

Anionic Polymerization of Terpene-based Monomers and Functional Styrenes for Thermoplastic Elastomers

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Christoph Hahn

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1. Berichterstatter: Prof. Dr. Holger Frey

2. Berichterstatter: Prof. Dr. Paul Blom

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Hiermit versichere ich gemäß § 10 Abs. 3d der Promotionsordnung vom 24.07.2007: Ich habe die jetzt als Dissertation vorgelegte Arbeit selbst angefertigt und alle benutzten Hilfsmittel (Literatur, Apparaturen, Material) in der Arbeit angegeben. Ich habe oder hatte die jetzt als Dissertation vorgelegte Arbeit nicht als Prüfungsarbeit für eine andere staatliche oder andere wissenschaftliche Prüfung eingereicht. Ich hatte weder die jetzt als Dissertation vorgelegte Arbeit noch Teile davon bei einer anderen Fakultät bzw. einem anderen Fachbereich als Dissertation eingereicht.

Christoph Hahn



“El Camino no tiene final, nuestros pasos sí”

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Collaborations

Some chapters contain contributions from other people.

Sebastian Becker contributed to the synthesis and characterization of the polystyrene copolymers in **Chapter 2** as part of his bachelor thesis.

Manfred Wagner performed the *online* NMR kinetic measurements and contributed to **Chapter 3** with his expertise on the microstructure investigations.

Moritz Rauschenbach and Christoph Hahn contributed equally to **Chapter 4.1**. Moritz Rauschenbach was responsible for the microstructure investigations upon the addition of THF and performed the kinetic studies.

Chapter 4.2 is a collaboration of the Johannes Gutenberg University Mainz and the University of Konstanz. George Floudas conducted and interpreted the SAXS measurements.

Moritz Simon contributed in parts to **Chapter 4.3** as a part of his master thesis. Moritz Simon performed synthesis and characterization of 4-isopropylene-vinylcyclohexene.

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Motivation and Objectives

The outstanding advantage of the carbanionic polymerization technique is the unreached level of control of the polymer architecture, enabling the preparation of high molecular weight block copolymers with very narrow molecular weight distributions by the sequential addition of different monomers. Copolymers of 1,3-butadiene, 1,3-isoprene and styrene are the most common polymers made by anionic polymerization for the manufacturing of elastomers.¹ Elastomers have enriched our everyday life in all areas, be it for personal transportation in car passenger tires, for industrial goods such as damping materials or for wire insulation in electronics. The demand for natural and synthetic rubber is growing because of the increasing world population and increasing industrial production. Dwindling petrochemical resources and an increasing environmental damage, caused by increasing emission of greenhouse gases, are motivating rapidly the interest in bio-based polymer materials from renewable sources.

However, society eventually desires independence of fossil resources, which places bio-based polymers in a new focus and perspective.² Among the bio-available resources that are already used in industry, such as carbohydrates, terpenes are a class of valuable hydrocarbons with structures, ranging from linear, cyclic, bicyclic, to aromatic moieties. Terpenes represent a large-scale available and structurally versatile class of bio-based compounds that are found in a large diversity of applications from natural flavors to natural rubber. Because of the nearly unlimited variety of structural compositions, terpenes offer a versatile library of renewable monomers for polymerization.³

The living anionic polymerization of isoprene in nonpolar solvents is a common procedure in industry and results in polyisoprene with high content of 1,4-regioisomers, which mimic the high flexibility of natural rubber.⁴ Recent studies have shown the vast potential of biomass-derived 1,3-diene monomers such as

β -myrcene and β -farnesene as alternatives to fossil-based isoprene.⁵ β -Myrcene as well as β -farnesene are already produced in large scale from biomass.⁶

Nevertheless, the functionalization of polydienes with polar groups remains a key challenge in the anionic polymerization. Functionalized polydienes feature important benefits mainly because of their improved interaction with polar fillers, that improve the wet skip performance of car passenger tires and additionally reduce the rolling resistance, resulting in more efficient fuel consumption.⁷ The addition of fillers in rubbers is crucial because of the reinforcement in mechanical and thermal properties at low costs. In contrast to butadiene and isoprene, in addition to the polymerizable 1,3-diene moiety, β -myrcene offers an additional double bond in the isopropylidene pendant group. This represents an advantage over the nonfunctionalized isoprene/butadiene rubbers. It facilitates further functionalization *via* post-polymerization modification reactions. In this context, the following central question of this thesis is intriguing:

Is it possible to introduce diol-functionalities into 1,3-diene and styrene copolymers despite the harsh conditions of living anionic polymerization, relying on biomass derived functional monomers?

This question directly leads to two of the main topics of this thesis. The introduction of diol-functionalities is a relevant problem in the field of the anionic polymerization of functional monomers, including 1,3-dienes and styrenes. In addition to the objective of functionalizing 1,3-dienes, the functionalization of polystyrene has generated significant interest to explore green alternatives from biomass. The objective is to develop greener synthesis routes for functional styrene monomers, for instance by employing cinnamic acid derivatives as starting materials.⁸ The most successful synthetic strategy towards functional polymers relies on the utilization of functional monomers and protecting group chemistry, giving access to functional polystyrene.

Within the nature of living carbanionic polymerizations, this polymerization method is very sensitive with respect to electrophilic functional groups and acidic protons, which chemically limits its use for functional polymers and specialty applications. Poly (hydroxystyrene) has been studied for a variety of applications ranging from surface coating and metal complexation. For this purpose, the second objective of this thesis was the incorporation of the bio-inspired adhesive catechol functionality into polystyrene. In nature, multi-hydroxy functional moieties are found in L-DOPA, the key amino acid in mussel adhesive proteins, being responsible for their strong attachment to almost every material in aqueous environment.⁹ The combination of the catechol functionality and polystyrene gives access to the design of materials properties such as solubility, hydrophobicity, and adhesion on metal surfaces.

The third main objective of this thesis deals with the design and synthesis of thermoplastic elastomers from bio-based resources. Thermoplastic elastomers (TPEs) are triblock copolymers that are typically composed of polystyrene (PS) as the glassy A block and polyisoprene (PI) or polybutadiene (PB) as the rubbery B block in an ABA triblock sequence.¹⁰ Cross-linking, which is required for the elastomer properties is achieved by vitrification of the glassy domains consisting of polymer A. In this case, the glassy end blocks (A) are connected covalently by flexible low T_g chains. In contrast to vulcanized rubbers that are chemically cross-linked by the addition of sulfur (and additives), these TPEs are thermally processable and recyclable.

In general, the replacement of the fossil sourced TPEs by renewable alternatives is a current objective in academic and industrial research. The previously discussed terpene-based 1,3-diene monomers β -myrcene is an ideal candidate for the low T_g flexible component of thermoplastic elastomers. However, there is no green alternative for polystyrene from sustainable feedstock at present. Thus, a central objective is the substitution of both the rubbery and glassy domains of TPEs with bio-based monomers. This aim can be summarized in the following question:

Is there a bio-based alternative that could mimic the properties of polystyrene in the field of thermoplastic elastomers, possessing a sufficiently high glass transition temperature for the high T_g block?

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Abstract

This thesis aims at the design and synthesis of multi-hydroxyl functional monomers for the field of living anionic polymerization, suitable for the preparation of polar elastomers. The obtained functional materials were characterized concerning their potential applications as highly flexible binders for silica particles in functionalized elastomers, based on their promising chelating properties. Another major topic of this work is the exploration of novel high T_g polydienes as a potential substitute of polystyrene in thermoplastic elastomers (TPEs). All topics combine the ambition of synthesizing high-performance polymers from bio-based resources. For this purpose, synthesis procedures relying on terpenes and other naturally available feedstocks were employed, producing tailor-made monomers suitable for synthetic strategies based on living anionic polymerization.

Chapter 1 introduces the living anionic polymerization of functional styrene and 1,3-diene monomers and describes the state of the art with a special focus on functional monomers. The chapter emphasizes the synthetic challenges of functional styrene monomers regarding polymerizability and stability of suitable protective groups under the harsh conditions of the anionic polymerization. The diversity of functional 1,3-dienes in anionic polymerization is rather limited. Therefore, Chapter 1 compiles previous studies on 1,3-dienes in living anionic polymerization with respect to their synthesis, substitution pattern, microstructure, and functionality. Dramatic changes in modern life and developing new approaches to adapt to the rapidly evolving demands of society have placed bio-based polymers in a new perspective. Hence, making a step towards sustainable chemistry, the utilization of terpene-based monomers in the field of living anionic polymerization was investigated.

Chapter 2 elaborates the anionic (co)polymerization of novel hydroxyl containing styrene monomers based on cinnamic acid derivatives. The hydroxyl functionality was protected by acetal and silyl protecting groups. Anionic polymerization of the protected monomers resulted in well-defined polymers after deprotection under mild

acidic conditions. In addition, the demethylation in a post-polymerization modification was performed to obtain polycatechols. The resulting polycatechols showed promising complexation properties, tested by pH-sensitive precipitation of iron cations. To enhance architectural complexity, the multi-hydroxyl polystyrenes were used as macroinitiators for graft-copolymers with L-lactide and 4-methyl- ϵ -caprolactone.

Chapter 3 describes the synthesis of a diol-functional 1,3-diene monomer (MyrDOL) for the living anionic polymerization. These works are motivated both by fundamental synthetic questions and potential applications, e.g., in filler reinforced rubbers. The copolymerizations of MyrDOL with β -myrcene, styrene and isoprene, respectively were investigated *via* ^1H NMR kinetic studies. The polar nature of the 1,3-dioxolane moiety is considered to have a “self-modifier” effect on the microstructure of P(MyrDOL) as typically known for polar additives (modifier) like THF, resulting in generally higher 3,4-microstructure incorporation. The selective introduction of dihydroxyl functionalities by the (co)polymerization of a dioxolane monomer enables unique control of the regiospecificity of the functionalization, which is not attainable by a postmodification functionalization of polymyrcene, e.g., by epoxidation and acidic ring-opening of the respective polymyrcene-epoxide.

Chapter 4 generally deals with the synthesis and anionic polymerization of novel cyclic 1,3-dienes. **Chapter 4.1** demonstrates the introduction of a cyclic 1,3-diene monomer with substitution in 1-and 2-position, i.e. 1-vinylcyclohexene. This monomer can be considered to be an intermediate between cyclic dienes and styrene. In order to gain a deeper understanding of the influence of different substitution patterns of cyclic 1,3-dienes, the polymerization of 1-vinylcyclohexene (VCH) was investigated as a model compound. A series of homo and-copolymers of VCH were synthesized and characterized in detail *via* NMR spectroscopy, SEC and DSC. After hydrogenation the polymers contained features of poly(vinylcyclohexane) and showed an increase of the T_g to 114°C, with a monomodal molecular weight distribution without any evidence of chain degradation.

Chapter 4.2 intensifies the studies on cyclic and more sterically demanding 1,3-dienes. This chapter describes the synthesis and characterization of nopadiene and the polymers of this natural compound, obtained by anionic polymerization for the first time. Together with catalytic polymerization approaches of nopadiene, the microstructure (1,4 - and 3,4 - units) of the resulting polydiene was investigated thoroughly by various NMR spectroscopy techniques. ABA triblock polymers with varied molar ratio and molecular weights were prepared by living anionic polymerization of the pinene-derivable monomers nopadiene and β -myrcene. The resulting thermoplastic elastomers displayed microphase separation at different molar ratios, an upper service temperature that was about 50 °C higher than for traditional petroleum-derived styrenic thermoplastic elastomers due to the high glass transition temperature of polynopadiene. In pronounced contrast to other 1,3-dienes, the bulkiness of polynopadiene caused elevated glass transition temperatures of up to 158 °C.

Chapter 4.3 expands the scope of cyclic 1,3-diene monomers with a *para*-menthane framework and an isopropyl-substituent for more bulkiness. This part describes the synthesis and anionic polymerization of 4-isopropyl-vinylcyclohexene (4IPVCH) based on natural perillaldehyde. The polymerization of the cyclic 1,2-disubstituted 1,3-diene proceeded quantitatively in cyclohexane at 25 °C with sec-butyllithium as initiator. The obtained polymers have well-controlled molecular weights in the range of 6 to 88 kg/mol, based on the molar ratio of monomer and initiator, with narrow molecular weight distributions ($\mathcal{D} < 1.06$ -1.23).

Appendix A1 reports on the synthesis and dynamics of a series of polymyrcene homopolymers, all with identical microstructures (95% 1,4-units and 5% of 3,4-units), which were investigated in detail by dielectric spectroscopy and rheology in close collaboration with the group of Prof. George Floudas (University of Ioannina, Greece).

Zusammenfassung

Ziel dieser Arbeit ist die Entwicklung und Synthese von multi-hydroxyl-funktionellen Monomeren unter Einsatz der lebenden anionischen Polymerisation für die Herstellung von polaren Elastomeren. Die hergestellten funktionellen Materialien wurden hinsichtlich ihrer vielversprechenden Komplexbildungseigenschaften untersucht. Diese Polymere finden potenziell Verwendung als hochflexible Bindemittel, die Siliziumdioxidpartikel in funktionalisierten Kautschuken stabilisieren. Bindemittel auf Siliziumdioxid-Basis sind in der Reifenherstellung weit verbreitet, da diese die Nasshaftung auf nasser Oberfläche verbessern, während der Rollwiderstand vergleichsweise minimiert wird. Ein weiteres wichtiges Thema dieser Arbeit ist die Synthese von Polydienen mit hoher Glasübergangstemperatur als potenzieller Ersatz für Polystyrol in thermoplastischen Elastomeren. Alle Themen verbindet das gemeinsame Ziel, Hochleistungspolymere aus biobasierten Ressourcen zu synthetisieren. Zu diesem Zweck wurden Syntheseverfahren ausgehend von Terpenen und anderen natürlich verfügbaren Rohstoffen entwickelt, um maßgeschneiderte Monomere herzustellen, die sich für die lebende anionische Polymerisation eignen.

Kapitel 2 befasst sich mit der anionischen (Co-)Polymerisation neuartiger hydroxylhaltiger Styrolmonomere auf der Grundlage von Zimtsäurederivaten. Die Hydroxylfunktionalität wurde durch Acetal- und Silylschutzgruppen geschützt. Die anionische Polymerisation der geschützten Monomere führte nach der Entfernung der Schutzgruppe unter milden, sauren Bedingungen zu definierten Polymeren. Nach Demethylierung zeigten die erhaltenen Polycatechole vielversprechende Komplexbildungseigenschaften im basischen Milieu. Die multi-hydroxyl-funktionellen Polymere wurden weiterhin als Makroinitiatoren für Pfropf-Copolymeren mit L-Lactid und 4-Methyl- ϵ -caprolacton verwendet.

Kapitel 3 beschreibt die Synthese eines diol-funktionellen 1,3-Dien-Monomers (MyrDOL) mittels lebender anionischer Polymerisation. Diese Arbeiten sind sowohl

durch grundlegende synthetische Fragen als auch durch potenzielle Anwendungen motiviert, wie z.B. in füllstoffverstärkten Kautschuken. Die Copolymerisationen von MyrDOL mit β -Myrcen, Styrol und Isopren wurden mittels ^1H NMR-Kinetik untersucht. Es wurde beobachtet, dass die polare Natur der 1,3-Dioxolan-Einheit einen "Selbstmodifizierungs"-Effekt auf die Mikrostruktur von P(MyxDOL) hat, wie er typischerweise für polare Additive (Modifizierungsmittel) wie THF bekannt ist, was zu einem allgemein höheren Einbau von 3,4-Mikrostrukturen führt. Die selektive Einführung von Diolen durch die (Co-)Polymerisation eines Dioxolan-Monomers ermöglicht eine einzigartige Kontrolle der Regiospezifität der Funktionalisierung.

Kapitel 4 behandelt die Darstellung und Polymerisation zyklischer 1,3-Diene. In **Kapitel 4.1** wird die Einführung eines zyklischen 1,3-Dien-Monomers demonstriert. Um ein tieferes Verständnis des Einflusses verschiedener Substitutionsmuster zyklischer 1,3-Diene zu erlangen, wurde die Polymerisation von 1-Vinylcyclohexen (VCH) als Modellverbindung in der carbanionischen Polymerisation untersucht. Die Mikrostruktur des Polydienes wurde mittels NMR-Spektroskopie untersucht. Nach der Hydrierung enthielten die Polymer Einheiten von Poly(vinylcyclohexan), einem hydrierten Analogon von Polystyrol. Weiterhin resultierte die Hydrierung der Polymere zu der Erhöhung der Glasübergangstemperatur auf 114°C mit einer monomodalen Molekulargewichtsverteilung ohne Anzeichen von Kettenbrüchen durch die Hydrierung.

Kapitel 4.2 vertieft die Studien über zyklische und sterisch anspruchsvollere 1,3-Diene. Dieses Kapitel beschreibt die Synthese und Charakterisierung von Nopadien und die Polymere dieser natürlich vorkommenden Verbindung. Die Mikrostruktur (1,4- und 3,4-Einbau) des resultierenden Polydiens wurde durch NMR-Spektroskopie untersucht. ABA-Triblockpolymere mit unterschiedlichen Molverhältnissen und Molekulargewichten wurden durch lebende anionische Polymerisation der biobasierten Monomere Nopadien und β -Myrcen hergestellt. Die resultierenden thermoplastischen Elastomere wurden durch SAXS-Messung auf

Mikrophasenseparation untersucht. Aufgrund der hohen Glasübergangstemperatur von Nopadien, bedingt durch die sterischen Anspruch und die Steifigkeit des Monomers, ist Polynopadien eine interessante Alternative zu Polystyrol, z.B. in Hochtemperaturanwendungen von thermoplastischen Elastomeren.

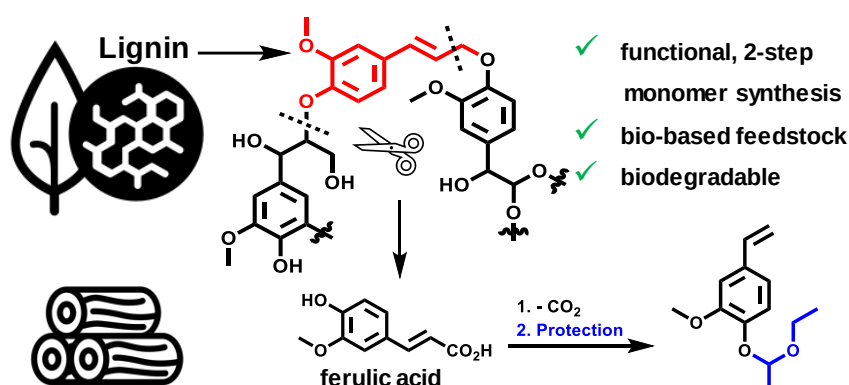
Kapitel 4.3 erweitert den Anwendungsbereich der zyklischen 1,3-Dien-Monomere mit einem einzigartigen Substitutionsmuster. Diese Arbeit beschreibt die Synthese und die anionische Polymerisation von 4-Isopropylvinylcyclohexen (4IPVCH). Ausgehend vom bio-basierten Terpenoid Perillaldehyd wurde zweistufigen Synthese 4-Isopropyl-vinylcyclohexen (4IPVCH) erhalten. Es wurde dargestellt, dass 4IPVCH anionisch polymerisiert mit enger Molekulargewichtsverteilung und präziser Molekulargewichtskontrolle.

Appendix A1 berichtet über die dynamischen Eigenschaften von Polymyrcene. Es wurde eine Reihe von Polymyrcen-Homopolymeren mit identischer Mikrostruktur (95 % 1,4-Einheiten und 5 % 3,4-Einheiten) mittels dielektrischer Spektroskopie und Rheologie untersucht.

Graphical Abstract

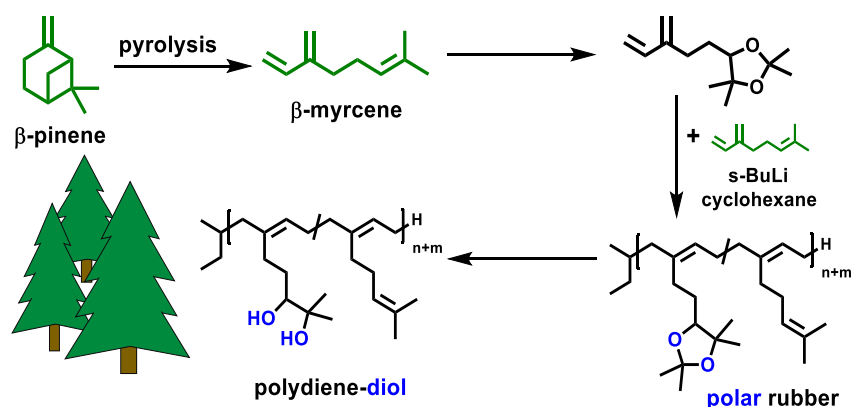
Chapter 2: Functional Styrene Monomers

Anionic Polymerization of Bio-based Functional Styrene Monomers - Convenient Access to Poly (hydroxystyrene) obtained from Renewable Resources



Chapter 3: Functional 1,3-Diene Monomers

MyrDOL - a Protected Dihydroxyfunctional Diene Monomer Derived from β -Myrcene: Functional Polydienes from Renewable Resources via Anionic Polymerization

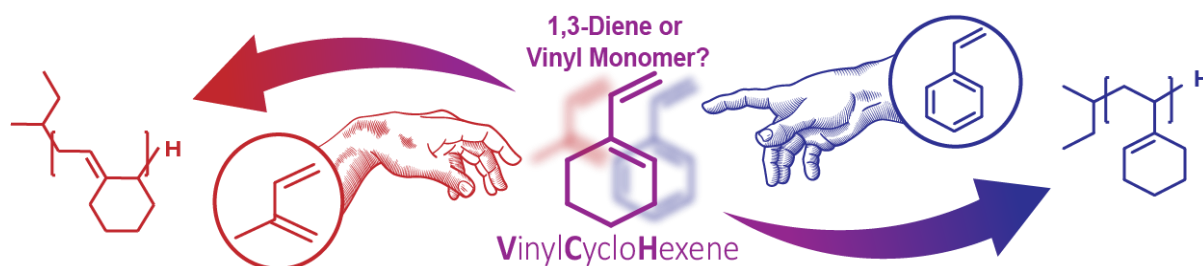


Published in *Macromolecules* 2022, 55, 10, 4046-4055, DOI: 10.1021/acs.macromol.2c00367

Chapter 4: Anionic Polymerization of Cyclic 1,3-Dienes

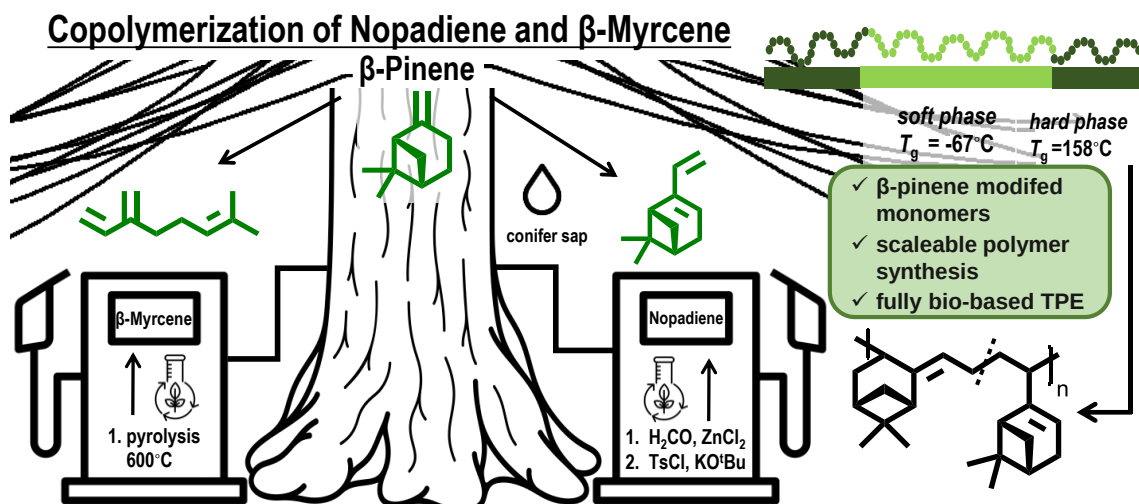
Chapter 4.1

Merging Styrene and Diene Structures to a Cyclic Diene: Anionic Polymerization of 1-Vinylcyclohexene (VCH)



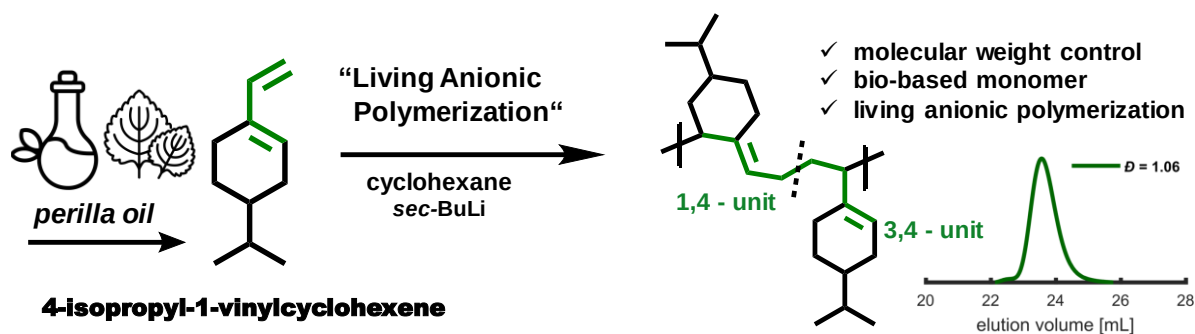
Chapter 4.2

Nopadiene: A Pinene-Based Cyclic Diene for Fully Bio-Based Thermoplastic Elastomers



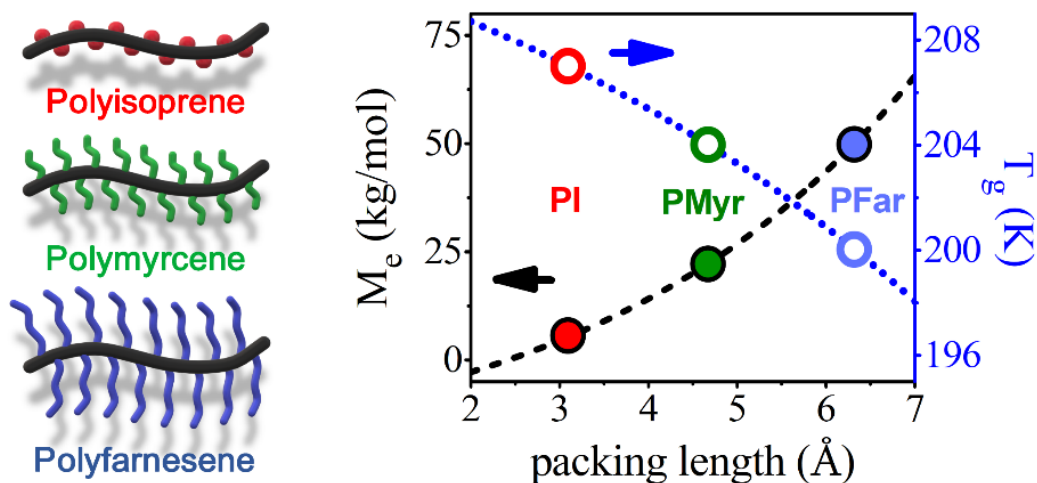
Chapter 4.3

Anionic polymerization of 4-isopropyl-1-vinylcyclohexene – expanding the scope of cyclic 1,3-diene monomers from natural resources



Appendix Chapter A1:

Molecular Dynamics and Viscoelastic Properties of the Biobased 1,4-Polymyrcene



Published in *Macromolecules* 2022, 55, 8766–8775, DOI: 10.1021/acs.macromol.2c01507

Chapter 1 Introduction

1 Introduction

1.1 Living anionic polymerization

1.1.1 Historic background

Living anionic polymerization of vinyl and 1,3-diene monomers using organo-lithium initiators is an established polymerization technique with precise control over molecular weight, molecular weight distribution, block copolymer sequence and microstructure. The discovery of the understanding of the living nature of the anionic polymerization goes back to 1956, when Michael Szwarc described the electron transfer of sodium naphthalide to styrene in THF.¹ However, the industrial utilization of the anionic polymerization in industry started much earlier in the 20th century, e.g., for the synthesis of synthetic rubber by the polymerization of butadiene and styrene using sodium.² The second world war accelerated the investigation of synthetic rubber in the United States and Europe, driven by the inability to secure the rubber supply with natural rubber (1,4-*cis*-polyisoprene) from international trading partners and by the naval blockade against Germany. The United States established the so-called US Government Synthetic Rubber (GR-S) program, to support the independent production of artificial rubber, all run by different companies.³ Shell chemical company was successful in developing a synthetic rubber called GR-S, Government Rubber–Styrene, the first large-volume commercial polymer produced in the United States. This material is nowadays known as SBR, a random or tapered copolymer of styrene and butadiene, which vulcanized by sulfur. Later, Shell sold shares of this division to create a still existing company named “Kraton”.

Today, nearly 46% of the worldwide rubber consumption relies on 1,4-*cis*-polyisoprene, obtained from *hevea brasiliensis*, grown in plantations in tropical regions. The global rubber market was valued at USD 45.18 Billion in 2021, and is expected to reach a value of USD 65.73 billion by 2028.⁴

1.1.2 Living anionic polymerization of functional monomers – functional styrenes

There are three distinctive approaches to introduce functionality to a polymer backbone: i) introduction of a functional end-group by applying functional end-capping agents or the use of functional initiators; ii) postmodification reactions; iii) utilization of functional monomers. The focus of the following chapter is on functional monomers in the field of living anionic polymerization.

The living anionic polymerization starts with a nucleophilic initiation reaction of an organometallic compound with a double bond, either of a vinyl or 1,3-diene monomer. The living anionic polymerization of styrene monomers generates a both reactive and stable benzyl-type polystyryl-anion at the chain-end, whereas 1,3-dienes are mesomerically stabilized by the adjacent double bond. Although the stabilization of the living carbanion in 1,3-diene polymerization is less pronounced, the resulting delocalization is fairly developed to stabilize the anion. These carbanions belong to the most reactive class among basic and extremely nucleophilic reagents. This translates to challenges whenever the living anionic polymerization of functionalized monomers is attempted. A key challenge of carbanionic polymerization is the reaction of functionalized styrene derivatives, since most functional groups are incompatible with anionic initiators and the propagating chain end.⁵

Nevertheless, numerous successful examples have been reported for the living anionic polymerization of functionalized styrene and 1,3-diene derivatives, relying on protective group chemistry.⁵ In addition to the employed protective groups, the choice of solvent plays a crucial role in the living anionic polymerization. Living anionic polymerization can be subdivided in two opposing strategies that both lead to controlled molecular weight and extremely narrow molecular weight distributions. The polymerization is performed either in polar solvents like THF at low temperatures (typically lower than -78°C) or in nonpolar hydrocarbons like cyclohexane or benzene at room temperature or higher.⁶ The polymerization in polar

solvents is accompanied by complete dissociation of the ions, resulting in a highly reactive “naked” carbanion.⁷ The polymerization in apolar media is described by a coordinative mechanism of aggregated chain-ends of organometallic complexes.⁸ These different solvents can influence the nucleophilicity of the carbanions by many orders of magnitude. In industry, polymerization in nonpolar media is the method of choice since the realization of low temperatures in THF is excessively energy intensive. It is noteworthy that 1,3-dienes cannot polymerize at temperatures below 0°C due to extremely slow propagation.⁹ For this reason, it remains a challenge to copolymerize functional styrenes and 1,3-dienes.

Functional styrene monomers have been investigated intensively by Hirao and coworkers in the early 1990s.^{10–12} A library of different substitution patterns and functional groups was investigated in great detail, including ether, sulfide, halogen, silyl, amino, phenol, hydroxyalkyl, acetal, formyl, ketone and ester functionalities (Figure 1).

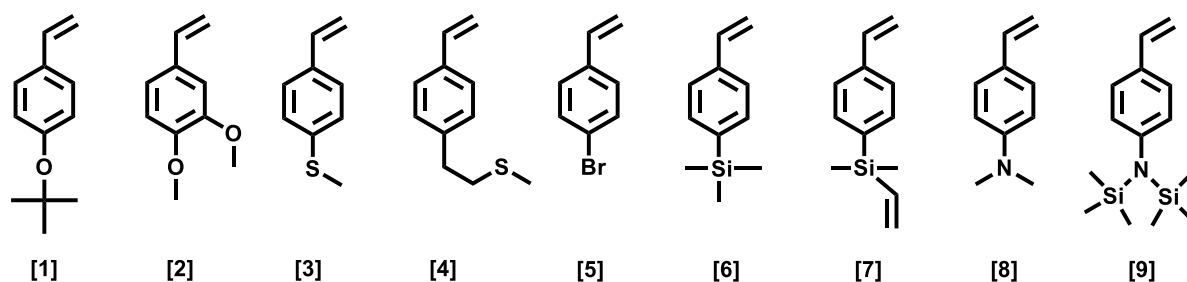


Figure 1: Overview of functional styrene monomers containing ether, sulfide, halogen, silyl, and amino functionalities.

Ether-functionalized styrene monomers have been described in literature.¹³ It was reported that *tert*-butoxystyrene [1], 2- and 4-methoxystyrene and 3,4-dimethoxystyrene [2] undergo living anionic polymerization in THF at -78°C to afford polymers with predictable molecular weights and narrow molecular weight distribution.¹³ The *tert*-butoxy group required harsh conditions with strong acids for its quantitative removal, to generate poly(4-hydroxystyrene). The introduction of polarity into the monomer is an elegant method to adjust the solubility of the polymers in polar solvents. Often the objective is to synthesize water-soluble

polymers.¹⁴ Indeed, these *tert*-butoxy ethers are utilized to prepare hydroxy-functional polystyrenes after removal of the *tert*-butoxy group.¹⁵ Tertiary amines and ethers are often used in industry as modifiers and additives in anionic polymerization to adjust monomer distribution and microstructure.¹⁶ This means they must be stable and indifferent towards strong nucleophiles.

3,4-Dimethoxystyrene [2] represents a compound bearing a protected catechol-functionality within its structures. However, the methoxy groups at the aromatic ring are prone to proton abstraction at elevated temperatures in toluene, leading to broad molecular weight distributions.^{17,18} Polymers of 3,4-dimethoxystyrene are often used as readily polymerizable precursors to polycatechols, as it is less prone to oxidation.¹⁷ It was demonstrated that 3,4-dimethoxystyrene and the resulting polymer is demethylated using boron bromide or chloride, resulting in polycatechols.¹⁹ This unique feature gives access to a versatile platform of multi-hydroxy functional polymers. 3,4-Dimethoxystyrene, known as vinylveratrole, is found in the essential oil of bee glue (propolis). The monomer possesses interesting bioactivity, e.g., antibacterial, antioxidative, and antifungal properties.

Sulfide and thiol containing styrene monomers can undergo living anionic polymerization under specific conditions.²⁰ However, it is challenging to introduce sulfides in anionic polymerization reactions. Sulfides as structural homologs of ethers, are considerably more reactive than ethers towards anionic, highly nucleophilic species. The carbon-sulfur bond in [3] is already cleaved by alkali-metal naphthalenides, much weaker nucleophiles than carbanions of living polymer chain ends or organo lithium initiators. However, the introduction of sulfides into polystyrene is of significant interest in the tire industry, because sulfur and sulfur containing additives are used in the vulcanization process to enhance matrix-filler interaction. On the contrary, the anionic polymerization of 4-methyl sulfide styrene [3], initiated with *sec*-BuLi at 0 °C or 20 °C in apolar solvents resulted in polymers with broad molecular weight distributions in low yields, indicating that side reactions occurred under such conditions.²⁰

The direct anionic polymerization of 4-halostyrene was demonstrated, although the results in literature are ambiguous. Shima, Königsberg and Jagur-Grodzinski reported on the living anionic polymerization of 4-chloro and 4-bromo styrene, whereas Prissette et al. stated that the polymerization was accompanied by severe side reactions.²¹⁻²³ Moreover, 4-bromostyrene as a starting material is of great interest, since the inertness of styrene toward Grignard reagents facilitates the rapid and convenient preparation of protected styrene monomers in *para*-position.²⁴ In general, the introduction of functionalities often relies on the nucleophilic addition or substitution using (4-vinylphenyl) magnesium bromide.^{25,26}

Publications on styrene derivatives with silyl groups and polymers thereof appeared in the 1950s and 1960s, albeit in the context of radical polymerization. The first report on living anionic polymerization of styrene derivatives with silyl groups was published in the early 1980s. The authors reported that 4-trimethylsilylstyrene [6] and 4-dimethylvinylsilylstyrene [7] undergo living anionic polymerization.^{27,28} However, 50 years later the copolymerization of 4-trimethylsilylstyrene and isoprene was investigated by detailed, real-time NMR kinetic studies, revealing a soft gradient-copolymer structure.²⁹

The polymerization of *N,N*-dimethyl amino styrene [8] and *N,N*-bis(trimethylsilyl)amino styrene [9] was reported as well.³⁰ The stability of the protecting group (*N,N*-bis(trimethylsilyl)) is remarkable. The Si-N bond is perfectly stable towards anionic initiators and polystyryl-lithium in THF at -78°C and at elevated temperature to even room temperature.³¹ The amino group of [9] can be generated by cleavage of the protecting group under rather mild conditions (pH =5).

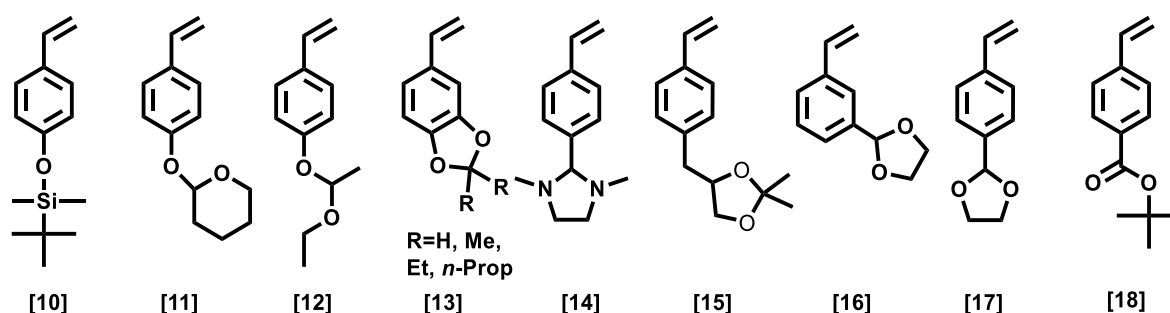


Figure 2: Overview of functional styrene monomers containing protected phenol groups, acetal, formyl, ketone, hydroxyalkyl and ester functionalities.

Polymers containing phenols or aliphatic hydroxyl groups are interesting macroinitiators for graft-copolymers. Evidently, hydroxyl and phenol groups have to be protected in anionic polymerization. Several strategies have focused on the preparation of poly(4-hydroxystyrene) using different protective groups. It is possible to protect the phenolic hydroxyl group by the corresponding *tert*-butylether, but the cleavage can be challenging, since it requires strongly acidic conditions.¹³ 4-Hydroxystyrene can be successfully protected by *tert*-butyldimethylsilyl chloride (TBDMS).³² This strategy is also suitable for the protection and polymerization of the *meta*-analog of [10].³³ It is interesting to note that the substitution position of the *tert*-butyldimethylsilyl group, i.e., *ortho*, *meta* or *para* is crucial for the stability of the protecting group. The anionic polymerization of 2-*tert*-butyldimethylsilyloxystyrene failed with several initiators.³³ It has been proposed that intramolecular silicon attack by the chain-end carbanion may occur in the polymerization in this case.

Anionic polymerization of acetal-protected monomers [11+12] proceeded quantitatively in THF at -78°C.^{34,35} Acetals and ketals are known in organic chemistry for their high stability towards strong basic conditions, but are easily hydrolyzed in acidic environment into their respective carbonyl and diol moiety. *Para*-1-ethoxyethoxy styrene [12] deserves special attention, because it possesses significant advantages over ether-functionalized styrenes, regarding the mild cleavage conditions of the acetal to gain access to hydroxyl-functional polystyrenes. In a facile addition reaction, the 1-ethoxyethoxy acetal is introduced *via* reaction of vinyl ethyl

ether with hydroxystyrene. The methylation of phenolic hydroxyl groups may lead to very stable protection, but these structures suffer from harsh deprotection conditions. In addition, *N,N*-acetals are suitable protecting groups in anionic polymerization. It was demonstrated that the *N,N*-acetal protected monomer [14] was polymerized in a living manner in THF at -78°C , using *sec*-BuLi as an initiator.³⁶

Catechol-functionalized styrene monomers with varying substitution pattern in 2,3 and 3,4-position have been reported.¹⁴ The catechols were protected with ketones to the corresponding ketals with different alkyl side chains (H, Me, Et, *n*-Prop). The introduction of such complex functionalities required tremendous effort and resources to selectively address the benzene ring Figure 3.

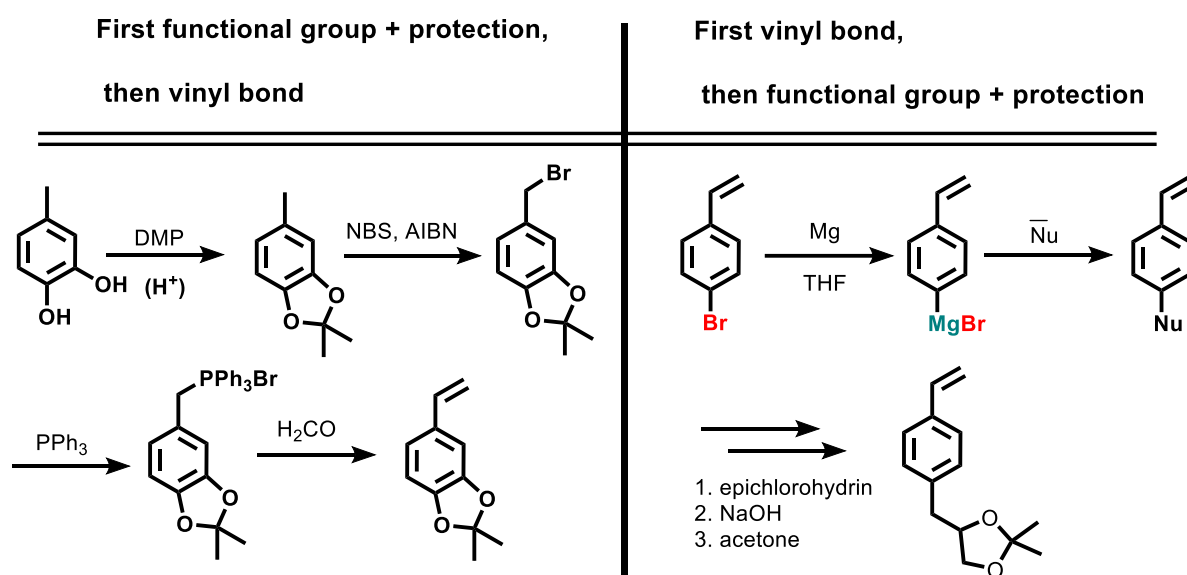


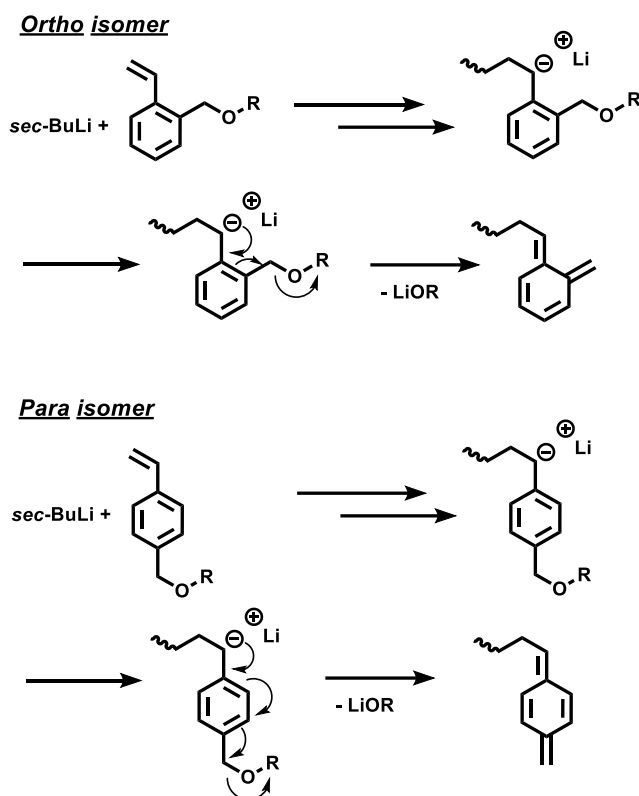
Figure 3: Opposing synthesis strategies for the preparation of functional styrene monomers.^{14,24}

In Figure 3 it is demonstrated that the preparation of functional styrene monomers can be subdivided in two fundamentally different strategies. The first strategy starts with the functional group and its protection and subsequently introduces the polymerizable vinyl bond *via* Wittig reaction.¹⁴ The synthesis route of functional styrenes has to be adjusted depending on the nature of the functional group. Acidic condition must be avoided under all circumstances, since this would readily cleave the protecting group.

Nevertheless, functional styrene monomers are accessible using 4-bromostyrene as a precursor (Figure 3, right). In contrast to the aforementioned synthesis route, the vinyl bond is already present in the structure of 4-bromostyrene.²⁴ Converting the latter into 4-vinylphenyl magnesium bromide, a variety of nucleophiles can attack the aromatic benzene ring. When the functional group is addressed after the introduction of the vinyl bond, the monomer is susceptible to polymerization, which is a drawback during workup and purification of the monomer.

It was demonstrated that the acetal protective groups work in both ways to protect either 1,2-diols or ketones. The copolymerization of styrene and monomer [15] resulted in controlled polymers with narrow molecular weight distributions ($M_w/M_n < 1.14$) in THF at -78°C and gave access to multi-hydroxy functional polystyrene after deprotection of the ketal protecting group.²⁴ The resulting diol of [15] can be used as a macroinitiator for graft copolymers. On the contrary, the polymerization of [15] in cyclohexane proceeded to only small amounts of homopolymer with dispersity $\bar{D} = 2.1$ after 192h.

Besides the nature of the substituent, its position at the styrene scaffold plays a key role. Monomer [16], possessing with an acetal protected formyl functionality in *meta*-position is polymerized under living anionic conditions to predictable molecular weights and narrow molecular weight distributions.³⁷ In contrast, the respective *para*-substituted (or *ortho*) monomer [17] shows no polymerization at all. As a proof of concept, Rickborn et al. demonstrated that the treatment of *ortho*-tolualdehyde dimethylacetal with lithium diisopropylamide resulted in an anion rearrangement followed by a 1,4-elimination of the alkoxide anion.³⁸ The same rearrangement and elimination occurred in the anionic polymerization of *ortho* and *para*-substituted benzylic ethers.



Scheme 1: Proposed reaction pathway of styrene derivatives possessing benzylic ether skeletons in anionic polymerization.⁵

As demonstrated in Scheme 1, styrene derivatives possessing benzylic ether skeletons may undergo rearrangement reactions, followed by a 1,6- or 1,4-elimination reaction of lithium alkoxide. The anionic polymerization of styrene derivatives having benzylic ether skeletons represents a challenging task. The rearrangement as demonstrated in Scheme 1, is not possible in the *meta*-position, which explains the suitability of [16] for the living anionic polymerization. In other positions an alkyl spacer between the functionality and the aromatic ring is required for the successful polymerization, as demonstrated in the polymerizable monomer [15].

Ester-functional styrene monomers have been reported. Esters are usually attacked by nucleophiles, but it has been reported that some sterically hindered esters such as *tert*-butyl esters can undergo living anionic polymerization even in the presence of organolithium and Grignard reagents under certain conditions. For instance, *tert*-

butyl 4-vinylbenzoate [18] was quantitatively polymerized with cumylpotassium and potassium naphthalenide in THF at -78°C.³⁹

1.1.3 Functional monomers from natural feedstocks

Sustainable polymers from lignocellulosic biomass do not only show the capability for reducing the environmental impact of commercial plastics. They also offer the facile introduction of functionalities compared to petrochemical-derived polymers. The additional benefit of natural compounds is the reasonable use of specific and refabricated molecular structures for special purposes as functional materials, which cannot be easily obtained from petrochemical resources. Although lignocellulosic biomass is the most abundant biomass source on earth, the separation and refinery of the material remains challenging. In this section, the focus is placed on the utilization of lignocellulosic biomass as a starting material for the synthesis of functional monomers. Figure 4 demonstrates how reductive catalytic fractionation of lignocellulosic biomass can provide a variety of valuable monomers covering bisphenol A (BPA) alternatives and vinyl monomers.⁴⁰

Different from these classical fossil-based approaches, the use of naturally occurring cinnamic acid derivatives as starting materials for functional styrene monomers has been demonstrated in literature. Kamigaito et al. reported on the synthesis of vinylcatechol *via* decarboxylation of caffeic acid and subsequent RAFT polymerization to obtain polyvinylcatechol.⁴¹ The decarboxylation of cinnamic acid derivatives represents an elegant synthesis pathway due to the neat reaction conditions and convenient workup. This route embodies the prefabricated styrenic structures of lignin and releases the polymerizable vinyl bond *via* decarboxylation. Even though RAFT polymerization is known for its large tolerance toward functional groups, phenols have to be masked by protecting groups, because they act as radical scavengers. Further studies based on ferulic acid (3-methoxy-4-hydroxy cinnamic acid), using silyl protecting groups, revealed the facile access to hydroxyl-functional polystyrenes after quantitative deprotection.⁴²

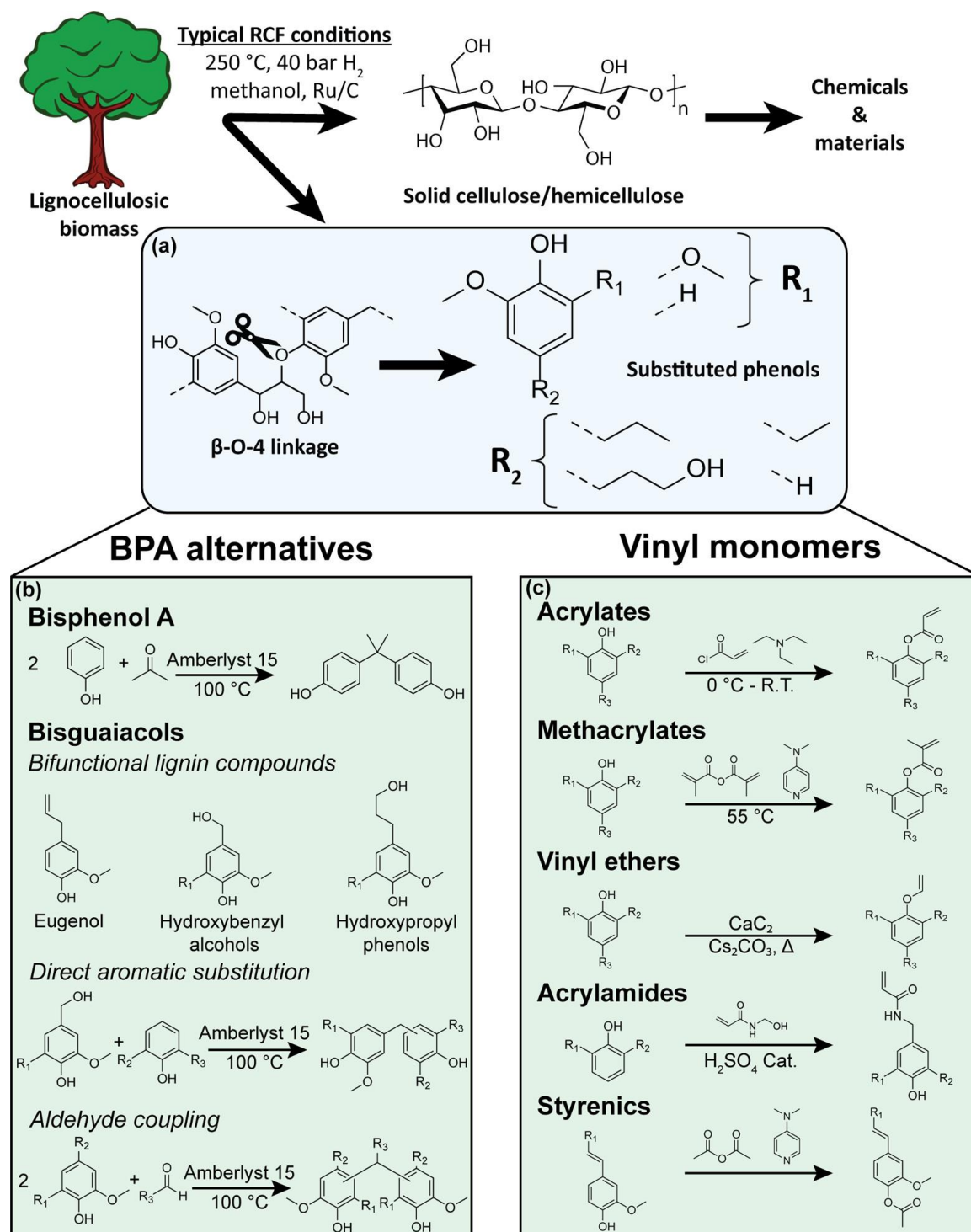


Figure 4: a) Reductive catalytic fractionation of lignocellulosic biomass to solid cellulose and substituted phenols. The R₁ and R₂ groups are influenced by the type of biomass and processing conditions. (b) BPA alternatives from lignin derivatives, including monoaromatics and coupled compounds. (c) Vinyl monomers from lignin derivatives and model compounds.⁴⁰

Hydroxyfunctional and hydroxyl terminated polystyrenes were used for the synthesis of graft copolymers consisting of a rigid polystyrene backbone and poly(L-

lactide) side chains by applying the “grafting from” approach^{43–45} These graft copolymers are promising candidates for water filtration systems.⁴⁶ The self-assembly of block copolymers can produce membranes with narrow pore-size distributions and high porosities. Copolymers of styrene and L-lactide phase separate into specific nano domain structures with cylindrical phase morphology. After the distinct phase separation, the L-lactide block is etched under acidic conditions, leaving only defined pores in the polystyrene matrix.

Besides the production of phenols, acrylates, methacrylates, vinyl ethers, acrylamides and styrenics, lignin can provide 4-alkylguaiacols in large quantity by means of catalytic depolymerization conditions.^{40,47} The 4-alkylguaiacols are converted into 4-alkylcyclohexanols, followed by dehydrogenation to form cyclohexanones, and subsequent Baeyer–Villiger oxidation yields 4-alkylcaprolactones.⁴⁸ The resulting polyesters of 4-alkylcaprolactones may be considered as a substitute for butadiene-based elastomers with low T_g . Fully bio-based copolymers are based on i.e., poly-4-methylcaprolactone and poly(L-lactide). Using a bifunctional initiator gives access to telechelic poly-4-methylcaprolactone.⁴⁸ Then, poly(L-lactide) is polymerized with $\text{Sn}(\text{Oct})_2$ as catalyst onto the polyester, resulting in well-defined ABA triblock copolymers of hard poly(L-lactide) end blocks and soft poly-4-methylcaprolactone midblock.⁴⁸

1.1.4 Living anionic polymerization of functional monomers – functional dienes.

1.1.4.1 Nonpolar 1,3-dienes

In general, conjugated 1,3-dienes undergo polymerization using different polymerization methods such as catalytic, radical, cationic, and anionic techniques. This section will outline the current state of functional diene monomers in living anionic polymerization and summarizes recent development and perspectives.

The widespread investigation of polybutadiene and polyisoprene both in academia and industry demonstrates the broad relevance of synthetic elastomers. Besides the native occurrence of natural rubber (*cis*-1,4 polyisoprene), most synthetic elastomers rely on the anionic polymerization of 1,3-butadiene or isoprene. Among synthetic elastomers, highly *cis*-1,4-configured polymers have attracted great attention, because of similar elastic properties as natural rubber. The stereochemistry is significant, since the elastic properties of 1,3-diene polymers strongly depend on the microstructure.

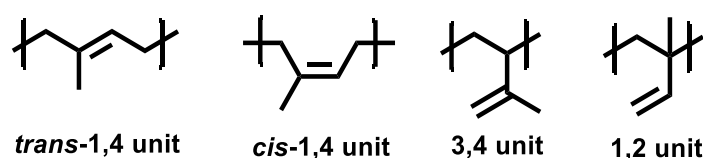


Figure 5: Possible microstructures of polyisoprene.

As demonstrated in Figure 5, multiple microstructures of polyisoprene exist, and they differ i.e., in their glass transition temperature (T_g) and surface binding properties. The glass transition temperatures of the *trans*-1,4 and *cis*-1,4 units are in the range of -58°C to -73°C , whereas the glass transition temperatures of PI consisting of 3,4 and 1,2 units are 33°C and 9°C , respectively.^{49,50} The contrasting flexibility of the accessible microstructures determine the mechanical properties and applications of synthetic rubbers. In carbanionic polymerization, the polydiene microstructure is affected by the choice of solvent, counter ion, as well as chain end concentration and

the temperature.⁸ The control over microstructure is attained by using polar additives.⁵¹

Ethers and tertiary amines as well as alkoxides which act as Lewis bases are representative examples of polar modifiers.⁵² These polar compounds have the ability to complex the respective counter ion and thereby the incorporation of the next monomer unit is influenced in a significant manner. Generally, it can be stated that the addition of polar modifiers leads to higher 3,4 and 1,2 units in 1,3-diene polymerization. Although the adjustment of the microstructure of 1,3-butadiene and other 1,3-dienes has been studied intensively, examples of functional diene monomer are rather limited because of their synthetic difficulty. 1,3-Dienes are highly reactive due to the possibility to react in cycloaddition reactions. The access to functional dienes is therefore restrained because synthetic approaches often fail when introducing the second double bond of the diene.

However, there are reports on the living anionic polymerization of 2-alkyl-butadienes with lithium initiator using hydrocarbon solvents such as heptane and benzene as well as polar solvents like THF.⁵³ It is considered that 2-alkyl-butadienes generally undergo living anionic polymerization under carefully selected conditions (temperature, solvent, initiator). The length of the alkyl or alkenyl chain can be extended even by an additional C₅ (β -myrcene) and C₁₀ (β -farnesene) unit.

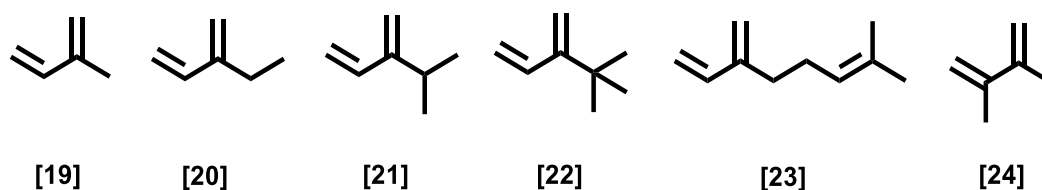


Figure 6: 2-Alkyl-1,3-butadiene and 2,3-dialkyl-1,3-butadiene derivatives.

Regarding the stereochemistry of the resulting polymers of [20-22], a general trend of higher *cis*-1,4 microstructures was observed when using the sterically bulkier alkyl-substituted 1,3-butadiene.^{6,54} The same results were observed for polymers obtained in polar solvents.

Introducing a second alkyl substituent at isoprene results in the formation of 2,3-dimethyl-1,3-butadiene [24] with fully different properties. 2,3-Dimethyl-1,3-butadiene was polymerized using *sec*-BuLi, Na, or K metal in THF and with *sec*-BuLi, EtLi, or K metal in benzene.⁵⁵ Fetters and Mays reported the living anionic polymerization of 2,3-dimethyl-1,3-butadiene in cyclohexane, resulting in almost exclusive 1,4-polymers (97 %), and in cyclohexane-triethylamine mixtures to provide a mixture of 1,4-polymer (55 %) and 1,2-polymer (45 %) with controlled molecular weights and narrow molecular weight distributions.⁵³ The structural isomer of 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, was polymerized using with *sec*-BuLi in benzene at 40 °C.⁵⁶ It is noteworthy that the resulting polymer exhibited an exclusively regulated 1,4-microstructure with a *cis:trans* ratio of 64:36. Hydrogenation of this polymer would result in atactic polypropylene.^{56,57}

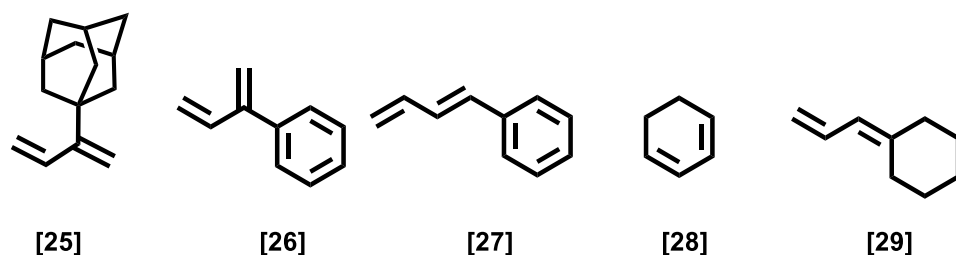


Figure 7: Alkyl- and aryl-1,3-butadienes with various substitution patterns.

Substituted 1,3-butadienes having bulky alkyl and aryl side chains have been reported in the field of living anionic polymerization. For instance, Ishizone et al. described the polymerization of the extremely sterically hindered 2-(1-adamantyl)-1,3-butadiene [25] by means of living anionic polymerization using either *sec*-BuLi in cyclohexane at 40 °C or potassium naphthalenide in THF at -78°C.⁵⁷

2-Phenyl and 1-phenyl 1,3-butadiene [26+27] were anionically polymerized in a living manner using hydrocarbon solvents at elevated temperatures and THF at -78°C, since they combine styrene and 1,3-diene structures.⁵⁸ The anionic polymerization of 1-phenyl-1,3-butadiene with *sec*-BuLi in hexane or benzene resulted in polymers composed of *cis*-1,4 (25–28 %), *trans*-1,4 (49–59 %), and 3,4-vinyl (16–23 %) contents.⁵⁹ On the contrary, polymers of 2-phenyl 1,3-butadiene were obtained under

the same conditions with high *cis*-1,4 microstructure of over 90 %. In addition, it was found that the temperature had an influence on the microstructure, as the highest *cis*-1,4 content was obtained in THF at 57 °C and gradually decreased from 98 to 72 % by lowering the polymerization temperature to -100 °C.

It was demonstrated that 1,3-cyclohexadiene [28] with a fixed *cisoid* 1,3-diene structure undergoes living anionic polymerization with *sec*-BuLi in the presence of tetramethylethylenediamine (TMEDA) in cyclohexane at 40 °C.⁶⁰ More recently, it was found that 1,2-dimethylene cyclohexane can be polymerized using *sec*-BuLi in toluene.⁶¹ The monomers 1,3-cyclohexadiene and 1,2-dimethylene cyclohexane have the same fixed *cisoid* 1,3-diene structure, but behave completely different regarding polymerization and solubility. However, the poor solubility of the resulting polymers in chloroform or THF made the molecular weight determination challenging.

The allylidene monomer [29], a 1,1-substituted 1,3-butadiene, was successfully polymerized using *sec*-BuLi as an initiator in benzene and THF as solvent.⁶² The obtained polymers have predictable molecular weights based on the molar ratios of monomer and initiator and narrow molecular weight distributions ($\mathcal{D}$ < 1.08-1.28). Interestingly, the obtained microstructure of the 1,1-substituted 1,3-diene polymer in benzene and THF show an inverse trend compared to the microstructures of polyisoprene. The results demonstrate that using THF as solvent, the polymer exhibits predominantly *trans*-1,4 (90%) microstructure. Using benzene as solvent, a mixture of 66% *trans*-1,4 and 34% 3,4-units is obtained.

1.1.4.2 Polar 1,3-dienes

Similar requirements and challenges as for functional styrene monomers apply for the living anionic polymerization of functional 1,3-diene monomers. In contrast to the living anionic polymerization of styrene in THF at low temperatures, the polymerization of 1,3-dienes is not possible below 0°C in THF.⁹ The anionic polymerization of 1,3-dienes requires unreactive and apolar hydrocarbon solvents at room temperature or higher. The accessibility of functional diene monomers for

carbanionic polymerization is strongly limited, due to the high susceptibility of the structures to the Diels-Alder reaction.

The scope of 1,3-dienes bearing protected functional groups is rather limited, but a few functional monomers have been reported to date, containing silyl or amine moieties.^{63,64} The polymerization of diisopropylaminomethyl-1,3-butadiene [30] using *sec*-BuLi and benzene resulted in lower M_n values than expected and possessed relatively broad molecular weights distributions.⁶³ Further studies on *N,N* dialkyl isoprenes [30] revealed that the functional groups influence the polydiene microstructure towards increased vinyl-content (1,2- and 3,4-units). It was found that alkyl substituents influence the ratio of *cis*- and *trans*-1,4 units. The tendency was that bulky substituents lead to preferred *cis*-configuration. As earlier mentioned, the polymerization of *N,N*-bis(trimethylsilyl)amino styrene [9] demonstrates the stability of the Si-N bond towards *sec*-Buli and carbanionic species.³¹ Attempts have been made to transfer the *N,N*-bis(trimethylsilyl) protecting group to functional 1,3-butadienes [31].

The polymerization of 2-(4-*bis*(trimethylsilyl)amino)butyl-1,3-butadiene [31] was carried out in toluene at 40°C in quantitative yield.⁶³ However, the molecular weight distribution appeared to be bimodal, and the expected M_n differs from the theoretical M_n , indicating that the polymerization was accompanied with side-reactions.⁶ Surprisingly, changing the initiator from *sec*-BuLi to polystyryl-lithium, the diblock-copolymer formation was realized with molecular weights distribution of $\mathcal{D}$ =1.09. As the authors state, the origin of the bimodality remains unknown and therefor the polymerization conditions should be optimized regarding the anionic polymerizability.

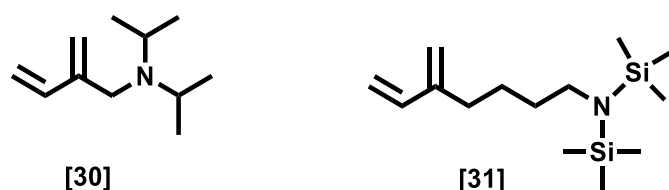


Figure 8: Amine containing 1,3-butadienes.⁶³

More importantly, attempts to anionically polymerize 2-ethoxymethyl-1,3-butadiene failed, because of an unexpected collapse of the monomer structure under the polymerization condition.⁶⁵ *sec*-BuLi, Li-Naph, K-Naph and polystyryl-lithium were used to initiate the polymerization. It was found that the highly reactive carbanion induces an elimination reaction of 2-alkoxy-1,3-butadienes, which leads to the so called “back side collapse”. This means that an alkyl spacer between the 1,3-butadiene unit and the functional group is required to successfully polymerize functional 1,3-dienes.

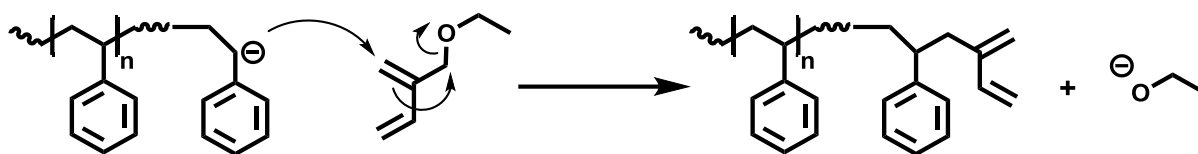


Figure 9: Back side collapse of 2-alkoxy-1,3-butadienes.⁶⁵

Recently, the first successful anionic polymerization of hydroxyl group containing 1,3-diene monomer, based on β -myrcenol, was reported.⁶⁶ β -Myrcenol was obtained by allylic oxidation of β -myrcene, a natural occurring terpene with the appropriate alkyl spacer within its structure. This hydroxyl group was protected with *tert*-butyldimethylsilyl chloride. This spacer indeed makes a difference, since the silyl-protected β -myrcenol was polymerized under living anionic polymerization conditions in cyclohexane at 25°C with controlled molecular weight and narrow molecular weight distribution.

One strategy to generate functional 1,3-diene monomers is the utilization of chloroprene as a precursor in a Grignard-reaction. The synthesis of alkoxy silane substituted 1,3-dienes has been reported but in the field of metal-catalyzed polymerization.⁶⁷ However, the handling and exposure of chloroprene is strongly regulated, because of its extreme toxicity and reactivity. This explains the necessity of the development of new monomer synthesis routes from natural resources, as described in the following chapter.

1.2 Polymerization of terpenes

1.2.1 General polymerization of terpenes

The basic building blocks of terpenes are mono or polyunsaturated C₅ units of isoprene. In nature, the synthesis of terpenes starts with the mevalonate pathway, also known as the isoprenoid pathway. This pathway produces isopentenyl pyrophosphate and dimethylallyl pyrophosphate, which are used to assemble higher isoprenoids, i.e., steroids and hormones. The biological function of terpenes is still an unexplored subject, and the purpose of terpenes has not been fully investigated. It is known that many plants produce volatile terpenes in order to attract specific insects for pollination. On the contrary, bitter-tasting, or toxic terpenes with a higher vapor pressure are produced to protect plants from being eaten by animals (antifeedant).⁶⁸ The practical application of terpenes originates from their olfactory properties as they are used in perfumes, flavors, fragrances, and pheromones. The pharmaceutical chemistry finds applications in terpenes because of the antibacterial, antiviral, and anti-inflammatory activities.⁶⁸

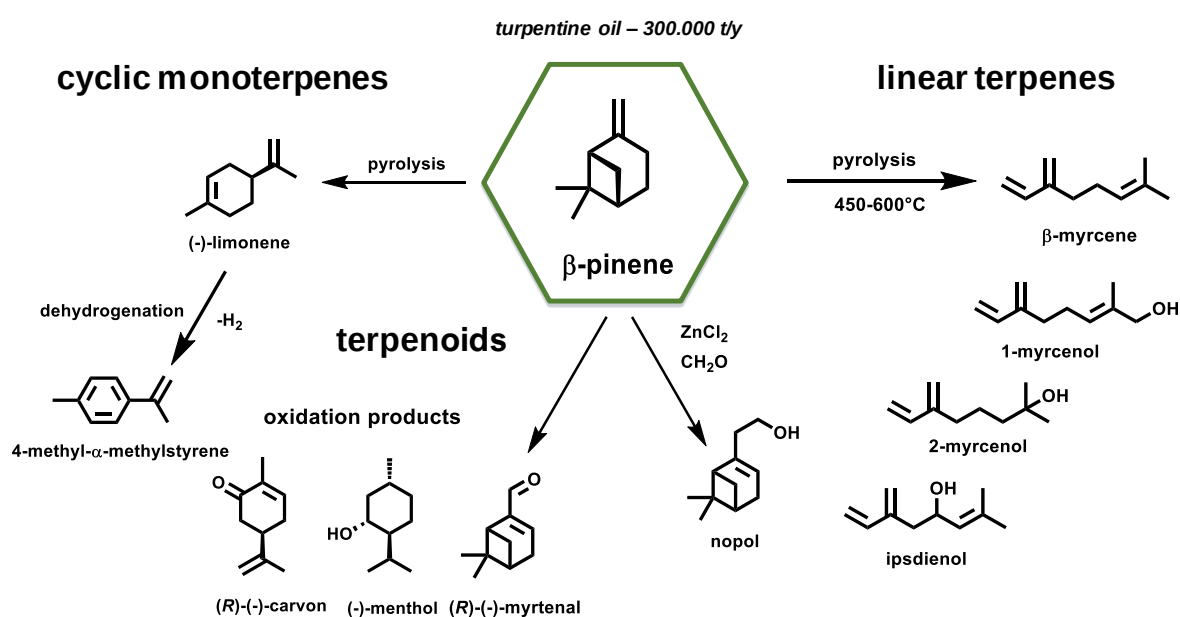


Figure 10: Overview of terpenes obtained from β -pinene.⁶⁹

Besides the pleasant smell of this material class, monoterpenes (C_{10}) and sesquiterpenes (C_{15}) gained great attention as starting materials for the synthesis of monomers in polymer and material science.⁷⁰⁻⁷⁴ The most prominent C_{10} monomers are β -pinene, β -myrcene and limonene. Even though the application of terpenes in chemical synthesis is divers and well supported by many publications, their applications in polymer science are mainly limited to a few monomers.⁷⁵ The direct polymerization of β -pinene by means of Lewis acids, was for a long time limited because only low number-average molecular weight ($M_n < 4000$ g/mol) and poor thermal properties were obtained.⁷⁶ Impressive process has been made in the field of advanced cationic polymerization using $AlCl_3$ etherate catalysts that yielded polymers of β -pinene with $M_n=9000-14000$ g/mol and glass-transition temperature values of $82-87^\circ C$.⁷⁷ Furthermore, Kamigaito et al. reported the direct polymerization of β -pinene in a living manner catalyzed by $EtAlCl_2$ with molecular weights up to 50.000 g/mol, but iterative monomer addition and cryogenic temperatures were required to achieve good conversion.⁷⁸

Among the vast diversity and versatility of naturally occurring terpenes, β -myrcene represents a valuable monomer for the synthesis of elastomers due to its structural similarity to isoprene.⁶⁹ Myrcene is industrially obtained from pyrolysis of β -pinene, a major compound of the turpentine oil.⁷⁹ Minor amount of natural β -myrcene is obtained from the essential oils of bay, basil and hops.⁶⁸ Turpentine oil, the volatile compounds of crude balsams from conifers, is mainly collected as waste product in the pulp and paper industry or is obtained by collecting the balsam of living conifer trees by cutting the bark. The thermal isomerization reaction of β -pinene to β -myrcene is conducted usually without catalyst at temperatures ranging from $450-600^\circ C$ with yields up to 95%.⁸⁰ This process is indeed quite energy intensive and would increase the carbon footprint of this bio-based resource.⁸¹

The first report on the polymerization of β -myrcene goes back to 1913, where Lautenschläger and Staudinger investigated that β -myrcene undergoes autooxidation and polymerization at $80^\circ C$.^{82,83} For most of the terpenes they have investigated, the

autooxidation is faster than the polymerization. However, β -myrcene easily forms polymeric products, which was later described as the radical polymerization of β -myrcene.⁸²

1.2.2 Anionic polymerization of terpenes

Nowadays, β -myrcene is known to be polymerizable by means of free radical, controlled radical, cationic, coordination and living anionic polymerization.⁸⁴⁻⁹¹ The structural requirement to be suitable for living anionic polymerization is the existence of a conjugated diene moiety (1,3-butadiene) or a vinyl bond, that is stabilized by, e.g., an aromatic substituent (phenyl, pyridyl, naphthalyl) or a carbonyl group (acrylates). The stabilization of the resulting carbanion is crucial for the living character of the polymerization. This key requirement is present in a variety of conjugated terpenes, such as in β -myrcene and β -farnesene.

Previous studies demonstrated that β -myrcene was polymerized with high *cis*-1,4 configuration using organo-lithium initiators in cyclohexane with great control over molecular weight and molecular weight distribution.^{91,92} The properties of polymyrcene mimic those of polyisoprene as it exhibits a good backbone flexibility and a low glass transition temperature of -67°C . The microstructure of polymyrcene can be controlled by the employed solvent in anionic polymerization.⁹³

Due to the longer alkyl side chain, polymyrcene (as well as polyfarnesene) features a higher entanglement molecular weight ($M_e = 22 \text{ kg}\cdot\text{mol}^{-1}$)^{94,95}, resulting in a reduced melt viscosity in comparison to polyisoprene. The effect of reduced melt viscosity is attributed to the unique bottlebrush-like structure. This can be advantageous regarding industrial processing of such materials. In addition, the benefit of the utilization of β -myrcene in elastomers can be attributed to the presence of additional cross-link points (higher cross-link density), because of the additional pendent isopropylidene unit within the polyterpene structure.⁹⁶

Various compositions and architectures of β -myrcene and styrene copolymers are obtained by living anionic polymerization.⁹⁷ The architectures range from statistical copolymers, that have a gradient-like structure to block-copolymers, obtained by sequential monomer addition.^{93,97} The statistical copolymerization of this monomer combination results in the formation of block-like or tapered copolymers due to the disparate reactivity ratios of myrcene ($r_{\text{mry}} = 36$) and styrene ($r_{\text{sty}} = 0.028$).⁹⁷ Moreover, the diblock copolymer synthesis including polystyrene and polymyrcene blocks is described *via* a temperature-induced block copolymer formation strategy in THF.⁹⁸ Gallei and colleagues investigated a method that uses the unreactive nature of myrcene in THF at $-78\text{ }^{\circ}\text{C}$. They started the living anionic polymerization with a mixture of styrene and myrcene, which fully converts the styrene fraction into living chain ends of polystyryl-lithium. Increasing the temperature ($-38\text{ }^{\circ}\text{C}$ to room temperature) leads to poly(styrene-*b*-myrcene) formation due to polymerization of myrcene at elevated temperatures.⁹⁸

Aiming at the synthesis of ABA triblock copolymers having polymyrcene as a mid-block, Hillmyer et al. investigated the copolymerization of α -methyl-*para*-methylstyrene and myrcene in THF.⁹⁹ They pursue a fully bio-based approach to gain thermoplastic elastomers obtained from pinene-derivable monomers. Limonene is dehydrogenated to yield α -methyl-*para*-methylstyrene, a monomer that potentially substitute styrene as a high T_g component. The direct synthesis of ABA structures by sequential monomer addition is not possible, because the living chain end of polymyrcene was not sufficiently reactive to reinitiate polymerization of α -methyl-*para*-methylstyrene. They achieved ABA triblock copolymers by the addition of dichlorodimethylsilane to a solution of living poly (α -methyl-*para*-methylstyrene-*b*-myrcene)-lithium, serving as a coupling agent. Moreover, the synthesis of ABA triblock polymers, where A is a α -methylstyrene derivative and B is a 1,3-diene, remains challenging because of mainly two reasons.¹⁰⁰ The first one is the low ceiling temperature, and the polymerization is therefore in equilibrium with residual amount of monomer at room temperature. The ceiling temperatures of a α -methylstyrene and

α -methyl-*para*-methylstyrene are 6°C and 15°C, respectively.^{99,100} The second reason is the slow rate of polymerization at room temperature or below in hydrocarbon solvents, and hence requires the presence of substantial amounts of aliphatic ethers to accelerate the rate. However, the polymerization of the employed 1,3-diene in polar media would significantly alter the microstructure and hence the T_g of the mid-block. The functionalization of polymers vastly expands their range of applications as dispersants, surfactants, or surface modifiers.¹⁰¹ Most studies of polymyrcene focus on the terminal functionalization, using functional initiators or termination agents.^{84,102,103} Haddleton described the synthesis of end-functionalized polymyrcene *via* a one-pot approach using living anionic polymerization of β -myrcene and propylene oxide, butylene oxide, allyl glycidyl ether, 1,2-epoxy-5-hexene and N,N-dibenzyl amino glycidol, for the introduction of a hydroxy functionality.¹⁰³ The polymers show high levels of regioselective termination combined with very high levels of functionalization. This approach has been adapted from the end functionalization of polystyrene with selective end-capping agents such as glycidyl ethers and glycidyl amines.¹⁰⁴ Those α,ω -functionalized polydienes are promising building blocks as they can be used as macroinitiators for graft-copolymers and ABA triblock copolymers.

One of the most straightforward techniques to obtain hydroxyl-functional polymyrcene is the hydrogen peroxide-initiated radical polymerization of β -myrcene in *n*-butanol solution at 100°C.⁸⁴ Besides considerable amounts of side products and oligomer species, the radical polymerization yield polymers with relatively low molecular weight in the range of 2000-4000 g/mol with dispersities of 1.3-1.4.⁸⁴ The obtained OH-functionalized polymers exhibits mainly 1,4-units (77–85% 1,4 and 15–23% 3,4), which translates in the low T_g of -50°C.

Anionic polymerization provides potential for the further functionalization.¹⁰⁵ Similar to other 1,3-diene polymers such as polybutadiene and polyisoprene, polymers of β -myrcene and β -farnesene form rubberlike materials. However, contrary to the

common 1,3-dienes, β -myrcene and β -farnesene provide additional double bonds in their alkyl side chain, which is attractive regarding postmodification reactions. These additional double bond can be epoxidized to increase the polarity of the rubbery material.¹⁰⁶

Schlaad and coworkers applied thiol-ene click chemistry to polymyrcene to introduce ester functionalities, differing in carboxylic acid and alcohol chain length.¹⁰⁷ It is noteworthy that the thiol addition to the side-chain double bonds of polymyrcene was 8–10 times (primary thiol) or 24 times (secondary thiol) faster than to the main-chain double bonds, which is attributed to the different accessibility of the double bonds and steric hindrance. The obtained polymers were further modified by hydrogenation or saponification of the esters, yielding amphiphilic polyelectrolytes.

The same polymerization technique, functionalization, and modification of β -myrcene can be applied to the sesquiterpene β -farnesene. β -Farnesene is obtained from natural resources by the fermentation of sugar cane. Wahlen et al. investigated that the direct (statistical) anionic copolymerization of β -farnesene and styrene in cyclohexane affords block-like, tapered copolymers due to the highly diverging reactivity ratios ($r_{\text{Far}} = 27$; $r_{\text{Sty}} = 0.037$).¹⁰⁵ This feature was used to synthesize a series of tri- (ABA) and pentablock (ABABA) copolymers of styrene and β -farnesene, varying the polydiene volume fraction between 0.50 and 0.68, respectively. The tapered multiblock copolymers showed, depending on composition and polydiene volume fraction, excellent phase-segregated domains of lamellar or hexagonally packed cylindrical structures. Using only nonpolar solvents in anionic polymerization, polyfarnesene results similar to polyisoprene and polymyrcene in high *cis*-1,4 configuration. However, compared to the aforementioned polydienes, the T_g of polyfarnesene is almost independent on microstructure, because the compact branched structure predominates the effect of the backbone.¹⁰⁷ The long side chains of the bottlebrush-like structure have a plasticizer effect and hinder the tight packing of the polymer chains.

1.3 Thermoplastic elastomers and architectures of block-copolymers

Thermoplastic elastomers (TPEs) include the benefits of a of rubbery material, while behaving as viscoelastic liquids (low T_g) and stiff thermoplasts (high T_g).¹⁰⁹ TPEs consist of a rubbery phase that is physically cross-linked by a hard and glassy phase. As a result of the block structure, each homopolymer segment maintains its unique properties, while the block copolymers' mechanical response is a combination of the individual properties of the segments. The incompatibility of the blocks forces the systems to minimize its interphase, resulting in distinct phase separation on nanometer scale.¹¹⁰ Prominent candidates are triblock copolymers based on poly(styrene-*b*-butadiene-*b*-styrene) (SBS) and poly(styrene-*b*-isoprene-*b*-styrene) (SIS).¹¹¹

The phase separation behavior of block copolymers is described by the Flory-Huggins theory.¹¹² In general, the incompatibility between the blocks is determined by the product of the Flory-Huggins interaction parameter (χ) and the degree of polymerization N . The Flory-Huggins interaction parameter describes the change in free energy per solvent molecule when a polymer-polymer and solvent-solvent contact is replaced by a polymer-solvent contact.¹¹³ As a result, the product $\chi \cdot N$ dominates the demixing of polymer blends. Such an incompatibility would generally force the system to undergo macroscopic phase separation if the material is a simple polymer blend. However, covalently linked block-copolymers prevent macroscopic phase separation and a microphase separated morphology results instead. Thus, the only control for the chemist over the phase morphology is determined by the degree of polymerization N .

The mechanical properties of TPEs based on polystyrene and butadiene are dictated by the molar composition, molecular weight and the architecture of the triblock copolymer. Due to a strong correlation between microphase separation and

mechanical properties, every compositional deviation alters morphology and mechanical behavior of the material.

To determine the mechanical properties of a material, tensile testing is the method of choice. In this method, the stress is measured that is applied to a material, as function of strain or displacement. The shape of the resulting stress-strain curve describes the mechanical behavior, as depicted in Figure 11 .

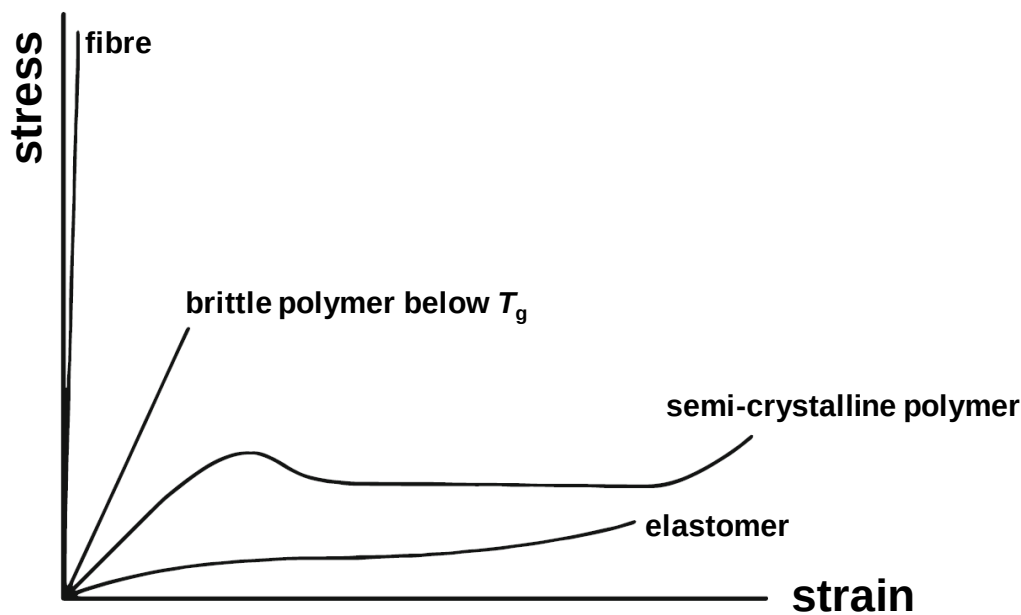


Figure 11: stress-strain curves of different polymer types.¹¹⁴

Figure 11 shows the stress-strain curves of different polymer types, varying from stiff fibers to brittle polymer below T_g over ductile semi-crystalline polymers to elastomers. The beginning of the strain-strains curves starts with a linear section, which slope is representing the Young-modulus. The integrated area under the curve represents the toughness of a material. Some polymers show a yield point, where a temporary drop in stress is observed. More flexible and ductile materials exhibit a necking event after the yield point.¹¹⁵

As mentioned earlier it was investigated that there is a linear correlation between molecular weight and mechanical properties, expressed in an enhancement of entanglements within the domains, providing a better mechanical response.^{116,117}

Furthermore, the morphology dictates the mechanical response. The variability in mechanical response of the morphologies is expressed by a higher Young modulus and toughness for lamellar and double-gyroid morphologies, attributed to an enhanced connectivity of the glassy domains.^{115,118} Differently, pherical and cylindrical morphologies of the glassy domains possess elastomeric behavior with the absence of a yield point.

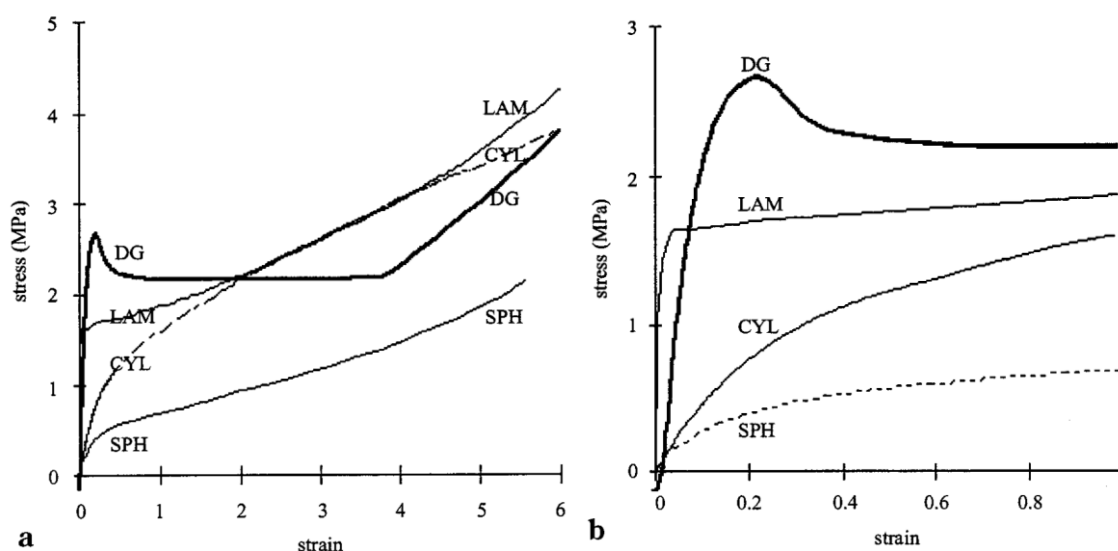


Figure 12: a) Stress-strain curves of isotropic, polygranular DG (bold), overlayed with the classical microdomain morphologies of spheres (SPH), cylinders (CYL), and lamellae (LAM). Key: (a) stress-strain behavior to 600% strain; (b) magnified portion of the stress-strain curve focusing on the 0-100% strain region.¹¹⁴

Terpolymers of butadiene as a major fraction, together with myrcene and styrene are however inferior in tensile strength but superior in elongation than butadiene/styrene copolymers. This can be attributed to the weaker phase separation of the soft and hard domains.

Styrene-butadiene copolymers are synthetic rubbers that are widely used in the tire industry. The styrene content is not only responsible to adjust the glass transition temperature of the rubber but also promotes the dispersion of fillers in the elastomer matrix. Among others, these fillers are carbon black and silica particles with precise definition that need to be dispersed thoroughly for good surface properties.⁹⁶ Moreover, special additives function as polar anchors in the flexible diene matrix to

bind the hydrophobic elastomer to the hydrophilic silica particles. Styrene facilitates the incorporation of carbon black due to the aromatic structure. The interaction of carbon black and styrene relies in the pi-pi stacking of polystyrene and the filler.¹⁰¹

Besides the applications in TPEs, polystyrene is widely used in packaging and insulations materials.¹¹⁹ Expanded polystyrene (EPS) is a lightweight foam with low thermal conductivity, low moisture absorption and excellent cushioning properties. EPS is offering benefits from energy efficiency, thermals resistance and insulation, chemical inertness, excellent impact strength, combined with cost-effectiveness. However, the resources of polystyrene materials are fossil-based and there is no adequate substitute from bio-available resources.

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Chapter 2 Functional Styrene Monomers

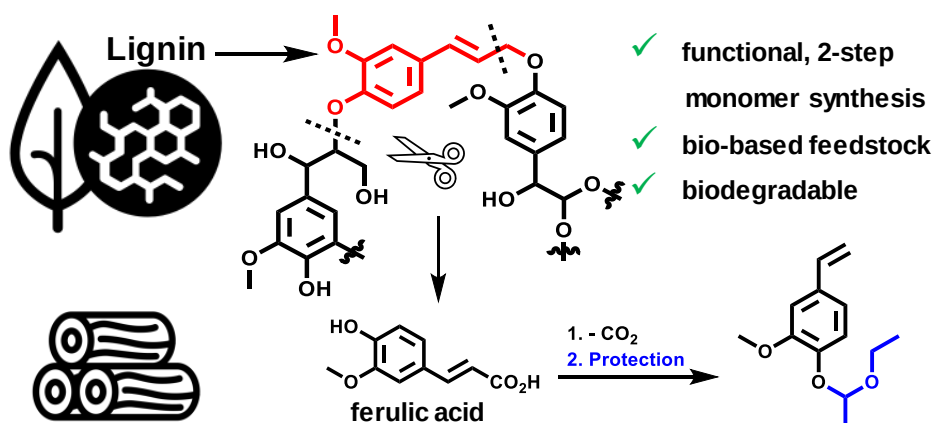
2 Functional Styrene Monomers

Anionic Polymerization of Bio-based Functional Styrene Monomers - Convenient Access to Poly (hydroxystyrene) obtained from Renewable Resources

Christoph Hahn,^{a,b} Sebastian Becker,^a Holger Frey^a

^a Department of Chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz (Germany)

^b Max Planck Graduate Center, MPGC, Staudingerweg 9, 55128, Mainz (Germany)
to be submitted.



2.1.1 Abstract

Ferulic acid, a cinnamic acid derivative with a hydroxyl and methoxy group in its structure, was quantitatively converted into protected functional styrene monomers *via* 4-vinyl guaiacol (VG) as an intermediate. In a facile and scalable two-step reaction including decarboxylation followed by protection reactions the monomers 1-ethoxy ethoxy-VG and tert-butyldimethylsilyl-VG were obtained with high yields. Living anionic polymerization of the acetal (1-ethoxy ethoxy) and silyl (*tert*-butyldimethylsilyl) protected styrenes proceeded to well-defined polymers with narrow MWD, although the reaction temperatures in THF were dependent on the protecting groups of the monomers. Deprotection of the acetal and silyl groups was easily attained under different acidic conditions in THF and water to result in well-defined poly(vinylguaiacol). In addition, the demethylation with boron tribromide was performed to obtain poly(vinylcatechol) copolymers, which was used to complex Fe³⁺ cations. Random copolymerization was observed for EE-VG and styrene copolymerization in THF at -95 °C. Aiming at a fully bio-based approach, 4-isopropylstyrene was synthesized from cuminaldehyde by Wittig reaction and the copolymerization of the latter with EE-VG was performed, resulting after deprotection in suitable multi-hydroxy macroinitiators for L-lactide and 4-methyl- ϵ -caprolactone grafting.

2.1.2 Introduction

The sustainable production of engineering materials, employing bio-based feedstocks, and biodegradable polymers, have been one of the most appealing research topics in our modern life.^{1,2} The applications of high-performance materials range from chemistry to medicine, diagnostics, packaging, energy, and electronics.³⁻⁸ To replace existing petroleum-based polymers, the sustainable feedstock-based compounds must exhibit at least complementary or even improved properties compared with the polymers available at present. The living anionic polymerization of styrene and diene monomers is crucial for the manufacturing of thermoplastic elastomers.⁹⁻¹² In literature it is well understood that a high degree of functionalization in linear polymers and block copolymers can be attained using anionic living polymerization.¹³⁻¹⁵ Complex architecture with a well-defined structure have been synthesized by anionic polymerization of hydrocarbon monomers or of monomers containing low reactive functional groups such as ethers, acetals and esters.¹⁶⁻¹⁸ Sustainable feedstock-based materials with specific molecular structures for special purposes can be used instead of the petroleum-derived, with reduced environmental impact.^{1,19-23}

When organic materials from plants are utilized as the renewable feedstock, the polymers are often referred to bioderived. Another important viewpoint of natural compounds is the true origin of the raw materials. In general, bio-based substances are divided in edible and non-edible parts of the plant or organic material. An interesting approach recently gained popularity in science and industry, where biological fermentation is used to produce chemical commodities from agricultural feedstocks.^{24,25} In most cases, such as poly(lactide acid) (PLA), this feedstock is based on glucose obtained from corn starch.

Lignin is a complex, polyphenolic, amorphous biopolymer with undefined and variable structure, depending on the origin. It is the second most abundant biomass, after cellulose, and produced large scale as a byproduct by the paper industry (~ 70

million tons annually).²⁶ Tremendous effort in both academia and industry have been made to recycle lignin waste into chemical commodities, although most recycling route use lignin for energy recovery.^{26–30} The minority of lignin waste is employed in high-value applications in upcycled products, such as a filler in tires^{31,32}, concrete and asphalt^{33,34}, and besides some specialized applications as polymer composites³⁵, epoxy resins^{36,37}, and other macromolecular systems.^{38–40}

Ferulic acid (3-methoxy-4-hydroxycinnamic acid) is a natural, aromatic compound that belongs to a variety of phytochemicals. It is one of the main constituents of many plant cell walls, e.g. in cereals, flax shives, oat, rice, and wheat bran.⁴¹ Cellulose and lignin are the key structural materials for the support tissue of cell wall, as they provide strength and rigidity.⁴² Lignin serves as a filler in the vacancies between cellulose, hemicellulose, and pectin, in particular in vascular and support tissues. Extraction of ferulic acid is attained by alkaline hydrolysis of lignin fibers.⁴³ Moreover, several works focused on the biotechnological production of ferulic acid from eugenol, which is obtained from clove oil.^{44,45} Fermentation-based processes offer apparent advantages, such as aqueous processing environments, nontoxic waste, besides the non-fossil-based feedstock. The outstanding prosperity of lignin is the prefabricated carbon skeleton of different cinnamic acids, that can be decarboxylated under mild condition to yield styrene derivates. Historically, researchers found that cinnamic acid was decarboxylated to form a until then unknown chemical compound called "cinnamene" or "cinnamol", which appeared to be styrene.^{46–48}

Terpenes, consisting of a carbon skeleton of condensed isoprene units, are together with cellulose and lignin another class of naturally occurring compounds with a large diversity of chemical structures and bioactivities. Cuminaldehyde (4-isopropylbenzaldehyde) is a terpene found in cumin and other related species. The aromatic aldehyde offers a natural substitute for styrene *via* the facile introduction of polymerizable vinyl bond by Wittig olefination. Polymer scientist have increasingly exploited naturally occurring aromatic molecules as building blocks for bio-based polymers. The application of bio-aromatics is often considered with improved

thermal and mechanical properties.⁴⁹ The aromatic components typically increase *glass transition temperatures* because of quadrupolar interactions, pi-pi stacking, and increased sterically hindrance (4-isopropylstyrene).

The common synthesis routes for functional styrene derivatives are divided into two opposing strategies. The functionality is either introduced at the beginning, along with the protection of itself, followed by the introduction of the vinyl double bond, or vice versa.^{13,50,51} The styrene vinyl group as well as the functional moiety are prone to undergo side reactions upon heating, strong electrophiles and nucleophiles.

Recently, Kamigaito and coworker published an elegant synthetic strategy to obtain bio-based functional styrenes by decarboxylation of cinnamic acids, followed by the introduction of various silyl-protecting groups.^{52,53} Reversible-addition-fragmentation chain transfer polymerization of the protected styrene derivatives yielded after deprotection poly(3-methoxy-4-hydroxy styrene).⁵²

Haraguchi *et al.* investigated the biodegradation of poly(3-methoxy-4-hydroxy styrene) by microorganisms (especially *Moraxella* and *Penicilium*) in soil.⁵⁴ They observed that vanillic acid seems to be the first biodegradation product, followed by further oxidation to monomethyl ester of β -carboxymuconic acid, maleic and oxalic acid. Evaluation of the intermediate degradation products reveals that the degradation pathway is similar to lignin by microorganisms.⁵⁴

The polymerization of monomers bearing pendent functional groups gives access to novel advanced polymers with precise functionalities, depending in the incorporated functional group. Special purpose materials, such as catechol containing polymers, are designed with respect to surface adhesion and antioxidant properties.^{55–59} Due to the incompatibility of protic OH-functionalities and the living carbanion during the polymerization, suitable protecting chemistry was employed.^{60–63} Historically, the first successful example of this strategy using a protective group is the synthesis of poly(4-vinylphenol), protected by *tert*-butyldimethylsilyl chloride, resulting in 4-*tert*-

butyldimethylsilyloxystyrene, which was subjected to carbanionic polymerization in THF at -78 °C.⁶¹

In previous works, catechol-containing vinyl monomers (4-vinylcatechol and 3-vinylcatechol acetonide) have been investigated with respect to kinetics, reactivity ratios, and formation of tapered block copolymers with pronounced monomer gradient.⁵¹ The acetonide-protecting group remained stable under the polymerization conditions, but was readily removed by the addition of diluted hydrochloric acid, resulting in well-defined poly(vinylcatechol)s. Acetal protecting groups recently gained increasing attention due to their convenient access and removal in post-modifications, along with excellent stability against nucleophiles.⁶⁴ In a previous report, we introduced *p*-(1-ethoxy-ethoxy) styrene, based on ethyl vinyl ether and the respective 4-vinylphenol, into the field of anionic polymerization, resulting in the rapid access to poly(hydroxy-styrene) after deprotection.⁶⁵

More importantly, 4-*tert*-butoxystyrene (*t*BuOS) is generally used as the favored protected precursor monomer for the synthesis of poly(hydroxy-styrene).⁶⁶ 4-*Tert*-butoxystyrene is suitable for carbanionic polymerization, but the latter suffers from harsh deprotection protocols. Indeed, this moiety exhibits simple benefits such as steric hindrance or stability that enriches the chemist's toolbox in many ways. Usually, the *tert*-butyl moiety is removed under strong acidic conditions using 1,1,1-trifluoroethanol as solvent and trifluoromethanesulfonic at -5 °C.⁶⁷

Here we report the synthesis of bio-based and biodegradable functional polystyrene (co)polymers with well-defined structure, relying on naturally occurring ferulic acid and the introduction of an acetal and a silyl protecting group. A series of different homopolymers, copolymers with styrene and 4-isopropylstyrene, and graft-block copolymers consisting of L-lactide and 4-methyl- ϵ -caprolactone (4MCL) respectively, have been prepared by living anionic polymerization to validate the versatility of the approach towards functional polymers based on renewable resources.

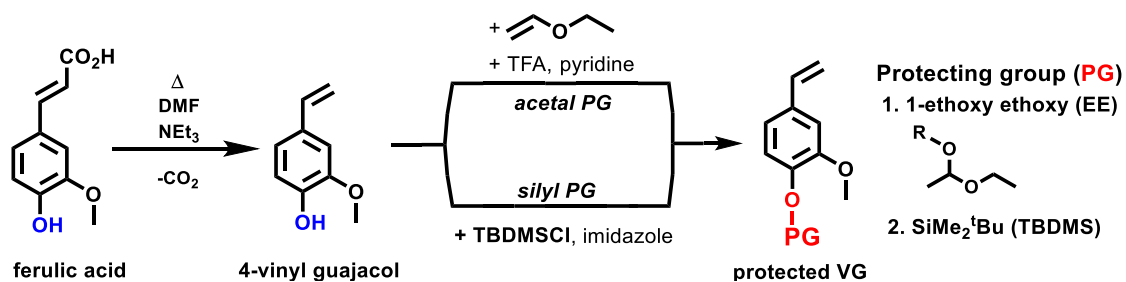
2.1.3 Results and Discussion

2.1.3.1 Polymerization of EE-VG and TBDMS-VG

Starting from the naturally available cinnamic acid derivative ferulic acid, 4-hydroxy-3-methoxystyrene (4-vinyl guaiacol, **VG**) was synthesized by decarboxylation in DMF at 100 °C in 99 % yield (Scheme 1). However, the phenolic group in the monomer typically needs to be protected by suitable protective groups. For this purpose, two different protective groups were introduced, and the polymerization thereof was studied regarding their polymerization behavior and deprotection. VG can be protected either by ethyl vinyl ether into its respective acetal, or by *tert*-butyldimethylsilyl chloride (TBDMSCl) to obtain silyl protected hydroxyl groups. Both protective groups represent stabile moieties towards nucleophiles but can be removed under acidic conditions.

The formation of acetals as a protecting group of ethyl vinyl ether with alcohols or phenols is a common synthesis strategy in organic chemistry. The protection of the phenol of VG with ethyl vinyl ether using trifluoroacetate/pyridine as catalyst proceeded quantitatively, nevertheless in only 80% isolated yield. However, quantitative consumption of VG was achieved after seven days and the conversion was tracked daily by NMR. The loss of EE-VG is attributed to the auto-polymerization of EE-VG (1-ethoxy ethoxy vinyl guaiacol) and VG during the distillation at elevated temperatures under reduced pressure.

TBDMSCl and imidazole were applied to protect the phenol of VG. The reaction proceeded without solvent in 82% yield. In contrast to literature, TBDMS-VG was purified *via* distillation under reduced pressure.⁵² This work demonstrates an improved purification method, avoiding column chromatography and additional work-up protocols.



Scheme 1: Synthesis of bio-based functional styrene monomers derived from ferulic acid with different protecting groups.

Living anionic polymerizations of all the synthesized protected VGs, were examined using *sec*-BuLi as initiator in THF at low temperatures. For both monomers, a series of homopolymers with increasing molecular weight was synthesized. The determination of the molecular weight was carried out by size exclusion chromatography, showing that larger molecular weights of P(EE-VG) and P(TBDMS-VG) are underestimated by GPC (eluent THF, PS calibration). Aiming even higher molecular weight (>50 kg/mol), pronounced tailing towards molecular weights was observed (Figure S 10).

EE-VG requires lower polymerizations temperatures of -95°C (acetone/ N₂(l)) in THF. Attempts have been made to polymerize EEVG at -78 °C (isopropanol/dry ice), but the results show that severe termination occurs during the polymerization, leading to a high molecular weight distribution. TBDMS-VG was polymerization under standard conditions at -78°C in THF.

In sharp contrast to the anionic polymerizations of EE-VG in THF at -95 °C, the polymerization of EE-VG in cyclohexane using *sec*-BuLi as initiator at 25 °C did not proceed at all, indicated by the immediate disappearance of the color of the anionic species after the addition of *sec*-BuLi. This can be attributed to the deactivation of the generated carbanion by the nucleophilic attack on the 1-ethoxy ethoxy group. In particular, the acidic proton in vicinity to the acetal can be abstracted by the nucleophilic organo-lithium initiator or living chain end. Furthermore, the TBDMS-VG with the bulky *tert*-butyldimethylsilyl groups resulted in a red colored solution, indicating the living chain end. However, the color of the living chain end disappeared

over the course of 15 min and only oligomers of <2000 g/mol were detected with SEC (Figure S 11). These observations hint that the TBDMS protective group is in general more stable towards strong nucleophiles. The nucleophilicity strongly depends on the temperature and on the employed solvent.

Table 1: Polymerization of protected VG, copolymers with styrene, molecular weight and glass-transition temperature.

entry	VG + protecting group	X _{feed} styrene %	Composition VG+/Sty	M _n (theo) kg/mol	M _n (GPC) ^a kg/mol	<i>D</i>	T _g °C
P1	1-ethoxy ethoxy	-	-	5.0	4.9	1.06	-
P2	1-ethoxy ethoxy	-	-	10.0	11.1	1.15	-
P3	1-ethoxy ethoxy	-	-	30.0	16.8	1.08	15
P4	TBDMS	-	-	5.0	4.8	1.10	79
P5	TBDMS	-	--	8.0	7.7	1.06	-
P6	TBDMS	-	-	20.0	14.6	1.06	-
P7	1-ethoxy ethoxy	88	10/90	10.0	11.2	1.06	81
P8	1-ethoxy ethoxy	77	25/75	10.0	9.6	1.07	95
P9	1-ethoxy ethoxy	47	50/50	10.0	12.1	1.08	45
P10	1-ethoxy ethoxy	38	75/25	10.0	9.2	1.08	35
P11	1-ethoxy ethoxy	23	90/10	10.0	11.8	1.11	30
P12	TBDMS	90	10/90	10.0	10.1	1.06	-
P13	TBDMS	75	25/75	10.0	10.8	1.08	-
P14	TBDMS	57	50/50	10.0	9.9	1.07	-
P15	TBDMS	35	75/25	10.0	15.5	1.08	-
P16	TBDMS	24	90/10	10.0	10.8	1.08	-

^a Determined by SEC in THF (UV signal, PS calibration),

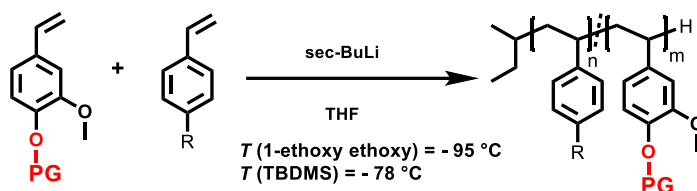
The resulting polymers of EE-VG and TBDMS-VG differ in glass transition temperature. It was observed that the 1-ethoxy-ethoxy acetal decreases the T_g to 15°C (Figure S 13), whereas the T_g of TBDMS-VG was determined to be 70°C (Figure S 14).

This can be attributed to the flexible ethyl side chains of EE-VG, whereas the bulky TBDMS provides rigidity.

The most pronounced difference of the monomers EE-VG and TBDMS-VG was observed in the deprotection of phenol groups. EE-VG is deprotected under mild conditions by the addition of diluted hydrochloric acid within one hour at 25°C. However, the removal of silyl group either requires tetra-butylammonium fluoride (TBAF) or concentrated hydrochloric acid under reflux for 24 h. The facile deprotection of acetals is a tremendous benefit of the 1-ethoxy ethoxy protecting group. In addition, the deprotection of P(EE-VG) can be performed in a one-pot reaction synthesis, when adding a mixture of degassed methanol and diluted hydrochloric acid directly into the polymerization medium at -95 °C to terminate the polymerization and to deprotect the polymer. After heating to room temperature and precipitation in cold methanol, the polymer was already deprotected, resulting in well-defined poly(4-hydroxy-3-methoxystyrene) in quantitative yield. The removal of the acetal protecting group increased the T_g of P(VG) to 77°C.

2.1.3.2 Copolymerization with styrene

It was demonstrated that EE-VG and TBDMS-VG can be copolymerized with styrene in different compositions, ranging from 23-88% styrene content and 24-90%, respectively.



Scheme 2: Copolymer synthesis with styrene (derivatives), R=H, styrene, R=isopropyl, 4-isopropylstyrene.

The ratio of VG to styrene precisely determines the T_g of the resulting copolymer. The exact incorporation of styrene was determined by NMR spectroscopy. It is shown that with increasing styrene content, the T_g increases in a linear trend. This linear dependance of increasing T_g is an indication that the copolymer sequence is randomly distributed. Using the Fox-equation, the polymers follow this linear tendency in Figure 1.

