New Methods for the Functionalization of Metathesis Polymers

Dissertation

zur Erlangung des Grades

"Doktor der Naturwissenschaften"

im Promotionsfach Makromolekulare Chemie

am Fachbereich Chemie, Pharmazie und Geowissenschaften

der Johannes Gutenberg-Universität

in Mainz

Stefan Hilf

geboren in Mainz

Mainz, den 17.03.2009

Dekan:

Prodekan:

1. Berichterstatter:

2. Berichterstatter:

Tag der mündlichen Prüfung: 13.05.2009

Hiermit versichere ich gemäß § 10 Abs. 3d der Promotionsordnung vom 24.07.2007, dass ich die als Dissertation vorgelegte Arbeit selbst angefertigt und alle benutzten Hilfsmittel (Literatur, Apparaturen, Material) in der Arbeit angegeben habe.

Die als Dissertation vorgelegte Arbeit wurde in der Zeit von September 2006 bis März 2009 am Institut für Organische und Makromolekulare Chemie der Johannes Gutenberg-Universität Mainz angefertigt.

“I am among those who think that science has great beauty. A scientist in his laboratory is not only a technician. He is also a child placed before natural phenomena which impress him like a fairy tale.”

Marie Curie (1867 - 1934)

Acknowledgements

Table of contents

Acknowledgements 7
Table of contents 11
Aim of this work 13
Abstract 15
Graphical abstract 19

Chapter 1: Introduction 23
1.1: Functional End groups for ROMP Polymers 25

Chapter 2: Synthesis of Precisely Functionalized Metathesis Polymers 53
2.1: Mono-functional Metathesis Polymers via Sacrificial diblock copolymers 55
Supporting Information 64
2.2: Sacrificial Synthesis of Hydroxy-Functionalized ROMP Polymers – An Efficiency Study 75
Supporting Information 93
2.3: Sacrificial Synthesis of Hydroxy-Telechelic Metathesis Polymers via Multiblock-copolymers 99
Supporting Information 120
2.4: Thiol-functionalized ROMP Polymers via Sacrificial Synthesis 125
Supporting Information 145
2.5: End-capping ROMP Polymers with Vinyl Lactones 149
Supporting Information 178
2.6: Well-defined Heterotelechelic Metathesis Polymers – A Combinatorial Approach 188

Chapter 3: Applications of functionalized Metathesis Polymers 201
3.1: An All-ROMP Route to Graft-Copolymers 203
Supporting Information 217
3.2: A “Click”-Approach to ROMP Block Copolymers. 221
3.3: Ugly Stars – Long-chain Branched ROMP Polymers 237
Supporting Information 255
Chapter 4: Cooperation Projects 261

4.0: Preface.....261

4.1: Janus Micelles Induced by Olefin Metathesis 263

Supporting Information 270

4.2: Polymerizable Well-defined Oligo(thiophene amide)s and their ROMP Block-copolymers 279

Supporting Information 300

4.3: Electroactive Linear-Hyperbranched Block Copolymers based on Linear Poly(ferrocenylsilane)s and Hyperbranched Poly(carbosilane)s 311

Supporting Information 335

Appendix..... 339

A.1: Future Work 341

A.2: Curriculum Vitae Stefan Hilf..... 345

A.2: List of Publications and Conference Contributions..... 347

Aim of this work

The development of modern Grubbs-type metathesis catalyst has had great impact in polymer chemistry. These highly reactive catalysts show tolerance to a variety of interesting functional groups such as alcohols, amines, amides and aldehydes while maintaining living polymerization characteristics for many types of monomer structures. They are compatible with bioactive molecules and are highly tolerant towards air and moisture. In fact, catalysts have been synthesized which facilitate a metathesis even in water.

This compatibility of ruthenium-based metathesis catalysts with an array of chemical and physical conditions, however, offers very few starting points for functionalization reactions at the polymer chain end. Ruthenium catalysts are reactive towards olefins only. This means, functionalizations are generally facilitated by adding an olefin that deactivates the catalyst, thus yielding monofunctional polymers, or non-cyclic olefins that react as a chain transfer agent, yielding telechelics. Substituted vinyl ethers are used as terminating agents. The catalyst is reactive towards them and is efficiently transformed into a metathesis-inactive Fischer-carbene. Such substituted vinyl ethers have to be synthesized by multi-step procedures typically involving Wittig-type chemistry.

On the other hand, reactive end-groups are required in many syntheses involving macromolecular building blocks. Higher polymer architectures, the functionalization of surfaces and the synthesis of conjugate and hybrid materials largely rely on the availability of precisely functionalized polymers and are particularly interesting when other interesting groups, e.g. stimuli responsive motives, can be present along the polymer chain. The high tolerance of the ruthenium-catalyzed ROMP towards such groups fosters the requirement of reliable methods for the synthesis of such materials.

It has therefore been the aim of this work to develop novel pathways for the precise introduction of highly reactive end-groups to metathesis polymers. Such methods should be easy to perform in order to grant broad applicability of the methods by research groups of a broad field. They should be realizable by non-specialists to the ROMP as well as appropriate for a maximum number of polymer structures. Work-up or deprotection conditions should be compatible with a maximum number of groups incorporated in and appending to the monomer structure.

Abstract

End-functionalization reactions for the ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) are scarce. The extremely high functional group tolerance of modern Grubbs-type initiators limits the number of reactions that place a precise number of functional groups on each polymer chain end.

Our research on the development of novel pathways for the functionalization has lead to the publication of two new functionalization strategies. Sacrificial Synthesis describes a pathway in which functionalization is induced by a polymerization reaction involving cleavable monomers in which the desired functional group is hidden and can be set free in a subsequent cleaving reaction. The second strategy, which represents a termination reaction, focuses on the use of vinyl lactones as a deactivating olefin. This termination reaction is particularly interesting as the terminated species self-deprotects setting the functional group free without addition of further reagents or a change of conditions.

Sacrificial Synthesis

By introducing *Sacrificial Synthesis*, many of the limitations of ruthenium-catalyzed ROMP have been overcome by introducing a sacrificial polymer block. There, the living ROMP polymer to be functionalized was turned into a diblock-copolymer by polymerizing dioxepine monomers onto the desired first polymer block. The second block could then later be cleaved to leave “half-a-dioxepine”, i.e. exactly one hydroxyl group, at the chain-end (**Chapter 2.1**). Cyclic acetals (dioxepines) have been used for the placement of hydroxyl-groups at the termini of polymer chains.

For the determination of the functionalization efficiency of *Sacrificial Synthesis*, a series of functionalization reactions involving different amounts of dioxepine monomer were performed. The degrees of functionalization obtained after hydrolysis were determined by ^{1}H-NMR (**Chapter 2.2**). This study has resulted that the success of the placement of functional groups is determined solely by the initiation kinetics of the sacrificial block. By correlation of the results with kinetic equations for macroinitiations known from classical

anionic living polymerizations, which also led to a correlation between the degree of functionalization and k_i/k_p of the polymerization of the sacrificial block. Therefore, the polymerization behavior and the degrees of functionalization at a given amount of cleavable monomer could be calculated and predicted.

The non-deactivating nature of Sacrificial Synthesis gave rise to the synthesis of polymers, which are also functionalized on the beginning of the chain (**Chapter 2.3**). This synthesis of telechelic ROMP polymers, therefore, involves the formation of triblock- or multiblock-copolymers. By application of different dioxepines, which can be cleaved sequentially under different conditions, the respective hydroxyl groups could be addressed specifically.

Thiol groups are of particular interest in polymer chemistry as a number of highly efficient functionalization reactions on surfaces and biomacromolecules rely on this functional group. The chemical relatedness of hydroxyl- and thiol-groups lead to the development of a sacrificial strategy towards thiol-functionalization based on the thio-analoga of the sacrificial monomers applied in the synthesis of hydroxyl-functionalized polymers. 2-Phenyl-1,3-dithiepin, a dithioacetal, represents a sulfur analogue to previously used 2-phenyl-1,3-dioxepine and exhibits similar polymerization characteristics. By hydrogenation of a polynorborneneimide-polythioacetal block copolymer with Raney-Nickel, we could remove the cleavable block and leave exactly one thiol group at every chain end (**Chapter 2.4**). The presence of thiol groups on the chain end has been proven by chemical means (derivatization) and by coating gold-nanoparticles.

Lactone Termination

Compared to functionalized vinyl ethers, similar deactivation and functionalization activity can be expected from vinyl esters. They also form Fischer-type carbenes with an electron withdrawing group. Small-ring vinyl lactones or carbonates feature two advantages. They incorporate both, an electron deficient double bond and strict *cis*-conformation, which reduces steric bulk and enhances the reaction kinetics. Vinylene carbonate is commercially available and *3H*-furanone can be synthesized from furfuraldehyde. These two reagents were tested for quenching reactivity, efficiency and degrees of functionalization. The two compounds gave rise to the placement of aldehydes and carboxylic acids at the polymer

chain ends. (**Chapter 2.5**) It was found that this method is very special in the sense, that the resulting carbene is unstable and self-decomposes to set an inactive ruthenium complex and the functional group free. Therefore, it is not necessary to perform any deprotection steps after the functionalization which is unique to functionalization reactions yielding reactive endgroups.

Kinetic measurements of the termination reaction gave rise to the related termination constants and unveiled the excellent termination characteristics of this method. Derivatization of the acid functionalized polymer allowed the determination of the degree of functionalization by ^{1}H-NMR by the comparison of start- and endgroups. Full functionalization was obtained for all polymer samples including vinylene carbonate and *3H*-furanone functionalization.

Applications

The successful development of the two above mentioned functionalization methods has also found application in several projects. By reacting hydroxyl-functionalized ROMP-polymers with norbornene acid, macromonomers were formed which were subsequently polymerized to the respective graft-copolymers (**Chapter 3.1**). A dependence of the DP of the secondary polymerization on the chain length of the side chains due do steric hindrance was found and the presence of a branched structure was proven by combined SEC-MALLS measurements.

The derivatization of hydroxyl-functionalized polynorborneneimides with propargylic acid gave rise to alkyne-functionalized polymers which could be used in a Huisgen-type 1,3-dipolar Cycloaddition with azides. This click-type reaction was performed with poly(ethylene glycol)-azide and gave amphiphilic block-copolymers in good definition under copper(I)-catalysis (**Chapter 3.2**).

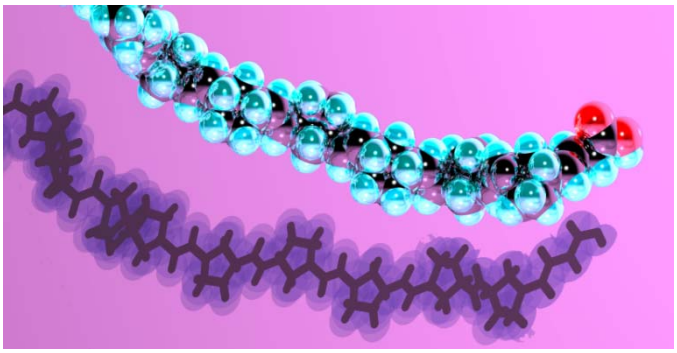
AB_n-type macromonomers were synthesized by application of *3H*-furanone termination. In this case, a protected hydroxyl-group bearing monomer was polymerized and the chain ends of these homo- or block-copolymers were functionalized with a carboxylic acid. Esterification of this acid with the hydroxyl groups along the chain resulted in the formation of “ugly stars”, i.e. highly branched star-like structures which do not possess a central defined core (**Chapter 3.3**).

Heterotelechelic polymers were synthesized in a combined Sacrificial Synthesis / Lactone Termination approach (**Chapter 3.4**). After formation of a diblock-copolymer consisting of a dioxepine block as the first and a polynorbornene as the second block, thus giving hydroxyl groups at the "start" of the polymer chain, addition of vinylene carbonate or *3H*-furanone facilitated the placement of an aldehyde or an acid endgroup at the "end" of it.

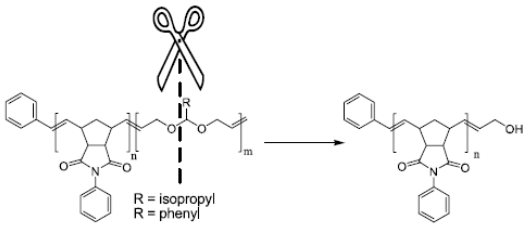
Chapter 4 describes several cooperation projects loosely related to the main topic of this thesis. A separate preface in this chapter gives details about the contributions to these projects.

Graphical abstract

1.1: Functional End-groups for ROMP Polymers.....25

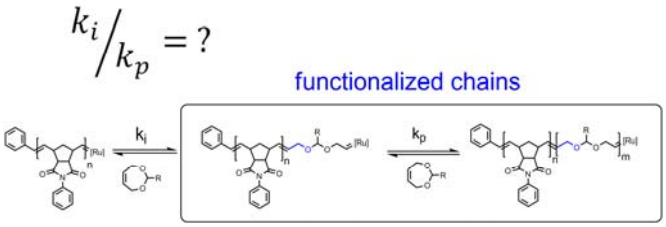


2.1: Mono-functional Metathesis Polymers via Sacrificial diblock copolymers 55



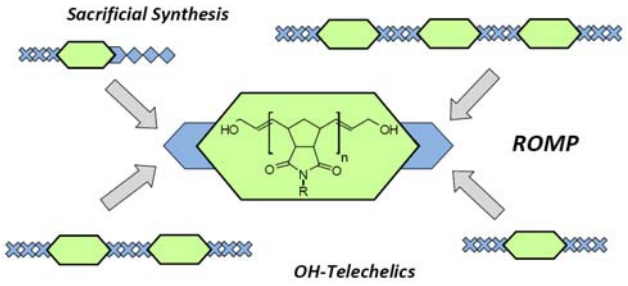
Supporting Information 64

2.2: Sacrificial Synthesis of Hydroxy-Functionalized ROMP Polymers – An Efficiency Study .. 75



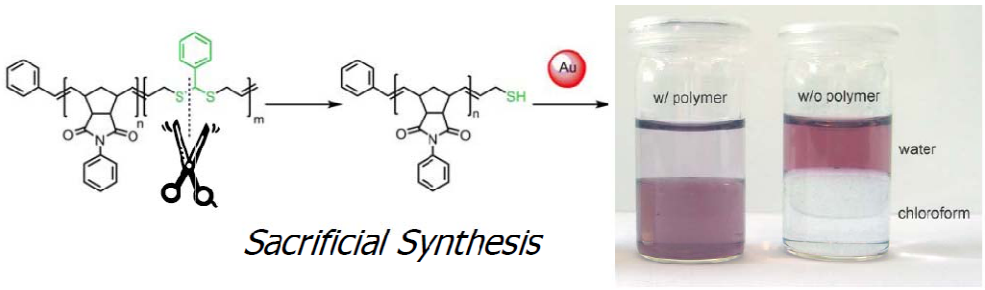
Supporting Information 93

2.3: Sacrificial Synthesis of OH-Telechelic Metathesis Polymers via Multiblock-copolymers 99



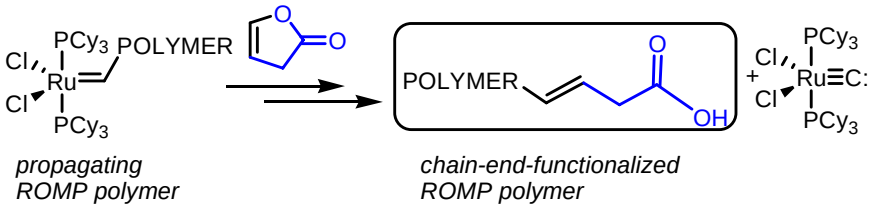
Supporting Information 120

2.4: Thiol-functionalized ROMP polymers via Sacrificial Synthesis..... 125



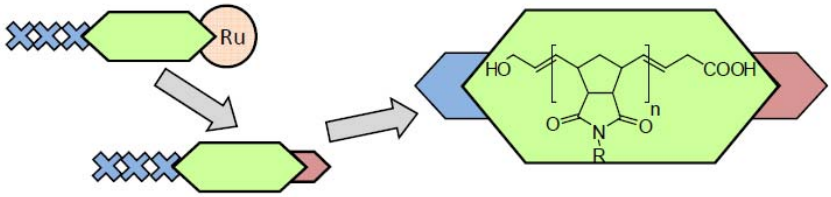
Supporting Information 145

2.5: End-capping ROMP Polymers with Vinyl Lactones 149

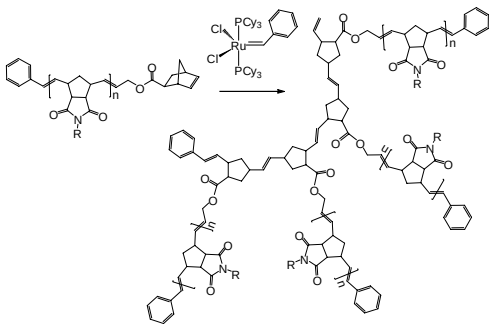


Supporting Information 178

2.6 Well-defined Heterotelechelic Metathesis Polymers – A Combinatorial Approach.....188

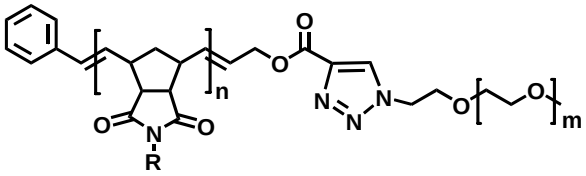


3.1: An All-ROMP route to graft-copolymers 203



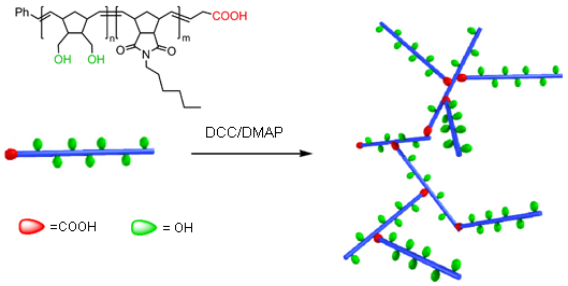
Supporting Information.....217

3.2: A “Click”-Approach to ROMP Block Copolymers. 221



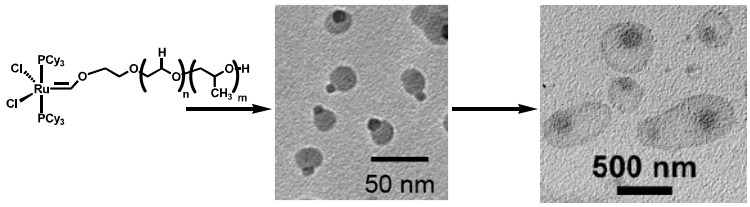
R = Ph, hexyl

3.3 Ugly Stars – Long-chain Branched ROMP Polymers.....237



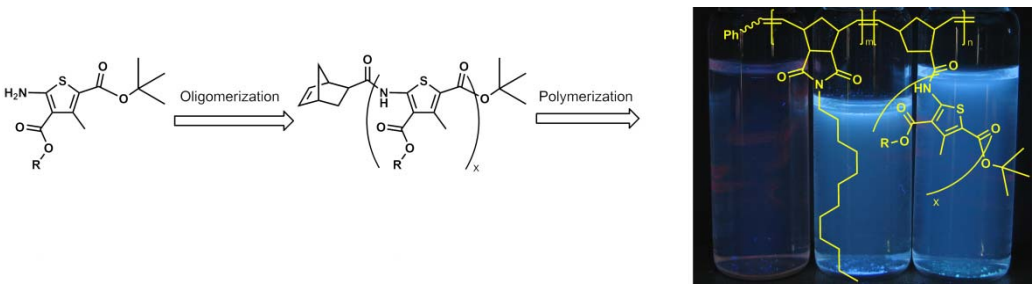
Supporting Information.....255

4.1: Janus Micelles Induced by Olefin Metathesis.....263



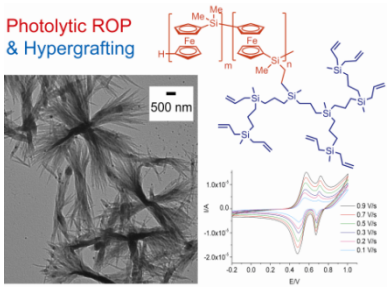
Supporting Information.....270

4.2 Polymerizable well-defined oligo(thiophenamide)s and their ROMP block-copolymers.....279



Supporting Information.....300

4.3: Electroactive Linear-Hyperbranched Block Copolymers based on Linear Poly(ferrocenylsilane)s and Hyperbranched Poly(carbosilane)s 311



Supporting Information..... 335

Chapter 1: Introduction

1.1: Functional End groups for ROMP Polymers

Stefan Hilf and Andreas F. M. Kilbinger

Submitted for publication in: Nature Chemistry

The precise placement of functional groups on the chain-ends of macromolecules is one of the major focuses of academic polymer research. Most living polymerisation techniques offer specific methods of end-functionalisation governed by the active propagating species and the kinetics of the polymerisation reaction. The ring-opening metathesis polymerisation (ROMP) is one of the most functional group tolerant living polymerisation techniques known. While the outstanding chemical tolerance has limited the number of functionalisation reactions, chemists have developed a variety of methods to place functional end-groups on ROMP-polymers. Each of them is adapted to the reactivity scheme of the particular catalysts used and tailored to the complexity of the group to be attached. This review presents an overview of the methods developed for different types and generations of metathesis catalysts typically employed. The review is divided into sub-sections according to the stages of polymerisation during which the functional group is introduced to the polymer chain.

Introduction

The ring-opening metathesis polymerisation represents a particularly interesting method among the living polymerisation techniques. Modern metathesis catalyst generations can polymerise a variety of monomer types ranging from cyclic olefins to bi- and oligocyclic structures such as norbornenes and cyclophanes. Also, additional double bonds can be present in the monomer, as long as they are sterically hindered or deactivated by low ring-strain or π-conjugation. All metathesis polymerisations perform under preservation of the double bonds involved in the polymerisation step, which makes this method unique to all olefin polymerisations.[1]

Olefin metathesis was once discovered as an obscure reaction present in a number of olefin transformations. The rationalisation of its unprecedented mechanism by Chauvin[2] gave rise to a chain of new catalyst developments. These featured extremely high metathesis activity, thermal and chemical stability and led to a better understanding and definition of the catalytic steps involved.

As soon as the development of well-defined catalysts based on titanium had emerged from their heterogeneous predecessors,[3] first examples of the living ROMP of norbornene were published.[4] The living character of this process was unexpected at first but soon led to groundbreaking developments of well-defined catalysts for the olefin metathesis reaction. Early efforts of synthesising organometallic compounds bearing metal centres of rhenium[5] and tantalum[6] were soon followed by those based on molybdenum and tungsten by Schrock et al. These featured much higher functional group tolerance as a consequence of being later transition metals.[7] This development eventually culminated in the introduction of late transition metal catalyst systems by Grubbs et al. based on ruthenium.[8] These complexes allow a whole new range of functionalities to be present in the polymers ranging from ionic to biologically active groups.[9]

The mechanism of metathesis, that is now generally accepted, was first described by Chauvin and proposes a metalla-cyclobutane transition state.[2] The metalla-cyclobutane is formed by a [2+2] cycloaddition of the metal-carbene double bond to an olefin. A better understanding of olefin coordination and the transition state stability have been the focus of recent catalysts developments and have led to the latest generation of highly reactive

catalysts. Kinetic measurements, in particular NMR studies,[10] have helped to understand and characterize functionalisation reactions, particularly in the case of termination reactions.

In terms of functional group tolerance, the ring opening metathesis polymerisation using new catalyst systems developed in recent decades has become superior to most other living polymerisation methods. In general, the functional group tolerance of each catalyst can be rated by the reactivity of the transition metal centre towards functional groups. Early transition metal complexes based on titanium are highly oxophilic and react readily with functional groups such as ketones and aldehydes in a Wittig-like reaction. Later transition metals such as those based on ruthenium even tolerate the presence of molecular oxygen, water or mild carboxylic acids. Table 1 gives a general reactivity scheme of transition metals used in most classical metathesis reactions.[1]

Table 1: Reactivity of transition metal complexes towards selected functional groups.

Titanium	**Tungsten**	**Molybdenum**	**Ruthenium**
Carboxylic acids	Carboxylic acids	Carboxylic acids	***Olefins***
Alcohols, Water	Alcohols, Water	Alcohols, Water	Carboxylic acids
Aldehydes	Aldehydes	Aldehydes	Alcohols, Water
Ketones	Ketones	***Olefins***	Aldehydes
Esters, Amides	***Olefins***	Ketones	Ketones
Olefins	Esters, Amides	Esters, Amides	Esters, Amides

Increasing reactivity

Possible reagents for the attachment of functional groups onto the polymer chain-end by a termination reaction can be found using the very same scheme. Table 1 shows that titanium-based catalysts react readily with ketones and aldehydes. Initiators based on molybdenum and tungsten still undergo the same termination reaction with aldehydes. However, ruthenium based metathesis catalysts are only reactive towards olefins. Therefore,

polymerisations involving ruthenium-catalysed ROMP have focussed mainly on other forms of end-functionalisation such as deactivation and chain-transfer of olefins. In some of these cases, the functional groups to be introduced to the chain-end can be well-hidden and difficult to spot at first glance.

Chain-end functionalised polymers have attracted interest among scientists across all disciplines. Such materials combine macromolecular properties with defined reactive sites at the chain-end. Polymers of this type can be used for the attachment of other compounds ranging from small tracers, to drugs or biomolecules[11] to other polymers. These conjugates have found manifold applications in medicine for drug immobilization and delivery,[12] in solid state chemistry for the modification of solid surfaces[13] and in polymer science as synthons for complex polymer architectures. In most application-driven studies, there is a need for precisely functionalised polymers bearing exactly one functional group at the chain-end. Partially and multi-functionalised polymers or those carrying the wrong functional group can quickly lead to unpredictable properties of the final conjugate or even to crosslinking during following reaction steps simply because the structure obtained within those reactions does not match the expected one. It is therefore essential to have reaction protocols at hand that allow the introduction of exactly one functional group with high precision. Best functionalisation experiences and results in terms of functionalisation precision and quantity have been made using living polymerisation techniques. The general kinetic criteria allocated to living polymerisations, such as the nonexistence of chain transfer, back-biting or self-termination reactions set the base for precise end group placement.

Functionalisation approaches in general

Functional groups can be introduced to the polymer chain in three ways during different stages of the polymerisation. By initiating the polymerisation with a metal complex that bears the functional carbene, it is ensured that all polymer chains initiated carry a defined functional group. Alternatively, a termination reagent added at the end of the polymerisation can transfer a functional group onto every polymer chain still containing an active site. The third functionalisation strategy is carried out by polymerisation. A functional group can, for example, be introduced by polymerising a second (cyclic) monomer onto the

first polymer block. Decomposition of the second block leaves one functional group at the end of the first polymer chain. Using an acyclic chain transfer agent, this method allows the synthesis of telechelic polymers, i.e. polymers that bear a functional group on both chain-ends.

All three strategies come with their own challenges. The success of termination reactions strongly depends on the stability and lifetime of the living species and the reactivity of the quenching reagent. Functional initiation, on the other hand, promises to guarantee high degrees of functionalisation since every chain that has been initiated will necessarily bear the functional group. The latter method, however, involves multiple organometallic transformations that a non-specialist to the field might be unwilling to carry out, thereby limiting the scope of this strategy. The third method, polymerisation, appears to be the easiest way of placing end-functional groups onto polymers. Nonetheless, it is limited by lack of control over the molecular weight distribution unless advanced strategies are applied.

Different catalyst systems have been applied to each of these strategies. The challenges that have been faced in developing versatile and efficient reactions for the three different methods outlined above will be highlighted, discussed and evaluated in the following sections.

Functional initiators:

Only very few functional initiators based on titanium metal centres have been synthesised. Due to the extreme reactivity of titanium towards any oxygen containing groups, all examples reported in the literature are bearing unreactive alkyl or aryl groups only.[14] Titanium-carbene complexes, which are formed from Tebbe's reagent[15] in most cases, neither tolerate reactive functional groups nor their protected counterparts to enable their use as metathesis catalysts.

An elegant way for the pre-functionalisation of a tungsten-initiator has been described by Amass et al., [16] who have formed a tungsten carbene from living polystyrene by addition of WCl_6 (Figure 1). The resulting tungsten-alkyl species eliminated HCl to form the metathesis active polymer-alkylidene complex from which norbornene was polymerised to give a block

copolymer using ROMP. This work was the first successful block copolymer synthesis using a conversion of polymerisation technique that involved ROMP.

The early commercial availability and the enormous chemical versatility of the Grubbs-type ruthenium based catalysts have facilitated their widespread use in the synthesis of functional initiators. Three strategies have been pursued in the synthesis of pre-functionalised catalyst moieties: A functionalised carbene can be introduced into the complex *ab initio* by applying the respective diazoalkane to the precursor complex $RuCl_2(PPh_3)_3$.[17] This method has been applied mainly by the Grubbs group for the synthesis of a catalyst that can be used both in ROMP and ATRP polymerisation, as well as for the formation of block-copolymers using both methods.[18] A modified strategy utilises a cross-metathesis reaction between the commercial ruthenium benzylidene and a functionalised olefin yielding a new carbene complex and styrene (Figure 1). This has been applied by Slugovc and co-workers who have attached luminescent dyes to Grubbs' 1st generation catalyst in order to study their behaviour on different polymeric materials.[19]

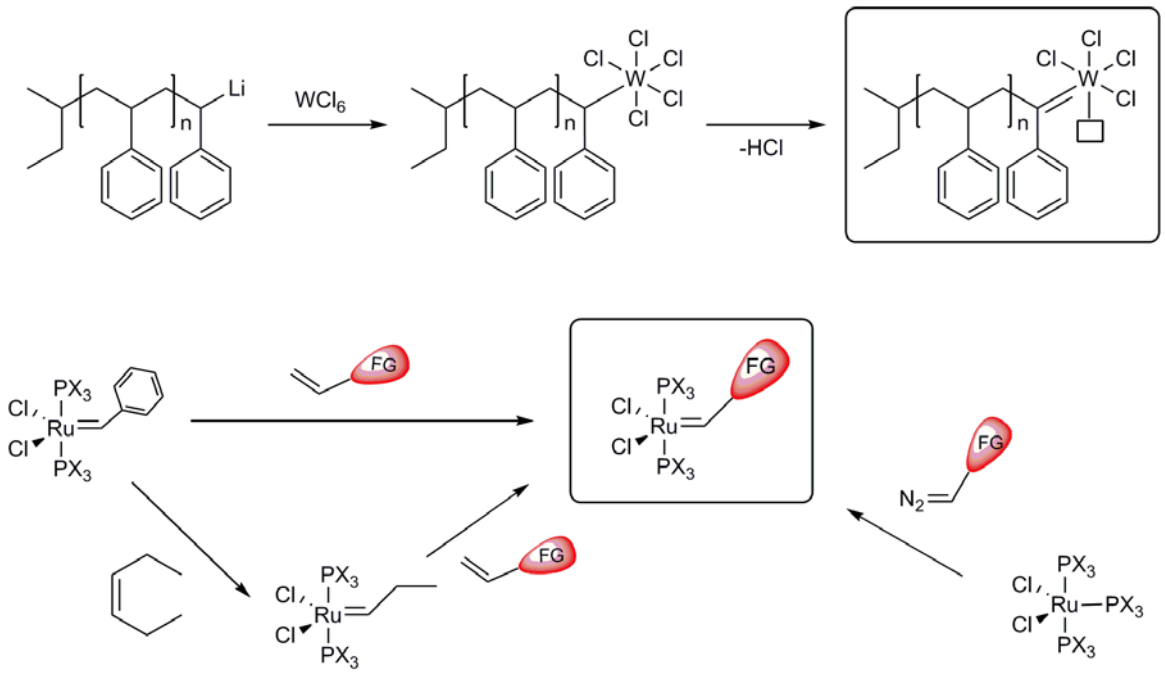


Figure 1: Synthesis of pre-functionalised initiators

The most advanced and synthetically challenging approaches have to be applied when the catalytically active species is to be pre-functionalised with a polymer. The difficulties in purification of polymeric materials require special reaction conditions during the organometallic transformations which promise high catalyst yields and simple removal of side products. Hutchings and Khosravi have found a pathway via a propenylidene intermediate complex and subsequent introduction of the polymer chain in a second cross-metathesis reaction with styrene-end capped poly(ethylene oxide) (Figure 1). In this case, the side product of this cross-metathesis reaction, propene, can easily be removed under vacuum.[20]

Termination Reactions:

Reaction with carbonyl groups:

Titanium metathesis catalysts follow the same reaction scheme as Tebbe's complex.[15] This complex can transfer its methylene group onto carbonyls in exchange for their oxo-group thus forming an olefin and a titanium oxide. Even amides and esters have been transformed to the respective enamines or vinyl ethers.[21]

This Wittig-like reaction, involving an oxo-metallacyclobutane intermediate, found its first application in polymer functionalisation by the Grubbs group, who were able to place a diphenylethenyl end-group on polynorbornene by adding benzophenone to the living titanium-initiated polymerisation.[22] Also, an early example of a more reactive end group was successfully attached to polynorbornene by the same group. The addition of an excess of a dialdehyde resulted in selective endcapping and the obtained terminal aldehyde was subsequently reduced to an alcohol end-group.[23] A general overview of the applications of this Wittig-like reaction is given in Figure 2.

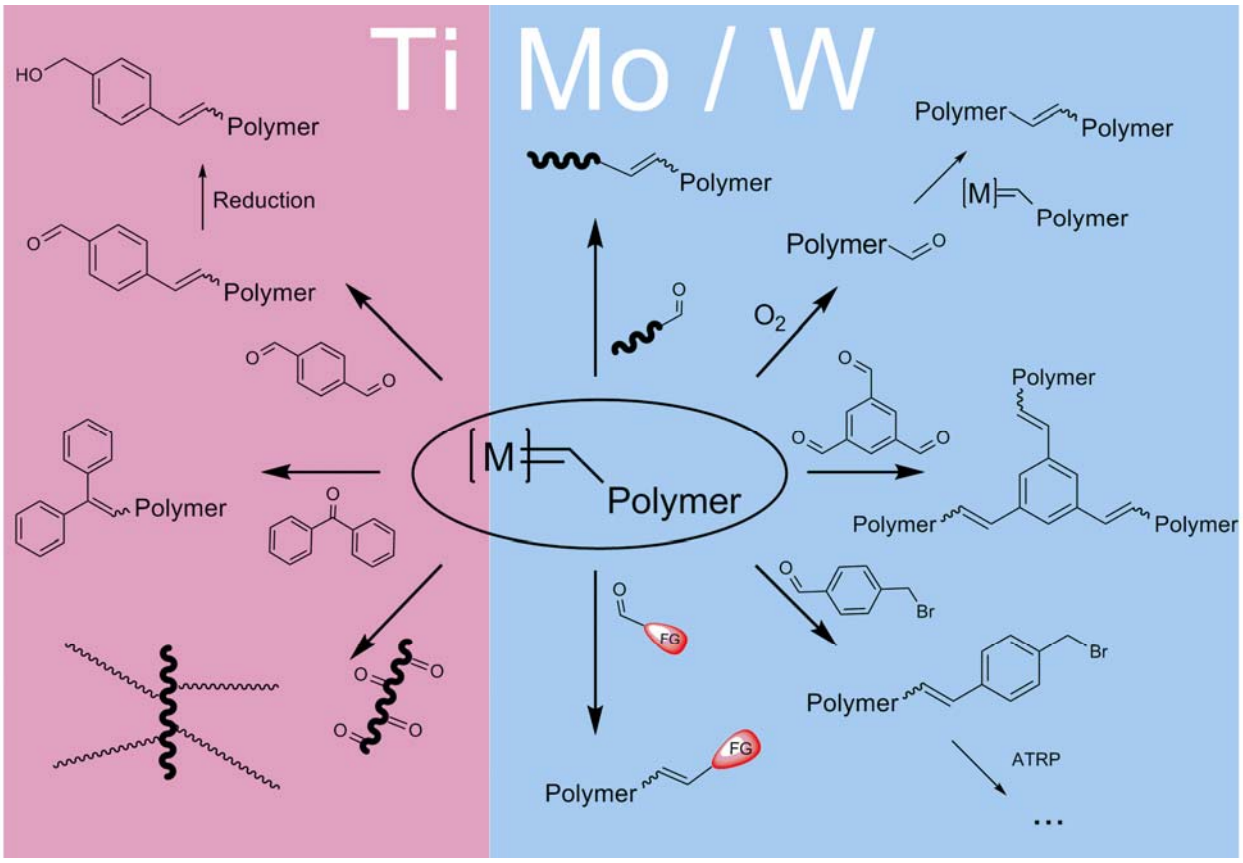


Figure 2: Application of functionalised carbonyls.

The same publication reports the use of polyaldehyde and aldehyde end-capped polymers as core molecules for block- and graft-copolymer synthesis. There, the extremely high reactivity of the Ti-alkylidene species towards aldehydes or ketones is used to scavenge the living chains on a multifunctional quencher, thereby building the new polymer architecture.[24]

Molybdenum and tungsten metathesis catalysts are also conveniently quenched by the addition of an aldehyde.[25] This termination reaction is mechanistically related to the Wittig-like reaction known from their titanium predecessors. The first application of this reaction on tungsten catalysts was reported by Schrock and Grubbs using benzaldehyde as the terminating agent.[26] The resulting styryl end-group, however, was not used for subsequent reactions. On molybdenum, the same terminating agent, benzaldehyde, was used with similar success.[27] A broader applicability of this reaction was shown in subsequent publications employing alkyl-substituted aldehydes such as pivalonaldehyde.[28] By application

of pyrenealdehyde, a fluorescence labelled polynorbornene was synthesised and studied in its fluorescence properties in the context of redox-active groups along the polymer chain.[29]

The aldehyde quenching was established as the standard termination reaction for metathesis polymerisations involving molybdenum or tungsten initiators.[30] The following developments led to two types of functionalised aldehydes. A variety of interesting end groups could be introduced without derivatisation, such as the pyrene label. Yet, the reactive functionalities had to be introduced in a suitably protected form in order to avoid side reactions and false capping. The compatibility of such protected functional groups bound to benzaldehydes with the reactivity of the initiating complexes was studied by the Schrock group. Quite a remarkable stability towards a number of functional groups such as amines and nitriles was found. Less reactive groups such as halides, ethers and alkylated amines performed accordingly.[31] Also, this strategy has been extended to the termination of polymerisations initiated by catalysts bearing two carbene moieties,[32] thus growing polymer chains in two directions. The termination of such polymers gives rise to homobifunctional polymers (homo-telechelics).[33]

The versatility of this reaction and the ready availability of the protected functionalised benzaldehydes have facilitated their use. Nomura et al. employed this strategy in a number of applications featuring hydroxy-functionalised polynorbornenes and sugar conjugates.[34] This group chose a TMS-protected *p*-hydroxybenzaldehyde as the terminating agent followed by mild removal of the protecting group. After formation of a terminal norbornene ester, a secondary metathesis polymerisation of the resulting macromonomers yielded graft-copolymers. The attachment of poly(ethylene glycol), yielded block copolymers. [35]

Star-shaped polymers were synthesised by Dounis and Feast when a trifunctional aldehyde-quencher, 1,3,5-benzene-tricarbaldehyde, was added to molybdenum-initiated polynorbornene.[36] More advanced polymer structures, particularly those featuring a change of polymerisation method, have been realized by termination of the living polymerisation with aldehydes bearing either an initiating or anchoring group for the second polymerisation technique. Alternatively, an aldehyde functionalised polymer was added to form a block-copolymer in one step. Similarly, p-fluorobenzaldehyde was used to form a terminal fluoride which could undergo a subsequent polycondensation.[37] Furthermore, *p*-bromomethylbenzaldehyde and *p*-vinylbenzaldehyde were added to synthesize polymers which can function as initiators for ATRP or anionic polymerisation.[38]

The reverse approach was described by Notestein and Register. There, an anionic polymerisation was terminated such that an aldehyde end group was obtained. This polymer was then added to the living ROMP polymer to form the conjugate. Block copolymers incorporating polynorbornene and polystyrene or polyisoprene were realized by this termination reaction.[39]

The addition of carbonyl groups to living ruthenium-initiated polymers does not terminate the polymerisation. In fact, polymerisations can be carried out in solvents such as ethyl acetate, acetone and DMF.[40]

Reaction with molecular oxygen:

In the early molybdenum and tungsten functionalisation reactions that involved aldehydes, high molecular weight shoulders could often be observed in the GPC traces. It was quickly noted that these could be avoided by careful removal of oxygen from all reagents. While this was considered as an unwanted side reaction initially, it was soon studied as a coupling reaction by Feast et al.[41] who found a reaction between the active carbene species and an oxygen molecule yielding a terminal aldehyde. This aldehyde group then undergoes bimolecular coupling to another carbene resulting in a polymer chain of twice the length. The possibility of rapidly applying large excesses of oxygen to the living polymerisation in order to facilitate the aldehyde formation and lower the chance for bimolecular coupling has, however, not been explored so far.

The same primary step was found by Biagini et al.[42] on ruthenium-carbenes. Differing from the aforementioned early transition metal carbenes, no secondary coupling reaction takes place due to the tolerance of ruthenium carbenes towards aldehydes. This reaction can therefore be used for the synthesis of aldehyde end-capped polymers. The reaction is, however, rather slow. Reaction times of 24h have to be expected in most cases which limits the scope of this reaction and its applicability when oxidisable functionalities are present along the polymer chain.

Reaction with vinyl ethers:

As ruthenium carbenes are reactive towards olefins only, deactivation reactions typically involve a metathesis step in which a carbene is formed that does not catalyse further metathesis steps. The most renowned and the first principal method for the introduction of functional groups at the chain-end of ruthenium initiated ROMP polymers is carried out by addition of substituted vinyl ethers. The carbene formed in this metathesis reaction represents an electronically deactivated Fischer-carbene (structure given in Figure 3), which does not re-initiate metathesis reactions on a considerable scale. During this step, the functional group attached to the vinyl ether is transferred to the polymer chain and forms the new end group.

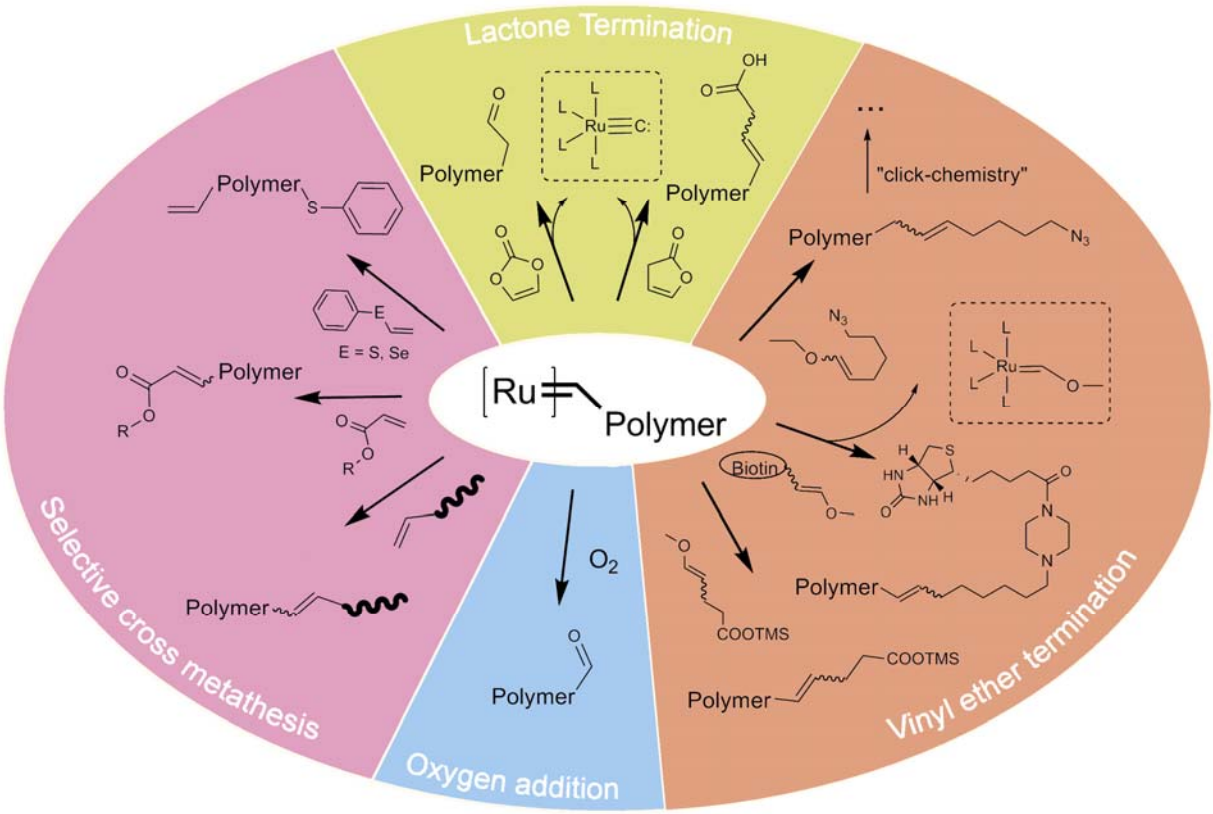


Figure 3: Termination reagents for the ruthenium-catalysed ROMP.

The first description of this process involved the reaction of neat catalyst with ethyl vinyl ether and 2,3-dihydrofurane which resulted in stoichiometric formation of the polymer-bound Fischer-carbene.[43] Soon after, the addition of ethyl vinyl ether was considered as a

standard termination reaction for ROMP polymerisations involving Grubbs-type ruthenium catalysts[44] since it is commercially available and the ruthenium complex is cleanly removed from the polymer chain. Therefore, both the stability and purity of the resulting polymer are enhanced since no secondary metathesis reaction within the polymer chains can take place and the catalyst is washed away during workup of the polymer. One advantage of vinyl ethers as quenching reagents is their straightforward functionalisation starting from the respective functional aldehydes in a Wittig reaction employing the phosphorus ylide based on e.g. chloromethyl ethyl ether.[45]

Vinyl ether termination has established itself as a versatile strategy for the introduction of complex functional end groups. The Kiessling group in particular has put forth this method featuring biocompatible labels on bio-active polymers and interesting binding motives bound to highly functional ROMP polymers. In their first publication, they managed to attach a fluorescein to a polymer that is capable of inhibiting L-selectin. By applying this polymer to living cells, the distribution of L-selectin moieties within the cell could be traced.[46] An even more advanced approach features an end group that can be bound to a surface carrying functionalities along the polymer chain which act as a multivalent ligand highly selective for several selectins. A sensoring chip for such selectins was built and shown to detect them more sensitively than regular detecting surfaces.[47] Also, binding of those functionalized polymers to a solid support has been developed by the same group in an effort to enable a functionalisation of the polymer chain similar to solid supported peptide synthesis (SPPS).[48] As depicted in Figure 3, also biotin molecules were bound to a vinyl ether in order to transfer them onto a polymer chain-end. Monofunctional amphiphilic block-copolymers capped with this agent were then micellised and exposed to streptavidine, which caused noncovalent aggregation of these structures.[49] These synthetic applications have been generalised in following publications.

A broad spectrum of vinyl ethers bearing protected reactive functional groups has been studied for capping efficiency and reaction conditions.[50] Also, an azide functionalised vinyl ether was used to introduce a universal group for the Huisgen 1,3-dipolar cycloaddition commonly known as the alkyne – azide “click” reaction.[51]

Metathesis catalysts are also known to isomerise double bonds, i.e. shift olefin groups along a hydrocarbon chain.[52] While this is considered a non disturbing side reaction in most polymerisation cases, the isomerisation of allyl ethers to vinyl ethers has to be considered as

it can lead to slow catalyst deactivation. The understanding of the isomerisation mechanism[53] might also give rise to new synthetic routes for vinyl ethers or their *in situ* formation in a tandem catalysis.

The addition of vinyl ethers to ruthenium carbenes does not terminate ROMP activity completely. Some studies have shown that the Fischer-carbenes formed in this reaction exhibit a residual capability to initiate a metathesis polymerisation, albeit with a rather low rate of initiation.[54] In this case, the vinyl ether acts as an acyclic chain transfer agent that reacts regioselectively to give a telechelic polymer bearing an ether group on one end and the functional group formerly bound to the vinyl ether on the other in fairly good definition. This selectivity is caused during the polymerisation deactivation step by the vinyl ether in which the energetically favourable Fischer-carbene is formed.

When sulphur or seleno-derivatives of vinyl ethers are applied, the deactivation is less pronounced, resulting in a more vivid chain transferring activity. While vinyl ether chain-transferred polymerisations required 1-3 days, sometimes at elevated temperatures, to complete, the reaction involving vinyl sulphides was finished after few hours at ambient temperatures.[55] Higher vinyl chalcogenides performed accordingly, while steric influences have to be considered. The selectivity remains considerably high when higher analogues of vinyl ethers are applied. The study of Katayama et al.,[56] which focused on the ring-opening cross metathesis of norbornene with vinyl ethers and their higher analogues, implies a very selective mechanism for the chain transfer directed by the resulting Fischer-carbenes produced in the cross metathesis step. Titanium, molybdenum and tungsten catalysts are not terminated when vinyl ethers are added.

Contrary to vinyl ethers, acyl carbenes form inactive and unstable Fischer-carbenes. They decompose to the respective carboxylic acid and another ruthenium complex containing a carbido ligand, i.e. a ruthenium-carbon triple bond.[57] This complex can not undergo further metathesis reactions unless reactivated by addition of a strong acid or an oxidant.[58] Furthermore, cyclic terminating agents can be applied in the case of vinyl esters, as the consecutive decomposition reaction will also cleave the catalyst off the chain. Another advantage of cyclic terminating agents is the fact that olefins in small cycles are purely *cis*-substituted. This enhances the reactivity of metathesis catalysts towards them due to lower steric hindrance at the double bond.

Two unsaturated lactones have been applied for the functionalisation of metathesis polymers.[59] Vinylene carbonate, which is also commercially available, can be used for the attachment of aldehydes at the chain-end. In this case decomposition of the acyl carbene gives a carbonic acid semi ester leaving the terminal aldehyde on the polymer chain-end. Addition of *3H*-furanone, readily synthesised from furfural in a Baeyer-Villiger oxidation, resulted in termination and the formation of a terminal polymeric carboxylic acid.

This strategy represents a particularly useful method for the end-functionalisation of polymers with aldehydes or carboxylic acids since no work-up such as deprotection is needed. Therefore, this approach not only yields two of the most interesting and reactive functional groups, but can also be applied when rather sensitive groups are present along the polymer chain. Due to its unique decomposition reaction to a non-carbene complex, this method is one of the very few real deactivation reactions involving olefins for the ruthenium catalysed metathesis known to date.

Reaction with neutral olefins:

When sterically hindered polymers are used, e.g. those of norbornene derivaties, a simple olefin can be applied to induce a functionalisation at the chain-end. In this case, the living characterisitics of the polymerisation are utilized to ensure the exact placement of one functional end group onto the polymer. Such sterically demanding structures virtually forbid the event of intra- and intermolecular cross metathesis with the olefin groups along the polymer chain or within other polymer chains. When no further monomer is present in the polymerisation mixture, addition of a functionalised acyclic olefin leads to a functionalising cross metathesis with the active polymer chain-end and to the formation of a new carbene complex. In the absence of monomer, the latter cannot initiate a new polymer chain.

The addition of acrylates (*c.f.* Figure 3, *left*) represents a particularly simple end-functionalisation method, as these are readily available. They give, however, only moderate degrees of functionalisation since the regiospecific direction of the metathesis step by the acrylate group is low.[60] The addition of symmetrically functionalised olefins, on the other hand, leads to quite appreciable functionalisation results. Intiator groups for the ATRP[61] and building blocks for “click”-reactions[62] have been attached to polynorbornenes by this method.

Polymerisation functionalisation:

By chain transfer agents:

The addition of chain transfer agents (CTA) in order to control the molecular weight of a polymer and to attach functional groups to the polymer chain-ends has been a very common method for other polymerisation techniques long before the metathesis polymerisation had been established. The method is based on the addition of an acyclic olefin which undergoes cross metathesis with the active chain-end (mechanism given in Figure 4), whereby the polymer chain is cleaved off the metal centre and a new polymer chain is initiated by the newly formed carbene. In addition, the cross metathesis of double bonds along the polymer chain with the chain transfer agent leads to an equilibration in which the average molecular weight is determined solely by the stoichiometry of the initial reagents, i.e. monomer and CTA. As far as the equilibration reaction is concerned, the structure of the polymer has to be taken into account. While polymers formed from monocyclic olefins are typically sterically non-demanding and equilibrate readily, polymers formed from norbornene, for example, are far less prone to undergoing secondary metathesis reactions along the polymer chain. While this is used by some groups for the formation of monofunctional polymers, telechel formations have to be triggered by more advanced strategies in this case.

CTA's were first used in the synthesis of telechelic polymers using molybdenum and tungsten catalysts. In an early approach, Schrock et al. chose an unprecedented way to activate chain transfer by employing olefin substituted cyclopentene derivatives. In this approach, the strained cyclopentene double bond is used to trigger the incorporation to the polymer chain. The second olefin is attached in such a manner that a cross metathesis with this double bond forms a favourable six-membered ring and a free carbene which can initiate a new chain.[63] The chain transferring activity of these agents, however, proved to be rather poor.

Later, it could be shown that activated double bonds showed increased cross metathesis activity and consequently better success with the incorporation into polyenes. Styrene and 1,3-butadiene, in particular, were used as chain transfer agents for the polymerisation of norbornene. In this case, where highly reactive monomers are used and the polymerisation is fast, impressively narrow molecular weight distributions can be obtained by pulsing the

polymerisation mixture with fresh monomer.[64] Reactive functional groups have not yet been introduced to polymer chains by this method.

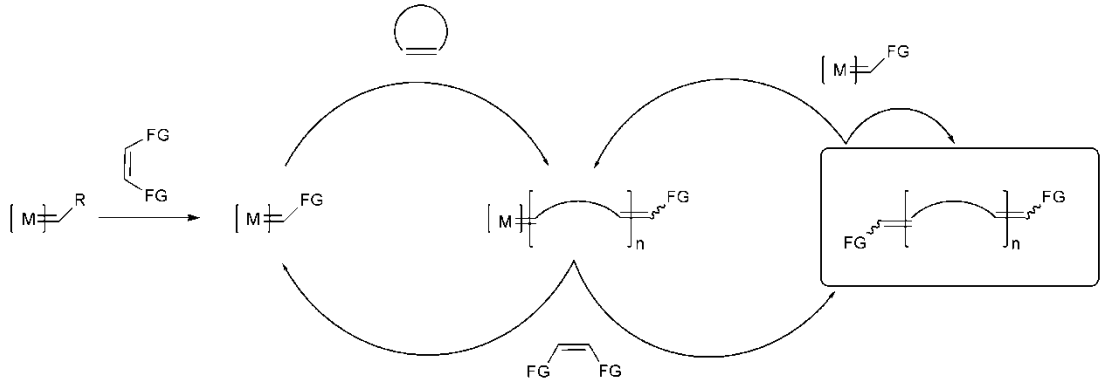


Figure 4: Mechanism for the formation of telechelic polymers by application of chain transfer agents.

The use of CTA's as functionalising agents for the ruthenium catalysed ROMP was studied largely during the early development of chain-end functionalised polymers due to the high functional group tolerance of the ruthenium carbenes. The theoretical base and a proposed mechanism of the chain transfer and the subsequent equilibration reaction have been studied in the Grubbs group.[65] Further studies involving the kinetics of the reaction and the influence of the monomer structure on the equilibration reaction followed,[66] which also set the base for the synthesis of monofunctional polymers (vide infra).

The use of CTA's in ruthenium catalysed ROMP has by far become the most applied method for the attachment of reactive termini on polymer chain-ends. First applications involved protected reactive functional groups such as alcohols,[67] amines and carboxylic acid.[68] Also, less reactive functional groups were introduced without protection. Especially groups like halides, pseudo-halides,[69] methacrylates and epoxides[70] which can function as initiating sites for different polymerisation techniques such as ATRP, free radical or ionic polymerisation were introduced this way. Furthermore, even complex CTA's bearing polymers[71] or groups that possess liquid crystalline properties[72] have been synthesised and applied.

The latest generation of extremely reactive ruthenium carbenes featuring pyridyl ligands has recently also been applied in a pulsed-addition ROMP, where fresh monomer is added to a catalyst – CTA solution.[73] While this method can also be used to form block-copolymers, it has, however, not been used yet to introduce reactive functional groups. This approach could drastically increase the number of well-defined polymer chains per catalyst molecule and has shown the impressive reactivity and selectivity of the latest catalyst developments. As such, this report also demonstrates how well these catalysts can compete with their molybdenum and tungsten parents in those terms.

A related method has been reported by Fraser et al.,[74] who have used cyclic cleavable monomers in a statistical copolymerisation with classical ROMP monomers. Here, the functional chain-ends are set free by a subsequent hydrolysis of those cleaving sites. Acetal monomers were found to be suitable for the synthesis of hydroxytelechelic polymers. As far as molecular weight control and the definition of the molecular weight distribution are concerned, this method is controlled not by the chemist, but by the kinetic characteristics of the reaction. The stable monomer has great influence on the equilibration reaction which gives the molecular weight control. Sterically demanding monomers would require an azeotropic copolymerisation in order to give polymers of the molecular weight that is predetermined by the stoichiometry of the reaction. The molecular weight distributions are generally expected to be rather broad as a statistical process takes place.

Sacrificial Synthesis:

In contrast to the majority of the aforementioned methods of mono-functionalisation, Sacrificial Synthesis is not based on a catalyst deactivation step. Rather, it represents an advanced strategy of polymerisation of cleavable cyclic monomers, thereby circumventing the negative kinetic aspects of a copolymerisation. In this approach, an additional block of a cleavable monomer is polymerised onto the desired polymer.[75] This block can then be destroyed in a subsequent deprotection reaction, thereby liberating the functional group as illustrated in Figure 5. This approach has shown potential, particularly in the placement of highly reactive functional groups which can be protected in such a way that cyclic monomers are formed.

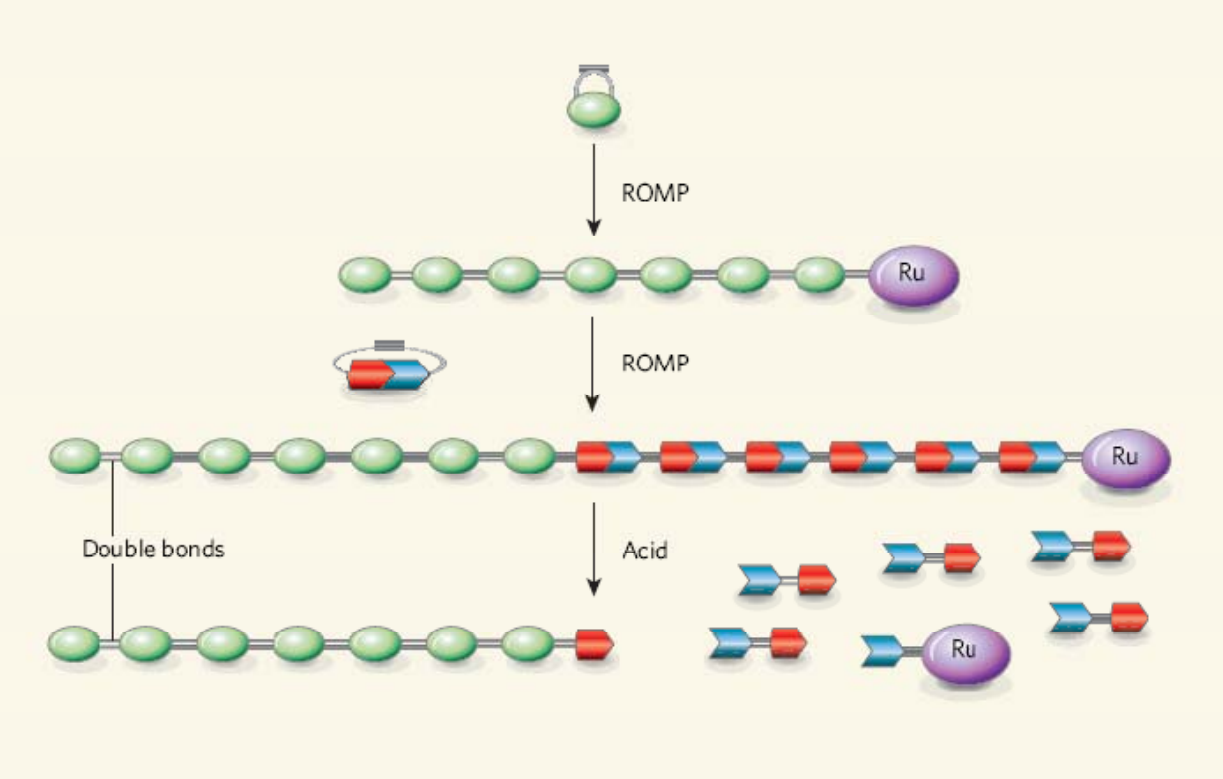


Figure 5: Synthetic concept of Sacrificial Synthesis

The first report on this strategy, which received significant attention,[76] focused on the formation of terminal alcohols. In this case, 1,3-dioxepines similar to the cyclic acetals used in the copolymerisation technique (see above) were used to form the sacrificial block. After removal by acidic hydrolysis or hydrogenation "half a dioxepine", i.e. an alcohol group was left on the polymer chain-end. The degree of functionalisation is primarily given by the degree of initiation of the sacrificial block. Any reaction of an additional sacrificial monomer unit does not contribute to the degree of functionalisation as it is removed later on. Therefore, excesses of the cleavable monomer have to be added to ensure high degrees of functionalisation.

The resulting precisely and reactively end-functionalised polymers have been applied in the construction of more complex polymeric architectures. By derivatisation with a norbornene acid, macromonomers were formed and polymerised to the respective graft-copolymers using the same catalyst that had been used for the synthesis of the side chains.

[77] Using the Huisgen-type azide-alkyne click reaction, block copolymers were formed with different polymers after esterification of the terminal alcohol with propargylic acid. [78]

Thiol end groups have also been accessed in the same fashion, polymerising 2-phenyl-1,3-dithiepine, which can be removed by hydrogenation with Raney-nickel. The resulting thiol end group was used to coat the surface of gold nanoparticles with the ROMP polymer.[79]

An efficiency study[80] has focused on the kinetic characteristics of the reaction and the block transfer in order to optimise the process and minimise the amounts of sacrificial monomer needed. By employing kinetic equations for the living anionic polymerisation, this key initiation step could be understood in detail. In summary, precise placement of exactly one alcohol or thiol group on the ROMP polymer chain-end has been accomplished by sacrificial synthesis.

Since the process of introducing the functional group by sacrificial synthesis is non deactivating, the method can also be used to place a functional group at the beginning of the polymer chain. Hydroxy-homotelechelic polymers, or polymers bearing an alcohol group at both ends, have been realised in this manner from sacrificial triblock copolymers where the outer blocks consisted of polyacetals. Using this method, the first well defined telechelic materials showing narrow molecular weight distribution have been synthesised by ruthenium-catalysed ROMP.[81]

The number of telechelic chains produced per molecule of catalyst could be increased by increasing the number of alternating blocks to five or seven. This means that two or three non-hydrolysable blocks are enclosed and separated by the respective number of sacrificial blocks. However, partial loss of molecular weight definition due to increasingly poor block transfers was observed. Nonetheless, this method is especially suitable for short telechelic polymers with narrow molecular weight distribution, which would otherwise require stoichiometric amounts of catalyst per polymer chain.

A general functionalisation guide:

A number of factors have to be considered in order to chose the most appropriate method of end-functionalisation: The chosen monomer has a great influence on the choice of catalyst, due to both potential functional group incompatibilities and the general reactivity of the catalyst. Secondly, the method of functionalisation has to be chosen with respect to the number of functional end-groups that have to be attached, i.e. monofunctional or telechelic polymers. Moreover, the desired molecular weight definition plays an important role in many application-oriented syntheses. Table 2 summarises the methods available and classifies them according to functional group classes, catalyst generations, polymer types and other factors to give a general navigation map through the wide field of methods.

Table 2: A field guide of functionalisation methods for the living ROMP

FG type	**catalyst**	**# FG**	**method**	**% FG**	**PDI**	**comment**	**ref**
-OH	Ti	1	$(CHO)_2$	med/high	med	reduction to OH	23
	Mo/W	1	CHO	high	good		34,35
	Ru	1	Sacr. Synth.	high	good		75, 76, 77, 78, 81
		2	CTA	high	low		66, 67, 71
		2	copo w/ acetals	high	low		74
		2	Sacr. Synth.	high	good		81
-COOH	Mo/W	1	CHO	high	good	As methyl ester	31
	Ru	1	VE	med	good		50
		1	3HF	high	good	no deprotection	59
		2	CTA	high	low		68
-NH_2	Mo/W	1	CHO	high	good		31
	Ru	1	VE	med	good		50
		2	CTA	high	low		68
-SH	Ru	1	Sacr. Synth.	high	high		79
-CHO	Ti	1	$(CHO)_2$	med/high	med	also coupling	23
	Mo/W	1	$(CHO)_2$	med/high	med	also coupling	31
	Ru	1	O_2-addition	med	good	reaction time	42
		1	VC	high	good		59
Initiator & polymerisable	Mo/W	1	CHO	high	high	ATRP, ionic PM, polycondensation	34, 35, 38

Initiator & polymerisable (cont.)	Ru	1	CTA	high	good	bulky monomers, ATRP, "click"	61, 62
		2	CTA	high	low	e.g. ATRP, rad. PM,	70
Polymer	Ti	1	Polym.-C=O	med/high	med	block- & star-copo.	24
	Mo/W	1	Polym.-CHO	med/high	med	block- & star-copo.	36, 39
	W	1	FI	high	good	living styrene + WCl_6	16
	Ru	1	FI	high	good	difficult!	20
		1-2	CTA	med	low		71
Biological Molecules	Ru	1	VE	med	good	e.g. biotin	47, 49
Labels	Ti	1	CHO/C=O	high	good	e.g. pyrene-CHO	14
	Mo/W	1	CHO	high	good	e.g. pivalonaldehyde	25, 27, 28, 29, 30, 31,
		1-2	CTA	med	low	e.g. styrene	64
		2	Aldehyde	high	good	bifunct. initiator	32, 33
	Ru	1	FI	med-high	good		18, 19
		1	Acrylate	med	good		60
		1	VE	high	good	e.g. ethyl vinyl ether	46, 48, 50, 51
		1-2	CTA	high	good		69, 72, 73

CHO: Addition of an aldehyde. $(CHO)_2$: Addition of a dialdehyde. VE: Addition of a vinyl ether. CTA: Addition of a chain-transferring agent. 3HF: Addition of 3H-furanone. VC: Addition of vinylene carbonate. C=O: Addition of a ketone. FI: use of a prefunctionalised initiator complex.

Conclusions and Outlook

An overwhelming number of functionalisation reactions have been developed for the ROMP. While most functionalisation strategies focus on the termination of the polymerisation reaction for the introduction of a functional group, others have employed a functional initiation step. A third group of methods has deployed specialised polymerisation techniques for the introduction of the desired functionalities. Owing to the fundamental differences of the different catalyst types and generations in terms of functional group tolerance, polymerisation activity and general reactivity towards substrates, every catalyst type requires its specific functionalisation techniques.

Catalysts based on molybdenum, ruthenium and tungsten play the most dominant role in recent ROMP research. In the case of molybdenum, catalysed metathesis polymerisation

functionalisation is affected in most cases by the addition of an aldehyde bearing the desired functional group. While this reaction is quick and efficient, only a limited variety of well-protected functional groups can be generated due to the relatively high reactivity of molybdenum towards such groups. Ruthenium carbenes, on the other hand, are reactive towards olefins only. As a consequence, olefins were employed which deactivate the catalyst after the metathesis step, thereby terminating the metathesis reaction. Electron deficient olefins, which can be found in vinyl ethers and vinyl lactones, are used for these purposes today.

The most modern ruthenium catalysts which combine both functional group tolerance and high metathesis activity will certainly play a key role in future metathesis development. The large variety of functionalisation methods for these complexes will also set the tone for future approaches to place functional sites on or along the polymer chain. Among the variety of methods, three have emerged as generally applicable strategies for the most useful functional groups. The termination with vinyl lactones and the Sacrificial Synthesis give rise to very reactive end groups and can be conducted conveniently. They can therefore be termed useful for the broad application as the resulting highly functionalised polymers can be reacted and derivatized easily, even by non-specialists. Vinyl lactone termination, in particular, promises an extremely broad applicability since the functional groups produces by this method are liberated during the termination reaction and need no further reaction steps. This in particular allows even labile groups to be present in the monomer structure as the functional end group is released under very mild conditions.

Vinyl ether termination is a much broader functionalisation technique with many more possible types of functional group available. Yet it is also a strategy which requires more knowledge and experience with the ROMP process and higher demands in the synthesis of the respective terminating agents. The method will, however, remain a driving force in the field of bio-related functional polymers, where complex molecular motifs have to be mildly reacted onto the polymer chain-end in order to conserve their function and specificity. Furthermore, this method will certainly remain the reference method for both the evaluation of other functionalisation techniques and a reliable work horse for all functional groups that can not be incorporated in cyclised monomers for Sacrificial Synthesis or lactone termination (such as azides or halides).

References

[1] Grubbs, R.H., *Handbook of Metathesis* (Wiley-VCH, Weinheim, 2003).

[2] Hérisson, J.-L. & Chauvin, Y. Catalyse de transformation des oléfines par les complexes du tungstène. II. Télomérisation des oléfines cycliques en présence d'oléfines acycliques. *Makromol. Chem.* **141,** 161-176 (1971).

[3] US Patent 3074918 (1963) Du Pont de Nemours and Company, Inv. H. C. Eleuterio. Calderon, N., Ofstead, E. A., Ward, J. P., Judy, W. A. & Scott, K. W. Olefin metathesis. I. Acyclic vinylenic hydrocarbons. *J. Am. Chem. Soc.* **90,** 4133-4140 (1968).

[4] Murdzek, J. S. & Schrock, R. R. Low polydispersity homopolymers and block copolymers by ring opening of 5,6-dicarbomethoxynorbornene. *Macromolecules* **20,** 2640-2642 (1987).

[5] Toreki, R. & Schrock, R. R. A well-defined rhenium(VII) olefin metathesis catalyst. *J. Am. Chem. Soc.* **112,** 2448 (1990)

[6] Wallace, K. C., Liu, A. H., Dewan, J. C. & Schrock, R. R. Preparation and reactions of tantalum alkylidene complexes containing bulky phenoxide or thiolate ligands. Controlling ring-opening metathesis polymerization activity and mechanism through choice of anionic ligand. *J. Am. Chem. Soc.* **110,** 4964 (1988).

[7] Schrock, R. R. Multiple Metal-Carbon Bonds for Catalytic Metathesis Reactions (Nobel Lecture). *Angew. Chem. Int. Ed.* **45,** 3748-3759 (2006).

[8] Grubbs, R. H. Olefin-Metathesis Catalysts for the Preparation of Molecules and Materials (Nobel Lecture). *Angew. Chem. Int. Ed.* **45,** 3760-3765 (2006).

[9] Grubbs, R. H. The Development of Functional Group Tolerant Romp Catalysts. *J. Macromol. Sci. A* **31**,1829-1933 (1994). Binder, J. B. & Raines, R. T. Olefin metathesis for chemical biology. *Current Opinion in Chemical Biology* **12**, 767–773 (2008).

[10] Ulman, M. & Grubbs, R.H. Relative Reaction Rates of Olefin Substrates with Ruthenium(II) Carbene Metathesis Initiators. *Organometallics* **17,** 2484-2489 (1998).

[11] Maynard, H. D., Okada, S. Y., & Grubbs, R. H. Inhibition of Cell Adhesion to Fibronectin by Oligopeptide-Substituted Polynorbornenes. *J. Am. Chem. Soc.* **123**, 1275-1279 (2001).

[12] Pasut, G. & Veronese, F.M. Polymer–drug conjugation, recent achievements and general strategies. *Prog. Polym. Sci.* **32,** 933-961 (2007).

[13] Nie, Z. & Kumacheva, E. Patterning surfaces with functional polymers. *Nature Materials* **7**, 277-290 (2008).

[14] Gilliom, L. R. & Grubbs, R. H. Titanacyclobutanes derived from strained, cyclic olefins: the living polymerization of norbornene. *J. Am. Chem. Soc.* **108,** 733-742 (1986).

