffusion coefficient  $[s]$  and the molar mass  $M$  according to the Gray-Bloomfield-Hearst theory (equation 16) of the triblock (series 1, top left), pentablock (series 2, top right), heptablock copolymers (series 3, bottom left) and copolymers with the same degree of polymerization per PS block (series 4, bottom right). The corresponding thermodynamic parameters  $\varepsilon$ , the slopes of the linear fits and the Kuhn segment lengths  $A$  derived thereof are given in Table 2.

The derived Kuhn segment lengths are listed in Table 2. With average Kuhn segment lengths of  $A_{\text{tap}} = 1.4$  nm and  $A_{\text{seq}} = 1.9$  nm, the tapered structures of the homologous series 1-3 exhibit shorter Kuhn lengths. In spite of the higher errors of the linear regression for series 4, this trend is also valid. Significantly longer Kuhn lengths are obtained, which again indicates that the block number affects the chain conformation.

The theoretical treatment of a polymer chain according to the Kuhn theory considers a polymer chain being composed of freely joined segments. These segments with their Kuhn segment

lengths being larger than the individual length of a repeating unit accounts for restricted bond and torsion angles. As a result, the Kuhn segment length is a measure for a polymer's stiffness, which translates to the sequential structures being stiffer than their tapered analogues.

**Table 2:** Thermodynamic parameters  $\varepsilon$  (equation 16), the slopes of the linear fits of Figure 5 according to the Gray-Bloomfield-Hearst theory (equation 16) and the Kuhn segment lengths  $A$  in toluene.

| multiblock series                           | (IS) <sub>n</sub> I block type | $\varepsilon$ | slope / $10^8 \text{ cm}^{-2}$ | $A$ / nm |
|---------------------------------------------|--------------------------------|---------------|--------------------------------|----------|
| <b>triblock copolymers</b>                  | tapered                        | 0.16          | $2.23 \pm 0.06$                | 1.61     |
|                                             | sequential                     | 0.12          | $1.76 \pm 0.04$                | 1.85     |
| <b>pentablock copolymers</b>                | tapered                        | 0.20          | $2.83 \pm 0.13$                | 1.39     |
|                                             | sequential                     | 0.12          | $1.71 \pm 0.06$                | 1.98     |
| <b>heptablock copolymers</b>                | tapered                        | 0.18          | $2.70 \pm 0.24$                | 1.23     |
|                                             | sequential                     | 0.14          | $1.95 \pm 0.08$                | 1.79     |
| <b><math>P_n(S)/\text{block}=150</math></b> | tapered                        | 0.16          | $2.06 \pm 0.27$                | 1.94     |
|                                             | sequential                     | 0.10          | $1.44 \pm 0.35$                | 2.38     |

In conclusion, the data from translational friction experiments imply that the sequential copolymer coils are more rigid than their tapered counterparts. This observation is in line with the data from rotational friction experiments (*vide supra*), also indicating a more extended coil conformation for the sequential structures.

On a molecular level, the higher flexibility of the tapered structures is rooted in the gradient distribution of the isoprene and styrene repeating units, which results from the statistical incorporation during copolymerization. The comonomer incorporation is controlled by the crossover rate constants, with  $k_{SI} \gg k_{IS}$ . With the fast crossover from styrene to isoprene, isoprene is strongly favored as the living chain end and hence isoprene is preferentially incorporated at the beginning of the copolymerization. Yet, the polyisoprene block is interrupted by single styrene repeating units. With proceeding copolymerization, the concentration of isoprene decreases and styrene is incorporated into the polymer chain to a larger extent. After all isoprene is consumed, the remaining styrene is polymerized resulting in a pure polystyrene block, which is effectively shortened compared to the sequential counterpart with an identical molar mass and molar ratio of the comonomers. Since the tapered structures are more flexible, one might speculate that the styrene repeating units adjacent to isoprene repeating units cause less restrictions with respect to bond and torsion angle.

## Conclusion

This work presents a systematic study of the gross solution conformation of sequential and tapered multiblock copolymers based on isoprene and styrene, the latter exhibiting a gradual transition between the comonomers per diblock sequence.

The solution properties in toluene as non-selective solvent have been studied comprehensively by velocity sedimentation experiments, viscometry, and densitometry. These experiments ensure a straightforward characterization of the polymer systems with high accuracy. Independent determination of the intrinsic viscosities confirmed the validity of the solution characterization. Absolute molar masses of the multiblock copolymers covering the range from 40 – 400 kg·mol<sup>-1</sup> were determined by complementary approaches, such as size exclusion chromatography with light scattering detection or with a combination of refractive index detection and differential viscometry. Even though narrow and unimodal size distribution were obtained, sometimes the absolute techniques failed. Based on the hydrodynamic invariants, the consistency between the solution properties and the determined molar masses was examined, allowing for averaging over the statistically most relevant values.

With the solid set of solution characteristics and molar masses at hand, the gross conformation of different polymer series was assessed implementing classical relationships between the hydrodynamic characteristics and the molar mass. Evaluating polymers with identical block numbers revealed good agreement, showing that the polymer series of triblock, pentablock and heptablock copolymers can be treated as homologues. The magnitude of the scaling indices lies in the range for flexible polymer systems in a thermodynamically good solvent, as it is expected for polyisoprene and polystyrene in toluene. The scaling behavior of the intrinsic viscosities (rotational friction) for different gradient types evidenced a more extended chain conformation for the sequential multiblock copolymers compared to their tapered counterparts. This is in line with the statistical chain parameters calculated from sedimentation analyses (translational friction), yielding higher Kuhn segment lengths and hence a higher rigidity for the sequential block copolymers of the homologous polymer series.

Polymers with varied molar mass by extending the chain architecture with a diblock sequence do not comply with the classical scaling behavior in the case of the intrinsic viscosity, which is expressed in poor correlation of the hydrodynamic characteristic with the molar mass. This indicates that the solution properties of multiblock copolymers in a good solvent do not only depend on the molar mass but also the number of heterocontacts, which increases with the block number. This is further emphasized by significantly higher magnitudes of the Kuhn segment lengths compared to the homologous tri-, penta- and heptablock copolymer series.

## References

- [1] a) M. O. Tuhin, J. J. Ryan, J. D. Sadler, Z. Han, B. Lee, S. D. Smith, M. A. Pasquinelli, R. J. Spontak, *Macromolecules* **2018**, *51*, 5173; b) L. Leibler, *Macromolecules* **1980**, *13*, 1602; c) D. Lairez, M. Adam, J.-P. Carton, E. Raspaud, *Macromolecules* **1997**, *30*, 6798; d) J. R. Urwin, M. Girolamo, *Eur. Polym. J.* **1971**, *7*, 785; e) L. Leibler, H. Orland, J. C. Wheeler, *J. Chem. Phys.* **1983**, *79*, 3550; f) C. Sinturel, F. S. Bates, M. A. Hillmyer, *ACS Macro Lett.* **2015**, *4*, 1044.
- [2] M. Steube, T. Johann, R. D. Barent, A. H. Müller, H. Frey, *Prog. Polym. Sci.* **2022**, *124*, 101488.
- [3] a) J. G. Drobny, *Handbook of thermoplastic elastomers*, Andrew Elsevier, Oxford, **2014**; b) K. Knoll, N. Nießner, *Macromol. Symp.* **1998**, *132*, 231; c) H.-C. Kim, S.-M. Park, W. D. Hinsberg, *Chemical reviews* **2010**, *110*, 146; d) J. Yan, R. J. Spontak in *Elastomer Blends and Composites*, Elsevier, **2022**, pp. 353–404.
- [4] a) L. R. Rudnick, *Lubricant Additives. Chemistry and Applications, Third Edition*, CRC Press, Portland, **2017**; b) A. Martini, U. S. Ramasamy, M. Len, *Tribol. Lett.* **2018**, *66*, 1; c) D. Clair, D. Evans, *Lubricating compositions*, US3772196, **1973**; d) D. H. Olson, D. L. Handlin, *Polymeric viscosity index improver and oil composition comprising the same*, US4788361A, **1988**; e) R. B. Rhodes, C. A. Stevens, *Star polymer viscosity index improver for oil lubricating compositions*, CA2152992C, **2006**; f) R. B. Rhodes, C. A. Stevens, *Asymmetric triblock copolymer viscosity index improver for oil compositions*, CA2155686A1, **2006**; g) R. J. A. Eckert, *Hydrogenated Star-Shaped Polymer*, US4116917A, **1978**; h) S. Briggs, C. Chu, *Viscosity index improvers for lubricating oil compositions*, US7163913B2, **2007**.
- [5] M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey, A. H. E. Müller, *Macromolecules* **2019**, *52*, 9299.
- [6] M. Steube, T. Johann, H. Hübner, M. Koch, T. Dinh, M. Gallei, G. Floudas, H. Frey, A. H. E. Müller, *Macromolecules* **2020**, *53*, 5512.
- [7] M. Morton, J. E. McGrath, P. C. Juliano, *J. Polym. Sci., Part C: Polym. Symp.* **1969**, *26*, 99.
- [8] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, *51*, 10246.
- [9] D. R. Paul, J. E. St. Lawrence, J. H. Troell, *Polym. Eng. Sci.* **1970**, *10*, 70.
- [10] J. E. Mark, *Physical properties of polymers handbook*, Springer Science & Business Media, New York, NY, **2007**.
- [11] a) C. Lai, W. B. Russel, R. A. Register, *Macromolecules* **2002**, *35*, 841; b) J. S. Higgins, J. V. Dawkins, G. G. Maghami, S. A. Shakir, *Polymer* **1986**, *27*, 931; c) J. S. Higgins, S. Blake, P. E. Tomlins, S. B. Ross-Murphy, E. Staples, J. Penfold, J. V. Dawkins, *Polymer* **1988**, *29*, 1968; d) Č. Koňák, G. Fleischer, Z. Tuzar, R. Bansil, *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 1312; e) W. Mandema, C. A. Emeis, H. Zeldenrust, *Makromol. Chem.* **1979**, *180*, 2163.
- [12] Q. Zhang, J. Lin, L. Wang, Z. Xu, *Prog. Polym. Sci.* **2017**, *75*, 1.
- [13] W. H. Stockmayer, M. Fixman, *J. Polym. Sci., Part C: Polym. Symp.* **1963**, *1*, 137.
- [14] P. A. Dondos, H. Benoît, *Makromol. Chem.* **1968**, *118*, 165.
- [15] A. Dondos, D. Froelich, P. Rempp, H. Benoit, *J. Chim. Phys.* **1967**, *64*, 1012.

- [16] J. Prud'Homme, J. Roovers, S. Bywater, *Eur. Polym. J.* **1972**, 8, 901.
- [17] a) N. Ho-duc, J. Prud'Homme, *Int. J. Polym. Mater.* **1976**, 4, 303; b) J. P. Plante, N. Ho-Duc, J. Prud'Homme, *Eur. Polym. J.* **1973**, 9, 77.
- [18] D. N. Cramond, J. R. Urwin, *Eur. Polym. J.* **1969**, 5, 35.
- [19] N. Corbin, J. Prud'Homme, *J. Polym. Sci., Polym. Phys. Ed.* **1977**, 15, 1937.
- [20] S. Schlick, M. Levy, *J. Phys. Chem.* **1960**, 64, 883.
- [21] Y. Tsunashima, M. Hirata, Y. Kawamata, *Macromolecules* **1990**, 23, 1089.
- [22] E. Raspaud, D. Lairez, M. Adam, J.-P. Carton, *Macromolecules* **1994**, 27, 2956.
- [23] B. H. Zimm, W. H. Stockmayer, *J. Chem. Phys.* **1949**, 17, 1301.
- [24] Y. Wang, W. L. Mattice, D. H. Napper, *Macromolecules* **1992**, 25, 4073.
- [25] J. Zhang, Z.-Y. Lu, Z.-Y. Sun, *Soft Matter* **2013**, 9, 1947.
- [26] S. Woloszczuk, M. Banaszak, P. Knychała, K. Lewandowski, M. Radosz, *J. Non-Cryst. Solids* **2008**, 354, 4138.
- [27] P. H. Brown, P. Schuck, *Biophys. J.* **2006**, 90, 4651.
- [28] V. N. Tsvetkov, P. N. Lavrenko, S. V. Bushin, *J. Polym. Sci., Polym. Chem. Ed.* **1984**, 22, 3447.
- [29] M. Grube, G. Cinar, U. S. Schubert, I. Nischang, *Polymers* **2020**, 12, 277.
- [30] O. Kratky, H. Leopold, H. Stabinger in *Methods Enzymol.*, Elsevier, **1973**, pp. 98–110.
- [31] D. J. Worsfold, *J. Polym. Sci., Part A-1: Polym. Chem.* **1967**, 5, 2783.
- [32] W. H. Beattie, C. Booth, *J. Appl. Polym. Sci.* **1963**, 7, 507.
- [33] R. Kniewske, W.-M. Kulicke, *Makromol. Chem.* **1983**, 184, 2173.
- [34] H. B. Gray, V. A. Bloomfield, J. E. Hearst, *J. Chem. Phys.* **1967**, 46, 1493.
- [35] G. M. Pavlov in *Prog. Colloid Polym. Sci., Vol. 119* (Eds.: W. Borchard, A. Straatmann), Springer Berlin Heidelberg, Berlin, Heidelberg, **2002**, pp. 149–158.
- [36] O. B. Ptitsyn, Y. E. Eizner, *Zh. Tekh. Fiz.* **1959**, 1105.

## Supporting Information

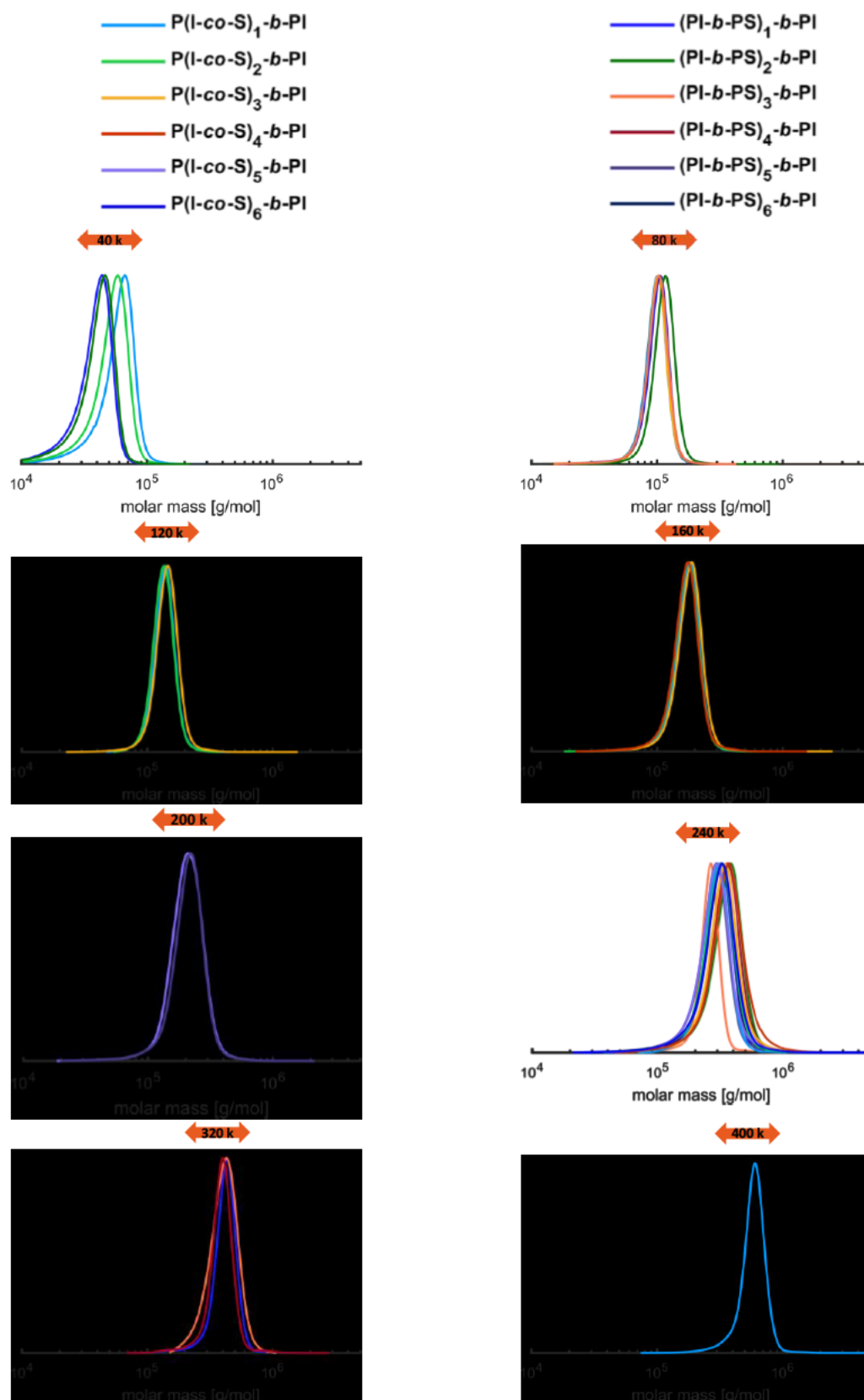


Figure S1: SEC traces (THF, RI detector) of the series with different molar masses (1<sup>st</sup> row left: 40, 1<sup>st</sup> row right: 80, 2<sup>nd</sup> row left: 120, 2<sup>nd</sup> row right: 160, 3<sup>rd</sup> row left: 200, 3<sup>rd</sup> row right: 240, 4<sup>th</sup> row left: 320, 4<sup>th</sup> row right: 400 kg·mol<sup>-1</sup>). Derived number average molar masses and dispersities are comprised in Table S1.



**Table S1: Overview of the characteristics of the statistically copolymerized multiblock copolymers P(I-co-S)<sub>n</sub>-b-PI with a tapered interface (tap) and the sequentially polymerized multiblock copolymers (PI-b-PS)<sub>n</sub>-b-PI (seq) obtained by SEC coupled to a RI detector as well as by <sup>1</sup>H NMR. The corresponding SEC traces are given in Figure S1.**

| (IS) <sub>n</sub><br>block type | block number<br>#=2n+1 | target $M_n$<br>[kg·mol <sup>-1</sup> ] | $M(PI)/\#$<br>[kg·mol <sup>-1</sup> ] | $M(PS)/\#$<br>[kg·mol <sup>-1</sup> ] | $M_n^a$<br>[kg·mol <sup>-1</sup> ] | $\mathcal{D}^a$ | $P_n(I)^b$<br>[%] | $\omega_{1,4}(I)^b$<br>[%] |
|---------------------------------|------------------------|-----------------------------------------|---------------------------------------|---------------------------------------|------------------------------------|-----------------|-------------------|----------------------------|
| tap                             | 3                      | 40                                      | 12                                    | 16                                    | 52.6                               | 1.14            | 70.3              | 94                         |
|                                 | 5                      | 40                                      | 8                                     | 8                                     | 45.9                               | 1.15            | 69.9              | 94                         |
| seq                             | 3                      | 40                                      | 12                                    | 16                                    | 33.8                               | 1.15            | 69.2              | 93                         |
|                                 | 5                      | 40                                      | 8                                     | 8                                     | 35.4                               | 1.16            | 69.5              | 93                         |
| tap                             | 3                      | 80                                      | 25                                    | 29                                    | 91.0                               | 1.08            | 72.4              | 94                         |
|                                 | 5                      | 80                                      | 17                                    | 15                                    | 96.3                               | 1.05            | 72.8              | 94                         |
|                                 | 7                      | 80                                      | 13                                    | 10                                    | 94.3                               | 1.06            | 72.7              | 94                         |
| seq                             | 3                      | 80                                      | 24                                    | 32                                    | 96.2                               | 1.06            | 67.3              | 94                         |
|                                 | 5                      | 80                                      | 16                                    | 16                                    | 109.0                              | 1.05            | 69.2              | 93                         |
|                                 | 7                      | 80                                      | 12                                    | 11                                    | 95.3                               | 1.06            | 69.3              | 93                         |
| tap                             | 3                      | 120                                     | 36                                    | 47                                    | 133.5                              | 1.04            | 68.7              | 94                         |
|                                 | 5                      | 120                                     | 24                                    | 24                                    | 130.8                              | 1.04            | 69.7              | 94                         |
|                                 | 7                      | 120                                     | 18                                    | 16                                    | 131.1                              | 1.06            | 70.4              | 94                         |
| seq                             | 3                      | 120                                     | 36                                    | 47                                    | 120.9                              | 1.07            | 69.0              | 94                         |
|                                 | 5                      | 120                                     | 24                                    | 24                                    | 132.4                              | 1.09            | 69.4              | 94                         |
|                                 | 7                      | 120                                     | 18                                    | 16                                    | 136.3                              | 1.08            | 69.8              | 94                         |
| tap                             | 3                      | 160                                     | 48                                    | 63                                    | 163.2                              | 1.07            | 69.9              | 94                         |
|                                 | 5                      | 160                                     | 32                                    | 32                                    | 158.9                              | 1.08            | 70.9              | 94                         |
|                                 | 7                      | 160                                     | 24                                    | 21                                    | 170.2                              | 1.08            | 70.0              | 95                         |
|                                 | 9                      | 160                                     | 19                                    | 16                                    | 158.6                              | 1.09            | 68.9              | 94                         |
| seq                             | 3                      | 160                                     | 48                                    | 63                                    | 155.9                              | 1.07            | 69.1              | 93                         |
|                                 | 5                      | 160                                     | 32                                    | 32                                    | 151.0                              | 1.09            | 70.2              | 93                         |
|                                 | 7                      | 160                                     | 24                                    | 21                                    | 168.6                              | 1.09            | 70.0              | 93                         |
|                                 | 9                      | 160                                     | 19                                    | 16                                    | 151.1                              | 1.10            | 71.6              | 94                         |
| tap                             | 11                     | 200                                     | 20                                    | 16                                    | 190.2                              | 1.12            | 70.5              | 94                         |
| seq                             | 11                     | 200                                     | 20                                    | 16                                    | 193.6                              | 1.12            | 69.2              | 94                         |
| tap                             | 3                      | 240                                     | 72                                    | 95                                    | 277.5                              | 1.08            | 69.2              | 94                         |
|                                 | 5                      | 240                                     | 48                                    | 47                                    | 273.9                              | 1.14            | 68.7              | 94                         |
|                                 | 7                      | 240                                     | 36                                    | 32                                    | 303.5                              | 1.14            | 68.9              | 94                         |
|                                 | 9                      | 240                                     | 29                                    | 24                                    | 324.9                              | 1.17            | 69.4              | 94                         |
|                                 | 11                     | 240                                     | 24                                    | 19                                    | 257.9                              | 1.15            | 69.4              | 94                         |
|                                 | 13                     | 240                                     | 21                                    | 16                                    | 272.8                              | 1.17            | 69.6              | 94                         |

|     |    |     |     |     |       |      |      |    |
|-----|----|-----|-----|-----|-------|------|------|----|
| seq | 3  | 240 | 72  | 95  | 268.7 | 1.14 | 69.3 | 94 |
|     | 5  | 240 | 48  | 47  | 306.1 | 1.18 | 69.6 | 93 |
|     | 7  | 240 | 36  | 32  | 246.9 | 1.06 | 68.9 | 93 |
|     | 9  | 240 | 29  | 24  | 304.5 | 1.15 | 70.0 | 93 |
|     | 11 | 240 | 24  | 19  | 254.8 | 1.13 | 68.7 | 93 |
|     | 13 | 240 | 21  | 16  | 275.1 | 1.14 | 69.2 | 93 |
| tap | 3  | 320 | 97  | 127 | 376.1 | 1.05 | 69.8 | 94 |
|     | 5  | 320 | 64  | 63  | 361.7 | 1.12 | 68.6 | 95 |
|     | 7  | 320 | 48  | 42  | 369.9 | 1.09 | 69.2 | 94 |
| seq | 3  | 320 | 97  | 127 | 400.5 | 1.06 | 69.9 | 93 |
|     | 7  | 320 | 48  | 42  | 387.8 | 1.08 | 69.1 | 94 |
|     | 9  | 320 | 39  | 32  | 373.6 | 1.07 | 68.4 | 93 |
| tap | 3  | 400 | 121 | 158 | 556.0 | 1.07 | 70.3 | 94 |
| seq | 3  | 400 | 121 | 158 | 558.6 | 1.08 | 70.0 | 94 |
|     | 5  | 400 | 81  | 79  | 476.9 | 1.07 | 69.6 | 94 |

<sup>a</sup> Determined by SEC (THF, PS calibration standard, RI detector). The number average molar masses are overestimated because of the incorporation of 70 mol% isoprene. <sup>b</sup> determined by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) integrating on the 1,4-polyisoprene ( $\delta$ =4.8-5.4 ppm), 3,4-polyisoprene ( $\delta$ =4.5-4.8 ppm), and polystyrene signals ( $\delta$ =6.2-7.4 ppm).

**Table S2: Overview of the average molar masses of the statistically copolymerized multiblock copolymers P(I-co-S)<sub>n</sub>-b-PI with a tapered interface (tap) and the sequentially polymerized multiblock copolymers (PI-b-PS)<sub>n</sub>-b-PI (seq) obtained by different characterization techniques, which include SEC measurements in THF using universal calibration ( $M_n$  and  $M_w$ ), a differential viscometer detector ( $M_{[\eta]}$ ) and a multi-angle light scattering detector ( $M_{LS}$ ) as well as AUC measurements in toluene ( $M_{sf}$ ). The mean values of the molar masses  $M_{av}$  were calculated by averaging over the molar masses which were validated by their hydrodynamic invariant. Excluded values are indicated by an italic front.**

| (IS) <sub>n</sub> I | #=2n+1 | target $M_n$<br>[kg·mol <sup>-1</sup> ] | $M_n$<br>[kg·mol <sup>-1</sup> ] | $M_w$<br>[kg·mol <sup>-1</sup> ] | $M_{[\eta]}$<br>[kg·mol <sup>-1</sup> ] | $M_{LS}$<br>[kg·mol <sup>-1</sup> ] | $M_{sf}$<br>[kg·mol <sup>-1</sup> ] | $M_{av}$<br>[kg·mol <sup>-1</sup> ] |
|---------------------|--------|-----------------------------------------|----------------------------------|----------------------------------|-----------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| seq - series 1      | 3      | 40                                      | 42.0                             | 44.0                             | 35.0                                    | 30.0                                | 24.3                                | 32.5                                |
|                     | 3      | 80                                      | 78.0                             | 85.0                             | 55.0                                    | 63.0                                | 77.1                                | 75.8                                |
|                     | 3      | 120                                     | 113.0                            | 125.0                            | 84.0                                    | 87.0                                | 76.3                                | 119.0                               |
|                     | 3      | 160                                     | 135.0                            | 152.0                            | 97.0                                    | 118.0                               | 194.9                               | 135.0                               |
|                     | 3      | 240                                     | 188.0                            | 243.0                            |                                         |                                     | 200.3                               | 243.0                               |
|                     | 3      | 320                                     | 315.0                            | 393.0                            |                                         |                                     | 256.8                               | 354.0                               |
|                     | 3      | 400                                     | 392.0                            | 524.0                            | 235.0                                   |                                     | 374.4                               | 430.1                               |
| tap - series 1      | 3      | 40                                      | 42.0                             | 45.0                             | 30.0                                    | 33.0                                | 35.6                                | 35.2                                |
|                     | 3      | 80                                      | 78.0                             | 87.0                             | 56.0                                    | 57.0                                | 62.5                                | 63.4                                |
|                     | 3      | 120                                     | 105.0                            | 118.0                            | 75.0                                    | 78.0                                | 101.6                               | 108.2                               |
|                     | 3      | 160                                     | 140.0                            | 172.0                            | 89.0                                    | 123.0                               | 131.5                               | 141.6                               |
|                     | 3      | 240                                     | 253.0                            | 277.0                            |                                         | 270.0                               | 177.2                               | 266.7                               |
|                     | 3      | 320                                     | 289.0                            | 367.0                            |                                         |                                     | 283.5                               | 313.2                               |

|                |    |     |       |       |       |       |       |       |
|----------------|----|-----|-------|-------|-------|-------|-------|-------|
| seq - series 2 | 3  | 400 | 375.0 | 509.0 |       |       | 368.8 | 417.6 |
|                | 5  | 40  | 44.0  | 47.0  | 36.0  | 28.0  | 35.8  | 33.3  |
|                | 5  | 80  | 93.0  | 104.0 | 70.0  | 80.0  | 92.9  | 92.5  |
|                | 5  | 120 | 123.0 | 141.0 | 91.0  | 101.0 | 120.1 | 121.3 |
|                | 5  | 160 | 126.0 | 144.0 | 82.0  | 121.0 | 132.4 | 130.8 |
|                | 5  | 240 | 230.0 | 310.0 | 140.0 |       | 254.1 | 282.1 |
|                | 5  | 400 | 367.0 | 466.0 |       |       | 350.5 | 394.5 |
| tap - series 2 | 5  | 40  |       |       |       |       | 32.2  | 32.2  |
|                | 5  | 80  | 72.0  | 81.0  | 50.0  | 60.0  | 35.7  | 52.6  |
|                | 5  | 120 | 102.0 | 121.0 | 75.0  | 89.0  | 85.7  | 99.4  |
|                | 5  | 160 | 138.0 | 174.0 | 85.0  | 138.0 | 142.1 | 148.0 |
|                | 5  | 240 | 266.0 | 326.0 |       | 276.0 | 153.8 | 289.3 |
|                | 5  | 320 | 314.0 | 388.0 |       |       | 239.1 | 351.0 |
| seq - series 3 | 7  | 80  | 73.0  | 84.0  | 56.0  | 66.0  | 59.3  | 70.6  |
|                | 7  | 120 | 100.0 | 136.0 | 82.0  | 121.0 | 93.8  | 106.6 |
|                | 7  | 160 | 133.0 | 154.0 | 88.0  | 128.0 | 145.2 | 140.0 |
|                | 7  | 240 | 174.0 | 212.0 |       |       | 224.6 | 203.5 |
|                | 7  | 320 | 308.0 | 379.0 |       |       | 294.0 | 327.0 |
| tap - series 3 | 7  | 80  | 75.0  | 83.0  | 52.0  | 52.0  | 109.1 | 59.7  |
|                | 7  | 120 | 107.0 | 124.0 | 71.0  | 86.0  | 59.3  | 78.5  |
|                | 7  | 160 | 130.0 | 161.0 | 58.0  | 134.0 | 63.3  | 132.0 |
|                | 7  | 240 | 201.0 | 368.0 | 223.0 | 343.0 | 156.9 | 212.0 |
|                | 7  | 320 | 243.0 | 332.0 | 154.0 |       | 276.0 | 304.0 |
| seq - series 4 | 3  | 40  | 42.0  | 44.0  | 35.0  | 30.0  | 24.3  | 32.5  |
|                | 5  | 80  | 93.0  | 104.0 | 70.0  | 80.0  | 92.9  | 88.0  |
|                | 7  | 120 | 100.0 | 136.0 | 82.0  | 121.0 | 93.8  | 112.7 |
|                | 9  | 160 | 136.0 | 154.0 | 96.0  | 119.0 | 121.6 | 132.6 |
|                | 11 | 200 | 199.0 | 230.0 | 162.0 | 180.0 | 154.9 | 180.3 |
|                | 13 | 240 | 182.0 | 262.0 | 24.0  |       | 78.1  | 140.0 |
| tap - series 4 | 3  | 40  | 42.0  | 45.0  | 30.0  | 33.0  | 35.6  | 35.2  |
|                | 5  | 80  | 72.0  | 81.0  | 50.0  | 60.0  | 35.7  | 71.0  |
|                | 7  | 120 | 107.0 | 124.0 | 71.0  | 86.0  | 59.3  | 105.7 |
|                | 9  | 160 | 140.0 | 169.0 | 66.0  | 124.0 | 61.7  | 132.0 |
|                | 11 | 200 | 141.0 | 183.0 | 88.0  | 167.0 | 193.6 | 181.2 |
|                | 13 | 240 | 110.0 | 335.0 | 453.0 | 467.0 | 99.0  | 169.1 |

For some polymers no  $M_{[n]}$  or  $M_{LS}$  is given. In case of the molar masses based on viscosity it was not possible to calculate a molar mass due to the narrow molar mass distribution. In case of MALLS detection, exceedingly high molar masses deviating by two orders of magnitude were obtained and hence are not given. This inaccuracy might arise from an imprecise evaluation due to small dependencies of the scattering intensity on the the concentration and the scattering angle or a limitation of the Zimm equation to very dilute samples, this way giving only high apparent molar masses.

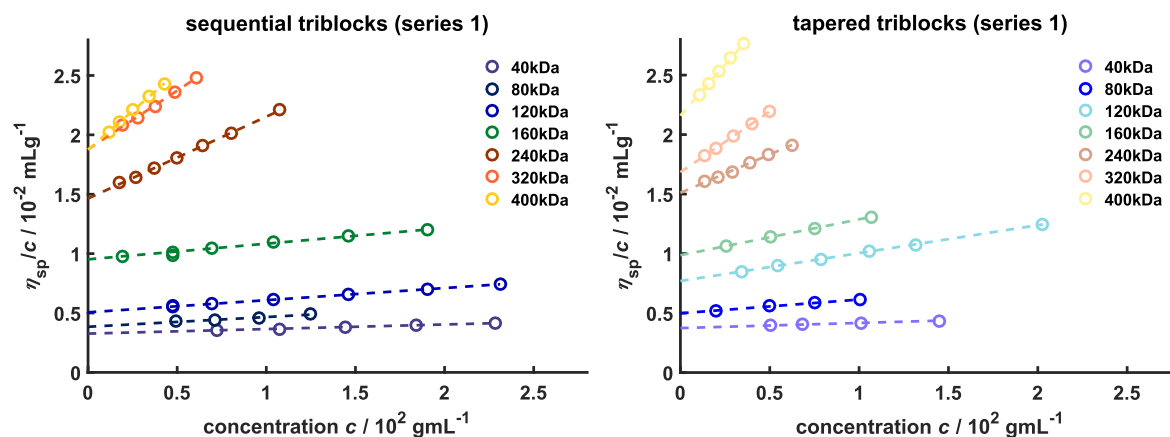


Figure S2: Huggins extrapolation plots for the determination of the intrinsic viscosities in toluene  $[\eta]_{\text{toluene}}$  for the sequential (left) and tapered (right) triblock copolymers (series 1).

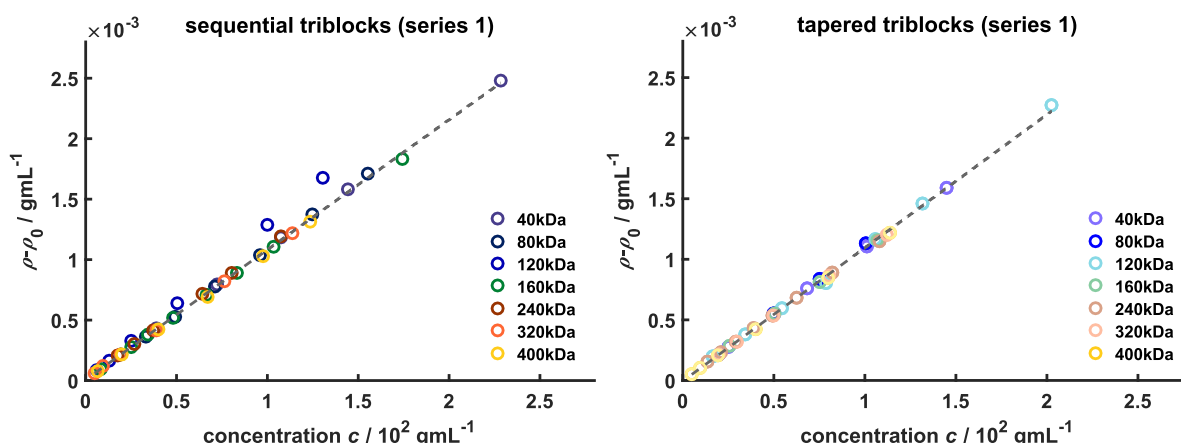


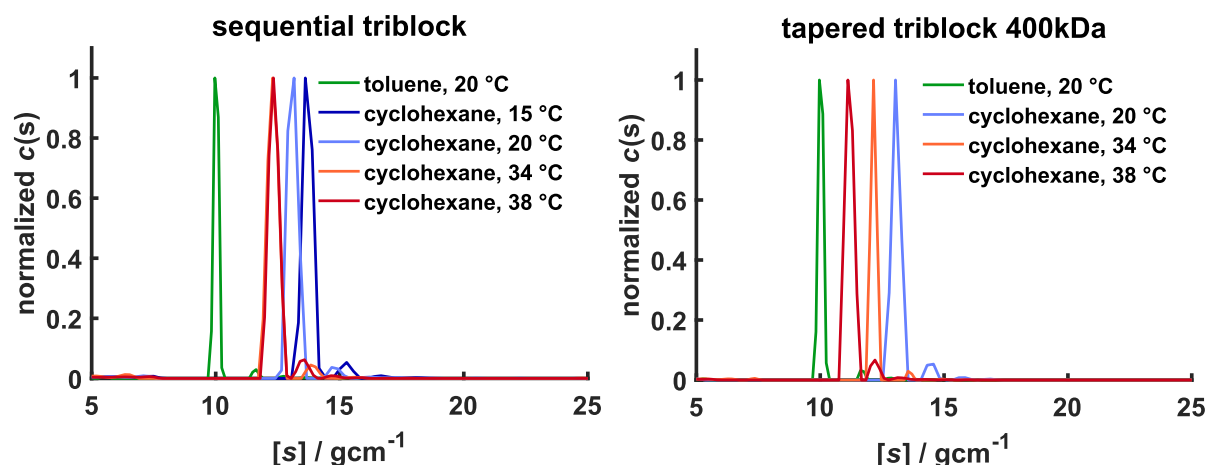
Figure S3: Dependence of the difference in density of the solute  $\rho$  and the solvent  $\rho_0$  on the polymer concentration  $c$  for the sequential (left) and tapered (right) triblock copolymers (series 1). The slope of the linear fit corresponds to the buoyancy factor  $(1 - \nu\rho_0)$ , from which the partial specific volume  $\nu$  is calculated.  $(1 - \nu\rho_0)_{\text{seq}} = 0.00107 \pm 6 \cdot 10^{-6}$ ;  $(1 - \nu\rho_0)_{\text{seq}} = 0.00110 \pm 6 \cdot 10^{-6}$ .

## Hydrodynamic Characteristics in Cyclohexane

By increasing the solvent quality towards one of the two blocks, the influence of the block profile on the gross conformation of the polymer coils in solution is prominent as well.

In the following, preliminary data on the sedimentation profiles of the highest molar mass triblock copolymers in cyclohexane at varying temperatures are discussed. With cyclohexane being a good solvent for polyisoprene and a theta-solvent for polystyrene at  $34.0^{[1]} - 34.5^\circ\text{C}^{[2]}$  (as indicated by their Hildebrand solubility parameters  $\delta_{\text{cyclohexane}}^{25^\circ\text{C}} = 16.8 \text{ MPa}^{0.5}$ ,  $\delta_{1,4\text{-PI}}^{25^\circ\text{C}} = 16.7 \text{ MPa}^{0.5}$  and  $\delta_{\text{PS}}^{35^\circ\text{C}} = 18.7 \text{ MPa}^{0.5}$ )<sup>[3]</sup> the change of the enthalpic contribution of polystyrene can be followed with increasing temperature. At the theta-temperature, the long-range forces between the polystyrene repeating units which cause a contraction are balanced by the interaction with the solvent which lead to coil expansion, thus resulting in unperturbed dimensions of the polystyrene blocks.

Figure S4 displays the distributions of the sedimentation coefficients for the sequential as well as the tapered triblock copolymer of  $400 \text{ kg}\cdot\text{mol}^{-1}$ . With only one polystyrene block, the triblock displays the simplest block structure incapable of intramolecular association of multiple polystyrene blocks per chain. Generally, an increase in the sedimentation coefficient at constant molar mass displays that the polymer coil becomes more compact, thus decreasing the frictional coefficient which results in a higher sedimentation speed.



**Figure S4:** Normalized differential distributions of the sedimentation coefficients of the sequential (left) and tapered (right) triblock copolymer with  $400 \text{ kg}\cdot\text{mol}^{-1}$  measured in toluene at  $20^\circ\text{C}$  being a good solvent for both comonomers isoprene and styrene (green) as well as in cyclohexane at increasing temperatures (dark blue:  $15^\circ\text{C}$ , blue:  $20^\circ\text{C}$ , orange:  $34^\circ\text{C}$ , red:  $38^\circ\text{C}$ ), with  $34^\circ\text{C}$  corresponding to the theta-temperature for polystyrene. The concentrations of the polymer solutions range between 0.15-0.2%.

Both polymers exhibit comparable sedimentation coefficients and hence dimensions in toluene at  $20^\circ\text{C}$  (green traces), which is a good solvent for both polyisoprene and polystyrene. In cyclohexane, the polymers contract, i.e., the sedimentation coefficients increase. At  $20^\circ\text{C}$  (blue traces) both the sequential and the tapered triblock show drastically increased sedimentation coefficients, which is reasoned in the collapse of the polystyrene block. Upon increasing the temperature to  $34^\circ\text{C}$  (orange traces), which corresponds to the theta-temperature for polystyrene, the polymer chains become more and more drained by solvent, which is reflected in smaller sedimentation coefficients. Again, both the block- and the block-like structure show comparable dimensions in solution.

Though, by further increasing the temperature to  $38^\circ\text{C}$  (red traces), the sedimentation profiles of the two types of block copolymers differ. For the sequential triblock, no change in the sedimentation coefficient can be observed, whereas for the tapered triblock the coil dimension further increases.

One can speculate that with the effective pure polystyrene block being shorter in the case of the tapered structure, polymers with a gradual block transition are more sensitive to changes of the interaction between the polymer and the solvent and more easily drained by the solvent.

Since cyclohexane is a model solvent for naphthenic oils<sup>[4]</sup>, understanding the relationship between the polymer structure and its solution behavior is not only of fundamental importance, but also of practical interest for lubricant formulations. In-deep investigation of the presented multiblock copolymers in a selective solvent will be subject of further studies.

## References

- [1] V. G. V. Schulz, H. Baumann, *Makromol. Chem.* **1963**, 60, 120.
- [2] J. W. Mays, N. Hadjichristidis, L. J. Fetters, *Macromolecules* **1985**, 18, 2231.
- [3] a) J. E. Mark, *Physical properties of polymers handbook*, Springer Science & Business Media, New York, NY, **2007**; b) D. Mangarj, S. K. Bhatnagar, S. B. Rath, *Makromol. Chem.* **1963**, 67, 75; c) J. Bandrup, E. H. Immergut, E. A. Grulke, *Polymer handbook*, **1999**.
- [4] P. Bezot, C. Hesse–Bezot, B. Elmakoudi, B. Constants, D. Faure, P. Hoornaert, *J. Appl. Polym. Sci.* **1994**, 51, 1715.







---

---

# CHAPTER 9

*Geometric Requirements for Living*  
*Anionic Polymerization: Polymerization of*  
**Rotationally Constrained 1,3-Dienes**

---

---



## CHAPTER 9

Published in Polymer Chemistry, 2022. DOI: 10.1039/D2PY00999D

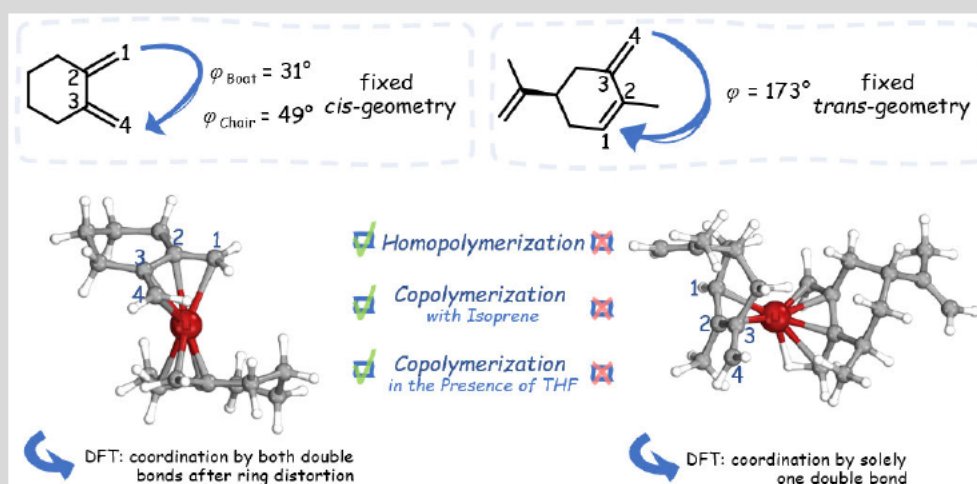
# Geometric Requirements for Living Anionic Polymerization: Polymerization of Rotationally Constrained 1,3-Dienes

Ramona D. Barent<sup>1,2</sup>, Manfred Wagner<sup>3</sup>, and Holger Frey<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Johannes Gutenberg-University, Duesbergweg 10-14, 55128 Mainz, Germany

<sup>2</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany

<sup>3</sup> Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany



The living anionic copolymerization of 1,3-dienes such as isoprene (I) or butadiene (B) can afford a variety of different polymer microstructures which determine the material's properties. One decisive factor for the stereochemistry is the polarity of the medium, which can be ascribed to the proposed coordinative mechanism in nonpolar media. In a combined synthetic, kinetic and theoretical study the homopolymerization of two new 1,3-diene monomers with a rigid, prescribed *cisoid* or *transoid* geometry as well as their copolymerization with isoprene is examined in cyclohexane as a typical nonpolar solvent. Real-time <sup>1</sup>H NMR spectroscopy provides kinetic data and hence the reactivity ratios at different temperatures. Furthermore, reaction pathways are modelled and followed by density functional theory (DFT) calculations to support the experimental observations. The results show that a *cisoid* geometry with in-plane double bonds is mandatory for propagation, and that the necessary ring distortion in case of the cyclic *cisoid* diene accounts for its higher activation barrier, leading to gradient formation in statistical copolymerization experiments with isoprene.

## Introduction

The significance of a high 1,4-stereoselectivity of polydienes derives from the low glass transition temperature, which enables a wide temperature range application window.<sup>[1]</sup> The stereochemistry of polydienes is known to depend on manifold parameters. The key parameters are (i) the counterion, which influences the aggregation strength with the living chain end, (ii) the solvent and (iii) the presence of polar modifiers, which profoundly alters the aggregation itself and thereby the polymerization mechanism.<sup>[2,3]</sup> A mechanistic hypothesis including a six-membered coordination of the propagating chain end and the incoming monomer was initially proposed by Bywater<sup>[4]</sup> in 1965 to explain the high 1,4-content in polydienes polymerized in nonpolar media with lithium as a counterion. This concept was further specified by Gebert and coworkers<sup>[5]</sup>, providing an explanation for the final *cis/trans*-ratio of the 1,4-units. Upon coordinative 1,4-addition of isoprene, a *cisoid* repeating unit is formed, which can isomerize between *cis* and *trans*. The isomerization rate is competitive with the timescale of monomer addition, explaining the mixture of *cis* and *trans* 1,4-units. (Figure 1).<sup>[6]</sup>

Since a high 1,4-microstructure content of polydienes is a result of the specific nature of the interaction between the carbanionic chain end, the lithium counterion and the diene, the microstructure control is lost, if other alkali counterions or Lewis bases coordinating the counterion are used.<sup>[7]</sup>

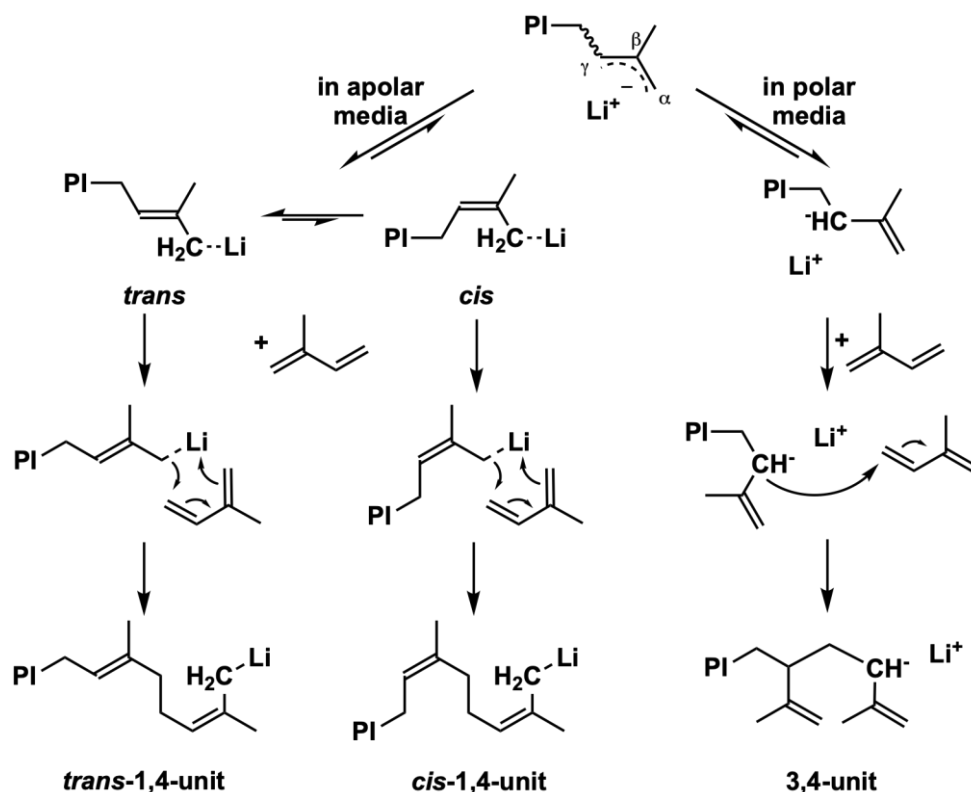
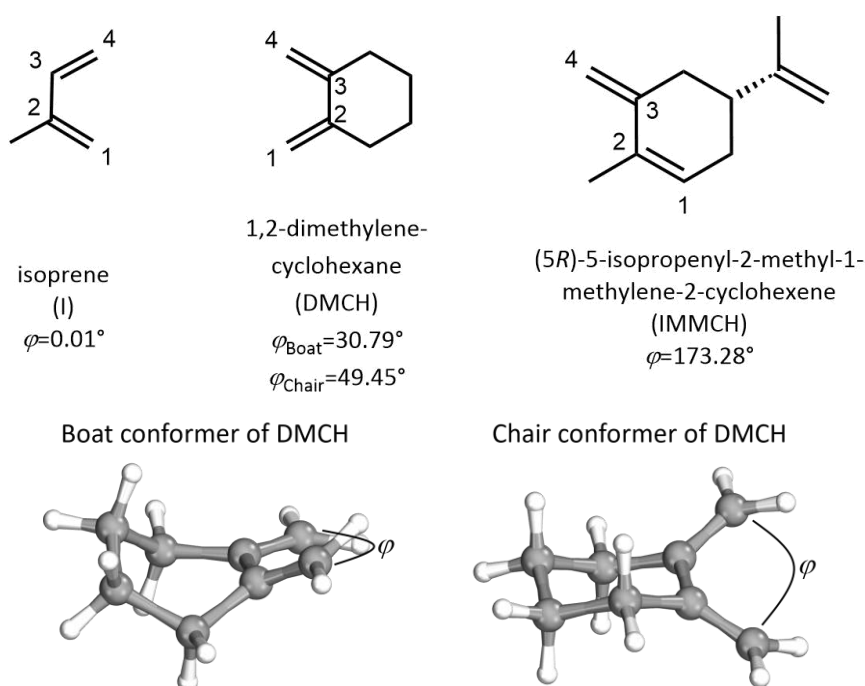


Figure 1: Proposed propagation mechanism for the carbanionic polymerization of 1,3-dienes. In nonpolar media, the chain end is strongly coordinated by the lithium counterion and the initially formed *cis*-unit can isomerize into the *trans*-form. The subsequent monomer addition via a six-membered transition state including the incoming monomer is faster in case of a *cis*-chain end. In nonpolar media, the living chain end has a pronounced ionic character, leading to higher vinylic contents. Modified from<sup>[3]</sup> (Scheme 1.10), showing the anionic propagation of 1,3-butadiene and neglecting the isomerization of 1,4-chain ends.

In this work, the importance of the cyclic coordination is examined relying on a combined experimental and theoretical approach based on the polymerization behavior of cyclic diene monomers with a prescribed *cisoid* or *transoid* geometry, the latter preventing the proposed cyclic six-membered transition state. This is achieved using the monomers 1,2-dimethylene-cyclohexane (DMCH) and (5*R*)-5-isopropenyl-2-methyl-1-methylene-2-cyclohexene (IMMCH) and is supported by density functional theory (DFT) calculations (Figure 2).

Besides these considerations, one should be aware that also substitution pattern and sterics strongly affect the microstructure. Due to the cyclic nature and the *transoid* geometry of IMMCH, a 1,3-disubstitution cannot be circumvented, encompassing a potential reason for differences in polymerizability.



**Figure 2:** Top: Monomer systems employed in this work. The numbering of DMCH and IMMCH does not correspond to IUPAC but describes the reactive moieties in analogy to isoprene. Bottom: 3D visualization of the DMCH conformers with assigned dihedral angle.

This is demonstrated on one hand at the example of 2,3-diphenylbutadiene<sup>[8]</sup>, resulting in a polymer with nearly exclusive 1,4-microstructure even in cyclohexane, with as little as 10 equivalents of THF to modify the *cis/trans*-1,4 ratio and to enhance solubility. On the other hand, the 3,4-content obtained when polymerizing allylidene monomers<sup>[9]</sup> (1,1-disubstituted butadienes) increases with the bulkiness of the substituents despite polymerization in benzene at elevated temperatures. Reviewing literature-known 1,3-dienes with constrained geometry, cyclohexadiene represents the simplest structure of a cyclic diene with fixed *cisoid* geometry. It was reported to be polymerizable by anionic techniques, however, this monomer is prone to side reactions like hydride elimination or allylic proton abstraction. Therefore, amine-(DABCO<sup>[10]</sup>, TMEDA<sup>[10,11]</sup>) or ether-type additives (DME<sup>[10]</sup>) were implemented. To date, DMCH has been polymerized only in a radical<sup>[12,13]</sup> or cationic<sup>[13]</sup> manner, and a high-melting, brittle polymer with poor solubility even in boiling toluene was obtained.