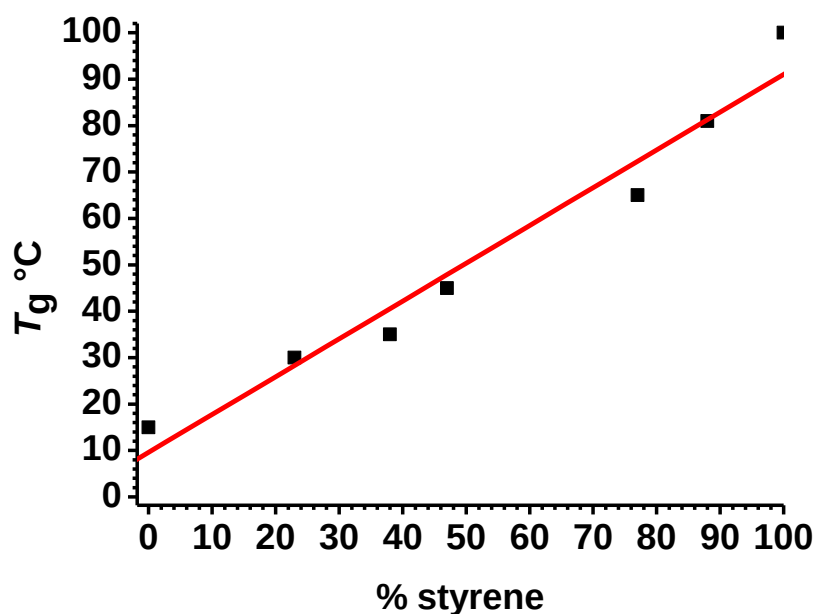


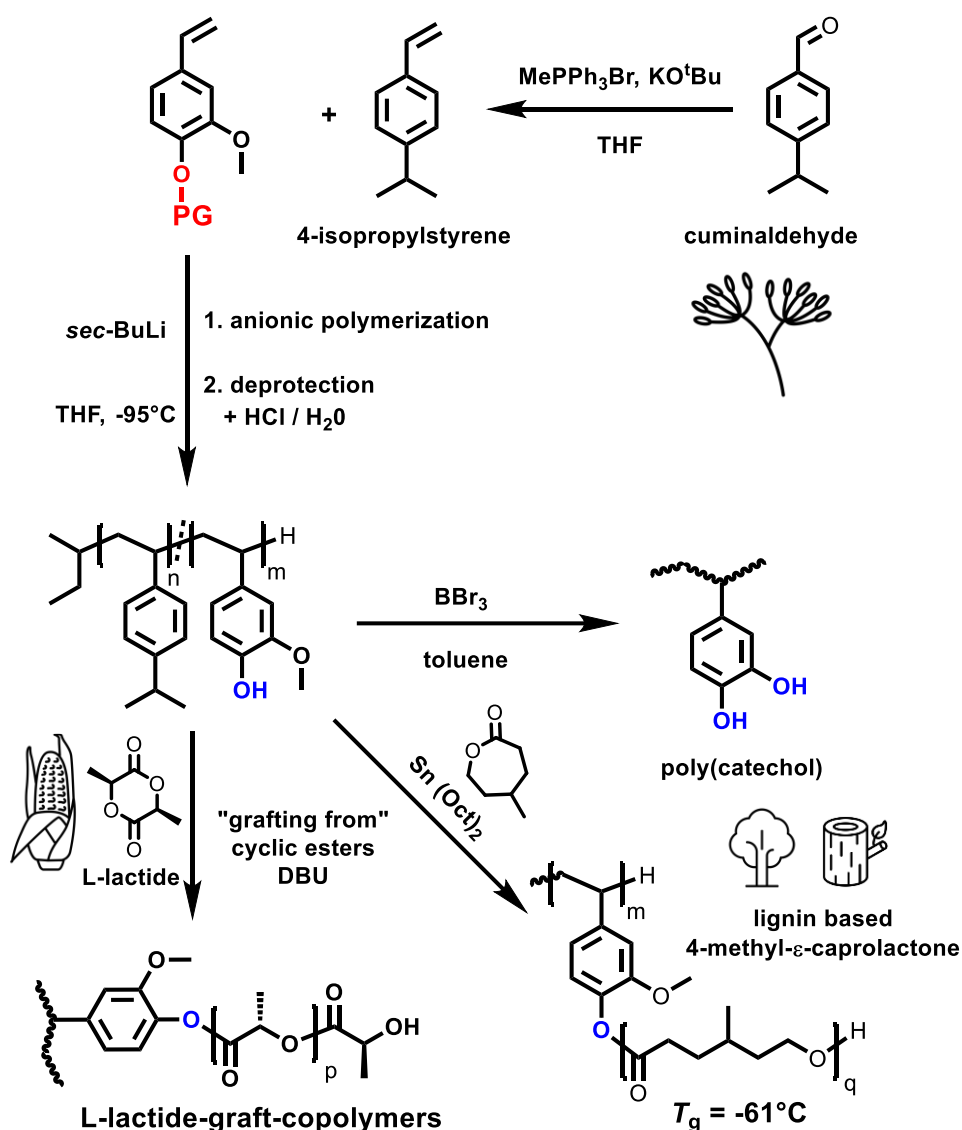
Figure 1: T_g vs. styrene content in copolymers of EE-VG and styrene (T_g of styrene taken from Literature ⁶⁸).

2.1.3.3 Copolymers with 4-isopropylstyrene

This study aims to contribute to the preparation of fully bio-based polymers. Hence, it was demonstrated that copolymers of 4-isopropylstyrene (4-ⁱPrS) and EE-VG are accessible *via* living anionic polymerization. Cuminaldehyde, the major terpene of the essential oil of cumin, is used as a starting material for the synthesis of 4-ⁱPrS. This monomer can be considered as a natural substitute for styrene to receive a fully bio-based copolymers from functional and non-functional monomers.

Cuminaldehyde was converted to 4-isopropylstyrene(4-ⁱPrS) *via* Wittig olefination (Scheme 3). In particular, the challenging step of the Wittig reaction the removal of the unavoidable by-product triphenylphosphine oxide (TPPO). Nevertheless, on a gram-scale TPPO can be removed by column chromatography, but targeting larger scales is inconvertible due to the complexation of the TPPO with the column matrix. However, this work demonstrates the synthesis of 4-ⁱPrS, without purification by column chromatography. The monomer was distilled under reduced pressure und dried over CaH₂ and trioctylaluminum. Poly(4-ⁱPrS) displays an interesting polymer regarding its thermal stability. It was found in literature that compared to other *para*-alkylstyrene derivates (4-ethyl-, 4-*tert*-butylstyrene, styrene), 4-ⁱPrS exhibits the larger thermal resistance, proven by TGA measurements under N₂ and O₂.⁶⁹

Copolymers consisting of a large excess of 4-ⁱPrS and EE-VG (10/1 molar ratio) were synthesized *via* anionic polymerization in THF under the same conditions as described for the styrene copolymers. This copolymer, P(4-ⁱPrS-*co*-VG), was then used after removal of the 1-ethoxy ethoxy protective group, in a proof-of-concept reaction to serve as a macroinitiator for graft copolymers.



Scheme 3: Synthesis of bio-based functional styrene monomers derived from naturally occurring ferulic acid and cuminaldehyde, anionic copolymerization in THF, defined synthesis of poly(catechol) by demethylation, “grafting from” copolymers by ring-opening polymerization of cyclic esters with L-lactide and 4-methyl- ϵ -caprolactone.

2.1.3.4 Graft Copolymers and demethylation

It was demonstrated in literature that poly(4-hydroxystyrene) can serve as the key material for the access to interesting polymer features, e.g. for macroinitiators for ethylene oxide grafting.^{65,66,70} The combination of the hydrophilic ethylene oxide and the hydrophobic polystyrene backbone results in amphiphilic block-copolymer with promising surfactant properties.^{65,70} To further expand the scope of graft copolymers

using hydroxy-functionalized polystyrenes, (4-*i*PrS₁₁₉-*co*-VG₁₂) was utilized as a versatile macroinitiator and precursor for the synthesis of graft copolymers. Applying “grafting from” technique, graft-copolymers of P(4-*i*PrS₁₁₉-*co*-VG₁₂) and cyclic esters were synthesized *via* ring-opening polymerization using DBU as catalyst. It was demonstrated that P(4-*i*PrS₁₀₉-*co*-VG₁₈) served as a good macroinitiator for L-lactide grafting. The number-average molecular weights M_n increased in direct proportion to L-lactide conversions (Figure 2) and maintained narrow molecular weight distributions ($\mathcal{D}$ = 1.11-1.13).

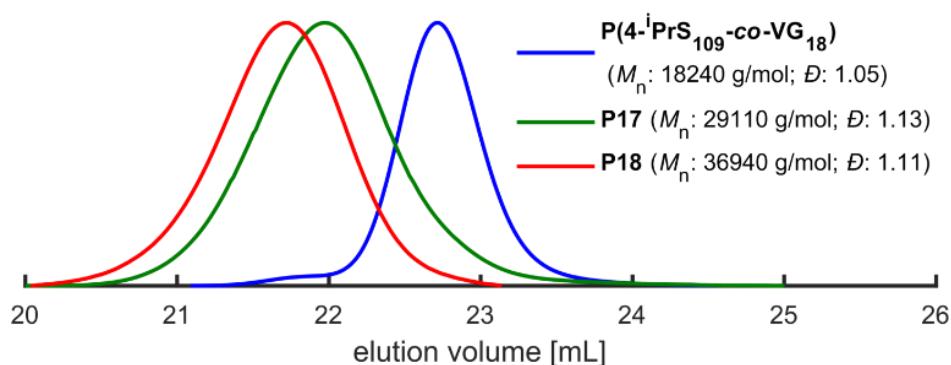


Figure 2: SEC traces (eluent THF, PS calibration) of P(4-*i*PrS₁₀₆-*co*-VG₁₈) and P(4-*i*PrS₁₁₉-*co*-VG₁₂-*g*-L-lactide); P17 and P18.

Table 2: Graft copolymers and demethylation of poly(4-isopropylstyrene-*co*-3-methoxy-4-hydroxystyrene).

entry	composition	Macroinitiator /precursor M_n (GPC) ^a kg/mol	% VG	monomer	M_n (GPC) ^a kg/mol	$\mathcal{D}$	T_g °C
P17	P(4- <i>i</i> PrS ₁₀₉ - <i>co</i> -VG ₁₈)	18.2	14	lactide	29.1	1.13	-
P18	P(4- <i>i</i> PrS ₁₀₉ - <i>co</i> -VG ₁₈)	18.2	14	lactide	36.9	1.11	49
P19	P(4- <i>i</i> PrS ₁₁₉ - <i>co</i> -VG ₁₂)	19.4	9	4MCL	31.9	1.40	-60
P20	P(4- <i>i</i> PrS ₁₁₉ - <i>co</i> -VG ₁₂)	19.4	9	4MCL	33.3	1.79	-58
		Demethylation with BBr ₃					
P21	P(4- <i>i</i> PrS ₁₁₉ - <i>co</i> -VG ₁₂)	19.4	9		20.9	1.09	93

%VG determined by NMR, GPC (eluent THF, PS calibration)

In addition, in a proof-of-concept reaction $P(4\text{-}^i\text{PrS}_{119}\text{-co-VG}_{12})$ was used as a macroinitiator to graft 4-methyl- ϵ -caprolactone from the free phenol groups using $\text{Sn}(\text{Oct})_2$ as catalyst. The bio-available 4MCL is a considerable alternative for flexible elastomers made from biodegradable polyester. 4MCL is obtained in multiple steps from lignin bio-oil. Lignin bio-oil provides a variety of cresols, that are hydrogenated into their respective alkyl-cyclohexanones. In the second step, Baeyer-Villiger oxidation with *m*CPBA yields methylcaprolactones.

The graft copolymer P19 was synthesized with $\text{Sn}(\text{Oct})_2$ in toluene solution at 130°C for 24h. The results show a bimodal molecular weight distribution with a shoulder towards higher molecular weights (Figure S 29). This is explained by the incomplete initiation of the phenol groups of VG. Due to the reduced nucleophilicity of phenolates compared to alkoxides, the initiation with $\text{Sn}(\text{Oct})_2$ can be hindered. In addition, the methoxy group in vicinity could influence the bulkiness of the macroinitiator. Moreover, the polymerization of 4MCL (P20) and $P(4\text{-}^i\text{PrS}_{119}\text{-co-VG}_{12})$ in bulk within one hour at 130°C was demonstrated. The rapid conversion of 4MCL was accompanied with a high increase in melt viscosity.

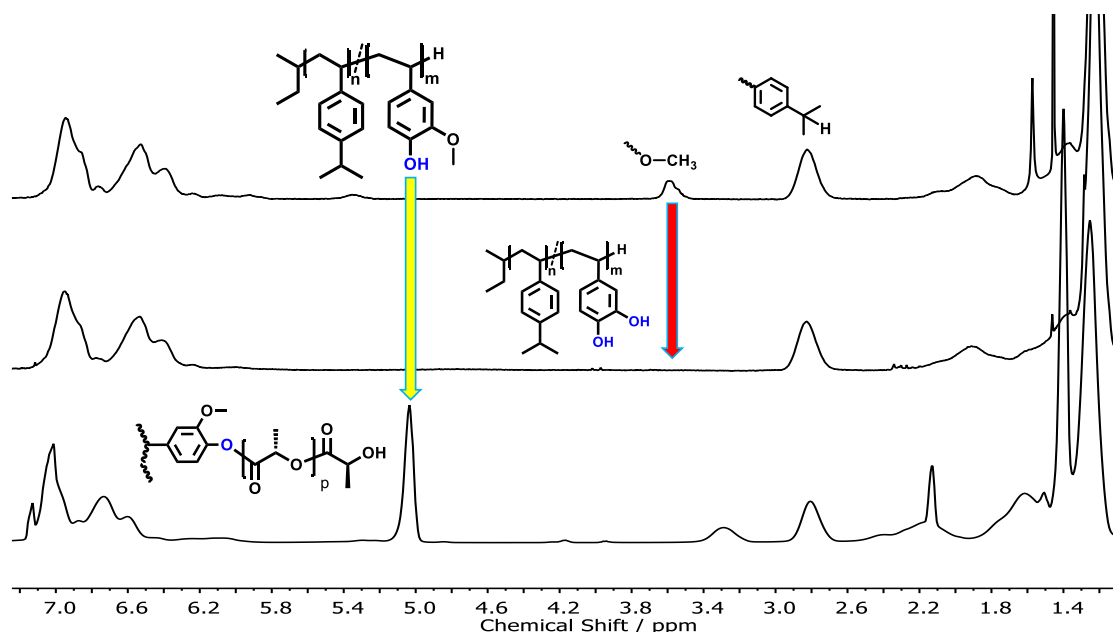


Figure 3: Deprotection, demethylation and “grafting from” copolymers of VG. Top: ^1H NMR spectrum of $P(4\text{-}^i\text{PrS}_{119}\text{-co-VG}_{12})$ (400 MHz, CDCl_3 , 25°C), middle: P21, $P(4\text{-}^i\text{PrS}_{119}\text{-co-VC}_{12})$ (400 MHz, CDCl_3 , 25°C), bottom: P19, $P(4\text{-}^i\text{PrS}_{109}\text{-co-VG}_{18}\text{-g-L-lactide})$ (400 MHz, toluene- d_8 , 25°C).

The versatility of P(4-*i*PrS₁₁₉-*co*-VG₁₂) is displayed by the clean removal of the methoxy substituent on the aromatic ring of vinyl guaiacol. The demethylation was performed using boron tribromide in dry toluene for 24h, resulting in poly(4-isopropylstyrene-*co*-vinylcatechol) P(4-*i*PrS₁₁₉-*co*-VC₁₂) in quantitative yield (Figure 2). The demethylation resulted in copolymers of P(VC) and P(4-*i*PrS) with a T_g of 93°C. The total disappearance of the methoxy signal at 3.58 ppm in ¹H NMR in Figure 3 confirmed the complete demethylation.

2.1.3.5 Complexation properties of P(4-*i*PrS-*co*-VC)

After the successful demethylation of vinyl guaiacol, the resulting polycatechol was investigated with respect to the complexation properties. It is known that catechols show remarkable complexation affinities to metal ions. It is noteworthy that iron (III, Fe³⁺) cations form stable tris-complexes with catechols. The catechol complexation activity with iron (III, Fe³⁺) cations depends on the pH value. Firstly, no complexation was observed when mixing a solution of FeCl₃ in methanol with a solution of P(4-*i*PrS-*co*-VC) in acetone. Only in alkaline conditions catechols show deprotonation of the hydroxyl groups. After the addition of sodium hydroxide in water, the formation of a dark precipitate was observed. The complexation leads to an insoluble polymer network (Figure 4). The reversibility of the complexation was demonstrated by adding hydrochloric acid to the solution to dissolve the complex, reducing the number of coordinating catechols on the iron center at low pH (Figure 4).

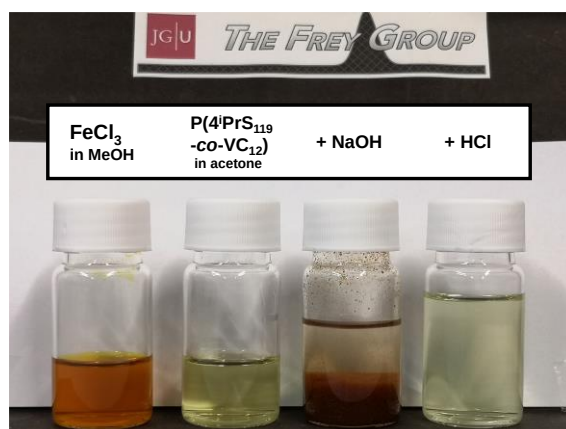


Figure 4: Complexation properties of P(4-*i*PrS-*co*-VC) in alkaline solution.

2.1.4 Conclusion

Bio-based ferulic acid was easily and quantitatively transformed into 4-vinyl guaiacol and novel hydroxyl-protected bio-based styrene monomers. Acetal and silyl protective group were introduced to protect the phenols of VG. Living anionic polymerization in THF at low temperatures of these protected phenolic styrene derivatives successfully proceeded in well-defined polymers with predictable molecular weights and narrow molecular weight distributions. The removal of the acetal and silyl protective group was accomplished by the treatment of different acidic conditions to result in multi-hydroxy-functional polystyrenes. The hydroxy-functional polystyrenes were used as macroinitiators for graft copolymers of L-lactide and 4-methyl- ϵ -caprolactone *via* ring-opening polymerization. Demethylation was successfully demonstrated to result in copolymers with catechol functionalities without any molecular weight broadening or backbone scission. In addition, the well-defined copolymers of 4ⁱPrS and VC containing catechol moieties can be applied as unique complexing agents and surface coatings with improved biodegradability.

2.1.5 References

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2.1.6 Supporting Information

2.1.6.1 Monomer synthesis

4-Vinylguaiaicol (VG) was synthesized *via* decarboxylation of ferulic acid. Ferulic acid (58.21 g, 300 mmol) was dissolved in DMF (300 mL) and triethylamine (139 mL, 1 mol) was added. The mixture was heated to 100 °C under stirring for 3 h, then the reaction mixture was cooled to room temperature. The full conversion of ferulic acid was tracked by ^1H NMR. The gas evolution of the decarboxylation stopped after full conversion of ferulic acid. The reaction mixture was concentrated by rotary evaporation to remove triethylamine. The residue was diluted with diethyl ether and washed with water. The organic layer was dried over MgSO_4 and then evaporated. VG was purified by distillation under reduced pressure. Without further purification, VG was used to synthesize EE-VG and TBDMS-VG.

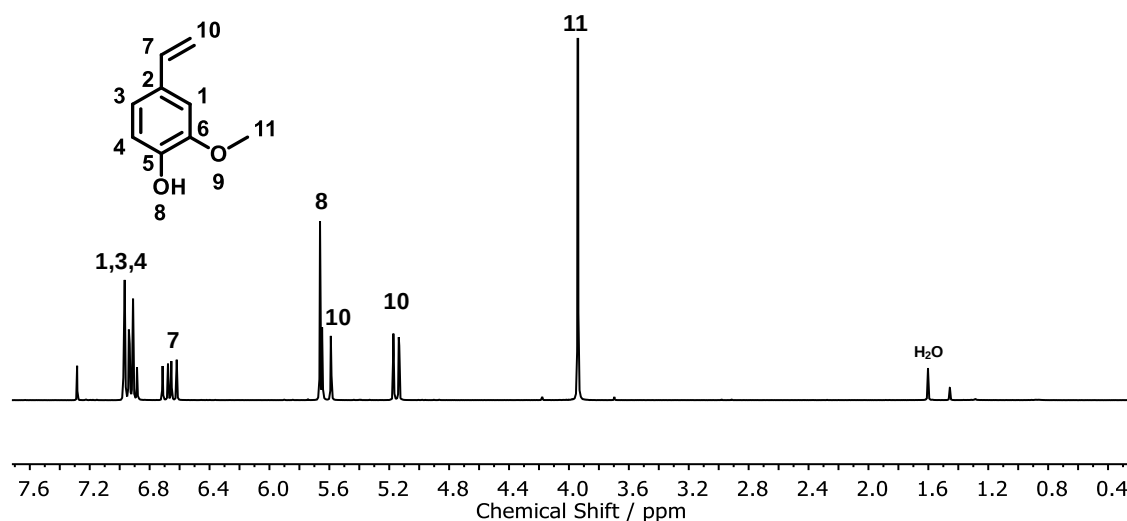


Figure S 1: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of VG.

EE-VG. Pyridine (1.58 g, 20 mmol) was carefully mixed with trifluoroacetic acid (0.52 ml, 6.7 mmol). Then VG (10g, 66 mmol) was dissolved in ethyl vinyl ether (25mL) and added to the pyridine trifluoroacetate. The mixture was stirred at room temperature for seven days. The solution was then diluted with diethyl ether and washed with 1M NaOH, water and brine. The ethereal phases were dried with MgSO₄, and the solvent was evaporated under reduced pressure. EE-VG was obtained in 80% yield and purified by fractional distillation at 90 °C and 1·10⁻³ mbar.

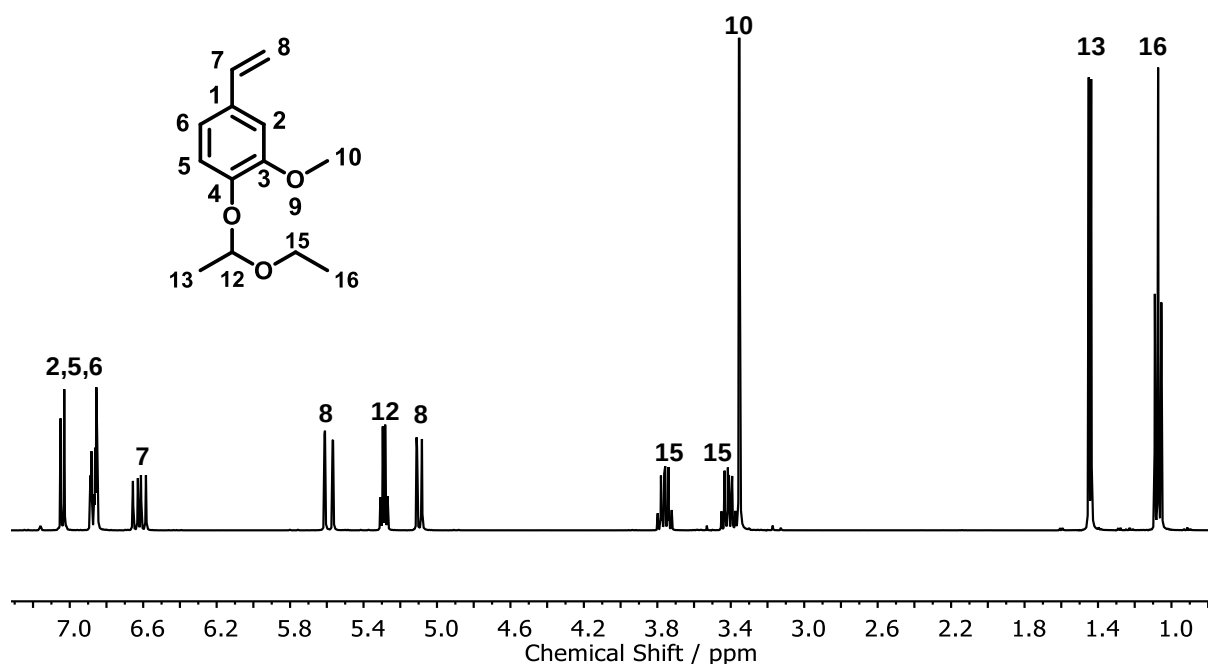


Figure S 2: ¹H NMR spectrum (400 MHz, C₆D₆, 25°C) of EE-VG.

TBDMS-VG. In a three-neck flask equipped with a condenser, thermometer and stirrer, VG (8 g, 53 mmol) was dissolved in THF (25 mL) and imidazole (7.9 g, 120 mmol) was added in small portions. The solution was cooled to 0°C under stirring. The stirring was continued for 48h at room temperature. The solution was mixed with cyclohexane (30 mL) and the organic phase was washed with water and dried with MgSO₄. After the removal of the solvent, TBDMS-VG was distilled at 99°C and 1·10⁻³ mbar in a yield of 82 %.

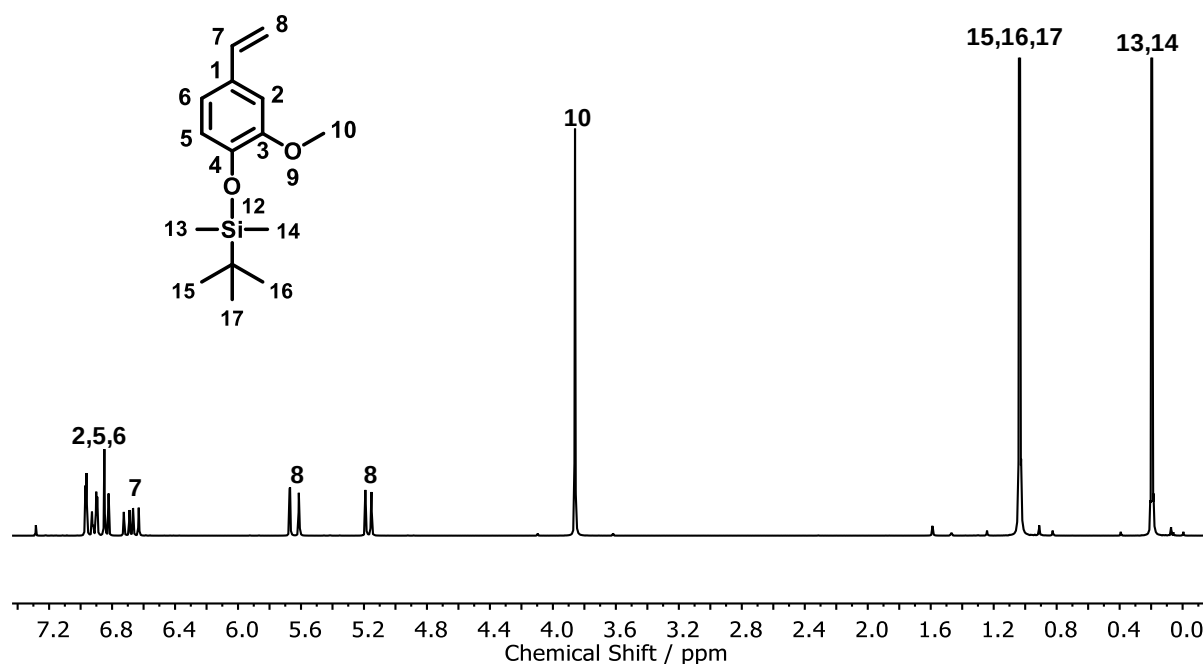


Figure S 3: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of TBDMS-VG.

2.1.6.2 Homopolymer synthesis

General Polymerization Procedure in THF. All (co)-polymerizations were performed in 250 mL Schlenk flasks equipped with a magnetic stir bar and Teflon stopper in dry THF under argon. THF was dried with *sec*-BuLi and 1,1-diphenylethylene and vacuum transferred into the polymerization reactor. The monomers were dried by stirring over CaH_2 overnight, followed by distillation into the polymerization flask. The polymerization reactor was cooled with a mixture of liquid nitrogen and acetone to -95°C (dry ice/acetone to -78°C respectively). The monomer/solvent (20 wt %) mixture was initiated with *sec*-BuLi (1.3 M in cyclohexane/hexane 92/8) via a 1 mL syringe. The solution was stirred for 30 min to ensure full monomer conversion. The polymerization was terminated by adding 0.5 mL of methanol (degassed with argon for 1 h prior to use) by a syringe. The polymers were precipitated in 100 mL of cold methanol and dried under reduced pressure.

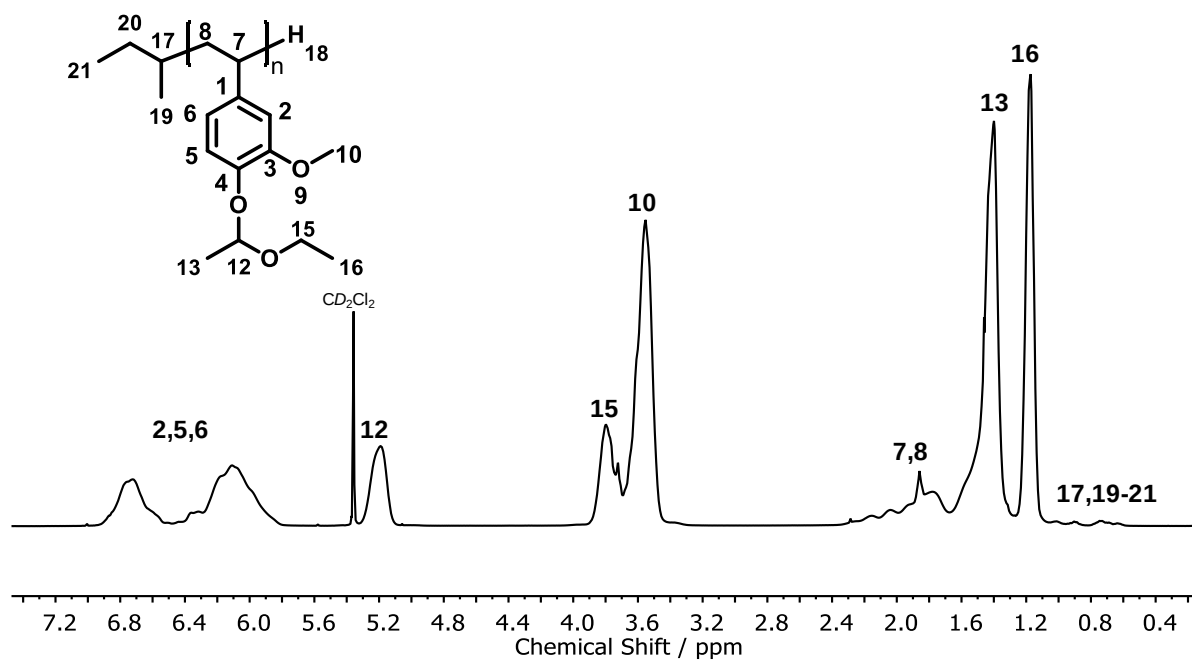


Figure S 4: ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 25°C) of P(EE-VG).

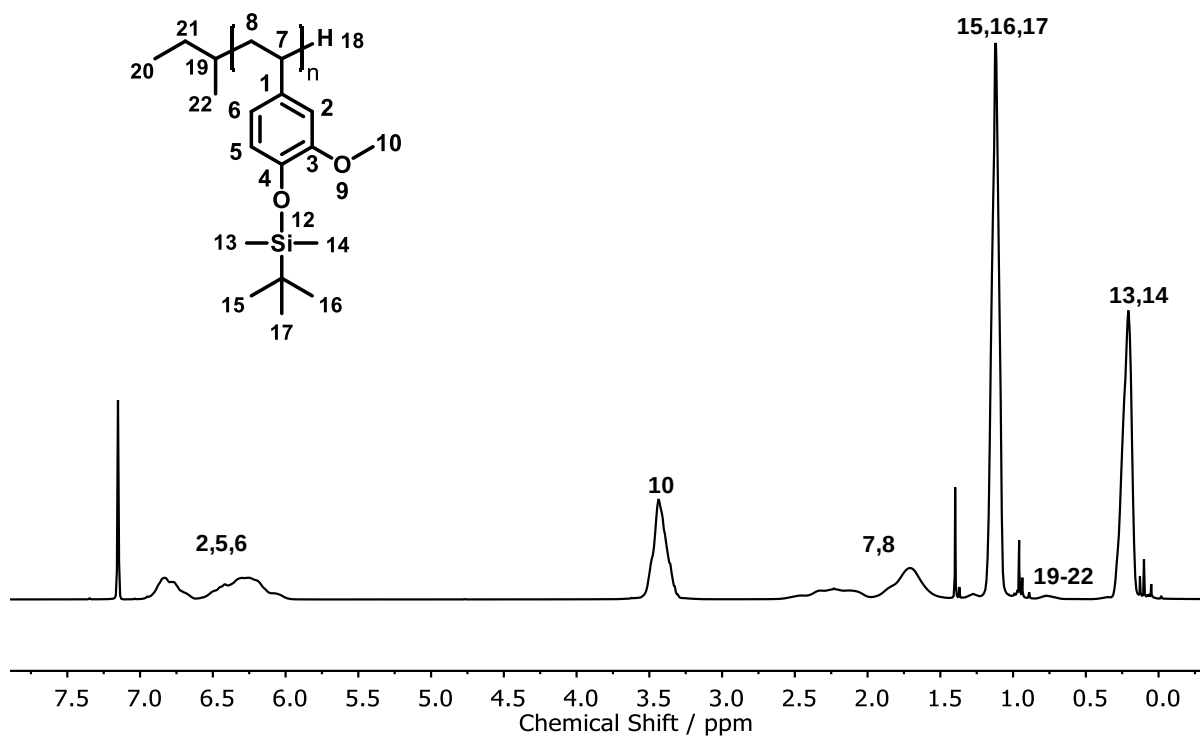


Figure S 5: ^1H NMR spectrum (400 MHz, C_6D_6 , 25°C) of P(TBDMS-VG).

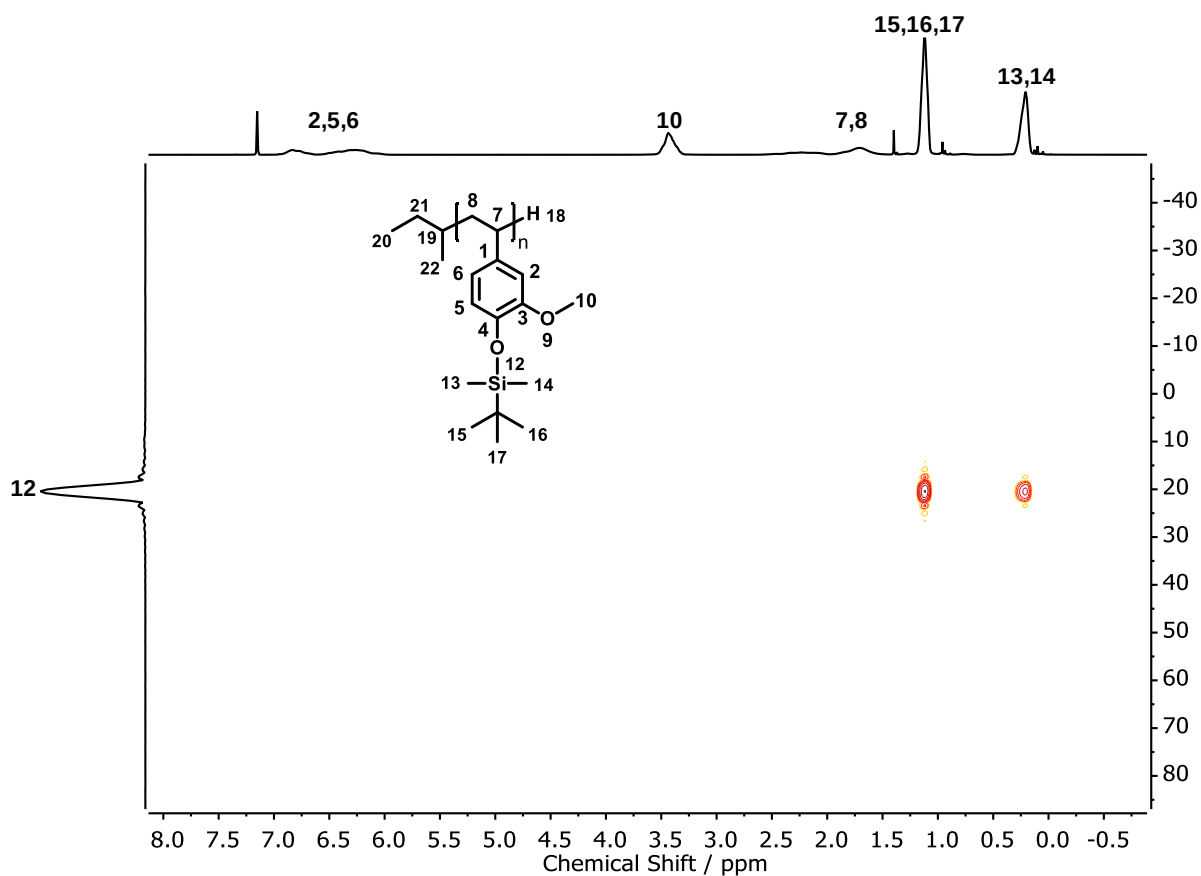


Figure S 6: $^1\text{H}/^{29}\text{Si}$ HMBC NMR spectrum (400 MHz, C_6D_6 , 25°C) of P(TBDMS-VG).

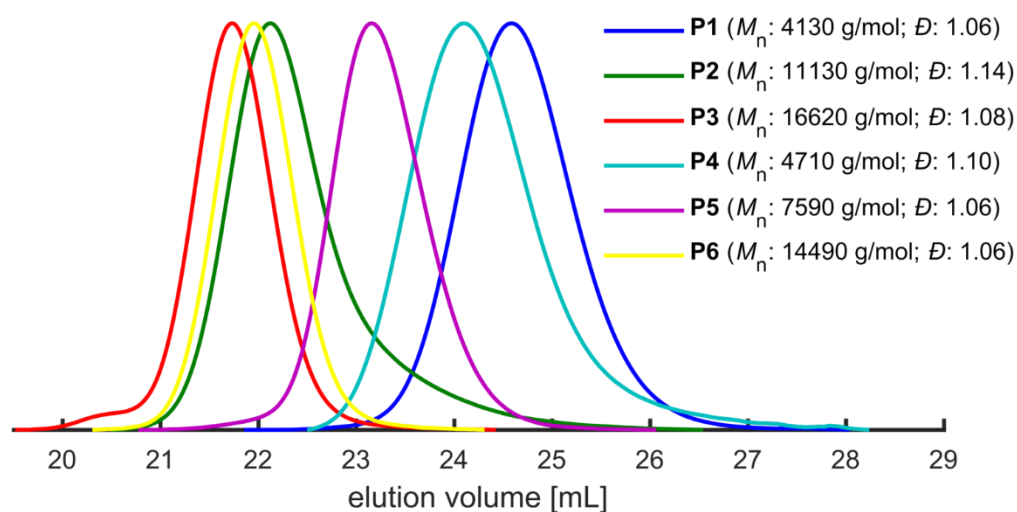


Figure S 7: SEC traces (eluent THF, PS calibration) of P1-6.

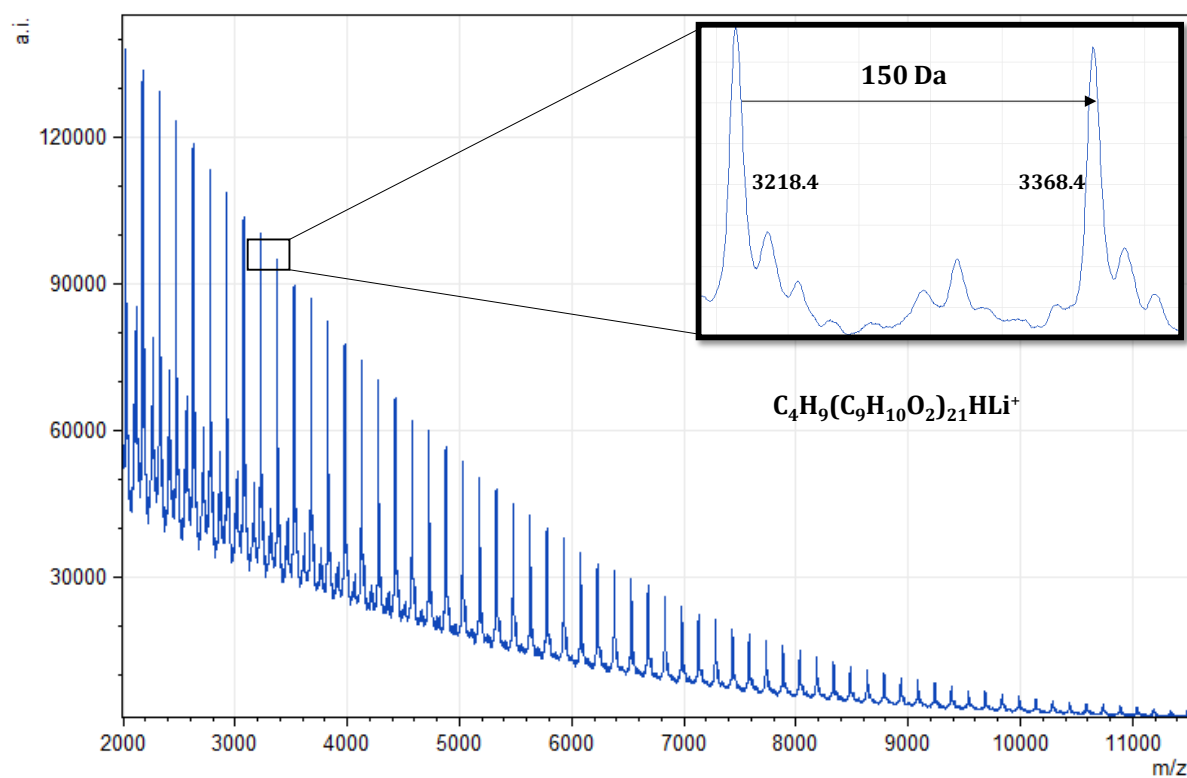


Figure S 8: MALDI-ToF MS spectra of P2 (Matrix: DCTB).

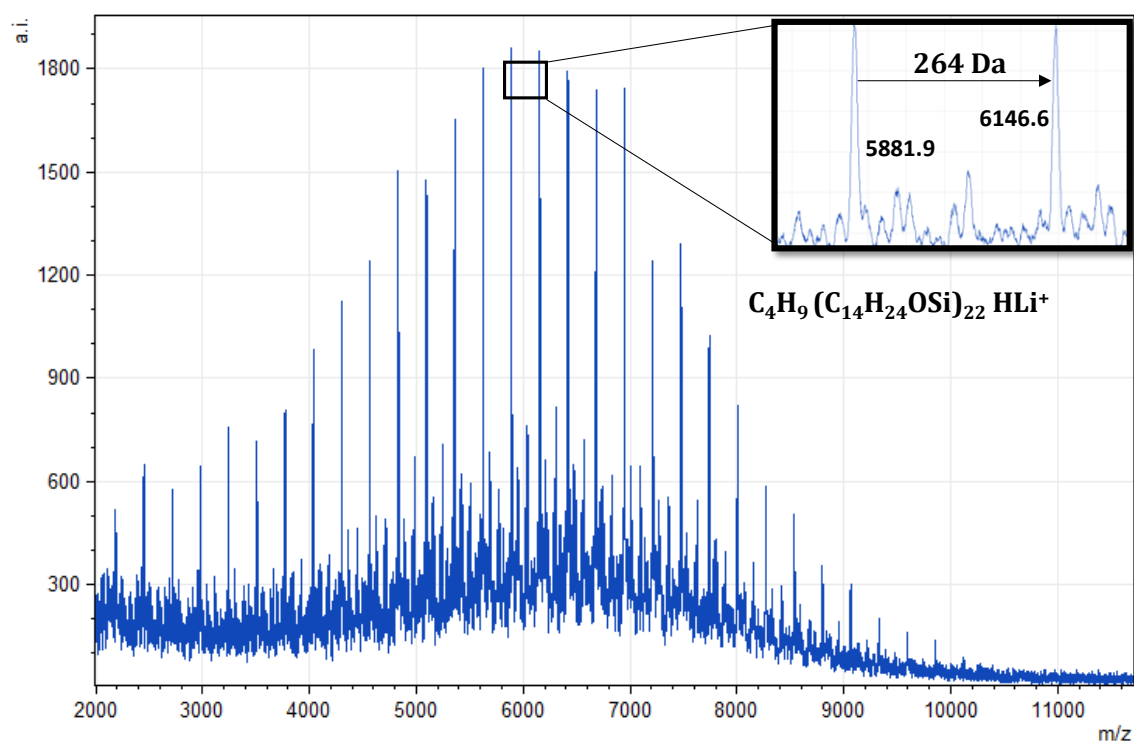


Figure S 9: MALDI-ToF MS spectra of P4 (Matrix: DCTB).

High molecular weight polymerization of EE-VG and TBDMS-VG. Attempts have been made to produce high molecular weight polymers of EE-VG and TBDMS-VG. The results show that with both monomers targeting higher molecular weights leads to the broadening of the molecular weight distribution.

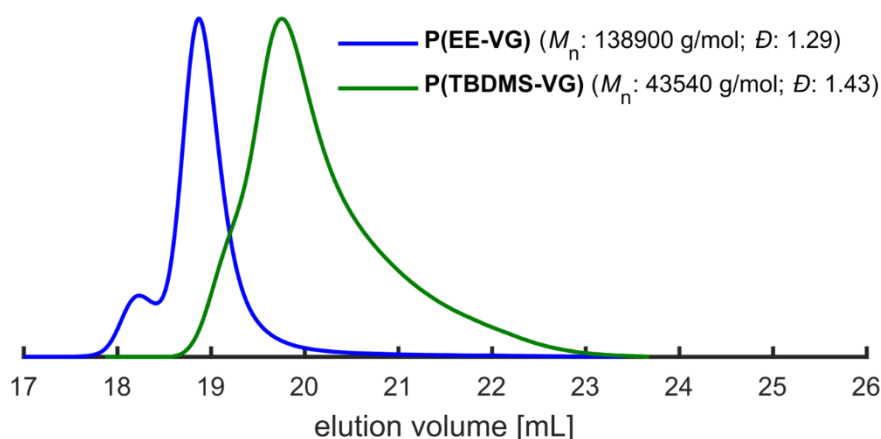


Figure S 10: SEC traces (eluent THF, PS calibration) of high molecular weight samples of P(EE-VG) and P(TBDMS-VG).

Polymerization of EE-VG and TBDMS-VG in cyclohexane. The polymerization of EE-VG in cyclohexane using *sec*-BuLi as initiator at 25 °C was not successful and the colors of the anionic species disappeared immediately after the addition of *sec*-BuLi. However, the red color of the living chain end of P(TBDMS-VG) remained for 15 min and vanished slowly. This demonstrated that the TBDMS group is not suitable for functional styrenes in cyclohexane at 25°C. The SEC traces in Figure S 12 of the polymerization attempt of TBDMS-VG show only low molecular weight species.

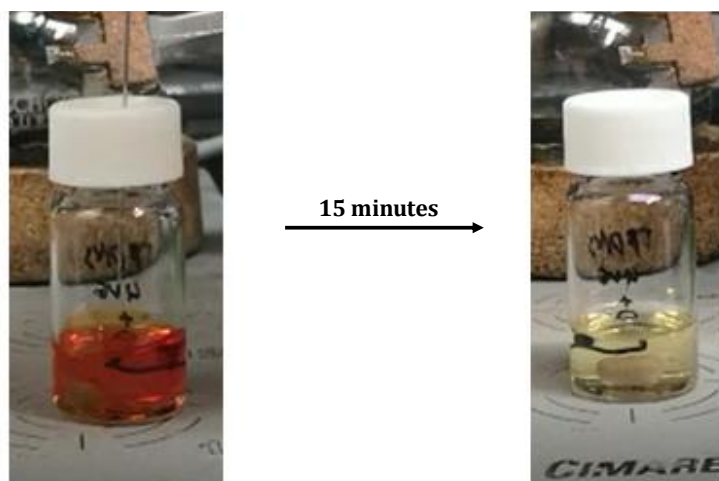


Figure S 11: Polymerization of TBDMS-VG in cyclohexane, left: directly taken after the initiation with *sec*-BuLi, right: after 15 minutes.

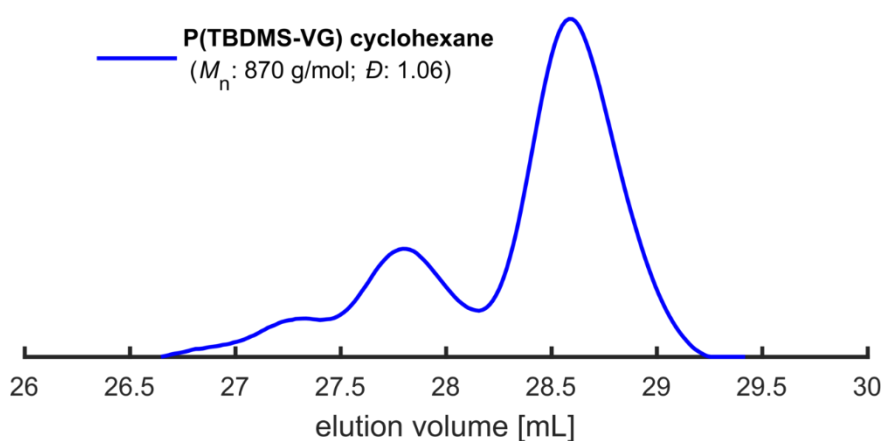


Figure S 12: SEC traces (eluent THF, PS calibration) of oligomers of TBDMS-VG polymerized in cyclohexane.

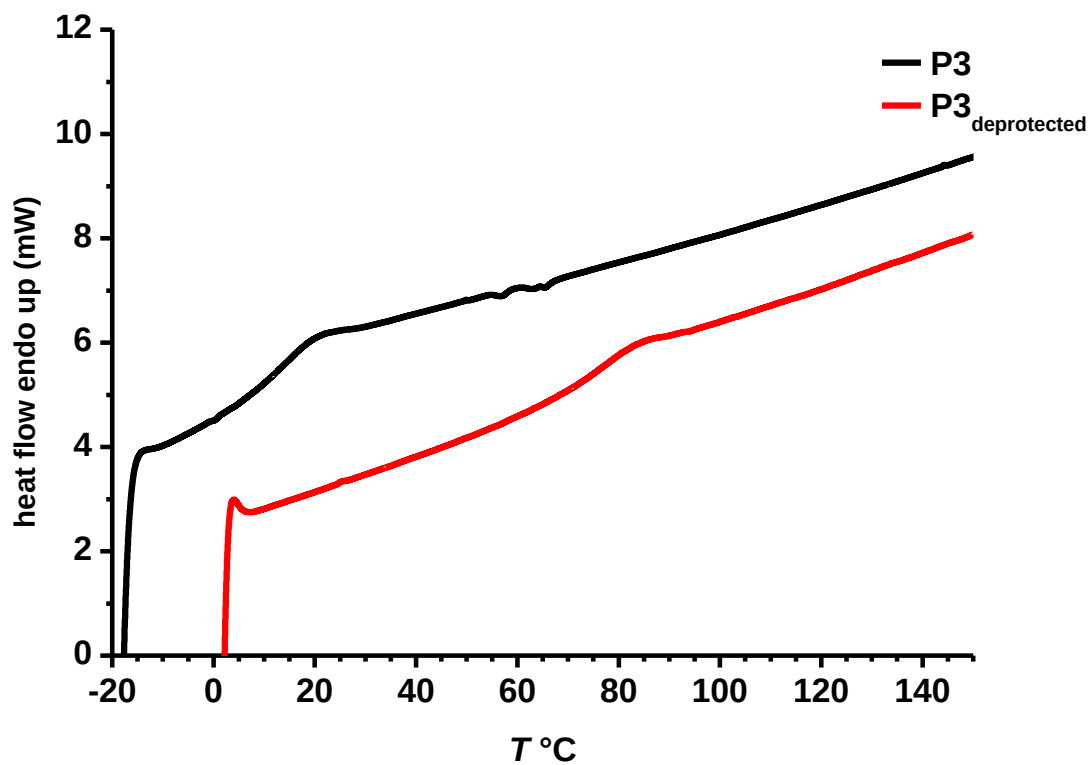


Figure S 13: Second heating curves from DSC of P3 ($T_g = 15^\circ\text{C}$) and P3_{deprotected} ($T_g = 77^\circ\text{C}$).

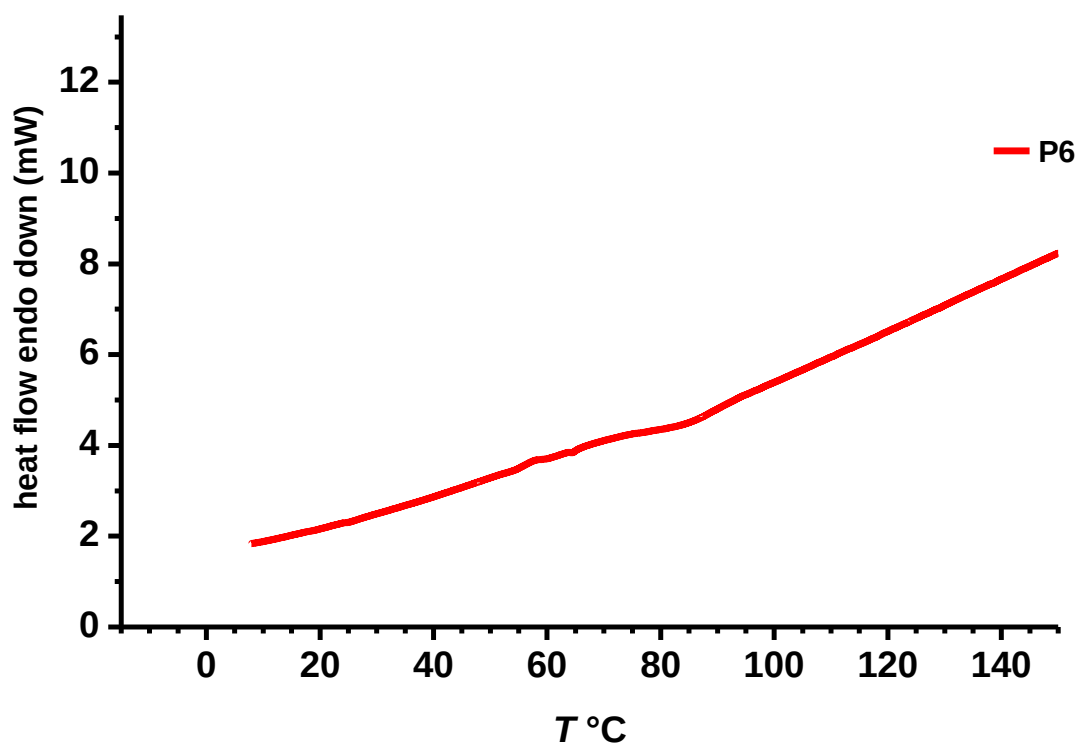


Figure S 14: Second heating curve from DSC of P4 ($T_g = 79^\circ\text{C}$).

2.1.6.3 Removal of the protecting groups

Removal of 1-ethoxy ethoxy protecting group. The (co)polymer of EE-VG (1 g) was dissolved in THF (30 mL), and 1 mL of 1 M HCl solution was added dropwise under stirring. The deprotection was completed after 1 h and the polymer was precipitated in cold methanol/isopropanol mixture.

Removal of TBDMS protecting group. The deprotection of TBDMS was performed using tetrabutylammonium fluoride as deprotecting agent. The (co)polymer of TBDMS-VG was dissolved in THF and tetrabutylammonium fluoride was added under argon atmosphere. Isopropanol was added after 30 min and the solution was allowed to stir for additional 30 min at 40°C. The solution was quenched by the addition of a saturated aqueous NH_4Cl solution. The polymer was precipitated in a methanol/isopropanol mixture.

Alternatively, the (co)polymer of TBDMS-VG (1 g) was dissolved in THF (30 mL), and 10 mL of conc. HCl solution was added dropwise under stirring. After the addition of HCl, THF was added again until the THF/water mixture was no longer cloudy, and the solution was heated to reflux. The resulting mixture was heated for 24 h before the deprotected polymer was precipitated in cold methanol/isopropanol mixture.

2.1.6.4 Copolymerization with styrene

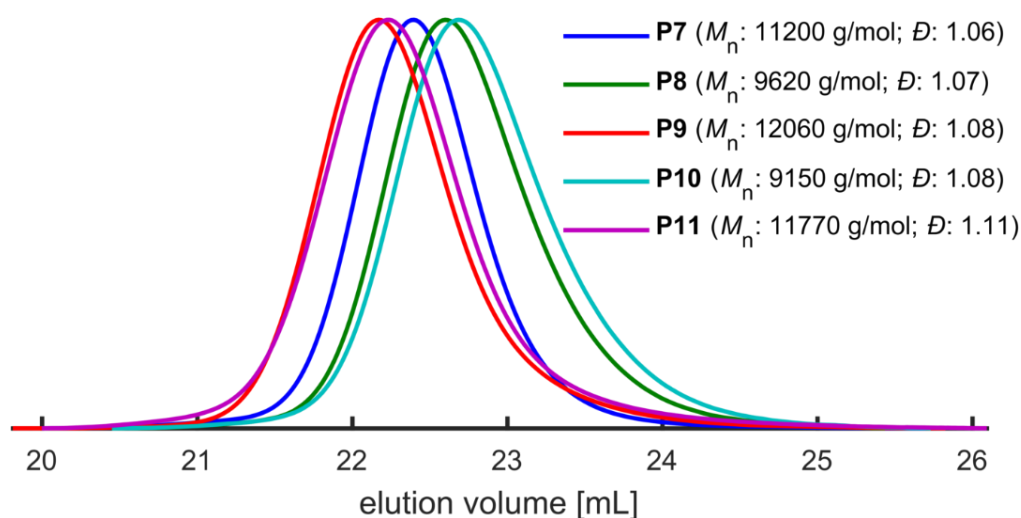


Figure S 15: SEC traces (eluent THF, PS calibration) of P7-11.

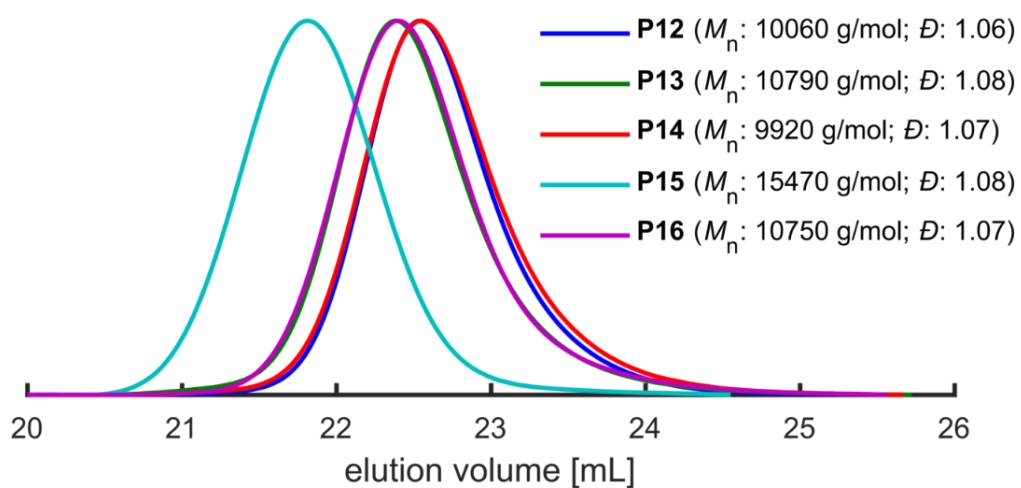


Figure S 16: SEC traces (eluent THF, PS calibration) of P12-16.

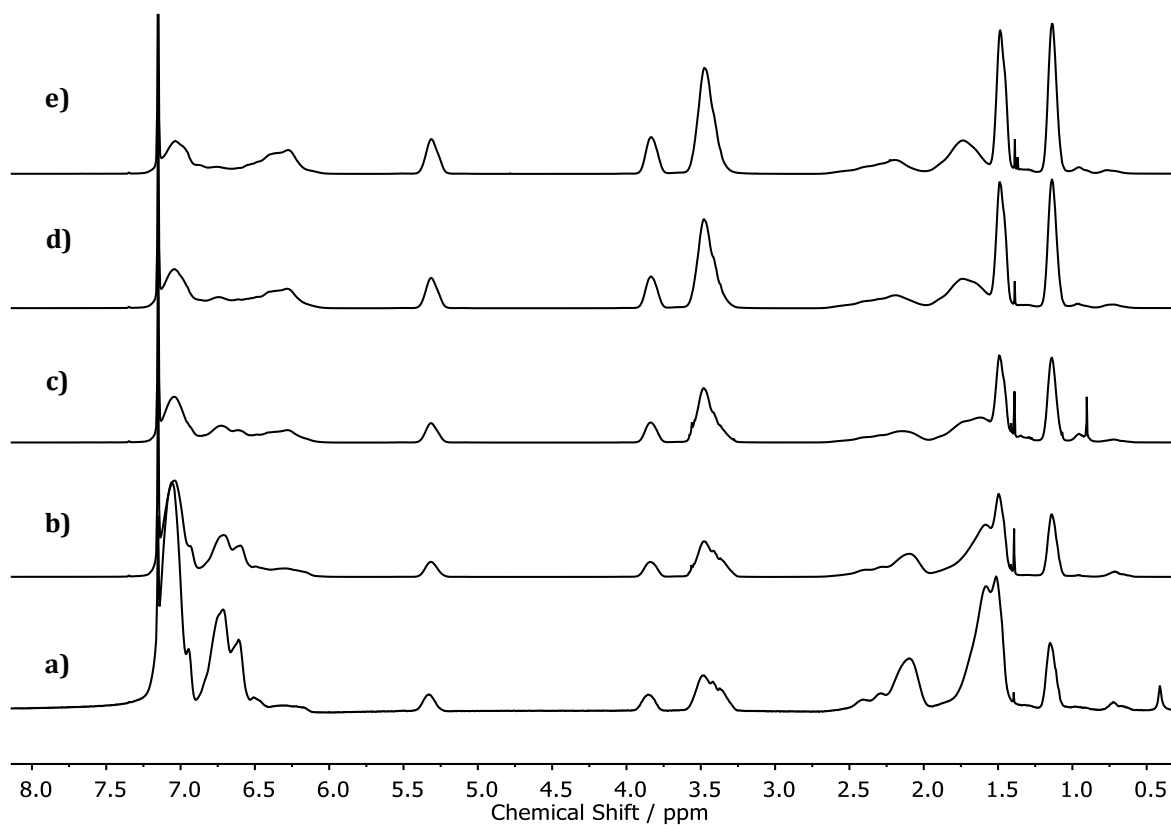


Figure S 17: Stacked ^1H NMR spectra (400 MHz, C_6D_6 , 25°C) of P7-11 (a-e).

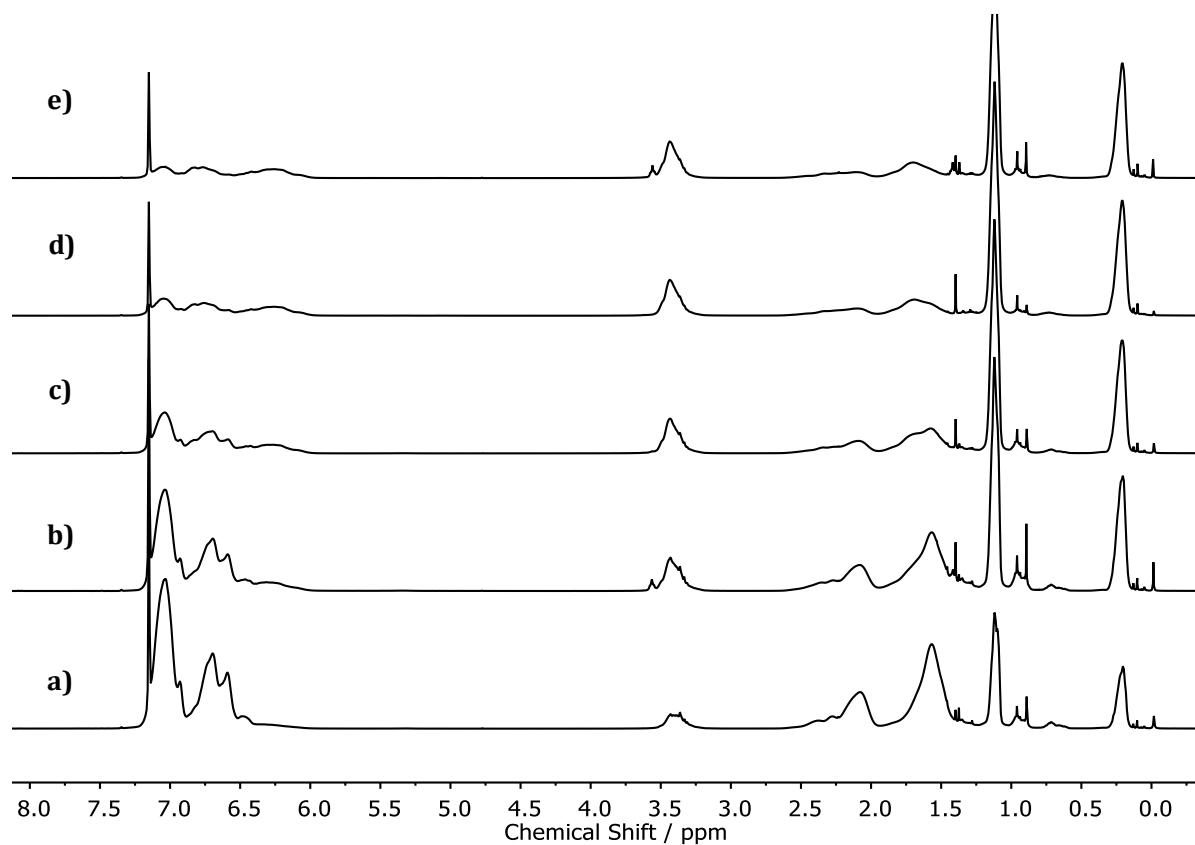


Figure S 18: Stacked ^1H NMR spectra (400 MHz, C_6D_6 , 25°C) of P12-16 (a-e).

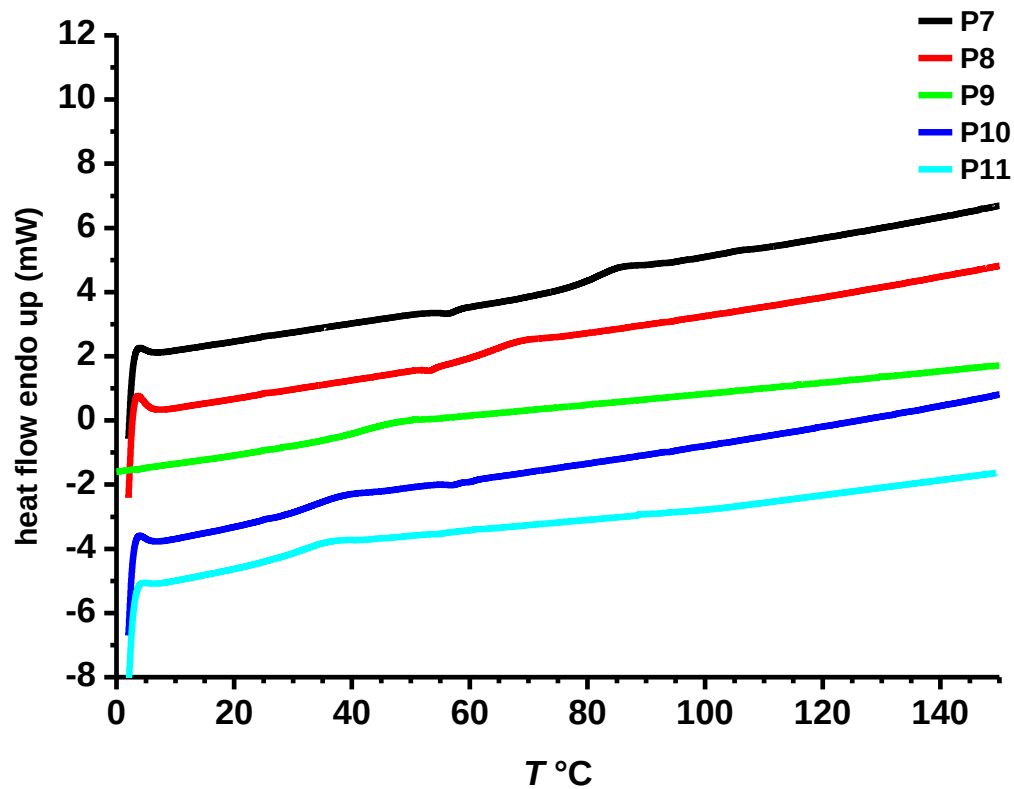


Figure S 19: Second heating curves from DSC of P7-11.

2.1.6.5 Copolymers with 4-isopropylstyrene

Synthesis of 4-isopropylstyrene. 4-Isopropylstyrene was synthesized *via* Wittig olefination of cuminaldehyde according to literature.⁶⁹

The copolymer of 4ⁱPrS and EE-VG was prepared in similar manner to the copolymerization of styrene and EE-VG. 4ⁱPrS was dried with CaH₂ overnight, followed by drying over trioctylaluminum. Two macroinitiators, P(4-ⁱPrS₁₀₉-co-VG₁₈) and P(4-ⁱPrS₁₁₉-co-VG₁₂), were synthesized for the graft-copolymerization of L-lactide and 4-methyl- ϵ -caprolactone.

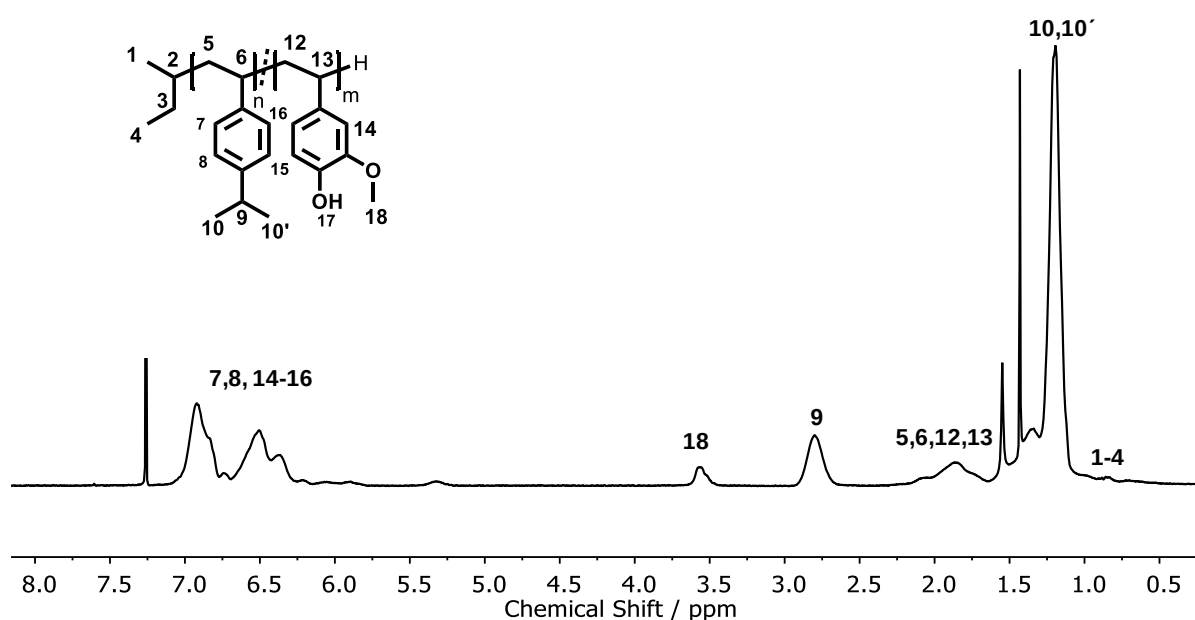


Figure S 20: ¹H NMR spectrum (400 MHz, CDCl₃, 25°C) of P(4-ⁱPrS₁₁₉-co-VG₁₂).

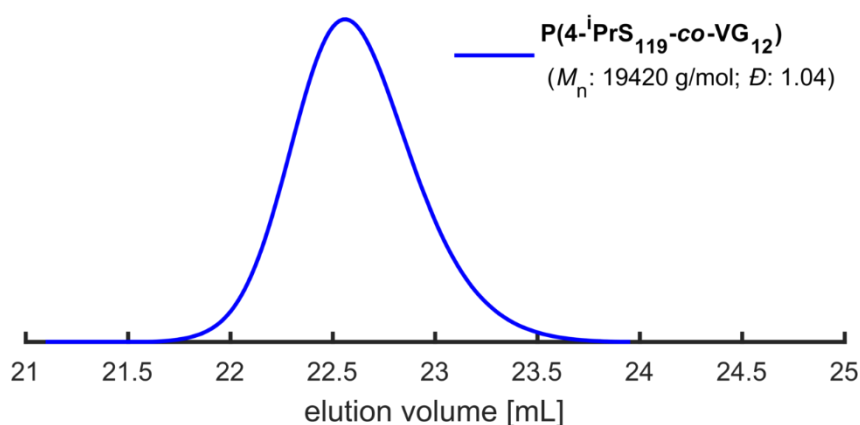


Figure S 21: SEC traces (eluent THF, PS calibration) of P(4-ⁱPrS₁₁₉-co-VG₁₂).

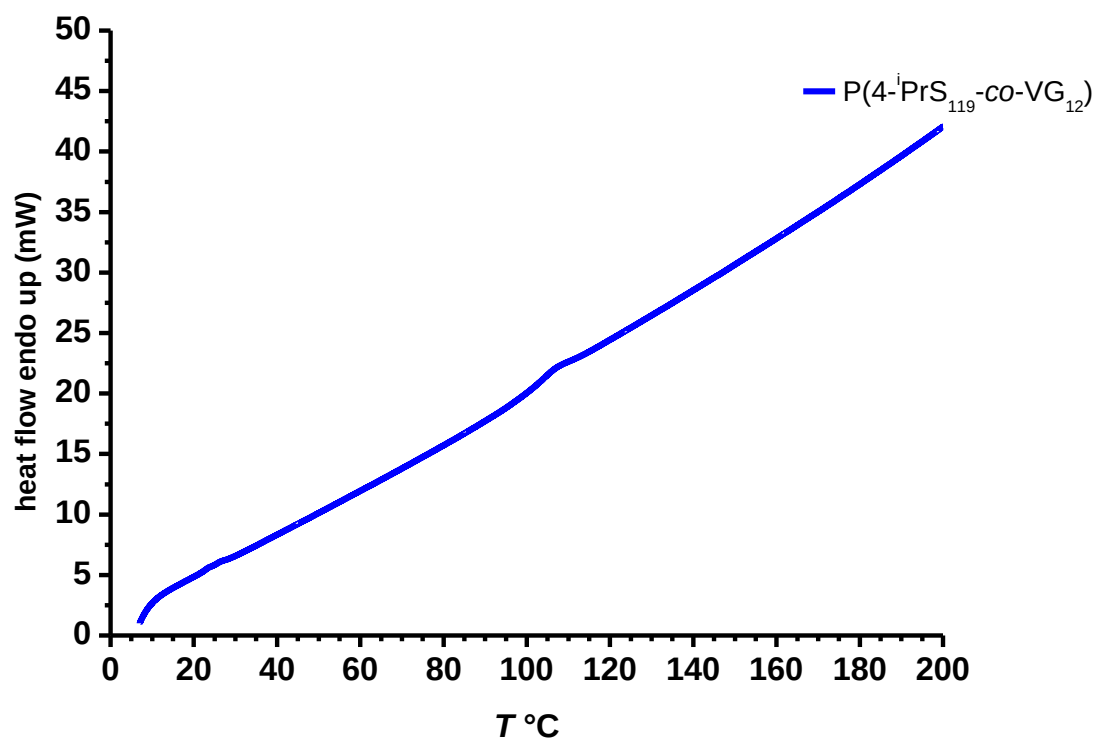


Figure S 22: Second heating curve from DSC of P(4-ⁱPrS₁₁₉-co-VG₁₂) ($T_g = 105^\circ\text{C}$).

2.1.6.6 Demethylation and graft-copolymers

L-Lactide grafting. The graft copolymerization of L-lactide using DBU as catalyst was performed under dry conditions in 25 mL vials with septum in a glove box. The deprotected macroinitiator P(4-ⁱPrS₁₀₉-co-VG₁₈) and L-Lactide were dissolved in dry chloroform. DBU was dried over CaH₂ prior to used and then a stock solution of DBU in chloroform was prepared. DBU (5 eq. /OH) was added to the macroinitiator and L-lactide solution under stirring at room temperature. The polymerization was terminated after 30 minutes by adding benzoic acid. The graft-copolymer was precipitated in cold methanol, centrifuged, and dried in vacuum.

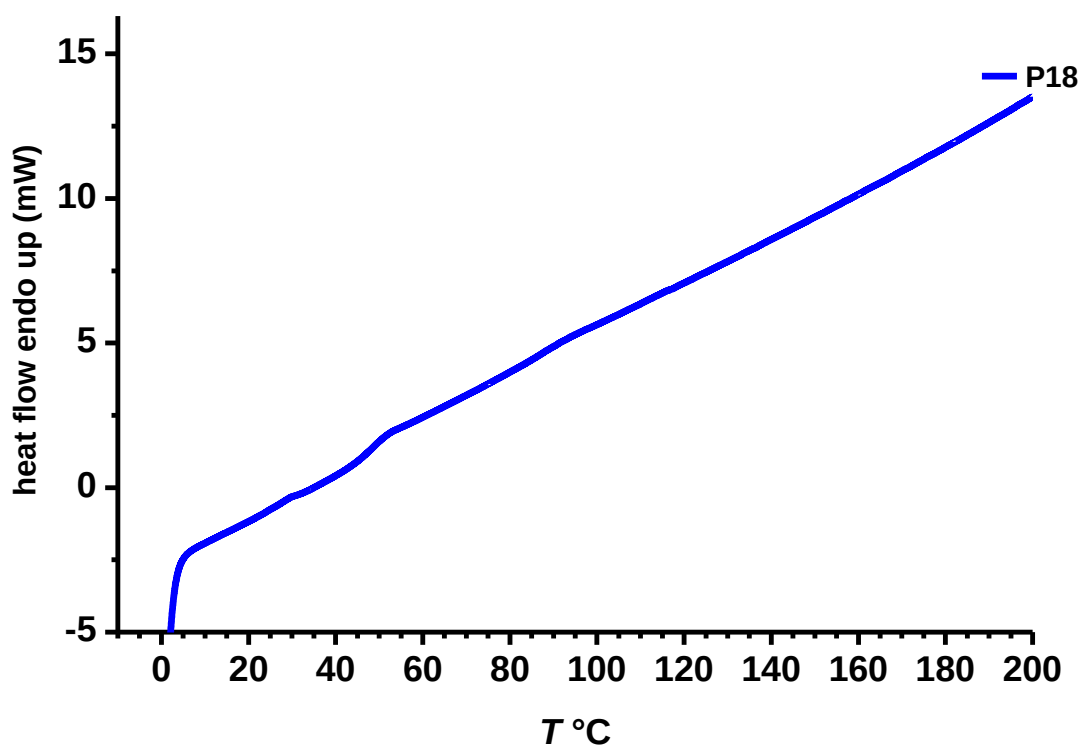


Figure S 23: Second heating curve from DSC of P18 ($T_g = 49^\circ\text{C}$).

4MCL grafting. The polymerization of 4-methyl- ϵ -caprolactone was conducted in bulk and in solution. The bulk polymerization was performed in an anionic flask equipped with a magnetic stir bar. The macroinitiator P(4-*i*PrS₁₁₉-*co*-VG₁₂) (100 mg) was dissolved in 4-methyl- ϵ -caprolactone (1g, 7.8 mmol), and Sn(Oct)₂ (11 mg, 0.026 mmol) was added under dry conditions. The reaction vessel was heated to 130°C in an oil bath for 1h. The clear, viscous polymer was dissolved in dichloromethane and precipitated in cold methanol.

The polymerization of 4-methyl- ϵ -caprolactone was performed in toluene at 130°C for 12h in a high-pressure reactor. The macroinitiator P(4-*i*PrS₁₁₉-*co*-VG₁₂) (250 mg) was dissolved in 4-methyl- ϵ -caprolactone (0.5 g, 3.9 mmol), and Sn(Oct)₂ (40 mg, 0.1 mmol) was added under dry conditions.

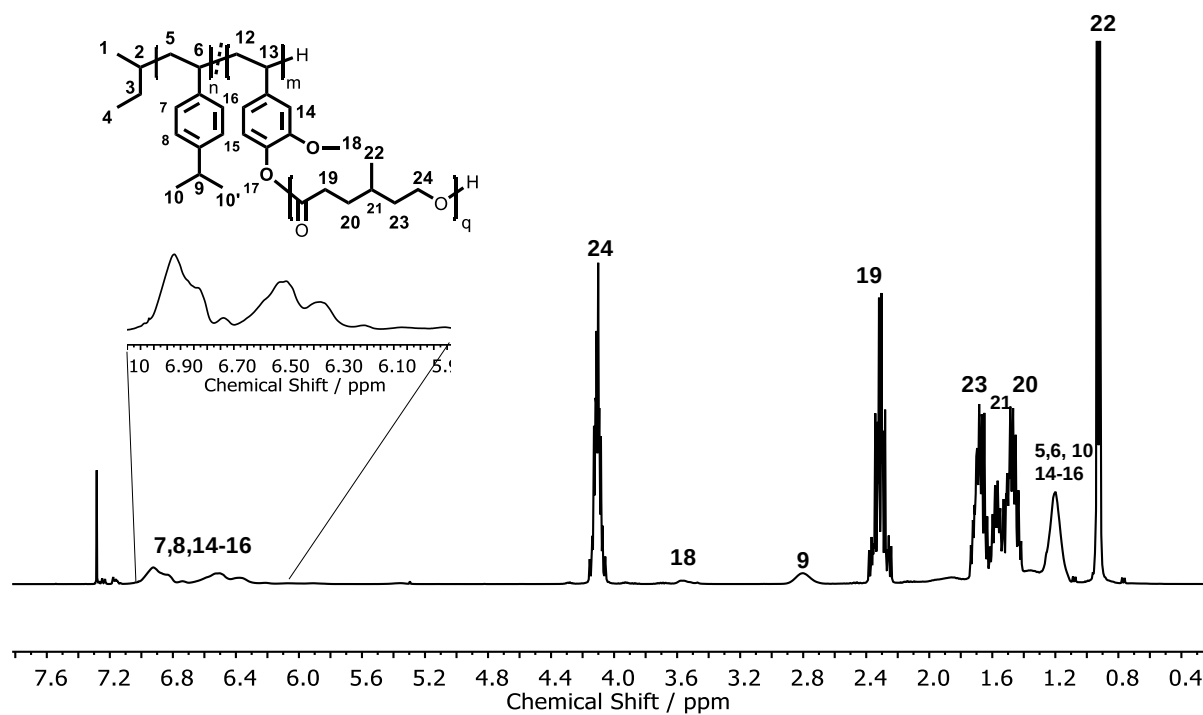


Figure S 24: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of P19.

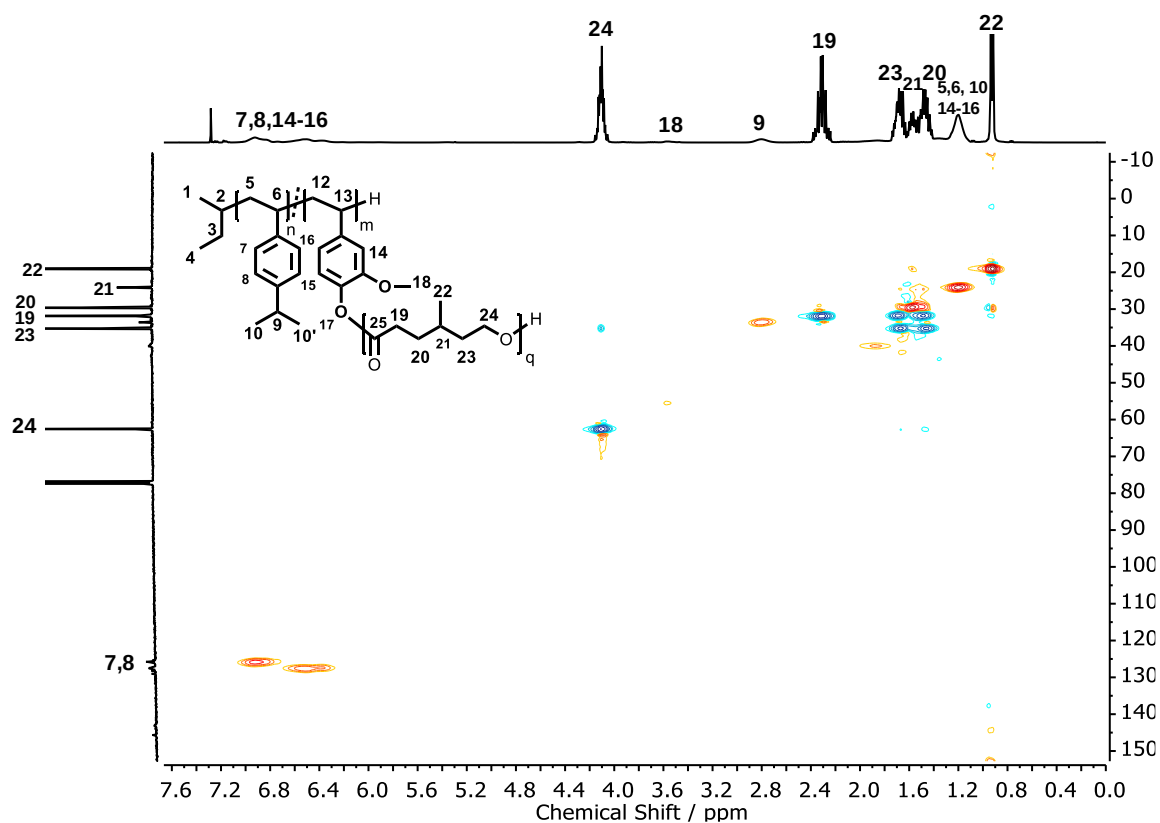


Figure S 25: HSQC NMR spectrum (400 MHz/100 MHz, CDCl_3 , 25°C) of P19.

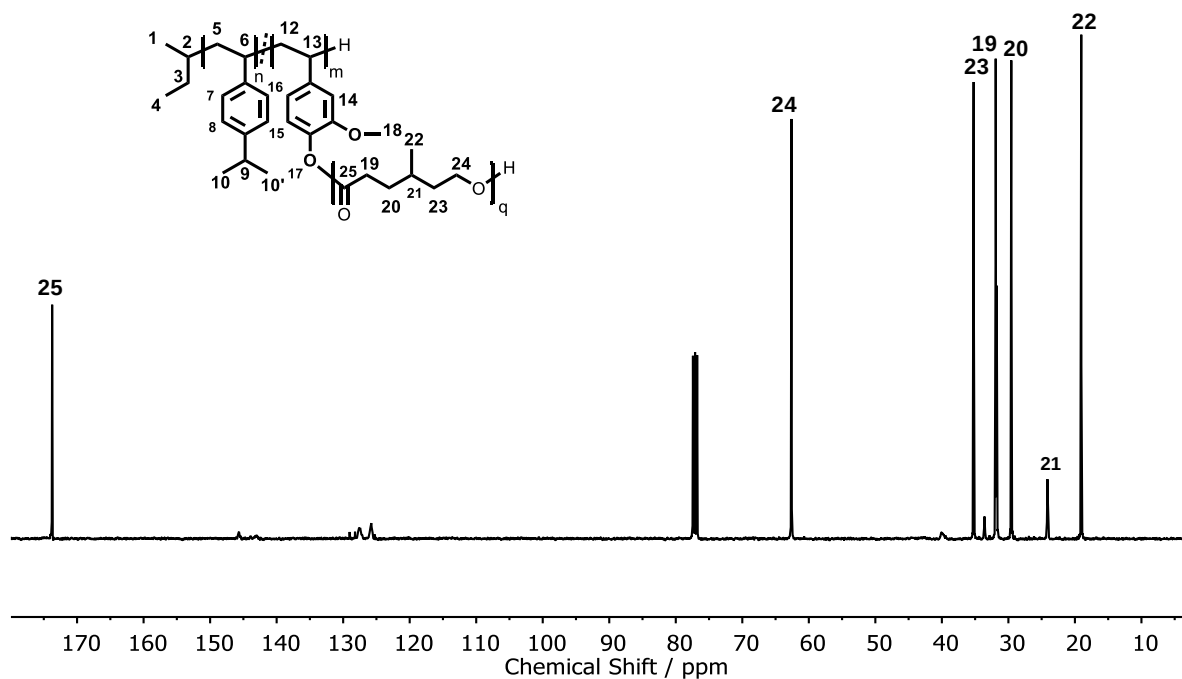


Figure S 26: ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25°C) of P19.

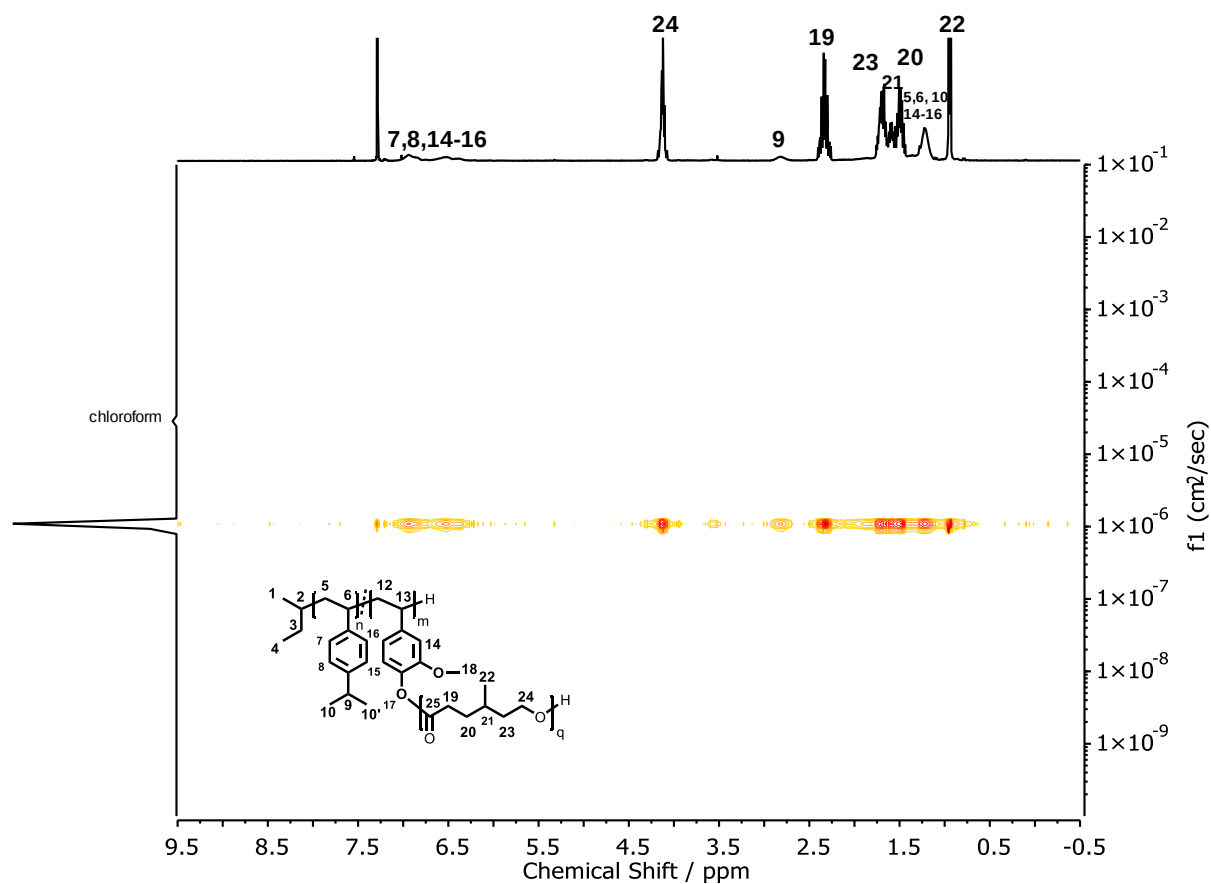


Figure S 27: DOSY NMR (400MHz, CDCl_3 , 25°C) of P19.

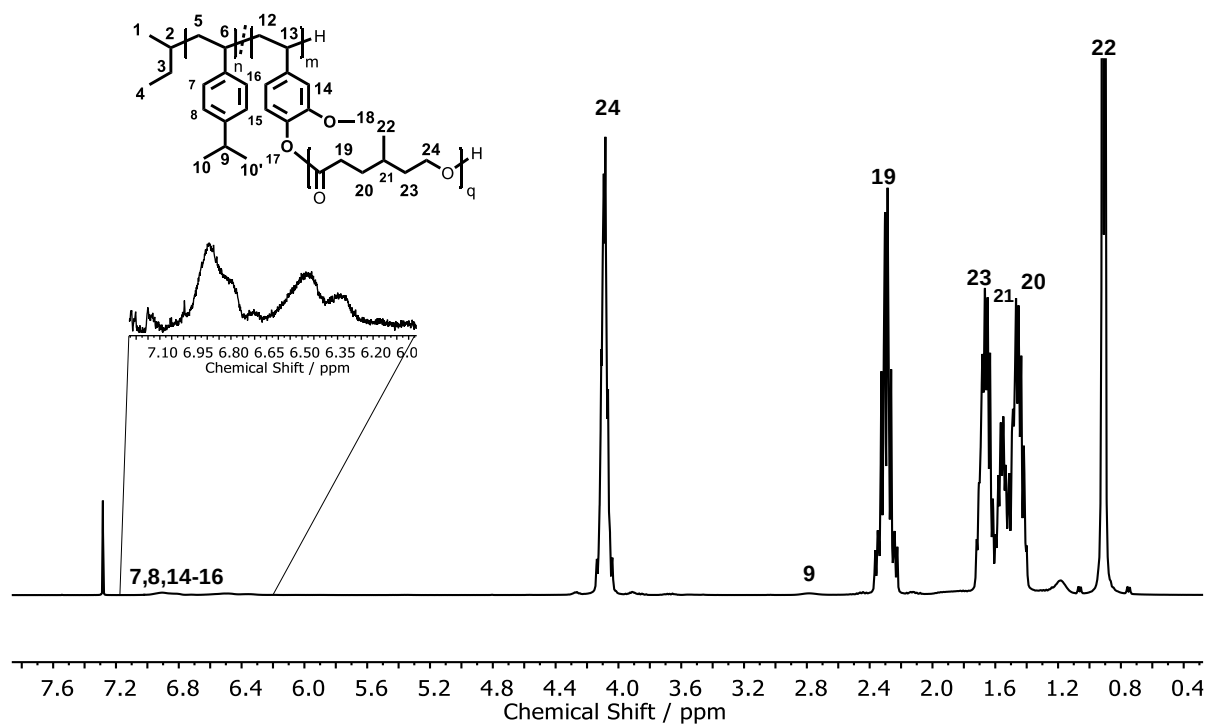


Figure S 28: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of P20.

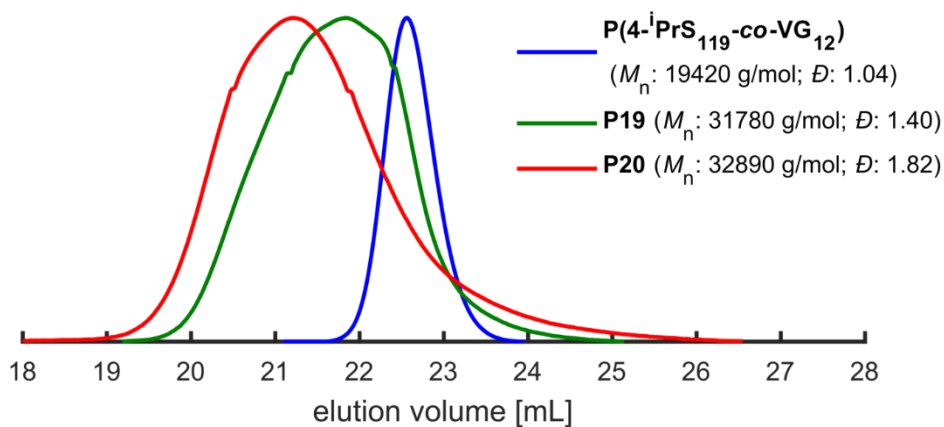


Figure S 29: SEC traces (eluent THF, PS calibration) of P(4-*i*PrS₁₁₉-co-VG₁₂), P19 and P20.

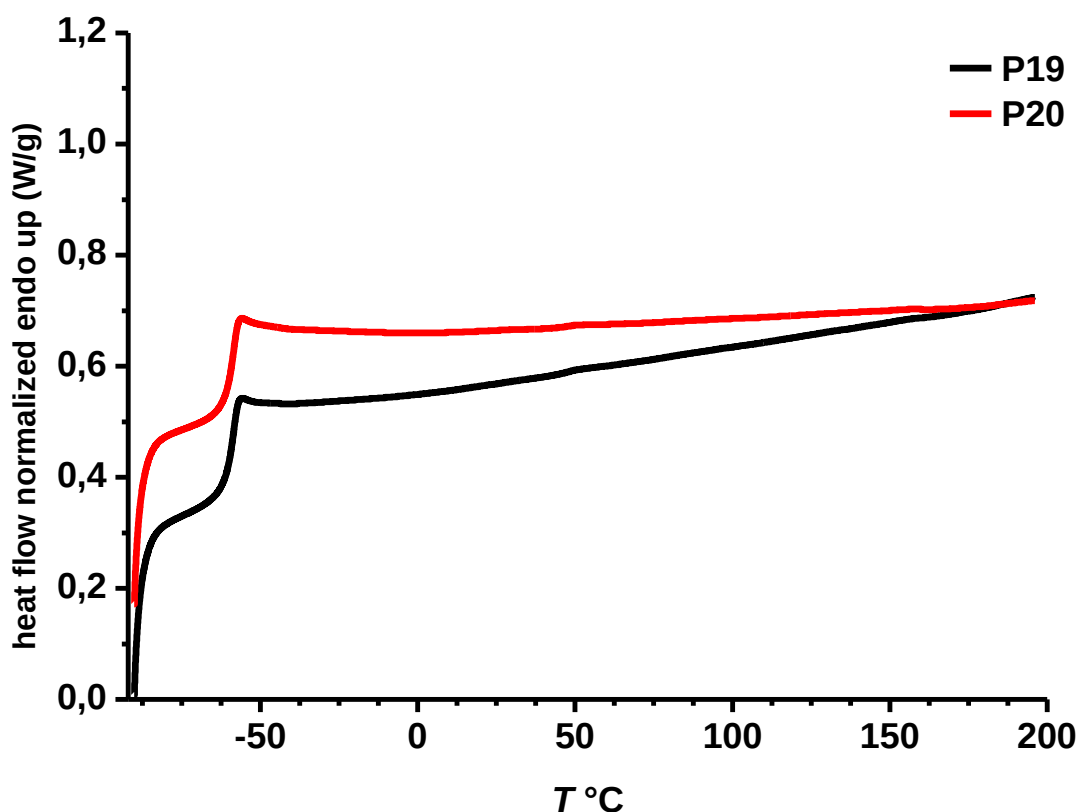


Figure S 30: Second heating curves from DSC of P19 ($T_g = -60^\circ\text{C}$) and P20 ($T_g = -58^\circ\text{C}$).

Demethylation. According to literature, boron tribromide has been found to be an effective reagent for the complete cleavage of methoxy groups in methoxyarene. The demethylation of P(4-*i*PrS₁₁₉-*co*-VG₁₂) and P(4-*i*PrS₁₀₉-*co*-VG₁₈) was performed according to a procedure of Carvalho et al.⁷¹ Boron tribromide in toluene (25 w%) was added to solution of P(4-*i*PrS₁₀₉-*co*-VG₁₈) in dichloromethane under cooling. Without cooling, the mixture was stirred for 24 h, and then poured into ice and water. The aqueous suspension was extracted with chloroform. After the removal of the solvent, the polymer was dissolved in toluene and precipitated in mixture of isopropanol and water (9/1) and dried in vacuum.

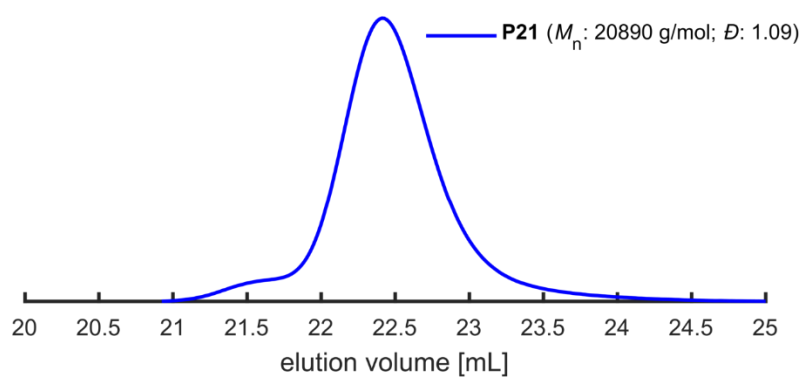


Figure S 31: SEC traces (eluent THF, PS calibration) of P21 (P(4-*i*PrS-*co*-VC)).

Chapter 3 Functional 1,3-Diene Monomers

3 Functional 1,3-Diene Monomers

MyrDOL - a Protected Dihydroxyfunctional Diene

Monomer Derived from β -Myrcene: Functional Polydienes from Renewable Resources *via* Anionic Polymerization

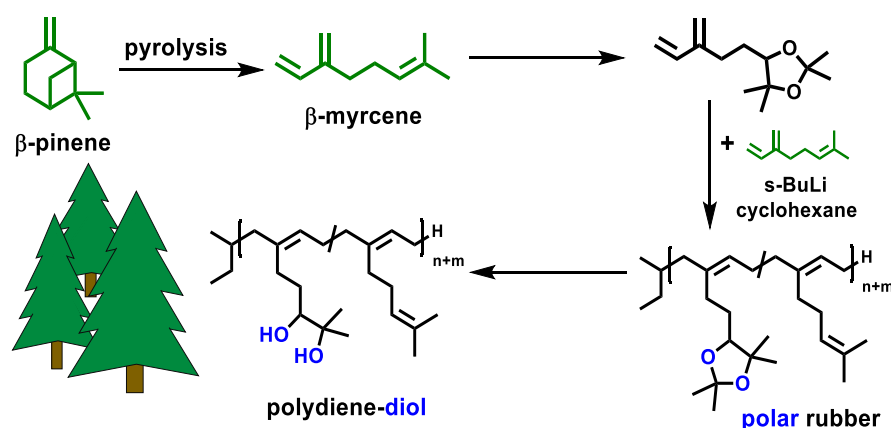
Christoph Hahn,^{a,b} Manfred Wagner,^c Axel H. E. Müller,^a Holger Frey^a

^a Department of Chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz (Germany)

^b Max Planck Graduate Center, MPGC, Staudingerweg 9, 55128, Mainz (Germany)

^c Max Planck Institute for Polymer Research, 55128 Mainz (Germany)

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3.1.1 Abstract

The protected functional diene monomer 2,2,4,4-tetramethyl-5-(3-methylenepent-4-en-1-yl)-1,3-dioxolane (myrcene dioxolane, MyrDOL) is introduced, based on β -myrcene. The monomer is suitable for carbanionic polymerization, since its acetal functionality as a protective group for diols is stable under carbanionic conditions. The polymerization of MyrDOL in cyclohexane at 25°C using *sec*-butyllithium as an initiator resulted in homopolymers with well-controlled molecular weights in the range of 4.0 to 31 kg mol⁻¹ (SEC, PMMA calibration) and low dispersities, $\bar{D}$, between 1.07 and 1.13. In pronounced contrast to polymyrcene, which contains 95% 1,4-myrcene microstructure (obtained in cyclohexane by anionic polymerization, T_g = -67°C), microstructure characterization of P(MyrdOL) shows 30-33% of 3,4-units and a T_g of 11°C. The acetal groups can be quantitatively removed under mild conditions, using acidic deprotecting agents (*e.g.* DOWEX resin), resulting in well-defined poly(myrcene-2,3-diol). The copolymerization of MyrDOL with the dienes myrcene, styrene and isoprene, respectively was investigated in great detail via *in-situ* ¹H NMR spectroscopy kinetics. The substitution pattern of the 1,3-diene in combination with the polarity of the monomer has significant influence on the copolymerization behavior, resulting in disparate reactivity ratios and formation of tapered copolymers in statistical copolymerizations. Myrcene copolymers with varying MyrDOL content, in the range between 10 - 100 mol% MyrDOL, were synthesized ($\bar{D} \leq 1.15$) and characterized regarding their glass-transition temperatures and polydiene microstructure. An increase in the 3,4-microstructure content was observed, as a consequence of both increasing MyrDOL content and polarity of the polymerization medium, resulting in an increase in T_g from -67 to 9 °C. The protected, functional MyrDOL monomer is promising with respect to polar, hydroxyl-functional rubbers.

3.1.2 Introduction

The development of new synthetic strategies towards bio-based materials is a current objective in academic and industrial research, motivated by dwindling petrochemical resources and increasing environmental awareness.^{1,2} Terpenes are a class of naturally occurring compounds, formally derived from isoprene units $(C_5H_8)_n$, and produced by many conifer species and other plants.³ By means of catalytic, biocatalytic or thermochemical processes, these natural compounds can be converted to novel functional monomers and fine chemicals for a wide range of applications.⁴⁻⁶ Bio-based terpenes offer promising potential because of their convenient availability and structural similarity to isoprene and butadiene.⁷ The living anionic polymerization of 1,3-diene monomers is a key step for the manufacturing of thermoplastic elastomers, established on a megaton scale for SBS and SIS-type materials in industry.⁸⁻¹¹

Natural feedstock-based materials can be used instead of their petroleum-derived diene counterparts.^{12,13} Recently, they emerged as promising candidates to serve as building blocks for bio-based polymers.¹⁴⁻¹⁹ Myrcene is obtained by the pyrolysis of β -pinene, which is a bicyclic monoterpene and the primary constituent of turpentine.³

Myrcene can be polymerized by various polymerization techniques like controlled and free radical polymerization, coordination polymerization and living anionic polymerization.²⁰⁻²⁴ As early as 1948, Goldblatt *et al.* initially synthesized a series of synthetic rubbers by emulsion polymerization and copolymerization of myrcene.²⁵ Recently, Gong *et al.* copolymerized polar myrcene derivatives with myrcene or isoprene using a neodymium or cobalt catalyst.^{26,27} In general, the coordination polymerization using rare-earth catalysts proceeds with complete monomer conversion and results in polyterpenes with high molecular weights. The drawback of this polymerization method is the rather broad molecular weight distribution ($\mathcal{D} > 1.3$) and the lacking possibility to generate block copolymer architectures, for instance for thermoplastic elastomers.

Unlike other polymerization techniques, carbanionic polymerization generally proceeds without termination or transfer reactions.²⁸ In addition, the living character of the anionic polymerization gives access to precise molecular weight control, low dispersity and complex macromolecular architectures.²⁹ Fully bio-based thermoplastic elastomers have gained increasing attention in the last decades. For this reason, several works focused on the copolymerization of β -myrcene with different comonomers and the synthesis of fully bio-based polymers.^{30–36}

The additional double bond of myrcene represents an advantage over the nonfunctionalized isoprene/butadiene rubbers. It facilitates further functionalization *via* post-polymerization modification reactions.^{25,37} Several works demonstrated that thiol-ene “click” chemistry can be employed to unsaturated terpenes and polymers, which offers the possibility to introduce a large variety of functional groups.^{38–40} However, when addressing the double bonds of polydienes after the polymerization, the disadvantage of post-modifications is the lack of regiospecificity, since the double bonds in the backbone compete with the pendant isopropylidene groups.^{37,41} The selective functionalization of these unsaturated sites of the polymer is not possible *via* post-modifications. It is important to note that Schlaad *et. al.* demonstrated that polymyrcene-2,3-diol is not attainable *via* regioselective epoxidation of polymyrcene and subsequent acidic hydrolysis of the resulting epoxide.³⁷

To date, functional polar rubbers have been produced only to a low extent.^{26,42–44} The synthesis of functional dienes can be challenging.⁴⁵ A small number of functional diene monomers have been reported to date, containing silyl or amine groups.^{46–48} In addition, the synthetic difficulties of such polar dienes are due to unexpected elimination of the monomer structure under the polymerization conditions, induced by the reaction of the living chain end with 2-alkoxy-1,3-butadienes, which leads to the so called “back side collapse”.⁴⁹ This undesired elimination reaction happens when the hydroxyl functionality is too close to the 1,3-diene system. The MyrDOL structure avoids this reaction due to the naturally present alkyl spacer between the polymerizable 1,3-diene moiety and the hydroxyl functionality.

Functional groups bearing acidic protons or electrophile groups (carbonyl), such as OH, SH, SiOH, NH₂, CHO, and COOH, are not compatible with carbanionic polymerization conditions.⁵⁰ Thus, suitable protective group chemistry has to be employed in the field of anionic polymerization.^{51,52} For instance, phenols were successfully protected by *tert*-butyldimethylsilyl chloride, resulting in 4-*tert*-butyldimethylsilyloxystyrene, which was subjected to carbanionic polymerization in THF at -78 °C.⁵³

Catechol-based monomers were investigated for different applications based on surface binding.⁵⁴ The catechol group shows outstanding adhesion and complexation properties, due to the chelate effect of catechol.⁵⁵⁻⁵⁷ 2,2-dimethyl-1,3-dioxolanes represent a base-stable protecting group for diol moieties and deprotection can readily be achieved by acidic hydrolysis under mild conditions after polymer formation.⁵⁸⁻⁶⁰ In pronounced contrast to the labile catechol moiety, aliphatic diols are stable and resistant to oxidation, which prolongs long-time storage stability.⁶¹ Such aliphatic diols present a promising class of polymer materials, as they can be used as macroinitiators for the synthesis of graft-copolymers.⁵⁸

Our group recently described the synthesis and polymerization of a novel bio-based hydroxy-functional diene monomer, silyl-protected β -myrcenol.⁴⁸ In general, silyl-protecting groups are quantitatively removed by means of tetrabutylammonium fluoride. New polar functional diene monomers for carbanionic polymerization should fulfill the following requirements: (i) stable protecting group, (ii) polymerization in apolar media at ambient temperature and (iii) convenient and scalable synthesis based on renewable resources.