[15] Tebbe, F. N., Parshall, G. W. & Reddy, G. S. Olefin homologation with titanium methylene compounds. *J. Am. Chem. Soc.* **100,** 3611-3613 (1978).

[16] Amass, A. J. & Gregory, D. Anionic to metathesis-transformation polymerization. *Br. Polym. J.* **19,** 263-268 (1987). Amass, A. J., Bas, S., Gregory, Denis, M. & Mathew C. Block copolymers by metathesis polymerization. *Makromol. Chem.* **186,** 325-330 (1985).

[17] Schwab, P., Grubbs, R. H. & Ziller, J. W. Synthesis and Applications of $RuCl_2(=CHR')(PR_3)_2$: The Influence of the Alkylidene Moiety on Metathesis Activity. *J. Am. Chem. Soc.*, **118,** 100-110 (1996).

[18] Bielawski, C., W., Louie, J. & Grubbs, R. H. Tandem Catalysis: Three Mechanistically Distinct Reactions from a Single Ruthenium Complex. *J. Am. Chem. Soc.*, **122,** 12872-12873 (2000).

[19] Burtscher, D., Saf, R. & Slugovc, C. Fluorescence-labeled olefin metathesis polymerization initiators. *J. Polym. Sci. A: Polym. Chem.* **44,** 6136-6145 (2006).

[20] Castle, T. C., Hutchings, L. R. & Khosravi, E. Synthesis of Block Copolymers by Changing Living Anionic Polymerization into Living Ring Opening Metathesis Polymerization. *Macromolecules* **37,** 2035-2040 (2004).

[21] Pine, S. H., Zahler, R., Evans, D. A. & Grubbs, R. H. Titanium-mediated methylene-transfer reactions. Direct conversion of esters into vinyl ethers. *J. Am. Chem. Soc.* 102, 3270-3272 (1980). Brown-Wensley, K. A., Buchwald, S. L., Cannizzo, L. F., Clawson, L., Ho, S., Meinhardt, D., Stille, J. R., Straus, D. & Grubbs, R. H. Cp_2TiCH_2 complexes in synthetic applications. *Pure & Appl. Chem.* **55,** 1733-1744 (1983).

[22] Gilliom, L. R. & Grubbs, R. H. Titanacyclobutanes derived from strained, cyclic olefins: the living polymerization of norbornene. *J. Am. Chem. Soc.* **108,** 733-742 (1986). Cannizo, L. F. & Grubbs, R. H. End capping of polynorbornene produced by titanacyclobutanes. *Macromolecules* **20,** 1488 (1987).

[23] Risse, W. & Grubbs, R. H. Block and graft copolymers by living ring-opening olefin metathesis polymerization. *J. Mol. Catal.* **65,** 211-217 (1991).

[24] Risse, W. & Grubbs, R. H. Application of Wittig-type reactions of titanacyclobutane end groups for the formation of block and graft copolymers. *Macromolecules* **22,** 4462-4466 (1989).

[25] Schrock, R. R. Living ring-opening metathesis polymerization catalyzed by well-characterized transition-metal alkylidene complexes. *Acc. Chem. Res.* **23,** 158-165 (1990).

[26] Schrock, R. R., Feldman, J., Cannizzo, L. F. & Grubbs, R. H. Ring-opening polymerization of norbornene by a living tungsten alkylidene complex. *Macromolecules*, **20,** 1169-1172 (1987).

[27] Murdzek, J. S. & Schrock, R. R. Low polydispersity homopolymers and block copolymers by ring opening of 5,6-dicarbomethoxynorbornene. *Macromolecules* **20,** 2640-2642 (1987).

[28] Schrock, R. R., Murdzek, J. S., Bazan, G. C., Robbins, J., DiMare, M. & O'Reagan, M. B. Synthesis of molybdenum imido alkylidene complexes and some reactions involving acyclic olefins. *J. Am. Chem. Soc.* **112,** 3875-3886 (1990). Bazan, G. C., Khosravi, E., Schrock, R. R., Feast, W. J., Gibson, V. C., O'Reagan, M. B., Thomas, J. K. & Davis, W. M. Living ring-opening metathesis polymerization of 2,3-difunctionalized norbornadienes by Mo(:CHBu-tert)(:NC6H3Pr-iso2-2,6)(OBu-tert)2. *J. Am. Chem. Soc.* **112,** 8378-8387 (1990).

[29] Albagli, D., Bazan, G. C., Schrock, R. R. & Wrighton, M. S. New functional polymers prepared by ring-opening metathesis polymerization: study of the quenching of

luminescence of pyrene end groups by ferrocene or phenothiazine centers in the polymers. *J. Phys. Chem.* **97,** 10211-10216 (1993).

[30] Albagli, D., Bazan, G. C., Schrock, R. R. & Wrighton, M. S. Surface attachment of well-defined redox-active polymers and block polymers via terminal functional groups. *J. Am. Chem. Soc.* **115,** 7328-7334 (1993).

[31] Mitchell, J. O., Gibson, V. C. & Schrock, R. R. Chain-end functionalization of living polymers formed by the ring-opening metathesis polymerization of norbornene. *Macromolecules* **24,** 1220-1221 (1991).

[32] Fox, H. H., Lee, J.-K., Park, L. Y. & Schrock, R. R. Synthesis of five- and six-coordinate alkylidene complexes of the type Mo(CHR)(Nar)[OCMe$(CF_3)_2]_2S_x$ and their use as living ROMP initiators or Wittig reagents. *Organometallics* **12,** 759-768 (1993).

[33] Singh, R., Verploegen, E., Hammond, P. T. & Schrock, R. R. Synthesis of ABA triblock copolymers via ring-opening metathesis polymerization using a bimetallic initiator: Influence of a flexible spacer in the side chain liquid crystalline block. *Macromolecules* **39,** 8241-8249 (2006).

[34] Murphy, J. J. & Nomura, K. Precise synthesis of poly(macromonomer)s containing sugars by repetitive ring-opening metathesis polymerization. *Chem Commun.* 4080-4082 (2005).

[35] Murphy, J. J., Takahashi, S. & Nomura, K. Synthesis of poly(macromonomer)s by repeating ring-opening metathesis polymerization (ROMP) with Mo(CHCMePh)(NAr)(OR) initiators. *Macromolecules* **34,** 4712-4723 (2001). Murphy, J. J., Kawasaki, T., Fujiki, M. & Nomura, K. Precise synthesis of amphiphilic polymeric architectures by grafting poly(ethylene glycol) to end-functionalized block ROMP copolymers. *Macromolecules* **38,** 1075-1083 (2005). Murphy, J. J., Furusho, H., Paton, R. M. & Nomura, K. Precise synthesis of poly(macromonomer)s containing sugars by repetitive ROMP and their attachments to poly(ethylene glycol): synthesis, TEM analysis and their properties as amphiphilic block fragments. *Chem. Eur. J.* **13,** 8985-8997 (2007).

[36] Dounis, P. & Feast, W. J. A route to low polydispersity linear and star polyethylenes via ring-opening metathesis polymerization. *Polymer* **37,** 2547 (1996).

[37] Albagli, D., Bazan, G. C., Schrock, R. R. & Wrighton, M. S. Surface attachment of well-defined redox-active polymers and block polymers via terminal functional groups. *J. Am. Chem. Soc* **115,** 7328-7334 (1993).

[38] Coca, S., Paik, H.-J. & Matyjaszewski, K. Block copolymers by transformation of living ring-openeing metathesis polymerization into controlled/"living" atom transfer radical polymerization. *Macromolecules* **30,** 6573-6576 (1997). Myers, S. B. & Register, R. A. Block copolymers synthesized by ROMP-to-anionic polymerization transformation. *Macromolecules* **41,** 5283 (2008).

[39] Notestein, J. M., Lee, L.-B. W. & Register, R. A. Well-defined diblock copolymers via termination of living ROMP with anionically polymerized macromolecular aldehydes. *Macromolecules*, **35,** 1985-1987 (2002).

[40] Slugovc, C., Demel, S. & Stelzer, F. Ring opening metathesis polymerization in donor solvents. *Chem. Commun.* 2572-2573 (2002).

[41] Feast, W. J., Gibson, V. C., Khosravi, E., Marshall, E. L. & Mitchell, J. P. Bimolecular termination in living ring opening metathesis polymerization. *Polymer* **33,** 872-873 (1992).

[42] Biagini, S. C. G., Davies, R. G., Gibson, V. C., Giles, M. R., Marshall, E. L. & North, M. Ruthenium initiated ting opening metathesis polymerization of amino-acid and –ester functionalsed norbornenes and a highly selective chain-end functionalisation reaction using molecular oxygen. *Polymer* **42,** 6669-6671 (2001).

[43] Wu, Z., Nguyen, S. T., Grubbs, R. H. & Zillier, J. W. Reactions of Ruthenium Carbenes of the Type (PPh3)2(X)2Ru:CH-CH:CPh2 (X = Cl and CF3COO) with Strained Acyclic Olefins and Functionalized Olefins. *J. Am. Chem. Soc.* **117,** 5503-5511 (1995).

[44] Schwab, P., Grubbs, R. H. & Zillier, J. W. Synthesis and applications of RuCl(CHR')(PR): The influence of the alkylidene moiety on metathesis activity. *J. Am. Chem. Soc.* **118,** 100-110 (1996).

[45] Earnshaw, C., Wallis, C. J. & Warren, S. Synthesis of E- and Z- vinyl ethers by the Horner-Wittig reaction. *J. Chem. Soc. Perkin Trans. 1,* **12,** 3099-106 (1979).

[46] Gordon, E. J., Gestwicki, J. E., Strong, L. E. & Kiessling, L. L. Synthesis of end-labeled multivalent ligands for exploring call-surface-receptor-ligand interactions. *Chem. Biol.* **7,** 9-16 (2000).

[47] Gestwicki, J. E., Cairo, C. W., Mann, D. A., Owen, R. M. & Kiessling, L. L. Selective immobilization of multivalent ligands for surface plasmon resonance and fluorescence microscopy. *Anal. Biochem.* **305,** 149-155 (2002).

[48] Pontrello, J. K., Allen, M. J., Underbakke, E. S. & Kiessling, L. L. Solid-phase synthesis of polymers using the ring-opening metathesis polymerization. *J. Am. Chem. Soc.* **127,** 14536-14537 (2005).

[49] Chen, B., Metera, K. & Sleiman, H. F. Biotin-terminated ruthenium bipyridine ring-opening metathesis polymerization copolymers: Synthesis and self-assembly with streptavidin. *Macromolecules* **38,** 1084-1090 (2005).

[50] Owen, R. M., Gestwicki, J. E., Young, T. & Kiessling, L. L. Synthesis and applications of end-labeled neoglycopolymers. *Org. Lett.* **4,** 2293-2296 (2002).

[51] Mangold, S. L., Carpenter, R., T. & Kiessling, L. L. Synthesis of fluorogenic polymers for visualizing cellular internalization. *Org. Lett.* **10,** 2997-3000 (2008).

[52] Maynard, H. D. & Grubbs, R. H. Synthesis of functionalized polyethers by ring-opening metathesis polymerization of unsaturated crown ethers. *Macromolecules* **32,** 6917-6924 (1999).

[53] Courchay, F. C., Sworen, J. C., Ghiviriga, I., Abboud, K. A. & Wagener, K. B. Understanding structural isomerization during ruthenium-catalyzed olefin metathesis: A deuterium labeling study. *Organometallics* **25,** 6074-6086 (2006).

[54] Katayama, H., Yonezawa, F., Nagao, M. & Ozawa, F. Ring-opening metathesis polymerization of norbornene using vinylic ethers as chain-transfer agents: Highly selective synthesis of monofunctional macroinitiators for atom transfer radical polymerization. *Macromolecules* **35,** 1133-1136 (2002).

[55] Katayama, H., Urushima, H. & Ozawa, F. Olefin metathesis reactions using vinylideneruthenium(II) complexes as catalyst precursors. *J. Organomet. Chem.* **606,** 16-25 (2000).

[56] Katayama, H., Urushima, H., Nishioka, T., Wada, C., Nagao, M. & Ozawa, F. Highly selective ring-opening/cross-metathesis reactions of norbornene derivatives using selenocarbene complexes as catalysts. *Angew. Chem. Int. Ed.* **39,** 4513-4515 (2000).

[57] Caskey, S. R., Stewart, M. H., Kivela, J. E., Sootsman, J. R., Johnson, M. J. & A., Kampf, J. W. Two generalizable routes to terminal carbide complexes. *J. Am. Chem. Soc.* **127,** 16750-16751 (2005).

[58] Caskey, S. R., Stewart, M. H., Johnson, M. J., A. & Kampf, J. W. Carbon-carbon bond formation at a neutral terminal carbide ligand: Generation of cyclopropenylidene and vinylidene complexes. *Angew. Chem. Int. Ed.* **45,** 7422-7424 (2006). Macnaughtan, M. L., Johnson, M. J. & A., Kampf, J. W. Olefin metathesis reactions with vinyl halides: Formation, observation, and fate of the ruthenium-monohalomethylidene moiety. *J. Am. Chem. Soc.* **129,** 7708-7709 (2007).

[59] Hilf, S., Grubbs, R. H. & Kilbinger, A. F. M. End capping ring-opening olefin metathesis polymerization polymers with vinyl lactones. *J. Am. Chem. Soc.* **130,** 11040-11048 (2008).

[60] Lexer, C., Saf, R. & Slugovc, C. Acrylates as termination reagent for the preparation of semi-telechelic polymers made by ring opening metathesis polymerization. *J. Polym. Sci. A: Polym. Chem.* **47,** 299-305 (2009).

[61] Li, M.-H., Keller, P. & Albouy, P.-A. Novel liquid crystalline block copolymers by ATRP and ROMP. *Macromolecules* **36,** 2284-2292 (2003). Matson, J. B. & Grubbs, R. H. ROMP#ATRP block copolymers prepared from monotelechelic poly(oxa)norbornenes using a difunctional terminating agent. *Macromolecules* **41,** 5626-5631 (2008).

[62] Gozgen, A., Dag, A., Durmaz, H., Sirkecioglu, O., Hizal, G. & Tunca, U. ROMP-NMP-ATRP combination for the preaparation of 3-miktoarm star terpolymer via click chemistry. *J. Polym. Sci. A: Polym. Chem.* **47,** 497-504 (2009).

[63] Schrock, R. R., Yap, K. B., Yang, D. C., Sitzmann, H., Sita, L. R. & Bazan, G. C. Evaluation of cyclopentene-based chain-transfer agents for living ring-opening metathesis polymerization. *Macromolecules* **22,** 3191-3200 (1989).

[64] Crowe, W: E., Mitchell, J. P., Gibson, V. C. & Schrock, R. R. Chain-transfer agents for living ROMP [ring opening metathesis polymerization] reactions of norbornene. *Macromolecules* **23,** 3534-3536 (1990).

[65] Benedicto, A. D., Claverie, J. P. & Grubbs, R. H. Molecular weight distribution of living polymerization involving chain-transfer agents: Computational results, analytical solutions, and experimental investigations using ring-opening metathesis polymerization. *Macromolecules* **28,** 500-511 (1995).

[66] Bielawski, C. W., Benitez, D., Morita, T. & Grubbs, R. H. Synthesis of end-functionalized poly(norbornene)s via ring-opening metathesis polymerization. *Macromolecules* **34,** 8610-8618 (2001).

[67] Hillmyer, M. A., Nguyen, S. & Grubbs, R. H. Utility of a ruthenium metathesis catalyst for the preparation of end-functionalized polybutadiene. *Macromolecules* **30,** 718-721 (1997).

[68] Morita, T., Maughon, B. R., Bielawski, C. W. & Grubbs, R. H. A ring-opening metathesis polymerization (ROMP) approach to carboxyl- and amino-terminated telechelic poly(butadiene)s. *Macromolecules* **33,** 6621-6623 (2000).

[69] Ji, S., Hoye, T. T. & Macosko, C. W. Controlled synthesis of high molecular weight telechelic polybutadienes by ring-opening metathesis polymerization *Macromolecules* ***37*****,** 5458-5489 (2004).

[70] Maughon, B. R., Morita, T., Bielawski, C. W. & Grubbs, R. H. Synthesis of cross-linkable telechelic poly(butenylene)s derived from ring-opening metathesis polymerization. *Macromolecules* **33,** 1929-1935 (2000).

[71] Scherman, O. A., Rutenberg, I. M. & Grubbs, R. H. Direct synthesis of soluble, end-functionaized polyenes and polyacetylene block copolymers. *J. Am. Chem. Soc.* **125,** 8515-8522 (2003).

[72] Xia, Y., Verduzco, R., Grubbs, R. H. & Kornfield, J. A. Well-defined liquid crystal gels from telechelic polymers. *J. Am. Chem. Soc.* **130,** 1735-1740 (2008).

[73] Matson, J. B., Virgil, S. C., & Grubbs, R. H. Pulsed-Addition Ring-Opening Metathesis Polymerization: Catalyst-Economical Syntheses of Homopolymers and Block Copolymers. *J. Am. Chem. Soc.* **Article ASAP** • DOI: 10.1021/ja809081h.

[74] Fraser, C., Hillmyer, M. A., Gutierrez, E. & Grubbs, R. H. Degradable cyclooctadiene/acetal copolymers: Versatile precursors to 1,4-hydroxytelechelic polybutadiene and hydroxytelechelic polyethylene. *Macromolecules* **28,** 7256-7261 (1995).

[75] Hilf, S., Berger-Nicoletti, E., Grubbs, R.H. & Kilbinger, A.F.M. Mono-functional metathesis polymers via sacrificial diblock copolymers. *Angew. Chem*. **118,** 8214-8217 (2006), *Angew. Chem. Int. Ed.* **45,** 8045-8048 (2006).

[76] Perrier, S. & Wang, X. Sacrificial synthesis. *Nature* **445,** 271 (2007).

[77] Hilf, S. & Kilbinger, A.F.M. An all-ROMP route to graft copolymers. *Macromol. Rapid Commun*. **28,** 1225-1230 (2007).

[78] Hilf, S., Hanik, N. & Kilbinger, A.F.M. A “click” approach to ROMP block copolymers. *J. Polym. Sci. A* **46,** 2913-2921 (2008).

[79] Hilf, S. & Kilbinger, A.F.M. Thiol functionalized ROMP polymers via sacrificial synthesis. *submitted.*

[80] Hilf, S., Grubbs, R.H. & Kilbinger, A.F.M Sacrificial synthesis of hydroxy-functionalized ROMP polymers: An efficiency study. *Macromolecules* **41,** 6006-6011 (2008).

[81] Hilf, S. & Kilbinger, A.F.M. Sacrificial synthesis of hydroxy-telechelic metathesis polymers via multiblock-copolymers. *Macromolecules* **42***, 1099-1106* (2009).

Chapter 2: Synthesis of Precisely Functionalized Metathesis Polymers.

2.1: Mono-functional Metathesis Polymers via Sacrificial diblock copolymers

Stefan Hilf, Elena Berger-Nicoletti, Robert H. Grubbs and Andreas F.M. Kilbinger

Published in: Angewandte Chemie International Edition **2006**, *45*, 8045-8048.

The ring opening olefin metathesis polymerization (ROMP) is a powerful tool for the synthesis of highly functionalized polymers. [1] The first well-defined catalyst systems based on titanium,[2] molybdenum and tungsten[3] exhibited relatively low functional group tolerance. This could be exploited in the end-functionalization of metathesis polymers. The high oxophilicity of the metal centers allowed end-functionalization via addition of aldehydes to the polymerization mixture.[4] Late transition metal catalysts based on ruthenium[5] do not allow for olefin metathesis functionalization with aldehydes. Nonetheless, several pathways have been described in the literature for the end-functionalization of ruthenium catalyzed metathesis polymers.

The most common method of terminating a ruthenium carbene at the chain end of a polymer is achieved by adding ethyl vinyl ether.[6] A methylene group is transferred onto the polymer while cleaving the catalyst off the polymer chain end at the same time. It could be shown that the cleaved-off Fischer-type carbene can undergo further olefin metathesis reactions under certain conditions.[7] For most polymer synthetic applications, however, it can be regarded as inactive. In the presence of vinyl sulfides it could be shown that such "Fischer-carbenes" react as chain transfer agents yielding mono-functional polymers.[8] The polymers prepared in this way show broad polydispersity indices (PDI between 1.3 and 3).

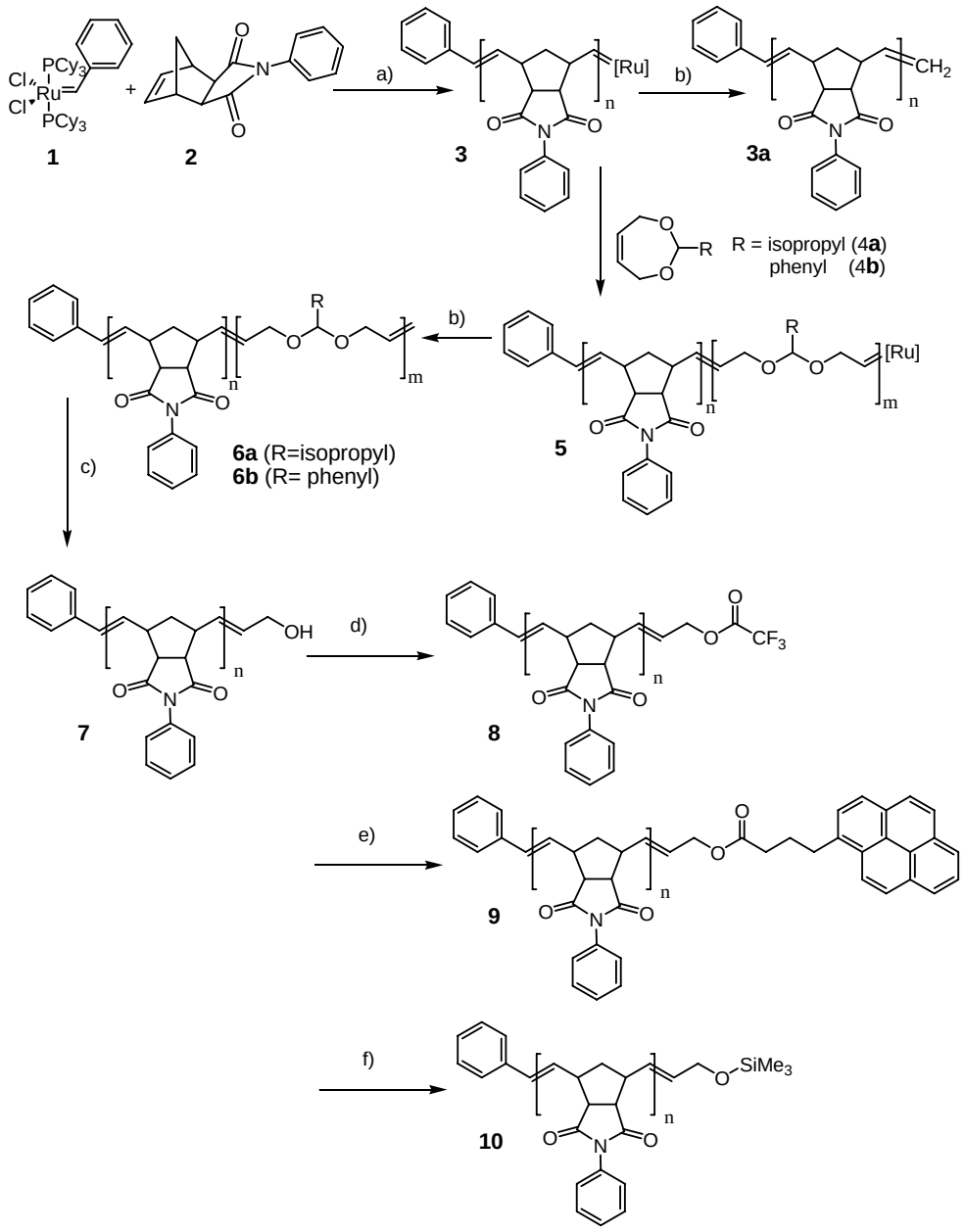
Substituted methyl vinyl ethers have also been used for the termination of living metathesis polymers.[9] In this way, a variety of functional groups could be transferred to the polymer chain end.

Gibson reported an end-capping reaction whereby the polymerization reaction mixture was exposed to an oxygen atmosphere which resulted in an aldehyde end-group after a reaction time of 24 h.[10] A further method describes the stoichiometric addition of one equivalent of functional monomer to the catalyst thereby turning the catalyst into a mono-functional initiator. [11]

The end-functionalization reactions described above suffer from several drawbacks. They typically take several hours to complete in which the metathesis active catalytic species can undergo further polymerization or secondary metathesis reactions. These end-capping methods can therefore not be employed in the presence of residual monomer without significant broadening of the molecular weight distribution. Even in the absence of residual monomer, long reaction times for the termination reaction can lead to molecular weight broadening due to chain transfer reactions to the polymer (back-biting), a fact that is exploited in the equilibration of telechelics.[12] True mono-functionality is also not guaranteed rigorously by some of the above examples. It is important to stress that the presence of exactly one functional group at the chain end is essential for many applications such as the synthesis of block copolymers, the synthesis of conjugates with biomacromolecules like proteins, polysaccharides or polynucleotides or the functionalization of surfaces and nano-particles. Today, many of these applications employ mono-functional polymers prepared by anionic polymerization.

Here we describe the mono-end-functionalization of ruthenium catalyzed metathesis polymers which can be carried out in the presence of residual monomer, yields narrow molecular weight distributions and allows the presence of functional groups in the monomer structure.

In order to prove our synthetic concept, we chose exo-*N*-phenyl-norbornene-2,3-dicarboximide (PNI) as the monomer as it can be polymerized in a living fashion.[13] PNI was initiated with catalyst **1** (Scheme 1) and polymerized to only 60% conversion.



Scheme 1. Synthesis of sacrificial diblock copolymers. a) PPh_3, dichloromethane, rt b) ethyl vinyl ether c) 6N HCl, methanol, dichloromethane d) trifluoroacetic anhydride, e) pyrenebutyroyl chloride f) trimethylsilyl chloride

Polymerization to low monomer conversion allowed us to evaluate the influence of residual monomer on the polydispersity of the mono-functional polymer. An analytical sample was taken and quenched with ethyl vinyl ether (**3a**). Next, a large excess of dioxepine monomer **4a** or **4b** was introduced to the reaction mixture which resulted in the formation of a diblock copolymer which was quenched with excess of ethyl vinyl ether.

Figure 1 shows GPC traces of the first block **3a** and diblock **6a** which clearly show that the living chain end of **3** was an effective initiator for the second monomer **4a**. As the first monomer had only been consumed to about 60%, the second block was most likely a statistical mixture of monomers **2** and **4a.**

Polymerization of **2** to higher conversions (i.e. 60-90%) before addition of the second monomer was also successful. Molecular weight control of the first polymer block is therefore possible by either varying the reaction time before adding the second monomer or via the monomer:catalyst ratio. After isolation and purification, the block copolymer was dissolved in a methanol/DCM/HCl mixture in order to cleave the acetal groups of the second block.[14] As can be seen in Scheme 1, cleavage of the acetal groups decomposes the second polymer block but leaves half a monomer unit of **4a** attached to the first block via a C-C-double bond.

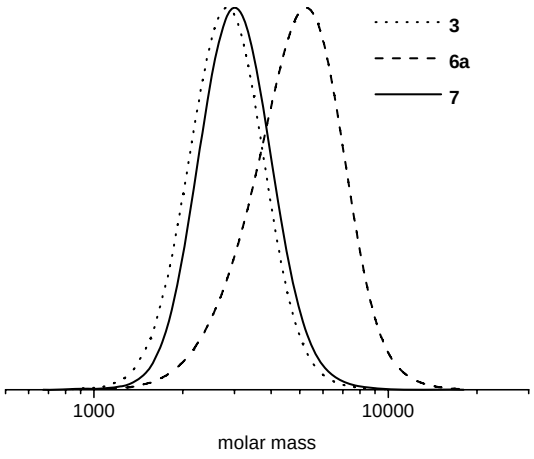


Figure 1. GPC traces (THF, PS calibration) showing the first polymer block of monomer **2** (polymer **3a**, dotted line), the diblock copolymer of monomers **2** and **4a** (polymer **6a**, dashed line) and mono-functional polymer **7**.

GPC analysis revealed that the molecular weight of the first block (**3a**, Figure 1) and mono-functional polymer (**7**, Figure 1) are almost identical. Additionally, the polydispersity indices for polymers **3a** and **7** (Figure 1) are identical and very narrow (PDI = 1.1). The presence of residual monomer (**2)** which can lead to severe molecular weight broadening in many of the previously reported end-capping procedures was shown not to have any effect on the polydispersity of the mono-functional polymer prepared here.

The same experiment was carried out with the dioxepine monomer **4b**. The GPC trace of diblock copolymer **6b** was also shifted towards higher molecular weights compared to that of **3a** indicating good re-initiation from the first to the second block (see supporting information). The mono-functional polymer **7** prepared via acidic cleavage of the poly-acetal block of **4b** shows a virtually identical molecular weight and polydispersity index (PDI=1.1) as the first block. It is important to stress at this point that the propagation rate of the dioxepine monomer is of no importance for successful end-functionalization of the first polymer block. As the second polymer block is eventually sacrificed, only the re-initiation of the first polymer block to the first unit of the dioxepine monomer is crucial. This incorporation of the first unit of the dioxepine monomer represents a breaking-point, the junction between the end-functionalized and sacrificed polymer block.

To obtain proof for the presence of a hydroxy functionality at the polymer chain end, polymer **7** (from 6a) was reacted with pyrenebutyroyl chloride to give the corresponding ester **9**. A GPC experiment with UV-detection at $\nu = 340$ nm (which is characteristic for pyrene butyric acid derivatives) showed a signal for the pyrene functionalized polymer (**9**) while hydroxyl-functionalized polymer **7** shows no absorption at the chosen wavelength (see supporting information).

This shows that the pyrene group was covalently attached to the polymer chain. The ^{1}H-NMR spectrum of polymer **7** reveals a singlet at $\delta = 4.14$ ppm which was attributed to the methylene group next to the hydroxy functionality (Figure 2 bottom). Addition of trifluoroacetic anhydride to the NMR-tube resulted in a shift of the peak to $\delta = 4.82$ ppm which is in agreement with the described assignment (Figure 2 top).

Additionally, the olefinic protons of the styrene-like initiator group can be observed in the ^{1}H-NMR spectrum of **7** (Figure 2, H2, $\delta = 6.33$ and H1, $\delta = 6.60$ ppm). Comparing the integrals of the olefinic protons at $\delta = 6.33$ and 6.60 ppm with the integral at $\delta = 4.7$ ppm reveals that end-functionalization >97% had occurred.

In the ^{1}H-NMR spectrum of the trifluoroacetate functionalized polymer (Figure 2 top), the terminal olefinic protons are separated from other olefinic peaks in the spectrum (H3, $\delta = 6.04$ ppm) and can also be used for end-group analysis.

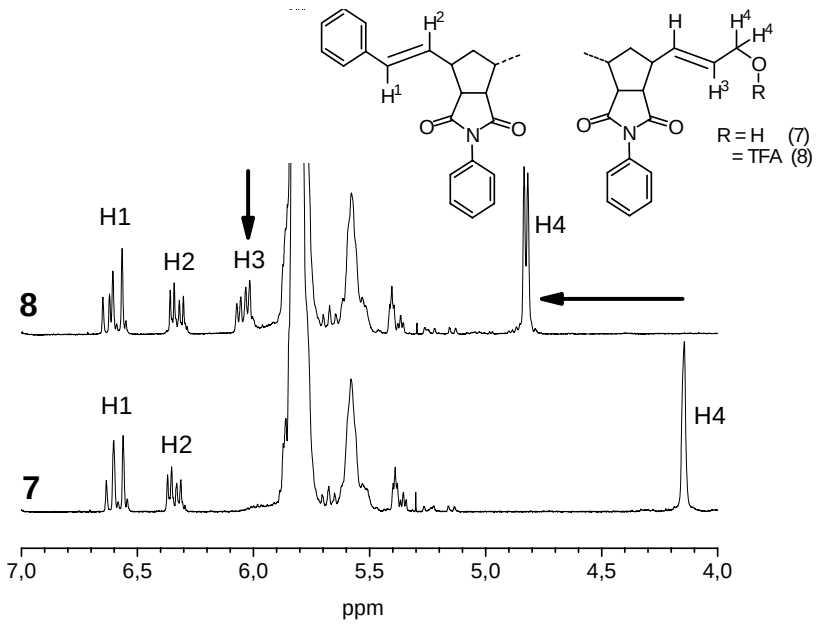


Figure 2. ^{1}H-NMR spectroscopic end-group analysis of polymers **8** (top) and **7** (bottom). The insets show the two end-groups of the polymer chain.

Reaction of polymer **7** with trimethylsilyl chloride gave the silyl-end-functionalized polymer **10**. ^{1}H-NMR analysis revealed the methyl-end groups at $\delta = 0.17$ ppm (see supporting information). Polymers **3a** and **7** were analyzed by MALDI-TOF mass spectroscopy (**7** from **6a** see Figure 3, **7** from **6b** see supporting information). The mass distribution of polymer 7 is shifted by m/z=30.09 compared to that of polymer 3 (the exact mass of CH_2O is 30.01 g mol^{-1}). This corresponds to the mass difference between the ethyl vinyl ether end-capped polymer **3a** and the hydroxy functionalized polymer **7**.

The mass distribution for polymer **7** provides no evidence for a second monomer distribution due to residual dioxepine monomer. However, a very small mass distribution due to unfunctionalized polymer **3** (which is structurally identical to **3a**) can be seen in the mass spectrum of **7** (Figure 3).

The functionalization of **7** with trimethylsilyl chloride to give the silyl protected alcohol was also successful and was confirmed by MALDI-TOF mass spectroscopy (see supporting information).

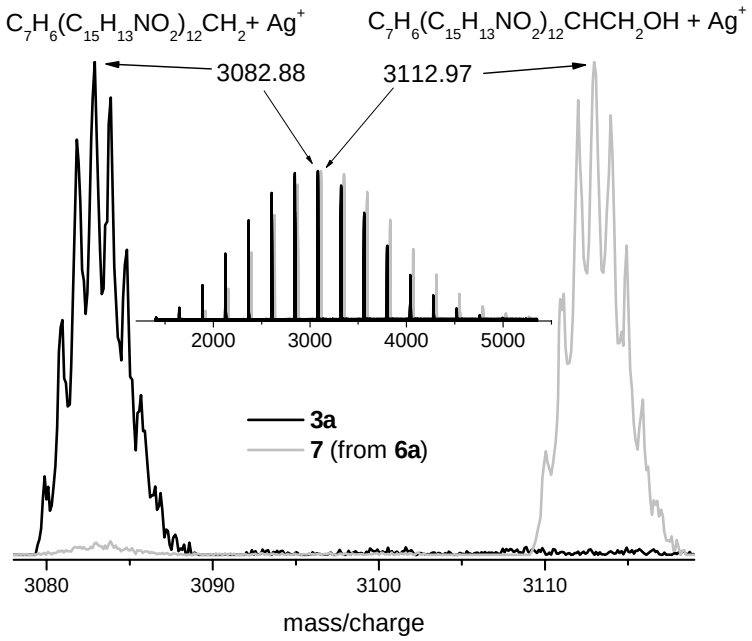


Figure 3. MALDI-TOF mass spectra of **3a** and **7** (from **6a**) showing isotopically resolved mass peaks of polymer **3a** and **7**. Inset: complete mass distribution.

In conclusion, we have presented a route to mono-hydroxy functionalized olefin metathesis polymers. This route allows the preparation of narrowly distributed polymers with commercially available ruthenium catalysts. Exo-*N*-phenyl-norbornene-2,3-dicarboximide was polymerized to the desired molecular weight and subsequently turned into a diblock copolymer by adding a cyclic olefinic acetal as second monomer. The second polymer block was decomposed under acidic conditions leaving exactly one hydroxyl group at the end of the initial polymer block.

We believe that this route to mono-functional ring opening metathesis polymers presents a viable and less laborious alternative to carbanionic polymerization. Mono-end-functional polymers with narrow polydispersity carrying functional groups along the polymer chain will allow numerous new applications in fields that previously relied on mono-functional carbanionic polymers.

Experimental Section

General procedure for the synthesis of blockcopolymers

Triphenylphosphine (6.3 eq) and **2** were sealed in a Schlenk-flask and evacuated and flooded with nitrogen (2x). Dichloromethane (ca. 10 mL per gram of monomer) was then added via canula transfer. Polymerization was initiated by quickly adding a solution of the appropriate amount of catalyst **1** in dichloromethane (ca. 1 mL per 100 mg of **1**) via syringe to the stirred solution. Reaction times were dependent on the desired molecular weight of the polymer (ca. 7h for 3000 g/mol, ca 13h for 5000 g/mol, ca 24h for 10000 g/mol, all reactions were carried out at rt). Upon completion of the reaction time, the cyclic olefinic acetal was added to the mixture (1 mL of **4a** or **4b** per gram of polymer) and allowed to react for another 10h. The reaction was quenched with 1 mL ethyl vinyl ether. The product was precipitated into methanol, dissolved in chloroform and re-precipitated into methanol. The block copolymer was dried to yield 70-80% of a brown solid.

General procedure for cleaving of the second block

To a solution of the block copolymer (1 g) in dichloromethane (10 mL) was added HCl (6M, 4 mL) and methanol (2 mL). The mixture was stirred for 12h at rt followed by precipitation into methanol. The solid was recovered, dissolved in chloroform and re-precipitated into methanol. The polymer was dried under vacuum to give a white solid (850mg, ca. 80%, depending on block ratios).

Detailed experimental procedures are described in the Supporting Information.

References:

[1] Frenzel, U.; Nuyken, O. *J. Polym. Sci. A* **2002**, *40*, 2895. Slugovc, C. *Macromol. Rapid. Commun*. **2004**, *25*, 1283.

[2] Gilliom, L.R.; Grubbs, R.H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

[3] O'Donoghue, M.B.; Schrock, R.R.; LaPointe, A.M.; Davis, W.M. *Organometallics*, **1996**, *15*, 1334. Murdzek, J.S.; Schrock, R.R. Macromolecules 1987, 20, 2640. Schrock, R.R.; Murdzek, J.S.; Bazan, G.C.; Robbins. J.; DiMare, M.; O'Regan.M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

[4] Brown-Wensley, K.A.; Buchwald, S.L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J.R.; Straus, D.; Grubbs, R.H. *Pure Appl Chem*. **1983**, *55*, 1733; Albagli, D.; Bazan, G.C.; Schrock, R.R.; Wrighton, M.S. *J. Phys. Chem*. **1993**, *97*, 10211. Albagle, D.; Bazan, G.C.; Schrock, R.R.; Wrighton, M.S. *J. Am. Chem. Soc*. **1993**, *115*, 7328. Nomura, K.; Takahashi, S.; Imanishi, Y. *Macromolecules* **2001**, *34*, 4712.

[5] Nguyen, S.T.; Johnson, L.K.; Grubbs, R.H. *J. Am. Chem. Soc*. **1992**, *114*, 3974. Nguyen, S.T.; Grubbs, R.H. *J. Am. Chem. Soc*. **1993**, *115*, 9858. Schwab, P.; Grubbs, R.H.; Ziller, J.W. *J. Am. Chem. Soc*. **1996**, *118*, 100. Chatterjee, A.K.; Morgan, J.P.; Scholl, M.; Grubbs, R.H. *J. Am. Chem. Soc*. **2000**, *122* ,3783. Scholl, M.; Ding, S.; Lee, C.W.; Grubbs, R.H. *Org. Lett*. **1999**, *1*, 953. Huang, J.; Stevens, E.D.; Nolan, S.P.; Peterson, J.L. *J. Am. Chem. Soc*. **1999**, *121*, 2674. Weskamp, T.; Kohl, F.J.; Hieringer, W.; Gleich, D.; Herrmann, W.A. *Angew. Chem. Int. Ed. Engl*. **1999**, *38*, 2416. Herrmann, W.A. *Angew. Chem. Int. Ed. Engl*. **2002**, *41*, 1291.

[6] Maynard, H.D.; Grubbs, R.H. *Macromolecules* **1999**, *32*, 6917. Weck, M.; Mohr, B.; Maughon, B.R.; Grubbs, R.H. *Macromolecules* **1997**, *30*, 6430.

[7] Katayama, H.; Urushima, H.; Ozawa, F. *Chem. Lett*. **1999**, 269. Katayama, H. Urushima, H.; Nishioka, T.; Wada, C.; Nagao, M.; Ozawa, F. *Angew. Chem. Int. Ed. Engl*. **2000**, *39,* 4513. van der Schaaf, P.A.; Kolly, R.; Kirner, H.-J.; Rime, F.; Mühlebach, A.; Hafner, A. *J. Organomet. Chem*. **2000**, *606*, 65. Louie, J.; Grubbs, R.H. *Organometallics*, **2002**, *21*, 2153.

[8] Katayama, H.; Urushima, H.; Ozawa, F. *J. Organomet. Chem*. **2000**, *606*, 16

[9] Owen, R.M.; Gestwicki, J.E.; Young, T.; Kiessling, L.L. *Org. Lett*. **2002**, *4*, 2293. Gestwicki, J.E.; Cairo, C.W.; Mann, D.A.; Owen, R.M.;Kiessling, L.L. *Anal. Biochem*. **2002**, *305*, 149. Gordon, E.J.; Gestwicki, J.E.; Strong, L.E.; Kiessling, L.K. *Chemistry and Biology*, **2000**, *7*, 9. Chen, B.; Sleiman, H.F. *Macromolecules* **2005**, *38*, 1084.

[10] Biagini, S.C.G.; Davie, R.G.; Gibson, V.C.; Giles, M.R.; Marshall, E.L.; North, M. *Polymer* **2001**, *42*, 6669.

[11] Roberts, K.S.; Sampson, N.S. *Org. Lett*. **2004**, *6*, 3253.

[12] Morita, T.; Maughon, B.R.; Bielawski, C.W.; Grubbs, R.H. *Macromolecules* **2000**, *33*, 6621.

[13] Bielawski,C.W., Grubbs, R.H. *Macromolecules* **2001**, *34*, 8838.

[14] Fraser, C.; Hillmyer, M.A.; Gutierrez, E.; Grubbs, R.H. *Macromolecules* **1995**, *28*, 7256.

Supporting Information for: Mono-functional metathesis polymers via sacrificial diblock copolymers

Experimental Section

General: Technical grade solvents were purchased from Acros Organics, those of analytical quality (p. a. grade) were purchased from Fisher Scientific. Dichloromethane was freshly distilled from P_4O_{10} and CaH_2 followed by two freeze-thaw cycles. Deuterated solvents were purchased from Deutero GmbH. Other reagents were purchased either from Acros Organics or Aldrich and used without further purification.

^{1}H-NMR spectra were recorded at 300 or 400 MHz on a Bruker AC 300 or AMX 400 and were referenced internally to residual proton signals of the deuterated solvent.

^{19}F-NMR-spectra were recorded at 276.47 MHz, ^{29}Si-NMR spectra (referenced externally to TMS) at 79.49 MHz on a Bruker DRX 400.

Gel permeation chromatography in chloroform was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P 100 pump and a set of three PSS SDV columns (10^4/500/50 Å). Signal detection occurred by use of a TSP Spectra System UV 2000 (UV 254 nm unless otherwise stated) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service.

Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) measurements were performed on a Shimadzu Axima CFR MALDI-TOF mass spectrometer equipped with a nitrogen laser delivering 3ns laser pulses at 337nm. Dithranol (1,8,9- trihydroxy-anthracene) was used as matrix. Samples were prepared by dissolving the polymer in $CHCl_3$ at a concentration of 10g/L. A 10µL aliquot of this solution was added to 10µL of a 10g/L solution of the matrix and 1µL of a solution of AgTFA (0.1M in methanol as cationization agent). A 1µL aliquot of the mixture was applied to a multistage target to evaporate $CHCl_3$ and create a thin matrix/analyte film. The samples were measured in positive ion and in linear or reflection mode of the spectrometer.

Polymerizations and polymer derivatizations were carried out under nitrogen using Schlenk techniques.

Field desorption mass spectra were measured on a Finnigan MAT 95

Exo-norbornene-2,3-dicarboxanhydride was synthesized as described by Craig et al.; *J. Am. Chem. Soc.*, **1951**, *73*, 4889-4892. Catalyst **1** was purchased from Aldrich.

Exo-*N*-phenyl-norbornene-2,3-dicarboximide (2)

A mixture of exo-norbornene-2,3-dicarboxanhydride (17g, 0.104mol) and aniline (10 mL, 10.02 g; 0.108mol) was heated to 190°C for 2h. The mixture was allowed to cool to rt. Further water was removed in a Dean-Stark apparatus using toluene (75 mL) as azeotrop until a clear solution was obtained. The product was then recrystallized from toluene (2x) to give colorless crystals (17.2g, 0.072mol, 69.2%).

FD-MS (m/z): 239.2, calc: 239.094. ^{1}H-NMR (300MHz, $CDCl_3$) δ[ppm]: 1.55 (dd, 2H, CH_2-bridge; ^{2}J=37.8Hz, ^{3}J=9.9Hz); 2.85 (s, 2H, C_3CH); 3.40 (s, 2H, C(O)CH); 6.34 (s, 2H, C=CH); 7.2-7.3 (m, 2H, o-Ph); 7,3-7,5 (m, 3H, m,p-Ph).

2-Isopropyl-4,7-dihydro-[1,3]-dioxepine (4a)

Isobutyric aldehyde (72g; 90mL; 1mol) was refluxed with 1,4-butenol (88 g; 80 mL; 1 mol) and p-toluenesulfonic acid monohydrate (1.5 g) in hexane (200 mL). All water was removed in a Dean-Stark apparatus. When one equivalent of water had been removed, the mixture was allowed to cool, was washed twice with dilute NaOH and once with water, dried with anhydrous $MgSO_4$ followed by removal of solvent.

The crude product was then distilled (80°C, 36 mbar) to give 97.8 g (63%) of a colorless liquid.

^{1}H-NMR (300MHz, $CDCl_3$) δ[ppm]: 0.82 (d, 2H, CH_3); 1.75 (hept, 1H, CH, ^{3}J=6.5Hz); 4.0-4.3 (m, 5H, allyl-H, acetal-H); 5.58 (s, 2H, HC=CH). FD-MS (m/z): 143.0 (142.10 calc.).

2-Phenyl-4,7-dihydro-[1,3]-dioxepine (4b)

Benzaldehyde (53 g; 47 mL; 0.5 mol) was refluxed with 1,4-butenol (44 g; 40 mL; 0.5 mol) and p-toluenesulfonic acid monohydrate (0.75 g) in toluene (150 mL). All water was removed in a Dean-Stark apparatus. When one equivalent of water had been produced, the mixture was allowed to cool, was washed twice with dilute NaOH and once with water, dried with anhydrous $MgSO_4$ followed by removal of solvent.

The crude product was then distilled twice (20 cm vigreux coloumn) (67°C, 0.1 mbar) to give 21.4 g (24.3%) of a colorless liquid.

^{1}H-NMR (300MHz, $CDCl_3$) δ[ppm]: 4.37 (m, 4H, allyl-H); 5.80 (s, 2H, HC=CH); 5.90 (s, 1H, acetal-H); 7.4 (m, 3H, m,p-Ph); 7.59 (m, 2H, o-Ph). FD-MS (m/z): 176.0 (176.08 calc.).

General procedure for the synthesis of block-copolymers (6a, 6b)

Triphenylphosphine (6.3 eq) and 2 were sealed in a Schlenk-flask and evacuated and flooded with nitrogen (2x). Dichloromethane (ca. 10 mL per gram of monomer) was then added via canula transfer. Polymerization was initiated by quickly adding a solution of the appropriate amount of catalyst 1 in dichloromethane (ca. 1 mL per 100 mg of 1) via syringe to the stirred solution. Reaction times were dependent on the desired molecular weight of the polymer (ca. 7h for 3000 g/mol, ca 13h for 5000 g/mol, ca 24h for 10000 g/mol, all reactions were carried out at rt). Upon completion of the reaction time, the cyclic olefinic acetal was added to the mixture (1 mL of 4a or 4b per gram of polymer) and allowed to react for another 10h. The reaction was quenched with 1 mL ethyl vinyl ether. The product was precipitated into methanol, dissolved in chloroform and re-precipitated into methanol. The block copolymer was dried to yield 70-80% of a brown solid.

Isopropyl-acetal as second block (6a):

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 0.9-1,0 (m, 9H, iPr); 1.5-1.8, 2.1-2.3 (m, 2H, CH_2-brigde); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, C(O)CH); 3.9-4.3 (m, 5H, acetal-H, C=C-CH2 acetal block); 5.5-5.9 (m, 2H, double bonds polymer); 6.3-6.4 (m, 1H, double bond CH_2-OH end);

6.5-6.7 (m, 1H, double bond Ph end); 7.2-7.6 (m, 5H, Ph). GPC 1st block (THF): Mn=2570; Mw=2820; PDI=1,10 (UV); Mn=2680; Mw=2940; PDI=1.10 (RI); blockcopolymer (THF): Mn=4280; Mw=4960; PDI=1.16 (UV); Mn=4520; Mw=5170; PDI=1.14 (RI).

Phenyl-acetal as second block (6b):

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2-brigde); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, C(O)CH); 4.2-4,5 (m, 4H, C=C-CH2 acetal block); 5.5-5.9 (m, 2H, double bonds polymer, acetal-H in acetal block); 6.3-6.4 (m, 1H, double bond CH_2-OH end); 6.5-6.7 (m, 1H, double bond Ph end); 7.2-7.5 (m, 5H, Ph, Ph in acetal block) . GPC 1st block (THF): Mn=2680; Mw=2950; PDI=1.10 (UV); Mn=2800; Mw=3070; PDI=1.10 (RI); blockcopolymer (THF): Mn=3890; Mw=4470; PDI=1.15 (UV); Mn=4040; Mw=4630; PDI=1.15 (RI).

General Procedure for cleaving the second block (7)

To a solution of the block copolymer (1 g) in dichloromethane (10 mL) was added HCl (4mL, 6M) and methanol (2mL). The mixture was stirred for 12h at rt followed by precipitation into methanol. The solid was recovered, dissolved in chloroform and re-precipitated into methanol. The polymer was dried under vacuum to give a white solid (850mg, ca. 80%)

^{1}H-NMR (400MHz, $CDCl_3$) d [ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2-brigde); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, C(O)CH); 4.16 (m, 2H, CH_2-O endgroup); 5.5-5.9 (m, 2H, double bonds polymer); 6.3-6.4 (m, 1H, double bond CH_2-OH end); 6.5-6.7 (m, 1H, double bond Ph end); 7.2-7.6 (m, 5H, Ph). GPC (from Isopropyl-acetal) (THF): Mn=2810; Mw=3070; PDI=1.10 (UV); Mn=2900; Mw=3170; PDI=1.10 (RI); GPC (from Phenyl-acetal) (THF): Mn=2940; Mw=3260; PDI=1.11 (UV); Mn=3030; Mw=3370; PDI=1.11 (RI).

Further GPC-results (Chloroform):

entry	Mn (UV)	Mw (UV)	PDI (UV)	Mn (RI)	Mw (RI)	PDI (RI)
1	1790	2010	1.12	1870	2110	1.12
2	2590	2920	1.13	2700	3040	1.13
3	4220	4750	1.12	4380	4900	1.12
4	5170	5910	1.14	5410	6140	1.13
5	5600	6510	1.16	5790	6740	1.16
6	9540	10260	1.08	9670	10370	1.07

Esterification of mono hydroxy-functional polymer with trifluoroacetic anhydride (8)

To a solution of 20 mg of OH-functional PNI in 1 mL dichloromethane-d_2 in an NMR-tube was added 50 µL trifluoroacetic anhydride. The mixture was allowed to stand for 20 minutes, then NMR spectra were taken.

^{1}H-NMR: shifted signals to OH-functional PNI: 4,82 (m, CH_2-O end-group). ^{19}F-NMR (376.47MHz $CDCl_3$) d[ppm]: -75.66.

Esterification of mono hydroxy-functional polymer with pyrenebutyric acid (9)

20 mg of pyrenebutyric acid were added 1 mL oxalyl chloride, 2 mL dry THF and were stirred over night. Then all liquids were evaporated in vacuo and 2mL dry dichloromethane, a solution of 20 mg OH-functionalized PNI in 3mL dichloromethane was added dropwise to the stirred mixture. After 3h 300 µL triethylamine were added. After one night the mixture was added excess methanol and the resulting polymer was re-precipitated from chloroform. In order to further purify the resulting polymer material from side products originating from the excess of pyrenebutyric acid, a preparative GPC was run.

GPC (Chloroform, UV: n=340 nm): Mn=3670; Mw=4090; PDI=1.12 (UV); Mn=3390; Mw=3840; PDI=1.13 (RI)

Reaction of mono hydroxy-functional polymer with TMS-Cl (10)

To a solution of 100mg of OH-functional PNI in 5mL dichloromethane was added 300 µL trimethylsilyl chloride and 300 µL triethylamine. The mixture was stirred over night, then precipitated into methanol and dried under vacuum to give 91 mg (91%) of a white solid.

^{1}H-NMR: additional signals to OH-functional PNI: 0.17 (s, 9H, $SiMe_3$-endgroup). ^{29}Si-NMR (79.49MHz $CDCl_3$) δ[ppm]: 18.25. GPC (Chloroform): Mn=3690; Mw=3950; PDI=1,070 (UV); Mn=3760; Mw=4030; PDI=1.07 (RI)

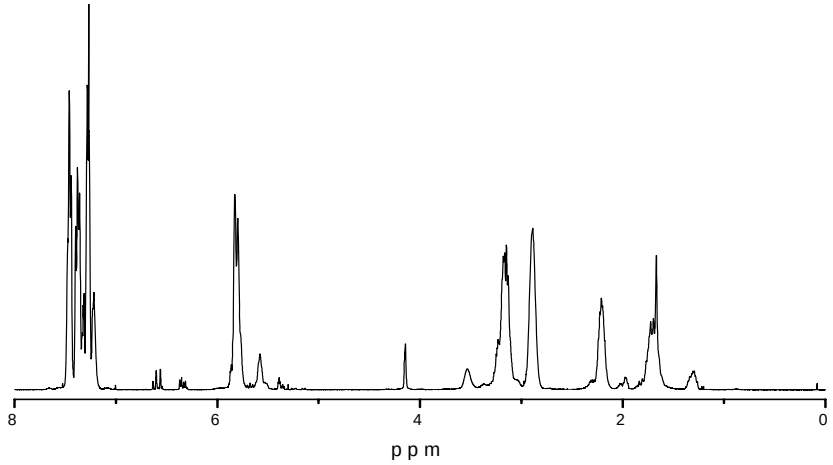


Figure SI-1 ^{1}H-NMR spectrum of **7**.

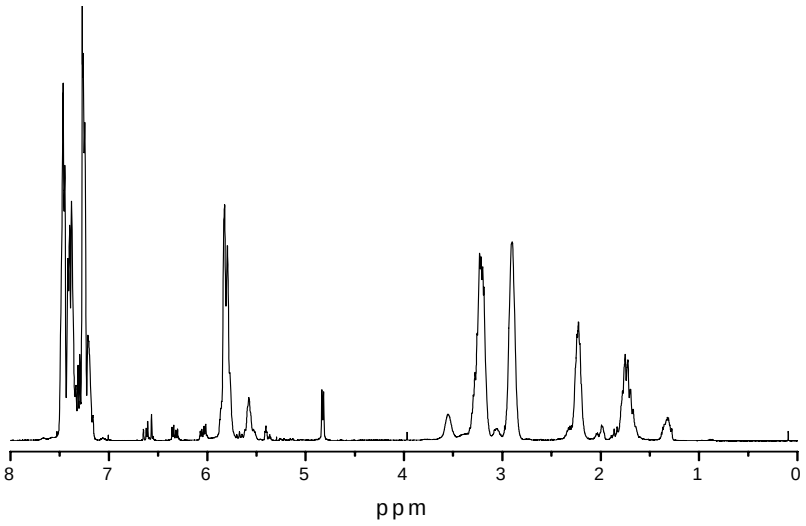


Figure SI-2 ^{1}H-NMR spectrum of **8**.

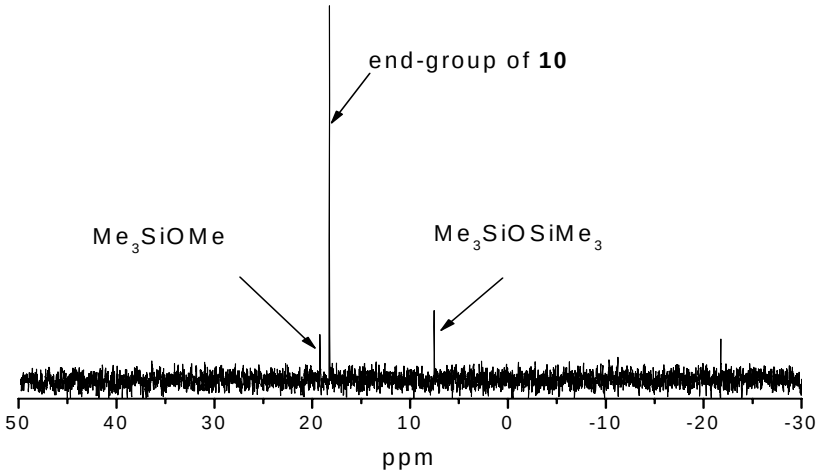


Figure SI-3 ^{29}Si-NMR spectrum of **10**.

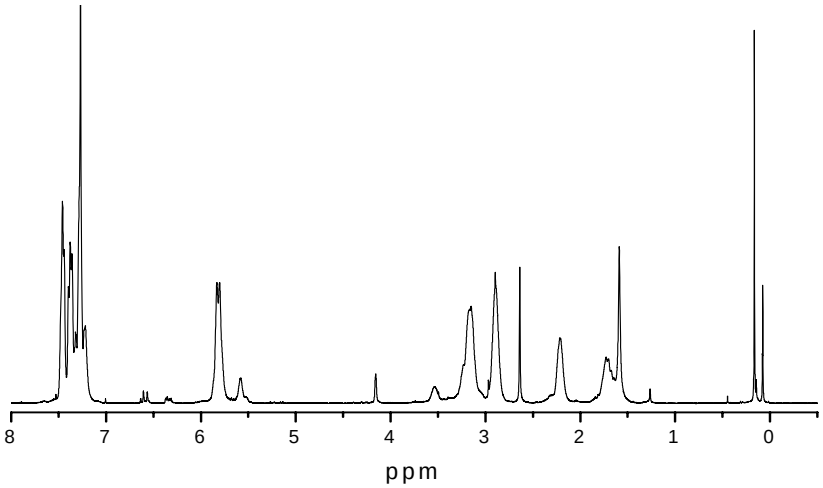


Figure SI-4 ^{1}H-NMR spectrum of **10**.

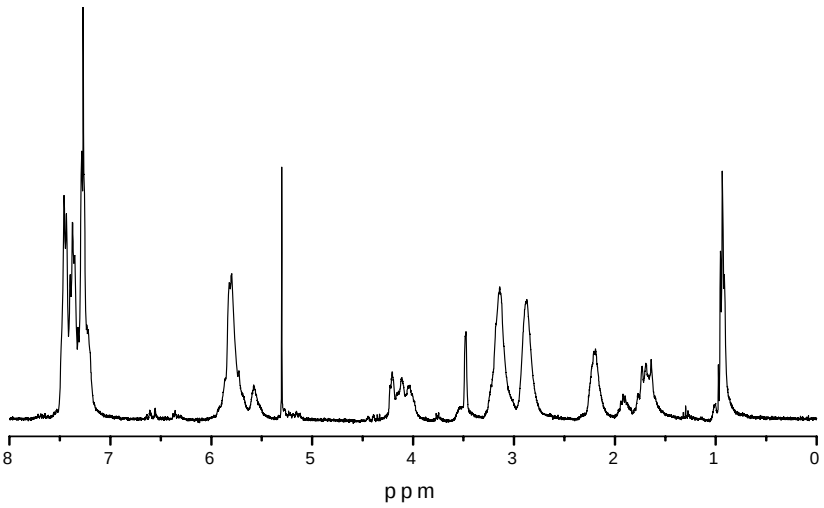


Figure SI-5 ^{1}H-NMR spectrum of **5** (from **4a**).

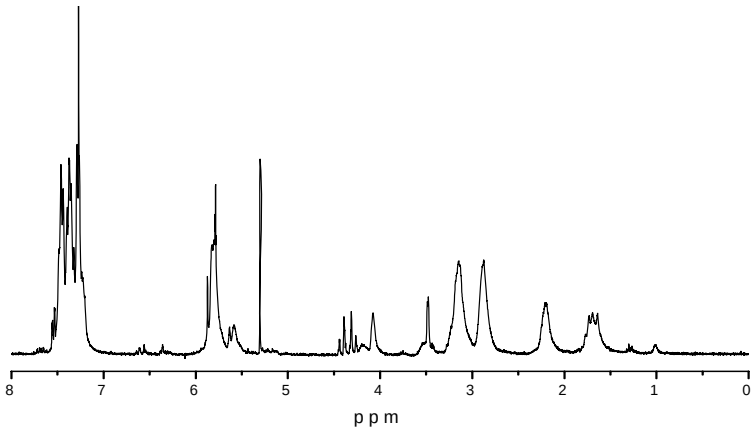


Figure SI-6 ^{1}H-NMR spectrum of **5** (from **4b**).

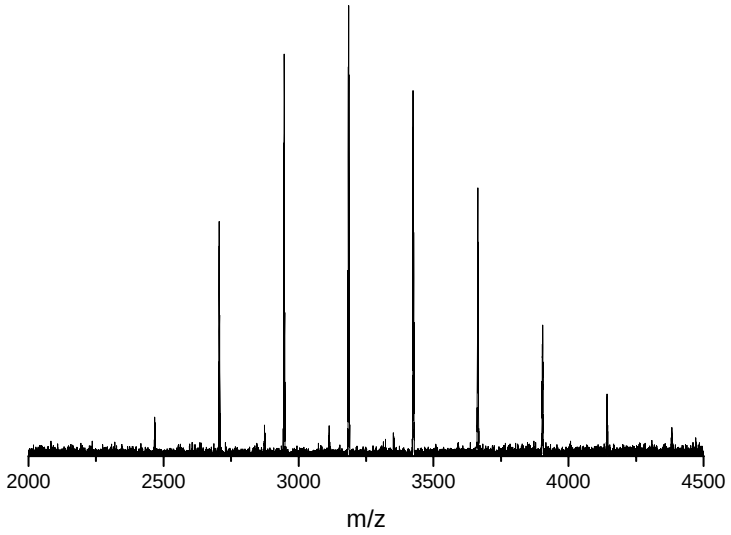


Figure SI-7 MALDI-ToF mass spectrum of **10**.

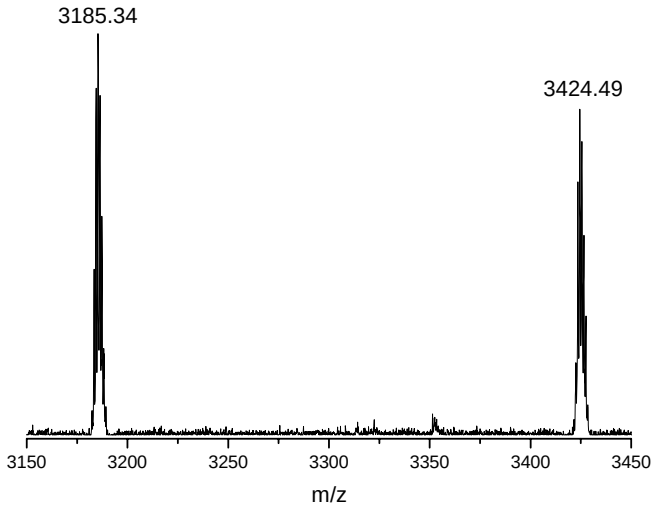


Figure SI-8 MALDI-ToF mass spectrum of **10**.

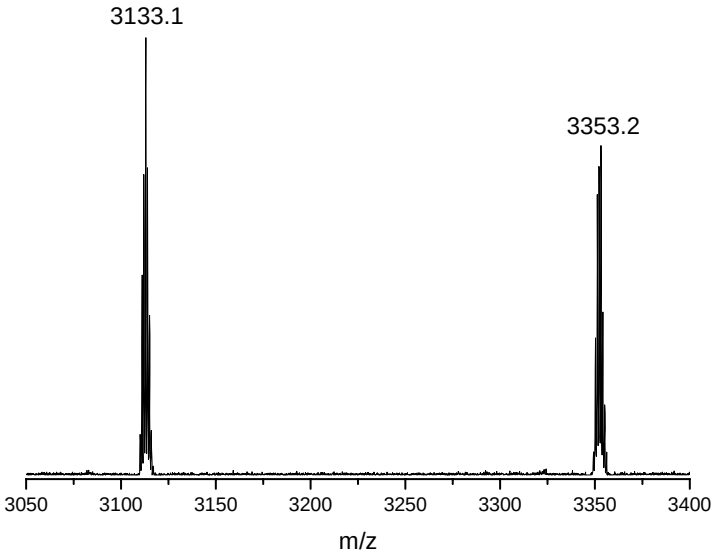


Figure SI-9 MALDI-ToF mass spectrum of **7** (from **6b**).

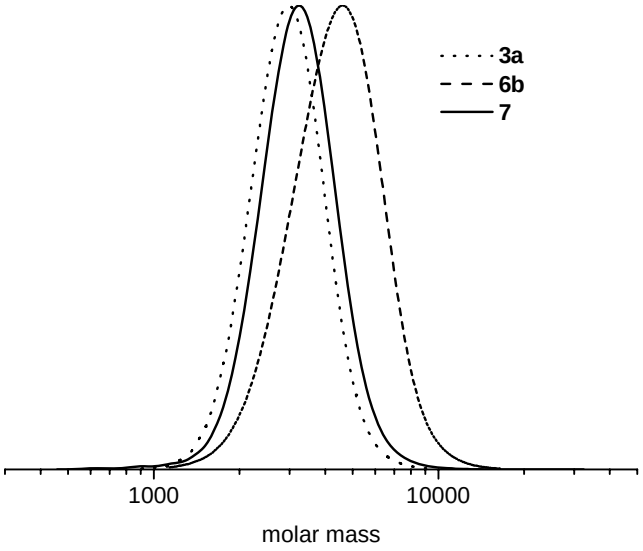


Figure SI-10 GPC traces (THF, PS calibration) showing the first polymer block of monomer **2** (polymer **3a**, dotted line), the diblock copolymer of monomers **2** and **4b**(polymer **6b**, dashed line) and mono-functional polymer **7**.

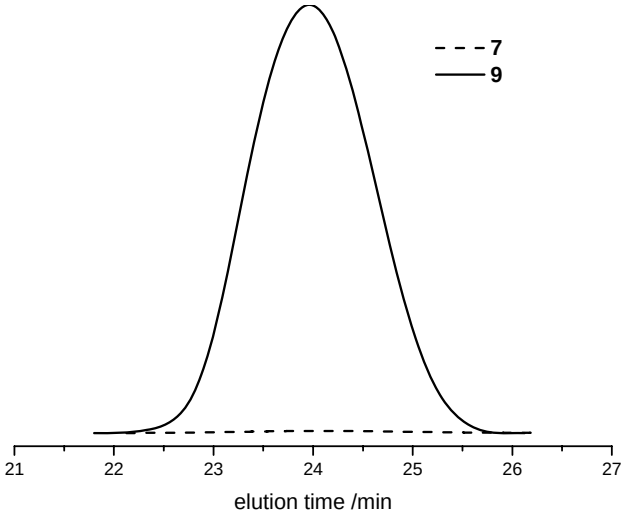


Figure SI-11 GPC traces ($CHCl_3$)of hydroxy terminated polymer **7** and pyrene functionalized polymer **9** with UV detection at d = 340 nm.

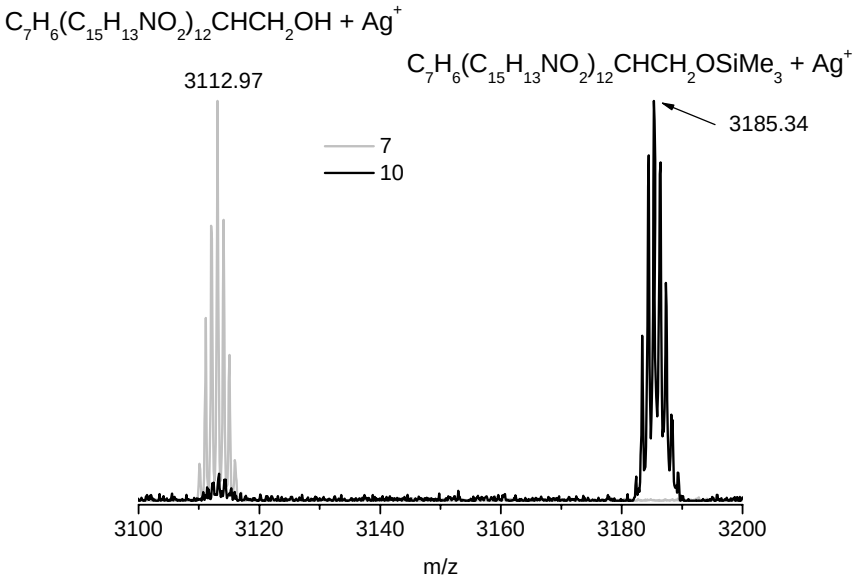


Figure SI-12 two isotopically resolved mass peaks from the MALDI-TOF mass spectra of **7** and **10** (from **6a**)

2.2: Sacrificial Synthesis of Hydroxy-Functionalized ROMP Polymers – An Efficiency Study

Stefan Hilf, Robert H. Grubbs and Andreas F.M. Kilbinger

Published in: Macromolecules **2008**, *41*, 6006-6011.

Abstract

We present here a ^{1}H NMR spectroscopy study of the kinetics of the ROMP macroinitiation of poly(*exo*-*N*-phenyl-2,3-norbornene dicarboximide) with various dioxepine derivatives and Grubbs first generation ruthenium initiators. We have recently demonstrated that this so-called "sacrificial block copolymer" approach yields hydroxy functionalized ROMP polymers with high end-group functionality. This study shows that the substituents on the dioxepine are important for functionalization efficiency, in the order phenyl > isopropyl > methyl. Addition of triphenylphosphine to the ruthenium carbene initiator resulted in lower ki/kp (rate of initiation / rate of propagation) values for the macroinitiation than in the absence of triphenylphosphine. We demonstrate that the value of k_i/k_p for macroinitiations can be estimated for new sacrificial monomers by analyzing one or two functionalization reactions. This provides an easy tool for the rapid screening and evaluation of new sacrificial monomers.

Introduction

Chain-end functionalized polymers are of immense interest in polymer chemistry but also across the interdisciplinary borders. They offer interesting and quite modular pathways to novel hybrid materials such as bio-active[1,2] and ionic groups[3] or non-covalent binding motifs.[4] The need for polymers bearing exactly one functional group at one chain-end requires the application of a living polymerization method thus eliminating the possibility of reinitiation, termination and chain transfer reactions.

Most living polymerization techniques, such as carbanionic polymerization,[5,6] RAFT,[7] ATRP[8] or anionic ring opening polymerization offer straightforward routes to either functionalize the living polymer chain-end or start the polymerization with a functional initiator.

Early well-defined catalyst systems based on titanium,[9] molybdenum and tungsten[10] did not tolerate many functional groups in the monomer structure. While limiting the choice of monomer, this feature could be exploited in the introduction of functional end-groups. The high oxophilicity of the metal carbenes allowed end-functionalization via addition of substituted aldehydes to the polymerization mixture.

As ruthenium-catalyzed ROMP is tolerant to most common organic functional groups, the functionalization reactions present in the literature mainly focus on olefins that deactivate the carbene species. The living end-group of a ROMP polymer can be terminated using substituted vinyl ethers or vinyl lactones[11] which deactivate and remove the catalytic center from the chain-end while leaving the desired functional group behind.[12] Applying specially functionalized ruthenium initiators[13] to place functional end-groups at exactly one chain-end also leads to mono-functionalized polymers, but involves challenging organometallic transformations which can be carried out by specialists to the field only.

Other groups have employed molecular oxygen,[14] which produces a terminal aldehyde. However, the functionalization reactions were often reported to be slow, gave low end-group conversions or were not applicable in general.