In contrast to the *cisoid* dienes, manifold *exo*-methylene dienes with a fixed *transoid* structure have been reported and were polymerized radically or cationically<sup>[14]</sup>, among them also IMMCH, resulting in a high  $T_g$ -polymer (113 °C<sup>[15]</sup>). Concerning an anionic approach, merely two

polymers of *transoid* dienes, benzofulvene and methylenecyclopentene, have been discussed so far. Benzofulvene was polymerized in benzene at temperatures ranging from 0 °C<sup>[16,17]</sup> to 55 °C<sup>[17]</sup>, giving 1,4-polydiene-contents above 74%. Nevertheless, this monomer can be regarded as a special case, because the planar cross-conjugated  $\pi$ -system results in a high reactivity.<sup>[18]</sup> The electronic structure relevance was proven by the comparison of benzofulvene with its acyclic counterpart, whose polymerizability is lower due a higher partial charge at the C4. Methylenecyclopentene was polymerized in pure cyclohexane in a controlled manner, giving a polymer with a dispersity of  $\bar{D}$ =1.12.<sup>[19]</sup> However, high temperatures of 70 °C and reaction times of 4 days were necessary to achieve full conversion. In contrast, 4 days of polymerization at 40 °C resulted in solely 21% conversion. Full conversion at moderate reaction times and conditions could only be realized with the addition of TMEDA.

Conclusively, no living anionic polymerization of a *transoid* diene in nonpolar solvents at mild conditions that are also suitable for the copolymerization with *i.e.*, isoprene was reported. Therefore, the deductions of this work are of general significance with respect to the introduction of new diene monomers for carbanionic polymerization in nonpolar media.

## Results and Discussion

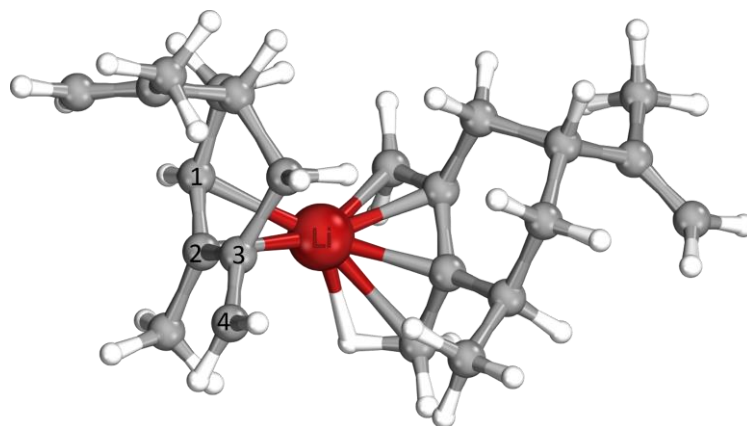
### Theoretical Considerations employing Computational Modelling

DMCH and IMMCH were chosen as model compounds due to their prescribed *cisoid* and *transoid* configuration, respectively. Firstly, the geometries of the monomers were simulated by DFT calculations, showing deviations in the torsion angle from 0° or 180°, leading to a diminished overlap of the double bonds'  $p_z$  orbitals. The ring strain twists the double bonds out of the plane by roughly 30° in case of DMCH having a boat conformation and by 7° for IMMCH (Figure 2). However, the chair conformation of DMCH with a torsion angle of 50° is energetically favored over the boat conformation. Secondly, the predicted partial charges are interpreted in terms of reactivity.

On a molecular level, different reactivities can be explained by the nucleophilicity of the living chain end and the electrophilicity of the propagating monomer. The comparison of the partial charges of the monomers' carbons 1-4 affords an insight into the most likely reaction center. All discussed monomers exhibit a lower partial charge at C1 compared to C4 (Figure S1), leading to the conclusion that this reaction site is most likely attacked in a 1,4-addition step. Furthermore, the C1 electron densities lead to the order IMMCH > I  $\geq$  DMCH<sub>Boat</sub> > DMCH<sub>Chair</sub> with respect to electrophilicity.

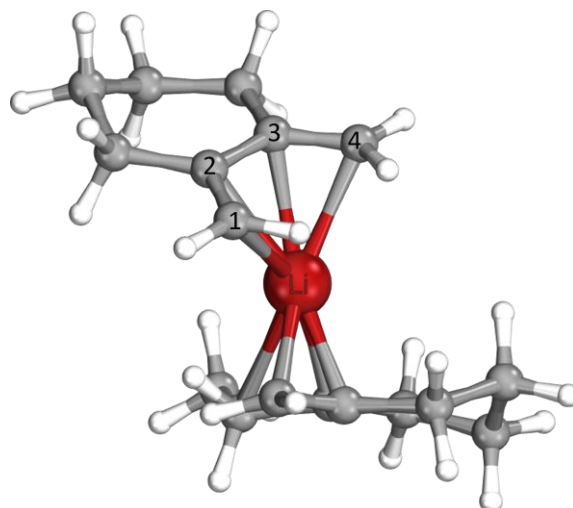
To support these predictions experimentally, the chemical shifts of the carbon-signals in <sup>13</sup>C NMR spectra can be considered. The more downfield shifted the signal is, the more likely is the nucleophilic attack. With  $\delta_{\text{IMMCH}}=127.6 \text{ ppm} > \delta_{\text{isoprene}}=113.6 \text{ ppm} > \delta_{\text{DMCH}}=107.9 \text{ ppm}$ , this ranking solely based on electron density can be confirmed.

Finally, the predicted geometry of the precursors and the reaction pathways are discussed. Despite a strong conjugation of the double bonds of IMMCH, the fixed *transoid* geometry prevents the coordination of the chain end by the lithium counterion by both double bonds (Figure 3).



**Figure 3:** 3D visualization of the chemical structure of the precursor of the IMMCH homopropagation (Me-IMMCH-Li + IMMCH) obtained by DFT calculations. The coordination solely by one double bond is clarified by assigning the carbon atoms 1-4.

On the contrary, DMCH can coordinate the reactive chain end with both double bonds, however under ring distortion allowing a significant overlap and hence  $\pi$ -conjugation ( $\varphi=8^\circ$ , Figure 4).



**Figure 4:** 3D visualization of the chemical structure of the precursor of the DMCH homopropagation (Me-DMCH-Li + DMCH) obtained by DFT calculations. The coordination by both double bond is clarified by assigning the carbon atoms 1-4.

This distortion is reflected in the trajectories of the reaction pathways for the addition of a DMCH monomer (Figure 5, blue trajectories). Generally, the addition of a monomer unit to a polydienyl-lithium chain end is simulated. The residual chain is simplified as a methyl group, and only the terminal unit is specified. All four pathways start with a precursor complex, wherein the incoming monomer coordinates the lithium counterion loosely by one double bond. During the reaction progress, the monomer is tilted and in case of DMCH also distorted, allowing a coordination by both double bonds. At the end of the reaction pathway, the covalent bond is formed, and the system's geometry is reorganized.

Examining the geometries at different stages of the reaction progress, the activation barrier of DMCH additions can be assigned to the ring flip from a chair conformation, that coordinates the lithium counterion with only one double bond (Figure S2, geometry 1), into a boat conformation (Figure S2, geometry 6), that is further distorted minimizing the torsion angle (Figure S2, geometry 8).

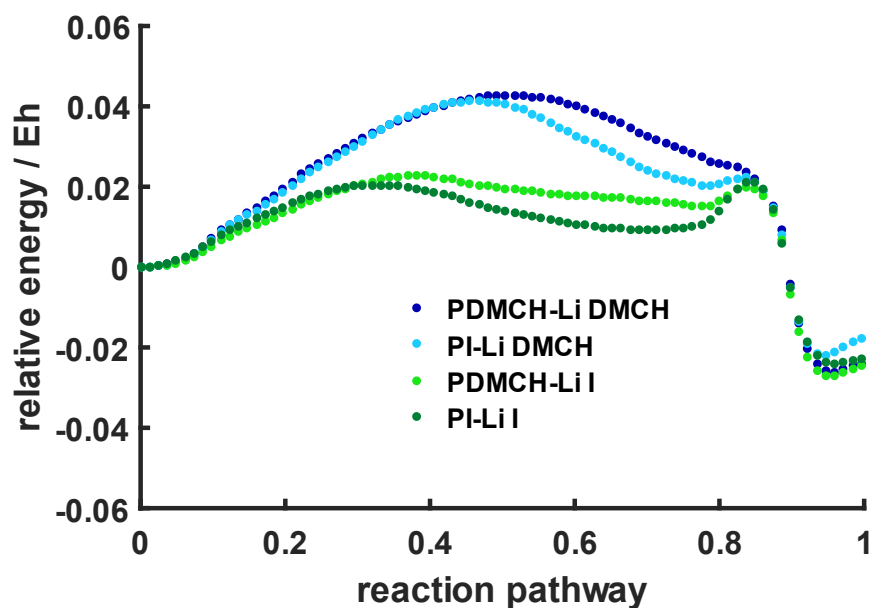


Figure 5: Reaction pathways for the four possible propagation steps copolymerizing isoprene with DMCH: homopropagation step of DMCH (dark blue, PDMCH-Li + DMCH), homopropagation step of isoprene (dark green, PI-Li + I), and the crossover propagation steps (light blue, PI-Li + DMCH, and light green, PDMCH-Li + I).

Although the absolute activation and reaction energies are not comparable due to neglecting aggregation phenomena, it is possible to draw a conclusion on a tendency, since the simulated additions of isoprene (Figure 5, green trajectories) also start with the coordination of solely one double bond. In systems comprising one monomer that rather adds the other monomer ( $k_{11} < k_{12} \Rightarrow r_1 < 1$ ) and a second monomer that rather homopolymerizes than crossing-over to the first monomer ( $k_{22} > k_{21} \Rightarrow r_2 > 1$ ), the statistical copolymerization experiment results in a steep gradient. The diverging activation energies of the isoprene and DMCH addition reasoned in the distortion of the latter monomer indicate, that this holds true for this system, *i.e.*, the formation of a tapered diblock structure in which first monomer 2 (I) is incorporated, followed by the formation of a block of monomer 1 (DMCH).

These conclusions coincide with the experimental results (*vide infra*), comprising the gradient formation in isoprene-DMCH copolymerizations, where only the *exo-cis* isomer reacts, and IMMCH lacks polymerizability.

### Real-time $^1\text{H}$ NMR Kinetics

The monomer incorporation in statistical copolymerization experiments of isoprene and DMCH was tracked by *in-situ*  $^1\text{H}$  NMR measurements (compiled in Table 1).

Pronounced gradient formation with a first block enriched in isoprene and a subsequent pure PDMCH block is observed, which is in agreement with the theoretically predicted reaction behavior. The gradient is flattened upon increasing the reaction temperature, which can be ascribed to a higher probability to overcome the activation barrier of the DMCH distortion.



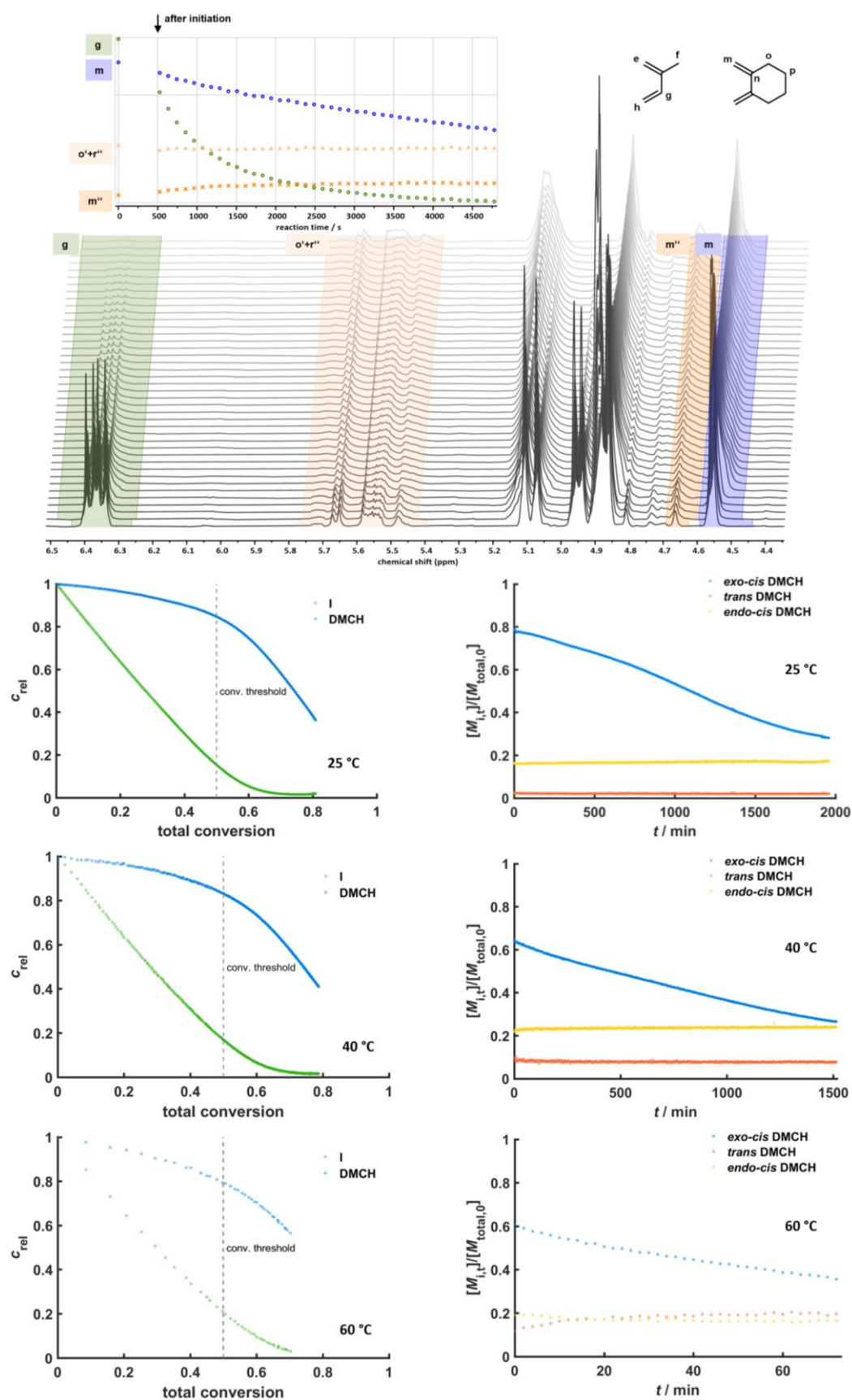


Figure 6: Top: Stacked  $^1\text{H}$  NMR spectra evaluated for the copolymerization at 60 °C. Bottom left: Plot of the monomer depletion against total conversion for isoprene (green, g) and *exo-cis* DMCH (blue, m) at 25 °C, 40 °C and 60 °C. Bottom right: Plot of the relative concentration  $[M_i]/[M_0]$  over time for the three DMCH isomers *exo-cis* (blue, m), *endo-cis* (yellow, o') and *trans* (orange, r''+m'') at 25 °C, 40 °C and 60 °C. All spectra were recorded with magnetic field strengths of 500 MHz.

This conclusion is further supported by the fact, that DMCH homopolymerizes slowly at room temperature but is readily consumed at elevated temperatures, as can be seen in the plot of the monomer consumption (Figure 6, Figure S3). For polymerizations using initiator concentrations of 1.3 M, the reaction at 25 °C is not completed even after 30 h, whereas full consumption is reached at 40 °C and 60 °C even at a time scale of a few hours (Figure S4). Thus, at comparably high concentrations only few data points are available for evaluation. Consequently, the estimated reactivity ratios are prone to fitting errors, and the experiments were repeated at a tenfold dilution.

**Table 1: Experimentally determined values for the reactivity ratios of isoprene ( $r_1$ ), and 1,2-dimethylenecyclohexane ( $r_{\text{DMCH}}$ ) in cyclohexane- $d_{12}$ .**

| temperature | initiator concentration | $r_1$ | $r_{\text{DMCH}}$ |
|-------------|-------------------------|-------|-------------------|
| 25 °C       | 1.3 M                   | 11.51 | 0.087             |
| 40 °C       | 0.13 M                  | 9.96  | 0.100             |
| 60 °C       | 0.13 M                  | 6.88  | 0.145             |

The calculated reactivity ratios were estimated by fitting the experimentally obtained monomer depletion of isoprene ( $\delta \approx 6.4$ –6.3 ppm) and DMCH ( $\delta \approx 4.6$ –4.5 ppm) (Figure 6) until a conversion threshold of 50% using the Jaacks equation (non-terminal model).

Looking at the plot of the logarithmic reciprocal concentration over time (Figure S3), the absence of termination reactions and moreover simultaneous initiation of all chains is manifest. Living conditions are visualized by a linear relation. This seems to be the case in all systems considered.

Furthermore, it can be concluded that the DMCH incorporation is accelerated after full isoprene consumption. Lastly, the relative concentrations of the different DMCH isomers are worth being discussed (Figure 6). While the amount of *exo-cis* isomer depletes during the reaction, no alteration in the signal intensity of the *trans* or even *endo-cis* isomer with a 1,4-disubstituted moiety is evident, implying that these isomers do not take part in the polymerization.

### Copolymerization of Isoprene and Dimethylenecyclohexane

These insights were used in copolymerization experiments on laboratory scale. Here, the major obstacle was to maintain proper solubility during copolymerization of isoprene and DMCH, which is a key parameter for uniform chain growth and hence living polymerization.

The growing chain with early repeating units consisting of isoprene is to a certain extent capable of keeping the polymer dissolved in cyclohexane. However, with increasing DMCH content or overall molecular weight, the reaction solutions became turbid, indicating precipitation of the still growing polymer chains. These polymers exhibited comparably low DMCH contents, further supporting the interpretation of a solubility-restricted polymerization behavior at late stages of the reaction.

**Table 2:** Entry 1-8: One-step tapered block copolymers based on isoprene (I) and dimethylenecyclohexane (DMCH) synthesized in cyclohexane at either room temperature, 40 °C or 60 °C. The initial concentrations of the monomers were calculated by the equation  $(n_I + n_{DMCH}) \cdot V_{cyclohexane}^{-1}$ . Entry 9: Homopolymer of DMCH synthesized in tetralin at 140 °C to maintain solubility of the formed polymer.

| # | reaction conditions |                            | $P_n$ (DMCH) [mol%] |                  | $M_n$ [kg·mol <sup>-1</sup> ] |                  |                  | $\bar{D}$        | DSC <sup>c</sup> |                     |
|---|---------------------|----------------------------|---------------------|------------------|-------------------------------|------------------|------------------|------------------|------------------|---------------------|
|   | $T$ [°C]            | $c$ [mol·L <sup>-1</sup> ] | target              | NMR <sup>a</sup> | target                        | NMR <sup>a</sup> | SEC <sup>b</sup> | SEC <sup>b</sup> | $T_g$ [°C]       | $T_{m(cryst)}$ [°C] |
| 1 | 25                  | 1.8                        | 7                   | 4.8              | 5                             | 5.25             | 5.78             | 1.04             | -66              | -                   |
| 2 | 25                  | 1.8                        | 15                  | 9.2              | 5                             | 6.23             | 6.18             | 1.04             | -65              | -                   |
| 3 | 25                  | 1.8                        | 23                  | 15.0             | 5                             | 6.35             | 6.14             | 1.04             | -61              | -                   |
| 4 | 25                  | 1.8                        | 31                  | 20.0             | 5                             | 6.20             | 6.73             | 1.04             | -53              | -                   |
| 5 | 25                  | 1.8                        | 41                  | 22.8             | 5                             | 6.35             | 6.45             | 1.04             | -51              | -                   |
| 6 | 40                  | 1.0                        | 30                  | 17.8             | 20                            | <i>n.d.</i>      | 29.4             | 1.04             | -48              | 120 (42)            |
| 7 | 40                  | 1.0                        | 30                  | 14.7             | 40                            | <i>n.d.</i>      | 43.6             | 1.06             | -55              | 130                 |
| 8 | 60                  | 1.0                        | 30                  | 19.9             | 40                            | <i>n.d.</i>      | 40.2             | 1.05             | -50              | 106 (45)            |
| 9 | 140                 | 0.9                        | 100                 | 100              | 5                             | 4.28             | -                | -                | 53               | 130                 |

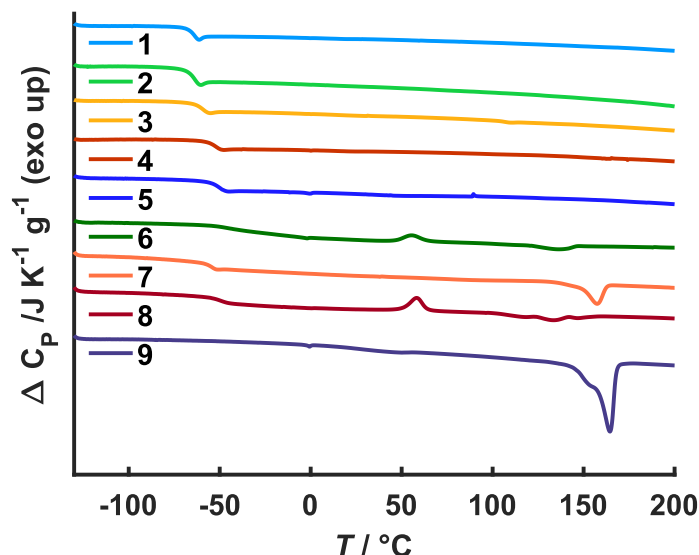
<sup>a</sup> Molar masses and monomer contents were determined by the integration on the quaternary carbons of 1,4-PDMCH (130.5 ppm), 1,4-PI (135.3 ppm), 3,4-PI (147.6 ppm), the methine (125.2 ppm) or methylene protons (111.6 ppm) of 1,4- and 3,4-PI in case of the 5 kg·mol<sup>-1</sup> and the methyl carbon of *sec*-BuLi (11.8 ppm) in an inverse gated <sup>13</sup>C NMR (CDCl<sub>3</sub>, 600 MHz,  $d_1 = 10$  s) in case of the copolymers or an inverse gated <sup>13</sup>C NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 100 °C, 126 MHz,  $d_1 = 15$  s) in case of the homopolymer. <sup>b</sup> Determined by SEC (THF, PI calibration standard, RI detector). Since the higher molecular weight samples tended to aggregate, full SEC traces and a detailed discussion are given in the ESI (Figure S24). The here given molar masses and dispersities rely only on the analysis of the main signals. <sup>c</sup> The glass transition or melting temperatures were determined by differential scanning calorimetry (-140 – 200 °C, 10 °C·min<sup>-1</sup>). *n.d.*: Molar masses could not be determined by NMR because of a too poor signal-to-noise-ratio to integrate on the methyl carbon of *sec*-BuLi (11.8 ppm).

In order to counteract precipitation, reaction conditions with lower monomer concentrations for higher molar mass polymers favoring solubility (Table 2, entries 6-8) and for entry 8 additionally a higher reaction temperature flattening the copolymer's gradient were chosen. In this way, several gradient copolymers with varied molar masses (5-40 kg·mol<sup>-1</sup>) and composition (at maximum 23 mol% DMCH) were realized and characterized by NMR and SEC (Table 2, Figures S24&S25). The 2D NMR experiments (Figures S27-S31) revealed an exclusive 1,4-incorporation of DMCH.

Copolymerization experiments at room temperature with 2 or 20 equivalents of THF only altered the ratio of the polyisoprene microstructures towards higher vinyl content, whereas the microstructure of PDMCH showed solely 1,4-units. Solubility of the formed copolymer remained an issue despite the increase in solvent polarity.

The polymers' thermal properties were examined by DSC (Table 2, Figure 7), revealing melting of PDMCH starting at 130 °C for the homopolymer (entry 9), whose synthesis is discussed in

the next section. A weak glass transition of PDMCH can be assigned at 53 °C. The second heating curves of the low molar mass copolymers (entries 1-5) only show a glass transition in the range of -66 – -51 °C, gradually increasing with increasing DMCH content. This observation of solely one  $T_g$  at intermediate temperatures together with the absence of melting indicates that no phase separation occurs.



**Figure 7:** Third cycles (heating curves) of the DSC measurements of the copolymers (1-8) and the PDMCH homopolymer (9) listed in Table 2. Temperature range: -140 – 200 °C, heating and cooling rates: 10 °C·min<sup>-1</sup>.

The DSC diagrams of the copolymers of higher molar mass (entries 6-8) feature a glass transition in the range of -48 – -55 °C, that increases when lowering the molar mass (entry 7 vs. 6) or the steepness of the gradient (entry 7 vs. 8). Furthermore, melting of PDMCH domains is most pronounced for entry 7 explained by the largest PDMCH block, presumably leading to the most extended domain size and segregation strength. This is also reflected in the onset of melting that equals the one of the homopolymer, whereas entry 6 and 8 exhibit lowered melting temperatures. Besides, entry 6 and 8 show cold crystallization starting at 42 – 45 °C, tentatively explained by the PDMCH domains being partially quenched into an amorphous structure that becomes sufficiently mobile accessing the glass transition temperature. Regardless of this crystallization, melting is comparably weak, further supporting the argument of less pronounced segregation.

### Homopolymerization of Dimethylenecyclohexane

Besides copolymerization experiments with isoprene, also the homopolymerization of DMCH was investigated. Enabling the homopolymerization requires a solvent, in which the formed polymer is soluble. Experiments in boiling cyclohexane, mixtures of cyclohexane with THF or toluene led to precipitation during polymerization and thus ill-defined specimens, whereas the reaction in tetralin at 140 °C was successful (Table 2, entry 9). The formation of a well-defined polymer was proven by DOSY NMR (Figure S23) and MALDI-ToF mass spectrometry (Figure S17). Again, exclusive 1,4-incorporation was confirmed by 2D NMR experiments (Figures S18-S22).

PDMCH synthesized by radical or cationic polymerization was described in literature published as early as 1954 as oily for low molar masses, but as a brittle and high-melting, colorless solid for high molar masses.<sup>[13]</sup> Due to limited possibilities at the time of publication, a detailed investigation by methods like SEC or DSC was not provided. We hereby quantify the thermal behavior by DSC (*vide supra*, Table 2, Figure 7), revealing a  $T_g$  around 50 °C and a melting onset at 130 °C.

### Copolymerization of Isoprene and Isoprenylmethylmethylenecyclohexene

In analogy to DMCH, IMMCH was employed for the copolymerization with isoprene. However, the copolymerization in pure cyclohexane did not lead to a notable incorporation of the *trans*-diene, as shown by NMR (Figure S32) and MALDI-ToF mass spectrometry (Figure S34). Therefore, experiments in mixtures of cyclohexane and THF ( $n_{\text{THF}}/n_{\text{Initiator}}=2, 20, 200$ ) were conducted in order to modify the reaction mechanism towards a more ionic character (Figure 1).

As proven by MALDI-ToF mass spectrometry (Figure S34), the presence of THF as a modifier increases the content of polyisoprene with one or two IMMCH repeating units, but no significant consumption of IMMCH was achieved. Even with 200 equivalents of THF, the MALDI-ToF mass spectrum shows that pure polyisoprene homopolymer is the main product (Figure 8, orange assignment), whereas polyisoprene with one or two IMMCH units incorporated (Figure 8, green and red assignments, respectively) are only observed as sub-distributions. NMR (Figures S35-S39) and SEC data (Figure S33) reveal the formation of well-defined polyisoprene. The molar masses of all polymers lie in the range of the targeted PI block, for which reason an inactivation of the chain end by IMMCH can be excluded. In conclusion, the *transoid* 1,3-diene IMMCH is not reactive under the given conditions.

In addition, homopolymerization experiments in pure cyclohexane as well as cyclohexane mixtures with THF were conducted, but again no polymerization was observed.

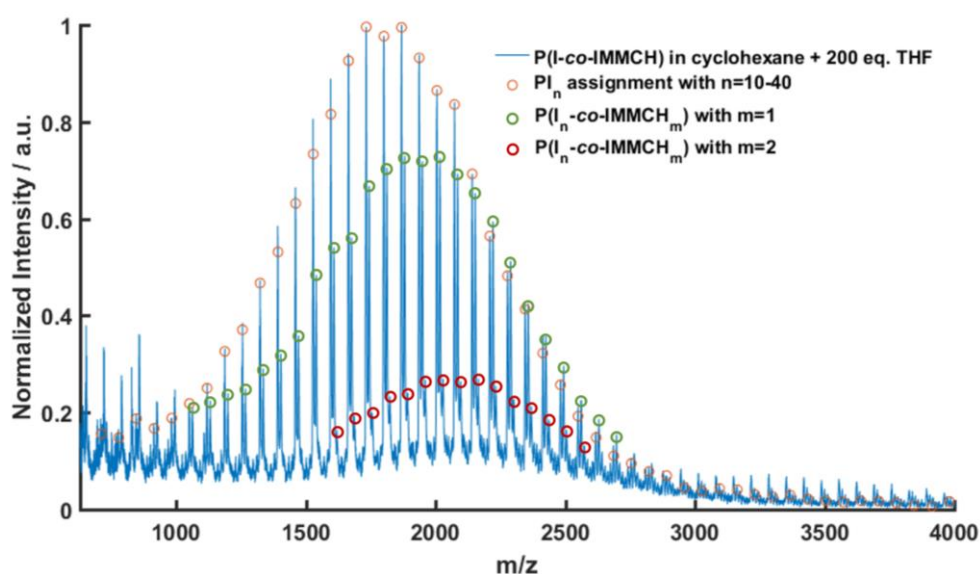


Figure 8: MALDI-ToF mass spectrum of P(I-co-IMMCH) in cyclohexane in the presence of 200 equivalents of THF. Matrix: DCTB, ionization agent: AgTFA, mode: linear. The distribution of pure polyisoprene  $PI_n$  with  $n=10-40$  (orange), the distribution of polyisoprene with one IMMCH repeating unit (green), and the distribution of polyisoprene with two IMMCH repeating units (red) are assigned.

## Experimental Section

A detailed experimental description of the monomers as well as polymer syntheses in batch can be found in the Supp. Inf.. Furthermore, supplemental spectra and results of DFT calculations are given.

### Real-Time $^1\text{H}$ NMR Method

The kinetic studies were performed with a 500 MHz Bruker Avance III system. All spectra were referenced internally to residual proton signals of the deuterated solvent. All kinetic experiments were performed in cyclohexane- $d_{12}$ . The comonomer mixtures (9-10 wt% in cyclohexane- $d_{12}$ ) were prepared in a glove box, and subsequently initiated with only one drop of a *sec*-butyllithium solution. The monomers as well as the deuterated solvent were purified by distillation over calcium hydride and in case of the monomers furthermore with trioctylaluminum prior to use. The mixtures were filled into a conventional NMR tube and sealed with a rubber septum.

One spectrum was recorded prior to initiation. After the initiation at 1.3 M (1.3 M in cyclohexane/hexane 92/8 in case of the kinetics at 25 °C; also 40 and 60 °C for comparison, although only few data points could be collected) and at 0.13 M obtained by dilution with cyclohexane in case of the kinetics at 40 and 60 °C, the NMR experiments were started without locking and shimming.

All spectra were measured with 1 scan at 500 MHz and the experiments were performed with time intervals between the spectra of 100 s, due to the long  $T_1$  relaxation times of isoprene and *exo-cis* DMCH ( $T_{1,I}^{25\text{ °C}}=40\text{ s}$ ,  $T_{1,I}^{60\text{ °C}}=37\text{ s}$ ;  $T_{1,\text{DMCH}}^{25\text{ °C}}=14\text{ s}$ ,  $T_{1,\text{DMCH}}^{60\text{ °C}}=29\text{ s}$ ).

Since the decrease of the monomer signal and hence mathematically spoken the derivative of the signal's integral is analyzed, insufficient relaxation has only a minor effect. Regardless of this fact,  $T_1$  relaxation times vary with the viscosity of the reaction solution. Therefore, experiments with longer  $d_1$  times are performed, even though fewer data points are especially disadvantageous for the fit of rapid reactions. The reaction temperature was held constant at 25, 40 or 60 °C.

The polymerization was terminated with degassed methanol after full conversion; the polymer was analyzed by SEC in THF with PI standard. The monomer depletion data were evaluated regarding the reactivity ratios using NIREVAL Software from Dr. Tobias Johann, Dr. Marvin Steube and Prof. Dr. Holger Frey.<sup>[20]</sup>

### NMR Spectroscopy

2D NMR spectra were recorded using a Bruker Avance III 600 with 600 MHz ( $^1\text{H}$ ) or 151 MHz ( $^{13}\text{C}$ ) and a 5 mm TCI-cryo probe with z-gradient and ATM, 500 MHz ( $^1\text{H}$ ) or 126 MHz ( $^{13}\text{C}$ ) or 400 MHz ( $^1\text{H}$ ) or 101 MHz ( $^{13}\text{C}$ ).

The spectra are referenced internally to residual proton signals of deuterated solvent.

## SEC Measurements

Size exclusion chromatography was carried out in THF on an instrument consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump, a set of three MZ-Gel SDplus columns based on SDV with particle sizes of 5  $\mu\text{m}$  (porosities of 100,  $10^3$  and  $10^5$  Å for molecular weight areas <3 000, 1 000-40 000 and 10 000-2 000 000 Da, respectively) and RI (35 °C) as well as UV detectors (254 nm). 100  $\mu\text{L}$  of the sample solution were loaded, and it was operated at room temperature at flow rates of 1  $\text{mL}\cdot\text{min}^{-1}$ . Polyisoprene standards used for calibration were provided by Polymer Standard Service.

## DSC Measurements

Thermal properties were studied using a Mettler-Toledo DSC 823 differential scanning calorimeter. The instrument was calibrated using indium, zinc and water as a standard. Two heating and one cooling cycle were performed at a rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$  in a temperature range between -140 and 200  $^{\circ}\text{C}$ . Glass or melting temperatures were extracted from the second heating cycle.

## MALDI-ToF Mass Spectrometry

Mass spectra were recorded using a Bruker Autoflex Max with a smartbeam-II solid state laser. The specimens were studied in linear positive mode, using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix and silver trifluoroacetate (AgTFA) as ionization agent in the ratio 10:10:1 (specimen/matrix/salt).

## DFT Calculations

DFT calculations were performed on MOGON II at the high-performance computing center of the Johannes Gutenberg-University Mainz using ORCA 4.2.1. software.<sup>[21]</sup> The B3LYP hybrid density functionals<sup>[22]</sup> were used as the calculation of the analytical Hessian matrix is available. Furthermore, the D3BJ<sup>[23]</sup> atom-pairwise dispersion correction to the DFT energy with Becke-Johnson damping was enabled. The def2-TZVP valence triple-zeta basis set<sup>[24]</sup> was selected and for an accurate single point energy TightSCF was chosen together with a Grid6 integration grid. The RIJCOSX approximation<sup>[25]</sup> was implemented together with a GridX8 for accurate geometry optimization, as it offers large accelerations. Finally, geometrical Counterpoise Corrections (gCP)<sup>[26]</sup> were enabled to prevent artificial overbinding effects. Solvation was not considered, since the experimentally used cyclohexane has a low dielectric strength ( $\epsilon_r=2.02$ ) and therefore only negligible solvent effects.

To simulate a complete reaction pathway with a climbing image (CI) including a transition state (TS), the NEB-TS method<sup>[27]</sup> (Nudged Elastic Band with Transition State optimization) was implemented, inputting the precursor and product geometries. Visualization of the geometries and orbitals were performed using IboView18.

## Conclusion

The copolymerization behavior of isoprene with the cyclic dienes DMCH and IMMCH exhibiting a rather rigid, prescribed *cisoid* and *transoid* geometry, respectively, was examined in cyclohexane via *in situ*  $^1\text{H}$  NMR measurements and DFT calculations. Remarkably, experimental observations correlated with the predicted reactivities.

Simulations revealed a high activation barrier for the 1,4-addition of DMCH ascribed to the ring distortion that is necessary to allow a coordination of the living chain end by both double bonds, which are in plane. On the contrary, in case of IMMCH no coordination of both double bonds was found and hence, no 1,4-addition predicted despite significant  $\pi$ -conjugation.

Copolymerization experiments verified this hypothesis, showing gradient formation in isoprene/DMCH copolymerizations in cyclohexane with exclusive 1,4-addition of DMCH, but hardly any IMMCH incorporation in isoprene/IMMCH copolymerizations in cyclohexane. Detailed understanding was achieved by  $^1\text{H}$  NMR kinetics, the derived reactivity ratios evidencing a flattening of the gradient's steepness upon temperature increase. Besides, no decrease of the two isomers of *exo-cis* DMCH could be detected, of which one comprises a fixed *transoid* geometry (*trans* DMCH). This suggests that at least an influence of the substitution in 2-position of IMMCH preventing anionic polymerization can be excluded. Still, the 1,3-disubstitution pattern of IMMCH could affect the polymerizability compared to DMCH. However, together with the partial charges of IMMCH, the inertness of *trans* DMCH further indicates that IMMCH did not copolymerize at the given conditions because of its *transoid* geometry and thus coordination by only one double bond of this monomer. Consequently, a possible sterical hindrance only plays a minor role. Furthermore, also the homopolymerization of DMCH could be implemented, using the high-boiling solvent tetralin, which is suitable for carbanionic polymerization.

In summary, we demonstrate the requirement of two *cisoid* oriented double bonds with strong  $\pi$ -conjugation for the 1,4-addition of a 1,3-diene in nonpolar media at moderate reaction conditions and timescales, in line with the commonly accepted reaction mechanism. DFT simulations are proven to be useful to gain an insight into comonomer systems prior to experiments and hence assess feasibility.

## Author Contributions

Ramona D. Barent and Holger Frey elaborated the conceptualization and administered the project. Manfred Wagner performed and validated the specialized real-time  $^1\text{H}$ -NMR methodology. Ramona D. Barent was responsible for the synthetic parts, theoretical calculations, formal analysis, writing of the original draft and visualization of the obtained data. All authors were involved in the writing process at review- and editing stage.

## Conflicts of interest

There are no conflicts to declare.



## Acknowledgements

This work was supported by the Max Planck Graduate Center with the Johannes Gutenberg-University Mainz (MPGC). We thank Jürgen Ludwig (JGU) for specialty glassware, Monika Schmelzer (JGU) for valuable support with SEC measurements and Dr. Elena Berger-Nicoletti (JGU) for MALDI-ToF measurements. Furthermore, we thank Petra Räder (MPI-P) for DSC measurements. Besides, the authors gratefully acknowledge the computing time granted on the supercomputer Mogon II at Johannes Gutenberg-University Mainz.

## References

- [1] a) M. Steube, T. Johann, R. D. Barent, A. H. Müller, H. Frey, *Prog. Polym. Sci.* **2022**, *124*, 101488; b) W. Wang, W. Lu, A. Goodwin, H. Wang, P. Yin, N.-G. Kang, K. Hong, J. W. Mays, *Prog. Polym. Sci.* **2019**, *95*, 1.
- [2] R. P. Quirk, *Anionic Polymerization. Principles and Practical Applications*, Taylor and Francis, Boca Raton, **1996**.
- [3] A. H. E. Müller, K. Matyjaszewski, *Controlled and living polymerizations. Methods and materials*, Wiley-VCH, Weinheim, **2009**.
- [4] S. Bywater in *Adv. Polym. Sci.*, *4/1* (Eds.: J. D. Ferry, W. Kern, G. Natta, C. G. Overberger, G. V. Schulz, A. J. Staverman, H. A. Stuart), Springer Berlin Heidelberg, Berlin, Heidelberg, **1965**, pp. 66–110.
- [5] W. Gebert, J. Hinz, H. Sinn, *Makromol. Chem.* **1971**, *144*, 97.
- [6] D. J. Worsfold, S. Bywater, *Macromolecules* **1978**, *11*, 582.
- [7] A. Forens, K. Roos, C. Dire, B. Gadenne, S. Carlotti, *Polymer* **2018**, *153*, 103.
- [8] Y. Yu, J. He, *Eur. Polym. J.* **2017**, *86*, 58.
- [9] S. Uchida, K. Togii, S. Miyai, R. Goseki, T. Ishizone, *Macromolecules* **2020**, *53*, 10107.
- [10] K. Hong, J. W. Mays, *Macromolecules* **2001**, *34*, 782.
- [11] I. Natori, S. Inoue, *Macromolecules* **1998**, *31*, 982.
- [12] A. T. Blomquist, D. T. Longone, *J. Am. Chem. Soc.* **1957**, *79*, 3916.
- [13] W. J. Bailey, H. R. Golden, *J. Am. Chem. Soc.* **1954**, *76*, 5418.
- [14] a) T. Nishida, K. Satoh, S. Nagano, T. Seki, M. Tamura, Y. Li, K. Tomishige, M. Kamigaito, *ACS Macro Lett.* **2020**, *9*, 1178; b) T. Nishida, K. Satoh, M. Tamura, Y. Li, K. Tomishige, M. Kamigaito, *Macromolecules* **2022**, 2300.
- [15] T. Nishida, K. Satoh, M. Tamura, Y. Li, K. Tomishige, S. Caillol, V. Ladmiral, M. Vayer, F. Mahut, C. Sinturel et al., *Polym. Chem.* **2021**, *12*, 1186.
- [16] W. Wang, R. Schlegel, B. T. White, K. Williams, D. Voyloy, C. A. Steren, A. Goodwin, E. B. Coughlin, S. Gido, M. Beiner et al., *Macromolecules* **2016**, *49*, 2646.
- [17] Y. Kosaka, R. Goseki, S. Kawauchi, T. Ishizone, *Macromol. Symp.* **2015**, *350*, 55.

- [18] Y. Kosaka, S. Kawauchi, R. Goseki, T. Ishizone, *Macromolecules* **2015**, *48*, 4421.
- [19] S. Kobayashi, C. Lu, T. R. Hoye, M. A. Hillmyer, *J. Am. Chem. Soc.* **2009**, *131*, 7960.
- [20] M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey, A. H. E. Müller, *Macromolecules* **2019**, *52*, 9299.
- [21] a) F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73; b) F. Neese, *WIREs Comput. Mol. Sci.* **2018**, *8*, 1.
- [22] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [23] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.
- [24] a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- [25] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2009**, *356*, 98.
- [26] H. Kruse, S. Grimme, *J. Chem. Phys.* **2012**, *136*, 154101.
- [27] a) V. Ásgeirsson, B. O. Birgisson, R. Bjornsson, U. Becker, F. Neese, C. Riplinger, H. Jónsson, *J. Chem. Theory Comput.* **2021**, *17*, 4929; b) G. Henkelman, H. Jónsson, *J. Chem. Phys.* **2000**, *113*, 9978.

## Supporting Information

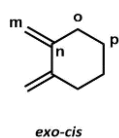
### Materials

The solvents cyclohexane (Fisher Science,  $\geq 99.8\%$ ) and tetrahydrofuran (THF, Fisher Science,  $\geq 99.8\%$ ) were dried over sodium with benzophenone as indicator. 1,2,3,4-Tetrahydronaphthalene (tetralin, TCI,  $>97\%$ ) was dried with *sec*-butyllithium and 1,1-diphenylethylene (DPE, abcr, 98%) as indicator. The solvents methanol (MeOH, Fisher Science,  $\geq 99.9\%$ ), pentane (Fisher Science,  $\geq 99\%$ ) and *N,N*-dimethylacetamide (DMAC, Acros Organics, 99.5%) were used as purchased. The chemicals 2-methylcyclohexanone (Acros Organics, 98%), *R*-(-)-carvone (Sigma Aldrich, 98%) dimethyl sulfone (abcr, 99%), potassium *tert*-butoxide ( $\text{KO}^t\text{Bu}$ , TCI,  $>97\%$ ) and methyl triphenylphosphonium bromide (Sigma Aldrich, 98%) were used without further purification.

The stabilizer of isoprene (I, Acros Organics, 98%) was removed filtering the monomer through a column containing basic aluminium oxide and purified hereafter by degassing and distillation over calcium hydride (Acros Organics, 93%) and trioctyl aluminum (Sigma Aldrich, 25 wt% in hexanes). The synthesized monomers DMCH and IMMCH were purified in analogy to isoprene. *Sec*-Butyllithium (*sec*-BuLi, Acros Organics, 1.3 M in cyclohexane/hexane (92/8)) was used as supplied for reactions on laboratory scale but diluted in dried cyclohexane for the kinetic investigations of fast polymerization reaction.

### Preparation of 1,2-Dimethylenecyclohexane (DMCH)

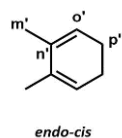
The monomer was synthesized in a modified procedure described by Garst *et al* <sup>[1]</sup>, dissolving the starting material 2-methyl-cyclohexanone (30.3 g, 32.78 mL, 0.27 mmol, 1 eq.) and dimethyl sulfone (58.5 g, 0.62 mmol, 2.3 eq.) in DMAC (377 mL). The solution was heated to 75 °C and subsequently potassium *tert*-butoxide (72.7 g, 0.65 mmol, 2.4 eq.) was added portionwise to avoid a huge temperature increase. After at least 3 hours the reaction was completed (tracked by  $^1\text{H}$ -NMR) and was allowed to cool down to room temperature. Then, the DMAC reaction solution was diluted with water (260 mL) and extracted against pentane (3 times  $\times$  180 mL). The combined organic phases were washed with water several times (5-6 times  $\times$  100 mL) to remove all DMAC traces. The organic phase was dried over magnesium sulfate and purified by distillation. First, pentane was removed (40 °C, 800 mbar), and then DMCH was fractionated with a Vigreux column (69-70 °C, 120 mbar), yielding a mixture of the three isomers that was enriched in *exo-cis* DMCH (43% yield). The ratio of the isomers can be deduced from NMR measurements (Figures S5-S10).

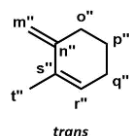


*exo-cis*:

$^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 4.92 (dt,  $J=2.4, 1.1$  Hz, 2H, m), 4.64 (dt,  $J=2.8, 1.5$  Hz, 2H, m), 2.25 (m, 4H, o), 1.63 (m, 4H, p).

$^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 149.83 (2C, N), 107.96 (2C, M), 35.43 (2C, O), 26.92 (2C, P).

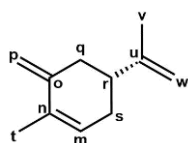
**endo-cis:**
 $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 5.56 (m, 2H, o'), 2.01 (m, 4H, p'), 1.77 (m, 6H, m').

 $^{13}\text{C}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 133.83 (2C, N'), 122.04 (2C, O'), 23.01 (2C, P'), 19.79 (2C, M').
**trans:**
 $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 5.68 (m, 1H, r''), 4.86 (s, 1H, m''), 4.74 (s, 1H, m''), 2.59 (s, 1H, q''), 2.35 (ddt,  $J=7.8, 4.4, 1.4$  Hz, 2H, o''), 2.12 (m, 2H, p''), 1.81 (m, 3H, t'').

 $^{13}\text{C}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 144.94 (1C, S''), 132.81 (1C, N''), 123.41 (1C, R''), 107.79 (1C, M''), 32.90 (1C, Q''), 32.52 (1C, O''), 26.53 (1C, P''), 19.38 (1C, T'').

### Preparation of (5R)-5-Isopropenyl-2-methyl-1-methylene-2-cyclohexene (IMMCH)

The monomer was synthesized via a Wittig reaction starting from (*R*)-(-)-carvone. The reaction flask was flame-dried and put under argon atmosphere before distilling the dried THF (170 mL) into the reaction flask. Methyltriphenylphosphonium bromide (27.51 g, 77 mmol, 1.1 eq.) was dissolved in THF and subsequently potassium *tert*-butoxide (8.64 g, 77 mmol, 1.1 eq.) was added to generate the corresponding ylide *in situ*. Afterwards, the carvone (10.52 g, 10.96 mL, 70 mmol, 1.0 eq.) was added via syringe and the reaction mixture was stirred for 14 hours at room temperature. After completion, the reaction mixture was diluted with roughly 15 mL of pentane, filtered two times and the solvents pentane and THF were removed by distillation under reduced pressure. Afterwards, the crude product was obtained by distillation out of the TPPO melt (oil bath temperature: 160 °C, crude product distilled at 80 °C and 160 mbar) and then fractionated with a Vigreux column (90-94 °C, 34 mbar), yielding pure IMMCH (56% yield). Figures S11-S15 show the 2D NMR analysis and the Figure S16 proves full removal of all TPPO residues by  $^{31}\text{P}$  NMR.


 $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 5.69 (ddq,  $J=5.4, 2.8, 1.4$  Hz, 1H, m), 4.90 (m, 1H, p), 4.79 (m, 1H, p), 4.74 (m, 2H, w), 2.46 (m, 1H, q), 2.30 (m, 1H, r), 2.28 (m, 1H, q), 2.20 (m, 1H, s), 2.09 (m, 1H, s), 1.82 (dt,  $J=2.4, 1.4$  Hz, 3H, t), 1.74 (t,  $J=1.1$  Hz, 3H, v).

 $^{13}\text{C}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 149.35 (1C, U), 144.98 (1C, N), 132.63 (1C, O), 127.77 (1C, M), 109.12 (1C, W), 108.41 (1C, P), 42.25 (1C, R), 37.49 (1C, Q), 31.89 (1C, S), 20.85 (1C, V), 19.40 (1C, T).

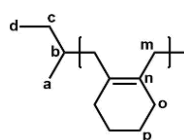
### General Procedure for Carbanionic Polymerization

The monomers were dried over calcium hydride and trioctylaluminium, and then distilled into an anionic flask. Polymerizations at room temperature were performed in an argon-flooded glove box and hence the solvents and reagents added volumetrically under argon atmosphere. For polymerizations at higher temperatures, the monomers were added to dried solvents in argon counterflow using syringes and the solution was tempered to the desired temperature. Afterwards, the required amount of *sec*-BuLi was added under vigorous stirring. The living chain ends were terminated by addition of methanol. The polymers were precipitated pouring the

reaction solution into a 5-10-fold excess of methanol, dried at reduced pressure for at least one week and stored in the absence of light at -20 °C under argon atmosphere.

### Homopolymerization of 1,2-Dimethylenecyclohexane (PDMCH)

Tetralin (4.6 mL) was cryotransferred into the reaction flask and the monomer DMCH (0.45 g, 0.54 mL, 4.6 mmol, 45.7 eq.) was added via a syringe under argon atmosphere. The reaction solution was heated up to 140 °C while stirring. Upon reaching the reaction temperature, the initiator *sec*-BuLi (0.07 mL, 1.3 M, 0.09 mmol, 1 eq.) was added using a syringe and the reaction solution was stirred vigorously. After 3 hours, the polymerization was terminated adding 0.1 mL of methanol. The hot reaction solution (105 °C to preserve solubility) was precipitated into 30 mL methanol. The polymer was dried at reduced pressure a white solid was obtained in quantitative yield. The raw NMR solution did not show any sign for unreacted monomer traces. An exclusive 1,4 incorporation can be proven by 2D NMR analysis (Figures S18-S23).



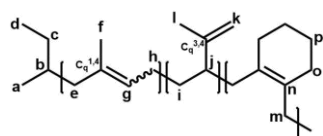
$^1\text{H}$  (500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ )  $\delta$ [ppm] = 2.11 (4H, m), 2.04 (4H, o), 1.63 (4H, p), 0.95 (3H per chain, d), 0.90 (3H per chain, a).

$^{13}\text{C}$  (126 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ )  $\delta$ [ppm] = 130.42 (2C, N), 32.36 (2C, M), 29.72 (2C, O), 23.52 (2C, P), 18.81 (1C per chain, A), 11.39 (1C per chain, D).

### Copolymerization of 1,2-Dimethylenecyclohexane with Isoprene (P(I-co-DMCH))

The preparations of the 5 000  $\text{g}\cdot\text{mol}^{-1}$  polymers with differing DMCH ratio were performed at room temperature inside a glove box; the preparations of the 20 000  $\text{g}\cdot\text{mol}^{-1}$  or 40 000  $\text{g}\cdot\text{mol}^{-1}$  polymers with 30 mol% DMCH at 40 °C or 60 °C were performed in a fume hood using Schlenk-technique. The reactions with a higher target molar mass of 20 000 and 40 000  $\text{g}\cdot\text{mol}^{-1}$  were first conducted with an initial monomer concentration of 1.8  $\text{mol}\cdot\text{L}^{-1}$ , as done for the 5 000  $\text{g}\cdot\text{mol}^{-1}$  polymers. Due to gelation issues, the initial monomer concentrations ( $c=(n_I+n_{\text{DMCH}})\cdot V_{\text{cyclohexane}}^{-1}$ ) had to be reduced to guarantee proper mixing and prevent gelation (see Table 2).

The procedure is exemplified for a 40 000  $\text{g}\cdot\text{mol}^{-1}$  polymer with 40 mol% DMCH. Dried cyclohexane (62 mL for an initial monomer concentration of 1.0 M) was freshly distilled and transferred into the reaction flask and the monomers DMCH (*exo-cis*: 2.67 g, 3.18 mL, 24.7 mmol, 190 eq.; the absolute amount of the isomeric mixture was factored in the purity determined by  $^1\text{H}$  NMR prior to use) and isoprene (2.52 g, 3.71 mL, 37.0 mmol, 285 eq.) were added via a syringe under argon atmosphere. The reaction solution was heated up to the targeted reaction temperature and then the initiator *sec*-BuLi (0.10 mL, 1.3 M, 0.13 mmol, 1 eq.) was added using a syringe while stirring the reaction solution vigorously. The next day (~16 hours), the polymerization was terminated adding 0.2 mL of methanol. The polymer was precipitated into 600 mL methanol, and dried at reduced pressure. A white solid was obtained in quantitative yield. The raw NMR solution did show complete conversion over night at elevated reaction temperatures, but unreacted DMCH traces for reactions over night at room temperature (Figure S26). The polymers were characterized by 2D NMR, what is exemplified for one specimen (Figures S27-S31).



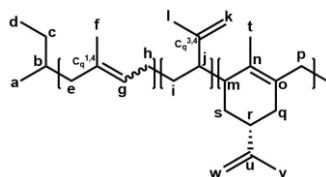
$^1\text{H}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 5.1 (1H, g), 4.8 (1H, k), 4.7 (1H, k), 2.0 (2H, h), 2.0 (2H,  $e^{\text{cis}}$ ), 2.0 (4H, m), 2.0 (2H,  $e^{\text{trans}}$ ), 2.0 (4H, o), 1.7 (3H,  $f^{\text{cis}}$ ), 1.6 (3H,  $f^{\text{trans}}$ ), 1.6 (3H, l), 1.5 (4H, p), 1.5 (2H, i), 0.9 (3H per chain, d), 0.8 (3H per chain, a).

$^{13}\text{C}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 147.6 (1C,  $\text{C}_q^{3,4}$ ), 135.2 (1C,  $\text{C}_q^{3,4}$ ), 130.4 (2C, N), 125.2 (1C, G), 111.6 (1C, K), 48.1 (1C, J), 39.9 (1C,  $E^{\text{trans}}$ ), 32.6 (2C, M), 32.3 (1C,  $E^{\text{cis}}$ ), 29.8 (2C, O), 29.1 (1C, l), 26.5 (1C, H), 23.8 (2C, P), 23.5 (1C,  $F^{\text{cis}}$ ), 18.7 (1C per chain, A), 18.2 (1C, L), 15.7 (1C,  $F^{\text{trans}}$ ), 11.8 (1C per chain, D).