3.1.3 Results

Terminology. 2,2,4,4-Tetramethyl-5-(3-methylenepent-4-en-1-yl)-1,3-dioxolane and styrene are abbreviated MyrDOL and S, respectively. Isoprene and myrcene are abbreviated as Iso and Myr, respectively. The deprotected polymer of MyrDOL, poly(myrcene-2,3-diol), will be denoted as P(Myrc(OH)₂).

Reagents. Chemicals and solvents were purchased from commercial suppliers (Acros, Sigma-Aldrich, Fisher Scientific, Alfa Aesar, TCI). Deuterated solvents were obtained from Deutero GmbH. Isopropyl alcohol and methanol were used as received without further purification. Cyclohexane was purified by stirring over diphenylhexyllithium (adduct of sec-butyllithium and 1,1-diphenylethylene), vacuum-transferred and degassed by three freeze-pump-thaw cycles prior to use. The monomers MyrDOL and Myr were purified by stirring over CaH₂ overnight, followed by distillation. MyrDOL was additionally dried over trioctylaluminum and vacuum-transferred prior to use. All monomers for the anionic polymerization were degassed by three freeze-pump-thaw cycles prior to use. Dowex® 50W x8 hydrogen form, strongly acidic, 200-400 mesh size, was purchased from Sigma-Aldrich and was recovered with diluted sulfuric acid for 30 minutes, when exhausted.

Instrumentation. All NMR spectra (¹H, ¹³C, ed. HSQC, HMBC, ¹H, ¹H-COSY and DOSY) were recorded on a Bruker Avance II 400 spectrometer equipped with a 5 mm BBFO-SmartProbe with z gradient and ATM, as well as a SampleXPress 60 sample changer. The kinetic studies were recorded with a 500 MHz Bruker Avance III system. All spectra are referenced internally to residual proton signals of the deuterated solvent. Size exclusion chromatography (SEC) measurements were performed using an Agilent 1100 Series, equipped with a SDV column set from PSS (SDV 103, SDV 105, SDV 106). Tetrahydrofuran (THF) was used as the mobile phase (flow rate 1 mL min⁻¹) and as the solvent. Poly(styrene) standards and PMMA were provided by PSS for calibration. The measurements were carried out at 30 °C with an RI and UV (275 nm)

detector. For analysis, the PSS WinGPC® UniChrom (V 8.31, Build 8417) software provided by PSS Polymer Standards Service GmbH was used.

Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) recorded on a Perkin Elmer 8500 differential scanning calorimeter. A temperature range from -90 °C to 130 °C was used. For the first cycle a heating rate of 10 °C min⁻¹ and a cooling rate of 10 °C min⁻¹ was employed. A second heating cycle (10 °C min⁻¹) was used to evaluate the thermal properties of the (co)polymers.

MALDI-ToF mass spectrometry measurements were performed using a Bruker autoflex maX. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) was used as a matrix (1:1 in CHCl₃) for P(MyrdOL) and silver trifluoroacetate was used as the cationization salt. The spectrum was measured in a linear positive mode with a laser wavelength of 337 nm. For all polymers 1 mg analyte was dissolved in 1 mL solvent.

General (co)polymerization procedure. All polymerizations were carried out in cyclohexane at room temperature in an argon-filled glovebox (Mbraun UNILAB, <0.1 ppm of O₂ and <0.1 ppm of H₂O) in 40 mL glass vials, equipped with a magnetic stir bar, screw caps and septa. Dry and degassed cyclohexane was distilled into a Schlenk flask equipped with a Teflon stopper. The monomer MyrdOL was dried for 24h over CaH₂ and then additionally 24h over trioctylaluminum, degassed and finally distilled into another Schlenk flask with Teflon stopper. Myrcene, isoprene and styrene were dried over CaH₂ for 24 h, degassed and then distilled into another Schlenk flask with Teflon stopper. Inside the glove box the monomer(s) and cyclohexane were added into a glass vessel with septum. For the synthesis of a homopolymer and copolymers the monomer/solvent (10-15 wt%) mixture (typically 1mL monomer/10mL cyclohexane) was initiated with 0.1 mL sec-butyllithium (1.3 M in cyclohexane/hexane 92/8) via 1 mL syringe. The solution was stirred for 24 h to ensure full monomer conversion. The polymerization was terminated by adding 0.5 mL of methanol (degassed with argon for 1h prior to use) by a syringe. The polymers were

precipitated in 30 mL of a cold methanol/isopropanol mixture and dried under reduced pressure.

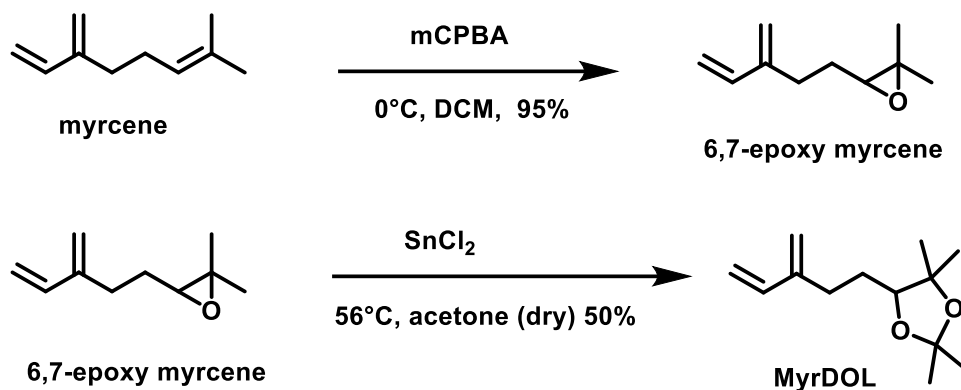
¹H NMR Kinetics. For the kinetic measurements, 0.6 mL dried cyclohexane-*d*₁₂ was used as solvent in conventional NMR tubes with rubber septa. The monomers ($[M]_0 = 3.5\text{--}7.5 \cdot 10^{-4}$ mol/mL, typically 20–30 mg of each monomer) were added in a 50/50 molar ratio under exclusion of air and humidity in a glove box. A ¹H NMR spectrum of the solution was measured prior to the initiation step. The polymerization was initiated with 0.005 mL sec-BuLi solution (1.3M) and the NMR tube was vigorously shaken and directly placed into the NMR sampler.

Deprotection. 500 mg of P(MyrdOL) homo- or copolymer was dissolved in 30 mL THF, 500 mg DOWEX was added and refluxed for 24h. The turbid solution was centrifugated and the THF solution was separated. THF was removed by rotatory evaporation.

Results and Discussion

3.1.3.1 Monomer synthesis

The monomer synthesis (Scheme 1) starts with the selective epoxidation of β -myrcene at the pendant double bond, while maintaining its 1,3-diene structure. 6,7-epoxy myrcene was prepared according to literature in 95% yield.⁶²



Scheme 1: Synthesis of MyrDOL starting from β -myrcene.

The second step of the MyrDOL synthesis, the transformation of the epoxide to the dioxolane was achieved by the SnCl_2 catalyzed reaction of 6,7-epoxy myrcene with acetone under dry conditions with a yield of 50%. The corresponding acetonide represents a suitable protective group for 1,2-diols. It was demonstrated in literature that this protective group is stable under carbanionic conditions in combination with styrene monomers.⁵⁸ Details and NMR spectra are given in the Supporting Information (Figures S1, S2).

3.1.3.2 Homopolymerization of MyrDOL

MyrDOL was subjected to carbanionic polymerization in the apolar solvent cyclohexane to achieve varying molecular weights. The polymerization at 25°C, using *sec*-butyllithium as an initiator, resulted in homopolymers with well-controlled molecular weights in the range of 4.0 to 31 kg mol⁻¹ (SEC, eluent THF, PMMA calibration) and dispersities between 1.07 and 1.13. Table 1 summarizes the homopolymerization results.

Table 1: Results of the homopolymerization of MyrDOL in cyclohexane.

Polymer^a	$M_{n,target}$ kg/mol	$M_{n,SEC}^b$ kg/mol	$M_{n,SEC}^c$ kg/mol	$\bar{D}^b$	3,4 units %	T_g, °C
P(MyrdOL) ₁₄	3.0	2.9	4.0	1.09	30	-
P(MyrdOL) ₂₄	5.0	3.3	4.7	1.08	31	9
P(MyrdOL) ₄₇	10.0	6.2	9.0	1.07	33	-
P(MyrdOL) ₁₅₆	30.0	20.6	31.4	1.13	33	11

^aThe index indicates the target degree of polymerization, $[M]_0/[I]_0$. ^bDetermined by SEC in THF (RI signal, PI calibration); ^cDetermined by SEC in THF (RI signal, PMMA calibration).

Molecular weights were determined by SEC measurements (Figure S3), calibrated to poly-isoprene (PI) and poly(methyl methacrylate) (PMMA) standards, respectively. The results suggest that the molecular weights of P(MyrdOL) are underestimated by SEC when using PI calibration. Hence, the polar polymer was referenced to PMMA standards, and the target molecular weights are in good agreement with the values obtained from SEC in THF using PMMA standards. The sample P(MyrdOL)₁₅₆ (31 kg mol⁻¹) demonstrates the accessibility of high molecular weight homopolymer, which is a precondition for polymer architectures and corresponding nanophase segregation.

The MALDI-ToF MS spectra (Figure S4) confirm the successful homopolymerization by showing a repeating unit of 210.3 g/mol, which is in agreement with the molar mass of MyrdOL. The number-average molecular weight determined by MALDI-ToF MS of sample P(MyrdOL)₄₇ is in good agreement ($M_p=7500$ g/mol) with the molecular weight determined by GPC (PMMA calibration).

3.1.3.3 Microstructure of P(MyrdOL) by NMR-spectroscopy

The microstructure of P(MyrdOL) was investigated via ^1H -NMR-Spectroscopy (Figure 1, Figures S5-7) based on the vinylic protons **a** and **a'** using equation S1 (Supporting Information). The content of 3,4-units is 30-33%, compared to only 6% for polymyrcene prepared under the same conditions in cyclohexane. The increase in 3,4-units is attributed to the increased polarity of the monomer, polymer and chain end.⁴⁸ The glass-transition temperature of P(MyrdOL) was determined to $T_g=9\text{-}11^\circ\text{C}$ by DSC (Figure S8). It is well-known that in carbanionic polymerization of dienes the polarity of the solvent has a key impact on the microstructure, resulting in generally increased content of 3,4-units.^{63,64} The strongly increased formation of the 3,4-myrcene units is comparable to the effect of the addition of THF to the carbanionic polymerization of dienes in apolar media.⁶⁵ This significant impact of the polar protecting group on the polymerization is discussed in more detail further below.

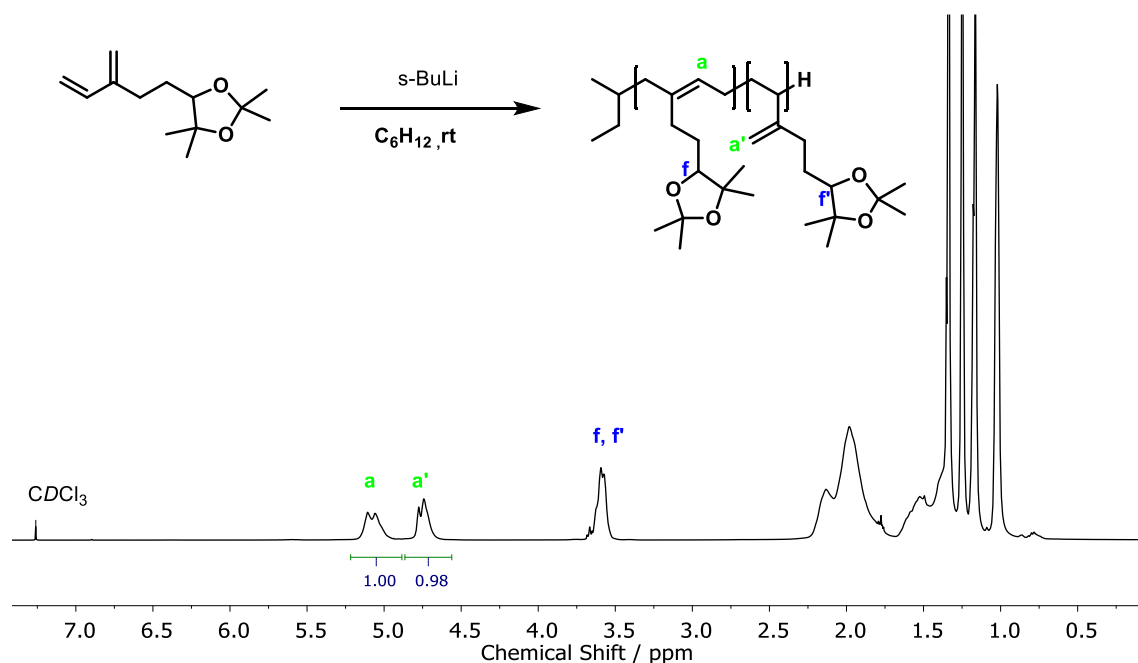


Figure 1: ^1H -NMR spectrum (400 MHz, CDCl_3 , 25°C) of P(MyrdOL)₄₇.

3.1.3.4 Copolymerization of MyrdOL with myrcene

A series of copolymers composed of MyrdOL and myrcene with constant molecular weight of 6 kg mol^{-1} and monomer ratio varied over the whole range from 10 - 100

mol% of MyrDOL was synthesized. The molecular weight distributions observed by SEC (Figure S 9) were generally narrow. An overview of all protected P(MyrdOL-co-Myr) copolymers is given in Table 2.

Table 2: Results of the copolymerization of MyrdOL with myrcene in cyclohexane at room temperature.

Polymer	x_{MyrdOL}^a mol-%	x_{MyrdOL}^b mol-%	$M_{n,\text{SEC}}^c$ kg/mol	$M_{n,\text{NMR}}^d$ kg/mol	$\bar{D}^c$	3,4-units %	T_g , °C
P(MyrdOL) ¹²	0	0	9.9	9.5	1.06	6	-67
P(MyrdOL _{0.1} -co-MyrdOL _{0.9})	10	13±3	6.7	8.8	1.14	7.5	-56
P(MyrdOL _{0.25} -co-MyrdOL _{0.75})	25	19±3	6.0	8.4	1.13	9.1	-53
P(MyrdOL _{0.5} -co-MyrdOL _{0.5})	50	49±3	6.2	6.7	1.12	16.7	-33
P(MyrdOL _{0.75} -co-MyrdOL _{0.25})	75	63±3	5.7	7.6	1.09	20.7	-14
P(MyrdOL _{0.9} -co-MyrdOL _{0.1})	90	76±3	5.6	7.8	1.07	24.5	-11
P(MyrdOL) ₂₈	100	-	5.0	6.3	1.15	31.0	9

$M_{n,\text{target}} = 6.0$ kg/mol, $[M]_0 = 1$ mol/L; $[I]_0 = 1.1 \cdot 10^{-2}$ mol/L.^a targeted feed, ^b composition determined by NMR, ^c determined by SEC in THF (RI signal, PI calibration), ^d determined by ¹H-NMR spectroscopy (CDCl₃) by referencing to the methyl protons of the initiator (Figure S11-15, i+i').

The molar amount of incorporated comonomers was determined by ¹H-NMR spectroscopy by comparing the integrals of methyl groups (Supp. Inf. Figures S10-14, myrcene: e+e'+e''+e''', MyrdOL: c+c'+d+d') of MyrdOL and myrcene. In addition, the content of 3,4-units of the polymer backbone was investigated by ¹H-NMR spectroscopy, the amount was calculated according to literature.⁶⁵ With increasing MyrdOL feed of the copolymer, a linear increase of the 3,4-units from 7.5 to 31% P(MyrdOL) was observed. It is important to note that the 3,4-units of MyrdOL and myrcene are not distinguished in this discussion.

The thermal properties of the copolymers are strongly dependent on the content of MyrdOL (Figure S15). With increasing MyrdOL content the glass transition

temperature of the polymers increased from $-56\text{ }^{\circ}\text{C}$ (13 mol% MyrDOL) to $11\text{ }^{\circ}\text{C}$ for the homopolymer P(MyxDOL). The T_g values follow the Fox relation (eq. S2, Figure S16), although our kinetic investigations (below) show that the comonomers are not randomly distributed.

As known from literature, polymyrcene with similar molecular weight, synthesized in apolar media, usually shows low content of 3,4-units in the range of 6%, with a T_g of $-67\text{ }^{\circ}\text{C}$.⁴⁸ The polar nature of the 1,3-dioxolane moiety is considered to have a “self-modifier” effect on the microstructure of P(MyxDOL). Lewis base polar modifiers, such as THF or the 1,3-dioxolane, possess free electron donor pairs, which can form a σ -complex with the living center.⁶⁶ This intrinsic polarity in the monomer can explain the relatively high extent of 3,4 addition, although the polymerization was performed in the apolar solvent cyclohexane.

The increasing T_g is tentatively explained by the sum of two effects: (i) polarity of the 1,3-dioxolane protecting group, resulting in increased dipole-dipole interactions of the polymer chains and (ii) increasing amount of 3,4-units. The effect of the polar 1,3-dioxolane group will be discussed in more detail below.

3.1.3.5 ^1H -NMR *in-situ* copolymerization kinetics with myrcene, styrene and isoprene

^1H -NMR online kinetic measurements are a valuable tool for the investigation of the monomer sequence statistics of the copolymers and the determination of the reactivity ratios of the comonomers.⁶⁷ Monitoring the incorporation of the comonomers during polymerization is only possible, when the monomers are structurally different, so that the monomer signals can be separated and are also distinguishable from the resulting copolymer resonances. Figure 2 shows the structures of MyrDOL and myrcene and the corresponding ^1H -NMR spectra. The overlapping signals at 6.24 ppm correspond to the vinyl protons (H_a and H_a') of MyrDOL and myrcene, respectively. These signals disappear with increasing conversion during the polymerization. The second decreasing signal at 2.43 ppm is assigned to MyrDOL (H_b), permitting the direct online-kinetic study of this monomer pair. Both decreasing signals do not overlap with resulting polymer signals.

Figure 3a quantitatively demonstrates that MyrDOL is consumed much faster than myrcene. In fact, about 60% of myrcene only reacts after MyrDOL has been fully consumed.

For the determination of the reactivity ratios the non-terminal (ideal) model was used because it fits the experimental results properly and has the least number of parameters. Both the Jaacks⁶⁸ and the “ideal integrated” equations⁶⁹ were used to fit the experimental data, as shown in the Supporting Information (Figures S17-21, Table S1).

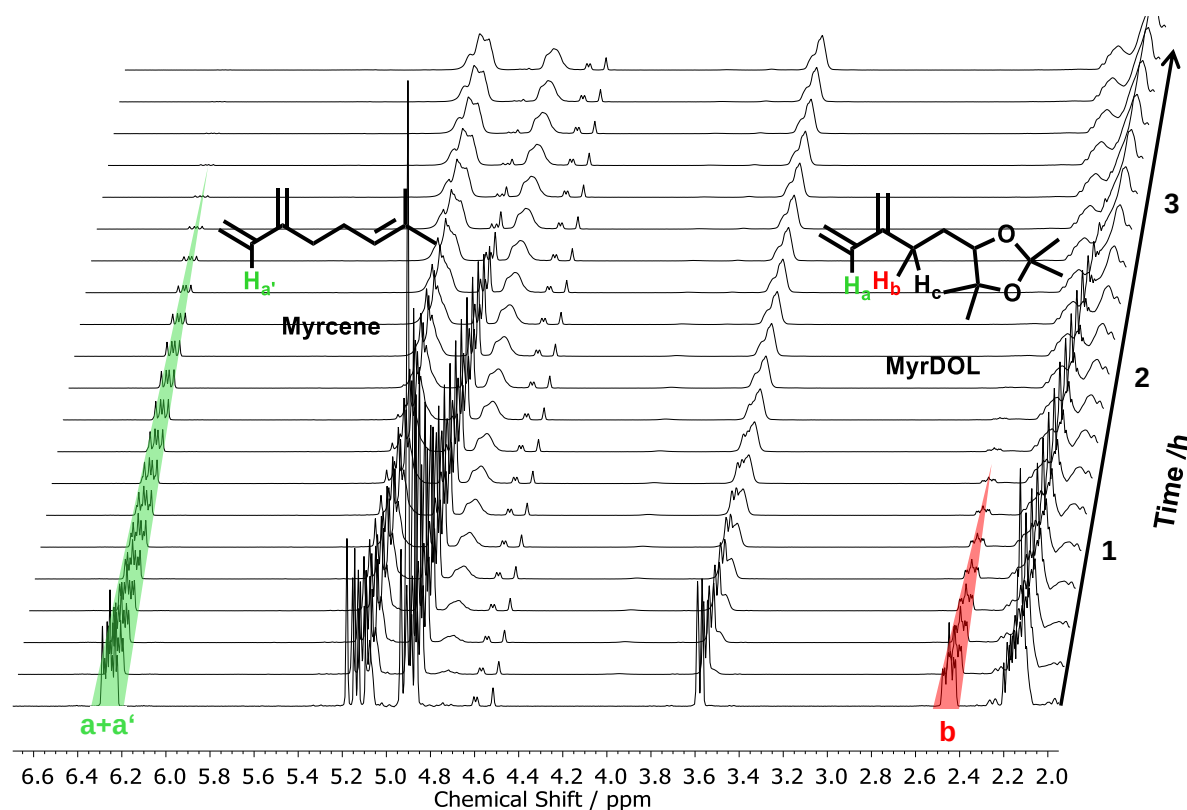


Figure 2: Stacked ^1H -NMR spectra (500 MHz, C_6D_{12} , 25°C) of the *in-situ* NMR kinetics study of MyrDOL and myrcene separated proton signals (region from 6.6 to 2.0 ppm) are used to determine monomer consumption. For the evaluation of the copolymerization parameters the decreasing signal at 2.45 ppm of MyrDOL was used. Due to the overlap of signals, the integral $a+a'$ is the sum of the signal $\text{H}_{a'}$ of myrcene and H_a of MyrDOL, respectively. Consequently, the difference of $a+a'$ and b gives the integral of $\text{H}_{a'}$.

In a similar way, the kinetics of the copolymerization of MyrDOL with styrene and isoprene, respectively, were studied. The detailed results are given in the Supporting Information (Figures S22-S35 and Tables S2 and S3). The determined reactivity ratios are given in Table 3. All these divergent reactivity ratios lead to a gradient structure of the copolymer with a block of pure monomer 2 at the end (Figure 3b). This behavior has also been demonstrated in the copolymerizations of styrene, 4-methylstyrene, isoprene, and myrcene in non-polar solvents.^{29,34}

Despite the distinct gradient structure, the copolymers with myrcene show only one T_g as a combination of the homopolymers (Table 2), which is tentatively attributed to the low degree of polymerization. ($\text{DP}=28$, $M_n=6.000$ g/mol) targeted in the online kinetics investigation, preventing microphase separation.

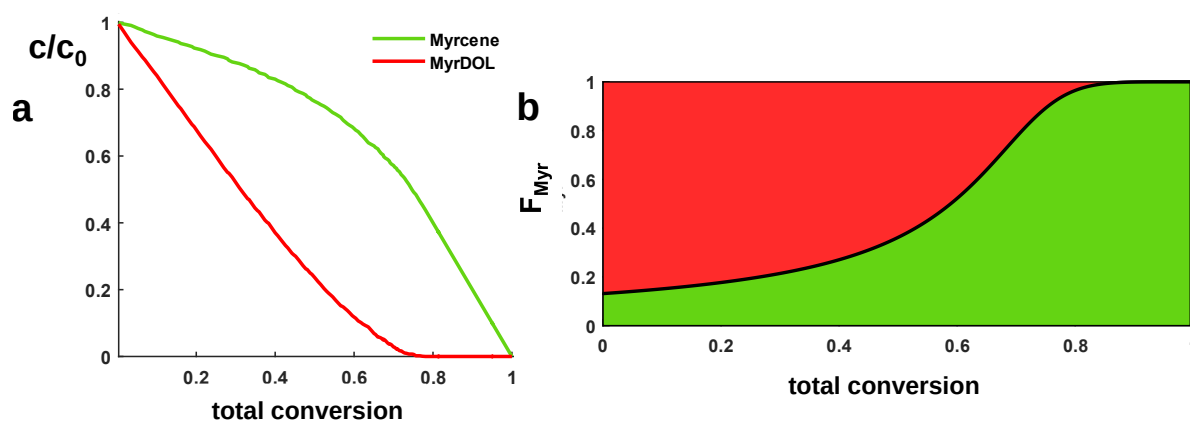


Figure 3: (a) Normalized comonomer concentrations vs. total conversion in the copolymerization of MyrDOL and myrcene. (b) Compositional gradient of the copolymer, red area= molar composition of MyrDOL, green area= molar composition of myrcene.

Table 3: Reactivity ratios in the copolymerization of MyrDOL with myrcene, styrene and isoprene in cyclohexane at 25°C.

Comonomer 2	r_{MyrDOL}	r_2
Myrcene	6.22	0.16
Styrene	5.20	0.19
Isoprene	9.22	0.11

While in homopolymerizations styrene reacts much faster than dienes, e.g. isoprene ($k_{\text{SS}} \gg k_{\text{II}}$), in copolymerizations the rates are inversed, i.e. dienes are incorporated much faster than styrene or styrene derivatives. This is due to large differences in the cross-over rate constants, where the polystyrene-Li chain ends are quickly converted to polydiene-Li termini, slowing down the styrene addition ($k_{\text{SI}} \gg k_{\text{SS}} > k_{\text{II}}$). Inversely the addition of diene to polystyryl-Li is very slow. ($k_{\text{IS}} \ll k_{\text{II}} < k_{\text{SS}}$). To determine the cross-over rate constants in our copolymerization systems, we studied the kinetics of homopolymerization of MyrDOL in cyclohexane at various concentrations. (Supporting Information, Figure S36). The aggregation number of living P(MyrdOL)-

lithium was determined to be close to 2 (Supp. Inf. Figure S37), similar to that of polymyrcene-Li.⁷⁰ This may be due to the steric requirements exerted by the bulky sidechain. Table S4 gives all homo-propagation and cross-over rate constants of our system. It is seen that in all cases the cross-over from the chain end of comonomer 2 to MyrDOL is the fastest of all reactions.

In earlier reports, our group investigated the copolymerization of myrcene with isoprene, styrene and 4-methylstyrene with respect to polymerization kinetics, reactivity ratios and morphology of the resulting tapered structures.^{34,36} The higher reactivity of myrcene for all monomer pairs was explained by the electron donating effect of the alkyl substituent. The reactivity can be correlated to the strength of the electron donating effect, which depends on the length of the alkyl substituent (isoprene < myrcene), resulting in an increased reactivity of myrcene compared to isoprene. Similar behavior is expected for MyrDOL.

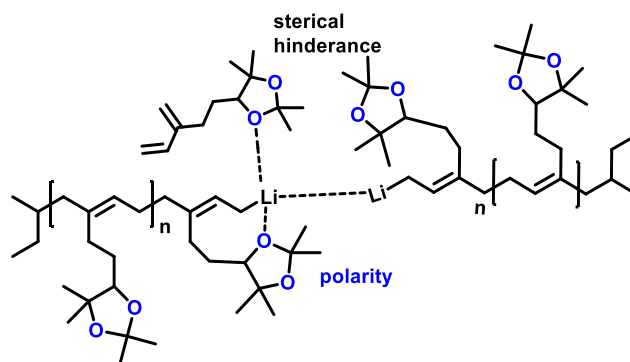


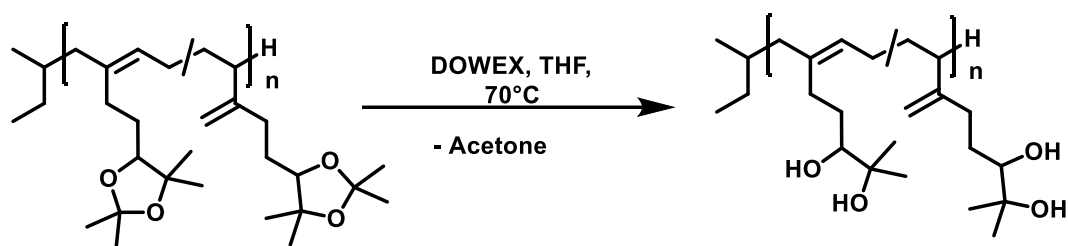
Figure 4: Tentative structure of the P(Myrdol)-Li chain end.

Based on our observations, copolymerization of Myrdol with different diene and styrene monomers is governed by two characteristic effects that are due to the specific structure of monomer and chain end: (i) the increased electron density and (ii) the polarity of the dioxolane group, which can co-ordinate with the Li counterion (Figure 4).

It is important to note that the effect of the increased polarity of the polymerization medium, caused by the dioxolane group of the Myrdol monomer, can be compared to the effect of modifying additives, such as THF. Polar modifiers cause (a) a generally

accelerated polymerization, along with an adjustment of the reactivity ratios at low concentrations of modifier or polar solvent, (b) a shift from 1,4- to 3,4 microstructure of the polydiene.^{66,71,72} This is also found for the MyrDOL/styrene monomer combination, showing less disparate reactivity ratios of $r_{\text{MyrDOL}} = 5.2$ and $r_{\text{Sty}} = 0.19$ in comparison to the extreme example myrcene/styrene $r_{\text{Myr}} = 40.6$, $r_{\text{Sty}} = 0.025$ (polymerization in cyclohexane, 25°C).³⁶ Furthermore, the polar protecting group of MyrDOL manipulates the kinetics of the polymerization in the same way as 1.5 eq. of THF relative to Li influences the copolymerization of styrene and myrcene (interpolated: $r_{\text{Myr}} = 5.62$, $r_{\text{Sty}} = 0.19$).³⁶ Similarly, the fraction of 3,4 structures is about 30% in P(MyrdOL) and 6% in polymyrcene. As observed previously, this fraction rises to 33% when polymerizing in presence of ca. 6 eq. THF.³⁶

3.1.3.6 Deprotection of the hydroxyl groups



Scheme 2: Deprotection of P(MyrdOL) resulting in P(My(OH)₂).

With DOWEX resin, a sulfonated styrene divinylbenzene (gel), P(MyrdOL) was deprotected, resulting in polymyrcene-2,3-diol, P(My(OH)₂). After acidic treatment with the deprotecting agent, the SEC traces in Figure 5 still show a monomodal molecular weight distribution. A shift of the molecular weight distributions to higher elution volume can be observed, which translates to lower molecular weight. Removal of the protective groups involves a slight broadening of the molecular weight distribution, with dispersity ($\bar{D}$) in the range of 1.13 to 1.19.

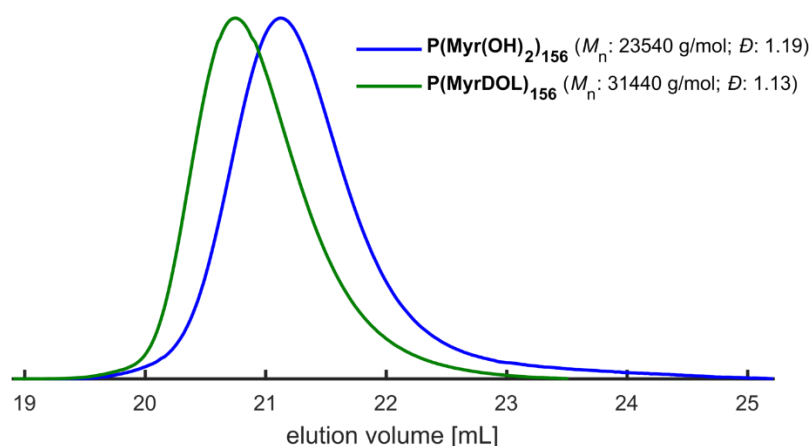


Figure 5: SEC traces of P(MyrdOL₁₅₆) (green) and deprotected polymer P(My(OH)₂)₁₅₆ (blue) in THF, PMMA calibration.

The copolymers were deprotected in the same manner as the homopolymers. The deprotection of the myrcene-copolymers is confirmed by ¹H-NMR spectroscopy, showing a shift of the two methyl signals of MyrdOL from 1.24 ppm and 1.10 ppm to 1.18 ppm and 1.09 ppm respectively, and by the disappearance of the two methyl signals 1.42 ppm and 1.33 ppm of the acetonide protecting group (Figure 6). After deprotection, a shift of the molecular weight distributions to higher elution volume can be observed, which translates to lower molecular weight (Figure S38). It is worth noticing that the NMR-spectrum of P(Myrc-co-Myr(OH)₂) was measured after a purification step *via* preparative GPC in chloroform to remove undesired impurities resulting from the deprotection. The homopolymers were not purified by this method due to the insolubility of the resulting deprotected polymer in chloroform.

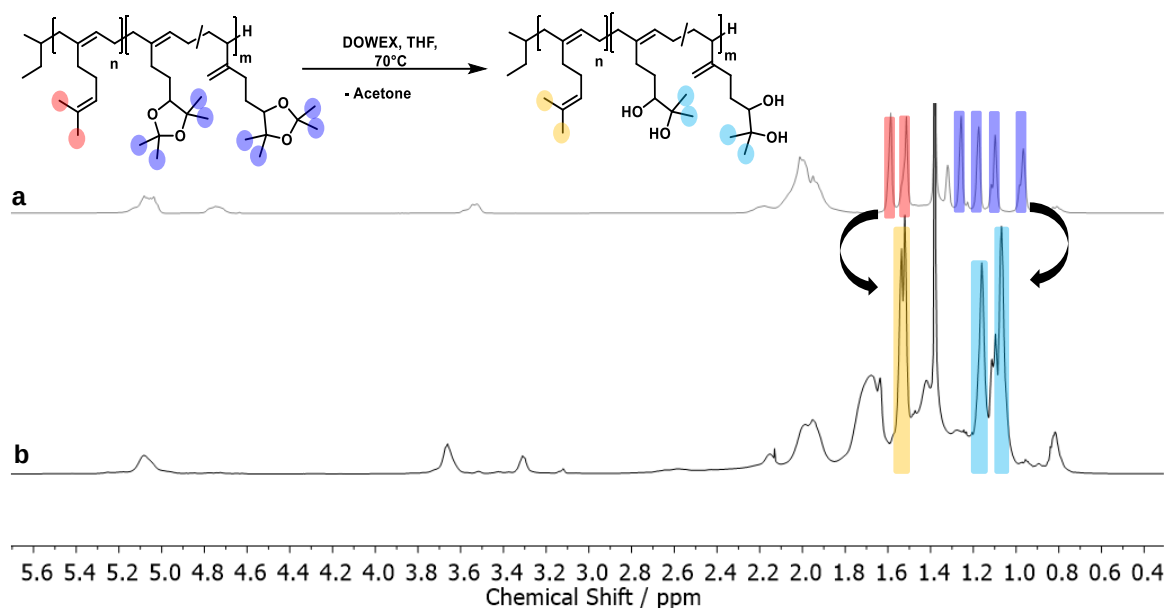


Figure 6: Deprotection of P(Myrc-co-MyrDOL) under acidic conditions; a) ^1H -NMR spectrum (400 MHz, C_6D_{12} , 25 °C) of P(Myrc-co-MyrDOL), b) ^1H -NMR spectrum (400 MHz, C_6D_{12} , 25 °C) of deprotected copolymer P(Myrc-co-Myr(OH) $_2$).

Thus, the removal of the protective group was not clearly demonstrated by NMR-spectroscopy. The SEC traces of the protected and deprotected styrene copolymers P(MyrcDOL-co-S) and P(Myrc(OH) $_2$ -co-S) are depicted in Figure S39. The ^1H -NMR-spectra of the deprotected styrene copolymers are shown in Figure S40. Furthermore, rigorous removal of solvents and low molecular structures appeared to be difficult, probably because of the high polarity of the polymer and the strong hydrogen bonds of the diol structure. The increased hydrophilicity of the deprotected polymer is manifest by swelling of the polymer in water. In addition, the deprotected sample P(Myrc(OH) $_2$) $_{156}$ was partial soluble in methanol (Table S5).

3.1.4 Conclusion

We present a new di-hydroxyfunctional functional, protected diene monomer (MyrDOL), obtained from renewable resources. Starting from β -myrcene, the selective epoxidation of the pendant double bond and the subsequent conversion of the resulting epoxide with acetone and SnCl_2 gave access to a functionalized 1,3-dioxolane diene monomer. This acetal functionality of MyrDOL as a protective group for diols was proven to be stable under carbanionic conditions but is readily removed after acidic treatment subsequent to polymerization. The investigation of the microstructure of P(Myrdol) revealed an increased 3,4-content (up to 33%) compared to other polydienes synthesized in apolar media. The increased amount of 3,4-units can be attributed to the “self-modifier” effect of the polar protecting group of MyrDOL. The statistical copolymerization of MyrDOL and myrcene was characterized in depth, as well as the reactivity and kinetics of copolymerization with myrcene, styrene and isoprene *via* online NMR kinetics. It was observed that MyrDOL is incorporated first in all statistical copolymerizations with myrcene, styrene and isoprene, resulting in copolymers with a strong gradient. The new diene monomer MyrDOL gives access to a large variety of polymer structures, gradient and tapered copolymer architectures and is generally valuable for polydiene-based materials with increased polarity.

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3.1.6 Supporting Information

3.1.6.1 Monomer synthesis

6,7-epoxy myrcene was prepared according to literature.⁶² To an ice-cooled solution of myrcene (20 g, 0.14 mol) in CH₂Cl₂ (300 mL) was added *m*CPBA (32 g, 0.15 mol) in small portions under stirring. After 5 min, 2 M aq. NaOH solution was added, and the reaction mixture was extracted with CH₂Cl₂ (3×300 mL). The combined organic layers were washed with water and then brine and dried over MgSO₄. Evaporation of solvent followed by distillation yielded 6,7-epoxy myrcene as a colorless oil (95 %).

¹H-NMR (400 MHz, chloroform-*d*₁): δ (ppm) = 6.39 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.25 (dd, *J* = 17.7, 0.9 Hz, 1H), 2.76 (t, *J* = 6.3 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.37 – 2.27 (m, 1H), 1.74 (dtd, *J* = 8.4, 7.4, 6.9, 2.5 Hz, 2H), 1.56 (d, *J* = 11.0 Hz, 1H), 1.31 (s, 3H), 1.26 (s, 3H).

The direct conversion of epoxides to the corresponding acetonides has been previously reported using mild Lewis acid catalysts (SnCl₂).⁷³ Anhydrous tin(II) chloride (2.8 g) was placed in a two-necked flask (500mL) equipped with a magnetic stir bar and a reflux condenser. The system was sequentially evacuated and filled with argon three times. Dry acetone (400 mL) was added through the septum and stirring was started. 6,7-Epoxy myrcene (18 g) was added dropwise, and the solution was heated to reflux and maintained at that temperature. The acetone was removed by rotary evaporation and the residue was taken up in CH₂Cl₂ (200 mL), and 10% NaOH solution (100 mL) and water (50 mL) were added. The layers were separated, and the aqueous layer was extracted CH₂Cl₂ (50 mL). The combined organic layers were dried over Na₂SO₄. After solvent evaporation, the residue was subjected to vacuum distillation. Yield 50%.

¹H-NMR (400 MHz, chloroform-*d*₁): δ (ppm) = 6.40 (dd, *J* = 17.6, 10.8, 0.6 Hz, 1H), 5.29 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.15 – 5.02 (m, 3H), 3.74 (dd, *J* = 9.7, 3.2 Hz, 1H), 2.52 (dddd, *J* = 14.9, 10.2, 4.8, 1.3 Hz, 1H), 2.28 (dddd, *J* = 14.7, 9.8, 6.6, 1.2 Hz, 1H), 1.74 (dtd, *J* =

13.6, 9.8, 4.8 Hz, 1H), 1.58 (dtd, $J = 13.7, 6.7, 3.3$ Hz, 1H), 1.45 (d, $J = 0.8$ Hz, 3H), 1.36 (d, $J = 0.7$ Hz, 3H), 1.26 (s, 3H), 1.12 (s, 3H), 1.05 – 0.92 (m, 1H).

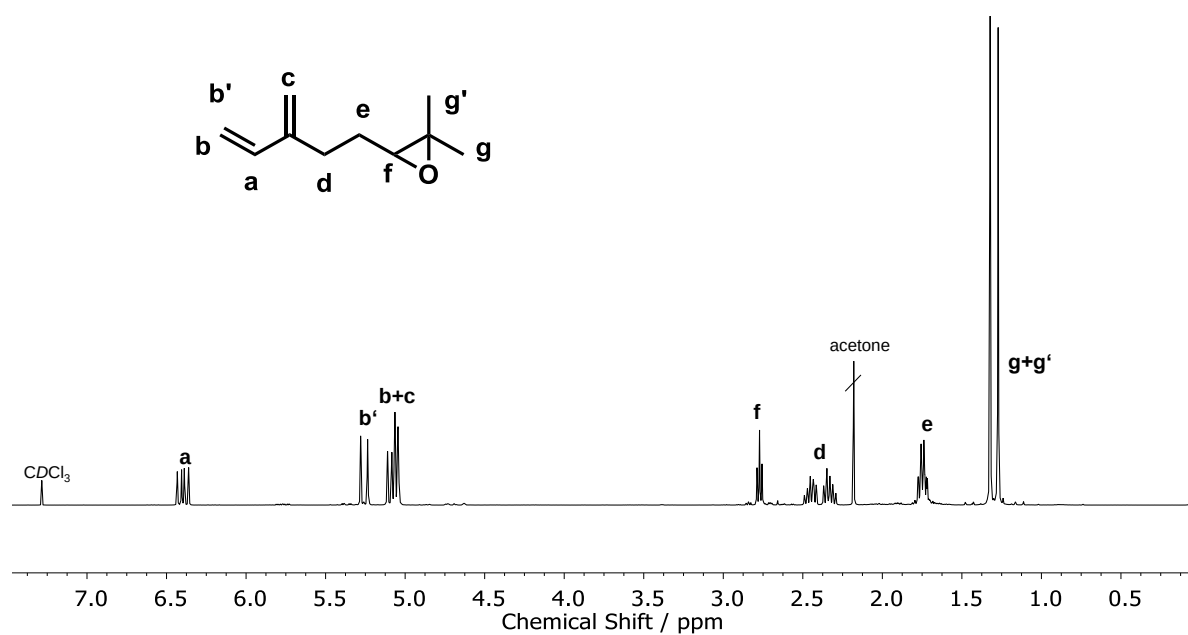


Figure S 1: ^1H NMR spectrum (400 MHz, CDCl_3) of 6,7-epoxy myrcene.

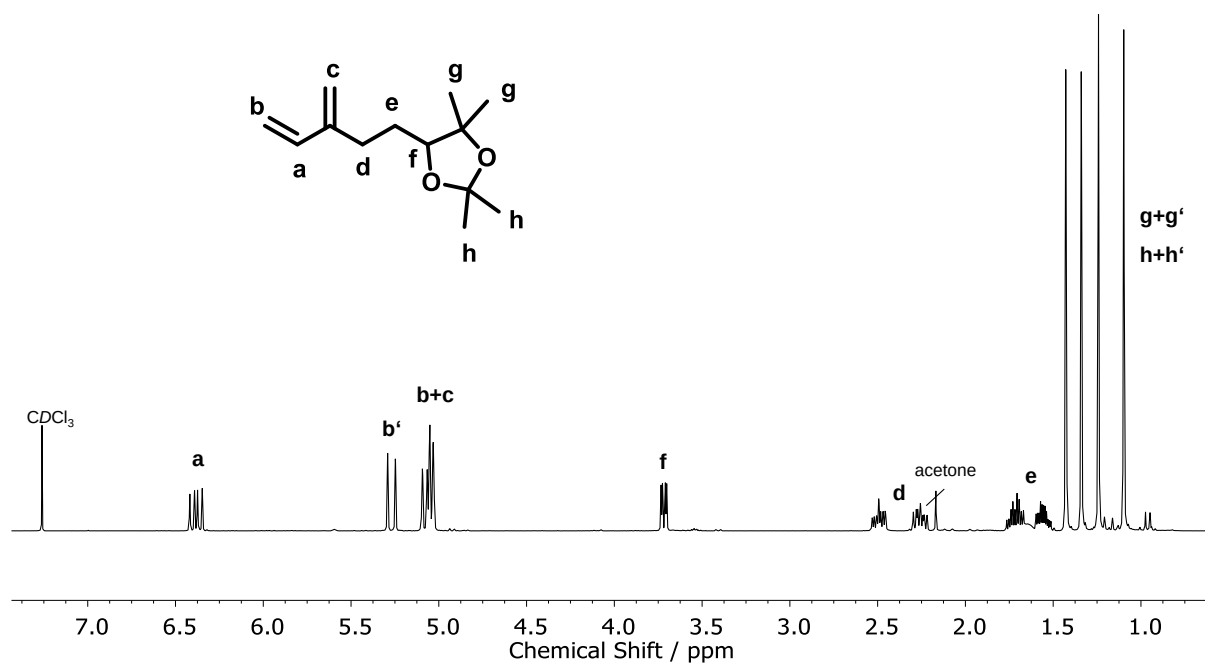


Figure S 2: ^1H NMR spectrum (400 MHz, CDCl_3) of MyrDOL.

3.1.6.2 SEC traces of Homopolymers and MALDI-ToF MS

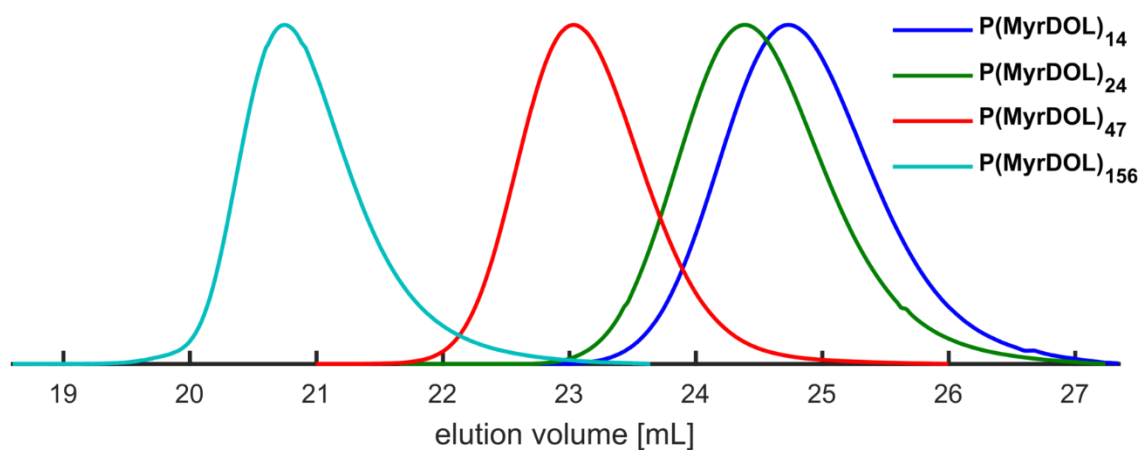
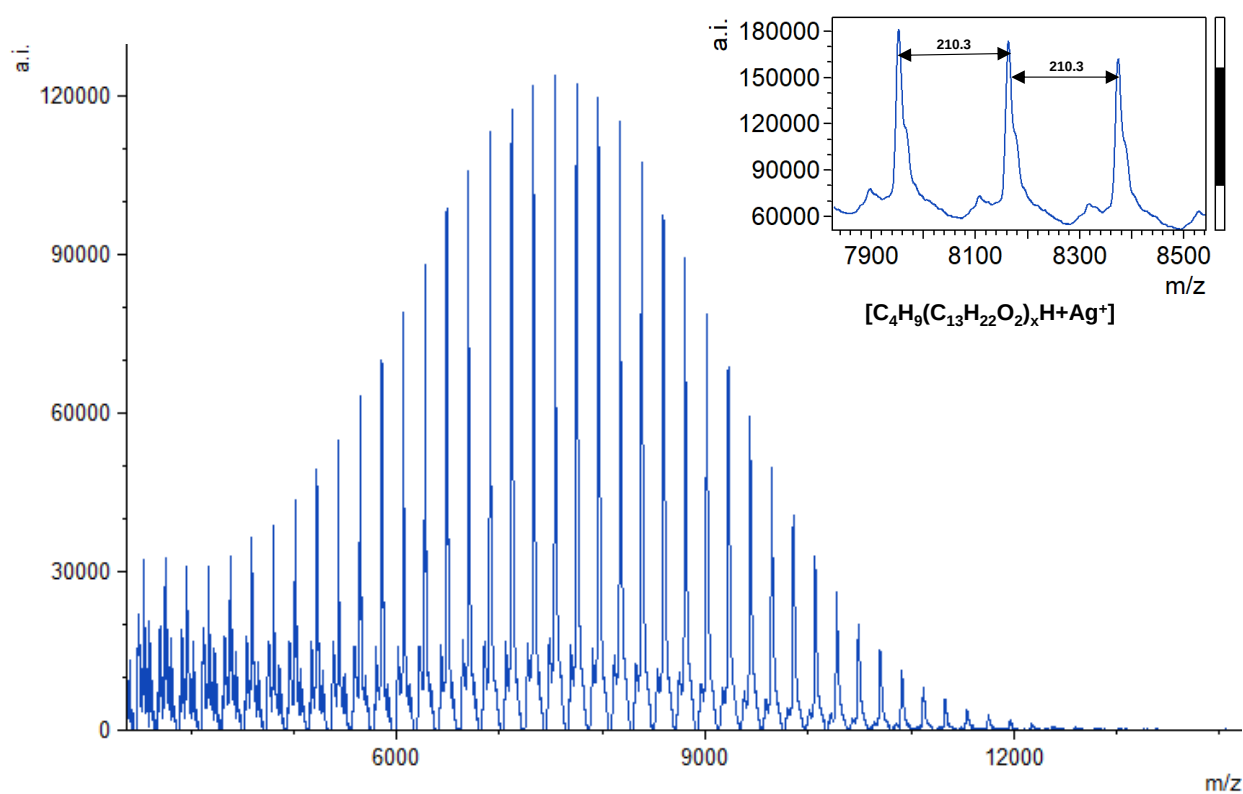
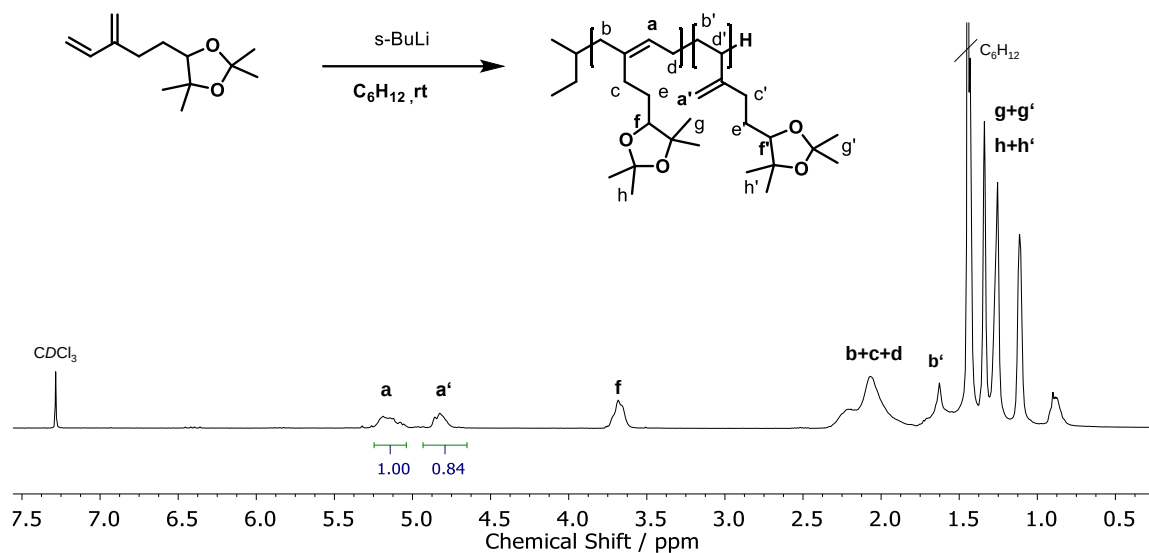
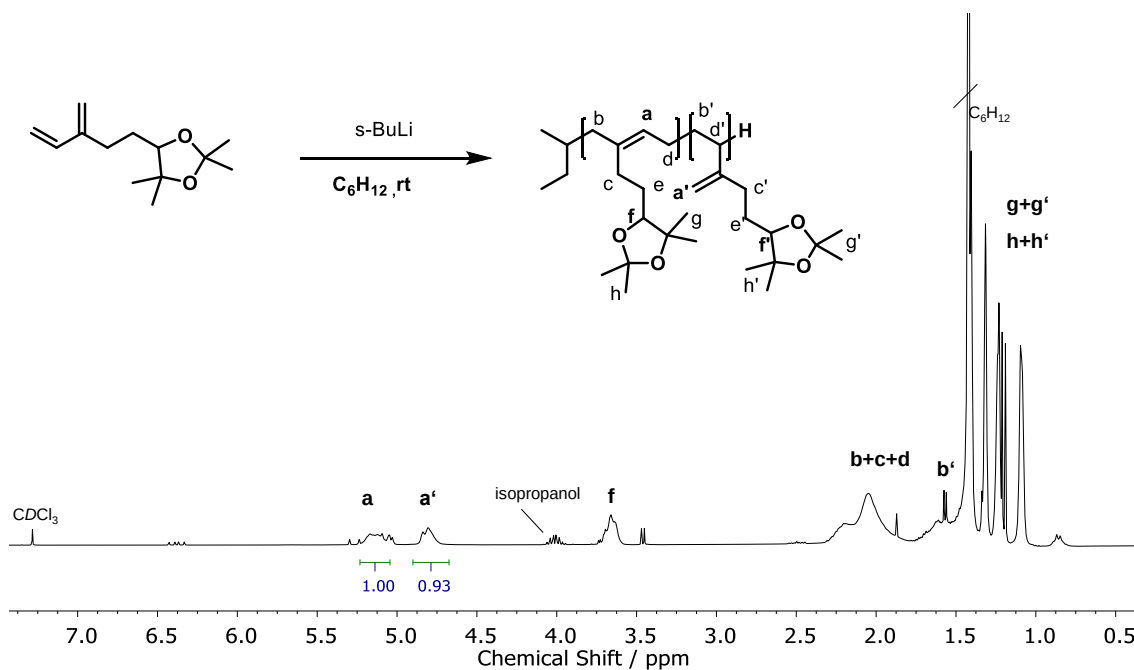


Figure S 3: SEC traces (eluent: THF) of P(MyrdOL) homopolymers.

Figure S 4: MALDI-ToF MS of P(MyrdOL)₄₇, Matrix DCTB, AgTFA.

3.1.6.3 Investigation of the microstructure of P(MyrdOL) by ^1H NMR

$$3,4 \text{ units (\%)} = 100 \frac{I(a')/2}{I(a)+I(a')/2} \quad (\text{S1})$$

Figure S 5: ^1H NMR spectrum (400 MHz, CDCl_3) of P(MyrdOL)_{14} .Figure S 6: ^1H NMR spectrum (400 MHz, CDCl_3) of P(MyrdOL)_{24} .

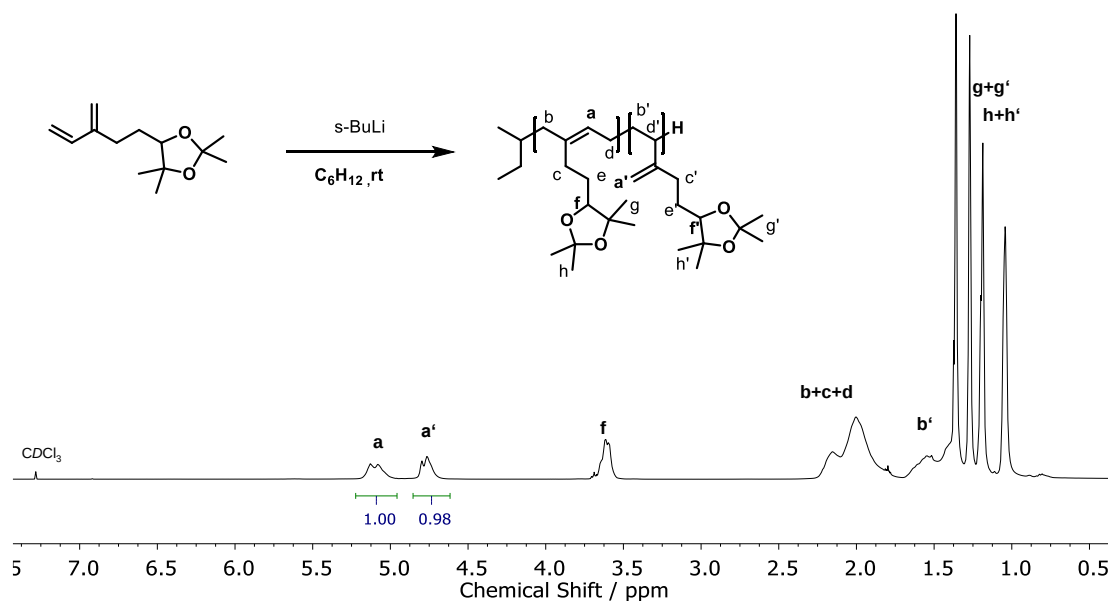


Figure S 7: ^1H NMR spectrum (400 MHz, CDCl_3) of $\text{P}(\text{MyrdOL})_{156}$.

3.1.6.4 Glass Transition Temperature Determination of $\text{P}(\text{MyrdOL})$

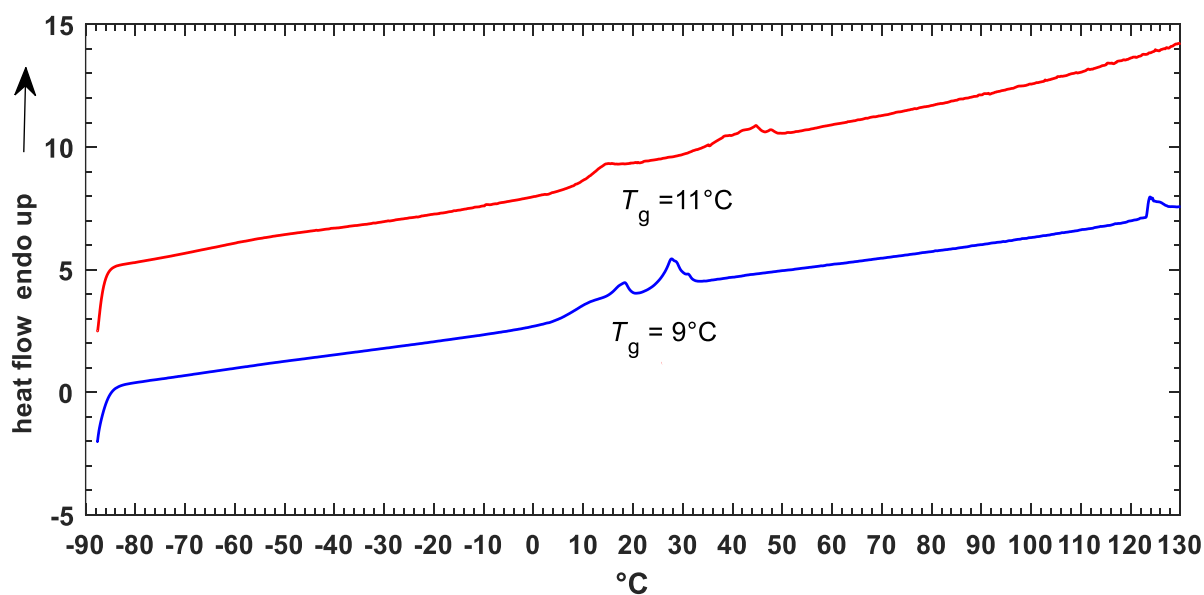


Figure S 8: DSC measurements of the homopolymers $\text{P}(\text{MyrdOL})_{24}$ (blue, $T_g = 9^\circ\text{C}$) and $\text{P}(\text{MyrdOL})_{156}$ (red, $T_g = 11^\circ\text{C}$).

3.1.6.5 SEC Traces of Copolymers

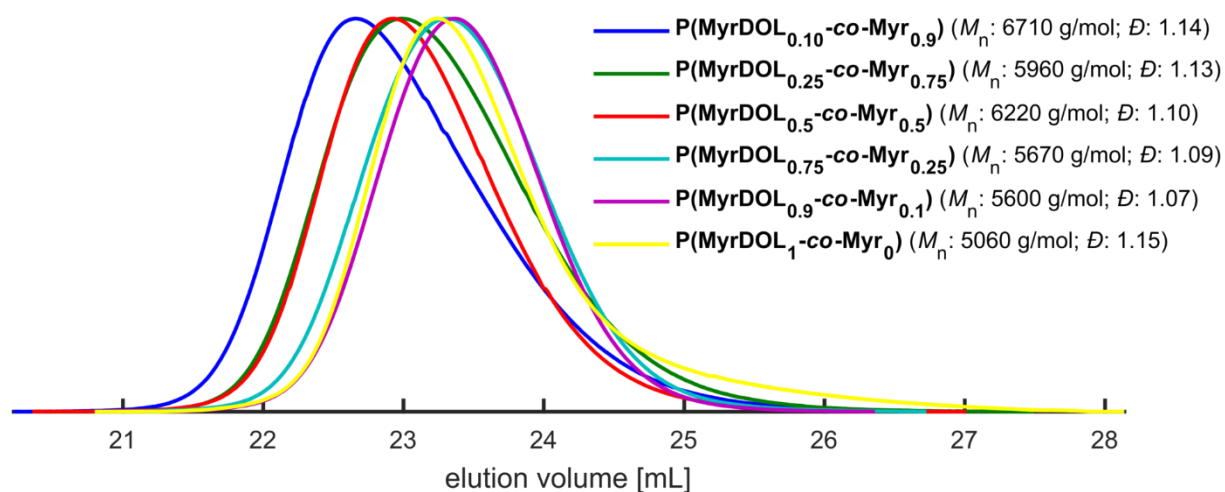
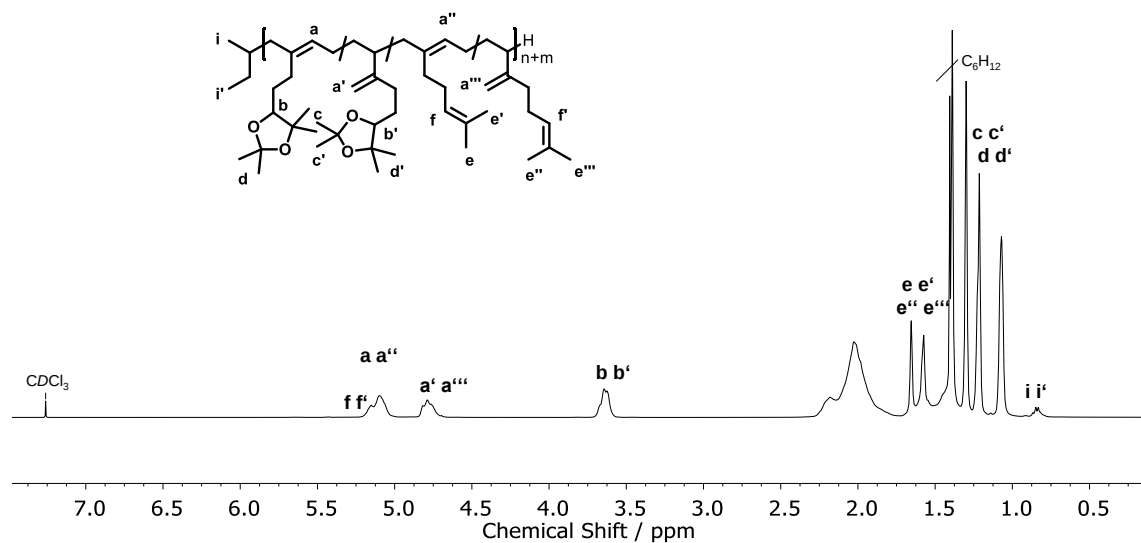


Figure S 9: SEC traces (THF, PI standard) of P(MyrdOL-co-Myr) copolymers.

3.1.6.6 NMR Spectra of Copolymers

Figure S 10: ¹H NMR spectrum (400 MHz, CDCl₃) of P(MyrdOL_{0.9}-co-Myr_{0.1}).

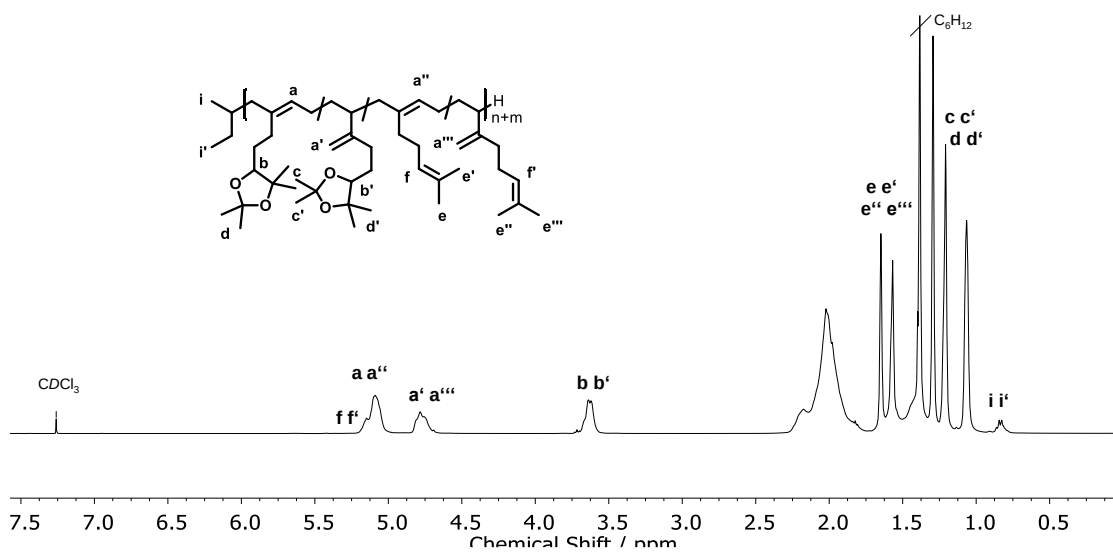


Figure S 11: ¹H NMR spectrum (400 MHz, CDCl₃) of P(MyrdOL_{0.75}-co-Myr_{0.25}).

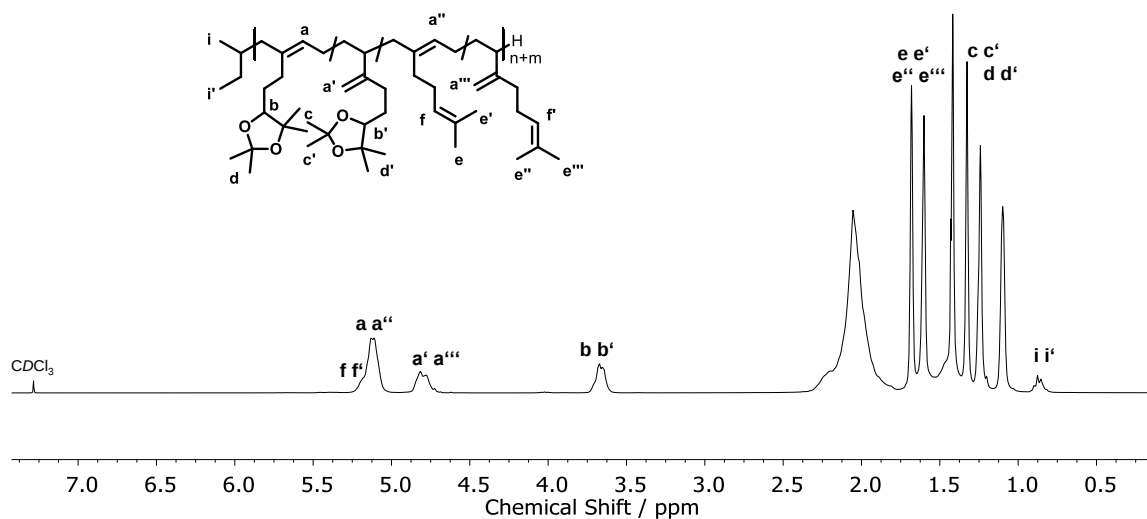


Figure S 12: ¹H NMR spectrum (400 MHz, CDCl₃) of P(MyrdOL_{0.5}-co-Myr_{0.5}).

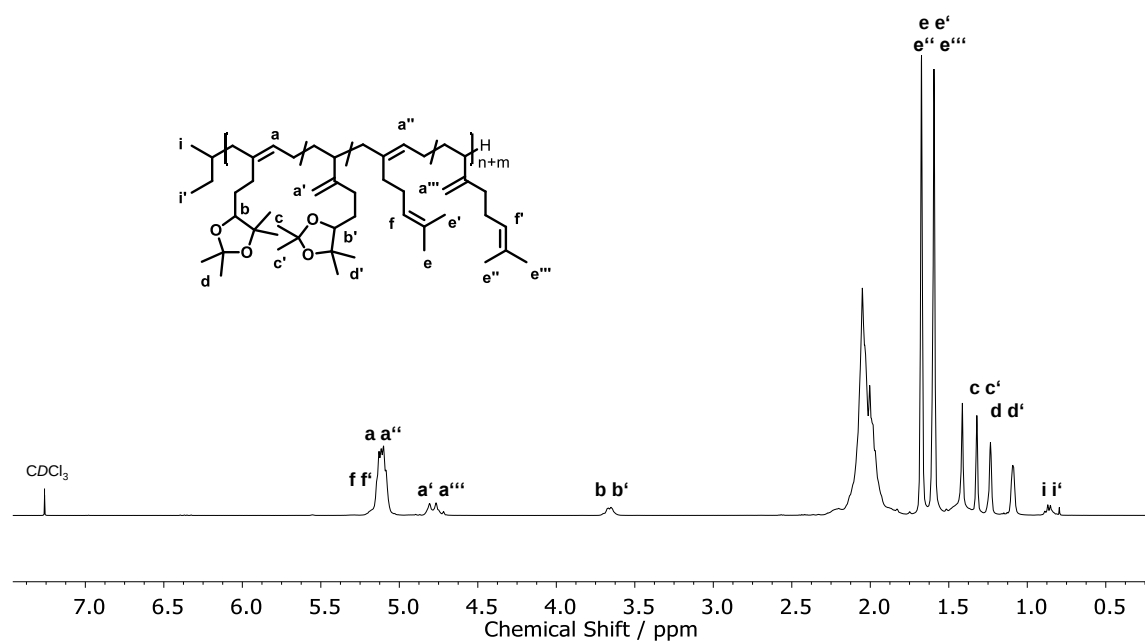


Figure S 13: ¹H NMR spectrum (400 MHz, CDCl₃) of P(MyrdOL_{0.25}-co-Myr_{0.75}).

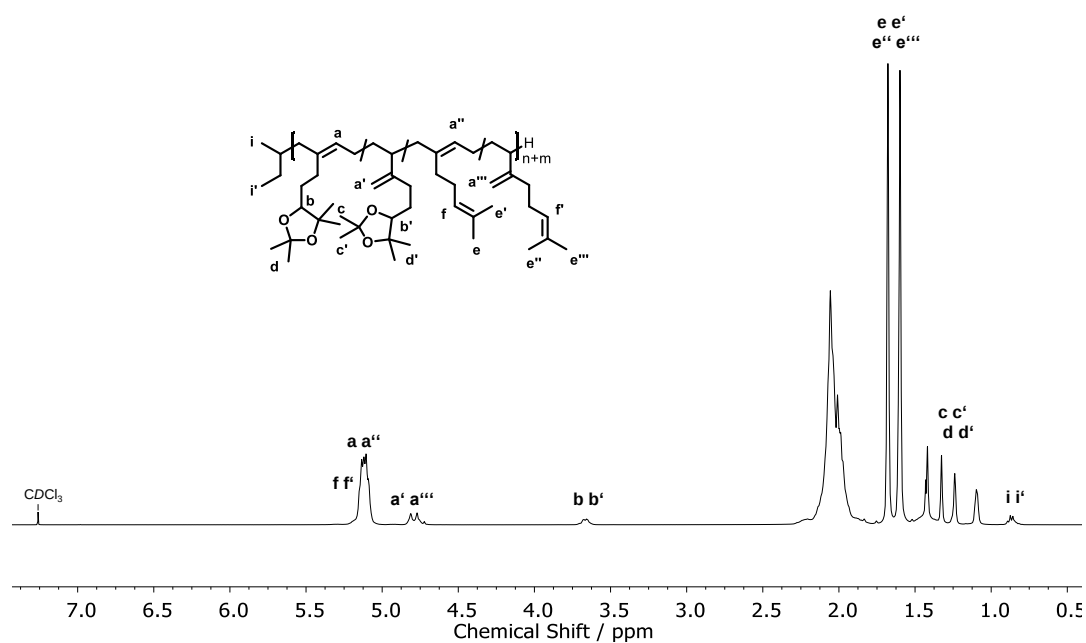


Figure S 14: ¹H NMR spectrum (400 MHz, CDCl₃) of P(MyrdOL_{0.1}-co-Myr_{0.9}).

3.1.6.7 Glass Transition Temperature Determination of Copolymers

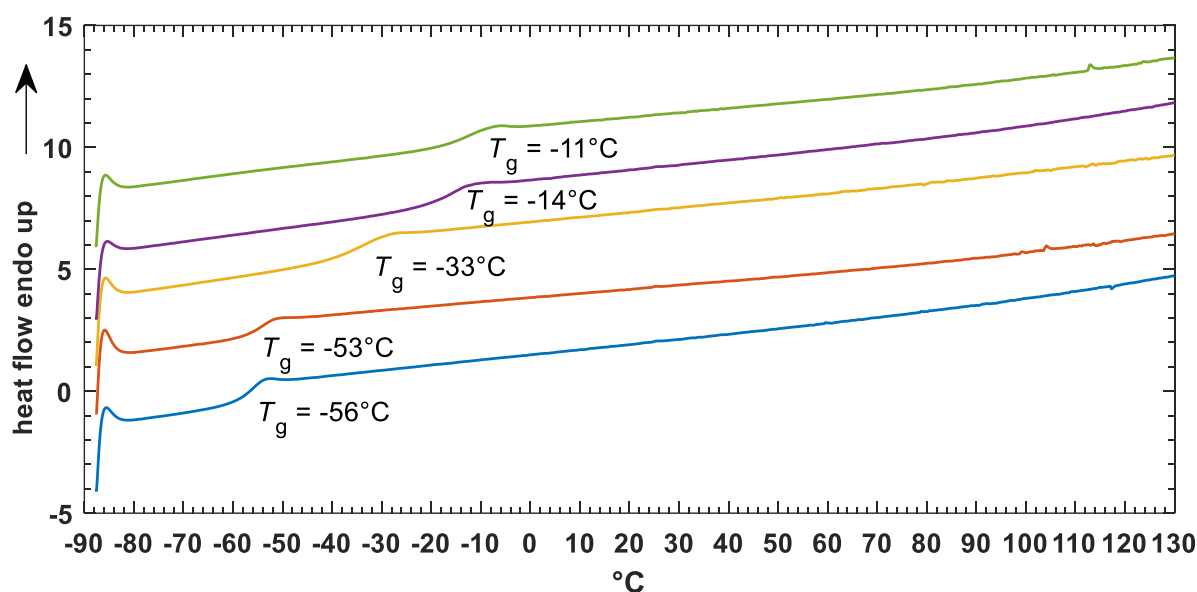


Figure S 15: DSC measurements of the copolymers P(MyrdOL_{0.9}-co-Myr_{0.1}) (green), P(MyrdOL_{0.75}-co-Myr_{0.25}) (violet), P(MyrdOL_{0.5}-co-Myr_{0.5}) (yellow), P(MyrdOL_{0.25}-co-Myr_{0.75}) (orange), P(MyrdOL_{0.1}-co-Myr_{0.9}) (blue).

T_g can be predicted by the Fox equation⁷⁴, when the copolymers possess a randomly distributed monomer sequence, depending on the incorporated weight fraction of the comonomers. The T_g of the copolymer is calculated as the sum of the inverse glass-transition temperatures of monomer A and monomer B, weighted by their mass fraction. The Fox equation (eq. S2) was used for prediction of the glass-transition temperatures.

$$\frac{1}{T_{g,mix}} = \frac{w_A}{T_{g,A}} + \frac{w_B}{T_{g,B}} \quad (S2)$$

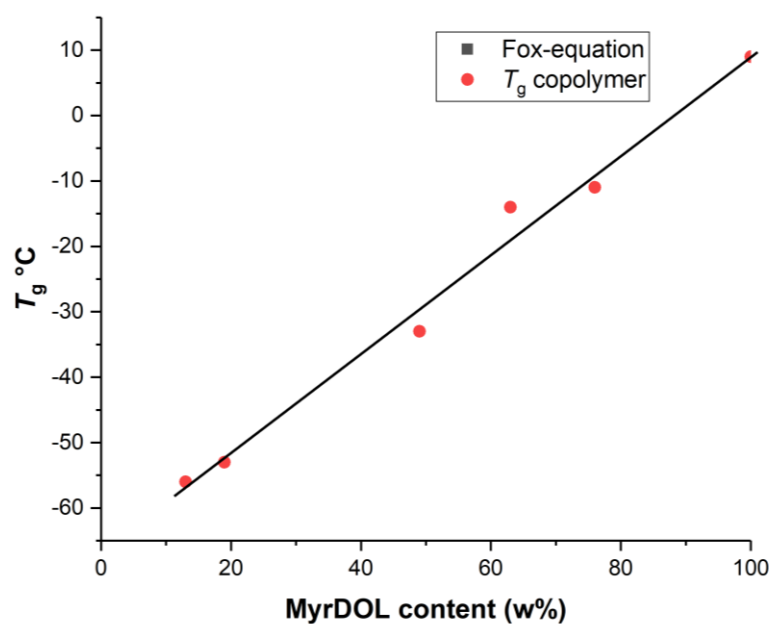


Figure S 16: Glass-transition temperatures of P(MyrdOL-*co*-Myr) copolymers.

The approximately good agreement of the glass-transition temperature of the copolymers of MyrDOL and myrcene with the prediction of the Fox equation is tentatively explained by the low degree of polymerization.

3.1.6.8 NMR Kinetic Studies

The data were evaluated by using NIREVAL Software from Johann, Steube and Frey.⁷⁵

Copolymerization of MyrDOL and myrcene

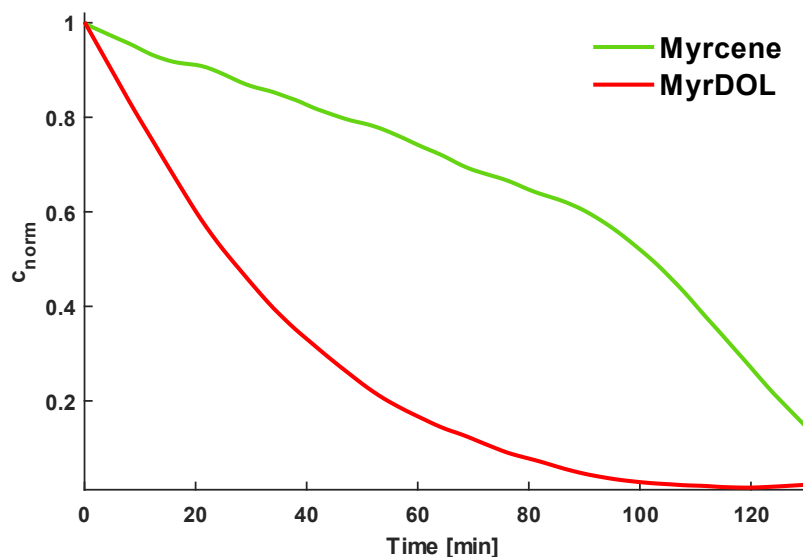


Figure S 17: Normalized comonomer concentrations c_{norm} vs. time in the copolymerization of MyrDOL and myrcene.

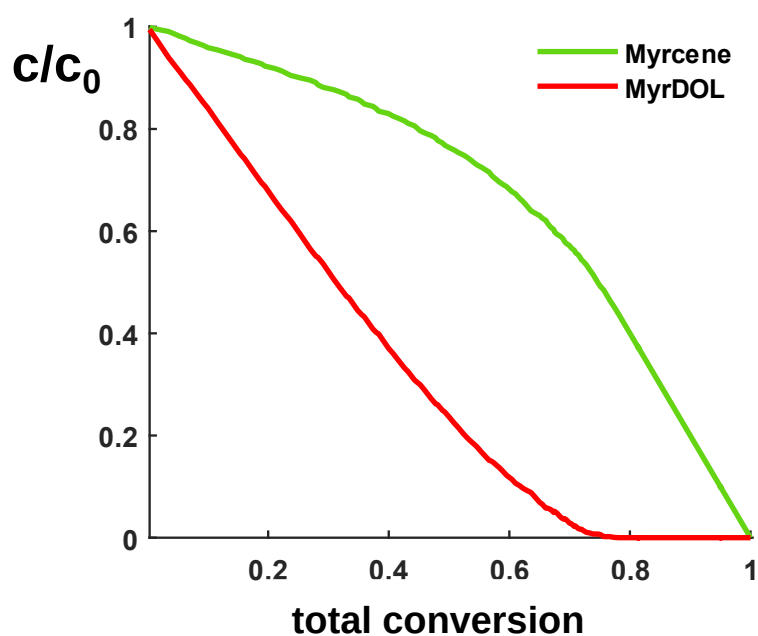


Figure S 18: Individual monomer concentrations as a function of the total monomer conversion time of the copolymerization of MyrDOL and myrcene.

For the determination of the reactivity ratios both the terminal and non-terminal models were tested. The ideal integrated model (Meyer-Lowry ideal) was used.⁷⁶ The non-terminal model applied because it uses the least number of parameters.

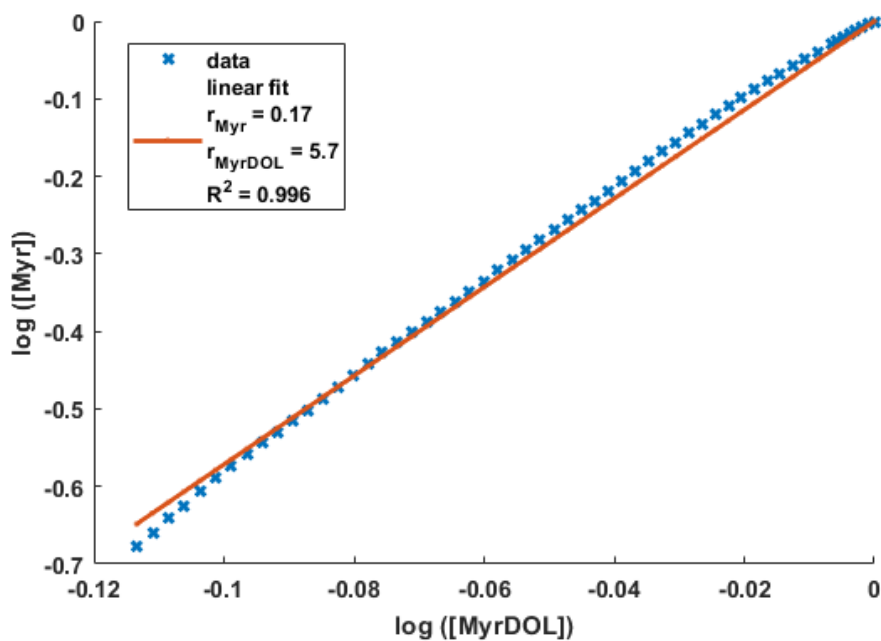


Figure S 19: Jaacks fit (red line) of the copolymerization of MyrDOL and myrcene.

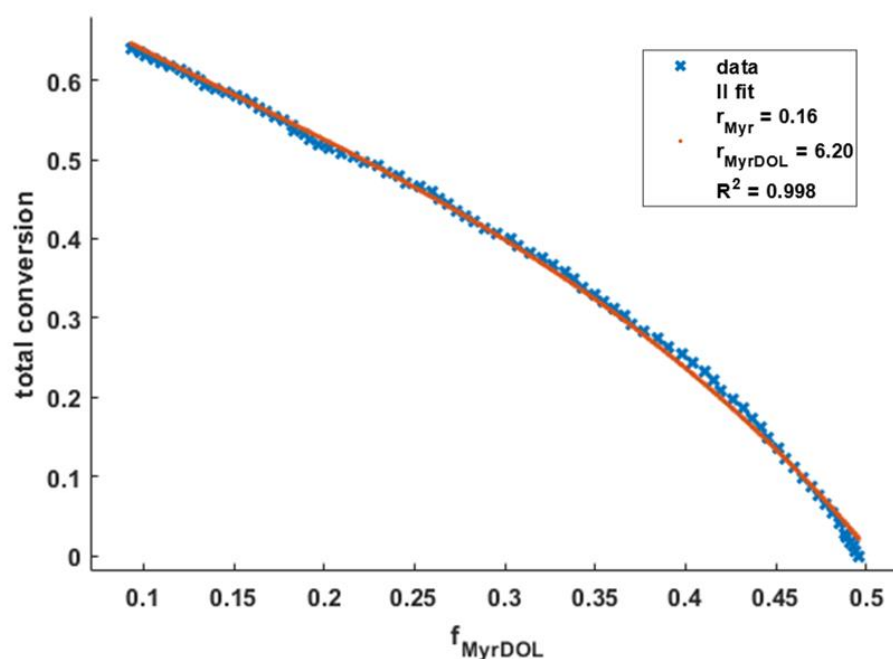


Figure S 20: Ideal integrated fit (red line) of the copolymerization of MyrDOL and myrcene.

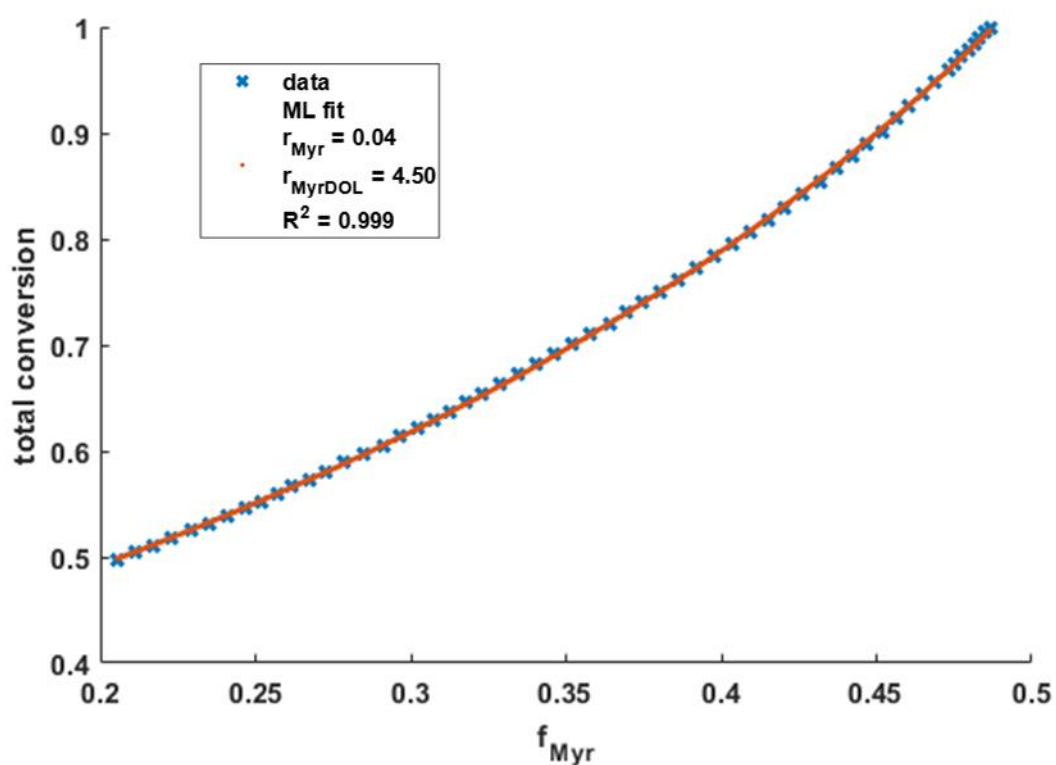


Figure S 21: Meyer-Lowry fits (red) ($1-X$ (total conversion)) versus actual fraction of styrene in the feed, f_{Myr} , used for the evaluation of the reactivity ratios, $R^2 = 0.999$, $r_1 \cdot r_2 = 0.17$.

Table S 1: Summary of fit results copolymerization of MyrDOL (r_2) and myrcene (r_1).

Method	r_1	r_1 error	r_2	r_2 error	$r_1 \cdot r_2$	$r_1 \cdot r_2$ error	R^2
Jaacks	0.1749	0.0017	5.7168	0.0556	1	0.0137	0.9961
Meyer-Lowry ideal	0.1617	0.0019	6.1842	0.0746	1	0.0170	0.9986
Meyer-Lowry	0.0394	0.0160	4.4906	0.1709	0.1706	0.072	0.999

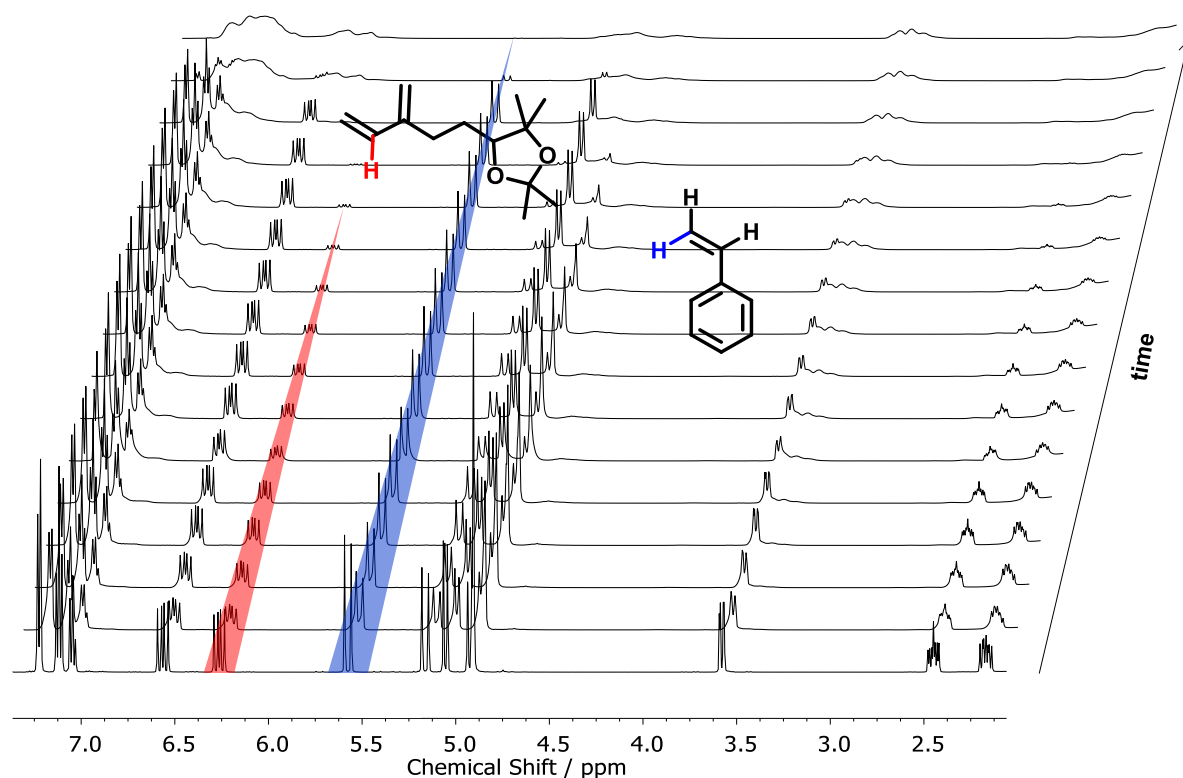
Copolymerization of MyrDOL and styrene

Figure S 22: Stacked ^1H -NMR spectra (400 MHz, C_6D_{12} , 25°C) of the *in-situ* NMR kinetics study of MyrDOL and styrene separated proton signals (region from 7.1 to 2.4 ppm) are used to determine monomer consumption. For the evaluation of the copolymerization parameters the decreasing signal at 6.25 ppm of MyrDOL and the decreasing signal at 5.57 ppm of styrene were used.

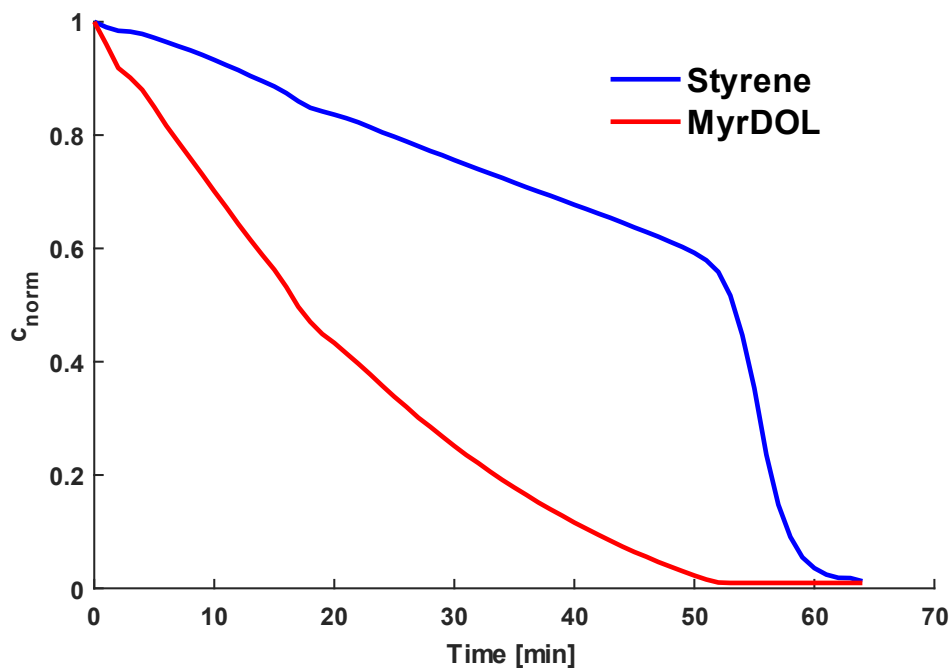


Figure S 23: Normalized concentration c_{norm} against time of the copolymerization of MyrDOL and styrene.

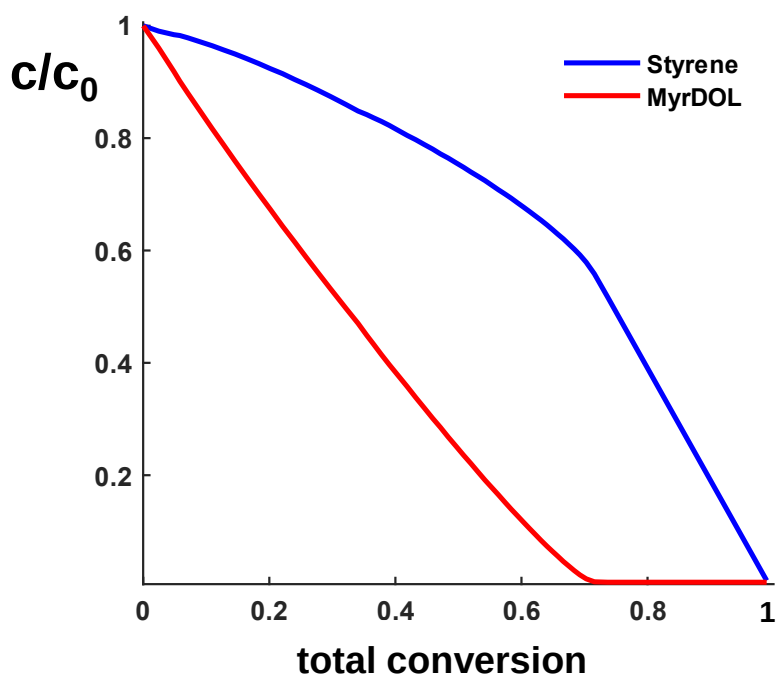


Figure S 24: Individual monomer concentrations as a function of the total monomer conversion time of the copolymerization of MyrDOL and styrene.

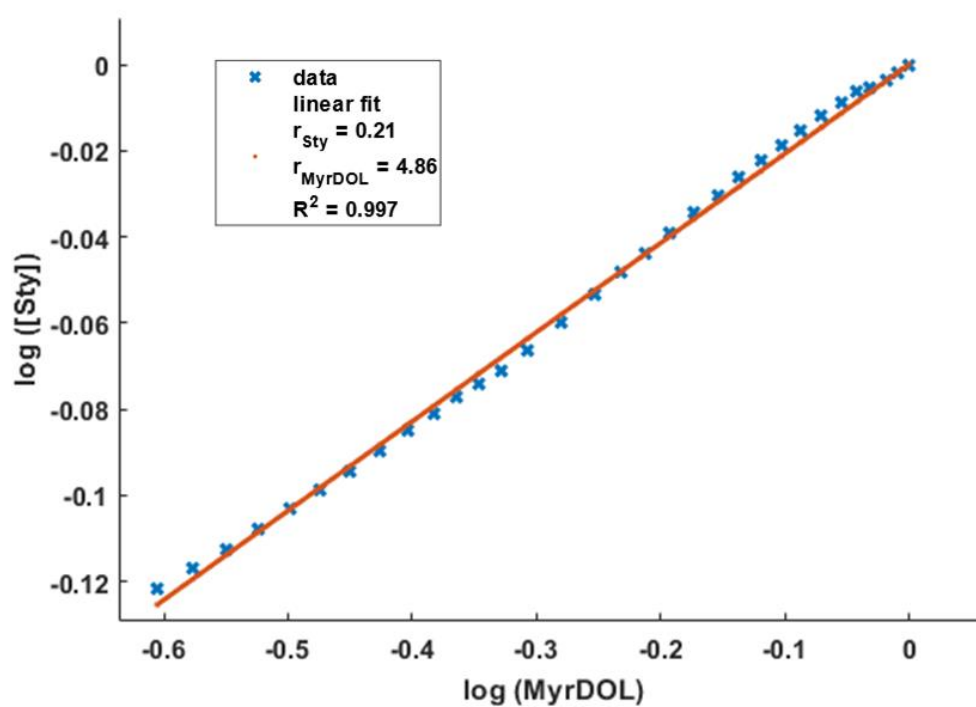


Figure S 25: Jaacks fit (red line) of the copolymerization of MyrDOL and Styrene.

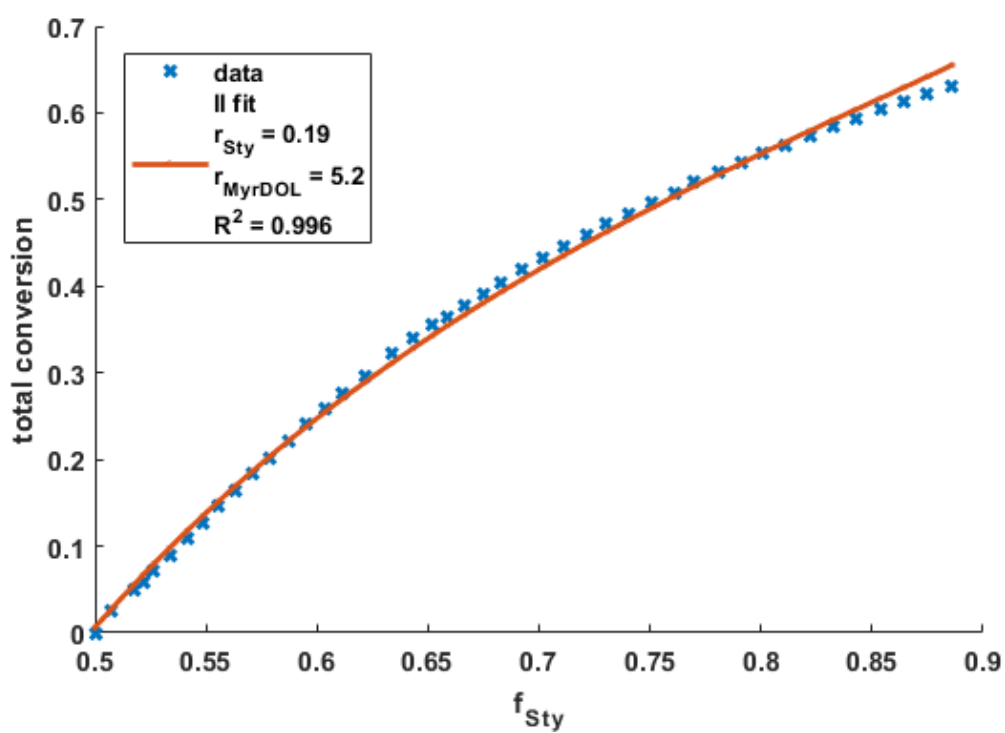


Figure S 26: Ideal integrated fit of the copolymerization of MyrDOL and Styrene.

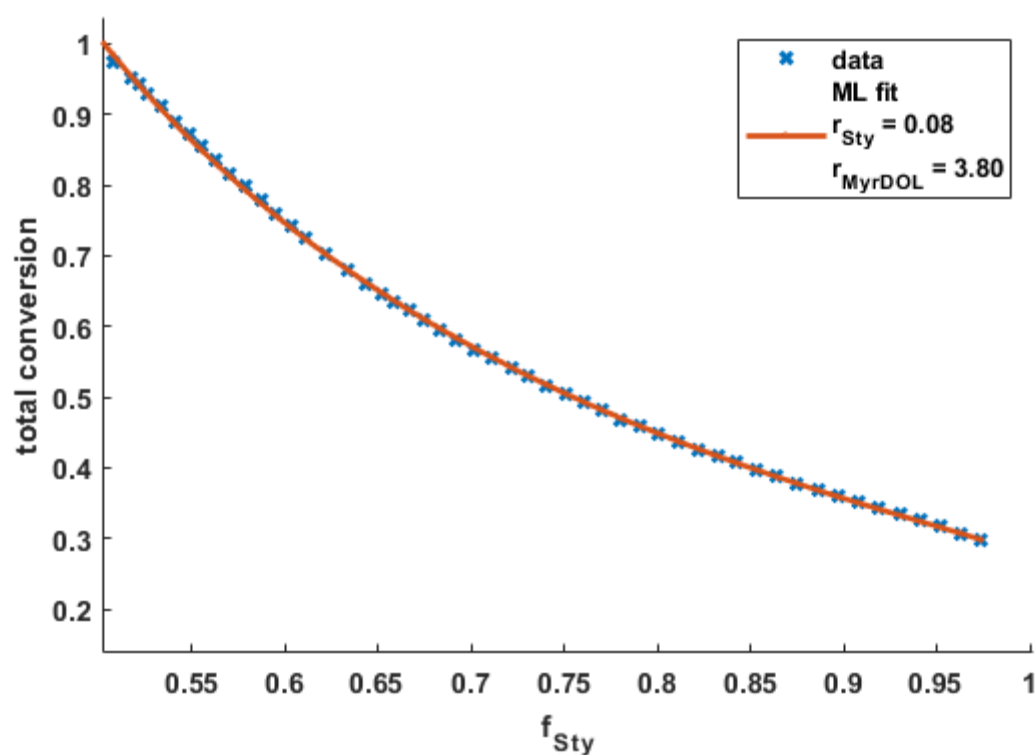


Figure S 27: Meyer-Lowry fits (red) ($1-X$ (total conversion)) versus actual fraction of styrene in the feed, f_{Sty} , used for the evaluation of the reactivity ratios, $R^2 = 0.999$, $r_1 \cdot r_2 = 0.33$.

Table S 2: Summary of fit results copolymerization of MyrDOL (r_2) and styrene (r_1).

Method	r_1	r_1 error	r_2	r_2 error	$r_1 \cdot r_2$	$r_1 \cdot r_2$ error	R^2
Jaacks	0.2038	0.0022	4.8617	0.0596	1	0.0172	0.9960
Meyer-Lowry ideal	0.1916	0.0038	5.2187	0.1613	1	0.0437	0.9963
Meyer-Lowry	0.0879	0.0499	3.7967	0.4111	0.3339	0.1931	0.999

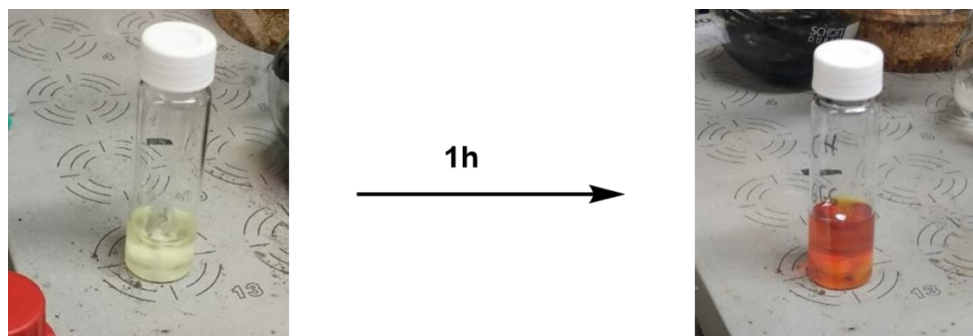


Figure S 28: Color change of poly(Myrdol)-lithium (left) to poly(styrene)-lithium (right).



Figure S 29: NMR tube of the kinetic study of Myrdol and styrene after 65 min. The red color indicates the living nature of the polymerization.

Copolymerization of MyrDOL and isoprene

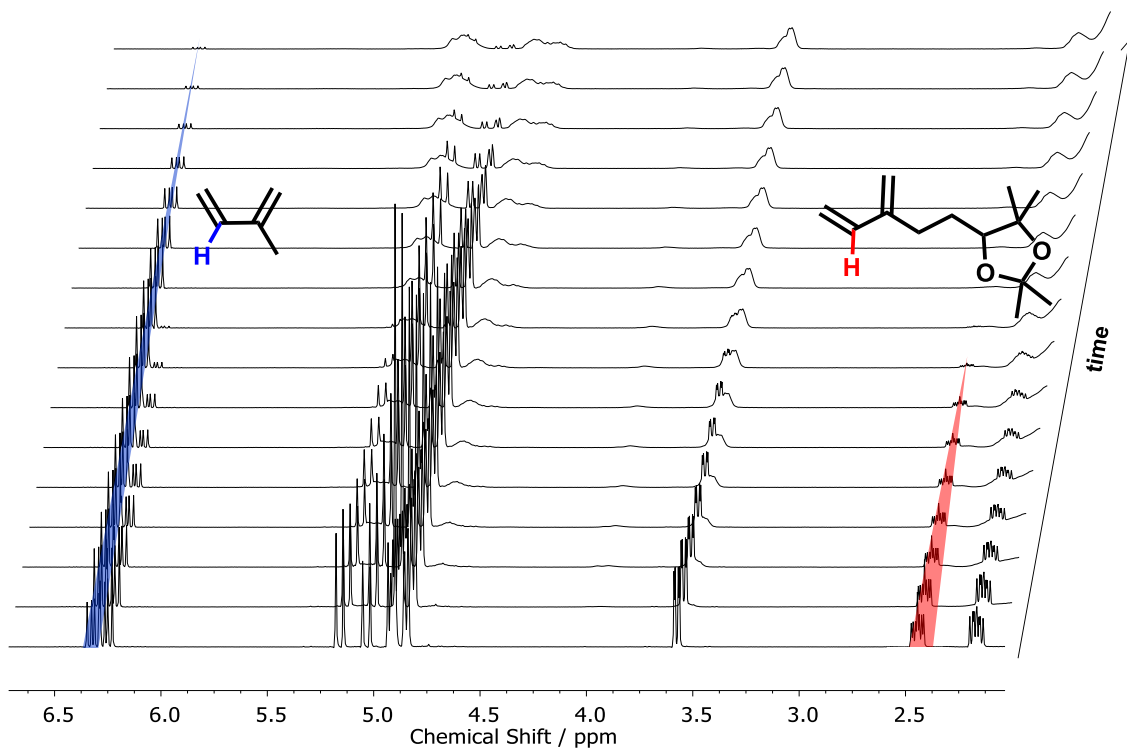


Figure S 30: Stacked ^1H -NMR spectra (400 MHz, C_6D_{12} , 25°C) of the *in-situ* NMR kinetics study of MyrDOL and isoprene separated proton signals (region from 6.6 to 2.4 ppm) are used to determine monomer consumption. For the evaluation of the copolymerization parameters the decreasing signal at 6.32 ppm of isoprene and the decreasing signal at 2.45 ppm of MyrDOL were used.

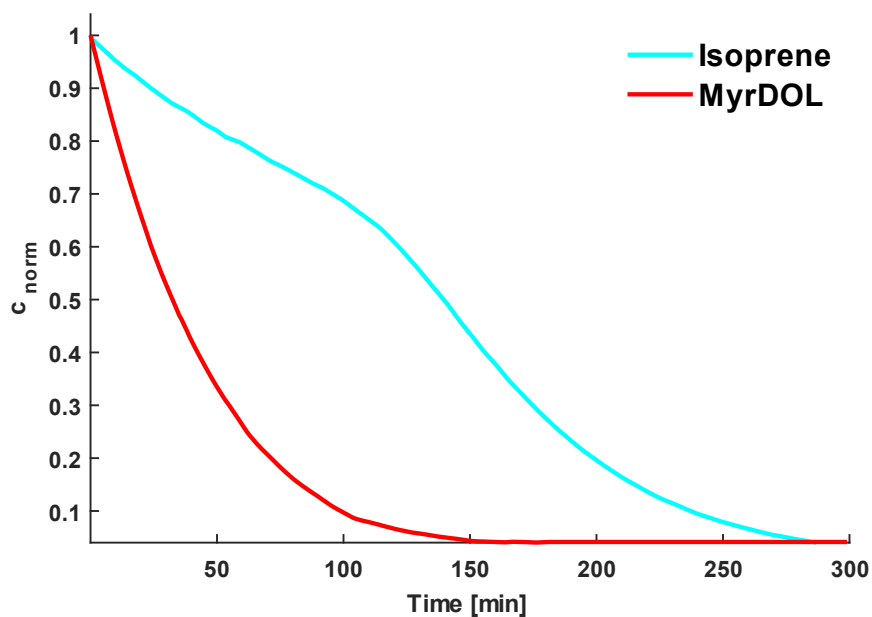


Figure S 31. Normalized concentration c_{norm} against time of the copolymerization of MyrDOL and isoprene.