End-functionalized telechelic polymers are also easily accessible using ruthenium carbene initiators in the presence of chain transfer agents. A number of functional groups such as hydroxyl groups[15] or amino and carboxylic acid groups[16] have been introduced in this manner; however, full control over the molecular weight distribution is lost. The necessity of precisely mono-functionalized polymer chains has limited the use of ruthenium-catalyzed

olefin metathesis polymerization to polymers with highly functional pendant groups by employing functional monomers for a long period.[17]

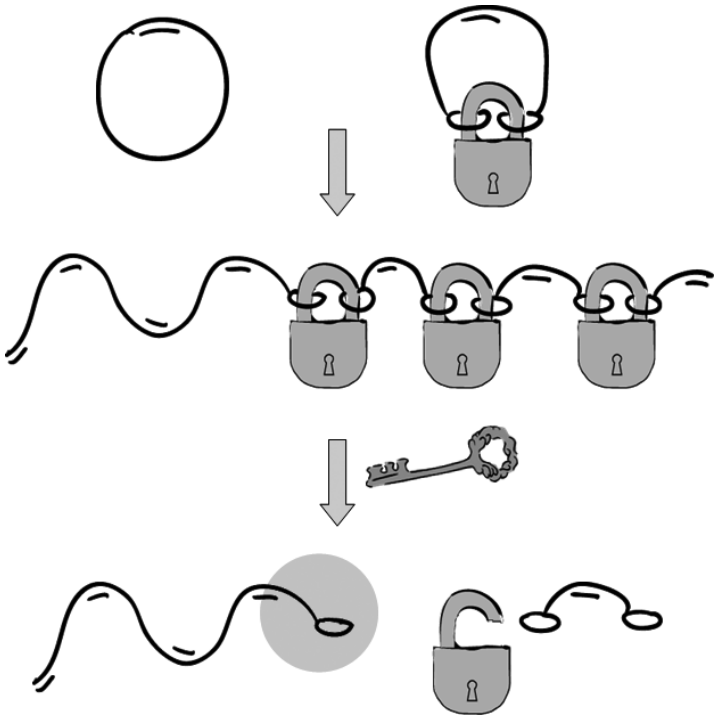


Figure 1. Concept of sacrificial synthesis.

Recently, we have reported a novel synthetic route to overcome many of the above mentioned limitations by introducing a sacrificial block copolymer synthesis.[18,19] There, the living ROMP polymer to be functionalized was turned into a diblock copolymer by polymerizing dioxepine monomers onto the desired first polymer block (c.f. Figure 1). The second (polyacetal) block could then later be cleaved, i.e. sacrificed, leaving exactly "half a dioxepine", i.e. a hydroxyl group, at the chain-end.

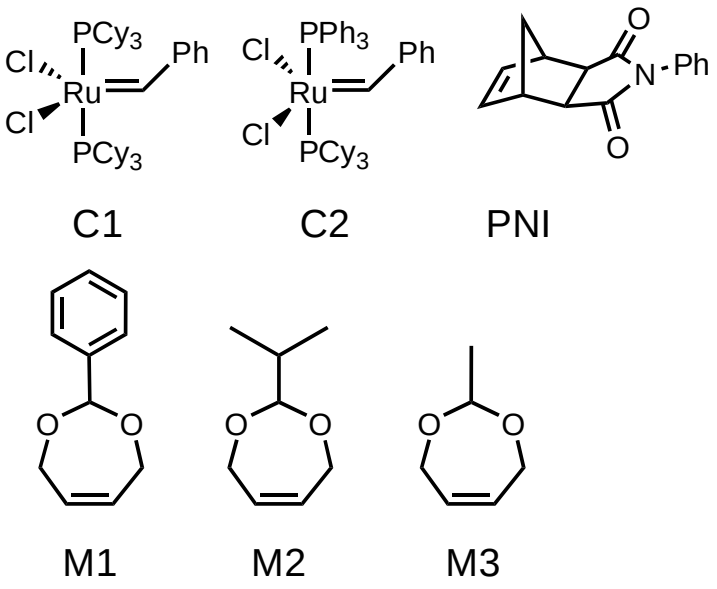
In this case, no termination step is required for the functionalization. It can therefore either be omitted or conducted with a terminating agent, such as ethyl vinyl ether, that does not give a functional group at all. Hydroxy-end-functional polymers prepared via this route have already been used for the synthesis of graft[20] and amphiphilic diblock copolymers.[21]

In a first communication, which has drawn significant attention in the metathesis community,[19] we were able to demonstrate that extremely high degrees of functionalization (>97% typically) can be achieved. Yet, little was known about the amount of functionalizing

agent necessary for a complete end-group conversion and therefore the atom economy could not be determined.

Here, we report a sacrificial synthesis study exploring both efficiency and versatility of this novel functionalization strategy by analyzing the kinetics of the key step to functionalization, i.e. the initiation of the sacrificial block. The results are compared to classical initiation reactions of living polymerizations.

Three cleavable monomers and two catalyst systems were chosen for this study (c.f. Scheme 1). The substituted 4,7-*2H*-dihydrodioxepine monomers **M1-M3** vary in both initiation and propagation behavior. In the presence of catalyst **C1** or **C2** the 2-phenyl-substituted dioxepine monomer **M1** and 2-isopropyl-substituted dioxepine **M2** do not form a homopolymer, but short oligomers. The 2-methyl-substituted derivative **M3** forms a homopolymer with a broad molecular weight distribution, when initiated with either catalyst **C1** or **C2**.



Scheme 1. Initiators and sacrificial dioxepine monomers studied.

Experimental Section

General. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AC300 or at 400 MHz on a Bruker AMX400. Kinetic ^{1}H NMR was conducted on a Varian Mercury 400 utilizing ACDLabs 10 for bulk processing. All spectra were referenced internally to residual solvent proton signals. Deuterated solvents were purchased from Deutero GmbH or Cambridge Isotopes. Size exclusion chromatography in chloroform was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P100 pump and a set of three PSS SDV columns (10^4/500/50 Å). Signal detection occurred by use of a TSP Spectra System UV2000 (UV 254 nm) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service.

Exo-*N*-phenyl-2,3-norbornene dicarboximide was synthesized as described in earlier publications.[18] Grubbs' 1st generation catalyst was obtained from Materia, inc. All solvents and other reagents were purchased from Aldrich or Acros. All polymerization reactions were carried out under argon using standard Schlenk techniques unless otherwise stated. Dichloromethane as the solvent was dried by a Grubbs-type solvent system and stored under nitrogen.

Preparation of kinetic ^{1}H NMR samples: 15mg (18µmol) of Grubbs 1st generation catalyst were added 0.3mL dichlormethane-d_2 under nitrogen. The solution was transferred into a nitrogen filled NMR-tube, which was sealed with a rubber septum. A solution of 43mg (15 equivalents) of **PNI** in 0.5mL dichlormethane-d_2 prepared under nitrogen was added by syringe. The polymerization mixture was allowed to stand for >30min to allow for full polymerization. Upon measurement of a reference spectrum, the dioxepin monomer (29mL **M1**, 26µL **M2** or 20µL **M3**) was added by microsyringe and kinetic measurement was commenced immediately with 4 scans per measurement (44 s) and a 1 s pause incremented by 1 s after every measurement.

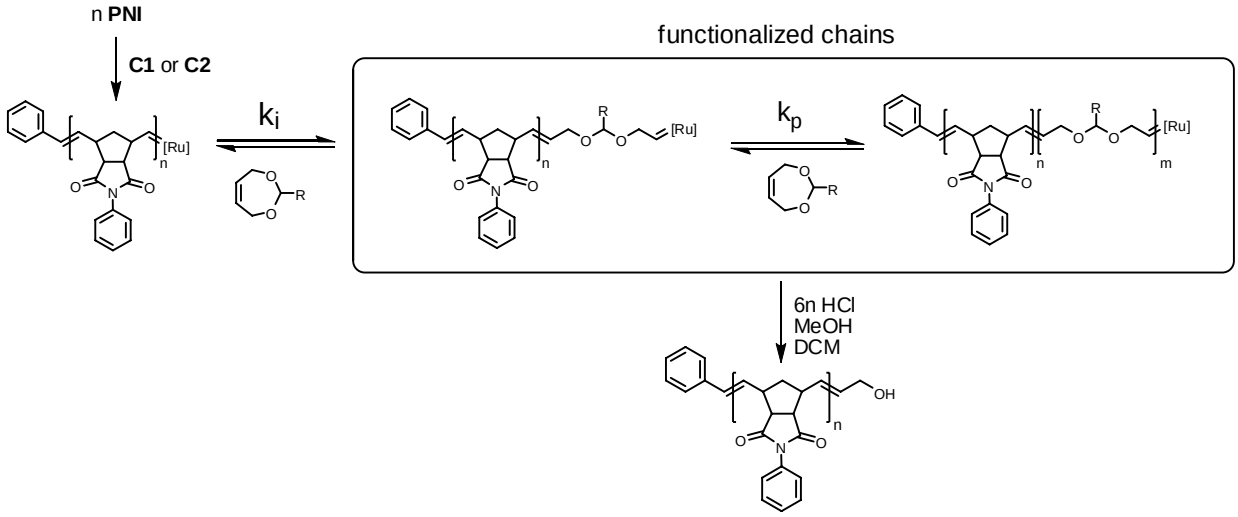
General procedure for the synthesis of functionalization series of Poly(PNI-b-Dioxepine): Five 30 mL glass vials equipped with a silicone septum and a small stirbar were charged with 600mg **PNI** and degassed by passing a stream of purified Ar over the solid for 20 min. The samples were charged with 10mL dry, degassed dichloromethane each and allowed to dissolve. A 2mL aliquot of a stock solution prepared from 690 mg Grubbs 1st generation catalyst (and 1.035 g PPh_3 (6.3 equivalents) in cases where catalyst **C2** was used) dissolved in 10mL of dry, degassed dichloromethane was added to the monomer solutions with stirring. After 30 min (6h in cases where **C2** was used to initiate the polymerization), a 3 mL aliquot of the living polymerization mixtures was taken and terminated with 100 µL ethyl vinyl ether. The appropriate amount of the respective dioxepin (14 µL for 1 equivalent Ph-dioxepin and Me-dioxepin or 18 µL for 1 equivalent of iPr-dioxepin, doubled for every subsequent sample) was added to the polymerization mixture. Further 3 mL aliquots of the polymerization mixtures were taken after 15, 30 and 60 minutes (1, 2 and 12 hours for polymerizations initiated with **C2**) and terminated by addition of 100 µL of ethyl vinyl ether each. All polymer samples were allowed to terminate for >1h, precipitated in methanol and dried over night in vacuo to give virtually colorless solids, typically yielding >90%.

General procedure for the hydrolysis of poly(PNI-b-Dioxepine) block-copolymers: The polymer samples were placed in a 12-vessel reaction carousel and dissolved in 5mL chloroform. 2 mL of methanol and 4 mL of 6n HCl were added and stirred vigorously for 14h. After the reaction time, the polymers were precipitated by addition of 15mL methanol, collected and redissolved in chloroform, reprecipitated in methanol. The precipitate was filtered isolated by filtration and dried over night in vacuo to give a colorless solid in 80-95% yield.

^{1}H NMR (400MHz, $CDCl_3$) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2-brigde); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, C(O)CH); 4.16 (m, 2H, CH_2-O end-group); 5.2-5.5 (m, 2H, Olefin end-group); 5.6-5.9 (m, 2H, double bonds polymer); 6.3-6.4 (m, 1H, double bond CH_2-OH end); 6.5-6.7 (m, 1H, double bond Ph end); 7.2-7.6 (m, 5H, Ph).

Results and Discussion

Sacrificial synthesis involves the polymerization of an additional block onto the desired polymer which is subsequently removed in order to set the terminal functionality free. The initiation kinetics of this cleavable block determine the efficiency of the entire synthetic strategy. The concurrent consumption of the sacrificial monomer during initiation and propagation of the sacrificial block limits the atom economy of this method because only chains bearing at least one unit of the cleavable monomer are functionalized as depicted in Scheme 2. In cases, where the initiation of the cleavable dioxepine monomer is much faster than its propagation, even low excesses of this monomer can be expected to lead to high degrees of functionalization. When the propagation is faster than the initiation, higher amounts of the sacrificial monomer have to be added.



Scheme 2. Concurrent reactions during initiation of the functionalizing sacrificial block.

In order to determine the efficiency of sacrificial synthesis, the optimum number of cleavable monomers per living chain-end had to be found. The polymerization of an additional block onto a living chain-end is commonly classified as an initiation reaction involving the new monomer and a macroinitiator. Furthermore, ruthenium-catalyzed ring-opening metathesis polymerization represents a living polymerization, as termination and chain transfer reactions do not occur with most common ROMP monomers such as

norbornene derivatives. Therefore, classical initiation kinetics of the living anionic polymerization can be applied to describe this reaction step.

The Grubbs 1st generation catalyst systems show rather slow initiation kinetics in comparison to many highly active living anionic polymerization initiators. However, the initiation kinetics of low-basicity intitiators[22] for the anionic polymerization can be applied to describe the concurrent reaction of initiation and propagation taking place during the macroinitiation step of the sacrificial block. As published by Szwarc et al.,[23,24] the initiation efficiency of an initiator can be calculated from the k_p/k_i factor and the equivalents of monomer applied to the initiator (c.f. Equation 1). In the case of sacrificial synthesis, M_{total}/C_{total} is defined by the number of equivalents of cleavable monomer per initiator (M_{total}: monomer concentration, C_{total}: initiator concentration) and the initiation efficiency *f* represents the degree of functionalization. However, as ROMP represents a theoretically reversible reaction, the values for k_i/k_p are apparent values.

$$\frac{M_{total}}{C_{total}} = \left(\frac{k_p}{k_i}\right) \cdot \left[\ln(1-f)^{-1} - f\right] + f \qquad (1)$$

The initiators chosen represent two readily available catalysts of the Grubbs 1st generation type. While catalyst **C1** is known for its commercial availability and good reactivity, the slower catalyst **C2** can be easily formed by addition of triphenylphosphine to **C1** and is known to give better control over molecular weight and PDI for lower molecular weight polymers. [25]

In order to determine the initiation kinetics of **M1-M3**, kinetic ^{1}H NMR spectroscopy was performed on catalyst **C1** initiated with 15 equivalents of **PNI**. To ensure pseudo-first order kinetics throughout the reactions, 10 equivalents of the sacrificial monomer were added to the living polymerization. Figure 2 shows the time resolved ^{1}H NMR spectra recorded for the reaction with **M2**. The signal at 19.2 ppm, representing the poly(**PNI**) carbene, vanishes over time, while a new signal at 19.5 ppm, which can be attributed to the newly formed dioxepine-carbene, develops at a similar rate. The benzylidene signal at 20.0 ppm is caused by non-initiated catalyst **C1.** It does not decrease noticeably owing to the lower reactivity of this carbene which has been reported previously.[26] By plotting the integrals of the carbene

signals versus time, the progress of the reaction can be quantified. The reaction follows pseudo-first order kinetics.

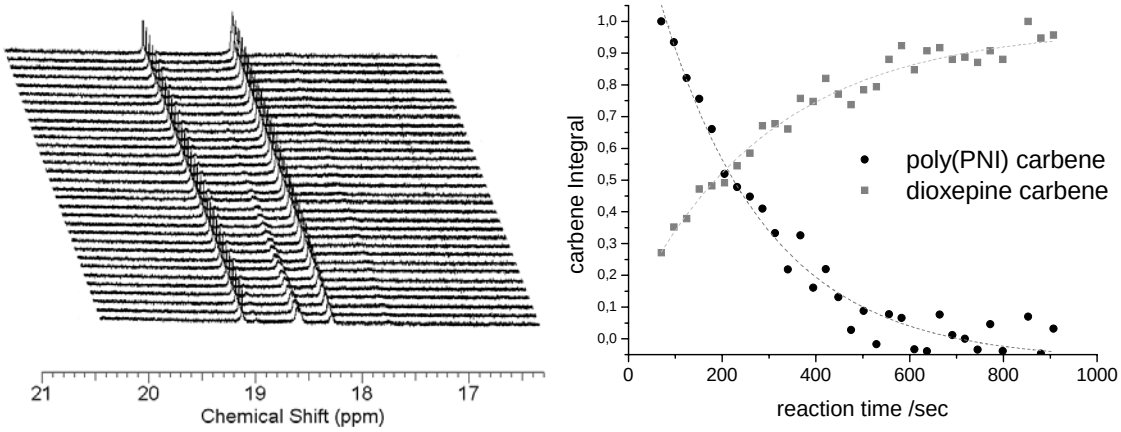


Figure 2. *Left:* Time-resolved ^{1}H NMR spectrum of the reaction of **C1** initiated with 15 equivalents of **PNI** after addition of 10 equivalents of **M2** (top = start of reaction. The time (t) between spectra increases from top to bottom. For details see experimental section). *Right:* Development of carbene signal integrals over time.

Reaction half lifes were determined for all dioxepines **M1-M3** (see Supporting Information **S-1** and **S-2** for further kinetic measurements). Second order initiation constants were calculated from the kinetic data which are summarized in Table 1.[27] Due to signal overlap of the dioxepine peaks with the poly(dioxepine) signals, the total monomer consumption could not be determined and no k_p values were calculated

Table 1: Half lifes and initiation constants for **M1-M3** with **PNI** initiated catalyst **C1**.

dioxepine	$t_{1/2}$ s	k_i L/mol s
M1	129	3.876
M2	237	1.596
M3	653	0.668

The obtained initiation constants correlate well with the general polymerization trend found for the three dioxepines, with **M3** giving broadly dispersed molecular weights and **M1** giving the best functionalization results. Similar kinetic results can be obtained when the formation of the new carbene is observed rather than the disappearance of the initial carbene. However, the signal of this carbene is broader and integration less exact. Generally, it has to be noted that quantitative evaluation of this active polymer end-group is particularly tedious. The high rate of the reaction requires quick measurements, inevitably leading to a rather low signal-to-noise ratio.

In summary, kinetic ^{1}H NMR spectroscopy was insufficient to determine the k_p/k_i factor. However, this vital factor is needed in order to describe the overall efficiency of sacrificial synthesis. Alas, the k_i/k_p value could be determined using the total degree of functionalization. As Equation 1 implies, with M_{total}/C_{total} set by the number of equivalents of the dioxepine monomer added and the degree of functionalization equaling the initiation efficiency *f*, the k_p/k_i factor can be calculated.

In order to obtain the total degree of functionalization, a series of sacrificial syntheses was carried out, employing poly(**PNI**) as the first block with either catalyst **C1** or **C2** and the three different dioxepines **M1-M3** to prepare the second block. A reference sample was collected before the cleavable dioxepine monomer was added. The reference sample was terminated with ethyl vinyl ether thus forming a terminal olefin which could be distinguished from the desired functional end-group by standard ^{1}H NMR spectroscopy. Upon addition of the cleavable dioxepine monomer, samples were taken at three representative reaction times (see experimental section) and treated with ethyl vinyl ether. All samples were subsequently hydrolyzed to liberate the terminal alcohol group.

The total degree of functionalization was determined by comparing the integral of the ^{1}H NMR signal of the functional end-group (H_f) to the integrals of the styryl end-group (H_{s1} & H_{s2}) introduced by the initiator (c.f. Figure 3). The signal of the terminal olefin group (H_o) created by ethyl vinyl ether termination served as a reference.

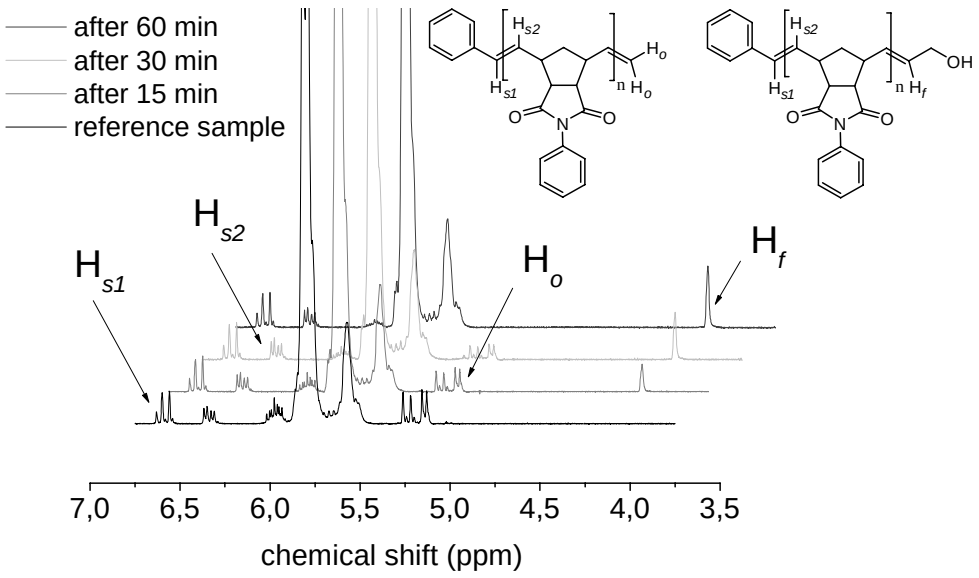


Figure 3. Determination of the degree of poly(**PNI**) end-functionalization by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra from bottom to top show the development of hydroxy-functionalization over time. 8 equivalents of **M1** were added to the reaction.

As demonstrated in Figure 3, the degree of functionalization with catalyst **C1** and dioxepine **M1** reaches a maximum after ca. 1h of reaction time indicating that the reaction has been completed at this point. Using catalyst **C2** (Figure 4 *right*), the functionalization reaction is much slower, as expected, and takes 12h to complete. A further increase of reaction time did not afford higher degrees of functionalization.

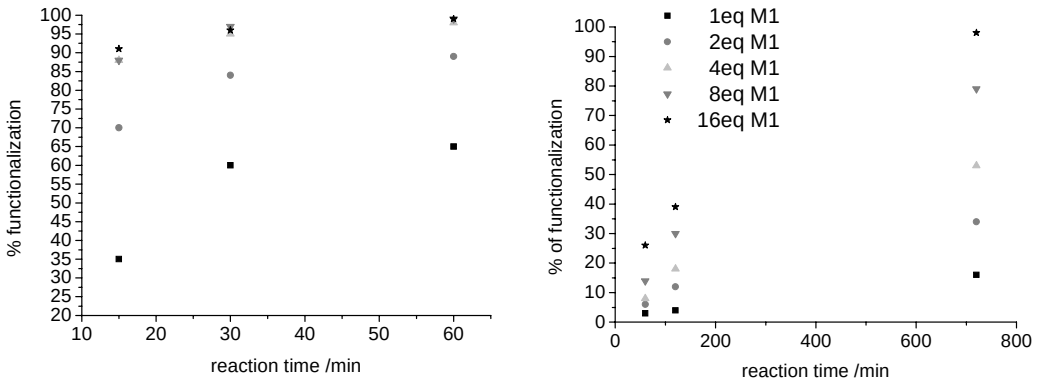


Figure 4. Degrees of poly(**PNI**) end-functionalization with different amounts of **M1**. *Left:* polymerization initiated with **C1**. *Right:* polymerization initiated with **C2**.

The results of the end-functionalization series with the other two dioxepines (**M2** and **M3**) are given in the Supporting Information (**S-3** and **S-4**). It was found that full end-functionalization can be achieved by adding as little as 4 equivalents of **M1** or 8 equivalents of **M2** to polymers initiated with catalyst **C1**. 80% functionalization was achieved by addition of 16 equivalents of the dioxepine **M3**.

When **C2** was used to initiate the polymerization of **PNI**, the degrees of end-functionalization were generally lower than with **C1**, but followed the same trend. Here, similar to the results presented above, dioxepine **M1** was the best functionalizing agent, giving nearly fully functionalized polymers (95%) employing 16 equivalents of the dioxepine.

M2 and **M3** gave 67% and 50% end-functionalization under the same conditions, respectively.

In order to obtain the k_i/k_p factor, the degrees of functionalization after the polymerization reaction had come to completion were plotted against the number of equivalents of the dioxepine monomer added. (c.f. Figure 5). A function generated from Equation 1 was then fitted to the raw data by varying k_p/k_i. For **M2** and **M3** (see **S-5** in the Supporting Information), adjusting the theoretical curve to the observed degrees of functionalization resulted in an excellent fit. When the functionalization results of **M1** were evaluated by the same method, a good agreement with theory could be found when catalyst **C1** was used. In the case of catalyst **C2**, however, the degrees of functionalization were underestimated for higher excesses of the dioxepine monomer. This effect can be explained taking into account that dioxepine **M1** cannot form a homopolymer due to steric and electronic reasons.[28] This means that the propagation of the monomer **M1** fades after a few monomer addition steps and large excesses of **M1** are available for the macroinitiation step.

It has to be noted that the ability to calculate k_i/k_p values from functionalization results is extremely useful for future developments of sacrificial monomers. Determining the end-functionalization with one or two test reactions at different excesses of the cleavable monomer, the entire functionalization behavior of a monomer can be estimated using Equation 1.

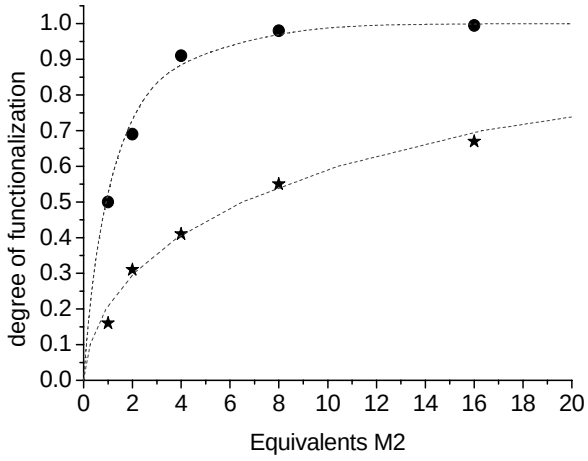


Figure 5. Degrees of end-functionalization vs. excess of dioxepine monomer **M2** and fitted theoretical values (dashed lines, according to Equation 1) for poly(**PNI**) initiated with catalyst **C1** (squares) and catalyst **C2** (stars).

The k_i/k_p values found for all dioxepine monomers studied are summarized in Table 2. The difference in initiation behavior between the various monomer and catalyst systems is quite significant. The general trend of the k_i/k_p values resembles the functionalization results of earlier experiments, with **M1** giving the best results and **M3** giving the lowest degree of functionality. The effect of the addition of PPh_3 to catalyst **C1** (thus forming **C2**) on the k_i/k_p ratio is contrary to the findings of Bielawski et al.[25] who saw a general increase of k_i/k_p when PPh_3 was added to the catalyst. However, the dioxepines **M1-M3** are rather low in polymerization reactivity and steric effects might have a significant influence on the initiation of the sacrificial block. The poly(**PNI**)-carbene certainly represents a larger steric hindrance than the comparably small carbene of the ring-opened dioxepine. Therefore, much higher excesses of the dioxepine monomers have to be added in order to reach full functionalization of the polymer when using catalyst **C2**.

Table 2: k_i/k_p values determined for the macroinitiation/propagation of poly(**PNI**) and the dioxepine monomers **M1**-**M3**.

Dioxepine	Initiator	Eq. PPh_3 added	k_i/k_p
M1	**C1**	0	0.625
M1	**C2**	6.3	0.065
M2	**C1**	0	0.472
M2	**C2**	6.3	0.032
M3	**C1**	0	0.040
M3	**C2**	6.3	0.012

On the other hand, the addition of PPh_3 does have positive effects on the molecular weight distribution and the initiation efficiency of the first polymer block that is not sacrificed. As demonstrated by the SEC data given in Table 3, the polymers synthesized during the functionalization series with catalyst **C1** show a higher polydispersity index (typically ca. 0.1 higher than polymers synthesized with catalyst **C2**) and a significantly higher molecular weight, indicating incomplete initiation which is typical for **C1** when aiming for low molecular weights. Also, a slight broadening of the molecular weight distribution can be monitored during the long reaction times required for quantitative functionalization with catalyst **C2**. However, the functionalization time can be reduced by addition of larger excesses of the respective dioxepine. The SEC characterization data for **M1** and **M3** can be found in the Supporting Information (**S-6** and **S-7**).

Table 3: SEC results (RI detection) for the end-functionalization of poly(**PNI**) using either catalyst **C1** or **C2** and employing different amounts of dioxepine monomer **M2**.

	Catalyst **C1**			Catalyst **C2**		
Excess **M2**	time (min)	M_n	PDI	time (h)	M_n	PDI
1	Reference	6400	1.23	Reference	2500	1.08
	15	6500	1.20	1	2400	1.15
	30	6700	1.15	2	2800	1.09
	60	6400	1.16	12	3100	1.10
2	Reference	6100	1.16	Reference	2600	1.08
	15	5800	1.15	1	2600	1.08
	30	6100	1.17	2	2800	1.10
	60	5900	1.17	12	3200	1.13
4	Reference	5900	1.16	Reference	2600	1.09
	15	5700	1.16	1	2500	1.07
	30	5900	1.17	2	2700	1.09
	60	6100	1.17	12	2900	1.16
8	Reference	6900	1.12	Reference	2300	1.09
	15	6000	1.16	1	2500	1.09
	30	5900	1.17	2	2600	1.10
	60	6000	1.17	12	2600	1.15
16	Reference	6000	1.16	Reference	2400	1.08
	15	5900	1.15	1	2500	1.10
	30	5600	1.19	2	2300	1.12
	60	5900	1.15	12	2500	1.13

The need to apply an excess of the functionalizing agent applies to most other functionalization methods such as for example the use of substituted vinyl ethers.[12] However, it is particularly pronounced in sacrificial synthesis when catalyst **C2** is used. Nonetheless, this is a small price to pay for obtaining well-defined and fully functionalized polymers, especially with commercially available or conveniently accessible dioxepine monomers and catalyst systems.

Conclusions

Sacrificial synthesis using the ring opening metathesis polymerization (ROMP) is an extremely useful and versatile functionalization method. The concept is unique in the sense that a macroinitiation step rather than a termination reaction is used to attach a desired functional group to the polymer chain end.

The efficiency of this functionalization concept was demonstrated by a series of functionalization reactions applying different amounts of the cleavable monomer and varying reaction times. Moreover, the functionalization results were found to be in good agreement with theoretically derived degrees of initiation on low-basicity initiators of the living anionic polymerization.

With the examination of the macroinitiation behavior of the dioxepine monomers involved in this study, the basis has been established to combine the characteristics of this functionalization reaction with the kinetic equation describing the initiation reaction of classical living polymerizations. This theoretical basis will aid future developments of new sacrificial monomers as it could be shown that the key factor to the efficiency of sacrificial synthesis, the value of k_i/k_p, can be estimated for each cleavable monomer by as little as one or two functionalization reactions.

Therefore, this study will be of major importance to further functionalization strategies applying sacrificial strategies and will simplify the comprehension of essential factors such as atom economy and reaction times.

References

[1] Maynard, H.D.; Okada, S.Y.; Grubbs, R.H. *Macromolecules* **2000**, *33*, 6239-6248.

[2] Maynard, H.D.; Okada, S.Y.; Grubbs, R.H. *J. Am. Chem. Soc*. **2001**, *123*, 1275-1279.

[3] Lynn, D.M.; Mohr, B.; Grubbs, R.H.; Henling, L.M.; Day, M.W. *J. Am. Chem. Soc*. **2000**, *122*, 6601-6609.

[4] Stubbs, L.P.; Weck, M. *Chem. Eur. J*. **2003**, *9*, 992-999.

[5] Jagur-Grodzinski, J.;*J. Polym. Sci:A*, **2002**, *40*, 2116-2133.

[6] Morton, M., *Anionic Polymerization: Principles and Practice*, Academic Press, New York, **1983**.

[7] Barner-Kowollik, C. *Handbook of RAFT Polymerization,* Wiley-VCH, Weinheim, **2008**.

[8] Matyjaszewski, K.; Xia, J.; *Chem. Rev*. **2001**, *101*, 2921-2990. Kamigaito, M.; Ando, T.; Sawamoto, M.; *Chem. Rev*. **2001**, *101*, 3689-3745.

[9] Gilliom, L.R.; Grubbs, R.H. *J. Am. Chem. Soc.* **1986**, *108*, 733-742.

[10] O'Donoghue, M.B.; Schrock, R.R.; LaPointe, A.M.; Davis, W.M. *Organometallics*, **1996**, *15*, 1334-1336. Murdzek, J.S.; Schrock, R.R. *Macromolecules* **1987**, *20*, 2640-2642. Schrock, R.R.; Murdzek, J.S.; Bazan, G.C.; Robbins. J.; DiMare, M.; O'Regan.M. *J. Am. Chem. Soc.* **1990**, *112*, 3875-3886.

[11] Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M *J. Am. Chem. Soc.* **2008** *accepted for publication* (ja-2008-022863.R1)

[12] Maynard, H.D.; Grubbs, R.H. *Macromolecules* **1999**, *32*, 6917-2924. Weck, M.; Mohr, B.; Maughon, B.R.; Grubbs, R.H. *Macromolecules* **1997**, *30*, 6430-6437. Owen, R.M.; Gestwicki, J.E.; Young, T.; Kiessling, L.L. *Org. Lett*. **2002**, *4*, 2293-2296. Gestwicki, J.E.; Cairo, C.W.; Mann, D.A.; Owen, R.M.;Kiessling, L.L. *Anal. Biochem*. **2002**, *305*, 149-155. Gordon, E.J.; Gestwicki, J.E.; Strong, L.E.; Kiessling, L.K. *Chemistry and Biology*, **2000**, *7*, 9-16. Chen, B.; Sleiman, H.F. *Macromolecules* **2005**, *38*, 1084-1090.

[13] Castle, T. C.; Hutchings, L. R.; Khosravi, E. *Macromolecules* **2004**, *37*, 2035-2040.

[14] Biagini, S.C.G.; Davie, R.G.; Gibson, V.C.; Giles, M.R.; Marshall, E.L.; North, M. *Polymer* **2001**, *42*, 6669-6671.

[15] Bielawski, C.W.; Benitez, D.; Morita, T.; Grubbs, R.H. *Macromolecules* **2001**, *34*, 8610-8618.

[16] Morita, T.; Maughon, B.R.; Bielawski, C.W.; Grubbs, R.H. *Macromolecules* **2000**, *33*, 6621-6623.

[17] Binder, W. H.; Kluger, C. *Macromolecules* **2004**, *37*, 9321-9330. Binder, W. H.; Kluger, C.; Josipovic, M.; Straif, C. J.; Friedbacher, G. *Macromolecules* **2006**, *39*, 8092-8101. Alfred, S.F.; Al-Badri, Z.M.; Madkour, A.E.; Lienkamp, K.; Tew, G.N. *J. Polym. Sci. A: Polym. Chem.* **2008**, *46*, 2640-2648.

[18] Hilf, S.; Berger-Nicoletti, E.; Grubbs, R.H.; Kilbinger, A.F.M. *Angew. Chem*. **2006**, *118*, 8214-8217; *Angew. Chem. Int. Ed.* **2006**, *45*, 8045-8048.

[19] Perrier, S.; Wang, X. *Nature* **2007**, *445*, 271.

[20] Hilf, S.; Kilbinger, A.F.M. *Macromol. Rapid Commun*. **2007**, *28*, 1225-1230.

[21] Hilf, S.; Hanik, N.; Kilbinger, A.F.M. *J. Polym. Sci. A* **2008**, *46*, 2913-2921.

[22] Arest-Yakubovich, A.A.; Nakhmanovich, B.I.; Litvinenko, G.I. *Polymer* **2002**, *43*, 7093-7100.

[23] Szwarc M. *Makromol. Chem.* **1960**, *35*, 132-158.

[24] Szwarc M.; van Beylen, M.; van Hoywegen, D. *Macromolecules* **1987**, *20*, 445-448

[25] Bielawski,C.W., Grubbs, R.H. *Macromolecules* **2001**, *34*, 8838-8840.

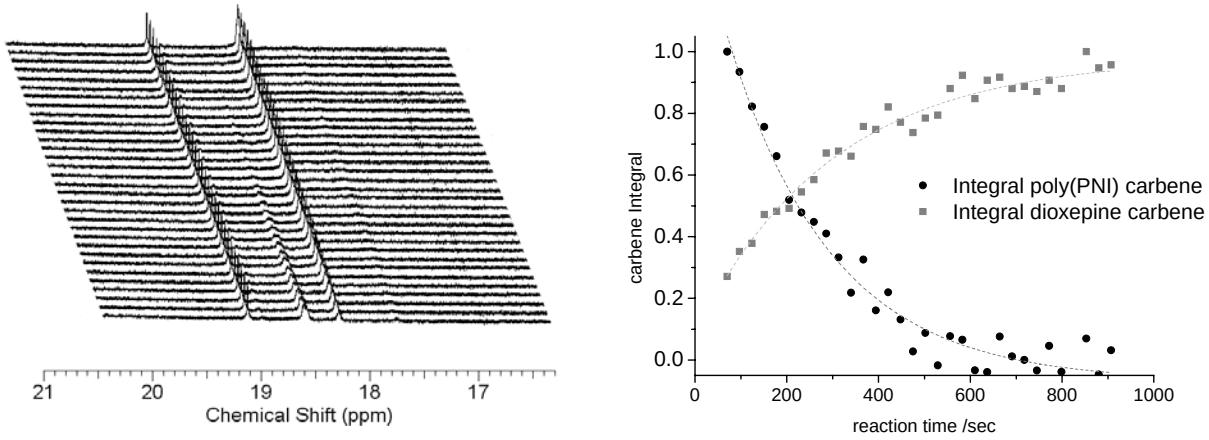
[26] Schwab, P.; Grubbs, R.H.; Ziller, J.W. *J. Am. Chem. Soc*. **1996**, *118*, 100-110.

[27] Ulman, M.; Grubbs, R.H. *Organometallics* **1998,** *17,* 2484-2489.

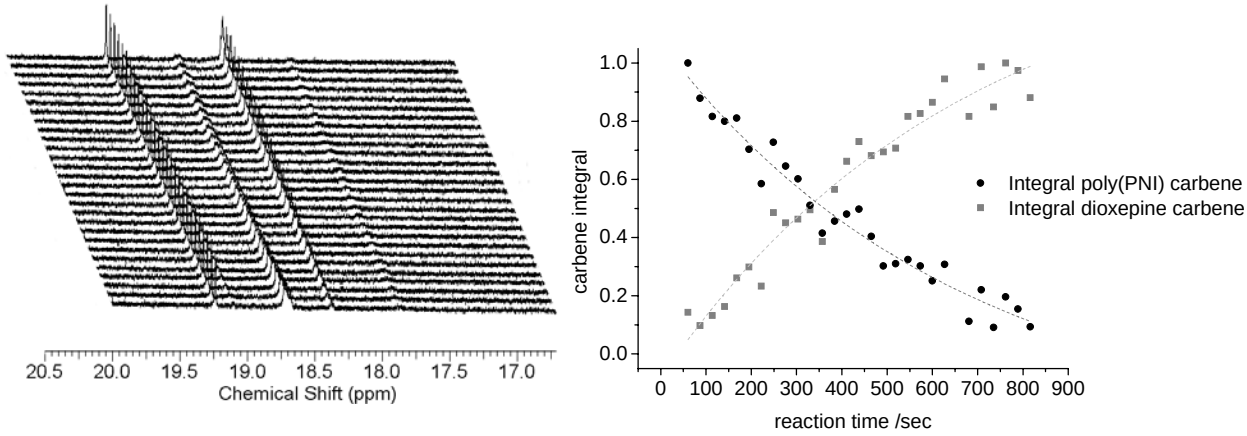
[28] Fraser, C.; Hillmyer, M.A.; Gutierrez, E.; Grubbs, R.H. *Macromolecules* **1995**, *28*, 7256-7261.

Supporting Information for: Sacrificial Synthesis of Hydroxy-functionalized ROMP polymers – An efficiency study

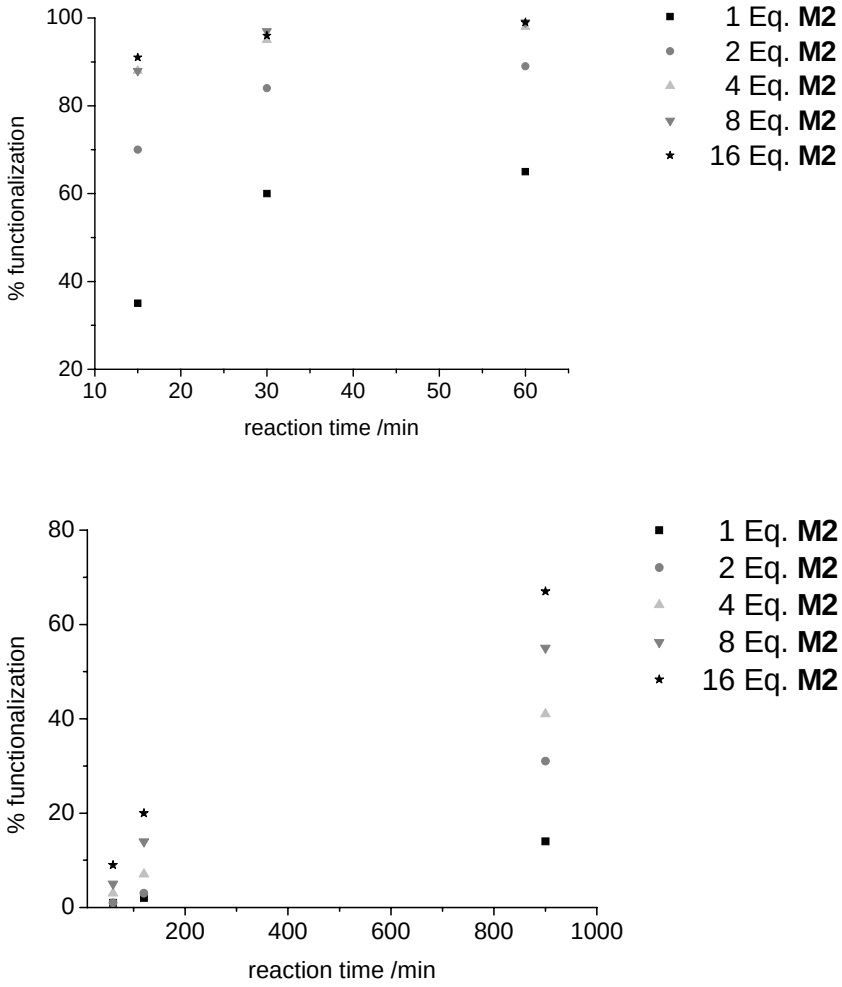
Stefan Hilf, Robert H. Grubbs and Andreas F.M. Kilbinger



S-1: *Left:* Kinetic ^{1}H-NMR of the raction of catalyst **C1** initiated with 15 equivalents **PNI** after addition of 10 equivalents of **M1**. *Right:* kinetic evaluation of carbene integrals.

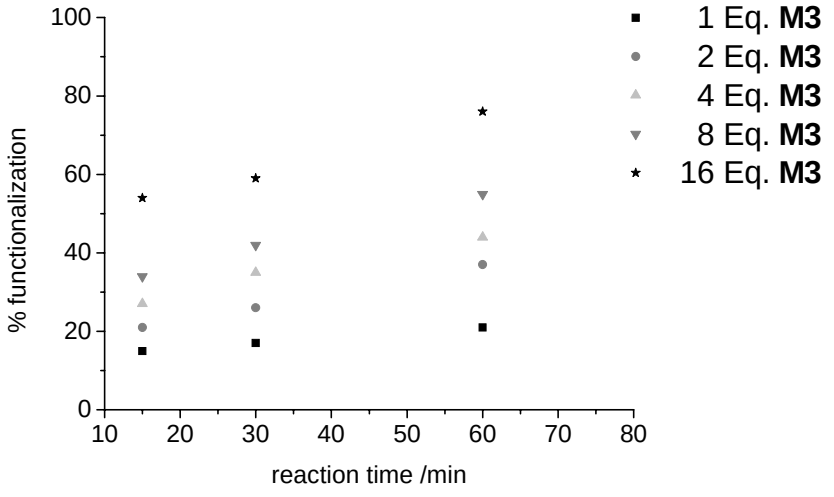


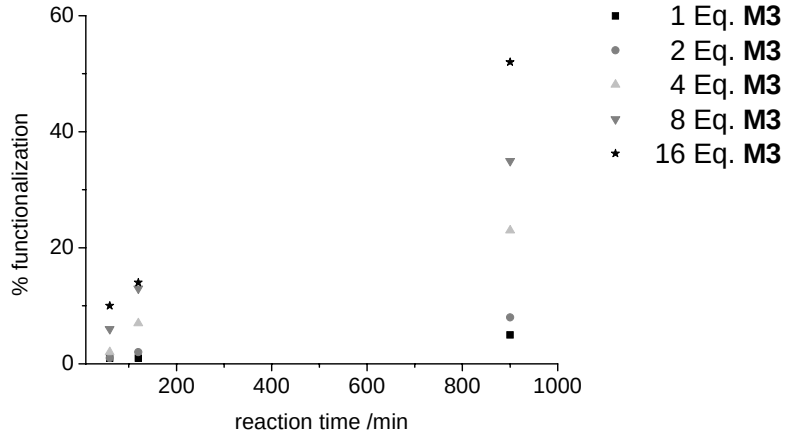
S-2: *Left:* Kinetic ^{1}H-NMR of the raction of catalyst **C1** initiated with 15 equivalents **PNI** after addition of 10 equivalents of **M3**. *Right:* kinetic evaluation of carbene integrals.



S-3: Degrees of polymer functionalization with different amounts of **M2**

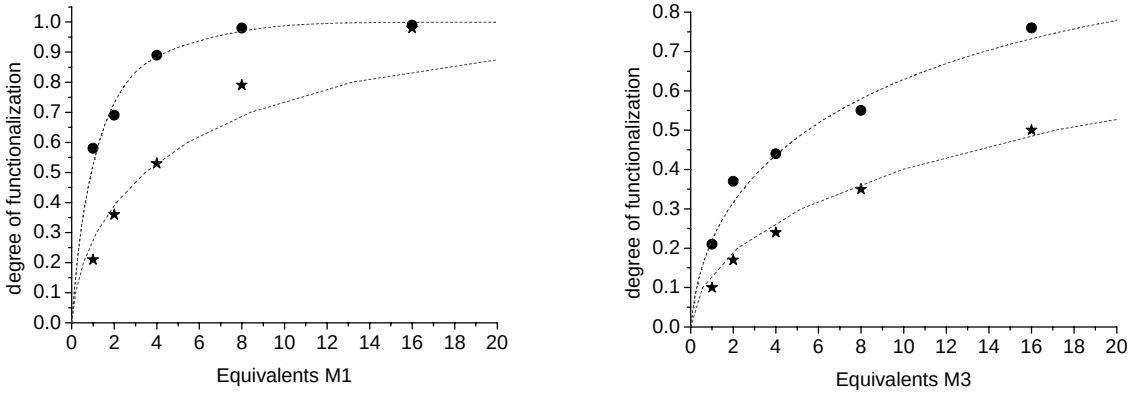
Top: with **C1**. *Bottom:* with **C2**.





S-4: Degrees of polymer functionalization with different amounts of **M3**

Prev. page bottom: with **C1**. *Top:* with **C2**.



S-5: Degrees of functionalization vs. Excess of dioxepin monomer **M1** *(left)* or **M3** *(right)* and fitted theoretical values (dashed lines) for poly(**PNI**) initiated with catalyst **C1** (squares) and catalyst **C2** (stars).

	Catalyst **C1**			Catalyst **C2**		
Excess **M1**	time (min)	M_n	PDI	time (h)	M_n	PDI
1	Reference	6400	1,23	Reference	2500	1,08
	15	6500	1,20	1	2400	1,15
	30	6700	1,15	2	2800	1,10
	60	6400	1,16	12	3100	1,10
2	Reference	6100	1,16	Reference	2600	1,08
	15	5800	1,15	1	2600	1,08
	30	6100	1,17	2	2700	1,10
	60	5900	1,17	12	3200	1,13
4	Reference	5900	1,16	Reference	2600	1,09
	15	5700	1,16	1	2500	1,07
	30	5900	1,17	2	2700	1,09
	60	6100	1,17	12	2900	1,16
8	Reference	6900	1,12	Reference	2300	1,09
	15	6000	1,16	1	2500	1,09
	30	5900	1,17	2	2600	1,10
	60	6000	1,17	12	2600	1,15
16	Reference	6000	1,16	Reference	2400	1,08
	15	5900	1,15	1	2500	1,10
	30	5600	1,19	2	2300	1,12
	60	5900	1,15	12	2500	1,13

S-6: SEC-RI results of the functionalization series with dioxepin monomer **M1.**

	Catalyst **C1**			Catalyst **C2**		
Excess **M3**	time (min)	M_n	PDI	time (h)	M_n	PDI
1	Reference	6000	1,24	Reference	2400	1,08
	15	6000	1,24	1	2300	1,08
	30	6100	1,22	2	2400	1,08
	60	6000	1,23	12	3200	1,10
2	Reference	5700	1,22	Reference	2500	1,07
	15	5500	1,24	1	2300	1,08
	30	5500	1,24	2	2500	1,07
	60	5500	1,25	12	3000	1,09
4	Reference	5800	1,20	Reference	2400	1,06
	15	5400	1,25	1	2300	1,07
	30	5500	1,22	2	2300	1,08
	60	5400	1,25	12	2700	1,12
8	Reference	5600	1,22	Reference	2400	1,06
	15	5900	1,21	1	2200	1,07
	30	5500	1,24	2	2300	1,09
	60	5300	1,26	12	2500	1,15
16	Reference	6300	1,19	Reference	2300	1,06
	15	5800	1,21	1	2200	1,07
	30	6000	1,22	2	2300	1,07
	60	5900	1,19	12	2700	1,14

S-7: SEC-RI results of the functionalization series with dioxepin monomer **M3.**

2.3: Sacrificial Synthesis of Hydroxy-Telechelic Metathesis Polymers via Multiblock-copolymers

*Stefan Hilf and Andreas F.M. Kilbinger**

Published in: Macromolecules **2009**, *42,* 1099-1106.

Abstract

The synthesis of well-defined telechelic ring-opening metathesis polymers has been achieved by Sacrificial Synthesis. With the formation of cleavable triblock-copolymers, precise control over the molecular weight and the degree of functionalization was achieved. Introducing cleavable monomers that can be addressed separately, sequential deprotection was accomplished which opened the path to more sophisticated polymeric materials bearing different substituents at their respective chain ends. Sacrificial penta- and heptablock-copolymers are also presented which allow the synthesis of well-defined telechelic polymers in good yields and significantly improved initiator efficiency.

Introduction

Telechelic polymers represent a special class of chain-end functionalized polymers. In contrast to monofunctional polymers which are generally used for many applications such as surface functionalization[1] or drug immobilization,[2] they offer an additional functional group on the second chain end. They can be used to combine different molecules such as biomacromolecules with e.g. dyes or inorganic tracers.[3] Therefore, they are particularly interesting for interdisciplinary applications. In polymer science, they have been applied in the formation of multiblock-copolymers by polycondensation of the telechelic prepolymers with other difunctional materials.[4]

Polymers bearing functional groups at both chain ends can be synthesized by a number of methods[5] reaching from step-growth[6] to chain growth polymerizations.[7] While step-growth polymerizations are easily accessible and typically give extremely high degrees of chain-end functionalization, they give broad molecular weight distributions and little control over the average chain length.

Chain growth polymerizations, on the other hand, can be used to synthesize telechelic polymers by the addition of functional chain transfer agents (CTA).[8] In this case, molecular weight control is given by the kinetic characteristics of the respective polymerization reaction, but narrow molecular weight distributions cannot be reached.

Only living polymerizations,[9] i.e. polymerizations without termination, chain transfer or reinitiation processes, are able to form narrowly dispersed, highly bifunctional polymers. Furthermore, they involve difunctional initiators or initiators bearing a protected functional group.[10] However, these molecules are not available for all types of living polymerizations or have to be synthesized in numerous steps and need to be cautiously purified. All functionalization reactions involving classical living ionic or radical polymerizations involve a termination of the active species. Since termination of one chain end while maintaining the other chain end's activity is impossible, polymerizations involving difunctional initiators are limited to homotelechelics.

Telechelics from ring-opening metathesis polymerization (ROMP) have been realized by two different approaches. Acyclic, homobifunctional olefins have been used as CTA for the synthesis of various telechelic polymers.[11] The statistical copolymerization of monomers with a cyclic cleavable olefin also gave telechelics after hydrolysis.[12] Due to the low regioselectivity of ROMP, only homotelechelic polymers, bearing the same functional group

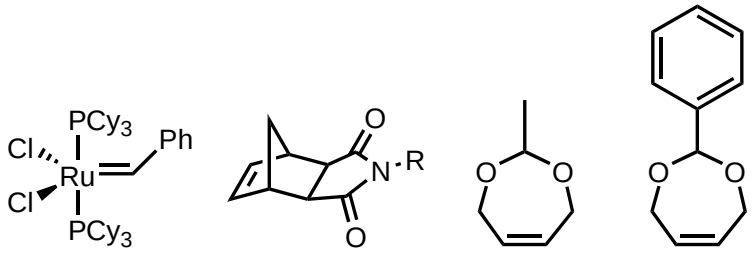
on both chain ends, are available by these methods. Difunctional initiators have only been realized for molybdenum based catalysts, but were limited to non-functional monomers due to the high oxophilicity of the active species.

Prefunctionalized ruthenium alkylidene complexes[13] have been used to place functional end-groups at one chain end. However, bifunctional polymers were never prepared using this route. Also, this method requires complex organometallic transformations and purifications which can be carried out by specialists only.

Recently, we have reported a different strategy for the functionalization of ROMP polymers. In contrast to classical functionalizing termination reactions involving vinyl ethers[14] or vinyl lactones,[15] *Sacrificial Synthesis*[16] does not require a termination reaction for the placement of the desired functional group, but a macroinitiation step. Therefore, the active species is kept and can be used to polymerize additional polymer blocks. Cyclic acetals (*c.f.* M1 and M2, scheme 1) were introduced for the formation of hydroxyl endgroups. The resulting polyacetal block could later be cleaved leaving exactly "half a dioxepine", *i.e.* a hydroxyl group at the chain-end. Such monofunctionalized polymers have already been used for the synthesis of graft[17] and block copolymers.[18] With the development of 2-methyl-1,3-dioxepine (M1) as sacrificial monomer was found that polymerized well and to high conversion. [19] For the first time, this allows the macroinitiation of a second monomer from a sacrificial block, thereby introducing a functional start-group.

Here, we present a new approach for the formation of telechelics based on the non-terminating functionalization principle of *Sacrificial Synthesis*. In contrast to the work of Fraser et al.[12] the cleavable sites are not introduced by statistical copolymerization, thereby scrambling the polymer chain into portions of statistically distributed sizes. Using blockwise polymerization of the hydrolyzable and the stable monomers, both polymer chain length and the order of cleavable and non-cleavable blocks remain under full control.

In order to introduce two functional groups on every polymer chain, two cleavable blocks containing easily hydrolyzable acetal functions formed from dioxepines M1 or M2 (*c.f.* scheme 1) are introduced on each side of the desired polynorborneneimide (*x*NI). Grubbs' 1st generation catalyst (C1) was chosen as the initiator since it has proven sufficient functional group and long-term stability to be deployed on complex block-copolymer formations.



C1 PNI: R=Ph DNI: R=Dodecyl HNI: R=Hexyl M1 M2

Scheme 1: Initiator and the monomers used for the synthesis of telechelics.

Furthermore, an advanced strategy is presented to cleave the two appending sacrificial blocks of an ABC triblock sequentially. Different conditions are used to cleave the two dioxepine blocks, thereby allowing for orthogonal derivatization of the two functional groups

An extension of this strategy to penta-, and hepta-blockcopolymers containing two or three non-hydrolyzable blocks leading to higher yields of telechelic polymer per molecule of initiator used is also described.

Experimental

General. ^{1}H-NMR spectra were recorded at 300 MHz on a Bruker AC300 or at 400MHz on a Bruker ARX400. All spectra were referenced internally to residual proton signals of the deuterated solvent. Deuterated solvents were purchased from Deutero GmbH. Gel permeation chromatography in chloroform was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P100 pump and a set of three PSS SDV columns ($10^5/10^3/10^2$ Å). Signal detection occurred by use of a TSP Spectra System UV2000 (UV 254 nm unless otherwise stated) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) measurements were performed on a Shimadzu Axima CFR MALDI-TOF mass spectrometer equipped with a nitrogen laser delivering 3ns laser pulses at 337nm.

Exo-N-phenyl-2,3-norbornene dicarboximide, *Exo-N*-dodecyl-2,3-norbornene dicarboximide and *Exo-N*-hexyl-2,3-norbornene dicarboximide, as well as 2-phenyl-1,3-dioxepine were synthesized as described in earlier publications.[18,17,18] Grubbs' 1st generation catalyst was obtained from Materia, inc. All solvents and other reagents were purchased

from Aldrich or Acros. All polymerization reactions were carried out under argon using standard Schlenk techniques unless otherwise stated. Dichloromethane as the polymerization solvent was dried over P_2O_5 and distilled under a nitrogen atmosphere. Dioxepine monomers were degassed by repeated freeze-pump-thaw-purge cycles using argon as the inert gas.

Synthesis of 2-methyl-1,3-dioxepine: To 130 mL of toluene in a 250 mL flask were given 43 mL *cis*-1,3-butenediol (0.5 mol), 29.5 mL acetaldehyde (0.52 mol) and 50 mg toluenesulfonic acid. The mixture was allowed to stand at r.t. for 30 minutes before it was connected to a Dean-Stark apparatus and refluxed until all produced water had been removed from mixture. After cooling, the content was washed with soda, water and brine and dried over MgSO4. The solvent was removed under reduced pressure and the product was distilled over a short Vigreux column (bp=135°C) to give a colorless liquid in good yield (49,5 g, 87%).

^{1}H NMR (300MHz, $CDCl_3$) δ[ppm]: 1.28 (3H, d, ^3J= 5.1 Hz, Me); 4.05-4.40 (4H, m, C=C-CH_2); 4.94 (1H, quart. , ^3J= 5.2 Hz, O-CH-O); 5.66 (s, 2H, C=CH).

General procedure for the synthesis of ABA and ABC triblock-copolymers: To a stirred solution of Grubbs' 1st generation catalyst (164 mg in 3 mL dichloromethane) was added 0.75 mL 2-methyl-1,3-dioxepine. After 1 hour, the solvent and all residual monomer was removed by high vacuum; the flask was evacuated for another 1 hour. The living polymer was then redissolved in 10 mL dichloromethane and the calculated amount of monomer (2 g in 10 mL dichloromethane for 10,000 g/mol) was added by syringe. After the polymerization had finished (typically 1 hour for 10,000 g/mol), 1 mL of the dioxepine monomer for the third block was added by syringe. After another 2 hours, the polymerization was terminated by addition of 0.5 mL ethyl vinyl ether in order to cleave the catalyst off the chain. The polymer was precipitated in methanol, collected and dried over night in a vacuum oven to give a brownish solid in good yield (>90% typically).

General procedure for the hydrogenation of the M2-block: The polymer bearing a poly(2-phenyl-dioxepine) block was dissolved in 50 mL dichloromethane, placed in a 100 mL hydrogenation reactor. 1 mL of a Raney-Ni slurry dispersed in methanol was added, the

reactor was sealed, evacuated and flushed with nitrogen three times, and allowed to react under 8 bar pressure of hydrogen for 20 hours with stirring. After the reaction time was completed, the mixture was filtered over a Celite pad, concentrated and precipitated in methanol. Te polymer was obtained as an off-white solid in good yield (>75% typically).

Attachment of pyrenebutyric acid to one hydroxyl-group and cleavage of the second dioxepine block: Pyrenebutyric acid (100 mg), *N,N'*-dicyclohexyl carbodiimide (80 mg) and *N,N*-dimethylaminopyridine (100 mg) were added to a solution of 150 mg poly(2-methyl-1,3-dioxepine-*b*-DNI)-OH in 15 mL dichloromethane and stirred at r.t. for 14 hours. The reaction mixture was then concentrated and precipitated in methanol. The polymer was collected, redissolved in chloroform, reprecipitated in methanol and dried in vacuo to give an off-white solid (135 mg, 92%). This polymer was then dissolved in dichloromethane (5 mL), 2 mL 1n HCl and 1 mL methanol was added and stirred over night. 20 mL methanol was then added to the mixture in order to precipitate the deprotected polymer. The collected solids were redissolved in chloroform, reprecipitated in methanol, collected and dried in vacuo to give a colorless solid weighing 84 mg (61% of starting material).

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 0.8-0.9 (m, 3H, C_{11}-CH_3); 1.1-1.4 (m, 18H, C_3H_2-$C_{11}H_2$); 1.5-2.2 (m, 4H, CH_2-brigde & N-C-CH_2); 2.6-2.7 (m, 2H, C_3CH); 2.9-3.1 (m, 2H, C(O)CH); 3.4-3.5 (m, 2H, N-CH_2); 4.07-4.14 (m, 2H, CH_2-OH endgroup); 4.58-4.67 (m, 2H, CH_2-O-PBA endgroup); 5.5-5.8 (m, 2H, double bonds); 7.7-8.3 (m, 9H, pyrene). GPC (chloroform): Mn=20200 ; PDI=1.30.

General procedure for the synthesis of ABABA and ABABABA multiblock-copolymers: A solution of 82 mg of Grubbs' 1st generation catalyst in 2 mL dichloromethane was added 0.5 mL 2-methyl-1,3-dioxepine. The mixture was stirred for 2 hours before a dichloromethane solution (5 mL) of the calculated amount of monomer (1 g for 10,000 g/mol) was added by syringe. After the polymerization of the second block had finished (ca. 1 hour), the second portion of 2-methyl-1,3-dioxepine (0.5 mL) was added and allowed to react for 2 hours. The monomer for the second polynorbornene block was added in the same manner as the first portion and was allowed to react for 1.5 hours. The third dioxepine portion was added again by syringe (0.5 mL). For the pentablock copolymer, the reaction was terminated after 2 hours by addition of 0.5 mL ethyl vinyl ether. For the

heptablock, another portion of the norbornenimide solution was added and allowed to react for 2 hours before the final portion of the dioxepin was added and allowed to react over night. Termination was conducted by addition of 0.5 mL ethyl vinyl ether in order to cleave the catalyst off the chain ends and stabilize the polymer. Precipitation of the polymer by addition of excess methanol followed by redissolution of the collected solids in chloroform and reprecipitation in methanol afforded an off-white solid in 80-90% yield.

General procedure for the hydrolysis of all cleavable blocks: To 1 g polymer dissolved in 15mL dichloromethane were given 5 mL 1n HCl and 2 mL methanol. This mixture was vigorously stirred to allow for good phase mixing for 14 hours before further methanol (50-100 mL) was added in order to precipitate the deprotected polymer. The resulting solids were collected, redissolved in chloroform, precipitated in methanol and dried over night in a vacuum oven to give a colorless solid in >70% yield compared to the staring material (depending on polydioxepin content).

Results and Discussion

Telechelics form ABA and ABC Triblock copolymers:

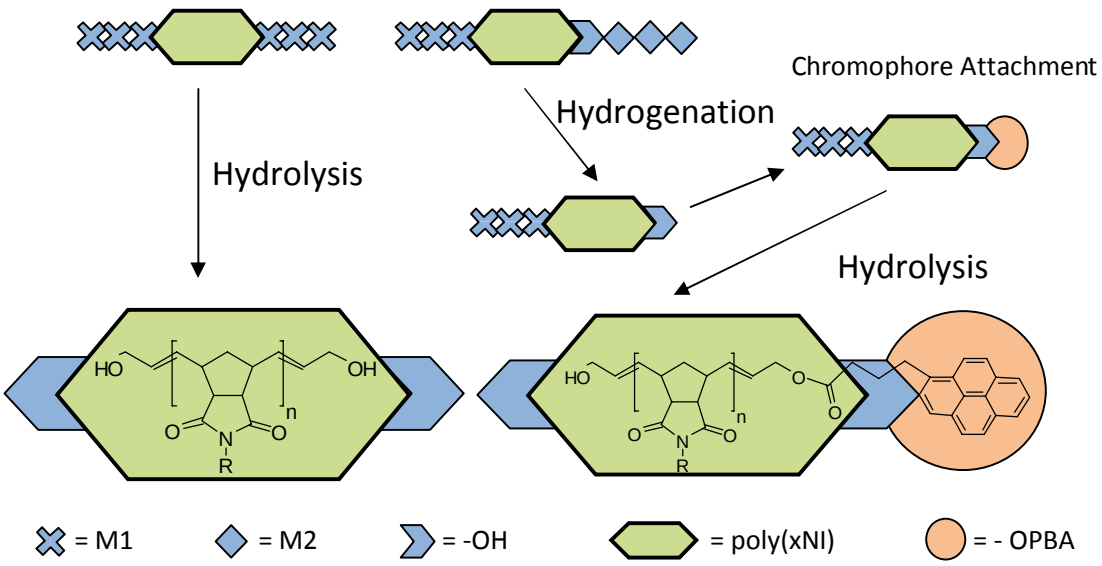
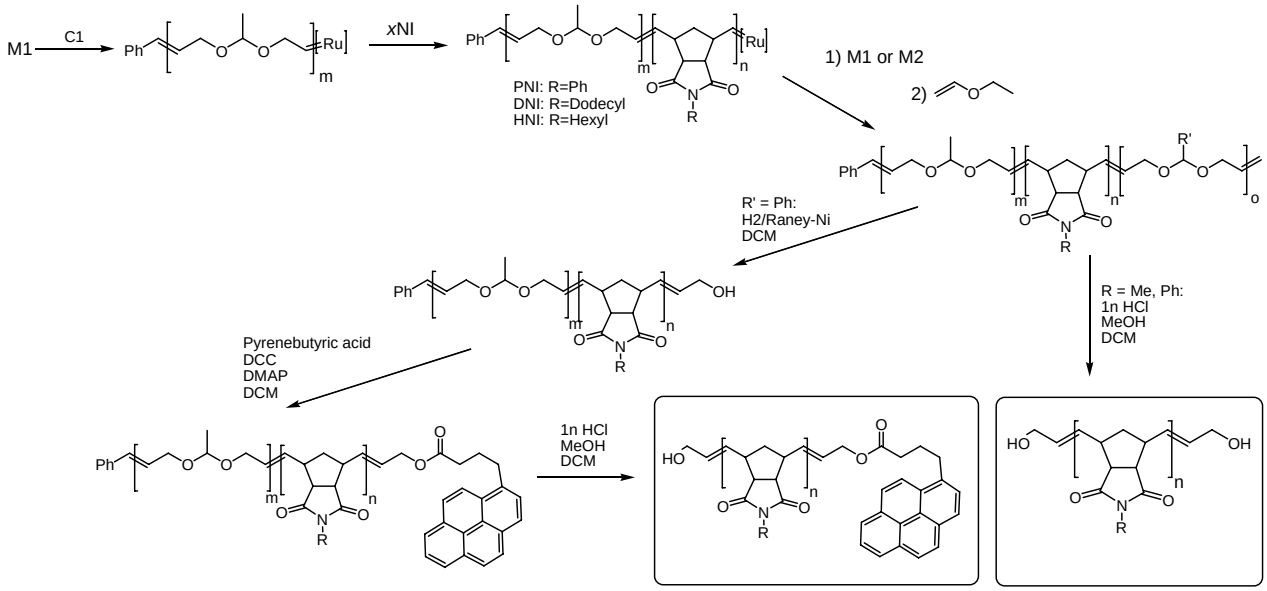


Figure 1. Principle of Sacrificial ABA and ABC Triblock-copolymers

The synthesis of telechelic ROMP polymers by a sacrificial approach involves the formation of triblock-copolymers. Two types of triblock copolymers can be prepared. The first type is a symmetric ABA-type (Fig.1 left) in which the stable polymer B-block is surrounded by hydrolyzable blocks made from monomer M1. The second type is a non-symmetric ABC-type (Fig. 1 right) in which A is poly-M1, B the stable polymer block and C poly-M2.

The latter approach involves two different dioxepines which can be addressed sequentially in subsequent cleaving reactions, allowing for precise placement of different substituents on the respective chain ends. For the synthesis of well-defined functionalized polymers by *Sacrificial Synthesis*, it is essential to ensure exact placement of the cleavable sites. Any infiltration of the stable polymer block with cleavable monomer units irrevocably leads to broad molecular weight distributions and loss of control over the average chain length. When cleavable monomers are polymerized prior to the stable block, it is therefore crucial to find a cleavable monomer that either polymerizes to completion or can be removed from the polymerization mixture without harming the living chain ends.

As outlined in Scheme 2, the synthesis of a polymer bearing hydroxyl-groups on each end of the polymer chain involves the polymerization of a polydioxepine homopolymer followed by the addition of the stable monomer and finally the second cleavable dioxepine block. Introducing monomer M2 as the second dioxepine, a different cleaving procedure can be utilized. Hydrogenation with Raney-Nickel is known to remove phenyl-acetals cleanly and leave deprotected hydroxyl-groups behind.[20]



Scheme 2. Synthesis of telechelic polymers by *Sacrificial Synthesis.*

Previously used dioxepine M2 and its isopropyl-derivative only form oligomers and can not be removed under reduced pressure due to their high boiling points. Yet, both M1 and its parent compound 1,3-dioxepine, have proven to polymerize to completion and can be removed under reduced pressure. 1,3-dioxepine, however, can be cleaved under chemically harsh conditions only, which limits its applicability in *Sacrificial Synthesis*.

Preliminary polymerizations of M1 exhibited broad molecular weight distributions of the resulting homopolymer. However, the subsequent polymerization of a second monomer that is known to polymerize in a living manner, gave a clean shift towards higher molecular weights, clearly showing that no termination reactions were induced by the polymerization of the first block. (c.f. Figure 2) When initiating monomer M1 with initiator C1, the low k_i/k_p value of M1 requires the addition of a large excess of M1 to the initiator in order to achieve full functionalization. Typically, 50-75 equivalents of M1 were applied in the first block.

After polymerization of the stable monomer block (xNI), the subsequent polymerization of the second M1 block performed in the same fashion as the first block. Similar amounts of M1 were applied as for the first block in order to ensure high functionalization. Interestingly, the low k_i/k_p-rate leads to the formation of a plateau-like maximum in the SEC trace. After hydrolysis of the polyacetal blocks, a polymer is retained that is well defined in is molecular weight and exhibits a Poisson-like molecular weight distribution as expected for a living polymerization (Fig. 2).

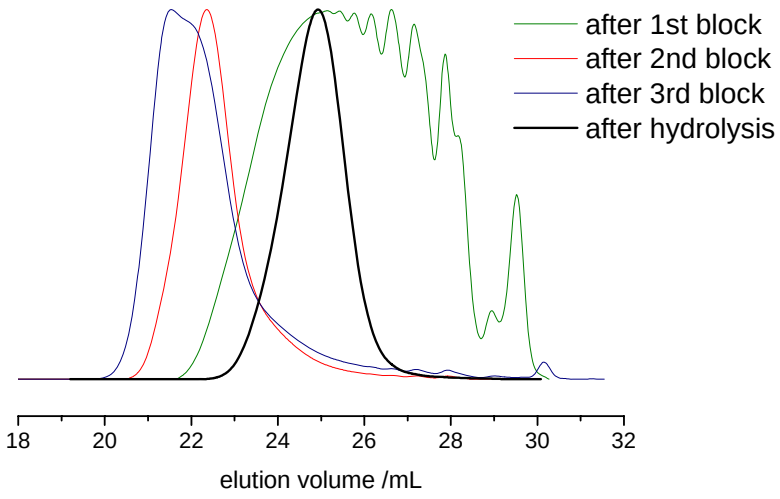


Figure 2. SEC-RI traces of poly(M1-*b*-PNI-*b*-M1) after each block and after hydrolysis of the polyacetal blocks.

When M2 is used as the second cleavable monomer, much smaller excesses of the dioxepine monomer are needed due to its lower k_i/k_p rate.[19] The respective SEC traces for the formation of a poly(M1-*b*-PNI-*b*-M2) triblock copolymer are given in the supporting information. It has to be noted at this point, that full conversion of the dioxepine monomer is needed in the case of subsequent addition of non-cleavable, i.e. stable monomers only. Complete conversion of the second dioxepine monomer to form the third block is not needed as long as every diblock chain has reacted with the second dioxepine at least once. In order to label chains that had not initiated the final dioxepine block, additional termination with ethyl vinyl ether was performed after the polymerization had finished. This termination leads to terminal olefins which can be assigned and quantified in the ^{1}H-NMR spectrum by their distinct signals.