Depending on the initial monomer concentration, the DMCH ratio and the reaction temperature, the reaction solutions became turbid or even gelled, what was tried to be avoided to ensure unhindered diffusion. However, the 0.5 m reaction solution of the 40 000 g·mol<sup>-1</sup> polymer 40 mol% was turbid, but of comparatively low viscosity and hence still stirrable.

### Copolymerization of (5R)-5-isopropenyl-2-methyl-1-methylene-2-cyclohexene with Isoprene (P(I-co-IMMCH))

All reactions were performed inside a glove box. Cyclohexane (6.6 mL), the monomers IMMCH (1.00 mL, 0.88 g, 5.94 mmol, 22.8 eq.) and isoprene (0.59 mL, 0.40 g, 5.94 mmol, 22.8 eq.) and in three out of four cases the modifier THF (0.04 mL, 2 eq. / 0.42 mL, 20 eq. / 4.22 mL, 200 eq.) were transferred into a glass vial equipped with a magnetic stirrer and sealed with a septum cap. Next, the initiator *sec*-BuLi (0.20 mL, 1.3 M, 0.26 mmol, 1 eq.) was added under stirred vigorously. After 24 hours, the polymerization was terminated adding 0.3 mL of methanol. The polymer was precipitated into 50 mL methanol. The polymer was dried at reduced pressure giving a colorless viscous liquid. The NMR of the raw reaction solutions (Figure S32 exemplified for the reaction without THF) and also of the precipitated polymers revealed that no isoprene was left after polymerization, but IMMCH remained within the reaction solution unreacted (integral ratio of PI(g)/IMMCH(m) (1.00/0.92)). Homopolymerization experiments of IMMCH in cyclohexane, mixtures of cyclohexane with 2, 20 or 200 equivalents of THF and pure THF at room temperature failed. The polymers were characterized by 2D NMR, what is exemplified for one specimen (Figures S35-S39).



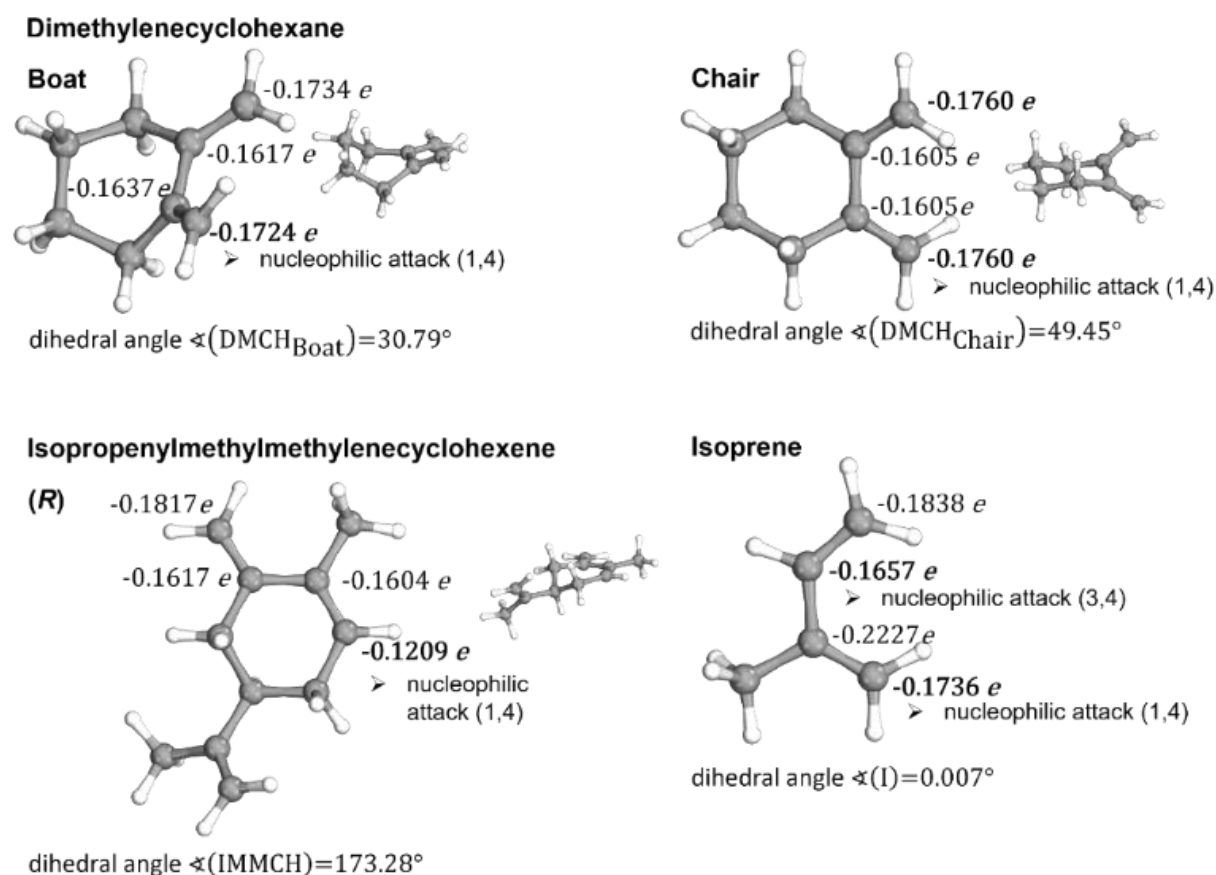
$^1\text{H}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 5.3 (1H, g), 4.9 (2H, k), 2.2 (2H, h), 2.2 (2H,  $e^{\text{cis}}$ ), 2.1 (2H,  $e^{\text{trans}}$ ), 2.1 (1H, j), 1.8 (3H,  $f^{\text{cis}}$ ), 1.7 (3H,  $f^{\text{trans}}$ ), 1.7 (3H, l), 1.5 (2H, i), 0.9 (3H per chain, d), 0.9 (3H per chain, a).

$^{13}\text{C}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$ [ppm] = 147.6 (1C,  $\text{C}_q^{3,4}$ ), 135.2 (1C,  $\text{C}_q^{3,4}$ ), 125.4 (1C, G), 111.7 (1C, K), 48.1 (1C, J), 40.1 (1C,  $E^{\text{trans}}$ ), 32.4 (1C,  $E^{\text{cis}}$ ), 31.4 (1C, l), 26.7 (1C, H), 23.5 (1C,  $F^{\text{cis}}$ ), 19.2 (1C per chain, A), 18.5 (1C, L), 16.0 (1C,  $F^{\text{trans}}$ ), 11.5 (1C per chain, D).

## Supporting Information obtained by DFT Calculations

Figure S1 summarizes the Loewdin electron densities, the dihedral angle between the two double bonds as well as the 3D visualization of the monomers used. In case of DMCH, both the chair as well as the boat conformation are shown.

Figure S2 illustrates the arrangement of the living PDMCH-Li chain end with a DMCH monomer molecule during the reaction pathway, showing the 3D geometries during polymerization and assigning these structures to different stages of the reaction progress. Here, the residual chain is simplified as a methyl group and only the terminal unit, i.e., DMCH, is specified.



**Figure S1:** Chemical structures of the monomers dimethylenecyclohexane (DMCH), (5*R*)-5-isopropenyl-2-methyl-1-methylene-2-cyclohexene (IMMCH) and isoprene (I) with assigned partial charges and dihedral angle between the double bonds obtained by DFT calculations.

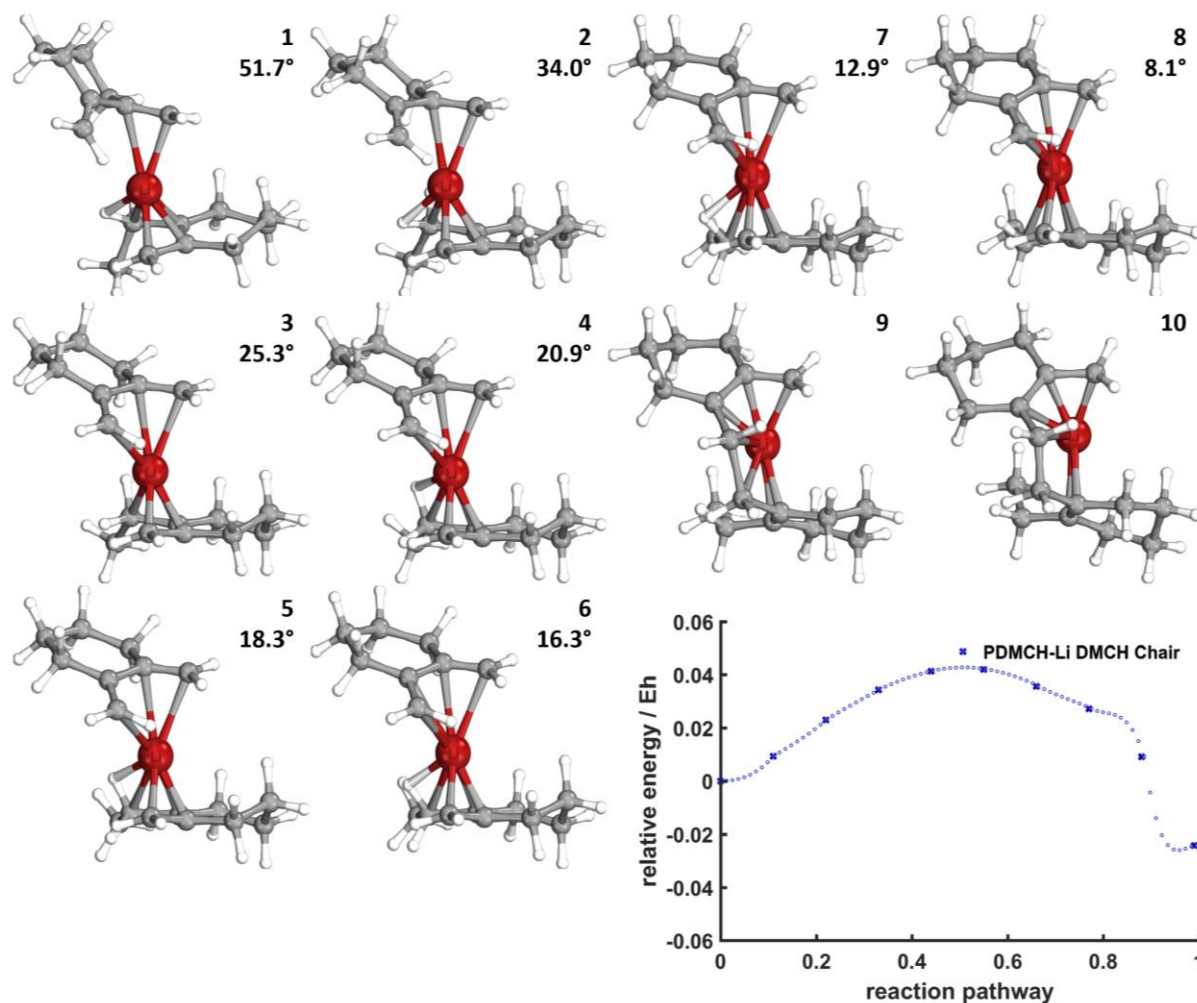


Figure S2: 3D visualization of the chemical structures along the reaction pathway of the DMCH homopropagation (PDMCH-Li + DMCH) obtained by DFT calculations. The dihedral angle between the double bonds is noted below the corresponding stage of reaction progress (values of x-axis: 0.00, 0.11, 0.22, 0.33, 0.44, 0.55, 0.66, 0.77, 0.88, 0.99 that are marked with a cross). For simplification and less computing effort, the residual chain is simulated by a methyl group, which is why influences of repeating units except the ultimate one are neglected.



Supporting Information concerning the *in situ*  $^1\text{H}$  NMR Kinetics

Figure S3 contains the plots of the logarithmic reciprocal concentration and the relative concentrations over time, respectively.

Figure S4 shows all plots for kinetical investigations at 40 and 60 °C, that were performed at higher initiator concentrations of (one drop of a 1.3M *sec*-BuLi solution), demonstrating the comparably speeded up reaction compared to room temperature.

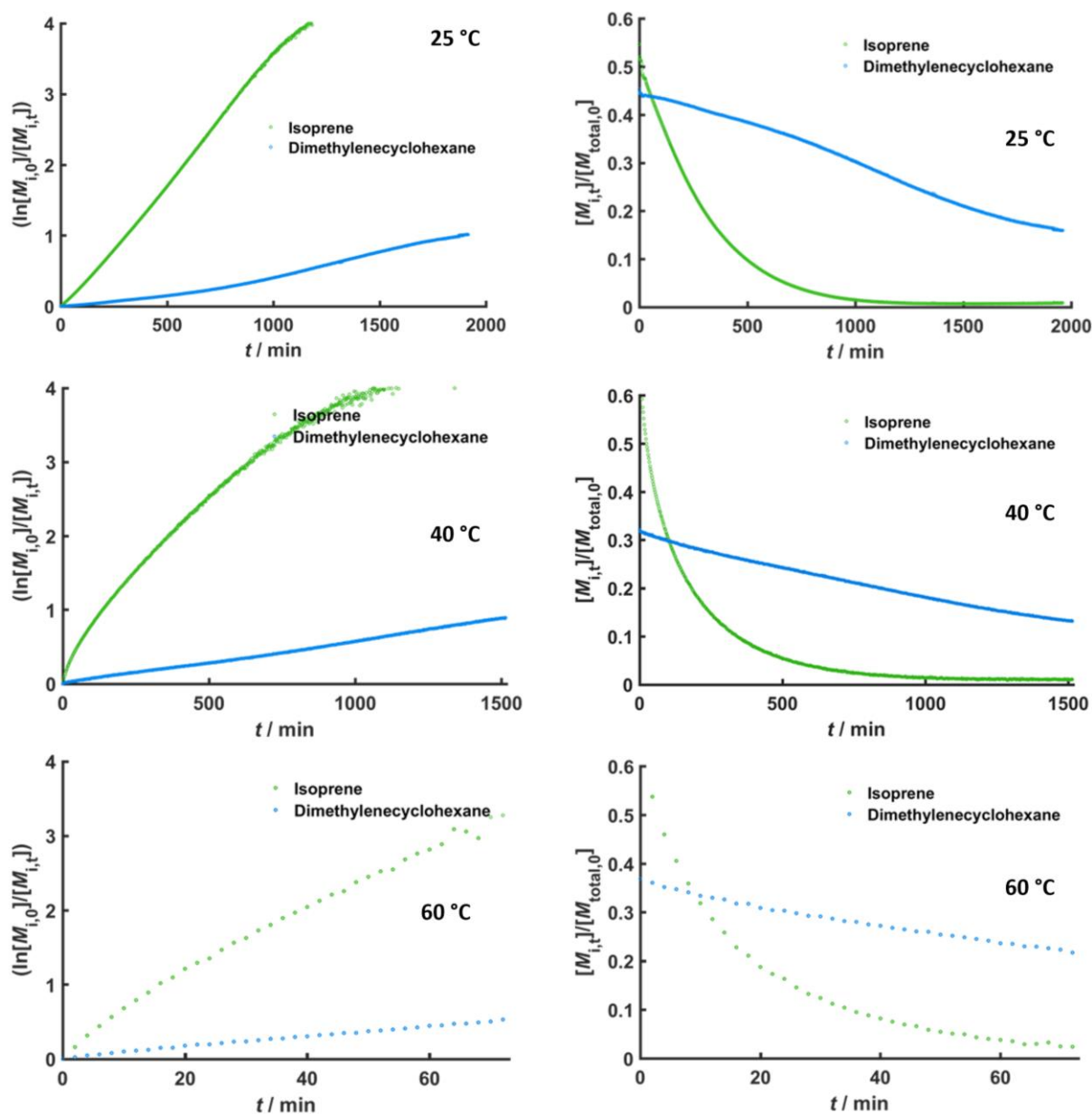


Figure S3: Left: Plot of the logarithmic reciprocal concentration  $\ln([M]_0/[M]_t)$  over time for both monomers isoprene (green) and DMCH (blue). Right: Plot of the relative concentrations ( $[M]_t/[M]_0$ ) over time for both monomers isoprene (green) and DMCH (blue). Top: Copolymerization at 25 °C, initiated with a 1.3M *sec*-BuLi solution. Middle, bottom: Copolymerizations at 40 and 60 °C, respectively, initiated with a 0.13M *sec*-BuLi solution.

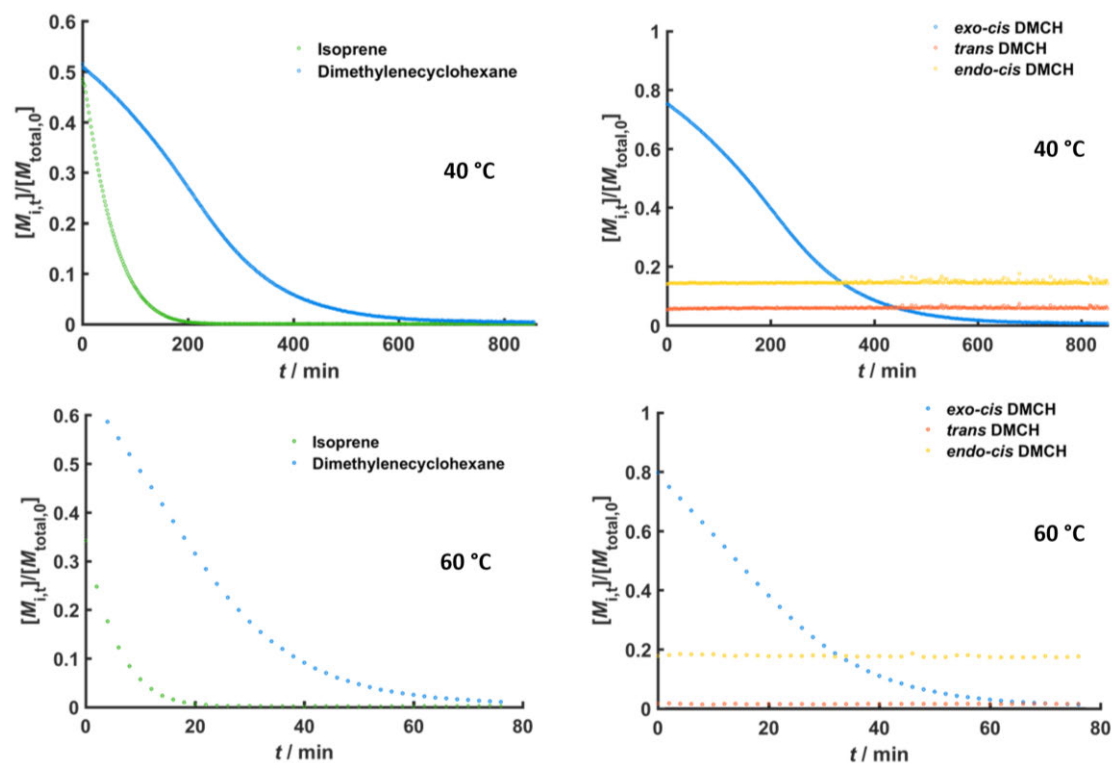


Figure S4: Left: Plot of the concentration  $[M_{i,t}]/[M_{total,0}]$  over time for both monomers isoprene (green) and DMCH (blue). Right: Plot of the relative concentration  $[M_i]/[M_0]$  over time for the three DMCH isomers *exo-cis* (blue), *endo-cis* (yellow) and *trans* (orange). Both kinetics were initiated with a 1.3M *sec*-BuLi solution.

### NMR spectra of DMCH

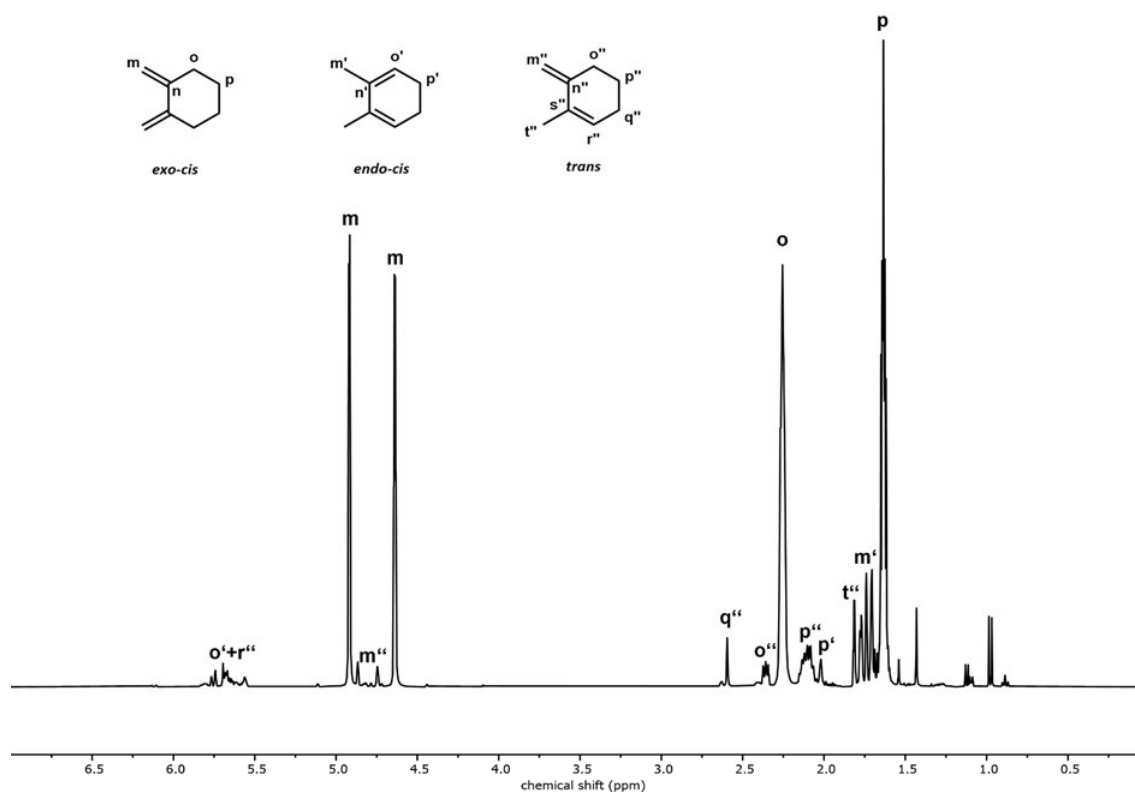


Figure S5:  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture is enriched in the reactive isomer *exo-cis* DMCH.

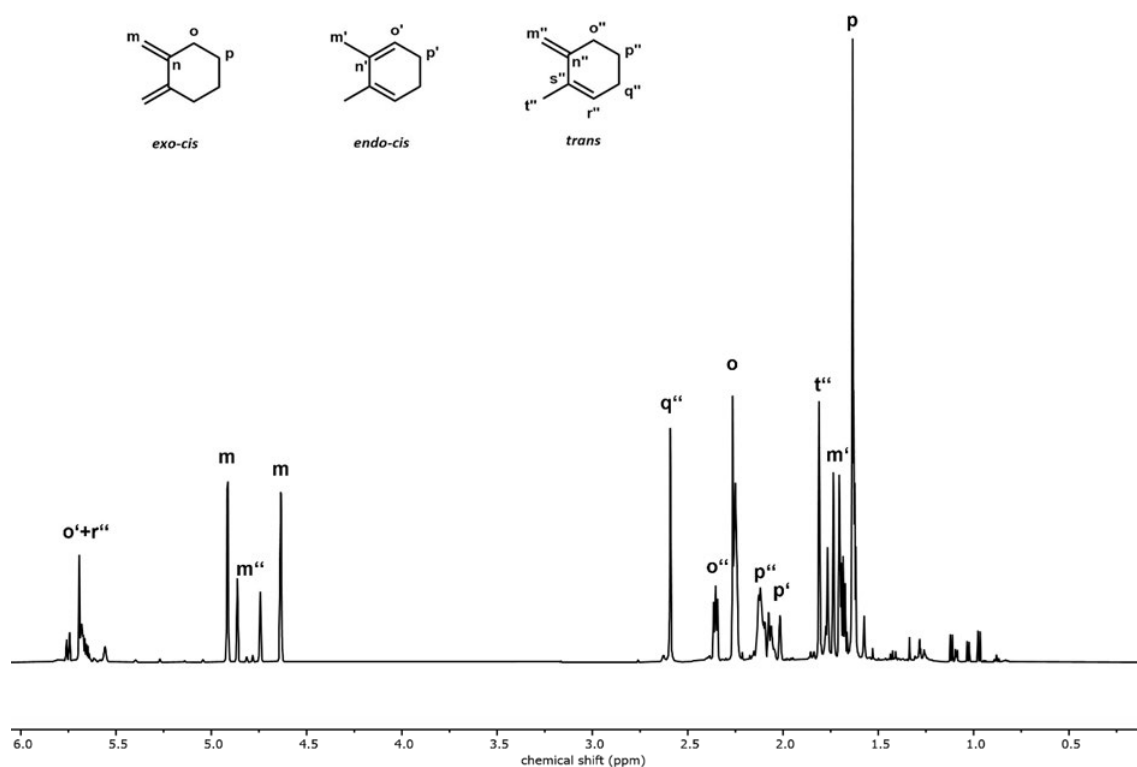


Figure S6:  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH with comparatively high amounts of the unreactive isomers.

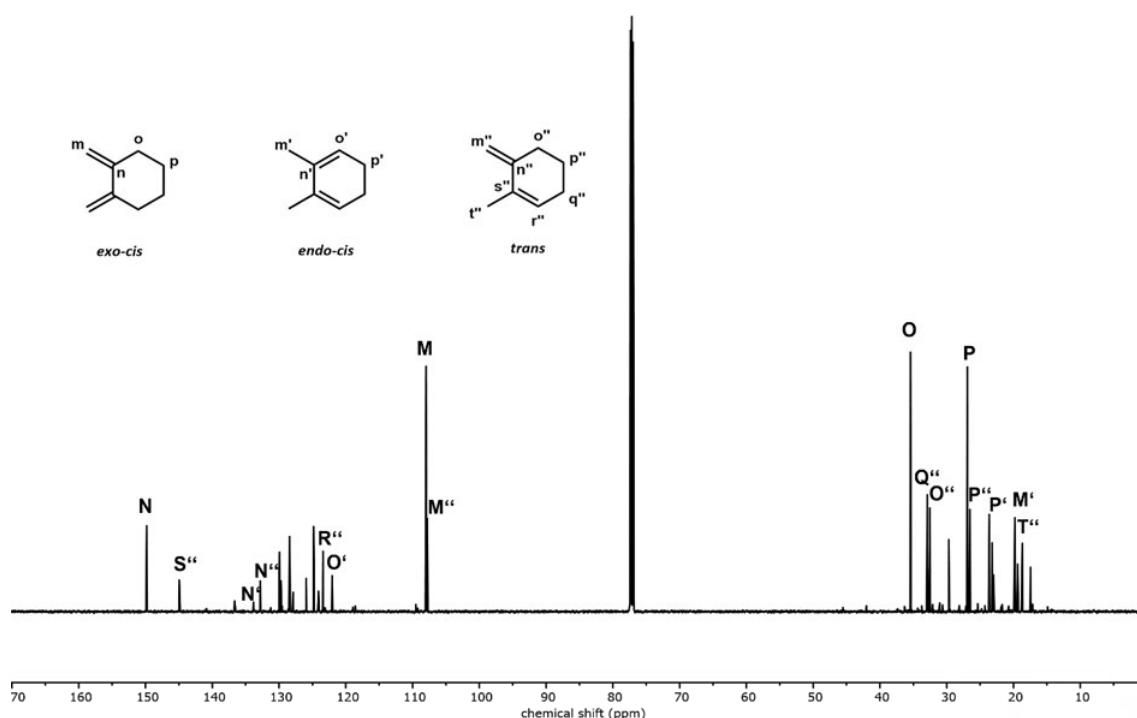


Figure S7:  $^{13}\text{C}$ -NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture contains comparatively high amounts of the unreactive isomers *endo-cis* and *trans* DMCH to facilitate assignments.

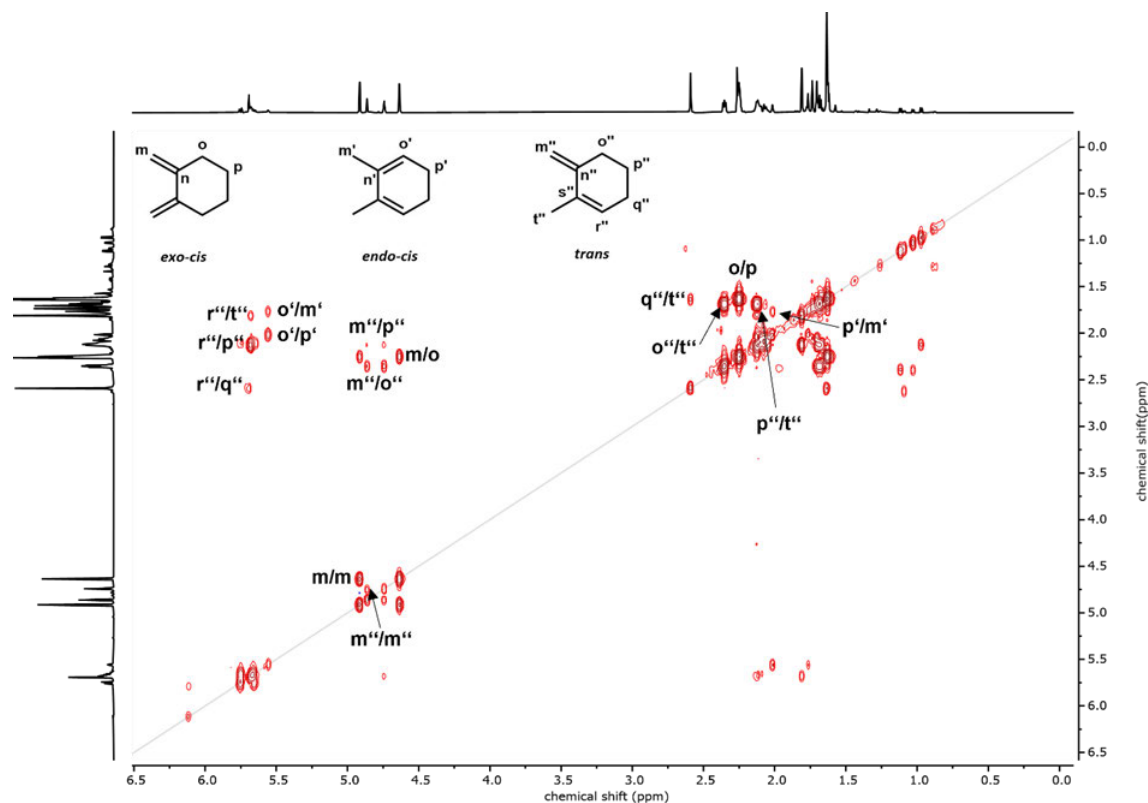


Figure S8:  $^1\text{H}$ -COSY-NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture contains comparatively high amounts of the unreactive isomers *endo-cis* and *trans* DMCH to facilitate assignments.

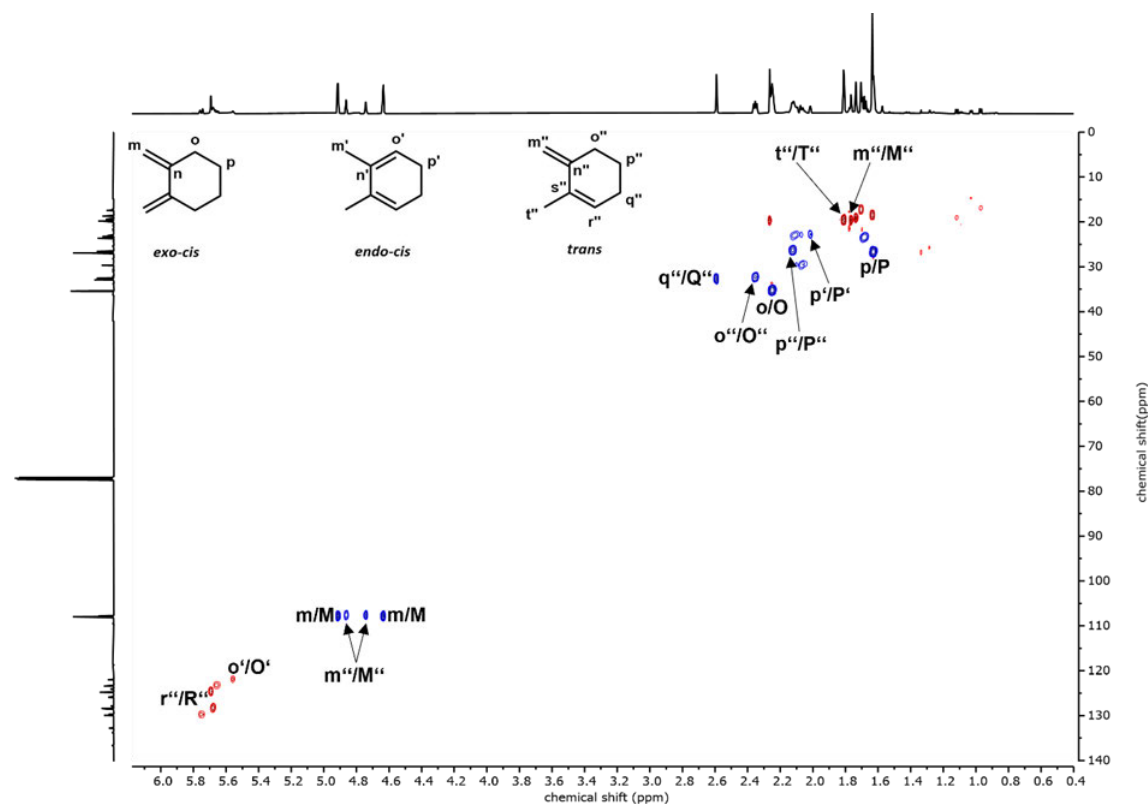


Figure S9:  $^1\text{H}$  $^{13}\text{C}$ -HSQC-NMR spectrum (400/101 MHz,  $\text{CDCl}_3$ ) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture contains comparatively high amounts of the unreactive isomers *endo-cis* and *trans* DMCH to facilitate assignments.

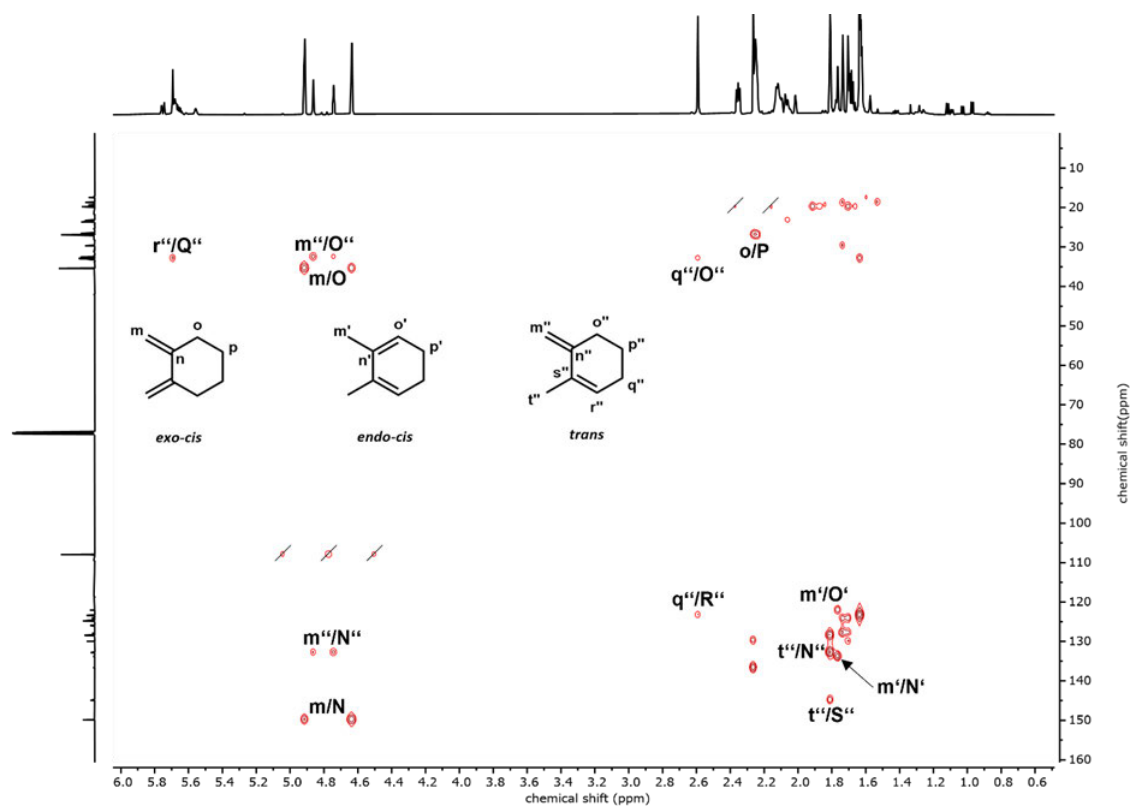


Figure S10:  $^1\text{H}^{13}\text{C}$ -HMBC-NMR spectrum (400/101 MHz,  $\text{CDCl}_3$ ) of *exo-cis* DMCH and its isomers *endo-cis* DMCH and *trans* DMCH. The mixture contains comparatively high amounts of the unreactive isomers *endo-cis* and *trans* DMCH to facilitate assignments.

### NMR spectra of IMMCH

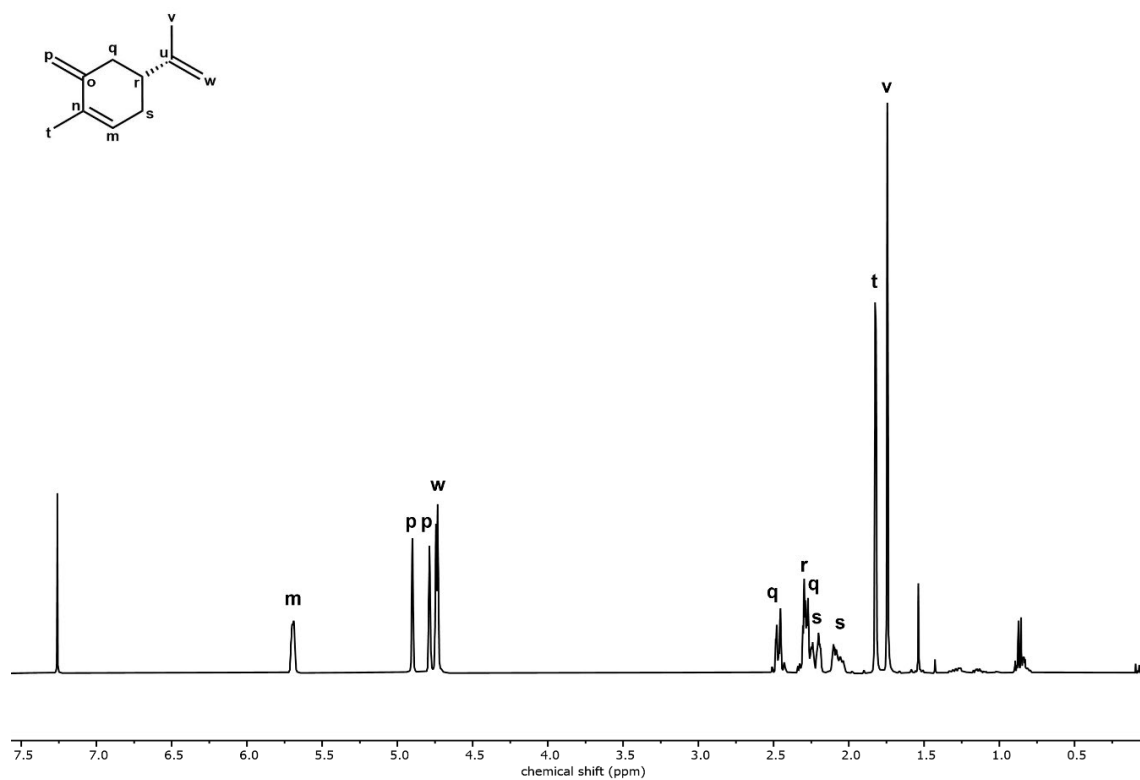


Figure S11:  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of IMMCH.

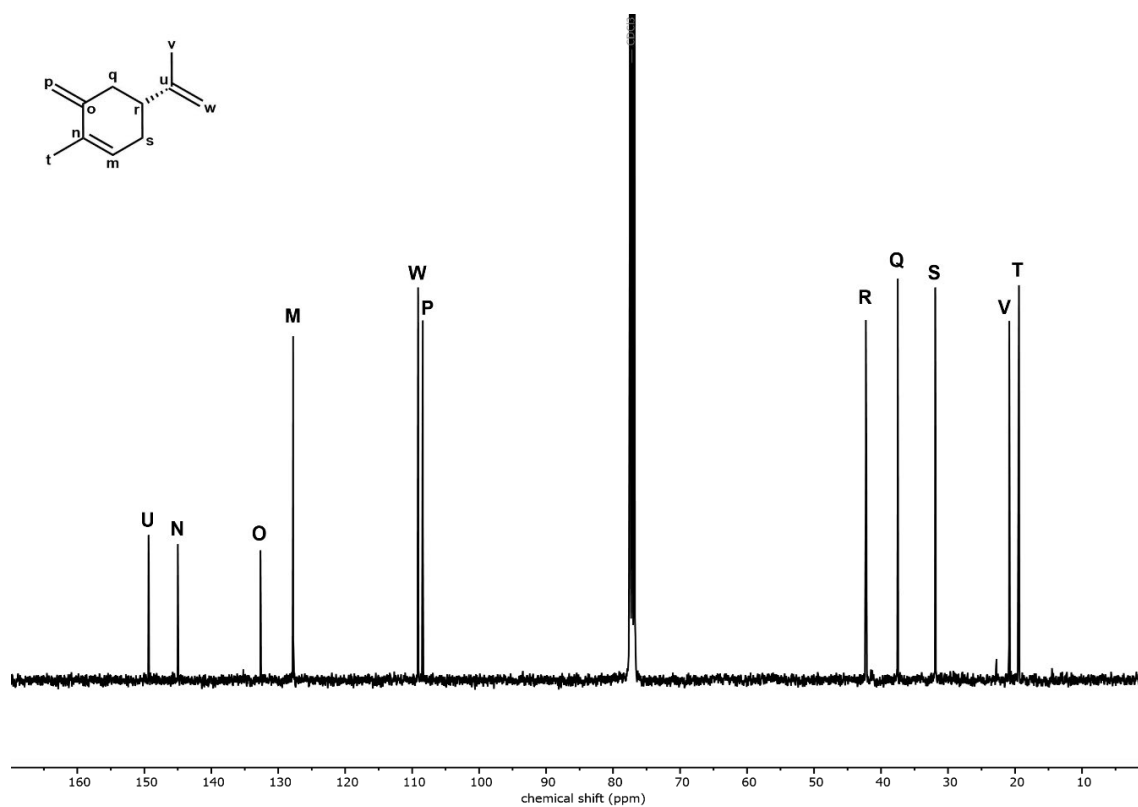


Figure S12:  $^{13}\text{C}$ -NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of IMMCH.

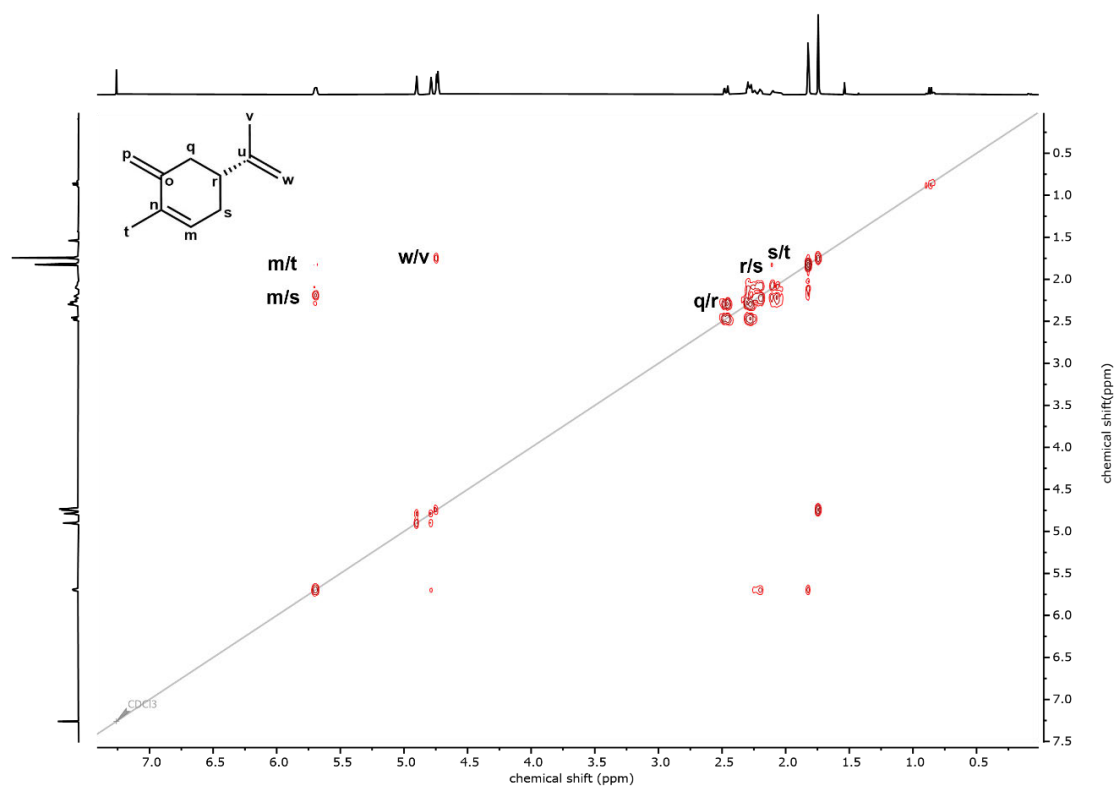


Figure S13:  $^1\text{H}$ - $^1\text{H}$ -COSY-NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of IMMCH.

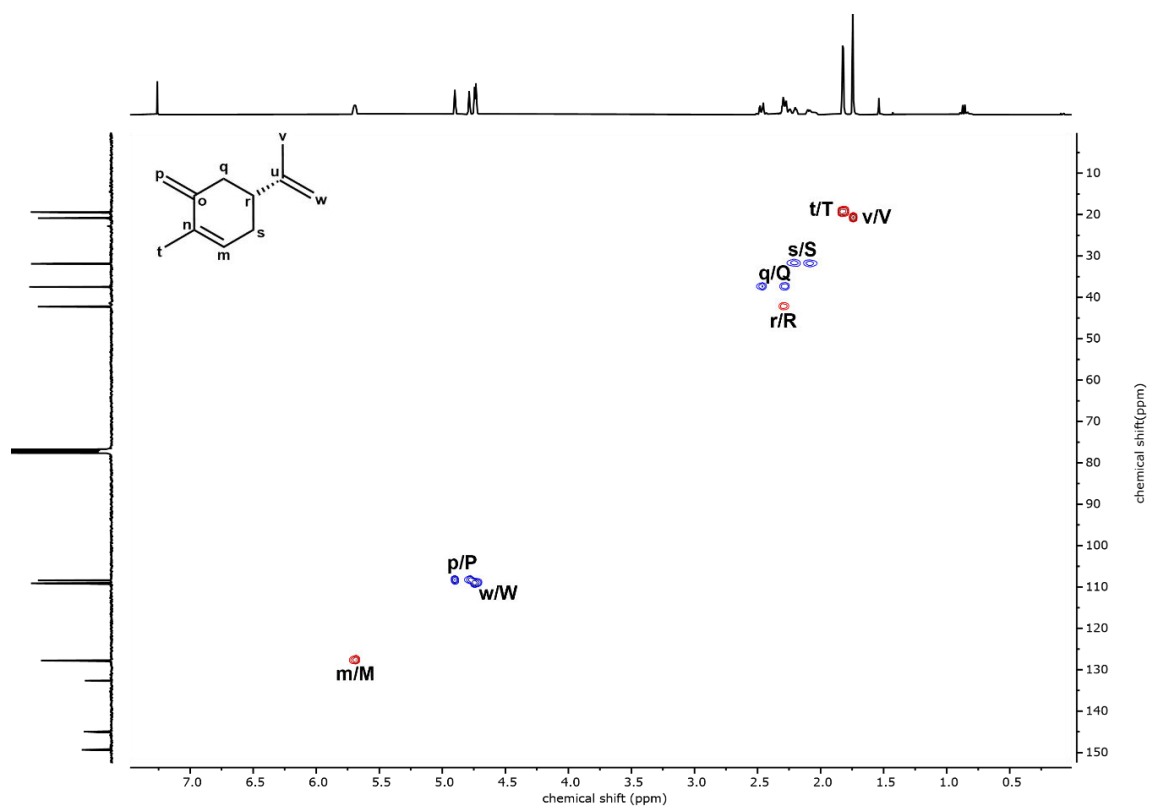


Figure S14:  $^1\text{H}^{13}\text{C}$ -HSQC-NMR spectrum (400/101 MHz,  $\text{CDCl}_3$ ) of IMMCH.

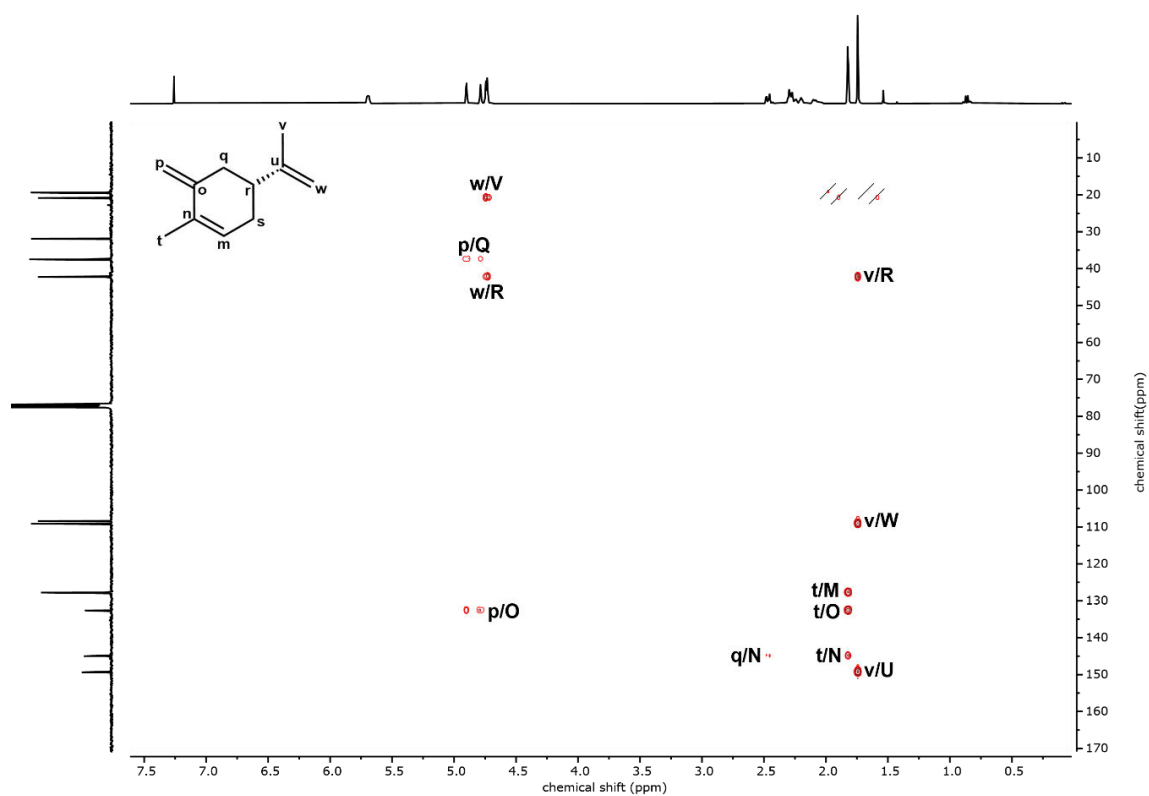


Figure S15:  $^1\text{H}^{13}\text{C}$ -HMBC-NMR spectrum (400/101 MHz,  $\text{CDCl}_3$ ) of IMMCH.

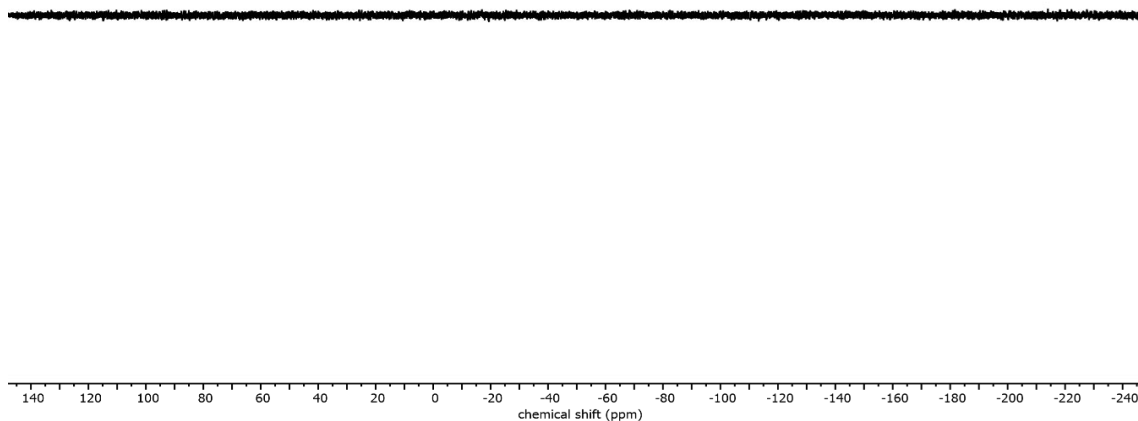
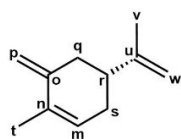


Figure S16:  $^{31}\text{P}$ -NMR spectrum (162 MHz,  $\text{CDCl}_3$ ) of IMMCH proving that no TPPO residues are present.