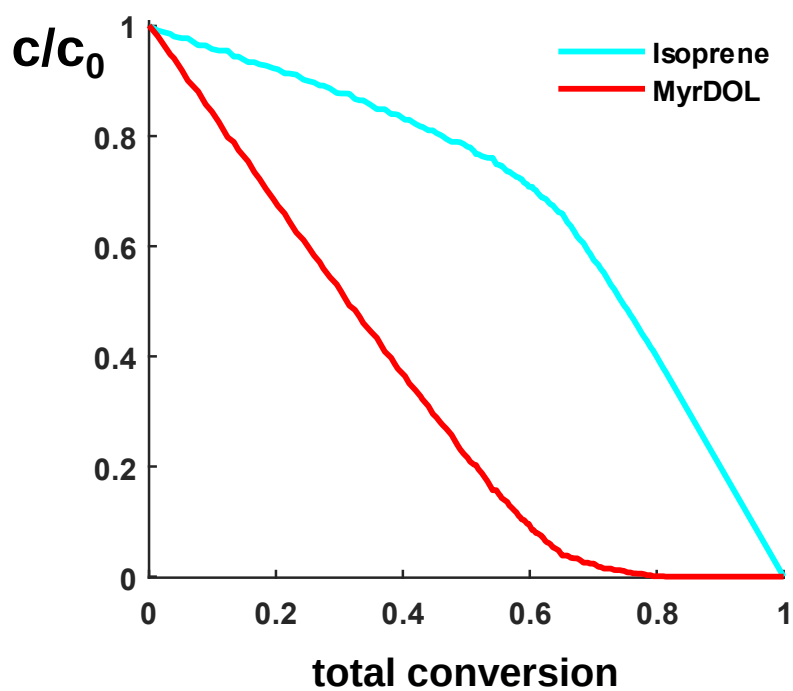


Figure S 32. Individual monomer concentrations as a function of the total monomer conversion time of the copolymerization of MyrDOL and isoprene.

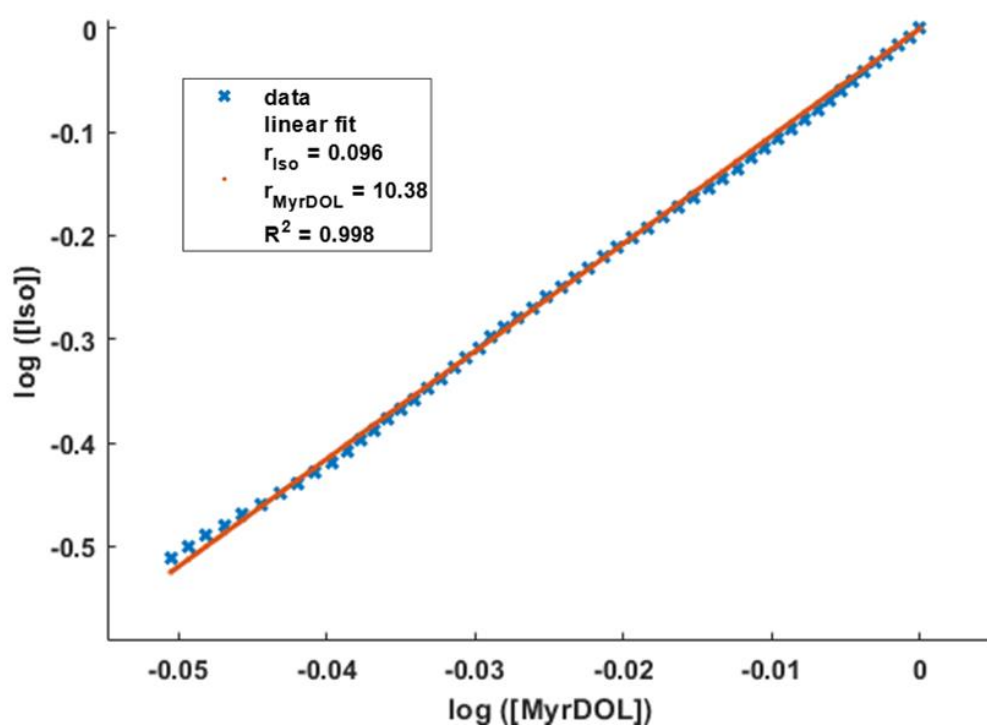


Figure S 33. Jaacks fit (red line) of the copolymerization of MyrDOL and isoprene.

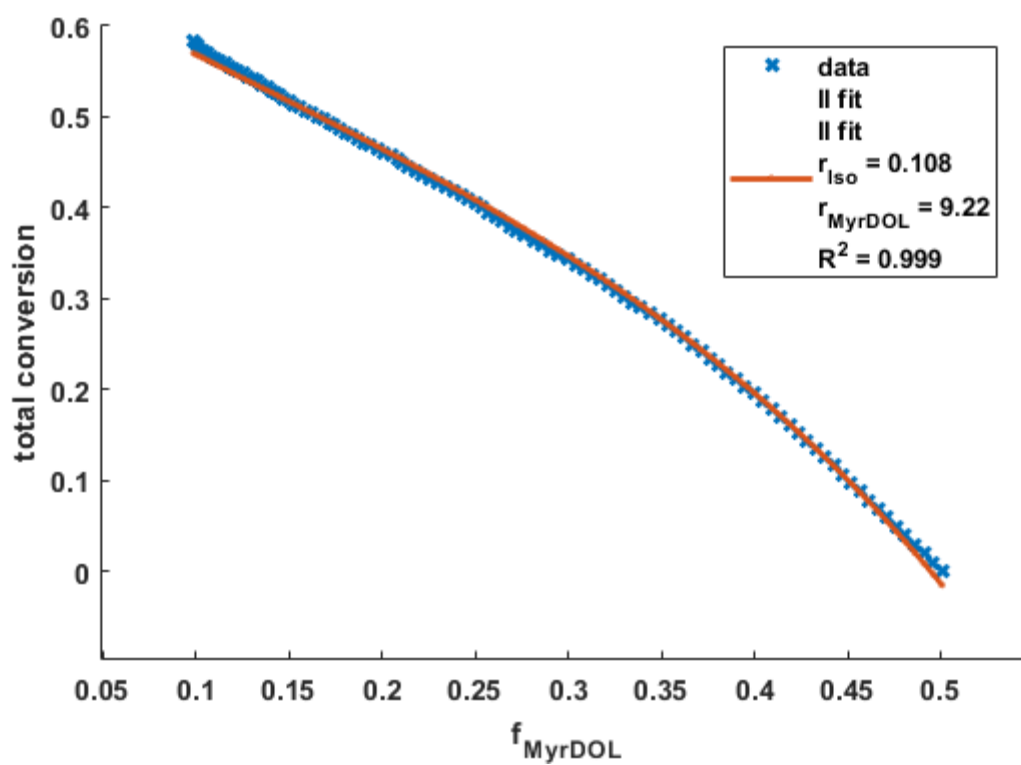


Figure S 34. Ideal integrated fit of the copolymerization of MyrDOL and isoprene.

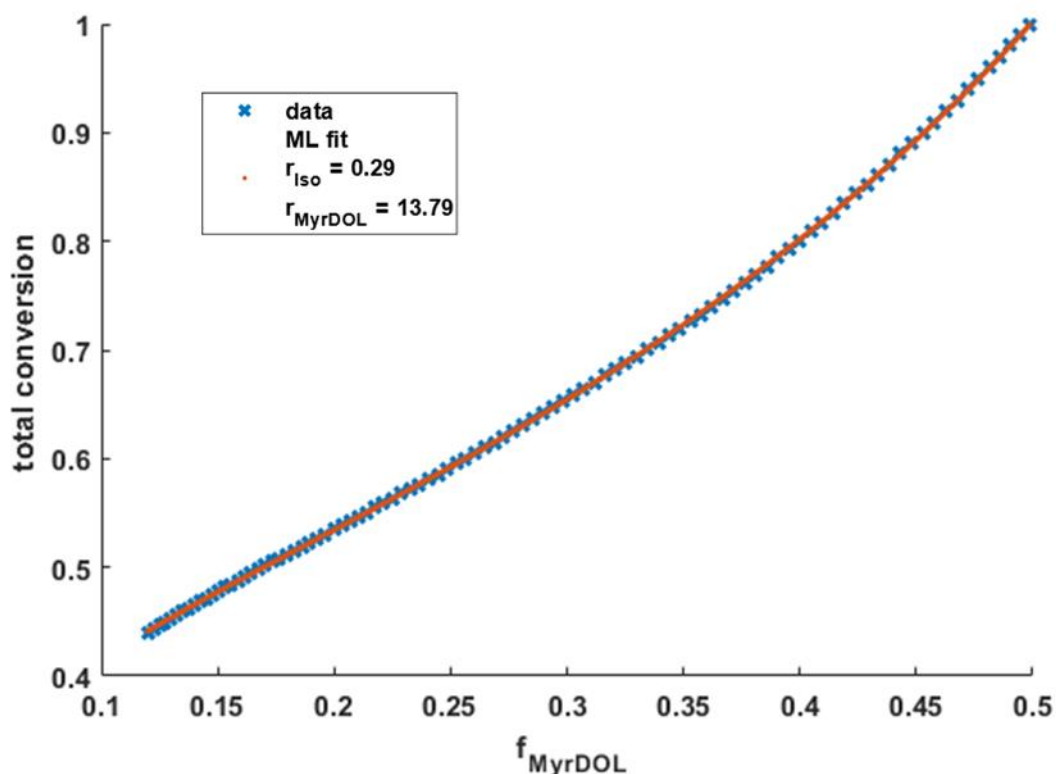


Figure S 35: Meyer-Lowry fits (red) ($1-X$ (total conversion)) versus actual fraction of styrene in the feed, f_{Iso} , used for the evaluation of the reactivity ratios, $R^2 = 0.999$, $r_1 \cdot r_2 = 4.12$.

Table S 3. Summary of fit results copolymerization of MyrDOL (r_2) and isoprene (r_1).

Method	r_1	r_1 error	r_2	r_2 error	$r_1 \cdot r_2$	$r_1 \cdot r_2$ error	R^2
Jaacks	0.0963	0.0004	10.3835	0.0497	1	0.0068	0.9989
Meyer-Lowry ideal	0.1084	0.0016	9.2215	0.1389	1	0.0213	0.9986
Meyer-Lowry	0.2990	0.0117	13.7899	0.2913	4.123	0.1831	0.9999

3.1.6.9 MyrDOL Homopolymerization Kinetics

To understand the observed copolymerization kinetics, we need rate constants of the homopolymerization. From these and the reactivity ratios we can calculate the cross-over rate constants. Since we are working in a non-polar solvent it is crucial to know the state of aggregation of the living chain ends. This was evaluated by kinetic

experiments at different concentrations (Fig. S34). In Figure S35, the inverse of the slope of the double logarithmic plot of k_{app} and the chain-end (Li) concentration gives the degree of aggregation of living P(MyrdOL)-Li, was determined to be close to 2. Similar results were obtained for living polymyracenyl-Li chain ends by Schlaad *et al.*⁷⁷ This differs from polyisoprenyl-Li, which is known to have a degree of aggregation of 4 at low chain-end concentrations.⁷⁸ The difference might be attributed to the steric demand of the P(MyrdOL)-Li, and polymyracenyl-Li chain ends. In the case of MyrdOL the electronic effect of the dioxolane oxygens might play an additional role.

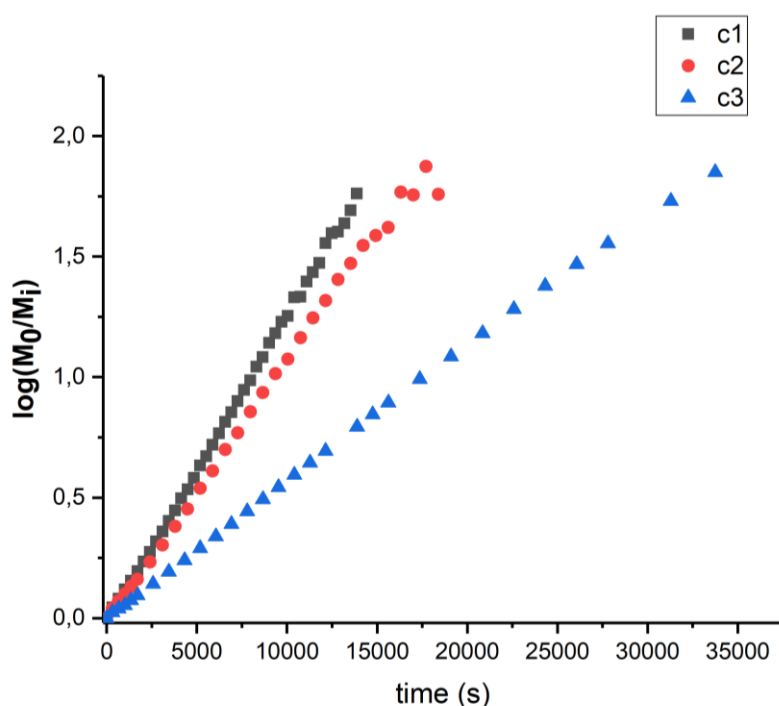


Figure S 36: Homopolymerization kinetics of MyrdOL at different concentrations, $[M]_0 = 3.9 \cdot 10^{-4}$ mol/mL, $c_1 = 6.619 \cdot 10^{-5}$ mol/L, $c_2 = 3.53 \cdot 10^{-5}$ mol/L, $c_3 = 8.50 \cdot 10^{-6}$ mol/L, 25°C in cyclohexane.

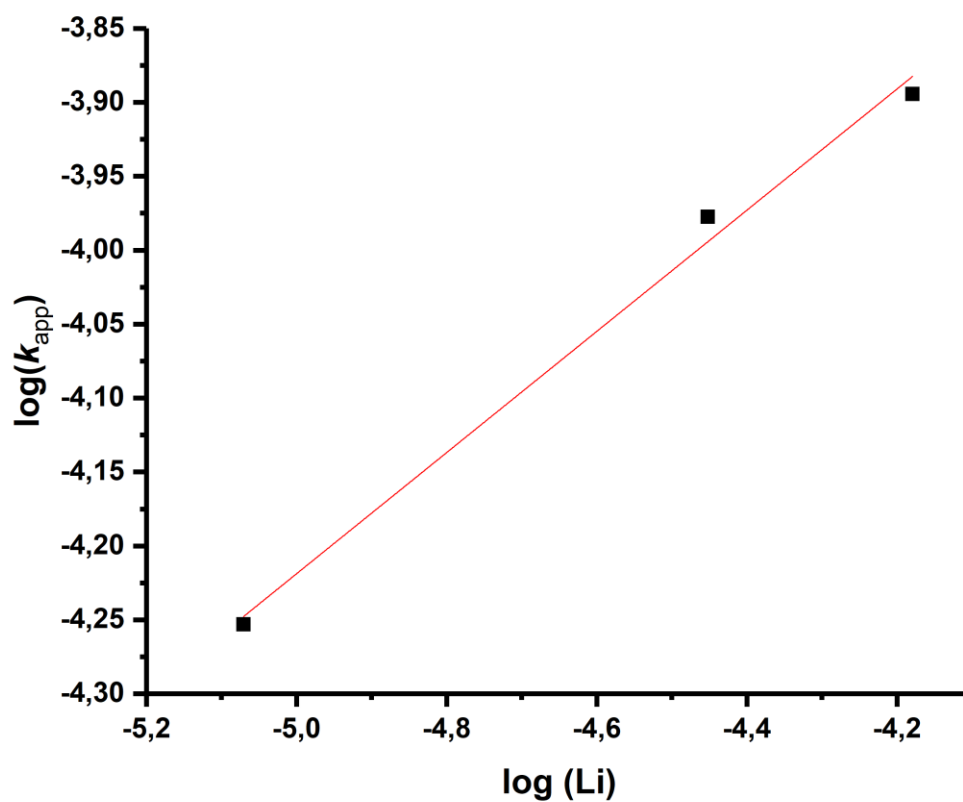
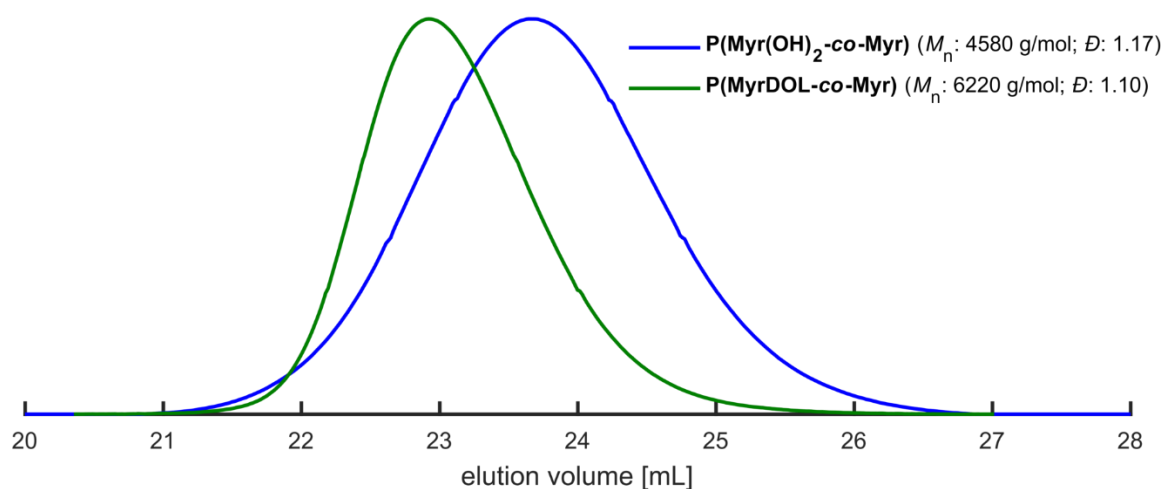


Figure S 37: Double logarithmic plot of k_{app} and the chain-end (Li) concentration. The slope of 0.41 ± 0.03 transforms into a degree of aggregation $N_{agg} = 2.4 \pm 0.2$, which is close to 2.

Table S 4: Reactivity ratios, homopolymerisation and cross-over rate constants in cyclohexane at 20 °C, calculated for a chain-end concentration of $3.53 \cdot 10^{-5}$ mol/mL.

Mon 1	Mon 2	r_1	r_2	$10^3 k_{11}$	$10^3 k_{12}$	$10^3 k_{22}$	$10^3 k_{21}$	k_{21} / k_{11}	k_{12} / k_{22}
				$(\text{L/mol})^{1/4} \text{s}^{-1}$	$(\text{L/mol})^{1/4} \text{s}^{-1}$	$(\text{L/mol})^{1/2} \text{s}^{-1}$	$(\text{L/mol})^{1/2} \text{s}^{-1}$	$(\text{L/mol})^{1/4}$	$(\text{L/mol})^{1/4}$
Isoprene ⁶⁵	Styrene ⁶⁵	10.03	0.015	0.612	0.061	6.39	426	696	0.0095
				$(\text{L/mol})^{1/2} \text{s}^{-1}$	$(\text{L/mol})^{1/2} \text{s}^{-1}$	$(\text{L/mol})^{1/2} \text{s}^{-1}$	$(\text{L/mol})^{1/2} \text{s}^{-1}$		
MyrDOL	Myrcene	6.22	0.16	0.56	0.090	8.82 ⁷⁹	55.1	612	0.0016
MyrDOL	Styrene	5.2	0.19	0.56	0.108	6.39 ⁶⁵	33.6	312	0.0032
				$(\text{L/mol})^{1/2} \text{s}^{-1}$	$(\text{L/mol})^{1/2} \text{s}^{-1}$	$(\text{L/mol})^{1/4} \text{s}^{-1}$	$(\text{L/mol})^{1/4} \text{s}^{-1}$	$(\text{L/mol})^{1/4}$	$(\text{L/mol})^{1/4}$
MyrDOL	Isoprene	9.22	0.11	0.56	0.061	0.61 ⁶⁵	5.56	91.6	0.0109

3.1.6.10 Deprotection of the hydroxyl groups

**Figure S 38: SEC traces of $\text{P(MyrceneDOL-co-Myr)}$ (green) and deprotected polymer $\text{P(Myrcene(OH)}_2\text{-co-Myr)}$ (blue) in THF, PI calibration.**

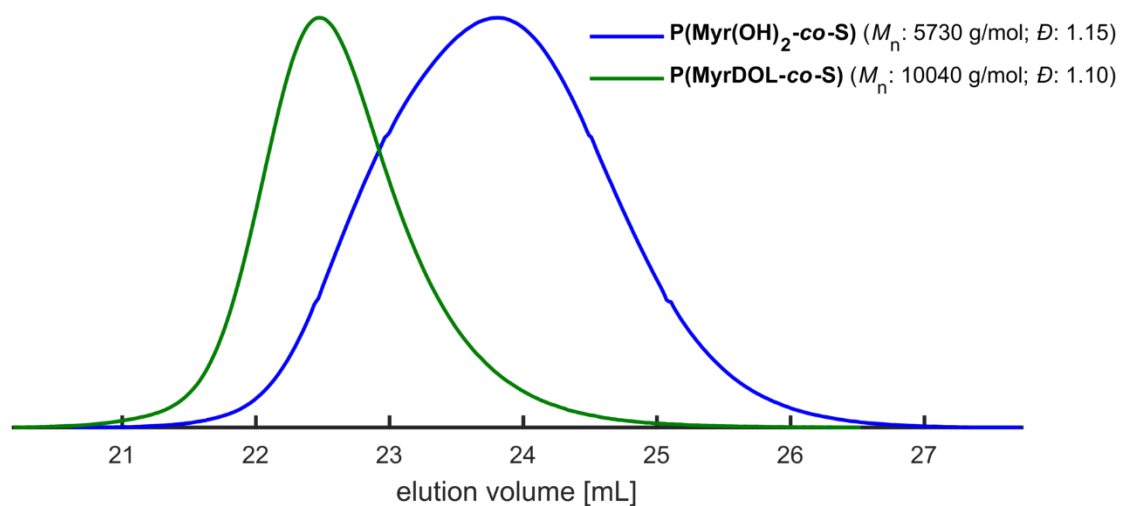


Figure S 39: SEC traces of deprotected polymer P(MyrdOL-co-S) (blue) and P(My(OH)₂-co-S) (green) in THF, PS calibration.

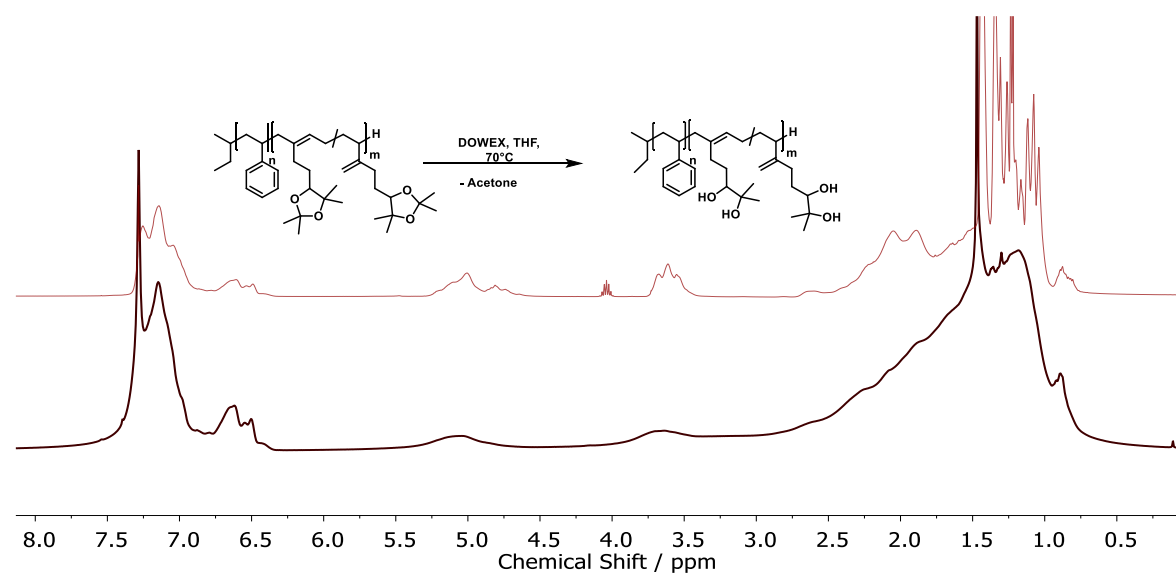


Figure S 40: Stacked ¹H- NMR spectra (400 MHz, C₆D₁₂, 25°C), top: P(MyrdOL-co-S), bottom: deprotected polymer P(My(OH)₂-co-S).

Table S 5: Solubility of P(MyrdOL)₁₅₆, P(My(OH)₂)₁₅₆ and P(MyrdOL_{0.1}-co-Myr_{0.9}).

Polymer	THF	Acetone	MeOH	H ₂ O	CHCl ₃	Pyridine	DMSO
P(MyrdOL)₁₅₆	+	-	-	-	+	+	+
P(My(OH)₂)₁₅₆	+	-	(+)	s	+	-	+
P(MyrdOL_{0.1}-co-Myr_{0.9})	+	-	-	-	+	-	+

+ = soluble (at least 10 mg / mL), - = insoluble, (+) = partially soluble, s= swelling

Chapter 4 Anionic Polymerization of Cyclic Dienes

4 Anionic Polymerization of Cyclic Dienes

4.1 Merging Styrene and Diene Structures to a Cyclic

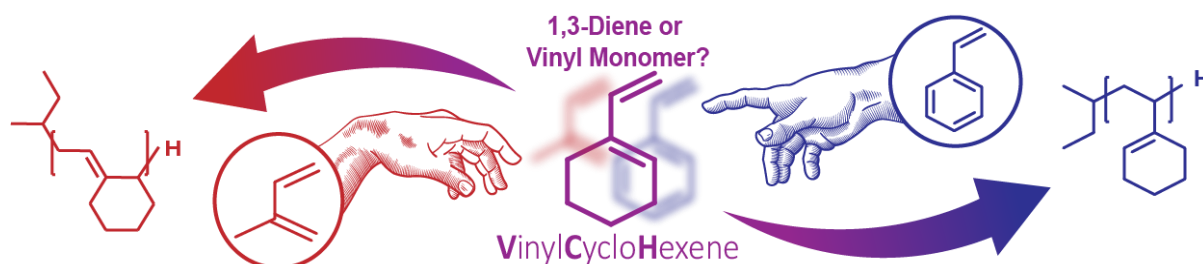
Diene: Anionic Polymerization of 1-Vinylcyclohexene (VCH)

Christoph Hahn,^{a,b} Moritz Rauschenbach,^a and Holger Frey,^a

^a Department of Chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz (Germany)

^b Max Planck Graduate Center, MPGC, Staudingerweg 9, 55128, Mainz (Germany)

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4.1.1 Abstract

We report the synthesis and first anionic polymerization of 1-vinylcyclohexene (VCH). The polymerization of the cyclic 1,2-disubstituted 1,3-diene proceeded quantitatively in cyclohexane at 25 °C with *sec*-butyllithium as initiator. The obtained polymers have well-controlled molecular weights in the range of 5 to 48 kg/mol, based on the molar ratio of monomer and initiator, with narrow molecular weight distributions ($\mathcal{D} < 1.07$ -1.20). *In situ* ^1H NMR kinetic characterization revealed a weak gradient structure for the copolymers of styrene and VCH, ($r_{\text{sty}} = 2.55$, $r_{\text{VCH}} = 0.39$). P(VCH) obtained in cyclohexane with *sec*-BuLi as an initiator showed both 1,4- and 3,4-incorporation mode (ratio: 64:36). It was demonstrated that the microstructure of the resulting P(VCH) can be altered by the addition of a modifier (THF), resulting in increasing 3,4-microstructure (up to 78%) and elevated glass-transition temperature up to 89°C. Thus, the monomer VCH polymerizes carbanionically like a 1,3-diene, however leading to rigid polymers with high glass transition temperature.

4.1.2 Introduction

Linear 1,3-dienes can be polymerized by various polymerization techniques such as emulsion polymerization, controlled and free radical polymerization, living anionic polymerization and catalytic or insertion polymerization.¹ Linear dienes play a key role for highly flexible polymers for manifold elastomer applications. However, cyclic 1,3-dienes with one vinyl double bond have been explored only to a limited extent. The first report on the polymerization of 1-vinylcyclohexene (VCH) was published in 1971 by Hara *et al.*² They polymerized VCH by cationic initiators and reported both 3,4- and 1,4-propagation mode albeit no SEC measurements were conducted. Bonnans-Plaisance investigated the polymerization of VCH by cationic or radical initiators.³ In 1997 Longo *et al.* reported that VCH was polymerized exclusively in 3,4-addition in the presence methylaluminoxane (MAO) and *rac*-[ethylene-bis(1-indenyl)]-ZrCl₂.⁴ However, the poor catalytic activity resulted in extremely low monomer conversion (0.1%). On the contrary, the (Flu)(Cp)ⁱPrZrCl₂-MAO system afforded polymers with 1,4-*trans* microstructure.

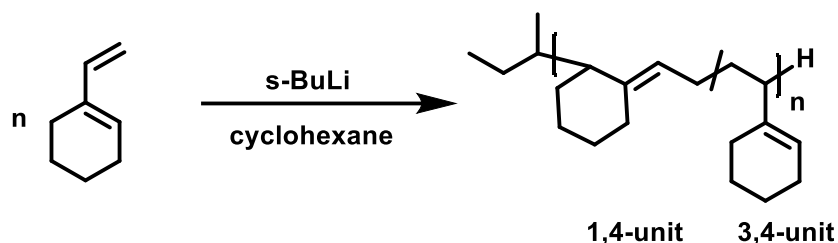
In general, it was demonstrated that cyclic 1,3-dienes with different substitution pattern can undergo living anionic polymerization.⁵ Ishizone *et al.* reported anionic polymerization of a series of extremely sterically hindered allylidene monomers. 1,1-disubstituted 1,3-butadiene derivatives were polymerized in a living manner, using *sec*-BuLi either in cyclohexane at 40 °C or in THF at 0-30°C.⁶ The substituents in 1,1-position studied were dimethyl, cyclohexyl, cycloheptyl, 2,2,5,5-tetramethylcyclopentyl, and bornane. It is noteworthy that less bulky substituents resulted in polymers wherein the 1,4-*trans* microstructure was predominant, whereas bulkier substituents resulted in an exclusively 3,4-microstructure under the very same conditions.⁶ The selective hydrogenation of PI in PS-*b*-PI-*b*-PS triblock copolymers is employed to enhance thermal stability and induces altered mechanical properties, such as pronounced strain hardening.⁷⁻⁹ Furthermore, the hydrogenation of polymers can increase the Flory-Huggins parameter (χ) and the order-disorder-

transition temperature (T_{ODT}). The key challenge lies in the selective hydrogenation of the PI block, retaining PS without saturation and without chain scission under the harsh conditions of the procedure.¹⁰ For full saturation of all double bonds in PI-PS copolymers (olefinic and aromatic), heterogeneous palladium catalyst supported on calcium carbonate can be utilized. The hydrogenated 3,4-microstructure of VCH is identical with a fully hydrogenated PS (i.e. polyvinylcyclohexane).^{4,11} In this work, we report on the polymerization of VCH by anionic polymerization in order to evaluate the behavior of a conjugated cyclic 1,3 diene, possessing one cyclic and one vinyl double bond. We aim at understanding, whether the behavior is comparable to a conjugated diene (as isoprene) or to styrene due to the related molecular structure. In terms of the resulting polymer materials, the cyclic 1,3-diene structure should provide sufficient rigidity to result in a high glass-transition temperature polymer comparable to PS. Additionally, the cyclic 1,3-diene may be viewed as a less delocalized styrene analog with a partially hydrogenated aromatic ring. In contrast to the catalytic polymerization mentioned above, we aimed at quantitative monomer conversion and a living polymerization mechanism.

4.1.3 Results and Discussion

The monomer 1-vinylcyclohexene (VCH) was synthesized according to literature, starting from 1-ethynylcyclohexene by partial hydrogenation of the terminal alkyne with Pd/CaCO₃, deliberately contaminated with Pb(OAc)₂.¹²

To the best of our knowledge, living anionic polymerization of VCH in apolar media with organo-lithium initiators has not been reported to date. The true living nature of the monomer was accompanied by an intense yellow color (Figure S20) upon initiation with *sec*-butyllithium, demonstrating the delocalization of the living



Scheme 7: Anionic polymerization of VCH in cyclohexane. (For reasons of clarity we exclude the *cis*-1,4 microstructure in the scheme. For details analysis of the microstructures see Supporting Information).

carbanion.

We synthesized a series of homopolymers with targeted molecular weights in the range of 5 to 48 kg/mol (SEC, THF, PS calibration). The resulting dispersities were in the range of $\bar{D} = 1.07$ -1.20. In addition, the absolute molecular weight of low molecular weight polymer was determined *via* MALDI-ToF MS, confirming the narrow distribution and incorporation of 1-vinylcyclohexene (108.18 g/mol). The MALDI-ToF spectrum (Figures S6+7) shows the different species assigned to the respective distributions with different cations. The relative molecular weight (GPC, 5130 g/mol) and absolute molecular weight according to MALDI-ToF MS (4800 g/mol) are in good

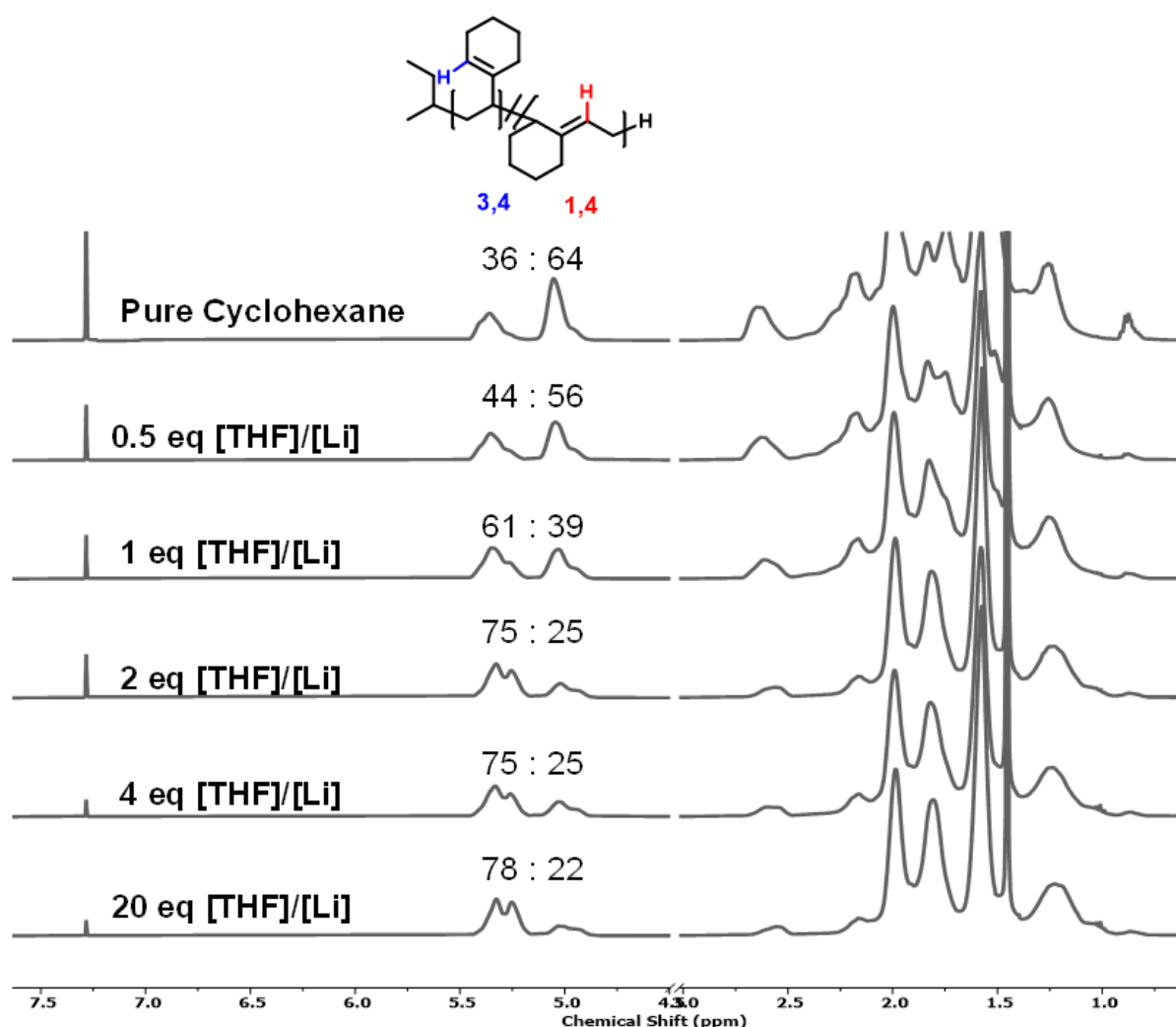


Figure 22: Stacked NMR spectra (CDCl₃, 25°C, 400 MHz) of P(VCH) with different equivalents (from top to bottom: pure cyclohexane, 0.5 eq, 1 eq, 2 eq, 4 eq, 20 eq) of THF as a modifier.

agreement.

DSC measurements reveal that the T_g values of the PVCH homopolymers are in the range of 62 to 78 °C, reaching a plateau value with constant T_g at 18.000 g/mol, i.e. somewhat lower than for polystyrene. The polymerization of VCH was investigated regarding the addition of modifiers with respect to their influence on the microstructure. The microstructure was determined by integration of the allylic protons (5.1 ppm and 5.3 ppm) in the ^1H NMR spectra of the resulting polymer (Figure 1).

Poly(vinylcyclohexene) (P(VCH)) obtained in cyclohexane by anionic polymerization with *sec*-BuLi as an initiator resulted in 64% 1,4-microstructure (36 % 3,4-microstructure, respectively). The determination of the 1,4- and 3,4-units by NMR spectroscopy was carried out in agreement with literature.⁴ Figure 1 shows the change of the structure of P(VCH) as a consequence of an increasing amount of the modifier THF towards 3,4-incorporation in ^1H NMR spectroscopy. Further investigation of the polymer structure by NMR spectroscopy is illustrated in the Supporting Information (Figure S9-12).

As seen in other studies based on catalytic polymerization, no 1,2-microstructure of VCH was observed (see Supporting Information (Figure S11)). Polar additives such as THF are known to alter the microstructure of 1,3-dienes towards higher 3,4-microstructure (and 1,2-microstructure) content.¹³ We utilized small quantities of polar modifiers to obtain a high content of 3,4-microstructure PVCH.

This microstructure is comparable to a (semi)-hydrogenated PS polymer. *Via* NMR spectroscopy it was observed that the polymers possess increasing 3,4-units with increasing ratio of THF/Li. Upon the addition of more than 20 eq. of THF, no further increase of 3,4-units was observed. As a result of the modified microstructures, we determined significantly higher glass-transitions temperatures upon addition of THF, compared to polymers obtained in cyclohexane (T_g = 74 to 89°C).

Statistical Copolymerization of VCH with styrene and isoprene. We further investigated VCH with respect to statistical copolymerization with styrene and isoprene since it is structurally related to both monomers. We were interested in understanding the behavior of the VCH monomer, particularly whether it is comparable to a 1,3-diene or rather to a vinyl monomer, such as styrene.

The results of the online kinetics of VCH with styrene and isoprene as well as a description of the method are shown in the Supporting Information. The reactivity ratios of styrene and VCH were determined to be $r_{\text{Sty}}=2.55$ and $r_{\text{VCH}}=0.39$. The cross-over of PS-Li to P(VCH)-Li is indicated by a significant color change in the block-copolymerization of P(S-*b*-VCH) (see Supporting Information Figure S20).

Table 1: Characterization data of the synthesized homopolymers of VCH in cyclohexene and with the addition of THF, microstructure and glass-transition temperatures are summarized.

entry	$M_n^{[a]}$ kg/mol	$\bar{D}$	[THF]/[Li]	1,4/3,4 %	T_g °C
P1	5.1	1.07	0	64/36	62
P2	6.5	1.15	0	64/36	65
P3	15.4	1.17	0	64/36	77
P4	18.7	1.20	0	64/36	76
P5	36.2	1.09	0	64/36	78
P6	48.7	1.07	0	64/36	77
P7	15.3	1.05	0.5	56/44	74
P8	15.2	1.07	1	39/61	75
P9	16.2	1.11	2	25/75	83
P10	18.1	1.08	4	25/75	83
P11	19.8	1.09	20	22/78	89

[a] SEC, eluent THF, PS calibration

To our surprise, we observed inverse reactivity ratios of VCH and styrene in comparison to those known from conventional diene/styrene copolymers. In general, copolymerization of styrene and 1,3-dienes (e.g. isoprene and butadiene) results in pronounced gradient or tapered structures due to the slow cross-over of PI-Li to styrene.^{14,15} The online NMR data show that styrene is consumed preferentially in the

statistical copolymerization of styrene/VCH. This finding suggests fast cross-over from P(VCH)-Li to styrene, in contrast to linear dienes, such as isoprene or myrcene.¹⁶ Generally, the reactivity of styrene derivatives can be estimated from their β -carbon shift in ^{13}C NMR spectroscopy. The reactivity of the monomer is mainly based on the electron charge density of the reactive vinyl bond which correlates with the chemical shift of the β -carbon. VCH shows a significantly decreased β -carbon shift (109.72 ppm) compared to styrene (113.36 ppm).¹⁷ Based on these observations, we conclude a lower reactivity of VCH compared to styrene. This is tentatively explained by the vinyl bond in the 1,3-diene being considerably less delocalized than the vinyl group at an aromatic ring in case of styrene. In other words, reduced stabilization is assumed compared to styrene.

Copolymerization of VCH with isoprene resulted in bimodal distributions with rather high dispersity of >1.35 . We attribute this to the high reactivity difference between isoprene and VCH, resulting in a very low crossover rate to the less favored monomer. To further elucidate the slow cross-over rate, we initiated VCH with living poly(isoprenyl)-lithium and vice versa. Consequently, the condition of fast initiation for a controlled polymerization is not fulfilled, leading to the observed bimodal molecular weight distribution. Surprisingly, the living chain ends of isoprene and VCH both showed incomplete initiation of the respective other monomer, leading to bimodal distributions in both ways (Figure S22).

Hydrogenation of P(VCH). P(VCH) generated by polymerization in cyclohexane (P3, 36% 3,4-addition) and P(VCH) obtained with 20 eq. of THF modifier (P11, 78% 3,4-addition) were hydrogenated, using palladium on carbon (10w%) as a catalyst under 30 bar H_2 pressure at 130°C in a Parr reactor. The hydrogenation led to full saturation of the polymer, confirmed by ^1H NMR spectroscopy (Figure S23+24). Poly(vinylcyclohexane) P(CHE) has been prepared previously by coordination polymerization of vinylcyclohexane or by complete catalytic hydrogenation of PS. In comparison to literature, we found identical shifts in ^1H and ^{13}C NMR signals to P(CHE) for hydrogenated P(VCH).⁴

For Sample P11, we observed an increase in T_g from 89 to 114°C after hydrogenation. The hydrogenated polymer consists of 78% poly(vinylcyclohexane) moieties with a T_g of 140°C.⁷ However, the thermal behavior of 1,4-P(VCH) remains unknown. No evidence of any chain scission or degradation of the polymer backbone after hydrogenation (see SEC traces Figure S25) was found. A T_g of 70°C was observed after hydrogenation of Sample P3 (Figure S26), which is tentatively explained by the increased freedom of rotation of the saturated polymer backbone.

4.1.4 Conclusion

The living anionic polymerization of VCH, which has not been reported to date, affords polymers with good control over molecular weights and moderate to narrow molecular weight distributions. Compared to the catalytic approach⁴ full conversion was always obtained due to the living character of the anionic polymerization. The results show that the microstructure of P(VCH) can be altered by the addition of THF, leading to a higher extent of 3,4 incorporation.¹⁸ In this case, a rigid polydiene with a tunable T_g in the range of 77-89°C is obtained. Initially, the question whether the monomer acts as a 1,3-diene or as a styrenic monomer was raised. Based on this study, VCH acts comparable to established dienes in the anionic polymerization, however the final material properties are similar to polystyrene, due to its rigidity. The hydrogenation of P(VCH) resulted in polymers containing poly(vinylcyclohexane) segments, causing an increase in T_g to 114°C with a monomodal molecular weight distribution without any evidence of chain degradation.

This work demonstrates the effect of one double bond in a 1,3-diene being sterically constrained on the anionic polymerization behavior. It is important to emphasize that VCH represents a model system for a variety of bio-based 1,3-dienes, derived from natural terpenes. VCH itself shows intriguing potential to produce fully hydrogenated high T_g materials with improved phase separation behavior and access to complex macromolecular architectures *via* living anionic copolymerization.

Acknowledgement

This research was partially supported by the Max-Planck-Graduate Center Mainz. The authors thank Philip v. Tiedemann for his initial conceptualization of the project. We thank Manfred Wagner for the *online-kinetic* measurements.

Keywords: living anionic polymerization • 1,3-dienes • copolymerization kinetics • polystyrene • polyisoprene

4.1.5 References

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4.1.6 Supporting Information

4.1.6.1 General information

Reagents. Chemicals and solvents were purchased from commercial suppliers (Acros, Sigma-Aldrich, Fisher Scientific, Alfa Aesar, TCI). Deuterated solvents were obtained from Deutero GmbH. Isopropyl alcohol and methanol were used as received without further purification. Cyclohexane was purified by stirring over diphenylhexyllithium (adduct of sec-butyllithium and 1,1-diphenylethylene), vacuum-transferred and degassed by four freeze-pump-thaw cycles prior to use. The monomers VCH, styrene and isoprene were purified by stirring over CaH₂ overnight, followed by distillation. All monomers for the anionic polymerization were degassed by four freeze-pump-thaw cycles prior to use.

Instrumentation. All NMR spectra (¹H, ¹³C, ed. HSQC, HMBC, ¹H, ¹H-COSY and DOSY) were recorded on a Bruker Avance II 400 spectrometer equipped with a 5 mm BBFO-SmartProbe with z gradient and ATM, as well as a SampleXPress 60 sample changer. All spectra are referenced internally to residual proton signals of the deuterated solvent.

Size exclusion chromatography (SEC) measurements were performed using an Agilent 1100 Series, equipped with a SDV column set from PSS (SDV 103, SDV 105, SDV 106). Tetrahydrofuran (THF) was used as the mobile phase (flow rate 1 mL min⁻¹) and as the solvent. Poly(styrene) standards were provided by PSS for calibration. The measurements were carried out at 30 °C with an RI and UV (275 nm) detector. For analysis the PSS WinGPC® UniChrom (V 8.31, Build 8417) software provided by PSS Polymer Standards Service GmbH was used.

Glass transitions temperatures (*T*_g) were determined by evaluating differential scanning calorimetry (DSC) curves recorded on a Perkin Elmer 8500 differential scanning calorimeter. A temperature range from 0 °C to 150 °C was used. For the first cycle a heating rate of 10 °C min⁻¹ and a cooling rate of 20 °C min⁻¹ was employed. A

second heating cycle ($20\text{ }^{\circ}\text{C min}^{-1}$) was used to evaluate the thermal properties of the (co)polymers. For the hydrogenated polymers a temperature range from 0°C to 200°C was used.

MALDI-ToF MS measurements were performed on a Bruker Rapiflex. 2-(4-hydroxyphenylazo)benzoic acid (HABA) was used as a matrix (1:1 in water) for P(VCH). The spectrum was measured in a linear positive mode with a laser wavelength of 337 nm. The mass spectrum was recorded in a reflector positive mode with a 337 nm laser. For all polymers 1 mg analyte was dissolved in 1 mL solvent.

General polymerization procedure in nonpolar media (cyclohexane). All polymerizations were carried out in cyclohexane at room temperature, or as indicated, in an argon-filled glovebox (MBraun UNILAB, <0.1 ppm of O_2 and <0.1 ppm of H_2O) in 40 mL glass vials equipped with a magnetic stir bar, screw caps and septa. Dry and degassed cyclohexane was distilled into a Schlenk flask equipped with a Teflon stopper. Dry and degassed THF was used as a modifier. Inside the glove box the monomer(s) and cyclohexane were added into glass vessel with septum. For the synthesis of a homopolymer and copolymer the monomer/solvent (10 wt%) mixture was initiated with 0.1 mL or 0.05 mL sec-butyllithium (1.3 M in cyclohexane/hexane 92/8) via 0.1 mL syringe. The polymerization was terminated after full conversion by adding 0.5 mL of isopropanol (degassed with argon for 1 h prior to use) by a syringe. The polymers were precipitated in 30 mL of a cold methanol/isopropanol mixture and dried under reduced pressure.

4.1.6.2 Monomer synthesis

1-Vinylcyclohexene. For the synthesis of this compound, 25 mL of 1-ethynylcyclohexene (Sigma-Aldrich) was hydrogenated selectively with Pd/CaCO_3 contaminated with $\text{Pb}(\text{OAc})_2$ in pentane and 1 bar of hydrogen atmosphere at room temperature.¹² The catalyst was removed by filtration and the solvent was distilled under reduced pressure. VCH was distilled over CaH_2 , followed by trioctylaluminum for 24 h and was freshly distilled under reduced pressure prior to use.

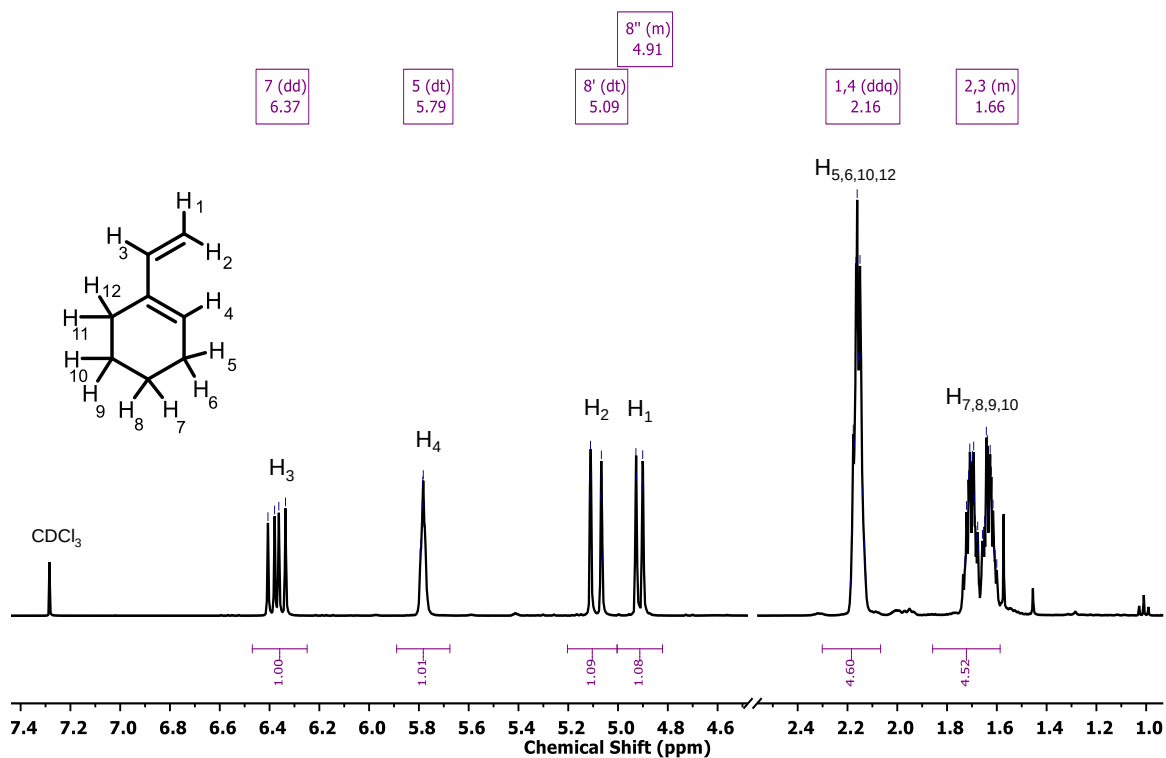


Figure S 1: ¹H NMR spectrum (400 MHz, CDCl₃, 25°C) of VCH.

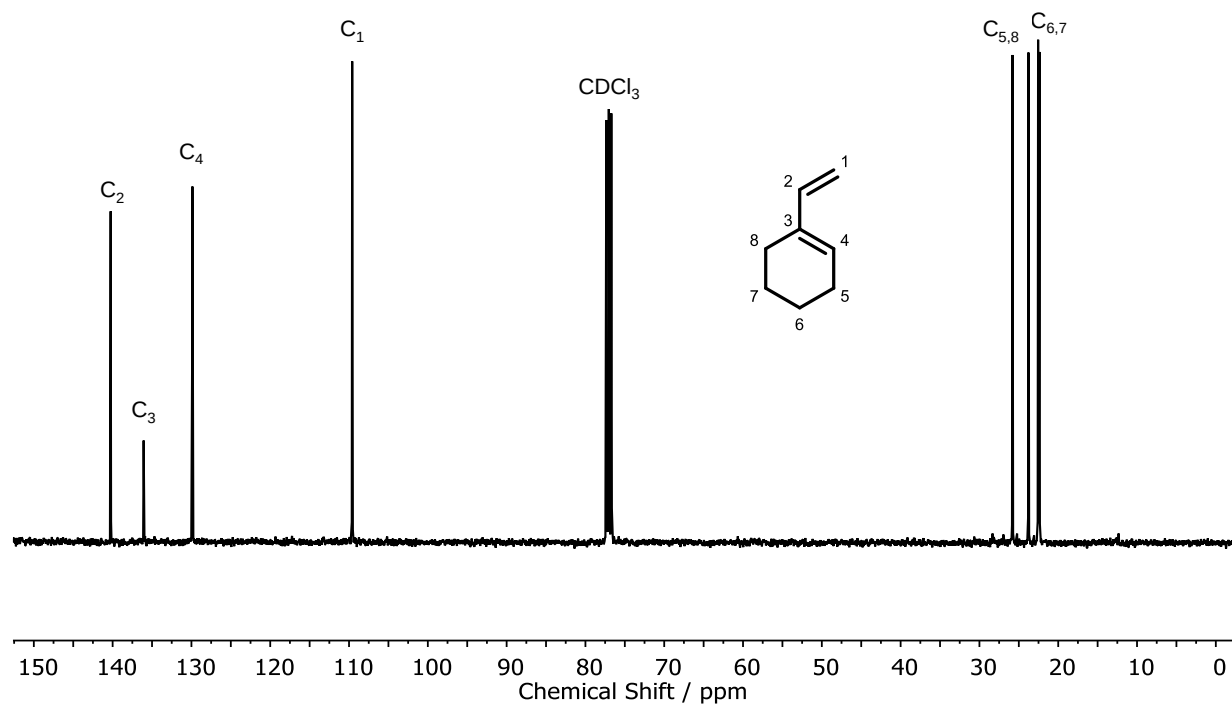


Figure S 2: ¹³C NMR spectrum (100 MHz, CDCl₃, 25°C) of VCH.

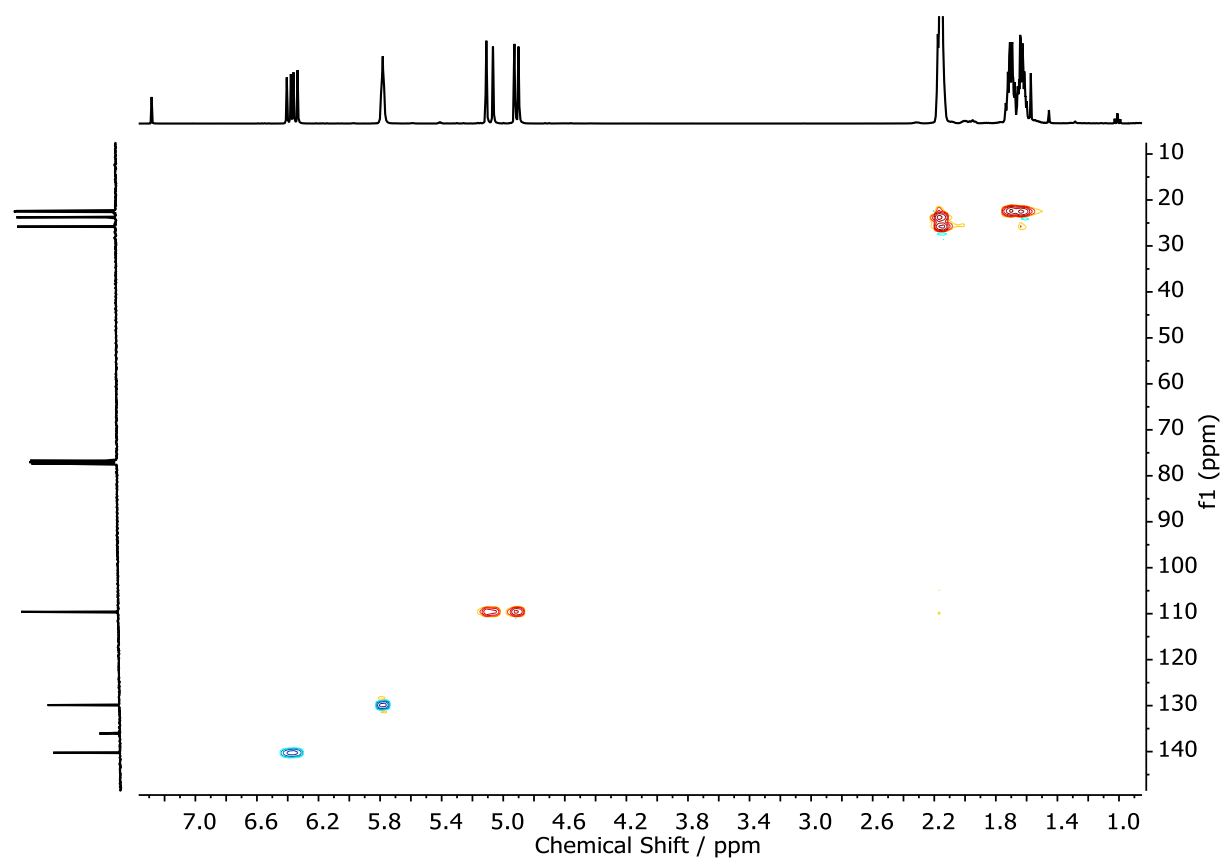


Figure S 3: HSQC NMR spectrum (400 MHz/100 MHz, CDCl_3 , 25°C) of VCH.

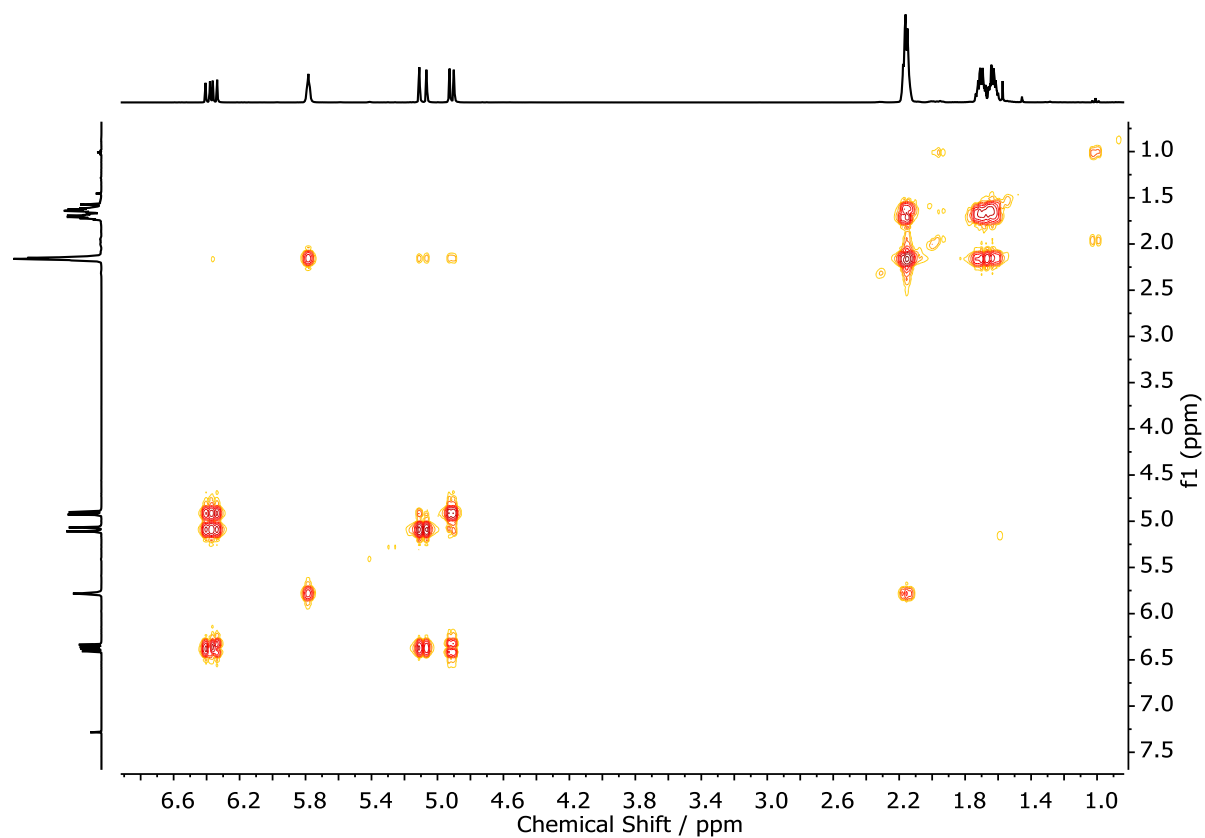


Figure S 4: COSY NMR spectrum of VCH (400 MHz, $CDCl_3$, 25°C)

4.1.6.2.1 Homopolymers

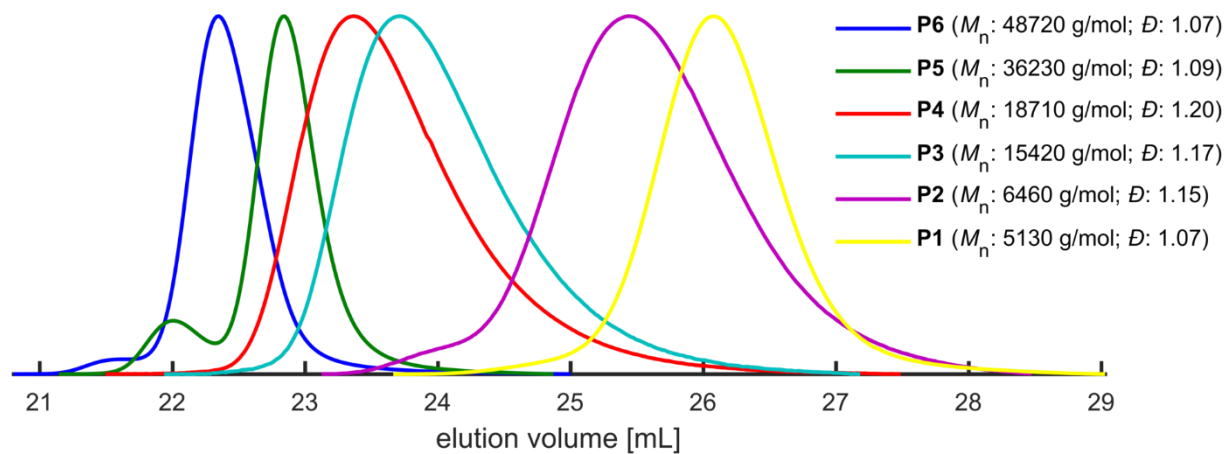


Figure S 5. SEC traces of homopolymers of VCH (Table 1); eluent THF, PS calibration.

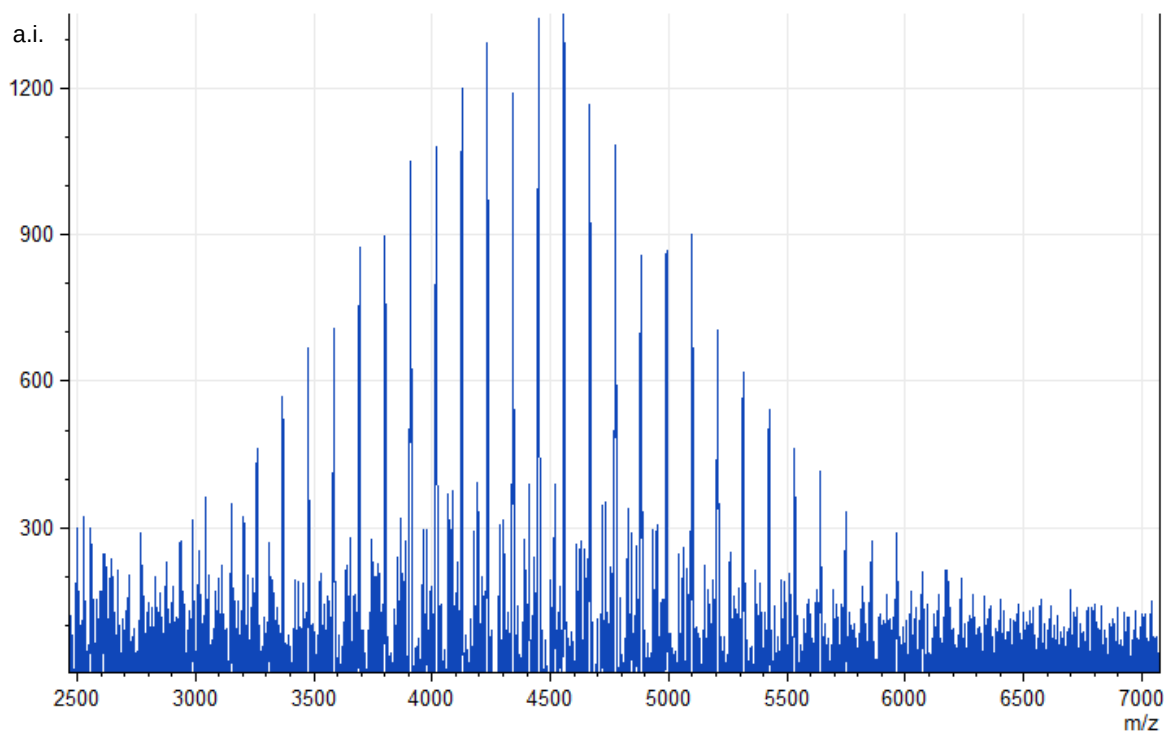


Figure S 6: MALDI ToF-MS of P1 (DCTB matrix).

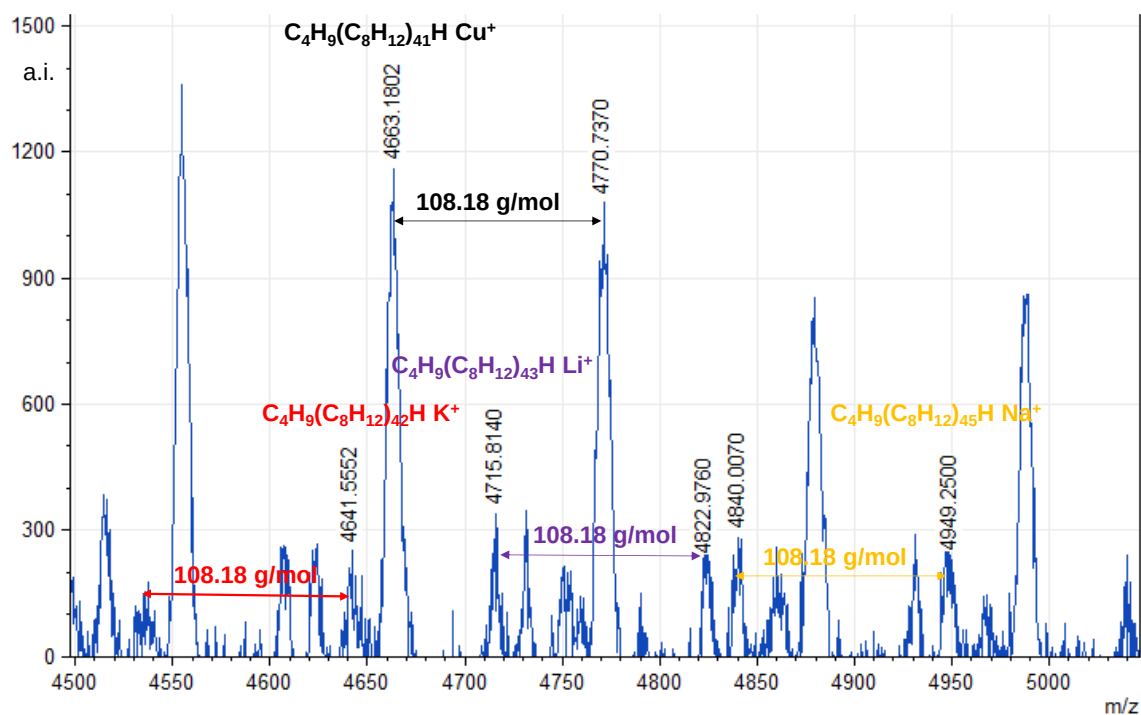


Figure S 7: MALDI ToF-MS of P1, zoom in of Figure 6.

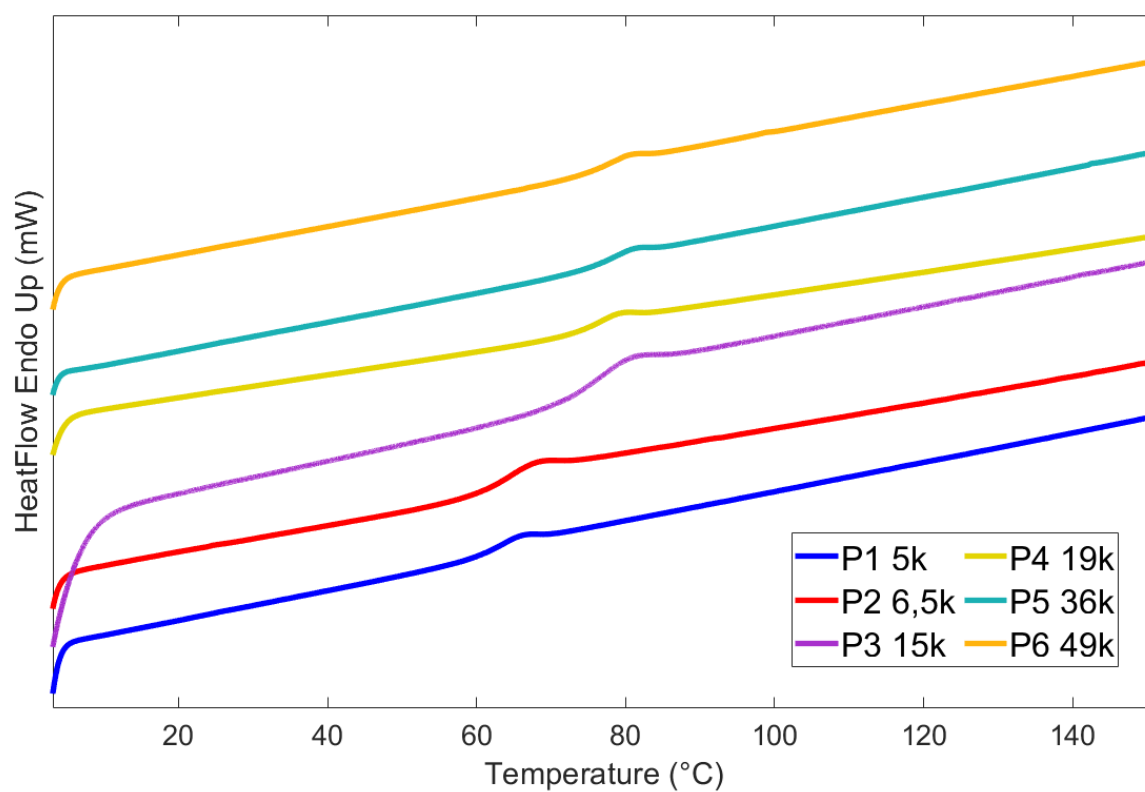


Figure S 8: DSC data of homopolymers P1-6 (Table 1).

4.1.6.2.2 Investigation of the microstructure

Here is an exemplary description of the microstructure of sample P11. The results agree with data from literature of poly(vinylcyclohexene), polymerized by Ziegler-Natta type catalysts.

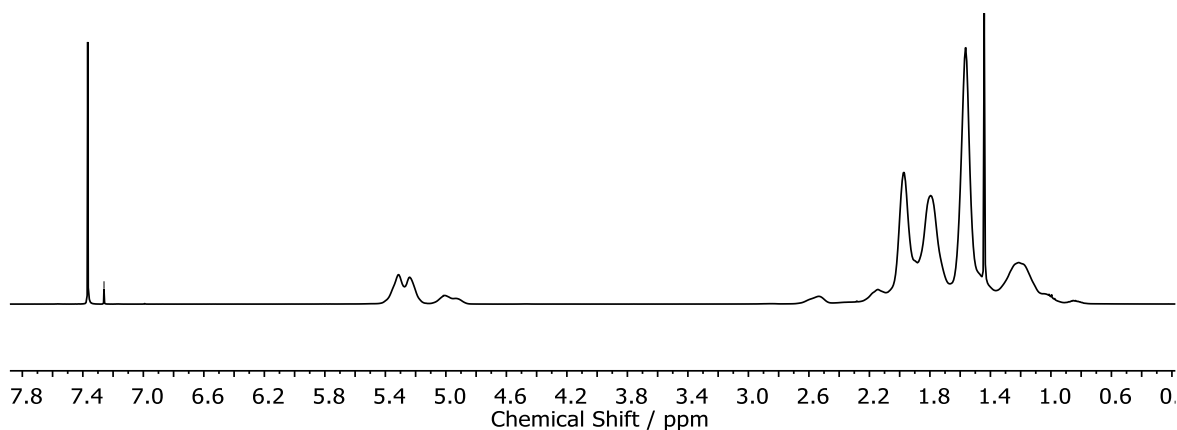


Figure S 9: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of PVCH sample (P11).

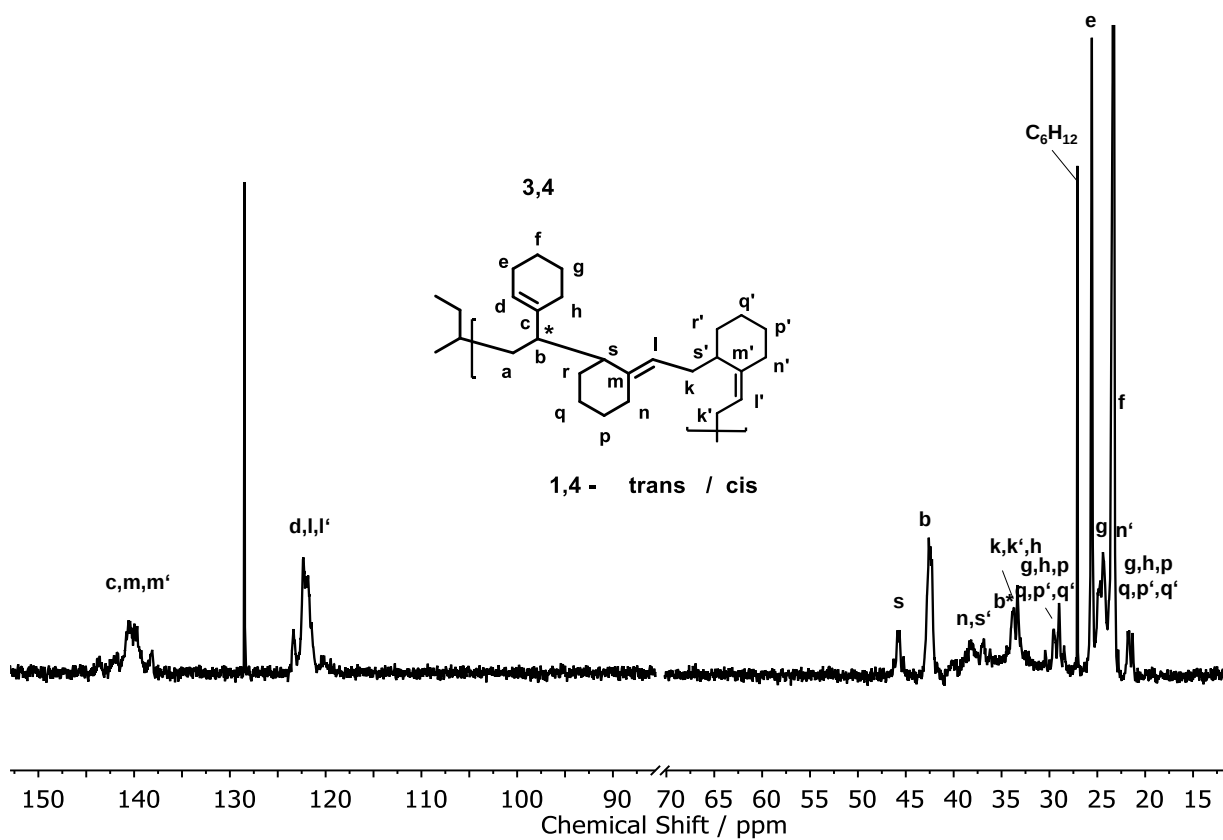


Figure S 10: ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25°C) of PVCH (P11).

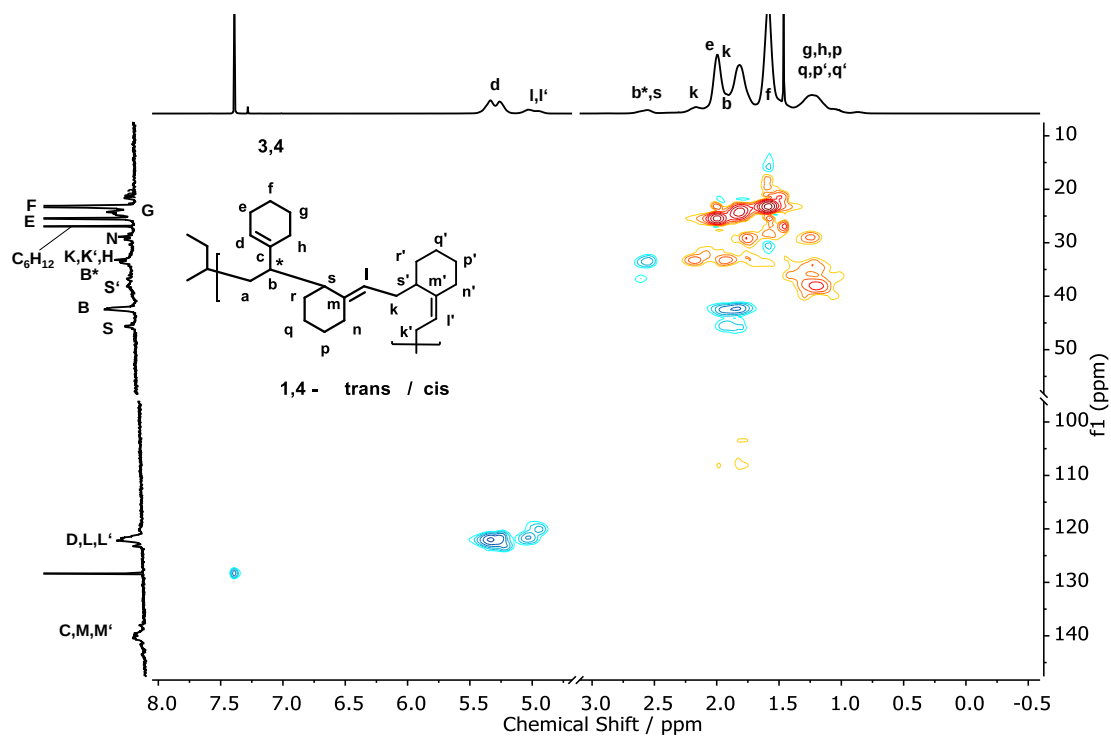


Figure S 11: HSQC NMR spectrum (400 MHz/100 MHz, CDCl₃, 25°C) of PVCH (P11).

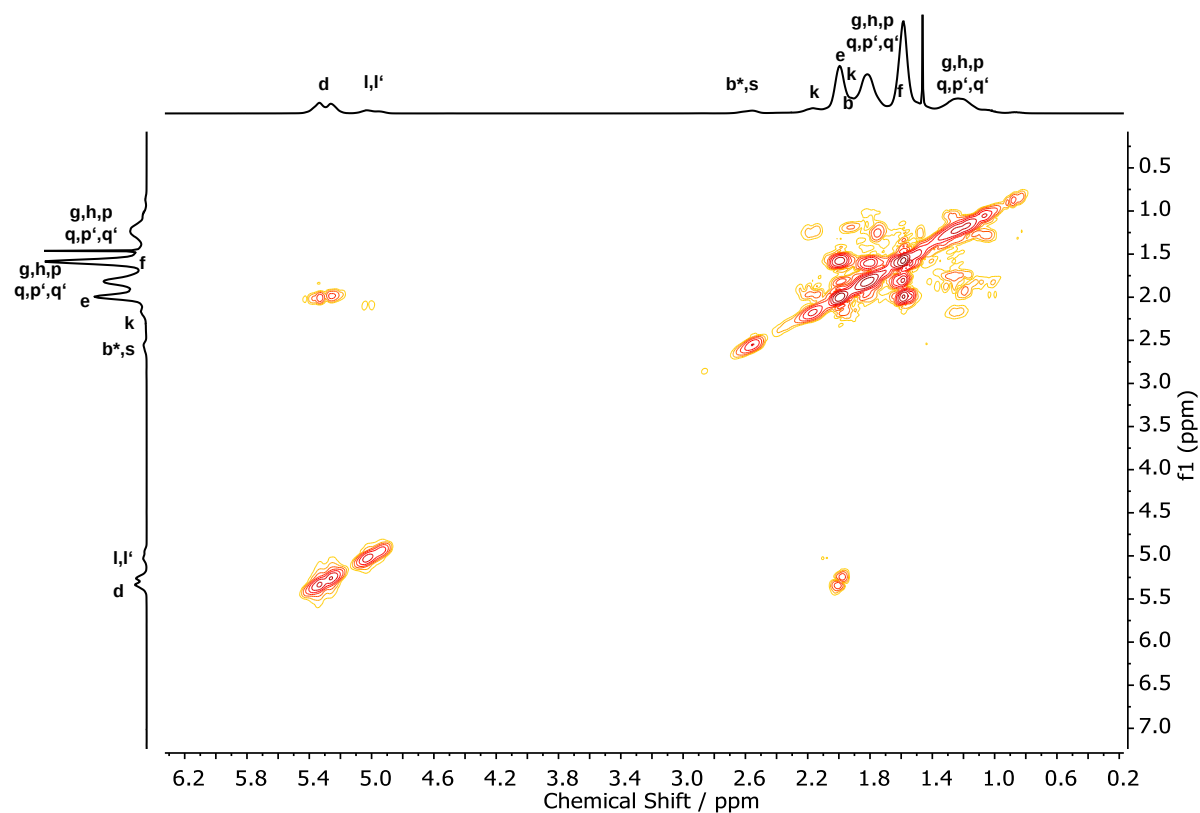


Figure S 12: ¹H/¹H COSY NMR spectrum (100 MHz, CDCl₃, 25°C) of PVCH (P11).

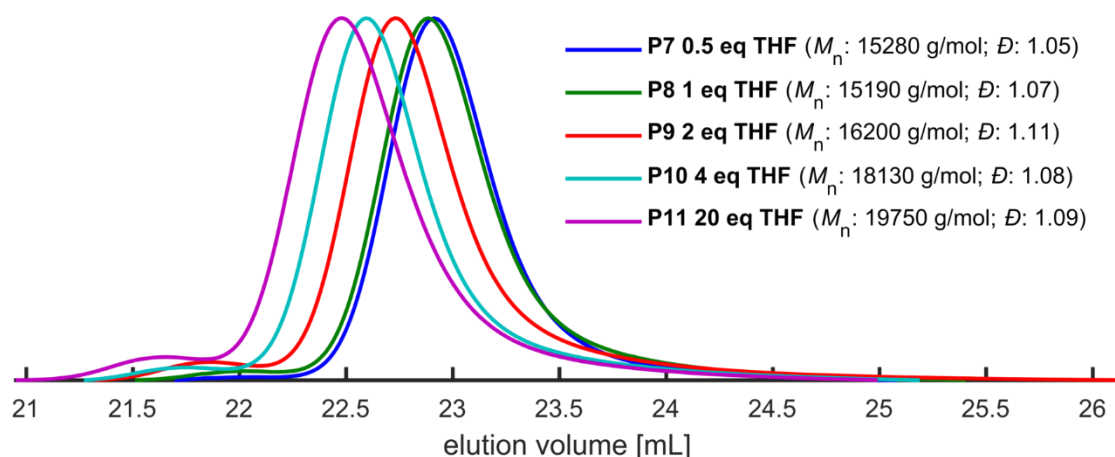


Figure S 13: SEC traces of the homopolymers of VCH obtained with different equivalents of THF as a modifier (eluent: THF, PS calibration).

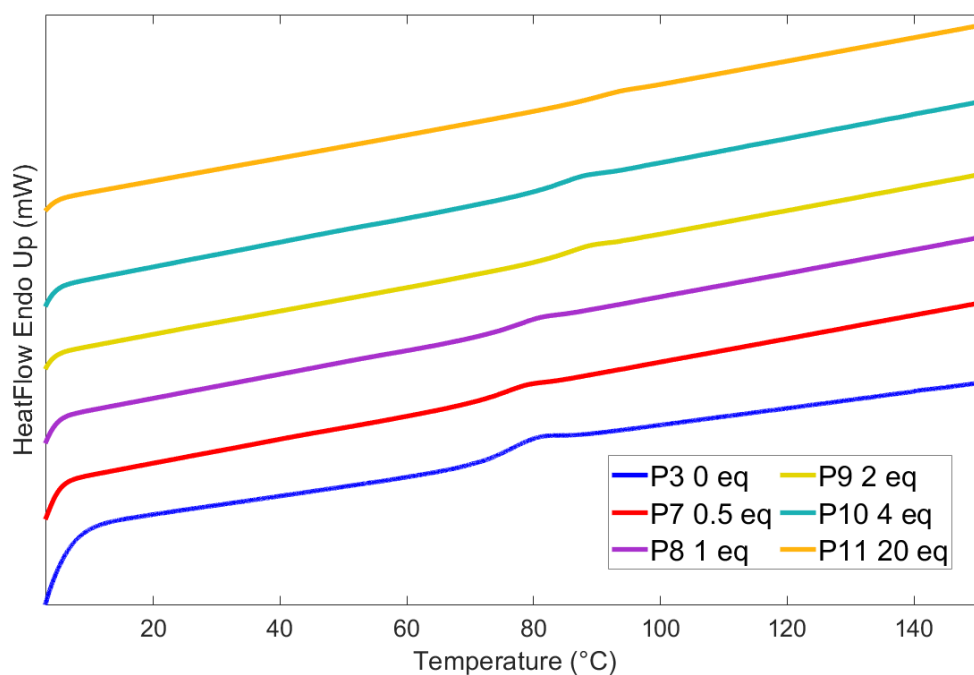


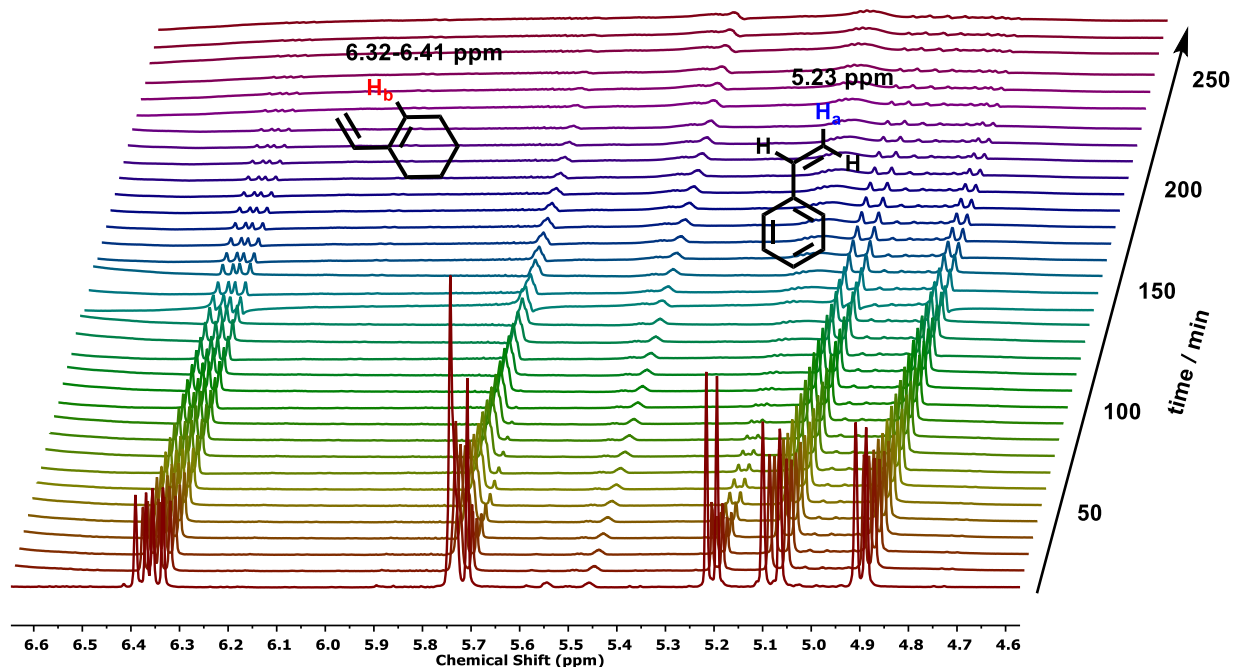
Figure S 14: DSC data of homopolymers P3+7-11 with different equivalents of THF.

4.1.6.2.3 Copolymerization kinetics

The copolymerization of VCH and styrene was investigated *via online* ^1H NMR kinetic studies. The integrated signals used for VCH and styrene are shown in Scheme 1. The diminishing signals of VCH are in the region of 6.32-6.41 ppm, whereas the decreasing signals for styrene are at 5.23 ppm.

For comparison reasons, we employed different models for the evaluation of the

copolymerization parameters. We utilized Jaacks, Meyer-Lowry, and the integrated version of the Meyer-Lowry model to fit the data.¹⁹ The summary of the fit results is demonstrated in Table S2.



Scheme 1: Chemical shifts of decreasing signal of VCH (6.32-6.41 ppm, H_b) and styrene (5.23 ppm, H_a) in the statistical copolymerization of both monomers.

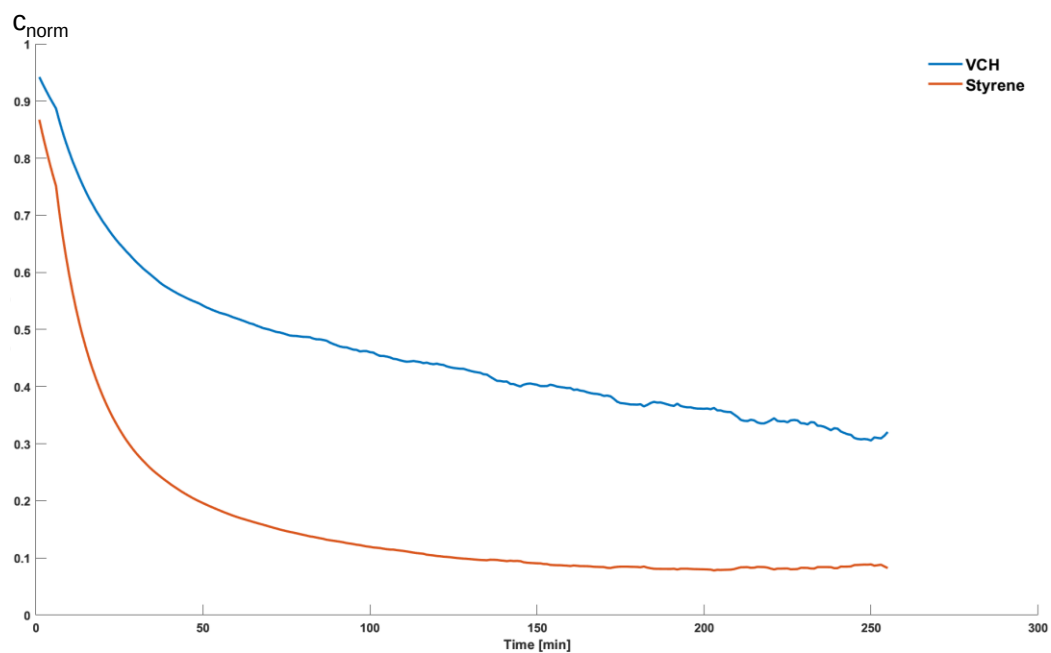


Figure S 15: Normalized comonomer concentrations c_{norm} vs. time in the statistical copolymerization of VCH and styrene in cyclohexane at 25°C.

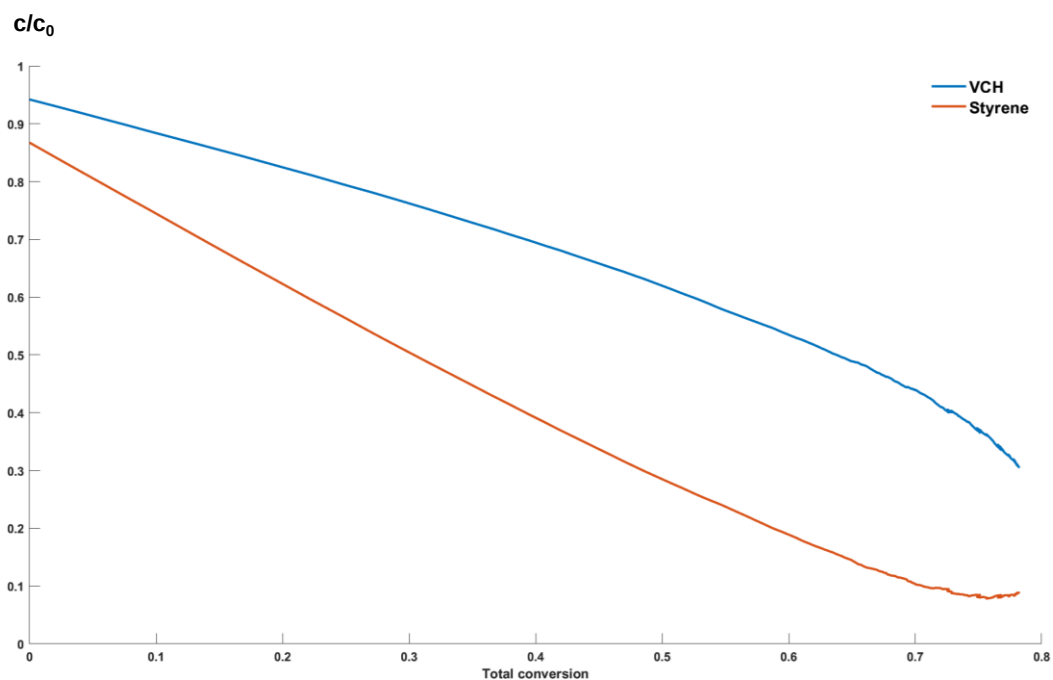


Figure S 16: Individual monomer concentrations as a function of the total monomer conversion in the statistical copolymerization of VCH and styrene.

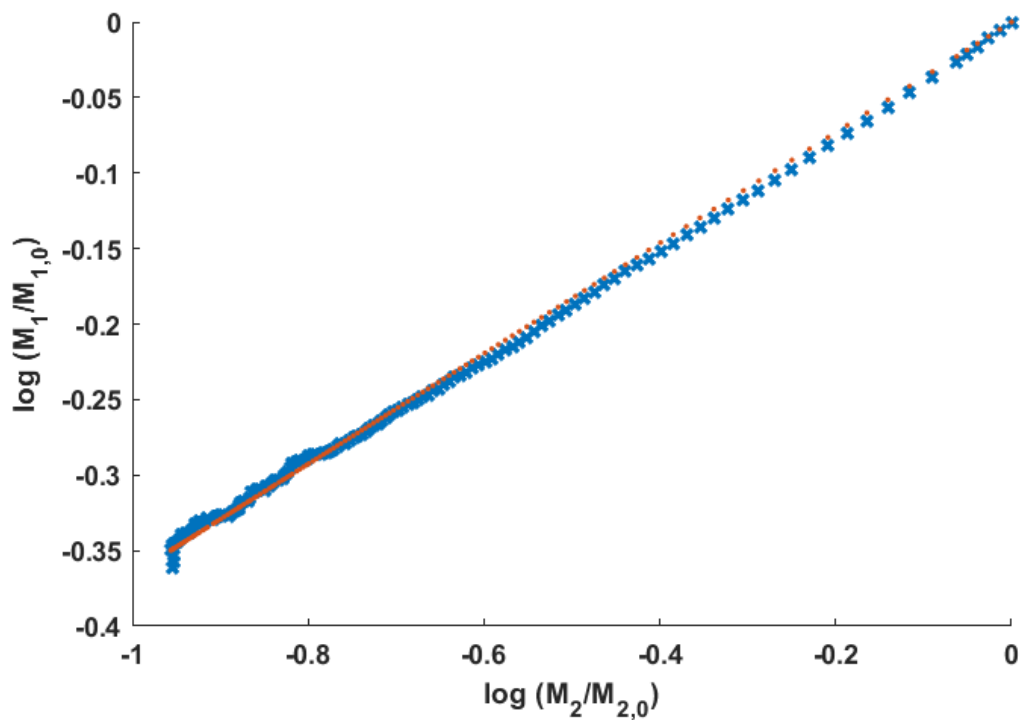


Figure S 17: Jaacks fit (red dots) of the copolymerization of VCH and styrene, showing excellent agreement with the experimental data obtained from online NMR.

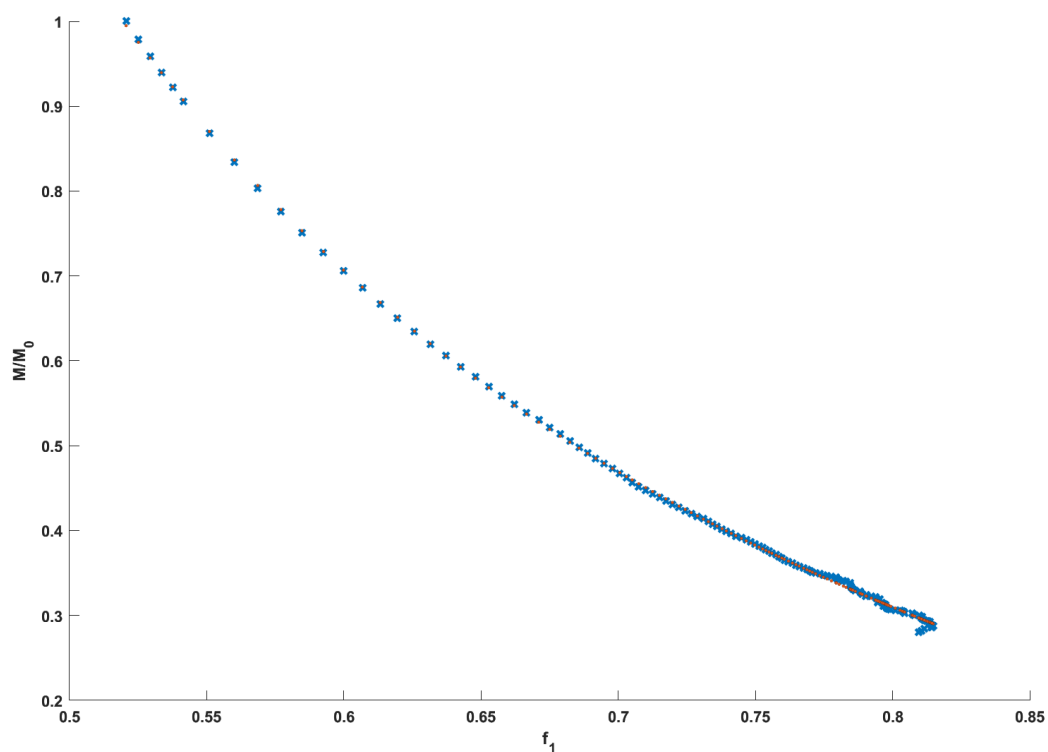


Figure S 18: Ideal integrated fit¹⁹ (red dots) of the copolymerization of VCH and styrene (f_1).

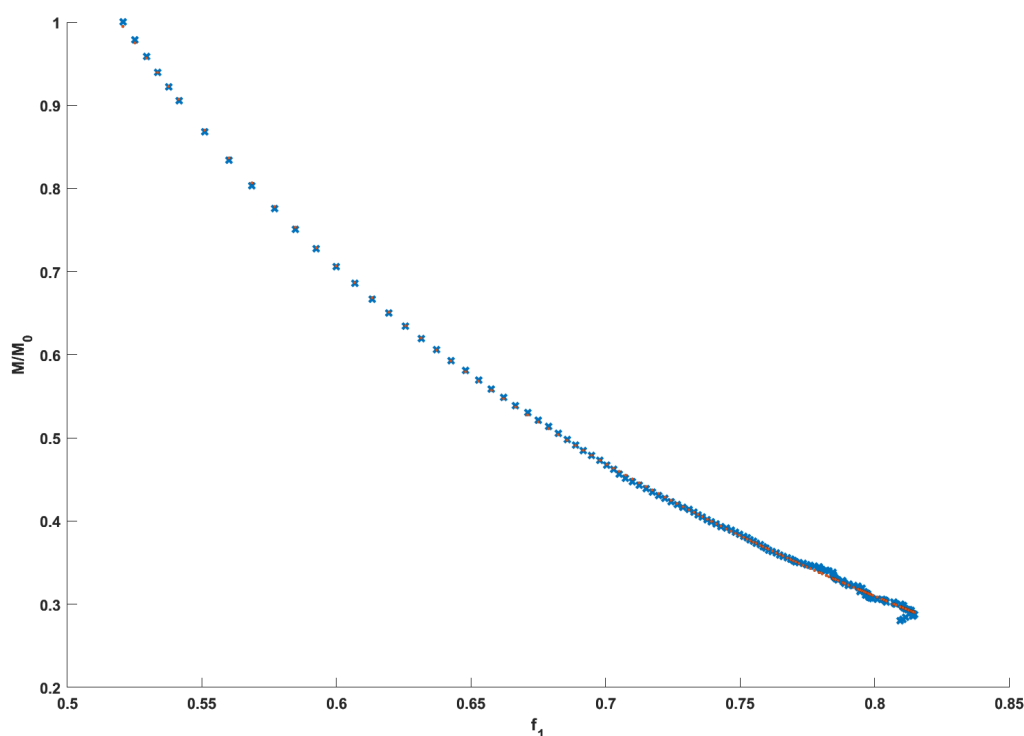


Figure S 19: Meyer-Lowry fits (red) (1-X (total conversion)) versus actual fraction of styrene in the feed, f_1 for the copolymerization of VCH and styrene in cyclohexane.

Table S 1: Summary of fit results copolymerization of VCH (r_2) and styrene (r_1).

Method	r_1	r_{1error}	r_2	r_{2error}	$r_1 \cdot r_2$	$r_1 \cdot r_2 error$	R^2
Jaacks	2.552	0.008	0.392	0.001	1	0.0043	0.9978
Meyer-Lowry ideal	2.770	0.014	0.361	0.002	1	0.007	0.9968
Meyer-Lowry	2.144	0.047	0.249	0.008	0.535	0.002	0.9995

Table S 2: β -carbon shift of styrene, 4-isopropylstyrene and VCH (^{13}C NMR).

Monomer	styrene	4-isopropylstyrene	VCH
$\beta\text{-C shift (ppm)}$	113.36	113.00	109.72

*400MHz, CDCl_3



Figure S 20. Typical colors of the living chain of P(VCH)-Li (left) and P(VCH-*b*-S)-Li (right).

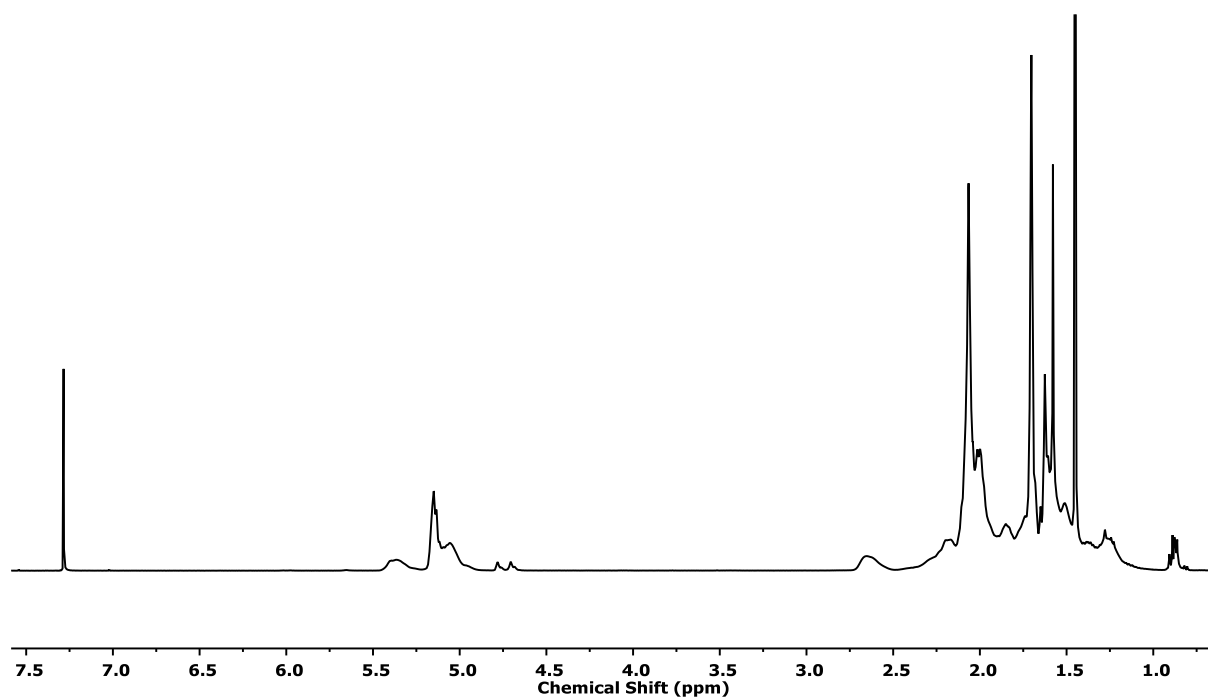


Figure S 21: ¹H NMR spectrum (400 MHz, CDCl₃, 25°C) of statistical copolymers P(VCH-co-I).

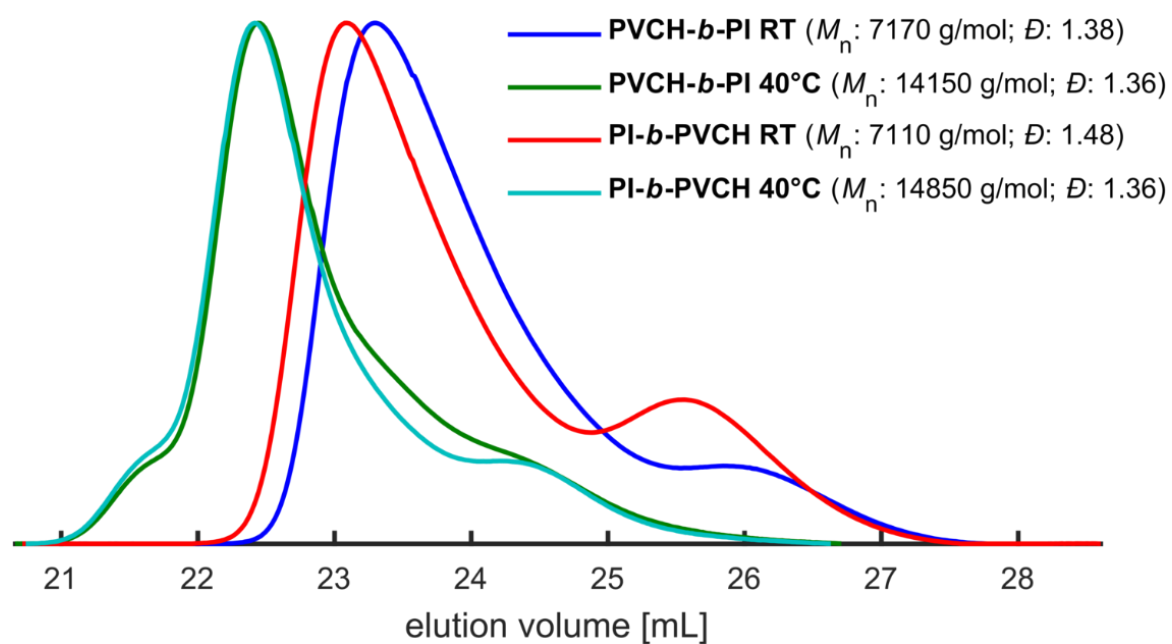


Figure S 22: SEC traces of the copolymers of VCH and isoprene.

4.1.6.2.4 Hydrogenation

The hydrogenation of P(VCH) was catalyzed with palladium on carbon (10w%) under 30 bar H₂ at 130 °C in a 300 mL Parr reactor. Typically, 100 mg polymer and 80 mg Pd/C were dissolved in 25 mL of *n*-decane and the hydrogenation reaction was conducted for 48h. The hydrogenation led to full saturation of the polymer, confirmed by ¹H NMR.