Hydrolysis of all dioxepine blocks (M1 and M2) could be performed by addition of dilute acid. The reaction performed in the same manner as described for monofunctional polymers in earlier publications.[18,19] In addition, the poly(M2)-blocks were successfully removed by hydrogenation using Raney-Nickel as the catalyst. In this case, it is of outmost importance to remove the Ru-polymerization initiator as well as possible, as it can also act as a hydrogenation catalyst, thus hydrogenating the double bonds of the polymer backbone.

In order to prove the selective sacrificial decomposition of only one of the two polyacetal blocks of the triblock copolymer, the resulting OH-group was derivatized with a dye. Pyrenebutyric acid (PBA) was chosen since it had been successfully attached to a polynorbornene before.[18] PBA is an excellent UV dye typically used in labeling nanoparticles[21] and biomolecules such as amylopectin.[22] PBA was attached under mild coupling conditions using the classical DCC/DMAP (dicyclohexylcarbodiimide / 4-dimethylaminopyridine) system.[23] These conditions were chosen in order to avoid the presence of free acid at any time since this could trigger cleavage of the methyl-acetal (M1) block. This remaining polyacetal (M1) block was then cautiously sacrificed by addition of dilute acid.

The degree of functionalization was determined by ^{1}H-NMR. Telechelics prepared by acidic cleavage of both acetal blocks exhibited one set of signals for the methylene group next to the hydroxyl-function (at δ=4.1 ppm). The mono-derivatized polymer showed two distinct endgroup signals (*c.f.* Figure 3). The signals could be assigned to the polymer-C*H*$_2$-OH group (δ =4.1 ppm) and the corresponding ester polymer-C*H*$_2$-O-PBA δ=4.6 ppm) in accordance

with earlier publications.[18] Both NMR signals show similar integrals, and the integrals for residual styryl-endgroups induced by incomplete initiation of the first dioxepine block are minimal. This clearly shows the selectivity of both deprotection steps and the high degree of functionalization reached by the two dioxepine blocks. The presence of the pyrene moiety on the polymer chains was shown by SEC detecting a UV-signal at the maximum absorption wavelength of pyrene (340 nm). The respective SEC traces can be found in the Supporting Information.

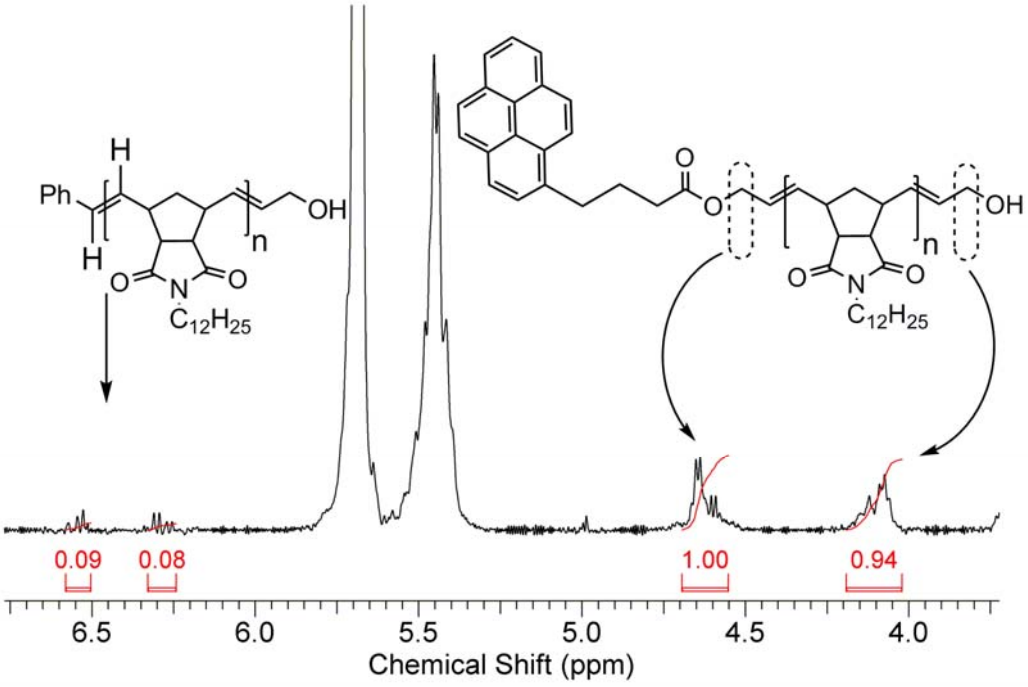


Figure 3. ^{1}H-NMR spectrum of HO-(DNI)$_n$-PBA showing both functional endgroups at 4.1 ppm (OH) and 4.6 ppm (PBA).

Similarly high degrees of functionalization are reached when both dioxepine blocks are removed in one acidic hydrolysis. A ^{1}H-NMR of the resulting polymer is given in the Supporting Information. In addition, the quality of the resulting materials could be shown by MALDI-ToF MS. The mass spectrum (Figure 4) shows no evidence at all for polymers bearing no functional group. The majority of signals observed correspond well to the calculated mass for the telechelic polymer (calc. 3785.01 m/z, observed 3787.1 m/z, both as Ag^{+} adducts).

Comparison with previously prepared mono-functional and non-functional polymers of the same monomer and similar molecular weight showed that only a small amount of mono-

functional impurity was present in the telechelic sample (Fig. 4). These monofunctionalized polymer chains are probably due to incomplete initiation of the first dioxepine block since they are bearing styryl starting groups originating from the initiator C1. However, these chains represent <4% of the total polymer as shown by ^{1}H-NMR experiments. It has to be noted, that the molecular weight of a polymer chain bearing two hydroxyl-endgroups is smaller than the monofunctional chain due to its lack of the styryl-endgroup generated by the initiator. The styryl group is removed during the cleavage of the first dioxepine block.

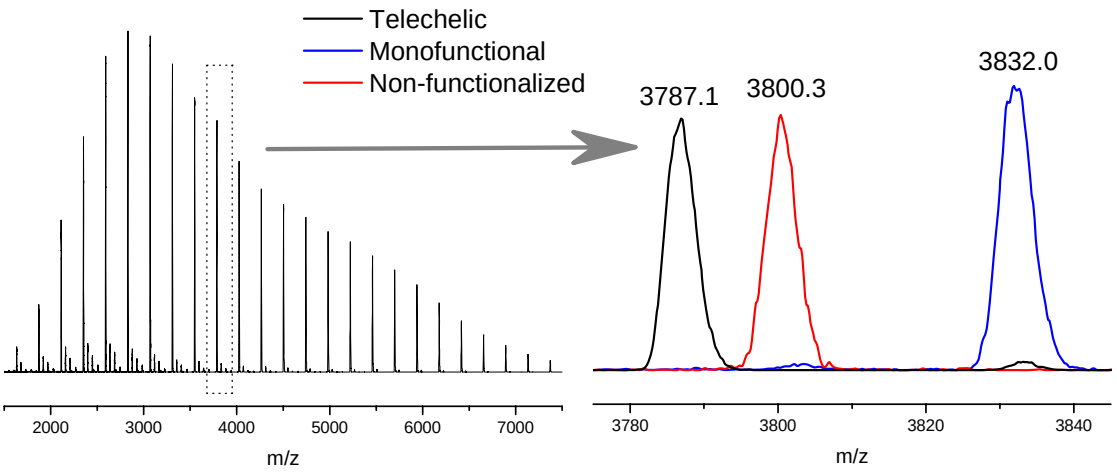


Figure 4. *Left*: MALDI-ToF MS spectrum of HO-(PNI)$_n$-OH. *Right*: Zoom of n=15 region and comparison to reference material (red and blue curve).

A number of different polymer materials were synthesized by this method, which are summarized in Table 1. Overall yields of this synthetic method ranged from 70-90% based on the norborneneimide monomer. As both dioxepine monomers are easy to synthesize even on large scale and work-up and cleavage of the protective dioxepine blocks is versatile, this method can be expected to be very useful for many applications.

Table 1. Characterization data of various telechelic polymers synthesized from triblock copolymers.

Entry	1st dioxepine	xNI	2nd dioxepine	FG[a]	Mn[b]	PDI
1	M1	PNI	M1	OH/OH	2700	1.30
2	M1	HNI	M1	OH/OH	3700	1.33
3	M1	PNI	M1	OH/OH	5500	1.25
4	M1	DNI	M2	OH/OH	6700	1.32
5	M1	PNI	M2	OH/OH	9600	1.21
6	M1	PNI	M2	OH/PBA	7800	1.23
7	M1	DNI	M2	OH/PBA	9700	1.25
8	M1	DNI	M2	OH/PBA	20200	1.29

[a)] functional groups; [b)] molecular weights given in g mol^{-1}

Polydispersity indices of all samples synthesized ranged from 1.2-1.3. They are a little higher than those obtained for monofunctional polymers by the *Sacrificial Synthesis* method using the same catalyst system, where PDI=1.2-1.25 is typically reached. This small difference, however, can be explained considering the different initiation behavior of a polydisperse poly(M1)-macroinitiator compared to the neat Grubbs 1st generation catalyst.

Telechelics from Multiblock copolymers

One drawback of the sacrificial triblock method for the synthesis of homotelechelic polymers is the consumption of one initiator molecule per telechelic chain. Since the characteristics of block copolymer formation between polynorborneneimides and dioxepine M1 had recently been established,[19] the question arose, as to what extent the addition of further alternating blocks of the two respective monomers would improve the yield of telechelic polymer chains per initiator molecule and thus lower cost of the desired material (Figure 5).

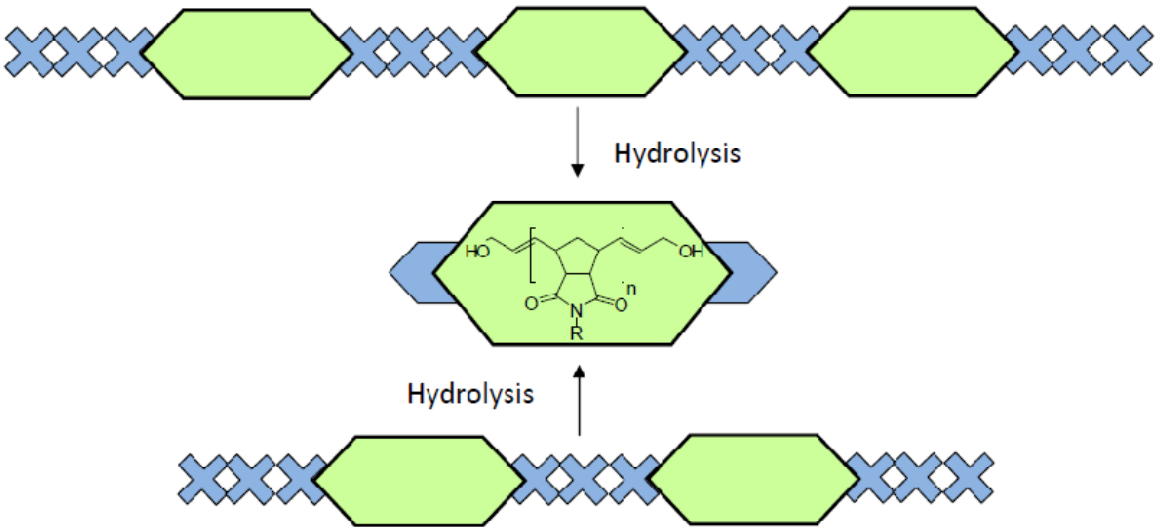


Figure 5. Formation of sacrificial multiblock copolymers and cleavage.

In order to test this concept, an ABABA pentablock-copolymer was synthesized and subsequently hydrolyzed by the same method as the triblocks (acidic hydrolysis). Figure 6 shows the GPC traces of the blockwise formation of the pentablock copolymer. A minor number of polymer chains can be found that were terminated during the polymerization of the second dioxepine block (3rd block) as these polymer chains did not reinitiate the 4th block (second polynorborneneimide block). However, hydrolysis of the final pentablock-copolymer resulted in cleavage of all dioxepine units and gave a polymer which showed a monomodal molecular weight distribution. In fact, the molar mass of the deprotected polymer is less than the masses of the individual multi-block samples, thus clearly showing the dioxepine separation between the two polynorborneneimide blocks. Any incomplete initiation at that point would have lead to a bimodal mass distribution of the final telechelic polymer.

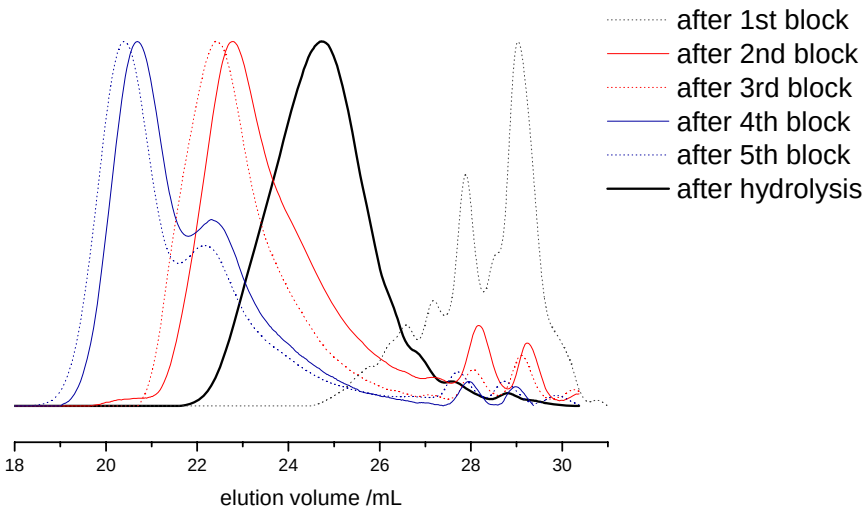


Figure 6. Formation of an ABABA pentablock-copolymer: SEC-RI traces of after each block (dotted lines after addition of acetal blocks, solid lines after stable blocks) and after hydrolysis of the polyacetal blocks (black solid line).

In analogy to telechelics synthesized from triblocks, the degree of functionalization was determined by ^{1}H-NMR. (see Supporting Information SI-6 top and SI-7 top for spectra) The total degree of functional endgroups was close to 100% in all cases. Minor signals could be found for styryl endgroups generated during the initiation of the first polynorborneneimide block (supporting information Figure SI-6, peaks at 6.3-6.6 ppm) . This shows that the efficiency of initiation of the first acetal monomer was greater than 95%. No signals could be found representing terminal olefin endgroups due to ethyl vinyl ether termination of the polynorborneneimide block.

The slightly higher total degree of functionalization is clearly a consequence of statistics: One initiator molecule forms two telechelic chains separated by a dioxepine segment. As this segment had been initiated in all chains, this could not create any non-functional groups. The probability of malformations at the beginning and the end of the pentablock copolymer due to incomplete initiation of the respective dioxepine blocks is the same as in the case of triblocks, however, these account for 50% of the functional groups in the case of sacrificial pentablocks only.

A further extension of the multiblock approach to a higher number of telechelics per initiator is especially interesting for short telechelics as their polymerization is fast and the

amounts of polymer obtained per catalyst molecule are particularly low. This consideration prompted us to explore ABABABA heptablock copolymers as a source for low molecular weight telechelics. The synthesis of the heptablocks performed quite well, as the blockwise GPC analysis given in Figure 7 demonstrates.

After hydrolysis, a monomodal telechelic polymer was retained; however, the PDI's of the telechelics synthesized from heptablock-copolymers were higher than those obtained from pentablock-copolymers (PDI around 1.5). Overall yields of the telechelic polymer as well as the degree of functionalization were similar to those obtained from sacrificial pentablock-copolymers, thus a higher number of telechelic polymer chains per initiator molecule had been reached.

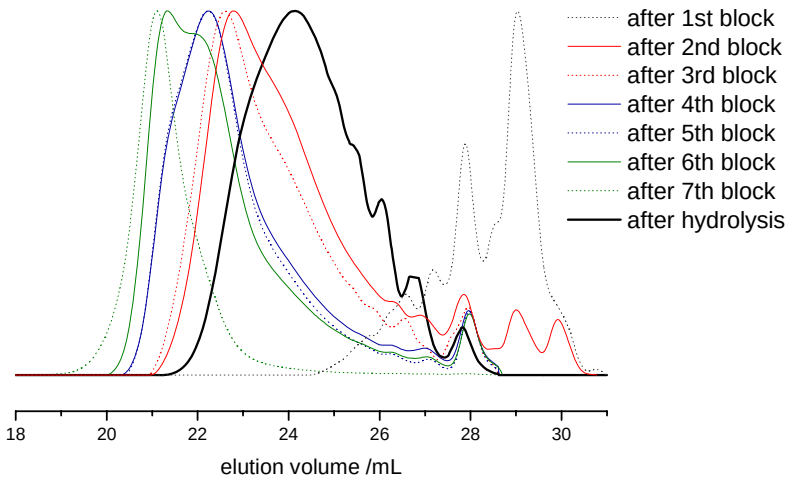


Figure 7. Formation of an ABABABA heptablock-copolymer: SEC-RI traces of each block (dotted lines after addition of acetal blocks, solid lines after stable blocks) and after hydrolysis of the polyacetal blocks (black solid line).

The average molecular weight of the telechelics is defined by the length of the polynorbornene blocks synthesized. It is of outmost importance to carefully tailor the amount of monomer added as the second and consecutive norborneneimide block in order to avoid broadening of the molecular weight distribution.

By choosing different segment lengths for the different polynorbornenimides in a multiblock copolymer, multimodally distributed telechelic polymers can be synthesized on purpose. An example for a trimodal polymer and its synthesis as a heptablock-copolymer and subsequent hydrolysis are given in the Supporting Information. The characterization

data for the bimodal pentablock equivalent is given in Table 2. Currently, telechelics with orthogonally deprotectable hydroxyl groups can not yet be prepared from multiblock-copolymers.

Table 2 summarizes a number of different materials synthesized by the multiblock approach. As careful purification of the monomers is a key factor in the formation of multiblock-copolymers, HNI and PNI were chosen as the non-cleavable monomer for this study since they can be obtained in excellent purity by high vacuum distillation or repeated recrystallization.

As expected, the degrees of functionalization that can be obtained by this heptablock approach lie close to 100%. The functionality of the synthesized polymer samples was confirmed by ^{1}H-NMR in the same manner as for those materials generated from the aforementioned tri- and pentablock copolymers. Two representative ^{1}H-NMR-spectra can be found in the Supporting Information (SI-6 bottom and SI-7 bottom)

Polydispersity indices increase with the number of blocks synthesized for the sacrificial block-copolymer. Multiple reinitiation and block transfer reactions cause broadening of the molecular weight distribution, presumably due to increasingly worsening block transfer reactions. A general trend can be found in which the controlled sacrificial block copolymer synthesis gives telechelics with narrowly distributed molecular weight distributions for low numbers of blocks. With an increasing number of blocks the polydispersity index approaches the statistical value of PDI =2.

The synthesis of sacrificial heptablock-copolymers clearly increases the amount of telechelic polymer that can be obtained per initiator. However, increasing the number of blocks also leads to a steady broadening of the molecular weight distribution.

In comparison to the previously reported method for telechel synthesis involving chain transfer agents, the method described here allows for both, control over molecular weight and molecular weight distribution. The metathesis kinetics of acyclic molecules differ largely from those of cyclic olefins. Therefore the metathesis polymerization of a CTA-monomer mixture will inevitably lead to long polymer chains with the CTA remaining unreacted at first. Reversible cross-metathesis between the primary polymer chain and the acyclic functionalizing agent leads to molecular weight control and the introduction of the functional endgroups. Therefore, the CTA-method is applicable mainly to polymers bearing unhindered double bonds, i.e. monocyclic monomer structures such as cyclooctene.[11]

The same holds for the statistical copolymerizations of cyclic hydrolyzable monomers and stable monomers.[12] Since copolymerization parameters of such monomer combinations can not be expected to give aceotropic copolymerizations at all times. Therefore the average molecular weight of the telechelic molecules cannot be expected to follow the stoichiometric ratio of monomer and CTA concentration initially.[24] These kinetic problems were overcome in the present approach with the blockwise addition of the two respective monomers leaving the control over the molecular weight distribution largely in the hands of the chemist.

Table 2. SEC-RI results of various telechelic polymers synthesized from sacrificial multiblock copolymers.

entry	xNI	# of blocks	# of Modes	Mn	PDI
9	HNI	5	1	2300	1.35
10	HNI	5	1	3700	1.33
11	HNI	5	1	5700	1.32
12	PNI	5	1	4800	1.36
13	HNI	5	2	7000	1.87
14	HNI	7	1	6100	1.49
15	PNI	7	1	3800	1.50
16	HNI	7	3	4100	2.4

Conclusion

Well-defined ROMP-polymers with narrow molecular weight distribution bearing exactly one functional group on both chain ends can be synthesized by *Sacrificial Synthesis*. Two cleavable polyacetal blocks were polymerized on either side of the desired polymer segment. Subsequent sacrificial cleavage of these blocks yields telechelics with hydroxy end-groups. By choosing two different dioxepines, two cleavable blocks that could be removed sequentially under different conditions could be achieved. A telechelic polymer was synthesized, whose functional end-groups could be addressed orthogonally.

For sacrificial triblock copolymers, high degrees of functionalization of both chain ends and good definition of the polymer molecular weight could be achieved.

Sacrificial penta and hepta-blocks in which the sacrificial and the desired polymer blocks alternate were prepared. These multi-block copolymers yield well-defined telechelic polymers after hydrolysis. The advantage of the latter approach is the reduced amount of ruthenium initiator consumed per telechelic chain. In addition, the successful synthesis of sacrificial hepta block copolymers can be seen as proof for the strength of the synthetic method.

The extension of Sacrificial Synthesis to telechelic polymers has opened a new field of interesting materials. As well-defined homo- and heterotelechelic polymers are of interest for many scientific applications, this versatile method may attract a number of polymer scientists.

Acknowledgements. The authors thank Materia, inc. for generous catalyst support. Ines Wollmer and Sabrina Samer are greatly acknowledged for laboratory assistance. S.H. thanks the POLYMAT Graduate School of Excellence and the IRTG International Research Training Group (DFG) for funding. AFMK thanks the Deutsche Forschungsgemeinschaft (DFG) for financial support.

References

[1] Rengifo, H. R.; Chen, L.; Grigoras, C.; Ju, J.; Koberstein, J. T. *Langmuir* **2008**, *24*, 7450-7456. Friedrich, J.; Kuehn, G.; Mix, R.; Fritz, A.; Schoenhals, A. *J. Adhes. Sci. Technol.* **2003**, *17*, 1591-1617.

[2] Pasut, G.; Veronese, F. M. *Prog. Polym. Sci.* **2007**, 933-961.

[3] Ribot, F.; Lafuma, A.; Eychenne-Baron, C.; Sanchez, C. *Adv. Mater.* **2002**, *14*, 1496-1499.

[4] Abadie, M. J. M.; Satibi, L. *Eur. Polym. J.* **1987**, *23*, 223-228.

[5] Nuyken, O. *Angew. Makromol. Chem.* **1994**, *223*, 29-46. Heitz, W. *Chem. Phys. Macromol.* **1991**, 61-95.

[6] Kricheldorf, H. R.; Adebahr, T. *Makromol. Chem.* **1993**, *194*, 2103-2115. Kricheldorf, H. R.; Chen, X; Masri, M. A. *Macromolecules* **1995**, *28*, 2112-2117.

[7] Guth, W.; Heitz, W. *Makromol. Chem.* **1976**, *177*, 3159-3175. Guth, W.; Heitz, W. *Makromol. Chem.* **1976**, *177*, 1835-1855.

[8] Otsu, T.; Yoshioka, M.; Tanaka, T. *Eur. Polym. J.* **1992**, *28*, 1325-1329

[9] Jagur-Grodzinski, J. *J. Polym. Sci:A*, **2002**, *40*, 2116-2133. Morton, M., *Anionic Polymerization: Principles and Practice*, Academic Press, New York, **1983**. Barner-Kowollik, C. *Handbook of RAFT Polymerization,* Wiley-VCH, Weinheim, **2008**. Matyjaszewski, K.; Xia, J.; *Chem. Rev*. **2001**, *101*, 2921-2990. Kamigaito, M.; Ando, T.; Sawamoto, M.; *Chem. Rev*. **2001**, *101*, 3689-3745.

[10] Hirao, A.; Hayashi, M. *Acta Polym.* **1999**, *50*, 219-231.

[11] Bielawski, C.W.; Benitez, D.; Morita, T.; Grubbs, R.H. *Macromolecules* **2001**, *34*, 8610-8618. Morita, T.; Maughon, B.R.; Bielawski, C.W.; Grubbs, R.H. *Macromolecules* **2000**, *33*, 6621-6623.

[12] Fraser, C.; Hillmyer, M. A.; Gutierrez, E.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 7256-7261

[13] Castle, T. C.; Hutchings, L. R.; Koshravi, E. *Macromolecules* **2004**, *37*, 2035-2040.

[14] Maynard, H.D.; Grubbs, R.H. *Macromolecules* **1999**, *32*, 6917-2924. Weck, M.; Mohr, B.; Maughon, B.R.; Grubbs, R.H. *Macromolecules* **1997**, *30*, 6430-6437. Owen, R.M.; Gestwicki, J.E.; Young, T.; Kiessling, L.L. *Org. Lett*. **2002**, *4*, 2293-2296. Gestwicki, J.E.; Cairo, C.W.; Mann, D.A.; Owen, R.M.; Kiessling, L.L. *Anal. Biochem*. **2002**, *305*, 149-155. Gordon, E.J.; Gestwicki, J.E.; Strong, L.E.; Kiessling, L.K. *Chemistry and Biology*, **2000**, *7*, 9-16. Chen, B.; Sleiman, H.F. *Macromolecules* **2005**, *38*, 1084-1090. Mangold, S. L.; Carpenter, R. T.; Kiessling, L. L. *Org. Lett.* **2008**, *10*, 2997-3000.

[15] Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M *J. Am. Chem. Soc.* **2008**, *130*, 11040-11048.

[16] Hilf, S.; Berger-Nicoletti, E.; Grubbs, R.H.; Kilbinger, A.F.M. *Angew. Chem*. **2006**, *118*, 8214-8217; *Angew. Chem. Int. Ed.* **2006**, *45*, 8045-8048. Perrier, S.; Wang, X. *Nature* **2007**, *445*, 271.

[17] Hilf, S.; Kilbinger, A.F.M. *Macromol. Rapid Commun*. **2007**, *28*, 1225-1230.

[18] Hilf, S.; Hanik, N.; Kilbinger, A.F.M. *J. Polym. Sci. A* **2008**, *46*, 2913-2921.

[19] Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M *Macromolecules* **2008**, *41*, 6006-6011.

[20] T. W. Green, P. G. M. **Wuts, *Protective Groups* *in Organic Synthesis***, Wiley- Interscience, New York, **1999**

[21] Wang, M.; Dykstra, T. E.; Lou, X.; Salvador, M. R.; Scholes, G. D.; Winnik, M. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 2221-2224.

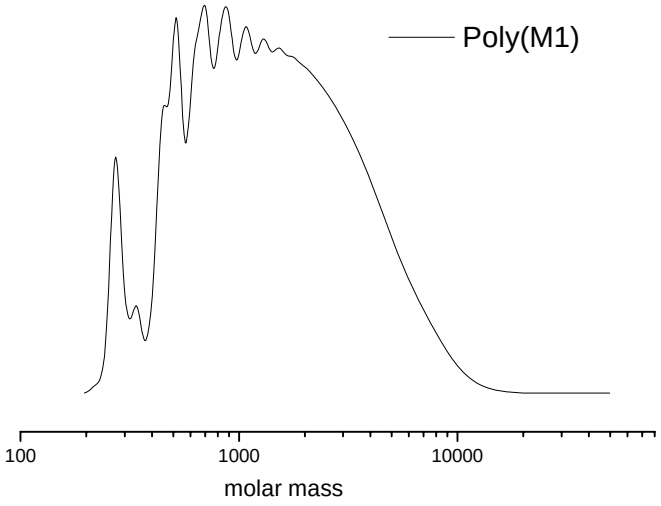
[22] Miranda, J. A.; Cacita, N.; Okano, L. T. *Colloids Surf., B* **2007**, *60*, 19-27.

[23] Williams, A.; Ibrahim, I.T. *Chem. Rev*. **1981**, *81*, 589-639.

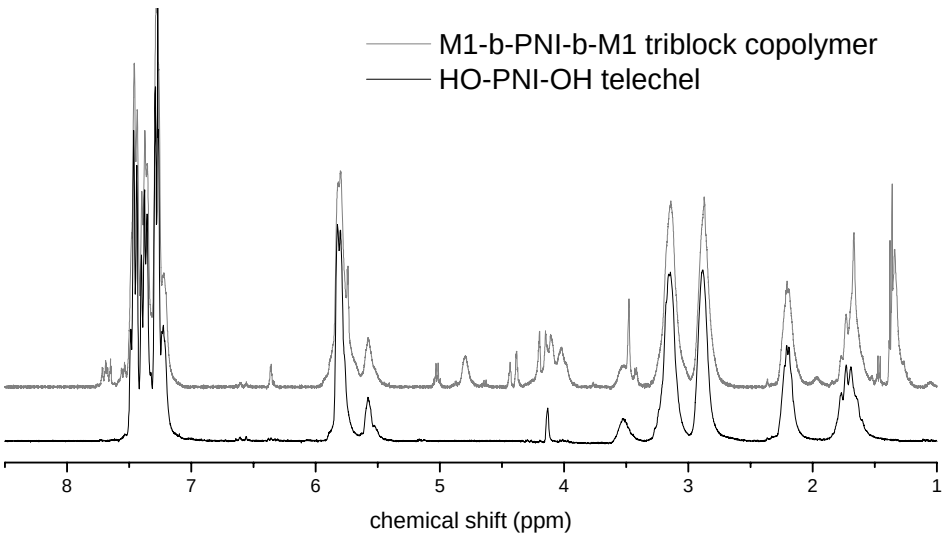
[24] Matson, J. B.; Grubbs, R. H. *Macromolecules* **2008**, *41*, 5626-5631.

Supporting Information for: Sacrificial Synthesis of Hydroxy-Telechelic Metathesis Polymers via Multiblock-copolymers

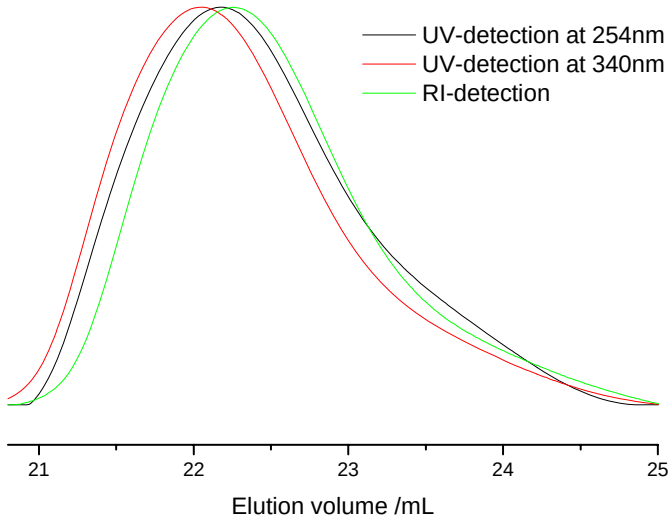
Stefan Hilf and Andreas F.M. Kilbinger



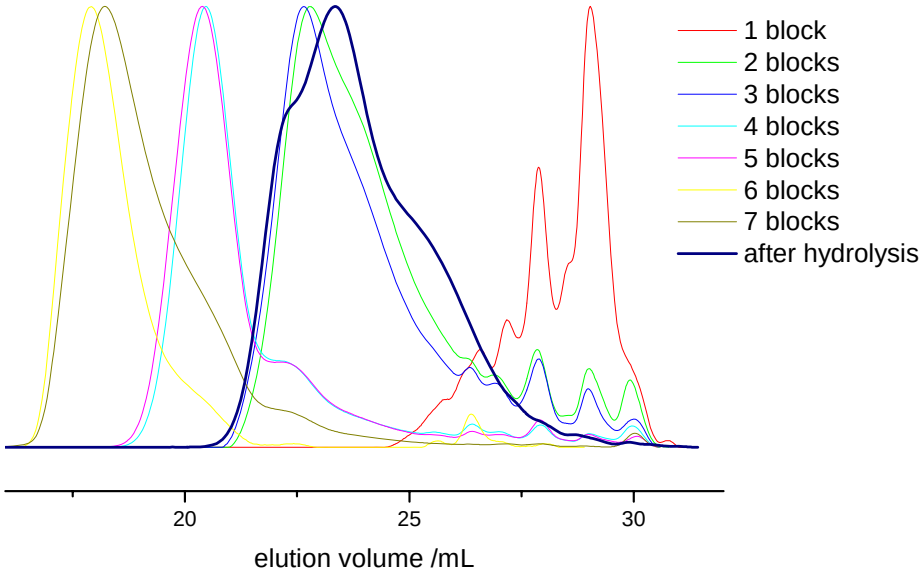
SI-1: SEC-RI trace of poly(M1).



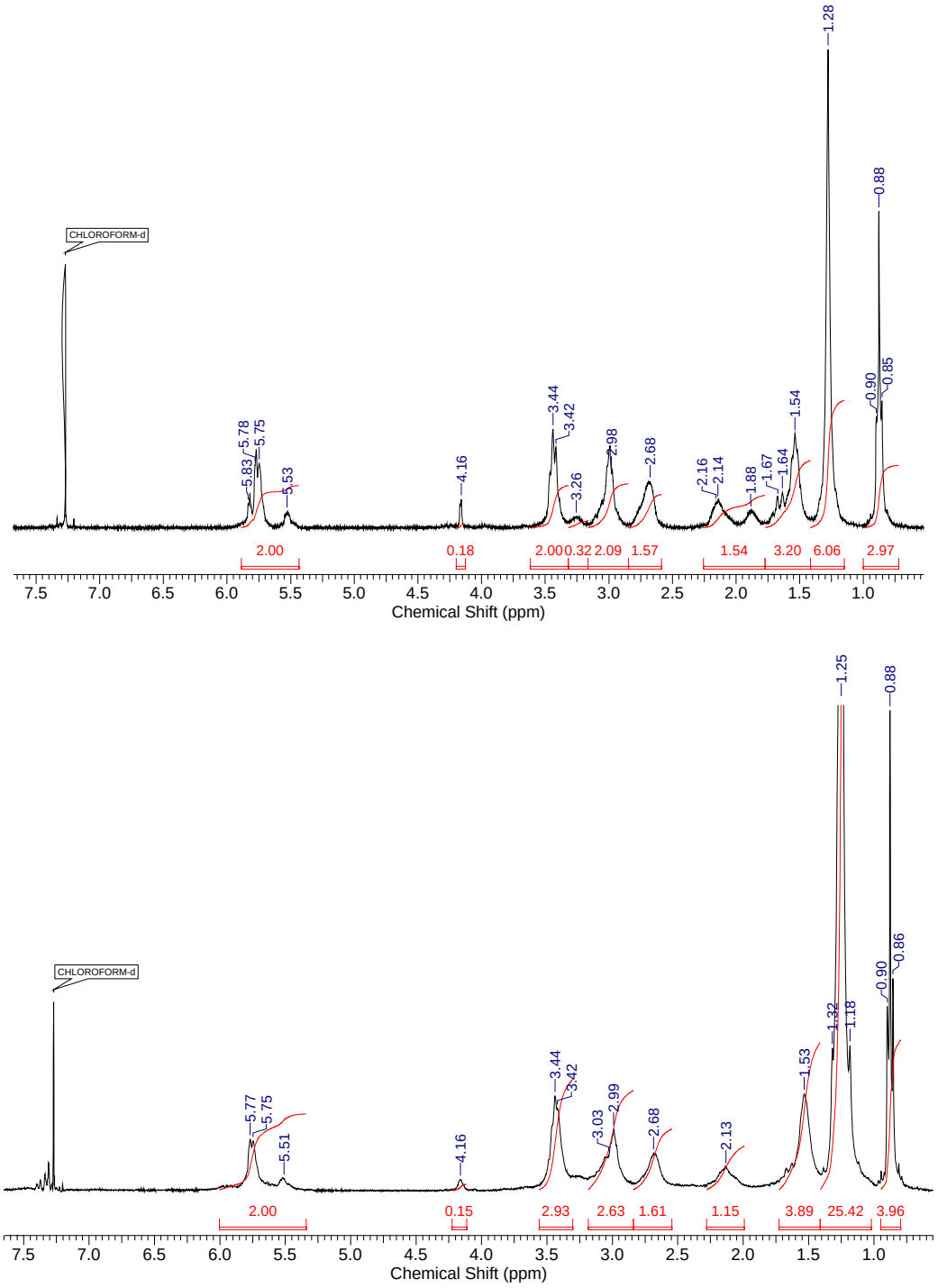
SI-2: ^{1}H-NMR of sacrificial triblock copolymer and resulting OH-telechelic poly(PNI)



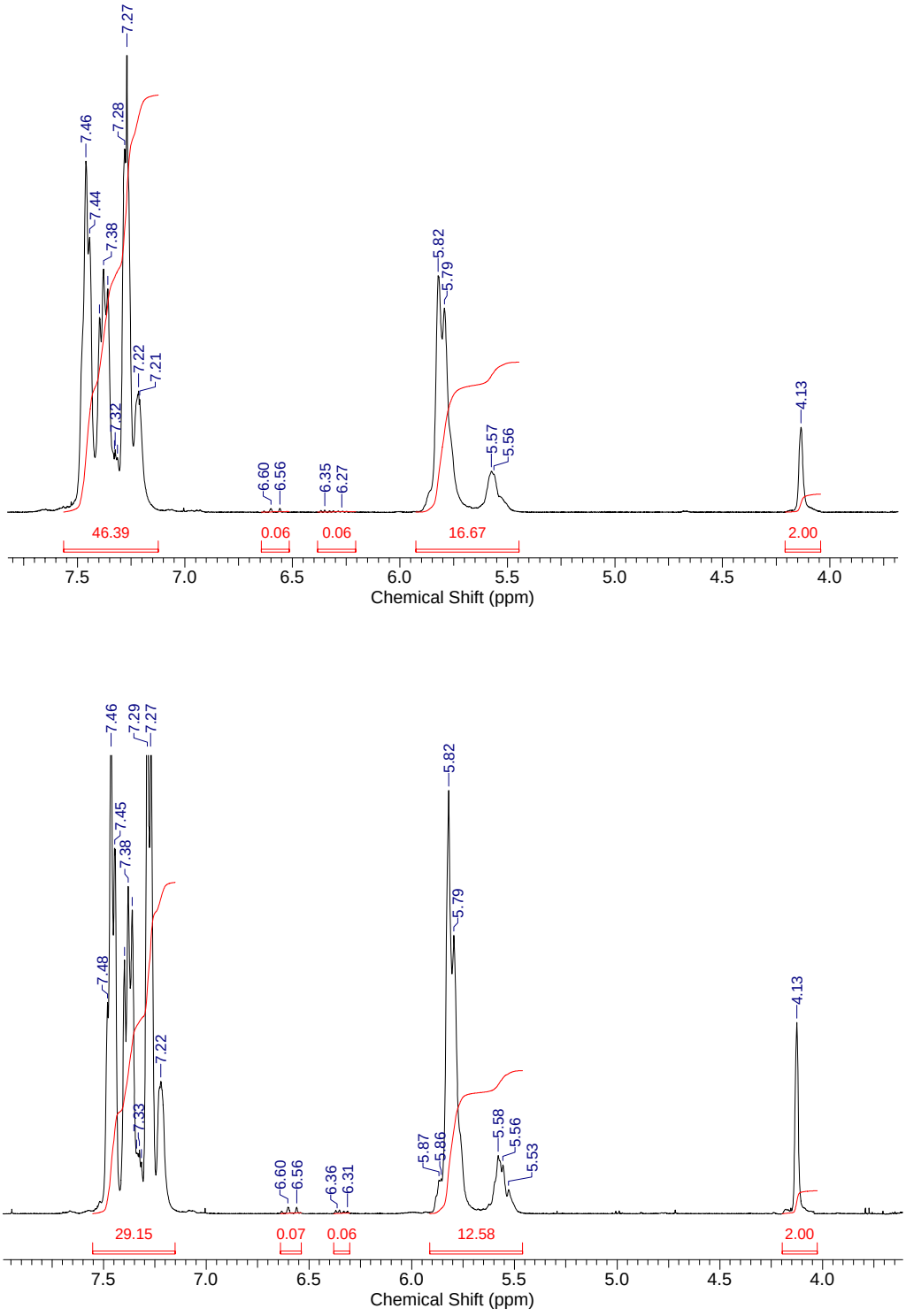
SI-3: SEC-traces of HO-poly(PNI)-OPBA with different detections.



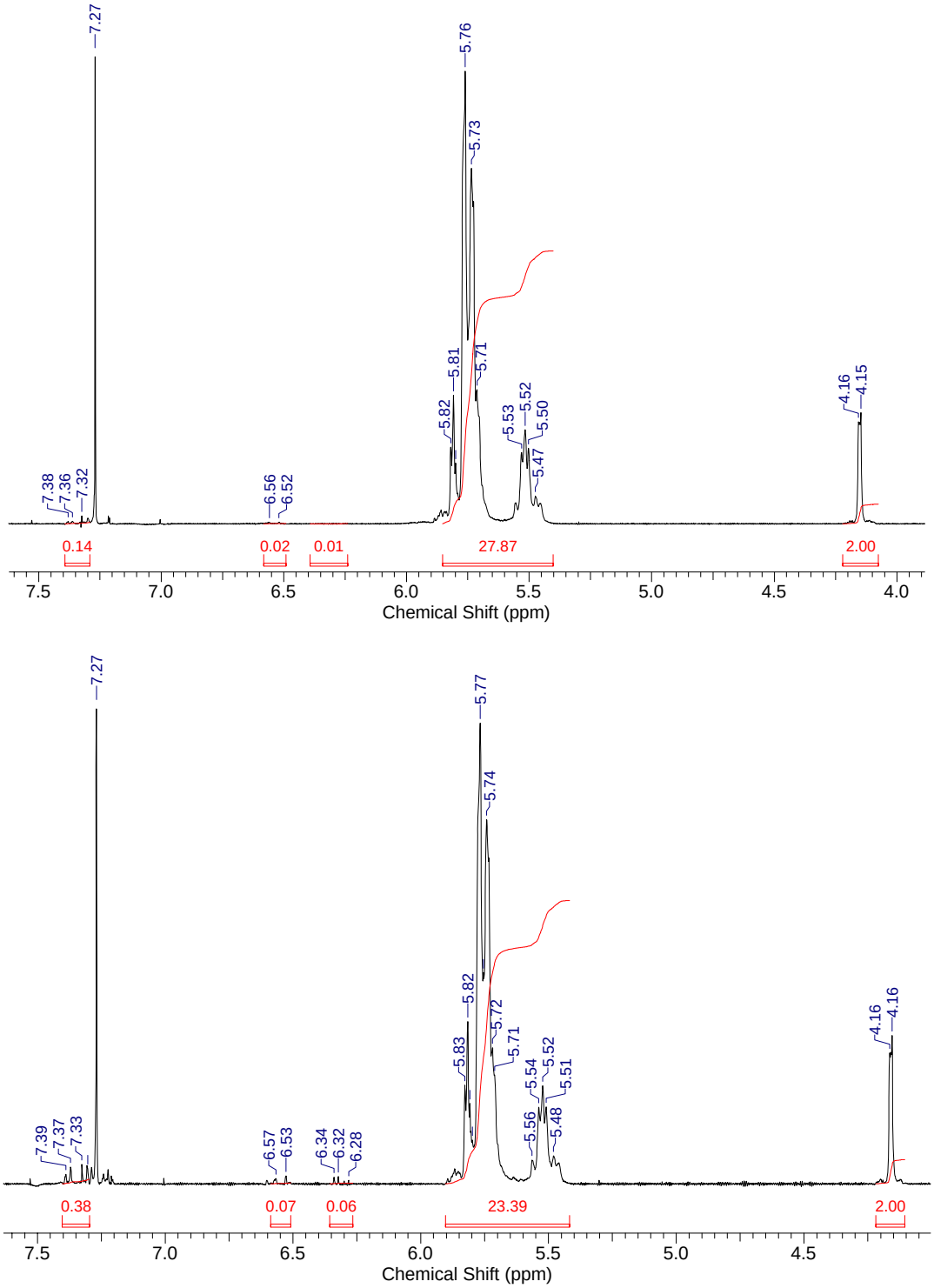
SI-4: SEC-RI traces of heptablock formation and trimodal molecular weight distribution after hydrolysis



SI-5: ^{1}H-NMR of OH-telechelic poly(HNI) (*top*) and poly(DNI) (*bottom*).



SI-6: ^{1}H-NMR of OH-telechelic poly(PNI) **12** (*top*) and **15** (*bottom*) hydrolyzed from their respective multiblock copolymers.



SI-7: ^{1}H-NMR of OH-telechelic poly(HNI) **11** (*top*) and **14** (*bottom*) hydrolyzed from their respective multiblock copolymers.

2.4: Thiol-functionalized ROMP polymers via Sacrificial Synthesis

Stefan Hilf and Andreas F.M. Kilbinger

Manuscript submitted on: 08.01.2009 to Macromolecules.

Abstract

The synthesis of well-defined and highly functionalized thiol-functionalized polymers has been accomplished via the ring-opening metathesis polymerization (ROMP). By choosing a synthetic approach based on the Sacrificial Synthesis concept, precise control over molecular weight and selective placement of the functional group was achieved. Thiol-functionalized ROMP-polymers were successfully synthesized employing thioacetal monomers, which can be cleaved by hydrogenation leaving the desired thiol group behind. The selective placement of this highly reactive functional group at exactly one chain end of a poly(norborneneimide) is demonstrated by analytical methods such as NMR and MALDI-ToF mass spectroscopy. By kinetic measurements, the functionalization efficiency and the polymerization characteristics of the used dithiepine monomer were determined. In a first demonstration, the coating of gold nanoparticles is shown as one interesting application of such functionalized metathesis polymers.

Introduction

Within the broad field of functional reactive polymers, the thiol group has established itself as a particularly interesting target.[1] Compared to their oxo-derivatives, thiols show increased reactivity in a number of reactions including nucleophilic substitutions, transition-metal complex formation and anionic binding to metal surfaces.[2] The electronic structure of sulfur, being able to occupy d-orbitals, can stabilize reaction intermediates such as radicals and ions in a manner inaccessible to alcohols.

These additional reaction pathways and the structural similarity of sulfur-containing connecting groups compared to their oxygen analoga have had great impact in the field of bio-conjugate and peptide chemistry. Especially the well-renown thiol-ene and thiol-maleimide "click" reaction[3] is of great importance in e.g. protein coupling to other synthetic molecules. There, a relatively stable radical species is formed which attacks the electron-deficient double bond of a maleimide bearing the desired counterpart for the respective conjugate.

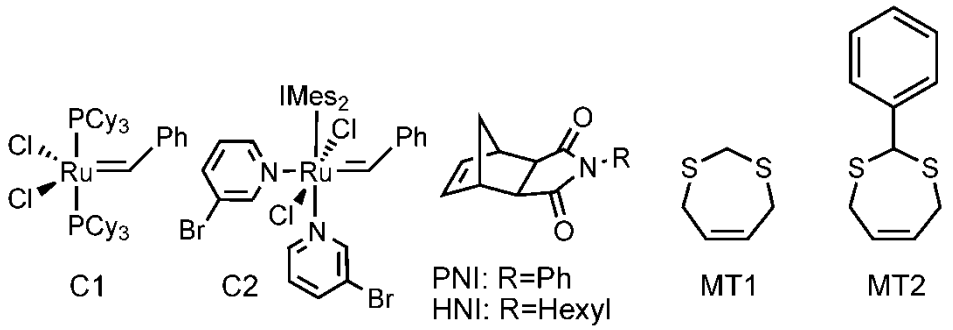
The thiol's tendency to form sulfur bonds to metal surfaces has been exploited largely in materials science and for analytical purposes. A number of thiol-functionalized low molecular weight molecules and polymers have been applied to gold nanoparticles and surfaces giving prefunctionalized electrode materials and synthons for derivatized nanoparticles in solid state chemistry. [4] By attaching various stimuli-responsive materials, sensoring properties[5] can be transferred to electrodes. Also, such thiol-bonding materials play an important role in surface plasmon resonance spectroscopy (SPR).[6]

Due to its high functional group tolerance, ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) has become a versatile tool in modern polymer and conjugate chemistry. A variety of interesting molecular motives have been polymerized by this ground-breaking method reaching from bio-active groups[7] to non-covalent binding motives.[8] Moreover, ROMP follows living polymerization characteristics for many monomer types, particularly strained and bicyclic olefins. The outstanding functional group tolerance, however, has limited the reaction pathways for efficient chain-end functionalization reactions to electron deficient olefins such as vinyl ethers[9] or the use of prefunctionalized catalysts[10] for a long time.

By introducing olefinic lactones[11] as a novel type of functionalizing agents, our group has recently managed to overcome many limitations of vinyl ether termination including slow kinetics of cis/trans isomeric double bonds and the need for subsequent deprotection reactions. This reaction strategy, as well as the classical vinyl ether termination, is not applicable for the attachment of thio-functionalities. It has been shown before, that vinyl thioethers rather act as a chain transfer agent as, in contrast to its oxo-analogue. The resulting thio-Fischer-carbene can undergo further metathesis steps. [12]

Sacrificial Synthesis[13] follows a completely different functionalization scheme. In this case, the functional group to be attached is hidden in a cyclic monomer that can be polymerized as an additional block. Therefore, it does not involve a termination reaction, but a macroinitiation. Cyclic acetal monomers, forming a polyacetal block were used, leaving exactly "half a dioxepine", *i.e.* a hydroxyl group at the chain-end after hydrolysis. Monofunctionalized polymers synthesized by this method have already found application in the synthesis of graft[14] and block copolymers.[15] Due to its unique, non-terminating functionalization,[16] it could also be used for the defined synthesis of hydroxy-telechelic polymers from tri-and multiblock copolymers.[17]

Thioacetals have been largely used in organic chemistry. Particularly the C-C coupling chemistry developed by Corey and Seebach[18] relies on the special stability of these structures allowing for umpolung reactions of carbonyl centers. They have also developed a variety of cleaving conditions for this protective group.[19]



Scheme 1. Initiators and the monomers used for the synthesis of thiol-functionalized ROMP polymers.

Here we present an extension of Sacrificial Synthesis to the introduction of thiol groups at precisely one chain end. By polymerizing the sulfur-analogues **MT1** and **MT2** of previously used dioxepines, a poly(thioacetal) block is built on the desired polymer which is then selectively cleaved by subsequent hydrogenation reaction. For this study, Grubbs' 1st generation catalyst **C1** and the bromopyridine complex **C2** were chosen as initiators and two different norborneneimide (***x*NI**) monomers which polymerize in a living fashion (*c.f.* Scheme 1). The successful placement of precisely one thiol endgroup on every polymer chain is proven by MALDI-ToF and ^{1}H-NMR of derivatized polymer samples. In addition, the polymerization characteristics are studied by kinetic analysis.

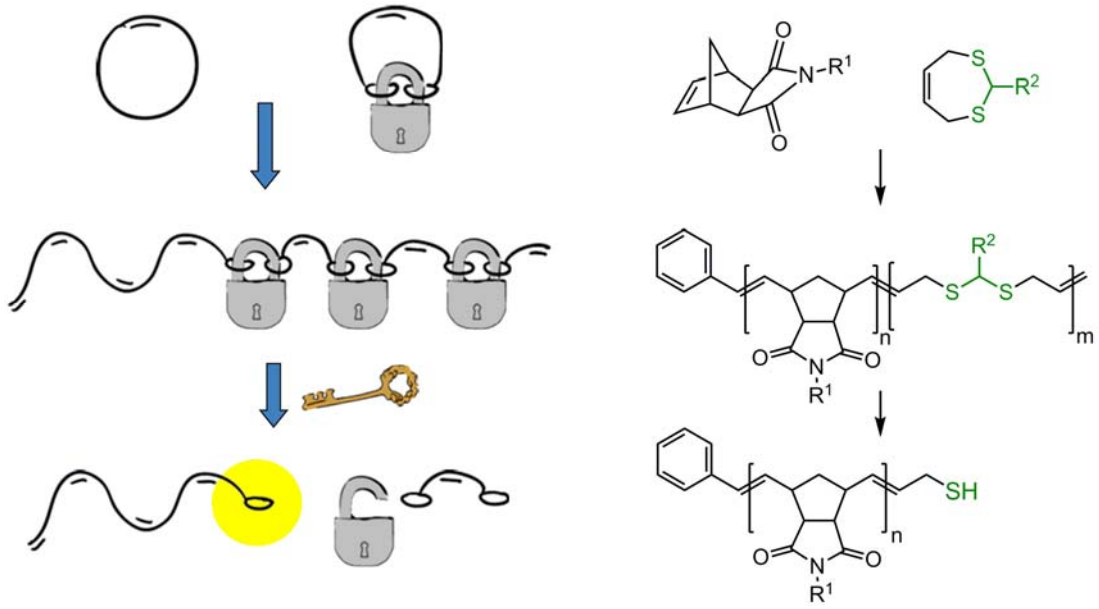


Figure 1. Principle of Sacrificial Synthesis of thiol-functionalized poly(norborneneimide)s. *Left*: Schematic representation. *Right*: Molecular structure.

Experimental

General. ^{1}H-NMR spectra were recorded at 300 MHz on a Bruker AC300 or at 400MHz on a Bruker ARX400. ^{13}C-NMR spectra were recorded at 75 MHz on a Bruker AC300. Time-resolved ^{1}H-NMR was conducted on a Bruker ARX400. All spectra were referenced internally to carbon or residual proton signals of the deuterated solvent. Deuterated solvents were purchased from Deutero GmbH. Size exclusion chromatography (SEC) in chloroform (poly(**PNI**)) or THF (poly(**HNI**)) was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P100 pump and a set of three PSS

SDV columns ($10^5/10^3/10^2$ Å). Signal detection occurred by use of a TSP Spectra System UV2000 (UV 254 nm unless otherwise stated) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-ToF) measurements were performed on a Shimadzu Axima CFR MALDI-ToF mass spectrometer equipped with a nitrogen laser delivering 3ns laser pulses at 337nm.

Exo-N-phenyl-2,3-norbornene dicarboximide (**PNI**), *exo-N*-hexyl-2,3-norbornene dicarboximide (**HNI**) and the bromopyridine complex **C2** were synthesized as described in earlier publications.[15] Grubbs' 1st generation ruthenium catalyst was obtained from Materia, inc. All solvents and other reagents were purchased from Aldrich or Acros and were used withous further purification. All polymerization reactions using initiator **C1** were carried out under argon using standard Schlenk techniques, polymerizations using initiator **C2** were conducted in a nitrogen filled glovebox. Dichloromethane as the polymerization solvent was dried over P_2O_5, distilled under a nitrogen atmosphere and stored over molecular sieves. Monodisperse gold nanoparticles with a diameter of 12.0 nm were prepared by the citrate-reduction method.[20] Substances **1**, **2** and **MT1** were synthesized as described by Harpp and Friedlander[21] with some variations:

*Synthesis of cis-1,4-dichlorobutene (**1**):*[21]

Thionyl chloride (100 mL, 1.4 mol) was added dropwise to *cis*-1,3-butenediol (50 mL, 0.6 mol) with rapid stirring under cooling with an ice bath. The reaction temperature was maintained below 10°C at all times in order to avoid isomerization. After all thionyl chloride had been added, the mixture was allowed to react for another 4 hours before the residual thionyl chloride was removed under reduced pressure. The resulting dark liquid was distilled under vacuum (bp=67°C, 23 mbar) to give a colorless liquid in good yield (58 g, 0.46 mol, 77%).

^{1}H-NMR (300MHz, $CDCl_3$) δ[ppm]: 4.12 (d, 4H, ^3J=5.9 Hz, CH_2); 5.84, t, 2H, ^3J=5.2 Hz, CH).

*Synthesis of cis-1,4-butene-dithioureate·2HCl (**2**):*[21]

A solution of 28 g (0.4 mol) of **1** in 200 mL ethanol were added 36 g (0.8 mol) thiourea. The solution was heated to 40°C until precipitation commenced. Heating was then discontinued as long as the reaction heat could maintain a gentle reflux. After refluxing for another 16 hours, the mixture was cooled with ice and the precipitate was filtered off and dried in vacuo to give 51 g (80%) of a pale solid which was used without further purification.

*One-pot synthesis of 2-methyl-1,3-dithiepine (**MT1**):*[21]

The thiouronium salt **2** (35 g, 0.22 mol) was dissolved in 600 mL methanol. KOH (solid, 66 g) was added in small portions over one hour under cooling with ice. The mixture was stirred over night to complete the formation of the dithiolate. Then, dibromomethane (18 mL, 43 g, 0.24 mol) dissolved in 200 mL methanol was added dropwise under cooling with ice. After the addition was completed, the reaction was allowed to finish over 60 hours before the methanol was removed at the rotary evaporator. The resulting solids were separated between ether and water (3x 200 mL) and the combined organic phases were dried with sodium sulfate. After removal of the solvent, the obtained solids were recrystallized from pentane to give colorless needles (15 g, 0.11 mol, 50%).

^{1}H-NMR (300MHz, $CDCl_3$) δ[ppm]: 3.47 (4H, d, ^{3}J= 6.6 Hz, CH_2); 4.01 (2H, s, S-CH_2-S); 5.9 (2H, m, double bonds).

*One-pot synthesis of 2-phenyl-1,3-dithiepine (**MT2**):*

Was synthesized under the same conditions as **MT1** starting with 8 g (0.05 mol) of the thiouronium salt **2** and subsequent addition of □□□-dibromotoluene to the dithiolate over 6h. The solids were cleaned by column chromatography over silica using petroleum ether / chloroform 9:2 (v:v) as the eluent (Rf=0.45) yielding 5.7 g (30 mmol, 60%) of a colorless solid.

^{1}H-NMR (300MHz, $CDCl_3$) δ[ppm]: 3.5-3.6 (4H, m, CH_2); 5.30 (1H, s, S-CH-S); 6.0-6.1 (2H, m, double bonds); 7.28-7.45 (m, 5H, Ph). ^{13}C-NMR (75MHz, $CDCl_3$) δ[ppm]: 30.39

(2C, CH2) ; 59.63 (1C, S-C-S); 127.89(1C, Ph: C_p); 128.43(1C, Ph: C_m); 128.72(1C, Ph: C_o); 129.17 (2C, C=C); 139.49 (1C, Ph: C_i). FD-MS: 208.1 m/z (calc. 208.34 g/mol).

*General synthesis of poly(norborneneimide-b-dithiepine) blockcopolymers using catalyst **C1**:*

The calculated amount of Grubbs 1st generation catalyst was dissolved in 5 mL dichloromethane in a Schlenk flask. The appropriate amount of monomer **xNI** was dissolved in dichloromethane (10 mL per 1 g monomer) and added to the solution by syringe. After the polymerization had finished (ca. 1h for 10000 g/mol), a 40-fold excess of **MT2** was added with continued stirring. The polymerization was terminated by adding 1 mL ethyl vinyl ether after another 4 hours. The polymer was obtained by precipitation in methanol and repeated redissolution in chloroform and precipitation in methanol to give a dark solid material in good yield (>80% typical).

*General synthesis of poly(norborneneimide-b-dithiepine) blockcopolymers using catalyst **C2**:*

In a glovebox, 42 mg of the initiator **C2** were dissolved in 2 mL dichloromethane in a septum-capped vial. The appropriate amount of monomer **xNI** dissolved in dichloromethane (10 mL per 1 g monomer) was added quickly by syringe with rapid stirring. After the polymerization had finished (ca. 15min for 10000 g/mol), the calculated amount of **MT2** was added with continued stirring. The polymerization was terminated by adding 100 µL ethyl vinyl ether after hour. The polymer was obtained by precipitation in methanol to give an off-white material in good yield (>85% typical).

General procedure for the hydrogenation of the dithiepine block:

The polymer was dissolved in dichloromethane (ca. 50 mL per 1 g polymer) and transferred into a hydrogenation reactor. A slurry of Raney nickel in methanol (solvent exchanged from water) was added (1 mL of the original 50% slurry in water per 1 g polymer) before the mixture was degassed and purged with hydrogen three times. After

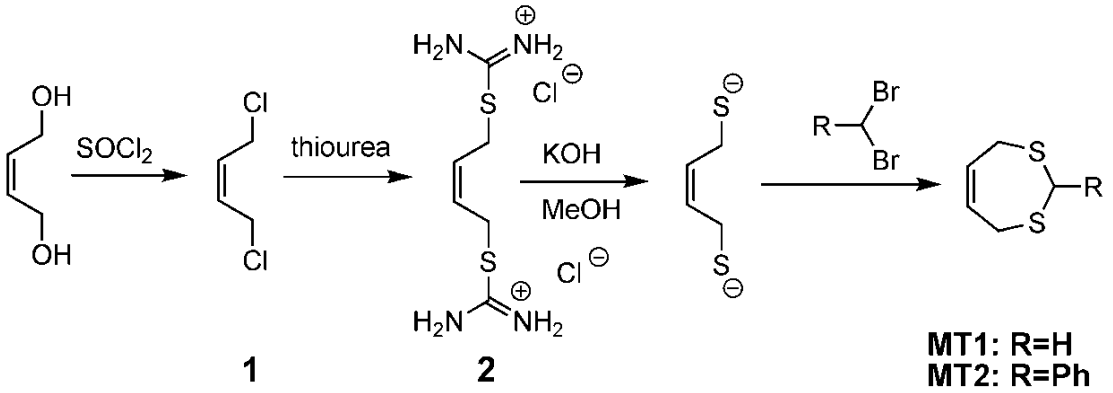
14 hours at 8 bar hydrogen pressure under stirring, the solution was filtered over Celite, the dichloromethane was evaporated and the polymer solution was precipitated in methanol, collected, redissolved in chloroform and reprecipitated in methanol. Colorless polymer samples were obtained when catalyst **C2** had been used to initiate the polymerization. Exemplary ^{1}H-NMR for poly(**PNI**) and poly(**HNI**)-SH are given in the Supporting Information (SI-1).

General procedure for the formation of 3,5-dinitrobenzyl-thioesters of the functionalized polymers:

100 mg of the thiol-bearing polymer (ca. 0,02 mmol) were dissolved in 2 mL dimethylformamide. 20 mg dimethylaminopyridine (0.17 mmol) and 30 mg 3,5-dinitrobenzoylchloride (0.13 mmol) were added and the mixture was stirred for 10 hours at r.t. before the solvent was removed in vacuo. The remaining solids were dispersed in chloroform, filtered and precipitated in methanol twice to give an off-white polymer material. Exemplary ^{1}H-NMR for poly(**PNI**) are given in the Supporting Information (SI-2)

Results and Discussion

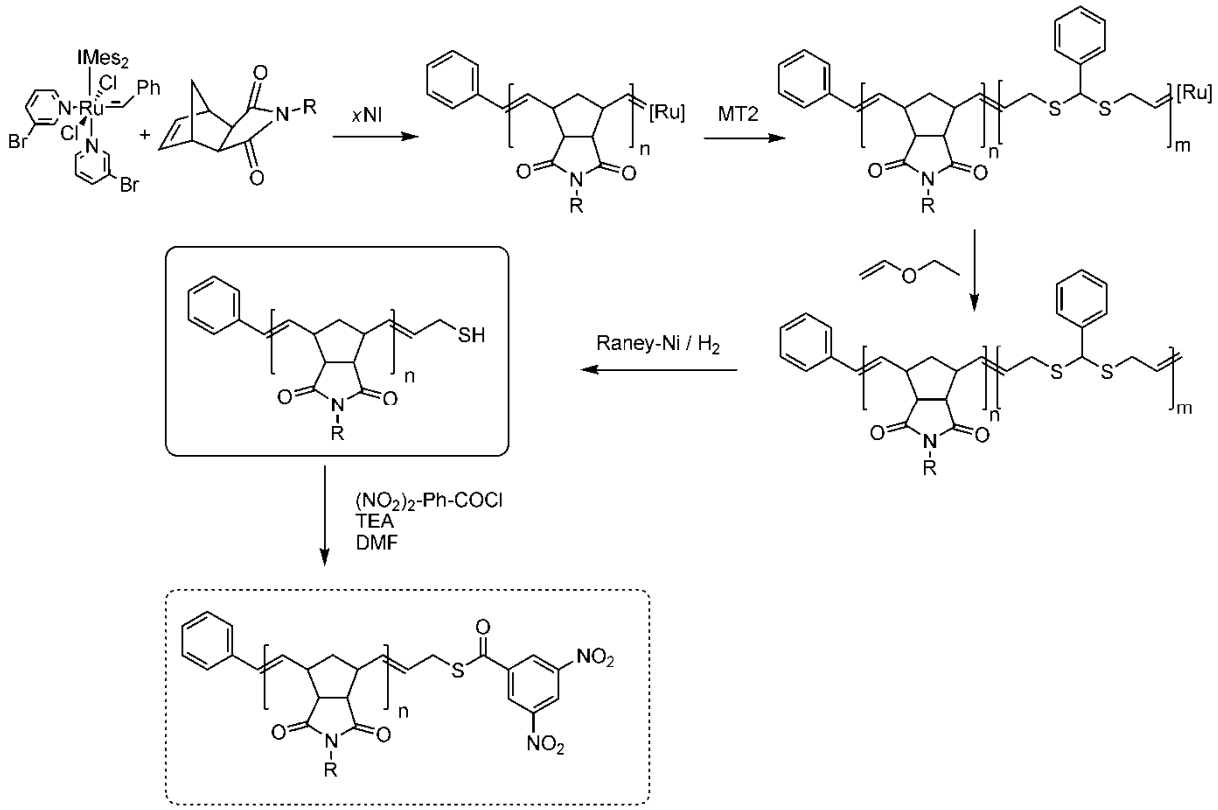
For the synthesis of monomers **MT1** and **MT2**, a method was chosen in which the thioacetal was formed from the readily accessible thioureate **2** precursor in a one-pot synthesis (Scheme 2). The handling of dithiol compounds could thus be avoided. The functional group in the 2-position could be varied using the respective geminal dihalide added to the dithiolate intermediate. Subsequent recrystallization or column chromatography gave pure compounds. The phenyl substituted dithiepine was chosen because aromatically substituted dithioacetals could be cleaved by catalytic hydrogenation before.[22] The unsubstituted dithiepine, on the other hand, imposes minimal steric hindrance to metathesis reactions and was expected to polymerize better than the oxo-analogues used by Fraser et al.[23] and by our group.



Scheme 2. Synthesis of dithiepines **MT1** and **MT2**.

From both thioacetal monomers, block copolymer synthesis was performed with catalyst **C1** and a norborneneimide monomer for the stable first block (Scheme 3). The GPC traces of the block-copolymerization with **MT1** revealed an incomplete block transfer to the second block (SEC given in the Supporting Information SI-3) and subsequent cleavage employing *N*-bromosuccinimide or Hg^{2+} salts resulted in cross linked polymers or did not cause cleavage at all.

Addition of **MT2** to a polymerization initiated by **C1** gave slightly better block transfer at the same excess of the thioacetal monomer as applied for **MT1**. Virtually complete block transfer was reached only by applying large excesses (>40 Equivalents) of **MT2** (*c.f.* Figure 2) indicating a very small k_i/k_p rate for this monomer. After the polymerization reaction had finished, ethyl vinyl ether quenching was performed in order to terminate all residual metathesis activity and remove the ruthenium species from the polymer chains.



Scheme 3. Sacrificial Synthesis of thiol-functionalized poly(norborneneimide)s

The polymer block formed from **MT2** was then removed by hydrogenation with Raney-nickel over night. At this point, it has to be emphasized that full macro-initiation (block transfer) is a key condition for the viability of the Sacrificial Synthesis method, as only chains that have initiated the cleavable monomer, remain functionalized after the removal of the sacrificial block.

Figure 2 shows as an example the GPC traces of poly(**PNI**)-*b*-poly(**MT2**), initiated with catalyst **C1**. 40 equivalents of **MT2** were employed in this reaction and complete block transfer can be observed. It has to be noted at this point, that the color of the polymer samples darkened strongly during the cleavage step. Almost black materials were obtained after work-up of the hydrogenation. Apparently, the ruthenium catalyst had strongly coordinated to the thioacetal block avoiding removal of the ruthenium after termination of the reaction.

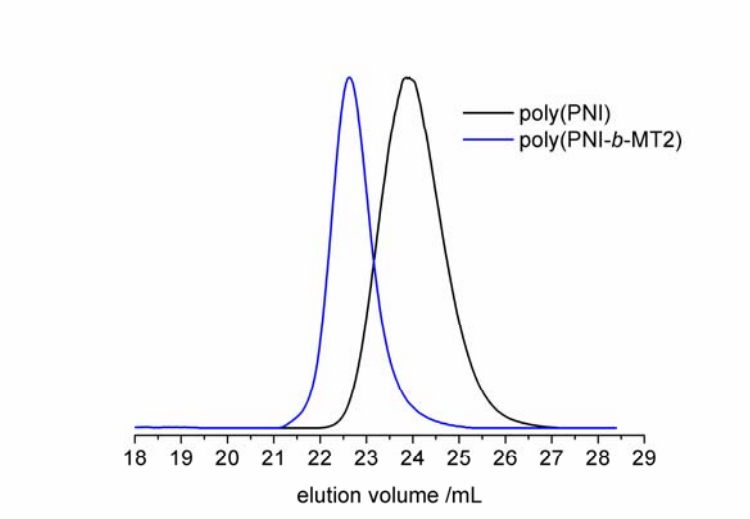


Figure 2: SEC-RI traces of poly(**PNI**) and poly(**PNI**-*b*-**MT2**) initiated by catalyst **C1** after addition of 40 equivalents **MT2**.

When catalyst **C2** was used to initiate the block-copolymerization, the shift of the molecular weight distribution after addition of **MT2** was minimal although 20 equivalents of **MT2** had been added (SEC given in the Supporting Information, SI-4). Given ample time to finish the metathesis reaction with the cleavable monomer, ethyl vinyl ether termination was conducted. Subsequent treatment of the obtained polymer with hydrogen under Raney-nickel catalysis resulted in the formation of thiols, as their characteristic smell revealed. Virtually colorless materials were yielded in all cases. Also, thiol endgroups could be found exclusively in the MALDI-Tof MS of the material (Figure 3). No indications for side reactions during the hydrogenation step such as backbone hydrogenation have been observed. This is in contrast to the hydrogenation cleavage involving Ph-dioxepine,[17] where such side reactions were observed. We believe that this is due to the poisoning of residual ruthenium by the liberated hydrogenation products thereby preventing it from hydrogenating olefins. Also, no signs of a desulfurization at the chain end has been found in the MALDI-ToF mass spectra. The degree of functionalization was determined by ^{1}H-NMR of the polymer after derivatization with 3,5-dinitrobenzoyl chloride (*c.f.* Figure 4).

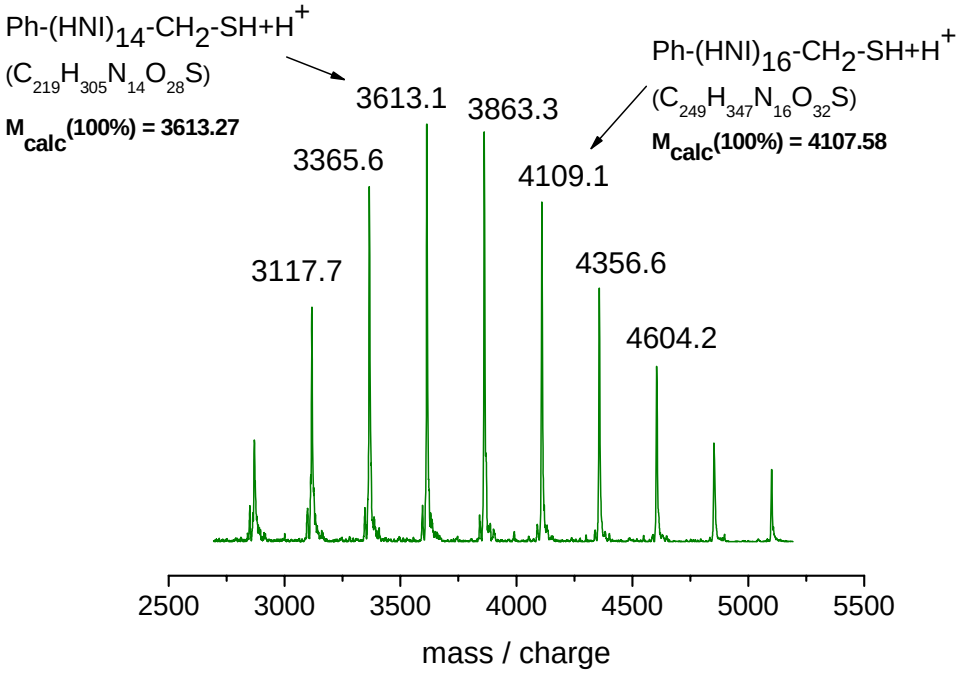


Figure 3. MALDI-ToF spectrum of poly(**HNI**)-SH. Matrix: dithranol, potassium triflate.