#### MALDI-ToF spectrum and NMR spectra of PDMCH

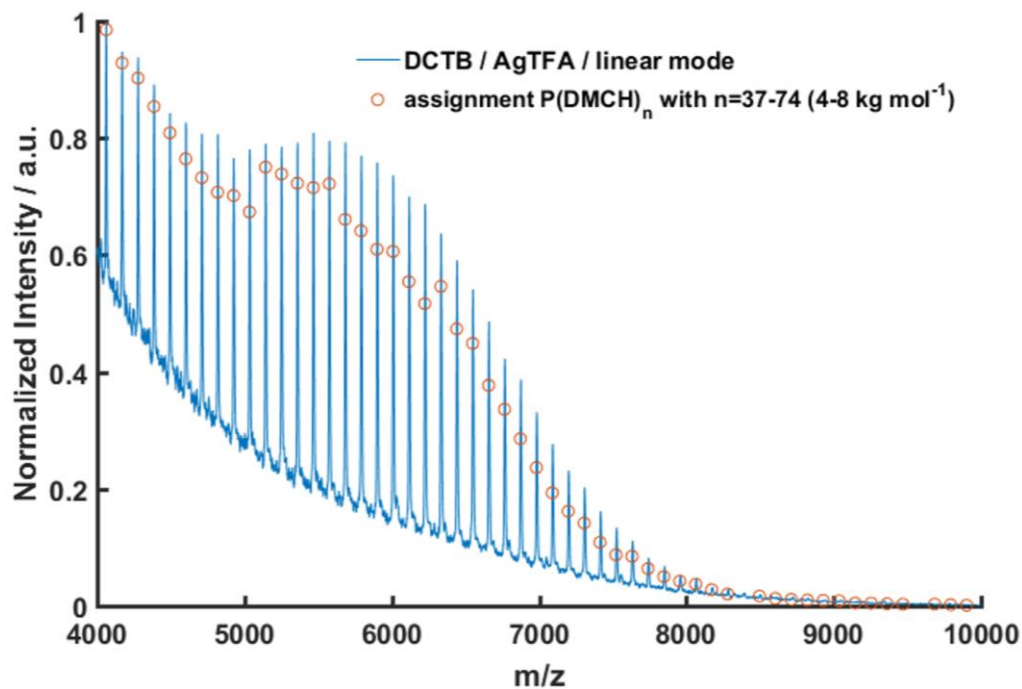


Figure S17: MALDI-ToF mass spectrum of PDMCH homopolymer. Matrix: DCTB, ionization agent: AgTFA, mode: linear.



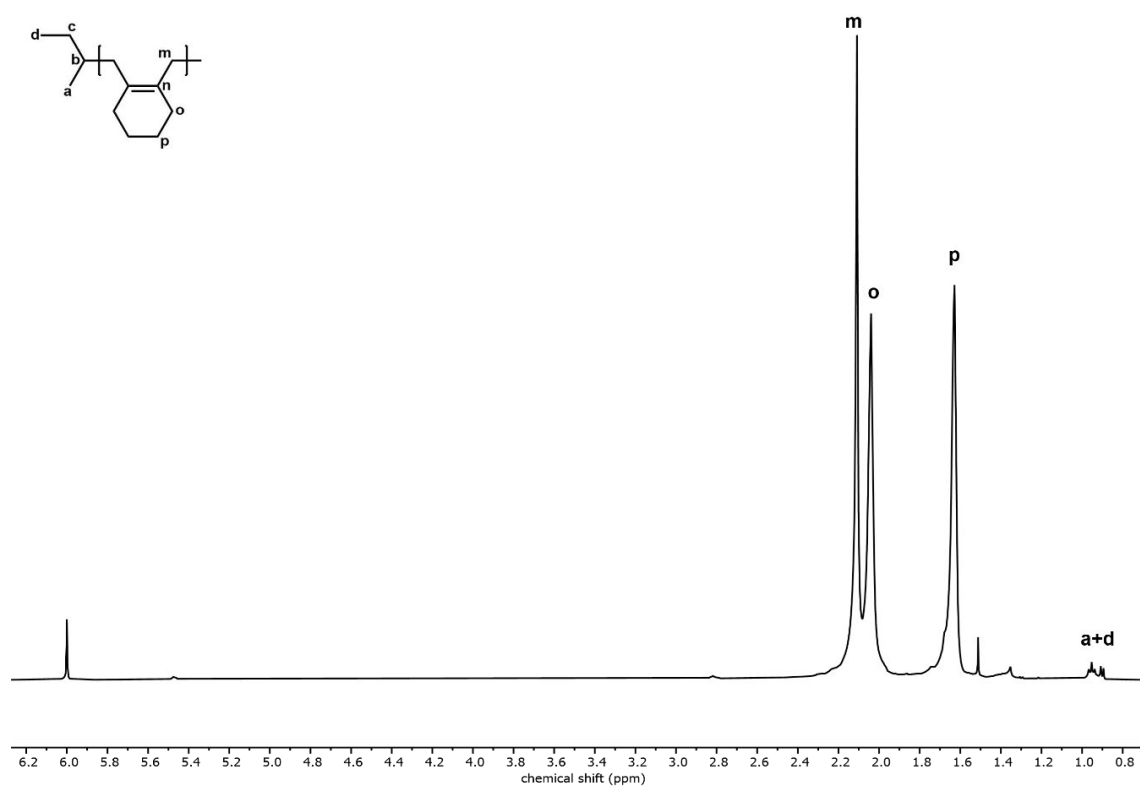


Figure S18:  $^1\text{H}$ -NMR spectrum (500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) of PDMCH measured at 100  $^\circ\text{C}$ .

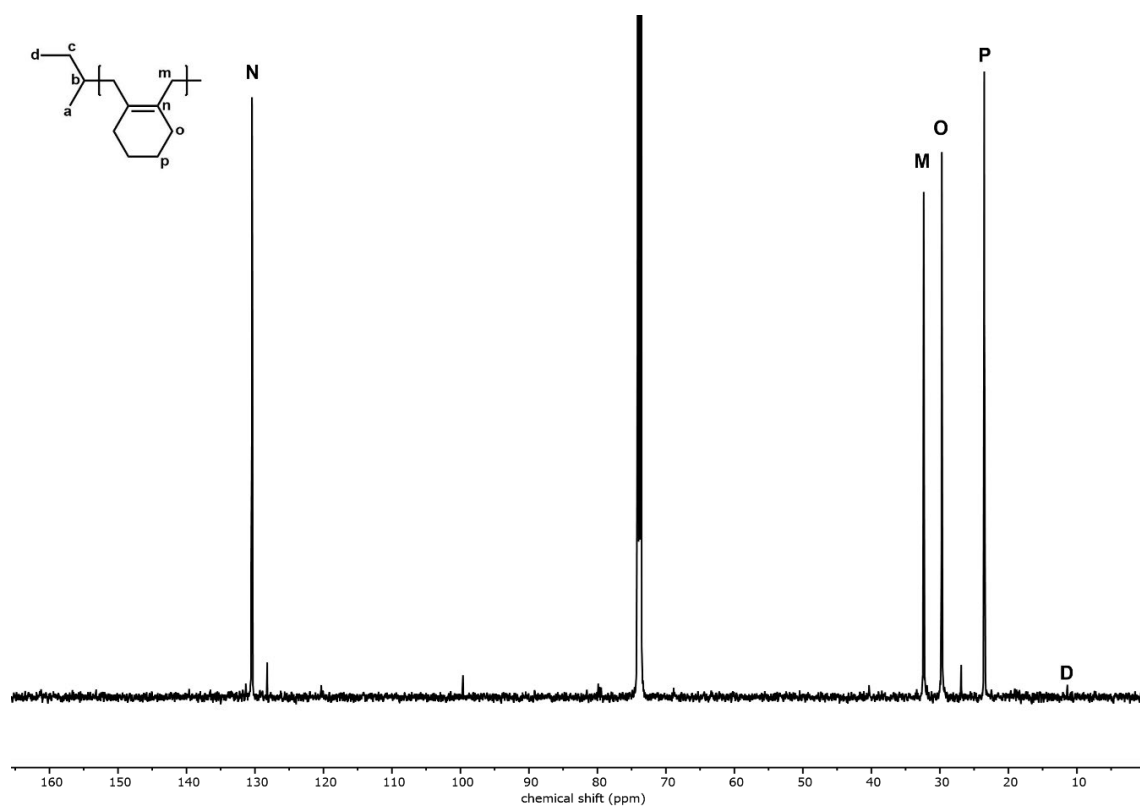


Figure S19: Inverse gated  $^{13}\text{C}$ -NMR spectrum (125 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) of PDMCH measured at 100  $^\circ\text{C}$ .

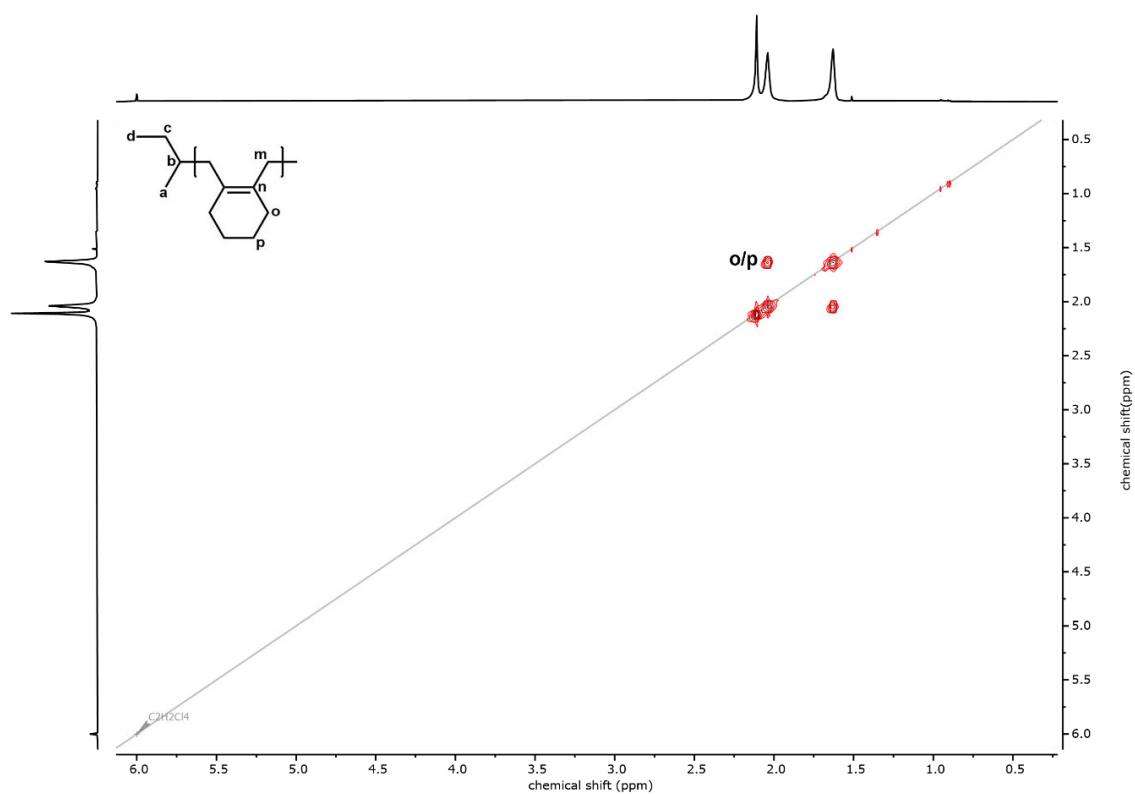


Figure S20:  $^1\text{H}$ -COSY-NMR spectrum (500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) of PDMCH measured at 100 °C.

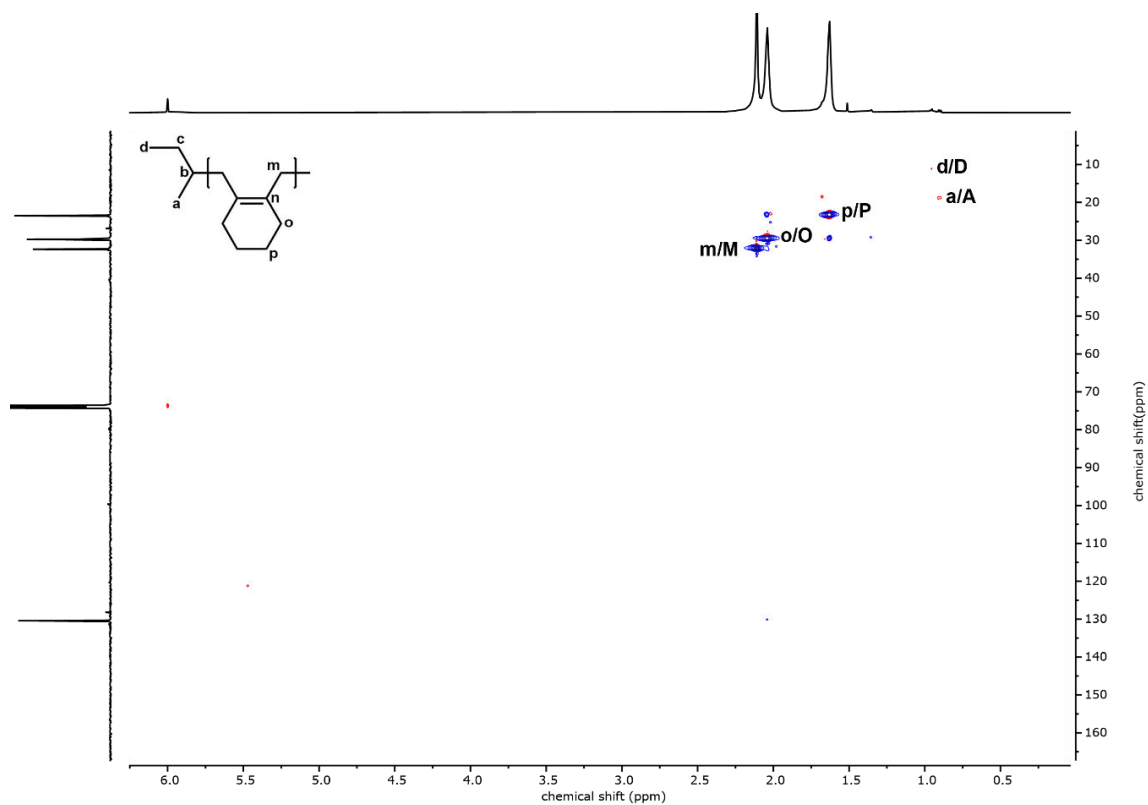


Figure S21:  $^1\text{H}$ - $^{13}\text{C}$ -HMBC-NMR spectrum (500/125 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) of PDMCH measured at 100 °C.

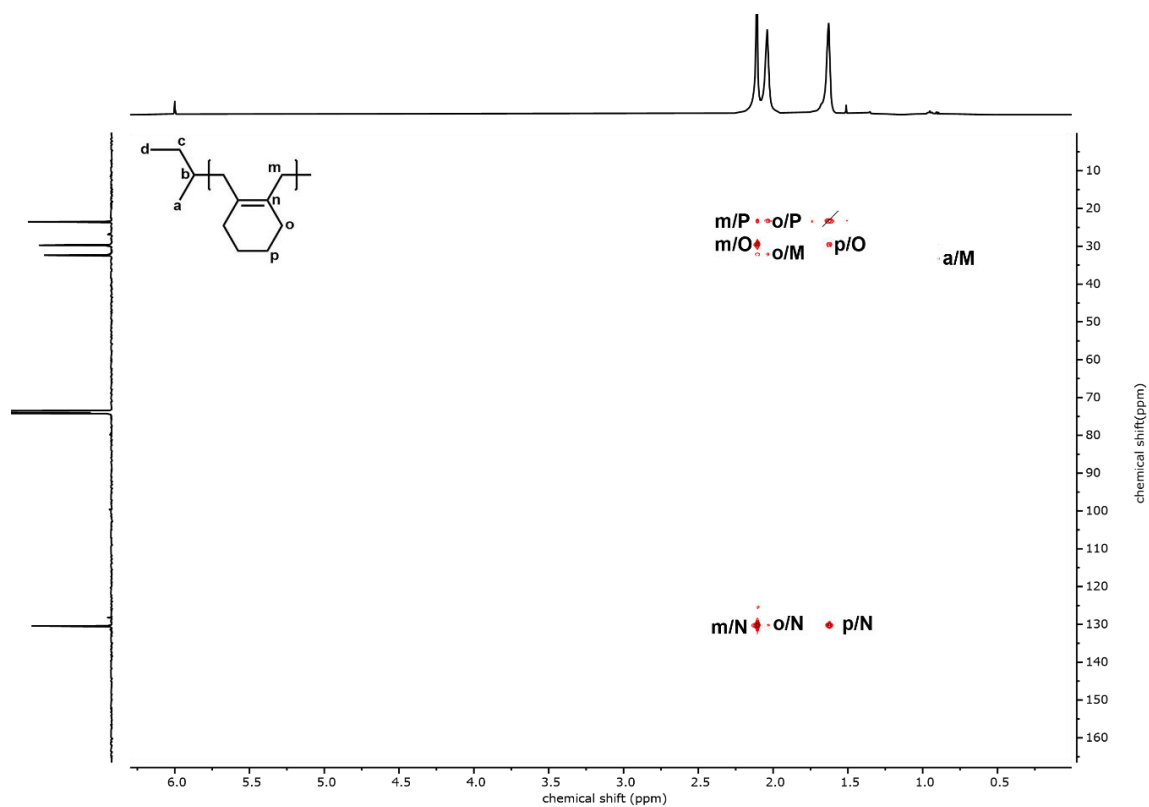


Figure S22:  $^1\text{H}^{13}\text{C}$ -HMBC-NMR spectrum (500/125 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) of PDMCH measured at 100 °C.

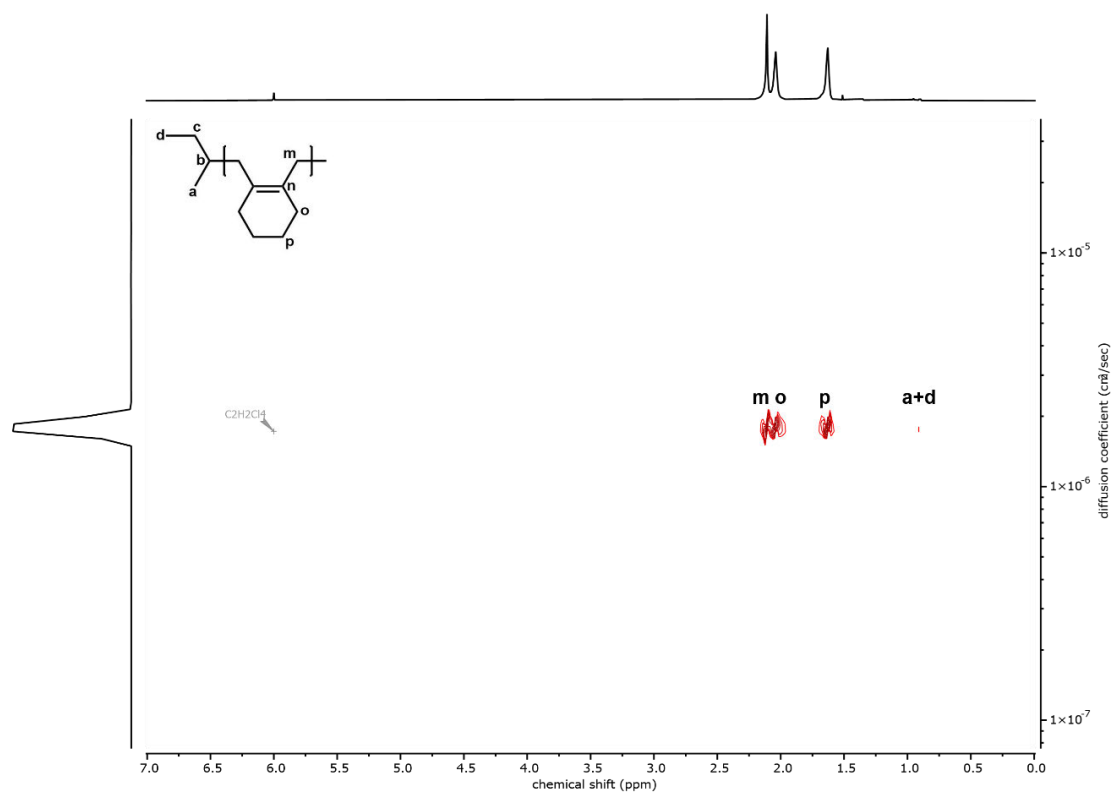


Figure S23:  $^1\text{H}$ -DOSY-NMR spectrum (500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) of PDMCH measured at 100 °C.

## SEC measurements and NMR spectra of P(I-co-DMCH)

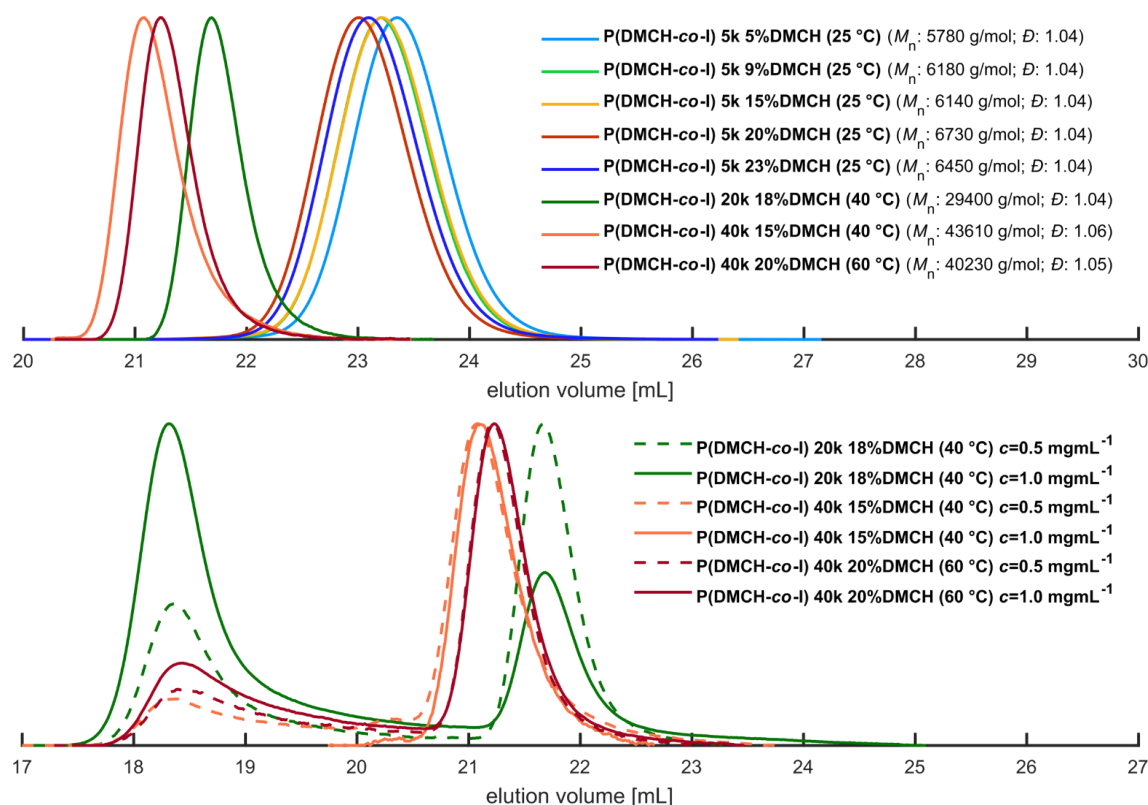


Figure S24: SEC traces (eluent: THF, detector: RI, calibration standard: PI) of the polymers obtained by copolymerization of isoprene and DMCH in cyclohexane. The SEC traces of copolymer of higher molecular weights show multimodality (bottom), what could be caused by partial aggregation of the polymer in THF. To reinforce this assumption, SEC measurements were performed at concentrations of 0.5 (dashed lines) and 1.0 mg·mL<sup>-1</sup> (solid lines) and the relative intensity of the peaks was compared. The alteration of this ratio with the concentration supports this theory, which is why only the main peak (top) is taken into account to determine the individual molar masses and dispersities.

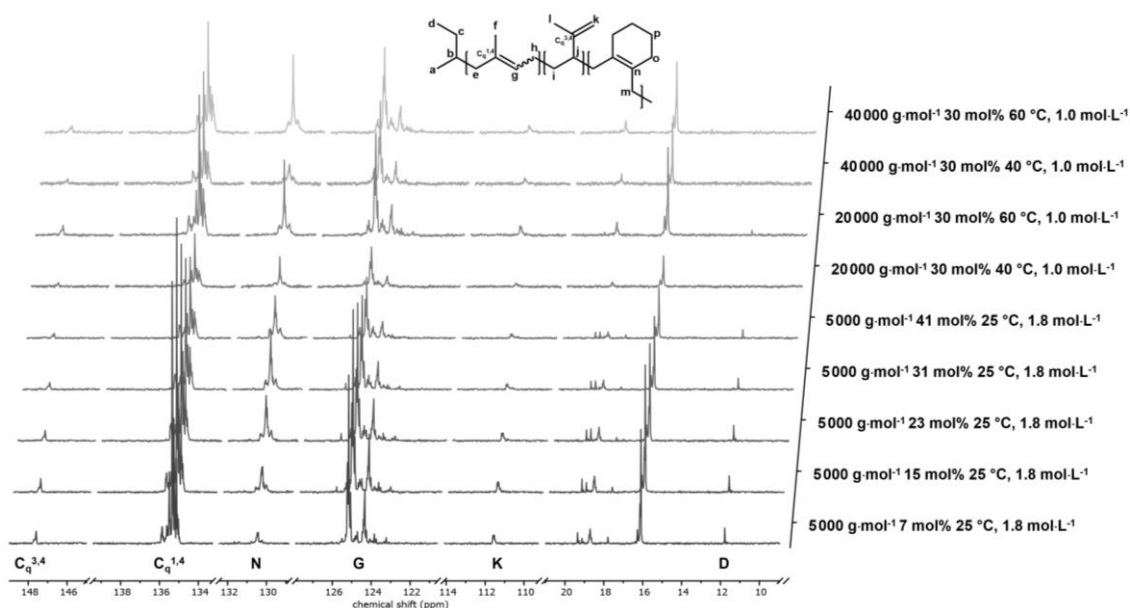


Figure S25: Inverse gated <sup>13</sup>C-NMR spectra (151 MHz, d<sub>1</sub>=10 s, CDCl<sub>3</sub>) of the polymers obtained by copolymerization of isoprene and DMCH in cyclohexane. The signals evaluated for the determination of the molar mass or incorporation ratio of isoprene and DMCH are shown.

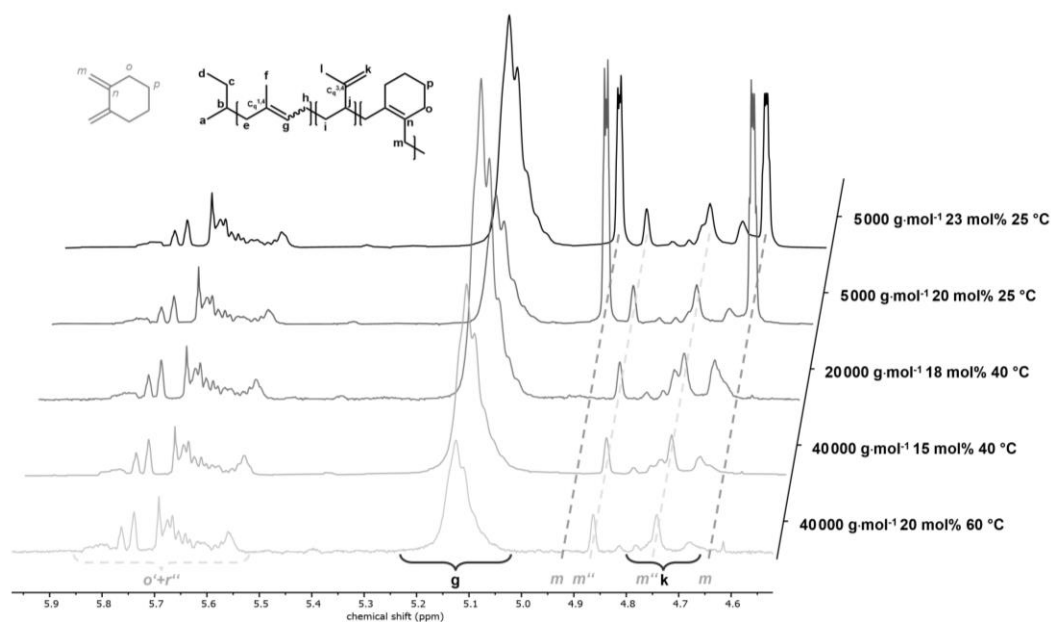


Figure S26:  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of the raw reaction solutions of the copolymerization experiments of isoprene and DMCH. Residual monomer signals are assigned in italic and grey; polymer signals are denoted in black. Since the methylene protons of *cis-exo* DMCH are still visible in case of the two spectra of the top, it can be concluded that the copolymerization was not completed after one night at room temperature, although the reaction solutions were higher concentrated. The raw reaction solutions of the polymerization experiments at 40 °C or 60 °C show no sign of residual monomers.

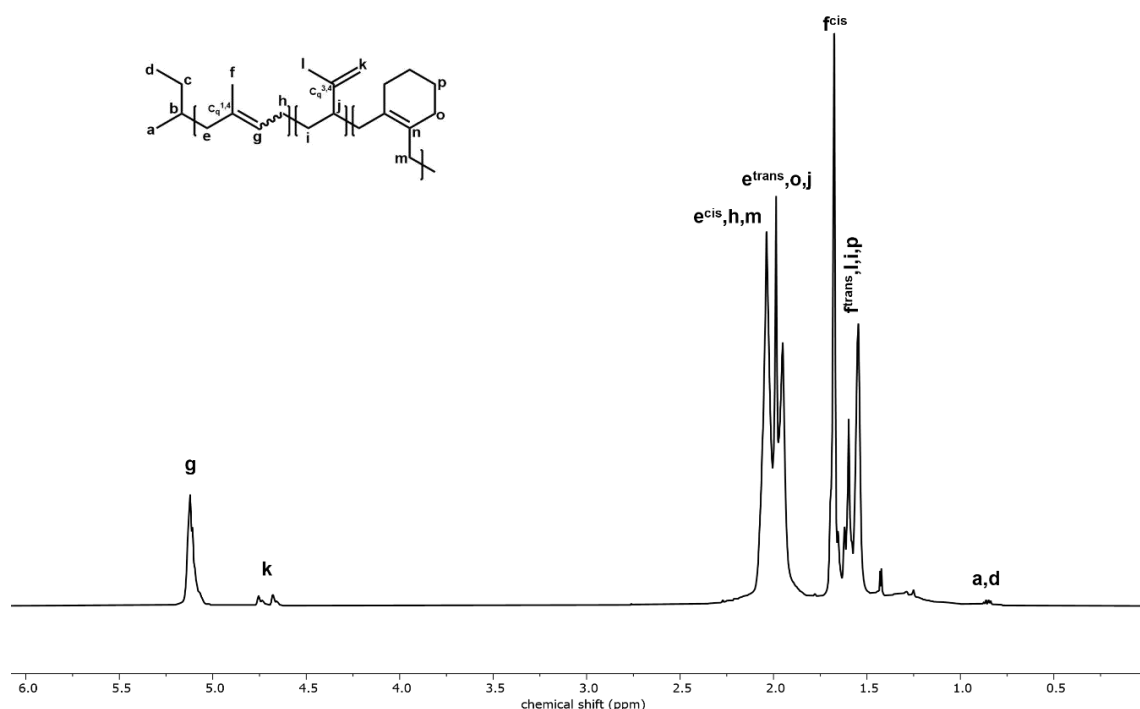


Figure S27:  $^1\text{H}$ -NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

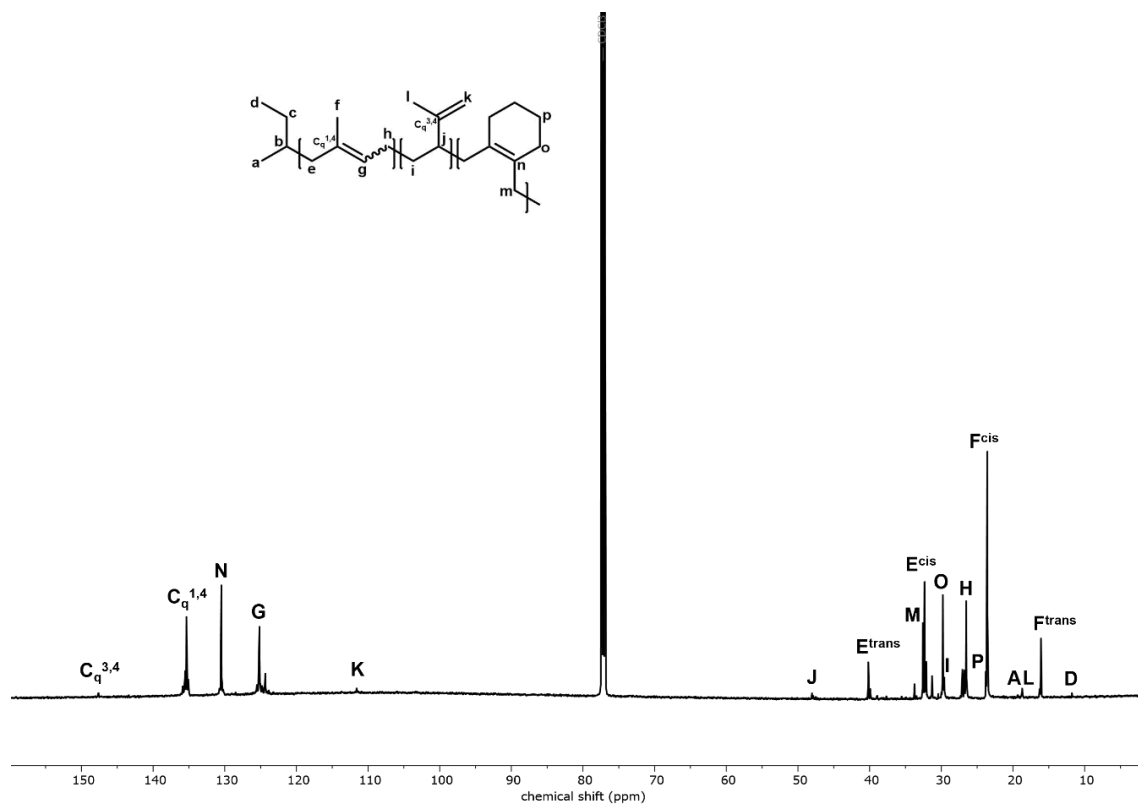


Figure S28: Inverse gated  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

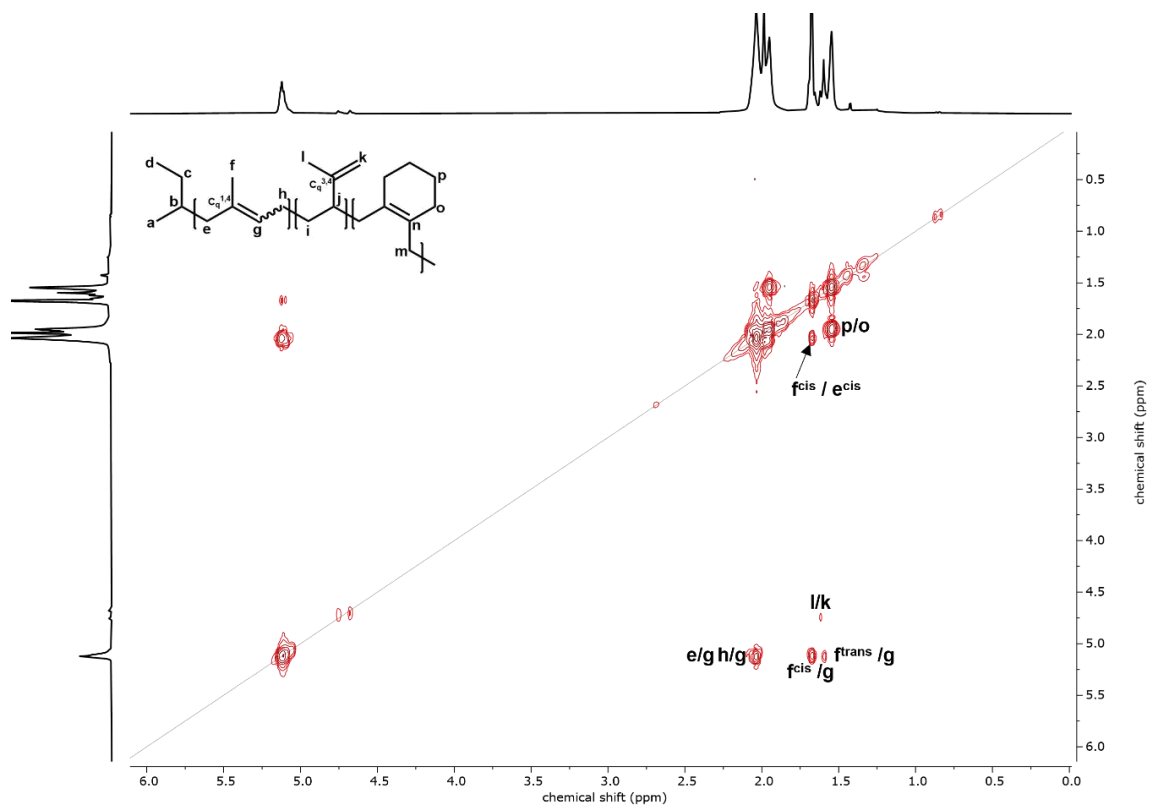


Figure S29:  $^1\text{H}$ -COSY-NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

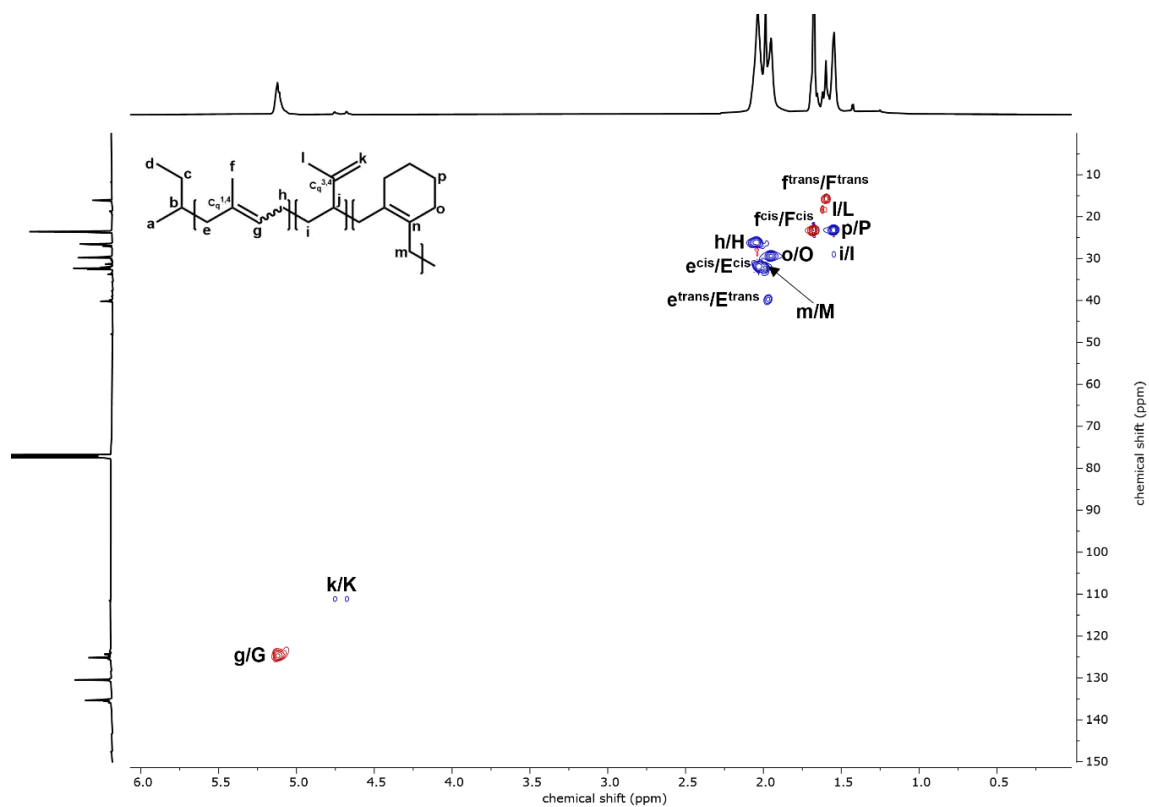


Figure S30:  $^1\text{H}/^{13}\text{C}$ -HSQC-NMR spectrum (600/151 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

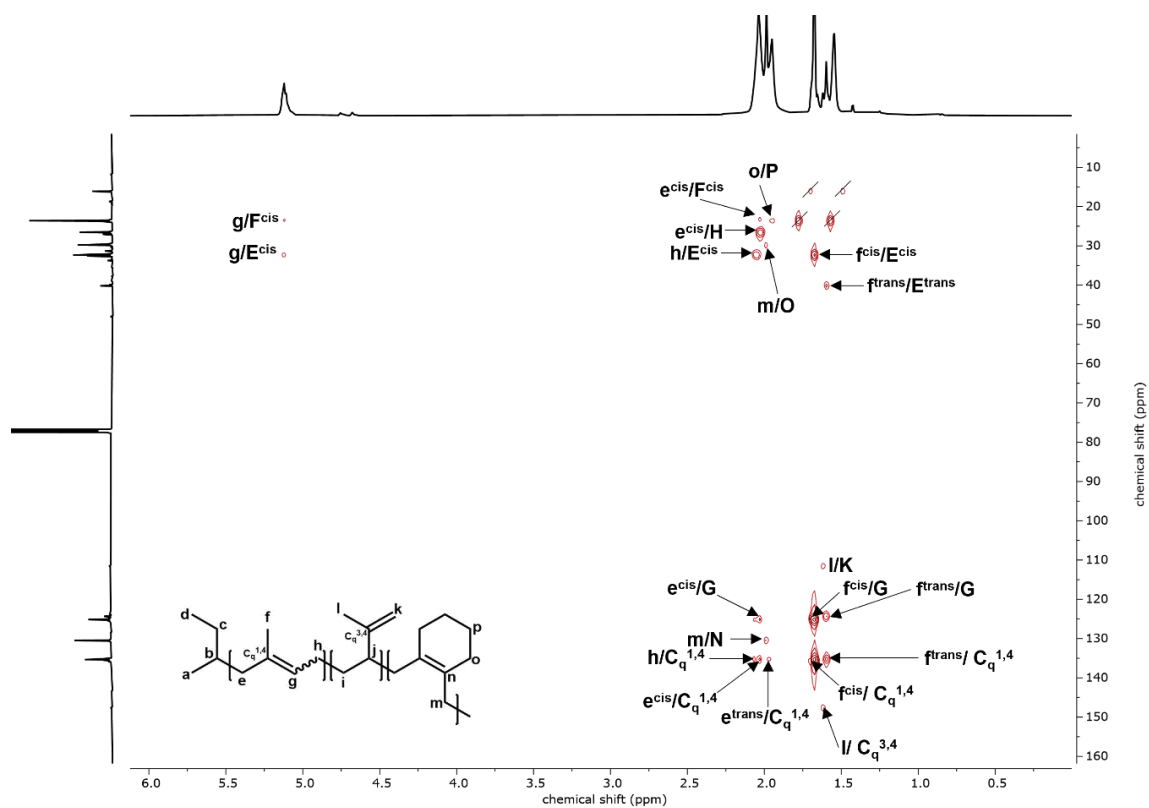


Figure S31:  $^1\text{H}/^{13}\text{C}$ -HMBC-NMR spectrum (600/151 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and DMCH in cyclohexane at 40 °C.

## MALDI-ToF spectra, SEC and NMR spectra of P(I-co-IMMCH)

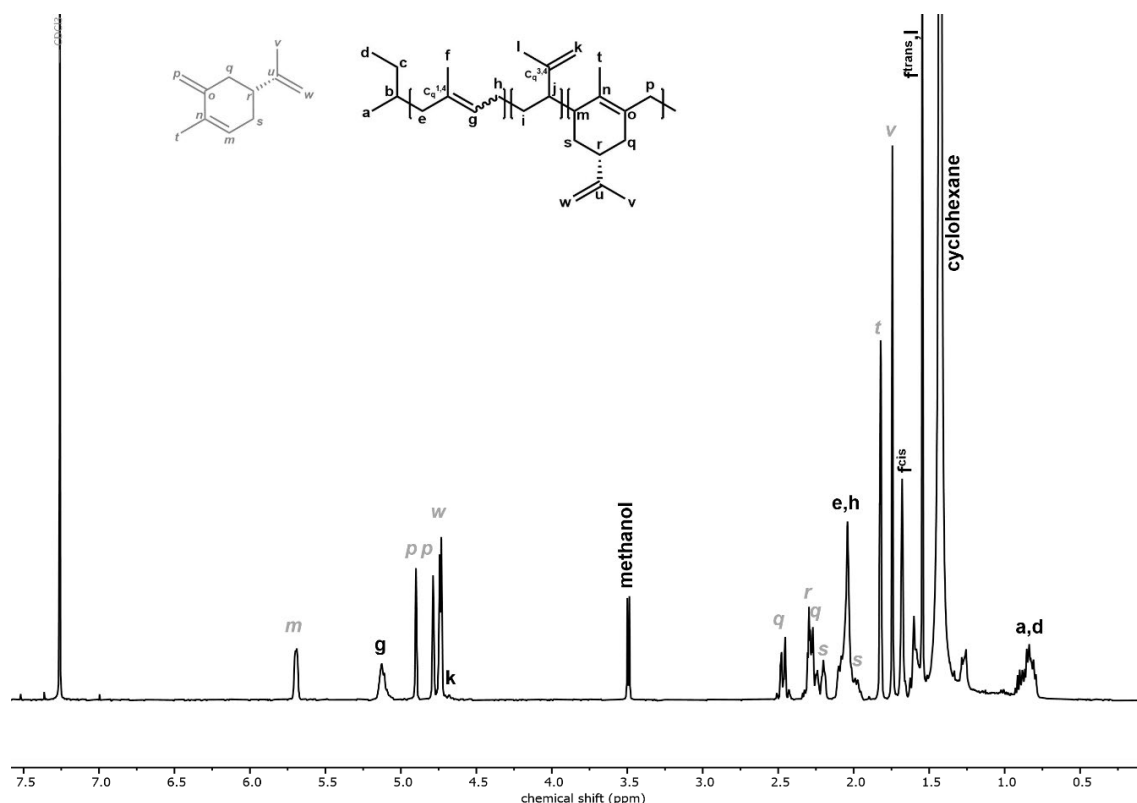


Figure S32:  $^1\text{H}$ -NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of the raw reaction solution of the copolymerization experiment of isoprene and IMMCH. Residual monomer signals are assigned in italic and grey; polymer signals are denoted in black.

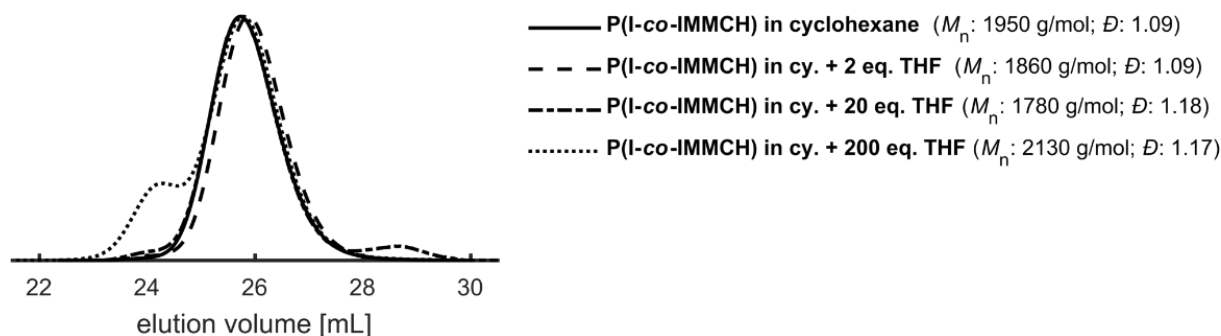
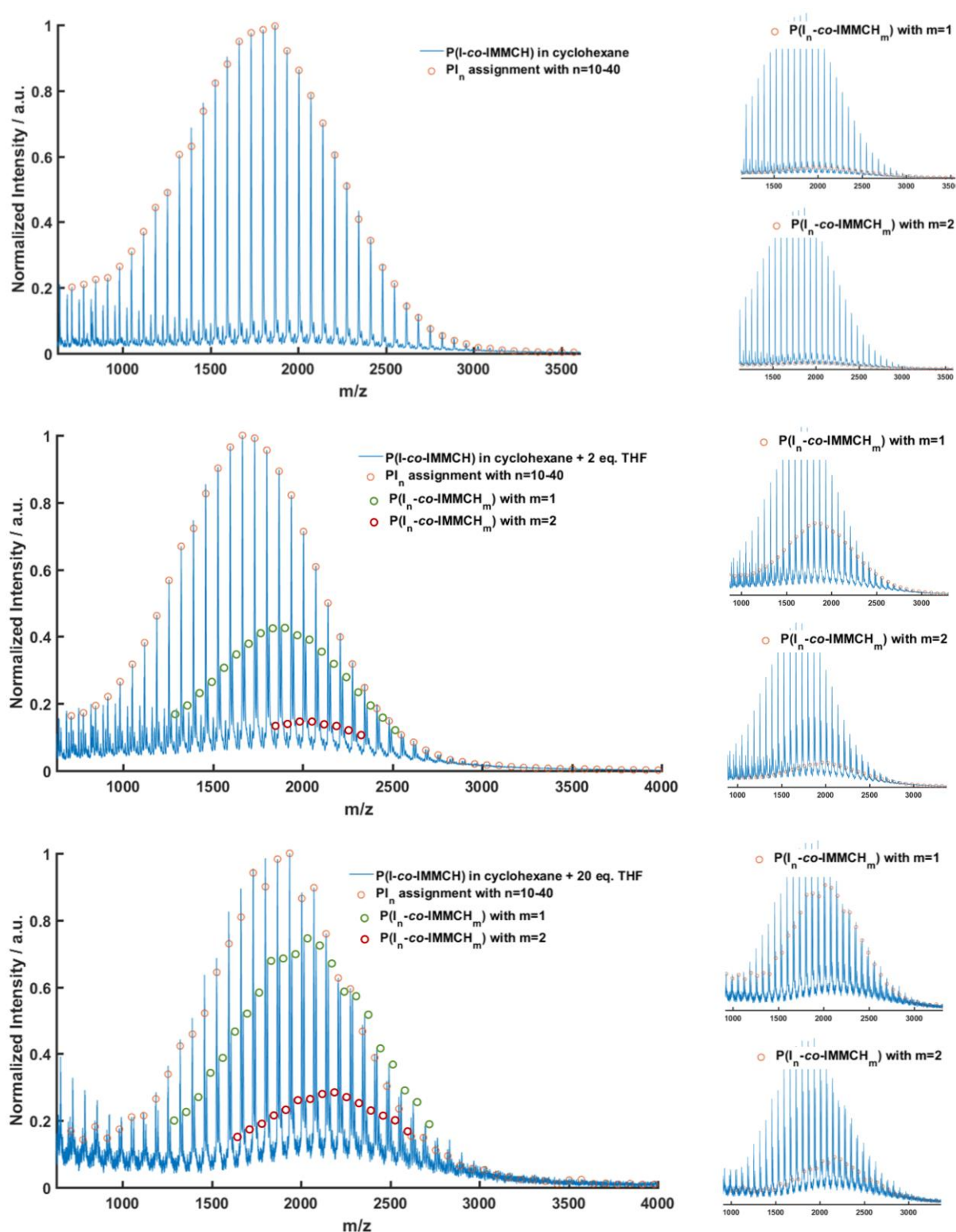


Figure S33: SEC traces (eluent: THF, detector: RI, calibration standard: PI) of the polymers obtained by copolymerization of isoprene and IMMCH in cyclohexane (black solid line), in cyclohexane with 2 equivalents of THF (black dashed line), in cyclohexane with 20 equivalents of THF (black dash-dotted line) and in cyclohexane with 200 equivalents of THF (black dotted line). Since  $5000 \text{ g}\cdot\text{mol}^{-1}$  and 50 mol% ( $\sim 23$  repeating units) of both isoprene and IMMCH were targeted, the observed molar masses together with the NMR and MALDI-ToF data show the consumption of all isoprene, but hardly no incorporation of IMMCH. The SEC trace of the polymer formed in the presence of 200 equivalents of THF shows multimodality, what could either be because of coupling in presence of oxygen during termination, or side reactions with THF. This could be the decomposition of THF by deprotonation at C2 and subsequent reverse [3+2] cycloaddition of the resulting anion, yielding ethylene and lithium enolate. Ethylene can react with alkyl lithium compounds giving a saturated carbanionic chain end, while the enolate terminates the chain if it is added and beyond this can coordinate the lithium counterion strongly.





**Figure S34:** MALDI-ToF mass spectra of  $P(I\text{-}co\text{-}IMMCH)$  in cyclohexane with 0 (top), 2 (middle) or 20 (bottom) equivalents of THF. Matrix: DCTB, ionization agent: AgTFA, mode: linear. The distributions of pure polyisoprene  $PI_n$  with  $n=10-40$  are assigned in the main plot, while the distributions of polyisoprene with one or two IMMCH repeating units are marked in the cutouts on the right.

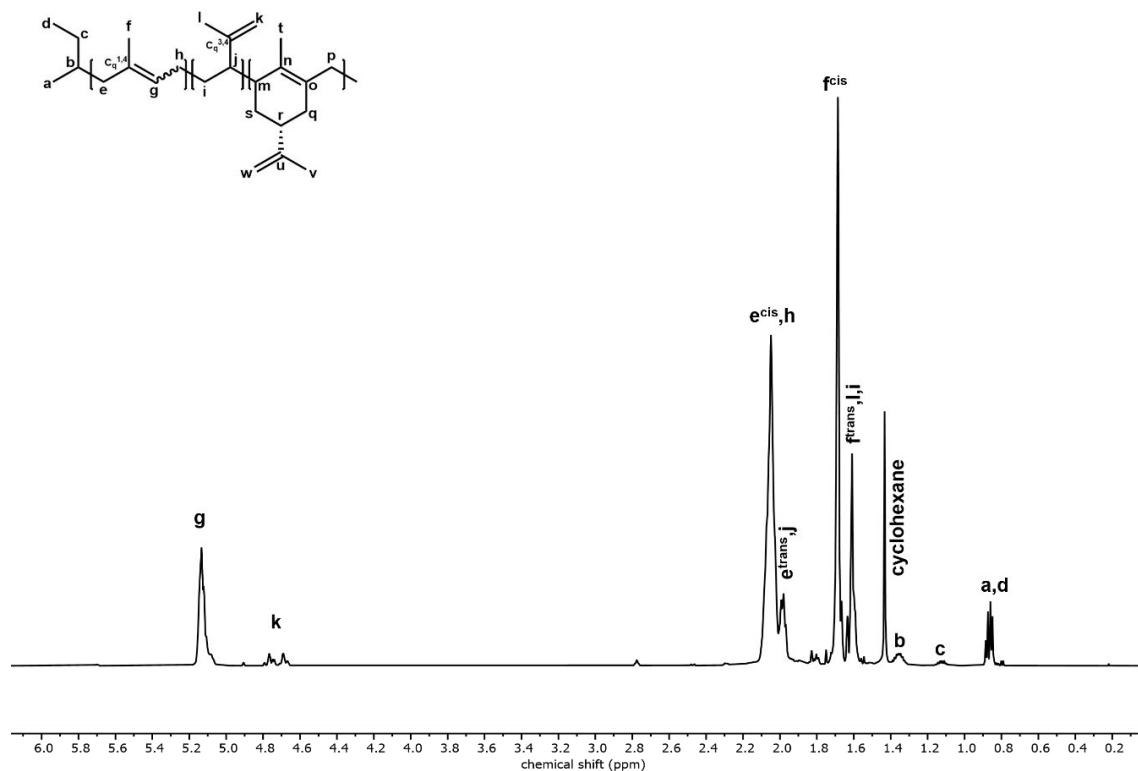


Figure S35:  $^1\text{H}$ -NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.