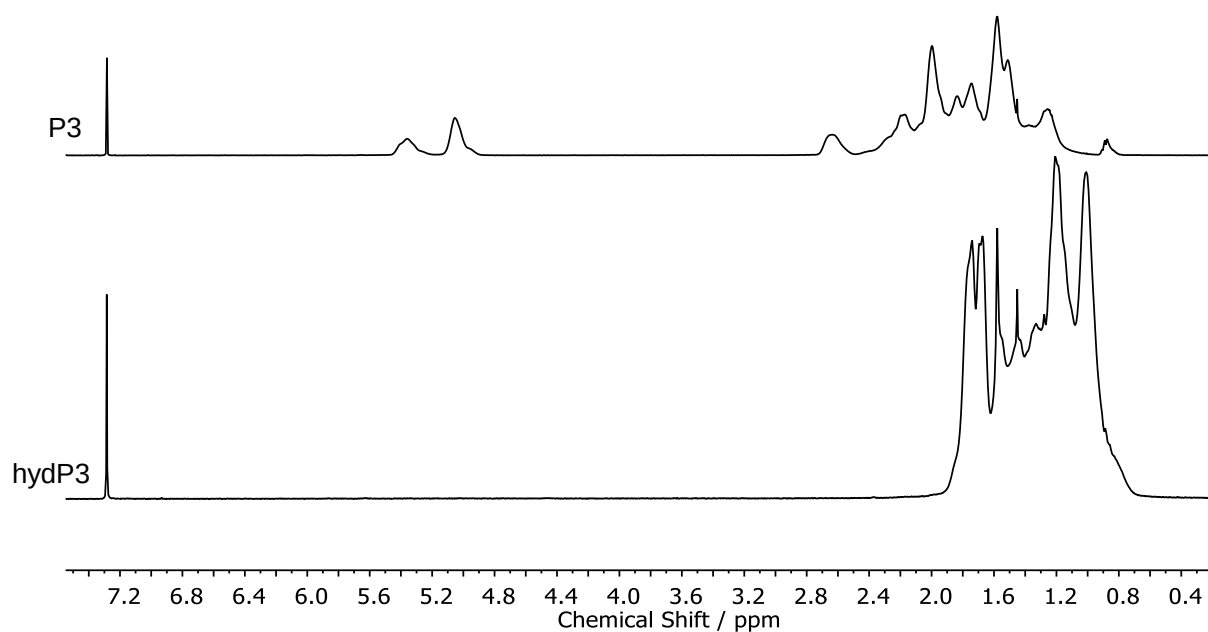


Figure S 23: Stacked ¹H NMR spectra (400 MHz, CDCl₃, 25°C) of PVCH (P3) before and after hydrogenation, sample hydP3.

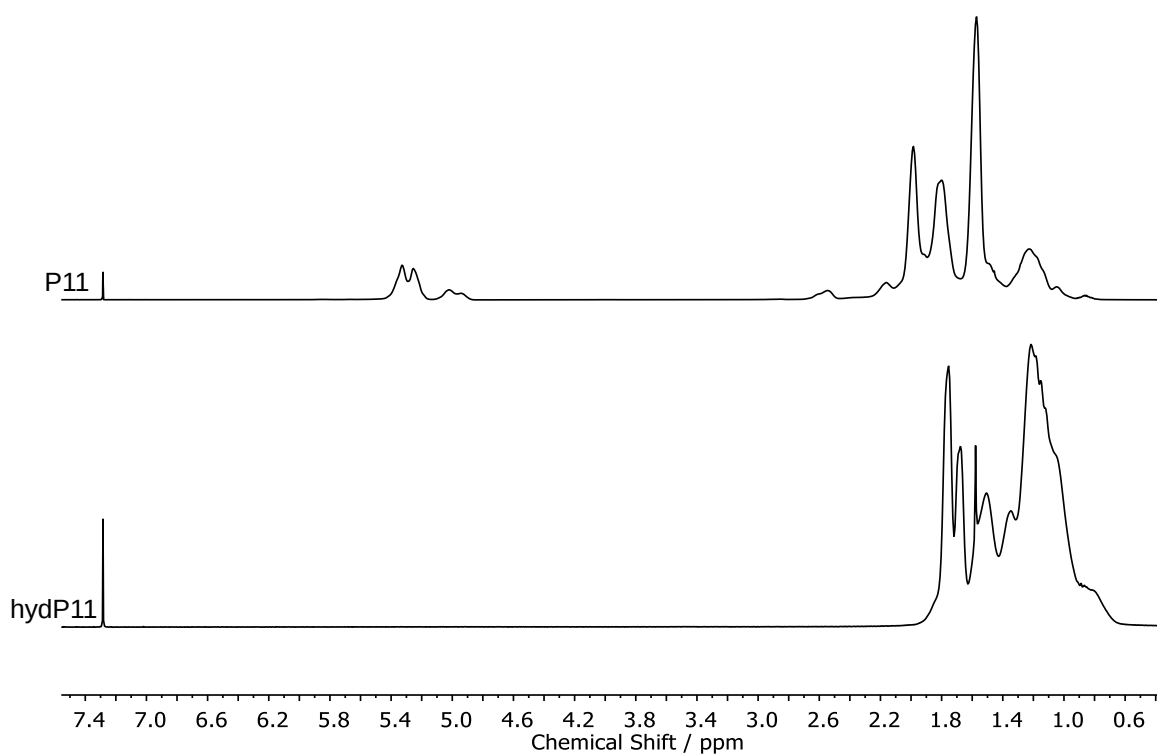


Figure S 24: Stacked ^1H NMR spectra (400 MHz, CDCl_3 , 25°C) of PVCH (P11) and its hydrogenated form hydP11.

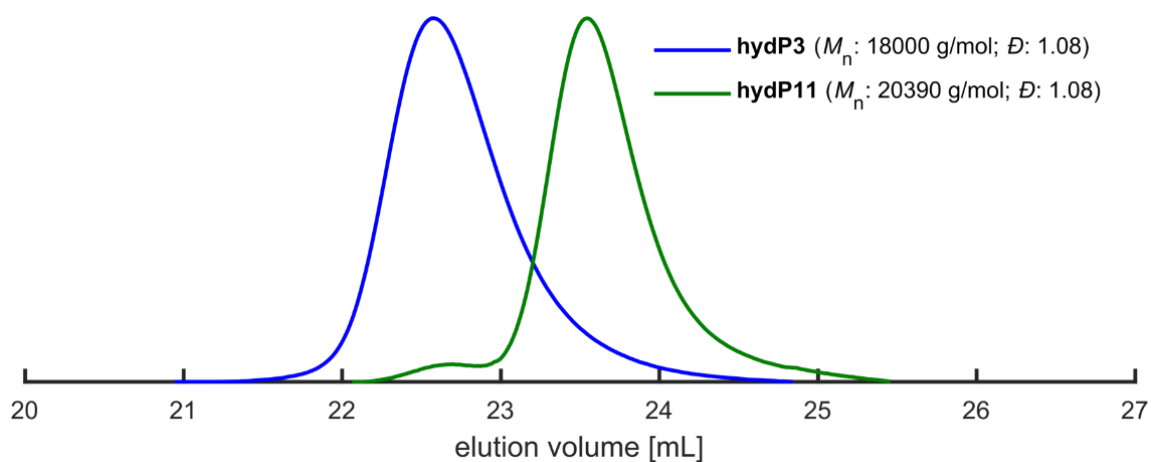


Figure S 25: SEC traces of the hydrogenated polymers hydP3 and hydP11 (Eluent: THF, PS calibration), showing that no chain degradation occurred.

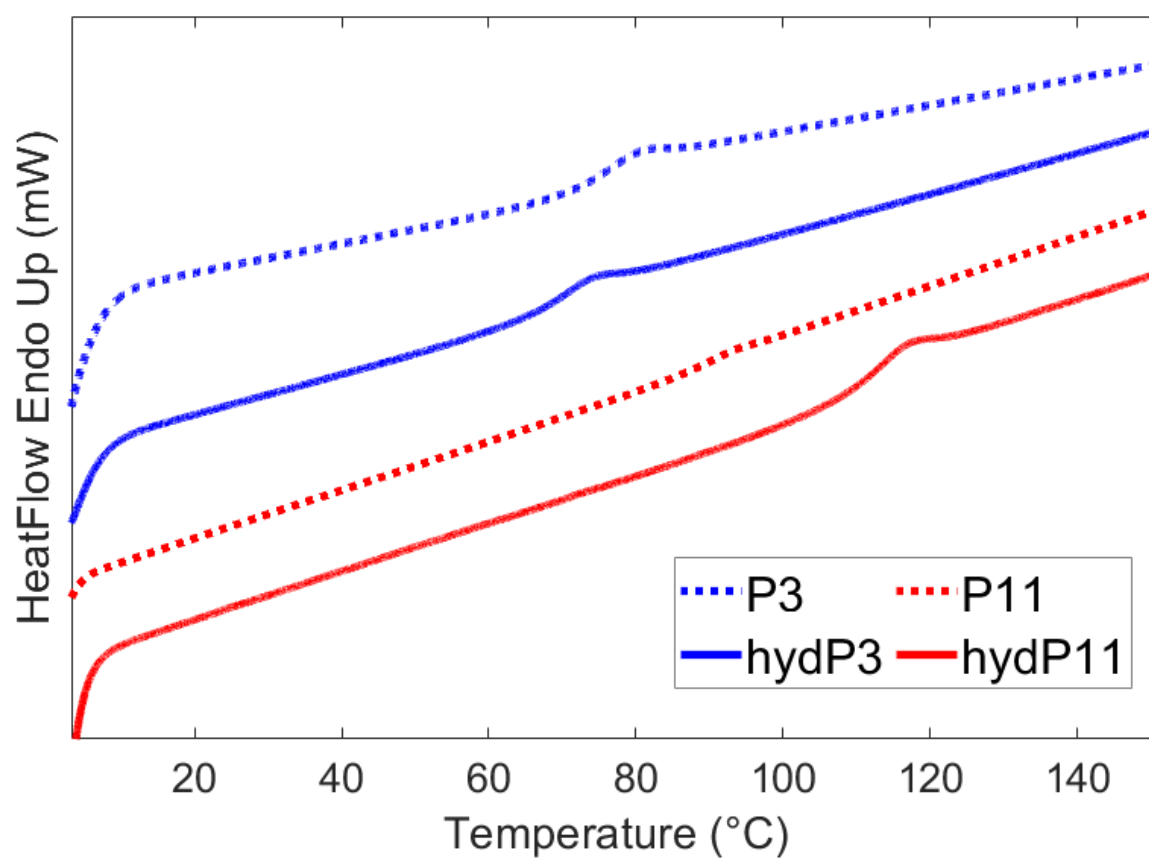


Figure S 26: DSC data of the hydrogenated polymers hydP3 and hydP11.

4.2 Nopadiene: A Pinene-Based Cyclic Diene for Fully Bio-Based Thermoplastic Elastomers

Christoph Hahn,^{a,b} Iniqui Göttker-Schnetmann,^c George Floudas,^d Stefan Mecking,^c
Holger Frey^a

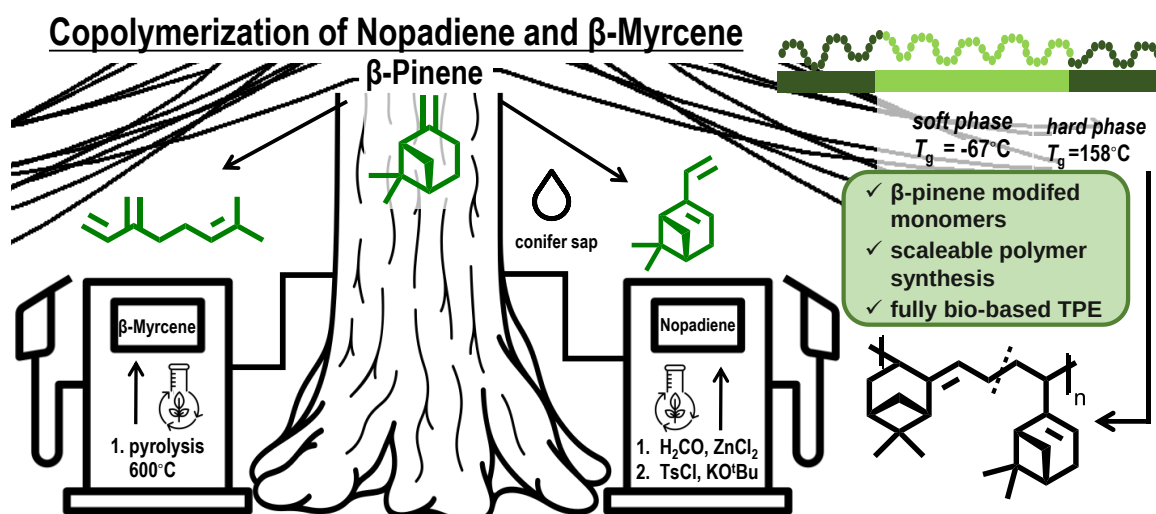
^a Department of Chemistry, Johannes Gutenberg University, 55128 Mainz (Germany)

^b Max-Planck Graduate Center, 55128, Mainz (Germany)

^c Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, 78457 Konstanz (Germany)

^d University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, 45110 Ioannina (Greece)

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4.2.1 Abstract

The bicyclic 1,2-substituted, 1,3-diene monomer nopadiene (1*R*,5*S*)-2-ethenyl-6,6-dimethylbicyclo[3.1.1]hept-2-ene) was successfully polymerized by anionic and catalytic polymerization. The monomer is produced either through a facile one-step synthesis from myrtenal *via* Wittig-olefination or *via* a scalable two-step reaction from nopol (10-hydroxymethylene-2-pinene). Both terpenoids originated from renewable β -pinene. The living anionic polymerization of nopadiene in apolar and polar solvents at 25 °C using organo-lithium initiators resulted in homopolymers with well-controlled molecular weights in the range 5.6–103 kg·mol⁻¹ (SEC, PS calibration) and low dispersities (*M_w*/*M_n*) between 1.06 and 1.18. By means of catalytic polymerization with Me₄CpSi(Me)₂N^tBuTiCl₂ and ((Flu)(Pyr)CH₂Lu(CH₂TMS)₂(THF), the 1,4 and 3,4-microstructure of nopadiene in excellent selectivity is accessible. ABA triblock polymers with a variety of nopadiene content (60-75 mol%) and molecular weights (100-200 kg/mol) were prepared by living anionic polymerization of the pinene-derivable monomers nopadiene and myrcene. The resulting thermoplastic elastomers displayed microphase separation at different molar ratios and an upper service temperature about 50 °C higher than traditional petroleum-derived styrenic thermoplastic elastomers due to the high glass transition temperature of nopadiene. In pronounced contrast to other 1,3-dienes, the sterically demanding and rigid polymers of nopadiene showed elevated glass transition temperatures of up to 158 °C. The polymers show advanced thermal stability up to 330°C, high tensile strength and ultimate elongations of up to 1610%.

4.2.2 Introduction

In consideration of increasing environmental concerns, climate change and the pursuit of sustainable materials, various bio-based polymers have been developed using renewable monomers. These building units can be obtained directly from natural feedstocks, by enzymatic conversion of biomass or indirectly by chemical transformation processes.¹⁻⁷ In recent years, the search for new options for bio-based polymers, motivated by governments and society, has increased greatly.⁸ Terpenes emerged as potential building blocks for a variety of applications ranging from flavors and fragrances to agricultural products such as pesticides and insect repellents to rubbers.⁹⁻¹¹ Cyclic monoterpenes such as α and β -pinene, consisting of two isoprene units ($C_{10}H_{16}$), are naturally abundant and found in many conifer species. The estimated production scale of turpentine is currently larger than 300,000 t per year.¹² The applications of turpentine oil range from solvents for binders, oils, coatings, resins, paints, floor and shoe polishes to starting material for pharmaceuticals, fragrances and food flavorings.¹³⁻¹⁶ Among other terpenes, turpentine oil contains α - and β -pinene as major ingredients.⁹ The composition and the percentual amount of the terpenes depend on the type of pine tree, climate, age, and the harvest season.¹³

Significant attempts have been made to replace butadiene-based rubbers by naturally occurring myrcene.¹⁷⁻¹⁹ Myrcene is obtained by pyrolysis of β -pinene. After polymerization the resulting polymyrcene is highly flexible with low glass transition temperature ($T_g = -60^\circ\text{C}$), depending on the microstructure.²⁰⁻²²

The nearly unlimited structural diversity of terpenes, ranging from linear to cyclic structures, bicyclic bridged and sterically hindered, as well as functional derivatives (terpenoids, mostly alcohols, aldehydes, ketones, ethers, or other oxidation products) gives access to tailor-made bio-based materials.¹³ Kamigaito *et al.* transformed carvone, a bio-based chiral cyclic α,β -unsaturated ketone-terpene, into cyclic *exo*-methylene conjugated diene (*trans*-diene). They investigated the respective *trans*-

dienes in the stereospecific living cationic polymerization and obtained cycloolefin polymers with enhanced thermal properties after hydrogenation.²³

Bio-based polymers with high T_g for the glassy domains in thermoplastic elastomers are rather rare, although biotechnological fermentation of glucose can produce styrene, albeit only on a small scale.^{24,25} Dehydrogenation of (+)-limonene at high temperature results in α -methyl-*p*-methylstyrene.²⁶ The first step towards the development of fully sustainable thermoplastic elastomers, meaning that both the rubbery and the “hard” phase polymer originate from natural resources, was reported by Bolton and Hillmyer. They synthesized ABA-type triblock copolymers of α -methyl-*p*-methylstyrene and myrcene by the sequential anionic polymerization in THF at low temperatures, followed by dichlorodimethylsilane coupling.²⁷ The triblock copolymers showed phase separation (hexagonally packed cylinders) with a rubbery low T_g of polymyrcene phase ($T_{g,PMYR} = -39\text{ }^{\circ}\text{C}$), and high T_g of poly(α -methyl-*p*-methylstyrene) cylinders ($T_{g,PAMMS} = 160 - 182\text{ }^{\circ}\text{C}$), that enables physical anchoring of the glassy domains. However, the re-initiation of α -methyl-*p*-methylstyrene by poly(myrcenyl)-lithium was not successful, requiring an additional coupling step with dichlorodimethylsilane. However, due to the polymerization in THF, an increased vinyl content (1,2- and 3,4-units) of the polymyrcene midblock cannot be avoided, resulting in an increased glass transition temperature of -39°C .

In general, conjugated 1,3 dienes are versatile monomers as they undergo polymerization using catalytic, radical, cationic, and anionic techniques.²⁸⁻³¹ The transition-metal catalyzed polymerization of conjugated dienes is an insertion polymerization, and its benefit is the control over regio- and stereoselectivity.³² On the other hand, the carbanionic polymerization offers the highest level of control of molecular weight, block sequence and polymer architecture, enabling the preparation of block copolymers with very narrow molecular weight distributions.

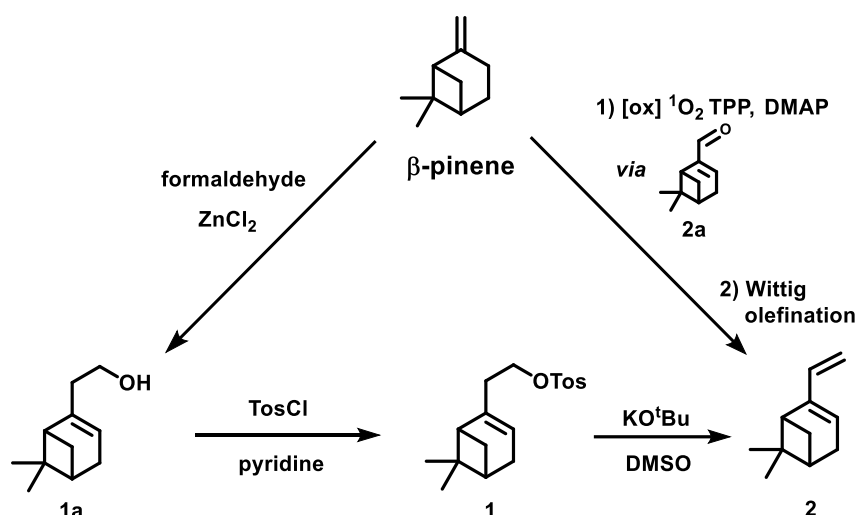
Thermoplastic elastomers (TPEs) include the benefits of a of rubbery material, while behaving as viscoelastic liquids (low T_g) and stiff thermoplastics (high T_g).³³ TPEs

consist of a rubbery phase that is covalently connected to a high T_g (“hard”), vitrified nanophase. The hard domains serve as reversible crosslinking sites of the flexible low T_g chains and provide a continuous three-dimensional network character. The physical crosslinks and the entanglements of the polymer chains result in a molecular composition that is very similar to a conventional rubber vulcanizate containing reinforcing filler. Prominent TPE examples are triblock copolymers based on poly(styrene-*b*-butadiene-*b*-styrene) (SBS) and poly(styrene-*b*-isoprene-*b*-styrene) (SIS).³⁴

Nopadiene (**2**, Scheme 1) is accessible *via* multiple routes starting from β -pinene. Among other terpenoids, myrtenal is a natural oxidation product of β -pinene, but it can also be obtained selectively by photocatalytic oxidation with tetraphenyl porphyrin and singlet oxygen.^{35,36} Myrtenal (**2a**) is converted to nopadiene by olefination according to the Wittig-reaction with methyltriphenylphosphonium bromide in THF.³⁷ For the preparation of nopadiene, nopol (**1a** Scheme 1, 10-hydroxymethylene-2-pinene) can be used as an intermediate product, that is converted to its respective tosylate and a subsequent base-catalyzed elimination yields nopadiene.³⁸ The Prins-condensation is an efficient method for preparation of nopol, consisting of the $ZnCl_2$ - catalyzed reaction of β -pinene and paraformaldehyde at high temperatures (150-230°C) and pressure.³⁹ Recently developed synthesis routes rely on double metal cyanide complexes (Fe-Zn) as solid acid catalysts for the synthesis of nopol from β -pinene.⁴⁰ Nopadiene is assumed to be fully bio-based under the assumption that formaldehyde is potentially renewable, obtained from methanol produced by biogas plants.

We hypothesized that an ABA triblock copolymer, having a high T_g from poly(nopadiene) end blocks flanking the low T_g polymyrcene central block, has value as a potentially sustainable TPE. For this purpose, we aimed at the development of a chemical equivalent to polystyrene with a high glass-transition temperature (>100°C), but with the benefits of a 1,3-diene with regard to its copolymerization behavior. The advantage of anionic copolymerization in non-polar media is the

control over the microstructure of the resulting polydiene with low vinyl content, for instance via the addition of small amounts of a so-called modifier.⁴¹ In addition, styrenic monomers generally require low temperatures in polar solvents (THF, -78°C) to stabilize the reactive living chain-end.⁴² The benefit of 1,3-dienes is that they readily undergo copolymerization with other 1,3-diene monomers in nonpolar media (cyclohexane) at ambient temperatures.



Scheme 1: Synthesis pathways of various terpenoids starting from β -pinene, 1a) nopol, 1) nopol tosylate, 2a) myrtenal, 2) nopadiene. TPP, meso-tetraphenylporphine; DMAP, 4-(dimethylamino) pyridine; TosCl, tosyl chloride, DMSO, dimethylsulfoxide.

4.2.3 Results and Discussion

4.2.3.1 Synthesis of nopadiene

Nopadiene is accessible by two different synthesis routes: i) *via* Wittig reaction of myrtenal and ii) *via* nopol dehydration. As is known to literature, full removal of the byproduct triphenylphosphine oxide (TPPO) in the Wittig reaction becomes a major challenge, when upscaling the monomer synthesis.⁴³ For this reason, alternatives to the Wittig reaction were investigated as well. An alternative route commences with the tosylation of the naturally occurring terpene nopol. The synthesis of nopadiene starting from nopol tosylate was conducted according to Salzer *et al.* on a 100g scale.⁴⁴ The tosylate is converted by a base-catalyzed elimination reaction to nopadiene (**Scheme 1**). The combined yield of the two-step synthesis of nopadiene based on nopol is up to 73 %. Despite the overall lower yield compared to the Wittig reaction of myrtenal (85%), this is a convenient alternative to circumvent the removal of TPPO and thus is the preferred synthetic route, because of the facility of monomer scale-up.

4.2.3.2 Polymerization of nopadiene in nonpolar media (cyclohexane)

In the first attempts to polymerize nopadiene in nonpolar solvents using organolithium initiators in the same manner as established for isoprene and myrcene, slow initiation with *sec*-BuLi was observed, leading to a high molecular weight distribution ($\bar{D} = 1.45$). The SEC traces of the slowly initiated polymers are shown in Figure S5.⁴⁵ The delayed initiation of nopadiene with *sec*-BuLi was observed via ¹H NMR kinetics studies, when the state of aggregation of the living chain ends was studied (see Supporting Information Figure S7). The data show that the rate constant of the initiation of the polymerization is lower than the rate constant of the propagation, the $M_w/M_n = 1.33$.⁴⁶ However, the more nucleophilic *tert*-BuLi, compared to *sec*-BuLi, showed a similar delayed initiation resulting in a dispersity of $\bar{D} = 1.29$, which is high for anionic polymerization. The aggregation of *sec*-BuLi, caused by its low solubility in apolar solvents like cyclohexane, together with the dissociation equilibrium of these aggregates to reactive unimers are important parameters of the initiation

kinetics.^{47,48} This result hints at a non-quantitative initiation step of nopadiene with *sec*-BuLi. In general, organo-lithium compounds form aggregates in apolar solution.⁴⁵ *Sec*-BuLi is known to aggregate in tetramers. On the contrary, poly(styryl)-lithium forms dimers that are sterically less crowded and thus appear to be more suitable for initiation of the bulky and sterically hindered nopadiene. It was found that oligo- or poly(styryl)-lithium served as a good macroinitiator for nopadiene, enabling the facile preparation of poly(*S-b*-nopa). Changing the organo-lithium initiator to living poly(styryl)-lithium, no induction period was observed. In the same manner living poly(α -methylstyryl)-lithium was used as an initiator and the results show a monomodal distribution with predictable molecular weights.

Using poly(α -methylstyryl)-lithium as initiator, the delayed initiation is suppressed (Figure S5). However, the low ceiling temperature of α -methylstyrene led always to residues of unreacted α -methylstyrene. In the following, oligo(styryl)-lithium (DP = 8) will be used as a most suitable initiator for nopadiene, permitting fast and complete initiation, as demonstrated below.

The initiation of nopadiene in polar solvents was also investigated to circumvent the aggregation of *sec*-BuLi. MTBE (methyl *tert*-butyl ether) and cyclohexane/THF were tested as solvents for the anionic polymerization of nopadiene. Remarkably, in pure MTBE immediate initiation of nopadiene occurred, resulting in monodisperse molecular weight distributions ($\mathcal{D}$ = 1.06). In addition, the polymerization of nopadiene in cyclohexane with only 8 eq. THF / Li also resulted in well-defined molecular weight distributions, concluding that even at low THF concentrations the aggregation of *sec*-BuLi was suppressed and the aggregates were dissipated. We hypothesize that the polar solvents break the aggregates into unimers. Typical SEC traces of the homopolymers of nopadiene with different initiators are depicted in Figure S10-12.

4.2.3.3 Homopolymerization of nopadiene in nonpolar solvents

A series of homopolymers of nopadiene with increasing molecular weights were synthesized in cyclohexane at room temperature (Figure1), using oligo(styryl)-lithium as an initiator. The polymerization of nopadiene in cyclohexane resulted in homopolymers with well-controlled and predictable molecular weights in the range of 5.6 to 103.4 kg·mol⁻¹ and dispersities between 1.06 and 1.18. Due to the living nature of the polymerization, predictable molecular weights are accessible, and measured molecular weights measured by GPC calibrated to PS standards were in good agreement with the targeted molecular weights. The high molecular weight shoulders in the SEC traces in PNopa_{40k} and PNopa_{103k} can be attributed to chain coupling by oxygen dimerization before the termination.

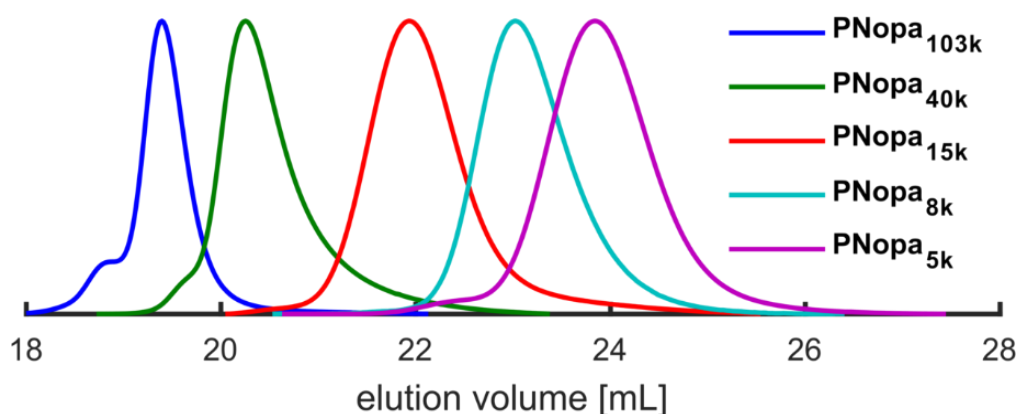
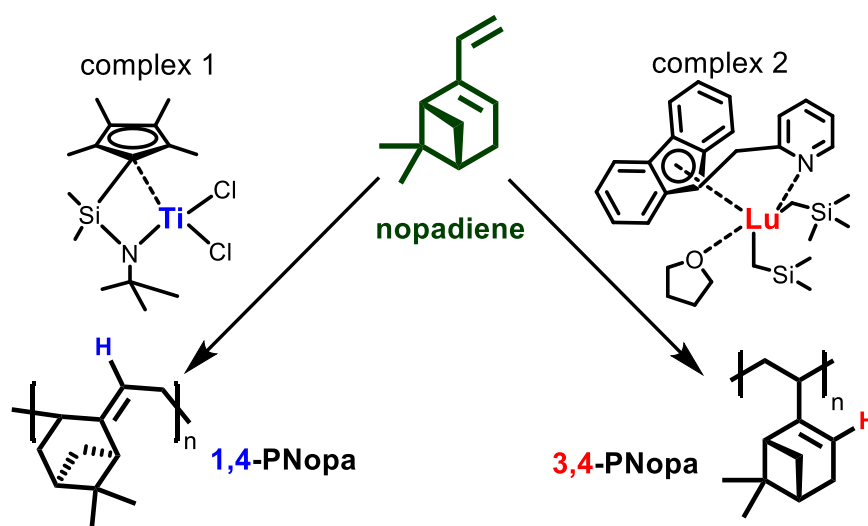


Figure 1: SEC traces (eluent THF, PS calibration) of the homopolymers of nopadiene PNopa_{5k-103k}. PNopa_{5k} M_n = 5.6 kg/mol, D = 1.07; PNopa_{8k} M_n = 7.8 kg/mol, D = 1.06; PNopa_{15k} M_n = 14.5 kg/mol, D = 1.12; PNopa_{40k} M_n = 39.6 kg/mol, D = 1.18; PNopa_{103k} M_n = 103.4 kg/mol, D = 1.15.

4.2.3.4 Microstructure investigation and catalytic polymerization of nopadiene

As it is obvious in the anionic polymerization of 1,3-dienes, the latter allows for the formation of different microstructures depending on solvent, temperature, addition of a modifier such as THF and polymerization method i.e. catalytic or anionic polymerization. The 1,3-diene system itself already determines the preferred mode of incorporation and the resulting microstructure in cyclohexane. However, due to the bicyclic and sterically hindered structure of nopadiene and the possibilities of head-to-head, head-to-tail and tail-to-tail incorporations modes, the signals in NMR spectroscopy are broad and do not allow direct determination of the microstructure in the anionic polymerization of nopadiene. Figure 2 shows the ^1H NMR spectrum of polynopadiene, prepared by anionic polymerization with *sec*-BuLi as an initiator. Because of signal broadening in the ^1H NMR spectra, no direct microstructure determination was possible. To fully understand and analyze the microstructure of nopadiene, catalytic polymerization of nopadiene was performed with transition-metal catalysts, that yield exclusively 1,4 and 3,4-microstructures.



Scheme 2: Catalytic polymerization of nopadiene with complex 1: MAO; and complex 2: TIBA:TritylBCF.

A series of transition-metal catalysts was tested for the polymerization of nopadiene. The respective NMR data of the polymers in Table 1 are shown in the Supporting Information in Figure S15-45. Herein, it is demonstrated that using complex 1 as

catalyst, $\text{Me}_4\text{CpSi}(\text{Me})_2\text{N}^t\text{BuTiCl}_2\text{:MMAO}$, the polymerization of nopadiene with perfect 1,4-*cis* regioselectivity (>99%) and high molecular weights ($M_n = 1.011 \times 10^6$ g/mol, $\bar{D} = 1.25$) can be achieved. These results were surprising because $\text{Me}_4\text{CpSi}(\text{Me})_2\text{N}^t\text{BuTiCl}_2\text{:MAO}$ is commonly used for vinyl monomer polymerization, i.e. to obtain atactic polypropylene, but it is not known to polymerize 1,3-dienes.⁴⁹ However, detailed NMR characterization revealed the formation of well-defined nopadiene in exclusive 1,4-*cis* addition.

The asymmetric fluorenyl-pyridyl lutetium complex 2, $((\text{Flu})(\text{Pyr})\text{CH}_2\text{Lu}(\text{CH}_2\text{TMS})_2(\text{THF})\text{:TIBA:TritylBCF})$, has been reported to show excellent 3,4-regio and syndio-selectivity for polymerization of isoprene and styrene in high activities.⁵⁰ In polymerization experiments with nopadiene, the latter produced low molecular weight 3,4-polynopadiene with a selectivity of 95% (2.400 g/mol, $\bar{D} = 1.87$) with a conversion exceeding 99%. The catalytic polymerization of nopadiene supports the rational understanding of the microstructure of polynopadiene, obtained by anionic polymerizations. The valuable insights obtained from the catalytic polymerization of nopadiene made it possible to assign all signal of the 1,4 and 3,4-units in polynopadiene obtained by anionic polymerization. The ratio of 1,4 to 3,4 - units of polynopadiene, synthesized in cyclohexane at room temperature, was determined as 51% 1,4 and 49 % 3,4 units by integrating ^{13}C signals of the allylic carbons at 121.5 ppm (Figure 2e, red) and 116.6 ppm (Figure 2c, blue). It is interesting to note that 1,2-addition of nopadiene was neither observed in anionic nor in the catalytic polymerization (more detailed analysis in Supporting Information Figures S15+16).

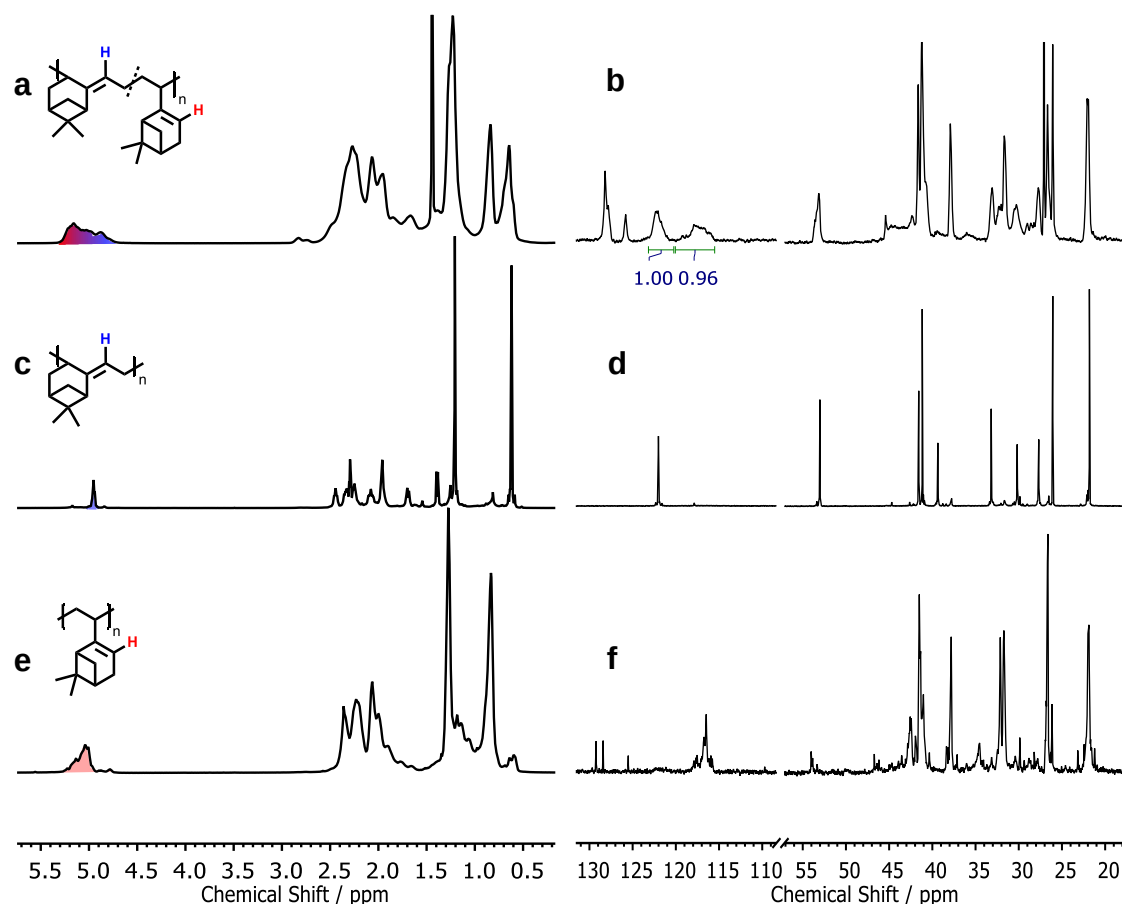


Figure 2: Stacked ^1H NMR and ^{13}C NMR spectra (CDCl_3) of: a and b) PNopa obtained by anionic polymerization in CyH; c and d) 1,4 -PNopa11; d+f) 3,4-PNopa13. Note that spectra a +e measured at 500 MHz, c at 600 MHz, b+d at 125 MHz, d at 150 MHz.

4.2.3.5 Addition of modifiers to the anionic polymerization of nopadiene

The addition of modifiers to a nonpolar polymerization medium significantly alters the ratio of microstructures of polydienes, as it has been investigated for several other 1,3 dienes.^{51,52} The change in polymer microstructure is correlated to the T_g . A series of modifiers like THF, MTBE, 2,2-di(2-tetrahydrofuryl)propane (DTHFP) and 1,2-dipiperidinoethane (DIPIPE) were employed to understand their influence on the microstructure of polynopadiene. MTBE as a modifier exhibited no significant influence on the microstructure on nopadiene. Even in pure MTBE as a solvent, the microstructure was similar as in cyclohexane (1,4-units 51%, 3,4-units 49%). The integrals of the two ^{13}C atoms at 121.5 ppm and 113.6 ppm are demonstrated in Figure 2b. This can be explained by the relatively low dipole character of MTBE,

resulting in only weak complexation of lithium. It is noteworthy that also small quantities of THF showed no influence on the microstructure compared to the polymerization in cyclohexane. However, the polymerization in pure THF resulted in mostly 1,4-polynopadiene (87% 1,4, 13% 3,4). The shift towards higher content of 1,4-units starts at a threshold of 20 eq. THF/Li. When adding 10 eq. of DTHFP/Li⁺, the microstructure of polynopadiene dramatically changed to 78% 3,4-units, and 22% 1,4-units, respectively. This change in microstructure resulted in an increase of the glass transition temperature from 125 °C to 143 °C (at approximately the same molecular weight of 10 kg/mol, Table 1). Regardless of the incorporation mode, 1,4 and 3,4-polynopadiene were found to show very similar thermal properties. The T_g of 3,4-polynopadiene was determined to be 158°C, whereas 1,4-polynopadiene exhibited a T_g of 161°C. The T_g of polynopadiene is in line with its structural polymer isomer of β -pinadiene (T_g =160°C).⁵³ The results of the microstructure analysis and the DSC measurements are summarized in Table 1.

Table 1: Polymerization of nopadiene via anionic and catalytic methods, solvent, modifier equivalents, molecular weight M_n , and dispersity $\bar{D}$, 1,4- and 3,4-microstructure and glass-transition temperature of polynopadiene.

No.	Initiator / catalyst	Solvent	Modifier	eq. Modifier /Li ⁺	M_n kg/mol SEC*	$\bar{D}$	1,4/3,4 micro-structure %	T_g °C
PNopa1	PS-Li	C ₆ H ₁₂	-	-	7.8	1.06	51/49	125
PNopa2	<i>sec</i> -BuLi	C ₆ H ₁₂	MTBE	5	18.0	1.05	51/49	158
PNopa3	<i>sec</i> -BuLi	C ₆ H ₁₂	THF	2	7.5	1.05	50/50	128
PNopa4	<i>sec</i> -BuLi	C ₆ H ₁₂	THF	8	21.6	1.05	49/51	156
PNopa5	<i>sec</i> -BuLi	C ₆ H ₁₂	THF	20	8.0	1.05	55/45	135
PNopa6	PS-Li	THF	-	1200	6.3	1.77	87/13	145
PNopa7	PS-Li	C ₆ H ₁₂	DTHFP	1	6.0	1.06	45/55	136
PNopa8	PS-Li	C ₆ H ₁₂	DTHFP	10	9.8	1.10	22/78	143
PNopa9	PS-Li	C ₆ H ₁₂	DIPIPE	1	11.2	1.09	49/51	138
PNopa10	PS-Li	C ₆ H ₁₂	DIPIPE	10	9.7	1.08	47/53	138
PNopa11*	complex 1	toluene	-	-	799.1	1.28	99/1	n.d.
PNopa12*	complex 1	toluene	-	-	1011.0	1.25	99/1	161
PNopa13*	complex 2	toluene	-	-	2.4	1.87	5/95	n.d.
PNopa14*	complex 2	toluene	-	-	4.0	4.06	5/95	158

Polymerization conditions for anionic polymerization 25°C, C₆H₁₂ cyclohexane, polymerization conditions for catalytic polymerization: 60°C, complex 1 co-catalyst MAO, complex 2 co-catalyst TIBA:TritylBCF, SEC eluent: THF, calibration PS, * SEC eluent CHCl₃, calibration PS.

4.2.3.6 Copolymerization kinetics

For the study of the monomer sequence of the copolymers resulting from the statistical copolymerization of nopadiene with myrcene and styrene in apolar media, *in situ* ¹H NMR kinetic investigations were performed. A detailed description of the copolymerization kinetic measurements is given in the Supporting Information. Figure 3 shows that myrcene is consumed faster in the early stage of the copolymerization with nopadiene. The living copolymerization of myrcene and nopadiene with reactivity ratios of $r_{\text{myr}} = 7.49$ and $r_{\text{nopa}} = 0.13$ translates to a pronounced gradient structure. Nopadiene is sterically hindered due to the bridged and bicyclic structure, and consequently it is assumed that the lower reactivity is mainly caused by the bulkiness of the monomer.

This interpretation is supported by the result that the copolymerization of styrene and nopadiene resulted in a rather weak gradient with reactivity ratios of $r_{\text{nopa}} = 3.26$ and $r_{\text{s}} = 0.31$. As is typical for 1,3-dienes, they form a gradient structure in the copolymerization with styrenic monomers. The shape of the gradient is determined by the combination of two effects: i) the relative reactivity of the monomers and ii) the cross-over reaction from a poly(styryl)-lithium to poly(nopadienyl)-lithium and vice versa. In general, this cross-over reaction from poly(styryl)-lithium to a poly(dienyl)-lithium is faster than the respective cross-over reaction. This phenomenon is known from several other diene/styrene combinations.^{10,54}

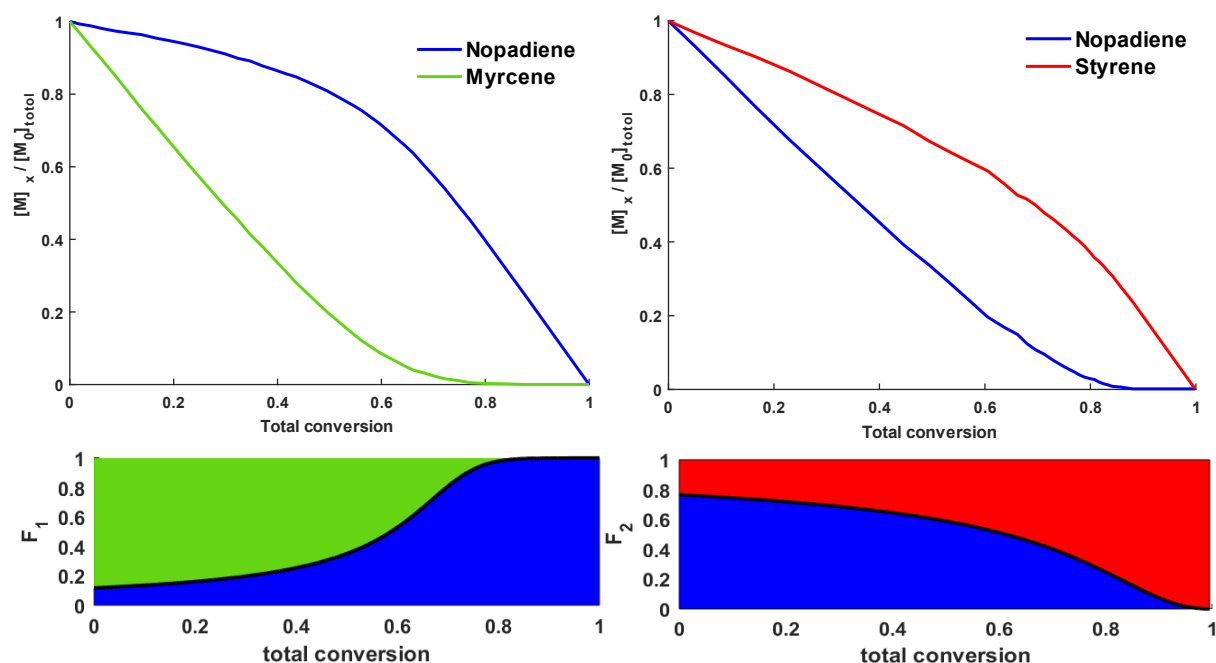


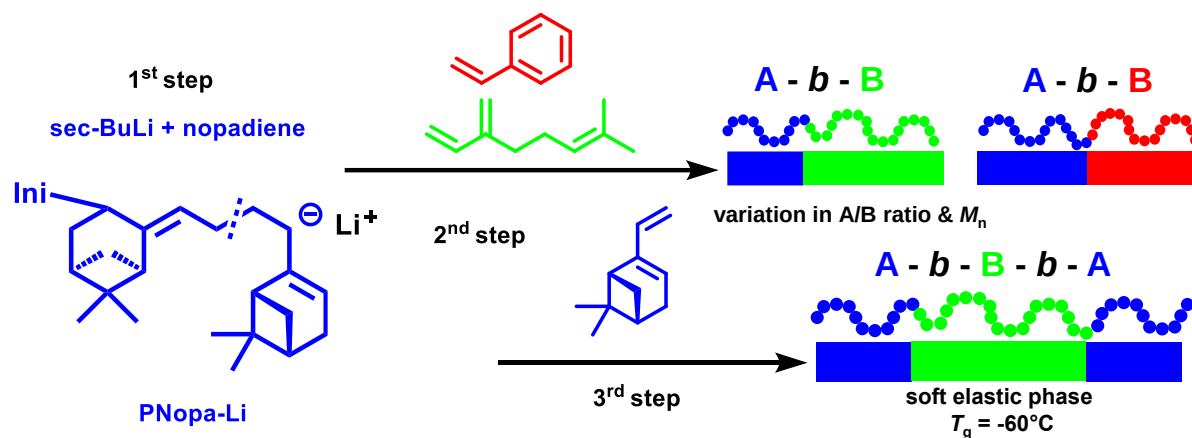
Figure 3: Copolymerization kinetics of nopadiene with myrcene (left) and styrene (right), above, individual monomer consumption as a function of total conversion, below, compositional illustration of the gradient structure.

The lower reactivity of nopadiene is tentatively attributed to the electron-donating alkyl groups in the 1,2-position of the diene system, which lower the reactivity with respect to the nucleophilic attack of carbanions. Whereas the electron donating alkyl substituent in 2-position in myrcene increases the nucleophilicity, the adjacent second alkyl substituent in 1-position in nopadiene compensates this effect. The cyclic ring structure of nopadiene counteracts this donating effect on the 1,3-diene system. In addition to the copolymerization kinetics, nopadiene homopolymerization was

performed at different concentrations to determine the state of aggregation of living poly(nopadienyl)-lithium chain ends. The results shown in Figure S 9 demonstrate that poly(nopadienyl)-lithium chains aggregate in dimers.

4.2.3.7 Block-Copolymers of nopadiene with myrcene and styrene

Both block and statistical copolymers of nopadiene with myrcene and styrene were synthesized in apolar media at room temperature on a 50g batch scale (Scheme 3). Statistical copolymers of nopadiene with myrcene and styrene were obtained by the initiation of the mixture of both monomers by *sec*-BuLi. In contrast to the homopolymerization of nopadiene described above, in the case of statistical copolymerization *sec*-BuLi was employed, since the copolymerization of nopadiene with other monomers (styrene and β -myrcene) lead to narrow molecular weight distributions. The aim of the block and statistical copolymers was the investigation of the phase separation of nopadiene with other comonomers.



Scheme 3: Synthetic strategy for block and tapered copolymers of nopadiene with myrcene and styrene.

Aiming at sustainable thermoplastic elastomers, we explored the combination of polynopadiene as the hard phase and polymyrcene as the soft phase to provide tough thermoplastic elastomers from fully renewable feedstocks. Together with the good scalability of the nopadiene monomer (100g scale), the benefit of full monomer conversion and the large-scale synthesis (50g scale) of the triblock copolymers of

nopadiene and myrcene, this approach *via* anionic polymerization represents a promising route for actual applications. With respect to processing the ABA triblock copolymers at elevated temperature, their stability at elevated temperatures was investigated by thermogravimetric analysis (TGA) under nitrogen. The results demonstrated that T2 is stable under N₂ up to 330°C (onset temperature T_{5%}, Figure S74). In Table 2, the diblock-copolymers will be denoted as D1-5, whereas the triblock-copolymer will be denoted as T1-4. Tapered copolymer obtained from statistical copolymerization are additionally labeled with *t*.

Table 2: Copolymers of nopadiene with myrcene and styrene with different comonomer content, molecular weight M_n (SEC) and dispersity $\mathcal{D}$, glass transition temperatures (DSC).

entry	Copolymer	monomer	monomer mol%	M_n kg/mol	$\mathcal{D}$	T_{g1} /°C	T_{g2} /°C
D1	P(Myrc- <i>b</i> -Nopa) _{50k}	myrcene	50	55.2	1.08	-	-
D2	P(Myrc- <i>b</i> -Nopa) _{100k}	myrcene	50	117.0	1.04	-59	-
D3- <i>t</i>	P(Myrc- <i>co</i> -Nopa) _{200k}	myrcene	50	199.9	1.18	-39	-
D4	P(S- <i>b</i> -Nopa) _{50k}	styrene	50	52.9	1.15	-	106
D5- <i>t</i>	P(Nopa- <i>co</i> -S) _{150k}	styrene	50	154.8	1.13	-	99
T1	P(Nopa- <i>b</i> -Myrc- <i>b</i> -Nopa) _{100k}	myrcene	60	80.5	1.08	-55	-
T2	P(Nopa- <i>b</i> -Myrc- <i>b</i> -Nopa) _{200k}	myrcene	60	198.1	1.12	-59	-
T3	P(Nopa- <i>b</i> -Myrc- <i>b</i> -Nopa) _{100k}	myrcene	75	89.1	1.10	-56	-
T4	P(Nopa- <i>b</i> -Myrc- <i>b</i> -Nopa) _{200k}	myrcene	75	196.1	1.11	-58	-

Molecular weight M_n determined by, SEC eluent: THF, PS calibration; the targeted molecular weight based on $[M]/[I]$ is indicated in the copolymer description.

The resulting bulk morphologies of (block) copolymers depend on the molar and volume ratio of the polymer blocks and their thermodynamic incompatibility.⁵⁵ Because the degree of phase separation has a significant impact on the related mechanical properties of block copolymers, understanding of the monomer gradient profile is essential. The product of the incompatibility parameter χ and the degree of polymerization N determine phase separation. Thus, copolymers of nopadiene/myrcene in a 50/50 molar ratio with molecular weights of 50-200 kg/mol were synthesized. A key requirement for thermoplastic elastomers is the phase

separation of the block copolymer domains. Since high molecular weights are required for phase separation in copolymers of nopadiene and myrcene, high molecular weights of 100 kg/mol and 200 kg/mol for the ABA triblock copolymers were targeted. Important features of the supramolecular network of a thermoplastic elastomer are high molecular weights, exceeding the entanglement molecular weight of polymyrcene ($M_e = 22$ kg/mol) as well as interdomain bridges.⁵⁶ The synthesis of ABA triblock copolymers of nopadiene and myrcene with varying composition (60-75mol% myrcene) and overall molecular weight of 100-200 kg/mol (SEC, $M_n = 80$ -198.1 kg/mol) was carried out by sequential monomer addition. The deviation of the SEC data in Table 2 from the theoretical molecular weight can be explained by the overestimated molecular weight of polymyrcene, when using a PS calibration.⁵⁷

Diblock-copolymer D2 shows one T_g close to polymyrcene ($T_g = -59^\circ\text{C}$), whereas the tapered copolymer of nopadiene and myrcene, D3-*t*, has a slightly higher T_g of -39°C , indicating miscibility of polynopadiene and polymyrcene microphases. The gradient structure of nopadiene and myrcene, represented by the disparate *r*-parameters, may cause a mixing of the polynopadiene and polymyrcene segments. No change in heat capacity corresponding to the T_g of the polynopadiene block were observed. The lack of a detectable T_g of the polynopadiene domains is caused by the sensitivity limitation of the DSC measurement (the heat capacity step ΔC_p at T_g , is inversely proportional to temperature).

The SAXS results of the symmetric copolymer with the lowest molar mass D1 show some featureless structures (Fig. S78, Supporting Information). The single broad peak indicates correlation hole scattering (with a period of ~ 25 nm) typical of copolymers in their disordered (DIS) state.^{55,58} Increasing the molar mass in D2 brings more features in the SAXS curves (Figure 4b). When heating to higher temperatures, the curves exhibit Bragg reflections with relative q values of 1:2:3, corresponding to a lamellar (LAM) structure. The periodicity is obtained as $d_0 = 2\pi/q^*$, where q^* is the modulus of the scattering vector corresponding to the first diffraction maximum (39.3

nm at 453 K). The suppressed intensity of the second Bragg peak indicates that the polymyrcene and polynopadiene domains of the lamellae have equal thickness.

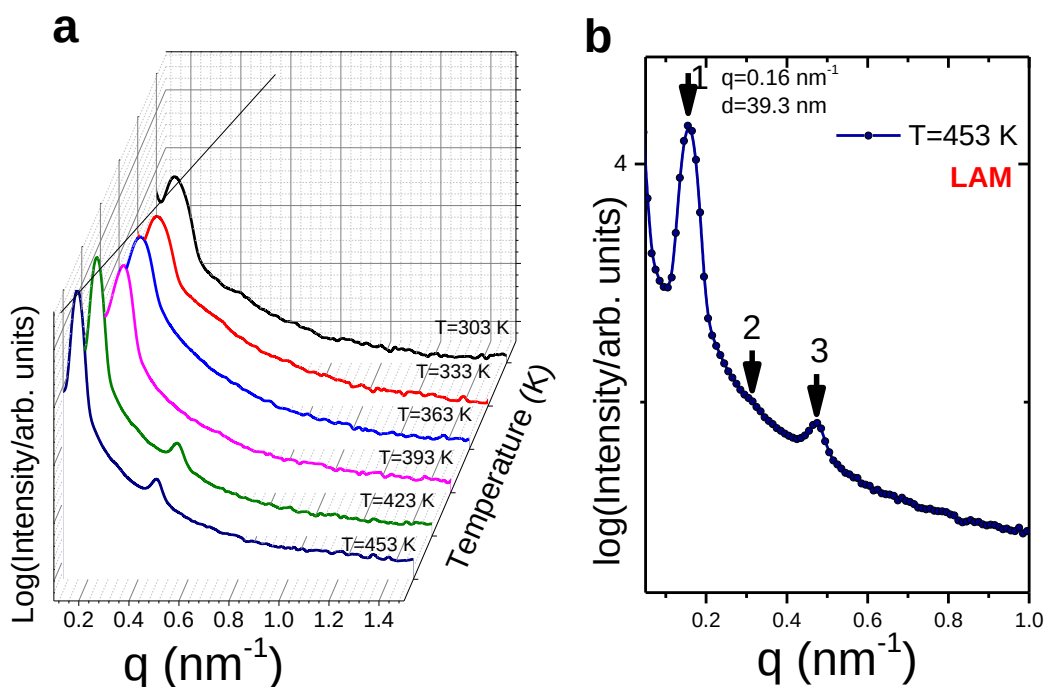


Figure 4: (a) Temperature-dependent SAXS patterns of D2 (P(Myrcene-*b*-Nopadiene)_{100k}, myrcene w%=50) obtained on heating from 303 K to 453 K. (b) The pattern obtained at 453 K shows Bragg reflections corresponding to a lamellar (LAM) morphology.

In going to the more asymmetric copolymers, T4 (P(Nopadiene-*b*-Myrcene-*b*-Nopadiene)_{200k}, myrcene w%=75), the SAXS pattern (Figure 5) exhibits weak Bragg reflections with relative q values of $1:3^{1/2}:2:7^{1/2}:3$ suggestive of a cylindrical (CYL) morphology without long-range order. At 453 K the periodicity is $d_0=41.3$ nm and the inter-cylinder distance, d , is $d=d_0(4/3)^{1/2}=47.7$ nm.

Keeping the same molar mass and going towards less asymmetric compositions in T2 (P(Nopadiene-*b*-Myrcene-*b*-Nopadiene)_{200k}, myrcene w%=60) drives the copolymer deeper into the ordered state (Figure 5). Now the SAXS patterns of T2 exhibit stronger Bragg reflections with relative q values of $1:3^{1/2}:2:7^{1/2}:3:12^{1/2}:4$ suggestive of a hexagonally packed cylindrical (HPC) structure. At 453 K the periodicity is $d_0=41.9$ nm and the inter-cylinder distance, d , is $d=d_0(4/3)^{1/2}=48.4$ nm. All SAXS patterns exhibit annealing effects, revealing better nanophase separation at higher

temperatures. This again exemplifies the non-equilibrium nature of the initial solvent-cast films showing incomplete phase separation.

4.2.3.8 Mechanical properties

The mechanical properties of the ABA triblock copolymers were investigated by uniaxial tensile and recovery measurements. The representative stress–strain plots for the samples T1-4 are shown in Figure 6. The mechanical properties of T1 with 60 mol% myrcene show typical characteristics of a thermoplastic elastomer. Significantly, it was found that T1 exhibited a definitive yield event, followed by a cold-drawing phase. This cold-drawing behavior dramatically increased strain-at-break up to 1230%. As demonstrated in Figure 5, T2 shows the better phase separation and thus, exhibits the highest Young's modulus of all samples. Samples T1 and T2 demonstrated strain at break values ranging from 6.6 to 10.3 MPa, respectively. T3 exhibits the typical mechanical properties of a soft elastomer. The extremely flexible sample T4 displays a remarkable strain-at-break of up to 1610%. Comparing the polymers with 60 and 75 mol% myrcene as a middle block, it is noticeable that with a higher nopadiene content both *E*-modulus (*E*) and stiffness increase, as expected. These results demonstrate that the mechanical properties of TPEs based on nopadiene and myrcene can be tuned, based on molar composition, molecular weight, morphology and architecture. Consequently, different types of elastomeric and tough thermoplastic materials are accessible with this bio-based monomer combination (myrcene/nopadiene).

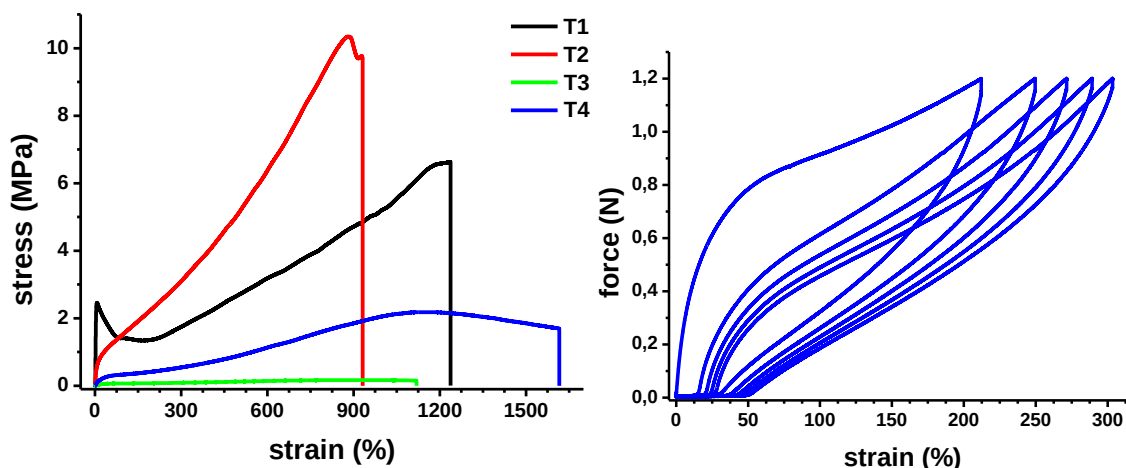


Figure 5: left - Stress-Strain curves of ABA triblock copolymer T1-4 at $50 \text{ mm}\cdot\text{min}^{-1}$; right - exemplary hysteresis curves of T4, $50 \text{ mm}\cdot\text{min}^{-1}$ to constant force of 1.2 N, average recovery 92,5 %.

The elastic properties were studied exemplarily for T4. Adapted hysteresis experiments have been performed in order to determine the recovery rate of thin film materials (Figure 6, down). Sample T4 was elongated to 1.2N and released to zero stress at a constant rate of $50 \text{ mm}\cdot\text{min}^{-1}$. T4 demonstrates a continuous decrease in *E*-modulus (flattening of slope) per cycle, a phenomenon that is referred to stress-softening. Consequently, hysteresis loops become narrower with increasing cycles. The average elastic recovery of T4 was 92,5%, using equation 3. The measurements prove that the recovery of T43 is in the range typical of SBS-TPEs.³⁴

4.2.4 Conclusion

Here we report the suitability of nopadiene as a novel monomer for living anionic polymerization. The unusual 1,3-diene system of nopadiene was investigated regarding the initiation reaction, microstructure formation, and its copolymerization behavior with styrene and myrcene. In addition to anionic polymerization, it was demonstrated that with the rational choice of catalytic polymerization techniques, both 1,4 and 3,4-polynopadiene are accessible in remarkable selectivity. The microstructures of the terpene-derived polymers were investigated in a detailed manner by a variety of NMR techniques. Thermal analysis revealed an exceptionally high T_g (158°C) of polynopadiene.

The statistical copolymerization of myrcene and nopadiene resulted in a gradient monomer profile with reactivity ratios of $r_{\text{myr}} = 7.49$ and $r_{\text{nopa}} = 0.13$, whereas the copolymerization of styrene and nopadiene showed reaction parameters of $r_{\text{nopa}} = 3.26$ and $r_{\text{s}} = 0.31$.

Aiming at novel high-performing, and sustainable TPEs, copolymers consisting of nopadiene, myrcene and styrene with predefined molecular weights (up to 200 kg/mol), narrow dispersity ($\mathcal{D} = 1.06\text{--}1.18$) and control over microstructures were synthesized. Microphase separation in these ABA triblock copolymers is supported by SAXS measurements. Lamellar/hexagonal packed morphologies with long range order were observed for these bio-based materials.

It is important to note that the natural source for these ABA triblock copolymers is the bio-based β -pinene, which represents a valuable and versatile natural compound, giving access to both flexible low T_{g} and rigid high T_{g} polymers.

Renewable β -pinene shows great potential to replace fossil feedstock-based monomers and shows once more the competitiveness of this natural resource. In summary, these results clearly demonstrate that bio-based monomers are useful for the carbanionic synthesis of thermoplastic elastomers.

4.2.5 References

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4.2.6 Supporting Information

Reagents. Chemicals and solvents were purchased from commercial suppliers (Acros, Sigma-Aldrich, Fisher Scientific, Alfa Aesar, TCI). Deuterated solvents were obtained from Deutero GmbH. (1R)-(-)- Myrtenal (97%) was purchased from Sigma-Aldrich.

(1R)-(-)-Nopol was purchased from BLD Pharmatech. Myrcene (95%) and styrene were purchased from Sigma-Aldrich. Cyclohexane was purified by stirring over diphenylhexyllithium (adduct of *sec*-BuLi and 1,1-diphenylethylene), vacuum-transferred and degassed by four freeze-pump-thaw cycles prior to use. The monomers nopadiene, styrene and myrcene were purified by stirring over CaH₂ and trioctylaluminum overnight, followed by distillation. All monomers for the anionic polymerization were degassed by four freeze-pump-thaw cycles prior to use.

Instrumentation. NMR spectra (¹H, ¹³C, ed. HSQC, ¹H, ¹H-COSY) were recorded on a Bruker Avance II 400 spectrometer equipped with a 5 mm BBFO-SmartProbe with z gradient and ATM, as well as a SampleXPress 60 sample changer. All ¹H NMR kinetic data were performed at 25 °C with a Bruker Avance III BR 500/51(500 MHz) spectrometer, which was also used to obtain the ¹³C NMR spectra. Detailed NMR analysis for the microstructure investigations of polynopadiene were recorded on a Bruker Avance III 600 MHz. All spectra are referenced internally to residual proton signals of the deuterated solvent.

Size exclusion chromatography (SEC) measurements were performed using an Agilent 1100 Series, equipped with a SDV column set from PSS (SDV 103, SDV 105, SDV 106). Tetrahydrofuran (THF) and chloroform were used as the mobile phase (flow rate 1 mL min⁻¹) and as the solvent. Poly(styrene) standards were provided by PSS for calibration. The measurements were carried out at 30 °C with an RI and UV (275 nm) detector. For analysis the PSS WinGPC® UniChrom (V 8.31, Build 8417) software provided by PSS Polymer Standards Service GmbH was used.

Glass transitions temperatures (T_g) were determined by evaluating differential scanning calorimetry (DSC) curves recorded on a Perkin Elmer 8500 differential scanning calorimeter. For the first cycle a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ and a cooling rate of $20\text{ }^{\circ}\text{C min}^{-1}$ was employed. A second heating cycle ($20\text{ }^{\circ}\text{C min}^{-1}$) was used to evaluate the thermal properties of the (co)polymers.

MALDI-ToF MS measurements were performed on a Bruker Rapiflex. trans-2-(3-(4-tert-butylphenyl)-2-methyl-2-propenylidene) malononitrile was used as a matrix and silver-trifluoroacetate as cationizing salt. The spectrum was measured in a linear positive mode with a laser wavelength of 337 nm. The mass spectrum was recorded in a reflector positive mode with a 337 nm laser. For all polymers 1 mg analyte was dissolved in 1 mL solvent.

Tensile tests were performed on a Shimadzu Universal Tester model EZ-LX. Thin films of 0.5 ± 0.05 thickness were prepared by solvent casting (CHCl_3) in Teflon templates. Dog-bone specimens were stamped with dimensions of 4.4 mm width and 60 mm length. The recovery rate of the hysteresis curves was determined by using equation 1, where R_n is the recovery rate of cycle n , $\text{strain}_{\text{max}}^n$ the maximum strain of cycle n , and $\text{strain}_{\text{max}}^{n+1}$ the maximum strain of next cycle.

$$R_n = \frac{\text{strain}_{\text{max}}^n}{\text{strain}_{\text{max}}^{n+1}} \cdot 100\% \quad \text{Eq.1}$$

Thermogravimetric analysis was measured on a PerkinElmer Pyris 6 instrument with a nitrogen flow rate of 10 K min^{-1} . The heating was carried out from 25 to $900\text{ }^{\circ}\text{C}$. The degradation onset temperature ($T_{5\%}$) was determined at 5% of mass loss.

4.2.6.1.1 Synthesis of nopadiene

Route 1: Myrtenal was converted to nopadiene by standard Wittig reaction according to literature.³⁷ Methyltriphenylphosphonium bromide (129.6 g, 0.36 mol, 1.10 eq.) was added to a solution of KO^tBu (40.7 g, 0.36 mol, 1.10 eq.) in 650 mL of freshly

distilled dry THF in a 1 L Schlenk flask under argon and the mixture was vigorously stirred for 30 min. Subsequently, myrtenal (49.6 g, 0.33 mol, 1.00 eq.) was added. When quantitative conversion was reached, the reaction mixture was concentrated under vacuum and then diluted with pentane (800 mL) and filtered through a plug of celite, eluting with pentane. The filtrate was concentrated under reduced pressure (600 mbar) at 40 °C to remove the solvent. The residue was subjected to vacuum distillation twice to remove residual triphenylphosphine oxide. The final product was distilled at reduced pressure (35°C, $1.0 \cdot 10^{-3}$ mbar), yielding 85 % of pure nopadiene. Prior to polymerization, the monomer was dried over CaH_2 and then over triocylaluminum and purified by distillation.

Route 2: Nopol-tosylate was prepared in a one-step synthesis following a modified literature procedure reported by Balczewski et al. To a solution of (1*R*)-nopol (99.7 g, 0.600 mol) in 400 mL of dry pyridine was added p-toluenesulfonyl chloride (125.7g, 0.66 mmol, 1.1 eq.) The resulting mixture was then poured into 300 mL of 12% hydrochloric acid. This mixture was then extracted three times with 75 mL diethyl ether and dried (K_2CO_3), and the solvent was removed by rotary evaporation, yielding 176.6g (92%) of crude nopol tosylate. The product was used as received without further purification.

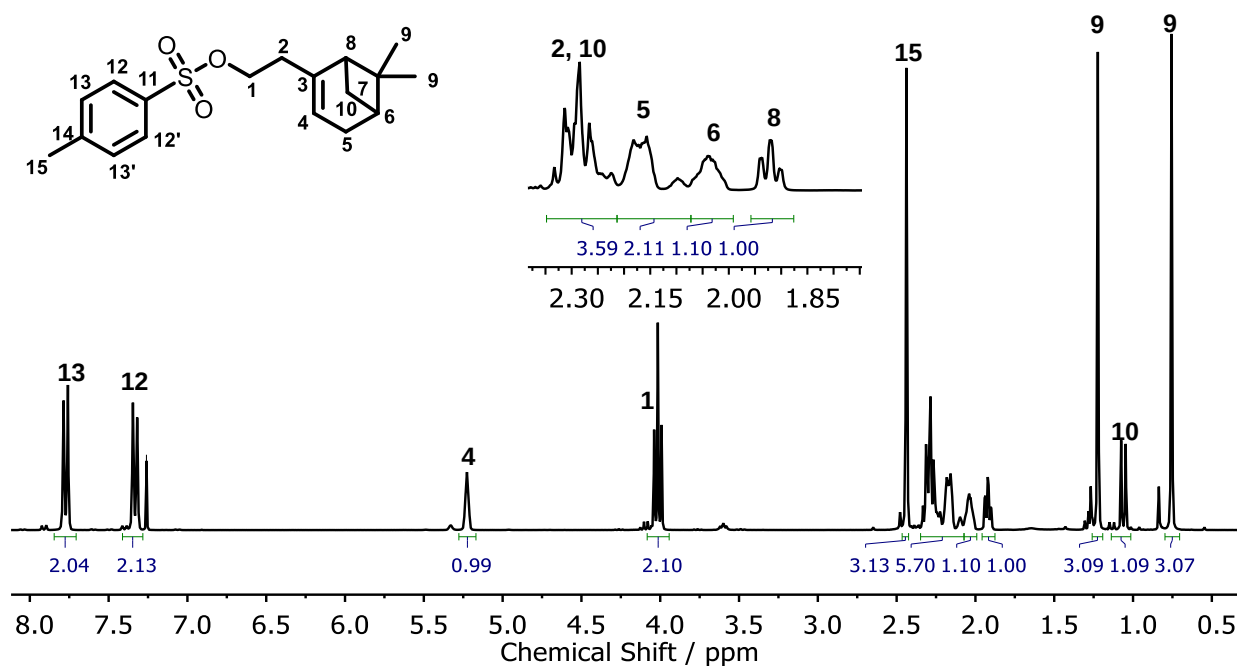


Figure S 1: ^1H NMR Spectrum (400MHz, CDCl_3 , 25°C) of nopol tosylate.

R_f: (cyclohexane:ethylacetate = 2:1) 0.78.

The synthesis of nopadiene starting from nopol tosylate was conducted accordingly to Salzer *et al.*⁴⁴ Nopol tosylate (166.4 g, 0.52 mol) was dissolved in DMSO (1000 mL) and KO^tBu (53.6 g, 0.48 mol, 0.92 eq.) was added. The resulting mixture was stirred for 6 h at 75 °C. After cooling, the product was extracted four times with 75 mL n-hexane and the combined organic extracts dried over MgSO_4 . The solvent was evaporated under reduced pressure and the crude product distilled at 35 °C and $1.0 \cdot 10^{-3}$ mbar. Nopadiene was obtained in 80% yield (61.5 g, 0.42 mmol) as a colourless liquid.

R_f: (cyclohexane:ethyl acetate = 2:1) 0.85.

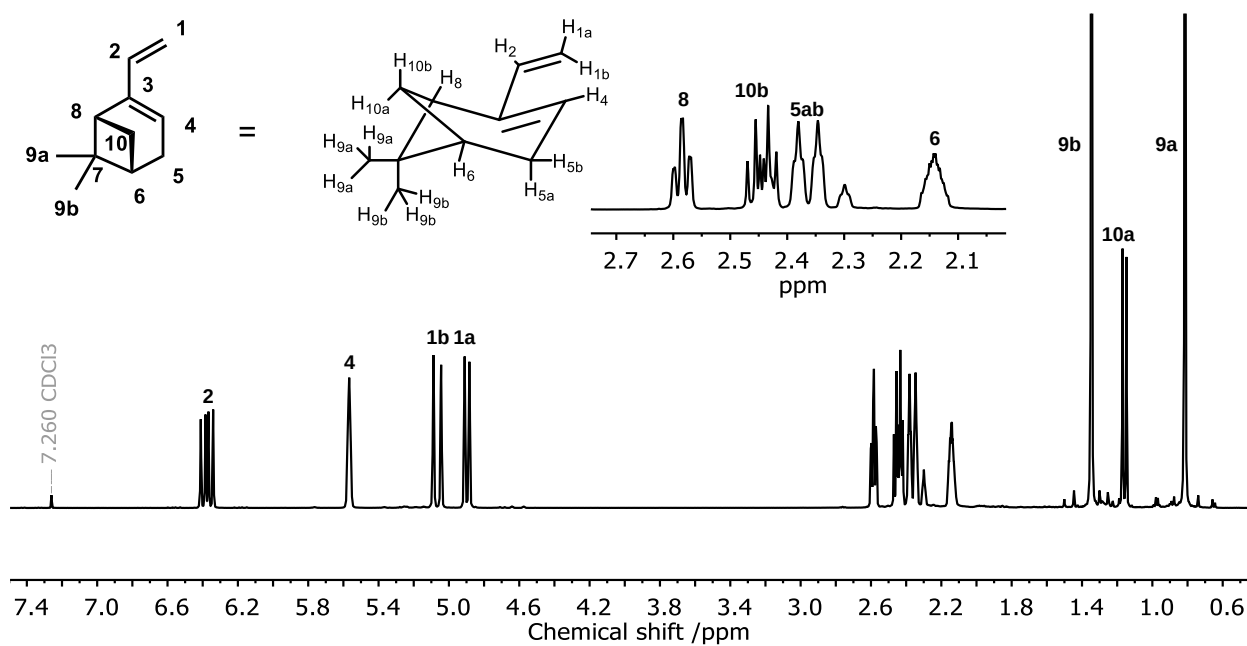


Figure S 2: ^1H NMR Spectrum (400MHz, CDCl_3 , 25°C) of nopadiene.

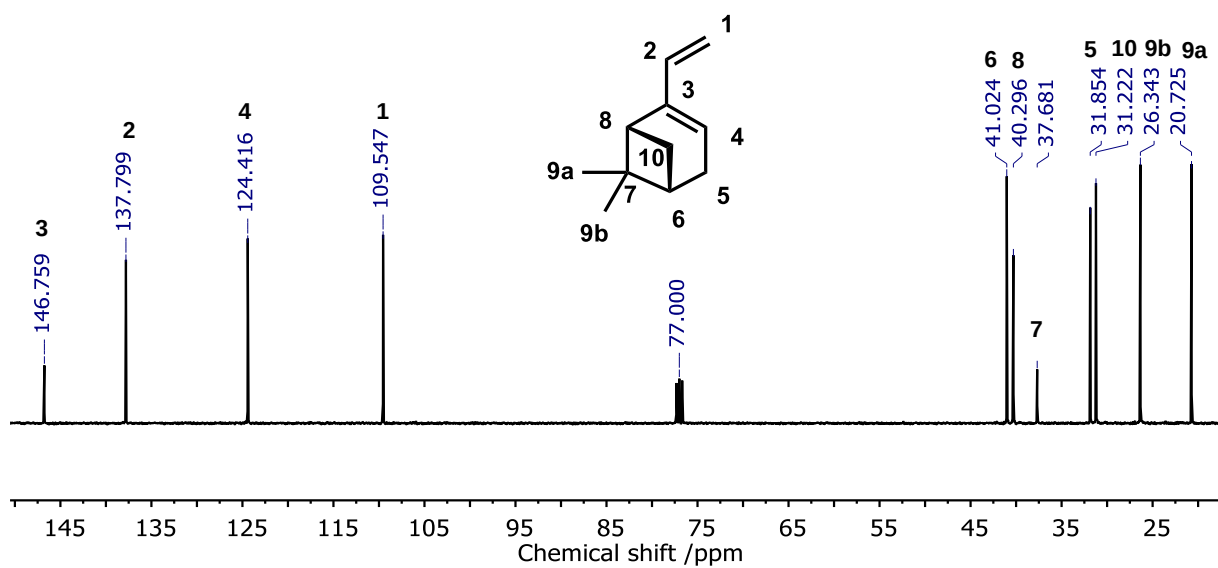


Figure S 3: ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25°C) of nopadiene.

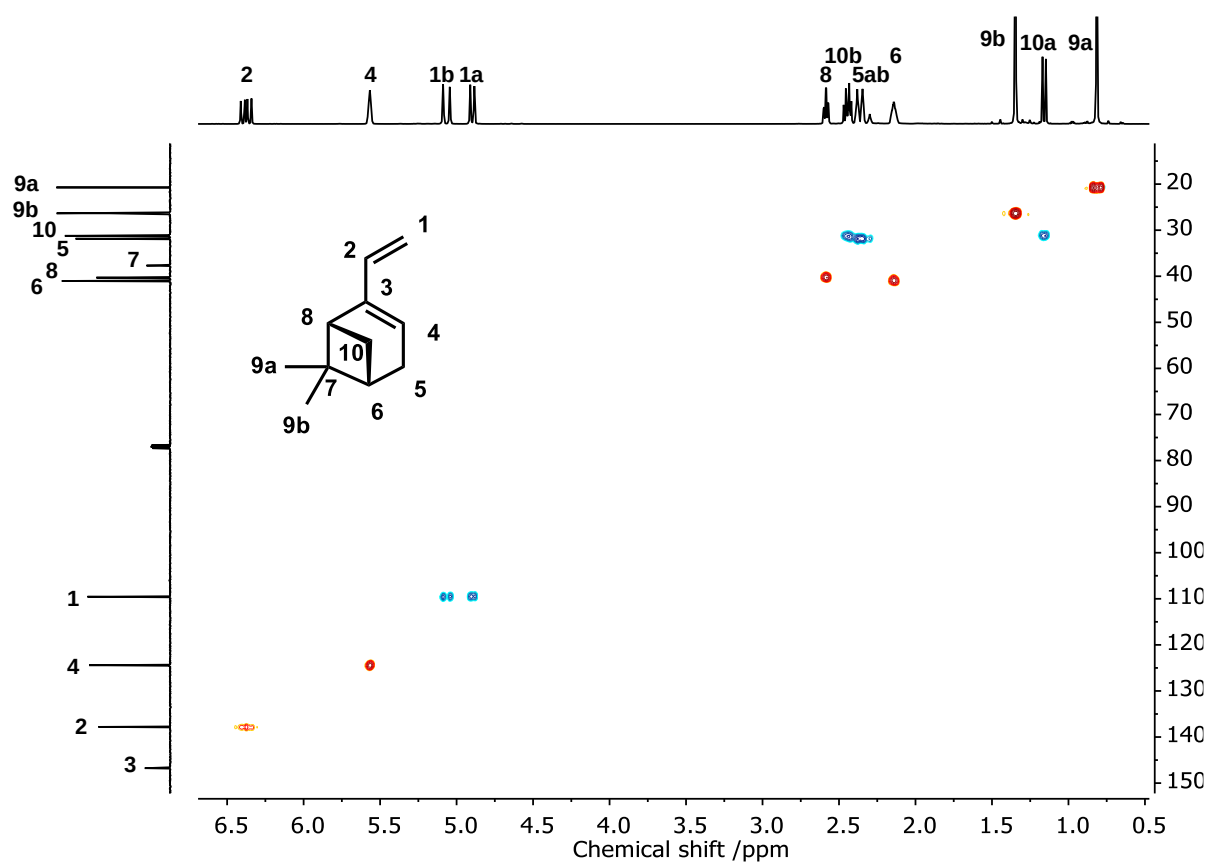
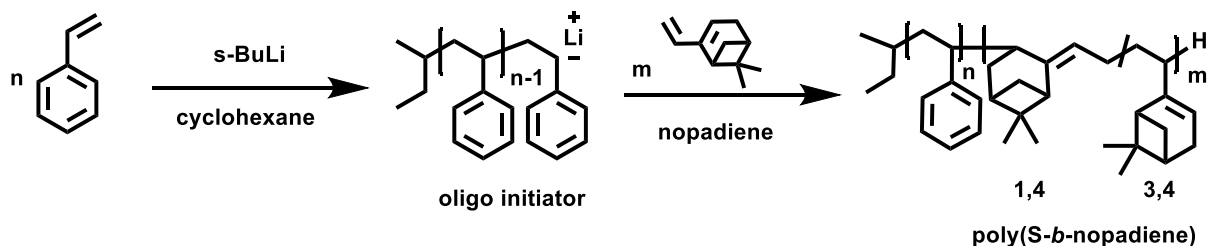


Figure S 4: HSQC NMR spectrum (100 MHz / 400 MHz, CDCl_3 , 25°C) of nopadiene.

4.2.6.1.2 General anionic polymerization procedure of nopadiene

Homopolymerizations were carried out in cyclohexane at room temperature in an argon-filled glovebox (MBraun UNILAB, <0.1 ppm of O₂ and <0.1 ppm of H₂O) in 40 mL glass vials, equipped with a magnetic stir bar, screw caps and septa. Dry and degassed cyclohexane was distilled into a Schlenk flask equipped with a Teflon stopper. The monomers (nopadiene, styrene, myrcene) were dried 24 h over CaH₂, and then additionally 24 h over trioctylaluminum, degassed and finally distilled into another Schlenk flask with Teflon stopper. Inside the glove box the monomer(s) and cyclohexane were added into glass vessel with septum. For the synthesis of the homopolymers with modifiers (THF, DTHFP, MTBE, DIPIPE) the monomer/solvent (10 wt%) mixture was initiated with 0.1 mL or 0.05 mL sec-BuLi (1.3 M in cyclohexane/ hexane 92/8) via 0.1 mL syringe. The modifiers were dried by stirring over CaH₂. The solution was stirred for 24 h to ensure full monomer conversion. For the synthesis of P(*S-b*-nopa) copolymers poly(styryl)-lithium was used as an initiator. Styrene was purified and dried as described before. For the preparation of the oligostyryl-initiator, 10-20 mg (3mol%) of styrene was initiated with sec-BuLi in cyclohexane. The solution was stirred until full styrene conversion. Subsequently, nopadiene was added via 1 mL syringe. The polymerization was terminated after full conversion by adding 0.5 mL of methanol (degassed with argon for 1 h prior to use) by a syringe. The polymers were precipitated in 30 mL of a cold methanol/isopropanol mixture and dried under reduced pressure.



Scheme S1: Initiation of nopadiene with poly(styryl)-lithium.

Initiation with various initiators. To circumvent the delayed initiation of nopadiene in apolar solvents using sec-BuLi, various other organo-lithium initiators were tested.

The SEC traces of the slowly initiated polymers are shown in Figure S5. However, the *tert*-BuLi, compared to *sec*-BuLi more nucleophilic, showed similar delayed initiation with a dispersity of $\bar{D} = 1.29$. Living chains as oligomeric initiators consisting of α -methylstyrene (aMS) and styrene (S) were utilized to initiate the polymerization of nopadiene. The results show a monomodal molecular weight distribution and the absence of a delayed initiation (Figure S5).

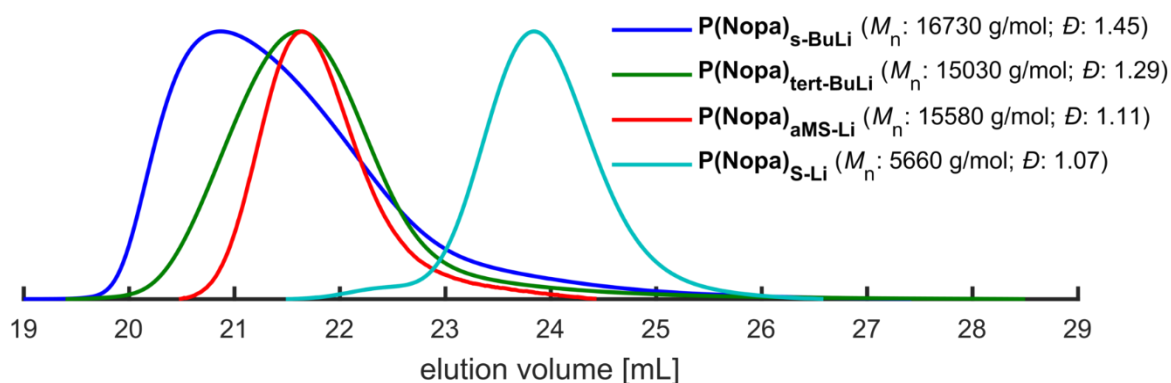


Figure S 5: SEC traces (eluent THF, PS calibration) of $P(Nopa)_{sec-BuLi}$ and $P(Nopa)_{tert-BuLi}$ and $P(Nopa)_{aMS-Li}$ and $P(Nopa)_{S-Li}$.

The polymerization of nopadiene in polar solvents, such as MTBE and cyclohexane/THF mixtures was conducted in a similar manner to the homopolymers. In contrast to the polymerization in cyclohexane, the initiator *sec*-BuLi and the polar solvent (MTBE, THF) was stirred for 1 hour before adding nopadiene to ensure full dissociation of the aggregates of *sec*-BuLi. The SEC traces of the polymers obtained in MTBE and cyclohexane/THF are shown in Figure S6. The results show that monomodal and well-defined polymers of nopadiene can be obtained in MTBE and cyclohexane/THF mixtures.

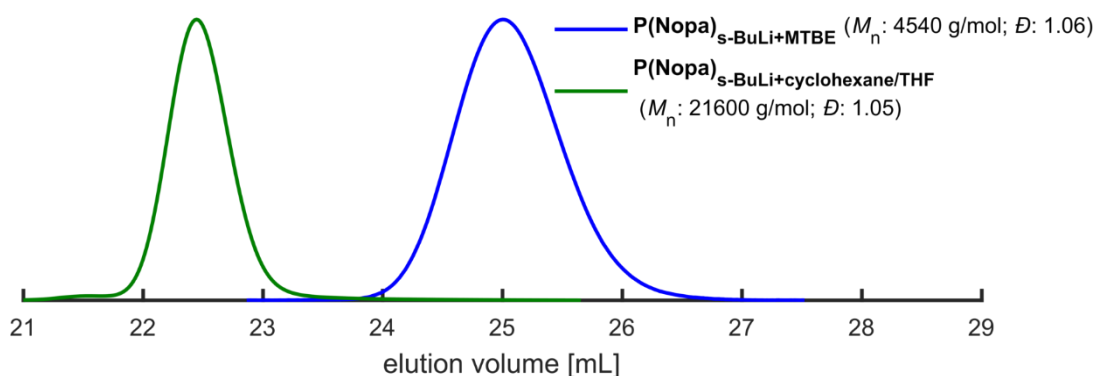


Figure S 6: SEC traces (eluent THF, PS calibration) of homopolymer samples $P(Nopa)_{\text{sec-BuLi+MTBE}}$ and $P(Nopa)_{\text{sec-BuLi+cyclohexane/THF}}$.

Aggregation of living $P(\text{nopadienyl})$ chain ends. The delayed initiation of the homopolymerization of nopadiene with sec-BuLi was investigated *via* ^1H NMR studies. The determination of the aggregation number of $P(\text{nopadienyl})$ chain ends will be discussed in the following section of the SI.

Living polymerization was defined by Szwarc⁵⁹ based on three preconditions: i) rate of initiation is considerably faster than the rate of propagation, ii) no termination reactions occur, and iii) all chains grow equally. As a consequence of these conditions, the active living chain end concentration $[\text{Li}]$ is always constant. The slope of $\log(M_0/M_i)$ is the apparent rate constant k_{app} , which is the product of the rate of propagation k_p and active chain end concentration $[\text{Li}]$.

The data shown in Figure S7 were obtained by following monomer consumption online by nopadiene polymerization in an NMR tube.

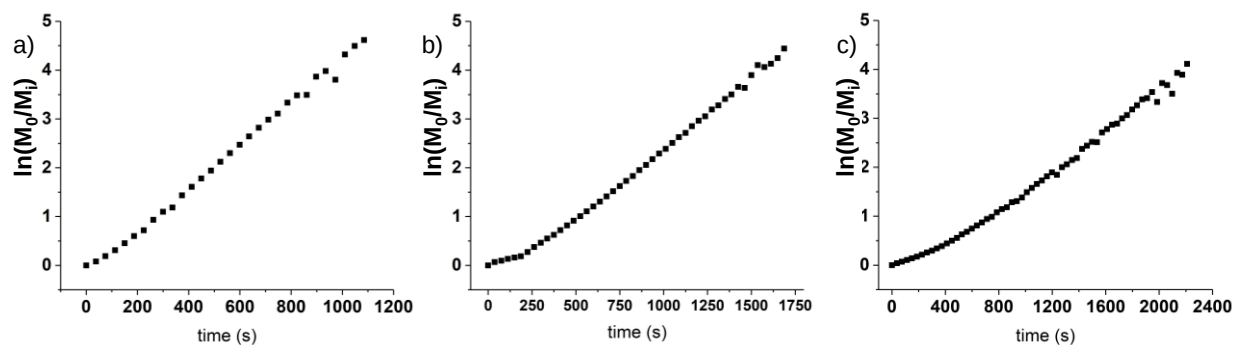


Figure S 7: Homopolymerization of nopadiene in cyclohexane- d_{12} , initiation with sec-BuLi , $\log(M_0/M_i)$ vs. time plot, lithium concentration $[\text{Li}]$ a) $c_1 = 1.19 \cdot 10^{-5} \text{ mol/mL}$, b) $c_2 = 3.85 \cdot 10^{-6} \text{ mol/mL}$, c) $c_3 = 1.73 \cdot 10^{-6} \text{ mol/mL}$.

In Figure S7 shows clearly that the living chain end concentration $[Li]$ is constant after an induction period, which is evident from the linearity of the plot after an induction period. The length of this induction period is concentration dependent. The shortest induction period for the three different concentrations c_{1-3} , is observed at high lithium concentration (c_1). In Figure 7a, the induction period appears to be hardly perceptible, because of the delay time (90 sec) between the initiation with *sec*-BuLi and the measurement of the first 1H NMR spectrum. The induction period increases up to 250 s for c_2 and up to 350 s for c_3 . The delayed initiation results in the rather high dispersities of the polymers. The respective SEC traces for c_{1-3} are shown in Figure S8.

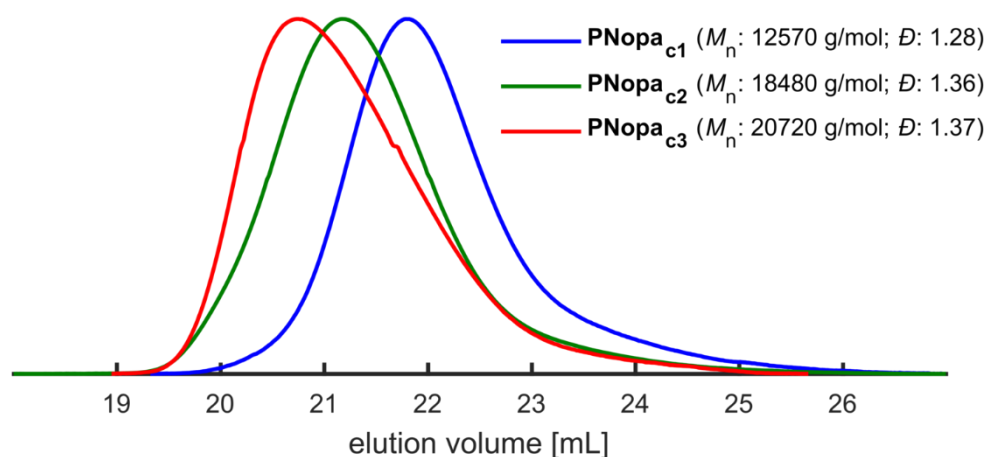


Figure S 8: SEC traces (eluent THF, PS calibration) of PNopa_{c1}, PNopa_{c2} and PNopa_{c3}.

The self-association of *sec*-BuLi, caused by its low solubility in nonpolar solvents such as cyclohexane, together with the dissociation of these aggregates to unimers, are important parameters of the initiation kinetics.^{47,48} For poly(styryl)lithium the well-known aggregation number is close to 2.⁴⁵ The aggregation of living chain ends of nopadiene was investigated in this work as well. In theory, the rate of polymerization is given by Equation 2.

$$R_p = \frac{d[M]}{dt} = k_p[M][Li] \quad \text{Eq.2}$$

In theory, the rate of polymerization is given by Equation 2 renders Equation 3.

$$\ln \left(\frac{[M]_0}{[M]} \right) = k_p [Li] t = k_{app} t \quad \text{Eq.3}$$

The slope of the linear region in the $\log([M]_0/[M])$ vs. time plot in Figure S7 gives the apparent rate constant k_{app} . Plotting the logarithm of the apparent rate constant k_{app} vs. the logarithm of the lithium concentration $[Li]$ employed results in a linear relationship, as demonstrated in Figure 4. The inverse of the slope (m) of this linear relationship gives access to the number of aggregated chain ends. It was found that the number of aggregated chains is 2.56 ± 0.1 , which indicates a mixed state of aggregation in this concentration regime. We assume that dimers, trimers and tetramers are present. It is known from butadiene in apolar media that the aggregation number of chains decreases with decreasing $[Li]$, changing from high concentrations where hexamers are formed to dimers under dilute conditions.

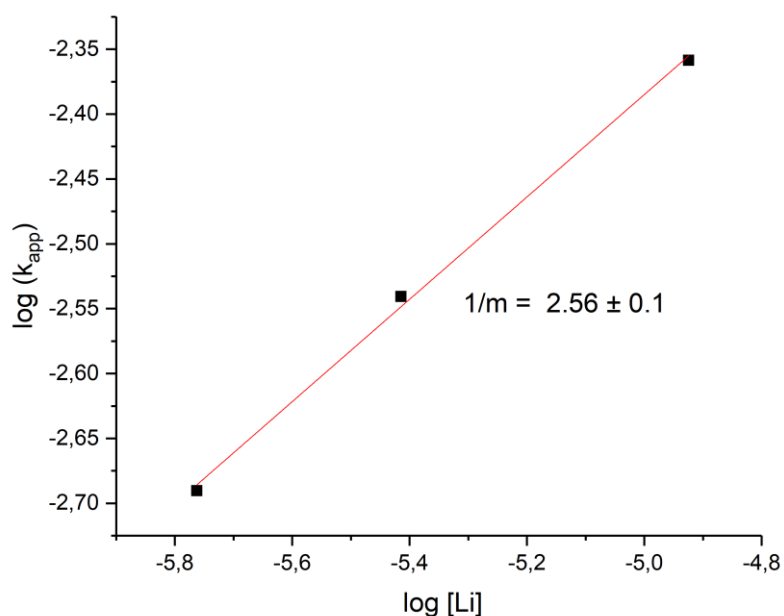


Figure S 9: Double logarithmic plot of the apparent rate constant k_{app} vs. lithium concentration $[Li]$, $\log(k_{app})$ vs. $\log [Li]$.

This result hints at a non-quantitative initiation step of nopadiene with *sec*-BuLi. In general, organo-lithium compounds form aggregates in apolar solution. *Sec*-BuLi aggregates in tetramers. On the contrary, oligo(styryl)-lithium forms dimers, which is sterically less demanding and thus is more suitable for initiation of the bulky nopadiene. Furthermore, styrene was used to prove the living nature of nopadiene and that higher molecular weight copolymers can also be prepared.

4.2.6.1.3 Microstructure investigation and catalytic polymerization of nopadiene

Anionic Polymerization of nopadiene. The addition of a modifier significantly alters the ratio of polymer microstructures, as it was investigated for several other 1,3 dienes.^{51,52} A series of modifiers like tetrahydrofuran, (THF), methyl-tertbutylether (MTBE), 2,2-di(2-tetrahydrofuryl)propane (DTHFP) and 1,2-dipiperidinoethane (DIPIPE) were employed to analyze their influence on the microstructure. The objective of the use of modifiers was to manipulate the microstructure of nopadiene towards higher 3,4 addition. ¹³C inversed gated NMR spectroscopy was employed to determine the respective microstructure of nopadiene. ¹H and ¹³C NMR spectra of the modified homopolymers of nopadiene are shown in Figures S8-S27. The ratio of 1,4 to 3,4 - units of polynopadiene is determined by integrating the ¹³C signals of the allylic carbons at 121.5 ppm (1,4-unit) and 116.6 ppm (3,4-unit) (Figure 9, main manuscript). To further confirm this assignment and to obtain defined spectra, catalytic polymerization of nopadiene with complex 1 and complex 2 (Scheme 2) was performed to yield exclusively 1,4 and 3,4-polynopadiene.

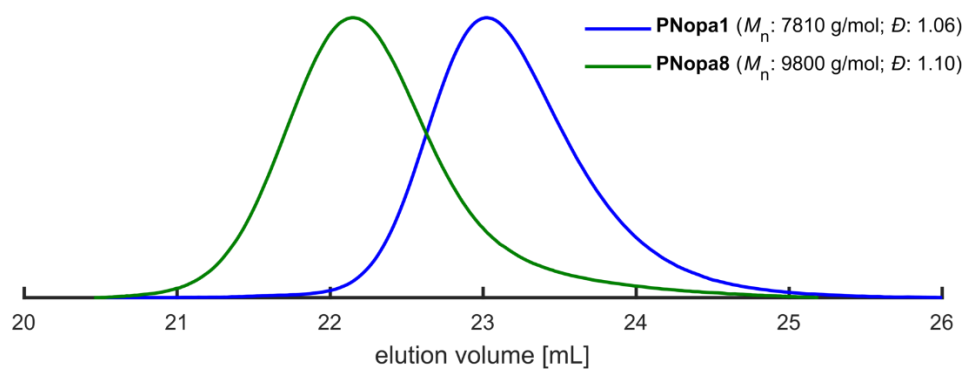


Figure S 10: SEC traces (eluent THF, PS calibration) of PNopa1 and PNopa8.

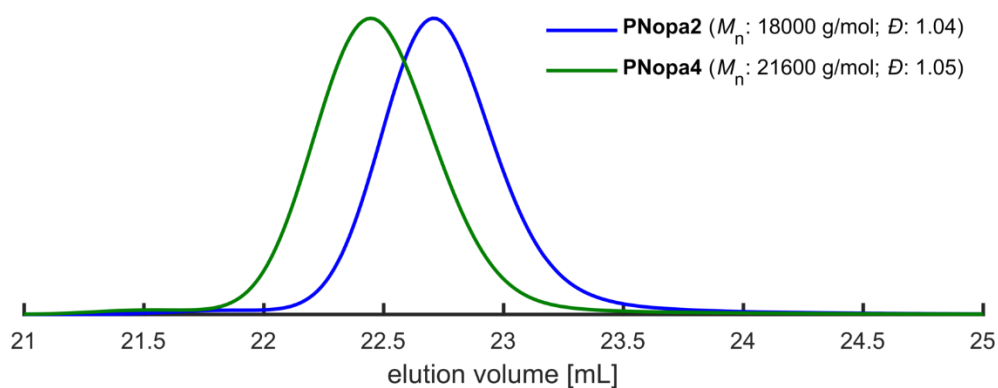


Figure S 11: SEC traces (eluent THF, PS calibration) of PNopa2 and PNopa4.

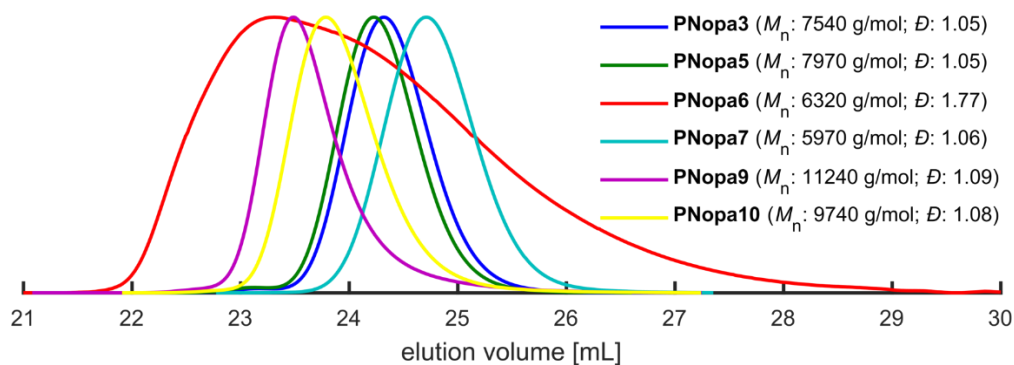


Figure S 12: SEC traces (eluent THF, PS calibration) of PNopa3, PNopa5-7 and PNopa9-10.

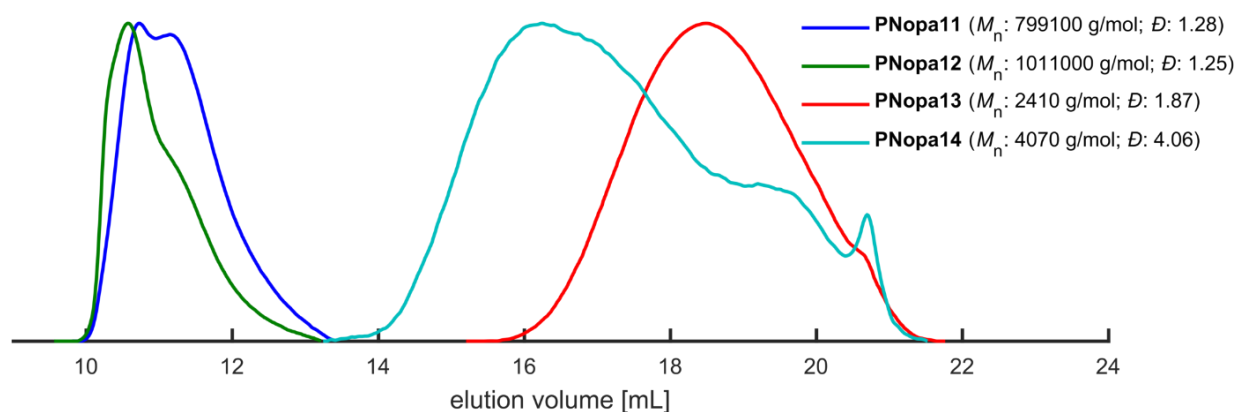


Figure S 13: SEC traces (eluent chloroform, PS calibration) of PNopa11-14.

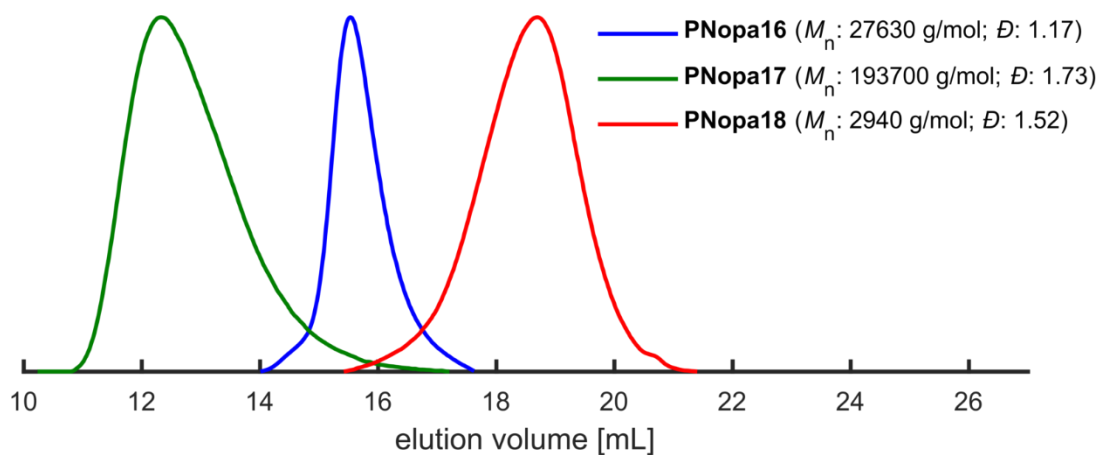


Figure S 14: SEC traces (eluent chloroform, PS calibration) of PNopa16-18.

4.2.6.1.4 Catalytic polymerization of nopadiene

Catalytic polymerization of 1,3-dienes has been studied intensively for decades. Besides $\text{Me}_4\text{CpSi}(\text{Me})_2\text{N}^t\text{Bu TiCl}_2$ and $((\text{Flu})(\text{Pyr})\text{CH}_2\text{Lu}(\text{CH}_2\text{TMS})_2(\text{THF}))$. The employed catalysts and co-catalyst are shown in Table S1.

Table S 1: Experimental results of the catalytic polymerization of PNopa11-18, temperature, time, conversion, and microstructure.

entry	catalyst	co-catalyst	Tem p. / °C	Time / h	Conv. / % (NMR)	1,4/3,4 microstructure %
PNopa11	$\text{Me}_4\text{CpSi}(\text{Me})_2\text{N}^t\text{BuTiCl}_2$	MAO	60	24	15	99/1
PNopa12	$\text{Me}_4\text{CpSi}(\text{Me})_2\text{N}^t\text{BuTiCl}_2$	MAO	60	24	15	99/1
PNopa13	$((\text{Flu})(\text{Pyr})\text{CH}_2\text{Lu}(\text{CH}_2\text{TMS})_2(\text{THF}))$	TIBA/Trityl BCF	60	24	99	5/95
PNopa14	$((\text{Flu})(\text{Pyr})\text{CH}_2\text{Lu}(\text{CH}_2\text{TMS})_2(\text{THF}))$	TIBA/Trityl BCF	60	24	99	5/95
PNopa15	$\text{Nd}(\text{BH}_3)(\text{THF})$	MgBu_2	60	72	99	13/87
PNopa16	$\text{Zr}(\text{EtInd})_2\text{Cl}_2$	MAO	50	72	traces	n.d.
PNopa17	CpTiCl_3	MAO	25	48	99	57/43
PNopa18	$[(\text{Mesitylene})\text{Ni}(\text{allyl})][\text{BAR}_4^{\text{F}}]$	-	50	48	10	93/7

Neodymium $(\text{BH}_3)(\text{THF})$ can polymerize nopadiene in 3,4-microstructure predominantly (87%), but not exclusively. When using zirconium $(\text{EtInd})_2\text{Cl}_2$ as a catalyst, only traces of polymer were obtained. It is known from literature that $\text{Zr}(\text{EtInd})_2\text{Cl}_2$ can polymerize vinylcyclohexene selectively in 3,4-addition. When using CpTiCl_3 , a mixture of 1,4 and 3,4-microstructures were obtained, which made the NMR analysis challenging. $[(\text{Mesitylene})\text{Ni}(\text{allyl})][\text{BAR}_4^{\text{F}}]$ successfully polymerized nopadiene in high 1,4-microstructure.

The respective ^1H and ^{13}C NMR spectra of polynopadiene, prepared by catalytic polymerization, are shown in Figure S35-55. The structure of the different microstructures is shown in Fig. S16. The NMR measurements reveal that in 1,4-polynopadiene the C_7 carbon is shifted to 41.41 ppm, whereas the C_7 carbon in 3,4-

polynopadiene appears at 37.65 ppm. Another remarkable difference in structure and chemical shift is seen for C₈ and H₈. The signals of H₈ and C₈ in the 3,4-microstructure can be assigned to 2.05 and 41.26 ppm, respectively. The signals of H₈ and C₈ in the 1,4-microstructure can be assigned to 2.92 and 52.83 ppm, respectively. ROESY and NOESY 2D NMR experiments further clarified the microstructure of 1,4-polynopadiene. It was found that the 1,4-microstructure of PNopa12 is *cis*-configured. The results demonstrate that NOE's are all in-phase and negative and in combination with the ROE's are all positive. This means no scalar J-coupling is visible that could appear in ROESY. In the ROESY spectrum of PNopa12 no scalar coupling from H₂ to H₁ is visible. This indicates that no TOCSY transfer occurs. In particular, the NOE (Figure S40) and ROE (Figure S39) from H₂ to H₈ is firm evidence for the 1,4-*cis* configuration of PNopa12. For visualization purposes, for all other samples the 1,4-*trans* microstructure is drawn.

The Figures S15-45 show the NMR spectra of the polymers in Table 1 (PNopa1-14).