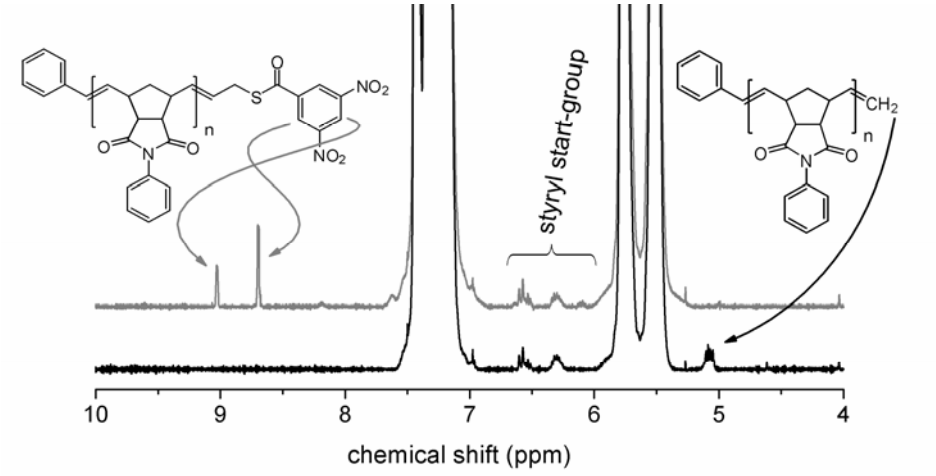


Figure 4. ^{1}H-NMR determination of the total degree of functionalization after derivatization of poly(**PNI**)-SH and non-functionalized reference material obtained from ethyl vinyl ether termination (Spectra including integrals are given in the Supporting Information).

By comparison of the resulting aromatic thioester signals (at δ=9.04 ppm and δ=8.70 ppm) to the signals representing the styryl endgroup (at δ=6.55 ppm and δ=6.30 ppm) (*c.f.* Figure 4), which is generated during the initiation step, the percentage of polymer chains bearing the desired functional group could be determined. The overall degree of functionalization obtained by this method was >95%.

In order to determine the efficiency of this functionalization method, kinetic aspects of the macroinitiation step and the following polymerization of the thioacetal block had to be determined. In analogy to our study on the behavior of different acetals, this included kinetic ^{1}H-NMR observation of the initiation step. This experiment was conducted with addition of 10 equivalents of **MT2** in order to ensure pseudo-first order conditions throughout the course of the reaction. It was performed on four different types of catalysts: **C1** and **C2**, as well both catalysts after initiation with 15 equivalents of **PNI**, which had proven to be far more reactive towards macroinitiation in the acetal study.

Catalyst **C1** showed no initiation activity on **MT2**, yet the carbene did not decompose significantly over the period of 10 hours. When **MT2** had been initiated by a norbornene monomer a slow initiation could be observed. This difference in the versatility of the initiation is typically observed on most ruthenium-based catalyst systems.[16] If initiated with **PNI**, the macroinitiation step to the **MT2**-block was slow (spectra given in the Supporting Information SI-5). The assumption that could be drawn from the preliminary test polymerization was therefore confirmed, which had shown that the rate of polymerization is high, while the rate of initiation is not. There, extremely large excesses of **MT2** had to be applied in order to approach complete initiation of the sacrificial block.

As a consequence, initiation of **MT2** was performed with the much more reactive catalyst **C2**. This latest-generation catalyst is well renowned for its ultra-fast initiation kinetics on all kinds of even mildly reactive cyclic olefins. Partly, this outstanding property is credited to the weakly associated pyridyl ligands which facilitate the coordination of olefins. When **MT2** was applied to catalyst **C2**, a quick initiation reaction could be monitored in time-resolved ^{1}H-NMR (*c.f.* Figure 5). The decay of the benzylidene signal followed clear first-order kinetics and k_i could be determined from the integration data obtained (k_i=5.5 L/mol s^{-1}). When **C2** had been initiated with 15 equivalents of **PNI** before **MT2** was added, the block transfer reaction was too fast to be

monitored by ^{1}H-NMR. No residual carbene signal originating from norbornenyl-carbenes (δ=18.54 ppm) could be found any more in the first measurement after the addition. The respective spectra are given in the Supporting Information (SI-6). Their complete conversion to a novel carbene species at δ=18.07 ppm demonstrated good stability of the initiator towards the thioacetal monomer. The rate of reaction was high, as more than 10 half-lives of the reaction had been passed during the first minute of the reaction.

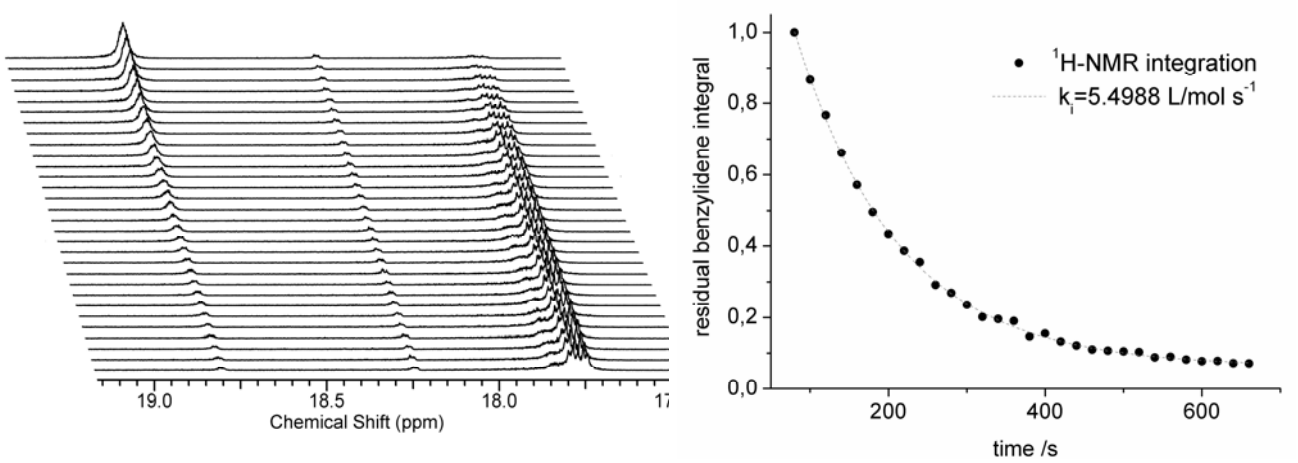


Figure5: Time-resolved ^{1}H-NMR of the reaction of initiator **C2** with 10 equivalents of **MT2** (Δt=20s) (*left*) and kinetic evaluation of the carbene integrals (signal at 18.8 ppm*, right)*.

However, no information about the actual polymerization reaction could be obtained from kinetic NMR due to strong signal overlap. Therefore, the k_i/k_p ratio could not be determined by this method. In order to fully comprehend the functionalization behavior of the thioacetal monomer, knowledge of this factor is vital. As we had shown in the acetal study, this key ratio can be obtained from a series of functionalizations at different amounts of functionalizing sacrificial monomer added. The degrees of functionalization could be used in order to calculate this factor from Swarcz's equation (1).[24,25]

$$\frac{M_{total}}{C_{total}} = \left(\frac{k_p}{k_i}\right) \cdot \left[\ln(1-f)^{-1} - f\right] + f \quad (1)$$

For this, a series of functionalization reactions was conducted, followed by hydrogenation cleavage of the sacrificial block and subsequent derivatization with 3,5-dinitrobenzoyl chloride. The functionalization was calculated from the resulting ^{1}H-NMR signals as shown in Figure 6. The results were used to fit equation (1) accordingly and thus obtain the k_i/k_p factor, which was determined to be k_i/k_p=0.31. It has to be noted, that the degrees of functionalization obtained from the experiment are higher than expected from the fit when fitting is based on the values for 1 and 2 equivalents of **MT2**. The same effect has been discovered for 2-phenyl-1,3-dioxepine in the Sacrificial Synthesis efficiency study. this effect can be explained by the polymerization characteristics of the sacrificial monomer. Evidently, monomers which do not polymerize to completion on a particular catalyst system, reach higher degrees of functionalization. This might be caused by a gradual deactivation of the catalyst by complexation of the newly formed polymer chain. Catalyst **C1** was not tested for k_i/k_p values due to its expected low k_i/k_p and the ruthenium removal difficulties observed, resulting in limited synthetic relevance of this reaction.

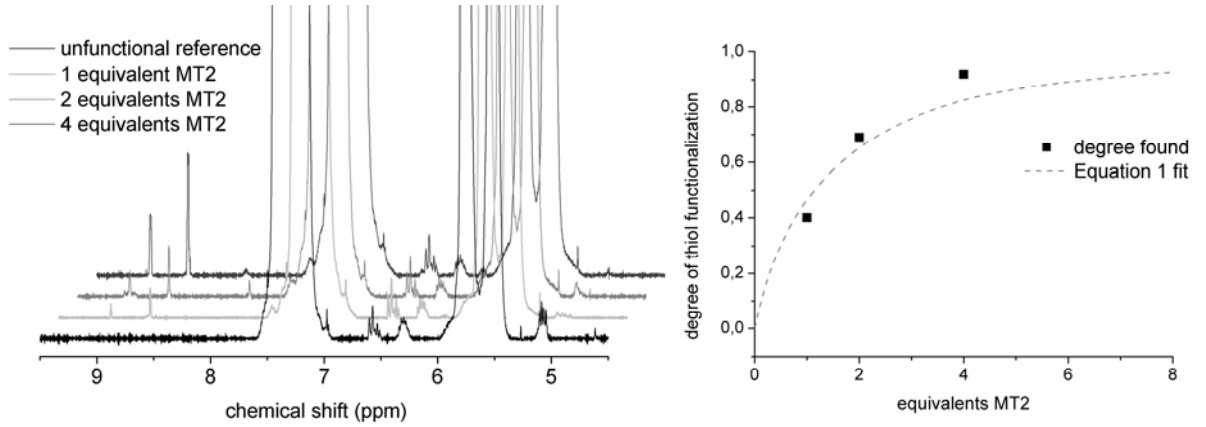


Figure 6. Functionalization series applying a different number of equivalents of **MT2**, ^{1}H-NMR results after hydrogenation (*left*) and derivatization for k_i/k_p determination (*right*).

Table 1. Thiol-functionalized polymers synthesized employing **MT2** as a sacrificial monomer.

entry	xNI	initiator	Mn /g mol^{-1}	PDI
1	**PNI**	**C1**	7300	1.24
2	**HNI**	**C1**	5600	1.27
3	**HNI**	**C1**	13800	1.28
4	**PNI**	**C2**	6900	1.13
5	**PNI**	**C2**	15200	1.16
6	**PNI**	**C2**	27300	1.13
7	**PNI**	**C2**	33000	1.15
8	**HNI**	**C2**	5900	1.11
9	**HNI**	**C2**	9500	1.09

A number of different polymers were synthesized by this method. The polymer characterization results are summarized in Table 1. The control over molecular weight and molecular weight distribution (PDI~1.2 for catalyst **C1**, 1.1 for catalyst **C2**) is in full agreement with values typically obtained for the used initiators.

The well-known coating reaction of thiols on gold surfaces was used to further prove the presence of a thiol group on the polymer chains. For this, a gold nanoparticle solution obtained from the citrate nanoparticle synthesis was added to a chloroform solution of the functionalized polymer. Upon shaking, the nanoparticles were drawn into the organic phase and stayed stable over months. UV/vis spectrometry of the phases proved quantitative phase transfer of the gold (Spectra given in the Supporting Information, SI-7). A transmission electron microscopy (TEM) image could verify the presence of a polymer layer that had forms around the nanoparticles (*c.f.* Figure 7).

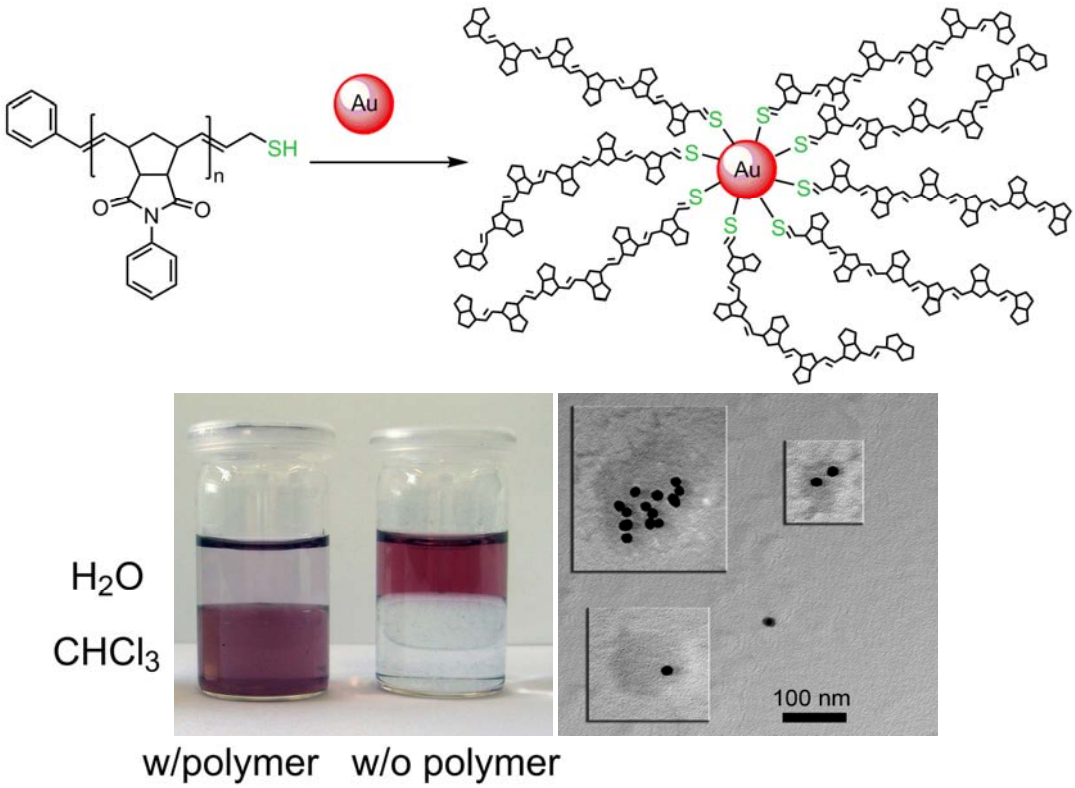


Figure 7. *Top*: Coating reaction of gold nanoparticles with poly(**PNI**)-SH. *Bottom left*: Phase transfer of gold nanoparticles after addition of poly(**PNI**)-SH. *Bottom right*: The three insets show TEM images of polymer coated gold nanoparticles.. One single nanoparticle (bottom right of the picture) is a nanoparticle reference sample that was not coated with the polymer.

Conclusion

With the introduction of dithiepine **MT2** as a novel cleavable monomer, we have successfully achieved a valuable extension of Sacrificial Synthesis. The successful placement of an additional block of this thioacetal monomer was accomplished by two different catalysts, **C1** and **C2**. While Grubbs 1st generation catalyst (**C1**) required a large excess of **MT2** in order to reach a high degree of functionalization, the bromopyridine complex **C2** required much smaller amounts of the sacrificial monomer in order to produce fully end-functionalized polymer chains. The precise and selective placement of the desired functional group was shown by MALDI-ToF MS giving no hint for falsely or non-functionalized polymer chains.

By a series of functionalization experiments and subsequent derivatizations, we have been able to determine the versatility of this method. Using the kinetic equation for the initiation efficiency of a living anionic polymerization, the k_i/k_p ratio of the key step for the functionalization by Sacrificial Synthesis has been determined which allowed us to establish the optimum conditions with the least amount of sacrificial monomer employed.

Furthermore, this new functional endgroup, which is of great importance to materials' science and biochemical research, has been employed in a first application. By coating gold nanoparticles with the novel material, the reactivity of the thiol endgroups was demonstrated. Considering the immense variety of functional polymers that can be synthesized by ruthenium-initiated ROMP using derivatized norbornene or other cycloolefin monomers, a number of different applications can be imagined ranging from electrode materials sensitive to complex stimuli to biomolecules bearing specially labeled polymer chains.

The synthesis of well-defined and highly functionalized thiol-functionalized polymers has been accomplished via the ring-opening metathesis polymerization (ROMP). By choosing a synthetic approach based on the Sacrificial Synthesis concept, precise control over molecular weight and selective placement of the functional group was achieved. Thiol-functionalized ROMP-polymers were successfully synthesized employing thioacetal monomers, which can be cleaved by hydrogenation leaving the desired thiol group behind. The selective placement of this highly reactive functional group at exactly one chain end of a poly(norborneneimide) is demonstrated by analytical methods such as NMR and MALDI-ToF mass spectroscopy. By kinetic measurements, the functionalization efficiency and the polymerization characteristics of the used dithiepine monomer were determined. In a first demonstration, the coating of gold nanoparticles is shown as one interesting application of such functionalized metathesis polymers.

References

[1] Duda, A.; Penczek, S. *Encycl. Polym. Sci. Eng*. **1989**, *16*, 246-368. Lee, C.-D. S.; Daly, W. H. *Fortschritte der Hochpolymeren-Forschung* **1974**, *15*, 61-90.

[2] Everhart, D. S *Handbook of Applied Surface and Colloid Chemistry* **2002**, *2*, 99-116.

[3] Dondoni, A.; *Angew. Chem. Int. Ed.* **2008,** *47,* 8995 – 8997. Shimada, K.; Mitamura, K.; *J. Chromatogr*. B **1994,** *659*, 227-241.Pounder, R. J.; Stanford, M. J.; Brooks, P.; Richards, S. P.; Dove, A. P. *Chem. Commun.* **2008**, *41*, 5158-5160. Killops, K. L.; Campos, L. M.; Hawker, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 5062-5064.

[4] J. Raula, J. Shan, M. Nuopponen, A. Niskanen, H. Jiang, E. I.Kauppinen, H. Tenhu, *Langmuir* **2003**, *19*, 3499 – 3504. M. Q. Zhu, L. Q.Wang, G. J. Exarhos, A. D. Q. Li, *J. Am. Chem.Soc.* **2004**, *126*, 2656 – 2657. I. Gorelikov, L. M. Field, E. Kumacheva, *J. Am. Chem. Soc.* **2004**, *126*, 15938 – 15939. M. Kuang,D. Y.Wang, H. Möhwald, *Adv. Funct. Mater.* **2005,** *15*, 1611 – 1616.

[5] Hanwell, M. D.; Heriot, S. Y.; Richardson, T. H.; Cowlam, N.; Ross, I. M *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* **2006**, *284+285*, 379-383.

Thery-Merland, F.; Methivier, C.; Pasquinet, E.; Hairault, L.; Pradier, C. M *Sensors and Actuators, B: Chemical* **2006**, *114*, 223-228.

[6] Rella, R.; Spadavecchia, J.; Manera, M. G.; Siciliano, P.; Santino, A.; Mita, G. *Biosensors & Bioelectronics* **2004**, *20*, 1140-1148.

[7] Maynard, H.D.; Okada, S.Y.; Grubbs, R.H. *Macromolecules* **2000**, *33*, 6239. Maynard, H.D.; Okada, S.Y.; Grubbs, R.H. *J. Am. Chem. Soc*. **2001**, *123*, 1275.

[8] Stubbs, L.P.; Weck, M. *Chem. Eur. J*. **2003**, *9*, 992.

[9] Maynard, H.D.; Grubbs, R.H. *Macromolecules* **1999**, *32*, 6917-2924. Weck, M.; Mohr, B.; Maughon, B.R.; Grubbs, R.H. *Macromolecules* **1997**, *30*, 6430-6437. Owen, R.M.; Gestwicki, J.E.; Young, T.; Kiessling, L.L. *Org. Lett*. **2002**, *4*, 2293-2296. Gestwicki, J.E.; Cairo, C.W.; Mann, D.A.; Owen, R.M.; Kiessling, L.L. *Anal. Biochem*. **2002**, *305*, 149-155. Gordon, E.J.; Gestwicki, J.E.; Strong, L.E.; Kiessling, L.K. *Chemistry and Biology*, **2000**, *7*, 9-16. Chen, B.; Sleiman, H.F. *Macromolecules* **2005**, *38*, 1084-1090. Mangold, S. L.; Carpenter, R. T.; Kiessling, L. L. *Org. Lett.* **2008**, *10*, 2997-3000.

[10] Castle, T. C.; Hutchings, L. R.; Koshravi, E. *Macromolecules* **2004**, *37*, 2035-2040.

[11] Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M *J. Am. Chem. Soc.* **2008**, *130*, 11040-11048.

[12] Katayama, H.; Urushima, H.; Ozawa, F. *J. Organomet. Chem*. **2000**, *606*, 16

[13] Hilf, S.; Berger-Nicoletti, E.; Grubbs, R.H.; Kilbinger, A.F.M. *Angew. Chem*. **2006**, *118*, 8214-8217; *Angew. Chem. Int. Ed.* **2006**, *45*, 8045-8048. Perrier, S.; Wang, X. *Nature* **2007**, *445*, 271.

[14] Hilf, S.; Kilbinger, A.F.M. *Macromol. Rapid Commun*. **2007**, *28*, 1225-1230.

[15] Hilf, S.; Hanik, N.; Kilbinger, A.F.M. *J. Polym. Sci. A* **2008**, *46*, 2913-2921.

[16] Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M *Macromolecules* **2008**, *41*, 6006-6011.

[17] Hilf, S.; Kilbinger, A.F.M. *Macromolecules* **2009**, *42,* 1099-1106.

[18] Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434-436. Seebach, D.; Jones, N. R.; Corey, E. J. *J. Org. Chem.* **1968**, *33*, 300-305. Corey, E. J.; Seebach, D. *Org. Synth.* **1970**, *50*, 72-74. Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *402*, 231-237.

[19] Corey, E. J.; Seebach, D. *Angew. Chem..* **1965**, 77, 1134-1136. Seebach, D. *Synthesis* **1969**, *1*, 17-36.

[20] Frens, G.; *Nat. (London) Phys. Sci.* **1973**, *241*, 20 – 22.

[21] Harpp, D. N.; Steliou, K.; Friedlander, B. T. *Org. Prep. Proced.* **1978**, *10*, 133-136.

[22] Corey, E. J.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1965,** *4,* 1075-1077.

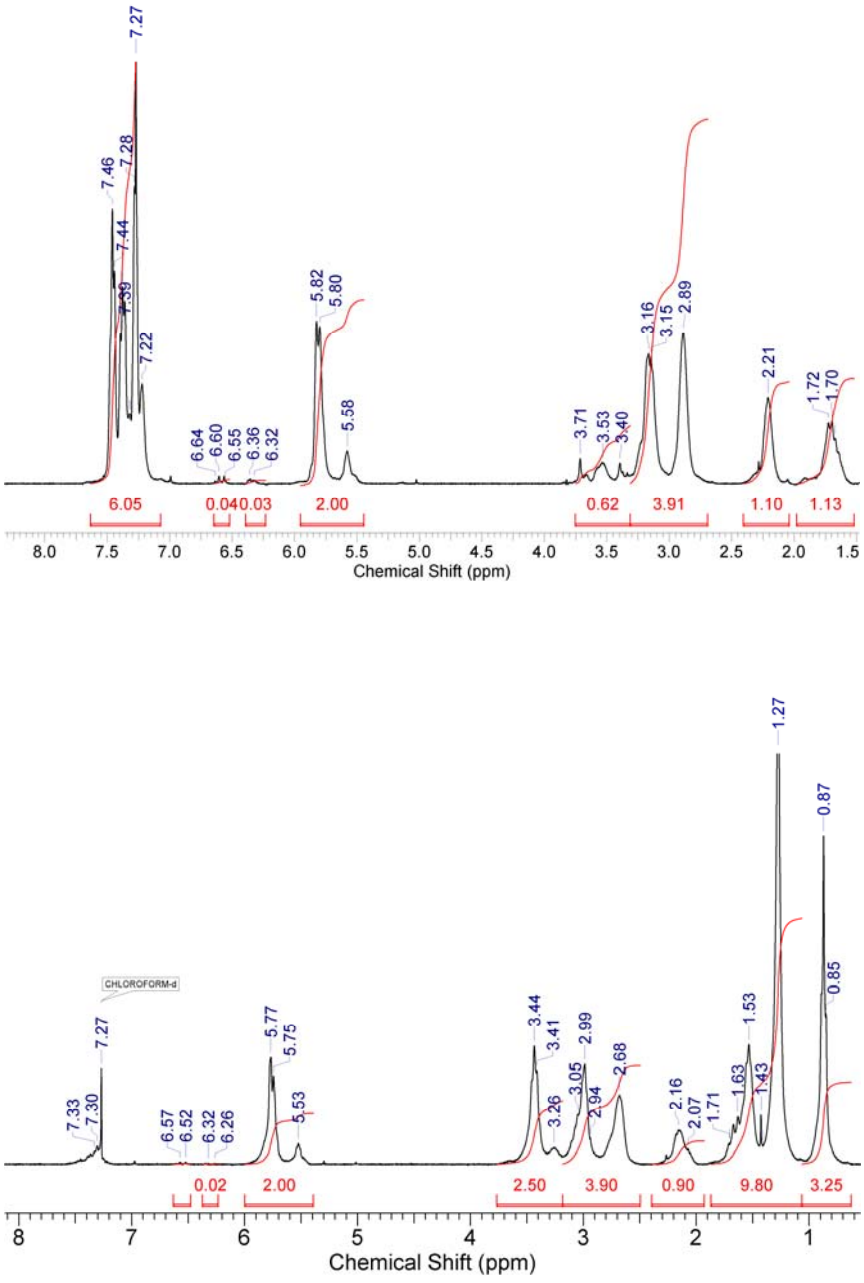
[23] Fraser, C.; Hillmyer, M. A.; Gutierrez, E.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 7256-7261

[24] Szwarc M. *Makromol. Chem.* **1960**, *35*, 132-158.

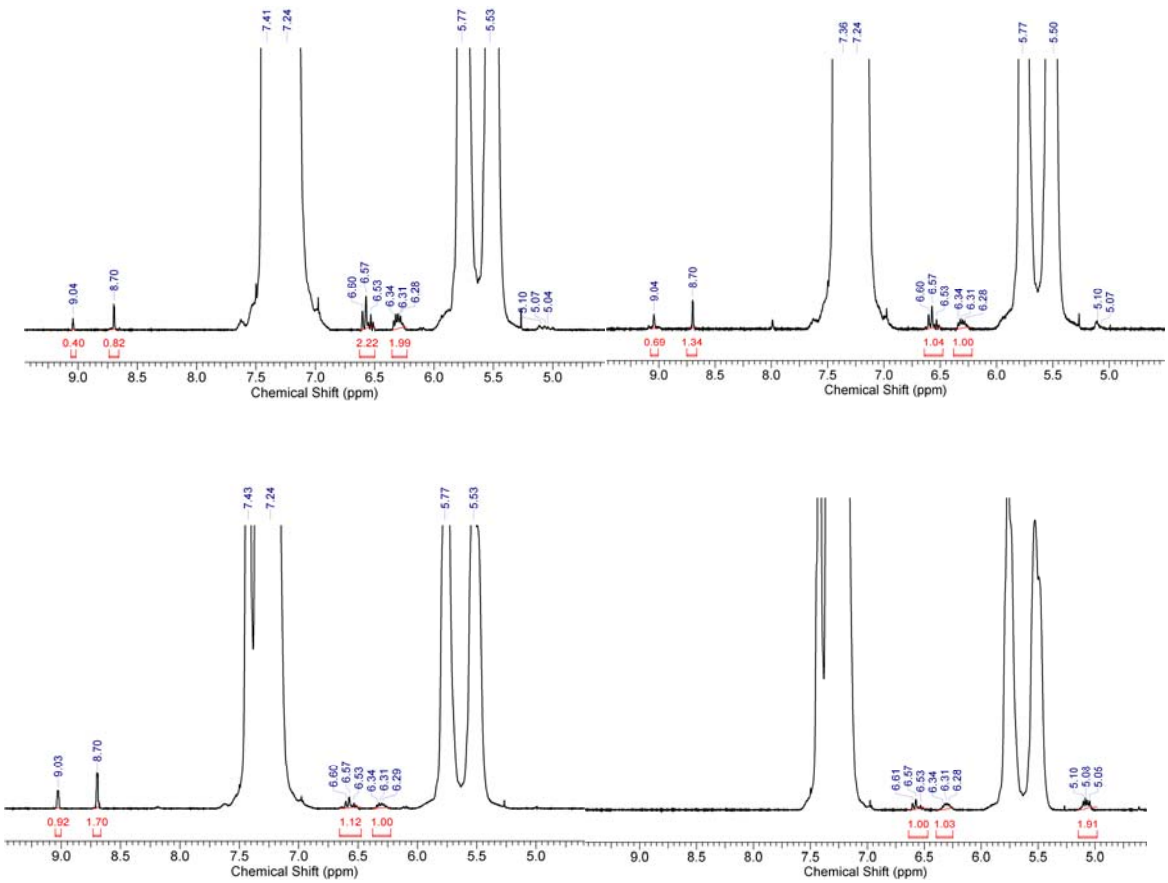
[25] Szwarc M.; van Beylen, M.; van Hoywegen, D. *Macromolecules* **1987**, *20*, 445-448

Supporting Information for: Thiol-functionalized ROMP polymers via Sacrificial Synthesis

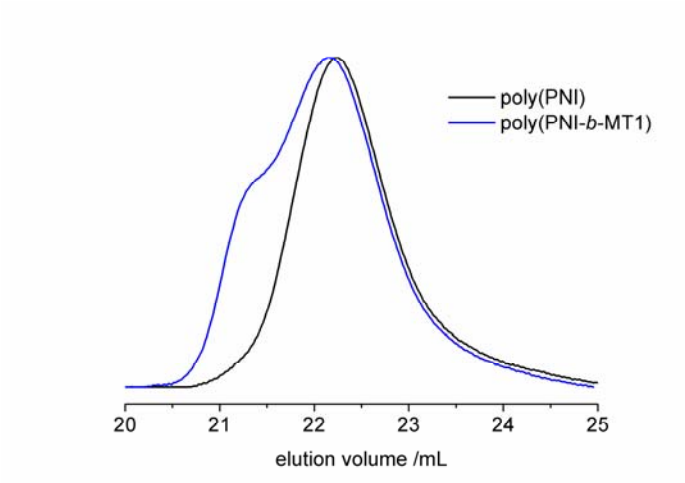
Stefan Hilf and Andreas F.M. Kilbinger



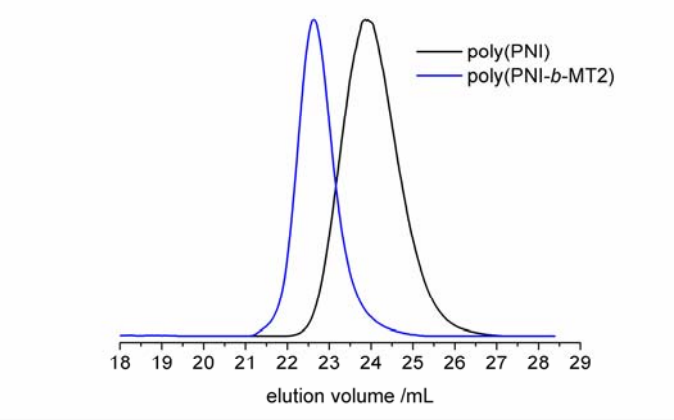
SI-1: ^{1}H-NMR of poly(PNI)-SH (top) and poly(HNI)-SH (bottom).



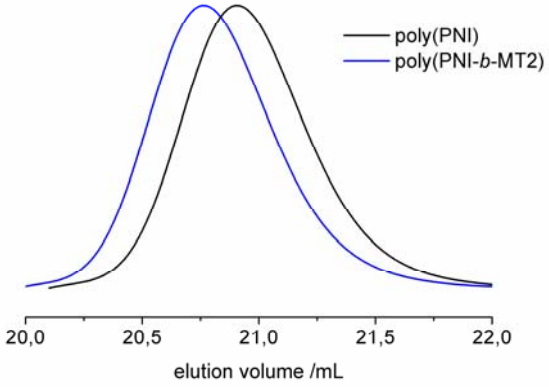
SI-2: ^{1}H-NMR of poly(PNI)-S-C(O)-ArNo_2 for determination of the degree of functionalization. After addition of 1 (top left), 2 (to right) or 4 (bottom left) equivalents MT2 and non-functionalized reference (bottom right).



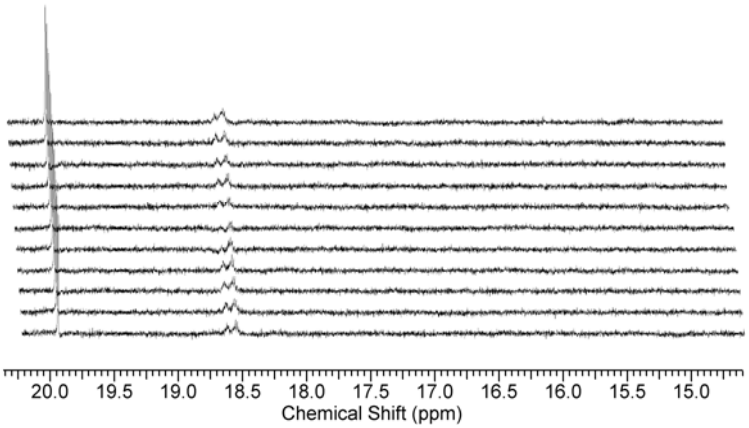
SI-3: SEC-RI traces of poly(PNI) and poly(PNI-*b*-MT1) initiated by catalyst C1 after addition of 10 equivalents MT1.



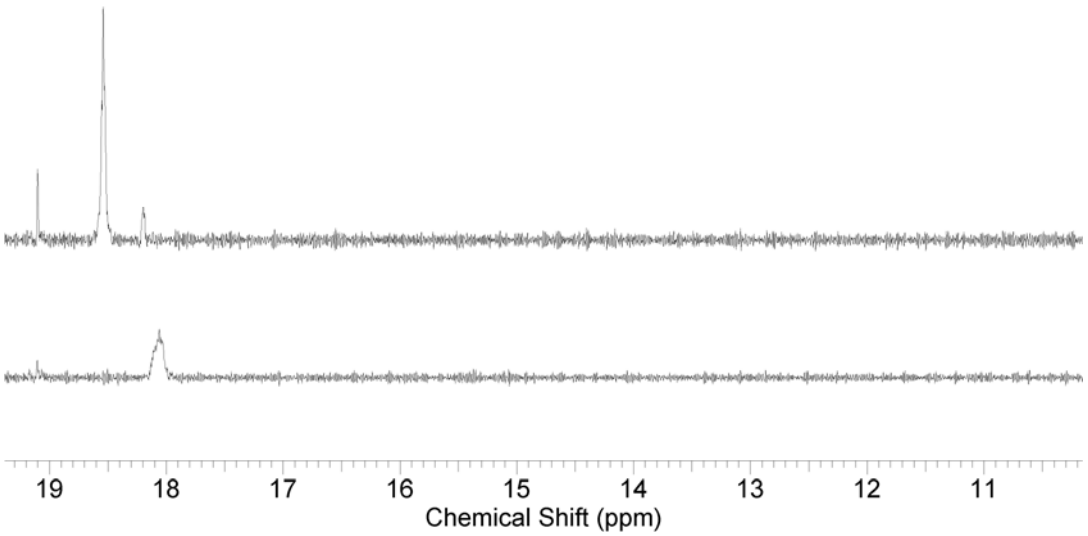
SI-4: SEC-RI traces of poly(PNI) and poly(PNI-*b*-MT2) initiated by catalyst C1 after addition of 40 equivalents MT2.



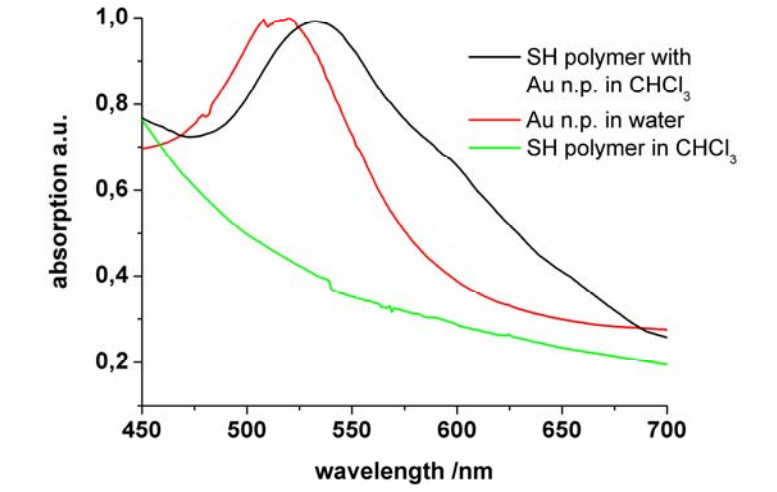
SI-5: SEC traces of poly(PNI) and poly(PNI-*b*-MT2) initiated by catalyst C2 after addition of 20 equivalents MT2.



SI-6: Time-resolved ^{1}H-NMR of the initiation of the MT2-block onto a poly(PNI) initiatied by catalyst C1 after addition of 10 equivalents MT2. The time difference between the spectra is 3 minutes (from top down). The signal at 18.7 ppm represents the norbonenylene, the signal at 20.1 ppm is caused by incompletely initiated C1 (benylidene).



SI-7: ^{1}H-NMR of the initiation of the MT2-block onto a poly(PNI) initiatied by catalyst C2 (top) after addition of 10 equivalents MT2 (bottom). The time difference between the two spectra is <60 seconds.



SI-8: UV/vis sprectra of neat gold nanoparticles and after coating with poly(PNI)-SH.

2.5: End-capping ROMP Polymers with Vinyl Lactones

Stefan Hilf, Robert H. Grubbs and Andreas F.M. Kilbinger

Published in: Journal of the American Chemical Society **2008**, *130*, 11040-11048.

Abstract

The selective placement of a functional group at the chain end of a ring opening metathesis polymer using ruthenium carbene initiators has been a significant limitation. Lack of synthetic routes towards end-functional materials has prevented this otherwise very attractive polymerization technique to gain ground in areas still dominated by the classical anionic polymerization. Here we demonstrate a highly effective and facile end-capping technique for ROMP with living ruthenium carbene chain ends using single-turnover olefin metathesis substrates. Vinylene carbonate and 3H-furanone are introduced as functionalization and termination agents for the ruthenium-initiated ring-opening metathesis polymerization. This leads directly to the formation of functional polymer end-groups without further chemical transformation steps. Aldehyde and carboxylic acid end-groups can be introduced by this new method which involves the decomposition of acyl carbenes to ruthenium carbides. The high degrees of chain-end-functionality obtained are supported by ^{1}H-NMR spectroscopy, MALDI-ToF mass spectrometry and end-group derivatization.

Introduction

The ring opening olefin metathesis polymerization (ROMP) is a powerful polymerization technique.[1] Early well-defined catalyst systems based on titanium,[2] molybdenum[3] and tungsten[4] showed rather low functional group tolerance. While this was undesirable for the polymerization of functional monomers, it could be exploited in the introduction of functional end-groups. The high oxophilicity of the metal carbenes allowed end-functionalization via addition of substituted aldehydes to the polymerization mixture.[5] Such functionalized polymers have been employed in a number of applications such as the formation of hybrid materials with interesting architectures.[6]

With the recent advances in functional group tolerant olefin metathesis catalysts based on ruthenium carbenes,[7] the ring opening metathesis polymerization (ROMP) has been established as a commonly employed polymerization technique.[8] Highly active ruthenium carbene initiators for instance those featuring pyridine ligands[9] (e.g. **C3**, see Figure 1) are able to polymerize a large variety of low strain cyclic olefins in a living manner while tolerating many polar functional groups and solvents.[10]

The selective placement of a functional group at the chain end of a ring opening metathesis polymer using ruthenium carbene initiators has been a significant limitation. Lack of synthetic routes towards end-functional materials has prevented this otherwise very attractive polymerization technique to gain ground in areas still dominated by classical anionic polymerizations. Most efforts to date have been conducted towards ROMP polymers with highly functional pendant groups via polymerization of functional monomers.[11] Many such examples have been described ranging from bio-active groups[12,13] to ionic groups[14,15] to non-covalent binding motives.[16]

End-functionalized telechelic polymers are also easily accessible using ruthenium carbene initiators in the presence of chain transfer agents. A number of functional groups such as hydroxyl groups[17] or amino and carboxylic acid groups[18] have been introduced in this manner.

One of the great limitations of the olefin metathesis polymerization has been the introduction of end-functional groups while maintaining full control over the molecular weight distribution. Most other living polymerization techniques, such as carbanionic polymerization,[19,20] RAFT,[21] ATRP[22] or anionic ring opening polymerization offer

straightforward routes to either functionalize the living polymer chain end or start the polymerization with a functional initiator.

The above mentioned route to telechelic polymers offers a very useful route to introduce functional end-groups to ROMP polymers, however, at the price of broad molecular weight distributions of the resulting polymers with typical polydispersity indices (PDI) of 2 and cannot give only one functional end-group exclusively.

Several attempts have been made at functionalizing the living end-groups of ROMP polymers using substituted vinyl ethers. These deactivate and remove the catalytic center from the chain end while leaving the desired functional group behind.[23] Other research groups have employed molecular oxygen,[24] stoichiometric amounts of a specifically functionalized monomer,[25] or specially functionalized ruthenium initiators[26] to place functional end-groups at exactly one chain-end of the ROMP polymer while maintaining the living nature of the polymerizations. However, the functionalization reactions were often reported to be slow, gave low end-group conversions or were not applicable in general.

Vinyl esters carry an electron deficient double bond that can deactivate ruthenium metathesis catalysts in a manner comparable to vinyl ethers.[27] Furthermore, they contain a fragile C-O bond which could be useful in releasing functional groups. In fact, as the pioneering work of the Johnson group demonstrated,[28] the carbenes of vinyl esters decompose readily forming a carboxylic acid and a ruthenium complex bearing a carbido-ligand.

We recently reported a general synthetic route to overcome many of the above mentioned limitations using a sacrificial diblock copolymer route.[29,30] There, the living ROMP polymer to be functionalized was turned into a diblock copolymer by polymerizing dioxepine monomers onto the first polymer block. The polyacetal block could then be cleaved under acidic conditions to leave exactly “half a dioxepine”, i.e. a hydroxyl group at the chain-end of the original polymer. Hydroxy-end-functional polymers prepared via this route have already been used for the synthesis of graft[31] and block copolymers.[32] While this route gives particularly high degrees of chain-end functionalitization (>97%) it requires a post-polymerization transformation, i.e. the hydrolysis of the acetal groups.

Here we present a new end-functionalization procedure for ROMP polymers. Polymers are initiated with the most common ruthenium initiators for living ROMP **C1**, **C2** or **C3** (Figure 1) and rapidly chain-end-functionalized using the quenching agents vinylene carbonate (**VC**) or *3H*-furanone (**3HF**) to give aldehyde- or carboxylic acid polymer end-groups without the need of further chemical transformations. **PNI** was chosen as the monomer in this study as poly(PNI) can be readily analyzed by MALDI-ToF mass spectrometry.

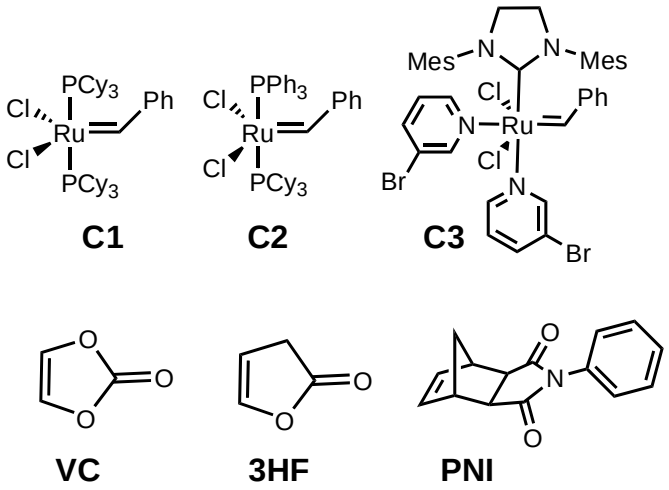


Figure 1. *Top:* Ruthenium carbene initiators **C1**, **C2** and **C3** employed in this study. *Bottom:* Polymer end-functionalization agents vinylene carbonate (**VC**) and *3H*-furanone (**3HF**) and monomer *exo-N*-phenyl-norbornene-2,3-dicarboximide (**PNI**).

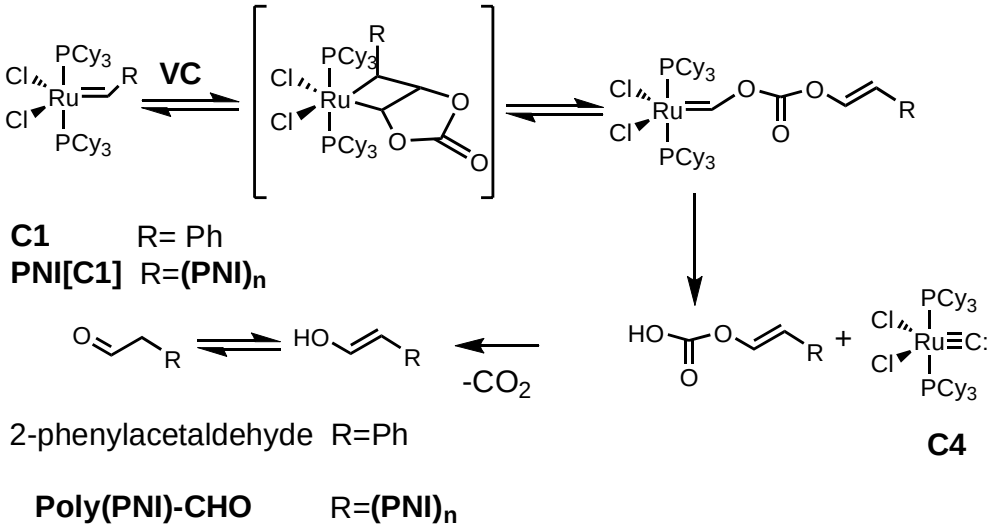
Results and Discussion

Functionalization with Vinylene carbonate. Vinylene carbonate (**VC**) is a small five-membered ring with little or no ring-strain. It therefore appears to be a poor choice for metathesis termination at first glance. However, this vinyl lactone contains a strongly electron deficient double bond which allows the formation of Fischer-type carbenes upon reaction with ruthenium carbenes. In addition, the *cis* double bond is substituted symmetrically, thus eliminating regioselectivity problems during the metathesis reaction. A reaction of **VC** with a living polymer ruthenium carbene end-group would result in the formation of a Fischer-type carbene linked to the polymer chain end via a carbonate (Scheme 1).

Acyl and halide substituted carbenes, such as the one shown in Scheme 1, are known to decompose to the corresponding acid and a ruthenium-carbido complex that cannot undergo further metathesis reaction unless reactivated.[33] The ring-opening of the vinylene carbonate would therefore trigger the cleavage of the ruthenium complex from the polymer chain end making further end-group modifications unnecessary.

We were interested whether this reaction would allow us to introduce functionality by applying the classical "quenching of living end-group" approach to ruthenium carbenes.

The proposed mechanism of the reaction of initiator or living polymeric end-group **C1** with **VC** is outlined in Scheme 1. After the ring-opening metathesis reaction of **VC** has occurred, the ester bond towards the ruthenium center is cleaved during the formation of the ruthenium-carbido complex **C4**. The resulting semi-ester of a carbonic acid then decomposes releasing carbon dioxide and phenylacetaldehyde or an aldehyde polymeric end-group.



Scheme 1. Proposed mechanism for the functionalization reaction with VC.

In a first model reaction, a large excess of **VC** was reacted with Grubbs 1st generation catalyst (**C1**). The reaction could be followed with the naked eye as the color of the reaction mixture changed from purple to yellow within few minutes with the

characteristic smell of phenylacetaldehyde emerging from the reaction vessel. In further model reactions catalysts **C1** and **C2** were used to initiate the polymerization of **PNI** to give living polymers with ruthenium carbene end-groups. Upon addition of **VC**, similar color changes of the solutions towards yellow were observed. An image of the solutions of the uninitiated, initiated and terminated catalyst **C1** can be found in the supporting information (S-1). The UV-vis absorption spectrum (see supporting information, S-2) showed complete loss of absorption bands characteristic of catalysts **C1** (absorption band at 520 nm) and catalyst **C2** initiated with *exo*-*N*-phenyl-norbornene-2,3-dicarboximide (**PNI**) (absorption bands at 400 nm and 330 nm). An FD-MS (field desorption mass spectrometry) analysis of the reaction mixture of initiated catalyst **C1** quenched with **VC** showed peaks that could be assigned to tricyclohexyl phosphine dissociated from the catalyst, short oligomers of the monomer bearing a terminal aldehyde (see supporting information for FD-MS) and phenylacetaldehyde from uninitiated catalyst **C1**.

In order to characterize the reaction kinetics and extent of reaction, time resolved ^{1}H-NMR spectroscopy was performed. The reaction of catalyst **C1** with **VC** proceeds at a moderate rate when equimolar amounts of the reactants were used (c = 0.026 mmol L^{-1}). The time-resolved ^{1}H-NMR spectrum given in Figure 2 shows the process of the reaction of **C1** with 8 equivalents of **VC**. The benzylidene signal (at 20.05 ppm) slowly diminishes over the course of the experiment (14 h) while the aldehyde signal forms at a similar rate (taking into account proton-deuterium exchange). A Fischer-carbene type intermediate can only be seen at the very beginning of the reaction, where the formation of the intermediate is faster than its decomposition. With higher excesses of **VC**, this carbene can be monitored for a longer period which shows that the formation and decomposition reaction steps are not concerted.

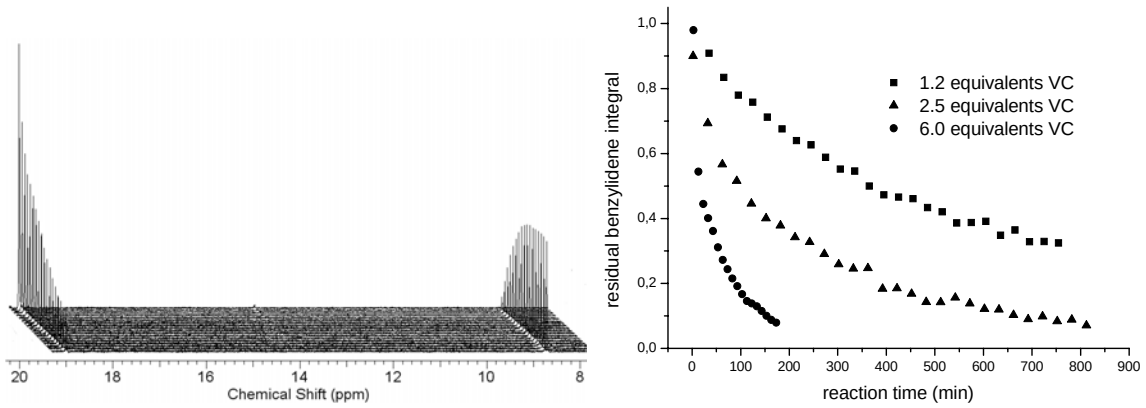


Figure 2. Reaction between benzylidene catalyst **C1** and **VC**. *Top*: Reaction with 8 equivalents of **VC** (time increases from back to front). The time difference between individual ^{1}H-NMR-spectra is 30 min. *Bottom*: Change of the benzylidene signal in the ^{1}H-NMR spectrum over time for 1.2, 2.5 and 6.0 equivalents of **VC**.

When the same reaction is carried out between catalyst **C2** and **VC**, the reaction is much slower than with catalyst **C1**. The reaction rate is strongly dependent on the amount of PPh_3 added to regulate the catalyst's activity. For **C2**, the equilibrium of phosphine dissociation, which is a key step for metathesis activity, is shifted towards the coordinated species. Due to the low reaction rate, no intermediates could be found by ^{1}H-NMR spectroscopy.

Adding **VC** to catalyst **C3**, the benzylidene signal in the ^{1}H-NMR spectrum disappears five times faster than in the case of catalyst **C1**. Two intermediate species can be found in the ^{1}H-NMR spectrum. The signal at 17.9 ppm presumably represents the ruthenium complex carrying **VC** as a ligand (see supporting information). The same observation is made with initiated catalyst **C3**. The resonance of the Fischer-carbene can be found at 14.3 ppm as expected, while the aldehyde group gives a signal at 9.6 ppm. Again, the decomposition of the Fischer-carbene is faster than its formation, so the signal of this intermediate state is small and vanishes over time.

Upon initiation of the three catalysts **C1**, **C2** and **C3** with **PNI,** the reaction with **VC** becomes much faster. The reactivity increase is caused by electronic effects as the rather stable benzylidene is replaced with a more reactive alkylidene.[27]

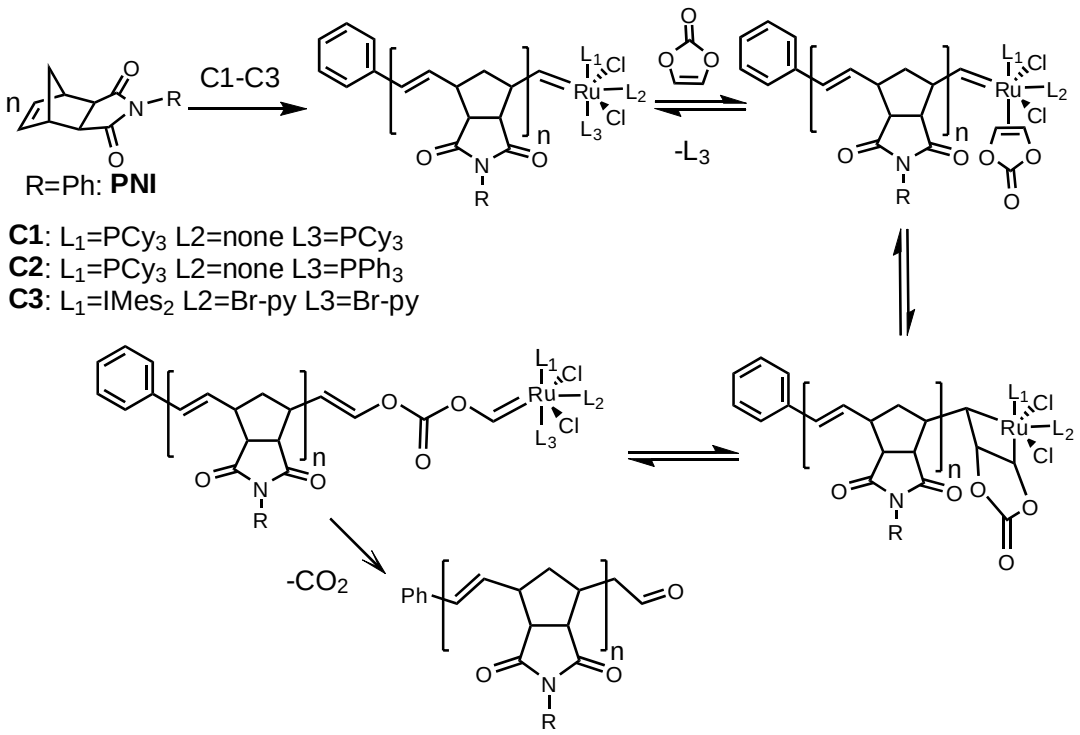
Addition of equimolar amounts of **VC** terminates the **PNI**-initiated catalyst **C1** much more rapidly than benzylidene catalyst **C1**. However, the determination of stoichiometrical factors is difficult due to incomplete initiation of **C1** even with 15 equivalents of monomer (PNI).

PNI-initiated catalyst **C2** reacts with **VC** at a rate similar to the uninitiated (benzylidene) catalyst **C1**. Both active species present in this catalytic system (18.7 ppm with PPh_3 dissociated and 17.6 ppm with PCy_3 dissociated, see supporting information)[34] react at a similar rate. No Fischer-carbene intermediate could be observed by ^{1}H-NMR spectroscopy, however, aldehyde formation proceeded cleanly.

The reaction between **PNI**-initiated catalyst **C3** and **VC** is extremely fast. Different reaction stages can be found in the ^{1}H-NMR spectrum. Similar to the uninitiated (benzylidene) catalyst **C3**, the **PNI**-initiated catalyst forms a complex with **VC** quantitatively within 5 minutes (carbene signal at 17.3 ppm, see supporting information) with little more than 1 equivalent of the terminating agent (**VC**) added. This complex then forms the intermediate Fischer-carbene before decomposing to the aldehyde functionalized polymer chain.

In order to prove formation of the proposed carbide-complex (Scheme 1), ^{13}C-NMR spectroscopy was performed on the reaction mixture of the above experiments. A carbon signal at 472 ppm could be detected. This matches the signal reported by the first group to synthesize **C4** (see supporting information).[35]

The mechanism for the termination reaction with **VC** is shown in Scheme 2. All intermediate steps proposed in Scheme 2 represent species that would be expected from the generally accepted mechanism of ruthenium catalyzed olefin metathesis.[36] All intermediates (except for the metalla-cyclobutane transition state) could be observed by ^{1}H-NMR spectroscopy (see above).



Scheme 2. Mechanism of the termination of ruthenium carbene end-groups with **VC**.

Kinetic measurements were repeated at different concentrations of **VC**. The termination reaction proceeds with first order kinetics with respect to the terminating agent (**VC**). The overall kinetics are expected to be second order, however, reactions on a polymer chain end typically suffer from steric hindrance and diffusion phenomena. From as little as 4-6 equivalents of **VC** with respect to ruthenium carbene end-groups, reactions followed a pseudo-first order behavior. In order to determine the kinetic rate constants, second order kinetic constants were calculated from the pseudo first-order constants obtained from integration of the benzylidene signals over time, according to literature procedures.[37] Kinetic constants derived from the time resolved ^{1}H-NMR spectroscopic measurements are summarized in Table 1. In all cases with initiated catalysts, reactions reached complete conversions even with small excesses of **VC**. The ^{1}H-NMR spectra indicated no side reactions.

Table 1. Termination constants with **VC**. [a] too slow to determine half life within 14h measurement, [b] too fast to be measured by ^{1}H-NMR spectroscopy ($t_{1/2}$ below 30 sec).

Catalyst	Eq. PPh_3	Eq. PNI	k_t L/mol*s
C1	0	0	0.073
C1	0	20	0.117
C2	3.4	0	<0.001[a]
C2	3.4	20	0.065
C2	1.2	20	0.104
C3	0	0	0.366
C3	0	20	>100[b]

For polymer synthesis the degree of functionalization and the molecular weight distribution are key factors. Catalysts **C1**-**C3** are known to polymerize many strained olefins in a living manner yielding polymers with narrow molecular weight distributions. In order to achieve full termination and chain-end-functionalization, chain transfer, re-initiation and non-functionalizing side reactions have to be excluded. Due to the nature of the termination reaction with **VC**, chain transfer and non-functionalizing termination can be excluded if the quenching reaction is given time to complete.

Re-initiation of monomer with a carbide-complex is a known phenomenon although it requires the addition of a strong acid. A moderate rate of termination is undesirable as it can lead to considerable broadening of the molecular weight distribution in cases where the polymerization was incomplete at the time the quenching agent was added. In order to facilitate the termination of polymer chains, 10-20 fold excesses of the terminating agent can be applied. If instant termination of all metathesis activity is needed, a large excess of the terminating agent (>50 equivalents) has to be added.

The intermediate Fischer-carbene chain end itself represents a vinyl ester which could, in theory, undergo a second metathesis reaction with a living chain end. This side reaction would yield two coupled polymer chains with no functional group at the chain end. The results of our kinetic study of the termination reaction, however, render the probability of this reaction diminishingly small since the decomposition of this carbene is

faster than its formation so that the concantration of this intermediate is extremely low. In addition, we found no evidence for the formation of stilbene as a coupling product in reactions with uninitiated (benzylidene) catalysts.

A number of polymers of **PNI** with different molecular weights were synthesized and functionalized with this method. GPC analysis of the resulting materials gave narrow molecular weight distributions typical of catalysts **C1**-**C3** as summarized in Table 2. The average molecular weight of the polymer matches the calculated values as expected from a living polymerization. In the case of catalyst **C1**, it has to be noted that the initiation efficiency is <1 as known from literature when aiming for low molecular weight polymers.[25] Any occurrence of broadened molecular weight distributions or higher molecular weight shoulders can be linked to incomplete polymerization reactions before the end-capping agent is added. In this case, unterminated chains continue to polymerize any residual monomer until all catalytic centers have been terminated. This can be avoided by addition of larger excesses of **VC** (see below).

Table 2. GPC-RI results for aldehyde terminated polymers.

entry	catalyst	n	M_n(theor.)	M_n(GPC)	M_w(GPC)	PDI
1	C1	18	4420	7500	9500	1.25
2	C1	25	6010	9000	10800	1.20
3	C1	60	14450	15500	18600	1.20
4	C2	10	2500	2500	3000	1.17
5	C2	12	2980	3000	3600	1.20
6	C2	18	4420	4600	5500	1.20
7	C2	50	12070	12600	14100	1.12
8	C3	18	4420	4600	4900	1.07

Aldehyde ^{1}H-NMR signals often give lower integrals than expected due to proton-deuterium exchange. Therefore, the total degree of functionalization was determined by absence of non-functional end-groups and also by derivatization of the terminal aldehyde with 2,4-dinitrophenyl hydrazine to give the respective hydrazone. In order to terminate all residually active catalyst, ethyl vinyl ether was added after the termination

reaction with **VC** was finished. The terminal olefinic end-groups produced by the reaction with ethyl vinyl ether can easily be detected by ^{1}H-NMR spectroscopy as demonstrated in Figure 3.

The derivatization reaction with 2,4-dinitrophenyl hydrazine gave distinct end-group signals that could be evaluated quantitatively in the ^{1}H-NMR spectra and compared to the end-group signals generated by the initiator (c.f. Supporting Information, S-8 for further details). Integration of the respective proton signals confirmed degrees of functionalizations exceeding 95%.

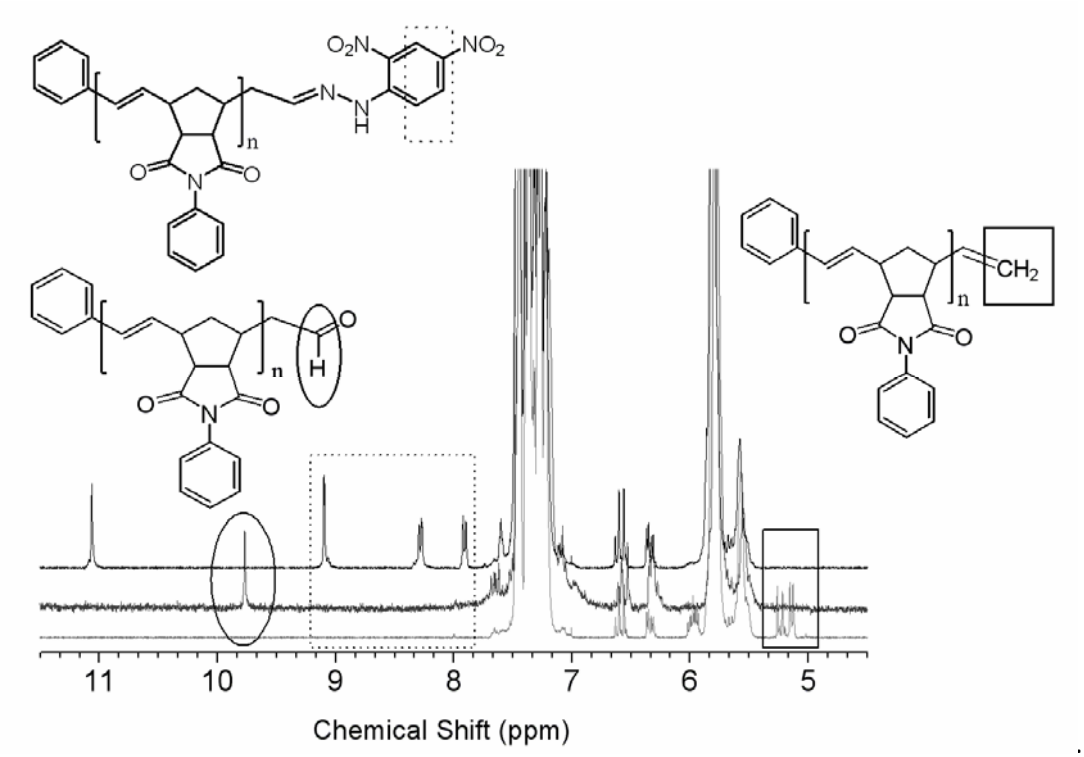


Figure 3. ^{1}H-NMR spectroscopic ($CDCl_3$) determination of the degree of functionalization. *Middle*: Poly(PNI)-CHO, *Top:* 2,4-dinitrophenyl hydrazone of Poly(**PNI**)-CHO, *Bottom:*Poly(**PNI**)=CH2 (all polymers entry 6 Table 2)

In addition, MALDI-ToF MS showed attachment of an aldehyde end-group to the polymer. As shown in Figure 4, the obtained mass spectrum reflects almost exclusively the aldehyde-functionalized polymer chains. The mass difference between signals corresponds to the molecular weight of the PNI repeat unit. The minor peaks represent polymer chains with an olefin end-group produced by termination with ethyl vinyl ether. However, the total amount of these chains is extremely low (invisible by NMR and <1% by MALDI ToF MS).

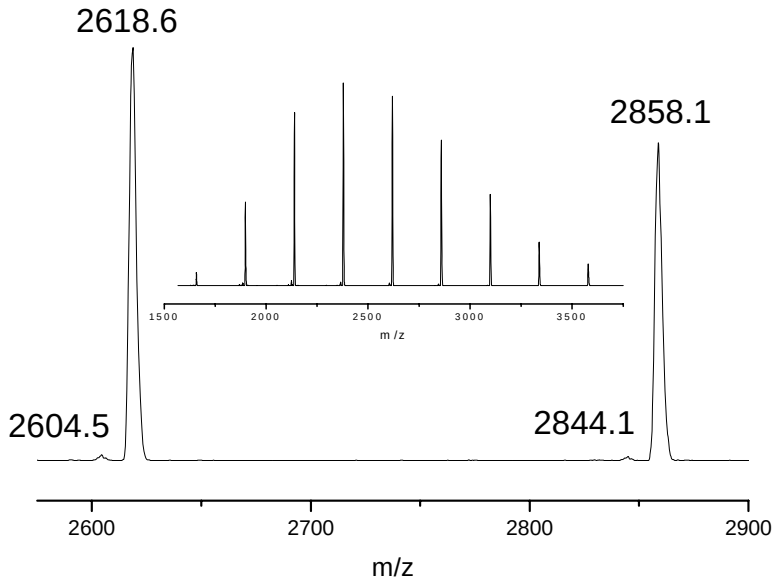


Figure 4. MALDI-ToF MS of aldehyde functionalized poly(**PNI**) (entry 5, Table 2).

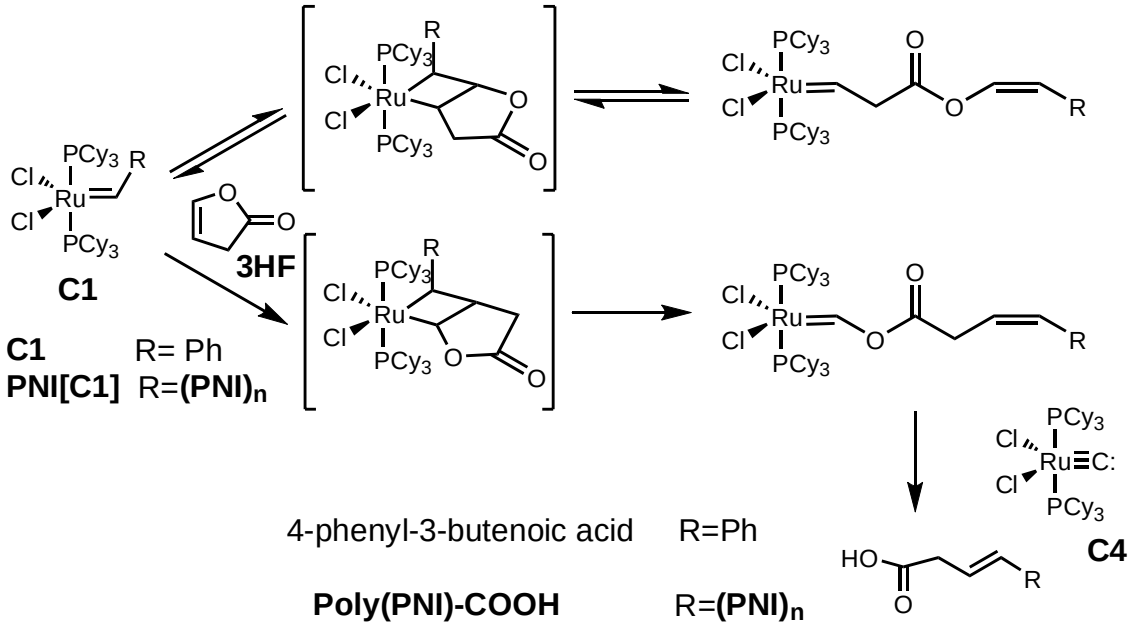
The functional group produced by addition of **VC** is set free during the course of the catalyst deactivation reaction without the need of further chemical transformations. This is a distinct advantage over the classical molybdenum-initiated ROMP polymerizations which cannot tolerate the unprotected functional group. In the case of molybdenum-initiated ROMP, the newly formed terminal aldehyde would undergo a secondary termination reaction giving incompletely functionalized and partially coupled polymer chains.

Vinylene carbonate is a particularly fast and efficient functionalizing agent for ROMP using ruthenium initiators. The reaction is applicable not only to small molecules, but

also to polymer chemistry. It proceeds by selectively attaching exactly one aldehyde group onto every polymer chain-end.

In order to prove that polymer functionalization with VC can be performed on highly functionalized polymers, the polymerization of *exo*-*N*-(2-hydroxy-ethoxy)ethyl-2,3-norbornene-dicarboximide (**HEENI**) was initiated with xxx and terminated with **VC** giving a polyalcohol bearing exactly one aldehyde group on every chain end (see Supporting Information, S-9).

Functionalization with *3H*-Furanone. *3H*-Furanone (**3HF**) is an asymmetric vinyl lactone, which can be easily synthesized in one step by the Baeyer-Villiger oxidation of furfural.[38] Given its lower degree of conjugation within the five-membered ring, it is expected to react more readily with ruthenium metathesis catalysts than **VC**. However, as **3HF** does not carry a symmetrically substituted double bond, the question of regioselectivity during the metathesis step is immanent. As shown in Scheme 3, two transition states of the metathesis step can be proposed, which lead to different products. Only the metathesis step leading to a Fischer-type carbene (Scheme 3, bottom pathway) is irreversible and leads to the desired acyl carbene which can subsequently decompose to release the acid functionality. The second pathway (Scheme 3, top), leading to another alkyl carbene, is reversible with the reverse reaction leading to a five-membered ring. This equilibrium should force the overall reaction into the Fischer-carbene pathway ensuring high degrees of functionalization. Upon treatment with **3HF**, catalyst **C1** showed the same color change as with **VC**, indicating a similar carbide-complex formation.



Scheme 3. Proposed mechanism for the termination of **C1** with **3HF**.

In order to determine the kinetics of this reaction, the progress of the transformation with a predetermined amount of **3HF** was followed by time-resolved ^{1}H-NMR spectroscopy. Upon addition of the quenching agent (**3HF**) to catalyst **C1**, the benzylidene signal vanished at a rate seven times higher than for **VC** (Figure 5, top). The intermediate Fischer carbene could be observed initially, confirming that the decomposition of this carbene is faster than its formation under these conditions (see Figure 5, top). The signal representing the carboxylic acid proton of the newly formed 4-phenyl-3-butenoic acid is very weak owing to rapid proton exchange with the deuterated solvent during the course of the reaction. If the same reaction is carried out with catalyst **C1** initiated with **PNI,** the termination reaction is more than 10 times faster.