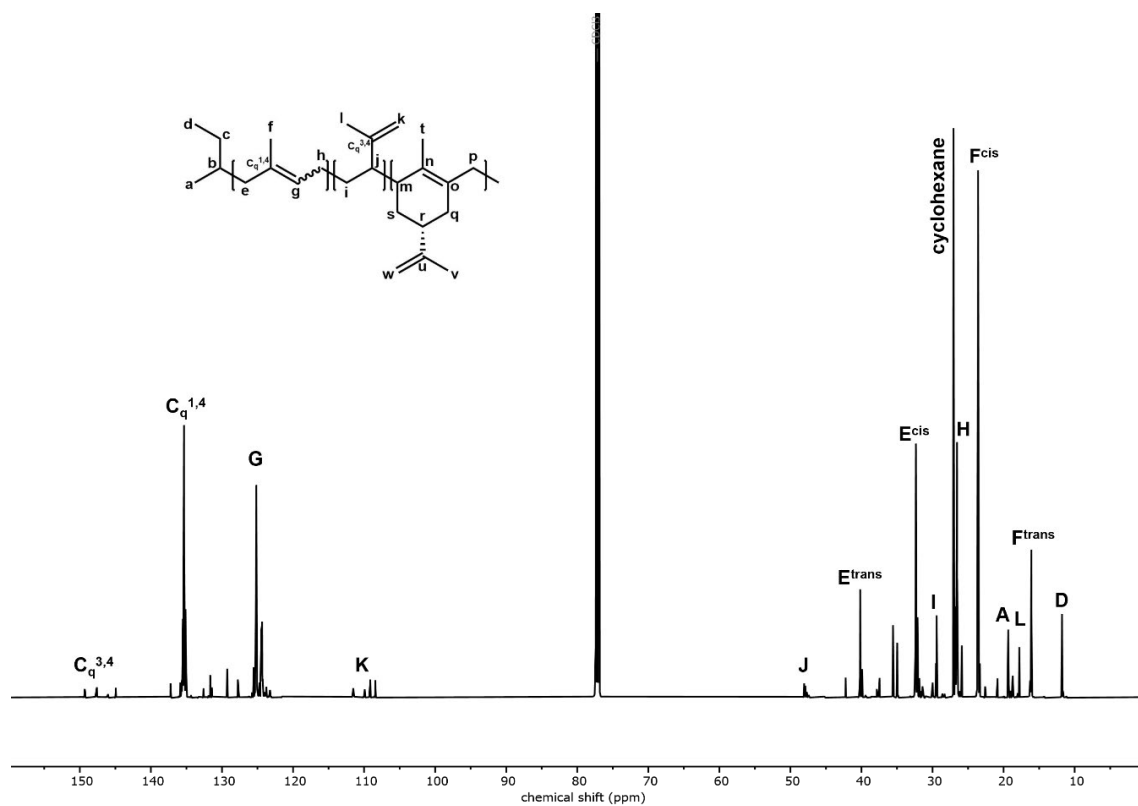


Figure S36:  $^{13}\text{C}$ -NMR spectrum (151 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.

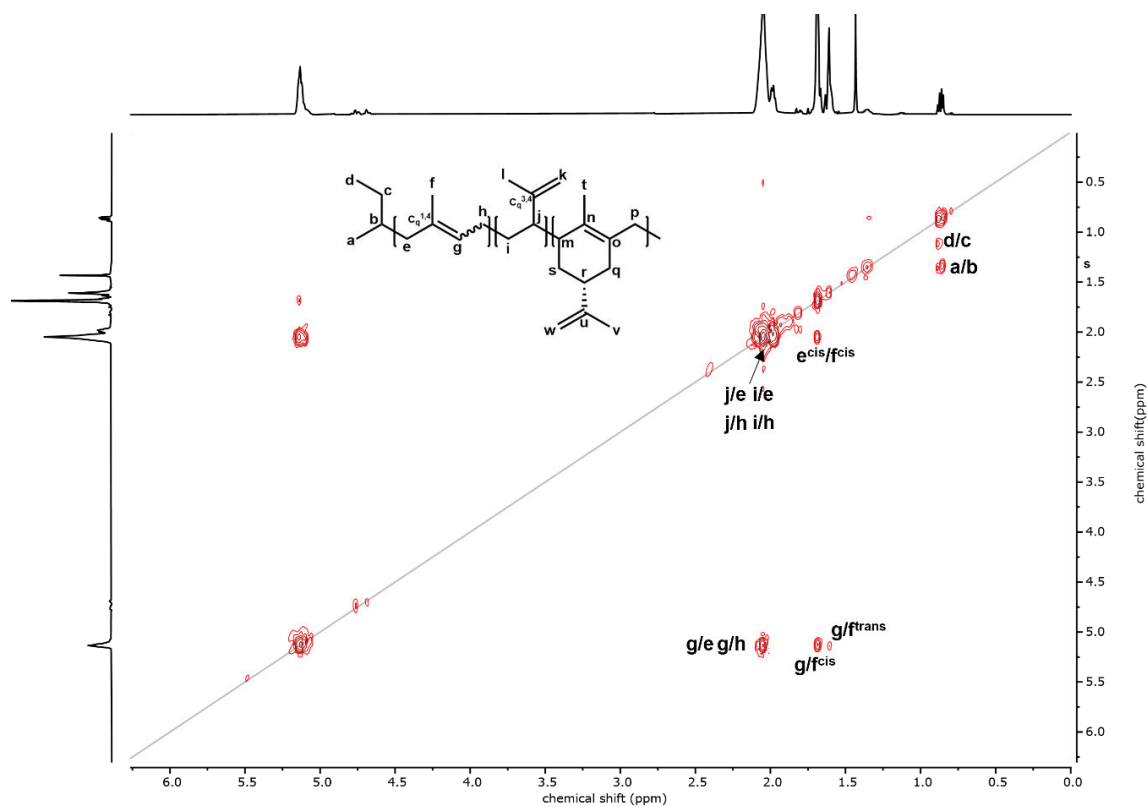


Figure S37:  $^1\text{H}$ - $^1\text{H}$ -COSY-NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.

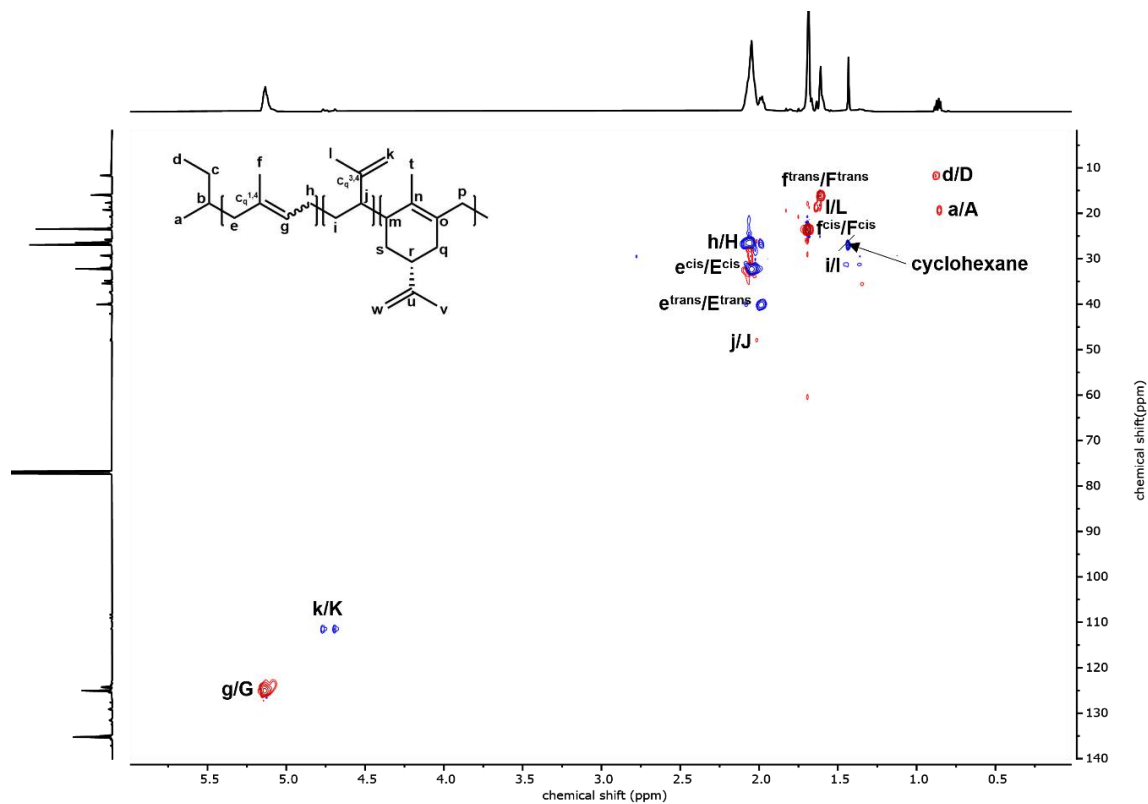
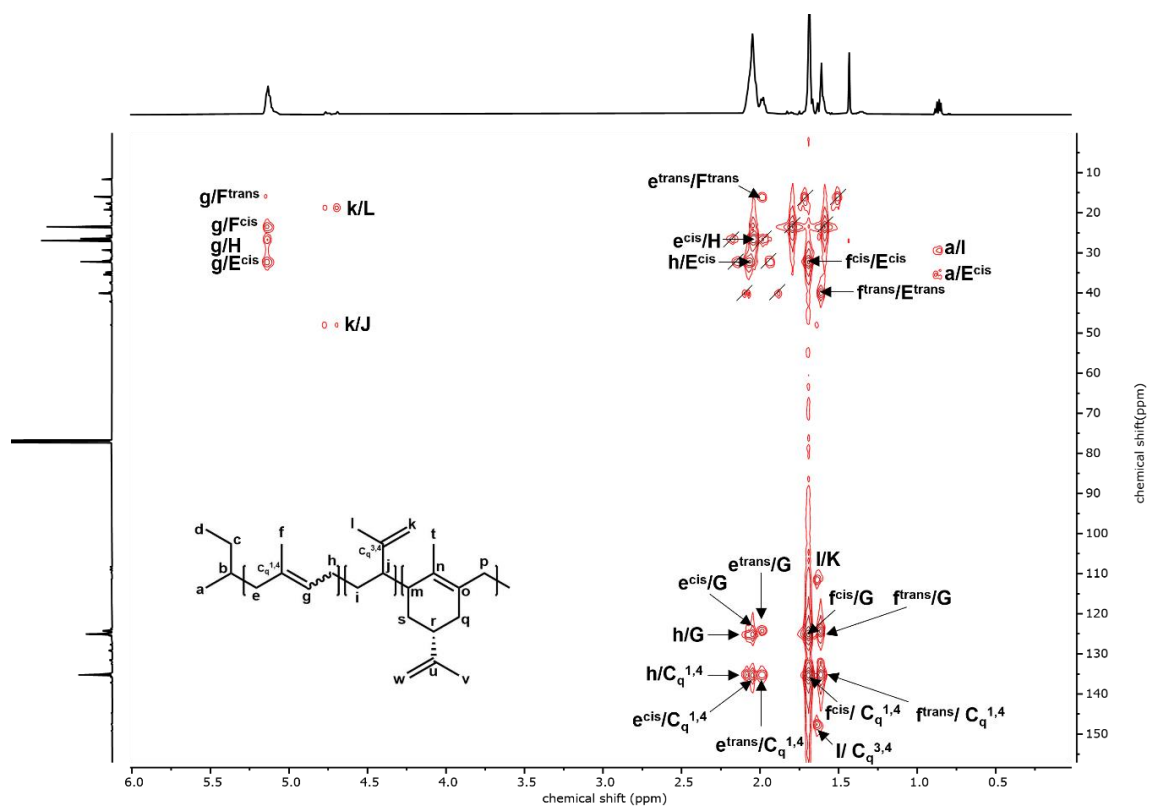


Figure S38:  $^1\text{H}$ - $^{13}\text{C}$ -HSQC-NMR spectrum (600/151 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.



**Figure S39:**  $^1\text{H}/^{13}\text{C}$ -HMBC-NMR spectrum (600/151 MHz,  $\text{CDCl}_3$ ) of the polymer obtained by copolymerization of isoprene and IMMCH in cyclohexane. Only signals of PI are detectable.

[1] M. E. Garst, L. J. Dolby, S. Esfandiari, R. A. Okrent, A. A. Avey, *J. Org. Chem.* **2006**, *71*, 553.





---

---

# **CHAPTER A1**

***Tapered Multiblock Star Copolymers:***  
**Synthesis, Selective Hydrogenation, and**  
**Properties**

---

---





# Macromolecules

pubs.acs.org/Macromolecules

Article

## Tapered Multiblock Star Copolymers: Synthesis, Selective Hydrogenation, and Properties

Philipp von Tiedemann, Jiaqi Yan, Ramona D. Barent, Richard J. Spontak, George Floudas,\*  
Holger Frey,\* and Richard A. Register\*



Cite This: *Macromolecules* 2020, 53, 4422–4434



Read Online

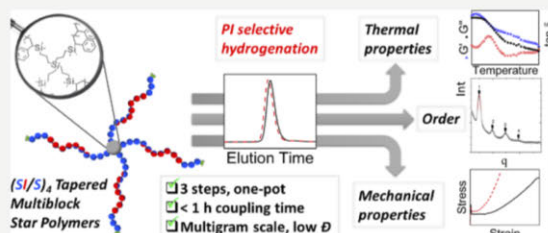
ACCESS |

Metrics &amp; More

Article Recommendations

Supporting Information

**ABSTRACT:** Two series of well-defined multiblock four-arm tapered star copolymers with “arms” of the type poly(styrene)-*block*-poly(isoprene-*grad*-styrene), (SI/S)<sub>4</sub>, were synthesized on a multigram scale with short reaction times. Targeted molecular weight (*M*) values ranged from 80 to 240 kg mol<sup>−1</sup> with polystyrene (PS) compositions of 40 and 60 wt %. Narrowly distributed (*Đ* = 1.04–1.12) copolymers were obtained regardless of *M* and without additional purification beyond precipitation. At sufficiently high *M*, members of the 40 wt % PS series possessed either a cylindrical or bicontinuous morphology, whereas the 60 wt % PS series yielded lamellae. The star copolymers outperformed their corresponding linear analogues with respect to ultimate toughness and elongation at break. Young’s moduli of up to 304 ± 11 MPa were reached, and the overall toughest (83 ± 2 MJ/m<sup>3</sup>) star copolymer exhibited the highest strain at break (1198 ± 34%). Catalytic hydrogenation of the PI segments was achieved selectively without saturation of styrene units at conversions of ≥98%. More pronounced strain hardening occurred upon hydrogenation. Modulus, toughness, and ultimate strength of the linear tapered copolymer increased substantially upon hydrogenation to poly(styrene)-*block*-poly((ethylene-*alt*-propylene)-*grad*-styrene), SEP/S. However, these mechanical properties for the star copolymer were found to decrease upon hydrogenation to (SEP/S)<sub>4</sub>. These materials, particularly the unsaturated multiblock stars of the highest *M*, are promising candidates for future advanced materials that require extremely tough elastomers.



### INTRODUCTION

Star copolymers with glassy (hard) microdomains linked into a network in a rubbery (soft) matrix represent a versatile polymer architecture as they exhibit a unique set of material properties, rendering them suitable for many commercial applications.<sup>1–7</sup> One of the most reliable pathways for the synthesis of star copolymers *via* living anionic polymerization utilizes the so-called “arm-first” approach wherein the linear polymer arms are synthesized in a first step and subsequently chemically linked at their chain ends *via* an effective coupling procedure. In contrast, the so-called “core-first” method capitalizes on multifunctional anionic initiators, which are effective for the synthesis of well-defined stars only if the growth of all arms can be initiated simultaneously.<sup>8</sup> Introduced in 1962 by Morton and co-workers,<sup>9</sup> chlorosilanes still represent one of the most useful classes of coupling agents (CAs) for the synthesis of well-defined star copolymers as they are known to undergo almost no side reactions. An excess of living polymer arms is typically reacted with a small quantity of the coupling agent. To ensure homogeneity, the crude product is subsequently fractionated to isolate the desired material in high purity. A variety of complex star architectures have been precisely designed, carefully synthesized, and extensively studied using this method.<sup>10–12</sup> We recently introduced

tetra[3-(chloro-dimethylsilyl)propyl]silane (TCDMSPS) as a new CA, with maximized reactivity toward living polymer chains and less-dense cores to improve the coupling efficiency.<sup>13</sup> The addition of tetrahydrofuran (THF) is known to increase the coupling rate of polybutadienyl- and polyisoprenyllithium with chlorosilanes, as first observed by Mays and co-workers<sup>14,15</sup> and quantified by Burns and Register.<sup>16</sup> Combining these two principles, the rapid synthesis of low-dispersity tapered star copolymers with arms of the type poly(isoprene-*grad*-styrene) was achieved without the need for further purification beyond precipitation.<sup>13</sup>

The formation of such “tapered” copolymers in a more general sense dates back to 1969 with the work of Kraus *et al.*<sup>7,17</sup> and Worsfold.<sup>18</sup> Diene monomers are known to form block-like structures with styrene or alkylstyrenes during statistical copolymerization in apolar media.<sup>19–21</sup> Although such copolymers can undergo microphase separation com-

Received: March 19, 2020

Revised: April 25, 2020

Published: May 19, 2020



ACS Publications

© 2020 American Chemical Society

4422

<https://dx.doi.org/10.1021/acs.macromol.0c00645>  
*Macromolecules* 2020, 53, 4422–4434



parable to block copolymers synthesized *via* sequential monomer addition, it was found that an increased tapered sequence induces mixing of the two different domains.<sup>4,22–30</sup> Consequently, the order–disorder transition temperature ( $T_{ODT}$ ) decreases. The possibility to thereby adjust morphological and mechanical properties was explored by Knoll and co-workers in their extensive studies of different ABA triblock copolymers consisting of styrene and butadiene.<sup>31–33</sup> Such triblock copolymers generally capitalize on chain anchoring by glassy polystyrene (PS) domains in a rubbery matrix of polybutadiene (PB) or polyisoprene (PI). The formation of bridges and entangled loops is known to be crucial for good material properties (e.g., high toughness and strain at break).<sup>34</sup> This bridging fraction is known to increase significantly for linear perfectly alternating multiblock copolymers.<sup>35–43</sup> Star block copolymers are also known to possess bridging fractions beyond normal ABA triblock copolymers, with a strong dependence on the number of arms.<sup>44</sup> Furthermore, star copolymers intrinsically exhibit advantageous properties such as superior ultimate strength and lower viscosity in solution, which are of great interest for industrial applications.<sup>45</sup> A prominent commercial product that capitalizes on such excellent properties is Styrolux.<sup>1</sup>

Increasing molecular weight ( $M$ ) and using different monomers are possibilities to increase the degree of interblock segregation. In addition, selective hydrogenation of specific polymer segments can increase the Flory–Huggins parameter ( $\chi$ ) and  $T_{ODT}$  dramatically.<sup>46</sup> PS-*b*-PI represents such a system when the PI block is selectively hydrogenated to poly(styrene)-*block*-poly(ethylene-*alt*-propylene), PS-*b*-PEP.<sup>47–49</sup> However, complete and selective hydrogenation of PI without PS saturation at high conversions, short reaction times, and without damaging the polymer chains or the macromolecular architecture is known to be challenging.<sup>50,51</sup> The well-researched diimide procedure<sup>52–56</sup> for the hydrogenation of polydienes can be accompanied by polymer chain scission, double bond addition products, and coupling or cyclization reactions, and requires relatively high temperatures.<sup>55</sup> In comparison, catalytic methods for selective polydiene hydrogenation are of great industrial interest<sup>57–60</sup> but are less frequently described in the literature.<sup>61–64</sup> The exact metal ratio ( $M/Al$ ) of Ziegler-type catalysts is known to be crucial to balance selectivity and reactivity.<sup>50,65</sup> Besides strongly enhanced thermal stability, altered mechanical properties such as pronounced strain hardening are known to result upon selective hydrogenation of PI in PS-*b*-PI-*b*-PS triblock copolymers.<sup>62,63,66</sup>

Multiair star copolymers of the type  $(SI)_x$ , where  $x$  represents the number of arms, have been studied extensively.<sup>67–77</sup> Compared to their linear counterparts, they are known to exhibit higher strength, lower strain at break, less permanent set, and pronounced yielding.<sup>12,70</sup> However, a systematic study of the mechanical properties of well-defined multiblock star copolymers of the type  $(SIS)_x$ , ideally with high enough  $\chi N$  to induce self-assembly into nanosegregated morphologies, has not yet been reported. Besides theoretical work<sup>78</sup> on (BAB)<sub>3</sub> star self-assembly, most synthetic pathways for such architectures rely on controlled radical polymerization techniques with individual block sizes not exceeding 5 kg mol<sup>−1</sup>.<sup>79–82</sup> Meyer and Widmaier<sup>83</sup> compared  $(SI)_x$  stars and  $(SIS)_x$  star copolymers with respect to their shear strength and adhesive properties as a function of their number of arms. Their finding of significantly increased shear strength of  $(SIS)_x$

as compared to  $(SI)_x$  star copolymers sparked our interest for a systematic study on the mechanical properties and self-assembly of such multiblock copolymers as a function of  $M$  and PS content (weight fraction of styrene,  $w_s$ ) while keeping the overall number of arms constant.

In this work, we present a three-step synthesis procedure (including coupling) for tapered multiblock four-arm star copolymers of the type  $(SI/S)_4$  based on the block-like copolymer formation of isoprene and styrene in apolar media, which produces a steep downchain gradient in a living statistical copolymerization, combined with a highly efficient coupling strategy. Two different series of star copolymers (overall PS compositions of 60 and 40 wt %, respectively) are presented and studied in detail with an emphasis on the phase state and its influence on thermal and mechanical properties. Material changes upon selective hydrogenation of the PI blocks were also of interest and thus analyzed with respect to order and mechanical properties.

## EXPERIMENTAL SECTION

**Reagents and Sample Designation.** All chemicals were purchased from commercial suppliers (Acros, Sigma-Aldrich, Fisher Scientific, and Alfa Aesar). Deuterated solvents were obtained from Deutero GmbH or Cambridge Isotope Laboratories. Isopropyl alcohol and methanol were used as-received without further purification. The detailed synthesis protocol for the coupling agent is described elsewhere.<sup>13,84</sup> In all of the copolymers synthesized, the first block (polystyrene) consists exclusively of styrene units, while the second block (poly(isoprene-*grad*-styrene)) consists of both isoprene and styrene units, but with a strong downchain gradient that is effectively a tapered isoprene–styrene diblock itself. The sample codes used to describe the copolymers are as follows:  $(SI/S)_4$ -60-240 represents a four-arm star with arms of the type poly(styrene)-*block*-poly(isoprene-*grad*-styrene). The targeted  $w_s$  was 60 wt % and the targeted  $M$  (on a number-average basis) was 240 kg mol<sup>−1</sup>. Additionally,  $(SI/S)$ -60-60 represents the corresponding linear analogue, while  $(SEP/S)_4$ -60-240 represents the hydrogenated star copolymer, where EP abbreviates ethylene-*alt*-propylene, the repeating unit of hydrogenated 1,4-PI.

**General Synthesis Procedure for  $(SI/S)_4$  Tapered Star Copolymers.** All polymerizations were conducted in 250 mL Schlenk flasks sealed with a fluoropolymer stopper and O-ring in dry cyclohexane at ambient temperature in an argon-filled glovebox (MBraun UNILAB, <0.1 ppm of O<sub>2</sub> and <0.1 ppm of H<sub>2</sub>O). Cyclohexane was purified by stirring over diphenylhexyllithium (adduct of *sec*-butyllithium and 1,1-diphenylethylene) and vacuum-transferred into the polymerization reactor. Styrene and isoprene were both dried by stirring over CaH<sub>2</sub> overnight, followed by vacuum distillation into another flask with a fluoropolymer stopper and O-ring. All flasks were transferred into the glovebox and 0.5 mL of *sec*-butyllithium (1.3 M in cyclohexane/hexane 92:8) was added to the polymerization flask *via* a syringe (1 mL, MBraun). The polymerization was initiated *via* the addition of the calculated charge of styrene *via* a syringe. The solution was stirred until full monomer conversion according to the reaction times of previous reports.<sup>13,85</sup> Subsequently, a mixture of isoprene/styrene was added to the living polystyryllithium (PSLi) solution in order to achieve the desired block/tapered copolymer sequence; the same quantity of styrene was used in the first and second monomer addition steps. The concentration of the final monomer/solvent mixture was generally 10–15 wt %. After complete monomer conversion, 0.25 equiv (typically 92 ± 0.5 mg) of TCDMSPS was added dropwise as a stock solution (100 equiv/equiv Li) in THF (dried over sodium benzophenone ketyl and vacuum-transferred onto activated 0.3 nm molecular sieves) to the living polymer. The coupling reaction was run until decolorization, which was typically achieved within less than 1 h. To precipitate the polymer, the mixture was added dropwise into a 10-fold excess of isopropyl alcohol with a small amount of butylated



hydroxytoluene (approximately 0.5 wt % based on polymer mass) for stabilization. The precipitate was separated by filtration and dried under reduced pressure for several days. Tapered linear copolymers of the same kind were synthesized similarly but excluded the coupling step. Instead, the living polymer chains were terminated with degassed methanol (1 mL) prior to precipitation.

**Selective PI Hydrogenation of Tapered Star and Linear Copolymers.** The PI blocks of the tapered star and linear copolymers were hydrogenated using the previously reported Ni/Al catalyst,<sup>47,57–61</sup> in a 1:4.25 Ni/Al atomic ratio. The hydrogenation was performed under 400 psi H<sub>2</sub> at room temperature in a 2 L Parr reactor with a mechanical stirrer. Typically, 5 g of the polymer was dissolved in 1.5 L of cyclohexane. The catalyst was freshly prepared for each charge *via* the addition of 10 mL of triethyl aluminum (AlEt<sub>3</sub>, 1 M in hexanes) to 1.04 g of Ni(II) 2-ethylhexanoate (78% in 2-ethylhexanoic acid) in 30 mL of cyclohexane in a separate vessel previously purged with N<sub>2</sub> for 45 min. Catalyst charges were added at 1 h intervals by connecting this vessel directly to the reactor. Aliquots for NMR analysis were sampled every 30 min after the catalyst addition; 3–4 catalyst charges were enough to result in at least 98% saturation regardless of the copolymer architecture and molecular weight. The reaction mixture was subsequently stirred with an equal volume of aqueous citric acid (10 wt %) until the dark color of the catalyst disappeared. The organic phase was first separated, then concentrated under reduced pressure *via* a rotary evaporator, and the polymer was finally precipitated in isopropyl alcohol before drying under vacuum overnight.

**Preparation of Polymer Films.** Polymer films were cast from chloroform (analytical grade, Fisher Scientific) using glass Petri dishes with a diameter of 3.5 cm. Typically, 2.5–3 g of the polymer (depending on *M* and *w*<sub>0</sub>) was dissolved in 20 mL of chloroform. The films were prepared by slow solvent evaporation over the course of one week. After removal of the films from the Petri dishes, they were dried under vacuum overnight. These as-cast films were used directly for all mechanical measurements (dynamic mechanical and stress–strain).

**Molecular, Property, and Phase Characterization.** Size-exclusion chromatography (SEC) measurements were performed using a Waters 515 HPLC pump, two 30 cm Polymer Laboratories PLgel Mixed-C columns, a Wyatt Technologies miniDAWN TREOS light-scattering detector ( $\lambda = 658$  nm, room temperature), and a Wyatt Optilab T-REX differential refractive index (dRI) detector ( $\lambda = 658$  nm, 298 K). Weight-average molecular weight (*M*<sub>w</sub>) values were calculated from the multiangle laser light-scattering (MALLS) detector signals and evaluated *via* the software ASTRA V6.1. The *dn/dc* values for the star and linear copolymers were weight-fraction-weighted<sup>66</sup> with respect to PS, PI, and PEP content from NMR analysis. The respective homopolymer *dn/dc* values (PS: 0.189 mL/g, PI: 0.130 mL/g, and PEP: 0.079 mL/g) were measured at 298 K and 658 nm. Apparent dispersities (*Đ*) were computed from the dRI signal, with the elution times calibrated with narrow-distribution linear PS standards. <sup>1</sup>H NMR spectra (400 MHz, 295 K) were recorded on a Bruker AVANCE II 400 spectrometer equipped with a 5 mm BBFO-SmartProbe with *z* gradient as well as a SampleXPress 60 sample changer. All hydrogenated polymers were measured on a Bruker AVANCE III (500 MHz, 295 K) equipped with a QCI (<sup>1</sup>H/<sup>13</sup>C/<sup>15</sup>N/<sup>2</sup>H) cryoprobe, a BACS-120 automated sample changer, and a BCU-05 temperature controller (Bruker BioSpin, Billerica, MA). Spectral features were referenced internally to the signal of the deuterated solvent (CDCl<sub>3</sub>).

The glass transition (*T*<sub>g</sub>) temperatures of the copolymers were characterized *via* differential scanning calorimetry (DSC) with PerkinElmer DSC 7 and DSC 8500 instruments, each with a type II intracooler and calibrated with indium and tin. All copolymers were evaluated at a heating rate of 10 K/min. Typically, a minimum of 10 mg of the polymer was used for the analysis and each polymer was measured at least twice to ensure data reproducibility. Dynamic mechanical thermal analysis (DMTA) was conducted on a TA Instruments RSA-3, using the shear sandwich fixture (0.5 mm gap); a frequency of 1 rad/s was employed at a heating rate of 5 K/min and a

strain amplitude of 1%. Measured *T*<sub>g</sub> values were discerned from the peak value of the  $\tan \delta$  curve or the temperature of the steepest descent in a plot of  $\log G'$  versus *T*, where *G'* denotes the dynamic storage modulus. Uniaxial tensile, initial (*R'*), and final (*R'*) recovery measurements<sup>87</sup> were performed on an Instron 5865 load frame. Specimens for the analysis were stamped out using an ASTM D1708 dogbone die. For all tests, a constant crosshead speed of 5.08 cm/min was applied. From the stress–strain measurements, the Young's modulus (*E*<sub>y</sub>) was calculated from the crosshead displacement by taking the steepest slope of the elastic regime in the stress–strain curve. The ultimate strength ( $\sigma_b$ ) and strain at break ( $\epsilon_b$ ) were extracted from the point of failure. The ultimate toughness of the materials was calculated by integrating the stress–strain curve. All reported average values are based on at least three replicates.

Small-angle X-ray scattering (SAXS) measurements were recorded using CuK $\alpha$  radiation (RigakuMicroMax 007 X-ray generator with Osmic Confocal Max-Flux curved multilayer optics). Two-dimensional diffraction patterns were recorded on a Mar345 image plate detector at a sample–detector distance of 2076 mm. Intensity distributions as a function of the modulus of the total scattering vector,  $q = (4\pi/\lambda) \sin(2\theta/2)$ , where  $\lambda$  is the radiation wavelength (0.154 nm) and  $2\theta$  is the scattering angle, were obtained by radial averaging of the 2D datasets. Samples in the form of thick films (~1 mm) were prepared as described above. Temperature-dependent measurements lasting 1 h were obtained by heating the films from 293 to 453 K in increments to obtain the structure factor and identify *T*<sub>ODT</sub> values. For transmission electron microscopy (TEM), to discern the real-space morphologies of the (SI/S)<sub>4</sub>-40-240 copolymer before and after thermal annealing, bulk films were cryosectioned with a diamond knife on a Leica UC7 ultramicrotome maintained at 153 K. Electron-transparent sections measuring *ca.* 100 nm thick were positioned on 400-mesh copper grids, which were then immediately contacted with a steel block after removal from the cryochamber to preclude condensation on (and damage to) the sections without introducing any other liquids. To enhance contrast between the microdomains, the sections were subsequently exposed to the vapor of a 2% OsO<sub>4</sub>(aq) solution for 90 min at ambient temperature in an isolated container to ensure the complete reaction of, and thus selectively stain, the unsaturated isoprene units. Finally, a thin (~5 nm) layer of carbon was evaporated onto the sections to reduce charging effects during imaging. Images were acquired on a field-emission FEI Talos F200X microscope operated at an accelerating voltage of 80 kV.

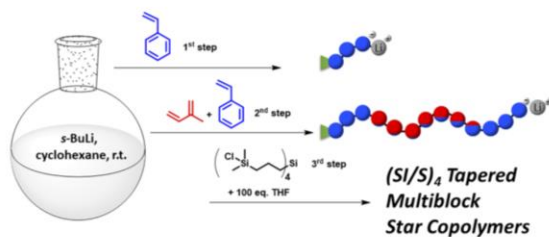
## RESULTS AND DISCUSSION

**Synthesis and Selective Hydrogenation.** The architecture and block sequence of the multiblock (SI/S)<sub>4</sub> tapered star copolymers were specifically designed to achieve tough, flexible, and transparent polymers with different morphologies. Analysis of the resulting mechanical properties as functions of *M*, architecture, copolymer composition, and phase state was of major interest. Therefore, the synthesis was optimized with respect to three major aspects: (i) few steps and short reaction times, (ii) highly efficient coupling without the need for painstaking purification protocols such as repeated fractionation, and (iii) multigram scale. Thus, a triblock sequence was chosen for the block sequence of each multiblock tapered star copolymer's "arm", with glassy PS outer blocks and rubbery polyisoprene inner blocks. Upon multifunctional linkage of the copolymer chains, a symmetrical pentablock architecture of the type SI/S-CA-S/IS, where CA denotes the coupling agent, is prepared. This block sequence does not generate any dangling ends from unanchored PI blocks, which are known to reduce the elasticity of the polymer network.<sup>34,88–91</sup>

Instead of a conventional five-step sequential synthesis procedure, three steps (Scheme 1) were followed: (1) initiation of styrene to form the first PS (outer) block, (2)



### Scheme 1. One-Pot Synthesis Route for Well-Defined Multiblock Tapered Star Copolymers



addition of a mixture of isoprene and styrene to form the rubbery PI midblock and second PS (inner) block, and (3) coupling with the previously reported CA tetra[3-(chlorodimethylsilyl)propyl]silane (TCDMSPS).<sup>13</sup> The same quantity of styrene was used in the first and second monomer charges. Based on the disparate reactivity ratios of isoprene ( $r_1 = 12.8$ ) and styrene ( $r_2 = 0.051$ ) in apolar media (cyclohexane), this monomer mixture forms a block-like gradient copolymer with a steep gradient within the blocks;<sup>19</sup> downchain composition profiles calculated with these reactivity ratios are plotted in Figure S1 in the Supporting Information. This CA possesses maximized reactivity with respect to living anionic polymer chain ends because of the monochlorosilane moieties and partially alleviates steric constraints because of the propyl spacers.<sup>13</sup> To further accelerate the coupling reaction, the CA was added as a solution in THF. The fading of the orange color of the solution (resulting from PSLi living chain ends, see Figure S2 in the Supporting Information) indicates coupling conversion and therefore was utilized to qualitatively assess the necessary reaction times. Complete decolorization generally occurred in less than 1 h.

With this approach, well-defined multiblock star copolymers with tapered triblock arms exhibiting the block sequence PS-*b*-P(I-*grad*-S) with overall 60 and 40 wt % PS and monomodal, narrow molecular weight distributions (apparent  $\bar{D} = 1.04$ – $1.12$ ) were synthesized. The SEC elution traces (Figure 1) reveal that only minimal levels of lower-molecular-weight side products (terminated PS first block, uncoupled arm) remain. All star copolymers possess  $\leq 3$  wt % uncoupled arms; note that, even when present, these SI/S arms do not form dangling ends in the polymer network as uncoupled diblock arms in (SI)<sub>x</sub> stars do, because the SI/S arms contain PS blocks at both ends. All SEC elution traces were recorded after precipitation without any further purification. The molecular weights ascertained *via* SEC with a MALLS detector (see the Experimental Section for details) generally agree with the target values. <sup>1</sup>H NMR analysis was used to determine the weight fraction ( $w_S^{\text{NMR}}$ ) of PS. Good agreement with the feed ratio ( $w_S^{\text{feed}}$ ) with only minor average variation ( $\pm 2\%$ ) was achieved, and the results of these molecular analyses are compiled in Table 1.

Selective hydrogenation of the PI blocks was carried out with the Ni/Al catalyst, at ambient temperature. Representative SEC elution traces of the unsaturated (SI/S)<sub>4</sub>-60-240 and PI-saturated (SEP/S)<sub>4</sub>-60-240 highest molecular weight tapered star copolymer before and after hydrogenation are presented for comparison in Figure 2a, and the corresponding <sup>1</sup>H NMR spectra are included in Figure 2b (more detailed spectra are provided in Figures S3 and S4 in the Supporting Information). The disappearance of the signals in the region of

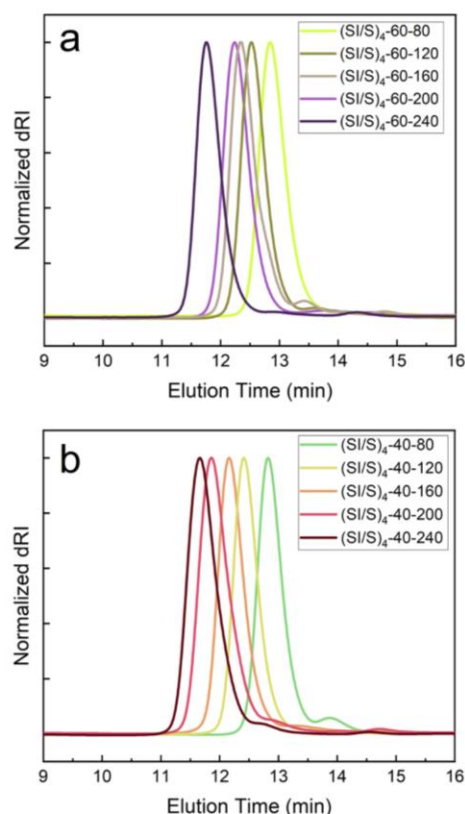


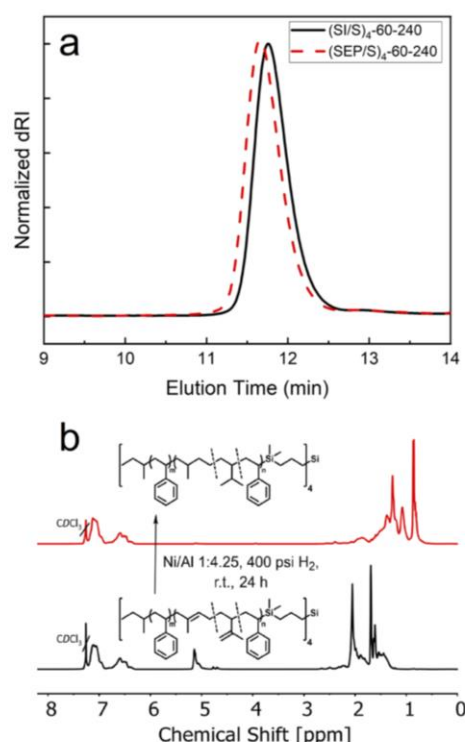
Figure 1. SEC elution traces (normalized dRI) of (SI/S)<sub>4</sub> tapered star copolymers with (a) 60 wt % PS and (b) 40 wt % PS.

Table 1. Overall Synthesis Results of (SI/S)<sub>4</sub> Tapered Star Copolymers with 60 and 40 wt % PS, Tapered Linear (SI/S) Copolymers, and Hydrogenated Derivatives

| polymer                      | $w_S^{\text{NMR}^a}$ (%) | $M_w^{\text{MALLS}^b}$ (kg mol <sup>-1</sup> ) | $\bar{D} = M_w/M_n^b$ |
|------------------------------|--------------------------|------------------------------------------------|-----------------------|
| (SI/S) <sub>4</sub> -60-80   | 65                       | 80                                             | 1.05                  |
| (SI/S) <sub>4</sub> -60-120  | 63                       | 101                                            | 1.06                  |
| (SI/S) <sub>4</sub> -60-160  | 60                       | 141                                            | 1.06                  |
| (SI/S) <sub>4</sub> -60-200  | 62                       | 197                                            | 1.09                  |
| (SI/S) <sub>4</sub> -60-240  | 58                       | 235                                            | 1.05                  |
| (SI/S) <sub>4</sub> -40-80   | 38                       | 69                                             | 1.12                  |
| (SI/S) <sub>4</sub> -40-120  | 39                       | 111                                            | 1.04                  |
| (SI/S) <sub>4</sub> -40-160  | 39                       | 138                                            | 1.05                  |
| (SI/S) <sub>4</sub> -40-200  | 40                       | 188                                            | 1.08                  |
| (SI/S) <sub>4</sub> -40-240  | 40                       | 235                                            | 1.09                  |
| (SI/S)-60-60                 | 62                       | 47                                             | 1.06                  |
| (SI/S)-40-60                 | 41                       | 54                                             | 1.06                  |
| (SEP/S) <sub>4</sub> -60-240 | 57                       | 249                                            | 1.04                  |
| (SEP/S) <sub>4</sub> -60-60  | 61                       | 50                                             | 1.05                  |

<sup>a</sup>Obtained from <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub>. <sup>b</sup>Determined from SEC measurements in THF (see the Experimental Section for details).

4.5–5.5 ppm and the appearance of the signal between 0.5 and 1 ppm prove the hydrogenation of the PI blocks with at least 98% conversion. Note that, spectra were always recorded on fairly concentrated samples (c.f. the CDCl<sub>3</sub> peak compared to

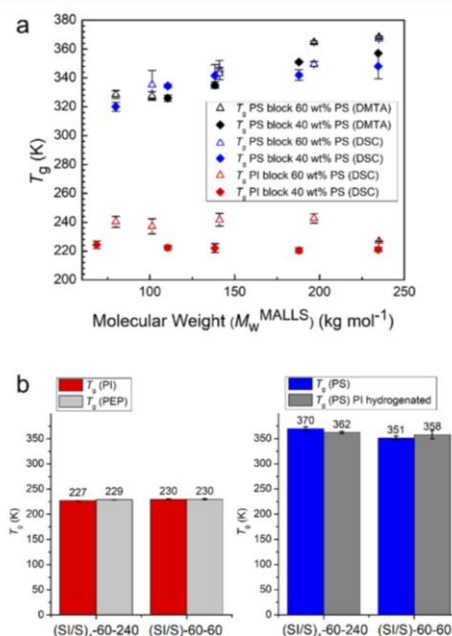


**Figure 2.** (a) SEC elution traces (normalized dRI) of (SI/S)<sub>4</sub>-60-240 (black) and (SEP/S)<sub>4</sub>-60-240 (red) tapered star copolymers. (b) Corresponding <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>, 295 K) are color-matched.

the aromatic signals) to ensure the maximum validity of the analysis. Whereas <sup>1</sup>H NMR spectroscopy is convenient to analyze the degree of PI hydrogenation, the possibility of partial hydrogenation of PS to poly(vinylcyclohexane), PVCH, cannot be assessed because of signal overlap. <sup>13</sup>C NMR analysis was used to ensure no hydrogenation of styrene units occurred. Figure S5 in the Supporting Information displays the <sup>13</sup>C NMR spectrum of (SEP/S)<sub>4</sub>-60-240. Two signals from the methylene carbon atoms of PVCH appear at 27 ppm in CDCl<sub>3</sub>.<sup>92</sup> As these two signals possess the highest intensities (as they correspond to three carbon atoms) in the spectrum and they do not overlap with resonances from PS, PI, or PEP, the region between 26 and 28 ppm was used to ensure that no hydrogenation of styrene occurred. If partial hydrogenation occurred, new olefinic signals (such as from poly(1-vinylcyclohexene))<sup>93</sup> would be visible in the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. No instances of these signals were detected. To reach near-quantitative hydrogenation, the catalyst was added 3–4 times in 1 h intervals and the conversion was checked *via* aliquots that were analyzed by <sup>1</sup>H NMR spectroscopy as described above. Following the first catalyst charge, the conversion was typically found to have reached or exceeded 90%. Further catalyst additions increased the degree of saturation stepwise within error to ≥98% (see Figure S6 in the Supporting Information). Upon hydrogenation of the PI blocks, the SEC elution traces slightly shifted toward lower elution times (see Figures 2a and S7 in the Supporting Information). The molecular weight by MALLS changed by

±5% for the hydrogenated copolymers, which is in good agreement with theoretical estimates considering the uncertainties in dn/dc and the MALLS analysis.

**Thermal Properties.** The thermal properties of the two series of (SI/S)<sub>4</sub> tapered star copolymer films, which appeared optically transparent to the unaided eye (see Figure S8 in the Supporting Information), were analyzed by DSC and DMTA according to the measurement conditions described in the Experimental Section. Nearly all copolymers exhibited two glass temperatures calorimetrically, but this does not necessarily confirm microphase separation between the blocks, as Lodge and McLeish<sup>94</sup> have reported that even miscible systems can exhibit two glass temperatures because of the phenomenon of self-concentration. For both star copolymer series, the two *T<sub>g</sub>* values approach each other upon decreasing *M* (Figure 3a), with the weaker *M* dependence for the PI *T<sub>g</sub>*



**Figure 3.** (a) *T<sub>g</sub>* values of (SI/S)<sub>4</sub> tapered star copolymers (60 and 40 wt % PS series) determined by both DSC (midpoint, 10 K min<sup>−1</sup>) and DMTA (steepest descent in log *G'*, 1 rad/s) as a function of *M<sub>w</sub>* MALLS. A comparison of *T<sub>g</sub>* values measured for hydrogenated and unhydrogenated star copolymers, as discerned by DSC, is given in (b).

reflecting the smaller Kuhn length of PI [*l<sub>k</sub>*(PI) = 0.74 nm] relative to PS [*l<sub>k</sub>*(PS) = 1.48 nm].<sup>95</sup> In addition, the *T<sub>g</sub>* values approach each other more closely in linear tapered copolymers compared to their star analogues, as evidenced by the DSC thermograms included in Figure S9 in the Supporting Information. The highest PS *T<sub>g</sub>* values (367 ± 1 and 348 ± 8 K), as well as the lowest PI *T<sub>g</sub>* values (227.0 ± 0.1 and 221 ± 1 K), are observed for the highest-molecular-weight star copolymer in each series: (SI/S)<sub>4</sub>-60-240 and (SI/S)<sub>4</sub>-40-240, respectively. The (SI/S)<sub>4</sub> tapered star copolymers with 40 wt % PS (*vs* 60 wt % PS) generally exhibit lower PS *T<sub>g</sub>* values at a given star *M<sub>w</sub>* because of their shorter PS blocks. Furthermore, the *T<sub>g</sub>* values of the PI domains (220–224 K at 40 wt % S;



238–243 K at 60 wt % S) increase with PS content and are significantly higher than that for PI homopolymers (204–208 K)<sup>96</sup> because of incorporation of styrene units into the PI-rich portions of the tapered microstructure (see Figure S1 in the Supporting Information). The  $T_g$  values measured by DMTA (see Figures S10 and S11 in the Supporting Information for representative results) and included in Figure 3a for comparison are seen to agree well with the values acquired from DSC, with the DMTA-derived values being slightly higher for the highest-molecular-weight star copolymers. Upon hydrogenation of the PI blocks, the soft block (PEP vs PI)  $T_g$  values increased by only 1 K on average, in agreement with previous reports,<sup>51,62,63</sup> the  $T_g$  value for PEP homopolymers is higher (by ~5 K) than that for PI.<sup>96</sup> According to DSC, the PS  $T_g$  values do not show a consistent change upon hydrogenation (Figure 3b), but DMTA (Figure S12 in the Supporting Information) reveals a consistent increase in PS  $T_g$  by 5–10 K. Both hydrogenated and nonhydrogenated copolymers of the 40 wt % PS series exhibit lower PI (PEP)  $T_g$  values (and lower PS  $T_g$  values) because of the greater overall PI (PEP) fraction in the copolymers. Additional insight regarding the degree of mixing is obtained from SAXS, as discussed in the following section.

**Order and Morphology.** The phase state of the (SI/S)<sub>4</sub> tapered star copolymers, the tapered linear (SI/S) copolymers, and their hydrogenated derivatives, as determined by SAXS analysis, is summarized in Table 2. Example SAXS results are

**Table 2. Phase State of Tapered Star and Linear Copolymers**

| copolymer designation        | $w_S$ (%) | phase state                                                        |
|------------------------------|-----------|--------------------------------------------------------------------|
| (SI/S) <sub>4</sub> -60-80   | 65        | DIS for $T > 293$ K                                                |
| (SI/S) <sub>4</sub> -60-120  | 63        | DIS, approaching $T_{ODT}$ by cooling to 293 K                     |
| (SI/S) <sub>4</sub> -60-160  | 60        | LAM, $T_{ODT} = 398 \pm 5$ K                                       |
| (SI/S) <sub>4</sub> -60-200  | 62        | LAM up to 453 K ( $T_{ODT}$ not accessible)                        |
| (SI/S) <sub>4</sub> -60-240  | 58        | LAM up to 453 K ( $T_{ODT}$ not accessible)                        |
| (SI/S) <sub>4</sub> -40-80   | 38        | DIS for $T > 293$ K                                                |
| (SI/S) <sub>4</sub> -40-120  | 39        | DIS for $T > 293$ K                                                |
| (SI/S) <sub>4</sub> -40-160  | 39        | DIS for $T > 293$ K                                                |
| (SI/S) <sub>4</sub> -40-200  | 40        | CYL without long range order up to 373 K, $T_{ODT} = 438 \pm 15$ K |
| (SI/S) <sub>4</sub> -40-240  | 40        | BIC up to 453 K ( $T_{ODT}$ not accessible)                        |
| (SI/S)-60-60                 | 62        | LAM, $T_{ODT} = 408 \pm 15$ K                                      |
| (SI/S)-40-60                 | 41        | hexagonally-packed CYL, $T_{ODT} = 408 \pm 15$ K                   |
| (SEP/S) <sub>4</sub> -60-240 | 57        | LAM, up to 453 K ( $T_{ODT}$ not accessible)                       |
| (SEP/S)-60-60                | 61        | LAM, up to 453 K ( $T_{ODT}$ not accessible)                       |

presented in Figures 4 and 5 for the tapered linear and star copolymers, respectively. Additional details for each of the copolymers studied by SAXS are provided in Figures S13–S25 in the Supporting Information. The intensity profile for the tapered linear (SI/S)-60-60 (Figure 4a) displays Bragg reflections with relative  $q$  values of 1:3, corresponding to a weakly ordered lamellar morphology (LAM) with a periodicity of 18.8 nm. In contrast, the tapered linear (SI/S)-40-60 (Figure 4c) reveals a weak higher-order peak at  $3^{1/2}$  times the  $q$  value of the primary peak (periodicity 21.9 nm), indicating a weakly ordered hexagonally packed cylindrical (CYL) morphology at 393 K. Both (SI/S)-60-60 and (SI/S)-40-60 transition to disorder at  $T_{ODT} = 408 \pm 15$  K (see Figure S13 in the Supporting Information). Selective hydrogenation of the PI blocks promotes microphase segregation, as evidenced by an

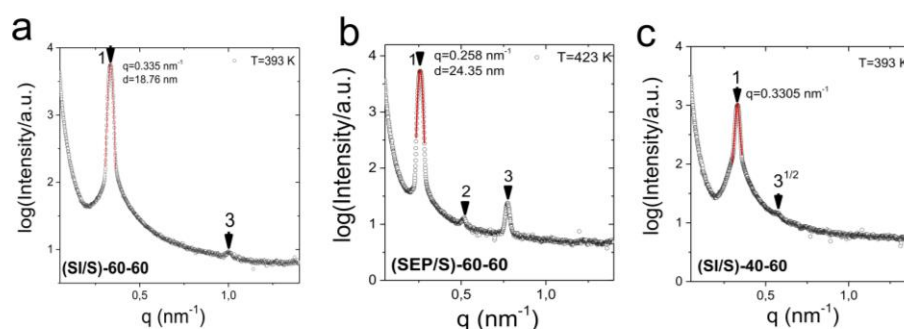
increase in the domain spacing from 18.8 to 24.4 nm in (SI/S)-60-60 compared to (SEP/S)-60-60, as well as an increased intensity of the third-order peak (Figure 4b).

Representative SAXS curves acquired for the tapered star copolymers are provided in Figure 5. In the case of (SI/S)<sub>4</sub> with 60 wt % PS (Figure 5a), the Bragg reflections at  $q$  ratios of 1:2:3 verify a lamellar morphology with a periodicity of 22.6 nm (at  $T = 423$  K). When the PS fraction is reduced to 40 wt % (Figure 5c), the as-cast film shows an indistinct scattering pattern; the structure at 293 K resembles CYL without long-range order (which would show higher-order peaks with relative  $q$  values of 1:2:7<sup>1/2</sup>:3). Heating to 423 K induces a sharpening of the peak and the emergence of a shoulder on the low- $q$  side of the principal peak, at a  $q$  ratio of 2<sup>1/2</sup>:3<sup>1/2</sup>, suggestive of an irregular bicontinuous (BIC) morphology; this structure is confirmed by TEM in the following section. Interestingly, the latter morphology is the one closer to equilibrium as it persists on cooling to ambient temperature. As with the linear copolymers, selective hydrogenation of the PI blocks drives the stars to stronger segregation (Figure S17 in the Supporting Information), producing a lamellar morphology exhibiting long-range order (Figure 5b).