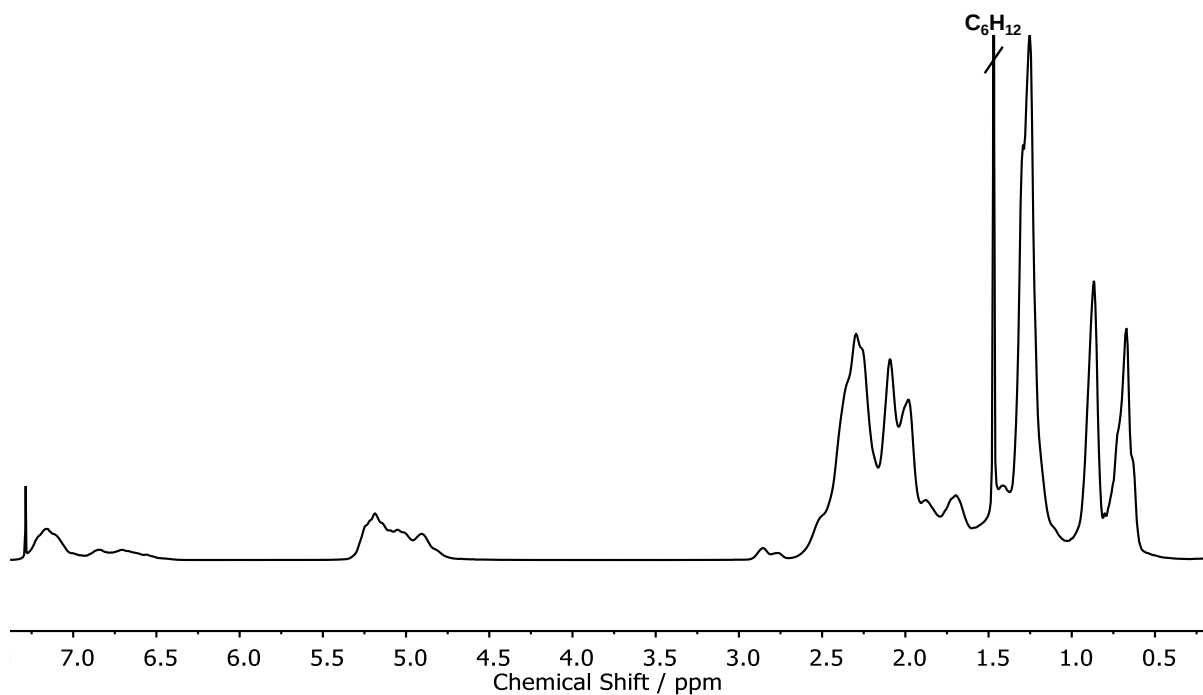


Figure S 15: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa1, obtained in cyclohexane.

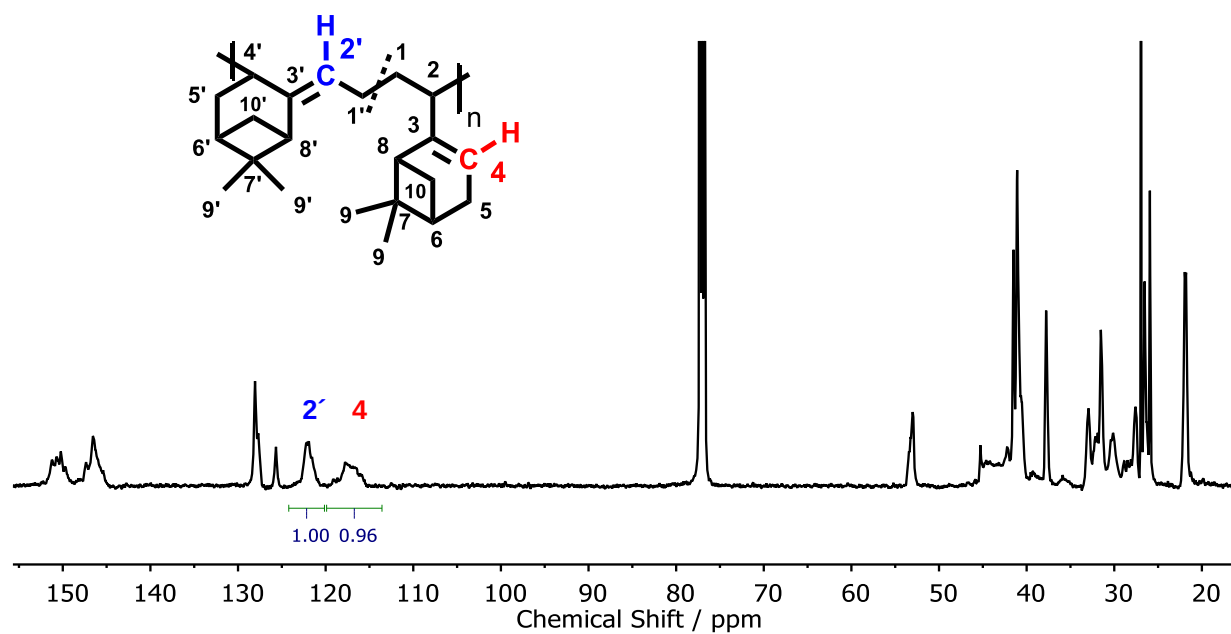


Figure S 16: ^{13}C NMR inverted-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa1, obtained in cyclohexane.

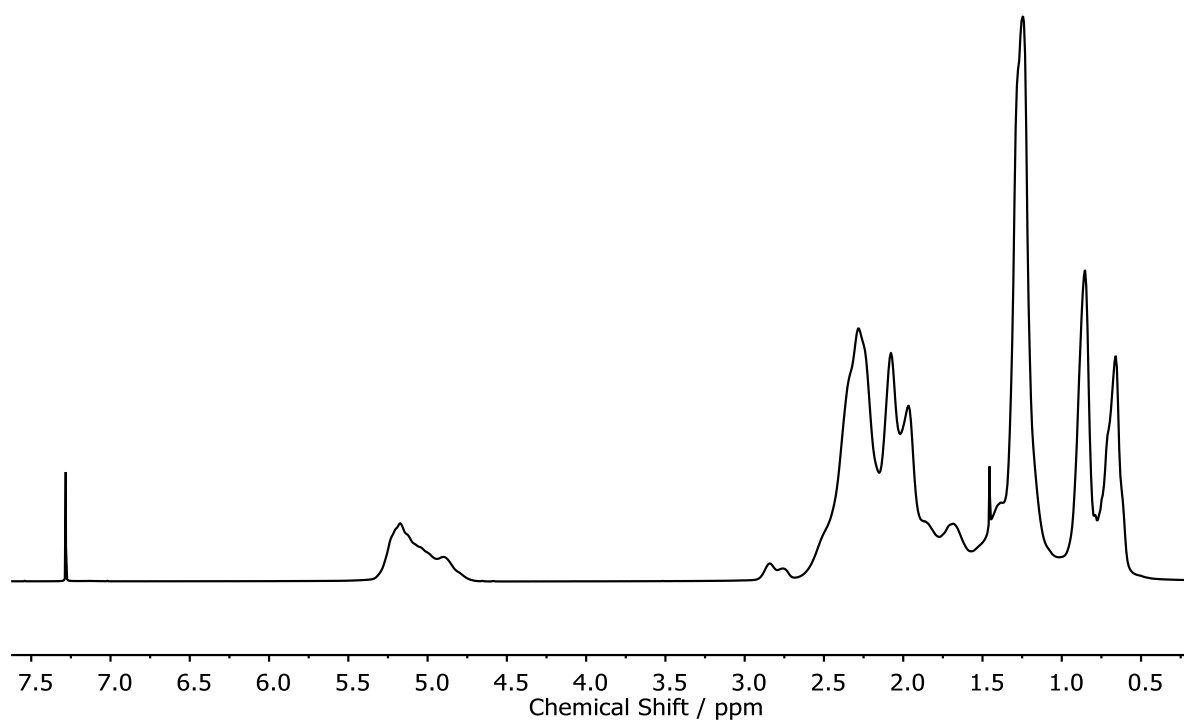


Figure S 17: ^1H NMR spectrum (600 MHz, CDCl_3 , 25°C) of PNopa2, obtained in cyclohexane and 5 eq. MTBE.

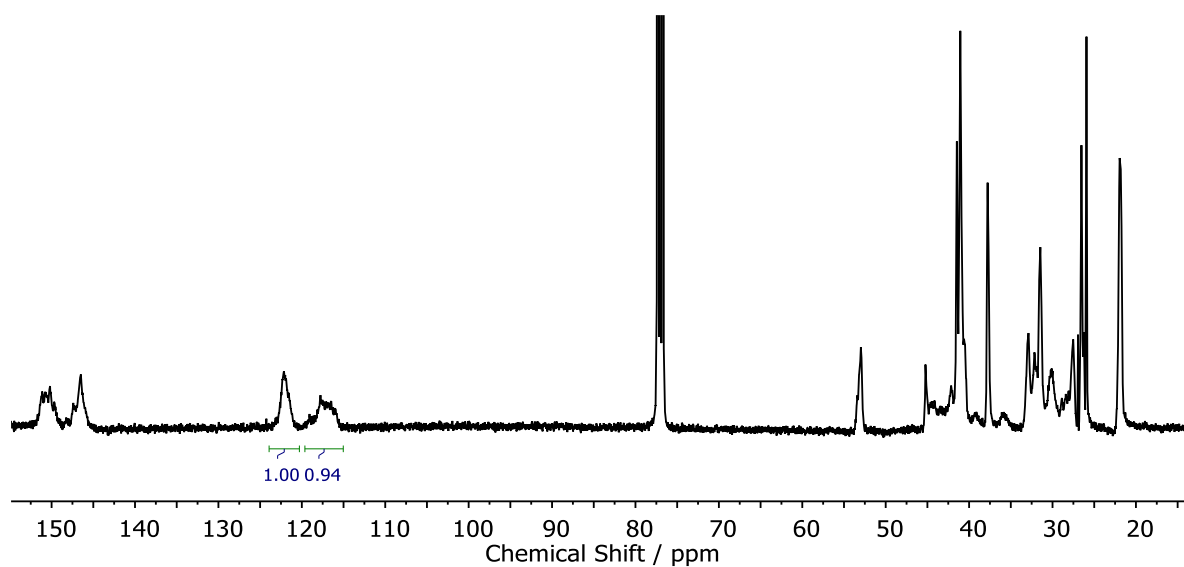


Figure S 18: ^{13}C NMR inverted-gated spectrum (150 MHz, CDCl_3 , 25°C) of PNopa2, obtained in cyclohexane and 5 eq. MTBE.

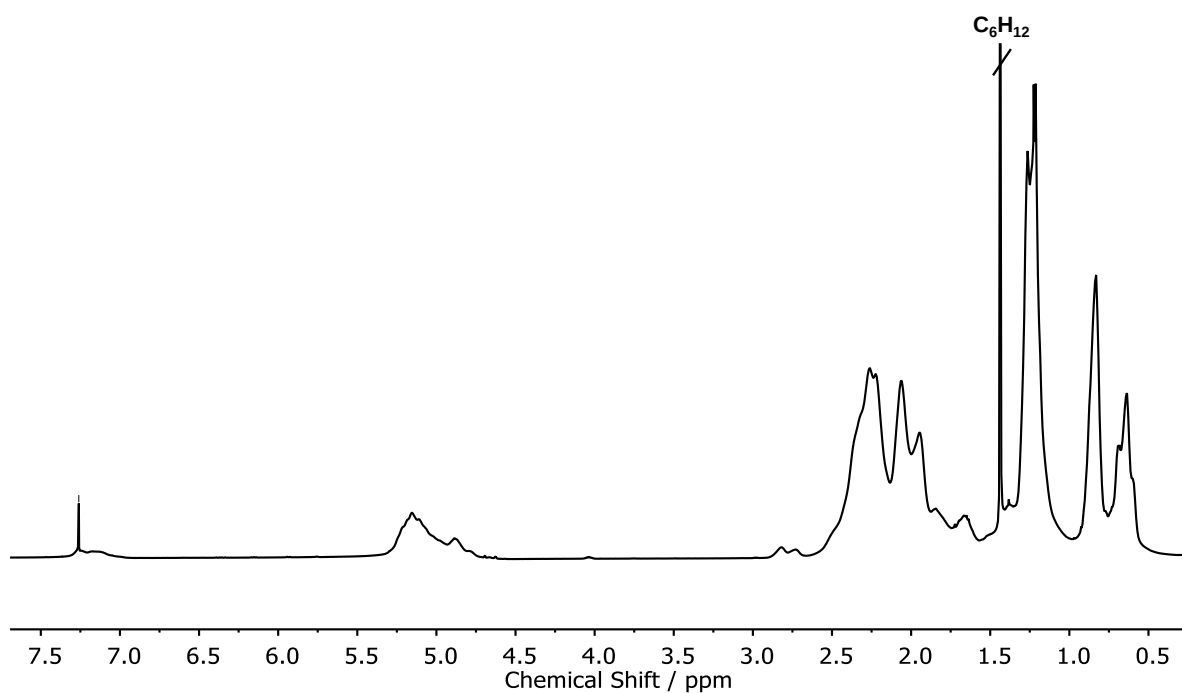


Figure S 19: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa3, obtained in cyclohexane and 2 eq. THF.

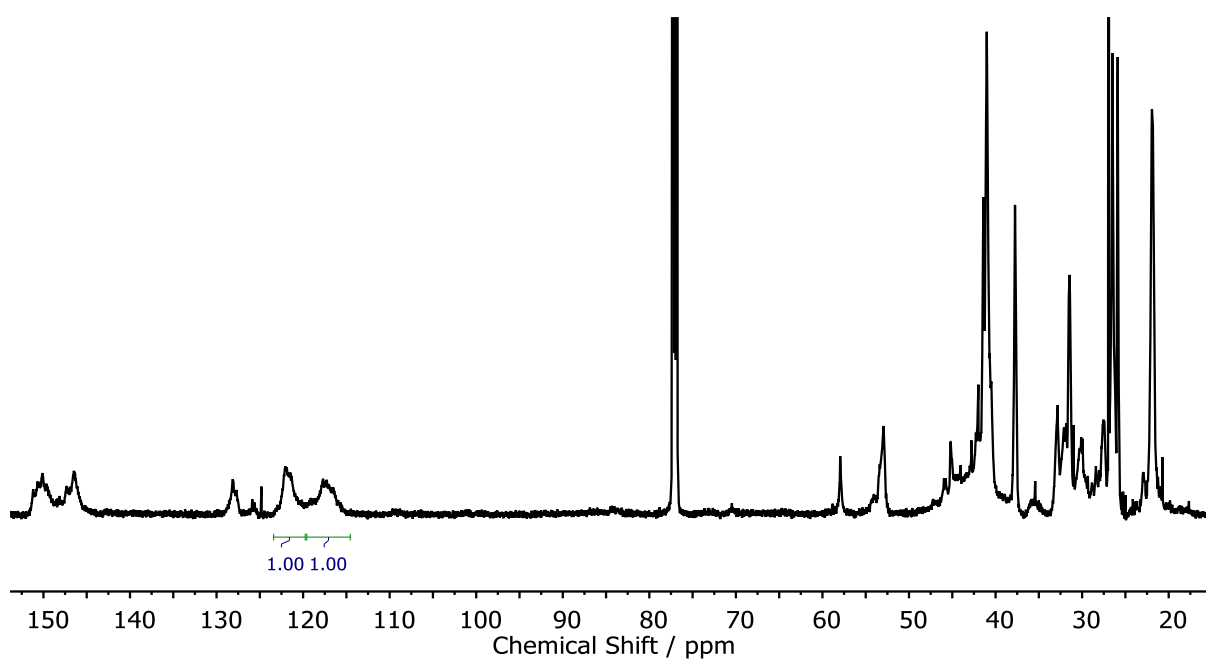


Figure S 20: ^{13}C NMR inverted-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa3, obtained in cyclohexane and 2 eq. THF.

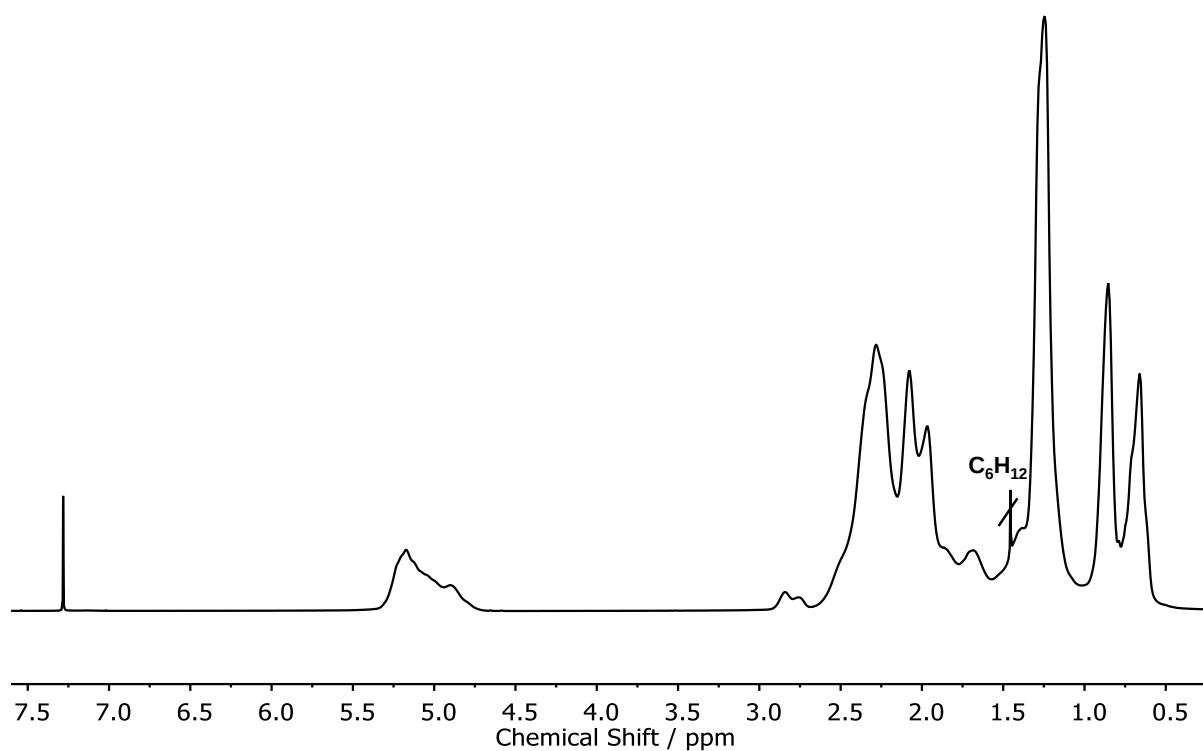


Figure S 21: ^1H NMR spectrum (600 MHz, CDCl_3 , 25°C) of PNopa4, obtained in cyclohexane and 8 eq. THF.

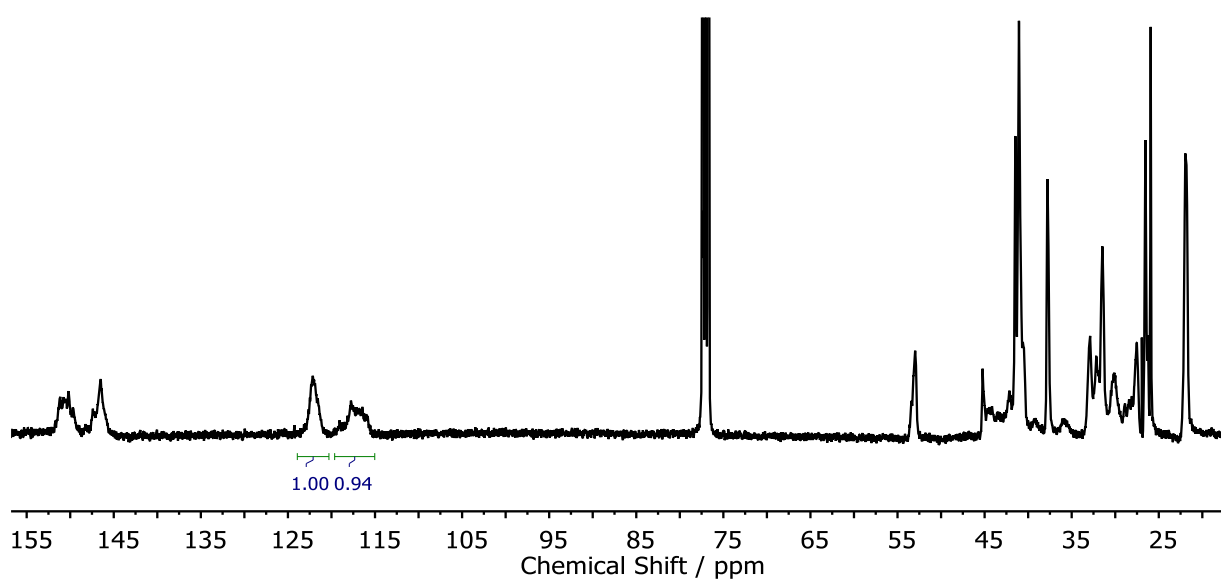


Figure S 22: ^{13}C NMR inverted-gated spectrum (150 MHz, CDCl_3 , 25°C) of PNopa4, obtained in cyclohexane and 8 eq. THF.

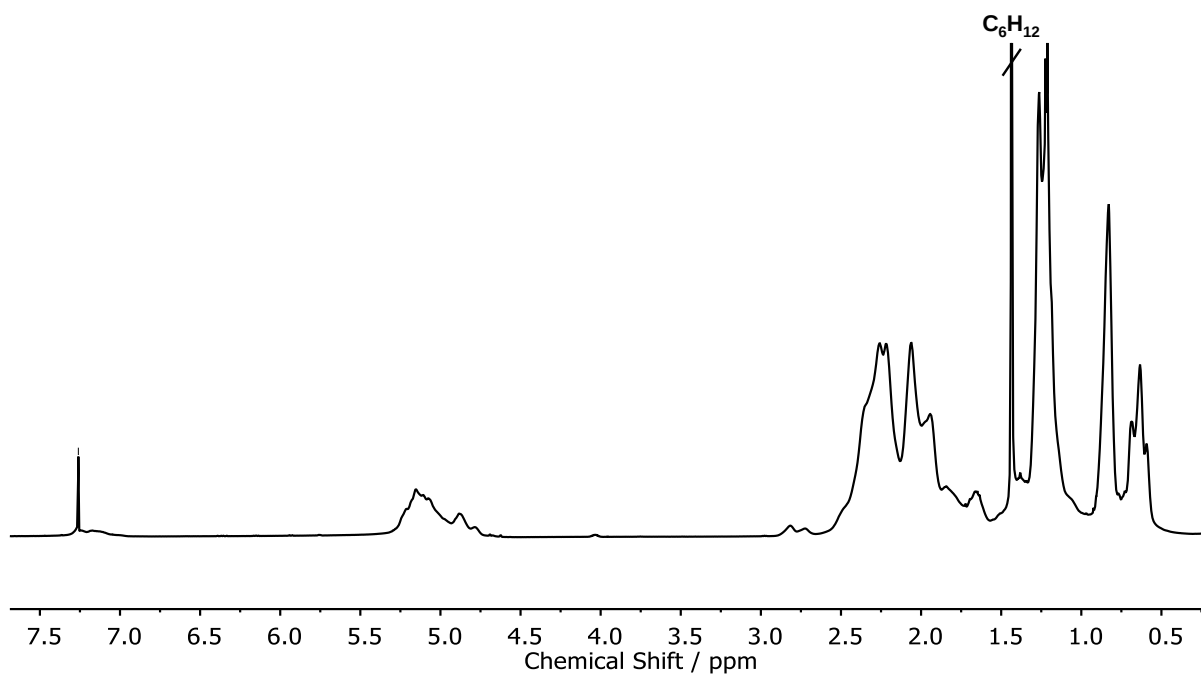


Figure S 23: ^1H NMR spectrum (600 MHz, CDCl_3 , 25°C) of PNopa5, obtained in cyclohexane and 20 eq. THF.

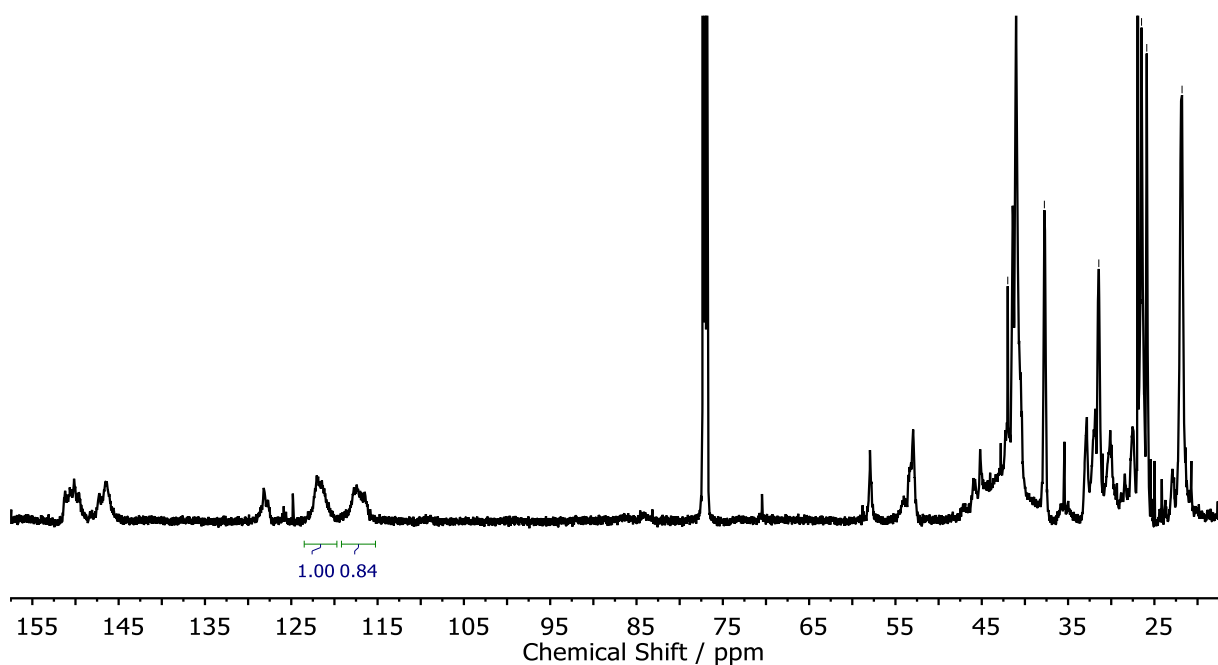


Figure S 24: ^{13}C NMR inverted-gated spectrum (150 MHz, CDCl_3 , 25°C) of PNopa5, obtained in cyclohexane and 20 eq. THF.

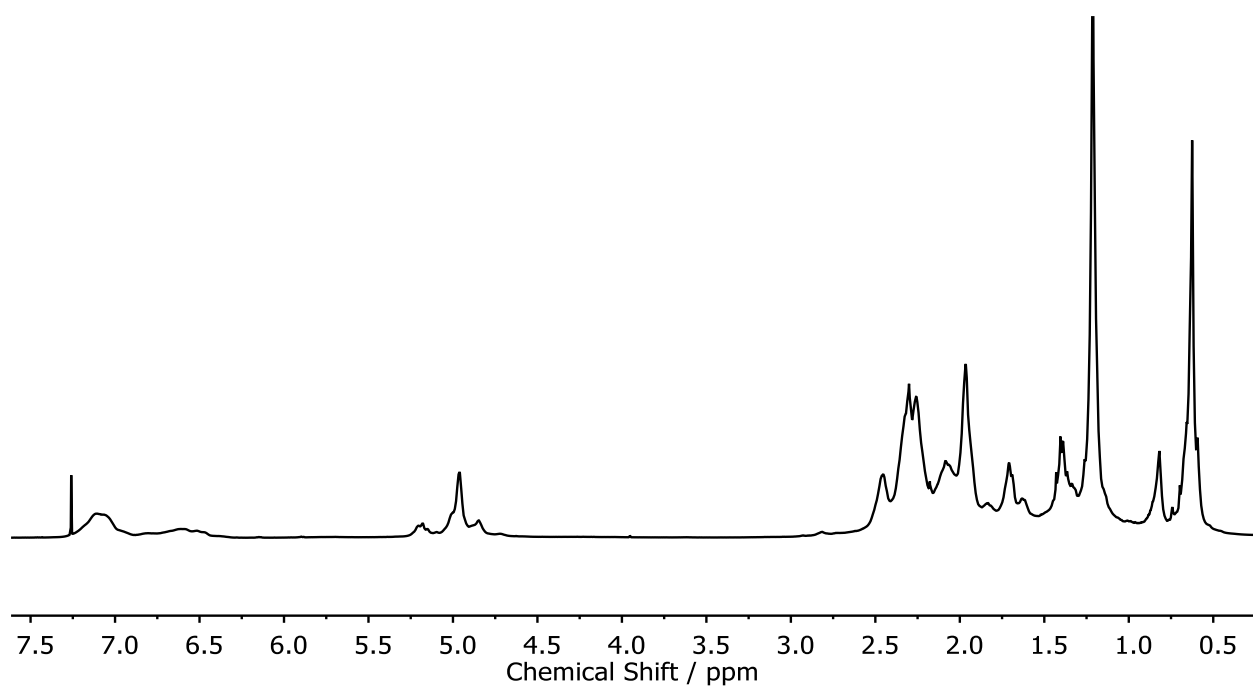


Figure S 25: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa6, obtained in THF.

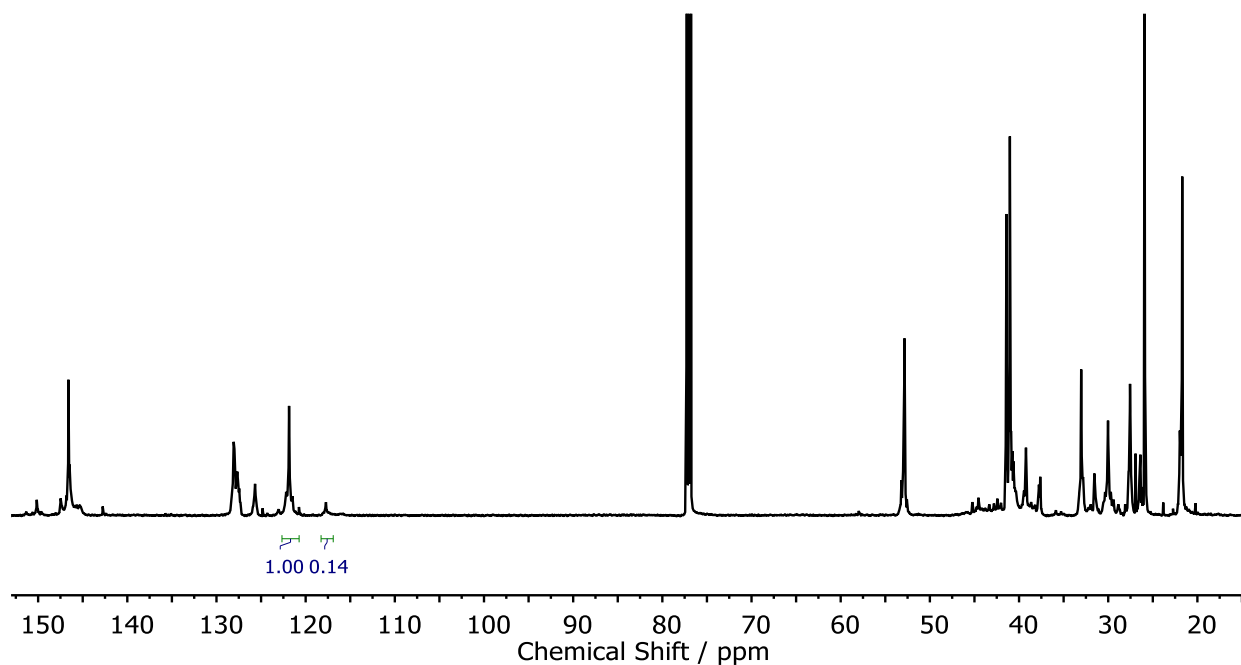


Figure S 26: ^{13}C NMR inverted-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa6, obtained in THF.

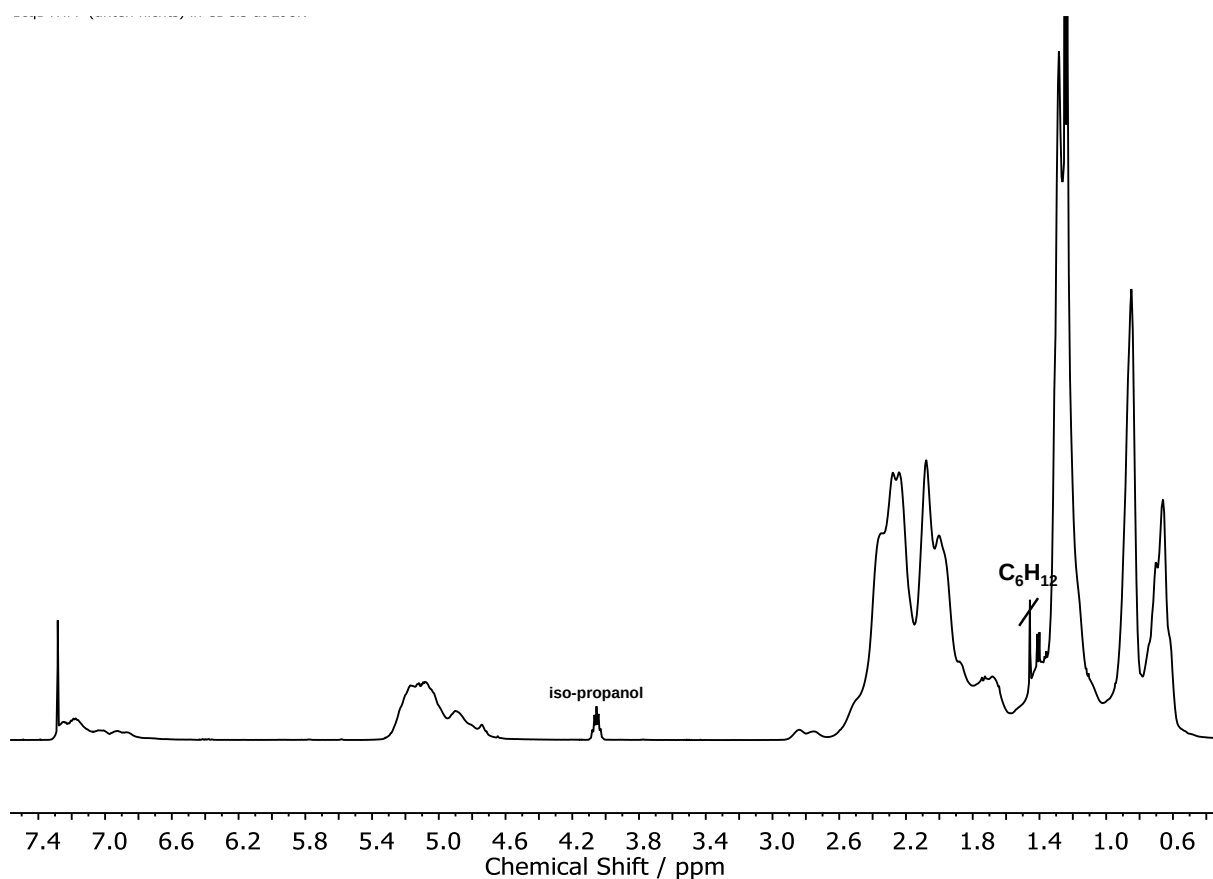


Figure S 27: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa7, obtained in cyclohexane and 1 eq. DTHFP.

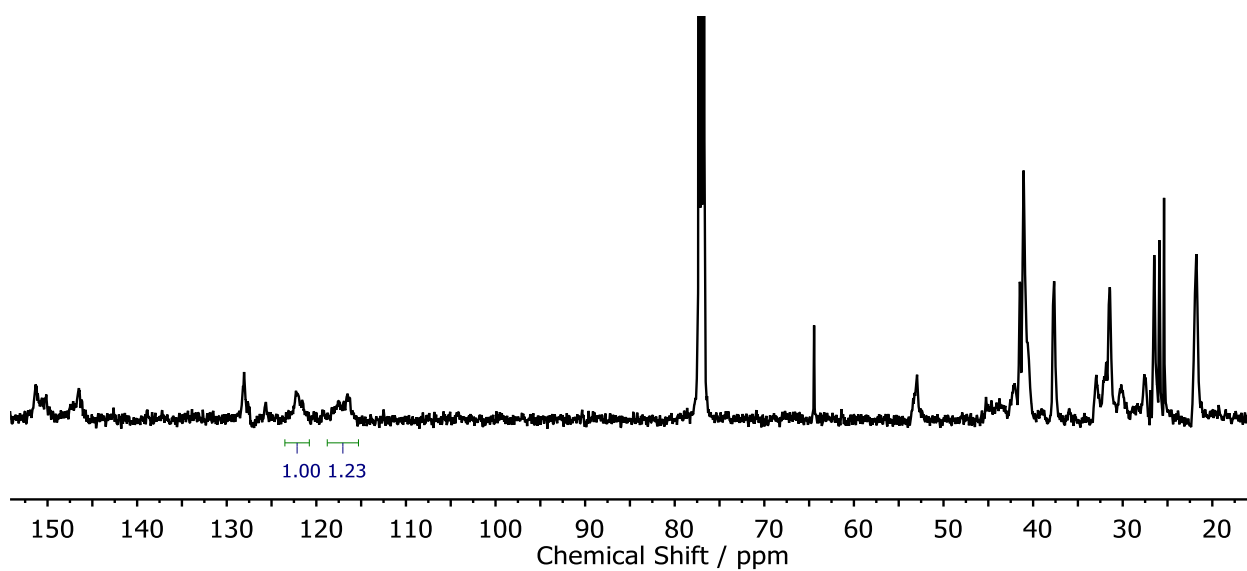


Figure S 28: ^{13}C NMR inverted-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa7, obtained in cyclohexane and 1 eq. DTHFP.

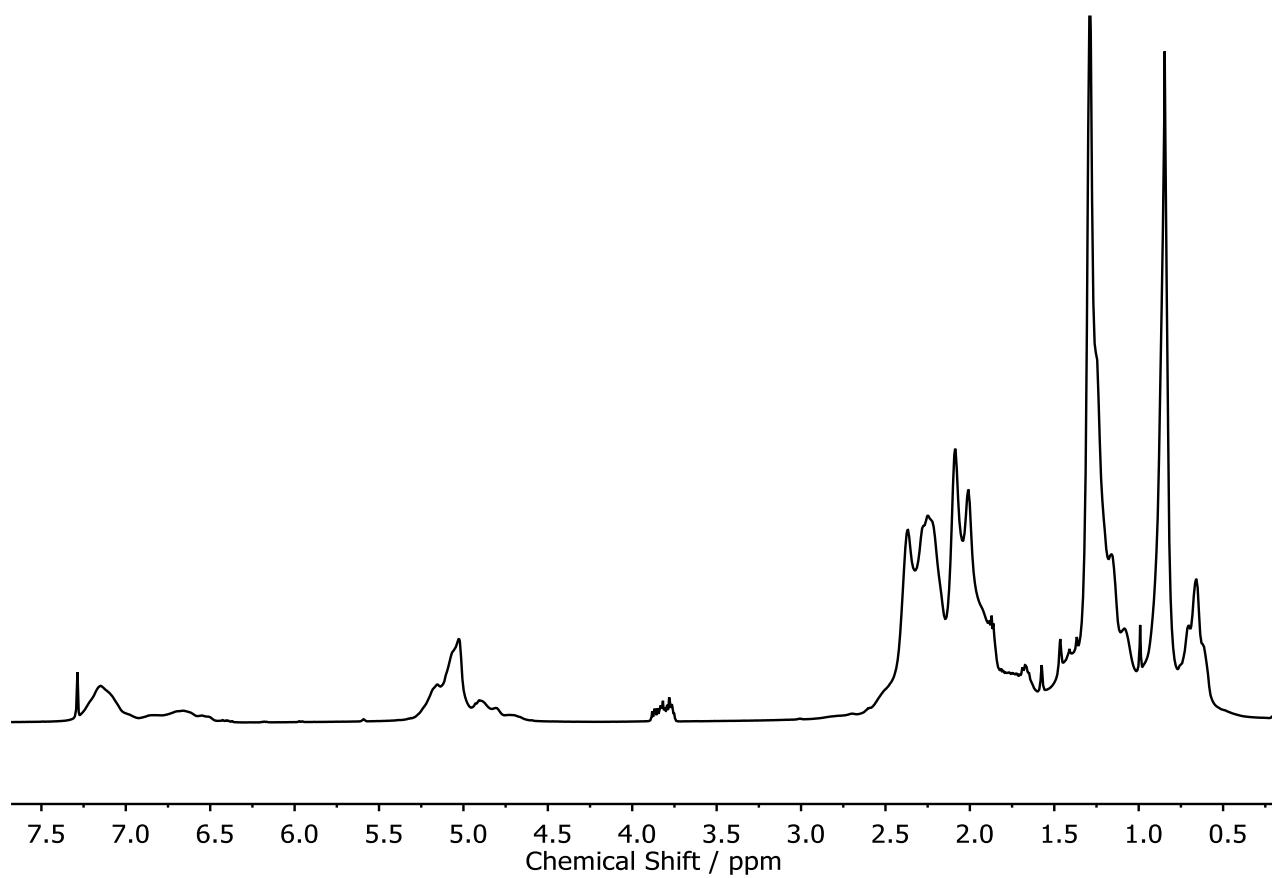


Figure S 29: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa8, obtained in cyclohexane and 10 eq. DTHFP.

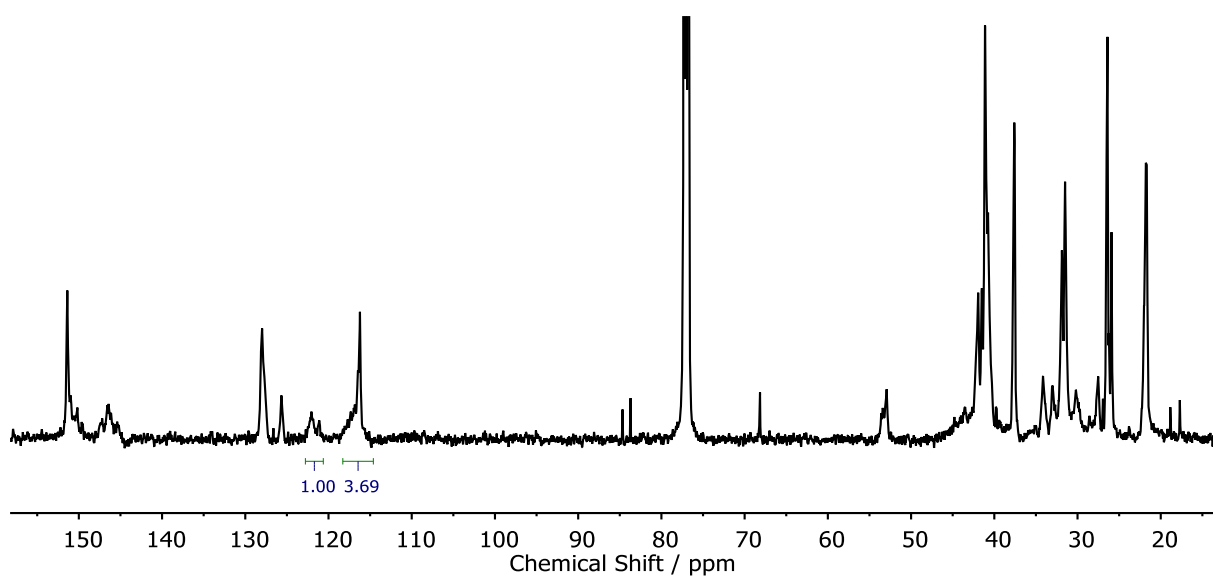


Figure S 30: ^{13}C NMR inversed-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa8, obtained in cyclohexane and 10 eq. DTHFP.

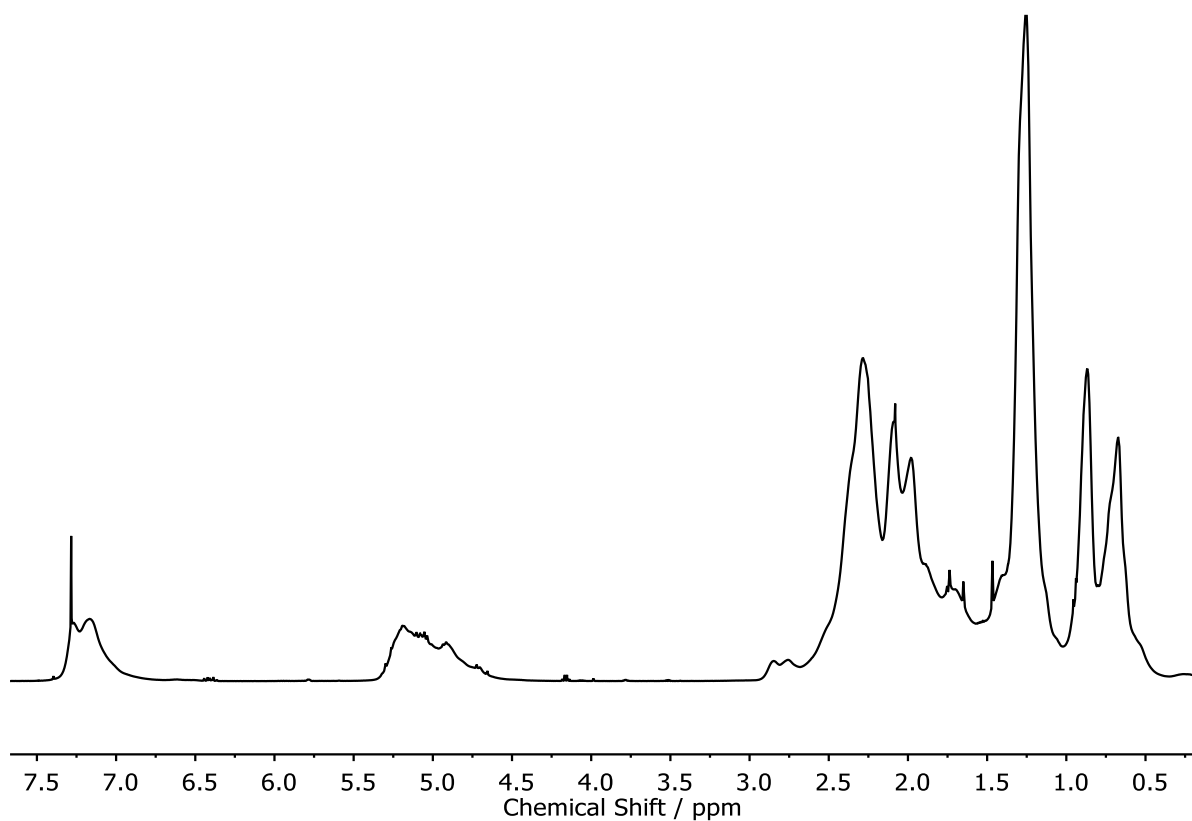


Figure S 31: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa9, obtained in cyclohexane and 10 eq. DIPIPE.

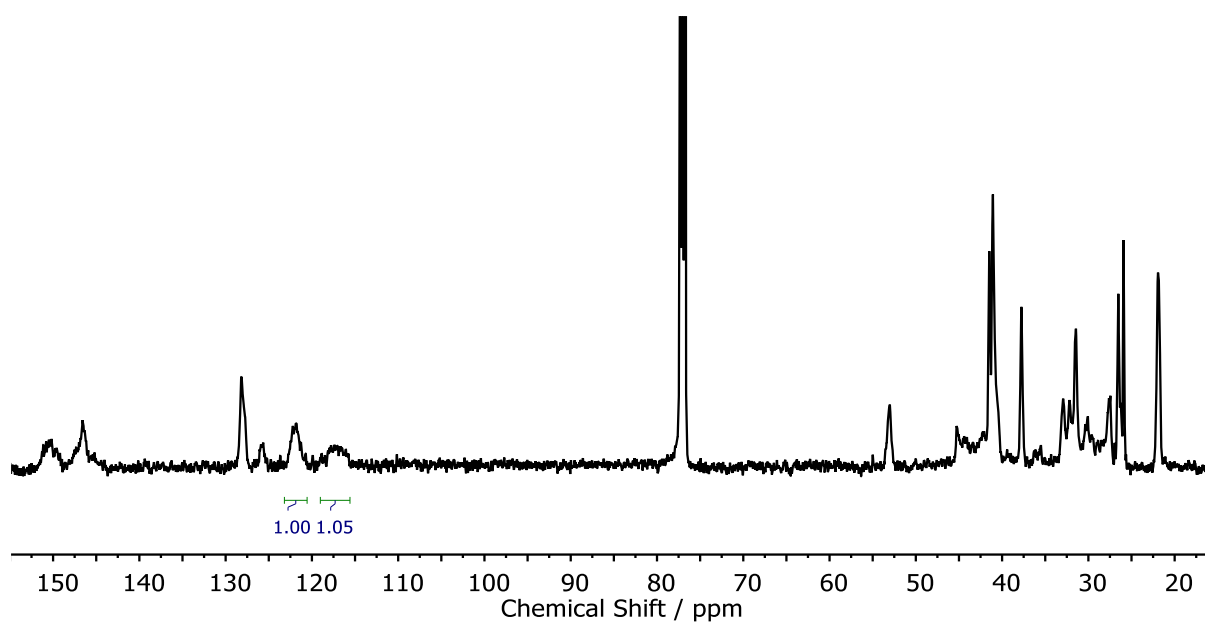


Figure S 32: ^{13}C NMR inversed-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa9, obtained in cyclohexane and 1 eq. DIPIPE.

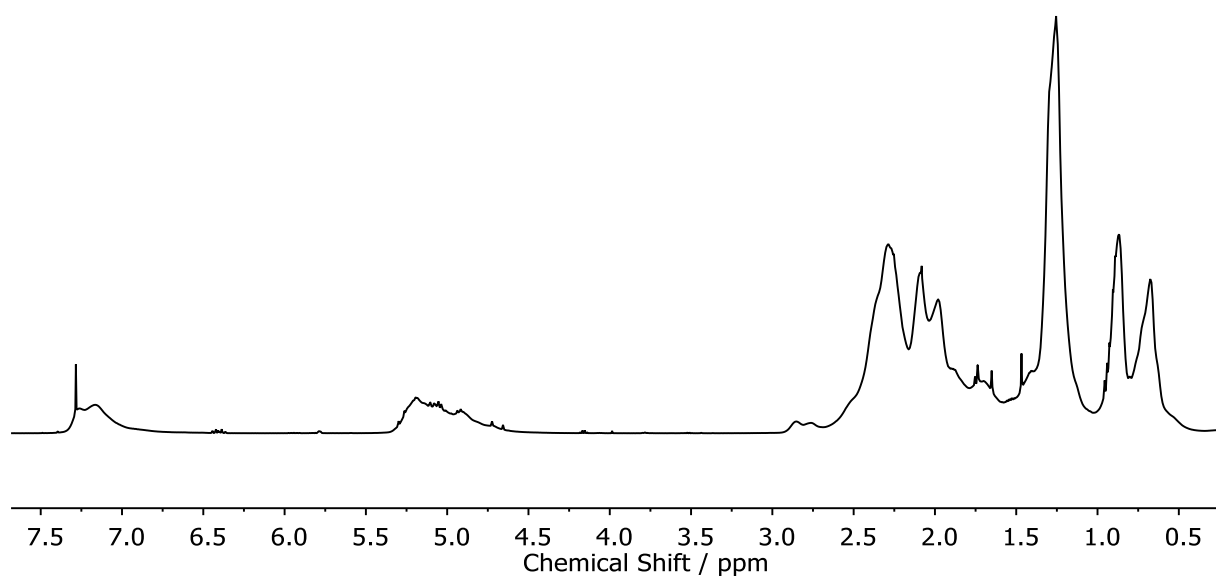


Figure S 33: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa10, obtained in cyclohexane and 10 eq. DIPIPE.

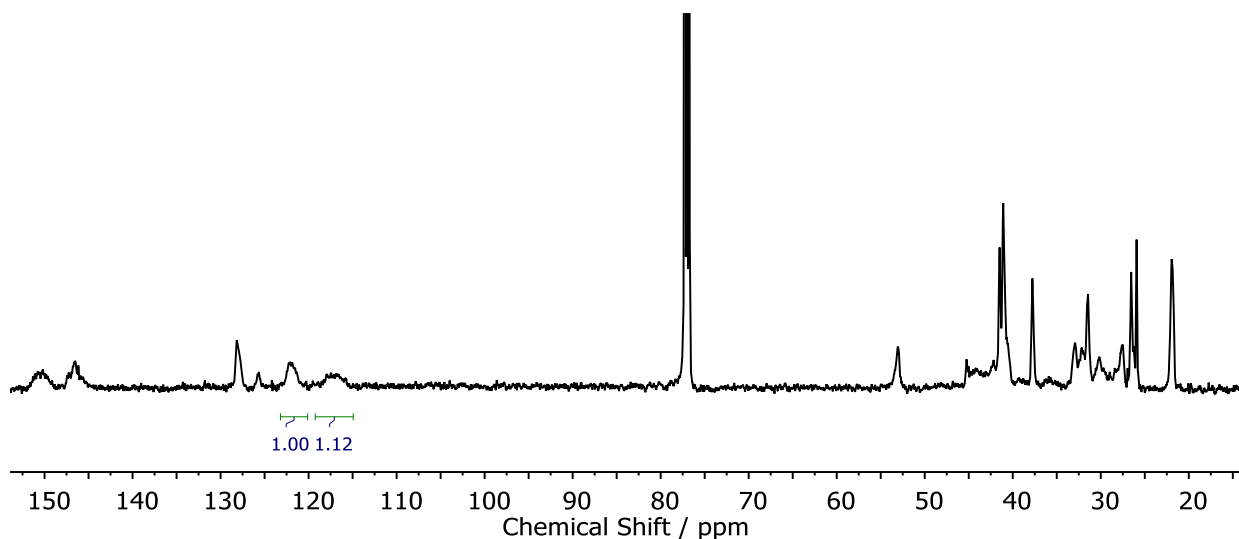


Figure S 34: ^{13}C NMR inversed-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa10, obtained in cyclohexane and 10 eq. DIPIPE.

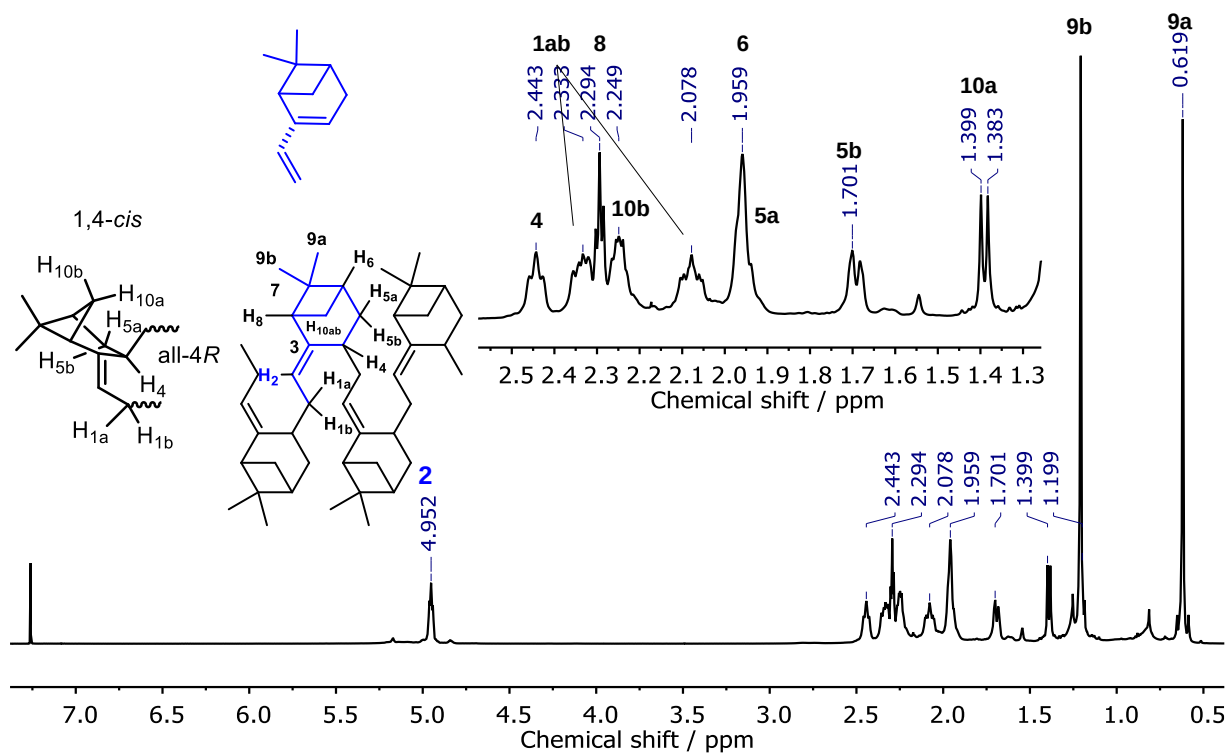


Figure S 35: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa12.

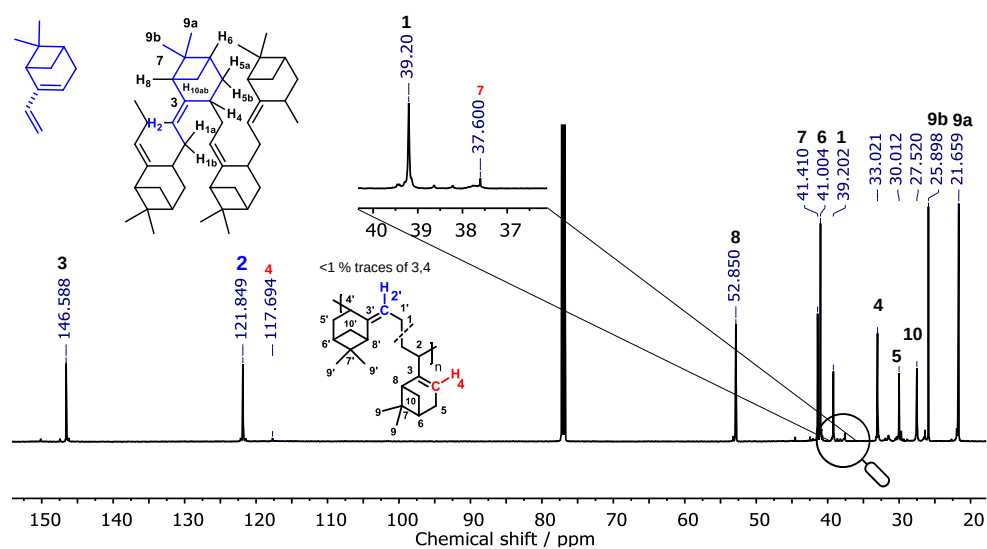


Figure S 36: ^{13}C NMR inverted-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa12.

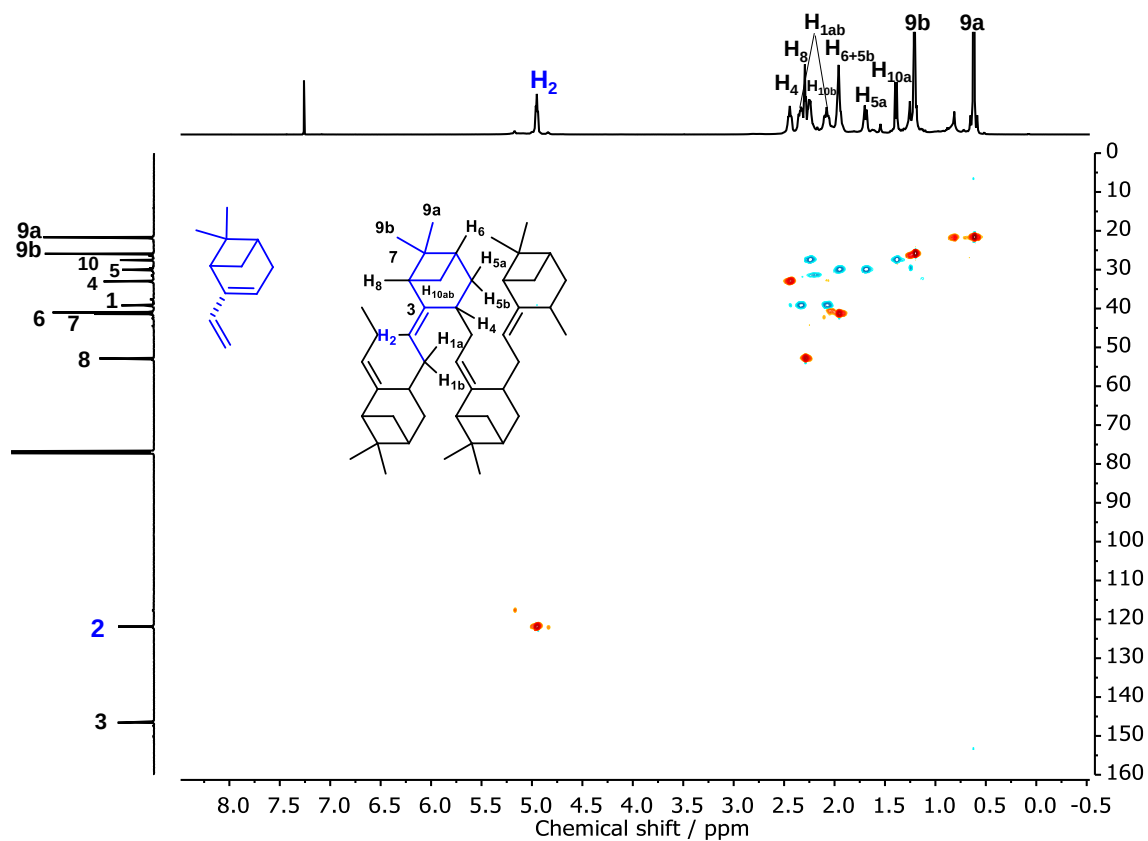


Figure S 37: HSQC NMR spectrum (125 MHz / 500 MHz, CDCl_3 , 25°C) of PNopa12.

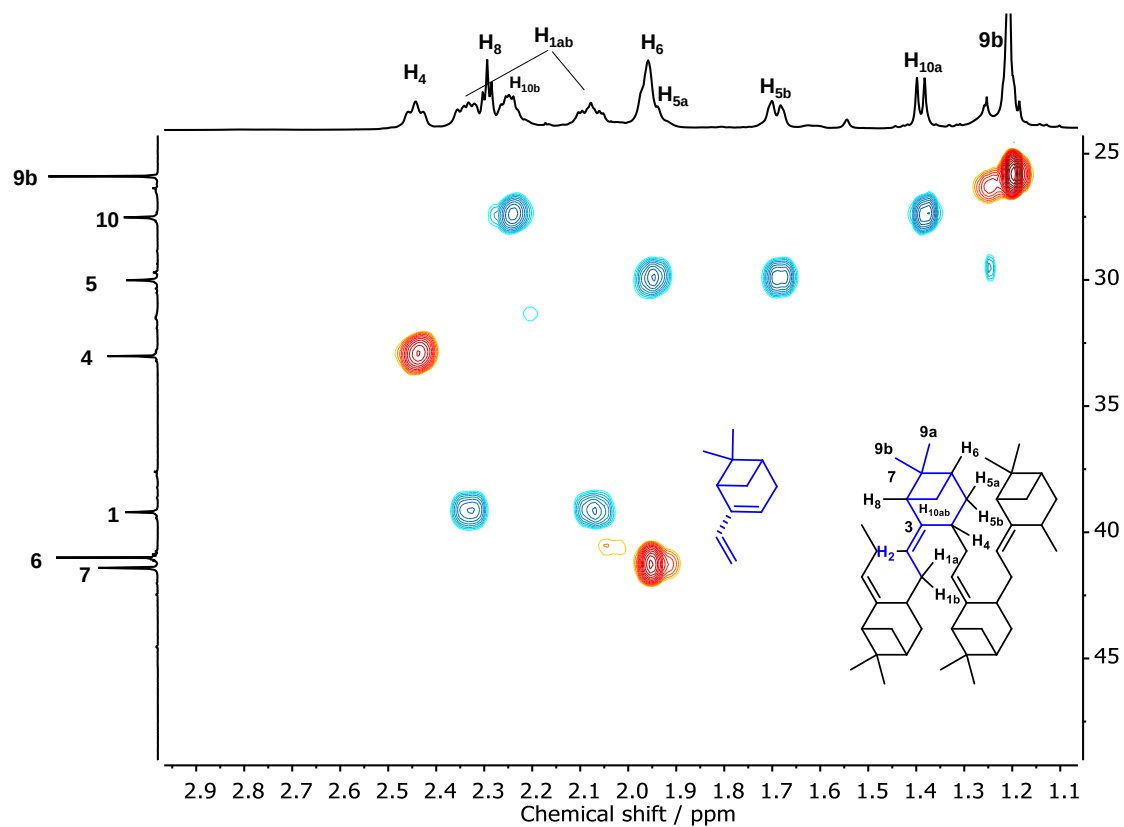


Figure S 38: HSQC NMR spectrum (125 MHz / 500 MHz, CDCl_3 , 25°C) of PNopa12.

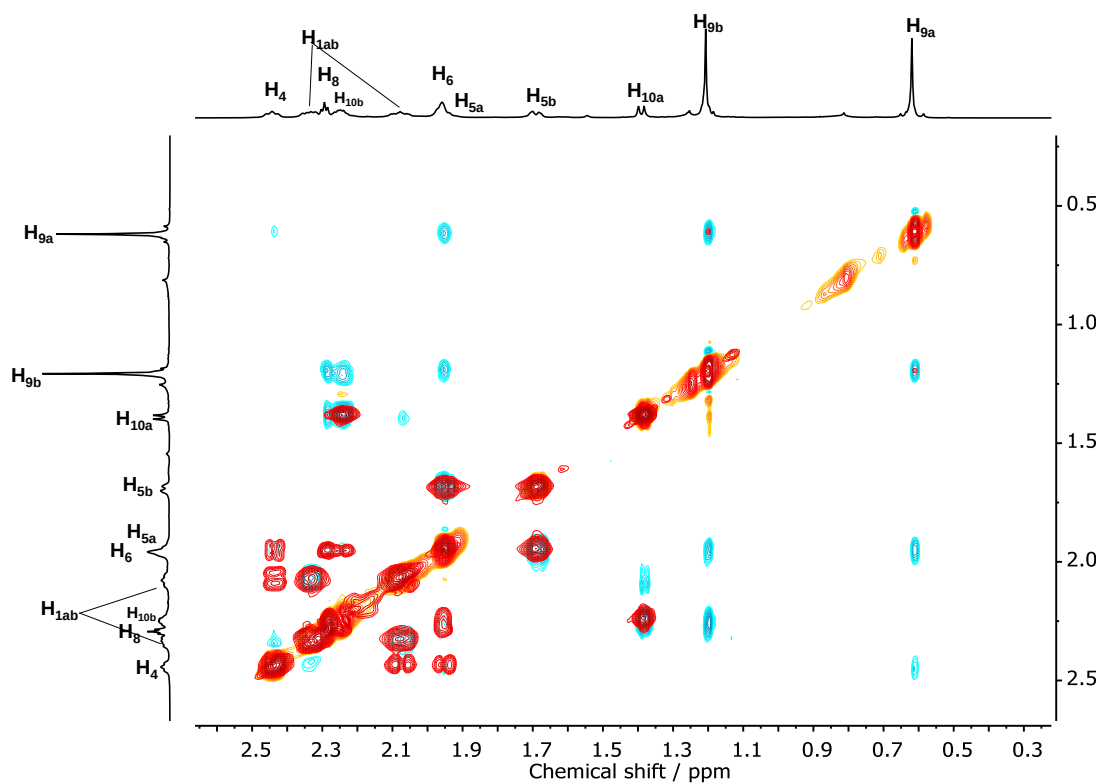


Figure S 39: ROESY (blue) /COSY (red) NMR spectrum (600 MHz, CDCl_3 , 25°C) of PNopa12.

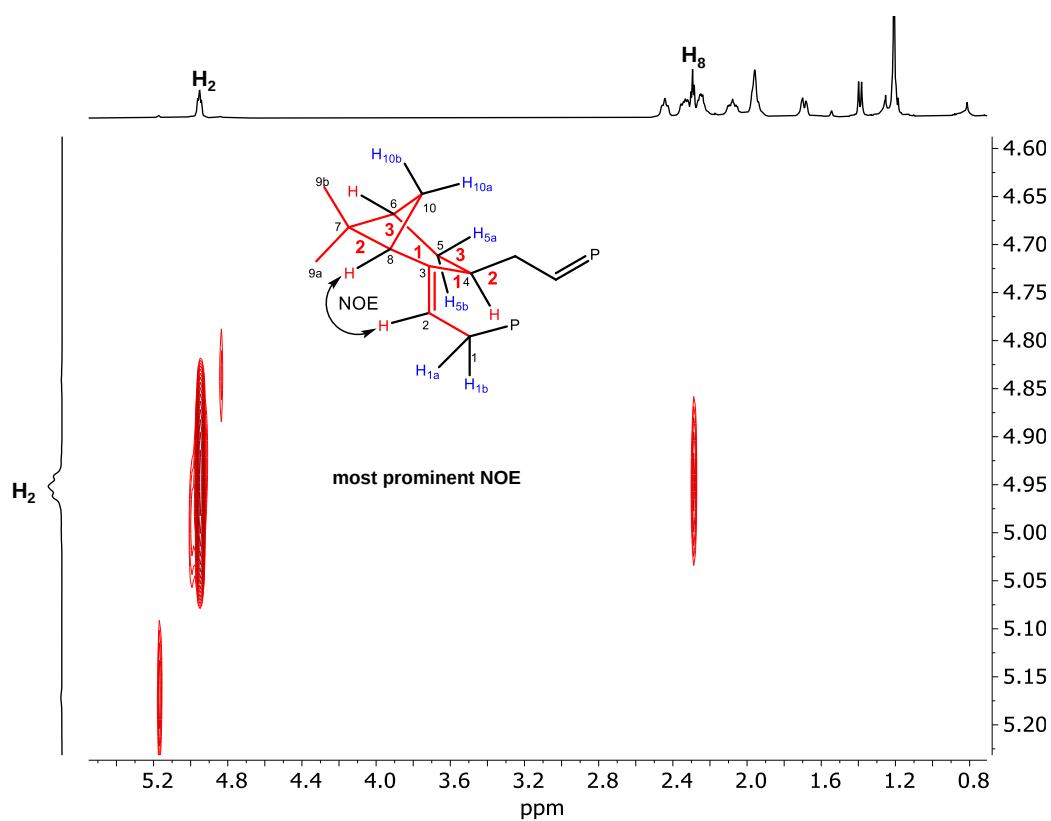


Figure S 40: NOESY NMR spectrum (600 MHz, CDCl₃, 25°C, 400 ms mixing time) of PNopa12.

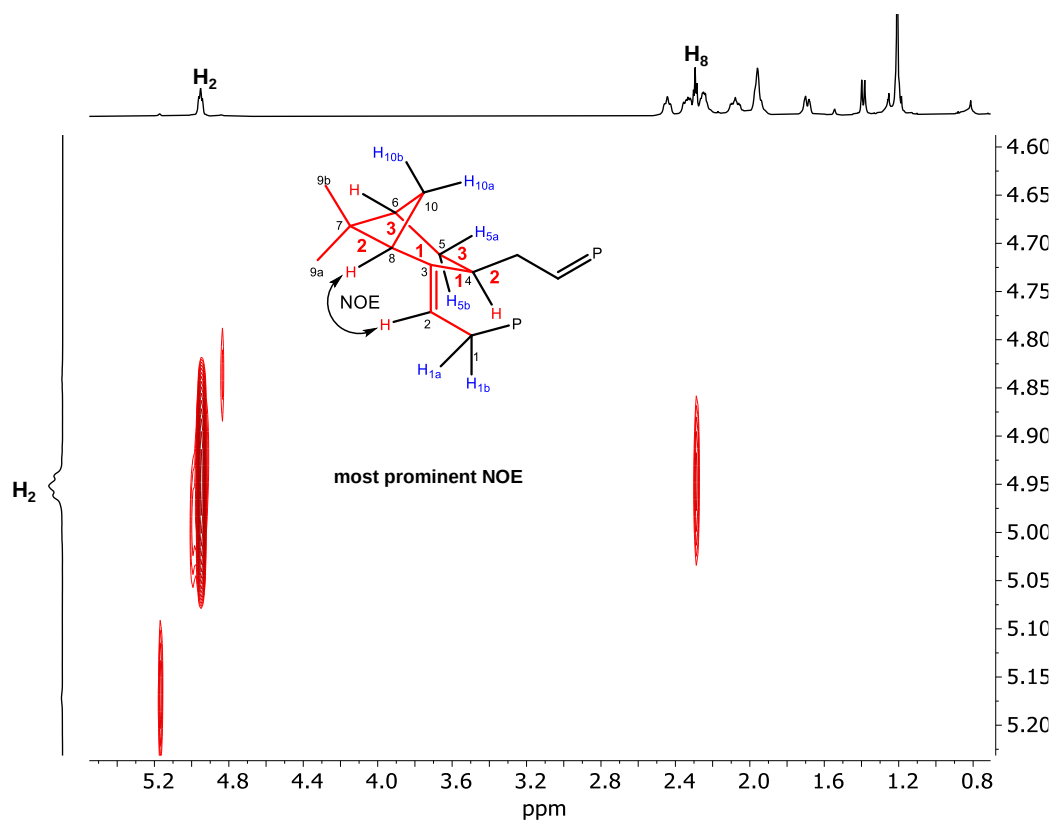


Figure S 41: ROESY NMR spectrum (600 MHz, CDCl₃, 25°C, 300 ms spinlock time) of PNopa12.

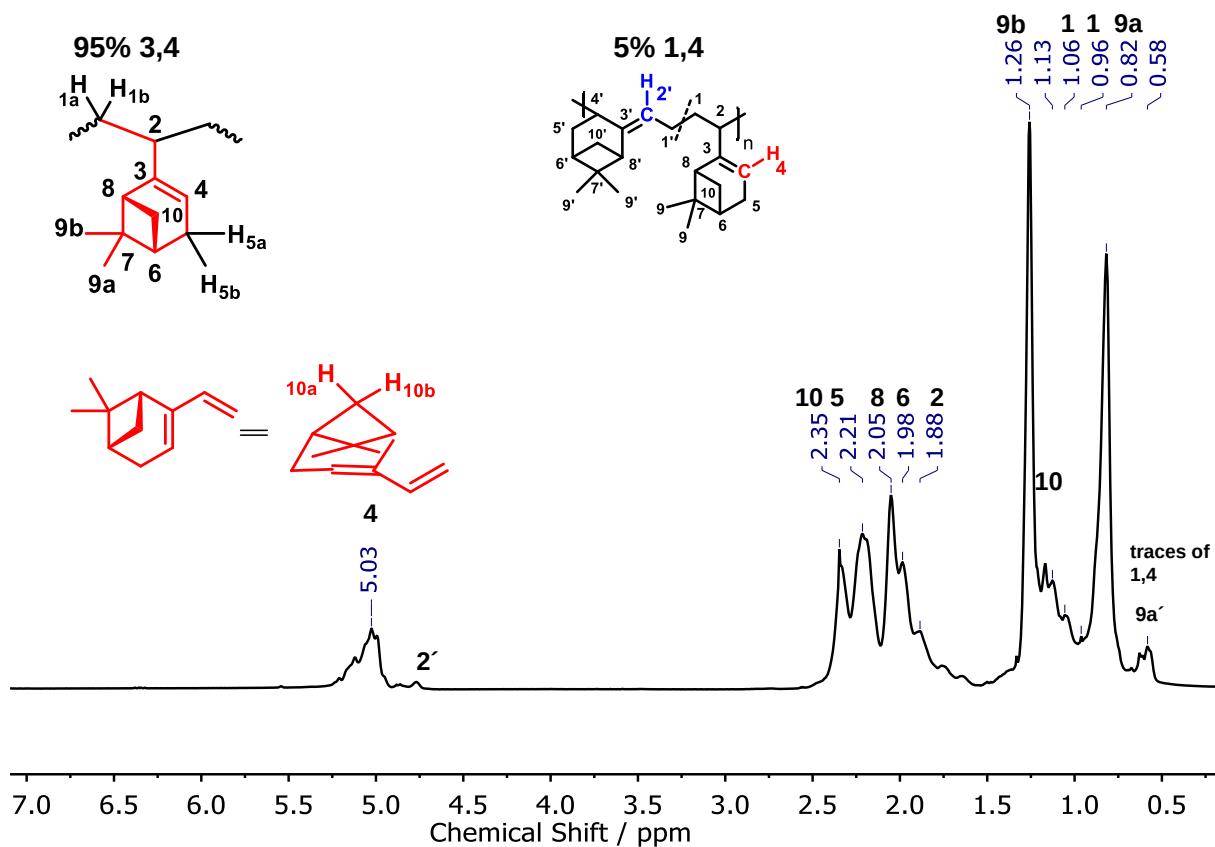
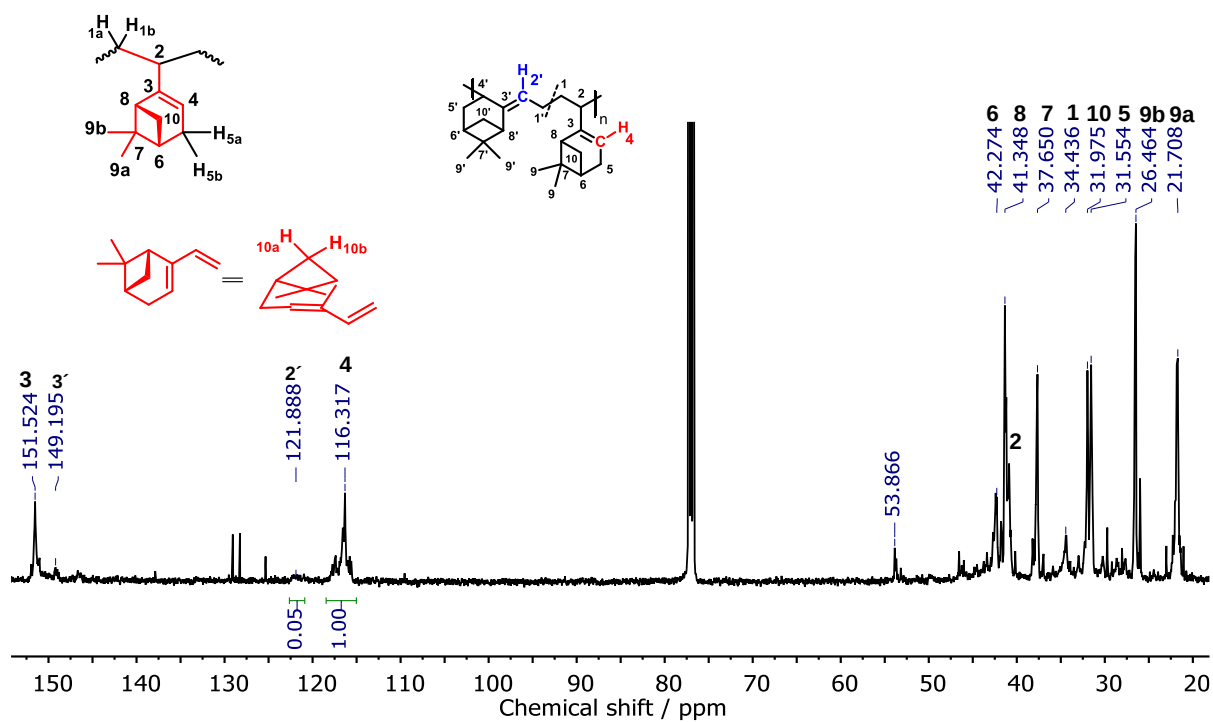


Figure S 42: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa14.**Figure S 43: ^{13}C NMR inversed-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa14.**

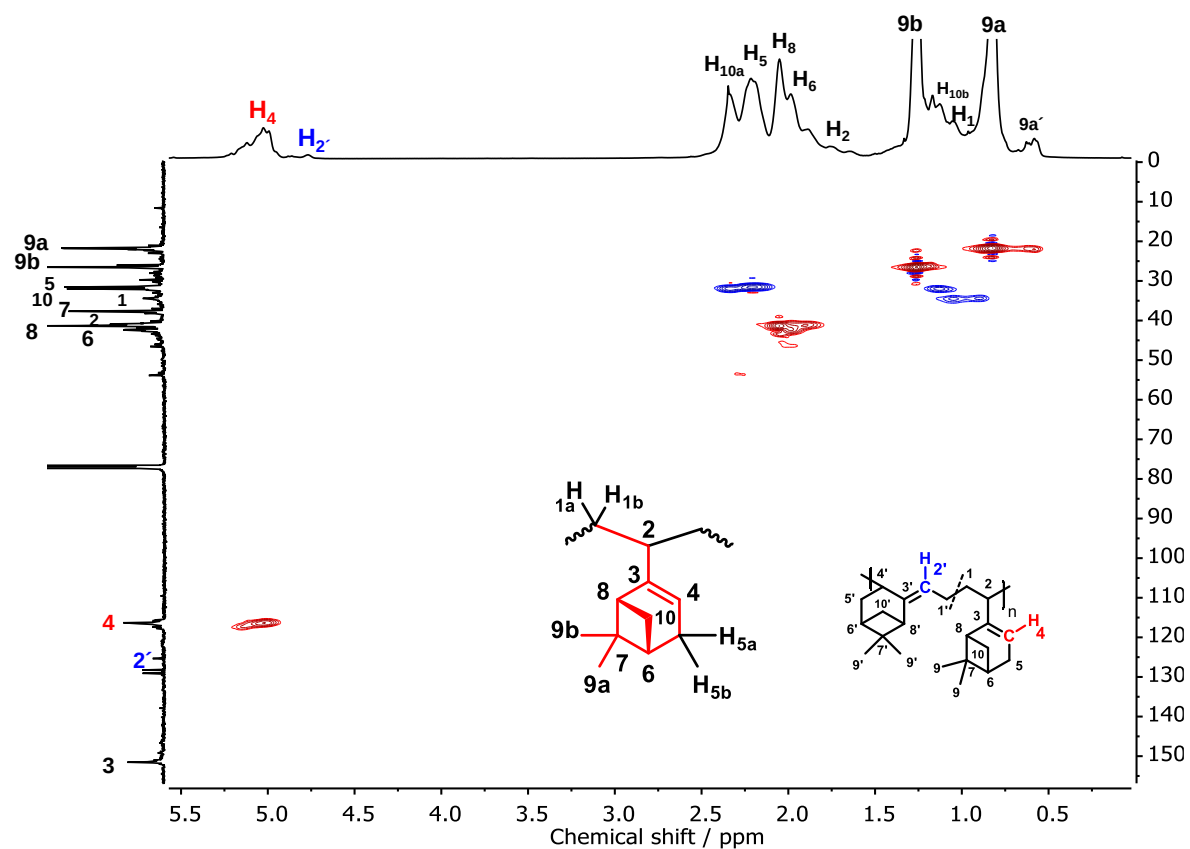


Figure S 44: HSQC NMR spectrum (125 MHz / 500 MHz, CDCl_3 , 25°C) of PNopa14.

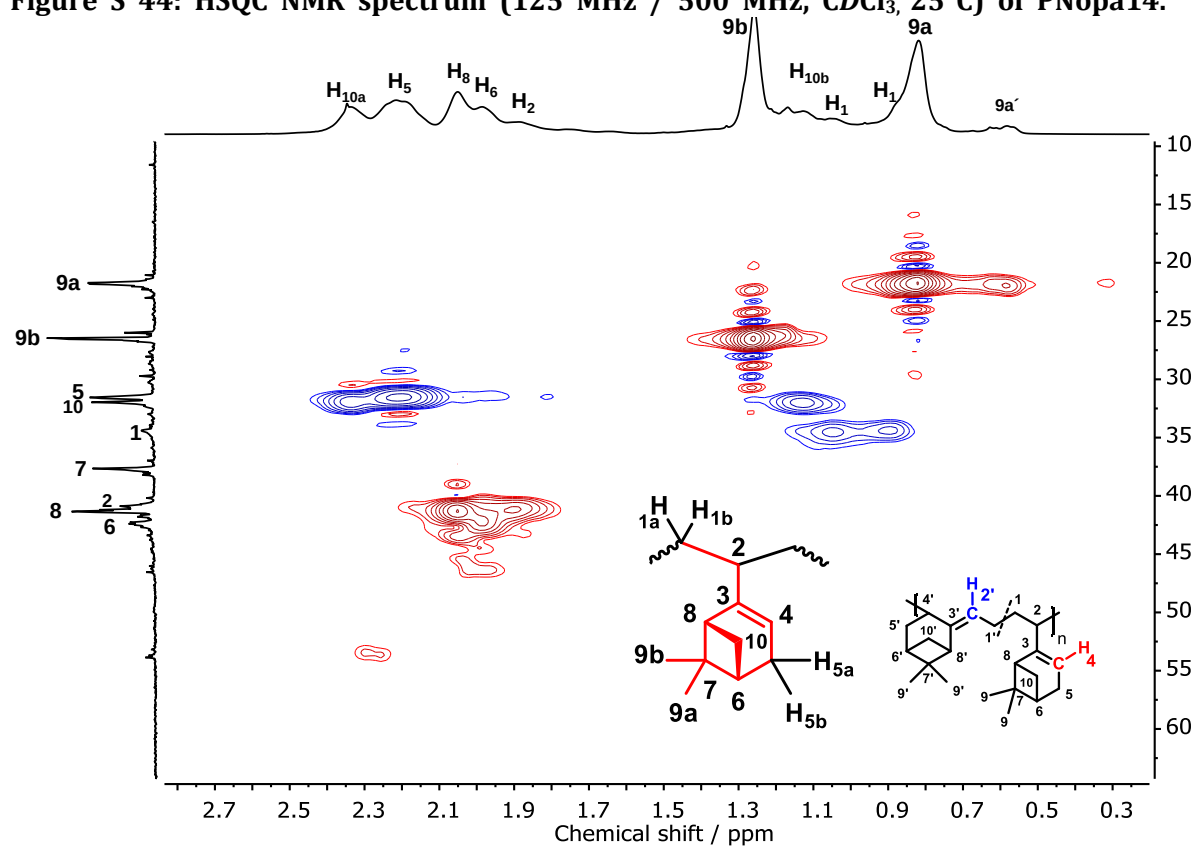
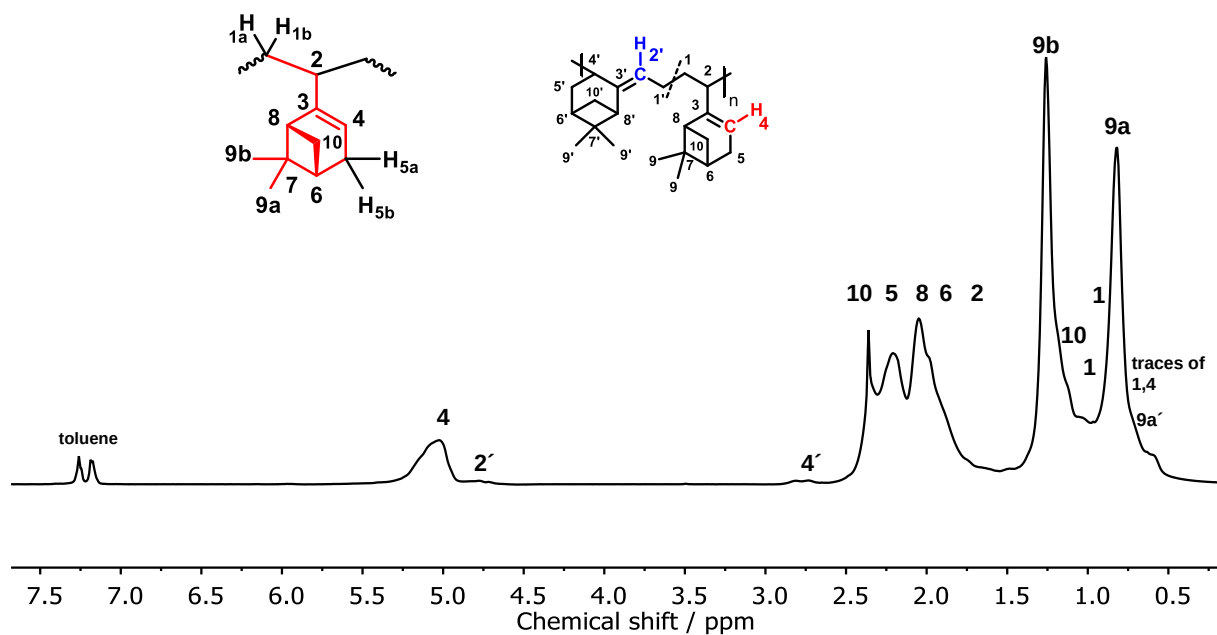
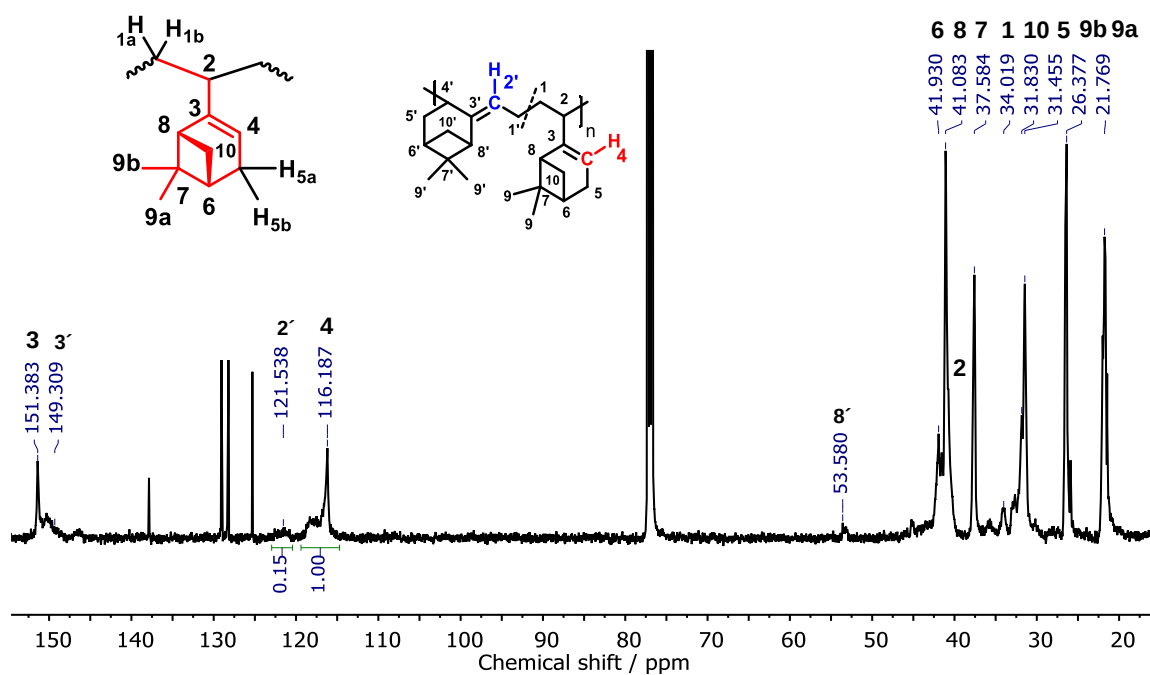


Figure S 45: HSQC NMR spectrum (125 MHz / 500 MHz, CDCl_3 , 25°C) of PNopa14.

Figure S 46: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa15.Figure S 47: ^{13}C NMR inverted-gated spectrum (125 MHz, CDCl_3 , 25°C) of PNopa15.

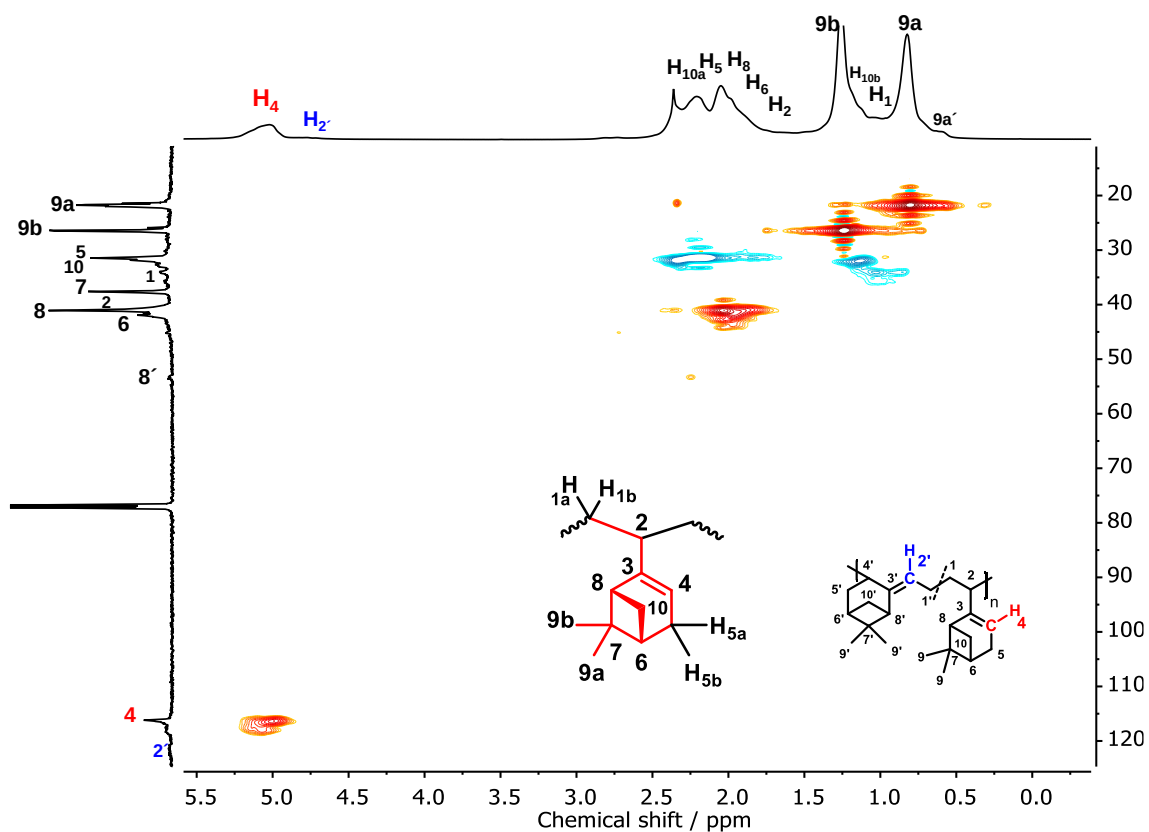


Figure S 48: HSQC NMR spectrum (125 MHz / 500 MHz, $CDCl_3$, 25°C) of PNopa15.

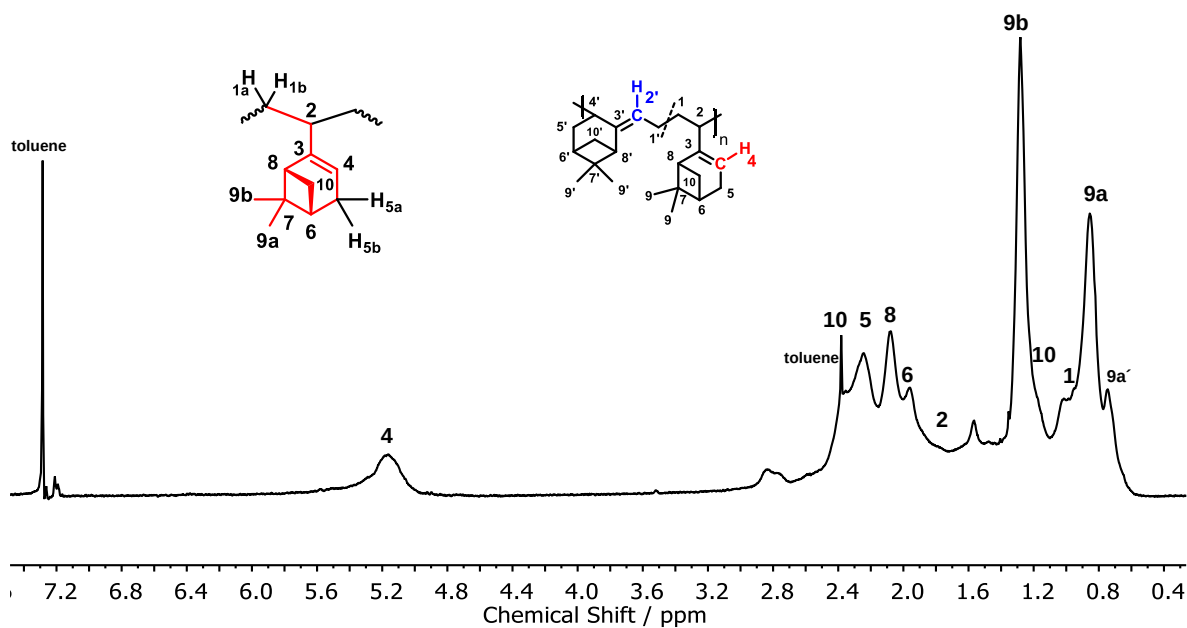


Figure S 49: 1H NMR spectrum (500 MHz, $CDCl_3$, 25°C) of PNopa16.

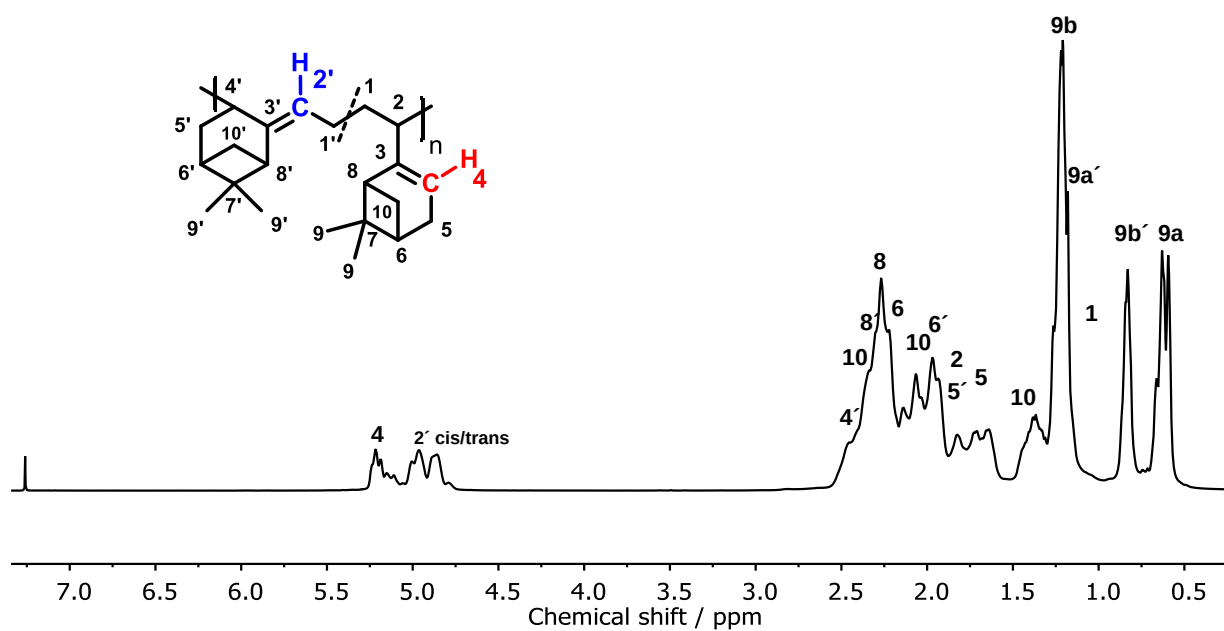


Figure S 50: ^1H NMR spectrum (600 MHz, CDCl_3 , 25°C) of PNopa17.

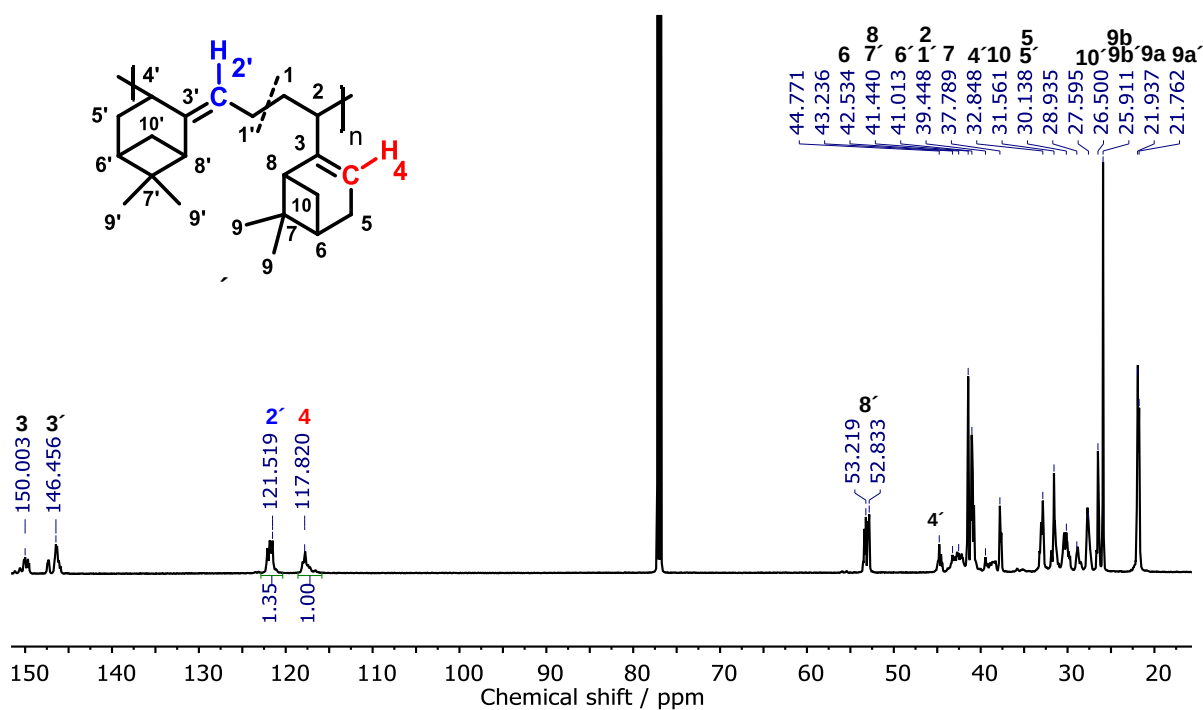
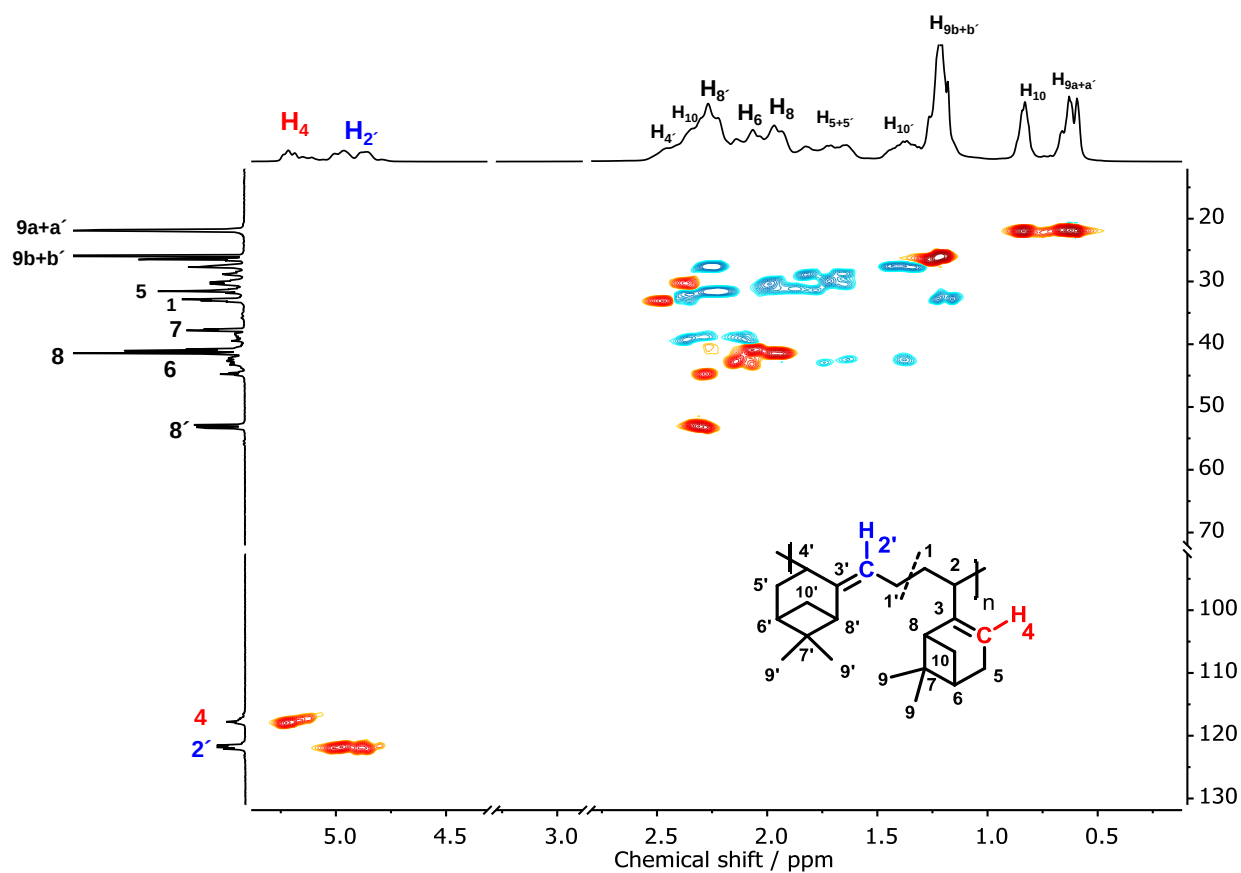
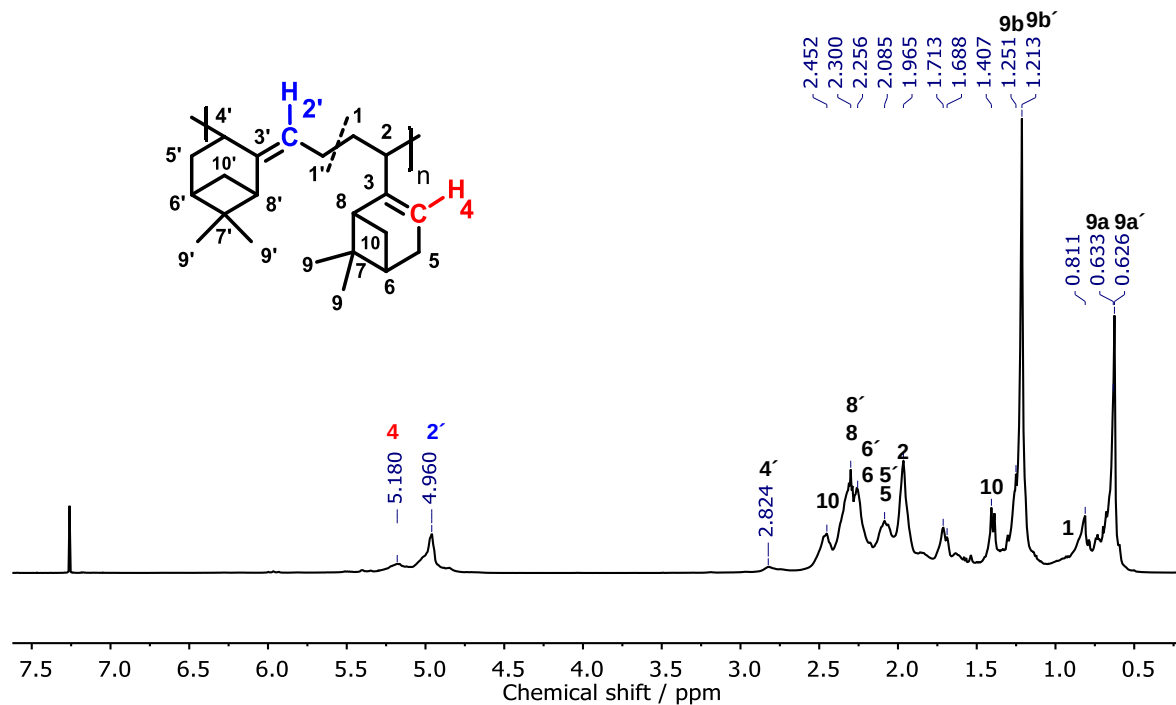
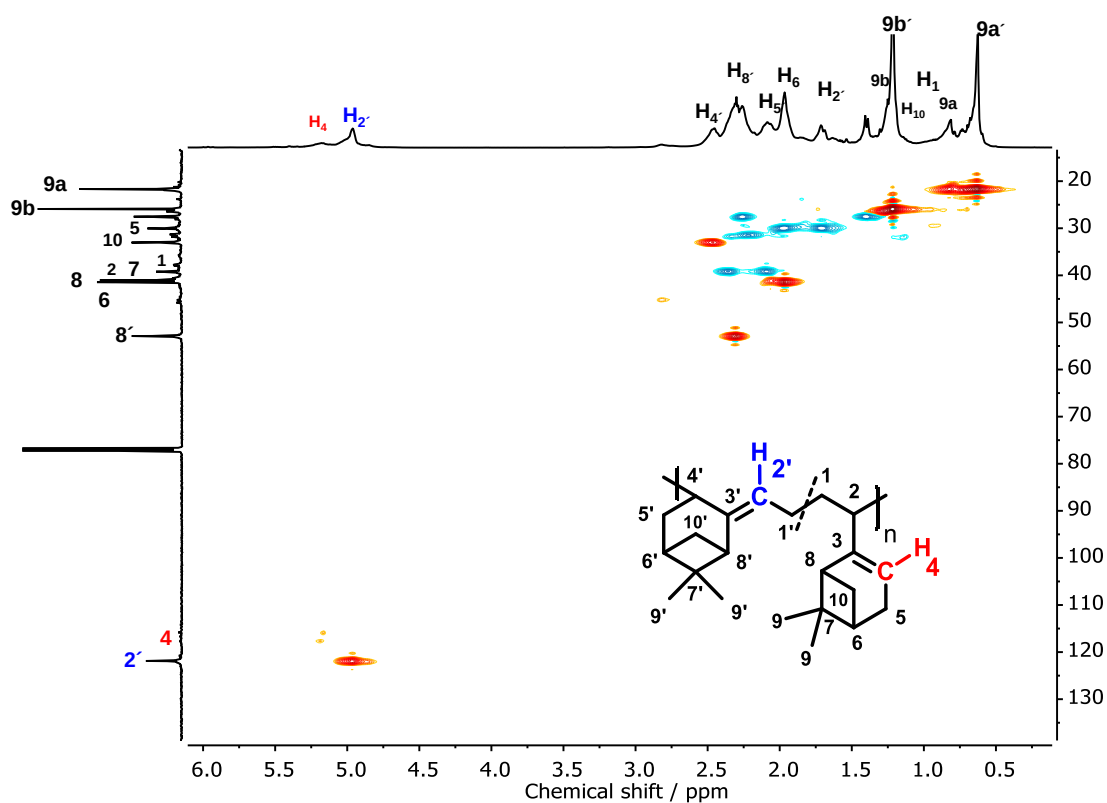
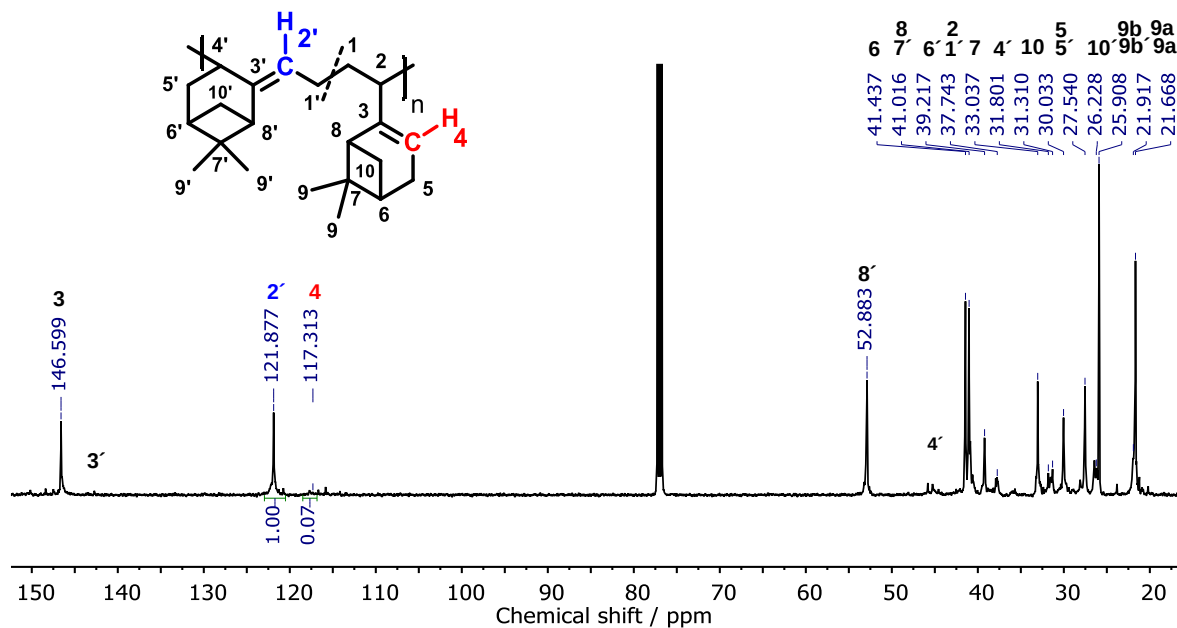


Figure S 51: ^{13}C NMR inverted-gated spectrum (150 MHz, CDCl_3 , 25°C) of PNopa17.