With initiated catalyst **C2**, a termination rate could be observed that is in the same range as uninitiated catalyst **C1**. In this case, the signal of the carboxylic acid group formed on the polymer chain-end can be detected in the ^{1}H-NMR spectra (see supporting information).

When the termination reaction was carried out on the 3-bromopyridine complex **C3**, the reaction rate jumped to 30 times the value of catalyst **C1**. This effect was even increased when the catalyst was initiated with **PNI**. In this case, even with low excesses (1.2 equivalents) of **3HF**, the reaction proceeded at such a high rate that several half-lives had passed by the time the sample had been placed in the spectrometer (see supporting information). Interestingly, in this case, the formation of the Fischer-carbene was much faster than its decomposition leading to an intense signal of this intermediate.

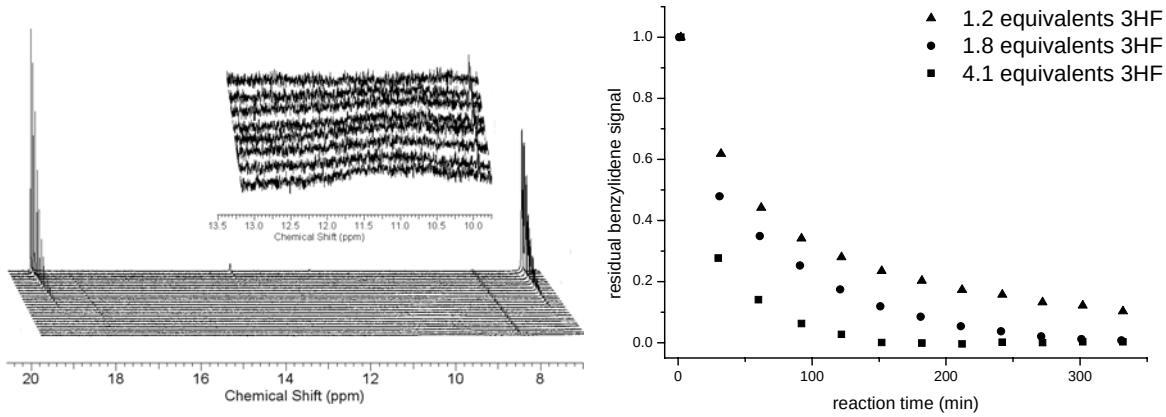


Figure 5. Reaction of benzylidene catalyst **C1** with **3HF**. *Top*: Reaction with 4 equivalents of **3HF** (from back to front). The time difference between individual ^{1}H-NMR-spectra is 30 min. *Bottom*: Change of the benzylidene signal in the ^{1}H-NMR spectrum over time for 1.2, 1.8 and 4.1 equivalents of **3HF**.

During the course of the reactions, no evidence for the presence a second carbene was found that would represent the regioisomer of the Fischer-carbene as described in Scheme 3. Therefore, this pathway of the proposed mechanism of **3HF**-functionalization can be excluded. The slightly higher amounts of Fischer-carbene observed during the time-resolved ^{1}H-NMR spectroscopic measurements with **3HF** compared to **VC** can be linked to the higher rate of formation of the intermediate due to electronic factors.

The time dependence of the catalyst deactivation could be shown by plotting the integrals of the carbene signals against time (Figure 5, bottom). Similar to the termination reaction with **VC**, all reactions showed second order overall kinetics and exhibited pseudo-first order behavior when greater 4-6 equivalents of **3HF** were employed. All reactions were first order with respect to the concentration of the quenching reagent (**3HF**). In order to calculate rate constants for the termination reaction, second order constants were calculated from the pseudo-first order constants obtained by integration of the benzylidene signals over time. All kinetic constants obtained are summarized in Table 3. With initiated catalysts, reactions reached 100% conversion even with small excesses of **3HF** and without any observed side reactions.

Table 3. Initiation constants with **3HF** [a] too fast to be measured by ^{1}H-NMR spectroscopy ($t_{1/2}$ below 30 sec).

Catalyst	**Eq. PPh_3**	**Eq. PNI**	k_t L/mol*s
C1	0	0	0.327
C1	0	20	3.56
C2	7.8	20	0.236
C3	0	0	11.7
C3	0	20	>100[a]

The functionalization of polymers with **3HF** proceeds in the manner outlined in Scheme 4. All intermediates with the exception of the metallacyclobutane transition state could be observed during kinetic measurements.

With ruthenium-carbido complexes being able to be reactivated to extremely metathesis-active carbenes by strong acids, the question could arise as to whether the acid end-group that is formed by this reaction is strong enough to reactivate the catalyst. During kinetic measurements, no signals were found that could be assigned to such a newly formed carbene proton.

3HF functionalization was deployed on an array of polymers, initiated by different catalysts and varying in molecular weight, in order to demonstrate the versatility of the method and the applicability to different catalytic systems. GPC analyses of the resulting polymers are summarized in Table 4. All polymerizations gave narrow molecular weight distributions typical of catalysts **C1**-**C3** and the average molecular weight could be controlled by the monomer-to-initiator ratio as expected for living polymerizations. This also demonstrates that no undesired metathesis reactivation by the carboxylic acid end-group occurred.

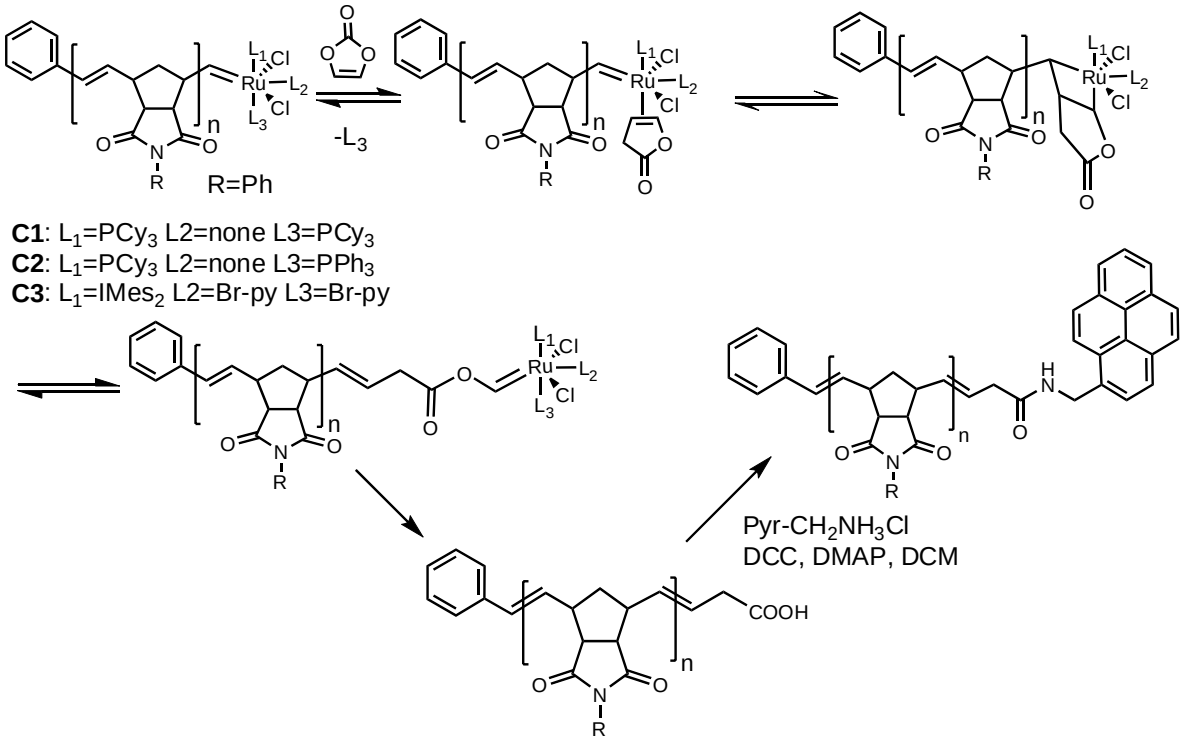
Similar to the reaction with **VC**, the termination reaction with **3HF** is slower than the polymerization of typical metathesis monomers based on norbornene derivatives. In order to obtain molecular weight distributions as narrow as possible, either full monomer conversion has to be reached before the terminating agent (**3HF**) is added or a large excess (20-50 equivalents) has to be added in order to terminate the metathesis reaction instantly.

Table 4. GPC-RI results for poly(PNI)-COOH with different catalysts.

entry	catalyst	n	M_n (theor.)	M_n (GPC)	M_w (GPC)	PDI
9	**C1**	18	4400	8400	10500	1.25
10	**C1**	25	6100	9300	11300	1.22
11	**C1**	50	12000	13300	15900	1.20
12	**C2**	18	4400	4400	5200	1.14
13	**C2**	25	6100	6200	7000	1.14
14	**C2**	50	12000	12600	14200	1.12
15	**C3**	18	4400	4300	4700	1.08

In order to confirm that the attachment of an acid functionality to the polymer chain, this end-group was derivatized with a chromophore. 1-Pyrenemethylamine hydrochloride was reacted to the terminal polymeric carboxylic acid using standard coupling chemistry, employing the well-established dicyclohexylcarbodiimide / *p*-dimethylaminopyridine system. Detection of the chromophore was performed by GPC-

UV detection at the absorption maximum of the dye (340 nm). The presence of a signal in the polymer region proved the attachment of the amine to the polymer and hence the presence of a carboxylic acid (supporting information).



Scheme 4. Polymer functionalization with **3HF** and attachment of a pyrene chromophore

The total degree of functionalization with **3HF** can be determined by the absence of non-functional groups in the ^{1}H-NMR spectrum and by esterification of the terminal carboxylic acid with an alcohol giving distinct ^{1}H-NMR signals. 2,2,2-Trichloroethanol was chosen for esterification since its methylene protons can be easily detected and analyzed quantitatively (c.f. Figure 6). ^{1}H-NMR quantification of the trichloroethyl ester and comparison to the styryl end-group generated by the initiator typically gave total degrees of functionalization >97% (c.f. Supporting Information, S-13.) This derivatization reaction as well as the one described above (see Figure 3) shows clearly that terminating with excess ethyl vinyl ether after functional capping with either **VC** or **3HF** is sufficient to evaluate the degree of end-functionalization by ^{1}H-NMR.

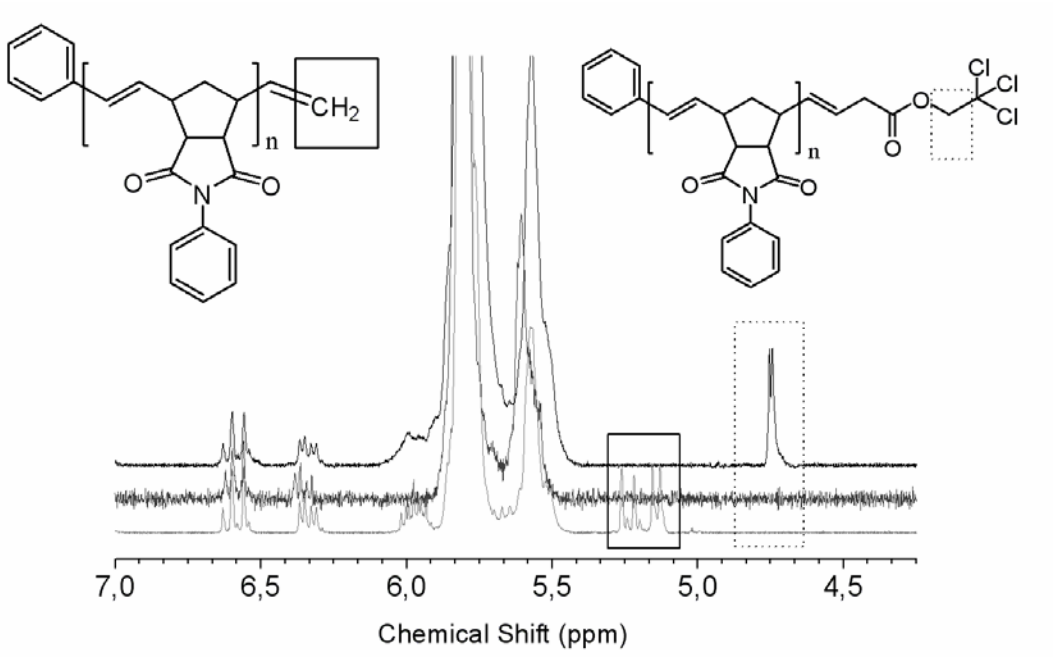


Figure 6. ^{1}H-NMR spectroscopic characterization ($CDCl_3$) of degree of functionalization. *Middle*: Poly(**PNI**)-COOH, *Top:* Trichloroethyl ester of Poly(**PNI**)-COOH *Bottom:*Poly(**PNI**)=CH2 (all polymers entry 13, Table 4)

The MALDI-ToF mass spectrum of polymers functionalized by **3HF** shows signals at masses that represent functionalized polymer chains exclusively. Olefin-terminated polymer chains could not be detected. Minor signals between the expected poly(PNI)-COOH signals most likely represent macromolecules with neutralized chain ends (Figure 7). These signals could not be assigned to any intermediate, side product or the product of regio-isomeric metathesis reactions of the **3HF**.

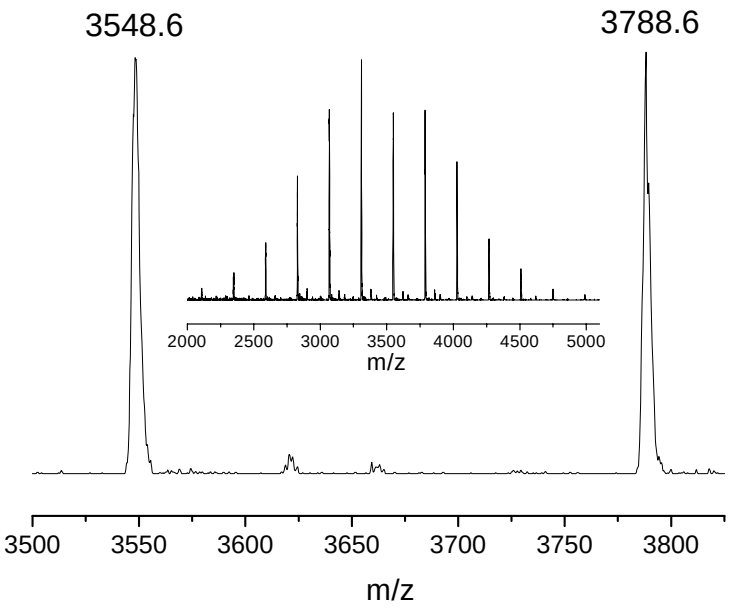


Figure 7. MALDI-ToF MS of acid functionalized poly(PNI) (entry 12, Table 4).

The feasibility of this functionalization reaction could be shown by functionalizing poly(norbornene-5-carbaldehyde) (initiated with **C1**) giving carboxylic acid functionalized polyaldehydes with excellent degrees of chain-end functionalization (ca. 95%, see Supporting Information, S-14).

3H-Furanone (**3HF**) can therefore be seen as a versatile functionalizing reagent for ROMP polymers. It terminates the catalytically active chain end efficiently and selectively. The formation of the terminal carboxylic acid functionality proceeds smoothly while the former catalytic center is cleaved off the polymer chain simultaneously. As with **VC**, **3HF** quenching can not be performed on molybdenum-initiated ROMP polymerizations since free carboxylic acids are incompatible with these catalysts.

Experimental Section

General. ^{1}H-NMR spectra were recorded at 300 MHz on a Bruker AC300 or a Bruker AMX400, kinetic ^{1}H-NMR was conducted on a Bruker ARX400. ^{13}C-NMR spectra were measured on a Bruker DRX400 at 100.15 MHz. All spectra were referenced internally to residual proton or carbon signals of the deuterated solvent. Deuterated solvents were purchased from Deutero GmbH. Gel permeation chromatography in chloroform was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P100 pump and a set of three PSS SDV columns (10^4/500/50 Å). Signal detection occurred by use of a TSP Spectra System UV2000 (UV 254 nm unless otherwise stated) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service. Field desorption mass spectra were measured on a Finnigan MAT 95. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) measurements were performed on a Shimadzu Axima CFR MALDI-TOF mass spectrometer equipped with a nitrogen laser delivering 3ns laser pulses at 337nm. Dithranol (1,8-dihydroxy-9(10H)-anthracetone, Aldrich, 97%) was used as matrix. Potassium (Aldrich, 98%) or silver trifluoroacetate(Aldrich, 99.99%) were added for ion formation. Best results were obtained for samples which were prepared from THF solution by mixing matrix (10 mg/mL), polymer (10 mg/mL), and salt (0.1 n solution) in a ratio of 10:1:1.A volume of 0.9 µL was given onto the MALDI sample slide and allowed to dry at room temperature for 2 h prior to measurement.

Exo-N-phenyl -2,3-norbornene dicarboximide and other monomers were synthesized as described in earlier publications. Vinylene carbonate was purchased from Aldrich and used as received, Grubbs' 1st and 2nd generation catalysts were obtained from Materia, inc. The bromopyridine complex **C3** was synthesized as described elsewhere[39]. All solvents and other reagents were purchased from Acros. All polymerization reactions were carried out under nitrogen using Schlenk techniques. Dichloromethane as the solvent was dried over P_2O_5 and freshly distilled under nitrogen. *3H*-Furanon was obtained in good yield and purity as described by Näsman et al.[38]

Preparation of kinetic ^{1}H-NMR samples: 15mg (18µmol) 1 were added 0.7mL Dichlormethane-d_2 in a nitrogen filled glovebox in cases where a phoshpine was added, the applicable amount of PPh_3 was added to this solution and was allowed to stand for 15min. The solution was transferred into an NMR-tube, which was sealed with a rubber septum. Upon measurement of a reference spectrum, the quenching reagent (1.2µL vinylene carbonate or 1.3µL *3H*-furanone for 1 equivalent) was added by microsyringe and kinetic measurement was commenced immediately.
Formation and decomposition of the Fischer carbene was monitored by ^{1}H-NMR spectroscopy in the 13-15 ppm region.

*General procedure for the synthesis of poly(PNI)-CHO and poly(PNI)-COOH with Grubbs' 1st generation catalyst (**C1**):* A solution of the monomer in dry, degassed dichloromethane (1mL per 100mg monomer) was added to an equal volume of a rapidly stirred dichloromethane solution of the calculated amount of catalyst at r.t. After the polymerization reaction was well finished (ca. 1h for 5000g/mol), a large excess of the quencher was added (50 equivalents of vinylene carbonate or 20 equivalents of *3H*-furanone) and the stirring was continued until the solution had turned yellow (Formation of **C4**). The Fischer carbene was not isolated and no further addition of reagents was needed to induce decomposition to the functional group and complex **C4**. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (>100 equivalents) and stirring was continued for another 30min. The resulting polymer was precipitated in methanol. The collected solids were re-dissolved in chloroform and re-precipitated in methanol, collected and dried under vacuum over night affording a colorless polymer material in good yield (>90% typical).

*General procedure for the synthesis of poly(PNI)-CHO and poly(PNI)-COOH with catalyst **C2**:* To a stirred dichloromethane solution of the calculated amount of catalyst (5mL dichloromethane per 100mg of catalyst) was added twice the mass of PPh_3 (6.3 equivalents) at r.t. The mixture was allowed to react for 15min. before a solution of the monomer in dichloromethane (1mL per 100mg monomer) was added. After the

polymerization reaction was finished (ca. 8h for 5000g/mol), a large excess of the quencher was added (50 equivalents of vinylene carbonate or 20 equivalents of *3H*-furanone) and stirring was continued over night or until the solution had turned yellow. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (>100 equivalents) and stirring was continued for another 2h. The polymer was precipitated in methanol, collected, re-dissolved in chloroform and re-precipitated in methanol, collected and dried under vacuum over night to give a virtually colorless solid in good yield (>90% typical).

*General procedure for the synthesis of poly(PNI)-CHO and poly(PNI)-COOH with bromopyridine complex (**C3**):* A solution of *exo-N*-Phenyl-2,3-dicarboximide in dry, degassed dichloromethane (1mL per 100mg monomer) was added to an equal volume of a rapidly stirred dichloromethane solution of the calculated amount of freshly prepared catalyst 3 at r.t. After the polymerization reaction was finished (ca. 15min for 10000g/mol), an excess of the quencher was added (20 equivalents of vinylene carbonate or 10 equivalents of *3H*-furanone) and the stirring was continued until the solution had turned yellow. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (>100 equivalents) and stirring was continued for another 10min. The polymer was precipitated in methanol and collected. The solids were redissolved in chloroform and reprecipitated in methanol, collected and dried under vacuum over night to give a colorless solid in good yield (>90% typical).

Synthesis of poly(PNI)-CONH-CH_2-Pyrene: 50mg of poly(PNI) (Mn=4400, PDI=1.13 (RI-detection); 11.4µmol), 20mg (84µmol) of 1-pyrenemethylamine hydrochloride, 50mg (242µmol) dicyclohexylcarbodiimide and 50mg (409µmol) of 4-dimethylaminopyridine were weighed into a 50mL Schlenk-flask, degassed and dissolved in 10mL dry dichloromethane. After stirring at r.t. for 14h, the turbid mixture was concentrated at the rotary evaporator, taken up with a small amount of chloroform and precipitated in methanol. The resulting solids were collected and dried in vacuo yielding 40mg (ca. 80%) of a colorless material. GPC: Mn=4200, PDI=1.13 (RI-detection).

Conclusions

Both, vinylene carbonate (**VC**) and *3H*-furanone (**3HF**) are powerful end-capping reagents for ruthenium-catalyzed ROMP. As vinyl lactones have not been used for the functionalization of polymers to date, they represent a new class of single-turnover metathesis functionalizing reagents. Both new quenching agents represent five-membered cyclic molecules that combine an easily cleavable lactone with an electron-deficient all-*cis* double bond. This reduces the steric hindrance for the coordination of the olefin to the metal centre. The self-deprotection of the functional group caused by the instability of the intermediate acyl carbene makes this innovative method uniquely versatile and exclusive to ruthenium-based ROMP catalysis.

Methods have been developed to quantify the total degree of functionalization by classical derivatization reactions. The functionalization efficiency of both **VC** and **3HF** could be shown to be extremely high or even quantitative. The simpler determination method of the degree of functionalization involving secondary termination with ethyl vinyl was proven to give reliable functionalization values.

In addition, further polymer analogous transformations become obsolete as the ring opening metathesis reaction of the quenching agent triggers its decomposition into a ruthenium carbide complex and the functionalized polymer chain end. Our study on the two reagents **VC** and **3HF** could show both, the selectivity and the efficiency of the catalyst deactivation and polymer functionalization.

In addition, **VC** is the first commercially available end-capping reagent for the metathesis polymerization that installs a functional group on the polymer chain-end. The regioselectivity of the metathesis step is not critical due to the symmetry of the double bond in **VC.**

The second end-capping reagent, **3HF**, which is readily available in one step from furfural, has demonstrated high regioselectivity during the metathesis step, thus producing carboxylic acid-functionalized polymer chain-ends exclusively. As carboxylic acids represent one of the most interesting functional end-groups that can be attached to a polymer, we believe that this functionalization method is of great synthetic value.

The progress of the functionalization reactions with **VC** and **3HF** is independent of the nature of the ruthenium-alkylidene or benzylidene as could be shown using a variety of

different catalyst systems. As no further chemical transformation is needed to release the functional end-group, even sensitive and labile functional groups can be present along the main chain of the polymer. Therefore, the functionalization with the two vinyl lactones presented here can be expected to be generally applicable.

Finally, the versatility of vinyl lactone functionalization, virtually eliminating the need for work-up and further deprotection steps, together with the ready availability of the quenching reagents, renders this new method extremely useful for polymer science.

References

[1] Frenzel, U.; Nuyken, O. *J. Polym. Sci. A* **2002**, *40*, 2895-2916. Slugovc, C. *Macromol. Rapid. Commun*. **2004**, *25*, 1283-1297.

[2] Gilliom, L.R.; Grubbs, R.H. *J. Am. Chem. Soc.* **1986**, *108*, 733-742.

[3] Schrock, R. R. *Acc. Chem. Res*. **1990**, *23*, 158-165;

[4] O'Donoghue, M.B.; Schrock, R.R.; LaPointe, A.M.; Davis, W.M. *Organometallics*, **1996**, *15*, 1334-1336. Murdzek, J.S.; Schrock, R.R. *Macromolecules* **1987**, *20*, 2640-2642. Schrock, R.R.; Murdzek, J.S.; Bazan, G.C.; Robbins. J.; DiMare, M.; O'Regan.M. *J. Am. Chem. Soc.* **1990**, *112*, 3875-3886.

[5] Brown-Wensley, K.A.; Buchwald, S.L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J.R.; Straus, D.; Grubbs, R.H. *Pure Appl Chem*. **1983**, *55*, 1733-1744. Albagli, D.; Bazan, G.C.; Schrock, R.R.; Wrighton, M.S. *J. Phys. Chem*. **1993**, *97*, 10211-10216. Albagli, D.; Bazan, G.C.; Schrock, R.R.; Wrighton, M.S. *J. Am. Chem. Soc*. **1993**, *115*, 7328-7334. Nomura, K.; Takahashi, S.; Imanishi, Y. *Macromolecules* **2001**, *34*, 4712-4723.

[6] Murphy, J. J.; Kawasaki, T.; Fujiki, M.; Nomura, K. *Macromolecules* **2005**, *38*, 1075-1083. Murphy, J. J.; Furusho, H.; Paton, R. M.; Nomura, K. *Chem. Eur. J.* **2007**, *13*, 8985-8997.

[7] Schwab, P.; France, M.B.; Ziller, J.W.; Grubbs, R.H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039-2041. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953-956. Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247-2250.

[8] Grubbs, R.H., *Handbook of Metathesis*, Wiley-VCH, Weinheim, **2003**; Buchmeiser, M. R. *Chem. Rev*. **2000**, *100*, 1565-1604; Khosravi, E.; Szymanska-Buzar, T., Eds. Ring-Opening Metathesis Polymerisation and Related Chemistry; Kluwer: Dordrecht, The Netherlands, **2002**; Imamoglu, Y. Dragutan, V., Eds. Metathesis Chemistry; Springer: Dordrecht, The Netherlands, **2007**.

[9] Love, J.A.; Morgan, J.P.; Trnka, T.M.; Grubbs, R.H. *Angew. Chem. Int. Ed*. **2002**, *41*, 4035-4037.

[10] Slugovc, C.; Demel, S.; Riegler,S.; Hobisch, J.; Stelzer, F. *J. Mol. Catal. A: Chemical* **2004**, *213*, 107-113. Slugovc, C.; Demel, S.; Stelzer, F. *Chem. Commun.* **2002**, 2572-2573.

[11] Binder, W. H.; Kluger, C. *Macromolecules* **2004**, *37*, 9321-9330. Binder, W. H.; Kluger, C.; Josipovic, M.; Straif, C. J.; Friedbacher, G. *Macromolecules* **2006**, *39*, 8092-8101. Alfred, S.F.; Al-Badri, Z.M.; Madkour, A.E.; Lienkamp, K.; Tew, G.N. *J. Polym. Sci. A: Polym. Chem.* **2008**, *46*, 2640-2648.

[12] Maynard, H.D.; Okada, S.Y.; Grubbs, R.H. *Macromolecules* **2000**, *33*, 6239-2648.

[13] Maynard, H.D.; Okada, S.Y.; Grubbs, R.H. *J. Am. Chem. Soc*. **2001**, *123*, 1275-1279.

[14] Lynn, D.M.; Mohr, B.; Grubbs, R.H.; Henling, L.M.; Day, M.W. *J. Am. Chem. Soc*. **2000**, *122*, 6601-6609.

[15] Rankin, D.A.; Lowe, A.B. *Macromolecules* **2008**, *41*, 614-622.

[16] Stubbs, L.P.; Weck, M. *Chem. Eur. J*. **2003**, *9*, 992-999.

[17] Bielawski, C.W.; Benitez, D.; Morita, T.; Grubbs, R.H. *Macromolecules* **2001**, *34*, 8610-8618.

[18] Morita, T.; Maughon, B.R.; Bielawski, C.W.; Grubbs, R.H. *Macromolecules* **2000**, *33*, 6621-6623.

[19] Jagur-Grodzinski, J.;*J. Polym. Sci:A*, **2002**, *40*, 2116-2133.

[20] Morton, M., *Anionic Polymerization: Principles and Practice*, Academic Press, New York, **1983**.

[21] Barner-Kowollik, C. *Handbook of RAFT Polymerization,* Wiley-VCH, Weinheim, **2008**.

[22] Matyjaszewski, K.; Xia, J.; *Chem. Rev*. **2001**, *101*, 2921-2990. Kamigaito, M.; Ando, T.; Sawamoto, M.; *Chem. Rev*. **2001**, *101*, 3689-3745.

[23] Maynard, H.D.; Grubbs, R.H. *Macromolecules* **1999**, *32*, 6917-2924. Weck, M.; Mohr, B.; Maughon, B.R.; Grubbs, R.H. *Macromolecules* **1997**, *30*, 6430-6437. Owen, R.M.; Gestwicki, J.E.; Young, T.; Kiessling, L.L. *Org. Lett*. **2002**, *4*, 2293-2296. Gestwicki, J.E.; Cairo, C.W.; Mann, D.A.; Owen, R.M.;Kiessling, L.L. *Anal. Biochem*. **2002**, *305*, 149-155. Gordon, E.J.; Gestwicki, J.E.; Strong, L.E.; Kiessling, L.K. *Chemistry and Biology*, **2000**, *7*, 9-16. Chen, B.; Sleiman, H.F. *Macromolecules* **2005**, *38*, 1084-1090.

[24] Biagini, S.C.G.; Davie, R.G.; Gibson, V.C.; Giles, M.R.; Marshall, E.L.; North, M. *Polymer* **2001**, *42*, 6669-6671.

[25] Roberts, K.S.; Sampson, N.S*. Org. Lett*. **2004**, *6*, 3253-3255.

[26] Castle, T. C.; Hutchings, L. R.; Khosravi, E. *Macromolecules* **2004**, *37*, 2035-2040.

[27] Schwab, P.; Grubbs, R. H.; Ziller, J.W . *J. Am. Chem. Soc.* **1996**, *118*, 100-110.

[28] Caskey, S. R.; Stewart, M. H.; Kivela, J. E.; Sootsman, J. R.; Johnson, M. J. A.; Kampf, J. W. *J. Am. Chem. Soc*. **2005**, *127*, 16750-16751. Caskey, S. R.; Stewart, M. H.; Johnson, M. J. A.; Kampf, J. W. *Angew. Chem. Int. Ed.* **2006**, *45*, 7422-7424.

[29] Hilf, S.; Berger-Nicoletti, E.; Grubbs, R.H.; Kilbinger, A.F.M. *Angew. Chem*. **2006**, *118*, 8214-8217; *Angew. Chem. Int. Ed.* **2006**, *45*, 8045-8048.

[30] Perrier, S.; Wang, X. *Nature* **2007**, *445*, 271.

[31] Hilf, S.; Kilbinger, A.F.M. *Macromol. Rapid Commun*. **2007**, *28*, 1225-1230.

[32] Hilf, S.; Hanik, N.; Kilbinger, A.F.M. *J. Polym. Sci. A* **2008**, *46*, 2913-2921.

[33] Macnaughtan M.L, Kampf, J.W., Johnson, M.J.A, *J. Am. Chem. Soc*. **2007,** *129*, 7708-7709.

[34] Bielawski,C.W., Grubbs, R.H. *Macromolecules* **2001**, *34*, 8838-8840.

[35] Carlson, R. G.; Gile, M. A.; Heppert, J. A.; Mason, M. H.; Powell, D. R.; Vander Velde, D.; Vilain, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 1580-1581.

[36] Sanford, M.S.; Love, J.A.; Grubbs, R.H. *J. Am. Chem. Soc.* **2001,** *123,* 6543-6554.

[37] Ulman, M.; Grubbs, R.H. *Organometallics* **1998,** *17,* 2484-2489.

[38] Näsman, J.-A. H.; Pensar K. G. *Synthesis* **1985**, 786-788.

[39] Love, J.A.; Morgan, J.P.; Trnka, T.M.; Grubbs, R.H. *Angew. Chem. Int. Ed.* **2002**, *41*, 4035-4037.

Supporting Information for: End-capping ROMP Polymers with Vinyl Lactones

Stefan Hilf, Robert H. Grubbs and Andreas F.M. Kilbinger

Experimental Section

^{1}H-NMR data for functionalized poly(PNI):

For poly(PNI)-CHO:

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2-brigde); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, C(O)CH); 5.5-5.9 (m, 2H, double bonds polymer); 6.2-6.4 (m, 1H, Ph-CH=C*H* end); 6.5-6.7 (m, 1H, Ph-C*H*=CH end); 7.2-7.6 (m, 5H, Ph); 9.6 (s, 1H, Aldehyde endgroup).

For poly(PNI)-COOH:

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2-brigde); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, C(O)CH); 5.5-5.9 (m, 2H, double bonds polymer); 6.2-6.4 (m, 1H, Ph-CH=C*H* end); 6.5-6.7 (m, 1H, Ph-C*H*=CH end); 7.2-7.6 (m, 5H, Ph); 11.3(s (br), 1H, COOH endgroup).

General procedure for the synthesis of 2,4-dinitrophenylhydrazones of CHO-functionalized polynorbornenes: 100mg of the aldehyde-functionalized polymer were dissolved in 5mL chloroform. 1mL acetic acid and 50mg 2,4-dinitrophenyl hydrazine (50% slurry in water) were added. The mixture was refluxed for 4 h, precipitated in hot ethanol and collected. The resulting polymer was redissolved in chloroform and precipitated in hot ethanol until the supernatant solution remained colorless. Vacuum drying afforded 60-85% of a yellow polymer material.

Exemplary characterization for poly(**PNI**):

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2-brigde); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, C(O)CH); 5.5-5.9 (m, 2H, double bonds polymer); 6.2-6.4 (m, 1H, Ph-CH=C*H* end); 6.5-6.7 (m, 1H, Ph-C*H*=CH end); 7.2-7.6 (m, 5H, Ph); 7.91 (d, 1H, 5-(NO_2-Ph)); 8.28 (d, 1H, 6-(NO_2-Ph)); 9.10 (s, 1H, 3-(NO_2-Ph)); 11.06 (s, 1H, N-H).

General Procedure for the Synthesis of 2,2,2-trichloromethyl ester of COOH-functionalized polynobornenes: 100mg polymer, 50mg dicyclohexyl carbodiimide and 100mg *N,N*-dimethylamino pyridine were dissolved in 5mL dry dichloromethane. 0.1 mL 2,2,2-trichloroethanol were added and the mixture was stirred at r.t. for 14h before the polymer was precipitated in methanol, collected, redissolved in chloroform and reprecipitated in methanol. The resulting polymer was dried in vacuo to give a brownish polymer material in good yields (>80% typically).

Exemplary characterization for poly(**PNI**):

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2-brigde); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, C(O)CH); 4.75 (m, 2H, CH_2-C-Cl_3 endgroup); 6.2-6.4 (m, 1H, Ph-CH=C*H* end); 6.5-6.7 (m, 1H, Ph-C*H*=CH end); 7.2-7.6 (m, 5H, Ph).

Synthesis of N-(2-hydroxy-ethoxy)-ethyl-2,3-norbornene dicarboximide (HEENI): 32g (0,2 mol) *exo*-norbornene-2,3-dicarboxanhydride were added 21g (0.2 mol) 2-aminoethoxy-ethanol. The mixture was allowed to stand for 30 min before 150mL toluene were added and the resulting slurry was refluxed under dean-stark conditions until all solids had dissolved and 3.2mL water had been collected (ca. 5 h). The solvent was then evaporated under reduces pressure and the resulting oil was passed through a silica column (eluent: chloroform: methanol 9:1 v:v, R_f=0.85) to give a colorless oil in good yield (42g, 82%).

^{1}H-NMR (300MHz, $CDCl_3$) δ[ppm]: 1.37 (dd, 2H, CH_2-bridge; ^2J=60Hz, ^3J=10Hz); 2.65 (s, 2H, C_3CH); 3.23 (s, 2H, C(O)CH); 3.5-3.7 (m, 8H, CH_2-O + CH_2-N) 6.24 (s, 2H, C=CH).

Synthesis of Poly(HEENI)-CHO and the hydrazone derivative: To a stirred solution of 49mg (56µmol) catalyst (in 3mL dichloromethane) **C1** was added a solution of 300mg **HEENI** in 12mL dichloromethane. After 1h, a large excess (200µL) of **VC** was added and stirring was continued over 8h. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (0.5mL) and stirring was continued for another 2h. The polymer was precipitated in methanol, collected, re-dissolved in chloroform and re-precipitated in methanol, collected and dried under vacuum over night to give 240mg (80%) of a slightly brown solid. The formation of the 2,4-dinitrophenyl-hydrazone was carried out following the general procedure.

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 1.6-1.7, 2.0-2.2 (m, 2H, CH_2-brigde); 2.6-2.8 (m, 2H, C_3CH); 2.9-3.1 (m, 2H, C(O)CH); 3.5-3.8 (m, 8H, CH_2-N and CH_2-O); 5.5-5.8 (m, 2H, double bonds polymer); 6.2-6.4 (m, 1H, Ph-CH=C*H* end); 6.5-6.7 (m, 1H, Ph-C*H*=CH end); 7.2-7.5 (m, 5H, Ph-endgroup); 7.91 (d, 1H, 5-(NO_2-Ph)); 8.31 (d, 1H, 6-(NO_2-Ph)); 9.12 (s, 1H, 3-(NO_2-Ph)); 11.10 (s, 1H, N-H).

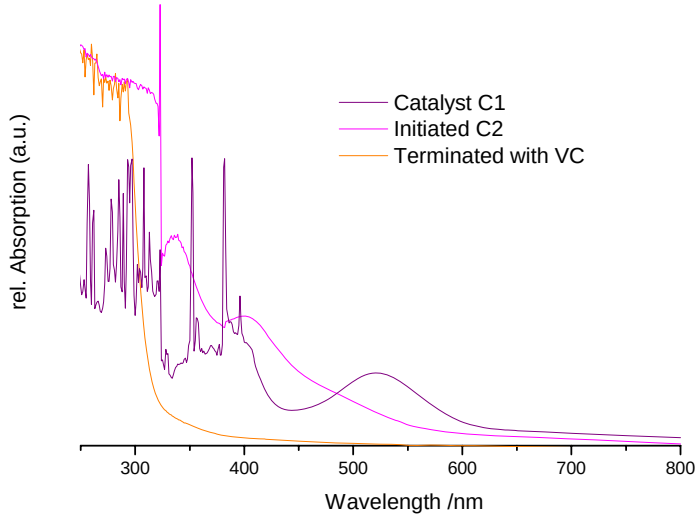
Synthesis of Poly(nobornene-aldehyde)-COOH and the trichloroethyl ester: To a stirred solution of 52mg (56µmol) catalyst (in 3mL dichloromethane) **C3** was added a solution of 300mg 5-norbornene-carbaldehyde (endo/exo-mixture) in 12mL dichloromethane. After 45min, an excess (200µL) of **3HF** was added and stirring was continued over 8h. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (0.5mL) and stirring was continued for another 2h. The polymer was precipitated in methanol, collected, re-dissolved in chloroform and re-precipitated in methanol, collected and dried under vacuum over night to give 265mg (85%) of a brown solid. The formation of the trichloroethyl ester was carried out following the general procedure.

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 1.2-1.3 (m, 2H, C*H*$_2$-CH-CHO); 1.6-2.2 (m, 2H, CH_2-brigde); 2.5-3.4 (m, 3H, C_3CH + C*H*-CHO); 5.3-5.5 (m, 2H, double bonds polymer); 6.2-6.3 (m, 1H, Ph-CH=C*H* end); 6.5-6.6 (m, 1H, Ph-C*H*=CH end); 7.2-7.5 (m, 5H, Ph-endgroup); 9.6-9.7 (m, 1H, CHO).

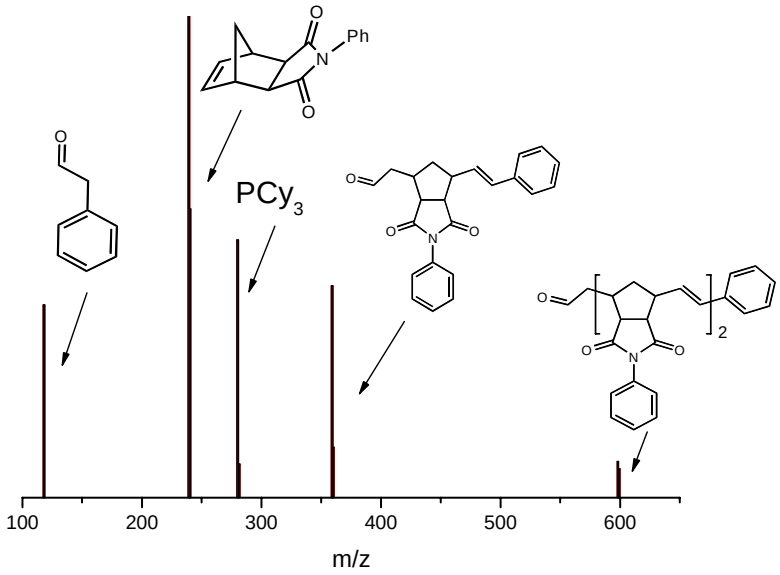
Synthesis of poly(PNI)-CONH-CH_2-Pyrene: 50mg of poly(PNI) (Mn=4400, PDI=1.13 (RI-detection); 11.4µmol), 20mg (84µmol) of 1-pyrenemethylamine hydrochloride, 50mg (242µmol) dicyclohexylcarbodiimide and 50mg (409µmol) of 4-dimethylaminopyridine were weighed into a 50mL Schlenk-flask, degassed and dissolved in 10mL dry dichloromethane. After stirring at r.t. for 14h, the turbid mixture was concentrated at the rotary evaporator, taken up with a small amount of chloroform and precipitated in methanol. The resulting solids were collected and dried in vacuo yielding 40mg (ca. 80%) of a colorless material.

GPC: Mn=4200, PDI=1.13 (RI-detection).

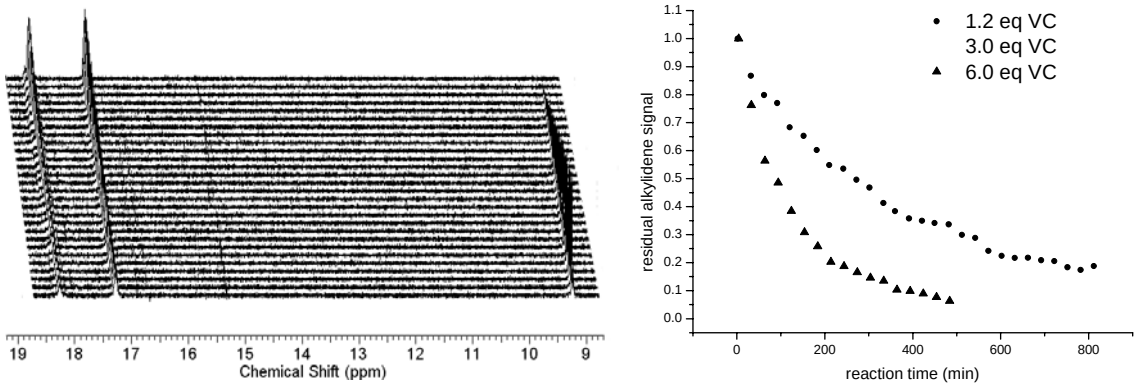
S-1: *Left:* Catalyst **C1** in dichloromethane *Middle:* Catalyst **C2** initiated with 15 equivalents of **PNI** *Right:* After termination with excess **VC**.



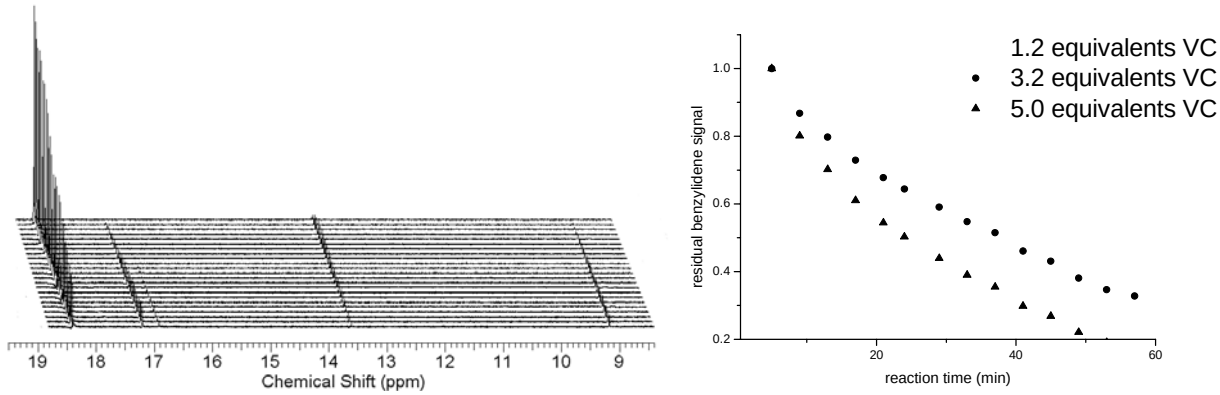
S-2: UV/vis spectra of the above mentioned (see **S-1**) solutions.



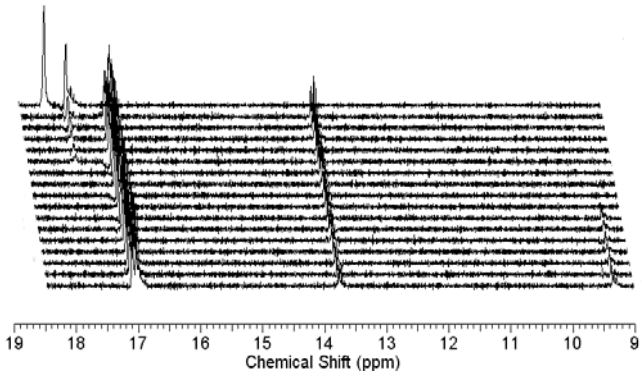
S-3: FD-MS of **VC**-terminated oligomer solution.



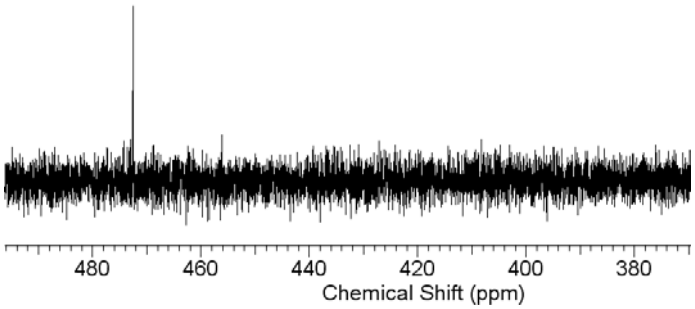
S-4: Reaction between initiated ruthenium benzylidene catalyst **C2** (15 eq**. PNI**) and vinylene carbonate (**VC**). The time resolved disappearance of the benzylidene signal is shown. (30 min between spectra)



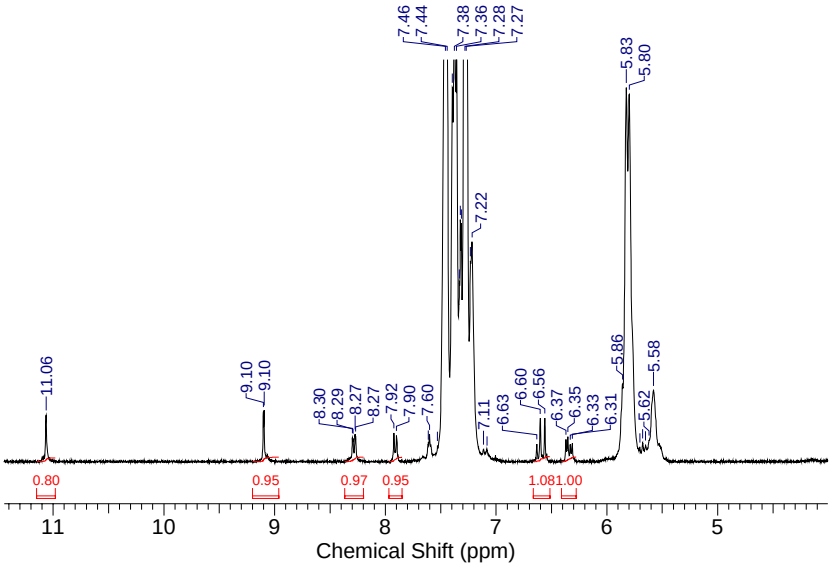
S-5: Reaction between ruthenium benzylidene catalyst **C3** and vinylene carbonate (**VC**). The time resolved disappearance of the benzylidene signal is shown. (90s between spectra)



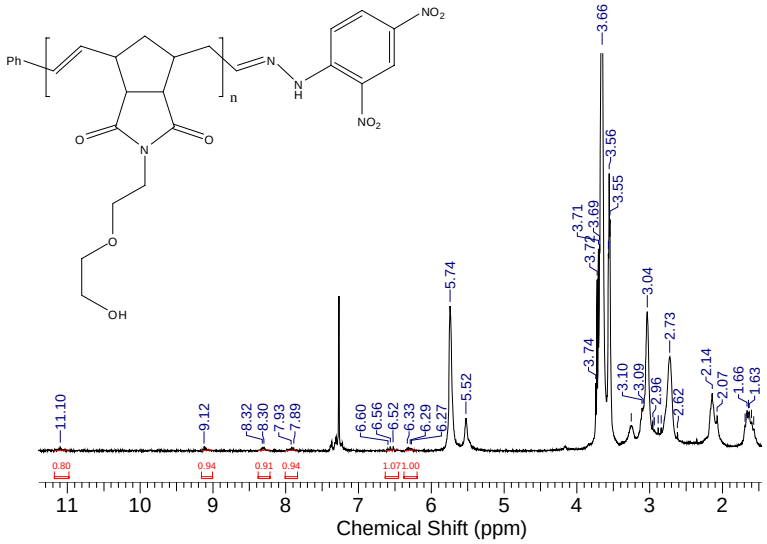
S-6: Reaction between initiated ruthenium benzylidene catalyst **C3** (15 eq. **PNI**) and vinylene carbonate (**VC**). (60s between spectra)



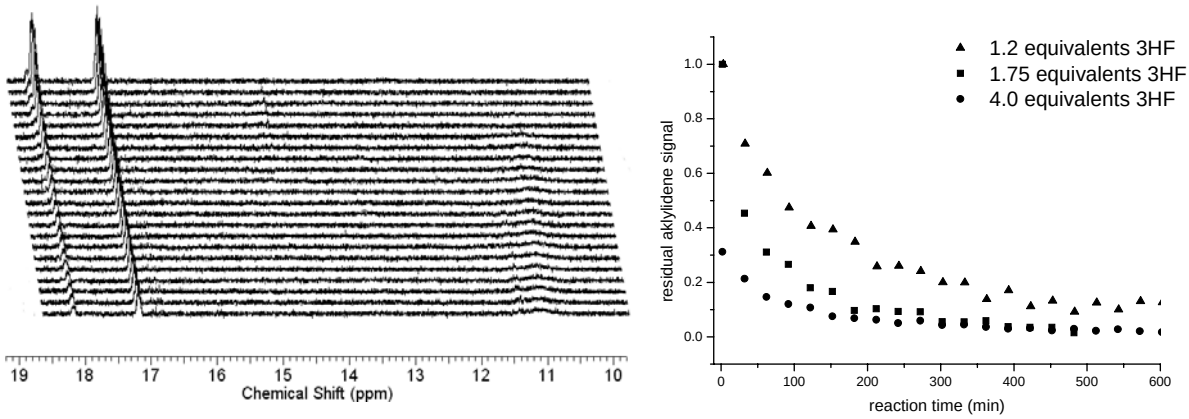
S-7: ^{13}C-NMR spectrum (CD_2Cl_2) of catalyst **C1** initiated with **PNI**, terminated with **VC**.



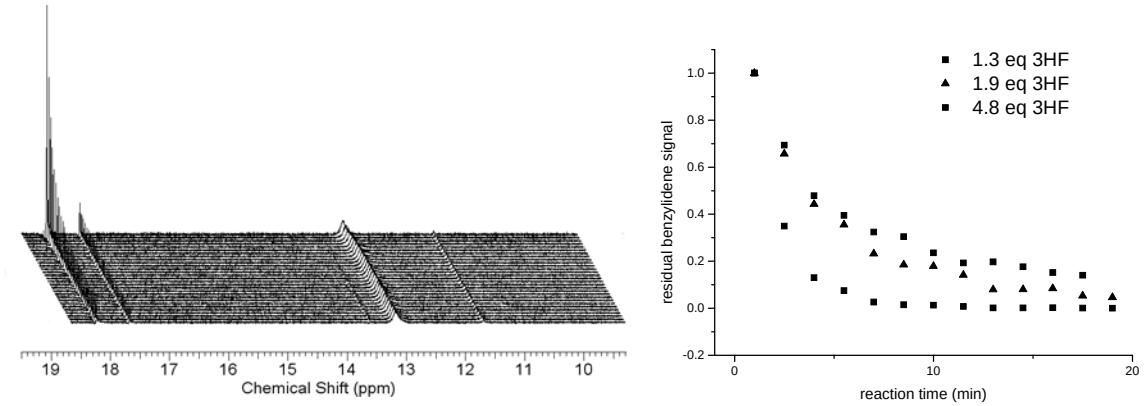
S-8: ^{1}H-NMR of 2,4-Dinitrophenylhydrazone of poly(PNI)-CHO for estimation of the total degree of functionalization.



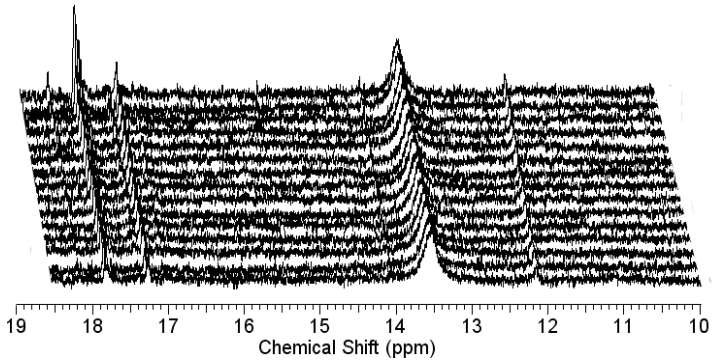
S-9: ^{1}H-NMR of 2,4-Dinitrophenylhydrazone of poly(HEENI)-CHO.



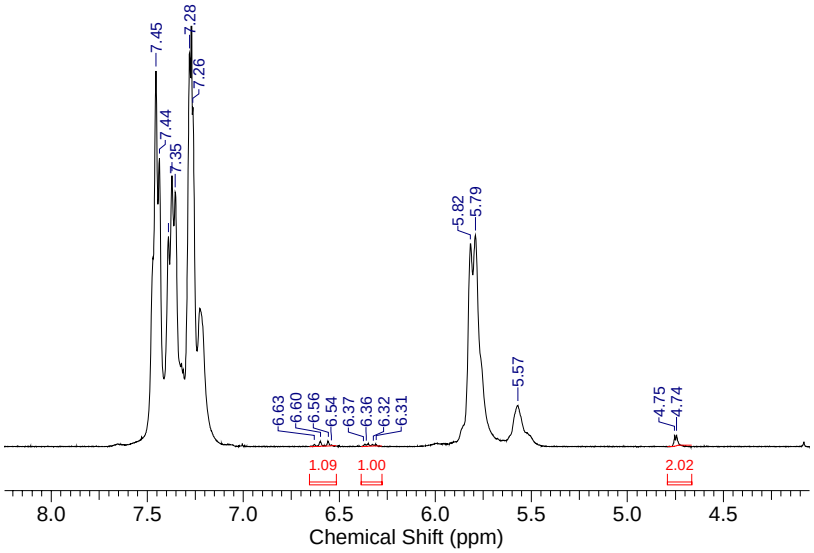
S-10: Reaction between initiated ruthenium benzylidene catalyst **C2** (15 eq**. PNI**) and 3H-furanone (**3HF**). The time resolved disappearance of the benzylidene signal is shown. (20 min between spectra)



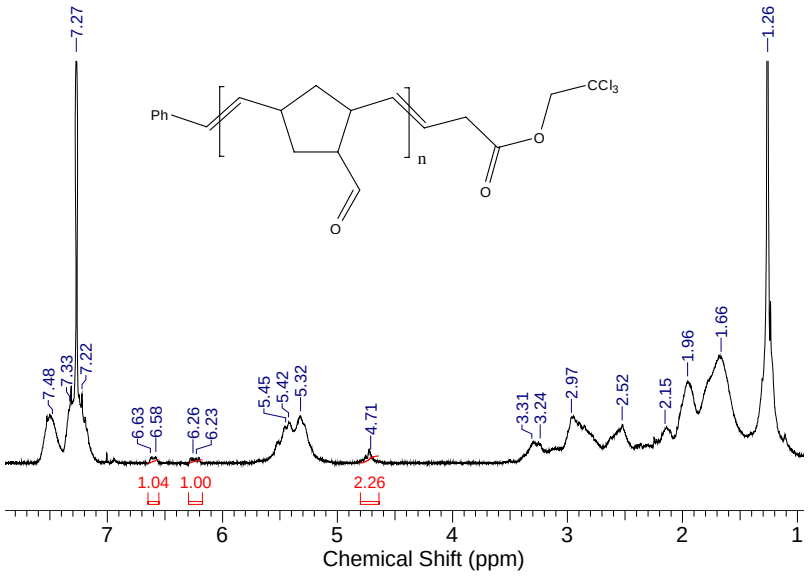
S-11: Reaction between ruthenium benzylidene catalyst **C3** and vinylene carbonate (**VC**). The time resolved disappearance of the benzylidene signal is shown. (90s between spectra)



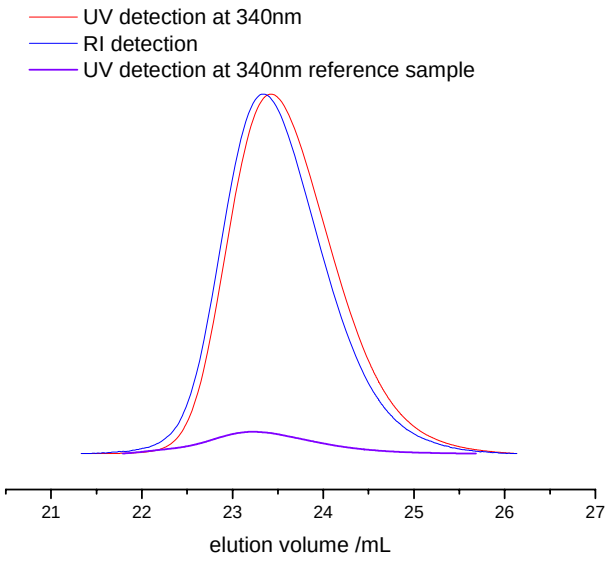
S-12: Reaction between initiated ruthenium benzylidene catalyst **C3** (15 eq. **PNI**) and vinylene carbonate (**VC**). (60s between spectra)



S-13: ^{1}H-NMR of 2,2,2-Trichloroethyl ester of poly(PNI)-COOH for estimation of the total degree of functionalization.



S-14: ^{1}H-NMR of 2,2,2-Trichloroethyl ester of poly(norbornenes-5-carbaldehyde)-COOH for estimation of the total degree of functionalization.



S-15: GPC traces of pyrene labelled Poly(PNI)-COOH with UV detection at 340 nm and non-labelled Poly(PNI)-COOH as reference.

2.6: Well-defined Heterotelechelic Metathesis Polymers – A Combinatorial Approach

Stefan Hilf and Andreas F. M. Kilbinger

Manuscript in praparation

Abstract

By combining Sacrificial Synthesis with the vinyl lactone termination technique, heterotelechelic polymers were synthesized. The non-terminatiing nature of Sacrificial Synthesis was utilized to introduce a hydroxyl group at the start of the polymer chain. Lactone termination was used to functionalize the chain ends with aldehydes or carboxylic acids. The synthesis of well-defined heterotelechelic polymers was thus accomplished employing the Grubbs' 1st generation catalyst as the initiator. The living nature of this polymerization allowed for precise control over the molecular weight and guaranteed full functionalization of both polymer chain ends. The presence of the functional groups is shown by MALDI-ToF and NMR measurements. Also, labeling experiments with chromophores were conducted to demonstrate the utility of such heterotelechelic polymer chains.

Introduction

The synthesis of heterotelechelic polymers is a particularly sophisticated element of macromolecular synthesis research. In contrast to their simpler homotelechelic relatives, this class of materials carries different reactive endgroups on both chain ends. Therefore, the different endgroups can be addressed specifically and selectively. Precision in placement of functional groups is the basis for the synthesis of complex macromolecular structures from heterotelechelic starting materials. It is of tremendous relevance in many fields of molecular research, materials- and life sciences. Such materials can be used to combine different molecules such as biologically active peptides or receptor sites[1] with e.g. fluorescent labels or proteins.[2] However, not only interdisciplinary applications, but also polymer synthesis require strategies for the synthesis of heterobifunctional polymer chains as they can act as linkers between different synthetic macromolecules or as building blocks in block-copolymer synthesis. They also give rise to a number of interesting polymer architectures in convergent conjugate formations.[3]

Most heterotelechel syntheses rely on living polymerization methods. Carb-anionic[4] and oxy-anionic polymerization methods are amongst the most utilized strategies for the formation of heterotelechelic polymers. This trend is mainly caused by both the availability of appropriate functionalizing termination agents which provide access to the chain-end functionality. They also offer potential for introducing functional groups at the start of every polymer chain using initiators which contain, sometimes heavily, protected functional groups. [5]

Furthermore, strategies for the use of controlled polymerization techniques for the synthesis of heterotelechels have been developed. They make use of the relatively high functional group tolerance of the controlled methods and therefore do not require heavy protective groups. Particularly elegant pathways are given by reactions that can derivatize and stabilize the dormant species involved in the polymerization and thus terminate it.[6]

Less well-defined telechelic polymers can be synthesized by step-growth polymerizations.[7] Polycondensations and polyadditions are easily accessible and typically give extremely high degrees of chain-end functionalization, however, they give broad molecular weight distributions and little control over the average chain length.

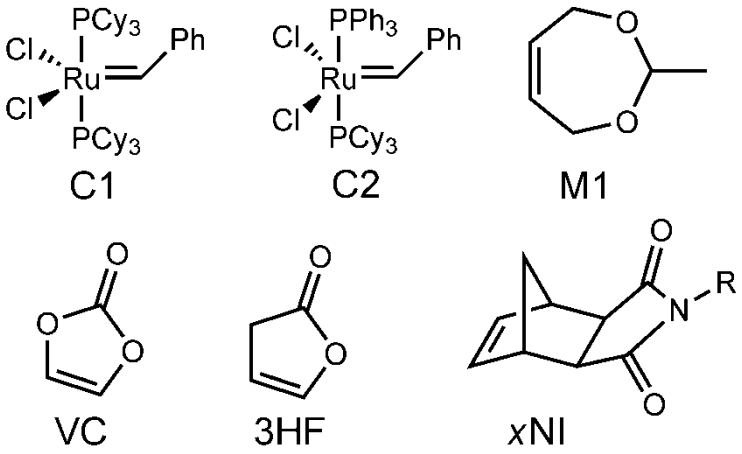
Telechelics are available via the ring-opening metathesis polymerization (ROMP). Three different approaches are known to literature, using two different synthetic methods. By the application of chain –transfer agents (CTA), homobifunctional olefins have been synthesized with a broad variety of functional groups including carboxylic acids, alcohols and amines.[8] Statistical copolymers of classical monomers with cyclic olefins which contain a cleavable site such as an acetal also gave telechelics after hydrolysis.[9] Both approaches, however, are strictly limited to homobifunctional telechelics due to the low regioselectivity of ROMP. Also, they give rather poorly defined polymer materials since both methods rely on statistical polymerizations or equilibration reactions which inevitably lead to broader molecular weight distributions. The third method is based on the concept of *Sacrificial Synthesis* for the placement of hydroxyl groups at ROMP-polymer chain ends. There, the controllable formation of (multi)block-copolymers of sacrificial and hydrolysis stable monomers gives rise to well-defined telechelic polymers.

Over the last three years, we have reported various strategies for the functionalization of ROMP polymers. The aforementioned unique *Sacrificial Synthesis*[10] strategy does, in contrast to the most renowned quenching reactions involving vinyl ethers[11], not require a termination reaction for the placement of the functional group, but a macroinitiation. [12] The living chain end retains its activity and can be used to polymerize additional polymer blocks. Cyclic acetals were introduced for the formation of hydroxyl endgroups. Monofunctionalized polymers synthesized by this method have already been used for the synthesis of graft[13] and block copolymers.[14]

The second method for precise and efficient functional group placement, we developed, is based on the termination reaction induced by vinyl lactones.[15] The deactivated Fischer-type carbene in this case represents an acyl carbene which self-decomposes, setting the functional group and a ruthenium-carbido complex free. This method is particularly mild as no work-up or deprotection reactions are required.

Here, we present a combinatorial for the synthesis of heterotelechelic polymers based on the non-terminating functionalization of *Sacrificial Synthesis* to introduce functionalities at the first chain end followed by polymerization of regular monomers and a lactone termination step to functionalize the second chain end. In order to introduce the functional group at the first chain end, first a cleavable block polymerized from 2-methyl-1,3-dioxepine (M1) was polymerized using Grubbs' 1st generation catalyst (C1) and its derivative C2

(c.f. Scheme 1) which gives better molecular weight distributions at low molecular weights.[16] These initiators were chosen as they had proven functional group tolerance and long-term stability before and also had shown efficient block transfers from a dioxepine block to classical ROMP monomer blocks. Norbornene imides were chosen as the stable monomer since this class of monomer is highly variable in its imide substituents and can be synthesized easily from the readily available anhydride. The termination of the living ruthenium sites on the active chains was conducted by application of vinylene carbonate (VC) to generate aldehyde endgroups or by addition of *3H*-furanone (3HF) when carboxylic acid endgroups were to be attached to the polymer chain ends.



Scheme 1: Monomers, initiators and terminating agents used in this study

Experimental

General. ^{1}H-NMR spectra were recorded at 300 MHz on a Bruker AC300 or at 400MHz on a Bruker ARX400. All spectra were referenced internally to residual proton signals of the deuterated solvent. Deuterated solvents were purchased from Deutero GmbH. Gel permeation chromatography in tetrahydrofuran or chloroform was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P100 pump and a set of three PSS SDV columns ($10^5/10^3/10^2$ Å). Signal detection occurred by use of a TSP Spectra System UV2000 (UV 254 nm unless otherwise stated) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) measurements were performed on a Shimadzu Axima CFR MALDI-TOF mass spectrometer equipped with a nitrogen laser delivering 3ns laser pulses at 337nm.

Exo-N-dodecyl-2,3-norbornene dicarboximide and *exo-N*-hexyl-2,3-norbornene dicarboximide, as well as 2-methyl-1,3-dioxepine were synthesized as described in earlier publications.[18,17,18] Grubbs' 1st generation catalyst was obtained from Materia, inc. All solvents and other reagents were purchased from Aldrich or Acros. All polymerization reactions were carried out under argon using standard Schlenk techniques unless otherwise stated. Dichloromethane as the polymerization solvent was dried over P_2O_5 and distilled under a nitrogen atmosphere. 2-methyl-1,3-dioxepine was degassed by repeated freeze-pump-thaw-purge cycles using argon as the inert gas.

General procedure for the synthesis of heterotelechelic polymers using catalyst C1:

To a stirred solution of Grubbs' 1st generation catalyst (164 mg in 3 mL dichloromethane) was added 0.75 mL 2-methyl-1,3-dioxepine. After 1 hour, the solvent and all residual monomer was removed by high vacuum; the flask was evacuated for another 1 hour. The living polymer was then redissolved in 10 mL dichloromethane and the calculated amount of monomer (2 g in 10 mL dichloromethane for 10,000 g/mol) was added by syringe. After the polymerization had finished (typically 1 hour for 10,000 g/mol), 1 mL of the dioxepine monomer for the third block was added by syringe. After another 2 hours, the polymerization was terminated by addition of 0.5 mL ethyl vinyl ether in order to cleave the catalyst off the chain. The polymer was precipitated in methanol, collected and dried over night in a vacuum oven to give a brownish solid in good yield (>90% typically).

General procedure for the synthesis of heterotelechelic polymers using catalyst C1:

To a stirred solution of Grubbs' 1st generation catalyst (C1) (164 mg in 3 mL dichloromethane) was added 1.0 mL 2-methyl-1,3-dioxepine. After 1 hour, the solvent and all residual monomer was removed by high vacuum under gentle warming with an r.t. waterbath. After evacuating the flask was evacuated for 30 minutes, 3 mL dichloromethane were added to dissolve the solid residues and the flask was evacuated again for 30 minutes. The living polymer was then redissolved in 10 mL dichloromethane and the calculated amount of monomer (1 g in 5 mL dichloromethane for 5000 g/mol, 1.4 g in 5 mL dichloromethane for 7000 g/mol or 2 g in 10 mL dichloromethane for 10000 g/mol) was added by syringe. After the polymerization had finished (typically 1 hour for 10000 g/mol),

300µL of the termination agent (VC for aldehydes 3HF for carboxylic acids) were added. After another 2 hours, after which the color of the solution had typically changed from a brown color to yellow, the polymer was precipitated in methanol, collected and dried over night in a vacuum oven to give a brownish solid in good yield (>90% typically).

General procedure for the synthesis of heterotelechelic polymers using catalyst C2:

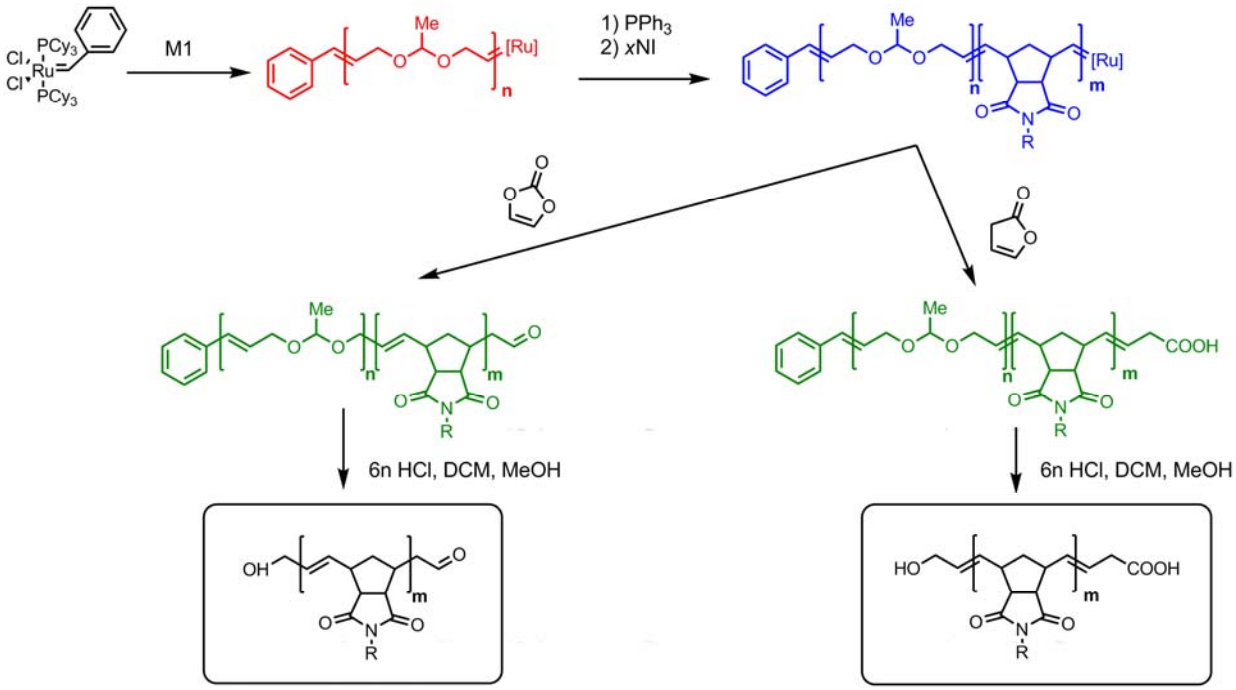
The polymerization of the dioxepine block was carried out under the same conditions and with the same catalyst as described for catalyst C1. Catalyst C2 was generated during the reaction as follows: After the vacuum removal of all solvents and residual M1 monomers, a solution of 240 mg triphenylphosphine (4 equiv. of the catalyst) dissolved in 10 mL dichloromethane was used to redissolve the living poly(M1). After 10 minutes, the calculated amount of monomer (2 g in 10 mL dichloromethane for 10000 g/mol) was added by syringe. After the polymerization had finished (typically 14 hours for 10000 g/mol, 7 hours for 5000 g/mol), 300 µL of the termination agent (VC for aldehydes 3HF for carboxylic acids) were added. The mixture was left to terminate for 14 hours. The color change during the termination of catalyst C2 is less pronounced than with C1. After the termination was finished, the polymer was precipitated in methanol, collected and dried over night in a vacuum oven giving a brownish solid in good yield (>90% typically).