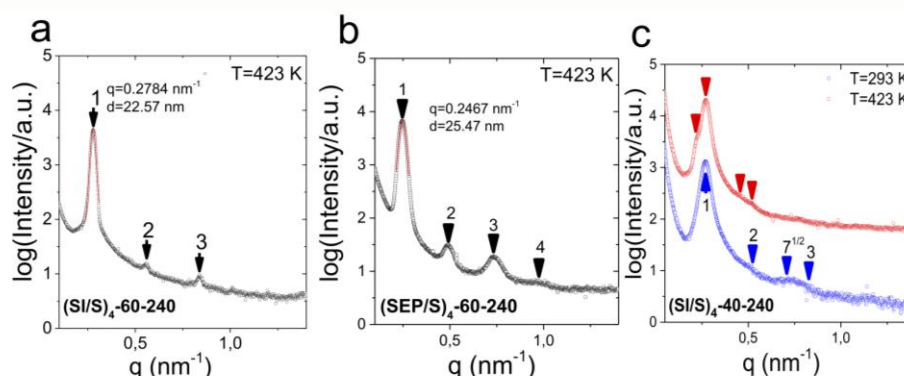
These results for the tapered (SI/S)<sub>4</sub> stars can be used to construct a phase diagram (c.f. Figure 6). Because of the unknown interaction parameter in the tapered systems, the quantity  $M_w/T$  is plotted instead of the pertinent  $\chi N$ . Nevertheless, the phase diagram indicates a lamellar morphology for the stars with 60 wt % PS and either a CYL or BIC morphology for 40 wt % PS, indicating that the CYL/BIC boundary lies close to 40 wt % PS. Several additional compositions would be required to generate a complete phase diagram.

To further elucidate the morphology of the tapered (SI/S)<sub>4</sub> star with 40 wt % PS, TEM images were collected from both an as-cast film and a film annealed at 423 K for 6 h to match the SAXS measurement. Representative images are displayed in Figure 7 and reveal that the morphologies in both cases appear qualitatively similar and spatially complex, not cylinders arranged on a hexagonal lattice. Because the tapered I/S sequences consist of both styrene and isoprene units, the thermodynamic incompatibility between the S-rich and I-rich blocks is expectedly lower than that of analogous S and I blocks of comparable size, as previously established in the related case of block-random copolymers.<sup>97</sup> In this latter class of diblock copolymers, the interblock thermodynamic incompatibility is not only reduced but, depending on the composition contrast between the blocks, fluctuations at the ODT can also be mitigated.<sup>98</sup> This decreased incompatibility, coupled with vitrification of the styrene units, is most likely responsible for incomplete microphase separation when the copolymer films are initially cast from solution at ambient temperature (Figure 7a,b).

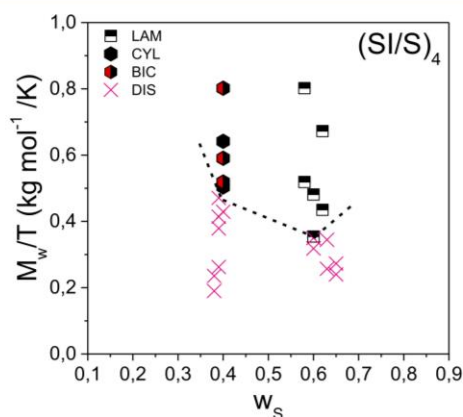
As a consequence, the electron contrast between the microdomains is lessened. Thermal annealing promotes an improvement in the extent of microphase separation in this copolymer because the microdomains appear more well-defined (Figure 7c,d), suggesting that the distribution of correlation distances narrows upon annealing, in agreement with the SAXS results presented in Figure 5c. Interestingly, however, the morphological dimensions and symmetry do not discernibly change in terms of lattice ordering upon annealing. For example, the microdomain periodicities determined from specimens before and after annealing are  $25.0 \pm 1.3$  and  $24.2 \pm$



**Figure 4.** SAXS patterns for (a) tapered linear (SI/S)-60-60, (b) hydrogenated derivative (SEP/S)-60-60, and (c) (SI/S)-40-60 copolymers. Arrows indicate the positions of the Bragg reflections corresponding to lamellar (a,b) or cylindrical (c) morphology. The associated temperatures are indicated.

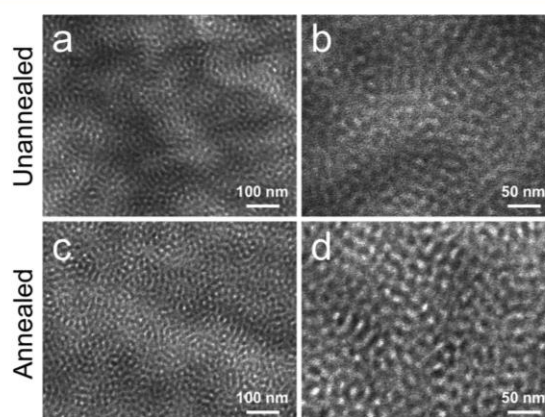


**Figure 5.** SAXS patterns for (a) tapered star (SI/S)<sub>4</sub>-60-240, (b) hydrogenated derivative (SEP/S)<sub>4</sub>-60-240, and (c) (SI/S)<sub>4</sub>-40-240 copolymers. Arrows indicate the positions of the Bragg reflections corresponding to lamellar (a,b) or CYL/BIC (c) morphologies. The associated temperatures are indicated.



**Figure 6.** Experimental phase diagram for tapered star (SI/S)<sub>4</sub> copolymers according to SAXS analysis, indicating the presence of lamellae (LAM), cylinders (CYL), BIC, and disordered (DIS) morphologies. For the BIC morphology, only data obtained during cooling are included. The ODT boundary (dashed line) serves as a guide for the eye.

1.5 nm, respectively (from 100 measurements of 10 different images), which also agrees favorably with findings from SAXS.



**Figure 7.** TEM images collected from the (SI/S)<sub>4</sub>-40-240 copolymer (a,b) as-cast from solution and (c,d) after thermal annealing at 423 K for 6 h. Electron-opaque (dark) regions identify stained isoprene-rich microdomains. Corresponding SAXS profiles are displayed in Figure 5c.

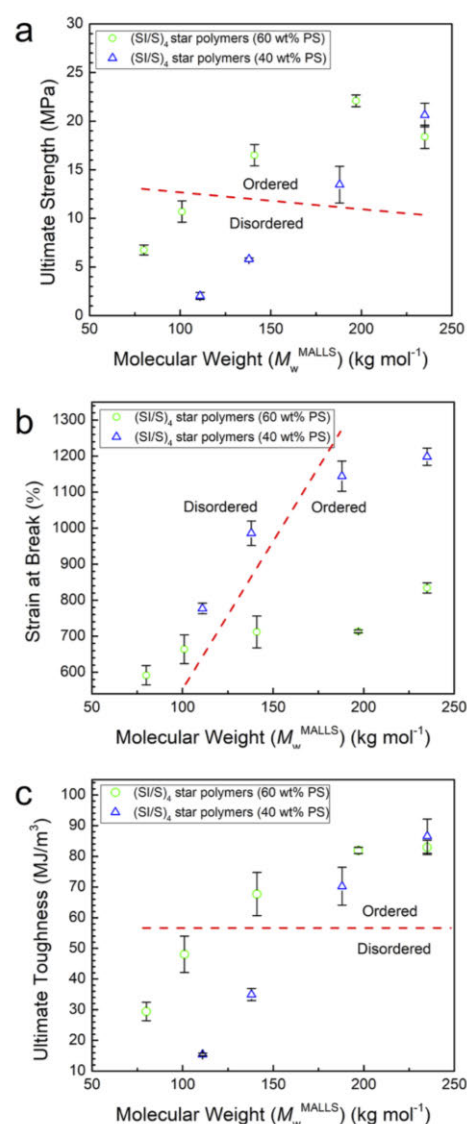
Although some of the unstained styrenic microdomains might exist as isolated cylinders in Figure 7, the overall morphologies in both cases appear to be weakly bicontinuous, although



without any particular symmetry (e.g., gyroid,<sup>99</sup> double diamond,<sup>100</sup> or *Fddd*<sup>101</sup>); rather, it appears to be a BIC structure, consistent with the absence of clearly resolved diffraction peaks in the SAXS pattern (Figure 5c). Previous studies have documented the presence of bicontinuous morphologies in both tapered block copolymers<sup>29,102</sup> and linear multiblock copolymers.<sup>103,104</sup> In diblock and triblock copolymer systems, most of these bicontinuous morphologies have been conclusively identified but not so in multiblock copolymers.<sup>105</sup> This suggests that the increased molecular complexity that accompanies an increased number of blocks per molecule can confound the development of a highly ordered bicontinuous morphology, which generally requires precise interfacial chain packing to ensure stability.<sup>106</sup>

**Mechanical Properties.** The ultimate properties of the multiblock tapered star copolymers produced here were investigated by uniaxial tensile measurements (see Figure S26 in the Supporting Information for representative stress–strain plots). Hysteresis and recovery data are presented in Figures S27–S32 in the Supporting Information and confirm that these materials behave as good thermoplastic elastomers. Here, we focus on the properties at the point of mechanical failure, which reveal clear trends with macromolecular characteristics; these property values are presented as a function of  $M_w$  in Figure 8. The stars with 60 wt % PS exhibit higher ultimate strength ( $\sigma_b$  up to  $22 \pm 1$  MPa in Figure 8a) but lower strain at break compared with the stars containing 40 wt % PS ( $\epsilon_b$  up to  $1198 \pm 34\%$  in Figure 8b). The multiblock tapered star copolymers with 60 wt % PS possess higher ultimate toughness ( $U$ ) values at low molecular weights compared to those with 40 wt % PS. This difference gradually decreases with increasing  $M_w$  to  $83 \pm 2$  and  $87 \pm 6$  MJ/m<sup>3</sup> for (SI/S)<sub>4</sub>-60-240 and (SI/S)<sub>4</sub>-40-240, respectively, in Figure 8c. Although the ordered copolymers display higher values of  $\sigma_b$ ,  $\epsilon_b$ , and  $U$  than the disordered ones, there is no obvious discontinuity; that is, all these attributes increase smoothly with increasing  $M_w$ . This demonstrates that even disordered copolymers show large local composition variations,<sup>94</sup> as evidenced by the two  $T_g$ s detectable by DSC. The PS blocks reside in regions where  $T_g$  is above ambient temperature and therefore act as effective physical cross-links even when the system is disordered. Note, however, that the lowest- $M$  star copolymer with 40 wt % PS, (SI/S)<sub>4</sub>-40-80, was too mechanically weak for tensile testing, which is consistent with our observation of only one clear  $T_g$  discernible by DSC (c.f. Figure 3a) and the anticipated absence of physical cross-links. Values of  $E_y$ , as well as the yield stress ( $\sigma_y$ ) and yield strain ( $\epsilon_y$ ), showed weaker trends with respect to  $M_w$  (see Figures S33–S35 and Table S1 in the Supporting Information), and again, no discontinuity is apparent upon passing from disordered to ordered. The (SI/S)<sub>4</sub>-40-120 copolymer with a disordered morphology does not reveal a distinguishable yield point. For the ordered star copolymers, the 60 wt % PS series (LAM) exhibits a higher  $E_y$  (by  $\sim 10\times$ ), higher  $\sigma_y$  (by  $\sim 4\times$ ), and modestly lower  $\epsilon_y$  than the 40 wt % PS series (CYL or BIC) because of the connectivity of the glassy PS microdomains.<sup>75</sup>

The mechanical behavior and property values for the linear (SI/S)<sub>4</sub>-40-60 and (SI/S)<sub>4</sub>-60-60 copolymers are generally similar to those reported in previous studies of SIS triblock copolymers with cylindrical and lamellar morphologies.<sup>75,107</sup> However, coupling the linear (SI/S) copolymers into star copolymers results in significant quantitative and even



**Figure 8.** Ultimate mechanical properties—(a)  $\sigma_b$ , (b)  $\epsilon_b$ , and (c)  $U$ —of (SI/S)<sub>4</sub> tapered star copolymers (60 and 40 wt % PS) as functions of  $M_w$ .

qualitative changes in mechanical behavior, resulting from changes in morphology. Most notably, the (SI/S)<sub>4</sub>-40-60 copolymer possesses a CYL morphology according to SAXS and does not exhibit a yield point, while the corresponding (SI/S)<sub>4</sub>-40-240 copolymer has a BIC structure with an unambiguous yield point at  $\sigma_y \approx 2$  MPa. These features are comparable to those for linear SIS triblock copolymers with CYL or gyroid morphologies, respectively.<sup>75</sup> At both 40 and 60 wt % PS, coupling the linear copolymers into star copolymers is responsible for significant increases in  $\sigma_y$ ,  $\sigma_b$ , and  $U$ , reflecting higher levels of stress throughout the deformation. The multiplicative factors by which these various properties increase upon coupling linear copolymers into star copolymers



are summarized in Table 3; the individual property values are available in Table S1 in the Supporting Information.

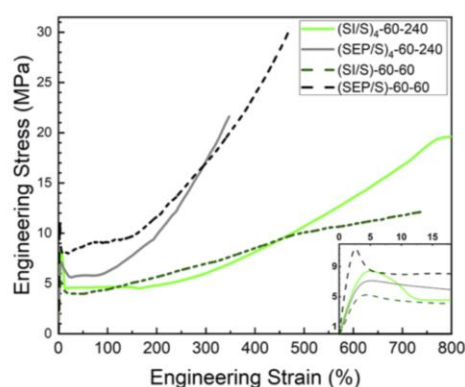
**Table 3. Relative Changes<sup>a</sup> in Mechanical Property Values after Coupling (SI/S) Tapered Linear Copolymers into (SI/S)<sub>4</sub> Tapered Star Copolymers**

| star copolymer              | $\Delta\epsilon_b$ | $\Delta\sigma_b$ | $\Delta U$ | $\Delta E_y$ | $\Delta\epsilon_y$           | $\Delta\sigma_y$ |
|-----------------------------|--------------------|------------------|------------|--------------|------------------------------|------------------|
| (SI/S) <sub>4</sub> -60-240 | 1.2                | 1.6              | 1.5        | 1.6          | 1.2                          | 1.6              |
| (SI/S) <sub>4</sub> -40-240 | 1.5                | 4.8              | 3.8        | 5.7          | yielding only after coupling |                  |

<sup>a</sup>Factors represent the ratio of values of property *P* for star versus linear, that is,  $\Delta P = P_{\text{star}}/P_{\text{linear}}$ .

At least three phenomena may contribute to such property enhancement: (1) an elevated bridging fraction in star copolymers relative to linear copolymers,<sup>44</sup> (2) additional fracture resistance imparted by bridging chains in the glassy domains,<sup>40</sup> which are absent in the linear copolymers but are formed by the central PS blocks in the stars, and (3) increased resistance to block “pullout” from the PS domains in the case of the stars, particularly for the second (gradient) PS blocks. In the linear copolymer, the chain length over which this gradient PS block is essentially pure PS is shorter than the length of the first PS block (by ~40%, see Figure S1 in the Supporting Information) because some of the styrene in the second monomer charge is statistically copolymerized into the isoprene-rich midblock. Considering the simple case of a difunctional CA, which yields an SI/S-CA-S/IS pentablock, the central PS blocks (S-CA-S) are twice the length of the second PS blocks in the precursor and are thus actually slightly longer (by ~20%) than the PS endblocks. A similar situation pertains to the four-arm star copolymers, which may be viewed as two pentablock copolymers (SI/S-CA-S/IS) joined at their central CA linkages. All three factors change simultaneously when linear copolymers are coupled into star copolymers, so it is difficult to identify their relative contributions, but they collectively produce the substantial property improvements evident in Table 3. An interesting comparison may be made between the results in Table 3, wherein the number of blocks per macromolecule is quadrupled by connecting four arms into a star architecture, and the results of ref 85, in which the number of blocks in tapered linear (I/S)<sub>n</sub> multiblock copolymers was varied (by varying *n*). At a fixed block *M*, the linear multiblock copolymers<sup>85</sup> display a moderate increase in  $\epsilon_y$  and  $\sigma_y$  with increasing *n* (from 3 to 5), although not as large as  $\Delta\epsilon_y$  and  $\Delta\sigma_y$  values for star copolymers versus linear copolymers in Table 3 (where the number of blocks per macromolecule is quadrupled). However, the observed increases in *U* and  $\epsilon_b$  for the present stars versus linear are not evident upon increasing *n* in the linear multiblocks<sup>85</sup> at a fixed block *M*. Thus, the arrangement of these blocks in a star architecture produces mechanical property improvements beyond those achieved by simply connecting the same blocks into a linear multiblock architecture.

The highest-*M* linear and star copolymers with 60 wt % PS were selectively hydrogenated; all four copolymers (linear, star, hydrogenated, and unhydrogenated) possess a LAM morphology at ambient temperature (Table 2). Their stress–strain curves are provided in Figure 9, and property changes upon hydrogenation are listed in Table 4. For the linear copolymer (SI/S)-60-60,  $E_y$  increased slightly (1.3×) upon hydrogenation to (SEP/S)-60-60, but  $E_y$  for the star copolymer actually



**Figure 9.** Stress–strain curves of the (SI/S)<sub>4</sub>, SI/S, (SEP/S)<sub>4</sub>, and SEP/S copolymers with 60 wt % PS.

**Table 4. Relative Changes<sup>a</sup> in Mechanical Property Values after Hydrogenation of (SI/S)<sub>4</sub> Tapered Star and (SI/S) Tapered Linear Copolymers to (SEP/S)<sub>4</sub> and (SEP/S)**

| hydrogenated polymer         | $\Delta\epsilon_b$ | $\Delta\sigma_b$ | $\Delta U$ | $\Delta E_y$ | $\Delta\epsilon_y$ | $\Delta\sigma_y$ |
|------------------------------|--------------------|------------------|------------|--------------|--------------------|------------------|
| (SEP/S) <sub>4</sub> -60-240 | 0.4                | 0.9              | 0.4        | 0.5          | 1.2                | 0.9              |
| (SEP/S)-60-60                | 0.7                | 2.5              | 1.3        | 1.3          | 0.7                | 2.0              |

<sup>a</sup>Factors represent the ratio of values of property *P* for hydrogenated versus unhydrogenated copolymer, that is,  $\Delta P = P_{\text{hyd}}/P_{\text{unhyd}}$ .

decreases upon hydrogenation (see Table 4), despite the fact that the rubbery modulus of PEP is ~3× that for PI.<sup>95</sup> This difference must reflect subtle changes in hard (PS) domain connectivity, for example, at grain boundaries or defects, as there is no qualitative change in morphology upon hydrogenation according to SAXS (see Table 2 and Figures S13 and S14 in the Supporting Information). Enhanced strain hardening is apparent for both linear and star copolymers upon selective hydrogenation (Figure 9) because of the decreased entanglement molecular weight (*M<sub>e</sub>*) of PEP relative to PI (by 3×).<sup>95</sup> As a consequence,  $\epsilon_b$  is reduced (by a factor of 0.4) for (SEP/S)<sub>4</sub>-60-240 compared to (SI/S)<sub>4</sub>-60-240, but less (by a factor of 0.7) for the tapered linear analogue (Table 4). Additional qualitative differences were observed between linear and star copolymers regarding the effect of hydrogenation on other large-strain properties. Values of  $\sigma_b$  increase significantly for the linear hydrogenated copolymer, by 2.5× for (SEP/S)-60-60, whereas a slight decrease (by a factor of 0.9) was recorded for the tapered star copolymer (SEP/S)<sub>4</sub>-60-240. For the tapered star copolymer, *U* decreased by a factor of 0.4 but increased by 1.3× for the tapered linear analogue (Table 4). These qualitative differences between the linear and star copolymers upon hydrogenation (increases in  $\sigma_b$  and *U* for the linear copolymer but decreases for the star copolymer) reflect differences in the high-strain behavior visible in Figure 9. In the case of the star copolymer, strong strain hardening is evident all the way up to break for both unsaturated and saturated copolymers; the lower  $\epsilon_b$  for the saturated copolymer thus leads to a lower *U* upon hydrogenation. However, for the linear copolymer, the unsaturated derivative undergoes weaker strain hardening at high strain than its saturated derivative, leading to a significant increase in  $\sigma_b$  upon hydrogenation.

We believe that these changes are related to differences in the ease of PS block “pullout,” as introduced above; the



increased segregation strength of SEP/S versus SI/S will hinder PS block pullout, increasing strain hardening and  $\sigma_b$ . By contrast, for the star copolymer, pullout is already disfavored by coupling together the second PS blocks, so no further improvement is observed upon hydrogenation. In summary, the mechanical properties of the linear tapered triblock copolymer benefit strongly from selective PI hydrogenation, whereas the mechanical properties of the star copolymer are adversely affected. The star copolymer behavior is similar to sequential linear SIS and SEPS copolymers described in prior reports,<sup>62,63</sup> while the hydrogenation-induced increase in mechanical properties of the present linear SI/S copolymers results from an increase in segregation strength and the corresponding impediment to PS block pullout.

## CONCLUSIONS

Multiblock four-arm tapered star copolymers with poly(styrene)-*block*-poly(isoprene-*grad*-styrene) “arms”, (SI/S)<sub>4</sub>, were synthesized in three steps with molecular weights ranging from 80 to 240 kg mol<sup>-1</sup>. Low dispersities (apparent  $\bar{D}$  = 1.04–1.12) were achieved regardless of  $M$  and without additional purification beyond precipitation. At sufficiently high  $M$ , an overall PS content of 60 wt % resulted in the lamellar order, while either a CYL or BIC morphology was observed at 40 wt % PS. Disordered morphologies prevailed at lower  $M$ . With decreasing  $M$ , the  $T_g$  values of PS and PI were found to approach each other but even disordered block copolymers typically displayed two  $T_g$ s because of local composition variations. Selective hydrogenation of the PI segments of the highest-molecular-weight star and the corresponding linear copolymers were achieved with high yields (78–94%), conversions of  $\geq 98\%$ , and without PS saturation via a Ni/Al (1:4.25) catalyst. The ultimate properties ( $\sigma_b$ ,  $\epsilon_b$ , and  $U$ ) of the star copolymers simultaneously increased as a function of  $M$  for both series, albeit without a discontinuity as the material passed from the disordered to an ordered state. The highest strain at break ( $\epsilon_b$  = 1198  $\pm$  34%), as well as the highest toughness ( $U$  = 83  $\pm$  2 MJ/m<sup>3</sup>), was recorded for the highest-molecular-weight star copolymer with 40 wt % PS. Selective hydrogenation of the PI segments of the (SI/S)<sub>4</sub> tapered star copolymer with 60 wt % PS and highest  $M$ , and the corresponding SI/S tapered linear copolymer resulted in more pronounced strain hardening and generally lower strain at break. Although the mechanical properties of the weakly segregated linear copolymer benefited significantly from selective hydrogenation, the mechanical properties of the star copolymer decreased in a similar fashion to those of sequential SIS copolymers. One-pot synthesis and facile hydrogenation of multiblock star copolymers permit access to tough, flexible, and transparent polymeric materials on a multigram scale while exhibiting comparably short reaction times and retaining low dispersity. Any uncoupled arms are still incorporated into the physical network and thus do not decrease the materials’ mechanical performance. Therefore, this approach holds great promise for the development of future complex macromolecular architectures. These materials are not only conceivably useful for a plethora of applications but also allow precise fundamental studies of structure–property relationships in nanostructured elastomers and their blends/composites.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.0c00645>.

Additional NMR spectra, SEC elution traces, representative DSC and DMTA data, and mechanical property details (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

**George Floudas** – Department of Physics, University of Ioannina, 45110 Ioannina, Greece; Max Planck Institute for Polymer Research, 55128 Mainz, Germany; Email: [gfloudas@uoi.gr](mailto:gfloudas@uoi.gr)

**Holger Frey** – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany; [orcid.org/0000-0002-9916-3103](https://orcid.org/0000-0002-9916-3103); Email: [hfrey@uni-mainz.de](mailto:hfrey@uni-mainz.de)

**Richard A. Register** – Department of Chemical and Biological Engineering, Princeton University, Princeton 08544, New Jersey, United States; [orcid.org/0000-0002-5223-4306](https://orcid.org/0000-0002-5223-4306); Email: [register@princeton.edu](mailto:register@princeton.edu)

### Authors

**Philipp von Tiedemann** – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany; Graduate School Materials Science in Mainz, 55128 Mainz, Germany; Department of Chemical and Biological Engineering, Princeton University, Princeton 08544, New Jersey, United States

**Jiaqi Yan** – Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh 27695, North Carolina, United States; [orcid.org/0000-0002-6540-698X](https://orcid.org/0000-0002-6540-698X)

**Ramona D. Barent** – Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany; Max Planck Graduate Center, 55122 Mainz, Germany

**Richard J. Spontak** – Department of Chemical & Biomolecular Engineering and Department of Materials Science & Engineering, North Carolina State University, Raleigh 27695, North Carolina, United States

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.macromol.0c00645>

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

P.V.T. acknowledges the Graduate School of Excellence MAINZ for financial support. This work was supported by the Max Planck Graduate Center with the Johannes Gutenberg-Universität Mainz (MPGC). Additional support was provided by the National Science Foundation, Polymers Program (DMR-1402180 to R.A.R.). P.V.T. thanks Christian Wahlen for his support with respect to sample shipment. J.Y. was financially supported by the NC State Nonwovens Institute, and TEM was performed at the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation (award number ECCS-1542015). This work made use of instrumentation acquired at the AIF with support from the National Science Foundation (DMR-1726294). The AIF is a member of the North Carolina



Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure (NNCI).

## REFERENCES

- (1) Knoll, K.; Nießner, N. Styrolux<sup>+</sup> and Styroflex<sup>+</sup> - from transparent high impact polystyrene to new thermoplastic elastomers. *Macromol. Symp.* **1998**, *132*, 231–243.
- (2) Adhikari, R.; Michler, G. H.; Goerlitz, S.; Knoll, K. Morphology and micromechanical deformation behavior of styrene-butadiene block copolymers. III. Binary blends of asymmetric star block copolymer with general-purpose polystyrene. *J. Appl. Polym. Sci.* **2004**, *92*, 1208–1218.
- (3) Knoll, K.; Fischer, W.; Gausepohl, H.; Koch, J.; Wünsch, J.; Naegle, P. (INEOS Styrolution Europe GmbH) Transparent, impact-resistant polystyrene on a styrene-butadiene block copolymer basis. U.S. Patent 6,593,430 B1, Jul 15, 2003.
- (4) Cunningham, R. E.; Treiber, M. R. Preparation and stress-strain properties of ABA-type block polymers of styrene and isoprene or butadiene. *J. Appl. Polym. Sci.* **1968**, *12*, 23–34.
- (5) Angelo, R. J.; Ikeda, R. M.; Wallach, M. L. Multiple glass transitions of block polymers. *Polymer* **1965**, *6*, 141–156.
- (6) Adhikari, R.; Michler, G. H.; Lebek, W.; Goerlitz, S.; Weidisch, R.; Knoll, K. Morphology and micromechanical deformation behavior of SB-block copolymers. II. Influence of molecular architecture of asymmetric star block copolymers. *J. Appl. Polym. Sci.* **2002**, *85*, 701–713.
- (7) Kraus, G.; Childers, C. W.; Gruver, J. T. Properties of random and block copolymers of butadiene and styrene. I. Dynamic properties and glassy transition temperatures. *J. Appl. Polym. Sci.* **1967**, *11*, 1581–1591.
- (8) Matmour, R.; Gnanou, Y. Synthesis of complex polymeric architectures using multilithiated carbanionic initiators—Comparison with other approaches. *Prog. Polym. Sci.* **2013**, *38*, 30–62.
- (9) Morton, M.; Helminiak, T. E.; Gadkary, S. D.; Bueche, F. Preparation and properties of monodisperse branched polystyrene. *J. Polym. Sci.* **1962**, *57*, 471–482.
- (10) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. Analysis and dilute solution properties of 12- and 18-arm-star polystyrenes. *Macromolecules* **1983**, *16*, 214–220.
- (11) Fetters, L. J.; Kiss, A. D.; Pearson, D. S.; Quack, G. F.; Vitus, F. J. Rheological behavior of star-shaped polymers. *Macromolecules* **1993**, *26*, 647–654.
- (12) Bi, L.-K.; Fetters, L. J. Synthesis and Properties of Block Copolymers. 3. Polystyrene-Polydiene Star Block Copolymers. *Macromolecules* **1976**, *9*, 732–742.
- (13) von Tiedemann, P.; Maciol, K.; Preis, J.; Sajkiewicz, P.; Frey, H. Rapid one-pot synthesis of tapered star copolymers via ultra-fast coupling of polystyryllithium chain ends. *Polym. Chem.* **2019**, *10*, 1762–1768.
- (14) Park, S.; Cho, D.; Im, K.; Chang, T.; Uhrig, D.; Mays, J. W. Utility of Interaction Chromatography for Probing Structural Purity of Model Branched Copolymers: 4-Miktoarm Star Copolymer. *Macromolecules* **2003**, *36*, 5834–5838.
- (15) Uhrig, D.; Mays, J. W. Experimental techniques in high-vacuum anionic polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6179–6222.
- (16) Burns, A. B.; Register, R. A. Strategies for the Synthesis of Well-Defined Star Polymers by Anionic Polymerization with Chlorosilane Coupling and Preservation of the Star Architecture during Catalytic Hydrogenation. *Macromolecules* **2016**, *49*, 2063–2070.
- (17) Kraus, G.; Rollmann, K. W. Some effects of monomer sequence on the viscoelastic behavior of random copolymers of butadiene and styrene. *Angew. Makromol. Chem.* **1971**, *16*, 271–296.
- (18) Worsfold, D. J. Anionic copolymerization of styrene and isoprene in cyclohexane. *J. Polym. Sci., Part A-1: Polym. Chem.* **1967**, *5*, 2783–2789.
- (19) Grune, E.; Johann, T.; Appold, M.; Wahlen, C.; Blankenburg, J.; Leibig, D.; Müller, A. H. E.; Gallei, M.; Frey, H. One-Step Block Copolymer Synthesis versus Sequential Monomer Addition: A Fundamental Study Reveals That One Methyl Group Makes a Difference. *Macromolecules* **2018**, *51*, 3527–3537.
- (20) Grune, E.; Appold, M.; Müller, A. H. E.; Gallei, M.; Frey, H. Anionic Copolymerization Enables the Scalable Synthesis of Alternating (AB)<sub>n</sub> Multiblock Copolymers with High Molecular Weight in *n*/2 Steps. *ACS Macro Lett.* **2018**, *7*, 807–810.
- (21) von Tiedemann, P.; Blankenburg, J.; Maciol, K.; Johann, T.; Müller, A. H. E.; Frey, H. Copolymerization of Isoprene with *p*-Alkylstyrene Monomers: Disparate Reactivity Ratios and the Shape of the Gradient. *Macromolecules* **2019**, *52*, 796–806.
- (22) Hadjichristidis, N.; Floudas, G.; Pispas, S.; Hadjichristidis, N. Microphase Separation in Normal and Inverse Tapered Block Copolymers of Polystyrene and Polyisoprene. 1. Phase State. *Macromolecules* **2001**, *34*, 650–657.
- (23) Corbin, N.; Prud'homme, J. Multiblock copolymers of styrene and isoprene. I. Synthesis and characterization. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1645–1659.
- (24) Zelinski, R.; Childers, C. W. Linear Elastomeric Block Polymers. *Rubber Chem. Technol.* **1968**, *41*, 161–181.
- (25) Corbin, N.; Prud'homme, J. Multiblock copolymers of styrene and isoprene. II. Microstructure and dilute solution properties. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1937–1951.
- (26) Luo, M.; Brown, J. R.; Remy, R. A.; Scott, D. M.; Mackay, M. E.; Hall, L. M.; Epps, T. H., III Determination of Interfacial Mixing in Tapered Block Polymer Thin Films: Experimental and Theoretical Investigations. *Macromolecules* **2016**, *49*, S213–S222.
- (27) Seo, Y.; Brown, J. R.; Hall, L. M. Effect of Tapering on Morphology and Interfacial Behavior of Diblock Copolymers from Molecular Dynamics Simulations. *Macromolecules* **2015**, *48*, 4974–4982.
- (28) Brown, J. R.; Seo, Y.; Sides, S. W.; Hall, L. M. Unique Phase Behavior of Inverse Tapered Block Copolymers: Self-Consistent Field Theory and Molecular Dynamics Simulations. *Macromolecules* **2017**, *50*, S619–S626.
- (29) Roy, R.; Park, J. K.; Young, W.-S.; Mastroianni, S. E.; Tureau, M. S.; Epps, T. H., III Double-Gyroid Network Morphology in Tapered Diblock Copolymers. *Macromolecules* **2011**, *44*, 3910–3915.
- (30) Singh, N.; Tureau, M. S.; Epps, T. H., III Manipulating ordering transitions in interfacially modified block copolymers. *Soft Matter* **2009**, *5*, 4757.
- (31) Adhikari, R.; Godehardt, R.; Lebek, W.; Weidisch, R.; Michler, G. H.; Knoll, K. Correlation between morphology and mechanical properties of different styrene/butadiene triblock copolymers: A scanning force microscopy study. *J. Macromol. Sci., Part B: Phys.* **2001**, *40*, 833–847.
- (32) Lach, R.; Weidisch, R.; Knoll, K. Morphology and mechanical properties of binary triblock copolymer blends. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 429–438.
- (33) Thunga, M.; Staudinger, U.; Satapathy, B. K.; Weidisch, R.; Abdel-Goad, M.; Janke, A.; Knoll, K. Influence of molecular architecture of S-S/B-S triblock copolymers on rheological properties. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2776–2788.
- (34) Watanabe, H.; Sato, T.; Osaki, K.; Yao, M.-L.; Yamagishi, A. Rheological and Dielectric Behavior of a Styrene-Isoprene-Styrene Triblock Copolymer in Selective Solvents. 2. Contribution of Loop-Type Middle Blocks to Elasticity and Plasticity. *Macromolecules* **1997**, *30*, S877–S892.
- (35) Matsumiya, Y.; Watanabe, H.; Takano, A.; Takahashi, Y. Uniaxial Extensional Behavior of (SIS)<sub>p</sub>-Type Multiblock Copolymer Systems: Structural Origin of High Extensibility. *Macromolecules* **2013**, *46*, 2681–2695.
- (36) Watanabe, H.; Matsumiya, Y.; Sawada, T.; Iwamoto, T. Rheological and Dielectric Behavior of Dipole-Inverted (SIS)<sub>p</sub>-Type Multiblock Copolymers: Estimates of Bridge/Loop Fractions for Respective I Blocks and Effect of Loops on High Extensibility of Bridges. *Macromolecules* **2007**, *40*, 6885–6897.



- (37) Karatasos, K.; Anastasiadis, S. H.; Pakula, T.; Watanabe, H. On the Loops-to-Bridges Ratio in Ordered Triblock Copolymers: An Investigation by Dielectric Relaxation Spectroscopy and Computer Simulations. *Macromolecules* **2000**, *33*, 523–541.
- (38) Shah, M.; Ganesan, V. Chain bridging in a model of semicrystalline multiblock copolymers. *J. Chem. Phys.* **2009**, *130*, 054904.
- (39) Nagata, Y.; Masuda, J.; Noro, A.; Cho, D.; Takano, A.; Matsushita, Y. Preparation and Characterization of a Styrene–Isoprene Undecablock Copolymer and Its Hierarchical Microdomain Structure in Bulk. *Macromolecules* **2005**, *38*, 10220–10225.
- (40) Mori, Y.; Lim, L. S.; Bates, F. S. Consequences of Molecular Bridging in Lamellae-Forming Triblock/Pentablock Copolymer Blends. *Macromolecules* **2003**, *36*, 9879–9888.
- (41) Tallury, S. S.; Spontak, R. J.; Pasquinelli, M. A. Dissipative particle dynamics of triblock copolymer melts: a midblock conformational study at moderate segregation. *J. Chem. Phys.* **2014**, *141*, 244911.
- (42) Tuhin, M. O.; Ryan, J. J.; Sadler, J. D.; Han, Z.; Lee, B.; Smith, S. D.; Pasquinelli, M. A.; Spontak, R. J. Microphase-Separated Morphologies and Molecular Network Topologies in Multiblock Copolymer Gels. *Macromolecules* **2018**, *51*, S173–S181.
- (43) Tuhin, M. O.; Woloszczuk, S.; Mineart, K. P.; Pasquinelli, M. A.; Sadler, J. D.; Smith, S. D.; Banaszak, M.; Spontak, R. J. Communication: Molecular-level description of constrained chain topologies in multiblock copolymer gel networks. *J. Chem. Phys.* **2018**, *148*, 231101.
- (44) Spencer, R. K. W.; Matsen, M. W. Domain Bridging in Thermoplastic Elastomers of Star Block Copolymer. *Macromolecules* **2017**, *50*, 1681–1687.
- (45) Ren, J. M.; McKenzie, T. G.; Fu, Q.; Wong, E. H. H.; Xu, J.; An, Z.; Shanmugam, S.; Davis, T. P.; Boyer, C.; Qiao, G. G. Star Polymers. *Chem. Rev.* **2016**, *116*, 6743–6836.
- (46) Ashraf, A. R.; Ryan, J. J.; Satkowski, M. M.; Smith, S. D.; Spontak, R. J. Effect of Systematic Hydrogenation on the Phase Behavior and Nanostructural Dimensions of Block Copolymers. *ACS Appl. Mater. Interfaces* **2018**, *10*, 3186–3190.
- (47) Adams, J. L.; Quiram, D. J.; Graessley, W. W.; Register, R. A.; Marchand, G. R. Interaction Strengths in Styrene–Diene Block Copolymers and Their Hydrogenated Derivatives. *Macromolecules* **1998**, *31*, 201–204.
- (48) Lai, C.; Russel, W. B.; Register, R. A.; Marchand, G. R.; Adamson, D. H. Phase Behavior of Styrene–Isoprene Diblock Derivatives with Varying Conformational Asymmetry. *Macromolecules* **2000**, *33*, 3461–3466.
- (49) Sakurai, S.; Hashimoto, T.; Fetters, L. J. Morphology of Polystyrene-block-poly(ethylene-alt-propylene) Diblock Copolymers in the Strong-Segregation Limit. *Macromolecules* **1995**, *28*, 7947–7949.
- (50) Alley, W. M.; Hamdemir, I. K.; Johnson, K. A.; Finke, R. G. Ziegler-type hydrogenation catalysts made from group 8–10 transition metal precatalysts and  $\text{AlR}_3$  cocatalysts: A critical review of the literature. *J. Mol. Catal. A: Chem.* **2010**, *315*, 1–27.
- (51) Yakubchik, A. I.; Tichomirov, B. I.; Sulimov, V. S. Hydrogenation of Natural and Synthetic cis-1,4-Polyisoprene. *Rubber Chem. Technol.* **1962**, *35*, 1063–1065.
- (52) Ricci, G.; Boccia, A.; Leone, G.; Pierro, I.; Zanchin, G.; Scoti, M.; Auriemma, F.; de Rosa, C. Isotactic and Syndiotactic Alternating Ethylene/Propylene Copolymers Obtained Through Non-Catalytic Hydrogenation of Highly Stereoregular cis-1,4 Poly(1,3-diene)s. *Molecules* **2017**, *22*, 755–769.
- (53) Mango, L. A.; Lenz, R. W. Hydrogenation of unsaturated polymers with diimide. *Makromol. Chem.* **1973**, *163*, 13–36.
- (54) Harwood, H. J.; Russell, D. B.; Verthe, J. J. A.; Zymonas, J. Diimide as a reagent for the hydrogenation of unsaturated polymers. *Makromol. Chem.* **1973**, *163*, 1–12.
- (55) Hahn, S. F. An improved method for the diimide hydrogenation of butadiene and isoprene containing polymers. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 397–408.
- (56) Gacal, B. N.; Filiz, V.; Shishatskiy, S.; Rangou, S.; Neumann, S.; Abetz, V. Modification of polyisoprene-block-poly(vinyl trimethylsilane) block copolymers via hydrosilylation and hydrogenation, and their gas transport properties. *J. Polym. Sci., Part B: Polym. Phys.* **2013**, *51*, 1252–1261.
- (57) Eckert, R. J. A. (Shell Oil Co) Hydrogenated Star-Shaped Polymer. U.S. Patent 4,156,673 A, May 29, 1979.
- (58) Baumgartner, H. J.; Balas, J. G. (Shell Oil Co) Hydrogenation Process. U.S. Patent 3,937,759 A, Feb 10, 1976.
- (59) Wald, M. M.; Quam, M. G. (Shell Oil Co) Partially Hydrogenated Block Copolymers. U.S. Patent 3,595,942 A, Jul 27, 1971.
- (60) Wald, M. M.; Quam, M. G. (Shell Oil Co) Selectively Hydrogenated Block Copolymers. U.S. Patent 3,700,633 A, Oct 24, 1972.
- (61) Velichkova, R.; Toncheva, V.; Antonov, C.; Alexandrov, V.; Pavlova, S.; Dubrovina, L.; Gladkova, E. Styrene–isoprene block copolymers. II. Hydrogenation and solution properties. *J. Appl. Polym. Sci.* **1991**, *42*, 3083–3090.
- (62) Laramée, A.; Goursot, P.; Prud'homme, J. Physikalische und mechanische Eigenschaften eines hydrierten Polystyrol/Polysopren/Polystyrol-Blockcopolymeren. *Colloid Polym. Sci.* **1977**, *255*, 1141.
- (63) Laramée, A.; Goursot, P.; Prud'homme, J. Propriétés physiques et mécaniques d'un copolymère séquencé polystyrène-polyisoprène-polystyrène hydrogéné. *Makromol. Chem.* **1975**, *176*, 3079–3088.
- (64) Falk, J. C. Coordination catalysts for the selective hydrogenation of polymeric unsaturation. *J. Polym. Sci., Part A: Polym. Chem.* **1971**, *9*, 2617–2623.
- (65) Beckingham, B. S. Mixing Thermodynamics of Block-Random Copolymers. Ph.D. Thesis, Princeton University, 2013.
- (66) Séguéla, R.; Prud'homme, J. Effects of Casting Solvents on Mechanical and Structural Properties of Polydiene-Hydrogenated Polystyrene-Polyisoprene-Polystyrene and Polystyrene-Polybutadiene-Polystyrene Block Copolymers. *Macromolecules* **1978**, *11*, 1007–1016.
- (67) Wang, W.; Lu, W.; Goodwin, A.; Wang, H.; Yin, P.; Kang, N.-G.; Hong, K.; Mays, J. W. Recent Advances in Thermoplastic Elastomers from Living Polymerizations: Macromolecular Architectures and Supramolecular Chemistry. *Prog. Polym. Sci.* **2019**, *95*, 1–31.
- (68) Matsushita, Y.; Takasu, T.; Yagi, K.; Tomioka, K.; Noda, I. Preparation and morphologies of 4- and 12-armed styrene-isoprene star-shaped block copolymers. *Polymer* **1994**, *35*, 2862–2866.
- (69) Hadjichristidis, N.; Fetters, L. J. Star-Branched Polymers. 4. Synthesis of 18-Arm Polyisoprenes. *Macromolecules* **1980**, *13*, 191–193.
- (70) Alward, D. B.; Kinning, D. J.; Thomas, E. L.; Fetters, L. J. Effect of arm number and arm molecular weight on the solid-state morphology of poly(styrene-isoprene) star block copolymers. *Macromolecules* **1986**, *19*, 215–224.
- (71) Floudas, G.; Pispas, S.; Hadjichristidis, N.; Pakula, T.; Erukhimovich, I. Microphase Separation in Star Block Copolymers of Styrene and Isoprene. Theory, Experiment, and Simulation. *Macromolecules* **1996**, *29*, 4142–4154.
- (72) Spontak, R. J.; Smith, S. D. Perfectly-alternating linear (AB) $_n$  multiblock copolymers: Effect of molecular design on morphology and properties. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 947–955.
- (73) Galanos, E.; Grune, E.; Wahlen, C.; Müller, A. H. E.; Appold, M.; Gallei, M.; Frey, H.; Floudas, G. Tapered Multiblock Copolymers Based on Isoprene and 4-Methylstyrene: Influence of the Tapered Interface on the Self-Assembly and Thermomechanical Properties. *Macromolecules* **2019**, *52*, 1577–1588.
- (74) Kelsey, J.; Pickering, N.; Clough, A.; Zhou, J.; White, J. L. Multiblock Inverse-Tapered Copolymers: Glass Transition Temperatures and Dynamic Heterogeneity as a Function of Chain Architecture. *Macromolecules* **2017**, *50*, 7233–7240.
- (75) Dair, B. J.; Honeker, C. C.; Alward, D. B.; Avgeropoulos, A.; Hadjichristidis, N.; Fetters, L. J.; Capel, M.; Thomas, E. L. Mechanical Properties and Deformation Behavior of the Double Gyroid Phase in



- Unoriented Thermoplastic Elastomers. *Macromolecules* **1999**, *32*, 8145–8152.
- (76) Kinning, D. J.; Thomas, E. L.; Alward, D. B.; Fetters, L. J.; Handlin, D. L. Sharpness of the functionality-induced structural transition in poly(styrene-isoprene) star block copolymers. *Macromolecules* **1986**, *19*, 1288–1290.
- (77) Pedemonte, E.; Dondero, G.; de Candia, F.; Romano, G. Correlation between physical-mechanical properties and morphological features of cruciform styrene-butadiene block copolymers. *Polymer* **1976**, *17*, 72–76.
- (78) Chen, L.; Qiang, Y.; Li, W. Tuning Arm Architecture Leads to Unusual Phase Behaviors in a (BAB)<sub>5</sub> Star Copolymer Melt. *Macromolecules* **2018**, *51*, 9890–9900.
- (79) Wenn, B.; Martens, A. C.; Chuang, Y.-M.; Gruber, J.; Junkers, T. Efficient multiblock star polymer synthesis from photo-induced copper-mediated polymerization with up to 21 arms. *Polym. Chem.* **2016**, *7*, 2720–2727.
- (80) Boyer, C.; Derveaux, A.; Zetterlund, P. B.; Whittaker, M. R. Synthesis of multi-block copolymer stars using a simple iterative Cu(0)-mediated radical polymerization technique. *Polym. Chem.* **2012**, *3*, 117–123.
- (81) Aksakal, R.; Resmini, M.; Becer, C. R. Pentablock star shaped polymers in less than 90 minutes via aqueous SET-LRP. *Polym. Chem.* **2016**, *7*, 171–175.
- (82) Matyjaszewski, K.; Miller, P. J.; Fossum, E.; Nakagawa, Y. Synthesis of block, graft and star polymers from inorganic macroinitiators. *Appl. Organomet. Chem.* **1998**, *12*, 667–673.
- (83) Meyer, G. C.; Widmaier, J. M. Adhesive properties of star-shaped block copolymers. *Polym. Eng. Sci.* **1977**, *17*, 803–805.
- (84) Rebrov, E. A.; Leshchiner, I. D.; Muzafarov, A. M. Synthesis of Carbosilane Dendrimers with Variable Distance between Branching Nodes. *Macromolecules* **2012**, *45*, 8796–8804.
- (85) Steube, M.; Johann, T.; Galanos, E.; Appold, M.; Rüttiger, C.; Mezger, M.; Gallei, M.; Müller, A. H. E.; Floudas, G.; Frey, H. Isoprene/Styrene Tapered Multiblock Copolymers with up to Ten Blocks: Synthesis, Phase Behavior, Order, and Mechanical Properties. *Macromolecules* **2018**, *51*, 10246–10258.
- (86) Bushuk, W.; Benoit, H. Light-Scattering Studies of Copolymers: I. Effect of Heterogeneity of Chain Composition on the Molecular Weight. *Can. J. Chem.* **1958**, *36*, 1616–1626.
- (87) Burns, A. B.; Register, R. A. Thermoplastic Elastomers via Combined Crystallization and Vitrification from Homogeneous Melts. *Macromolecules* **2016**, *49*, 269–279.
- (88) Watanabe, H.; Sato, T.; Osaki, K. Concentration Dependence of Loop Fraction in Styrene-Isoprene-Styrene Triblock Copolymer Solutions and Corresponding Changes in Equilibrium Elasticity. *Macromolecules* **2000**, *33*, 2545–2550.
- (89) Takahashi, Y.; Song, Y.; Nemoto, N.; Takano, A.; Akazawa, Y.; Matsushita, Y. Effect of Loop/Bridge Conformation Ratio on Elastic Properties of the Sphere-Forming ABA Triblock Copolymers under Uniaxial Elongation. *Macromolecules* **2005**, *38*, 9724–9729.
- (90) Curro, J. G.; Pearson, D. S.; Helfand, E. Viscoelasticity of randomly crosslinked polymer networks. Relaxation of dangling chains. *Macromolecules* **1985**, *18*, 1157–1162.
- (91) Berglund, C. A.; McKay, K. W. Viscoelastic properties of a styrene-isoprene-styrene triblock copolymer and its blends with polyisoprene homopolymer and styrene-isoprene diblock copolymer. *Polym. Eng. Sci.* **1993**, *33*, 1195–1203.
- (92) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. Dramatic enhancement of activities for living Ziegler-Natta polymerizations mediated by “exposed” zirconium acetamidate initiators: the isospecific living polymerization of vinylcyclohexane. *J. Am. Chem. Soc.* **2001**, *123*, 6197–6198.
- (93) Longo, P.; Grassi, A.; Grisi, F.; Milione, S. Polymerization of 1-vinylcyclohexene in the presence of group 4 metallocenes – MAO catalysts. *Macromol. Rapid Commun.* **1998**, *19*, 229–233.
- (94) Lodge, T. P.; McLeish, T. C. B. Self-Concentrations and Effective Glass Transition Temperatures in Polymer Blends. *Macromolecules* **2000**, *33*, 5278–5284.
- (95) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties. *Macromolecules* **1994**, *27*, 4639–4647.
- (96) Gotro, J. T.; Graessley, W. W. Model hydrocarbon polymers: rheological properties of linear polyisoprenes and hydrogenated polyisoprenes. *Macromolecules* **1984**, *17*, 2767–2775.
- (97) Beckingham, B. S.; Register, R. A. Regular Mixing Thermodynamics of Hydrogenated Styrene-Isoprene Block-Random Copolymers. *Macromolecules* **2013**, *46*, 3084–3091.
- (98) Ashraf, A. R.; Ryan, J. J.; Satkowski, M. M.; Lee, B.; Smith, S. D.; Spontak, R. J. Bicomponent Block Copolymers Derived from One or More Random Copolymers as an Alternative Route to Controllable Phase Behavior. *Macromol. Rapid Commun.* **2017**, *38*, 1700207.
- (99) Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J. The Gyroid: A New Equilibrium Morphology in Weakly Segregated Diblock Copolymers. *Macromolecules* **1994**, *27*, 4063–4075.
- (100) Chu, C. Y.; Jiang, X.; Jinnai, H.; Pei, R. Y.; Lin, W. F.; Tsai, J. C.; Chen, H. L. Real-space evidence of the equilibrium ordered bicontinuous double diamond structure of a diblock copolymer. *Soft Matter* **2015**, *11*, 1871–1876.
- (101) Takenaka, M.; Wakada, T.; Akasaka, S.; Nishitsuji, S.; Saijo, K.; Shimizu, H.; Kim, M. L.; Hasegawa, H. Orthorhombic Fddd Network in Diblock Copolymer Melts. *Macromolecules* **2007**, *40*, 4399–4402.
- (102) Samseth, J.; Spontak, R. J.; Smith, S. D.; Ashraf, A.; Mortensen, K. Microphase-separated tapered triblock copolymers. *J. Phys. IV* **1993**, *03*, C8.
- (103) Laurer, J. H.; Hajduk, D. A.; Fung, J. C.; Sedat, J. W.; Smith, S. D.; Gruner, S. M.; Agard, D. A.; Spontak, R. J. Microstructural Analysis of a Cubic Bicontinuous Morphology in a Neat SIS Triblock Copolymer. *Macromolecules* **1997**, *30*, 3938–3941.
- (104) Avgeropoulos, A.; Dair, B. J.; Hadjichristidis, N.; Thomas, E. L. Tricontinuous Double Gyroid Cubic Phase in Triblock Copolymers of the ABA Type. *Macromolecules* **1997**, *30*, 5634–5642.
- (105) Laurer, J. H.; Hajduk, D. A.; Dreckötter, S.; Smith, S. D.; Spontak, R. J. Bicontinuous Morphologies in Homologous Multiblock Copolymers and Their Homopolymer Blends. *Macromolecules* **1998**, *31*, 7546–7549.
- (106) Matsen, M. W.; Bates, F. S. Block copolymer microstructures in the intermediate-segregation regime. *J. Chem. Phys.* **1997**, *106*, 2436–2448.
- (107) Hsieh, W. V. Properties of Block Copolymers in Non-equilibrium Morphologies. B.S.E. Thesis, Princeton University, 1993.

## - Supporting Information -

### **Tapered Multiblock Star Copolymers: Synthesis, Selective Hydrogenation, and Properties**

Philipp von Tiedemann,<sup>a,b,c</sup> Jiaqi Yan,<sup>d</sup> Ramona D. Barent,<sup>a,e</sup> Richard J. Spontak,<sup>d,f</sup> George Floudas,<sup>g,h\*</sup>

Holger Frey,<sup>a\*</sup> Richard A. Register<sup>c\*</sup>

<sup>a</sup> Department of Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128

Mainz, Germany

<sup>b</sup> Graduate School Materials Science in Mainz, Staudinger Weg 9, 55128 Mainz, Germany

<sup>c</sup> Department of Chemical and Biological Engineering, Princeton University, Olden Street, Princeton,

New Jersey 08544, United States

<sup>d</sup> Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh,

North Carolina 27695, United States

<sup>e</sup> Max Planck Graduate Center, Forum Universitatis 2, 55122 Mainz, Germany

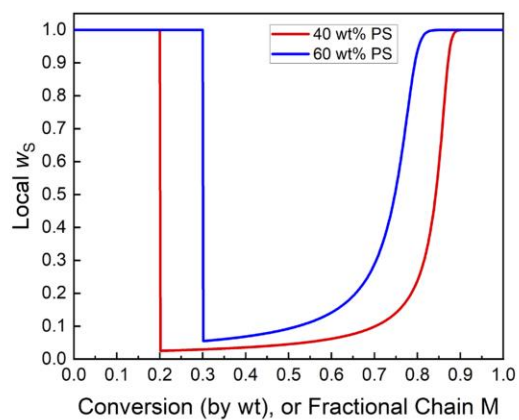
<sup>f</sup> Department of Materials Science & Engineering, North Carolina State University, Raleigh,

North Carolina 27695, United States

<sup>g</sup> Department of Physics, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece

<sup>h</sup> Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

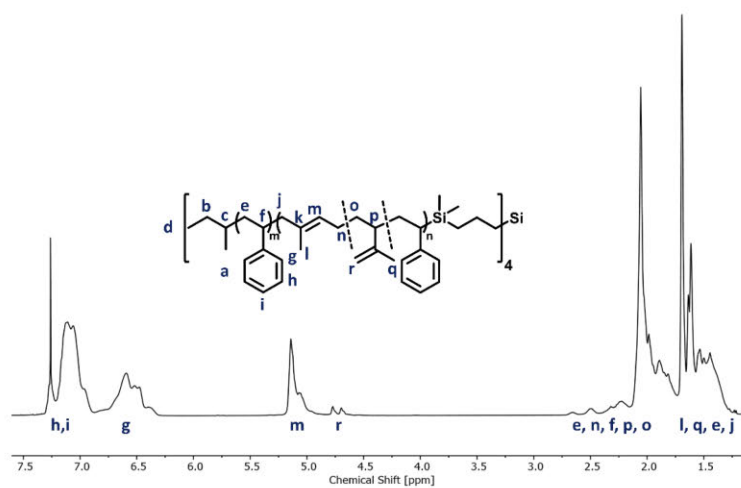
\*E-mail: register@princeton.edu (R.A.R.), hfrey@uni-mainz.de (H.F.), gfloudas@uoi.gr (G.F.)