Figure S 52: HSQC NMR spectrum (150 MHz / 600 MHz, CDCl_3 , 25°C) of PNopa17.Figure S 53: ^1H NMR spectrum (500 MHz, CDCl_3 , 25°C) of PNopa18.



4.2.6.1.5 MALDI-ToF MS

MALDI-ToF MS revealed the existence of masses of 148.24 g/mol, i.e., the molar mass of nopadiene. Due to the initiation with oligostyrenyl-Li, masses of 104.15 g/mol were detected in combination with nopadiene as well. Higher masses of polynopadiene suffer from mass discrimination effects.

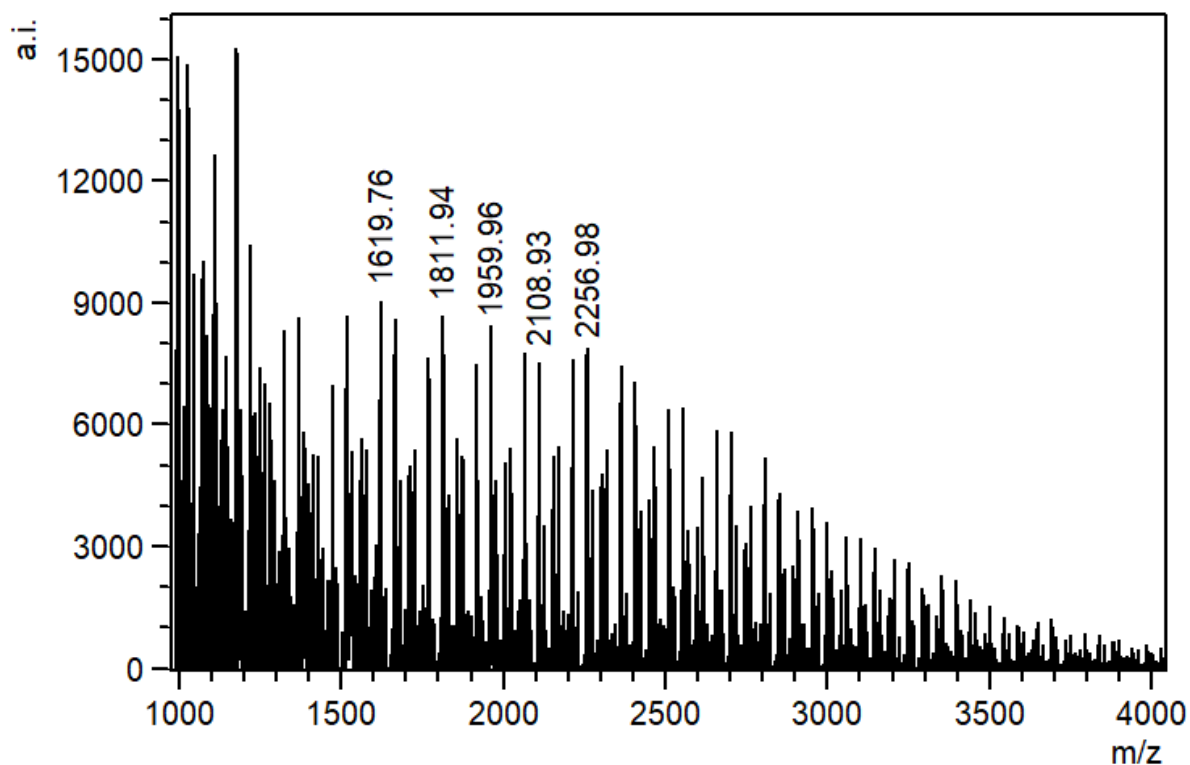


Figure S 56: MALDI ToF MS spectrum of the homopolymer of nopadiene PNopa_{5k}.

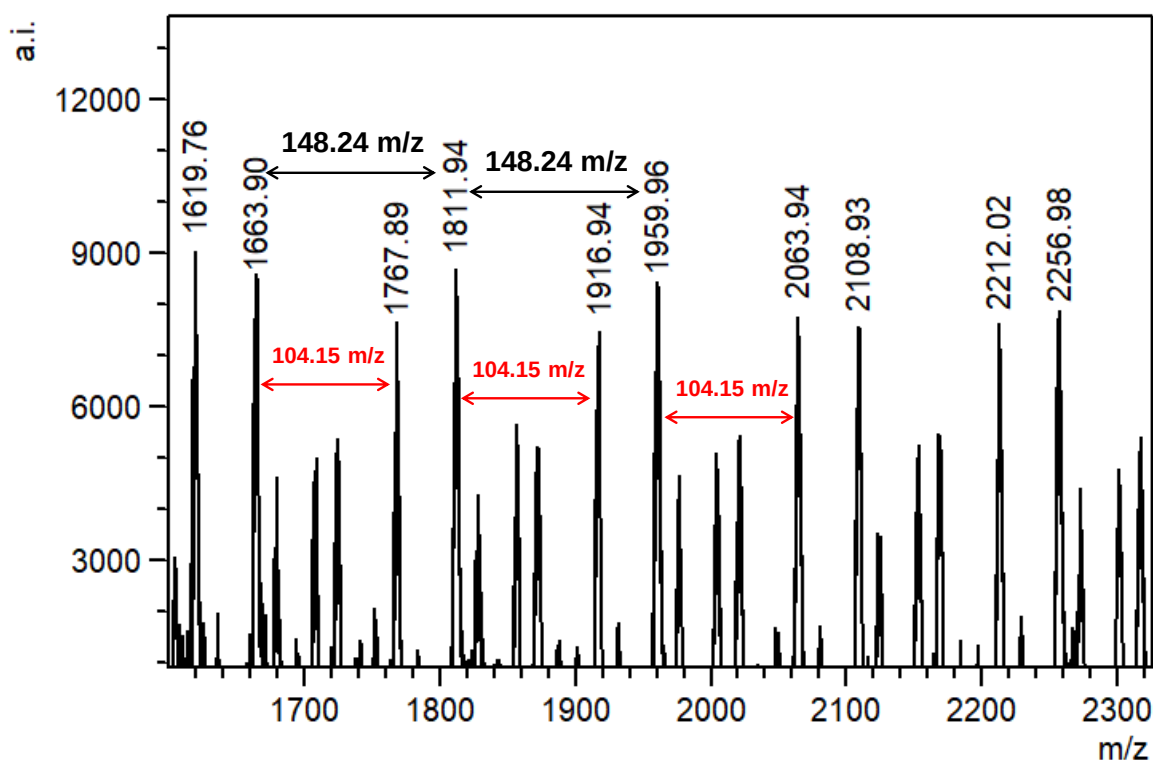


Figure S 57: Zoom-in of MALDI ToF MS spectrum of the homopolymer of nopadiene PNopa_{5k}.

4.2.6.1.6 Kinetic studies of statistical nopadiene copolymerization

The monomer sequence distribution of statistical copolymers of nopadiene and myrcene was investigated by ^1H NMR online kinetic measurements. For the kinetics measurements, 0.6 mL of dried cyclohexane- d_{12} was used as a solvent in conventional NMR tubes with rubber septa. The monomers ($[\text{M}]_0 = (3.5\text{--}7.5) \times 10^{-4}$ mol/ mL, typically 20–30 mg of each monomer) were added in a 50/50 molar ratio under exclusion of air and humidity in a glovebox. A ^1H NMR spectrum of the solution was measured prior to the initiation step. The polymerization was initiated with *sec*-BuLi solution, and the NMR tube was vigorously shaken and directly placed in the NMR sampler.

Copolymerization of styrene and myrcene with nopadiene were investigated via *online* ^1H NMR kinetic studies. For the calculation of the reactivity ratios, the Jaacks method was employed. All methods show tapered structures with comparable

reactivity ratios. The diminishing integrals of myrcene and nopadiene are shown Figure S58. Due to the overlapping signals in the region of 6.19-6.27 ppm of myrcene and nopadiene, the integral H_1 is calculated by the difference between the sum of the integral of H_1 and H_2 (H_{total}), subtracted by the integral of H_4 ($H_1 = H_{\text{total}} - H_4$). H_1 and H_4 was then used for the calculation of the reactivity ratios.

The diminishing integrals of styrene are at 5.55-5.60 ppm and of nopadiene at 6.19-6.27 ppm.

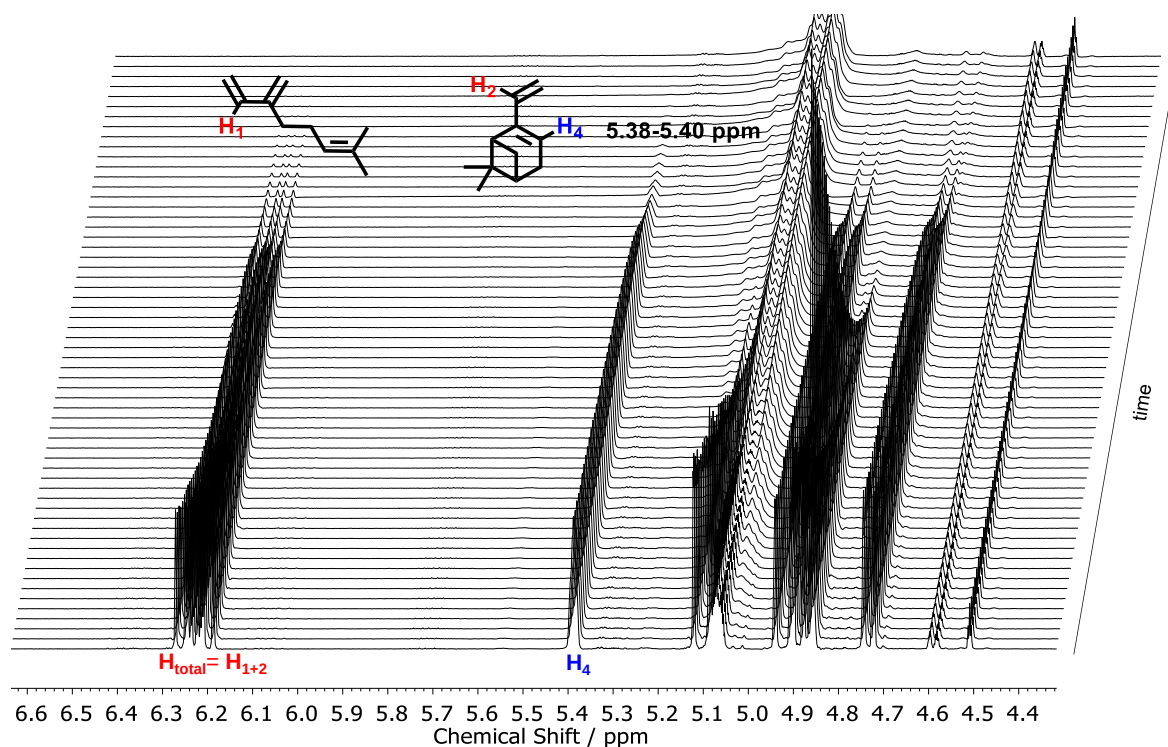


Figure S 58: Stacked ^1H NMR spectra (500 MHz, C_6D_{12} , 25°C) of the copolymerization of myrcene and nopadiene.

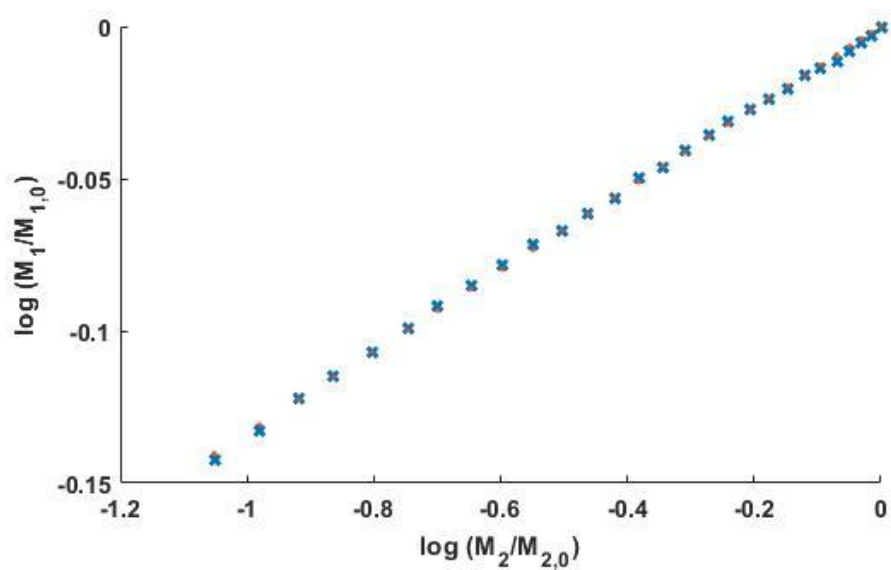


Figure S 59: Jaacks fit of the copolymerization of myrcene and nopadiene.

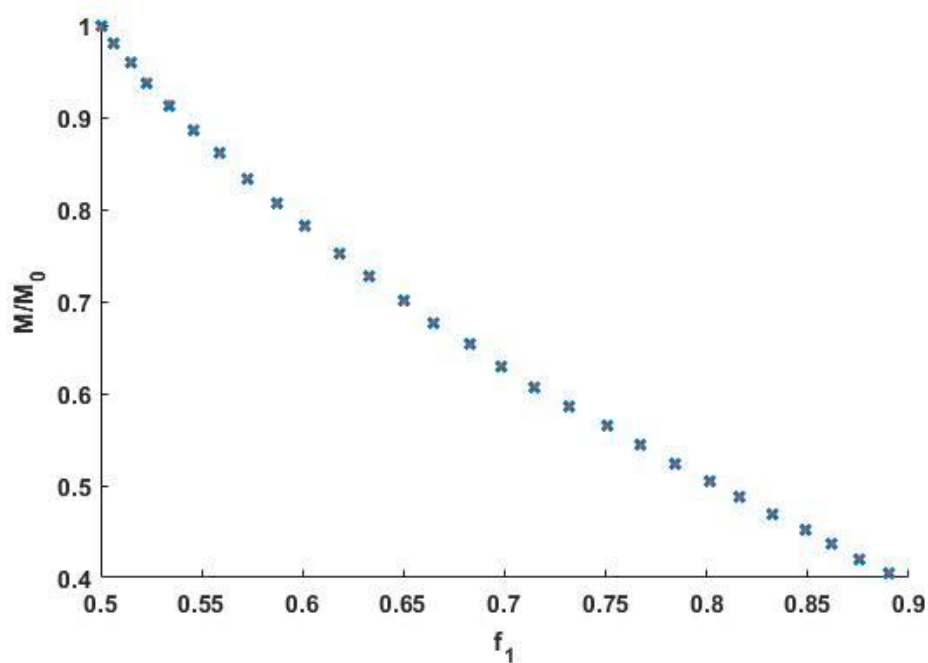


Figure S 60: Meyer-Lowry fit of the copolymerization of myrcene and nopadiene.

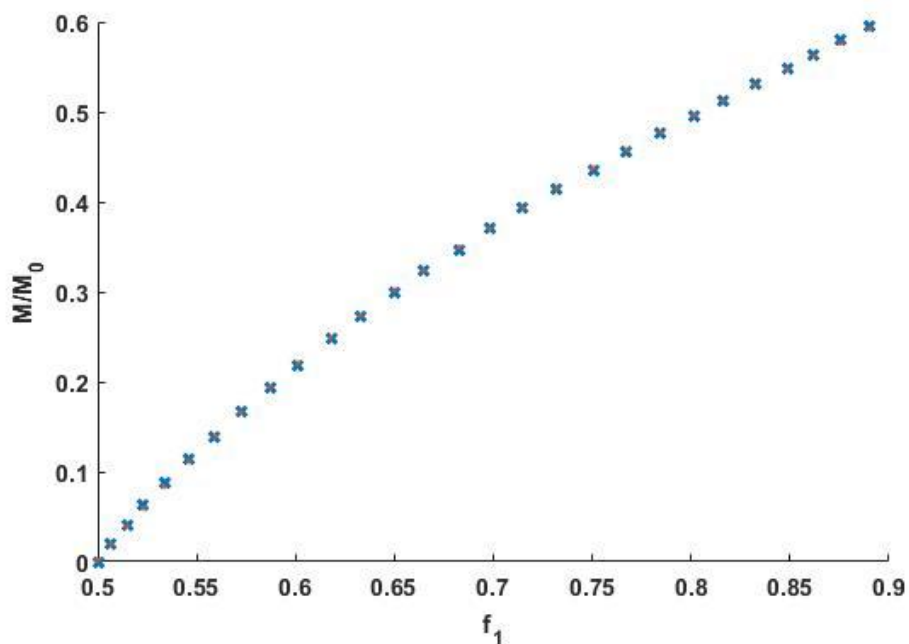


Figure S 61: Ideal integrated (Meyer-Lowry ideal) fit of the copolymerization of myrcene and nopadiene.

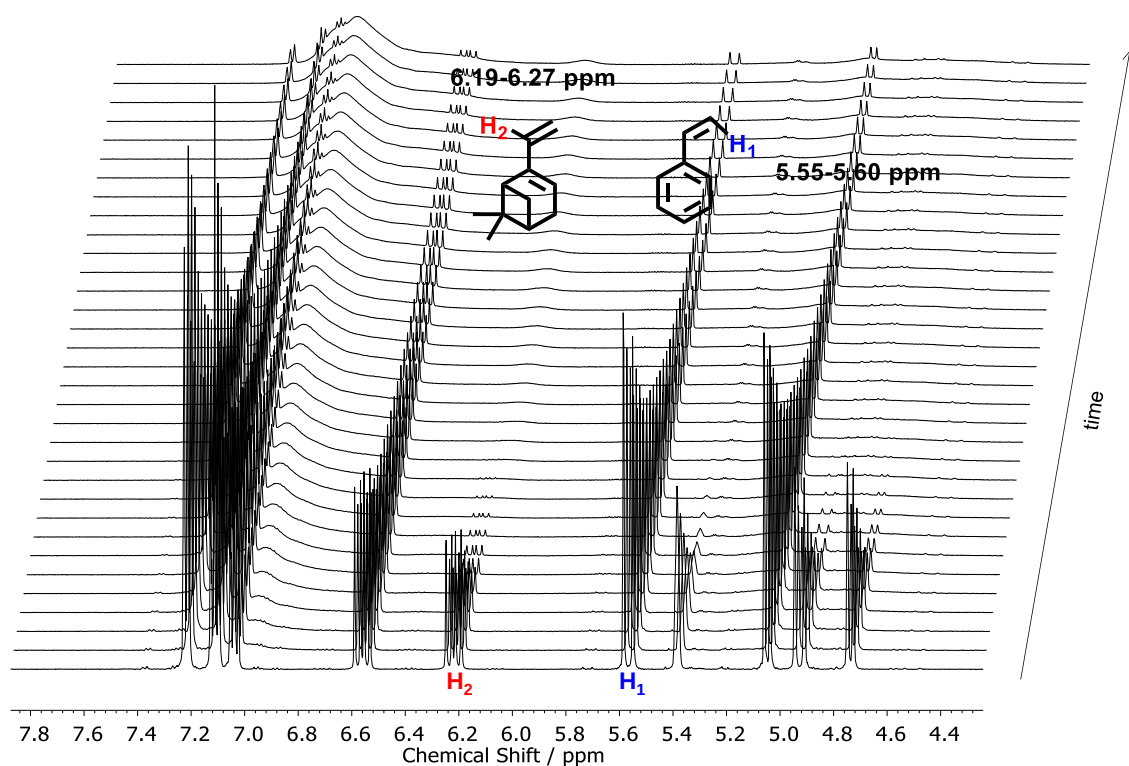


Figure S 62: Stacked ^1H NMR spectra (500 MHz, C_6D_{12} , 25°C) of the copolymerization of styrene and nopadiene.

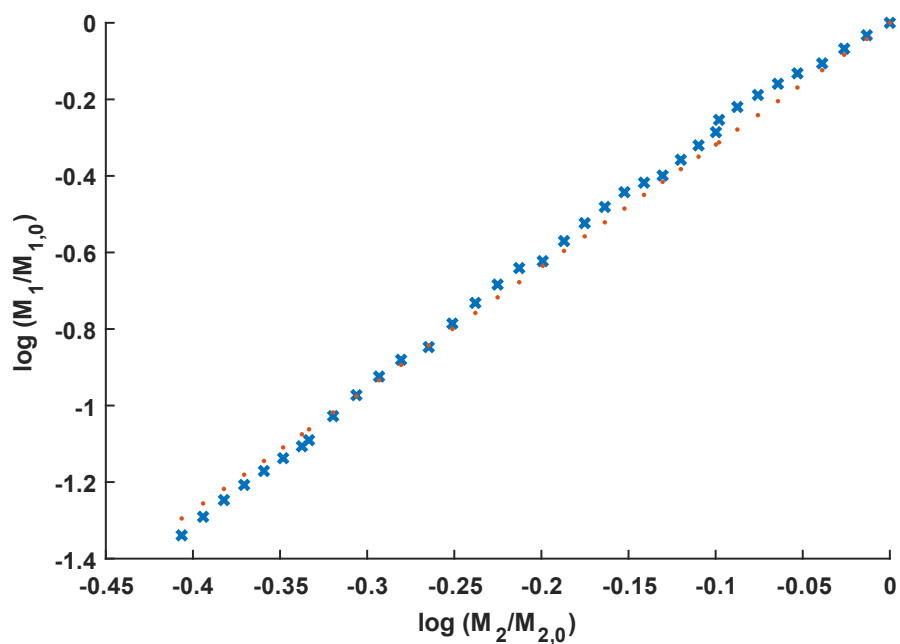


Figure S 63: Jaacks fit of the copolymerization of styrene and nopadiene.

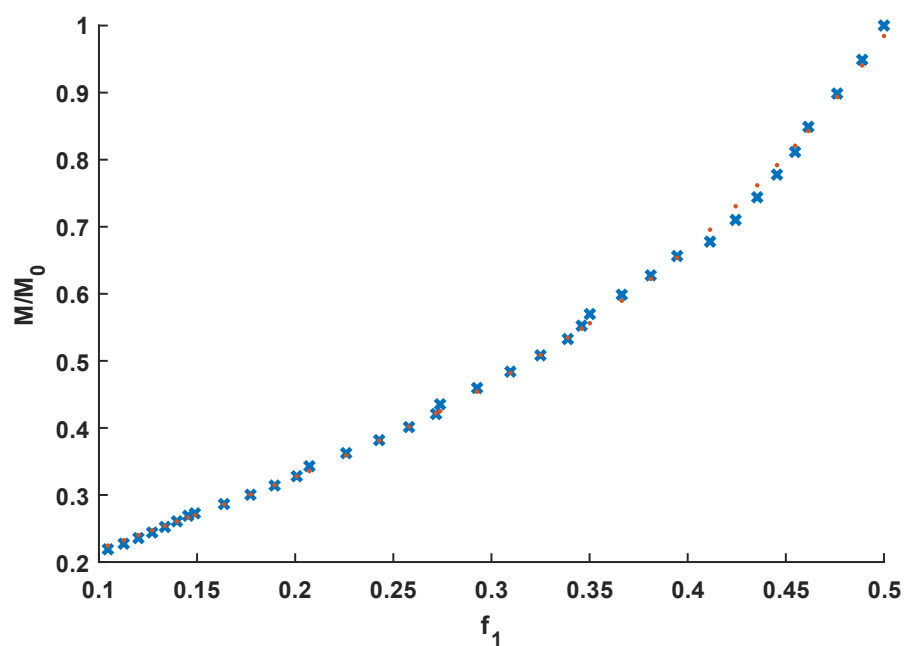


Figure S 64: Meyer-Lowry fit of the copolymerization of styrene and nopadiene.

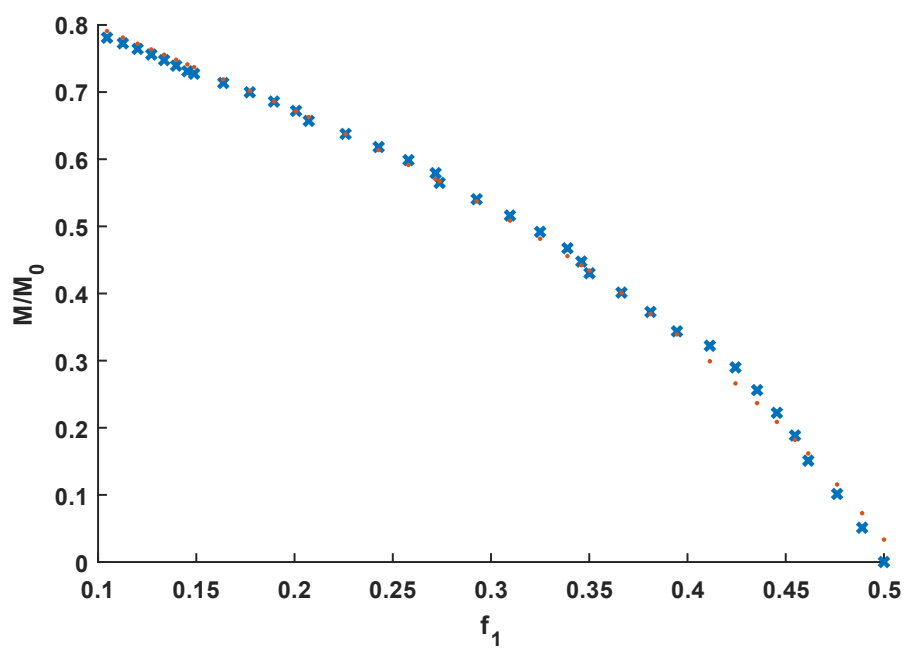


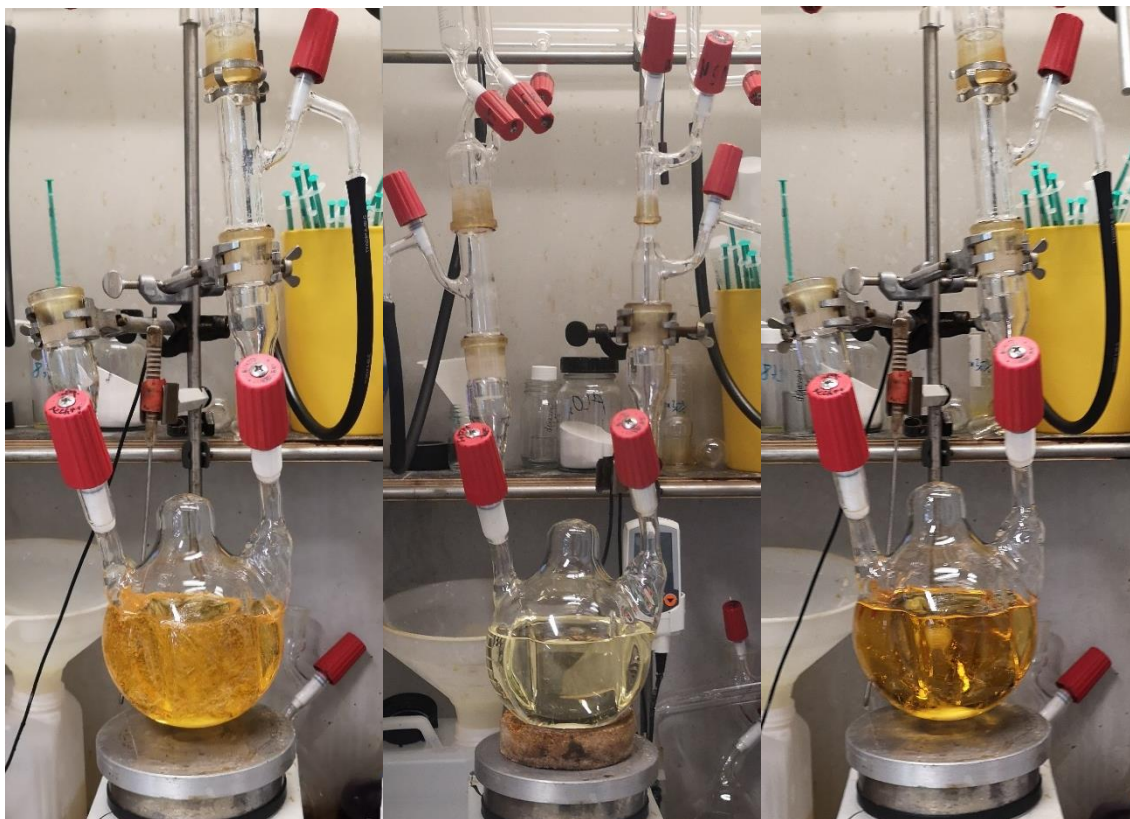
Figure S 65: Ideal integrated (Meyer-Lowry ideal) fit of the copolymerization of styrene and nopadiene.

4.2.6.1.7 General procedures for the synthesis of statistical and block copolymers of nopadiene with myrcene and styrene

Statistical copolymerization of nopadiene with myrcene and styrene. The monomer mixture of nopadiene with myrcene/styrene was dried over CaH_2 and trioctylaluminum. All monomers and solvents were degassed by three freeze-thaw cycles prior to use. The monomer mixture was distilled into a graduated ampule equipped with a teflon stop cock. Cyclohexane was distilled directly into the all-glass reactor under reduced pressure. The polymerization was initiated by the addition of sec-BuLi via syringe. The polymerizations were carried out at 25 °C and argon atmosphere.

Block copolymerization of nopadiene with myrcene and styrene. A dual series of triblock copolymers with molecular weights of 100 and 200 kg/mol has been prepared, changing the ratio of hard to soft phase in the range of 60-75 mol% myrcene (40-25 mol% nopadiene, respectively). Nopadiene and myrcene were dried over CaH_2 and trioctylaluminum. Cyclohexane was dried as described before. All monomers and solvents were degassed by three freeze-thaw cycles prior to use. Herein we provide an exemplary description of the block copolymer synthesis. Cyclohexane (600 mL) was distilled directly into the all-glass reactor equipped with a neodymium stir bar under reduced pressure (Picture S1). Sec-BuLi (0.5 mL) and 2 eq. of MTBE/Li (120 mg) were added to the reactor via syringe and stirred for 30 minutes. To the initiator solution, nopadiene (24.1 g) was added via syringe. Myrcene (37 mL) was distilled into a graduated ampule equipped with a teflon stop cock. After full consumption of nopadiene, myrcene was added. Depending on the block sizes of myrcene, the next load of nopadiene (24 mL) was added after 6-12 hours via a graduated ampule. Polymerization of myrcene was observed by a significant increase in viscosity of the reaction medium. To accelerate the polymerization and to avoid elevated viscosity, the temperature was increased to 50°C. The color change from the slightly colored poly(myrcenyl)lithium to the orange poly(nopadienyl)lithium confirmed the

successful crossover from polymyrcene to the polynopadiene block segment, as depicted in Picture S1.



Picture S1: *left*; poly(nopadienyl)lithium of the first block, *middle*; after the addition of myrcene *right*; poly(nopadienyl)lithium of the third block after second addition of nopadiene.

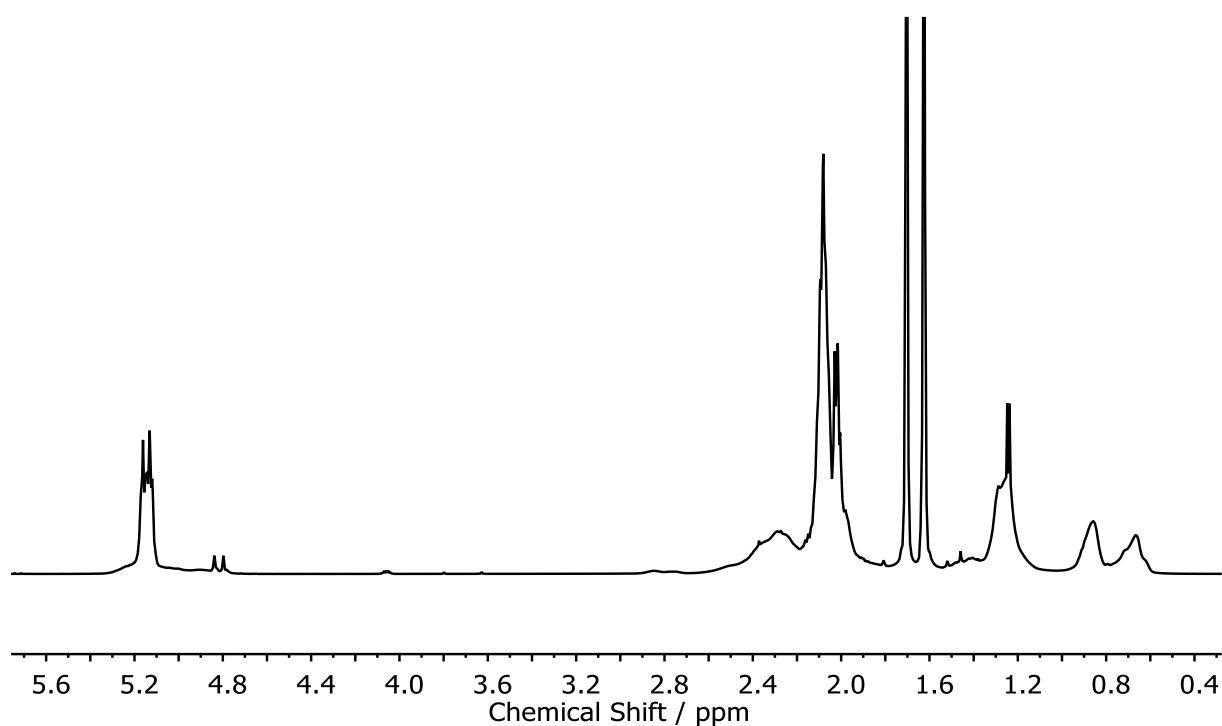


Figure S 66: ^1H NMR spectrum (600 MHz, CDCl_3 , 25°C) of T1 (P(Nopa-*b*-Myr-*b*-Nopa)_{100k}).

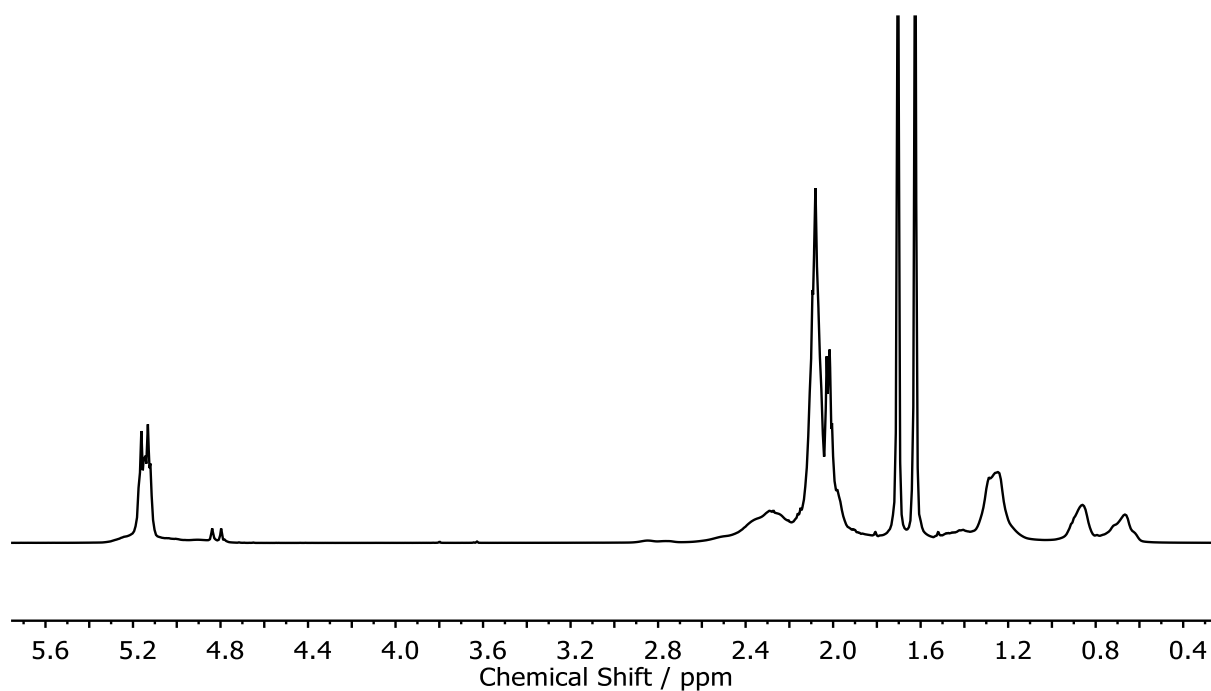


Figure S 67: ^1H NMR spectrum (600 MHz, CDCl_3 , 25°C) of T2 (P(Nopa-*b*-Myr-*b*-Nopa)_{200k}).

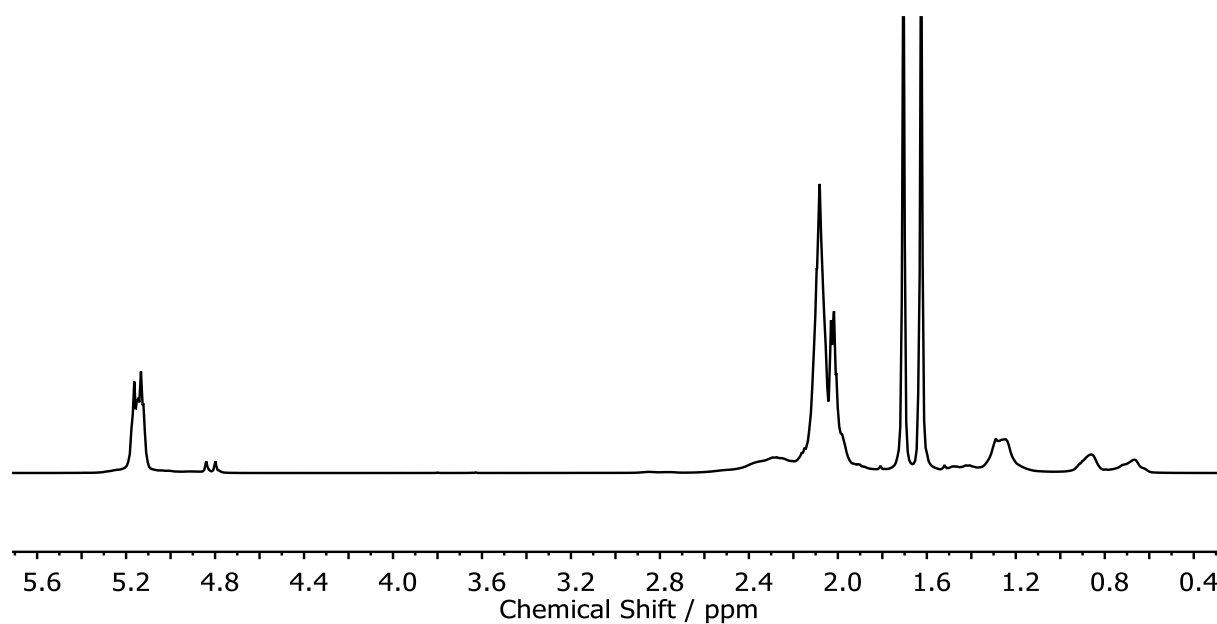


Figure S 68: ^1H NMR spectrum (600 MHz, CDCl_3 , 25°C) of T3 (P(Nopa-*b*-Myr-*b*-Nopa)_{100k}).

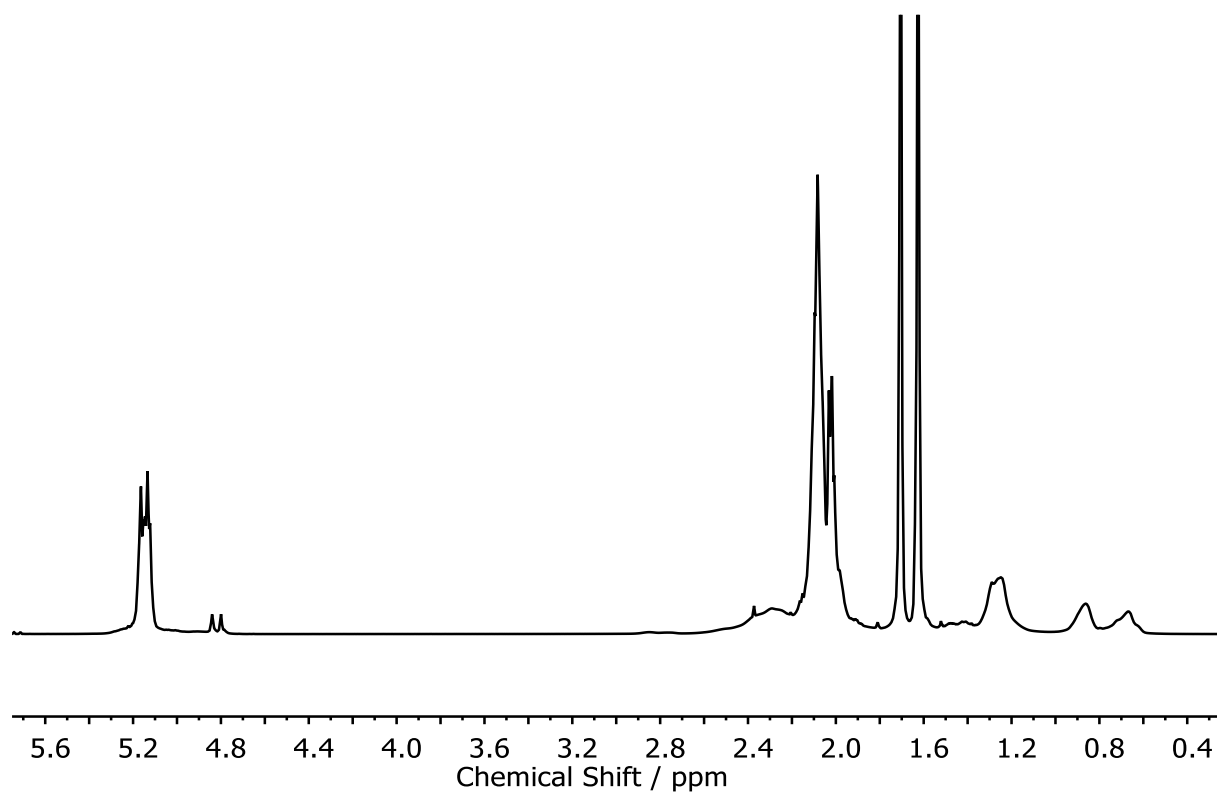


Figure S 69: ^1H NMR spectrum (600 MHz, CDCl_3 , 25°C) of T4 (P(Nopa-*b*-Myr-*b*-Nopa)_{200k}).

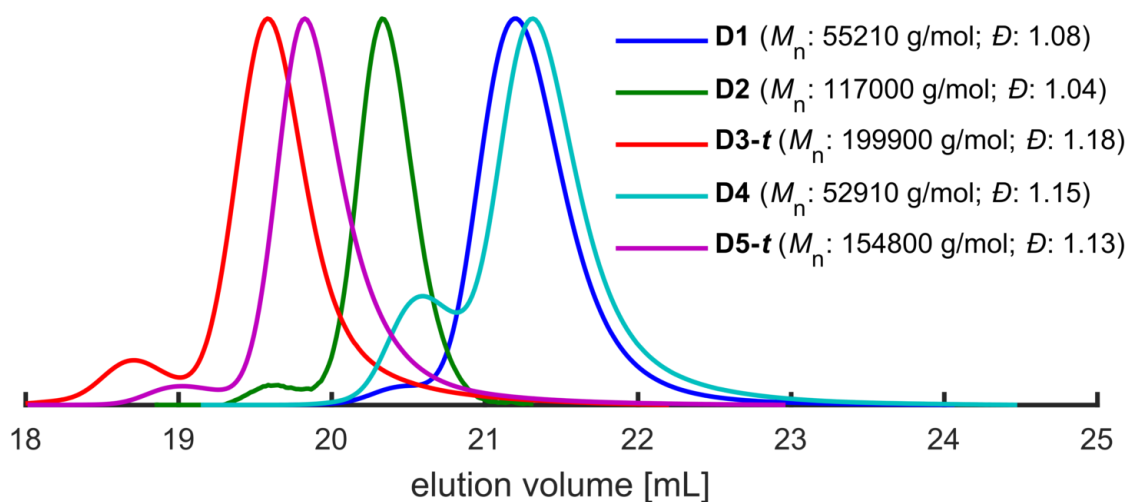


Figure S 70: SEC traces (eluent THF, PS calibration) of D1, D2 D3-t, D4 and D5-t.

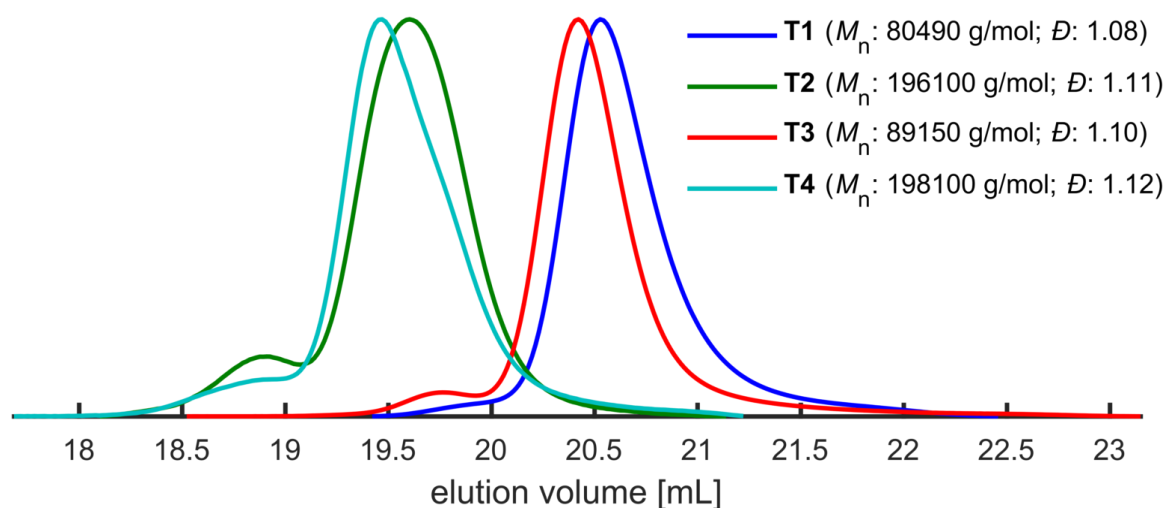


Figure S 71: SEC traces (eluent THF, PS calibration) of T1-4.

4.2.6.1.8 DSC measurements

Thermal properties of PNopa1-14. The change in microstructure results in variations of the glass transition temperature.

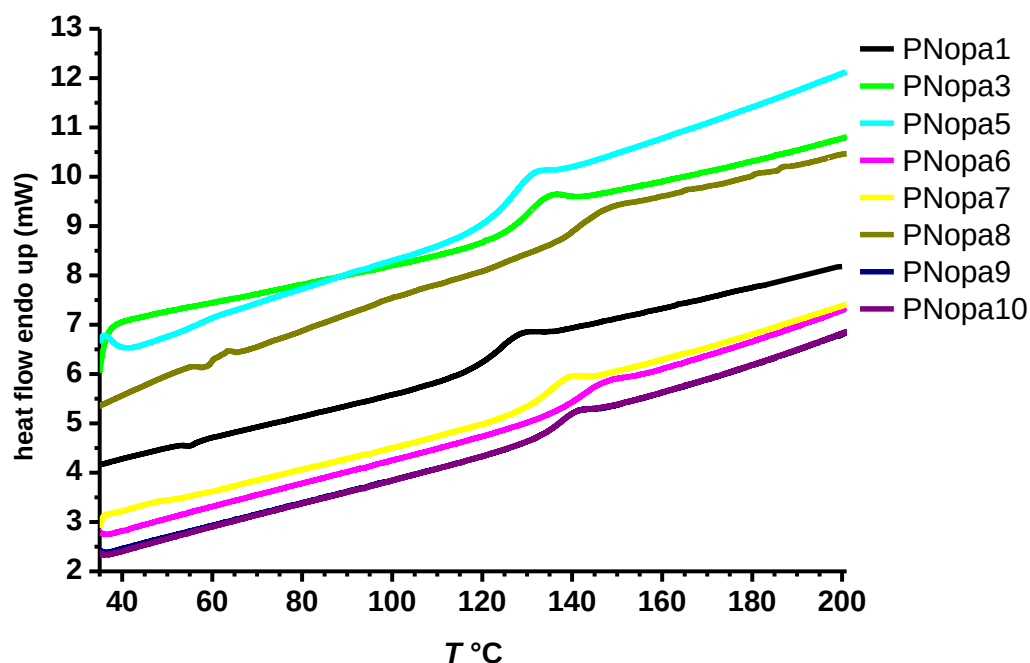


Figure S 72: DSC curves of PNopa 1, PNopa 3 and PNopa5-10.

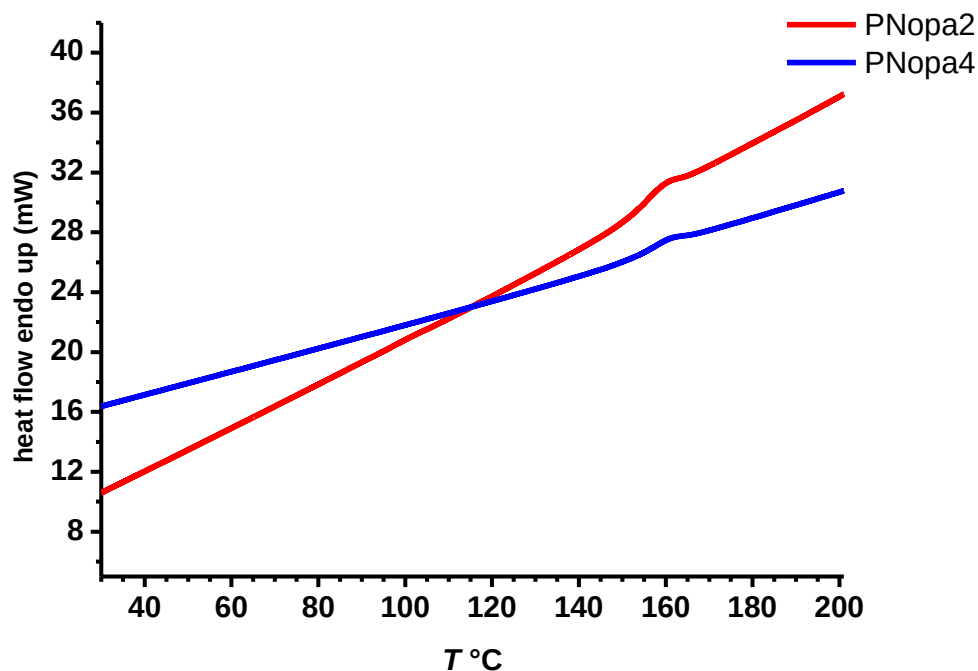


Figure S 73: DSC curves of PNopa 2 and PNopa4.

Thermogravimetric measurements

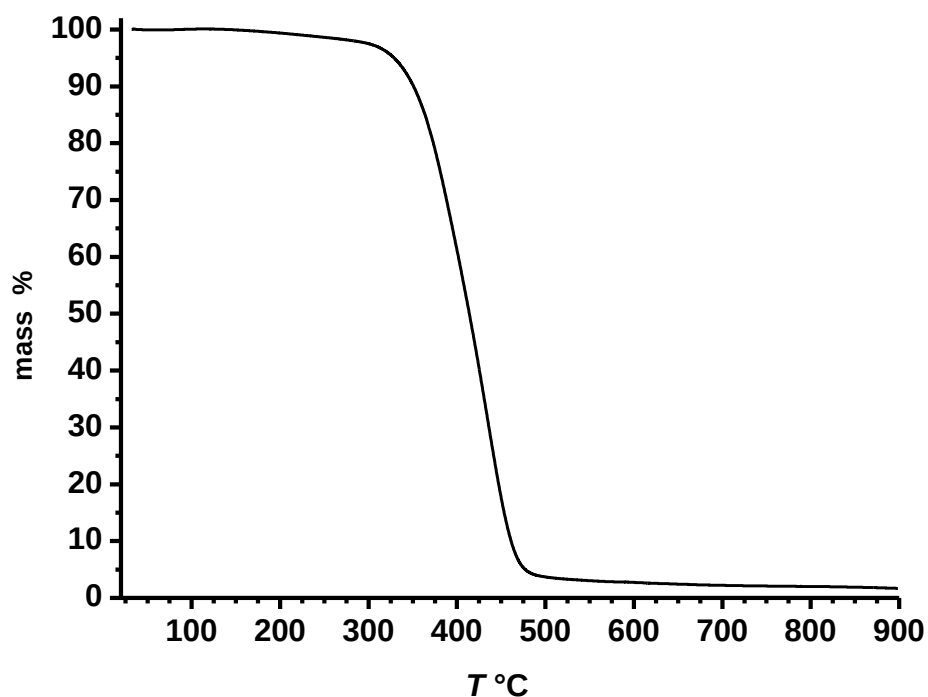


Figure S 74: Thermogravimetric analysis (TGA) under N₂ of T2.

DSC measurements of the diblock and triblock copolymers.

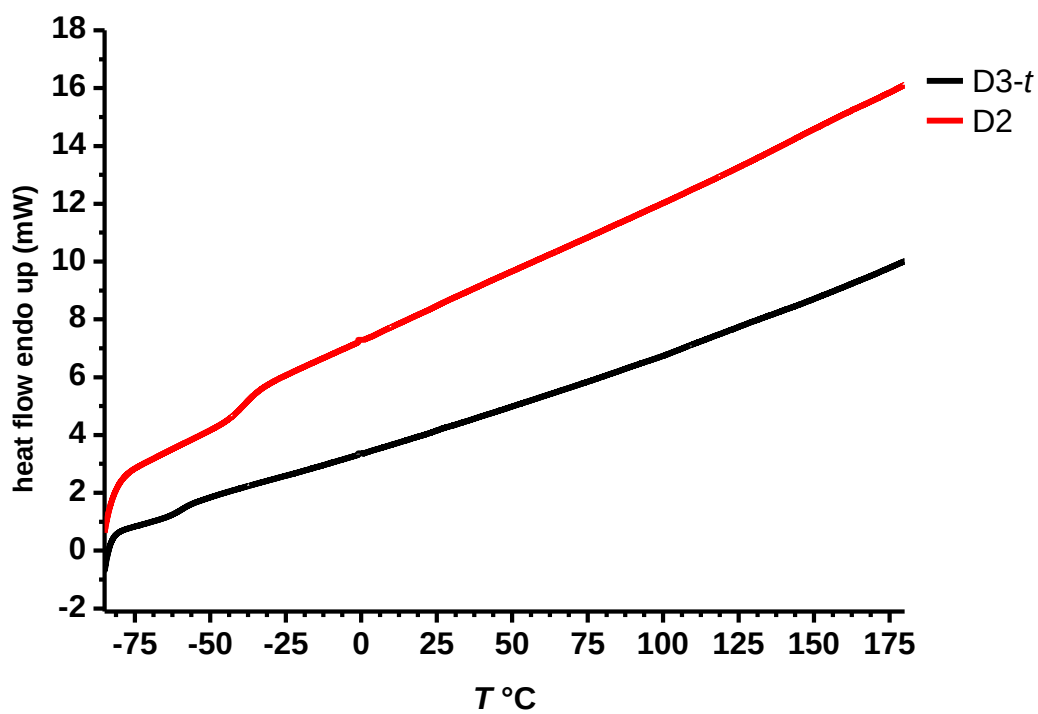


Figure S 75: DSC curves of D2 and D3-t.

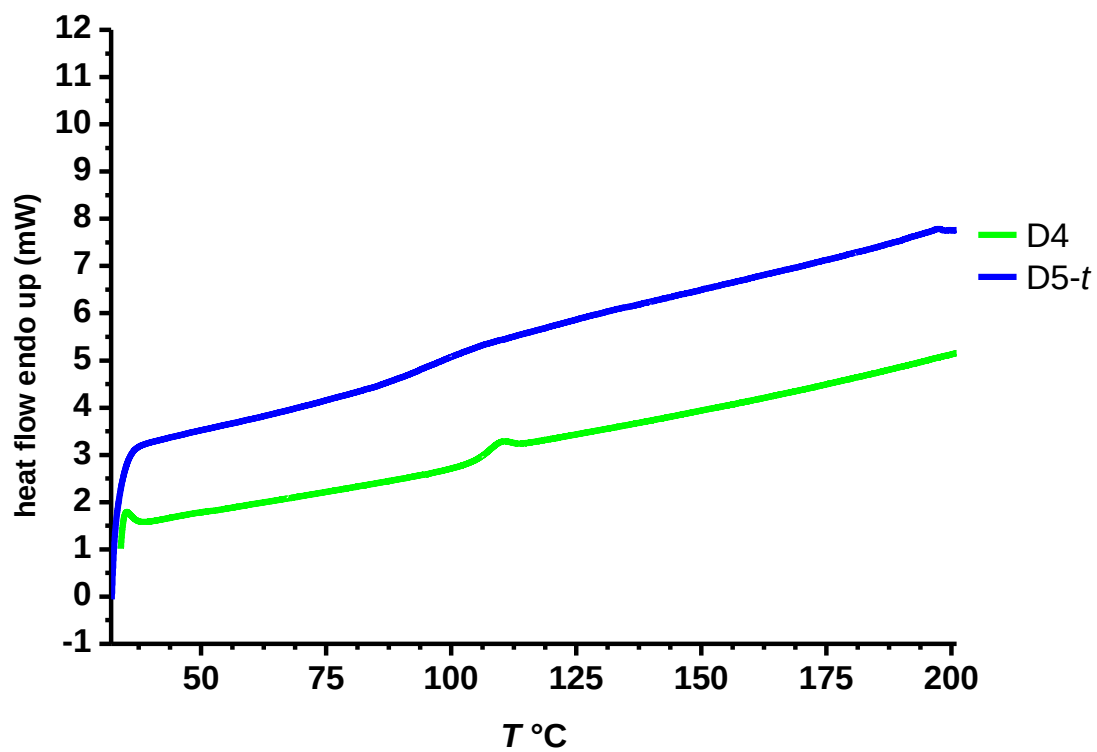


Figure S 76: DSC curves of D4 and D5-t.

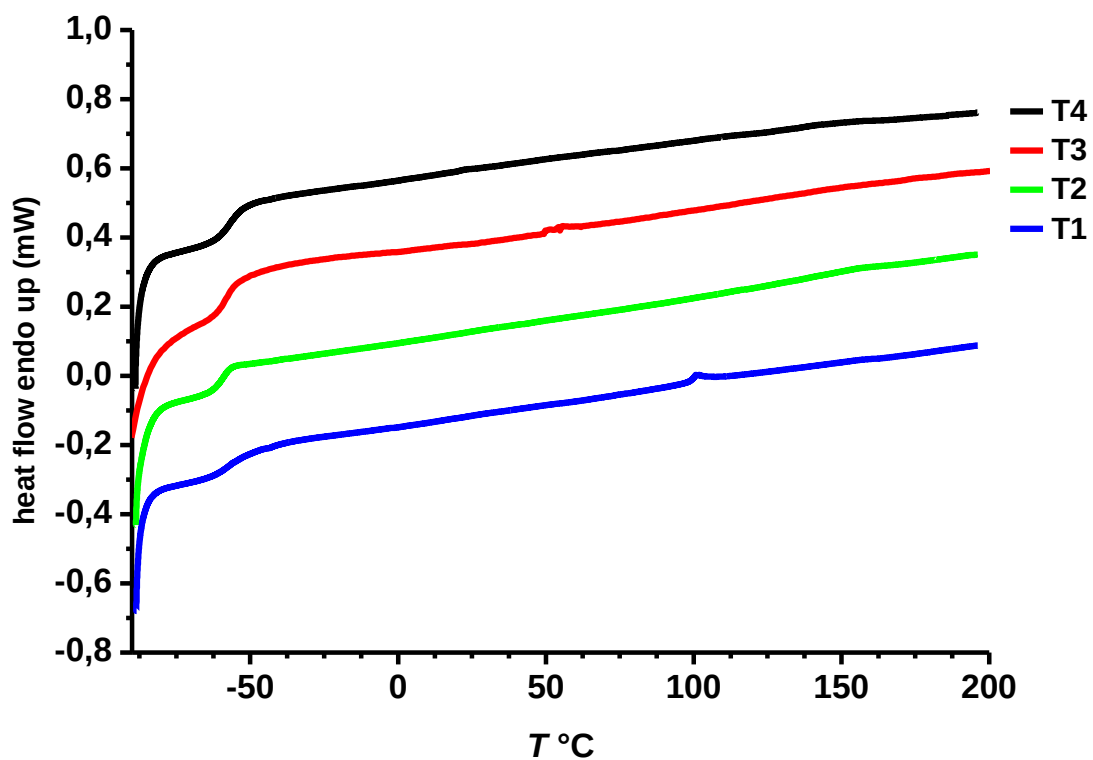


Figure S 77: DSC curves of T1-4.

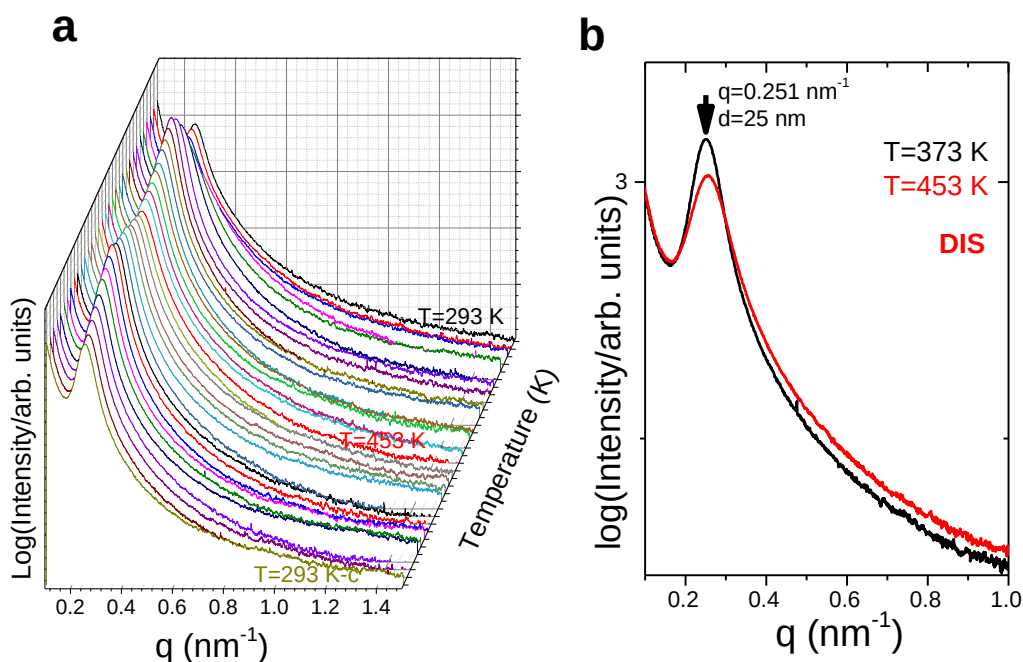


Figure S 78: (a) Temperature-dependent SAXS patterns of D1 (P(My r - b -Nopa) $_{50k}$, myrcene w%=50) obtained on heating from 293 K to 453 K and back to 293 K. (b) All patterns exhibit a broad peak associated with correlation hole scattering e.g., disordered state (DIS).

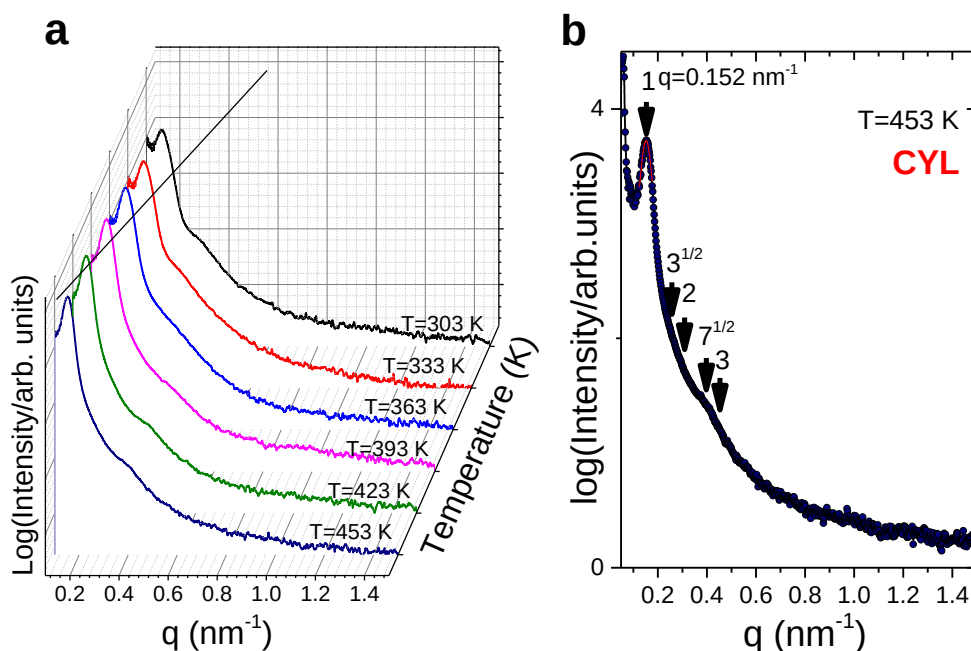


Figure S 79: (a) Temperature-dependent SAXS patterns of T4, obtained on heating from 303 K to 453 K. (b) The pattern obtained at 453 K shows Bragg reflections corresponding to a cylindrical (CYL) morphology in the absence of long-range order.

4.2.6.1.9 Mechanical properties

The mechanical properties of the triblock copolymers T1-4 were investigated by tensile testing. The different colors in the stress-strain experiments represent individual specimens.

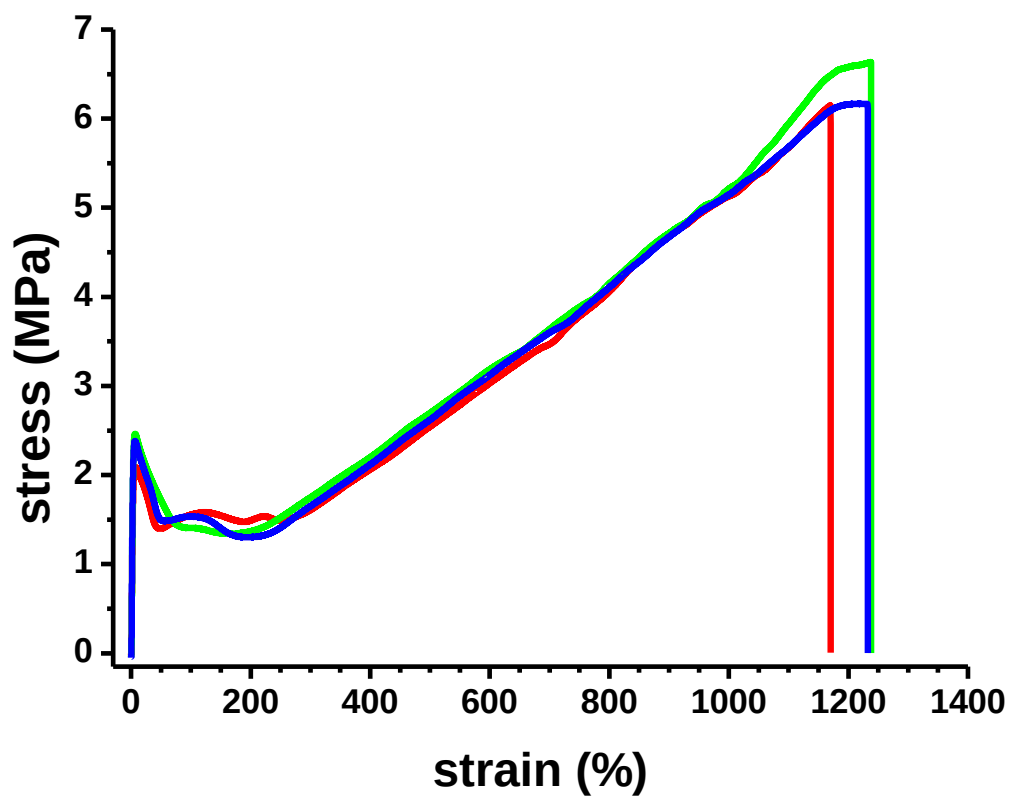


Figure S 80: Stress-strain curves of T1.

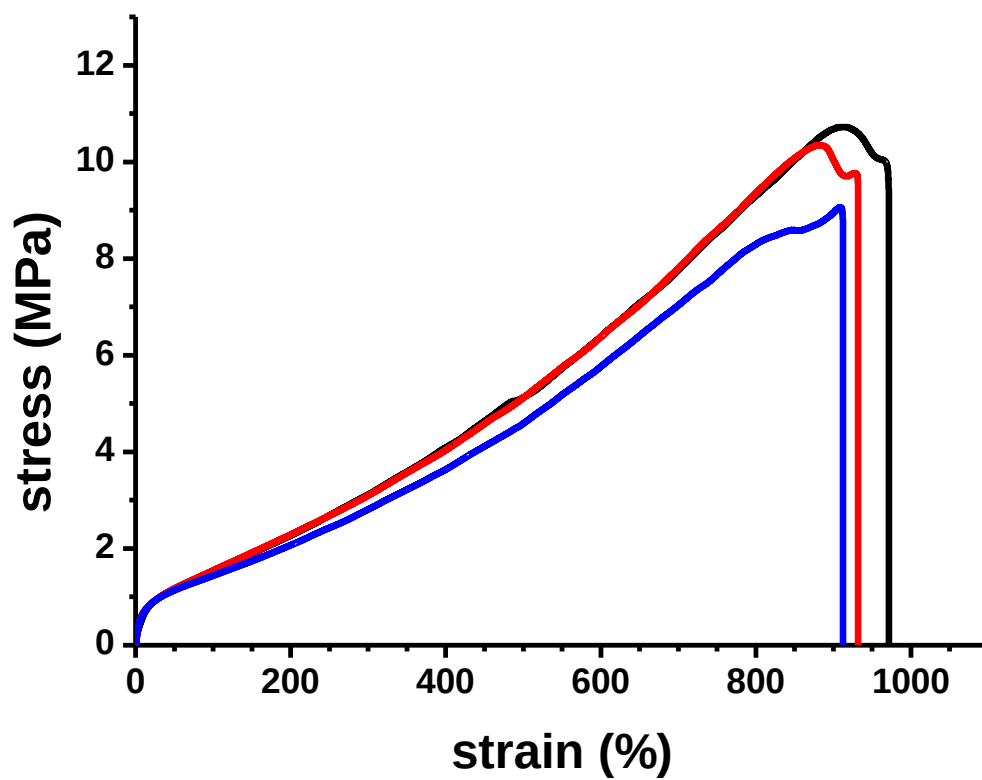


Figure S 81: Stress-strain curves of T2.

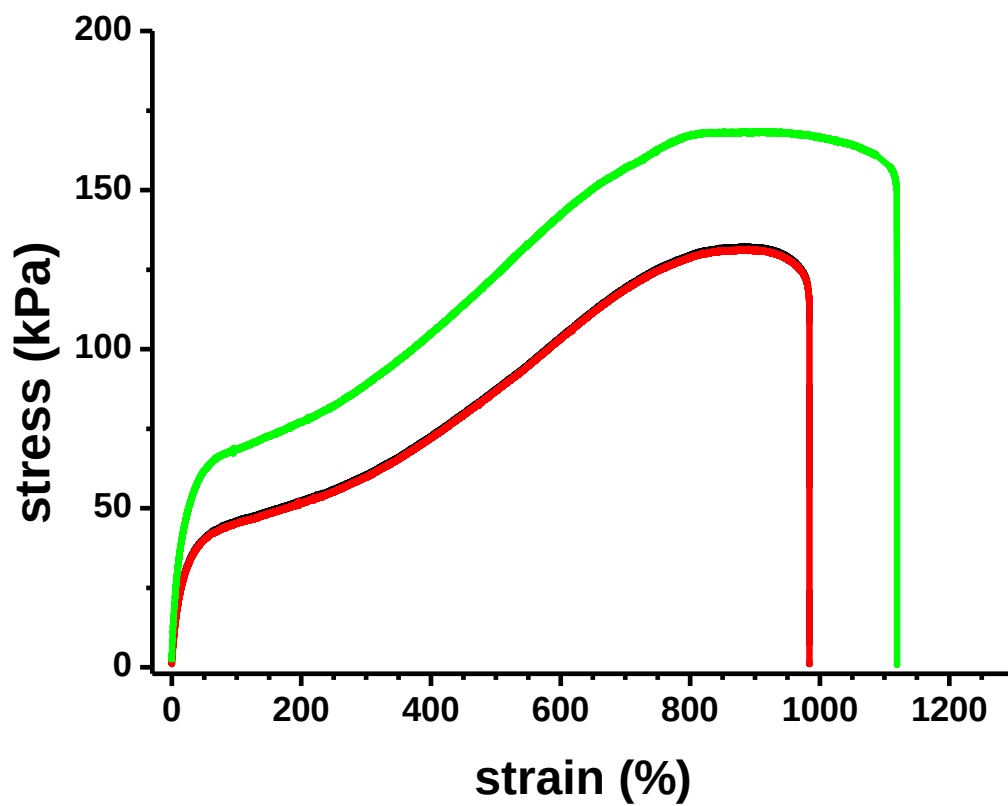


Figure S 82: Stress-strain curves of T3.

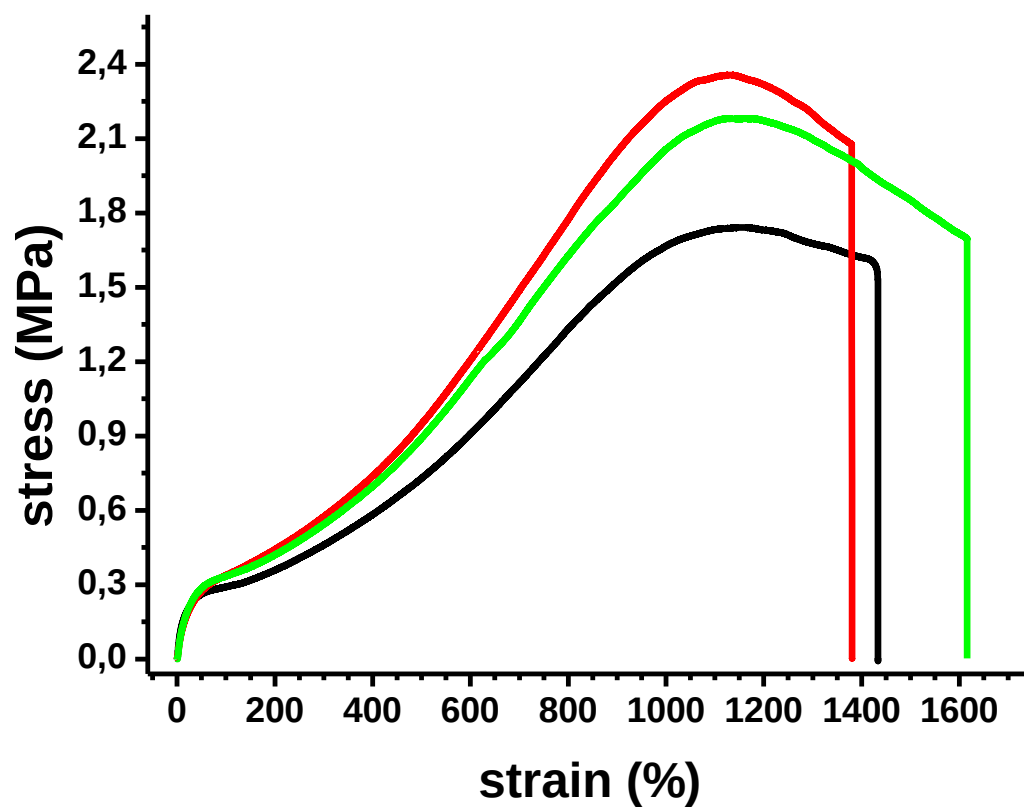


Figure S 83: Stress-strain curves of T4.

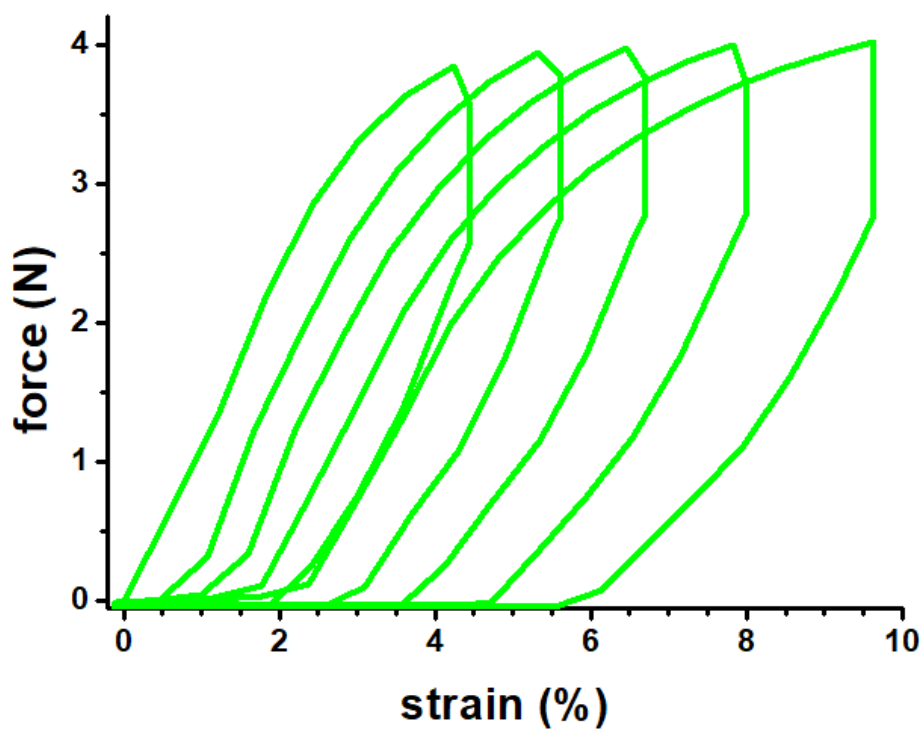


Figure S 84: Hysteresis curves of T1, average recovery 81,4%.

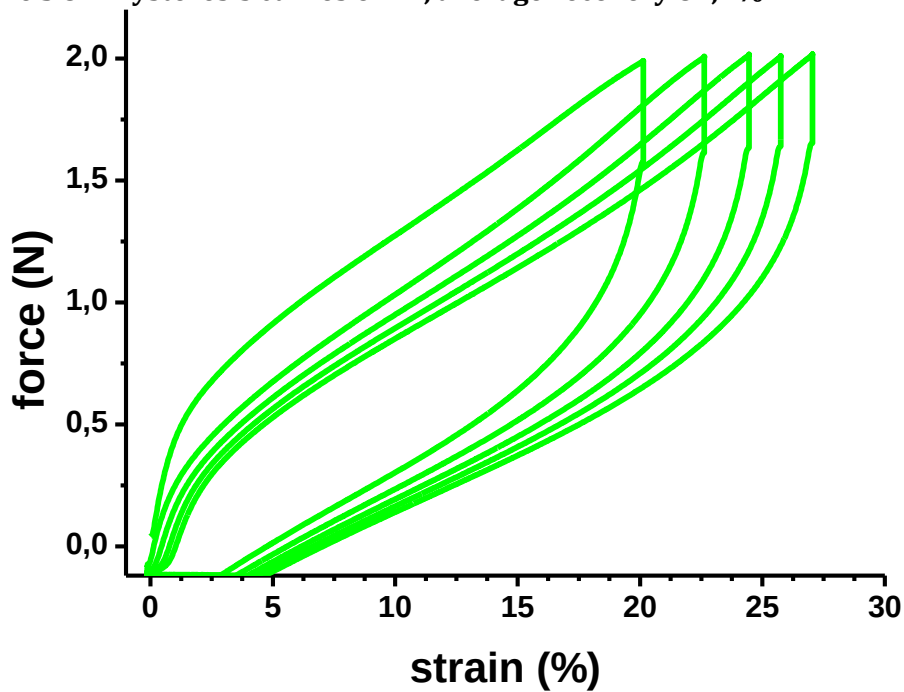


Figure S 85: Hysteresis curves of T2, average recovery 93,1%.

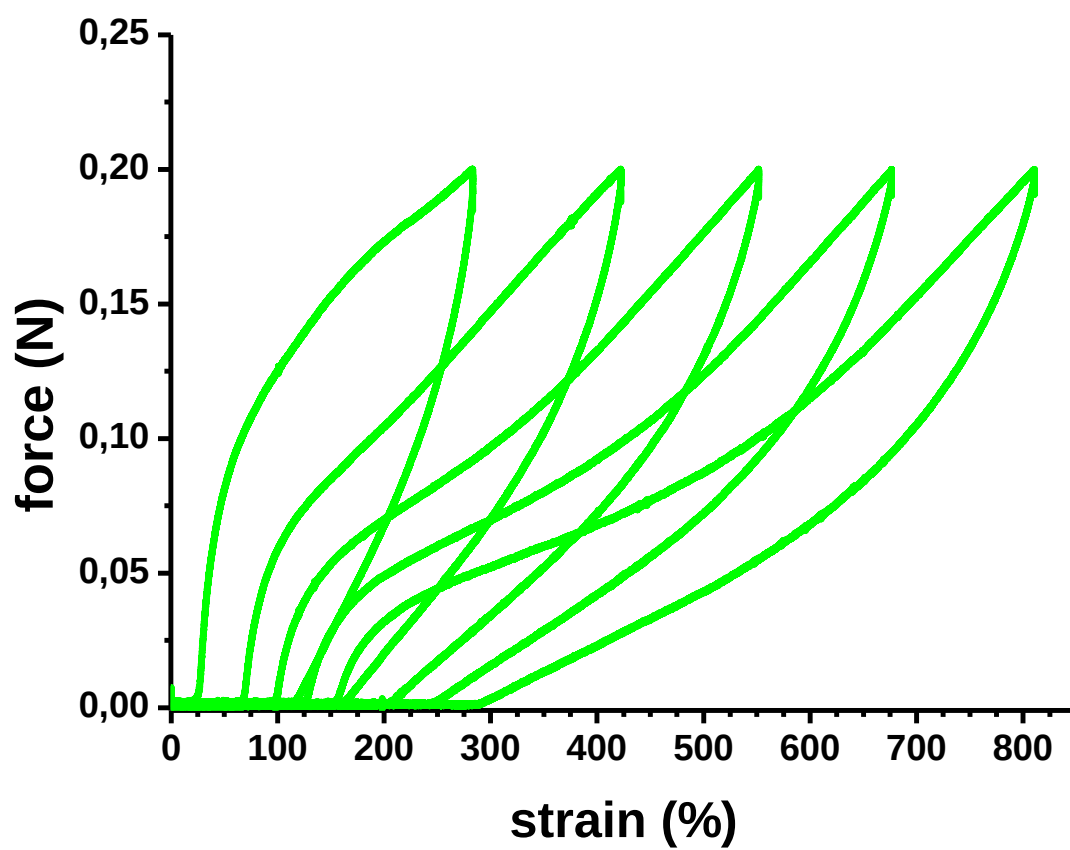


Figure S 86: Hysteresis curves of T3, average recovery 75,5%.

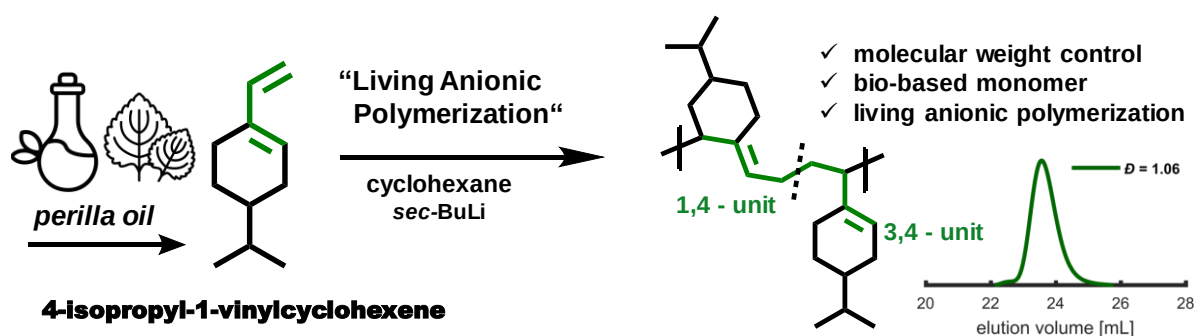
4.3 Anionic polymerization of 4-Isopropyl-1-vinylcyclohexene – expanding the scope of cyclic 1,3-diene monomers from natural resources

Christoph Hahn,^{a,b} Moritz Simon,^a and Holger Frey,^a

^a Department of Chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz (Germany)

^b Max Planck Graduate Center, MPGC, Staudingerweg 9, 55128, Mainz (Germany)

To be Submitted.



4.3.1 Abstract

Aiming at a fully bio-based approach in polymer synthesis, the utilization of cyclic terpene monomers motivated the investigation of the novel monomer 4-isopropyl-1-vinylcyclohexene (4IPVCH) obtained from perillaldehyde. The terpene derived monomer 4IPVCH was polymerized by means of living anionic polymerization in cyclohexane using *sec*-BuLi as an initiator with M_n up to 88 kg mol⁻¹. The polymers were studied with respect to molecular weight control, dispersity, microstructure of the 1,3-diene, and glass transition temperature. Employing 4-isopropylstyrene (4ⁱPrS) as a comonomer, which is due to natural impurities of cuminaldehyde that after Wittig olefination result in 4-isopropylstyrene (4ⁱPrS), the copolymerization proceeded under excellent molecular weight control and resulted in narrow molecular weight distributions. P(4IPVCH) obtained in cyclohexane with *sec*-BuLi as an initiator showed both 1,4- and 3,4-incorporation mode (ratio: 55:45). The microstructure of the resulting polydiene can be altered by the addition of THF or DTHFP, resulting in increasing 3,4-microstructure (up to 84%). Copolymers of 4IPVCH with styrene and β -myrcene were accessible as well.

4.3.2 Introduction

Among the various controlled polymerization techniques, anionic polymerization of styrene and 1,3-diene monomers is known as the best method for control of molecular weight, molecular weight distribution and microstructure. In literature a variety of monomers, ranging from linear 1,3- dienes to cyclic and bicyclic structures, have been demonstrated to undergo living anionic polymerization in nonpolar solvents.¹⁻⁴ Numerous studies focused on elucidating the polydiene synthesis under various polymerization conditions, with the final objective of controlling the microstructure and physical properties of the polymer. However, these polydienes are commonly based on isoprene and butadiene. We have recently shown that cyclic 1,3-dienes with a 1,2-substitution pattern, e.g., 1-vinylcyclohexene, can be polymerized under living anionic conditions using *sec*-BuLi as an initiator in cyclohexane at 25°C.⁵ The resulting poly(vinylcyclohexene) exhibited 66% 1,4 and 34 % 3,4 microstructure resulting in a T_g of 78°C. In addition to these findings, the microstructure of the resulting rigid and cyclic polydiene is controllable toward higher 3,4 incorporation by the addition of THF to the polymerization medium. To further expand the scope of bio-based monomers, perillaldehyde was converted to a cyclic 1,3-diene monomer, 4IPVCH, with an isopropyl substituent in *para*-position in the vinylcyclohexene framework. Perillaldehyde is obtained from the essential oil of *perilla frutescens*, an edible oil often used in the Korean cuisine because of its aromatic and strong mint-like flavor. This valuable natural resource contains an unique carbon skeleton of a six-membered ring and a α,β -unsaturated aldehyde with an isopropylene unit in *para*-position.

Cuminaldehyde (4-isopropylbenzaldehyde) is a terpene found in cumin and other related plants. This aromatic aldehyde offers a natural substitute for styrene *via* the facile introduction of polymerizable vinyl bond by Wittig olefination. Polymer scientists have increasingly exploited naturally occurring aromatic molecules as building blocks for bio-based polymers. The application of aromatic moieties is often considered with improved thermal and mechanical properties due to their chemical

stability.⁶ The aromatic components typically increase T_g values because of quadrupolar interactions, $\pi - \pi$ stacking, and increased sterical hindrance (4-isopropylstyrene).⁷

Here we report the synthesis of a bio-based substitute for polystyrene (co)polymers with well-defined structure, relying on naturally occurring perillaldehyde. Initially, the question was whether the monomer acts as a 1,3-diene or as a styrenic monomer. 4IPVCH exhibits a unique cyclic substitution pattern in 1 and 2-position of the 1,3-diene. In contrast to 2-alkyl-1,3-dienes, the 1,2-disubstituted 1,3-diene is cyclic and this constrained structure can influence not only the steric orientation but also the electron density at the 1,3-diene moiety. Hence, it is expected that these constraints and the bulky isopropylene group in *para*-position show a strong influence on the thermal properties of the polymer, especially regarding the glass transition temperature.

4.3.3 Results and Discussion

4.3.3.1 Synthesis of 4IPVCH from perillaldehyde.

Starting from the naturally available perillaldehyde, 4IPVCH was selectively hydrogenated using PtO_2 as a catalyst.⁸ The selectivity of PtO_2 enables the hydrogenation of the isopropylene unit, by maintaining the α,β -unsaturated aldehyde. This selectivity of the PtO_2 catalyst for hydrogenation of the double bond of the isopropylene unit was demonstrated for a series of terpenes, including carvon and limonene.⁹ This is crucial for the preparation of the 1,3-diene structure. The resulting phellandral (4-Isopropylcyclohexenecarbaldehyde) is converted to 4IPVCH by Wittig olefination in 99 % yields (Scheme 1).¹⁰ However, commercially available perillaldehyde is contaminated with cuminaldehyde, a dehydrogenated derivative. Perillaldehyde contains 5-10% cuminaldehyde, because of the natural origin of the compound. *Perilla frutescens* and other cumin related species produce a variety of monoterpenes with a *para*-menthane framework. Interestingly, Wittig-reaction of cuminaldehyde yields 4-isopropylstyrene, a common monomer in anionic

polymerization with similar steric hindrance and thermal properties, such as a $T_g > 100^\circ\text{C}$.¹⁰

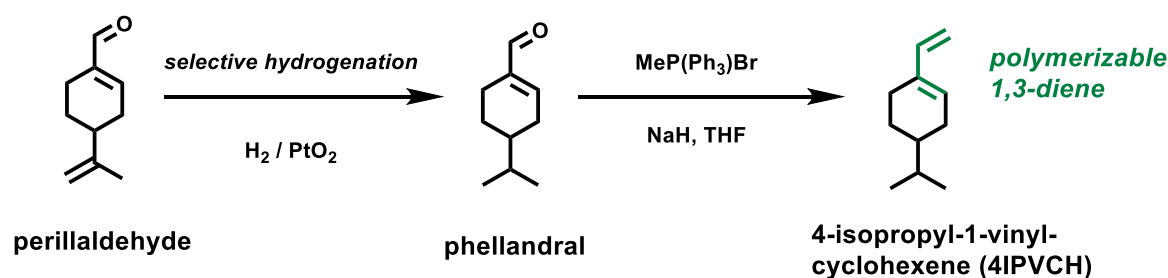


Figure 1: Synthesis of bio-based 4IPVCH derived from perillaldehyde.

As demonstrated in previous works, the challenging step of the Wittig reaction is the removal of the unavoidable by-product triphenylphosphine oxide (TPPO).¹⁰ 4IPVCH and impurities of 4ⁱPrS were purified by distillation from TPPO in melt. In the following section 4IPVCH is always contaminated with 5 % of 4ⁱPrS, unless noted otherwise. The two monomers could not be separated by distillation, due to the similar boiling points. As demonstrated later in this section, 4ⁱPrS can be separated by column chromatography or by means of polymerization of 4ⁱPrS in THF at -78°C .

4.3.3.2 Anionic copolymerization of 4IPVCH and 4ⁱPrS

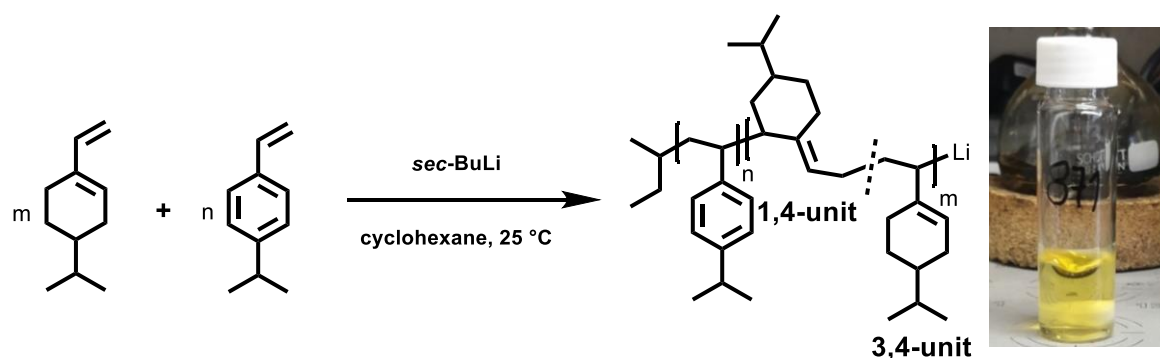


Figure 2: Anionic copolymerization of 4IPVCH and 4ⁱPrS in cyclohexane using *sec*-BuLi as initiator.

As mentioned above, the homopolymerization of 4IPVCH is in fact a copolymerization of 4IPVCH and 4ⁱPrS. Polymers consisting of these two monomers with different molecular weights were synthesized in cyclohexane using *sec*-BuLi as an initiator.

Figure 2 highlights the living character of the polymerization of 4IPVCH and 4ⁱPrS as indicated by the typical color due to the living chain end. The color of the living chain-end changed within the first minutes of the polymerization from red to yellow (Figure 2). This observation suggests that the 4ⁱPrS is incorporated first in the copolymerization of 4IPVCH and 4ⁱPrS, resulting in a weak gradient copolymer sequence. The molecular weights and molecular weight distributions are demonstrated in Table 1 and Figure 3. The polymerization of 4IPVCH resulted in polymers with controlled molecular weights and narrow molecular weight distribution as expected for living anionic polymerization. However, targeting higher molecular weights exceeding 68 kg/mol, the molecular weight distribution showed evidence of tailing towards lower molecular weights. At higher molecular weights the determination of the molecular weight with SEC leads to underestimated values (P5 and P6). Due to impurities with 4ⁱPrS, the polymerization of 4IPVCH is always accompanied by small amounts of 4ⁱPrS.

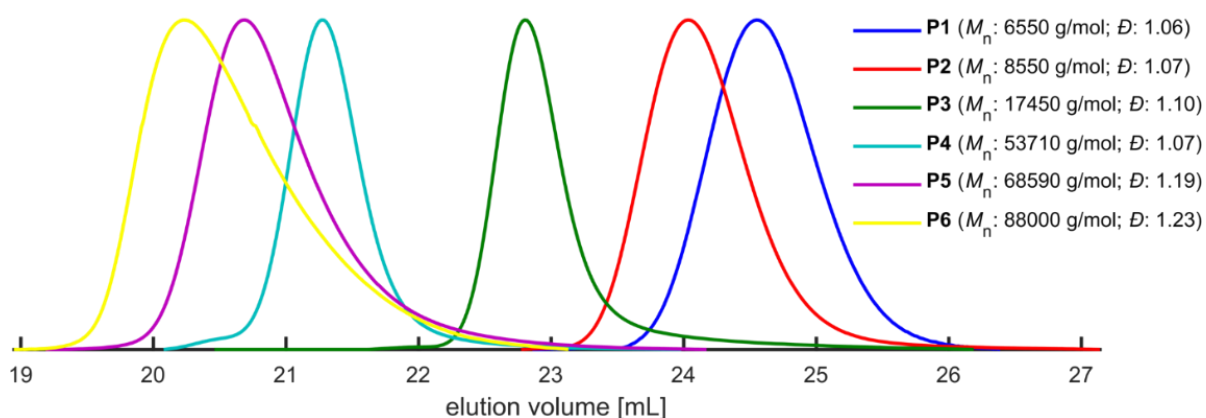


Figure 3: SEC traces (Eluent THF, PS calibration) of P1-6.

As described in other studies, the initiation of sterical hindered 1,3-dienes can be delayed when using *sec*-BuLi.¹¹ It is hypothesized that the impurities of 4ⁱPrS support the initiation with *sec*-BuLi, leading to well-defined polymers. Thus, 4IPVCH has to be separated and initiated in the absence of any other monomer. A series of different organo-lithium initiators were tested to study the initiation reaction and it was observed that polystyryl-lithium and *sec*-BuLi initiated the polymerization if 4IPVCH

instantly, resulting in narrow molecular weight distributions ($\bar{D}$ = 1.06-1.18). On the contrary, with *tert*-BuLi an extreme broadening of the molecular weight distribution was detected. In addition, the targeted molecular weight and the molecular weight obtained from SEC deviate greatly, which hints at incomplete initiation.

Employing living anionic polymerization in THF at -78°C using the inseparable mixture of pure 4IPVCH and 4ⁱPrS (P9), it was possible to polymerize only 4ⁱPrS. Thus, this method was applied to obtain pure 4IPVCH. Despite the complete consumption of 4ⁱPrS in the polymerization in THF, the diene monomer showed no polymerization, even after increasing the temperature gradually from -78°C to 25°C under inert atmosphere. No further propagation of the diene was observed even after 3 days, as proven by NMR spectroscopy.

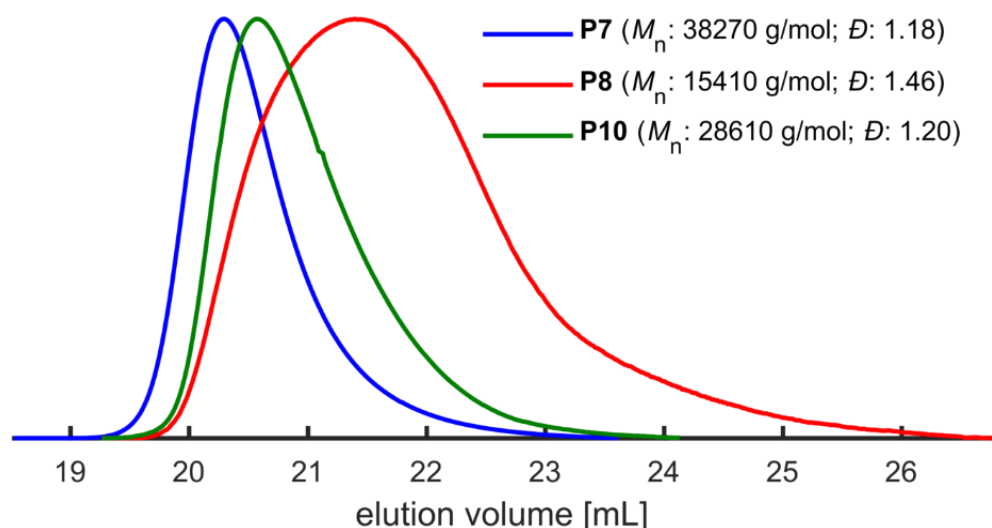


Figure 4: SEC traces (Eluent THF, PS calibration) of P7, P8 and P10.

Thus, after removal of P4ⁱPrS, the purified monomer 4IPVCH was distilled and dried and subjected to polymerization in cyclohexane using *sec*-BuLi as an initiator. The polymerization of pure 4IPVCH (P10) proceeded successfully with moderate dispersity ($\bar{D}$) of 1.20.

Table 1: Polymerization of 4IPVCH by means of living anionic polymerization in cyclohexane and THF using different organo-lithium initiators.

entry	Monomer (+4 ⁱ PrS)	Initiator	equivalents modifier/Li ⁺	solvent	<i>M_n</i> <i>target</i>	<i>M_n</i> (GPC)* kg/mol	<i>D</i>	<i>T_g</i> °C
P1	4IPVCH	<i>sec</i> -BuLi	-	cyclohexane	7.5	6.6	1.06	-
P2	4IPVCH	<i>sec</i> -BuLi	-	cyclohexane	10	8.6	1.07	-
P3	4IPVCH	<i>sec</i> -BuLi	-	cyclohexane	20	17.5	1.10	72
P4	4IPVCH	<i>sec</i> -BuLi	-	cyclohexane	50	53.7	1.07	-
P5	4IPVCH	<i>sec</i> -BuLi	-	cyclohexane	75	68.6	1.19	87
P6	4IPVCH	<i>sec</i> -BuLi	-	cyclohexane	100	88.0	1.23	-
P7	4IPVCH	polystyryl-lithium (20kg/mol)	-	cyclohexane	40	38.3	1.18	-
P8	4IPVCH	<i>tert</i> -BuLi	-	cyclohexane	10	15.4	1.46	-
P9	4IPVCH ^a	<i>sec</i> -BuLi	-	THF	10	1.6	1.29	-
P10	4IPVCH ^b	<i>sec</i> -BuLi	-	cyclohexane	20	28.6	1.20	-
P11	4IPVCH	<i>sec</i> -BuLi	2 eq. THF	cyclohexane	10	24.2	1.19	84
P12	4IPVCH	<i>sec</i> -BuLi	20 eq. THF	cyclohexane	10	18.3	1.17	89
P13	4IPVCH	<i>sec</i> -BuLi	1 eq. DTHFP	cyclohexane	10	15.6	1.12	80
P14	4IPVCH	<i>sec</i> -BuLi	10 eq. DTHFP	cyclohexane	10	13.0	1.10	82

*Determined by SEC (eluent THF, UV signal, PS calibration),^a polymerization in THF accompanied by incomplete conversion. ^b pure 4IPVCH without 4ⁱPrS, purified by column chromatography or from (P9).

It is hypnotized that 4IPVCH can react as a 1,3-diene monomer or as a vinyl monomer like styrene, in anionic polymerization, leading to contrasting microstructures. Therefore, the determination of the microstructure of the resulting (co)polymer of 4IPVCH and 4ⁱPrS was investigated by NMR spectroscopy.

The differentiation of the 1,4 and 3,4 units of P(4IPVCH) was easily determined by the olefinic methine signals at 5.32 ppm and 4.99 ppm, respectively (Figure 4). The microstructure of P(4IPVCH) that was obtained in cyclohexane exhibited 55 % 1,4-microstructure and 45 % 3,4-microstructure.

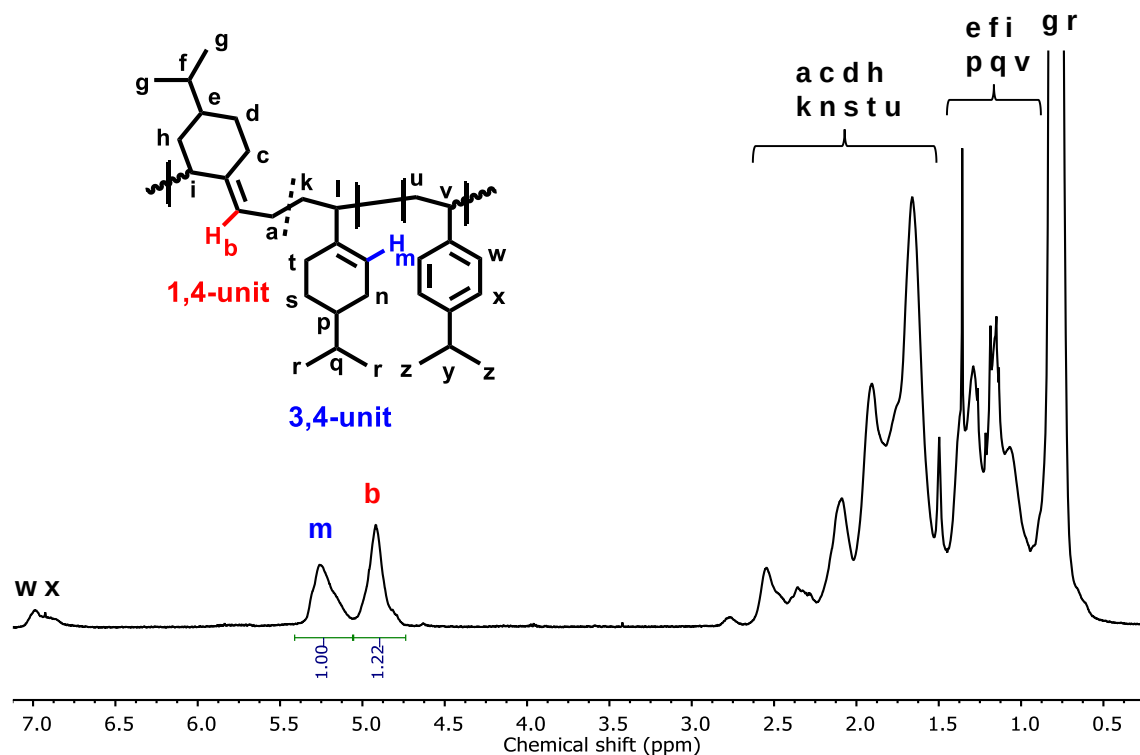


Figure 5: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of P(I4PVCH).

The ratio of 1,4 to 3,4-units can be altered by the addition of polar additives.¹² The amount of modifier was referred to the amount of initiator (*sec*-BuLi). THF and DTHFP in different oxygen to Li^+ ratios were used to change the microstructure of P(4IPVCH). In NMR spectroscopy it was observed that the polymers possess increasing 3,4-units with increasing ratio of THF / Li. Upon the addition of more than 20 eq. of THF, no further increase of 3,4-units was observed. Figure 4 shows the change of the structure of P(4IPVCH) as a consequence of increasing amount of the polar modifier THF and towards 3,4-incorporation. Further investigation of the polymer structure revealed that no 1,2-microstructure of VCH was observed (see). The 3,4-unit of 4IPVCH is comparable to a (semi) hydrogenated 4ⁱPS polymer. As a result of the modified microstructures, slightly higher glass-transitions temperatures upon the addition of THF and DTHFP, compared to polymers obtained in cyclohexane, were observed. It is assumed that the 3,4-microstructure exhibited a higher glass-transition temperature due to the sterically demanding isopropyl substituent within the cyclic ring structure. Adding 1 or 10 eq. DTHFP to the polymerization medium, the amount of 1,4-units

drops to 33% while the 3,4-units increased to 67%. The further increase of modifier equivalents did not lead to higher 3,4-units.