General procedure for the hydrolysis of the M1-block:

The polymer bearing a poly(2-methyl-dioxepine) block was dissolved in dichloromethane (ca. 20 mL per 1 g polymer). 10 mL methanol and 10 mL 6n HCl were added and the mixture was stirred vigorously. After one night, the polymer was precipitated by adding methanol. After collecting, redissolving in chloroform and reprecipitation in methanol, the polymer was obtained as an off-white solid in good yield (>75% typically).

Results and Discussion

This strategy towards the synthesis of heterotelechelic polymers is based on the non-deactivating characteristics for the functional group placement via sacrificial block copolymers. If such a sacrificial block is synthesized as the first block of a block-copolymer, the "start"-group of this chain is functionalized. The second endgroup of a polymer chain thus be terminated with a different method giving the second functional endgroup. The synthetic pathway leading to heterotelechelic is illustrated in Scheme 2. Here, a methyl-dioxepine block is polymerized as the first block, the block copolymer is formed by addition of norbornene imide monomers and termination is facilitated by addition of a vinyl lactone which produces the second functional endgroup. The first functionality is then set free by acidic hydrolysis of the poly(M1)-block with cleavage of the acetal moieties included in the monomer units.



Scheme 2: Synthesis of heterotelechelic ROMP polymers.

In a first attempt, the polymerization of the sacrificial diblock-copolymer was carried out using catalyst C1. The synthesis of the diblock-copolymer perfomed well, according to a blockwise analysis of the construction of the material. The polymers were obtained in good definition (PDI~1.2). After hydrolysis of the sacrificial block, however, a material was retained that showed a significantly broadened molecular weight distribution in all cases (*c.f.* Figure 1). PDIs ranged around 1.35-1.5. Apparently, the termination in presence of poly(M1) led to side reactions such as secondary metatheses which had not been observed in the Lactone Quenching technique before.

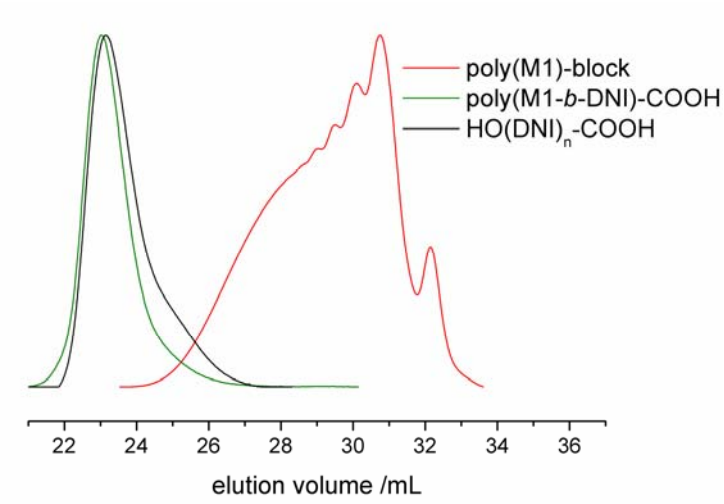


Figure 1: Blockwise SEC analysis of the construction of heterotelechels under C1 catalysis

In order to improve the definition of the final polymer, the method of Bielawski was tested, adding an excess of PPh_3 to the polymerization mixture. A test-polymerization of M1, however, unveiled incomplete polymerization of this acetal monomer presumably due to an extremely slow polymerization after 10 h. An extensive purification of the poly(M1) macroinitiator would therefore have been necessary in order to avoid an infiltration of the second polymer block with residual M1.

Hence, we decided to perform a mixed approach using the polymerization characteristics of C1 for the M1-block and making use of the easy conversion from C1 to C2, whose improved polymerization characteristics for norbornene imides should then lead to better polymer definition in the second, stable, polymer block. Again, the construction of the block-copolymer and the termination were monitored by stage-wise analysis by SEC. All samples were terminated additionally by conventional ethyl vinyl ether termination in order to avoid

further reactions in the analytical samples. The SEC traces obtained for the formation of OH/COOH and OH/CHO telechelics are given in Figure 3

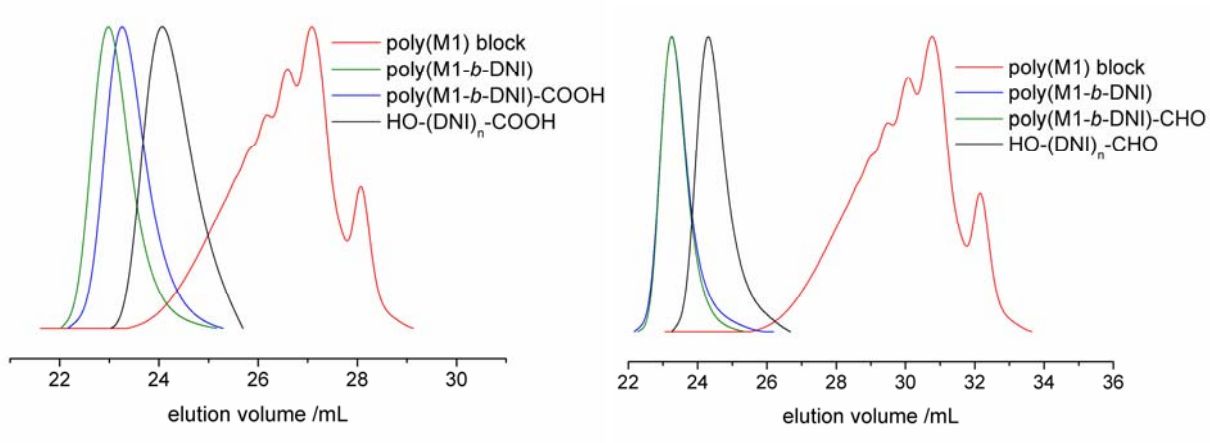


Figure 3: Blockwise analysis of the contruction of OH/COOH (left) anf OH/CHO (right) telechelics.

From the block samples, the clean construction of the sacrificial diblock-copolymer can be observed. Interstingly, a small decrease in the average molecular weight can be found after termination of the diblock-copolymer with 3HF, which is not observed when the reaction was terminated with VC. Considering the chemical nature of the newly formed functional group, a carboxylic acid, a slow cleavage of the M1 block can be imagined, which is also conducted by acidic hydrolysis. The cleavage of the sacrificial block performed well and gave exceptionally well-defined heterotelechelic polymers (PDI~1.15).

The heterotelechelic polymers were analyzed by MALDI-ToF MS. Figure 4 shows the spectrum obtained for a poly(HNI) heterotelechel carrying a hydroxyl function and a carboxylic acid. In the case of heterotelechelic polymers, the carboxylic acid was a sodium salt in contrast to the monofunctional polymers observed in our lactone termination study under the same conditions. No matrix/ionization agent could yet be found for the OH/CHO telechels.

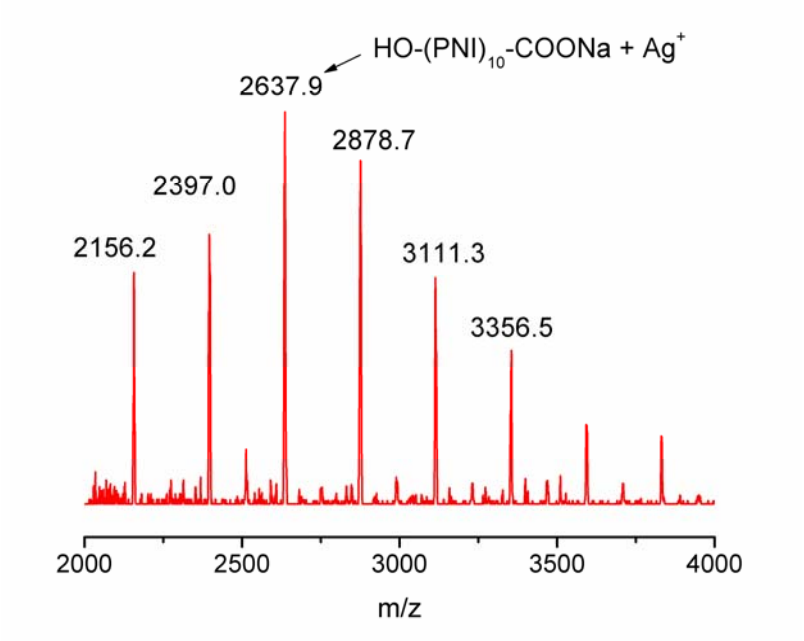


Figure 4: MALDI-ToF MS of HO-(HNI)$_n$-COOH (entry 1 in Table 1)

Table 1: Polymerization results for the heterotelechelic polymers

entry	*x*NI	FG	Mn_{calc} /g mol^{-1}	Mn_{SEC} /g mol^{-1}	PDI
1	HNI	OH/COOH	6000	6700	1.18
2	HNI	OH/COOH	7500	8400	1.20
3	HNI	OH/COOH	10000	9000	1.12
4	DNI	OH/COOH	4000	4600	1.27
5	DNI	OH/COOH	6000	6400	1.14
6	DNI	OH/COOH	7000	7100	1.20
7	HNI	OH/CHO	5000	6800	1.26
8	HNI	OH/CHO	10000	10300	1.29
9	HNI	OH/CHO	15000	15500	1.13
10	DNI	OH/CHO	5000	5700	1.23
11	DNI	OH/CHO	7000	7500	1.24
12	DNI	OH/CHO	10000	12000	1.22

A number of polymers was synthesized and bifunctionalized using this strategy. The characterization results for the various samples are listed in Table 1. The use of catalyst C2, which has an increased initiation efficiency when rather short polymer chains are synthesized, allowed for the precise synthesis of defined polymers. We have therefore been able to develop a feasible and versatile method for the synthesis of heterotelechelic polymers by ROMP using commercially available catalysts as well as readily available monomers and functionalization agents.

Conclusion

The synthesis of heterotelechelic polymers bearing hydroxyl groups on one chain end and an aldehyde or a carboxylic acid at the other has been accomplished by a combined approach using Sacrificial Synthesis and the vinyl lactone termination. The non-terminating placement of exactly one hydroxyl group via a cleavable acetal polymer allowed for the precise functionalization of the fist chain end, while the second functionality was introduced by a termination reaction.

The polymerization of the chain-end functionalized sacrificial diblock-copolymer was carried out using initiators of the first generation of Grubbs' catalysts. Best polymerization results were achieved when the catalyst activity was tailored to the necessities of each polymer block. For the polymerization of the first, sacrificial, block, catalyst C1 was used to promote the polymerization. Before the second, stable, monomer was added, the catalysts activity was changed by addition of PPh_3, thus forming C2.

This pathway gave rise to very well-defined heterotelechelic material which will certainly be of considerable interest in polymer chemistry as now, ROMP polymers can not only bear a variety of interesting functional groups along the chain, but also two different, precisely placed, reactive endgroups on the two chain ends.

References:

[1] Boyer, C.; Liu, J.; Bulmus, V.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *Macromolecules* **2008**, *41*, 5641-5650. Hereida, K. L.; Grover, G. N.; Tao, L.; Maynard, H. D. *Macromolecules* **ASAP**, doi: 10.1021/ma8022712.

[2] Ribot, F.; Lafuma, A.; Eychenne-Baron, C.; Sanchez, C. *Adv. Mater.* **2002**, *14*, 1496-1499.

[3] Abadie, M. J. M.; Satibi, L. *Eur. Polym. J.* **1987**, *23*, 223-228.

[4] Quirk, R. P.; Ma, J.-J.; Lizarraga, G.; Ge, Q.; Hasegawa, H.; Kim, Y. J.; Jang, S. H.; Lee, Y. *Macromol. Symp.* **2000**, *161*, 37-44.

[5] Hirao, A.; Hayashi, M. *Acta Polym.* **1999**, *50*, 219-231.

[6] Guth, W.; Heitz, W. *Makromol. Chem.* **1976**, *177*, 3159-3175. Guth, W.; Heitz, W. *Makromol. Chem.* **1976**, *177*, 1835-1855. Nuyken, O. *Angew. Makromol. Chem.* **1994**, *223*, 29-46. Heitz, W. *Chem. Phys. Macromol.* **1991**, 61-95.

[7] Kricheldorf, H. R.; Adebahr, T. *Makromol. Chem.* **1993**, *194*, 2103-2115. Kricheldorf, H. R.; Chen, X; Masri, M. A. *Macromolecules* **1995**, *28*, 2112-2117.

[8] Bielawski, C.W.; Benitez, D.; Morita, T.; Grubbs, R.H. *Macromolecules* **2001**, *34*, 8610-8618. Morita, T.; Maughon, B.R.; Bielawski, C.W.; Grubbs, R.H. *Macromolecules* **2000**, *33*, 6621-6623.

[9] Fraser, C.; Hillmyer, M. A.; Gutierrez, E.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 7256-7261

[10] Hilf, S.; Berger-Nicoletti, E.; Grubbs, R.H.; Kilbinger, A.F.M. *Angew. Chem*. **2006**, *118*, 8214-8217; *Angew. Chem. Int. Ed.* **2006**, *45*, 8045-8048. Perrier, S.; Wang, X. *Nature* **2007**, *445*, 271.

[11] Maynard, H.D.; Grubbs, R.H. *Macromolecules* **1999**, *32*, 6917-2924. Weck, M.; Mohr, B.; Maughon, B.R.; Grubbs, R.H. *Macromolecules* **1997**, *30*, 6430-6437. Owen, R.M.; Gestwicki, J.E.; Young, T.; Kiessling, L.L. *Org. Lett*. **2002**, *4*, 2293-2296. Gestwicki, J.E.; Cairo, C.W.; Mann, D.A.; Owen, R.M.; Kiessling, L.L. *Anal. Biochem*. **2002**, *305*, 149-155. Gordon, E.J.; Gestwicki, J.E.; Strong, L.E.; Kiessling, L.K. *Chemistry and Biology*, **2000**, *7*, 9-16. Chen, B.; Sleiman, H.F. *Macromolecules* **2005**, *38*, 1084-1090. Mangold, S. L.; Carpenter, R. T.; Kiessling, L. L. *Org. Lett.* **2008**, *10*, 2997-3000.

[12] Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M *Macromolecules* **2008**, *41*, 6006-6011.

[13] Hilf, S.; Kilbinger, A.F.M. *Macromol. Rapid Commun*. **2007**, *28*, 1225-1230.

[14] Hilf, S.; Hanik, N.; Kilbinger, A.F.M. *J. Polym. Sci. A* **2008**, *46*, 2913-2921.

[15] Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M *J. Am. Chem. Soc.* **2008**, *130*, 11040-11048.

[16] Bielawski,C.W., Grubbs, R.H. *Macromolecules* **2001**, *34*, 8838.

Chapter 3: Applications of functionalized Metathesis Polymers

3.1: An All-ROMP route to graft-copolymers

Stefan Hilf and Andreas F. M. Kilbinger.

Published in: Macromolecular Rapid Communications **2007**, *28*, 1225-1230.

A new versatile synthesis strategy for macromonomers has been developed that uses the living ring-opening metathesis polymerization (ROMP) with commercial Grubbs 1st generation ruthenium initiators. Homopolymers as well as diblock copolymers were end-functionalized with norbornene derivatives to serve as macromonomers. The graft copolymerization of the macromonomers was also carried out employing ROMP. Well-defined and highly functional graft copolymers are accessible with this new synthetic route.

Introduction

With the advancements in living polymerization techniques over the last decades, chemists today can choose from a variety of polymerization procedures yielding well-defined polymers. Careful combination of these polymerization techniques has allowed the synthesis of ever more complex, yet well-defined polymeric architectures.

Graft copolymers represent one type of hyperbranched polymeric architecture in which polymer chains are attached along a polymer backbone.[1] Graft copolymers are important macromolecular architectures and have received interest for compatibilizing immiscible polymer blends or improving mechanical properties of composites. They also represent a form of multi-branched structure in which full control over the density of branching points as well as the length of the grafts and the backbone can be achieved.

Using living polymerization techniques, the molecular weight and the molecular weight distribution of backbone and grafts as well as the grafting density can be controlled.

Two synthetic routes are commonly employed to prepare these macromolecular architectures. The first is the macromonomer route in which a mono-end-functional polymer chain is prepared and modified with a polymerizable group.[2] A subsequent second polymerization joins these end-groups to form a graft copolymer. The grafts in this approach are typically prepared via carb-anionic,[3,4,5,6,7,8] oxy-anionic,[9,10,11,12] atom transfer radical polymerization (ATRP)[13,14,15] or ring opening polymerization.[16] The ring-opening metathesis polymerization (ROMP) has often been used for backbone polymerization. Early transition metal initiators based on molybdenum[3,4,5,6,8,11,12,13,14] or tungsten[5] as well as late transition metal initiators[7,9,10,15,16] have been used for the polymerization of macromonomers.

In the second approach, a functional monomer is first polymerized to the desired molecular weight. Then, pre-formed polymeric grafts are attached via their chain-ends to these functional groups (grafting onto) or, alternatively, a second polymerization is initiated from those functional groups (grafting from). Here, as well as above, the grafts are most often prepared by anionic polymerization techniques[17] or ATRP[18] while ROMP as well as ATRP has been reported for backbone polymerization. A one-pot procedure using ATRP for the grafts and ROMP for the backbone has also been reported recently.[19]

ROMP using well-defined ruthenium initiators is an attractive polymerization technique due to its high tolerance towards polar functional groups. In addition to the presence of polar functional groups, ROM-polymers also provide a large number of C-C-double bonds along the polymer chain. These can also be turned into functionalities in post-polymerization transformations.

While early transition metal initiators based on molybdenum turn inactive in the presence of aldehydes or alcohols, the late transition metal ruthenium initiators tolerate such functional groups. Ruthenium initiators can be handled in air and tolerate exposure to moisture. Molybdenum and tungsten initiators are typically handled using Schlenk techniques under inert atmosphere. Polymerizations using ruthenium initiators are therefore more accessible to non-specialists in the field.

Until recently,[20,21] general techniques to produce mono-end functional ROM polymers were scarce. ROMP could therefore only be employed in the backbone polymerization but not for the synthesis of grafts. Only early transition metals, such as molybdenum and tungsten, that do not tolerate many polar functional groups have been used to prepare macromonomers via ROMP.[22] A macromonomer synthesis employing late transition metal ROMP would, however, be particularly useful, as a large variety of polar functional groups could be present in the monomer structure without interfering with the polymerization control.

Here we present an all-ROMP route to graft copolymers in which the grafts as well as the backbone are polymerized by ROMP using a Grubbs 1st generation ruthenium initiator.

Experimental Part

Materials

Technical grade solvents were purchased from Acros Organics, those of analytical quality (p. a. grade) were purchased from Fisher Scientific. Dichloromethane was dried over P_4O_{10} and freshly distilled under a dry nitrogen atmosphere. Deuterated solvents were purchased from Deutero GmbH. All reagents were obtained from Acros Organics and used without further

purification unless otherwise stated. Grubbs 1st generation initiator ($RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2$ was obtained from Aldrich.

Norbornene-5-carboxylic acid chloride was synthesized in good yield by Diels-Alder reaction of acryloyl chloride and freshly cracked cyclopentadiene as reported by Arehart and Pugh.[23]

*Synthesis of exo-N-Dodecyl-norbornene-2,3-dicarboximide (**DNI**):*

16.4g (0.1 mol) of *exo-N*-Norbornene-dicarboxylic acid anhydride and 18.6g (0.1 mol) of *n*-Dodecylamine were combined and allowed to stand for 15 min. Then 150 mL toluene was added and the mixture was refluxed under Dean-Stark conditions until all solid had dissolved and all reaction water had been removed. The solvent was evaporated and the resulting imide was purified by flash chromatography over a silica column (Solvent: petroleum ether : ethyl acetate 1:1 (v:v)). Evaporation of the solvent yielded 28.5 g of a colourless liquid.

^{1}H-NMR (300MHz, $CDCl_3$) δ[ppm]: 0.88 (t, 3H, CH_3, ^3J=8Hz); 1.1-1.3 (m, 20H, dodecyl-chain); 1.4-1.5 (m, 2H, CH_2-bridge); 2.67 (s, 2H, C_3CH); 3.27 (s, 2H, C(O)CH); 3.45 (t, 2H, N-CH_2, ^3J=7.7Hz); 6.29 (s, 2H, C=CH). ^{13}C-NMR (100.75MHz, $CDCl_3$) δ[ppm] 14.04 (*C*H_3); 22.60, 22.70, 29.07, 29.25, 29.53, 31.83 (*C*H_2-chain); 38.64 (N-*C*H_2); 42.62 (*C*H_2-bridge); 45.07 (C_3*C*H); 47.70 (CO-*C*H); 137.74 (*C*=*C*); 177.99 (*C*O). FD-MS: 331.6m/z (331.49 g/mol calc.).

*General Procedure for **PxN, DxN, D3P2N** and **P8D4N:***

To a stirred solution of the hydroxyl-functional polynorbornene in dry dichloromethane a ten-fold excess of norbornene-5-carboxylic acid chloride is given at rt. After 1h, a 3-fold excess of TEA was added and stirred for another 10h. The norbornene ester-functionalized polynorbornene was precipitated in methanol, redissolved in chloroform and reprecipitated into methanol. The yield of the dried polymer ranged from 60-80% depending on functionality and length of the polymer chain.

General Procedure for ROMP of macromonomers, ***3-10:***

The macromonomer (200mg typical) was dissolved in dry, degassed dichloromethane. A solution of the calculated amount of Grubbs 1st generation catalyst in dichloromethane was added by syringe. The mixture was stirred for 40h at rt, quenched with excess ethyl vinyl ether and precipitated into methanol. Any unreacted polymer and catalyst was removed by preparative GPC in chloroform. Evaporation of the solvent under vacuum for 15h gave 50-75% of the graft copolymer.

Instrumentation:

Standard nuclear magnetic resonance spectra were recorded at 300 MHz (^{1}H-NMR) or 75 MHz (^{13}C-NMR) on a Bruker AC 300 or at 400 MHz (^{1}H-NMR) or 100 MHz (^{13}-NMR) on a Bruker AMX 400. All NMR-signals were referenced internally to residual solvent signals.

DSC curves were recorded on a Perkin Elmer DSC 7 and a Perkin Elmer Thermal Analysis Controler TAC 7/DX.

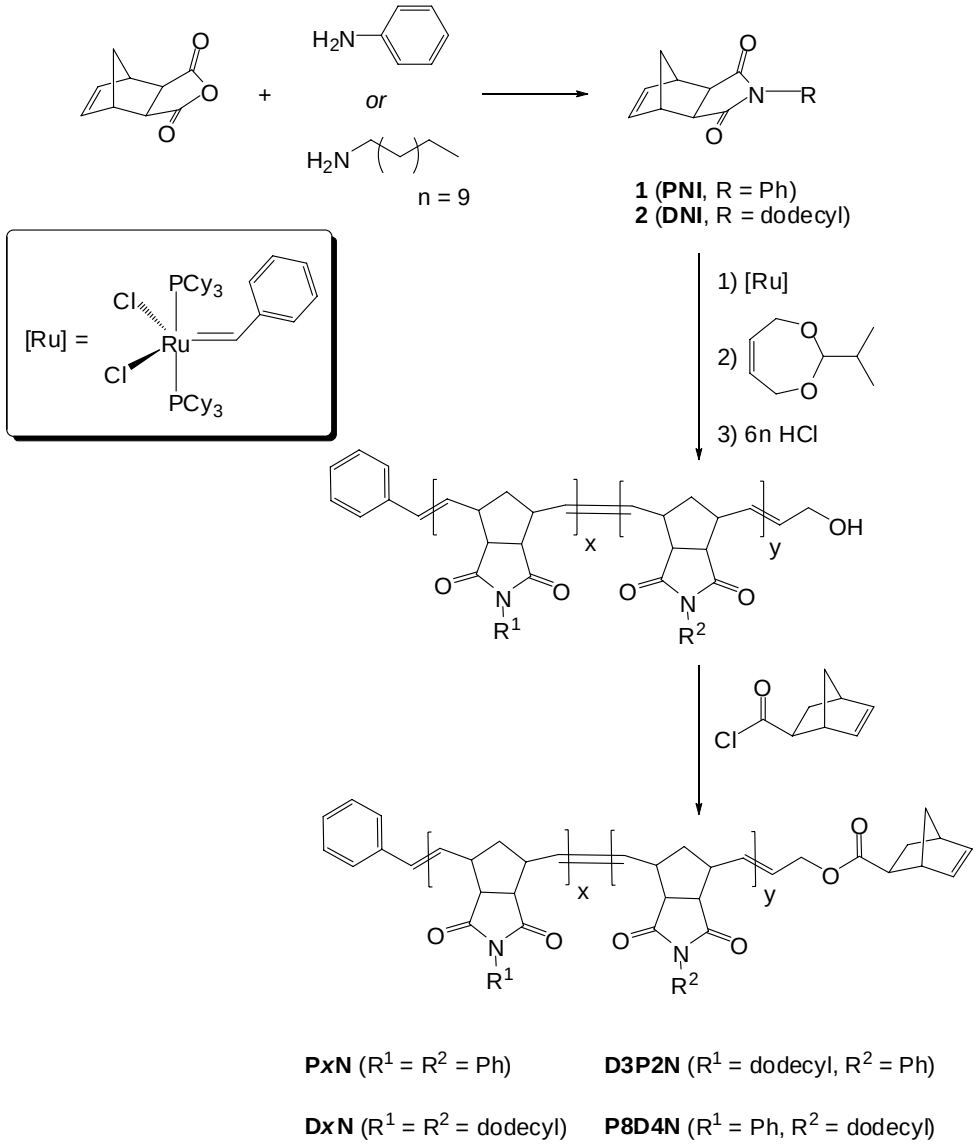
Gel permeation chromatography with chloroform was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P 100 pump and a set of three PSS SDV columns (10^{4}/10^{3}/10^{2} g/mol). Signal detection occurred by use of a TSP Spectra System UV 2000 (UV 254 nm) and a Wyatt Optilab DSP (refractive index). MALLS-detection was carried out on a Wyatt Dawn 18 angle online light scattering detector. Calibration was done using poly(styrene) standards provided by Polymer Standards Service.

Field desorption mass spectra were measured on a Finnigan MAT 95.

Results and Discussion

In order to exemplify the versatility of our synthetic route to graft copolymers, we prepared two different monomers **1** and **2,** one carrying a phenyl the other a dodecyl chain on the imide nitrogen (see Scheme 1). From these monomers we prepared mono-hydroxy terminated polymers via a sacrificial block copolymer synthesis employing 2-isopropyl dioxepine as the sacrificial monomer and a Grubbs 1st generation initiator as described previously.[18] Homopolymers of **1** (**P3N**, **P7N**, **P10N**) and **2** (**D3N**, **D5N**) with varying molecular weights as well as two diblock copolymers from **1** and **2** (**D3P2N**, **P8D4N**) were synthesized with hydroxy end-groups. Subsequent reaction with freshly prepared norbornene-5-carboxylic acid chloride (endo:exo = 80:20) gave macromonomers carrying norbornene end-groups via ester linkages. It has been well-documented that often exo-isomers propagate faster and more readily than the corresponding endo-isomers.[24,25] In the case of the macromonomers polymerized here, the difference in propagation rate is negligible as the propagation rate is slowed drastically down due to steric bulk of the macromonomer chain.

Table 1 shows GPC data for all macromonomers prepared. The molecular weights of the macromonomers were determined by calibration against poly(styrene) standards (Table 1, refractive index (RI)) and multi angle laser light scattering (MALLS). Both sets of data are in good agreement. Polydispersity indices of PDI ≈ 1.1 or below were obtained for all macromonomers. It is especially worth mentioning that the sacrificial block copolymer synthesis for the introduction of terminal hydroxy groups is also applicable to diblock copolymers. The macromonomers **D3P2N** (Mn = 6000 g mol^{-1}) and **P8D4N** (Mn = 15000 g mol^{-1}) are norbornene end-functionalized diblock copolymers which were prepared from sacrificial triblock copolymers. The low PDIs (< 1.1) of both end-functional diblock copolymers show once more the high levels of control achievable with the sacrificial copolymer method. The fact that block copolymers could be produced which elute in a narrow polydispersity mono-modal gpc-trace indicates that the polymerization was living.



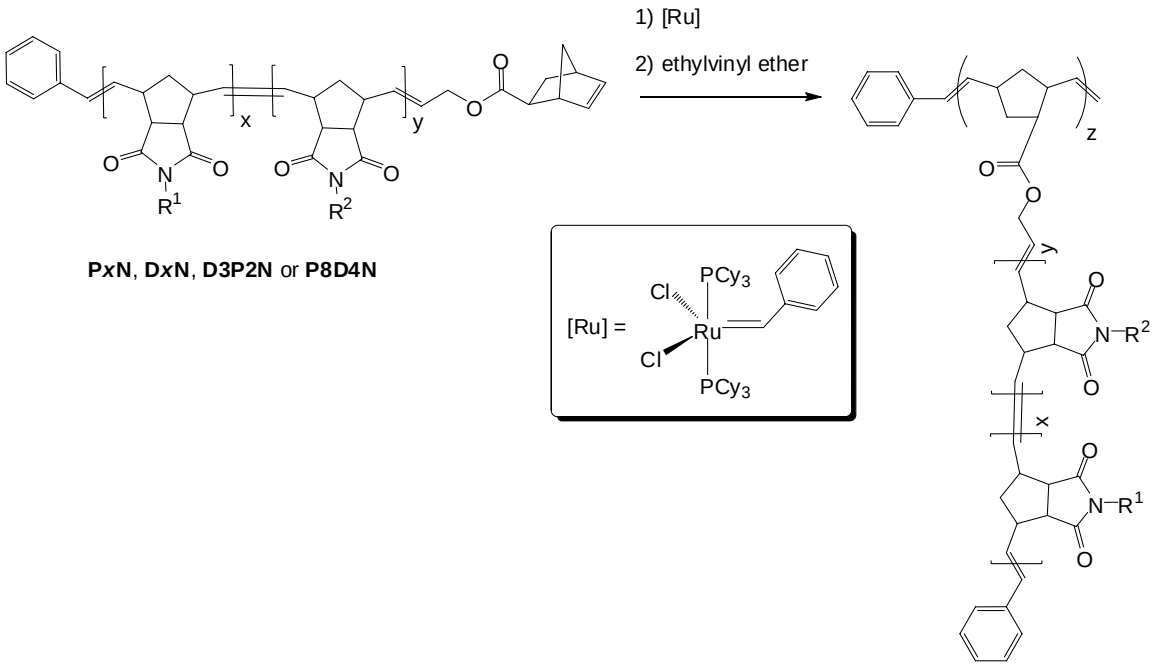
Scheme 1 Synthesis of monomers (**1**,**2**) and hydroxy as well as norbornene terminated macromonomers (**P*x*N**, **D*x*N**, **D3P2N**, **P8D4N**; *x* represents the approximate molecular weight in 10^3 g mol^{-1}, see Table 1). The detailed synthesis of mono-end functional polymers via sacrificial block copolymers is reported elsewhere.[18]

Table 1 GPC-MALLS characterization of macromonomers.

		RI-detection		MALLS-detection	
macromonomer	monomer	Mn	PDI	Mn	PDI
P3N	**1**, PNI	2700	1.08	3300	1.04
P7N	**1**, PNI	4900	1.11	6900	1.06
P10N	**1**, PNI	9700	1.12	11800	1.04
D3N	**2**, DNI	3800	1.08	3800	1.06
D5N	**2**, DNI	6100	1.09	5600	1.04
D3P2N	DNI:PNI 3:2	6700	1.19	6200	1.04
P8D4N	PNI:DNI 8:4	12200	1.10	15300	1.06

All macromonomers were subsequently polymerized with a 1st generation Grubbs catalyst (see Scheme 2) and non-functionally terminated by quenching with ethylvinyl ether.

It has been well-documented that the degree of polymerization obtainable for polymerizations of macromonomers is highly dependent on the molecular weight of the graft itself.[3,4] Feast et al. could show that with growing degree of polymerization of a polystyrene macromonomer two distinct peaks were observed in the gpc of the graft copolymer reaction mixture.



Scheme 2 Synthesis of graft-copolymers via ROMP of macromonomers.

It was unambiguously shown that the macromonomer ceases to propagate as a consequence of steric hindrance induced by the size of the macromonomer.[4]

All macromonomers were polymerized to their maximum molecular weight. In practice, a high molecular weight graft copolymer was aimed for and the polymerization continued until no further increase in molecular weight was observed by GPC. A typical GPC trace would at this stage show two peaks, one representing unreacted macromonomer the other the graft copolymer at higher molecular weight. The macromonomers polymerized here therefore showed a similar polymerization behavior as the ones polymerized by Feast et al.[4] MALLS-GPC allowed us to determine the exact molecular weight and thus the degree of polymerization of the graft copolymer. This information was used to calculate the correct amounts of initiator needed to obtain quasi-monodisperse GPC traces with none or little residual macromonomer impurities and the maximum molecular weight possible. Lower molecular weight graft copolymers can of course also be achieved, as was shown for the polymerization of **P7N** to **4** (vide infra).

The fact that almost no macromonomer residues were left over using the calculated amounts of initiator also proves the very high degree of norbornene-functionalization of the

macromonomer. All graft copolymers were purified by preparative GPC in order to remove traces of residual macromonomer.

Figure 1 shows GPC traces for an optimized polymerization of macromonomer **P7N** to graft copolymer **5** as an example. A molecular weight increase, i.e. elution at an earlier retention time, can clearly be observed for the polymerization of the macromonomer. After 48h of polymerization most of the macromonomer has been consumed. During polymerization, the molecular weight and molecular weight distribution of the macromonomer (Figure 1, peak at 21 mL elution volume) changes very little. This is, in our view, an indication for a fast initial ring-opening oligomerization with sterical retardation at a critical degree of oligomerization.

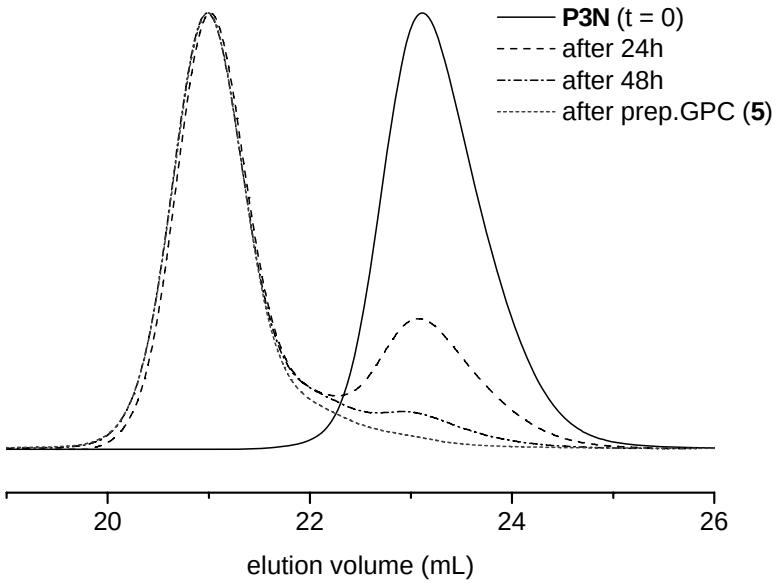


Figure 1 GPC traces showing the conversion of macromonomer **P7N** to graft copolymer **5** Unreacted macromonomer could be removed after 48h by preparative GPC in chloroform.

Figure 2 shows as an example the ^{1}H-NMR spectra of the hydroxy-functionalized macromonomer precursor (Figure 1 bottom) as well as the macromonomer **P3N** (Figure 2 middle). The allylic methylene protons shift downfield from δ = 4.1 ppm to ca. 4.5 ppm after formation of the terminal ester (functionalization with norbornene). No residual OH-terminated polymer can be observed in the ^{1}H-NMR spectrum. This is further evidence that the macromonomer functionalization with norbornene was quantitative. Figure 2 (top) shows the macromonomer after purification by preparative GPC. As expected, the allylic methylene protons at $\delta \approx$ 4.5 ppm have become very broad due to their immobility close to

the graft copolymer backbone. The styrenic protons at the chain ends of the grafts (Figure 2, protons H1 and H2) remain well-resolved in all ^{1}H-NMR spectra shown in Figure 2. This behavior is expected for unrestrained polymer chain ends such as the chain ends of a graft copolymer.

Table 2 summarizes the molecular weight data for all graft copolymers. The degrees of polymerization varied between 3 and 8 with polydispersity indices PDI ≈ 1.1 for most samples. Table 2 also shows that the macromonomers prepared from monomer **2** yield lower numbers of arms (3-4 arms) per graft copolymer than the ones prepared from monomer **1** (5-8 arms). This is most likely due to the higher sterical demand of the macromonomers carrying the bulkier dodecyl chains.

The low PDIs indicate good control over the oligomerization, i.e. the absence of secondary metathesis reactions (backbiting). It is worth noting that the molecular weight determination by GPC against poly(styrene) standards grossly underestimated the molecular weight of the sample compared to the data obtained by MALLS. This behavior is expected for a core branched structure.

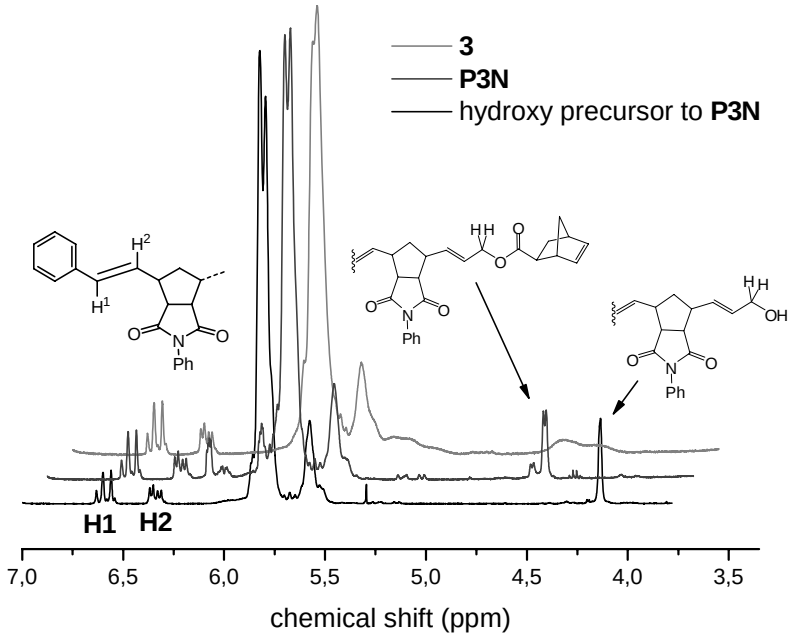


Figure 2 Series of ^{1}H-NMR spectra following the conversion of hydroxy-terminated macromonomer precursor (bottom) to macromonomer (**P3N**, middle) to graft copolymer(**3**, top). The methylene protons indicated by arrows show the conversion of hydroxy terminated polymer to norbornene terminated macromonomer. The graft copolymer shows a broad peak in the same region.

Table 2 Graft copolymers produced by ROMP of macromonomers. The number of arms were calculated using the MALLS GPC data.

		RI-detection		MALLS-detection		No. of arms (calc.)
graft copolymer	macromonomer	Mn	PDI	Mn	PDI	
3	**P3N**	12300	1.17	17300	1.14	5.24
4	**P7N**	20800	1.20	38000	1.16	5.56
5	**P7N**	25000	1.18	56600	1.11	8.20
6	**P10N**	39500	1.21	63200	1.38	5.36
7	**D3N**	12600	1.14	13500	1.10	3.55
8	**D5N**	22800	1.15	26400	1.18	4.71
9	**D3P2N**	21000	1.22	25700	1.14	4.15
10	**P8D4N**	33000	1.12	52400	1.10	3.42

All macromonomers and graft copolymers were examined by differential scanning calorimetry (DSC). In all cases, the glass transition temperatures (Tg) of the macromonomers were higher than those of the corresponding graft copolymers. The energies associated with the glass transition (ΔCp) were higher for the macromonomers than for the graft copolymers. The macromonomer end-groups are linked-up to form a graft copolymer. The resulting copolymer has therefore effectively lost half of its end-groups (per macromonomer unit) and the chain segments close to the graft copolymer backbone are less flexible than the ones at the ends of the grafts. This is expected to lead to lower ΔCp values, as observed. Table 3 shows exemplary DSC data for the two macromonmers **P7N** and **D5N** as well as their corresponding graft copolymers **4** and **8** respectively.

Table 3: DSC-results of macromonomers and graft-copolymers. Measurements were conducted at a heating rate of 40°C per minute.

Polymer	Tg/°C	ΔCp/J g^{-1}
P7N	187.9	0.77
4	179.6	0.40
D5N	17.6	0.27
8	11.2	0.22

In conclusion, we have employed a recently developed end-functionalization strategy for a ruthenium complex initiated ROMP in the preparation of an all-olefin metathesis route to graft copolymers. Macromonomer synthesis as well as macromonomer polymerization was carried out using ROMP. Homopolymers as well as diblock copolymers were used as macromonomers. ROMP using ruthenium initiators allows the living polymerization of functional monomers. This versatile new approach opens the way to many highly functional graft copolymer architectures. Future work will deal with the copolymerization of low molecular weight monomers and macromonomers in order to achieve higher molecular weight copolymers. This approach will allow the presence of polar functional groups in the polymer backbone as well as the grafts.

References:

[1] D.W. Jenkins, S.M. Hudson *Chem. Rev*. **2001**, *101*, 3245.

[2] J.-F. Lahitte, F. Pelascini, F. Peruch, S. Plentz Meneghetti, P.J. Lutz, *C.R. Chimie*, **2002**, *5*, 225.

[3] A.C.M. Rizmi, E. Khosravi, W.J. Feast, M.A. Mohsin, A.F. Johnson, *Polymer* **1998**, *39*, 6605.

[4] W.J. Feast, V.C. Gibson, A.F. Johnson, E. Khosravi*, J. Mol. Catal. A* **1997**, *115*, 37.

[5] R.L. Norton, T.J. McCarthy, *Macromolecules* **1989**, *22*, 1022.

[6] V. Heroguez, Y. Gnanou, M. Fontanille *Macromol. Rapid Commun* **1996**, *17*, 137.

[7] V. Heroguez, J.-L. Six, Y. Gnanou, M. Fontanille *Macromol. Chem. Phys.* **1998**, *199*, 1405.

[8] V. Heroguez, E. Amedro, D.Grande, M. Fontanille, Y. Gnanou *Macromolecules* **2000**, *33*, 7241.

[9] A. Chemtob, V. Héroguez, Y. Gnanou, *Macromolecules* **2004**, *37*, 7619.

[10] K. Breitenkamp, J. Simeone, E. Jin, T. Emrick, *Macromolecules* **2002**, *35*, 9249.

[11] V. Heroguez, Y. Gnanou, M. Fontanille *Macromolecules* **1997**, *30*, 4791.

[12] V. Heroguez, S. Breunig, Y. Gnanou, M. Fontanille *Macromolecules* **1996**, *29*, 4459.

[13] G. Morandi, V. Montembault, S. Pascual, S. Legoupy, L. Fontaine, *Macromolecules* **2006**, *39*, 2732.

[14] M.B. Runge, S. Dutta, N.B. Bowden, *Macromolecules* **2006**, *39*, 498.

[15] D.-J. Liaw, C.-C. Huang, J.-Y. Ju *J. Polym. Sci. A* **2006**, *44*, 3382.

[16] D. Mecerreyes, D. Dahan, Ph. Lecomte, Ph. Dubois, A. Demonceau, A.F. Noels, R. Jerome *J. Polym. Sci. A* **1999**, *37*, 2447.

[17] C. Cheng, N.-L. Yang, *Macromol. Rapid Commun*. **2005**, *26*, 1395.

[18] R.M. Kriegel, W.S. Rees, M. Weck, *Macromolecules* **2004**, *37*, 6644.

[19] R. Charvet, B.M. Novak, *Macromolecules* **2004**, *37*, 8808.

[20] S. Hilf, E. Berger-Nicoletti, R.H. Grubbs, A.F.M. Kilbinger, *Angew. Chem*. **2006**, *118*, 8214

[21] S. Perrier, X. Wang, *Nature* **2007**, *445*, 271

[22] Y. Imanishi, K. Nomura, *J. Pol. Sci. A* **2000**, *38*, 4613; K. Nomura, S. Takahashi, Y. Imanishi, *Polymer* **2000**, *41*, 4345; K. Nomura, S. Takahashi, Y. Imanishi, *Macromolecules* **2001**, *34*, 4712.

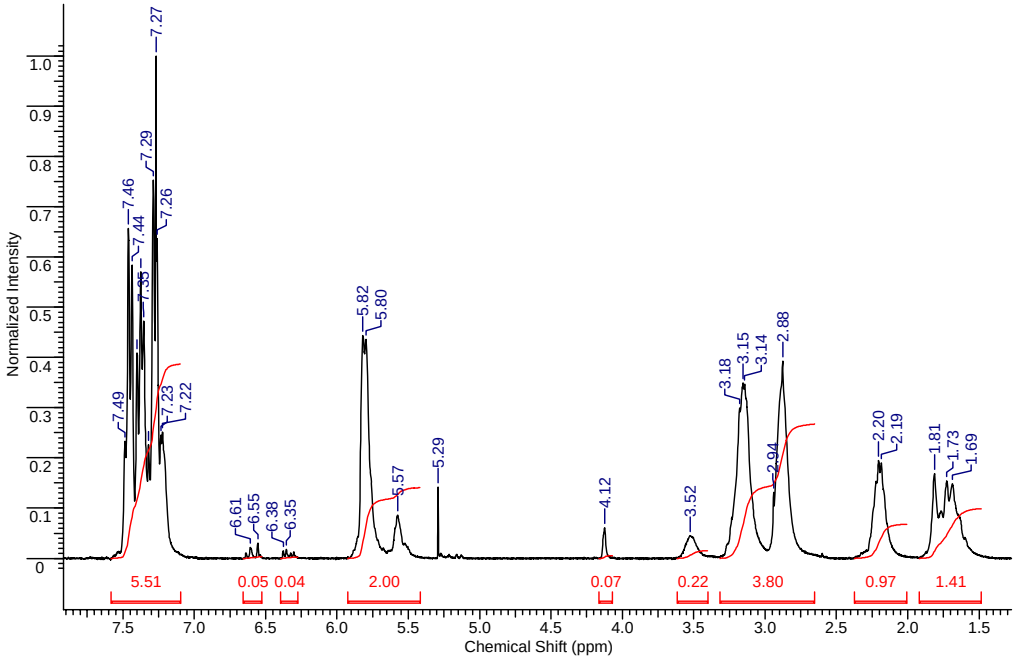
[23] S.V. Arehart, C. Pugh, C., *J. Am. Chem. Soc*. **1997**, *119*, 3027.

[24] see chapter 13 in K.J. Ivin, J.C. Mol, "Olefin Metathesis and Metathesis Polymerization", Academic Press, **1997**, San Diego.

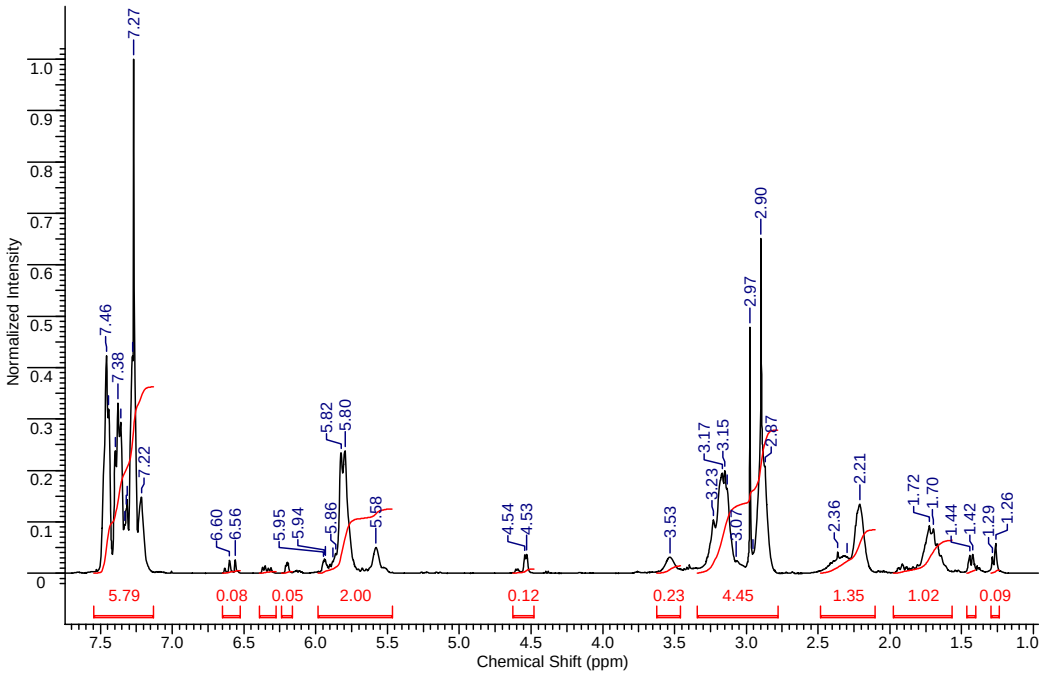
[25] K.J. Ivin, J. Kress, J.A. Osborn *J. Mol. Catal.* **1988**, *46*, 351-358.

Supporting Information for: An All-ROMP route to graft-copolymers

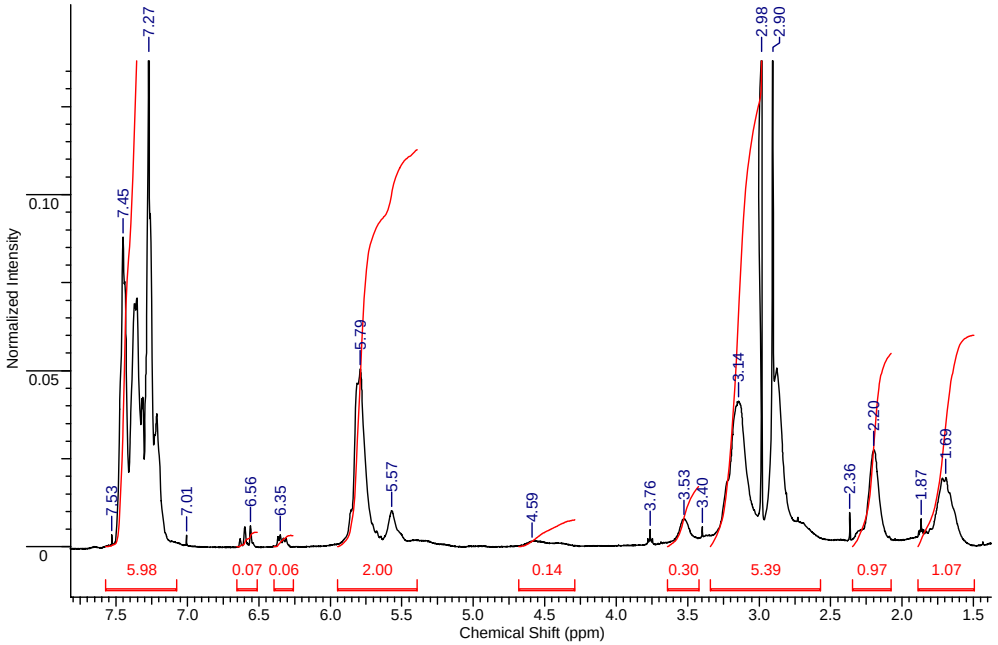
Stefan Hilf, Robert H. Grubbs and Andreas F.M. Kilbinger



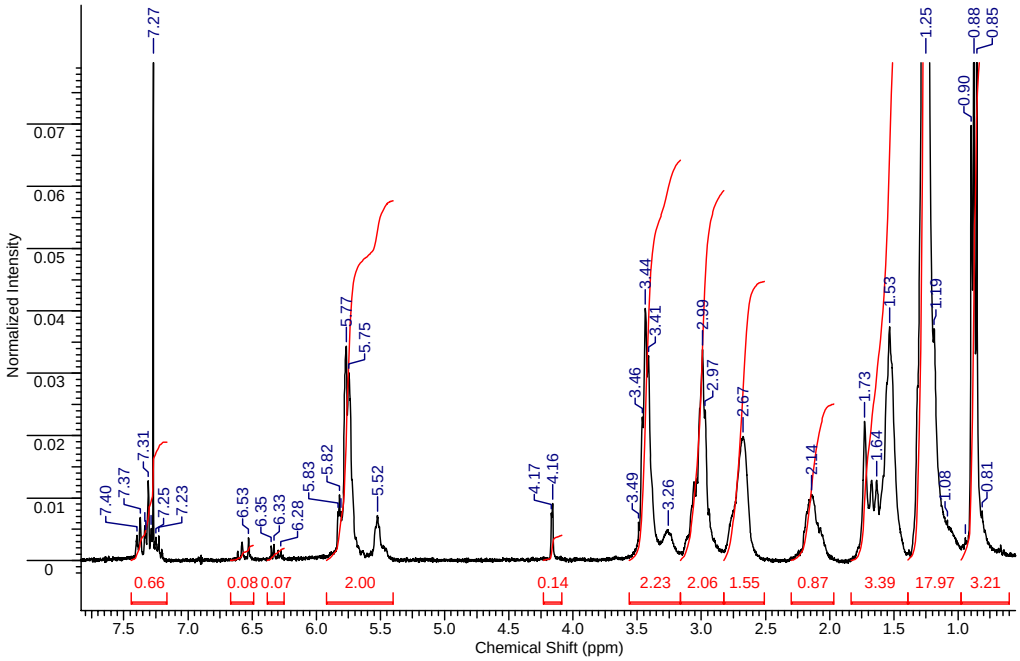
S-1: ^{1}H-NMR spectrum of OH-functional precursor for **P7N**.



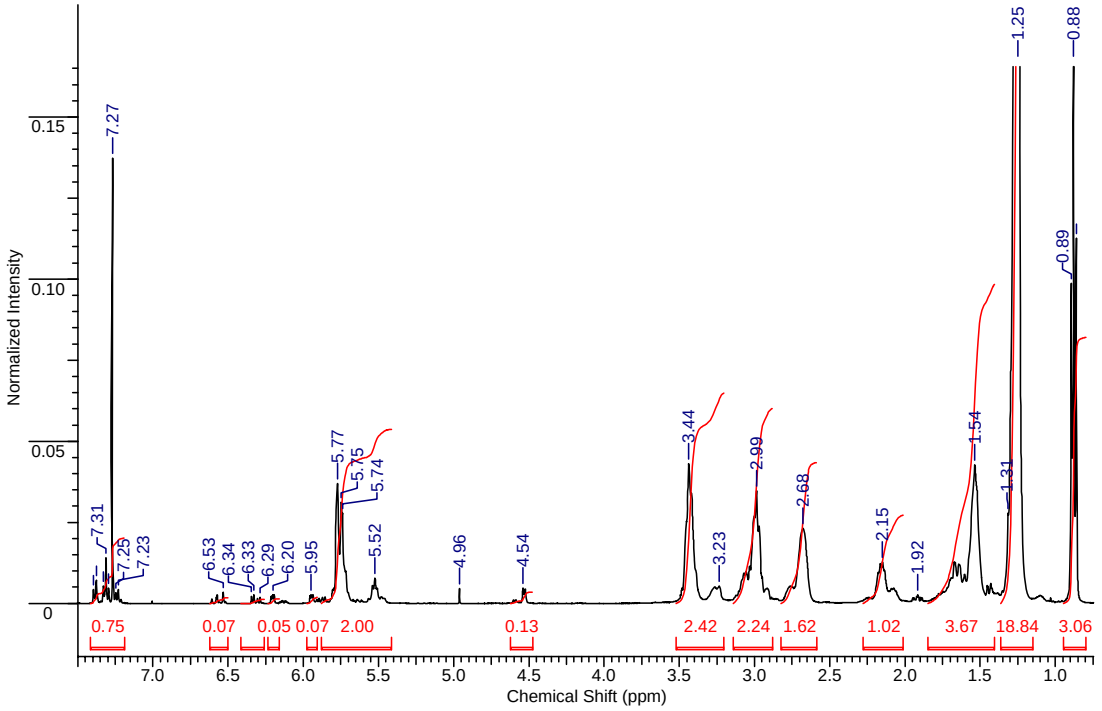
S-2: ^{1}H-NMR spectrum of **P3N.**



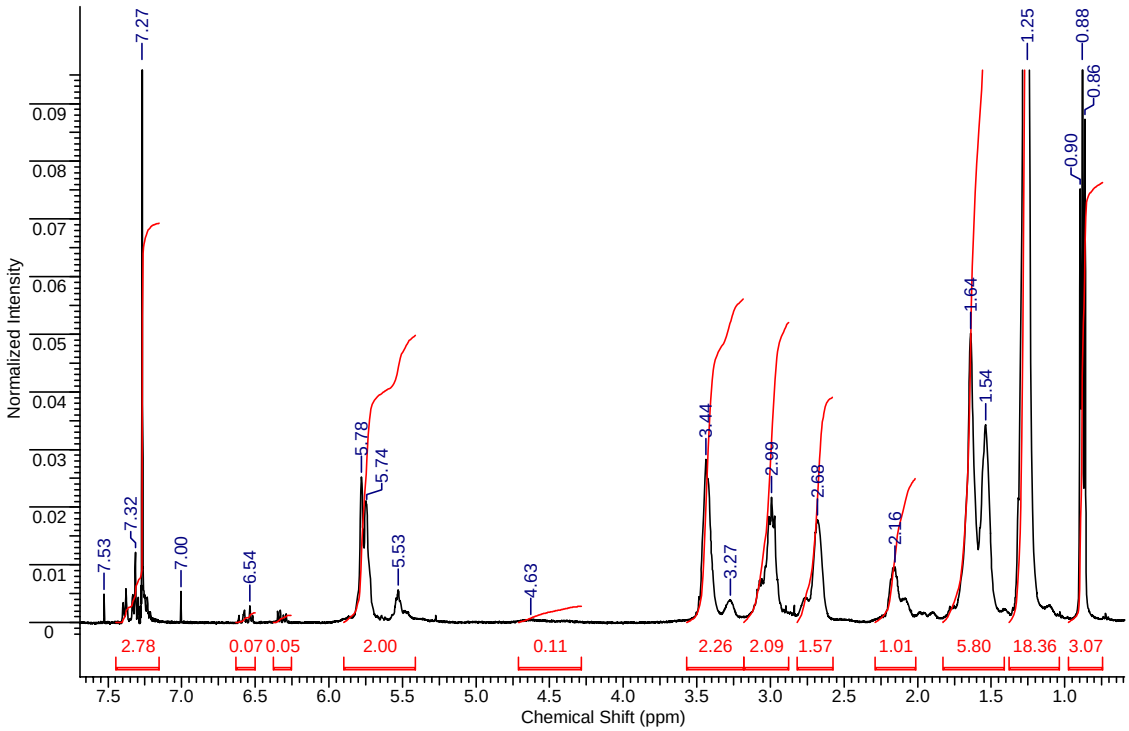
S-3: ^{1}H-NMR spectrum of **4.**



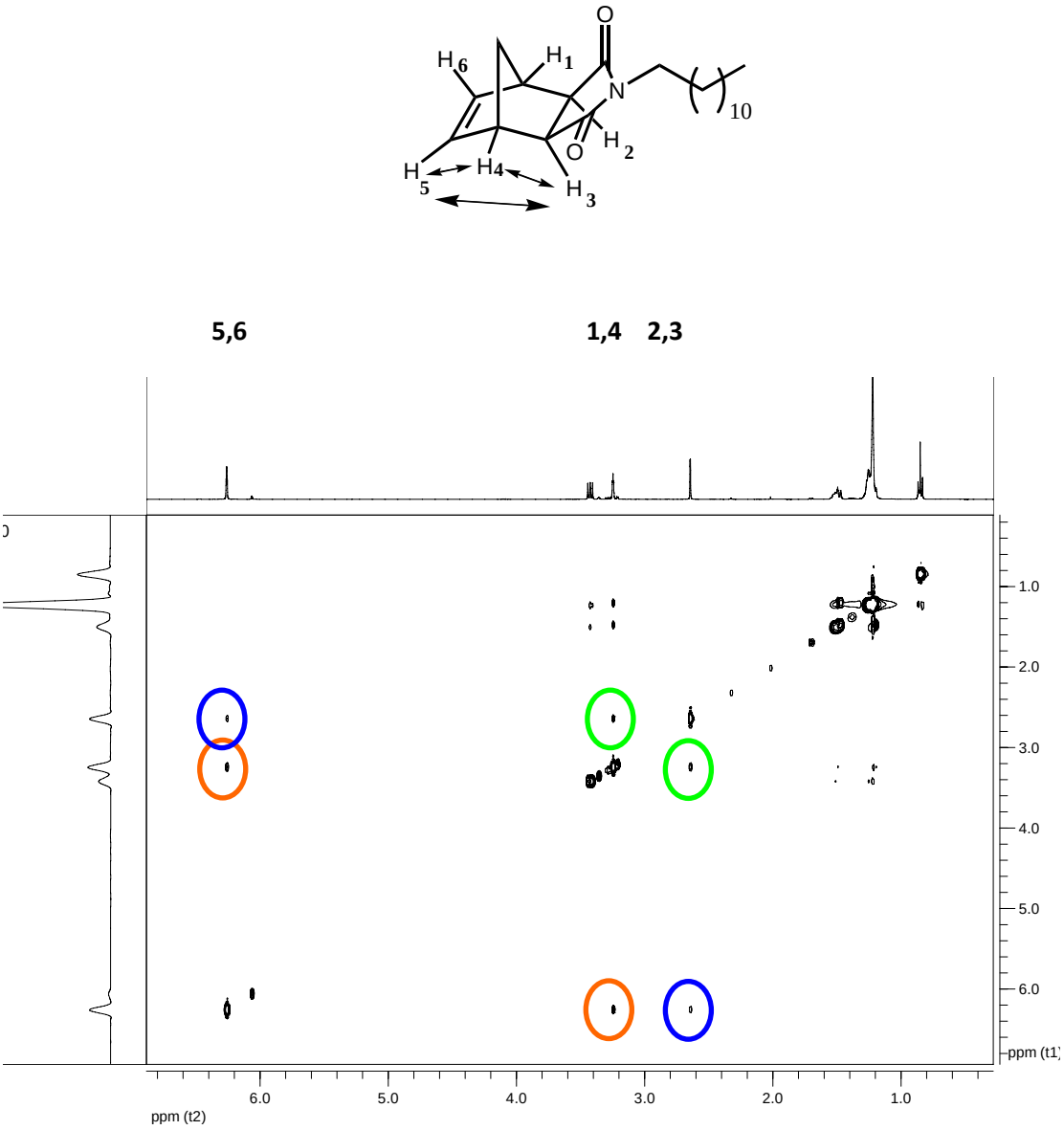
S-4: ^{1}H-NMR spectrum of OH-functional precursor for **D5N.**



S-5: ^{1}H-NMR spectrum of **D5N.**



S-6: ^{1}H-NMR spectrum of **8.**



S-7: NOESY-NMR spectrum of **DNI**: exo-conformation is shown by coupling of double bond protons ($H_{5,6}$: 6.25 ppm) to CH-CO protons ($H_{2,3}$: 2.6 ppm) with coupling to $H_{1,4}$ at 3.2 ppm representing the brigde heads of the norbornene structure.

3.2: A “Click”-Approach to ROMP Block Copolymers.

Hilf, Stefan; Hanik, Nils; Kilbinger, Andreas F.M.

Published in: Journal of Polymer Science Part A: Polymer Chemistry **2008**, *46*, 2913-2921.

Abstract: Amphiphilic block copolymers can be conveniently prepared via convergent syntheses, allowing each individual polymer block to be prepared via the polymerization technique that gives the best architectural control. The convergent "click"-chemistry route presented here, gives access to amphiphilic diblock copolymers prepared from a ring opening metathesis polymer and polyethylene glycol. Due to the high functional group tolerance of ruthenium carbene initiators, highly functional ROMP polymer blocks can be prepared. The described synthetic route allows the conjugation of these polymer blocks with other end-functional polymers to give well-defined and highly functional amphiphilic diblock copolymers.

Introduction

Blockcopolymers are important macromolecular architectures as they can self-assemble into ordered micellar structures in solution or form microphase separated structures in the bulk.[1,2] Many living polymerization techniques are known today that allow the preparation of multi-block copolymers. In most cases, the same polymerization technique is used to create all blocks of a block copolymer in one single reaction. Today's vast choice of different polymerization techniques allows the polymerization of a large number of structurally diverse monomers. Block copolymers have been synthesized by various approaches. Living anionic polymerizations, for example, have been used extensively for the synthesis of well-defined block-copolymers, yet are highly limited in monomer choice and block sequence due to difficult block transfer reactions.[3] However, not all polymerization methods tolerate the presence of functional groups or give the same amount of control over molecular weight and molecular weight distribution for all monomers. End-functionalized polymers can be used as macroinitiators for a different polymerization technique. Those block copolymers can be much more diverse in terms of monomer functionality and structure. In this case, the degree of functionalization and the initiation activity of the macroinitiator have to be known in order to retain control over the molecular weight of the second block. Also, the initiating polymer must by now means interfere with the second polymerization step. Bielawski et al. prepared telechelic ROMP polymers carrying bromo-alkane end-groups which allowed ATRP polymerization to give ABA triblock copolymers.[4]

It is therefore of great interest to develop synthetic techniques that allow block copolymer syntheses in which the individual blocks have been prepared by different polymerization techniques. Such synthetic approaches give access to functionally more diverse materials. However, these reactions suffer from extremely slow reaction kinetics due to steric hindrance.

The ring opening metathesis polymerization using well-defined ruthenium initiators is an example for a polymerization technique that allows many functional groups to be present in the monomer structure.[5]

"Click-chemistry" has become a synonym for a variety of reactions lately, all of which feature a side-reaction free, rapid and stereospecific reaction that is of general applicability, easy to work up and uses simple reaction conditions.[6] The most common reaction of this type is the 1,3-dipolar cycloaddition of azides to terminal alkynes. It can be conducted either

thermally in a Huisgen-type reaction[7,8] or catalytically using various copper catalysts, as Sharpless reported.[9] This reaction is tolerant towards most types of functional groups and many biologically active motifs.[10]

The huge variety of catalyst systems can be divided into two general classes. Highly basic systems using strong amino bases such as pentamethyl diethylene tetramine (PMDETA),[11,12] DBU[13], DIPEA[14] or bipyridine[15] as both ligating and deprotonating agents in combination with CuBr[16] or CuI[17,18] were used in most polymer-related reactions, where high catalyst activity was needed. Use of a tris(triazole) amine[19] could further increase activity and selectivity of the process. These systems can, however, not be applied if any one reaction component is base sensitive.

Rather neutral catalysts have been developed for the more delicate conjugations of polymers with biologically active and other base labile molecules. This class of catalysts includes copper(I) complexes such as $(PPh_3)_3CuBr$,[20] which can also be used in combination with a base[14] and $(CH_3CN)_4Cu(I)PF_6$.[21] A number of systems makes use of redox chemistry in order to generate the active Cu(I) species in situ such as $CuSO_4$ / sodium ascorbate[22] and Cu(II)/Cu.[23] The latter two are therefore especially suitable for reactions that have to be carried out in aqueous solutions.

The 1,3-dipolar cycloaddition of azides to alkynes has had impact in a vast field of polymer chemistry and materials science using catalysts systems of all kinds.[24] Macromolecules featuring various functional groups,[25,26,27] interesting architectures such as dendritic structures,[28] macrocycles,[15,29] star copolymers[30,31] and hydrogels[32] have been accessed utilizing this type of "click"-reaction, as well as nanoparticles[33,34] and functionalized carbon nanotubes.[35] Conjugates with biologically relevant molecules have been formed using particularly mild neutral conditions with *in situ* formation of the catalytically active species.[36]

Few block copolymer syntheses have been reported to date, all of which apply highly basic catalyst systems in order to drive this highly hindered coupling reaction to an optimum.[11,37,38]

A combination of these two concepts, convergent synthesis involving functional ROMP polymers and "click"-chemistry, would in principle be perfectly suited to provide highly functional polymer blocks for conjugation with polymers from other polymerization techniques.

For the preparation of graft copolymers this has already been extensively exploited. There, macromonomers are typically prepared which carry a strained olefin at the chain terminus, allowing the subsequent ring opening metathesis polymerization to give graft copolymers.[17,39,40,41]

Due to the difficulty to obtain mono-chain end-functionalized polymers via ROMP using ruthenium initiators, reports of block copolymer syntheses have been rare to date. The less functional group tolerant molybdenum initiators can, however, be easily end-functionalized using aldehydes, which was employed by Coca et al. to prepare block copolymers by ROMP and ATRP.[42] Similarly, the group of Nomura synthesized hydroxy end-functional ROMP polymers using Mo-initiators and conjugated them with poly(ethylene glycol).[43] Due to the high reactivity of the molybendum catalysts towards most polar or protonic functional groups, the ROMP polymer block is limited to a rather small variety of structures in this case.

Hutchings and Khosravi reported an elegant way to prepare poly(ethylene glycol)-polynorbornene block copolymers using a macromolecular ruthenium carbene initiator, thereby overcoming the need for an end-functional ROMP polymer.[44] Although this route represents a particularly aesthetic way to prepare block copolymers, it is very labor intensive and can typically be carried out by specialists in the field only.

We recently reported a general synthetic route for the synthesis of mono-hydroxy end-functionalized ROMP polymers using Grubbs' 1st generation ruthenium initiators.[45,46] The concept of *Sacrificial Synthesis* ensures high degrees of chain end functionalization and yields narrowly distributed polynorbornenes. These polymers represent valuable macromolecular building blocks for the construction of complex polymer architectures such as graft[47] or block copolymers, as the terminal hydroxy-groups can be derivatized easily, e.g. by esterification with a functional carboxylic acid.

The work of Binder, Kluger et al. who have developed 1,3-dipolar cycloaddition reactions on polyoxanorbornenes,[17] has shown that ROMP polymers can be functionalized by "click-chemistry" either by functionalizing the monomer or after polymerization of a precursor monomer bearing an alkyl bromide.

Here, we describe the synthesis of diblock copolymers via conjugation of ROMP polymers with poly(ethylene glycol) using the Cu-catalyzed 1,3-dipolar cycloaddition of azides to alkynes.

Experimental Section

Instrumentation

^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 MHz (100.15 MHz for ^{13}C) on a Bruker AMX 400 or a Bruker ARX 400 and were referenced internally to residual proton signals of the deuterated solvent. Gel permeation chromatography in chloroform or tetrahydrofuran was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P 100 pump and a set of three PSS SDV columns (10^4/500/50 Å). Signal detection occurred by use of a TSP Spectra System UV 2000 (UV 254 nm) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service. MALLS-detection was carried out on a Wyatt Dawn 18 angle online light scattering detector. IR spectra were recorded on a Nicolet 5DXC FTIR spectrometer. Field desorption mass spectra were measured on a Finnigan MAT 95. A Philips EM 420 transmission electron microscope using a tungsten cathode at an acceleration voltage of 100 kV was used to obtain TEM-images.

Materials

All polymerizations and polymer derivatizations were carried out under Schlenk-conditions in a dry nitrogen atmosphere. Monomethyl-polyethyleneglycol-azide (PEG-N3) was synthesized as described elsewhere.[48] Monohydroxy-poly(PNI) (PPNI-OH) was synthesized as described in earlier publications.[45] *Exo*-norbornene-2,3-dicarboxylic acid anhydride was synthesized by the method described by Craig et al.[49] Dichloromethane was dried over phosphorus pentoxide and distilled under nitrogen. All other chemicals were purchased from Acros or Aldrich and were used as received. TEM grids (carbon film on copper, 300 mesh) were obtained from Electron Microscopy Sciences, Hatfield, PA, USA.