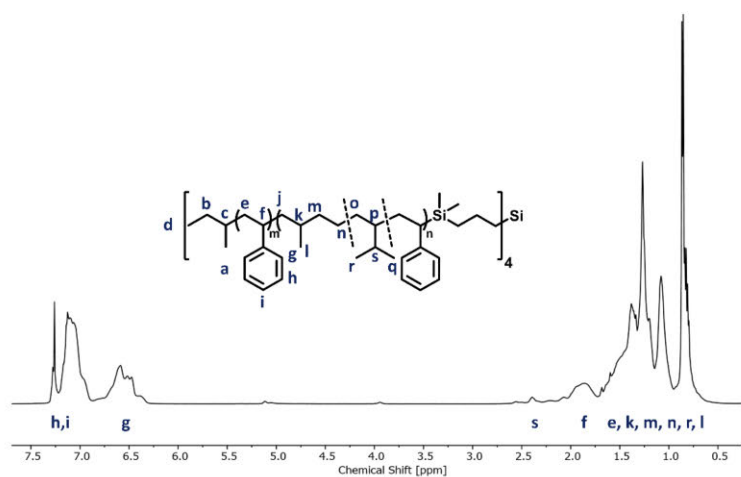
**Figure S1.** Calculated down-chain composition profiles for SI/S copolymers (linears and star arms). The gradient block composition was calculated using the copolymerization equation,<sup>1</sup> with the reported values<sup>2</sup> of  $r_1 = 12.8$  and  $r_s = 0.051$ , accounting for the continuous change in monomer mixture composition with conversion.



**Figure S2.** Polymerization reactor with orange color due to polystyryllithium (PSLi) chain ends before coupling reaction.

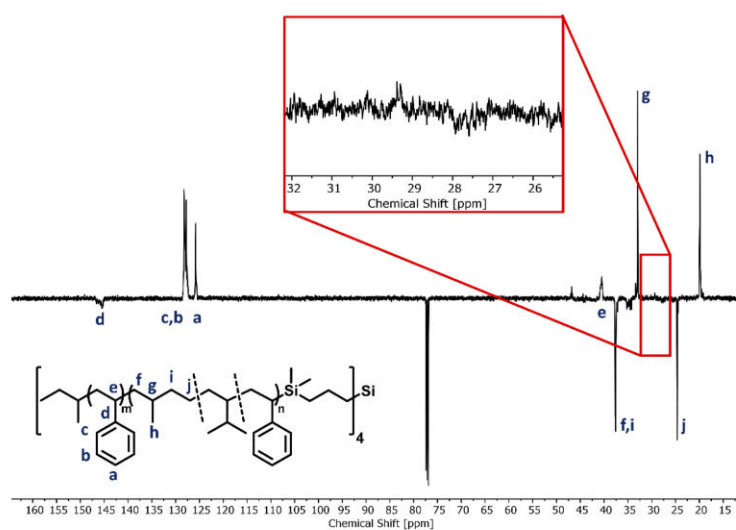


**Figure S3.**  $^1\text{H}$  NMR spectrum of  $(\text{SI/S})_4\text{-60-240}$ , 400 MHz,  $\text{CDCl}_3$ , 295 K.

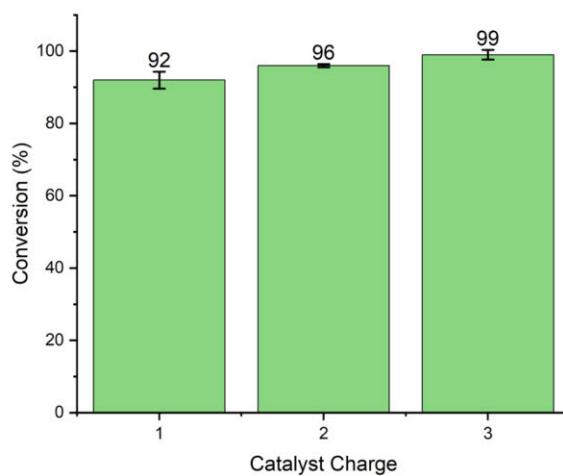


**Figure S4.**  $^1\text{H}$  NMR spectrum of  $(\text{SEP/S})_4\text{-60-240}$ , 500 MHz,  $\text{CDCl}_3$ , 295 K.

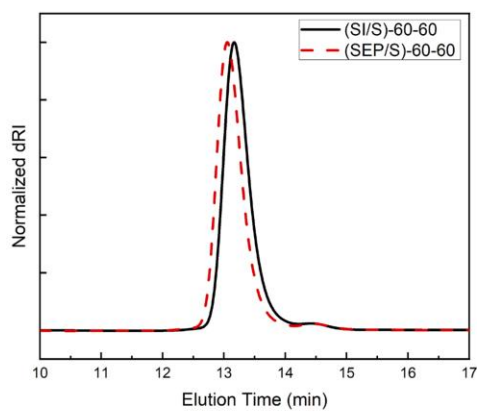




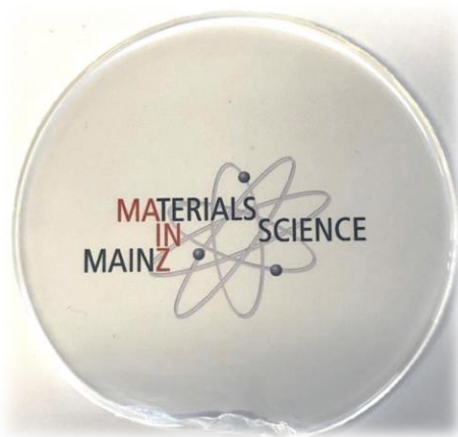
**Figure S5.**  $^{13}\text{C}$  NMR spectrum (attached proton test, APT) and expanded region of (SEP/S)<sub>4</sub>-60-240, 500 MHz,  $\text{CDCl}_3$ , 295 K.



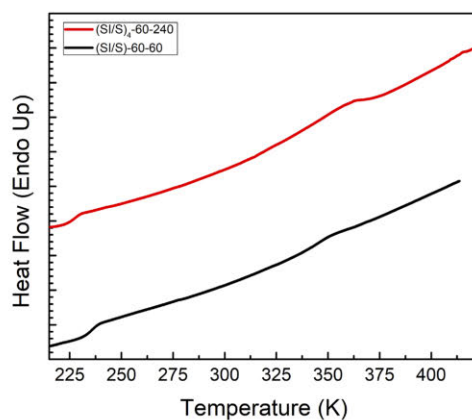
**Figure S6.** Conversion as a function of the number of successive catalyst charges for PI-selective hydrogenation of (SI/S)<sub>4</sub>-60-240 using a Ni/Al ratio of 1:4.25.



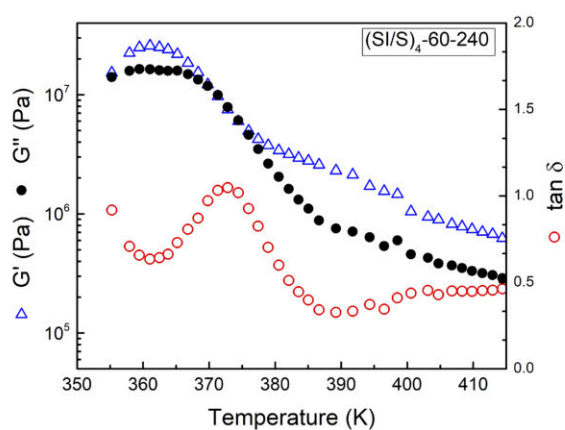
**Figure S7.** SEC elution traces (normalized dRI) of (SI/S)-60-60 (solid black line) and (SEP/S)-60-60 (dashed red line).



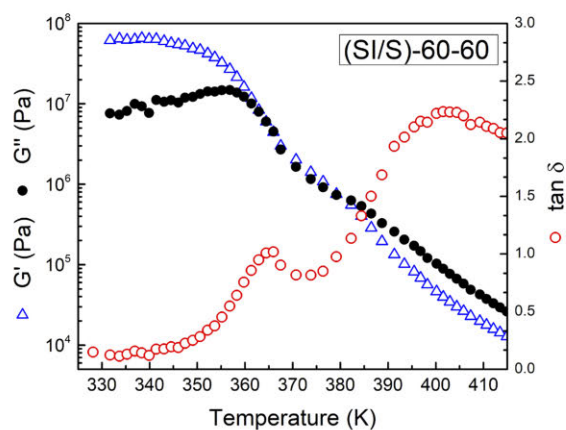
**Figure S8.** Solution processed (SI/S)<sub>4</sub>-40-240 tapered star copolymer transparent film.



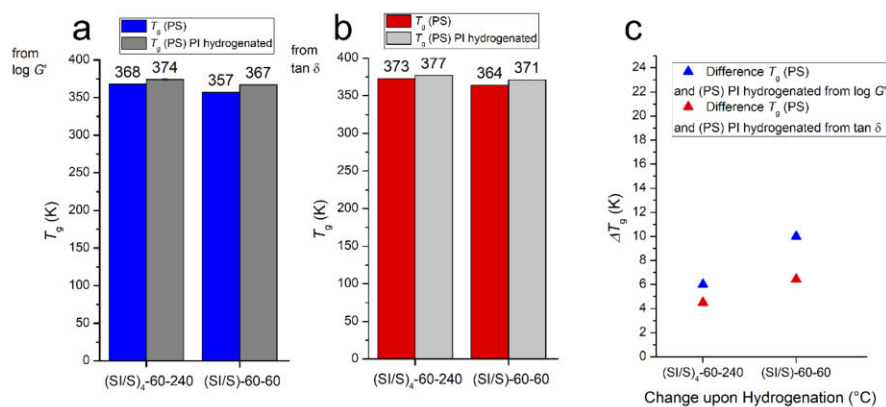
**Figure S9.** DSC thermograms (2<sup>nd</sup> heating cycle) of  $(SI/S)_4-60-240$  and  $(SI/S)-60-60$ .



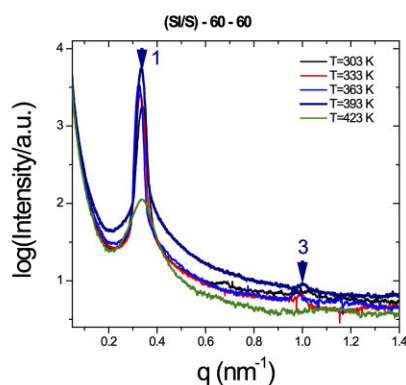
**Figure S10.** Isochronal DMTA thermal sweeps (storage modulus,  $G'$ ; loss modulus,  $G''$ ; and  $\tan \delta$ ) of  $(SI/S)_4-60-240$ .



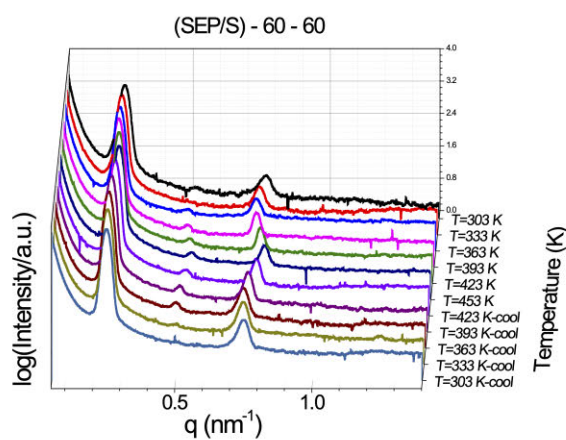
**Figure S11.** Isochronal DMTA thermal sweeps (storage modulus,  $G'$ ; loss modulus,  $G''$ ; and  $\tan \delta$ ) of (SI/S)-60-60.



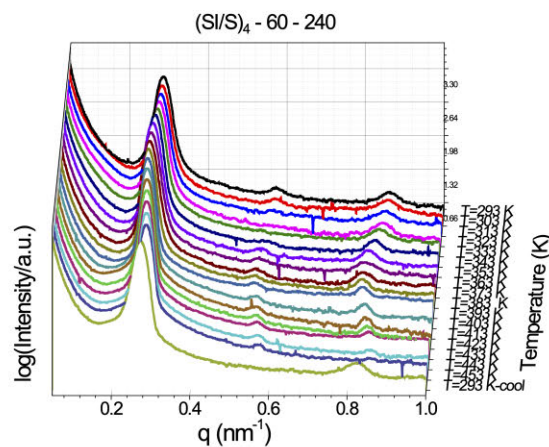
**Figure S12.** PS  $T_g$  values from  $\log G'$  (a), from  $\tan \delta$  (b), along with differences between PS  $T_g$  for hydrogenated vs. unhydrogenated star copolymers (c).



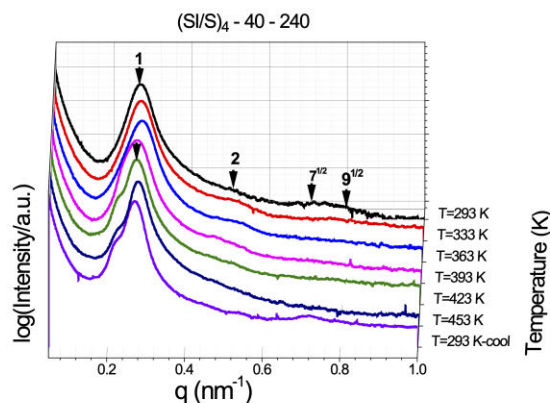
**Figure S13.** SAXS patterns for the tapered linear (SI/S)-60-60 at the indicated temperatures. Arrows identify the positions of the Bragg reflections corresponding to a lamellar morphology at 393 K. The  $T_{ODT}$  is estimated at  $408 \pm 15$  K.



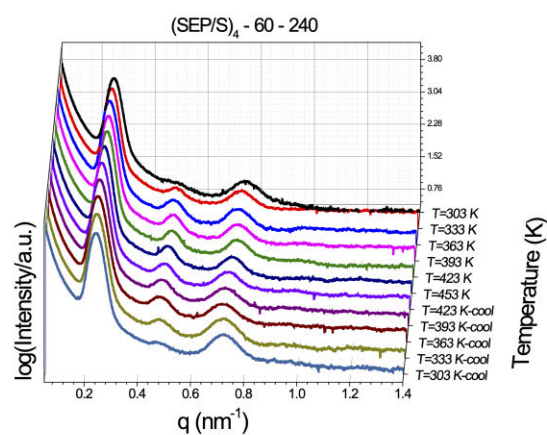
**Figure S14.** SAXS patterns for the hydrogenated tapered linear (SEP/S)-60-60 at the indicated temperatures, obtained on heating and subsequent cooling. The patterns confirm the existence of a lamellar morphology up to the highest temperature (453 K).



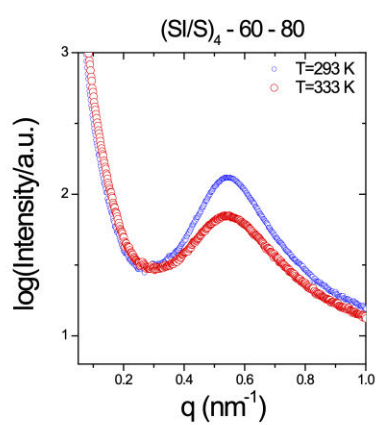
**Figure S15.** SAXS patterns for the tapered star (SI/S)<sub>4</sub>-60-240 at the indicated temperatures, obtained on heating and subsequent cooling to 293 K. The patterns confirm the existence of a lamellar morphology up to the highest temperature (453 K).



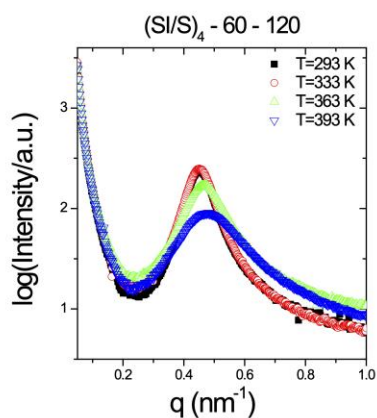
**Figure S16.** SAXS patterns for the tapered star (SI/S)<sub>4</sub>-40-240 at the indicated temperatures, obtained on heating and subsequent cooling to 293 K. Upon heating to 393 K, the main peak sharpens and reveals a shoulder at low  $q$ , which persists upon heating to 453 K and subsequent cooling. While the absence of clear higher-order peaks prevents an unambiguous assignment from SAXS alone, TEM reveals an irregular bicontinuous (BIC) morphology both prior to and after heating.



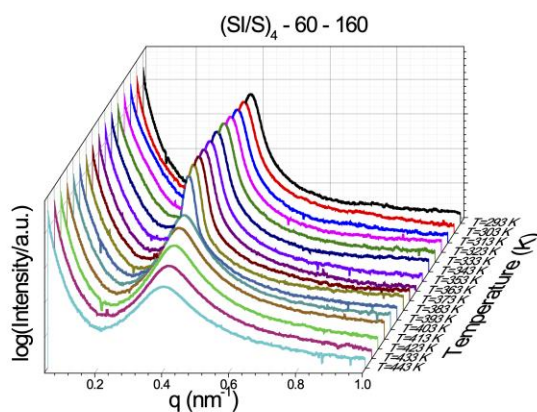
**Figure S17.** SAXS patterns for the tapered star (SEP/S)<sub>4</sub>-60-240 at the indicated temperatures, obtained on heating and subsequent cooling. The patterns confirm the existence of a lamellar morphology up to 453 K.



**Figure S18.** SAXS patterns for the tapered star (SI/S)<sub>4</sub>-60-80 at two temperatures as indicated. The patterns confirm the existence of a DIS state.

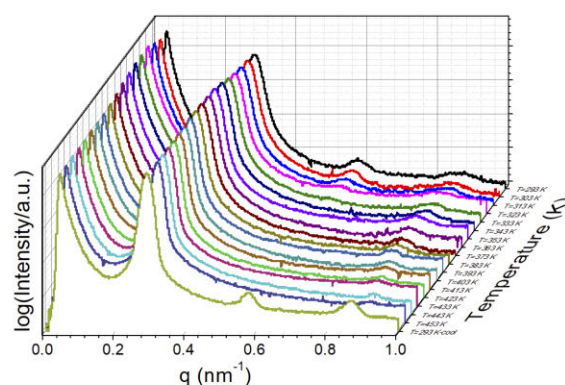


**Figure S19.** SAXS patterns for the tapered star (SI/S)<sub>4</sub>-60-120 at the indicated temperatures. The patterns confirm the existence of a DIS state. Peak narrowing at lower temperatures reveals its proximity to  $T_{ODT}$ .

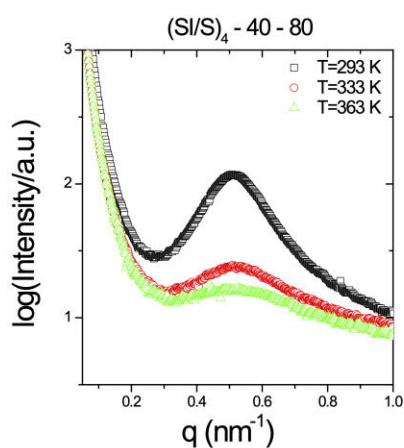


**Figure S20.** SAXS patterns for the tapered star (SI/S)<sub>4</sub>-60-160 at the indicated temperatures, obtained on heating. The patterns indicate a weakly-segregated lamellar phase at lower temperatures and a transformation to the disordered phase at  $T_{ODT} = 398 \pm 5$  K.

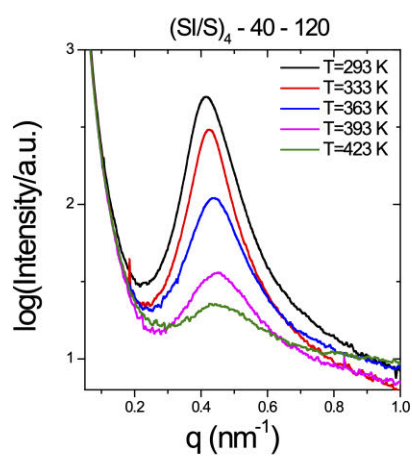




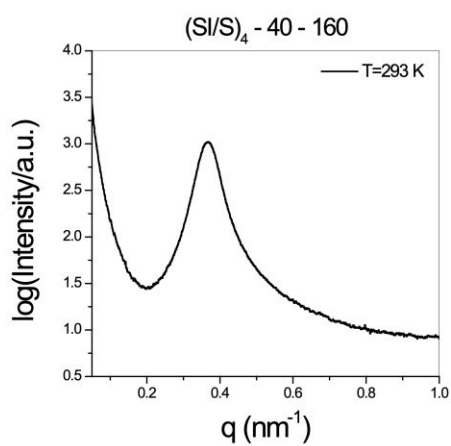
**Figure S21.** SAXS patterns for the tapered star (SI/S)<sub>4</sub>-60-200 at the indicated temperatures, obtained on heating and subsequent cooling to 293 K. The patterns confirm the existence of a lamellar phase up to 453 K.



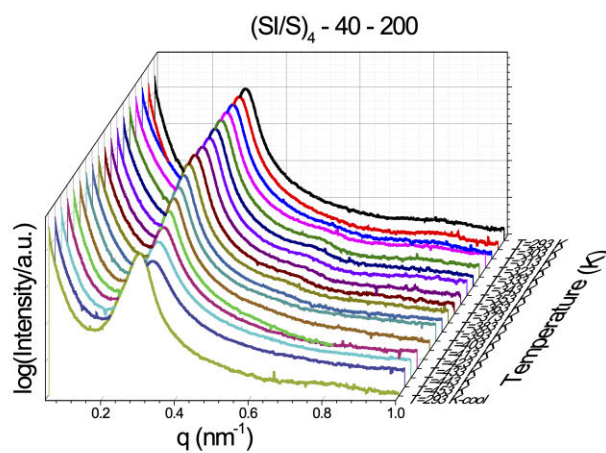
**Figure S22.** SAXS patterns for the tapered star (SI/S)<sub>4</sub>-40-80 at the indicated temperatures, obtained on heating. The patterns confirm the existence of a disordered phase for all  $T > 293$  K.



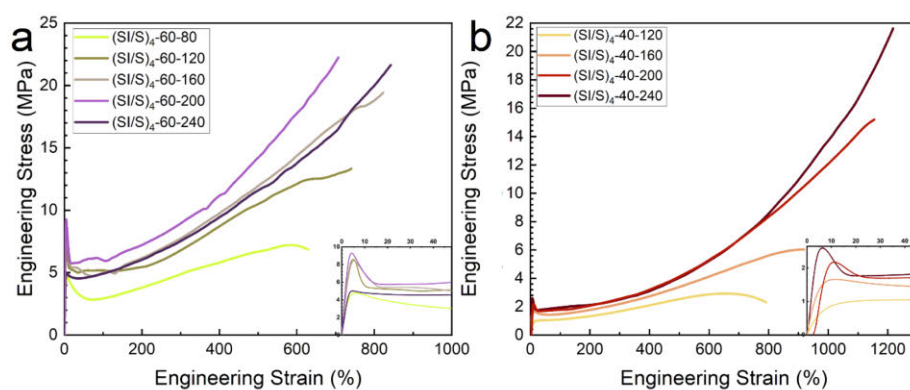
**Figure S23.** SAXS patterns for the tapered star (SI/S)<sub>4</sub>-40-120 at the indicated temperatures, obtained on heating. The patterns confirm the existence of a disordered phase for all  $T > 293 \text{ K}$ .



**Figure S24.** SAXS pattern for the tapered star (SI/S)<sub>4</sub>-40-160 at 293 K, confirming the existence of a disordered phase.



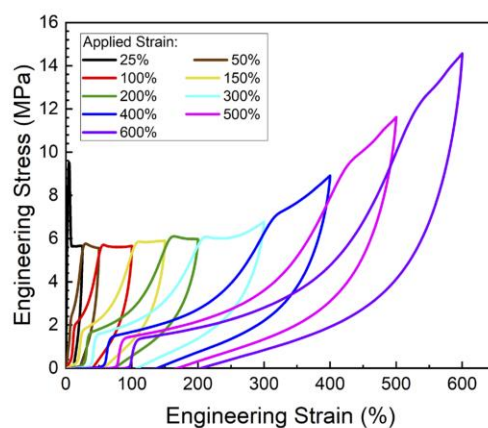
**Figure S25.** SAXS patterns for the tapered star (SI/S)<sub>4</sub>-40-200 at the indicated temperatures, obtained on heating. The patterns confirm the existence of a CYL structure without long-range order at  $T \leq 423$  K and a DIS structure at  $T \geq 453$  K, or  $T_{ODT} = 438 \pm 15$  K.



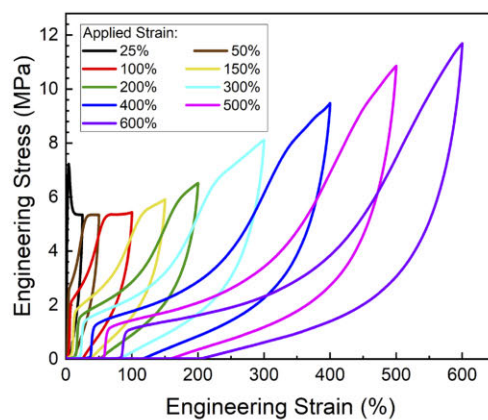
**Figure S26.** Stress-strain curves of (SI/S)<sub>4</sub> tapered star copolymers with (a) 60 and (b) 40 wt% PS.

### Strain hysteresis testing

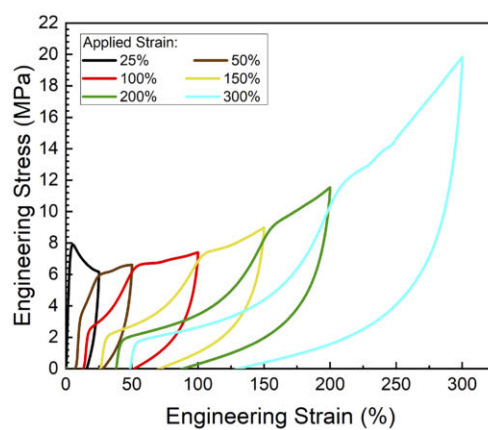
The initial ( $R^i$ ) and final recovery ( $R^f$ ) of the copolymers listed in Table 1 have been studied by uniaxial extension with an Instron 5865 according to the method of Burns *et al.*<sup>3</sup> with a preset strain ( $\varepsilon_a$ ) at a speed of 5.08 in/min. When  $\varepsilon_a$  was reached, the crosshead was reversed until the initial position was reached again. After the sample was allowed to rest for 5 min, the process was repeated with increased strain. The applied strain values were chosen to be 25, 50, 100, 150, 200, 300, 400, and 500%. The initial strain ( $\varepsilon_s^i$ ) was taken from the point where the stress reached zero upon unloading. The final strain ( $\varepsilon_s^f$ ) was determined from the values where the stress first became greater than zero again upon the subsequent loading curve of the next strain cycle. The recovery was thus calculated as  $R = (1 - \varepsilon_s/\varepsilon_a)$  and plotted in percent.



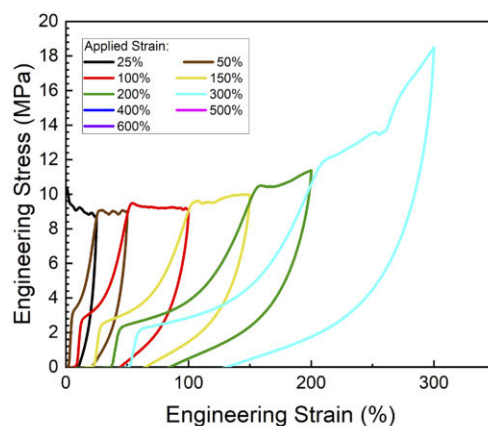
**Figure S27.** Strain hysteresis of the (SI/S)<sub>4</sub>-60-240 star copolymer.



**Figure S28.** Strain hysteresis of the (SI/S)-60-60 linear copolymer.

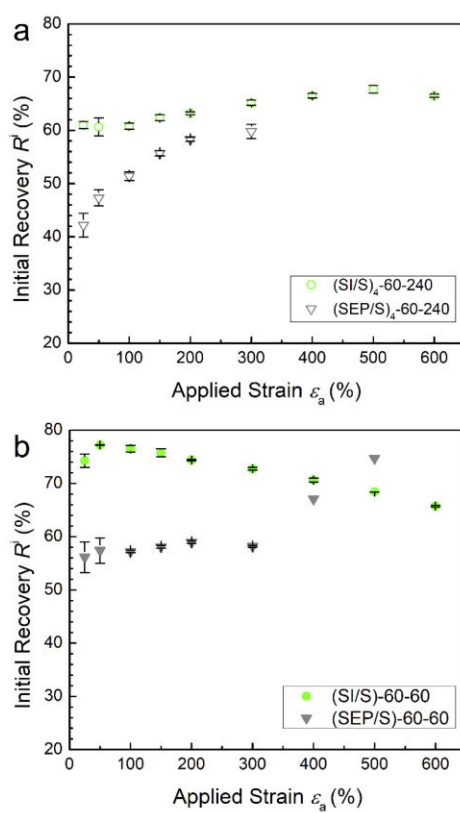


**Figure S29.** Strain hysteresis of the hydrogenated (SEP/S)<sub>4</sub>-60-240 star copolymer.

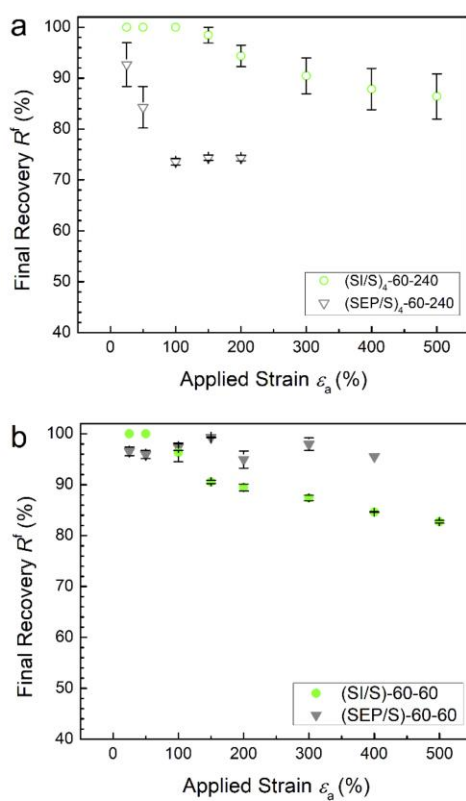


**Figure S30.** Strain hysteresis of the hydrogenated (SEP/S)-60-60 linear copolymer.

As a function of applied strain,  $R^i$  was found to change differently depending on copolymer architecture and block chemistry (PI vs. PEP), as demonstrated in **Figure S31**. For a given composition (60 wt% PS, saturated or unsaturated), recovery (both  $R^i$  and  $R^f$ ) is generally similar for star vs. linear copolymers. Hydrogenation also does not have a major influence on recovery (either  $R^i$  and  $R^f$ ). It is perhaps worth noting that, despite modest variations across the series, all of these copolymers behave as good thermoplastic elastomers, showing final fractional recoveries  $> 90\%$  at modest strain levels ( $< 50\%$ ) and  $> 70\%$  at high strain levels (up to  $600\%$ ).

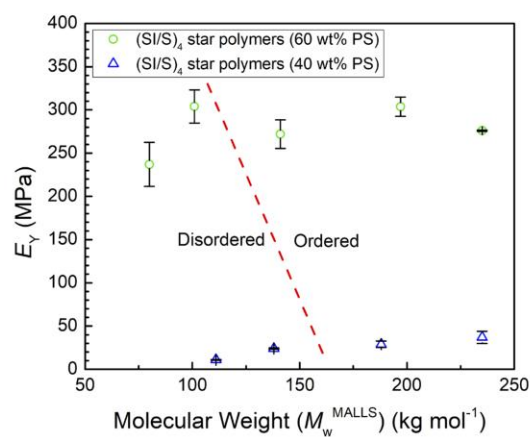


**Figure S31.** Initial recovery from strain results of (a)  $(SI/S)_4$  and  $(SEP/S)_4$  tapered star copolymers and (b) corresponding linear copolymers  $(SI/S)$  and  $(SEP/S)$ .

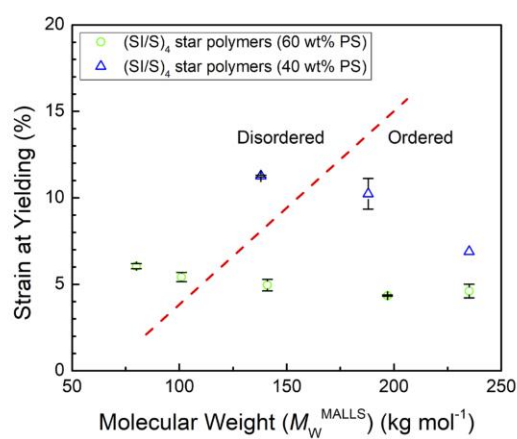


**Figure S32.** Final recovery from strain results of (a) (SI/S)<sub>4</sub> and (SEP/S)<sub>4</sub> tapered star copolymers and (b) corresponding linear copolymers (SI/S) and (SEP/S).

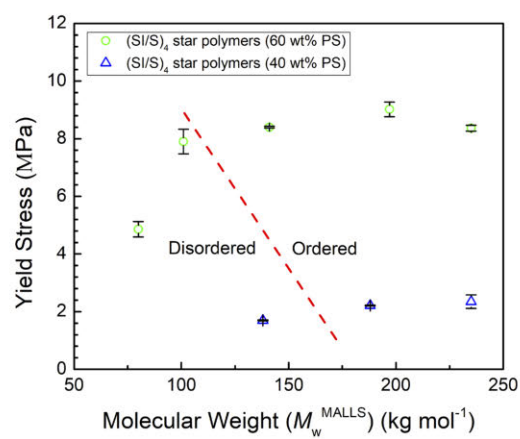




**Figure S33.** Young's moduli ( $E_Y$ ) of (SI/S)<sub>4</sub> tapered star copolymers with 60 and 40 wt% PS.



**Figure S34.** Strain at yielding ( $\epsilon_y$ ) of (SI/S)<sub>4</sub> tapered star copolymers with 60 and 40 wt% PS.



**Figure S35.** Yield stress ( $\sigma_y$ ) of (SI/S)<sub>4</sub> tapered star copolymers with 60 and 40 wt% PS.

**Table S1.** Room-temperature mechanical property values for SI/S and SEP/S tapered star and tapered linear copolymers with 60 and 40 wt% PS.

| Copolymer                    | $\alpha_b$ (%) | $\sigma_b$ (MPa) | $U$ (MJ/m <sup>3</sup> ) | $E_Y$ (MPa) | $\epsilon_Y$ (%) | $\sigma_Y$ (MPa) |
|------------------------------|----------------|------------------|--------------------------|-------------|------------------|------------------|
| (SI/S) <sub>4</sub> -60-80   | 592 ± 27       | 7 ± 0.5          | 29 ± 3                   | 237 ± 26    | 6 ± 0.3          | 5 ± 0.3          |
| (SI/S) <sub>4</sub> -60-120  | 664 ± 40       | 11 ± 1           | 48 ± 6                   | 304 ± 19    | 5 ± 0.7          | 8 ± 0.4          |
| (SI/S) <sub>4</sub> -60-160  | 712 ± 44       | 17 ± 1           | 68 ± 7                   | 272 ± 17    | 5 ± 0.7          | 8.4 ± 0.3        |
| (SI/S) <sub>4</sub> -60-200  | 713 ± 4        | 22 ± 1           | 82 ± 1                   | 304 ± 11    | 4 ± 0.1          | 9 ± 0.3          |
| (SI/S) <sub>4</sub> -60-240  | 834 ± 14       | 18 ± 1           | 83 ± 2                   | 276 ± 1     | 4.6 ± 1          | 8.3 ± 0.1        |
| (SI/S) <sub>4</sub> -40-80   | n.d.           | n.d.             | n.d.                     | n.d.        | n.d.             | n.d.             |
| (SI/S) <sub>4</sub> -40-120  | 777 ± 15       | 2 ± 0.3          | 15 ± 0.4                 | 11 ± 0.4    | -                | -                |
| (SI/S) <sub>4</sub> -40-160  | 986 ± 34       | 6 ± 0.1          | 35 ± 2                   | 24 ± 0.4    | 11 ± 0.1         | 1.7 ± 0.1        |
| (SI/S) <sub>4</sub> -40-200  | 1144 ± 42      | 14 ± 2           | 70 ± 6                   | 29 ± 4      | 10 ± 1           | 2.2 ± 0.1        |
| (SI/S) <sub>4</sub> -40-240  | 1198 ± 34      | 21 ± 1           | 87 ± 6                   | 37 ± 7      | 7 ± 1            | 2.3 ± 0.3        |
| (SI/S)-60-60                 | 707 ± 31       | 12 ± 0.3         | 55 ± 3                   | 173 ± 32    | 4 ± 0.2          | 5 ± 0.1          |
| (SI/S)-40-60                 | 818 ± 40       | 4 ± 0.8          | 23 ± 1                   | 8 ± 3       | -                | -                |
| (SEP/S) <sub>4</sub> -60-240 | 344 ± 19       | 17 ± 2           | 34 ± 3                   | 148 ± 16    | 5 ± 0.2          | 7 ± 0.1          |
| (SEP/S)-60-60                | 477 ± 3        | 29 ± 1           | 73 ± 1                   | 231 ± 30    | 3 ± 0.1          | 10 ± 0.1         |

**REFERENCES**

- (1) Wall, F. T. The Structure of Copolymers. II. *J. Am. Chem. Soc.* **1944**, *66*, 2050–2057.
- (2) Grune, E.; Johann, T.; Appold, M.; Wahlen, C.; Blankenburg, J.; Leibig, D.; Müller, A. H. E.; Gallei, M.; Frey, H. One-Step Block Copolymer Synthesis versus Sequential Monomer Addition: A Fundamental Study Reveals That One Methyl Group Makes a Difference. *Macromolecules* **2018**, *51*, 3527–3537.
- (3) Burns, A. B.; Register, R. A. Mechanical Properties of Star Block Polymer Thermoplastic Elastomers with Glassy and Crystalline End Blocks. *Macromolecules* **2016**, *49*, 9521–9530.





---

---

# **CHAPTER A2**

**In Situ Kinetics Reveal the Influence of Solvents  
and Monomer Structure on the Anionic Ring-  
Opening Copolymerization of Epoxides**

---

---





## RESEARCH ARTICLE

# In Situ Kinetics Reveal the Influence of Solvents and Monomer Structure on the Anionic Ring-Opening Copolymerization of Epoxides

Philip Dreier, Rebecca Matthes, Ramona D. Barent, Sandra Schüttner, Axel H. E. Müller,\* and Holger Frey\*

Dedicated to Brigitte Voit on the occasion of her 60th birthday

In-depth understanding of copolymerization kinetics and the resulting polymer microstructure is crucial for the design of materials with well-defined properties. Further, insights regarding the impact of solvents on copolymerization kinetics allows for precisely tuned materials. In this regard, in situ  $^1\text{H}$  NMR spectroscopy enables precise monitoring of the living anionic ring-opening copolymerization (AROP) of ethylene oxide (EO) with the glycidyl ethers allyl glycidyl ether (AGE) and ethoxy vinyl glycidyl ether (EVGE), respectively. Determination of reactivity ratios reveals slightly higher reactivity of both glycidyl ethers compared to EO, emphasizing a pronounced counterion chelation effect by glycidyl ethers in AROP. Implementation of density functional theory (DFT) calculations further illustrates the complexation capability of ether-containing side groups in glycidyl ethers, in analogy to crown ethers ("crown ether effect"). Investigation of the copolymerization in i) THF- $d_8$  and ii) DMSO- $d_6$  shows an increasing disparity of reactivity ratios for both glycidyl ethers compared to EO, clearly related to decreasing solvent polarity.

## 1. Introduction

In depth kinetic studies of the statistical copolymerization of different monomers have received renewed interest in recent years, particularly for living polymerization techniques. In this case, reactivity ratios mirror the monomer gradients along the chain and thus "mapping" of the chain composition from initiator to

chain end is feasible. Besides controlled radical polymerization, living anionic polymerization (LAP) remains the most efficient method for the synthesis of well-defined copolymers with narrow molecular weight distributions and controlled monomer gradients. Detailed understanding of the compositional profile of the comonomers along the polymer chains is of key importance in gradient or tapered copolymers to adjust the thermal properties in bulk<sup>[1–6]</sup> and consequently to control the morphology<sup>[1,4,7]</sup> and properties of the resulting materials.

To date, common methods for the evaluation of reactivity ratios and the corresponding comonomer gradient in the copolymer chains formed have relied on the determination of the comonomer content at different stages of copolymerization. After termination at different stages of the reaction,<sup>[8,9]</sup> samples were analyzed by gas chromatography to determine residual monomer

content.<sup>[10]</sup> These monitoring techniques are time-consuming, often rather difficult to implement and may hold uncertainties due to missing reproducibility, since the data are obtained from different polymerization experiments. In comparison, triad analysis via  $^{13}\text{C}$  inverse gated (IG) spectroscopy<sup>[11,12]</sup> is a reliable method for the determination of the global microstructure, but a large variety of samples must be synthesized for correct assignment and evaluation of the corresponding triads. In addition, it is not possible to derive the gradient structure. More recently, in situ monitoring via near infrared (NIR) spectroscopy<sup>[7,13,14]</sup> was established as a feasible analytical tool to directly correlate the polymerization kinetics with the copolymer microstructure for carbanionic copolymerization. The in situ methods advantageously permit to follow the mean composition over the whole conversion range, that is, at all given chain positions, resulting in a full compositional profile of the copolymers.<sup>[7,15]</sup> For instance, the influence of temperature<sup>[7]</sup> and polar additives<sup>[13,14]</sup> on the compositional drift and steepness of the gradient in isoprene/styrene-based tapered block copolymers, synthesized via carbanionic copolymerization, was recently investigated in great detail via NIR spectroscopy.

P. Dreier, R. Matthes, R. D. Barent, S. Schüttner, A. H. E. Müller, H. Frey  
Department of Chemistry  
Johannes Gutenberg-University  
Duesbergweg 10–14, D-55128 Mainz, Germany  
E-mail: axel.mueller@uni-mainz.de; hfrey@uni-mainz.de

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/macp.202200209>

© 2022 The Authors. Macromolecular Chemistry and Physics published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

DOI: 10.1002/macp.202200209



The rather slow polymerization kinetics of the anionic ring-opening polymerization (AROP) in polar aprotic solvents facilitates NMR spectroscopic monitoring at room temperature. This has been exploited to follow the monomer consumption of epoxides<sup>[16–22,12,23]</sup> as well as activated aziridines<sup>[24–27]</sup> via in situ <sup>1</sup>H NMR spectroscopy. Depending on the comonomer employed, the copolymerization of EO with monosubstituted epoxides may result in rather different polymer microstructures. For instance, preferred addition of EO over alkylene oxides<sup>[19]</sup> and glycidyl amines<sup>[16]</sup> to the active chain end has been observed. In anionic copolymerization with EO, both propylene oxide ( $r_{EO} = 2.8$ ,  $r_{PO} = 0.25$ )<sup>[11]</sup> and butylene oxide ( $r_{EO} = 6.46$ ,  $r_{BO} = 0.148$ ) exhibit significantly lower reactivities compared to EO.<sup>[22]</sup> In contrast, the copolymerization of EO with various glycidyl ethers (GE) generally revealed an almost ideally random distribution of the comonomer units along the polyether backbone.<sup>[17,20,28,21]</sup> Considering the underlying reactivity ratios,  $r$ , and rate constants,  $k$  ( $r_{EO} = k_{EO,EO}/k_{EO,GE}$ ,  $r_{EO} = k_{GE,GE}/k_{GE,EO}$ ), this copolymerization behavior necessitates  $k_{EO,EO} = k_{GE,EO}$  as well as  $k_{GE,GE} = k_{EO,GE}$  and thus the product  $r_{EO} \cdot r_{GE}$  equals unity. Consequently, non-terminal models, for example, the Jaacks method<sup>[29]</sup> can be employed to investigate the underlying copolymerization kinetics in AROP.<sup>[28,23,17]</sup>

In addition to the chemical nature of the monomers, the polarity of the solvent and its potential interaction with the counterion affects the kinetics of AROP copolymerization. EO or substituted epoxides have been investigated with regard to polymerization kinetics in different aprotic polar solvents ranging from linear and cyclic ethers<sup>[30–33]</sup> to polar solvents like dimethyl sulfoxide (DMSO)<sup>[34–38]</sup> and hexamethylphosphoramide (HMPA).<sup>[36,39]</sup> Depending on the polarity of the solvents, ion pairs were observed as reactive species in ethers,<sup>[33,31]</sup> whereas free ions were found to be present in the case of the more polar DMSO<sup>[40]</sup> and HMPA.<sup>[39]</sup> Nevertheless, although the homopolymerization kinetics in these solvents is well understood, the influence of the solvent on the copolymerization kinetics of EO with monosubstituted epoxides remains largely unexplored.

In 2011, our group investigated the microstructure of copolymers consisting of ethoxy vinyl glycidyl ether (EVGE) and EO copolymerized with cesium alkoxides in THF via <sup>13</sup>C NMR triad analysis. The post-polymerization analysis revealed a random distribution of EVGE units along the polymer backbone while no specific reactivity ratios were calculated.<sup>[41]</sup> One year later, Lynd, Hawker and coworkers reported a novel initiator-based method for the calculation of the reactivity ratios based on post-polymerization <sup>1</sup>H NMR spectroscopy. Here, the AROP copolymerization of EO and monosubstituted epoxides, namely EVGE and allyl glycidyl ether (AGE), was investigated in THF with potassium alkoxides as active chain ends.<sup>[42]</sup>

To the best of our knowledge, merely the variation of the reactivity ratios in the presence of electron donors has been investigated in detail for the copolymerization of epoxides to date.<sup>[10]</sup> Further, online monitoring of the comonomer consumption during copolymerization of EO with EVGE/AGE has not been compared in-depth regarding the influence of substituents as well as solvent variation.

In the current work we utilize in situ <sup>1</sup>H NMR kinetics to evaluate and compare the reactivity ratios of the copolymerization of EO with EVGE and AGE, respectively, both in tetrahydrofuran-

$d_8$  (THF- $d_8$ ) and DMSO- $d_6$  as solvents (Scheme 1). DFT calculations were employed, leading to an in-depth understanding of the copolymerization kinetics.

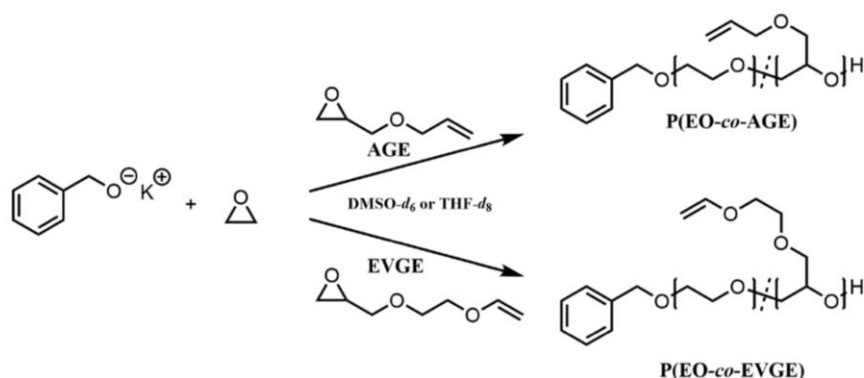
## 2. Results and Discussion

### 2.1. Impact of Solvents on Copolymerization Kinetics of EO and Glycidyl Ethers

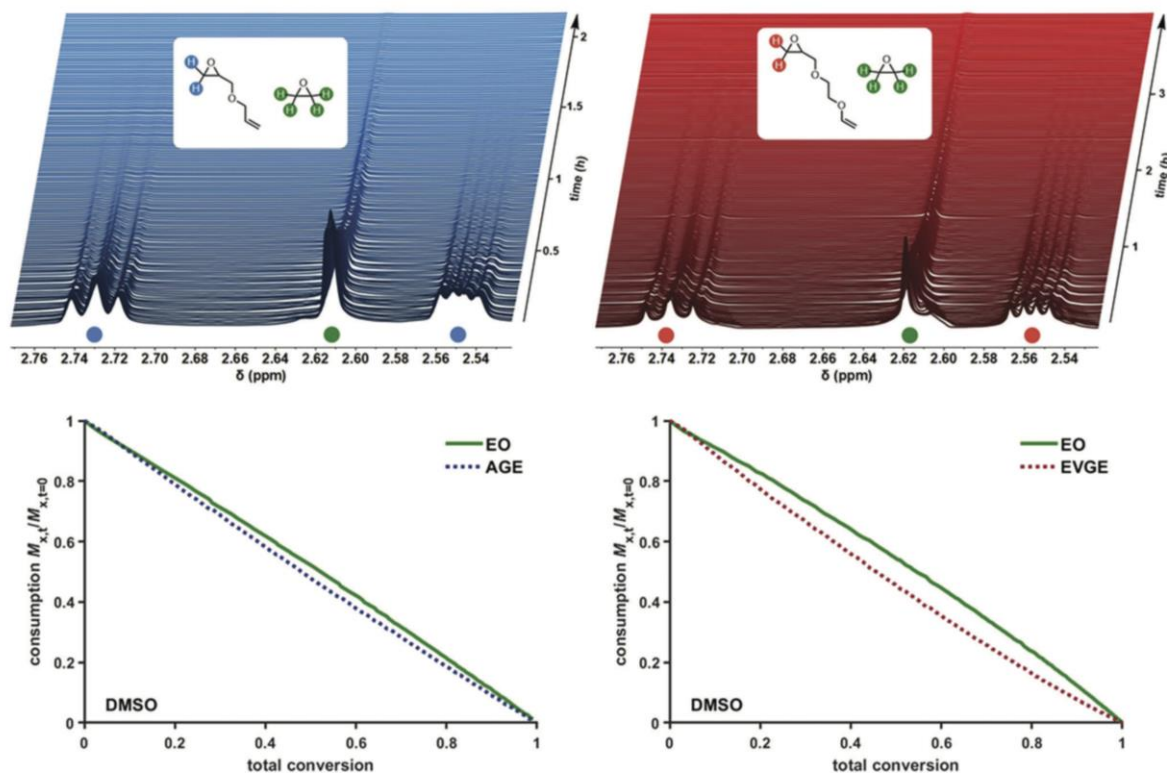
The anionic ring-opening polymerization (AROP) of epoxides is often performed in polar solvents to achieve ion pair separation and consequently accelerate the polymerization. DMSO with a dipole moment of 3.96 D is the solvent with the highest polarity that can be utilized in AROP, besides the carcinogenic HMPA, which was not used in this study for safety reasons. Thus, DMSO can be considered as the ideal polar system with a high extent of ion dissociation and free ions as the active species.<sup>[40]</sup> On the contrary, THF exhibits a lower dipole moment of 1.63 D and accordingly is a less polar solvent implemented in AROP, permitting only partial dissociation of alkali metal alkoxides.<sup>[43]</sup> The reactive species of the alkoxide chain ends in THF can be characterized as ion pairs. These ion pairs are in equilibrium with unreactive aggregates,<sup>[31]</sup> and polymerization in THF most likely mimics the behavior in bulk polymerizations of epoxides. Therefore, DMSO and THF represent a strongly polar and a comparably nonpolar example to perform AROP of epoxides. Although several studies targeting the copolymerization of EO with various substituted epoxides have been conducted in either THF, DMSO, or mixtures of both, their influence on the copolymerization kinetics has not been compared in a detailed manner to date. Based on this lack of data, we elucidated the impact of solvent polarity on the incorporation of different epoxides in the polyether during the copolymerization of EO with monosubstituted epoxides via in situ <sup>1</sup>H NMR kinetics. To this end, model copolymerization reactions of EO with the two typical glycidyl ethers AGE and EVGE, respectively were performed, initiated by potassium benzyl alkoxide at 45°C in DMSO- $d_6$  and THF- $d_8$ , respectively. Potassium benzyl alkoxide was selected as initiator as a commonly employed example in AROP.<sup>[44,42]</sup> By recording one spectrum every 30 s, the monomer consumption was monitored over time (Figure 1, top),

As shown in Figure S1, Supporting Information, in DMSO, the copolymerization of EO with AGE and EVGE exhibits high propagation rates, with a half-life (50% conversion) of the respective glycidyl ether of 13 (AGE) and 20 min (EVGE), respectively. A plot of comonomer consumption versus total conversion, as shown in Figure 1 (bottom), shows that in both cases the glycidyl ether is incorporated slightly faster than EO.

Implementation of the Jaacks equation<sup>[29]</sup> enabled the calculation of reactivity ratios for both copolymerizations with a coefficient of determination ( $R^2$ ) of 0.9995 (AGE) and 0.998 (EVGE), respectively (Figure S2, Supporting Information). The Jaacks model is a non-terminal, integrated model for ideal copolymerizations that originates in the simplification  $r_1 = r_2^{-1}$  and relies on the linearization of the Meyer–Lowry equation. The latter is applicable, if the rate of monomer incorporation does not show a strong dependence on the identity of the terminal unit, but on the nature of the reacting monomers. Its strength lies in the reduction of potential errors caused by overfitting. The implementation of the non-terminal model is further justified by DFT cal-



**Scheme 1.** Copolymerization for P(EO-co-AGE) and P(EO-co-EVGE), initiated by potassium benzyl alkoxide in DMSO- $d_6$  and THF- $d_8$ .