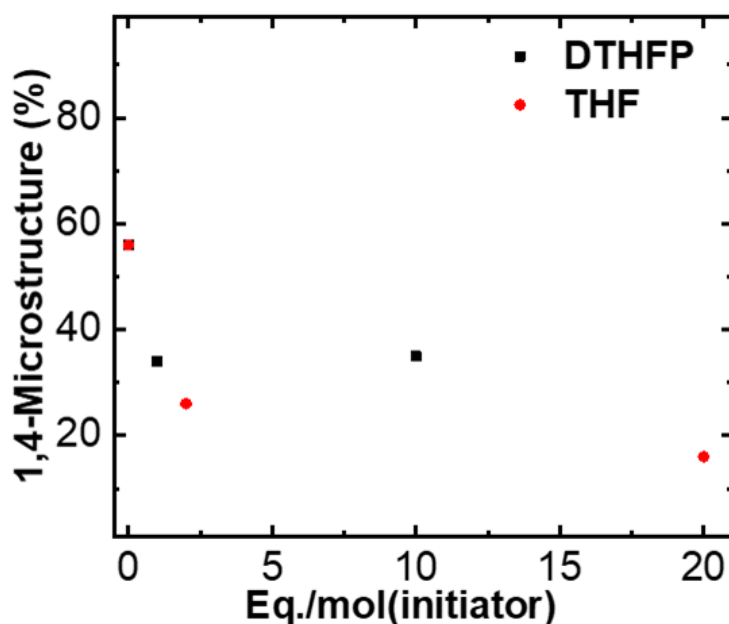


Figure 6: Microstructure of P(4IPVCH) with the addition of polar modifiers, THF and DTHFP.

4.3.3.3 Copolymerization with styrene

It was demonstrated that 4IPVCH can be copolymerized with styrene in different compositions, ranging from 25-75% styrene content (P15 25%, P16 50%, P17 75% styrene respectively). The SEC traces of 4IPVCH/styrene copolymers P15-17 are shown in Figure 6.

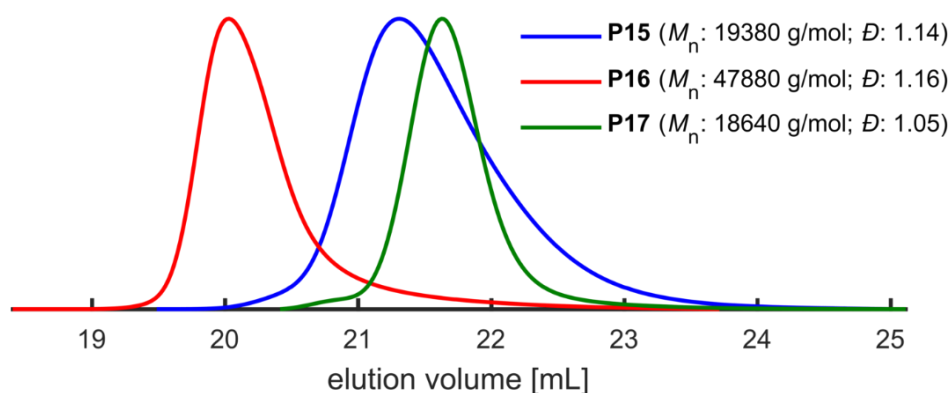


Figure 7: SEC traces (Eluent THF, PS calibration) of the 4IPVCH/styrene copolymers P15-17.

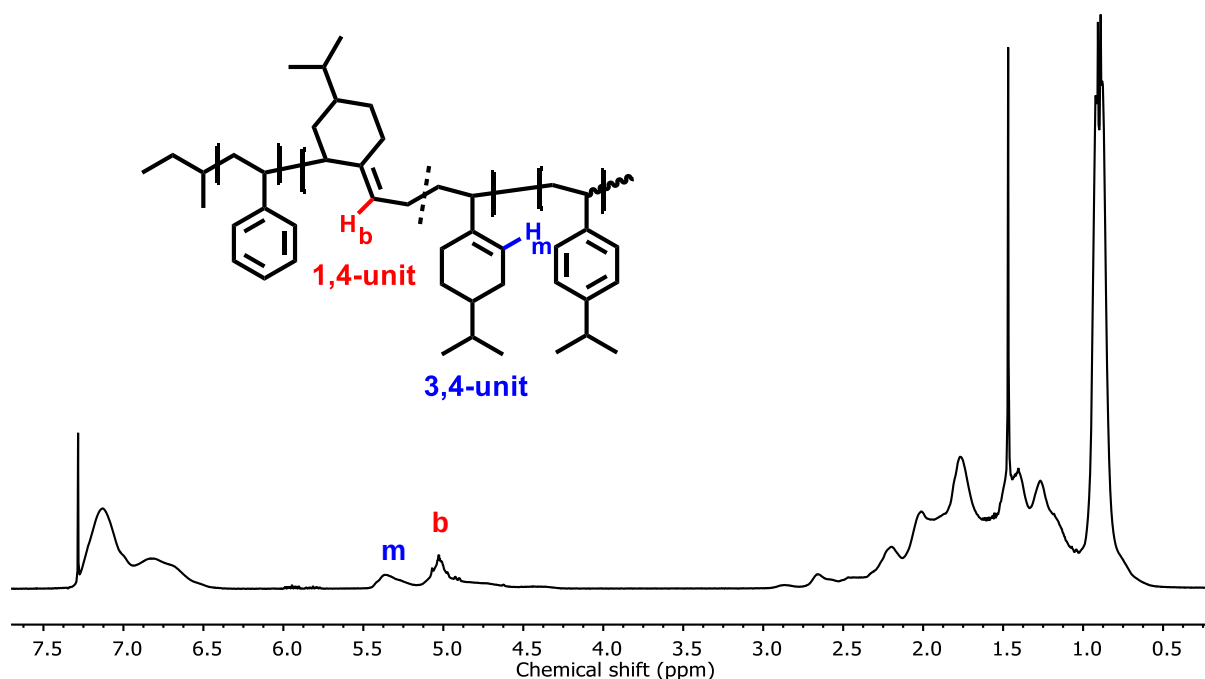


Figure 8: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of P15.

4.3.3.4 Copolymerization with β -myrcene

It was demonstrated that 4IPVCH can be copolymerized with β -myrcene in cyclohexane using *sec*-BuLi as initiator in different compositions, ranging from 25–90% β -myrcene content (P18 25%, P19 50%, P20 75%, P21 90% β -myrcene, respectively). However, the copolymerization of 4IPVCH with β -myrcene lead to bimodal molecular weight distributions, with distributions toward larger elution volumes. The bimodality can be explained by the cross-over reaction from living chain-ends of P(4IPVCH) to polymyrcene. In the case of slow cross-over, bimodal distributions can occur.

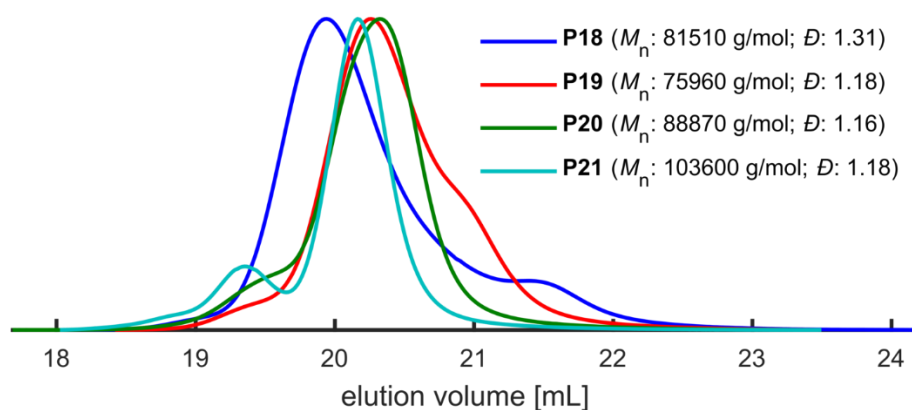


Figure 9: SEC traces (Eluent THF, PS calibration) of the 4IPVCH/ β -myrcene copolymers P18-21.

In the statistical copolymerization of 4IPVCH and β -myrcene molecular weights of 80 kg/mol were targeted. Except P21, the molecular weights determined by SEC are in good agreement with the targeted molecular weight. The deviation of P21 can be attributed to lower initiator concentrations and by that to higher molecular weights.

4.3.3.5 Polymerization of 4-isopropylene-vinylcyclohexene (4IPenVCH)

Inspired by the polymerization of β -myrcene in limonene as a solvent, the synthesis of the unsaturated derivate of 4IPVCH, 4-isopropylene-vinylcyclohexene (I4PenVCH), was investigated.¹³ It was found that the isopropylene unit is stable against the nucleophilic chain end but the stability of I4PenVCH needs to be verified.

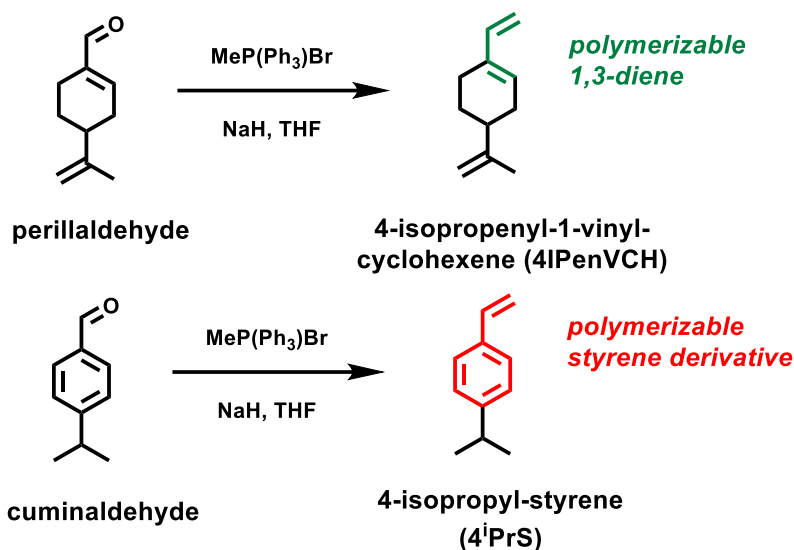


Figure 10: Synthesis of 4IPenVCH from perillaldehyde and synthesis of 4ⁱPrS from cuminaldehyde via Wittig reaction.

Nevertheless, the anionic polymerization of the unsaturated derivate of 4IPVCH, 4-isopropylene-vinylcyclohexene (I4PenVCH), proceeded quantitatively to afford defined homopolymers with narrow molecular weight distributions (P22). Like phellandral, I4PenVCH shows after the Wittig reaction impurities of 4ⁱPrS, that cannot be removed by distillation but by the polymerization in THF at -78°C by means of living anionic polymerization or by column chromatography. This procedure was applied to obtain pure 4IPenVCH, that was subsequently polymerized in cyclohexane using *sec*-BuLi as an initiator. The SEC traces of the resulting polymer (P22) are shown in Figure 10.

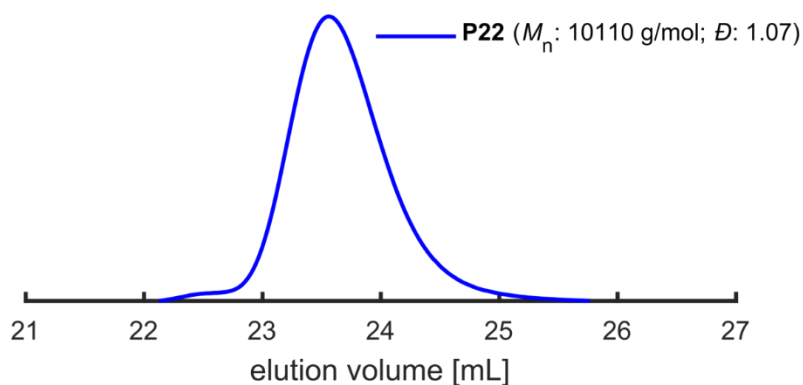


Figure 11: SEC traces (Eluent THF, PS calibration) of the P(4IPenVCH) sample P22.

The monomer for the polymer of P22 was purified by anionic polymerization of the 4ⁱPrS in THF at -78°C. In Figure 10 is the ¹H NMR spectrum of P22 demonstrated.

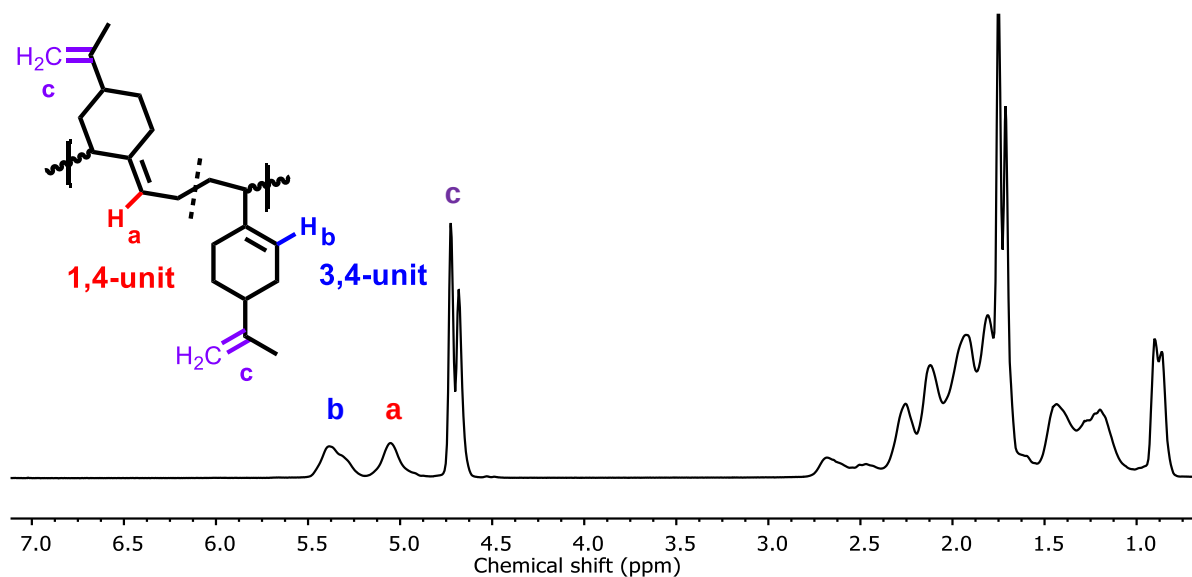


Figure 12: ¹H NMR spectrum (400 MHz, CDCl₃, 25°C) of P(I4PenVCH).

4.3.4 Conclusion

This study aims to contribute to the preparation of fully bio-based polymers with glass transition temperatures comparable to polystyrene. Hence, it demonstrated that copolymers of 4IPVCH and 4ⁱPrS are accessible *via* living anionic polymerization. This work demonstrates the impact of a sterically hindered cyclic 1,3-diene with a *para*-menthane framework in the field of anionic polymerization with respect to initiation reaction, molecular weight and molecular weight distribution. The living anionic polymerization of 4IPVCH affords polymers with good control over molecular weights and moderate to narrow molecular weight distributions. The results show that the microstructure of P(4IPVCH) can be influenced by the addition of THF and DTHFP, leading to a higher extent of 3,4-microstructure. A high *T_g* polydiene in a range of 87°C is obtained as potential substitution for polystyrene materials. The monomer 4IPVCH can be considered as a natural substitute for styrene to receive a fully bio-based materials with similar thermal and mechanical properties.

4.3.5 References

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4.3.6 Supporting Information

4.3.6.1.1 Monomer synthesis 4IPVCH

The synthesis of 4IPVCH from perillaldehyde in a two-step synthesis proceeded via the initial selective hydrogenation of the pendent isopropenyl moiety with PtO₂ according to a procedure of Kamigaito.⁸ (-)-Perillaldehyde (24.60 g, 0.164 mol) was added to a reactor containing PtO₂ (60 mg, 0.25 mmol) and a magnetic stirrer, then ethanol (25 mL) was added. The reactor chamber was sealed and flooded with hydrogen and subsequently pressurized with hydrogen (30 bar, 0.36 mol). The hydrogenation was checked for complete conversion *via* NMR after the pressure diminished no further after 3 h. Diverging from literature, the obtained suspension was reduced under vacuum resulting in a yellowish oil. This crude product was then purified under vacuum (1·10⁻³ mbar, 47-60°C) to give a colorless liquid (22.90 g, 0.15 mol) of approximately 90% purity as (-)-perillaldehyde naturally contains the cuminaldehyde.

The product of the hydrogenation, phellandral, is shown in Figure 12.

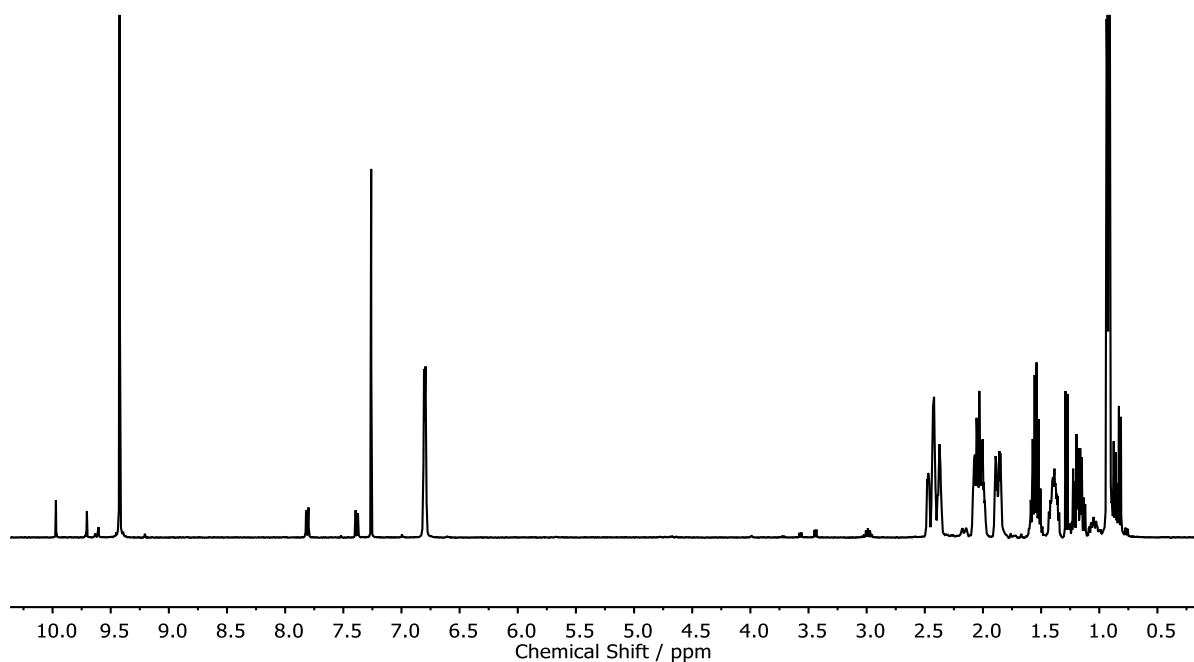


Figure S 1: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of phellandral.

The subsequent Wittig olefination of phellandral was performed according to literature.¹⁰ The NMR analysis of 4IPVCH is shown in Figure 13-16.

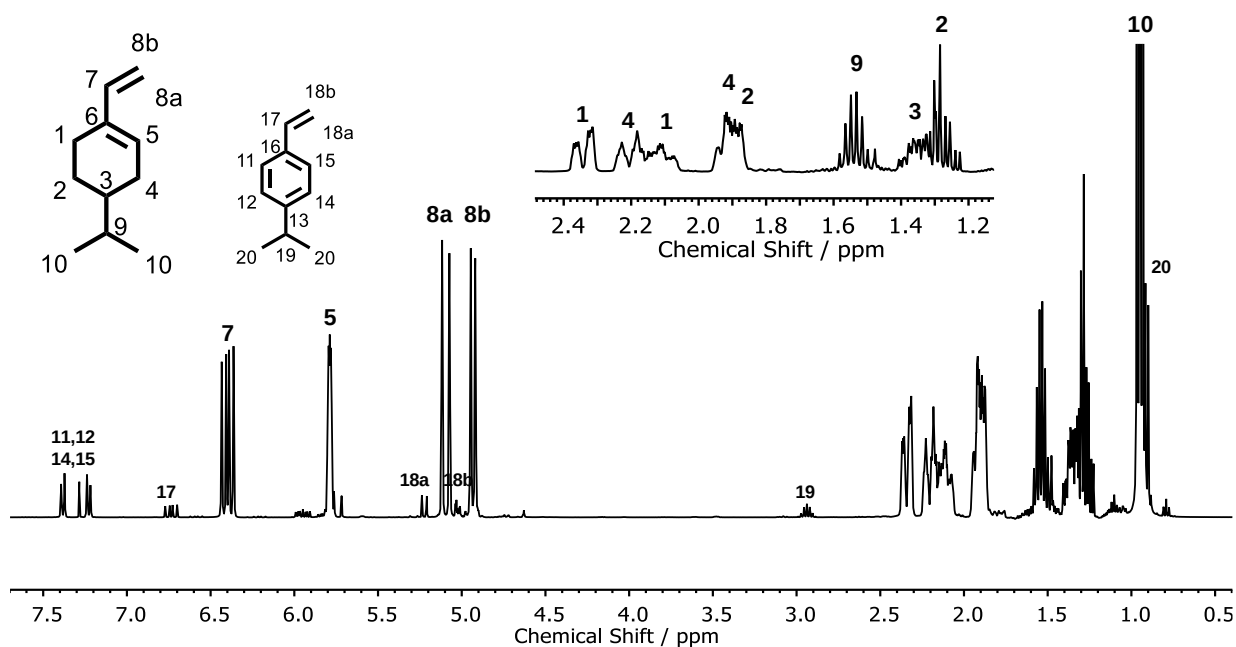


Figure S 2: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of 4IPVCH contaminated with 4*i*PrS.

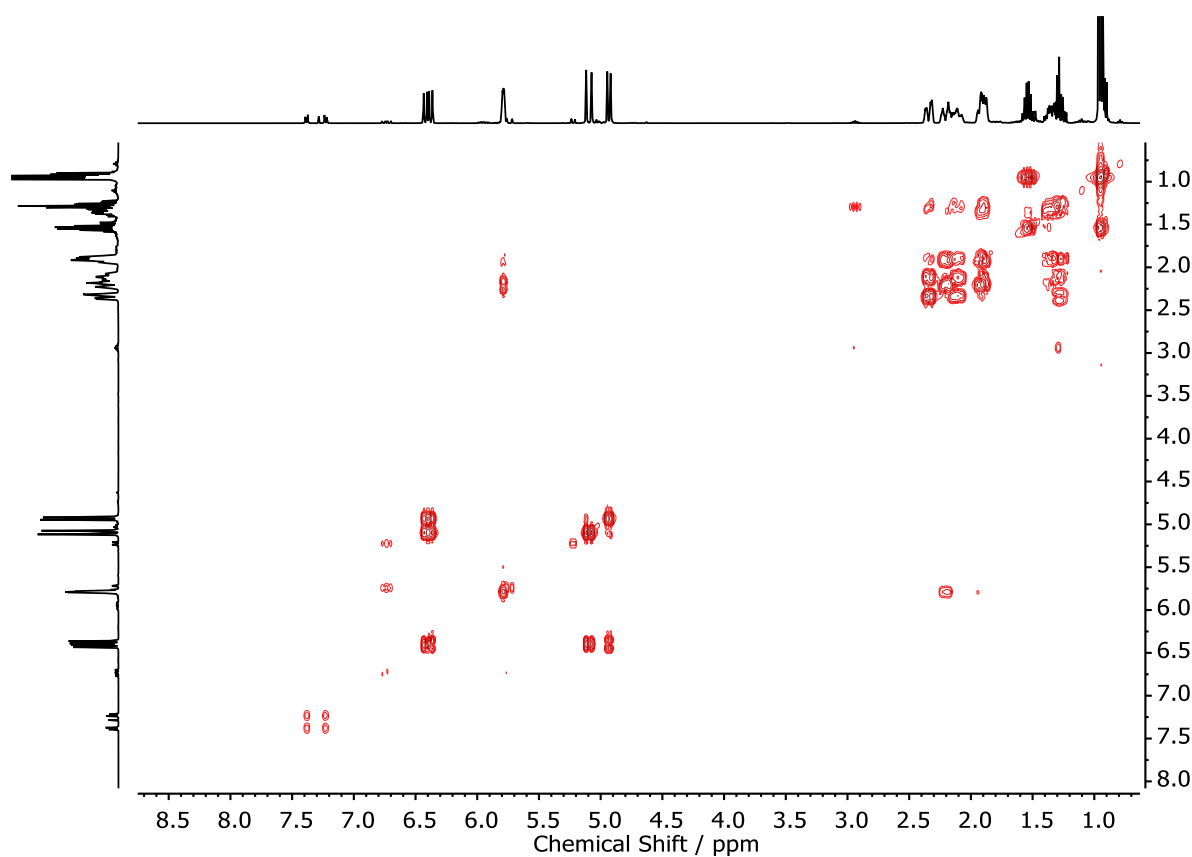


Figure S 3: COSY NMR spectrum (400 MHz, CDCl_3 , 25°C) of 4IPVCH contaminated with 4iPrS.

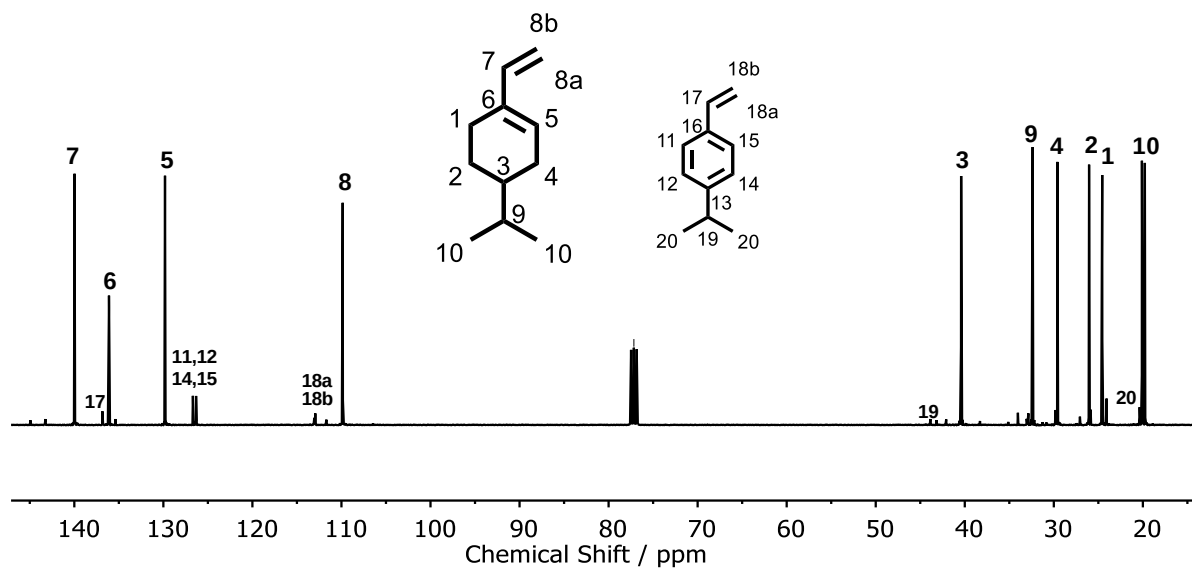


Figure S 4: ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25°C) of 4IPVCH contaminated with 4iPrS.

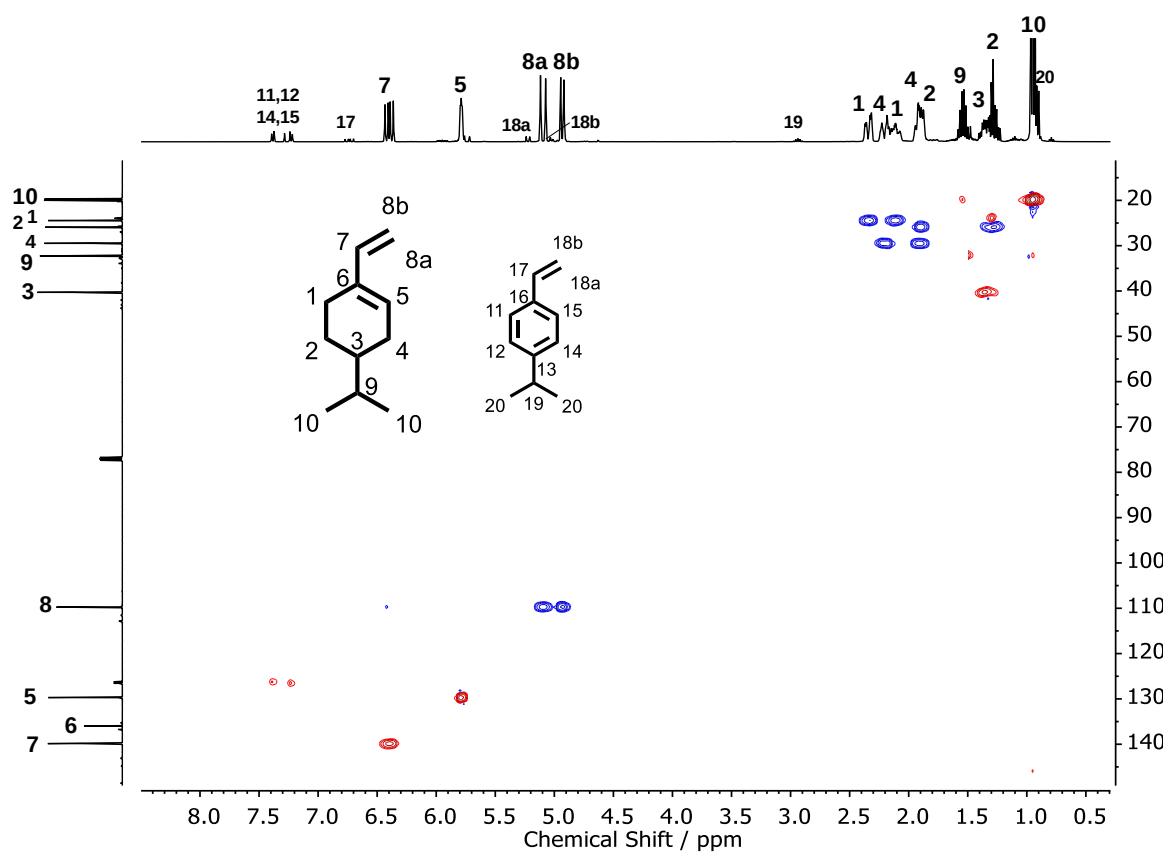


Figure S 5: HSQC NMR spectrum (400/100 MHz, CDCl₃, 25°C) of 4IPVCH contaminated with 4ⁱPrS.

4.3.6.1.2 Polymerization of 4IPVCH

The following spectra in Figure 18-20 are taken from the polymer of 4IPVCH that was contaminated with 5% 4ⁱPrS.

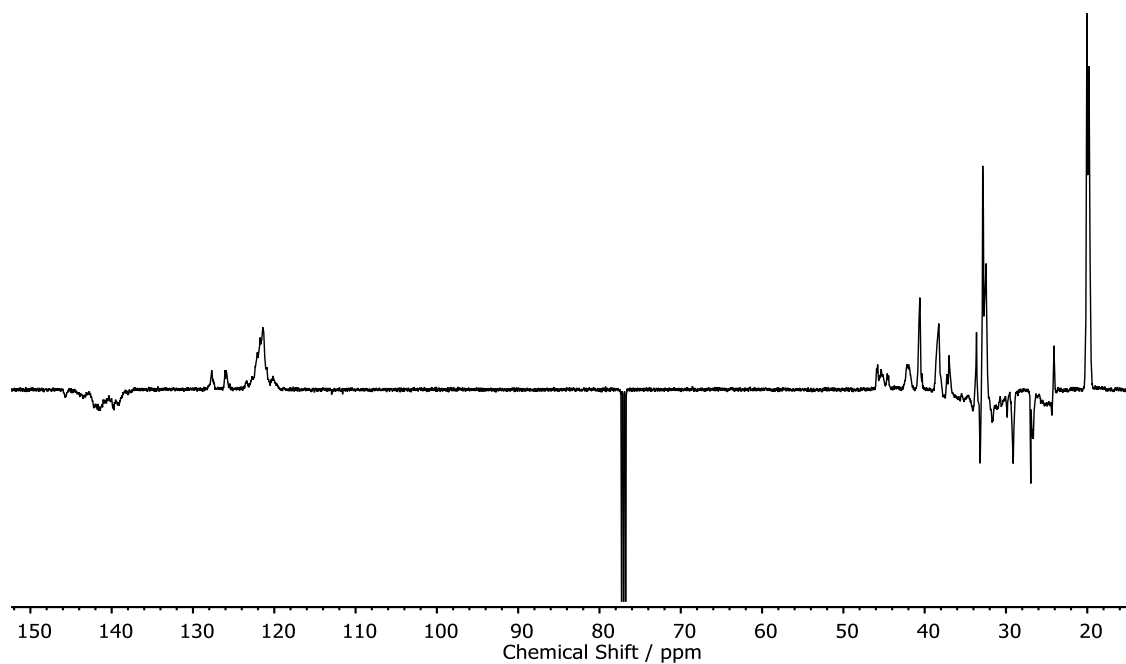


Figure S 6: ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25°C) of P(4IPVCH).

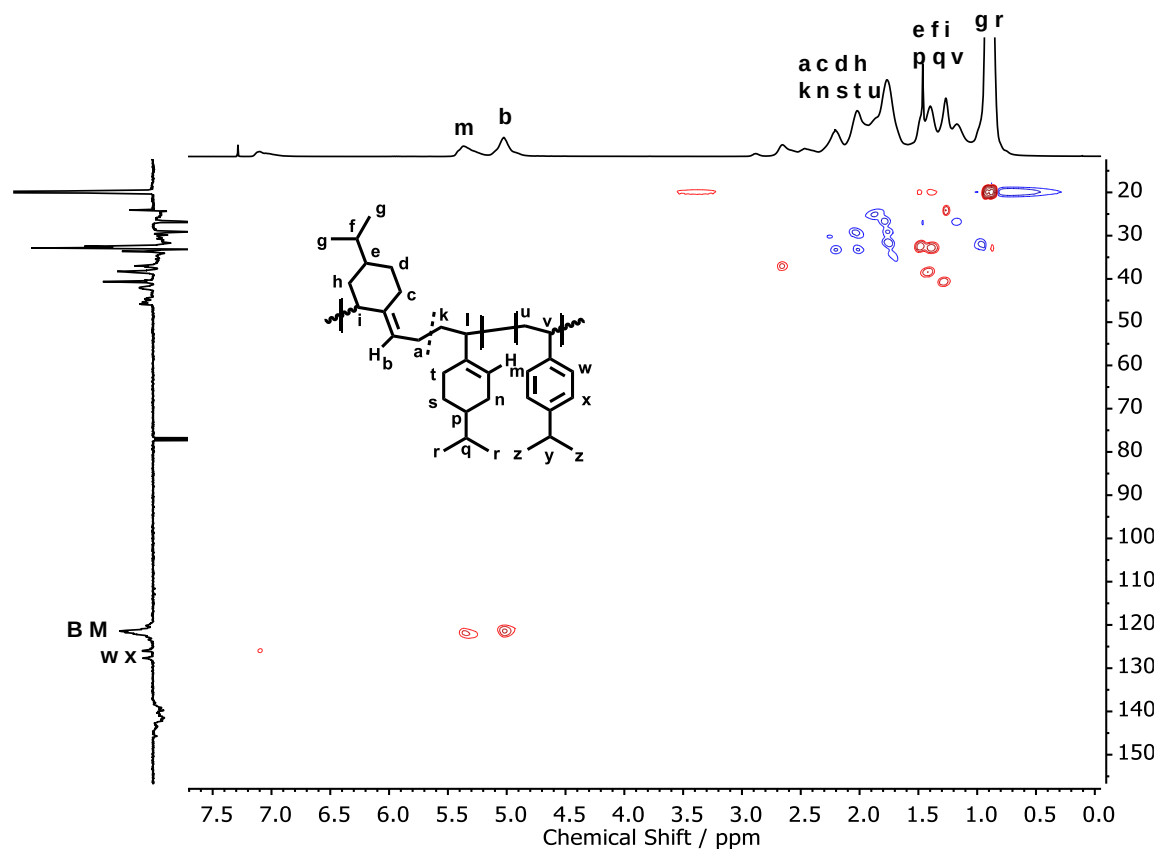


Figure S 7: HSQC NMR spectrum (400/100 MHz, CDCl_3 , 25°C) of P(4IPVCH).

Polymerization in THF at -78°C. Dry and degassed THF was distilled into the reaction flask, and the dry and degassed monomer (4IPVCH contaminated with 4ⁱPrS) was added into the flask via syringe in argon atmosphere. The solution was cooled down to -78 °C, and the polymerization was initiated with *sec*-BuLi. The solution turned red immediately and the polymerization was allowed to stir for 1h. After complete conversion of 4ⁱPrS the polymerization was terminated with degassed methanol. The NMR spectra in Figure 19 shows the purified 4IPVCH by means of living anionic polymerization in THF at -78°C.

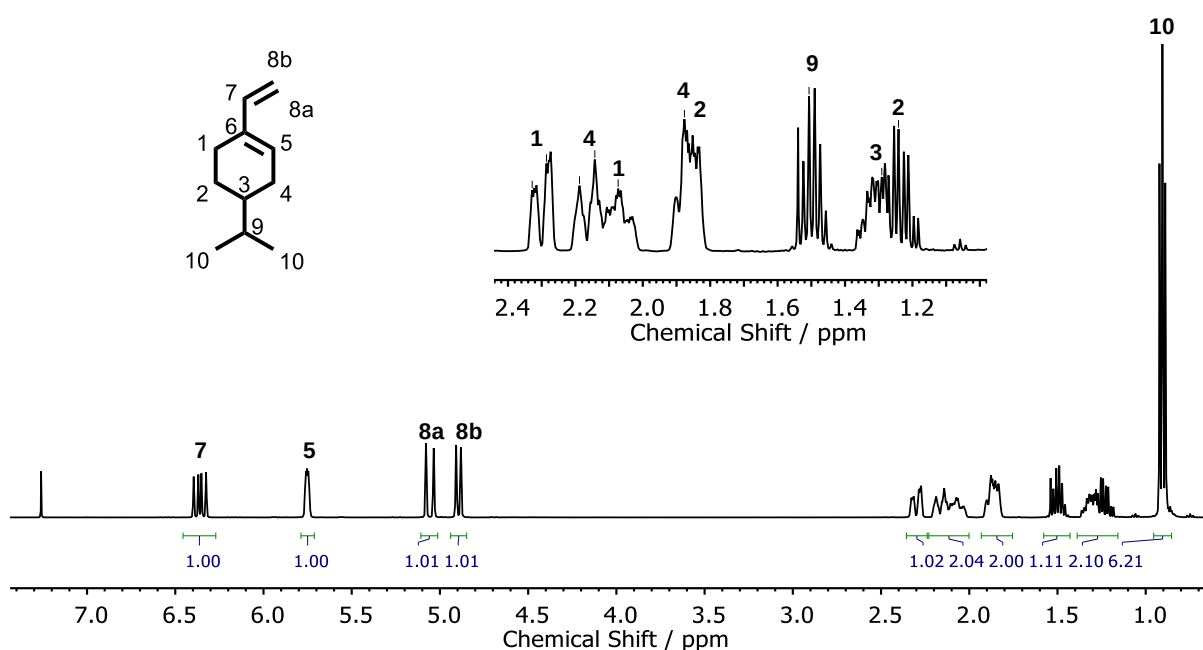


Figure S 8: ¹H NMR spectrum (400 MHz, CDCl₃, 25°C) of 4IPVCH.

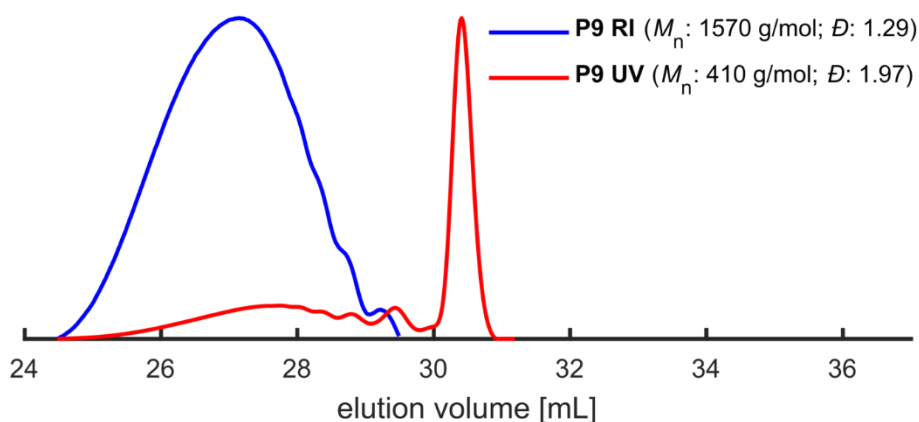


Figure S 9: SEC traces (Eluent THF, PS calibration) of P9, blue refractive index detector, red UV detector.

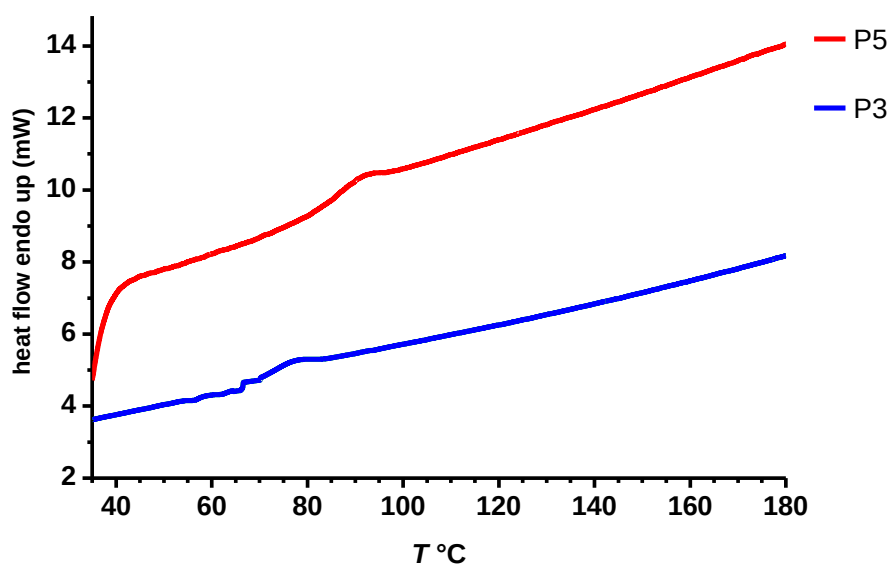


Figure S 10: DSC curves of P3 ($T_g = 72^\circ\text{C}$) and P5 ($T_g = 87^\circ\text{C}$).

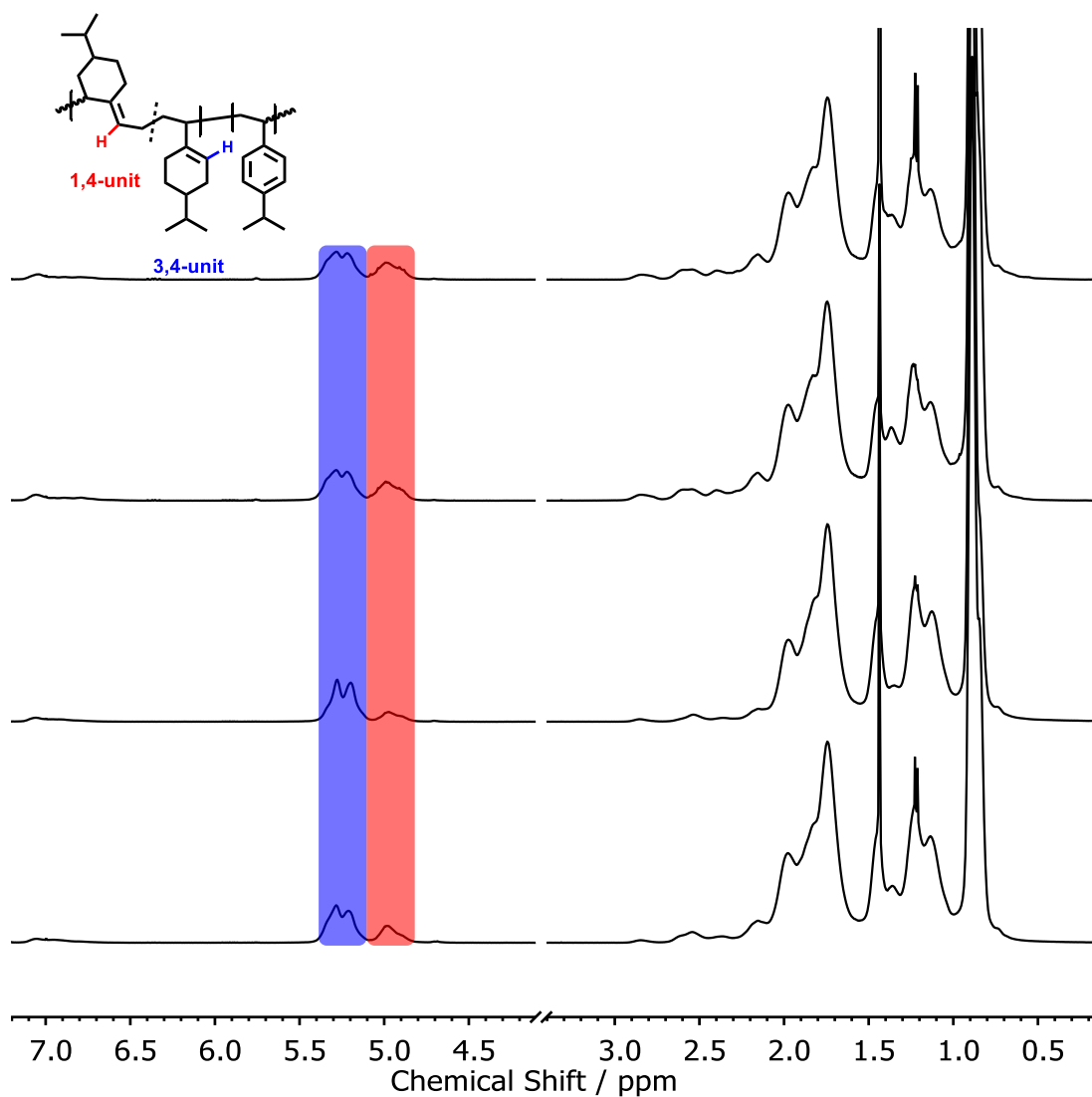


Figure S 11: Stacked ^1H NMR spectra (400 MHz, CDCl_3 , 25°C) of P11-14.

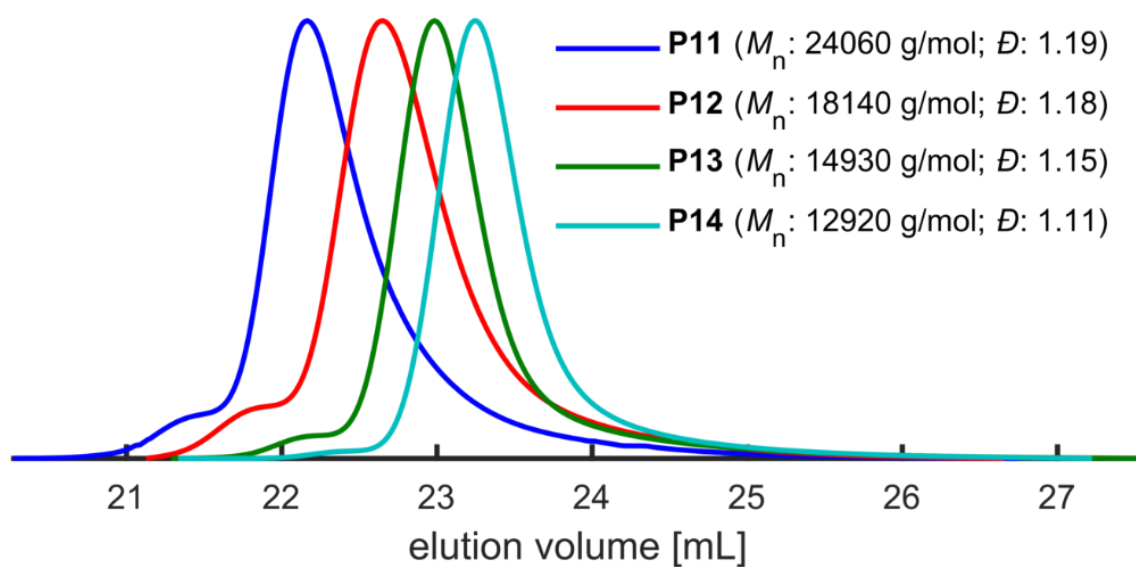


Figure S 12: SEC traces (eluent THF, PS calibration) of P11-14.

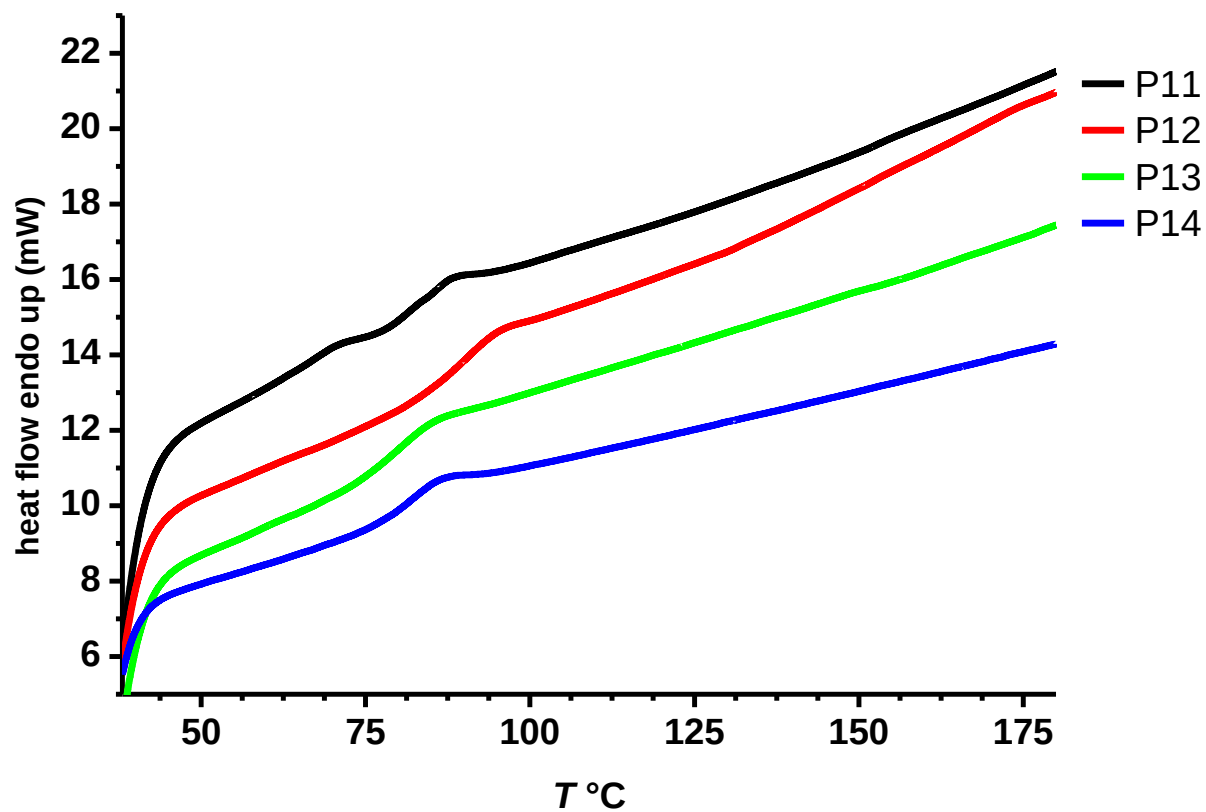


Figure 24: DSC curves of P11 ($T_g = 84^{\circ}\text{C}$), P12 ($T_g = 89^{\circ}\text{C}$), P13 ($T_g = 80^{\circ}\text{C}$) and P14 ($T_g = 82^{\circ}\text{C}$).

4.3.6.1.3 Monomer synthesis 4IPenVCH

4IPenVCH was synthesized according to modified procedure from literature.¹⁴ The NMR spectra of 4IPVCH are demonstrated in . However, before the polymerization, 4IPenVCH was purified from 4ⁱPrS by means of living anionic polymerization in THF at -78°C. After distillation and drying over CaH₂ 4IPenVCH was polymerized under similar conditions as the homopolymers in cyclohexane at 25°C using *sec*-BuLi as initiator.

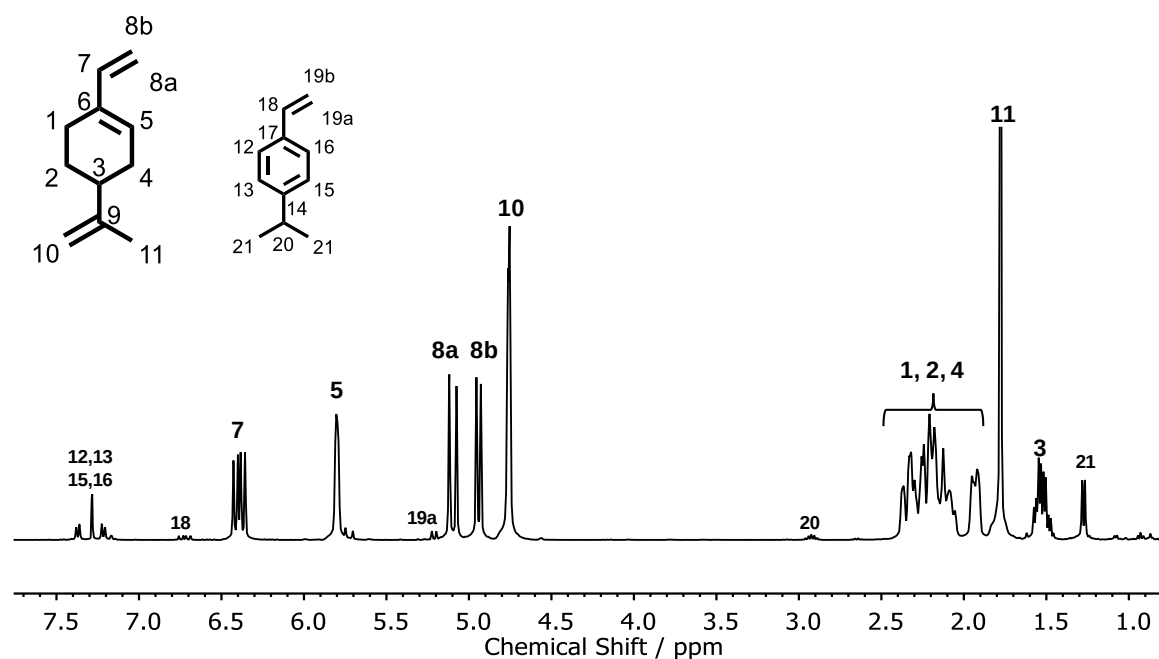


Figure S 13: ¹H NMR spectrum (400 MHz, CDCl₃, 25°C) of 4IPenVCH contaminated with 4ⁱPrS.

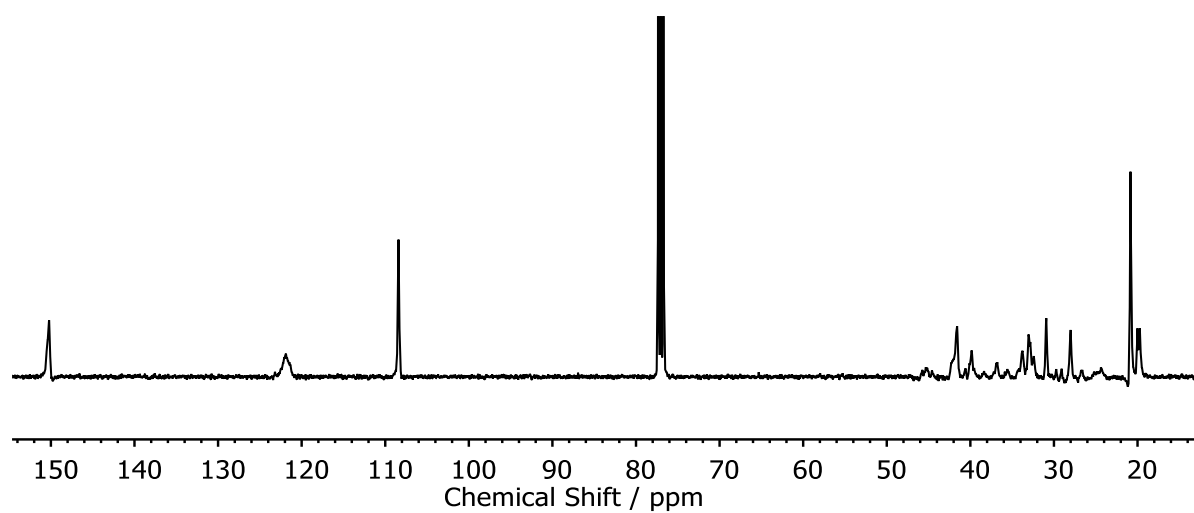


Figure S 14: ^{13}C NMR spectrum (100 MHz, CDCl_3 , 25°C) of P22.

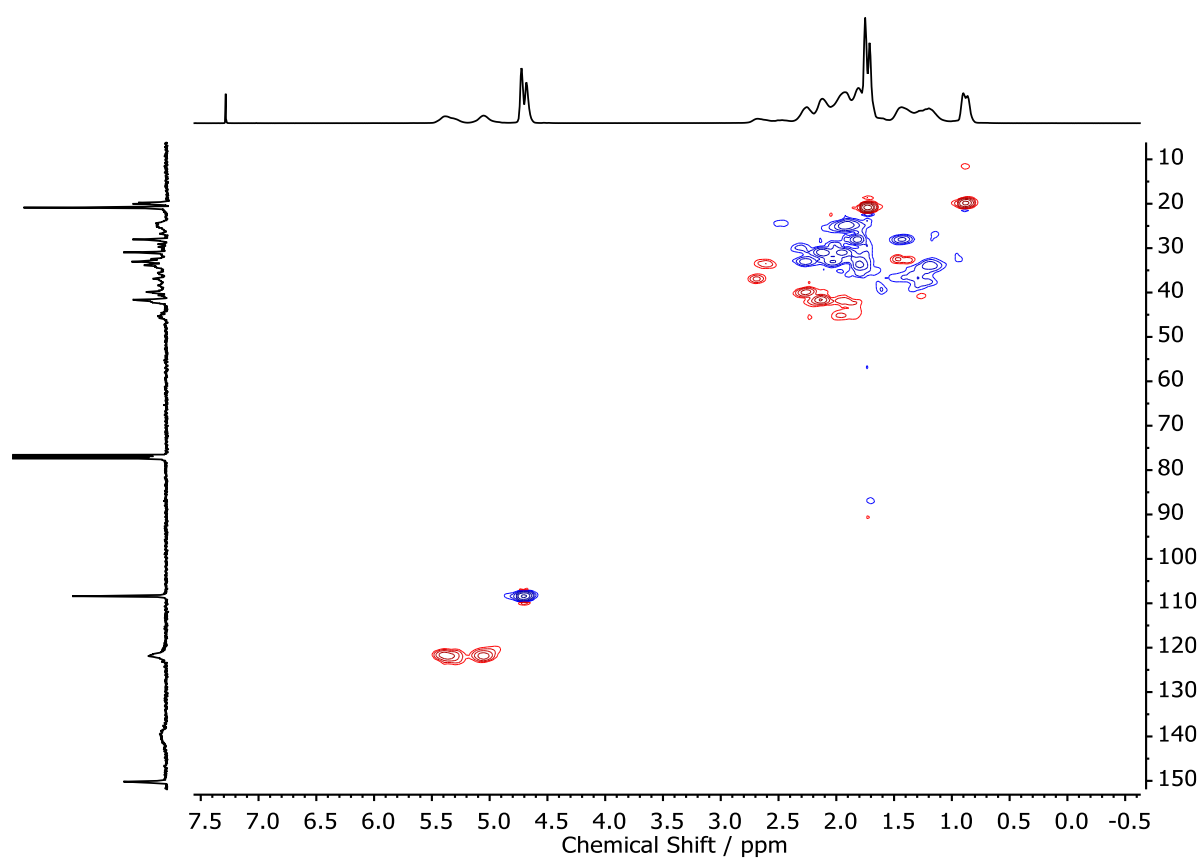


Figure S 15: HSQC NMR spectrum (400/100 MHz, CDCl_3 , 25°C) of P22.

Appendix A1

5 Appendix A1

Molecular Dynamics and Viscoelastic Properties of the Biobased 1,4-Polymyrcene

Ioannis Tzourtzouklis,^a Christoph Hahn,^{b,c} Holger Frey,^b and George Floudas^{a,d}

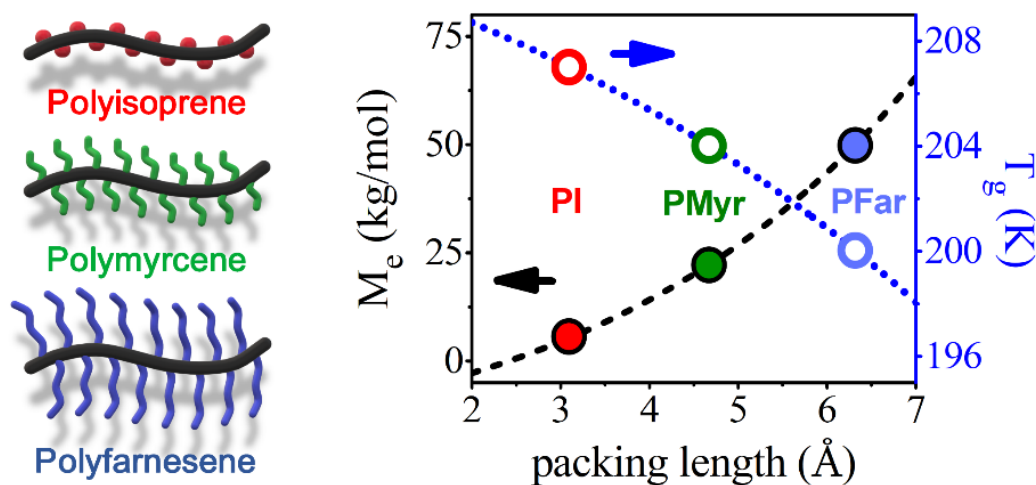
^a Department of Physics, University of Ioannina, Ioannina 45110 (Greece)

^b Department of Chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz (Germany)

^c Max Planck Graduate Center, MPGC, Staudingerweg 9, 55128, Mainz (Germany)

^d University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, Ioannina 45110 (Greece)

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Molecular Dynamics and Viscoelastic Properties of the Biobased 1,4-Polymyrcene

Ioannis Tzourtzouklis, Christoph Hahn, Holger Frey,* and George Floudas*

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ABSTRACT: We report the synthesis and dynamics of a series of polymyrcene homopolymers, all with identical microstructures (95% 1,4-units and 5% of 3,4-units), the latter by dielectric spectroscopy and rheology. Polymyrcene belongs to an important class of bio-based polymers (polyterpenes) with known members, the *cis*-1,4-polyisoprene and the *cis*-1,4-polyfarnesene. Polyterpenes constitute a class of type-A polymers where by architectural design, one can control the thickness of chains and henceforth the segmental and chain dynamics. The dielectric, rheology, and thermodynamic results showed a lower glass temperature in *cis*-1,4-polymyrcene as compared to *cis*-1,4-polyisoprene. A weak dependence of the segmental and longest normal mode on pressure revealed the dominant effect of the backbone. Furthermore, comparing polymyrcene with available literature data of polyisoprene and polyfarnesene, we report the effect of chain thickening on the viscoelastic properties. The plateau modulus, G_N^0 , decreased, the entanglement molar mass increased (from 5 kg·mol⁻¹ in *cis*-1,4-polyisoprene to 22 kg·mol⁻¹ in *cis*-1,4-polymyrcene), and the packing length, p , increased (from 3.1 Å in *cis*-1,4-polyisoprene to 4.7 Å in *cis*-1,4-polymyrcene) as anticipated by chain thickening. The plateau modulus, G_N^0 , followed the proposed empirical relation: $G_N^0 = 0.00226k_B T/p^3$, further reflecting the proportionality between the tube diameter and the packing length.

INTRODUCTION

Limited fossil feedstock along with the environmentally adverse effects of petrochemical products have increased the necessity of finding sustainable alternatives to replace the petroleum-based 1,3-diene monomers isoprene and butadiene (commercially used for the synthesis of synthetic rubber thermoplastic elastomers).¹ Hence, an increasing interest in bio-based polymer materials from renewable sources is generally observed.^{1–3} Terpenes are an important class of biomass compounds.^{4–8} They are naturally abundant, originating from plants that are used, e.g., in pharmaceutical products. The most well-known example of polyterpenes is natural rubber, i.e., *cis*-1,4-polyisoprene (PI) comprising about 40% of the total rubber consumption worldwide. Among the variety of bio-based monomers, myrcene (Myr) has garnered considerable attention due to its convenient availability and structural similarity to isoprene and butadiene.^{9–11} Myrcene belongs to the class of monoterpenes that can be found in plants like conifers, wild thyme, hop, and bay leaves.¹² Similar to its petroleum-derived diene counterparts, myrcene can be polymerized by various polymerization techniques like emulsion polymerization, controlled and free radical polymerization, and living anionic polymerization.^{6–8} Polymyrcene provides similar properties to polyisoprene, such as a low glass temperature, T_g , and high content of 1,4-units when polymerized in nonpolar solvents. Regarding the possible microstructures, the actual incorporation mode is 4,1-*trans* and 4,1-*cis* since the carbanionic chain end attacks preferentially the more reactive 3,4-double bond of the monomer.

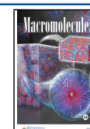
From an architectural/topological point of view, polymyrcene (PMyr) is related to PI and polyfarnesene (PFar). While polyisoprene can be considered as a linear polymer with methyl side groups, the length of the side groups increases from polymyrcene to polyfarnesene, with the latter having a bottlebrush-like structure (Scheme 1).⁶ From a dynamics point of view, all three polyterpenes exhibit an asymmetric structure with dipole moment having components both along and perpendicular to the chain contour (they are type-A polymers according to the classification by Stockmayer^{13–23}). This fact makes them ideal candidates for studying the effect of chain thickening on the viscoelastic and dielectric properties by investigating the effect of the repeat unit asymmetry on the segmental and chain dynamics.

Herein, we report the synthesis of a series of polymyrcene homopolymers with molar masses in the range from 1600 to 126,000 g mol⁻¹ with identical microstructures (95% 1,4-polymyrcene units and 5% 3,4-units). In the first dynamics investigation of PMyr – with dielectric spectroscopy and rheology – we address the question of how the thickening of the chain as well the difference in stiffness of the side groups

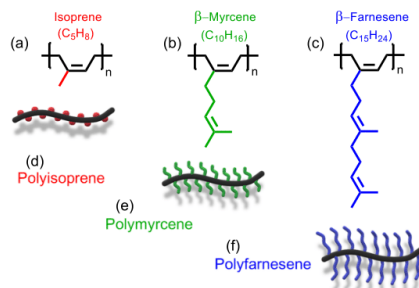
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Scheme 1. Chemical Structure of (a) *cis*-1,4-Polyisoprene, (b) *cis*-1,4-Polymyrcene, and (c) *cis*-1,4-Polyfarnesene (Pictorial Representation of the Chain Architecture, Respectively, in Panels (d–f))



associated with variations in chemistry (Scheme 1) affects the segmental and chain dynamics, including the effect on viscoelastic properties (plateau modulus and entanglement molar mass). We find that chain packing, through the packing length, affects all relevant dynamic properties, from the segmental to the chain length scales. The results are compared with *cis*-1,4-polyfarnesene studied recently by DS and rheology.²⁴ Overall, polyterpenes constitute a class of type-A polymers, where by architectural design, one can control the thickness of chains and henceforth the viscoelastic response.

EXPERIMENTAL SECTION

Instrumentation. All NMR spectra (¹H, D1 30 s.) were recorded on a Bruker Avance II 400 spectrometer equipped with a 5 mm BBFO-SmartProbe with a *z* gradient and ATM as well as a SampleXpress 60 sample changer. All spectra are referenced internally to residual proton signals of the deuterated solvent (CDCl₃). Representative ¹H NMR curves are provided in Figures 1 and 2. Size exclusion chromatography (SEC) measurements were performed using an Agilent 1100 Series, equipped with an SDV column set from PSS (SDV 103, SDV 105, SDV 106). Tetrahydrofuran (THF) was used as the mobile phase (flow rate 1 mL min⁻¹) and as the solvent. Polyisoprene standards were provided by PSS for calibration. All measurements were carried out at 303 K, with RI and UV (275 nm) detectors. In the analysis, we have employed the PSS WinGPC UniChrom (V 8.31, Build 8417) software provided by PSS Polymer Standards Service GmbH.

Synthesis. All polymerizations were carried out in cyclohexane at 298 K (except for the samples with the higher molar masses: PMyr₅₀₀, PMyr₇₁₃, and PMyr₉₂₆) in an argon-filled glovebox (MBraun

UNILAB, <0.1 ppm O₂, and <0.1 ppm H₂O) in 40 mL glass vials equipped with a magnetic stir bar, screw caps, and septa. Dry and degassed cyclohexane (or *n*-heptane, respectively) was distilled into a Schlenk flask equipped with a Teflon stopper. Myrcene was dried for 24 h over CaH₂ and then additionally for 24 h over triethylaluminum, degassed, and finally distilled into another Schlenk flask with a Teflon stopper. Inside the glove box, the monomer and cyclohexane (*n*-heptane) were added into a reaction flask with a septum. For the synthesis of polymyrcene, the monomer/solvent (10 wt %) mixture was initiated with 0.1 mL or 0.05 mL of *sec*-butyllithium (1.3 M in cyclohexane/hexane 92/8) via a 0.1 mL syringe. The solution was stirred for 24 h at room temperature to ensure full monomer conversion. For the synthesis of the PMyr₅₀₀, PMyr₇₁₃, and PMyr₉₂₆, *n*-heptane was used as a solvent at 313 K. To reduce the increasing viscosity of the polymer solution when targeting high molar masses, a slightly higher reaction temperature (313 K) and, consequently, the higher boiling solvent *n*-heptane were employed. The SEC traces of the samples are shown in Figure 3, and the obtained molar masses are summarized in Table 1. In two samples, PMyr₇₁₃ and PMyr₉₂₆, oxygen coupling is observed. This is not surprising because a certain (small) extent of oxygen coupling can occur at high molecular weights due to the high viscosity. In both cases, the couplings can be estimated to be less than 10%. The DS and rheology measurements suggest that the fraction of coupled higher molar mass polymer does not have a major impact on the dielectric and viscoelastic properties. To show this, we provide rheology data at different temperatures for PMyr₇₁₃ in Figure S6, Supporting Information.

Microstructure of PMyr. The microstructure of polymyrcene was investigated via ¹H NMR spectroscopy. For the quantification of the 1,4-units of polymyrcene (C_{1,4}), eq 1 was used.

$$C_{1,4} = \frac{I_{1,4}}{I_{3,4} + I_{1,4}}, \text{ where } I_{1,4} = \frac{I(4.97 - 5.29 \text{ ppm}) - I_{3,4}}{2}$$

$$\text{and } I_{3,4} = \frac{I(4.76 - 4.85 \text{ ppm})}{2} \quad (1)$$

Figures 1 and 2 show the respective ¹H NMR spectra (400 MHz, CDCl₃, 298 K) of PMyr₇₂ and PMyr₅₀₀. The spectra confirm that all samples (regardless of the synthesis in cyclohexane or *n*-heptane) showed an identical microstructure with 95% 1,4-polymyrcene units and 5% 3,4-units. 1,2-Incorporation of myrcene was not observed.

Differential Scanning Calorimetry (DSC). The thermal properties of the polymyrcene samples were investigated by differential scanning calorimetry through the QA 2000 (TA Instruments). The instrument was calibrated for the baseline using a sapphire standard, for the enthalpy and temperature using indium as a standard, and for the heat capacity using sapphire as a standard.

Dielectric Spectroscopy (DS). Dielectric spectroscopy measurements as a function of temperature (*i.e.*, under "isobaric" conditions) were performed with the Novocontrol Alpha high-resolution frequency analyzer within the frequency range from 10⁻² to 10⁷ Hz

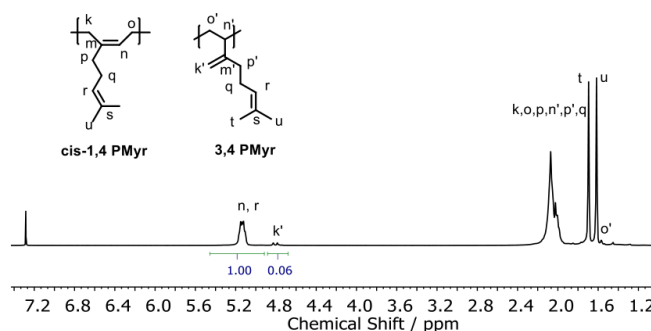


Figure 1. ¹H NMR spectrum (400 MHz, CDCl₃, 25 °C) of PMyr₇₂ (synthesized in cyclohexane, 25 °C).

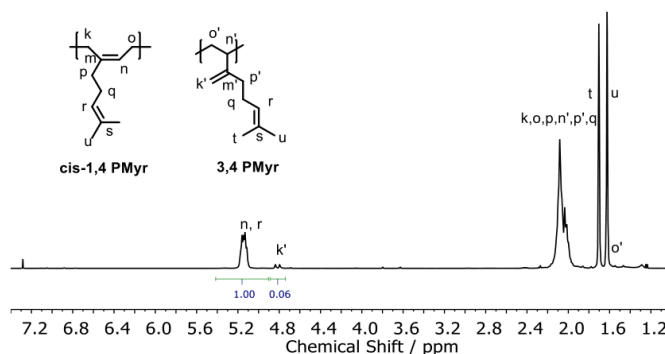


Figure 2. ^1H NMR spectrum (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) of PMyr_{300} (synthesized in *n*-heptane, 40 $^\circ\text{C}$).

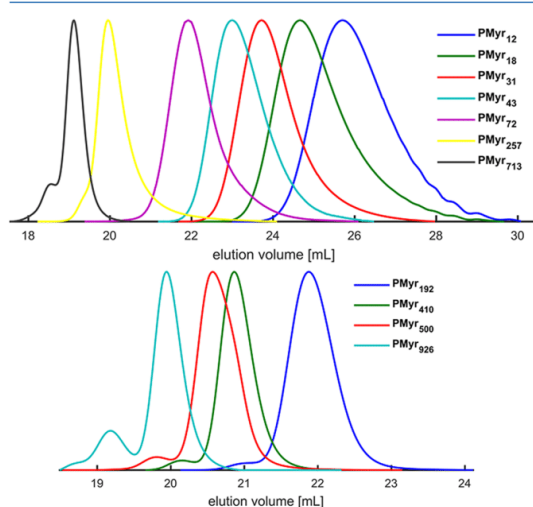


Figure 3. SEC traces (eluent: THF, calibration polyisoprene) of polymyrce with varying molar masses. Samples PMyr_{192} , PMyr_{410} , PMyr_{500} , and PMyr_{926} were measured using a different calibration set of polyisoprene standards.

Table 1. Molar Masses and Dispersities as Determined by GPC (Eluent: THF, PI Calibration) for the *cis*-1,4-Polymyrce Homopolymers

sample ID	M_n ($\text{g}\cdot\text{mol}^{-1}$)	$\bar{D}$
PMyr_{12}	1600	1.21
PMyr_{18}	2500	1.21
PMyr_{31}	4200	1.13
PMyr_{43}	5900	1.11
PMyr_{72}	9900	1.15
PMyr_{192}	26,100	1.06
PMyr_{257}	34,900	1.21
PMyr_{410}	55,800	1.05
PMyr_{500}	68,000	1.07
PMyr_{713}	97,000	1.12
PMyr_{926}	126,000	1.11

and for temperatures in the range from 173.15 to 353.15 K. All samples, before measurement, were placed into an oven under vacuum conditions in order to remove any humidity. The DS

measuring cell consisted of two platinum electrodes (of 20 mm diameter) forming a capacitor. A Teflon spacer was inserted in the sample so as to keep the distance of the electrodes fixed (about 50 μm). By applying an alternating electric field to the capacitor, the complex dielectric function (ϵ^*) is obtained as a function frequency (ω), temperature (T), and pressure (P). The latter is defined as $\epsilon^* = \epsilon' - i\epsilon''$, where the real part (the dielectric permittivity) refers to the energy that is reversibly stored in the dielectric and the imaginary part to the dielectric losses. The analysis of the DS curves was based on the empirical equation of Havriliak and Negami (eq 2).^{25,26}

$$\epsilon_{\text{HN}}^*(\omega, T, P) = \epsilon_\infty(T, P) - \frac{\Delta\epsilon(T, P)}{[1 + (i\omega\tau_{\text{HN}}(T, P))^m]^n} + \frac{\sigma_0(T, P)}{i\epsilon_0\omega} \quad (2)$$

where $\epsilon_\infty(T, P)$ is the high frequency permittivity, $\epsilon_0(T, P)$ is the permittivity of free space, $\tau_{\text{HN}}(T, P)$ refers to the characteristic relaxation time of this model, $\Delta\epsilon(T, P) = \epsilon_0(T, P) - \epsilon_\infty(T, P)$ is the relaxation strength of the process under investigation, $\sigma_0(T, P)$ introduces the DC conductivity, m and n describe, respectively, the symmetrical and asymmetrical broadening of the relaxation times distribution, and finally $\omega (= 2\pi f = 1/\tau)$ is the angular frequency of the external electric field. From the τ_{HN} , the relaxation times at maximum loss, τ_{max} were obtained analytically from the HN equation as follows:

$$\tau_{\text{max}} = \tau_{\text{HN}} \sin^{-1/m} \left(\frac{\pi m}{2(1+n)} \right) \sin^{1/m} \left(\frac{\pi mn}{2(1+n)} \right) \quad (3)$$

In the temperature range where two, or more, relaxation processes contribute to ϵ^* , a summation of HN functions was used, assuming statistical independence in the frequency domain. Exemplary fits to a summation of HN functions are provided in Figure S1, Supporting Information section.

Dielectric measurements under pressure (*i.e.*, under "isothermal" conditions) were carried out, within the pressure range 20 to 260 MPa, in 20 MPa steps.^{27–30} The experimental setup consisted of a Novocontrol BDS system with the frequency response analyzer Solartron Schlumberger FRA 1260, a temperature-controlled cell, in which the sample was placed into a closing hydraulic press with an air pump and an air pump for hydrostatic test pressure. The sample capacitor consisted of two electrodes (diameter 20 mm) and a 50 μm Teflon spacer, wrapped with Teflon tape and placed into a Teflon ring. Following this, epoxy resin was applied to the area between the electrodes and the ring, in order to ensure that the sample is fully insulated. Subsequently, the sample was submerged into the temperature-controlled cell where the pressure is uniformly exerted by the silicon oil DOW CORNING 550 Fluid. The "isothermal" frequency sweeps were made with a temperature stability of approximately ± 0.1 K and pressure stability of about ± 2 MPa.

Rheology. The viscoelastic properties of polymyrce have been studied with the TA Instruments Rheometer AR-G2 equipped with a magnetic bearing that allows for nanotorque control. Measurements were performed in an environmental test chamber (ETC). Samples were prepared on the lower rheometer plate (8 mm), and the upper plate was adjusted aptly to ensure a uniform gap thickness. Temperature control was achieved through a nitrogen convection oven. The linear and non-linear viscoelastic regimes were determined by the strain amplitude dependence of the complex shear modulus $|G^*|$, at $\omega = 10 \text{ rad s}^{-1}$. Data of complex shear modulus as a function of frequency were obtained by frequency sweeps into the range of $0.1\text{--}100 \text{ rad s}^{-1}$ for several temperatures near and above the glass temperature. According to the principle of time–temperature superposition (tTs), the frequency dependence of the complex shear modulus G^* at any temperature can be obtained from a master curve at a reference temperature (T_r) according to the equation: $G^*(\omega, T) = b_T G^*(a_T \omega; T_r)$. When the tTs is valid, then at each temperature, a single frequency-scale shift factor a_T and a single modulus-scale shift factor b_T allow superposition of all viscoelastic data at any temperature T . Our attempted superpositions involved independent estimation of the two shift factors by first shifting the loss tangent data ($\tan \delta = G''/G'$) on the frequency scale, thus obtaining a_T and subsequently determining b_T by an independent modulus-scale shift of G^* . Horizontal shift factors a_T were fitted according to the Williams–Landel–Ferry (WLF) equation³¹ (eq 4).

$$\log a_T = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)} \quad (4)$$

where C_1 and C_2 are empirical parameters at the reference temperature (T_r).

RESULTS AND DISCUSSION

Dielectric Spectroscopy. The results of the DS study as a function of temperature and pressure are discussed with respect to Figures 4–7 and 8, respectively. Representative

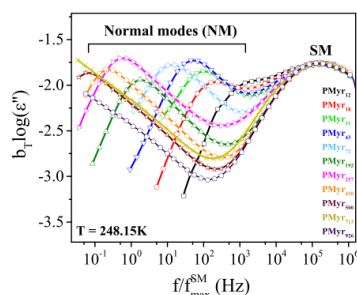


Figure 4. Dielectric loss curves as a function of frequency for the different molar masses (black: PMyr₁₂, red: PMyr₁₈, light green: PMyr₃₁, blue: PMyr₄₃, light blue: PMyr₇₂, olive: PMyr₁₉₂, magenta: PMyr₂₅₇, orange: PMyr₄₁₀, dark magenta: PMyr₅₀₀, yellow: PMyr₇₁₃, dark blue: PMyr₉₂₆) at a reference temperature of 248.15 K. Two distinct loss peaks are observed known as the longest normal mode (longest NM), at lower frequencies and segmental mode (SM) at higher frequencies. The curves have been normalized so as to coincide at the SM peak frequency.

dielectric loss curves for the PMyr homopolymers of Table 1 are compared at a common temperature ($T = 248.15 \text{ K}$) in Figure 4. The loss curves depict a faster segmental process (SM) and a slower spectrum of normal modes (NM) with peak frequencies that depend strongly on molar mass. The curves have been slightly shifted on the horizontal (frequency) axis and subsequently on the vertical axis so as to coincide at

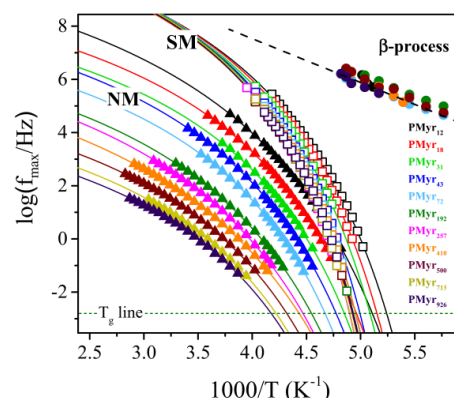


Figure 5. Relaxation map of the different processes in PMyr homopolymers depicting the β -process (filled symbols), the segmental (open squares), and longest normal mode (filled triangles). Solid lines represent VFT fits to the characteristic frequencies corresponding to the SM and longest NM at temperatures above T_g . The horizontal dashed line at a characteristic time of 100 s ($\tau = 1/2\pi f_{\max}$) defines the corresponding T_g 's. At lower temperatures, the β -process is fitted to an Arrhenius equation (dashed line).

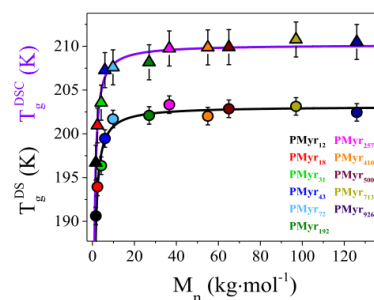


Figure 6. Molar mass dependence of the glass temperature of polymyrce. Data refer to DS (circles; T_g is defined at a characteristic time of 100 s) and to DSC (triangles). This dependence can be described by the Fox–Flory equation (solid lines).

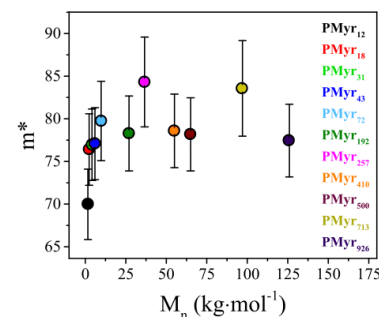


Figure 7. Fragility or steepness index, m^* , as a function of molar mass calculated for the different molar masses, which are indicated by different colors.

the SM peak frequency. The asymmetric shape of the spectrum of normal modes (with a low-frequency slope of 1 in a log–log representation) and especially the contribution of the shorter

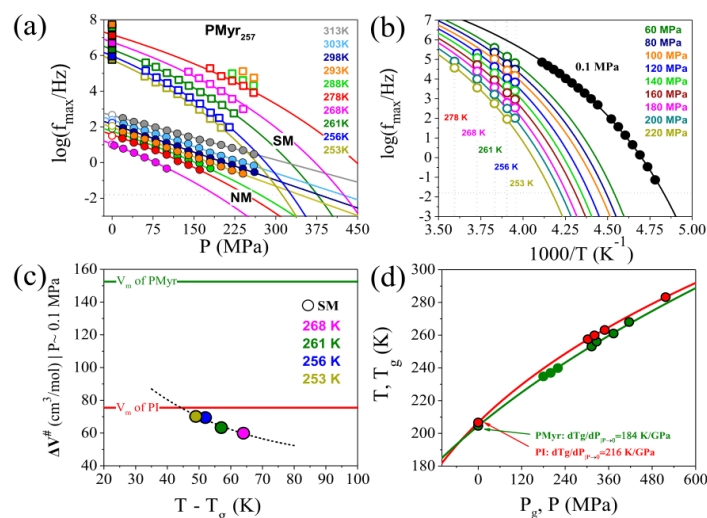


Figure 8. (a) Frequency at maximum loss corresponding to the segmental (open squares) and longest normal (filled circles) mode as a function of pressure for the following temperatures: 313 K (gray), 303 K (light blue), 298 K (navy), 293 K (orange), 288 K (green), 278 K (red), 268 K (magenta), 261 K (olive green), 256 K (blue), and 253 K (gold). Solid lines are fits to the experimental data according to eq 8. Filled squares and open circles at 0.1 MPa are extracted from “isobaric” DS measurements. (b) Frequency at maximum loss corresponding to the segmental mode as a function of temperature at different pressures; 0.1 MPa (black), 60 MPa (olive green), 80 MPa (navy blue), 100 MPa (orange), 120 MPa (blue), 140 MPa (green), 160 MPa (red), 180 MPa (magenta), 200 MPa (dark green), and 220 MPa (gold). (c) Apparent activation volume ($\Delta V^\#$) as a function of temperature for the segmental process plotted as a function of the temperature difference from T_g . Red and green solid lines give the volume of the repeat unit of PI and PMyr, respectively. (d) Pressure dependence of glass temperatures (T_g) for polymyrcene and polyisoprene. Solid lines are fits to eq 10.

Table 2. VFT Parameters for the Segmental (SM) and the Longest Normal Mode (NM) Obtained by DS

sample ID	segmental mode (SM)			longest normal mode (NM)		
	$-\log(f_{\max}/\text{Hz})$	B (K)	T_0 (K)	$-\log(f_{\max}/\text{Hz})$	B (K)	T_0 (K)
PMyr ₁₂	-12^a	1347 ± 9	151 ± 1	-10.1 ± 0.1	1460 ± 38	147 ± 1
PMyr ₁₈	-12^a	1308 ± 10	156 ± 1	-9.3 ± 0.1	1322 ± 26	154 ± 1
PMyr ₃₁	-12^a	1305 ± 4	158 ± 1	-8.6 ± 0.2	1274 ± 56	157 ± 2
PMyr ₄₃	-12^a	1280 ± 4	162 ± 1	-8.5 ± 0.1	1371 ± 27	157 ± 1
PMyr ₇₂	-12^a	1243 ± 9	165 ± 1	-7.9 ± 0.1	1380 ± 22	158 ± 1
PMyr ₁₉₂	-12^a	1287 ± 13	164 ± 1	-7.3 ± 0.1	1550 ± 32	153 ± 1
PMyr ₂₅₇	-12^a	1232 ± 5	168 ± 1	-6.7 ± 0.1	1421 ± 22	159 ± 1
PMyr ₄₁₀	-12^a	1322 ± 11	162 ± 1	-6.1 ± 0.1	1427 ± 40	156 ± 2
PMyr ₅₀₀	-12^a	1229 ± 12	165 ± 1	-5.5 ± 0.1	1351 ± 15	161 ± 1
PMyr ₇₁₃	-12^a	1221 ± 8	168 ± 1	-4.9 ± 0.1	1301 ± 37	163 ± 2
PMyr ₉₂₆	-12^a	1280 ± 11	165 ± 1	-4.4 ± 0.1	1181 ± 62	169 ± 3

^afixed value

normal modes to the dielectric loss have been discussed earlier.^{22,23} Both processes conform to the Vogel–Fulcher–Tammann (VFT) dependence as

$$f_{\max} = f_0 \exp\left(-\frac{B}{T - T_0}\right) \quad (5)$$

Here, f_0 is the limiting frequency at very high temperatures, B is the activation parameter, and T_0 is the “ideal” glass temperature located below the conventional T_g . The VFT parameters for the segmental and longest normal mode are summarized in Table 2.

The temperature dependence of the characteristic peak frequencies for the SM and the longest NM are shown in Figure 5. The figure depicts an SM and the longest NM

processes that display, respectively, moderate to strong molar mass dependence.

At lower temperatures, a faster process (β process) is observed that has an Arrhenius temperature dependence as

$$f_{\max} = f_0 \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

where f_0 ($= 1.26 \times 10^{14}$ Hz) is the characteristic frequency in the limit of very high temperatures and E_a is the activation energy (31 ± 1 kJ mol⁻¹) associated with restricted motion of the side group. The latter assignment is based on the lower activation energy in comparison to the β -process of *cis*-1,4-PI and the similarity to *cis*-1,4-PF₂.²⁴

The SM displays a molar mass dependence (Figure 6) that can be fitted with the Fox–Flory equation: $T_g(K) = T_g^\infty - K/M_n$, resulting in $T_g^\infty = (203 \pm 2)$ K and $K = 21900$ g·mol⁻¹ (data refer to DS). This strong dependence for the lower molar masses has historically been interpreted in terms of the mobile chain ends that effectively speed-up the backbone segmental dynamics. However, recent simulations³² and generalized entropy theory³³ on polymers with different topologies suggested that chain branch points give rise to correlations in the fluid, which can compete with property changes associated with free ends, which can make thermodynamic properties and dynamic properties, such as T_g , vary in a more complicated fashion than envisioned by Fox and Flory. Additional T_g data obtained by DSC and temperature-modulated DSC are discussed in the Supporting Information, Figures S2 and S3.

A property of the segmental dynamics closely related to the liquid-to-glass formation is the fragility parameter or steepness index, m (Figure 7). It is used to quantify the steepness in the temperature dependence of the segmental relaxation times as the glass is approached from higher temperatures. It is defined as $\partial \log \tau / \partial (T_g/T)|_{T=T_g}$ and can be calculated directly from the VFT parameters (Table 2) as

$$m^* = \frac{BT_g}{2.303(T_g - T_o)^2} \quad (7)$$

The data for the steepness index display (Figure 7) an increasing fragility with increasing molar mass, in agreement with several homopolymers.^{34–37} This fact implies that mobile chain ends not only determine the absolute value of T_g but also the temperature dependence of the associated segmental dynamics.

Important information on the origin of the dynamic arrest at T_g can be obtained by pressure-dependent measurements (Figure 8). In general, increasing pressure brings about the same effect as decreasing temperature (hence the $P \leftrightarrow T^{-1}$ equivalence). However, there exist certain thermodynamic parameters that are only accessible by pressure. The characteristic frequencies at maximum loss follow the pressure equivalent relation to the normal VFT as³⁸

$$f_{\max} = f_a \exp\left(-\frac{D_p P}{P_o - P}\right) \quad (8)$$

where f_a is the segmental relaxation frequency at atmospheric pressure at a given temperature, D_p is a dimensionless parameter, and P_o is the pressure corresponding to the "ideal" glass. The pressure dependence of the segmental mode and longest normal mode are depicted, respectively, in Figure 8a,b, under "isothermal" and "isobaric" conditions. Notice the different pressure sensitivity of the two modes. The faster SM is more prone to pressure variations resulting in the crossing of the SM and longest NM at a finite pressure, *i.e.*, in sharp contrast to the expectations born by the Rouse model.²⁸

Importantly, pressure-dependent dynamics provide access to a quantity only accessible by pressure, namely, the apparent activation volume, $\Delta V^\ddagger$, of the underlying dynamic processes as^{39,27}

$$\Delta V^\ddagger = 2.303RT \left(\frac{\partial \log \tau}{\partial P} \right)_T \quad (9)$$

Earlier studies suggested a coupling of $\Delta V^\ddagger$ with the molecular volume of relaxing species.^{27–29,39} This quantity, obtained at atmospheric pressure, is plotted in Figure 8c as a function of the temperature difference from the glass temperature. The figure includes the repeat unit volume of PI and PMyr. Interestingly, the measured apparent activation volume is lower than the molecular volume of the PMyr repeat unit, being closer to the corresponding PI value. This suggests that responsible for the segmental relaxation process is a part of the repeat unit, *i.e.*, similar to PI. The reason for this could be the asymmetry of the PMyr repeat unit having a longer side group. This feature of PMyr can be explored further in, *e.g.*, PI/PMyr blends.

On the other hand, the $T_g(P)$ (the latter determined here at $\tau \sim 10$ s) exhibits a non-linear P dependence (Figure 8d) that conforms to the following empirical equation⁴⁰

$$T_g(P) = T_g(0) \left(1 + \frac{\nu P}{\mu} \right)^{1/\nu} \quad (10)$$

Here, $T_g(0)$ ($= 204.6 \pm 0.6$ K) is the T_g at ambient pressure and ν and μ are polymer specific parameters (with values $\nu = 2.4 \pm 0.3$ and $\mu = 1120 \pm 50$ for the SM process). These values can be compared to *cis*-1,4-PI ($T_g(0) = 206.2 \pm 0.2$ K, $\nu = 3.05 \pm 0.06$ and $\mu = 977 \pm 11$, all defined at $\tau \sim 10$ s in order to avoid long extrapolations). Specifically, the pressure coefficient of T_g^{high} in the limit of ambient pressure, $d T_g / d P|_{P \rightarrow 0}$ is 184 K·GPa⁻¹. This value compares favorably with *cis*-1,4-PI (216 K·GPa⁻¹).³⁰ Such values are typical for low T_g flexible polymers.²⁷

An important parameter of flexible polymers is the entanglement molar mass, M_e . This quantity is usually obtained from the plateau modulus, G_N^0 , in rheology (see below). Alternatively, it can be obtained from DS by examining the relaxation times of the longest normal mode when plotted versus the number averaged molar mass in a double logarithmic representation (Figure 9). The plot indicates two regimes; one at lower molar masses with an approximate dependence of $\tau_{\text{NM}}/\tau_{\text{SM}} \sim M^{2.3 \pm 0.1}$ signifying the Rouse regime pertinent to bottlebrush polymers⁴¹ and another at higher molar masses, with an approximate dependence as $\tau_{\text{NM}}/\tau_{\text{SM}} \sim M^{4.1 \pm 0.2}$, suggesting a modified reptation regime.⁴²

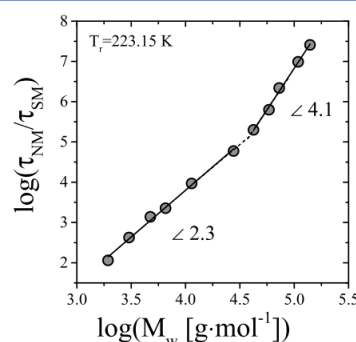


Figure 9. Longest normal mode relaxation times for PMyr normalized by the segmental times plotted versus the molar mass at a reference temperature of 223.15 K, in a double logarithmic representation. Lines with slopes of 2.3 and 4.1 are fits to the two regimes (see text).

Rheology. The entanglement molar mass, M_e , can be readily obtained from rheology by employing the principle of time–temperature superposition (tT s) by constructing the master curves for the storage (G') and loss (G'') shear moduli. The construction of the master curves for the different molar masses is shown in Figure 10, together with the shift factors

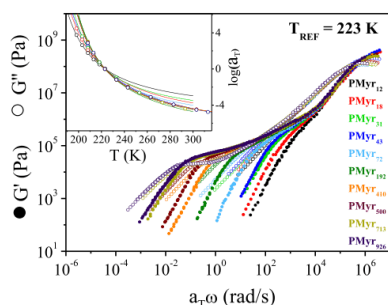


Figure 10. Master curves of storage (filled symbols) and loss (open symbols) shear moduli, at the same reference temperature of 223 K. Different colors correspond to different molar masses. Lines with slopes of 1 and 2 are also shown. The inset depicts the shift factors fitted with the WLF equation (parameters at the glass temperature are provided in Table S1).

(the values of the WLF parameters C_1 and C_2 are summarized in Table S1). The plateau modulus, G_e , defines the entanglement spacing of a polymer melt as^{42–46}

$$M_e = \frac{4}{5} \frac{\rho RT}{G_e} \quad (11)$$

By employing the higher molar mass polymer and the value of the mass density ($\rho = 0.892 \text{ g/cm}^3$),^{43,44} we obtain $M_e \sim 22 \pm 2 \text{ kg/mol}$. This estimate is consistent with the one obtained from the molar mass dependence of the zero shear viscosity (Figure 11). In the latter, two regimes with approximate slopes of $\eta_0 \sim M^{1.1 \pm 0.1}$ and $\eta_0 \sim M^{3.3 \pm 0.2}$ define a critical molar mass of $M_c \sim 40 \text{ kg/mol}$ ($M_c/M_e \sim 2$). The presence of M_c in the zero shear viscosity dependence on molar mass is distinctly

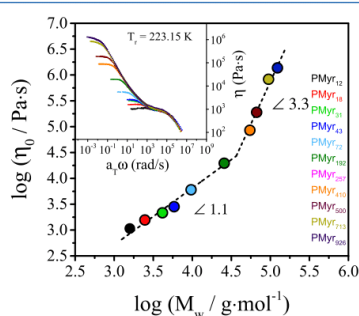


Figure 11. Zero shear viscosity of PMyr as a function of molar mass in a double logarithmic representation. The two lines with slopes of ~ 1.1 and 3.3 represent linear fits to lower and higher molar masses, respectively. In the inset, the complex viscosity versus angular frequency is shown, at a reference temperature of 223 K. Different colors correspond to the different molar masses as shown.

different from the extended Rouse-like scaling found in high molar mass bottlebrush polymers of atactic polypropylene.⁴¹

Earlier works⁴⁶ suggested that the static structure of polymer melts is controlled by two length scales: the Kuhn length (l_k) and the packing length, p . The Kuhn length characterizes the conformations of individual chains. It relates to the mean-square end-to-end distance ($\langle R^2 \rangle_0$) and the contour length, L , as $l_k = \langle R^2 \rangle_0 / L$. The packing length is defined as the volume occupied by a chain ($M / \rho N_A$; M is the molar mass and N_A is the Avogadro number) divided by the mean-square end-to-end distance, as $p = M / (\langle R^2 \rangle_0 \rho N_A)$. It also reflects the characteristic length scale at which polymers start to interpenetrate. It can be obtained from the entanglement density and the plateau modulus, respectively, as $M_e = 218 \rho p^3$ and $G_N^0 \sim T/p^3$. Certain correlations of dynamic and static quantities with respect to the packing length or the number of double bonds on the side group for the three structurally related polyterpenes (Scheme 1, polyisoprene, polymyrcene, and polyfarnesene) are shown in Figure 12. Figure 12a shows the dependence of the glass temperature on the number of double bonds on the side group. It reveals a decreasing glass temperature with increasing chain thickness (by $\sim 8 \text{ K}$). The effect of the elongated side group on the packing length is shown in Figure 12b.

However, the more drastic dependencies are the $G_N^0(p)$ and $M_e(p)$ shown, respectively, in Figure 12c,d. Figure 12c depicts the decreasing plateau modulus with increasing p . It follows $G_N^0 = 1 - 2.95p$, close to the predicted dependence ($G_N^0 = 10.5p^{-3}$).⁴⁴ Figure 12d displays a strong increase of the entanglement molar mass, M_e , with increasing chain thickness. The dependence agrees well with the proposed scaling⁴⁴ ($M_e = 218 \rho p^3$) tested in Figure S7 for PI, PMyr, and PFar. In addition, the data for PI, PMyr, and PFar are in excellent agreement with the scaling of the dimensionless plateau moduli $G_N^0 l_k^3 / k_B T$, when plotted as a function of the dimensionless ratio l_k/p (Figure 13). The data points follow the proposed empirical relation:⁴⁶ $G_N^0 = 0.00226 k_B T / p^3$, that also implies a simple proportionality between the tube diameter and the packing length.

Hence, increasing the side group length in going from PI to PMyr to PFar effectively increases the tube diameter. At the same time, the glass temperature is decreasing as a result of increasing density of chain ends. Polyterpenes constitute a class of type-A polymers where by architectural design, one can control the thickness of chains and henceforth the viscoelastic response. A ten-fold increase in the entanglement molar mass is obtained going from PI to PFar, with PMyr producing a 4-fold increase. In this respect, it would be interesting to investigate binary blends (PI/PFar and PI/PMyr) with respect to the chain dynamics. A limiting factor here is the decreasing dielectric strength of the longest normal mode in going from PI to PMyr and to PFar (Figure S4). This reflects the weaker dipole moment component along the chain.

CONCLUSIONS

The synthesis of a series of monodisperse polymyrcenes, all with identical microstructures (95% 1,4-polymyrcene units and 5% 3,4-units) and molar masses in the range from 1600 to 126,000 $\text{g}\cdot\text{mol}^{-1}$, allowed the first investigation of the dynamics at the segmental and chain length scales by dielectric spectroscopy and rheology. "Chain thickening" by increasing the size of the side group in polyterpenes affected both the local segmental and the chain dynamics. At the segmental level, the glass temperature was found to decrease with increasing

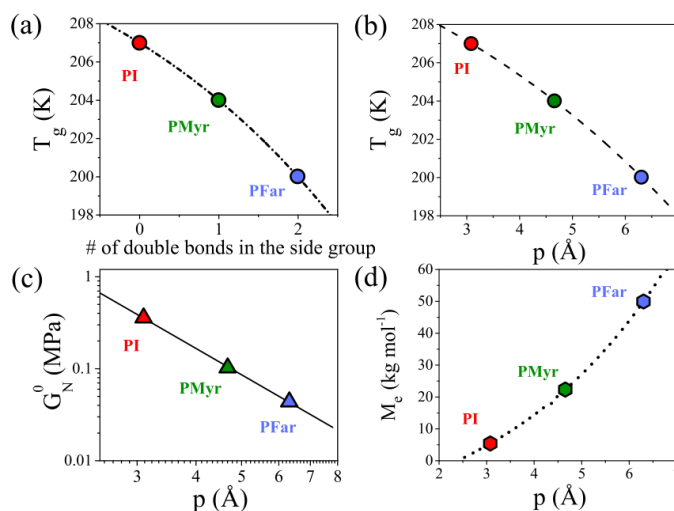


Figure 12. (a) Glass temperature in the limit of high molar masses, plotted as a function of the number of double bonds in the side group and (b) as a function of the packing length for polyisoprene (red), polymyrcene (olive), and polyfarnesene (blue). The lines are guides for the eye. (c) Double logarithmic representation of the plateau modulus over the packing length, following a linear dependence, described by $G_N^0 = 1 - 2.95p$. (d) Dependence of the entanglement molar mass on packing length.

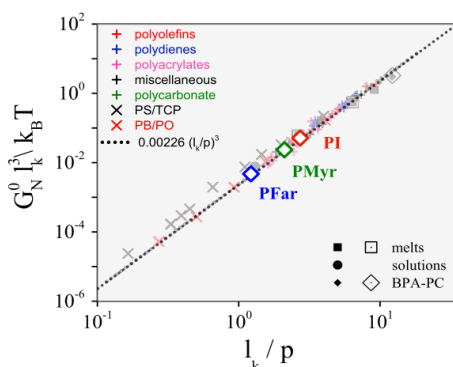


Figure 13. Dimensionless plateau moduli $G_N^0 l_k^3 / k_B T$ plotted as a function of the dimensionless ratio l_k / p . Blurred data are from ref 46. Open rhombi refer to the PFar, PMyr, and PI data.

chain thickness (by ~ 8 K). The decrease was attributed to the increasing density of end groups that effectively mobilize the polymer backbone. The glass temperature had a strong dependence on molar mass becoming independent of molar mass above $M \sim 30$ kg·mol⁻¹. The application of pressure revealed a small sensitivity of the segmental (and normal) mode, suggesting the dominant effect of the backbone. Chain thickening greatly affected the viscoelastic properties: The entanglement molar mass increased (from 5 kg·mol⁻¹ in PI to 22 kg·mol⁻¹ in PMyr to 50 kg·mol⁻¹ in PFar). Likewise, the packing length increased (from 3.1 Å in PI to 4.7 Å in PMyr and to 6.3 Å in PFar) and the plateau modulus decreased. The latter followed the proposed empirical relation: $G_N^0 = 0.00226 k_B T / p^3$ consistent with the proportionality between the tube diameter and the packing length.

Polyterpenes with their distinctly different viscoelastic properties can be employed as model – athermal – binary

blends, whereby differences in the plateau modulus and packing of the homopolymers can be employed to trigger the flow behavior. Experiments in this direction are currently planned in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.2c01507>.

Additional DSC, temperature-modulated DSC, DS data, and proposed scaling of the viscoelastic properties with the packing length (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Holger Frey – Department of Chemistry, Johannes Gutenberg, Universität Mainz, Mainz 55099, Germany; orcid.org/0000-0002-9916-3103; Email: hfrey@uni-mainz.de

George Floudas – Department of Physics, University of Ioannina, Ioannina 45110, Greece; University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, Ioannina 45110, Greece; orcid.org/0000-0003-4629-3817; Email: gfloudas@uoi.gr

Authors

Ioannis Tzourtzouklis – Department of Physics, University of Ioannina, Ioannina 45110, Greece

Christoph Hahn – Department of Chemistry, Johannes Gutenberg, Universität Mainz, Mainz 55099, Germany; Max Planck Graduate Center Mainz, Mainz 55128, Germany

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.macromol.2c01507>

Notes

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Christoph Hahn

Am Römerlager 23

55131 Mainz

+491773682044

Born: 30.08.1994 in Kirchheimbolanden

Nationality: German

Education

11/2019 – 04/2023	PhD Student, Research group of Prof. Dr. Holger Frey Johannes Gutenberg-Universität Mainz, in cooperation with the Max-Planck Graduate Center, co-advisor Paul Blom PhD topic: <i>“Anionic polymerization of bio-based dienes and functional styrenes”</i> Research interest: General investigation of pine chemicals and bio-based feedstocks for the invention of new monomers
04/2019 – 09/2019	Master thesis on “Synthesis, characterization and ferroelectric properties of nylon-3” Research group of Prof. Dr. Holger Frey Johannes Gutenberg-Universität Mainz, in cooperation with the Max-Planck Institute for Polymer Research, co-advisor Kamal Asadi
09/2017 – 03/2018	Semester abroad at University of Massachusetts Amherst (USA), Department of Polymer Science and Engineering, Research group Prof. Lesser, research topic: Frontal polymerization of pre- impregnated carbon fiber epoxy resin
07/2017 – 09/2019	Master studies in chemistry Johannes Gutenberg-Universität Mainz (Ø 1.6)

04/2019 – 09/2019	Bachelor thesis on „Multi-aldehyde functionalized polyethers” Research group of Prof. Dr. Holger Frey
04/2014 – 07/2017	Bachelor studies in chemistry, Johannes Gutenberg-Universität Mainz (Ø 2.5)
08/2011 – 03/2014	High school diploma (Abitur) Priv. Gymnasium Weierhof Bolanden (Ø 2.2)

Conference contributions

09/2022	Ionic Polymerization '22 , Conference, oral presentation , Ghent, BE.
06/2022	Bordeaux Polymer Conference , polymer materials, poster presentation , Bordeaux, FRA.
11/2021	Brightland Polymer Days 2021 , polymer materials, poster presentation , Eindhoven, NL.

Skills and Interests

Languages	German (mother tongue), English (fluent), Spanish (basic)
Interests	Soccer Hiking
Teaching	Scientific Assistant for Organic and Polymer Chemistry Johannes Gutenberg University, Mainz, Germany Mentoring of Bachelor and Chemical Lab Course Students

List of publications:

- (1) Hahn, C., Wagner, M., Müller, A. H., & Frey, H. (2022). MyrDOL, a Protected Dihydroxyfunctional Diene Monomer Derived from β -Myrcene: Functional Polydienes from Renewable Resources via Anionic Polymerization. *Macromolecules*, 55(10), 4046-4055.
- (2) Hahn, C., Becker, S., & Frey, H. (2023). Anionic Polymerization of Bio-based Functional Styrene Monomers - Convenient Access to Poly (hydroxystyrene) obtained from Renewable Resources, *to be submitted*.
- (3) Hahn, C.; Rauschenbach, M. & Frey, H. (2023). Merging Styrene and Diene Structures to a Cyclic Diene: Anionic polymerization of 1-Vinylcyclohexene (VCH), *submitted to Angewandte Chemie*.
- (4) Hahn, C.; Göttker-Schnetmann, I.; Floudas, G.; Mecking, S.; Frey, H. (2023). Nopadiene: A Pinene-Based Cyclic Diene for Fully Bio-Based Thermoplastic Elastomers, *submitted to J. Am. Chem. Soc.*
- (5) Hahn, C.; Simon, M. & Frey, H. (2023). Anionic polymerization of 4-isopropyl-1-vinylcyclohexene – expanding the scope of cyclic 1,3-diene monomers from natural resources, *to be submitted*.
- (6) Hahn, C.; Anwar, S. Asadi, K. & Frey, H. (2023). Ferroelectric Properties of Nylon-3- Synthesis and Characterization, *to be submitted*.

Mainz, 16.02.2023