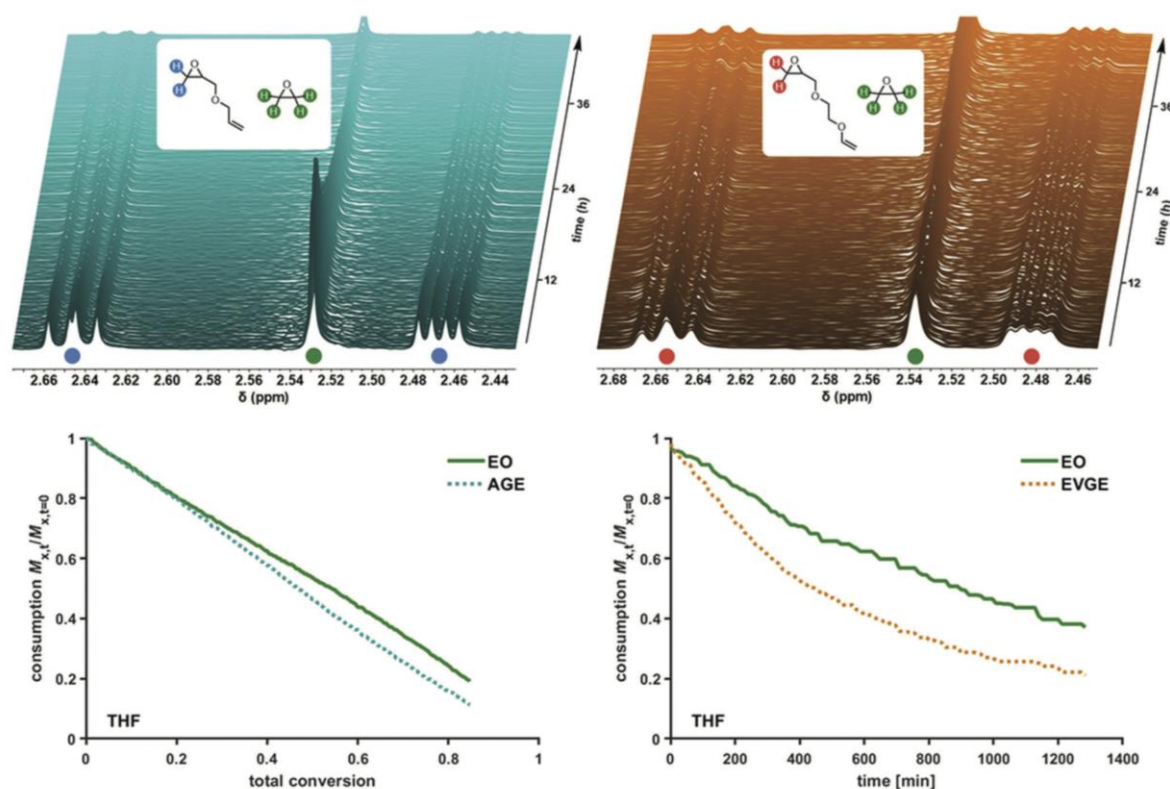


**Figure 1.** Top: in situ  $^1\text{H}$  NMR kinetics of the anionic copolymerization of EO with AGE in DMSO- $d_6$  (left) and with EVGE (right), initiated by potassium benzyl alkoxide at  $45^\circ\text{C}$ ; bottom: conversion of both comonomers versus total conversion.

culations, as discussed in a later section. Note that reactivity ratios are defined as  $r_1 = k_{1,1}/k_{1,2}$  and  $r_2 = k_{2,2}/k_{2,1}$  with index 1 representing EO and 2 the respective glycidyl ether. Both glycidyl ethers demonstrate rate constants of  $k_{\text{AGE,AGE}} > k_{\text{AGE,EO}}$  and  $k_{\text{EVGE,EVGE}} > k_{\text{EVGE,EO}}$ , resulting in the preferential incorporation of AGE and EVGE in the early stages of the copolymerization. The herein performed in situ kinetic experiments in DMSO con-

sequently revealed reactivity ratios of  $r_{\text{EO}}^{\text{DMSO}} = 0.92 \pm 0.002$  and  $r_{\text{AGE}}^{\text{DMSO}} = 1.08 \pm 0.002$  as well as  $r_{\text{EO}}^{\text{DMSO}} = 0.81 \pm 0.001$  and  $r_{\text{EVGE}}^{\text{DMSO}} = 1.23 \pm 0.002$ . Collectively, the copolymerization of EO and AGE in DMSO shows nearly ideally random character, whereas the copolymerization with EVGE results in a very slight gradient microstructure. Based on the obtained reactivity ratios, the molar composition diagrams  $F_{\text{GE}}$  versus total conversion il-





**Figure 2.** Top: in situ  $^1\text{H}$  NMR kinetics in THF- $d_8$  of the anionic copolymerization of EO/AGE (left) and EO/EVGE (right), initiated by potassium benzyl alkoxide at 45 °C; bottom: consumption  $M_{x,t}/M_{x,t=0}$  versus total conversion for P(EO-co-AGE) (left) and for P(EO-co-EVGE) (right).

illustrate the close to random (AGE) and slight gradient (EVGE) microstructure (Figure S3, Supporting Information).

Subsequently, analogous in situ  $^1\text{H}$  NMR kinetic experiments were performed in THF to determine the polymerization kinetics of ion pairs in equilibrium with unreactive aggregates. As expected, in THF both copolymerizations revealed significantly decreased propagation rates compared to DMSO, leading to half-lives of 17.3 h (AGE) and 7.6 h (EVGE), respectively (Figures 2 and Figure S4, Supporting Information). The experiment was not carried out to full conversion due to limited measurement time. Nevertheless, the amount of data points reaching >70 % conversion ensures a reliable evaluation of reactivity ratios by the Jaacks equation ( $R^2$  of 0.997 (AGE) and 0.992 (EVGE)) (Figure S5, Supporting Information).

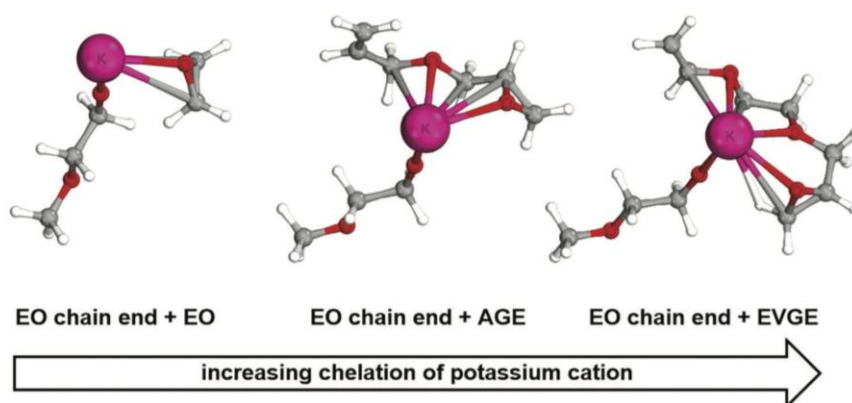
The differences in reactivity between EO and both glycidyl ethers are notably more pronounced in THF in comparison to the polar DMSO system, albeit without changing the overall trend. Accordingly, reactivity ratios were determined as  $r_{\text{EO}}^{\text{THF}} = 0.78 \pm 0.001$  and  $r_{\text{AGE}}^{\text{THF}} = 1.29 \pm 0.002$  as well as  $r_{\text{EO}}^{\text{THF}} = 0.48 \pm 0.004$  and  $r_{\text{EVGE}}^{\text{THF}} = 2.05 \pm 0.015$ . In THF, both copolymerizations exhibit soft gradient microstructures, illustrated in the molar composition diagrams (Figure S6, Supporting Information). In the case of P(EO-co-EVGE), the gradient determines the nature of the terminal units, consisting almost exclusively of EO repeating units, which can be important for further trans-

formation of the chain end. The investigated polymerizations in DMSO as well as THF resulted in polymers of low to moderate dispersities ( $\bar{D} < 1.19$ ) (see Figure S7, Supporting Information).

A summary of the evaluated reactivity ratios compared to the values reported by Lynd, Hawker and coworkers<sup>[42]</sup> based on a different method, that is, the end-group dyad (EGD) method as well as the current results of our group evaluated by  $^{13}\text{C}$  NMR triad analysis (for EVGE)<sup>[41]</sup> is given in Table 1. The reactivity ratios evaluated for the copolymerization of EO and AGE in THF are in good agreement for both methods (in situ and EGD), while the error is decreased for in situ kinetics due to the large amount of data points. However, the copolymerization of EO and EVGE shows a pronounced discrepancy when comparing the different methods. The EGD analysis yielded a more pronounced reactivity of EVGE compared to the established in situ method as well as the  $^{13}\text{C}$  NMR triad analysis. Analysis via EGD enables facile and quick first access to reactivity ratios subsequent to several polymerization experiments via  $^1\text{H}$  NMR spectroscopy, but it relies on the first monomer addition steps at the initiator. In contrast, in situ experiments reveal online results with a multitude of data points over minutes up to hours reaction time, however necessitating a demanding reaction set-up within the NMR spectrometer. Nevertheless, the calculated reactivity ratios are independent of the nature of the utilized initiator and enable precise results with low error values, notably up to full monomer conversion.

**Table 1.** Reactivity ratios evaluated by in situ  $^1\text{H}$  NMR experiments using the Jaacks method,<sup>[29]</sup> by EGD<sup>[42]</sup> and  $^{13}\text{C}$  triad analysis.<sup>[41]</sup>

| Monomer | Method         | Solvent | $r_{\text{EO}}$ | $r_{\text{EO}}^{\text{eff}}$ | $r_{\text{GE}}$                                 | $r_{\text{GE}}^{\text{eff}}$ | $r_{\text{EO}} \times r_{\text{GE}}$ | $R^2$  |
|---------|----------------|---------|-----------------|------------------------------|-------------------------------------------------|------------------------------|--------------------------------------|--------|
| AGE     | Jaacks         | DMSO    | 0.92            | 0.002                        | 1.08                                            | 0.002                        | 1.00                                 | 0.9995 |
|         | Jaacks         | THF     | 0.78            | 0.001                        | 1.29                                            | 0.002                        | 1.00                                 | 0.997  |
|         | EGD            | THF     | 0.54            | 0.03                         | 1.31                                            | 0.26                         | 0.71                                 | -      |
| EVGE    | Jaacks         | DMSO    | 0.81            | 0.001                        | 1.23                                            | 0.002                        | 1.00                                 | 0.998  |
|         | Jaacks         | THF     | 0.48            | 0.004                        | 2.05                                            | 0.015                        | 1.00                                 | 0.992  |
|         | EGD            | THF     | 0.32            | 0.10                         | 3.50                                            | 0.90                         | 1.12                                 | -      |
|         | triad analysis | THF     |                 |                              | $r_{\text{EO}} \approx r_{\text{GE}} \approx 1$ |                              |                                      | -      |



**Figure 3.** Complexation of potassium by EO chain end with EO, AGE, and EVGE calculated by DFT.

## 2.2. Impact of Transition State on Monomer Reactivity

The described results demonstrate that the influence of cation complexation on monomer reactivities during the polymerization is more pronounced in THF rather than DMSO. Following these findings, we postulate a transient “crown ether-effect” of the investigated glycidyl ethers, causing the enhanced reactivity of both glycidyl ethers compared to EO in THF, as also mentioned by Lynd, Hawker et al.<sup>[42]</sup> It is a known phenomenon that the addition of 18-crown-6, a cyclic oligo(ethylene glycol) consisting of six EO repeating units, strongly complexes potassium cations in THF.<sup>[45]</sup> The distance of two methylene units between the oxygens of 18-crown-6 is similarly found for the three oxygens in EVGE. Based on this rationale, a preferential combined complexation of the potassium cation with EVGE monomer and the alkoxide of the propagating chain via chelation can be hypothesized and investigated by quantum chemistry methods, namely density functional theory (DFT) (Figure 3, right). In contrast, EO exhibits only one coordination site per monomer and therefore a lower complex coordination constant with potassium cations. Consequently, this results in a higher probability to find EVGE rather than EO in the chain segments close to the initiator, explaining the preferential incorporation of EVGE ( $r_{\text{EVGE}} > r_{\text{EO}}$ ) during chain propagation. The chelation of potassium cations is less pronounced for AGE, as only two possible coordination sites are present in each AGE monomer (Figure 3, center). Therefore, the stability constant of AGE complexes is lower than that of EVGE,

but still somewhat higher than for EO, resulting in a merely slightly preferred addition of AGE to the chain end in THF ( $r_{\text{AGE}} > r_{\text{EO}}$ ).

The propagating chain ends of the three investigated monomers were simulated using DFT calculations. As visualized in Figure S8, Supporting Information, the presence of a glycidyl ether, namely AGE or EVGE, as an ultimate or penultimate repeating unit of the growing chain allows for a complexation by not merely the backbone oxygens of the former epoxide moiety, but also by the glycidyl ether's side chain. In the case of AGE, the number of oxygens potentially coordinating to the potassium counterion equals the number of coordinating atoms when the backbone aligns with the counterion. On the contrary, with the two oxygen atoms of the side chain of EVGE, the propagation chain end with (pen)ultimate EVGE units further saturates the complexation sites of the potassium counterion. As discussed, the coordination capability of the monomers to be added follows the trend  $\text{EO} < \text{AGE} < \text{EVGE}$  (Figure 3).

The enhanced coordination of the potassium counterion by the monomer going from EO and AGE to EVGE was observed as a local energy minimum. Hence, the inherent entropic benefit is a determining factor for the preferred chelation of the potassium cation. Furthermore, we compared the electron densities of the electrophilic methylene groups of the epoxides calculated by DFT, which are attacked by the alkoxide during polymerization. Since the bond angles of the different epoxides and hence the ring strain of the monomers are comparable, the electron density is



**Table 2.** Partial charges of the unsubstituted methylene carbon of the epoxide moiety of the monomers ethylene oxide (EO), allyl glycidyl ether (AGE), and ethoxy vinyl glycidyl ether (EVGE) calculated by DFT without taking solvation into account or rather in THF and DMSO using CPCM.

| System | EO       | AGE      | EVGE     |
|--------|----------|----------|----------|
| Vacuum | −0.285 e | −0.251 e | −0.251 e |
| THF    | −0.275 e | −0.242 e | −0.249 e |
| DMSO   | −0.273 e | −0.240 e | −0.243 e |

the pivotal parameter for the monomer reactivity. In **Table 2**, the partial charges of the three monomers simulated in vacuum as well as in THF and DMSO are given, using the implicit solvation model CPCM.

Both investigated glycidyl ethers exhibit lower electron density at their electrophilic carbon relative to EO. The trend is further decreased for all epoxides with increasing dipole moment of the respective solvent. Consequently, the partial charges give a first indication for preferential incorporation of the glycidyl ethers at the chain end compared to EO. The observed trend in monomer reactivity is further verified by evaluating the electron densities of the electrophilic epoxide methylene groups once coordinated to the propagating chain end, (see Table S1, Supporting Information).

This is in accordance with the observed trend from the in situ  $^1\text{H}$  NMR kinetic experiments. Surprisingly, the unsubstituted methylene carbon of AGE exhibits a higher electrophilicity than the respective carbon of EVGE in all solvents. Considering the afore described reactivity ratios, the potassium complexation of glycidyl ethers appears to be the major contributing factor to the copolymerization kinetics in THF, rather than the electrophilicity itself. These findings suggest that the monomer, but not the respective chain, primarily affects the incorporation with its specific complexation behavior. This further supports the implementation of the non-terminal model for the determination of reactivity ratios by in situ  $^1\text{H}$  NMR measurements.

Additional considerations are required to understand the impact of solvent polarity on the differences of the reactivity ratios in THF and DMSO ( $r_{\text{GE}}^{\text{DMSO}}$  and  $r_{\text{GE}}^{\text{THF}}$ ). Compared to THF, DMSO is a solvent with a high dipole moment. The resulting high polarity of the solvent allows an excellent dissolution of ions. Therefore, free ions are the primary active species, which mainly contribute to propagation.<sup>[40]</sup> The strong solvation effect of DMSO has a documented impact on complexes, for example, it is known to decrease the stability constants of crown ether complexes.<sup>[46]</sup> This influence is clearly visible when comparing the reactivity ratios obtained via in situ  $^1\text{H}$  NMR measurements in the different solvents. In DMSO, only a slightly preferred incorporation of EVGE over EO is observed. Therefore, the previously proposed crown ether-effect of EVGE in THF (Figure 3) is less pronounced in the case of DMSO. This is additionally confirmed by the increasing  $r_{\text{EO}}$  values from THF (0.57) to DMSO (0.81) and the increasing similarity of  $r_{\text{EVGE}}^{\text{DMSO}}$  (1.23) and  $r_{\text{AGE}}^{\text{DMSO}}$  (1.08). The described influence of DMSO is equally observed in the copolymerization of EO with AGE, resulting in an almost ideally random copolymerization with  $r_{\text{EO}} \approx r_{\text{AGE}}$ . Similar values of the reactivity ratios were previously reported by our group for the

copolymerization of ethoxyethyl glycidyl ether (EEGE) with EO in DMSO under AROP conditions.<sup>[17]</sup>

In summary, variation of the chemical structure of a glycidyl ether, for example, the addition of an ethylene glycol spacer at the monomer side chain, has a distinct influence on the behavior of epoxide monomers in the copolymerization with EO and consequently the microstructure of the resulting copolymers. In this context, the choice of solvent thus has a pronounced effect on the copolymerization reaction kinetics.

Further, the choice of a non-polar solvent enables the synthesis of “EO-rich” terminal segments within the polymer microstructure. If post-modification of the  $\omega$ -terminus is desired, a decreased reactivity of EO in copolymerization leads to an increase of primary hydroxy functionalities in the resulting polyether. Consequently, the reactivity of the polyether copolymers for post-modification reactions is largely enhanced.

### 3. Conclusion

With this study we aim at a general understanding of the anionic ring-opening copolymerization kinetics of ethylene oxide (EO) with glycidyl ethers (GE), relying on online  $^1\text{H}$  NMR monitoring of the reaction. Allyl glycidyl ether (AGE) and ethoxy vinyl glycidyl ether (EVGE) were chosen as typical and synthetically valuable representatives of glycidyl ether monomers, and copolymerization was carried out either in THF or DMSO. Online  $^1\text{H}$  NMR kinetics enables in situ monitoring of monomer consumption, leading to precise and reliable determination of reactivity ratios by common non-terminal models. Both investigated glycidyl ethers exhibited slightly higher reactivity ratios than EO in DMSO as well as in THF. However, the reactivity difference increased with reduced solvent polarity. These results further emphasize the crown ether effect and the underlying multidentate cation complexation as the driving force for the enhanced reactivity of glycidyl ethers compared to EO in the anionic copolymerization. The impact of the crown ether-like complexation consequently increased with reduced cation dissociation in less polar media going from DMSO to THF. Supplementary calculations by density functional theory (DFT) support the presented crown ether-effect, showing the stronger complexation with increasing number of oxygen atoms comparing EO with ethylene glycol spacer containing GEs (EO < AGE < EVGE).

Overall, the results disclose the underlying effects of the slightly preferred glycidyl ether incorporation over EO. This is crucial for the design of glycidyl ether-based copolymers since the resulting microstructure is tunable to a certain extent by choice of solvent as well as the introduction of ethylene glycol spacers in the monomer structures. The monomer gradient governs the behavior of the resulting materials in bulk or solution. In summary, this study provides in-depth insights in epoxide reactivity with respect to the design of the respective monomers as well as its solvent dependence. The results emphasize the vast value of in situ experiments for the control of chemical properties via precise tuning of polymer microstructures.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

P.D. and R.M. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Open access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

anionic ring-opening polymerization, copolymerization, epoxide monomers, in situ kinetics, polyethers

Received: June 28, 2022

Revised: July 27, 2022

Published online: September 1, 2022

- [1] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, *51*, 10246.
- [2] E. Grune, T. Johann, M. Appold, C. Wahlen, J. Blankenburg, D. Leibig, A. H. E. Müller, M. Gallei, H. Frey, *Macromolecules* **2018**, *51*, 3527.
- [3] P. Hodrokoukes, G. Floudas, S. Pispas, N. Hadjichristidis, *Macromolecules* **2001**, *34*, 650.
- [4] R. Lach, R. Weidisch, K. Knoll, *J. Polym. Sci. B Polym. Phys.* **2005**, *43*, 429.
- [5] N. Singh, M. S. Tureau, T. H. Epps, III, *Soft Matter* **2009**, *5*, 4757.
- [6] M. Thunga, U. Staudinger, B. K. Satapathy, R. Weidisch, M. Abdel-Goad, A. Janke, K. Knoll, *J. Polym. Sci. B Polym. Phys.* **2006**, *44*, 2776.
- [7] M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey, A. H. E. Müller, *Macromolecules* **2019**, *52*, 9299.
- [8] A. A. Korotkov, G. V. Rakova, *Polym. Sci. U.S.S.R.* **1962**, *3*, 990.
- [9] C. C. Price, Y. Atarashi, R. Yamamoto, *J. Polym. Sci. A-1 Polym. Chem.* **1969**, *7*, 569.
- [10] A. Stolarzewicz, H. Becker, G. Wagner, *Acta Polym.* **1980**, *31*, 743.
- [11] F. Heatley, G.-E. Yu, C. Booth, T. G. Bleas, *Eur. Polym. J.* **1991**, *27*, 573.
- [12] V. S. Reuss, B. Obermeier, C. Dingels, H. Frey, *Macromolecules* **2012**, *45*, 4581.
- [13] M. Steube, T. Johann, H. Hübner, M. Koch, T. Dinh, M. Gallei, G. Floudas, H. Frey, A. H. E. Müller, *Macromolecules* **2020**, *53*, 5512.
- [14] J. M. Kim, S. B. Chakrapani, B. S. Beckingham, *Macromolecules* **2020**, *53*, 3814.
- [15] A. Natalello, M. Werre, A. Alkan, H. Frey, *Macromolecules* **2013**, *46*, 8467.
- [16] B. Obermeier, F. Wurm, H. Frey, *Macromolecules* **2010**, *43*, 2244.
- [17] J. Herzberger, D. Leibig, J. C. Liermann, H. Frey, *ACS Macro Lett.* **2016**, *5*, 1206.
- [18] J. Herzberger, D. Kurzbach, M. Werre, K. Fischer, D. Hinderberger, H. Frey, *Macromolecules* **2014**, *47*, 7679.
- [19] J. Blankenburg, E. Kersten, K. Maciol, M. Wagner, S. Zarbakhsh, H. Frey, *Polym. Chem.* **2019**, *10*, 2863.
- [20] J. Blankenburg, K. Maciol, C. Hahn, H. Frey, *Macromolecules* **2019**, *52*, 1785.
- [21] K. Niederer, C. Schüll, D. Leibig, T. Johann, H. Frey, *Macromolecules* **2016**, *49*, 1655.
- [22] W. Zhang, J. Allgaier, R. Zorn, S. Willbold, *Macromolecules* **2013**, *46*, 3931.
- [23] P. Verkoyen, P. Dreier, M. Bros, C. Hils, H. Schmalz, S. Seiffert, H. Frey, *Biomacromolecules* **2020**, *21*, 3152.
- [24] T. Homann-Müller, E. Rieger, A. Alkan, F. R. Wurm, *Polym. Chem.* **2016**, *7*, 5501.
- [25] E. Rieger, A. Alkan, A. Manhart, M. Wagner, F. R. Wurm, *Macromol. Rapid Commun.* **2016**, *37*, 833.
- [26] E. Rieger, J. Blankenburg, E. Grune, M. Wagner, K. Landfester, F. R. Wurm, *Angew. Chem.* **2018**, *57*, 2483.
- [27] T. Gleede, J. C. Markwart, N. Huber, E. Rieger, F. R. Wurm, *Macromolecules* **2019**, *52*, 9703.
- [28] J. Herzberger, K. Fischer, D. Leibig, M. Bros, R. Thiermann, H. Frey, *J. Am. Chem. Soc.* **2016**, *138*, 9212.
- [29] V. Jaacks, *Makromol. Chem.* **1972**, *161*, 161.
- [30] T. C. Majdanskii, J. Vitz, A. Meier, M. Brunzel, S. Schubert, I. Nischang, U. S. Schubert, *Polymer* **2018**, *159*, 86.
- [31] K. S. Kazanskii, A. A. Solovyanov, S. G. Entelis, *Eur. Polym. J.* **1971**, *7*, 1421.
- [32] N. V. Pitsyna, V. K. Kazakevich, K. S. Kazanskii, *Polym. Sci. U. S. S. R.* **1977**, *19*, 3218.
- [33] A. A. Solov'yanov, K. S. Kazanskii, *Polym. Sci. U. S. S. R.* **1972**, *14*, 1186.
- [34] C. E. H. Bawn, A. Ledwith, N. R. McFarlane, *Polymer* **1967**, *8*, 484.
- [35] C. Bawn, A. Ledwith, N. McFarlane, *Polymer* **1969**, *10*, 653.
- [36] C. C. Price, M. K. Akkapeddi, *J. Am. Chem. Soc.* **1972**, *94*, 3972.
- [37] C. C. Price, D. D. Carmelite, *J. Am. Chem. Soc.* **1966**, *88*, 4039.
- [38] A. A. Solov'yanov, K. S. Kazanskii, *Polym. Sci. U. S. S. R.* **1972**, *14*, 1196.
- [39] J. E. Figueruelo, D. J. Worsfold, *Eur. Polym. J.* **1968**, *4*, 439.
- [40] K. S. Kazanskii, A. A. Solovyanov, S. A. Dubrovsky, *Makromol. Chem.* **1978**, *179*, 969.
- [41] C. Mangold, C. Dingels, B. Obermeier, H. Frey, F. Wurm, *Macromolecules* **2011**, *44*, 6326.
- [42] B. F. Lee, M. Wolffs, K. T. Delaney, J. K. Sprafke, F. A. Leibfarth, C. J. Hawker, N. A. Lynd, *Macromolecules* **2012**, *45*, 3722.
- [43] S. Penczek, M. Cypryk, A. Duda, P. Kubisa, S. Slomkowski, *Prog. Polym. Sci.* **2007**, *32*, 247.
- [44] A. Lee, P. Lundberg, D. Klinger, B. F. Lee, C. J. Hawker, N. A. Lynd, *Polym. Chem.* **2013**, *4*, 5735.
- [45] J. Ding, F. Heatley, C. Price, C. Booth, *Eur. Polym. J.* **1991**, *27*, 895.
- [46] V. P. Solov'ev, N. N. Strakhova, O. A. Raevsky, V. Rüdiger, H.-J. Schneider, *J. Org. Chem.* **1996**, *61*, 5221.

WILEY-VCH

## Supporting Information

***In Situ* Kinetics Reveals the Influence of Solvents and Monomers on the Anionic Ring-Opening Copolymerization of Epoxides**

*Philip Dreier, Rebecca Matthes, Ramona D. Barent, Sandra Schüttner, Axel H. E. Müller,\*  
and Holger Frey\**

**1. Materials and Experimental Procedures****1.1. Reagent and Equipment**

All chemicals and solvents were purchased from Acros Organics, TCI, Sigma-Aldrich and Fluka. Deuterated solvents were received from Deutero GmbH. Ethoxy vinyl glycidyl ether (EVGE) was synthesized according to the procedure established by our group in 2011.<sup>[1]</sup> Allyl glycidyl ether (AGE) was purchased from TCI and purified before use by fractional distillation. Both glycidyl ethers were dried prior to the experiments by cryo-transfer after stirring over CaH<sub>2</sub> for 30 min.

**1.2. *In situ* <sup>1</sup>H NMR Kinetic Experiments**

Online <sup>1</sup>H NMR kinetic measurements were performed according to a protocol by Herzberger et al.<sup>[2]</sup> in a Norell S-500-VT-7 NMR tube. The *in situ* <sup>1</sup>H NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer equipped with a 5 mm BBFO SmartProbe. An exemplary protocol for P(EO-*co*-AGE) in DMSO-*d*<sub>6</sub> is described in the following, other experiments were performed equivalently.

KOtBu (24.6 mg, 219 μmol) was dissolved in a THF/water mixture and transferred in a flame-dried Schlenk flask equipped with a septum and stop cock. Benzyl alcohol (24.9 mg, 23.9 μl, 230 μmol) was dissolved in benzene and added to the base solution. After slow evaporation of the solvent under high vacuo, the initiator salt was dried at 60 °C under high vacuum. The dried initiator salt was then dissolved in 1.12 ml DMSO-*d*<sub>6</sub> and stirred for 30 min. Concurrently, EO (0.05 ml, 23 eq) was cryo-transferred to the evacuated NMR tube attached to the Schlenk-line under static vacuum at -50 °C with an acetone/nitrogen bath. Subsequently, 0.21 ml of the initiator solution and AGE (0.11 ml, 20 eq) were transferred to



## WILEY-VCH

the NMR tube under an inert argon-atmosphere. The reaction mixture was then cooled by liquid nitrogen, evacuated and finally sealed with a Teflon stop cock. The reaction mixture was warmed to room temperature, shaken vigorously to ensure a homogenous solution and placed in the preheated (45 °C) NMR spectrometer. One spectrum every 30 sec. was recorded in DMSO-*d*<sub>6</sub> with 1 scan after the temperature was stable ( $\Delta T = 0.1$  K). In THF, spectra were recorded in a 2-min interval. The experimental data was analyzed by using NIREVAL software from Johann, Steube and Frey.<sup>[3]</sup>

Note regarding ethylene oxide: EO is a highly flammable and toxic gas. It therefore has to be handled with care and the necessary precautions. The addition of EO throughout this study was carried out in a reproducible procedure. Yet, small deviations in the measured volumes are possible considering the very small amounts utilized (< 0.1 ml). The evaluated reaction times depend on the overall concentration, which may therefore vary with each measurement. The targeted monomer ratios might differ to a small extent as well.

### 1.3. DFT Calculations

DFT calculations were performed on MOGON II at the high-performance computing center of the Johannes Gutenberg University Mainz using ORCA 4.2.1. software.<sup>[4] [5]</sup> The B3LYP hybrid density functionals<sup>[6] [7]</sup> were used as the calculation of the analytical Hessian matrix is available. Furthermore, the D3BJ<sup>[8] [9]</sup> atom-pairwise dispersion correction to the DFT energy with Becke-Johnson damping was enabled. The def2-TZVP valence triple-zeta basis set<sup>[10] [11]</sup> was selected and for an accurate single point energy TightSCF was chosen together with a Grid6 integration grid. The RIJCOSX approximation<sup>[12]</sup> was implemented together with a GridX8 for accurate geometry optimization, as it offers large accelerations. Finally, geometrical Counterpoise Corrections (gCP)<sup>[13]</sup> were enabled to prevent artificial overbinding effects. To take solvation into account, the implicit solvation model of the conductor-like polarizable continuum (CPCM)<sup>[14]</sup> simulating the solvate in a solvent cavity was utilized where appropriate.

Furthermore, the maximum amount of memory to be used for integral buffering was defined by %maxcore and parallel jobs were invoked by %pal nprocs. The number of parallel jobs was set to the threefold of the number of atoms. The SCF calculations were specified in terms of their integral direct integration, by a maximal number of iterations and by a very tight convergence as threshold.

## WILEY-VCH

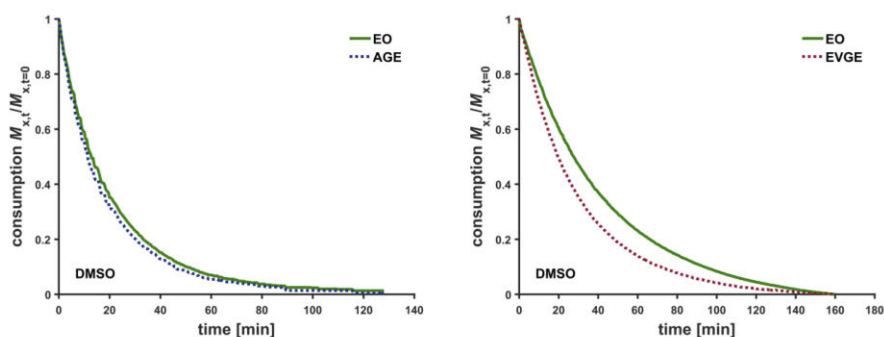
An exemplary ORCA inputfile allowing the calculation of a local energy minimum is shown below:

```
!B3LYP D3BJ def2-TZVP CPCM(solvent) TightSCF RIJCOSX Opt Grid6 NoFinalGrid
GridX8 FREQ NORMALPRINT GCP(DFT/TZ)
%maxcore 8000
%PAL NPROCS 64 END
%scf
MaxIter 2000
SCFMode Direct
Convergence VeryTight
End
* xyzfile Charge Multiplicity 3d_coordinates.xyz
```

#### 1.4. Size Exclusion Chromatography

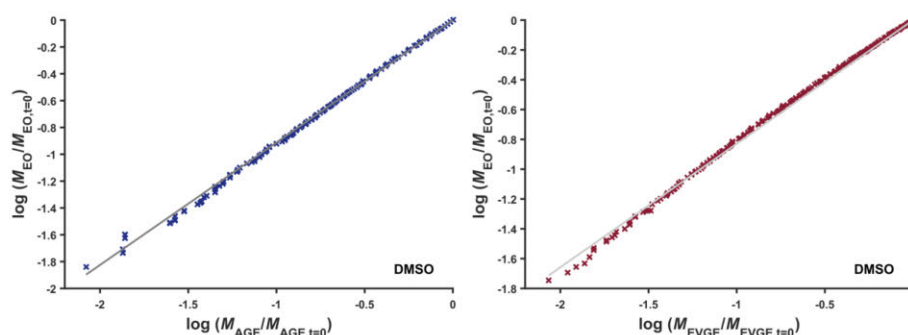
Size exclusion chromatography (SEC) measurements were performed in dimethylformamide (DMF) with 1 g/l lithium bromide as an eluent at 50 °C. An Agilent 1100 Series was used, equipped with HEMA 300/100/40 columns, and calibration was carried out using polyethylene glycol (PEG) standards, both provided by Polymer Standard Service (PSS), Mainz.

## 2. Results of *in situ* $^1\text{H}$ NMR Kinetic Experiments

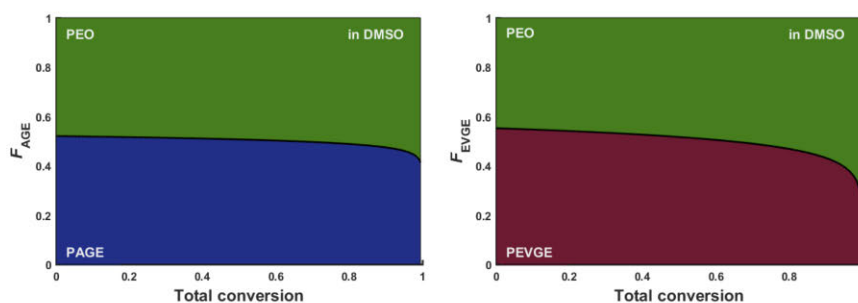


**Figure S1.** Time-conversion plot of the copolymerization of EO with AGE (left) and with-EVGE (right) determined via *in situ*  $^1\text{H}$  NMR kinetics in  $\text{DMSO-}d_6$  at 45 °C.

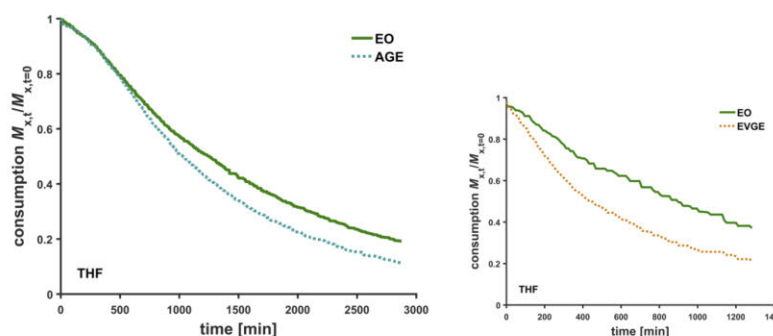
WILEY-VCH



**Figure S2.** Jaacks plot for the copolymerization of EO with AGE (left,  $r_{\text{EO}}^{\text{DMSO}} = 0.92 \pm 0.002$  and  $r_{\text{AGE}}^{\text{DMSO}} = 1.08 \pm 0.002$ ;  $R^2 = 0.99$ ) and with EVGE (right,  $r_{\text{EO}}^{\text{DMSO}} = 0.81 \pm 0.001$  and  $r_{\text{EVGE}}^{\text{DMSO}} = 1.23 \pm 0.002$ ;  $R^2 = 0.99$ ) determined via *in situ*  $^1\text{H}$  NMR kinetics in  $\text{DMSO}-d_6$  at  $45^\circ\text{C}$ .

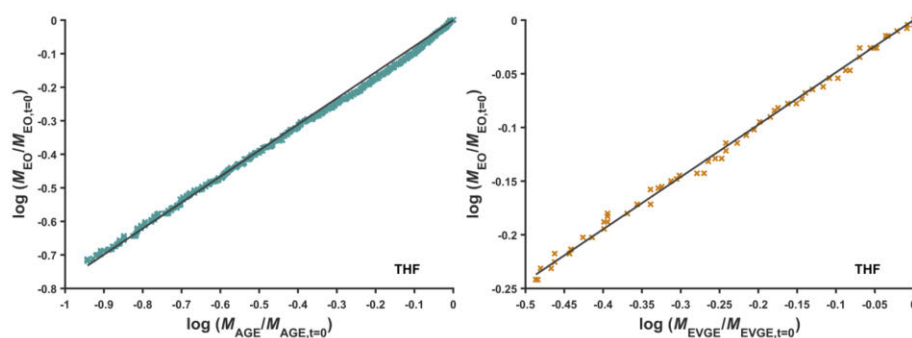


**Figure S3.** Molar-based composition diagram of  $\text{P}(\text{EO}-co\text{-AGE})$  (left) and  $\text{P}(\text{EO}-co\text{-EVGE})$  (right) in  $\text{DMSO}-d_6$  with an initial equimolar ratio.  $F_{\text{AGE}}$  = AGE incorporation,  $F_{\text{EVGE}}$  = EVGE incorporation.

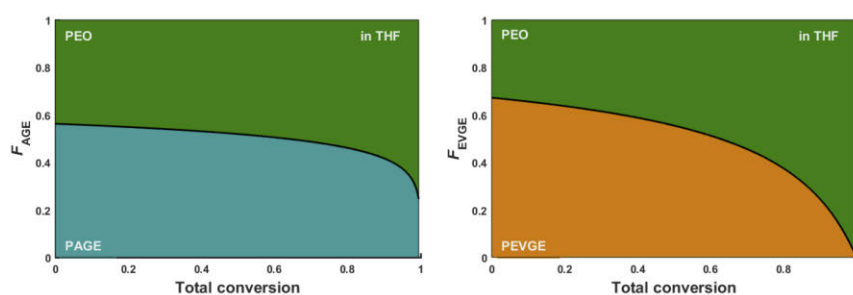


**Figure S4.** Time-conversion plot of the copolymerization of EO with AGE (left) and with EVGE (right), determined via *in situ*  $^1\text{H}$  NMR kinetics in  $\text{THF}-d_8$  at  $45^\circ\text{C}$ .

WILEY-VCH



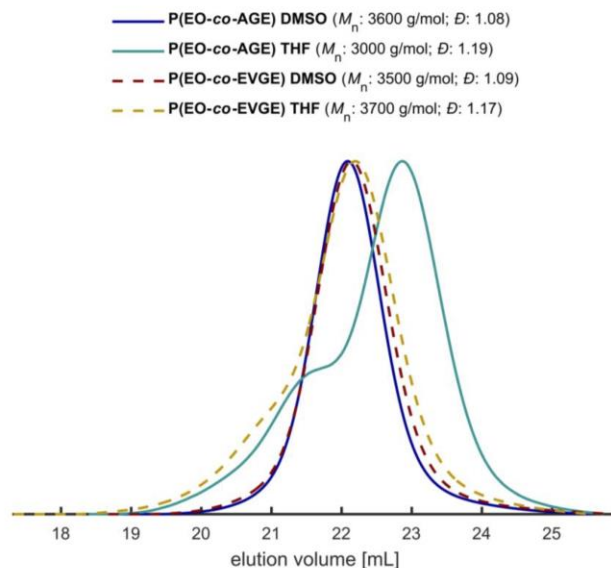
**Figure S5.** Jaacks plot for the copolymerization of EO with AGE (left,  $r_{\text{EO}}^{\text{THF}} = 0.78 \pm 0.001$  and  $r_{\text{AGE}}^{\text{THF}} = 1.29 \pm 0.002$ ;  $R^2 = 0.99$ ) and with EVGE (right,  $r_{\text{EO}}^{\text{THF}} = 0.48 \pm 0.004$  and  $r_{\text{EVGE}}^{\text{THF}} = 2.05 \pm 0.015$ ;  $R^2 = 0.99$ ) determined via *in situ*  $^1\text{H}$  NMR kinetics in  $\text{THF-}d_8$  at  $45^\circ\text{C}$ .



**Figure S6.** Molar-based composition diagram of P(EO-*co*-AGE) (left) and P(EO-*co*-EVGE) (right) in  $\text{THF-}d_8$  with an initial equimolar monomer ratio.  $F_{\text{AGE}}$  = AGE incorporation,  $F_{\text{EVGE}}$  = EVGE incorporation.

WILEY-VCH

## 3. Molecular Weight Distributions of Copolymers

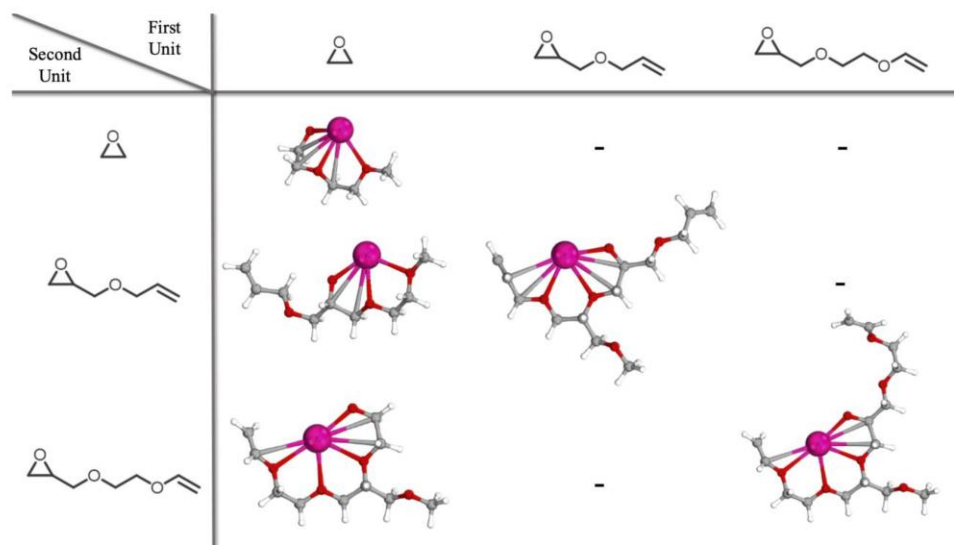


**Figure S7.** SEC traces of P(EO-co-AGE) and P(EO-co-EVGE) copolymers synthesized in DMSO- $d_6$  und THF- $d_8$  at 45 °C (solvent: DMF, standard: PEG).

The SEC traces of the *in-situ*  $^1\text{H}$  NMR kinetic show molecular weight distribution from 3000 to 3700 g mol $^{-1}$  with dispersities ranging from 1.08 to 1.19 (Figure S7). Please note that the samples were formed in the NMR tube. In the case of the THF samples, high molecular weight shoulders can be observed, which can be explained by the presence of traces of water in the polymerization process. However, the presence of water has no influence on the concentration of active chain ends and the monomer consumption because the concentration of active chain ends is equal to the amount of alkoxides present in the system. Further, water is consumed at the beginning of the polymerization as an initiator and therefore does not change the polarity of the solvent during the copolymerization. As a result, online monitoring results regarding monomer consumption via *in situ*  $^1\text{H}$  NMR measurements are independent of the dispersity of the samples.

WILEY-VCH

## 4. Supplementary DFT Calculations



**Figure S8.** Complexation of the potassium counterion within the two penultimate monomer units. Potassium methanolate was utilized as a model initiator for this simulation. The multidentate chelation with the potassium counterion is shown for combined incorporated monomer units, visualizing the comparably poor complexation by solely EO repeating units.

Table S1 opposes electron densities of the precursors with the ones of the uncoordinated monomers, showing that with the coordination to the propagating chain end the electron density is lowered in all cases, further increasing the electrophilicity of the reaction site. Besides, for both comonomer pairs implemented (EO/AGE and EO/EVGE) the partial charge at the electrophilic methylene group of the epoxide moiety to be attacked is lower for the glycidyl ethers than for ethylene oxide, further supporting the experimentally observed slight gradient formation upon copolymerization.

WILEY-VCH

**Table S1.** Partial charges of the unsubstituted methylene carbon of the epoxide moiety of the monomers ethylene oxide (EO), allyl glycidyl ether (AGE) and ethoxy vinyl glycidyl ether (EVGE) calculated by DFT without taking solvation into account within the precursor complex of propagating chain end, potassium counterion and incoming monomer. The electron densities of the single monomer is given for comparison.

| System                                    | EO                                | AGE             | EVGE            |
|-------------------------------------------|-----------------------------------|-----------------|-----------------|
| precursor complex with ultimate EO unit   | -0.250 <i>e</i> & -0.251 <i>e</i> | -0.225 <i>e</i> | -0.206 <i>e</i> |
| precursor complex with ultimate AGE unit  | -0.262 <i>e</i> & -0.245 <i>e</i> | -0.199 <i>e</i> | –               |
| precursor complex with ultimate EVGE unit | -0.240 <i>e</i> & -0.264 <i>e</i> | –               | -0.212 <i>e</i> |
| single monomer                            | -0.285 <i>e</i>                   | -0.251 <i>e</i> | -0.251 <i>e</i> |

WILEY-VCH

## 5. References

- [1] C. Mangold, C. Dingels, B. Obermeier, H. Frey, F. Wurm, *Macromolecules*. **2011**, *44*, 6326.
- [2] J. Herzberger, D. Leibig, J. C. Liermann, H. Frey, *ACS Macro Lett.* **2016**, *5*, 1206.
- [3] M. Steube, T. Johann, M. Plank, S. Tjaberings, A. H. Gröschel, M. Gallei, H. Frey, A. H. E. Müller, *Macromolecules*. **2019**, *52*, 9299.
- [4] F. Neese, *WIREs Comput Mol Sci.* **2012**, *2*, 73.
- [5] F. Neese, *WIREs Comput Mol Sci.* **2018**, *8*.
- [6] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372.
- [7] Lee, Yang, Parr, *Phys. Rev. B.* **1988**, *37*, 785.
- [8] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
- [9] S. Grimme, S. Ehrlich, L. Goerigk, *J. Compu. Chem.* **2011**, *32*, 1456.
- [10] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571.
- [11] F. Weigend, R. Ahlrichs, *PCCP*. **2005**, *7*, 3297.
- [12] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chemical Physics*. **2009**, *356*, 98.
- [13] H. Kruse, S. Grimme, *J. Chem. Phys.* **2012**, *136*, 154101.
- [14] V. Barone, M. Cossi, *J. Phys. Chem. A.* **1998**, *102*, 1995.









## RAMONA DENISE BARENT

Address

[REDACTED]  
[REDACTED]

Telephone

[REDACTED]

e-Mail Address

[REDACTED]

Date and Place of Birth

[REDACTED] [REDACTED]

## EDUCATIONAL BACKGROUND

05/2019 – 03/2023

PhD Studies, Polymer Chemistry, JGU Mainz within the fellowship Max Planck Graduate Center (MPGC)

‘Copolymerization of Dienes: From Mechanistic Insights towards Material Properties of Multiblock Copolymers’ Prof. Dr. Frey

*Main Topics:*

- Polymer chemistry and organic synthesis
- Reaction kinetics
- Block copolymer synthesis based on dienes and styrene
- Correlation of monomer sequences with morphological (SAXS) and mechanical properties (tensile tests)
- Correlation of monomer sequences with solution properties (DLS, FCS, viscometry, sedimentation velocity analysis)
- Density functional theory simulation of reaction pathways

*Collaborations:*

- 1 industrial collaboration project
- Collaboration partners at the St. Petersburg University, Friedrich-Schiller-University Jena, University of Ioannina, and the Max Planck Institute for Polymer Research

*Supervision of:*

- 1 bachelor student, 3 research module candidates, and a laboratory technician
- Supervision of students in 4 lab courses

|                          |                                                                                                                                                                                                                                                                                                                                                                                              |
|--------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>03/2016 – 03/2019</b> | <b>Master of Science, Chemistry (1.1)</b> , JGU Mainz<br>‘Functional Termination of Polyisoprene and Linear-Branched Structures’ (1.0), Prof. Dr. Frey<br><i>Main Topic:</i> <ul style="list-style-type: none"> <li>Synthesis of advanced structures by the combination of carbanionic and oxyanionic polymerization techniques</li> </ul>                                                   |
| <b>10/2012 – 03/2016</b> | <b>Bachelor of Science, Chemistry (1.8)</b> , JGU Mainz<br>‘Synthesis of Selenium-Containing Polycarbonates’ (1.6), Prof. Dr. Waldvogel<br><i>Main Topic:</i> <ul style="list-style-type: none"> <li>Correlation of polymer characteristics with refractive properties</li> </ul> <i>Collaboration:</i> <ul style="list-style-type: none"> <li>1 industrial collaboration project</li> </ul> |
| <b>03/2012</b>           | <b>Abitur (1.4)</b> , Hans-Purrmann-Gymnasium Speyer                                                                                                                                                                                                                                                                                                                                         |
| <b>02/2009 – 01/2010</b> | <b>Stay Abroad</b> in Santiago de Puriscal in Costa Rica<br><i>Experience:</i> Life in a host family, school attendance at 10 <sup>th</sup> grade, participation in a mountain bike racing team                                                                                                                                                                                              |

## WORK AND TEACHING EXPERIENCE

|                    |                                                                           |
|--------------------|---------------------------------------------------------------------------|
| <b>2017 – 2018</b> | Tutor in the module ‘Physical Chemistry IV’, 3 semesters                  |
| <b>2016 – 2019</b> | Tutor in the module ‘Organic Chemistry I’, 5 semesters                    |
| <b>2014 – 2017</b> | Tutor in the module ‘Inorganic and Analytical Chemistry I’, 6 semesters   |
| <b>06/2011</b>     | Voluntary one-week internship at BASF SE as chemical laboratory assistant |

## SCIENTIFIC PUBLICATIONS

|                     |                                                                                                                                                                                                                                           |
|---------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Publications</b> | <b>Several publications in peer-reviewed journals</b><br>See attached detailed list                                                                                                                                                       |
| <b>Conferences</b>  | <b>3 international conferences</b><br>14 <sup>th</sup> International Symposium on Ionic Polymerization in Ghent<br>Bordeaux Polymer Conference in Bordeaux<br>13 <sup>th</sup> International Symposium on Ionic Polymerization in Beijing |

## SKILLS AND COMPETENCES

|                      |                                                                                                                                                                                                                                                                         |
|----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Languages            | <b>German:</b> first language                                                                                                                                                                                                                                           |
|                      | <b>English:</b> business fluent                                                                                                                                                                                                                                         |
|                      | <b>Latin:</b> basic knowledge<br>intermediate Latin certificate                                                                                                                                                                                                         |
|                      | <b>Spanish:</b> fluent                                                                                                                                                                                                                                                  |
| IT Knowledge         | <b>Working Knowledge</b><br>Microsoft Office                                                                                                                                                                                                                            |
|                      | <b>Scientific Computing Software</b><br>MATLAB, OriginPro, ChemDraw, MestreNova, WinGPC Unichrom, Kinetic Monte Carlo Simulations using a self-written in-house software, Density Functional Theory calculations (computational quantum mechanical modeling) using ORCA |
|                      |                                                                                                                                                                                                                                                                         |
| Continuing Education | <b>Participation in the yearlong Mentoring Program</b> offered by MAINZMentoring including KODE® Profiling, coaching on the professional orientation, and exchange with a mentor from Freudenberg Performance Materials                                                 |
|                      | <b>Examined Project Manager in Business Chemistry</b> offered by the GDCh with focus on the competitive analysis and balance sheet analysis                                                                                                                             |
|                      | <b>Time- &amp; Self-Management</b> for doctoral students offered by the MPGC                                                                                                                                                                                            |
|                      | <b>Defense Training</b> offered by the MPGC                                                                                                                                                                                                                             |

## INTERESTS

Tennis, volleyball, skiing since the age of four, acrylic painting

## LIST OF PUBLICATIONS

### CONTRIBUTION AS FIRST AUTHOR OR EQUALLY

- 08/2022** Ramona D. Barent, Manfred Wagner, and Holger Frey 'Geometric Requirements for Living Anionic Polymerization: Polymerization of rotationally constrained 1,3-Dienes' In: *Polymer Chemistry*, **2022**, 13, 5478-5485.  
DOI: 10.1039/D2PY00999D

### CONTRIBUTION AS COAUTHOR

- 08/2022** Philip Dreier, Rebecca Matthes, Ramona D. Barent, Sandra Schüttner, Axel H.E. Müller and Holger Frey 'In Situ Kinetics Reveal the Influence of Solvents and Monomer Structure on the Anionic Ring-Opening Copolymerization of Epoxides' In: *Macromolecular Chemistry and Physics*, **2022**, 2200209.  
DOI: 10.1002/macp.202200209
- 01/2022** Marvin Steube, Tobias Johann, Ramona D. Barent, Axel H.E. Müller and Holger Frey 'Rational Design of Tapered Multiblock Copolymers for Thermoplastic Elastomers' In: *Progress in Polymer Science*, **2022**, 124, 101448.  
DOI: 10.1016/j.progpolymsci.2021.101488
- 05/2020** Philipp von Tiedemann, Jiaqi Yan, Ramona D. Barent, Richard J. Spontak, George Floudas, Holger Frey, and Richard A. Register 'Tapered Multiblock Star Copolymers: Synthesis, Selective Hydrogenation, and Properties' In: *Macromolecules* **2020**, 53, 4422–4434.  
DOI: 10.1021/acs.macromol.0c00645
- 07/2019** Tobias Johann, Ulrike Kemmer-Jonas, Ramona D. Barent and Holger Frey 'Multifunctional Fe(III)-Binding Polyethers from Hydroxamic Acid-Based Epoxide Monomers' In: *Macromolecular Rapid Communications* **2019**, 41, 1900282.  
DOI: 10.1002/marc.201900282

### CONFERENCES

- 09/2022** **14th International Symposium on Ionic Polymerization in Ghent**  
Oral contribution 'Geometric Requirements for Living Anionic Polymerization in Hydrocarbon Media: Polymerization of Rotationally Constrained 1,3-Dienes'

**06/2022**

***Bordeaux Polymer Conference in Bordeaux***

Poster presentation 'Correlation between the Solution as well as Mechanical Properties of Multiblock Copolymers based on Isoprene and Styrene (IS)<sub>n</sub>I and their Chemical Composition'

**09/2019**

***13<sup>th</sup> International Symposium on Ionic Polymerization in Beijing***

Poster presentation 'General Approach towards Telechelic Multihydroxyl Functionalized Polymers and Star-Shaped Amphiphiles'