Synthesis of *N*-hexyl-*exo*-norbornene-2,3-dicarboximide (HNI)

32.8 g (0.2 mol) of *exo*-norbornene-2,3-dicarboxylic acid anhydride and an equimolar amount of *n*-hexylamine (25.7 g) were combined and allowed to stand for 15 min. Toluene (200 mL) was added to the salt and refluxed under Dean-Stark conditions until all solid was dissolved and the reaction water had been removed (ca. 1h). All volatiles were removed at

the rotary evaporator and the residue was distilled at 130°C (0.05 mbar) to give a clear colorless oil that solidified below room temperature (45g, 83%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ[ppm]: 0.81 (t, 3H, ^{3}J=6.8Hz, CH_3); 1.15-1.25 (m, 7H, hexyl-C$^{3-5}H_2$ + C*H*2-bridge imide side); 1.40-1.50 (m, 3H, hexyl- C$^{2}H_2$ + C*H*2-bridge double bond side); 2.61 (s, 2H, C*H*-bridgeheads); 3.21 (s, 2H, C*H*-CO); 3.39 (t, 2H, 3J=6.5Hz, N-CH_2); 6.23 (s, 2H, *H*C=C*H*). ^{13}C-NMR (100.25 MHz, $CDCl_3$) δ[ppm]: 13.82 (1C, hexyl-C^6); 22.28 (1C, hexyl-C^5); 26.43 (1C, hexyl-C^4); 27.54 (1C, hexyl-C^3); 31.13 (1C, hexyl-C^2); 38.55 (1C, hexyl-C^1); 42.53 (1C, *C*H2-bridge); 44.99 (2C, *C*H-CO); 47.61 (2C, *C*H-bridgeheads); 137.65 (2C, double bond); 177.87 (2C, CO). FD-MS: 247.2 m/z (calc. 247.16 g/mol).

General procedure for the synthesis of PHNI-OH

The calculated amount of *N*-hexyl-*exo*-norbornene-2,3-dicarboximide (HNI) was transferred into a Schlenk flask, degassed by repeated freeze-pump-thaw cycles and dissolved in ca. 5 mL dichloromethane per gram HNI. The correct amount of Grubbs' 1st generation catalyst ($RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2$) and twice the mass (6.3 equivalents) of triphenylphosphine, dissolved in a small amount of dichloromethane, were quickly added to the stirred solution of monomer. After the polymerization was finished (ca. 4 h for 3000 g/mol and ca. 7 h for 5000 g/mol), an excess (20-25 equivalents) of 2-isopropyl-4,7-dihydro-1,3-dioxepine were added and allowed to react for another 15 h. After termination of the polymerization by addition of ethyl vinyl ether (0.2mL), the polymer solution was precipitated into ice-cold methanol. The resulting brown polymer was dissolved in a mixture of dichloromethane (20 mL), HCl (6M, 15 mL) and methanol (10 mL) and stirred at r.t. for 10 h. The solution was then poured into ice-cold methanol, collected (100 mL), dissolved in chloroform and re-precipitated into ice-cold methanol to give the colorless sticky polymer product (ca. 60-75% depending on molecular weight) that solidified upon vacuum drying.

^{1}H-NMR (400 MHz, $CDCl_3$) δ[ppm]: 0.88 (m, 3H, CH_3); 1.28 (m, 6H, hexyl C$^{3-5}H_2$); 1.5-1.8, 2.0-2.2 (m, 4H, CH_2-brigde + hexyl C$^{2}H_2$); 2.5-2.8 (m, 2H, C_3CH); 2.9-3.1 (m, 2H, 3.3-3.5 (m, 2H, N-CH_2); C(O)CH); 4.16 (m, 2H, CH_2-O endgroup); 5.5-5.9 (m, 2H, double bonds polymer); 6.3-6.4 (m, 1H, double bond CH_2-OH end); 6.5-6.7 (m, 1H, double bond Ph end); 7.2-7.6 (m, 5H, Ph-endgroup).

General Procedure for Esterification of Hydroxy-functional Polynorbornenes with Propiolic acid, PPNI-CCH and PHNI-CCH

A mixture of 1.00 g mono-hydroxy-polynorbornene (typically 0.2-0.33 mmol), 5 equivalents of DCC (dicyclohexyl carbodiimide (200-300 mg), 2 equivalents of DMAP (50-750 mg) and 5 equivalents of propiolic acid (75-113 mg) was dissolved in dry DCM (15 mL) and stirred for 12 h. The red turbid solution was precipitated into methanol, dissolved in chloroform, re-precipitated into methanol and dried to give 80-90 mg (80-90%) of a red solid.

For PPNI-CCH:

^{1}H-NMR (400 MHz, $CDCl_3$) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH_2-brigde); 2.8-3.0 (m, 2H, C_3CH); 3.1-3.3 (m, 2H, C(O)CH); 4.68 (m, 2H, CH_2-O end-group); 5.5-5.9 (m, 2H, double bonds polymer); 6.3-6.4 (m, 1H, double bond at alkyne terminus); 6.5-6.7 (m, 1H, double bond Ph terminus); 7.2-7.6 (m, 5H, Ph).

For PHNI-CCH:

^{1}H-NMR (400 MHz, $CDCl_3$) δ[ppm]: 0.88 (m, 3H, CH_3); 1.28 (m, 6H, hexyl C$^{3-5}H_2$); 1.5-1.8, 2.0-2.2 (m, 4H, CH_2-brigde + hexyl C$^{2}H_2$); 2.5-2.8 (m, 2H, C_3CH); 2.9-3.1 (m, 2H, 3.3-3.5 (m, 2H, N-CH_2); C(O)CH); 4.68 (m, 2H, CH_2-O end-group); 5.5-5.9 (m, 2H, double bonds polymer); 6.3-6.4 (m, 1H, double bond at alkyne end); 6.5-6.7 (m, 1H, double bond Ph end); 7.2-7.6 (m, 5H, Ph-end-group)

General Procedure for 1,3-dipolar cycloaddition of polynorbornene-alkyne and monomethyl-polyethyleneglycol-azide

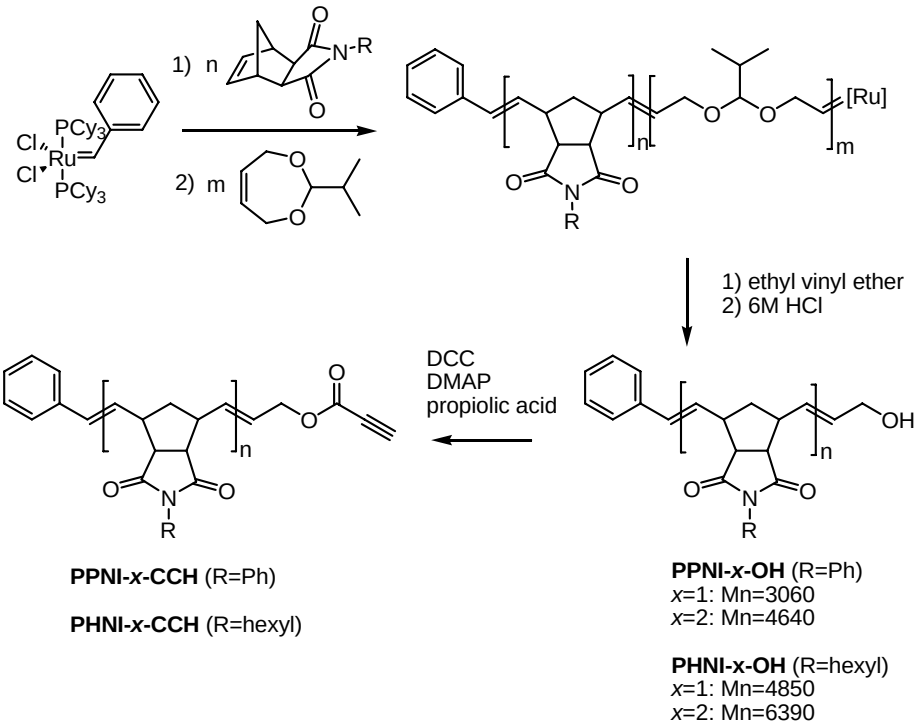
200mg of an alkyne-functionalized polynorbornene, 2.5 equivalents of the respective PEG-azide (200-2500 mg) and a half equivalent of bromotris(triphenylphosphino)copper(I) (25-50 mg) were dissolved in dry DMF (10 mL). The mixture was stirred at 100°C. Progress of the reaction was monitored by GPC. After 4 days, when the reaction had subsided, the mixture was pumped to dryness and 200mg of the solid were separated from unreacted polymer and catalyst by preparative GPC in THF. Yields ranged from 62-73%.

Exemplary ^{1}H-NMR data (here forPPNI-1-PEG2k):

^{1}H-NMR (400 MHz, $CDCl_3$)) δ[ppm]: 1.5-1.8, 2.1-2.3 (m, 2H, CH2-brigde); 2.8-3.0 (m, 2H, C3CH); 3.1-3.3 (m, 2H, C(O)CH); 3.39 (s, 3H, Me endgroup PEG); 3.66 (m, 4H, PEG-chain); 4.23 (m, 2H, O-C-CH2-Triazole)5.5-5.9 (m, 2H, double bonds polymer); 6.3-6.4 (m, 1H, double bond CH2-OH end); 6.5-6.7 (m, 1H, double bond Ph end); 7.2-7.6 (m, 5H, Ph).

Results and Discussion

Using the previously described sacrificial diblock copolymer synthesis, we prepared mono-hydroxy end-functionalized poly(*N*-hexyl-*exo*-norbornene-2,3-dicarboximide), PHNI-OH and poly(*N*-phenyl-*exo*-norbornene-2,3-dicarboximide), PPNI-OH (see Scheme 1). Two PHNI-OH as well as two PPNI-OH polymers were prepared differing in molecular weight and exhibiting very narrow polydispersity indices (PHNI-1-OH: Mn=4850 g mol^{-1}, PHNI-2-OH: Mn=6390 g mol^{-1}, PPNI-1-OH: Mn=3060 g mol^{-1}, PPNI-2-OH: Mn=4640 g mol^{-1}, PDI: see Table 1).



Scheme 1 Sacrificial block copolymer synthesis yielding mono-alkyne end-functionalized metathesis polymers.

Table 1 Molecular weight determination of mono-hydroxy-polynorbornenes:

polymer	RI-detection		MALLS detection		^{1}H-NMR	Calc.		Yield
	Mn	PDI	Mn	PDI	Mn	Mn	DP	
PPNI-1-OH	3060	1.12	2490	1.05	2514	2989	12	76%
PPNI-2-OH	4640	1.12	4410	1.04	4445	4909	20	84%
PHNI-1-OH	4850	1.15	3200	1.02	3166	3083	12	69%
PHNI-2-OH	6390	1.12	5020	1.04	4997	5049	20	75%

The degree of OH-functionalization was estimated to be close to 100% as comparison of molecular weight average determined by MALLS and by ^{1}H-NMR (derived from C=C-CH_2-OH-endgroup signal) as well as the complete absence of olefin signals of unfunctionalized polymer chains could show. The hydroxy terminal polymers were subsequently esterified using propiolic acid to give compounds **PPNI-CCH** and **PHNI-CCH** carrying exactly one terminal alkyne necessary for the Cu-catalyzed 1,3-dipolar cycloaddition (Scheme 1) at every chain end. Dicyclohexylcarbodiimide (DCC) allowed the use of mild reaction conditions for the esterification, which typically proceeded to complete conversion. Mild reaction conditions are particularly important, as the acid chloride of propiolic acid tends to decompose violently.[50] Figure 1 shows as an example the ^{1}H-NMR spectra of the reaction between **PPNI-1-OH** with propiolic acid. Comparing the two ^{1}H-NMR spectra shows clearly that all allylic alcohol end-groups (Figure 1 top, δ = 4.1 ppm) were converted to the ester. The new signals observed after esterification (bottom, δ = 4.5-5.0 ppm) are rather broad, most likely due to the coexistence of various hydrogen bonded species aggregated via the propiolic ester end-group.

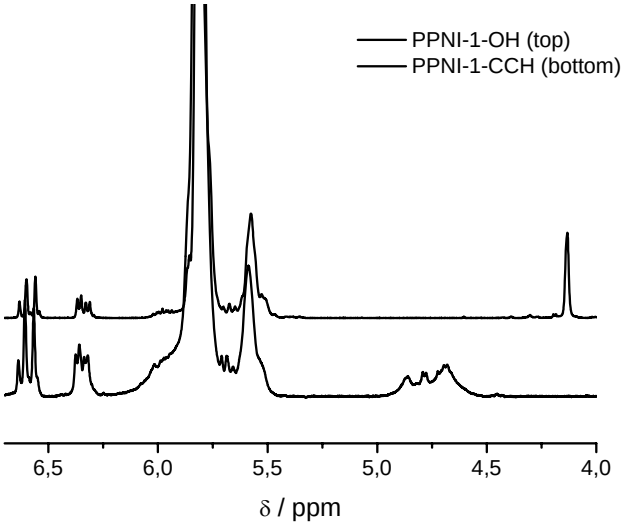


Figure 1 ^{1}H-NMR spectra of **PPNI-1-OH** (top) and **PPNI-1-CCH** (bottom). The methylene protons next to the hydroxy group can be seen at δ = 4.1 ppm (top). The new signals observed after esterification (bottom, δ = 4.5-5.0 ppm) are rather broad, most likely due to the coexistence of various hydrogen bonded species aggregated via the propiolic ester end-group.

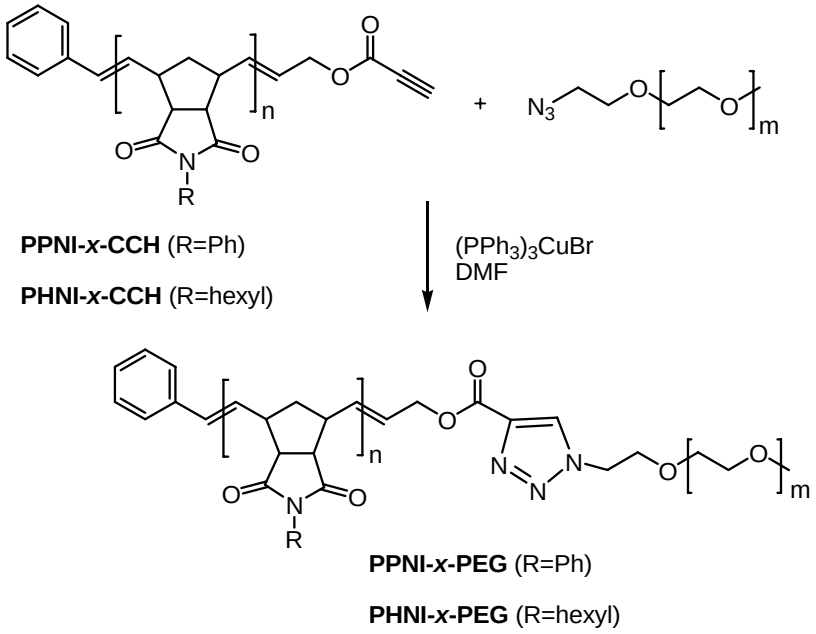
Table 2 Evaluation of reaction conditions for the 1,3-dipolar cycloaddition. The test reaction was carried out between **PPNI-1-CCH** and **PEG2k-N3**.

Entry	Catalyst	Solvent	Temperature	Reaction time	**PPNI-1-CCH** consumption[a]
1	CuI/DBU	THF	55°C	7d	<10%
2	CuI/DBU	DMF	100°C	7d	<15%
3	$CuSO_4$/Na ascorbate	DMF/water	90°C	7d	ca. 20%
4	$(PPh_3)_3CuBr$	DCM	r.t.	3 weeks	>80%
5	$(PPh_3)_3CuBr$	THF	55°C	2 weeks	>90%
6	$(PPh_3)_3CuBr$	DMF	100°C	4d	>80%

[a]estimated by GPC

In order to optimize reaction conditions for the "click"-reaction, several catalyst systems were evaluated with **PPNI-1-CCH** (Table 2) and poly(ethylene glycol) mono azide (Mn=2000 g mol^{-1}), **PEG2k-N3**. Samples were taken from the reaction mixture and diblock copolymer formation as well as **PPNI-1-CCH** consumption was analyzed via GPC (Table 2). Using CuI/DBU, a highly reactive, yet basic catalytic system, only small amounts of product could be observed after 7days of reaction time (Table 2, entries 1 and 2). The in-situ reduction of $CuSO_4$ with Na-ascorbate (Table 2 entry 3) gave slightly higher yields of product (20%), however not sufficient amounts for isolation. ^{1}H-NMR analysis of the reaction mixture after 7d showed evidence for the decomposition of the propiolic ester of the polynorbornene. An efficient catalyst would therefore have to be non-basic and non-aqueous in order to avoid competing hydrolysis and decomposition of any of the compounds. Owing to the relative instability of the imid groups present on **PPNI-CCH** and **PHNI-CCH** to strong bases and the sensitivity of the propiolic ester towards aqueous media, a catalyzing copper complex was chosen. $(PPh_3)_3CuBr$, which is rather neutral and highly soluble in nonpolar organic solvents had previously been reported by Binder et al. to work well in 1,3-dipolar cycloadditions on ROMP polymers. In our hands it also gave significantly higher yields (80-90%) for the diblock copolymer formation in all solvents examined (DCM, THF and DMF). In DMF, however, the product was formed in ca. 80% yield after 4 days (Table 2, entry 6) due to the fact that this solvent allowed the use of a higher reaction temperature (100°C). Reaction times exceeding 4 days did not significantly improve the yield. Therefore, these reaction conditions were used for all subsequent diblock copolymer formations.

The convergent block copolymer synthesis is shown in Scheme 2. Poly(ethylene glycol) mono-azides of two molecular weights, **PEG2k-N3** (Mn=2000 g mol^{-1}) and **PEG5k-N3** (Mn=5000 g mol^{-1}) were coupled via a 1,3-dipolar cycloaddition to the alkyne functionalized poly(norbornene imides) **PPNI-CCH** and **PHNI-CCH** (Table 3). All eight combinations of poly(norbornene imide) with poly(ethylene glycol) were carried out. The PEG-azides were used in excess. After a reaction time of 4 days, the block copolymer product was isolated by preparative GPC (THF) cutting at the first minimum of the elution curve (RI-signal). The isolated yields varied between 62% and 73%. In all cases, block copolymers with narrow molecular weight distribution (PDI = 1.13-1.20) were obtained.



Scheme 2 Block copolymer synthesis employing the Cu-catalyzed 1,3-dipolar cycloaddition between ROMP-azides and PEG-alkynes. The values of x correspond to those shown in Scheme 1. Poly(ethylene glycol) of molecular weight Mn=2000 g mol^{-1} (m = 44) and Mn=5000 g mol^{-1} (m = 110) was used.

A typical GPC trace for the reaction between **PPNI-1-CCH** and **PEG5k-N3** is shown in Figure 2. The left most peak at ca. $2x10^3$ g mol^{-1} corresponds to **PPNI-1-CCH**, the peak at $4x10^3$ g mol^{-1} to **PEG5k-N3**. From Figure 2 it can clearly be seen that during the course of the reaction the amount of **PPNI-1-CCH** strongly decreases relative to **PEG5k-N3**. The crude reaction mixture after 4 days of reaction time shows both individual blocks as well as the block copolymer. After preparative GPC in THF, the product peak (**PPNI-1-PEG5k**) at $7x10^3$g mol^{-1} (Figure 2, solid line) could be separated from the starting material.

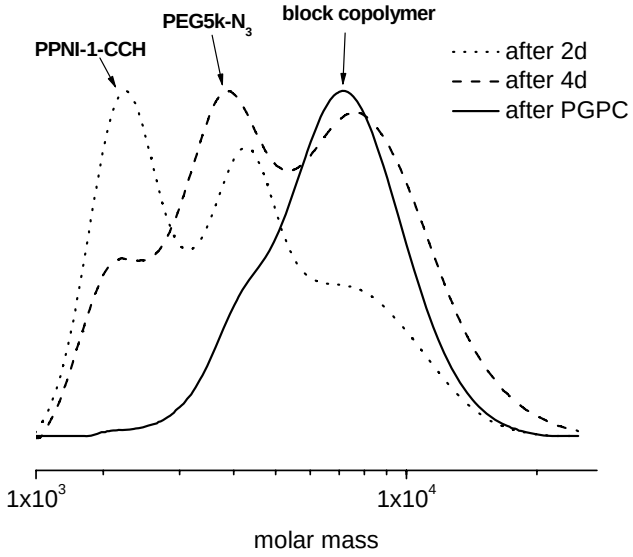


Figure 2 "Click"-reaction between **PPNI-1-CCH** and **PEG5k-N3** followed by GPC over several days. The dotted line shows the isolated block copolymer after preparative GPC (PGPC). The peak at ca. $2x10^3$ g mol^{-1} corresponds to **PPNI-1-CCH**, the peak at $4x10^3$ g mol^{-1} corresponds to **PEG5k-N3**. The curves are normalized to the most intensive peak, their absolute intensities cannot be compared.

All block copolymers prepared show amphiphilic behavior. Water was added dropwise to THF solutions of **PPNI-2-PEG2k** and **PPNI-1-PEG5k** in order to induce micellization. The THF/water mixtures were then drop cast onto carbon coated copper grids and the aggregates visualized by transmission electron microscopy (TEM). Figure 3 shows two representative examples for spherical micelles observed for **PPNI-2-PEG2k** and **PPNI-1-PEG5k**. As expected from the hydrophobic to hydrophilic block ratio, the micelles formed by **PPNI-2-PEG2k** are larger in diameter (Fig. 3 left) than the ones formed from **PPNI-1-PEG5k** (Fig. 3 right).

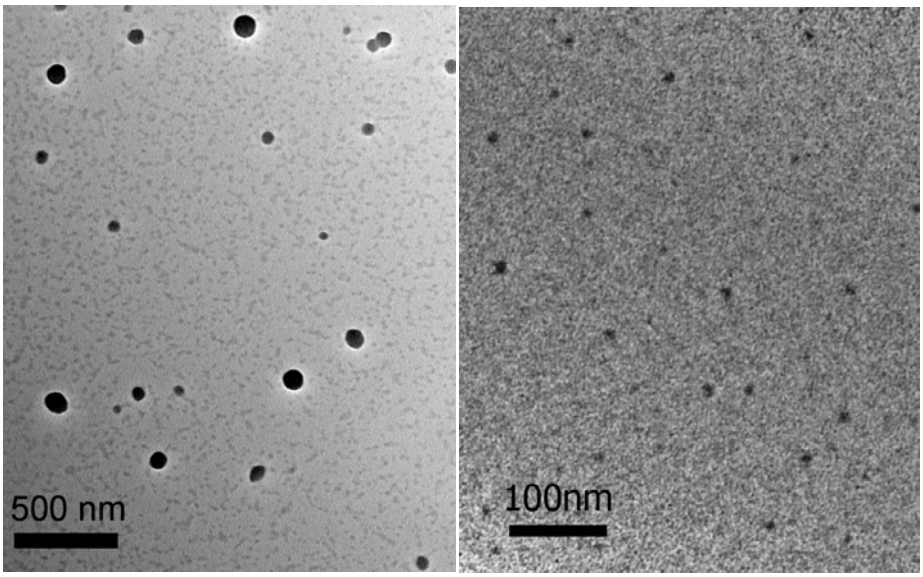


Figure 3 TEM images of **PPNI-2-PEG2k** (left) and **PPNI-1-PEG5k** (right) drop cast from THF/water mixture onto carbon coated copper grids

Conclusion

We have prepared highly functional mono-hydroxy end-functionalized ROMP polymers and conjugated them with polyethylene glycol in a 1,3-dipolar cycloaddition to yield amphiphilic diblock copolymers. The synthetic route described here allows the use of the highly functional group tolerant Grubbs' 1st generation ruthenium initiator for the preparation of one of the two polymer blocks. The second polymer block can, in principle, be freely chosen. In the examples described here, polyethylene glycol was used to prove the synthetic concept. In order to optimize the 1,3-dipolar cycloaddition reaction, the catalyst system had to be tenuously selected with respect to stability of the components and reaction time. The amphiphilic diblock copolymers prepared, form micelles in THF/water mixtures as could be shown by transmission electron microscopy.

References:

[1] Forster, S.; Plantenberg, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 689.

[2] Rodriguez-Hernandez, J.; Checot, F.; Gnanou, Y.; Lecommandoux, S. *Prog. Polym. Sci.* **2005**, *30*, 691.

[3] Morton, M. *Anionic Polymerization: Principles and Practice*, Academic Press: New York, 1983

[4] Bielawski, C. W.; Morita, T.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 678.

[5] Slugovc, C.; Demel, S.; Riegler, S.; Hobisch, J.; Stelzer, F. *J. Mol. Catal. A* **2004***, 213,* 107.

[6] Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.

[7] Huisgen, R.; Szeimies, G.; Möbius, L. *Chem. Ber.* **1967**, *100*, 2494.

[8] Huisgen, R. *Angew. Chem. Int. Ed.* **1968**, *7*, 321.

[9] Rostovtsev, V. V.; Green, L. G.; Dr., Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596.

[10] H. C. Kolb, K. B. Sharpless, *Drug Discovery Today* **2003**, *8*, 1128.

[11] Opsteen, J. A.; van Hest, J. C. M. *Chem. Commun.* **2005**, *26*, 57.

[12] Agut, W.; Taton, D.; Lecommandoux, S.*Macromolecules* **2007**, *40,* 5653.

[13] Quémener, D.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *Chem. Commun*. **2006**, *27*, 5051.

[14] Fleischmann, S.; Komber, H.; Appelhans, D.; Voit, B. I. *Macromol. Chem. Phys*. **2007**, *208*, 1050.

[15] Laurent, B. A.; Grayson, S. M. *J. Am. Chem. Soc.* **2006**, *128,* 4238.

[16] Opsteen, J. A.; van Hest, J. C. M. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2913.

[17] Bodine, K. D.; Gin, D. Y.; Gin, M. S. J. *Am. Chem. Soc.* **2004**, *126*, 1638.

[18] Mantovani,G.; Ladmiral, V.; Tao, L.; Haddleton, D. M. *Chem. Commun*. **2005**, *27*, 2089.

[19] Wang, Q.; Chan, T. R.; Hilgraf, R.; Fokin, V. V.; Sharpless, K. B.; Finn, M. G. *J. Am. Chem. Soc.* **2003**, *125*, 3192.

[20] Binder, W. H.; Kluger, C. *Macromolecules* **2004**, *37*, 9321.

[21] Binder, W. H.; Kluger, C.; Josipovic, M.; Straif, C. J.; Friedbacher, G. *Macromolecules* **2006**, *39*, 8092.

[22] Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem. Int. Ed.* **2004**, *43*, 3928.

[23] Díaz, D. D.; Punna, S.; Holzer, P.; McPherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 4392.

[24] Binder, W. H.; Sachsenhofer, R. *Macromol. Rapid Commun* **2007**, *28*, 15.

[25] Lutz, J.-F.; Börner, H. G.; Weichenhan, K. *Macromol. Rapid Commun*. **2005**, *26*, 514.

[26] Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 3558.

[27] Thomsen, A. D.; Malmström, E.; Hvilsted, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6360.

[28] Malkoch, M.; Schleicher, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P.; Wu, P.; Fokin, V. V. *Macromolecules* **2005**, *38*, 3663.

[29] Helms, B.; Mynar, J. L.; Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc*. **2004**, *126*, 15020.

[30] Whittaker, M. R.; Urbani, C. N.; Monteiro, M. J. *J. Am. Chem. Soc*. 2006, *128*, 11360.

[31] Altintas, O.; Hizal, G.; Tunca, U. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5699.

[32] Ossipov, D. A.; Hilborn, J. *Macromolecules* **2006**, *39*, 1709.

[33] O'Reilly, R. K.; Joralemon, M. J.; Wooley, K. L.; Hawker, C. J. *Chem. Mater.* **2005**, *17*, 5976.

[34] Joralemon, M. J.; O'Reilly, R. K.; Hawker, C. J.; Wooley, K. L. *J. Am. Chem. Soc.* **2005**, *127*, 16892.

[35] Li, H.; Cheng, F.; Duft, A. M.; Adronov, A. *J. Am. Chem. Soc.* **2005**, *127*, 14518.

[36] Lee, L. V.; Mitchell, M. L.; Huang, S.-J.; Fokin, V. V.; Sharpless, K. B.; Wong, C.-H. *J. Am. Chem. Soc.* **2003**, 125, 9588.

[37] Reynhout, I. C.; Cornelissen, J. J. L. M.; Nolte, R. J. M. *J. Am. Chem. Soc*. **2007**, 129, 2327.

[38] Agut, W.; Taton, D.; Lecommandoux, S. *Macromolecules* **2007**, 40, 5653.

[39] Kluger, C.; Binder, W. H. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 485.

[40] Binder, W. H.; Kluger, C.; Josipovic, M.; Straif, C. J.; Friedbacher, G. *Macromolecules* **2006**, *39*, 8092.

[41] Murphy, J. J.; Nomura, K. *Chem. Commun.* **2005**, 4080.

[42] Coca, S.; Paik, H. J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 6513.

[43] Murphy, J. J.; Kawasaki, T.; Fujiki, M.; Nomura, K. *Macromolecules* **2005**, *38*, 1075.

[44] Castle, T. C.; Hutchings, L. R.; Khosravi, E. *Macromolecules* **2004**, *37*, 2035.

[45] Hilf, S.; Berger-Nicoletti, E.; Grubbs, R. H.; Kilbinger, A. F. M. *Angew. Chem. Int. Ed.* **2006**, *45*, 8045.

[46] S. Perrier, X. Wang, *Nature* **2007**, *445*, 271

[47] Hilf, S.; Kilbinger, A. F. M. *Macromol. Rapid Commun.* **2007**, *28*, 1225.

[48] Konig, H. M.; Gorelik, T.; Kolb, U.; Kilbinger, A. F. M. *J. Am. Chem. Soc.* **2007**, *129*, 704.

[49] Craig, D. *J. Am. Chem. Soc.* **1951**, *73*, 4889.

[50] Blush, J. A.; Park, J.; Chen, P. *J. Am. Chem. Soc.* **1989**, *111*, 8951.

3.3: Ugly Stars – Long-chain Branched ROMP Polymers

Stefan Hilf, Frederik Wurm and Andreas F. M. Kilbinger

Manuscript prepared for submission in March 2009

Abstract

The ring-opening metathesis polymerization (ROMP) has enabled chemists to synthesize well-defined, highly functionalized linear polymers in good definition. The development of methods for the synthesis of branched polymer structures, however, is emerging rather slowly. This publication describes the construction of branched ROMP-polymer architectures via polycondensation of AB_n-type macromonomers. For this convergent strategy, a polymer was synthesized that bears hydroxyl-groups along the chain and a terminal carboxylic acid which was used to condensate these macromonomer chains to long-chain branched polymers. As the DPn for these systems is limited, we call them ugly-stars. These novel materials were analyzed by NMR and SEC in order to monitor the condensation reaction.

Introduction

Branched polymer structures exhibit very distinct properties compared to their linear analogues.[1] A much denser structure and severe limitations in the degrees of freedom of the polymer chain, such as the number of conformations, and the lack of entanglements between individual polymer chains, have great influence on solution properties such as the hydrodynamic volume of the polymer, and the number of chain ends, and thus often functional groups,[2] appending to a single polymer molecule. This microstructure also has substantial influence on macroscopic properties such as viscosity and thermal behavior (lower T_g) which can deviate immensely from the linear analogues.[3]

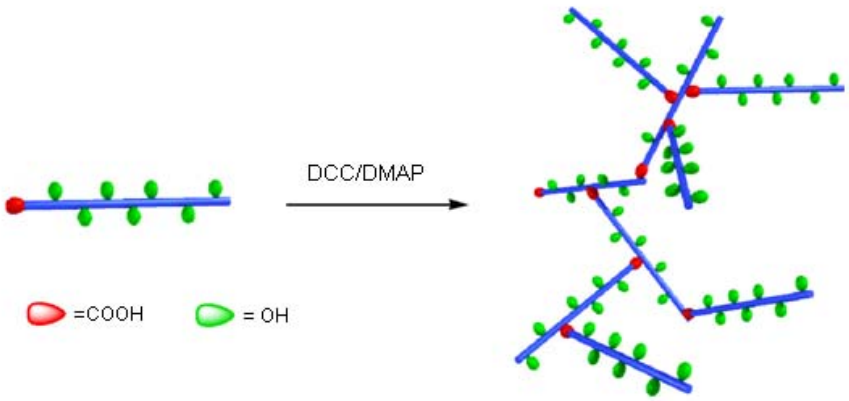
While the metathesis polymerization has had enormous impact in polymer chemistry,[4] especially in the living synthesis[5] of highly functional polymers which can bear even biologically active groups,[6] the availability of pathways towards branched polymer structures is very limited to date. The very first approaches towards branched polymers were developed on catalyst systems based on titanium, tungsten and molybdenum. Here, ketone- and aldehyde-functionalized core molecules served as multifunctional terminating agents.[7] The high oxophilicity of those catalyst types promised a high degree of attachment to those cores by a Wittig-type reaction.

As ruthenium is extremely functional group tolerant and the metathesis activity of this type of catalysts can only be quenched with highly electron deficient olefins,[8] thus rendering the possibility of a convergent branching strategy based on ruthenium-initiated ROMP difficult. Via the acyclic diene metathesis (ADMET), branched structures have been achieved elegantly in a classical AB_2-monomer approach by Gorodetskaya and Grubbs.[9] Here, the different reactivity of free double bonds and conjugated olefinic bonds have been utilized to guarantee an A-type and a B-type functional group thus avoiding the crosslinking which would be expected from an A_3-type monomer. A different ROMP based approach was described by Mathers et al.,[10] who have utilized dicyclopentadiene, which can also act as a crosslinking agent, to interconnect active polymers along the chains and in a central core. This approach can be compared to the synthesis of star-polymers by Matyjaszewski for other polymerization methods involving a branching agent with two polymerizable groups[11] such as divinyl benzene in classical vinyl polymerizations.

A completely different pathway towards branched polymers is based on the synthesis of macromonomers. These can be either of a chain-growth nature, such as macromonomers[12]

used for the synthesis of graft-copolymers, or of a step-growth functionality which can be condensated in a manner similar to small AB_x-monomers, a strategy developed as HyperMacs by Hutchings[13] based on Williamson-coupling of polystyrene-based AB_2-macromonomers. A similarconcept has also found application on polyaddition reactions via hydrosilylation for AB_n-macromonomers.[14] A major drawback for a (hyper)branching polycondensation process is the resulting broad PDI, exceeding 5-10 in many cases. Only a few systems allow control over Mn and PDI.

The facility of such a convergent approach is based on the precision of the placement of the single A-function since any oligo-functionalization in this part would inevitably lead to crosslinking during the polycondensation. Convenient methods for ROMP, giving exactly one reactive[15] functional group at one chain end have been reported recently by our group.[16] Particularly the termination reaction utilizing vinyl lactones for the introduction of carboxylic acids and aldehydes, which does not require extensive work-up or deprotection reactions, offers access to reactive terminal functional groups which can be places with high precision.[17]



Scheme 1: Concept of polycondensation of AB_n-macromonomers to form branched polymers.

Here we present the synthesis of branched ROMP polymers based on the latter pathway, i.e. AB_n-type macromonomers. The introduction of orthogonal reactive functionalities at the chain end and at along the polymer was accomplished by *3H*-furanone termination[17] of a polymer having protected hydroxyl groups along the entire or one block of the polymer chain. This involved the synthesis of a monomer that bears two protected hydroxyl groups

per molecule which are as reactive as possible, i.e. primary alcohols. **NDBA** (c.f. Scheme 1) was developed for this purpose and was copolymerized by means of the Grubbs 1st generation catalyst **C1** with norborneneimide (**xNI**) monomers which acted as a spacer block between the orthogonal functional groups to minimize cyclization.

Experimental

General. ^{1}H-NMR spectra were recorded at 300 MHz on a Bruker AC300 or at 400MHz on a Bruker ARX400. All spectra were referenced internally to residual proton or carbon signals of the deuterated solvent. Deuterated solvents were purchased from Deutero GmbH. Size exclusion chromatography in tetrahydrofuran was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P100 pump and a set of three PSS SDV columns ($10^5/10^3/10^2$ Å). Signal detection occurred by use of a TSP Spectra System UV2000 (UV 254 nm unless otherwise stated) and a Wyatt Optilab DSP (refractive index). MALLS measurements were performed on a Dawn EOS, data evaluation was implemented using the WinGPC Unity software provided by PSS. Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service (PSS).

Exo-norbornene-2,3-dicarboxanhydride, *exo*-*N*-hexyl-2,3-norbornene dicarboximide and *exo*-*N*-dodecyl-2,3-norbornene dicarboximide *3H*-furanone were synthesized as described in earlier publications. Grubbs' 1st generation catalyst was obtained from Materia, inc. All solvents and other reagents were purchased from Aldrich or Acros. All polymerization reactions were carried out under argon using standard Schlenk techniques unless otherwise stated. Dichloromethane as the polymerization solvent was dried over P_2O_5 and distilled under a nitrogen atmosphere.

Synthesis of exo-norbornene-2,3-dimethanol:

Exo-norbornene-2,3-dicarboxanhydride (15 g, 91 mmol) were reduced to the di-alcohol as described by the procedure described by Zhan and Hanson[18] for the *endo*-derivative employing g of $LiAlH_4$ (4.3 g, 0.11 mol) in 150 mL THF. Workup was performed by dropwise

addition of water followed by conc. Hydrochloric acid until the aluminum oxides were dissolved. Then, the THF was removed under reduced pressure and the product was extracted with multiple portions of ether (4 x 150 mL). The combined organic phases were deacidified with a conc. soda solution, dried over anhydrous sodium sulfate and filtered before the ether was removed. The crude product obtained (10.5 g, mol, %) was pure enough for further reactions. Distillation of the product under high vacuum causes partial decomposition and solidification.

^{1}H-NMR (300 MHz, $CDCl_3$) δ[ppm]: 1.2-1.4 (m, 2H, CH_2-bridge); 1.79 (m, 2H, O-C-CH); 2.50 (s, 2H, bridgeheads); 3.71 (m, 4H, O-CH_2); 4.45 (s, 2H, OH); 6.16 (s, 2H, HC=CH).

Synthesis of exo-norbornene-2,3-dimethanol benzylidene acetal (NDBA):

To 9 g exo-norbornene-2,3-dimethanol (60 mmol) dissolved in 100 mL toluene were added 7.1 g benzaldehyde (67 mmol) and 50 mg toluenesulfonic acid monohydrate. The mixture was refluxed under Dean-Stark conditions until all reaction water had been removed (ca. 2 h). After cooling, the solvent was removed under reduced pressure and the resulting solids were recrystallized twice from petroleum ether to give colorless crystals in 9.5 g yield (0.39 mol, 65 %).

^{1}H-NMR (300 MHz, $CDCl_3$) δ[ppm]: 1.5-1.8 (m, 2H, CH2-bridge); 1.8-2.1 (m, 2H, O-C-CH); 2.19 (s, 2H, bridgeheads); 3.7-3.8 (m, 2H, O-CH_2); 4.0 (m, 1H, O-CH-O); 4.1-4.3 (m, 2H, O-CH_2); 5.36 (s, 2H, HC=CH); 7.3-7.5 (m, 5H, Ph).

Synthesis of poly(NDBA)-COOH:

To a dichloromethane solution (4 mL) of 164 mg Grubbs 1st generation catalyst (0.2 mmol) and 200 mg triphenylphosphine (0.8 mmol) in a Schlenk flask was added 4, 6 or 8 mL of a stock solution of NDBA (1.1 g dissolved in 17 mL dichloromethane, 4 mL corresponds to 10 equivalents). The mixtures (brown solutions) were allowed to stir for 9 h at r.t. to allow for full reaction before 300µL *3H*-furanone were added to each reaction vessel. The polymerization mixtures were left to terminate over night (orange solutions), then

precipitated in methanol, recollected and reprecipitated to give brown solids in good yield (79 - 85%).

^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 1.1-1.4 (m, 2H, CH_2-brigde); 1.7-2.5 (m, 6H, C_2-CH-CH_2-O); 3.4-4.0 (m, 3H, bridgeheads + O-CHPh-O); 5.1-5.5 (m, 2H, double bonds polymer); 6.0-6.1+6.5-6.7 (m, 2H, double bond Ph endgroup); 6.8-7.6 (m, 5H, Ph).

Synthesis of poly(NDBA-b-xNI)-COOH:

To a dichloromethane solution (4 mL) of 164 mg Grubbs 1st generation catalyst (0.2 mmol) in a Schlenk flask was added 4, 6 or 8 mL of a stock solution of NDBA (1.1 g dissolved in 17 mL dichloromethane, 4 mL corresponds to 10 equivalents). After 2 h, the calculated amounts of norborneneimide monomer were added in solution (ca. 5 mL dichloromethane). The mixtures were allowed to stir for another 2 h at r.t. to complete the polymerization before 300µL *3H*-furanone were added to each flask. The polymerization mixtures were left to terminate over night before they were precipitated in methanol, recollected and reprecipitated to give slightly brown solids in good yield (83 - 95%).

An exemplary ^{1}H-NMR of the polymer is given in the Supporting Information.

Deprotection of NDBA-containing polymers:

The polymer to be deprotected was dissolved in chloroform (ca. 20 mL per 1 g), methanol (half the volume of chloroform) and 1n HCl (half volume of chloroform) were added and the mixture was stirred vigorously for 3 h before the organic solvents were removed under reduced pressure. The water was decanted off the polymer and the polymer was redissolved in THF, and then precipitated in methanol (block-copolymers) or diethyl ether (homopolymers). Redissolution and precipitation under the same conditions yielded slightly brown polymer materials (yields ca. 60-80% of the starting material depending on block rate).

Without *x*NI-block: ^{1}H-NMR (400MHz, $CDCl_3$) δ[ppm]: 1.0-1.35 (m, 2H, CH_2-brigde); 1.6-2.0 (m, 6H, C_2-CH-CH_2-O); 3.4-4.0 (m, 4H, bridgeheads + OH); 5.2-5.4 (m, 2H, double bonds

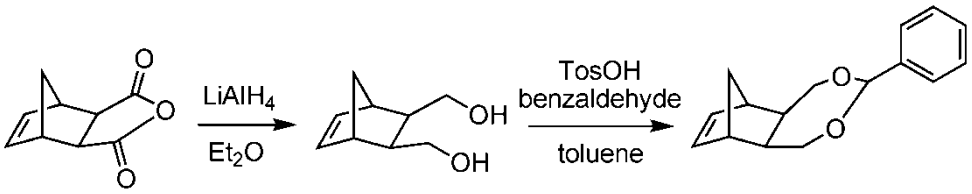
polymer); 6.0-6.1+6.5-6.7 (m, 2H, double bond Ph endgroup). An exemplary ^{1}H-NMR of a deprotected block-copolymer is given in the Supporting Information.

Polycondensation of macromonomers:

A thin (ca. 1 cm in diameter) Schlenk tube was charged with 100 mg of the macromonomer, 10 mg *N,N*-dimethylaminopyridine, 30 mg dicyclohexyl carbodiimide and a small stirbar. After three cycles of evacuating and purging with argon, the tube was heated to 80°C in an oil bath before 100 µL dimethyl formamide were added by syringe. The thick solution was stirred for another 4 h. After the reaction time was completed, the tube was left to cool to r.t., 0.5 mL chloroform were added and the polymer was precipitated by dropwise addition of the solution to methanol (block-copolymers) or ether (homopolymers). The polymers were obtained as a brown solid (yields ranging from 75 to 87%).

Results and Discussion

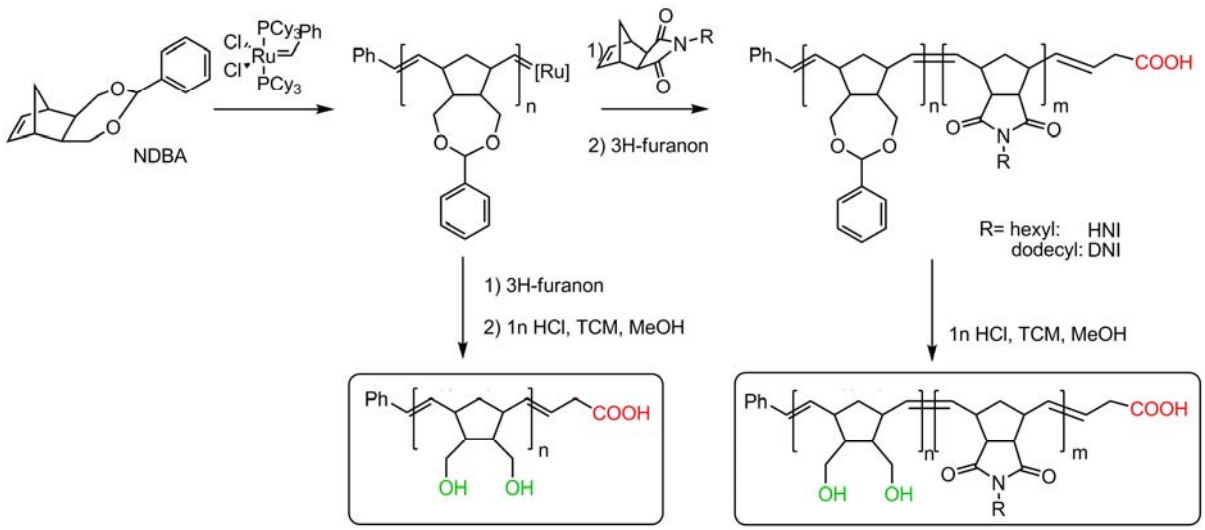
Carboxylic acids and Alcohols were chosen as the A- and B-type functionalities the highly selective and very efficient *3H*-furanone quenching technique was selected for the introduction of exactly one carboxylic acid at every chain end, while the alcohol groups along the polymer chains were introduced via a monomer carrying acetal protected alcohols in order to ensure a maximum of control over the polymerization. In order to attach a maximum number of hydroxyl groups on every monomer and to avoid the use of asymmetrically norbornenes which are generally harder to synthesize, we developed a new monomer that, after removal of the protective groups, carries two highly reactive primary alcohol groups. Therefore, *exo*-norbornene-dimethanol benzylidene acetal (NDBA) was synthesized as illustrated in Scheme 1 by reduction of the readily available *exo*-anhydride and subsequent acetal formation with benzaldehyde under Dean-Stark conditions.



Scheme 1: Synthesis of NDBA.

The polymerization of NDBA performed smoothly with Grubbs 1st generation catalyst in dichloromethane. In order to obtain well-defined polymer materials at low molecular weight, the method of Bielawski[5] adding triphenylphosphine to the catalyst in order to enhance the initiation efficiency and lower PDIs of the final materials, was applied. After termination with *3H*-furanone, narrowly distributed polymers were obtained with degrees of polymerization ranging from 10-20 (c.f. Table 1). Deprotection of those materials with aqueous acid gave rise to the respective macromonomers which retained their good definition as shown by the SEC data.

The polycondensation of the macromonomers was performed using DCC/DMAP coupling to form an ester bond between the different functionalities present on the macromonomer chains. In order to avoid a coupling of two groups of the same chain, which would lead to cyclization rather than star-formation, the reaction was carried out in highly concentrated solutions. In a typical experiment, 100 mg of the macromonomer were therefore reacted in as little as 100 µL DMF and excesses of the coupling agents. The progress of the polycondensation reaction came to an end after ca. 2h reaction time under the typical reaction conditions given in the experimental part (SEC- traces given in Figure 3). Addition of further amounts of coupling agents did not promote additional condensation reactions.



Scheme 2: Synthesis and deprotection of the (block-co)polymers.

The poly(macromonomer)s were analyzed by SEC. As they exhibited very low dn/dc values, an analysis via MALLS detection did not give sufficient data to quantify the degree of polycondensation. The SEC traces do, however, demonstrate that higher-MW materials have been generated. The number of macromonomer chains that have been fused to one branched polymer can be estimated from the portions of polymer that exceed the molecular weight distribution of the starting material. This number, which appears to be in the order of 2-8 in these cases, can be seen as a lower limit as branched polymers are generally underestimated by SEC due to the lower hydrodynamic volume, branched polymers take in compared to their linear counterparts. The actual branching of such AB_n type poly(macromonomer)s has been shown by our group[14] and can be expected for this type of ugly star polymer as well.

The percentages of polymer chains which have undergone a condensation reaction were determined by identifying the point of the SEC traces where the normalized molecular weight distributions of the macromonomers and the polycondensation products cross and integrating over the molecular weight distribution from this point on. Under the three macromonomers synthesized from NDBA only, two trends were observed. Shorter macromonomers gave higher degrees of polycondensation and higher amounts of branched polymer (c.f. Table 2). These trends follow the findings of our earlier study,[14] in which we have attributed this effect to the probability of cyclization against a branching condensation

due to the dilution of the A-type functionality, i.e. “dilution” of the endgroup in the polymer matrix. As longer chains contain less endgroups per volume of material, cyclization is more likely to occur.

A-spacer-B_n block-copolymer-based macromonomers are of considerable interest, since the additional polymer block between the two functional parts of the macromonomer, can act as a separator which avoids direct cyclization of the terminal functional group A with B groups in its direct vicinity. Also, it can act as a block to trigger the properties of the final material such as glass transition temperature or solubility.

For the synthesis of the block-copolymers, Grubbs 1st generation catalyst was used to first initiate NDBA followed by the addition of HNI or DNI as the second block. *3H*-furanone termination then was applied to attach the terminal functionality. The success of the block-copolymer formation could be monitored by blockwise SEC analysis (c.f. Figure 2).

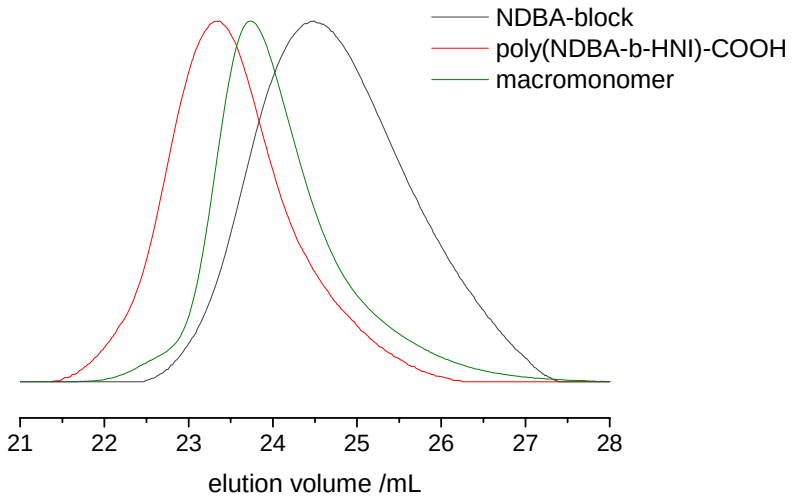


Figure 2: SEC in THF monitoring of the construction of the deprotected macromonomer 5.

A variety of macromonomers was synthesized by this method varying in block rate and total chain length. The characterization results of the macromonomers are summarized in Table 1. All polymers were obtained in good yield and definition according to the general capability of the used initiator. At this point it has to be noted that, due to the initiation characteristics typically observed for Grubbs 1st generation catalyst, a degree of

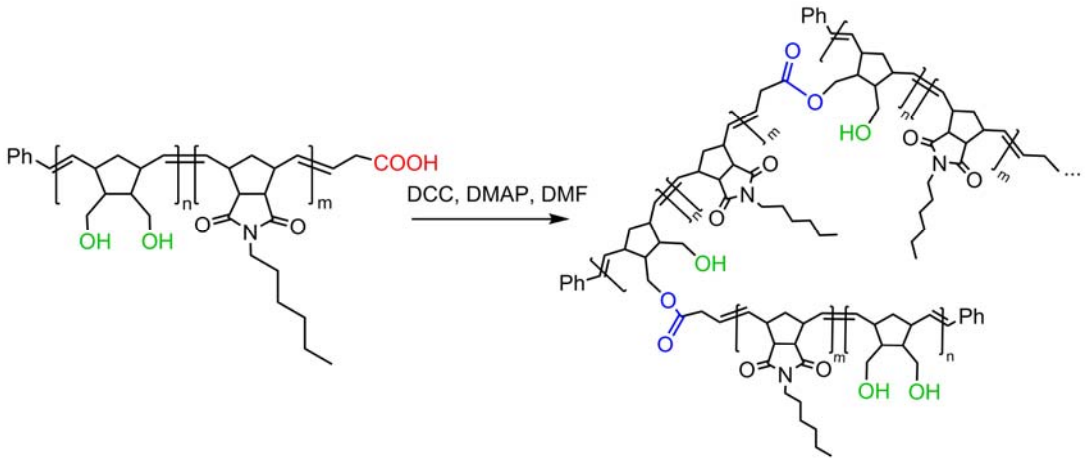
polymerization of 5 (*c.f.* polymers 4-7 does not warrant the placement of an NDBA monomer on every polymer chain as the k_i/k_p value for this catalyst is not sufficiently high.[25] This does, however, not have a major influence on the result of a later polycondensation since function A, i.e. the carboxylic acid, is present on every polymer chain. Such chains can therefore still be incorporated during the branching step.

Table 1: Characterization data of the macromonomers.

Macromonomer #	n(NDBA)	n(*x*NI)	*x*NI	Mn_{SEC} /g mol^{-1}	PDI
1	10	--	--	8 00	1.30
2	15	--	--	9 50	1.35
3	20	--	--	1 400	1.25
4	5	10	HNI	7 300	1.17
5	5	20	HNI	8 600	1.21
6	10	10	HNI	5 900	1.27
7	10	20	HNI	10 700	1.24
8	10	30	HNI	14 000	1.28
9	15	10	HNI	6 700	1.23
10	15	30	HNI	15 200	1.22
11	10	10	DNI	7 600	1.34
12	10	20	DNI	11 700	1.34
13	10	30	DNI	13 600	1.33

The polycondensation reactions of the AB_n-functional block-copolymers (*c.f.* Scheme 3) were carried out under the same conditions as the homopolymers. The reaction times were prolonged to 4 h due to the higher molecular weight due to which slower reaction kinetics were expected. Again, the DCC/DMAP promoted ester formation necessary for the branching reaction was carried out under maximum concentrations in order to suppress

cyclization reactions. Higher dilutions resulted in lowered amounts of the branched polymer. SEC traces of the products of a polycondensation of macromonomer 4 under different reaction conditions can be found in the Supporting Information.



Scheme 3: Polycondensation of HNI block-copolymer based macromonomers.

The resulting polymers were analyzed by SEC, the portion of the polymer chains which had formed higher molecular weight materials was determined by the same method that had been used for the homopolymers and which is illustrated in Figure 3 (dashed line) comparison of the average molecular weight of this fraction to the molecular weight of the original macromonomers gave rise to the degree of polymerization achieved.

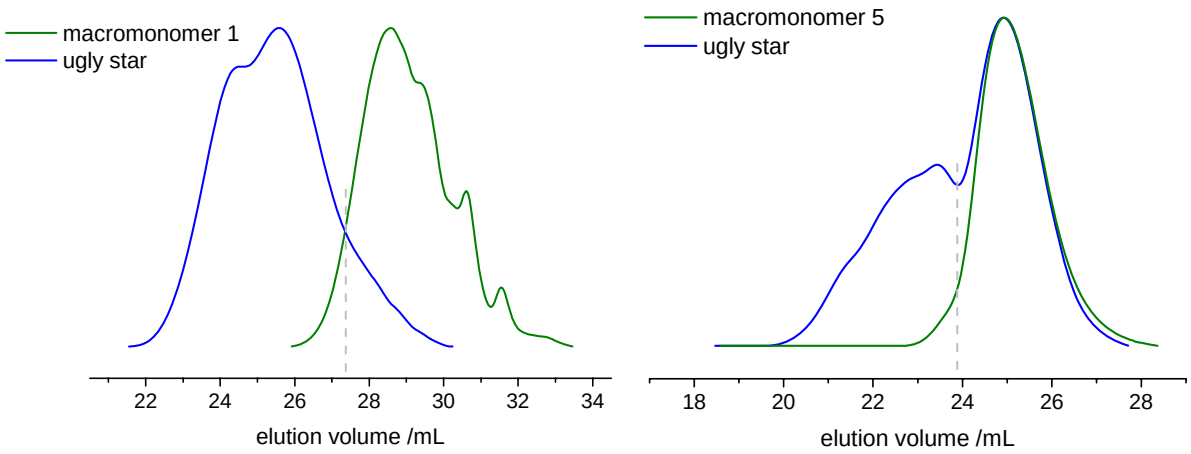


Figure 3: SEC traces of polymer 1 (*left*) before and after polycondensation and polymer 5 (*right*).

The results of the polymerization of the AB_n-functional block-copolymers as well as their ugly-star content and degree of polycondensation are summarized in Table 2. Polydispersity indices of the complete product ranged between 1.5 – 2.0. Considering the polydispersities observed for the homopolymer-macromonomers, where the incorporation of macromonomers into the star-like structures was generally higher, the molecular weight distributions are fairly narrow compared to the observations of earlier convergent star-like polymer formations.

The fate of the unreacted macromonomer chains remains uncertain. On the one hand, the terminal carboxylic acid might have undergone side reactions under the polycondensation reaction conditions, e.g. reaction with fragments of DMF, by decarboxylation or with DCC as an acyl urea. An analysis by MALDI-ToF did not give any information since no matrix / ionization agent combination was applicable to produce reliable spectra for the present polymer. For longer polymer chains, intramolecular esterification is the most expected side reaction reducing the overall DPn.

When analyzed with respect to chain length and block ratio between the spacer block and the polymer block which carries the B-type functionality, several trends can be extrapolated. Figure 4 categorizes the ugly star-formation results with respect to the degree of polycondensation of the macromonomers and the percentage of polymer chains which have been incorporated in such a branched structure. In general, best polycondensation results have been achieved when polymer chains were short. The spacer block ratio had influence on the degree of polycondensation rather than the portion of polymer chains which had undergone a condensation reaction.

Table 2: Results of the polycondensations and ugly-star content of the samples.

Macromonomer #	Mn^{*}_{total} /g mol^{-1}	PDI_{total}	Mn^{*}_{star}/g mol^{-1}	DP_{star}	$\%_{star}$
1	3 700	1.89	5 100	6.4	89%
2	2 400	2.16	4 500	4.7	70%
3	1 400	1.60	3 200	2.3	53%
4	9 000	1.83	24 300	3.3	40%
5	10 000	1.87	45 500	5.3	38%
6	7 300	1.88	19 800	3.4	41%
7	14 400	1.76	36 000	3.4	40%
8	14 900	1.90	40 800	2.9	38%
9	7 300	1.57	19 400	2.9	31%
10	16 300	2.00	44 700	2.9	38%
11	8 300	1.70	29 400	3.9	18%
12	12 500	1.72	42 100	3.6	25%
13	13 800	1.75	18 000	1.5	24%

*Determined in THF vs. PS standards

The chart clearly illustrates that long spacer blocks do not efficiently suppress the intramolecular cyclization unless the total chain length remains low. Considering the chain stiffness of norbornene derivative-based ROMP polymers, this indicates that the spacer block can, in this case, act as a cyclization aid, as a certain unfunctional chain length is needed for the A-type function to reach B-type functions along its own polymer chain. Thus, the influence of the chemical nature of this spacer block was also of considerable interest

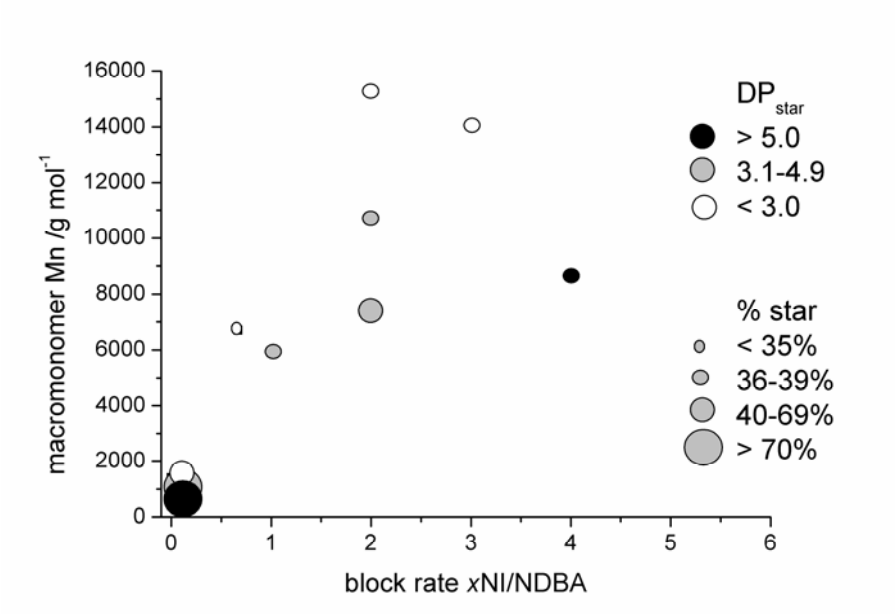


Figure 4: dependence of the ugly star formation on macromonomer block rate and molecular weight (block rate = 0 : homopolymers).

In order to study the influence of the chemical nature of the spacer block, macromonomers bearing a dodecyl-substituted polynorborneneimide (DNI) block were synthesized by the same technique used for the synthesis of the aforementioned A-spacer-B_n type macromonomers. The macromonomers (polymers 11-13), which were obtained in similar definition as the previous ones, underwent polycondensation under the same conditions as the other block-copolymers. The polycondensation results, however, were less successful than those obtained for the HNI-based block copolymers. The portions of polymer chains which had been incorporated in the ugly stars did not reach the values obtained for their HNI-equivalents (polymers 6-8). This can be reasoned by thelarge difference in the chemical nature of the two blocks of the macromonomer, resulting in phase separation during polycondensation, thus lowering the efficiency.

Therefore, the spacer block must not only be selected by the properties desired for the final material, but also with respect to the miscibility of the polymer blocks in order to avoid an encapsulation of certain functional groups necessary for the polycondensation reaction. Furthermore, the total chain length of the A-spacer-B_n macromonomer should not exceed a critical length, after which the rather stiff polynorbonenes can undergo intramolecular condensation more feasible. Moreover, the influence of the B_n-block structure, i.e.

functional group density, the possibility of a statistical copolymer in this section, as well as the influence of the block-order, which might play a crucial role in the polycondensation step, will be studied.

Conclusions

Long-chain branched structures have been synthesized from ROMP polymers in a convergent strategy using AB_n-type macromonomers. The synthesis of poly(NDBA)-COOH gave rise to an easy access to such macromonomers after deprotection. Application of conventional DCC/DMAP coupling chemistry allowed for the construction of ester bonds between the carboxylic endgroups and the hydroxyl groups along the macromonomer chains. Both, intra- and intermolecular esterifications were observed after the polycondensation. The extent of the desired intermolecular coupling varied on the chain length. Lower molecular weight macromonomers could be reacted almost entirely to long-chain branched polymers.

The synthesis of A-spacer-B_n type macromonomers via a block-copolymer approach allowed the synthesis more complex of long-chain branched in which the overall properties of the final branched materials can be tuned by the monomer structure of the spacer block. The polycondensation of those macromonomers performed less efficiently than when the simpler homopolymer were used, but higher molecular weight materials were formed to a reasonable extent. A synopsis over the success of the reaction depending on the total chain length and the block ratios of the two blocks present in the macromonomers resulted that particularly a low molecular weight of the macromonomers enhances the extent of the intramolecular condensation, while a high spacer / B_n block ratio adds to this effect. The introduction of poly(DNI) as the spacer block did not enhance the results, presumably due to an increased immiscibility of the two macromonomer blocks whereby the two respective functionalities are shielded from each other and can not undergo the condensation reaction efficiently.

[1] Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and Other Dendritic Polymers* (John Wiley & Sons Ltd., New York **2001**) 647.

[2] Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 4240. H. Frey, D. Hölter, *Acta Polym.* **1999**, *50*, 67.

[3] Hult, A.; Johansson, M.; Malmström, E. *Adv. Polym. Sci.* **1999**,*143*, 1.

[4] Grubbs, R.H., *Handbook of Metathesis* (Wiley-VCH, Weinheim, 2003).

[5] Bielawski,C.W., Grubbs, R.H. *Macromolecules* **2001**, *34*, 8838.

[6] Maynard, H.D.; Okada, S.Y.; Grubbs, R.H. *Macromolecules* **2000**, *33*, 6239. Maynard, H.D.; Okada, S.Y.; Grubbs, R.H. *J. Am. Chem. Soc*. **2001**, *123*, 1275.

[7] Risse, W.; Grubbs, R. H. *Macromolecules* **1989**, *22*, 4462-4466. Dounis, P.; Feast, W. J. *Polymer* **1996**, *37*, 2547.

[8] Wu, Z., Nguyen, S. T., Grubbs, R. H. & Zillier, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503-5511.

[9] Gorodetskaya, I. A.; Choi, T.-L.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 12672-12673.

[10] Mathers, R. T.; Damodaran, K.; Rendos, M. G.; Lavrich, M. S. *Macromolecules* **2009** ASAP.

[11] Gao, H.; Matyjaszewski, K. *Macromolecules* **2006,** *39,* 7216-7223. Lapienis, G.; Penczek, S. *J. Polym. Sci. A: Polym. Chem*. **2004**, *42*, 1576–1598. Lapienis, G.; Penczek, S. *Macromol. Symp.* **2003***, 195*, 317-327.

[12] Hilf, S.; Kilbinger, A.F.M. *Macromol. Rapid Commun*. **2007**, *28*, 1225-1230.

[13] Hutchings, L. R. *Soft Matter* **2008**, *4*, 2150-2159. Clarke, N.; De Luca, E.; Dodds, J. M.; Kimani, S. M.; Hutchings, L. R. *Europ. Polym. J.* **2008**, *44*, 665-676. Dodds, J. M.; De Luca, E.; Hutchings, L. R.; Clarke, N. *J. Polym. Sci. B: Polym. Phys.* **2007**, *45*, 2762-2769. Hutchings, L. R.; Dodds, J. M.; Roberts-Bleming, S. J. *Macromolecules* **2005**, *38*, 5970-5980.

[14] Wurm, F.; Lopez-Villanueva, F.-J.; Frey, H *Macromol. Chem. Phys.* **2008**, *209*, 675-684. Lopez-Villanueva, F.-J.; Wurm, F.; Kilbinger, A. F. M.; Frey, H. *Macromol. Rapid Commun.* **2007**, *28*, 704-709.

[15] Hilf, S.; Hanik, N.; Kilbinger, A.F.M. *J. Polym. Sci. A* **2008**, *46*, 2913-2921.

[16] Hilf, S.; Berger-Nicoletti, E.; Grubbs, R.H.; Kilbinger, A.F.M. *Angew. Chem*. **2006**, *118*, 8214-8217; *Angew. Chem. Int. Ed.* **2006**, *45*, 8045-8048. Perrier, S.; Wang, X. *Nature* **2007**, *445*,

271. Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M *Macromolecules* **2008**, *41*, 6006-6011. Hilf, S.; Kilbinger, A.F.M. *Macromolecules* **2009**, *42,* 1099-1106.

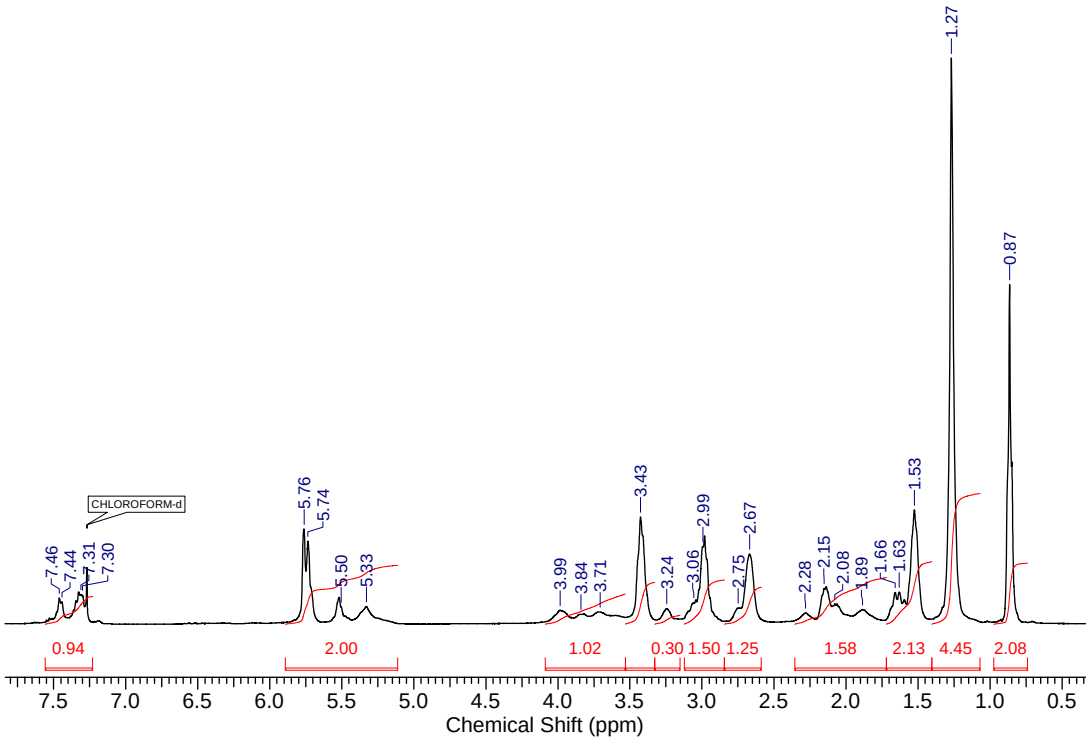
[17] Hilf, S.; Grubbs, R.H.; Kilbinger, A.F.M *J. Am. Chem. Soc.* **2008**, *130*, 11040-11048.

[18] Zhang, M.; Flynn, D. L.; Hanson, P. R. *J. Org. Chem.* **2007**, *72*, 3194-3198.

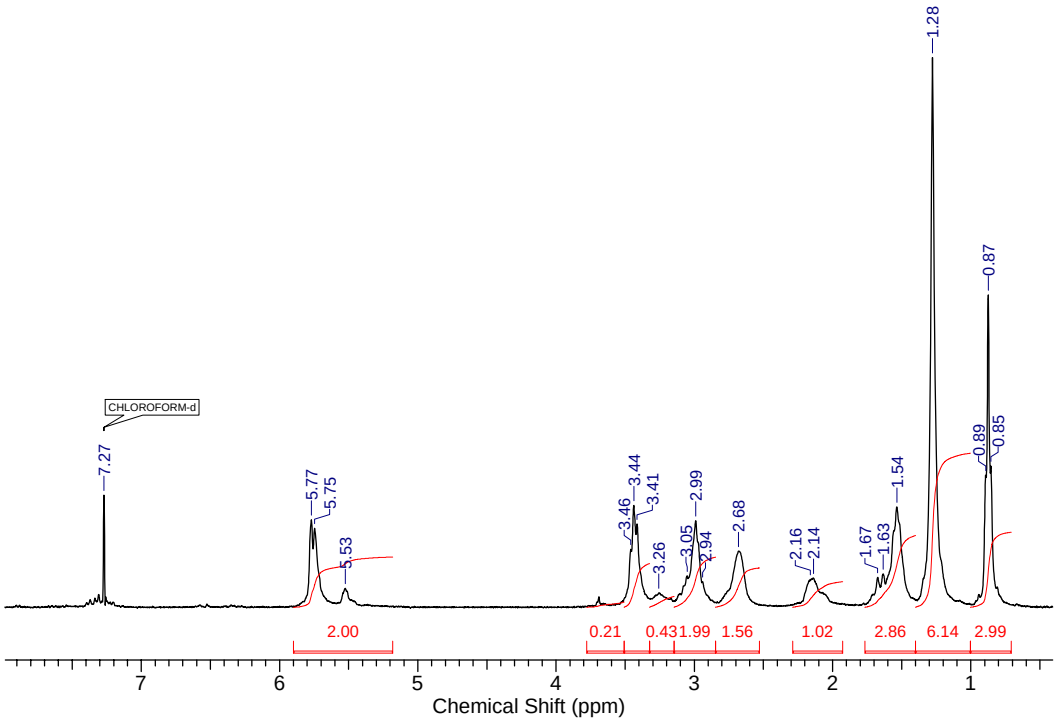
Supporting Information for: Ugly Stars – Long-chain Branched ROMP Polymers

Stefan Hilf, Frederik Wurm and Andreas F.M. Kilbinger

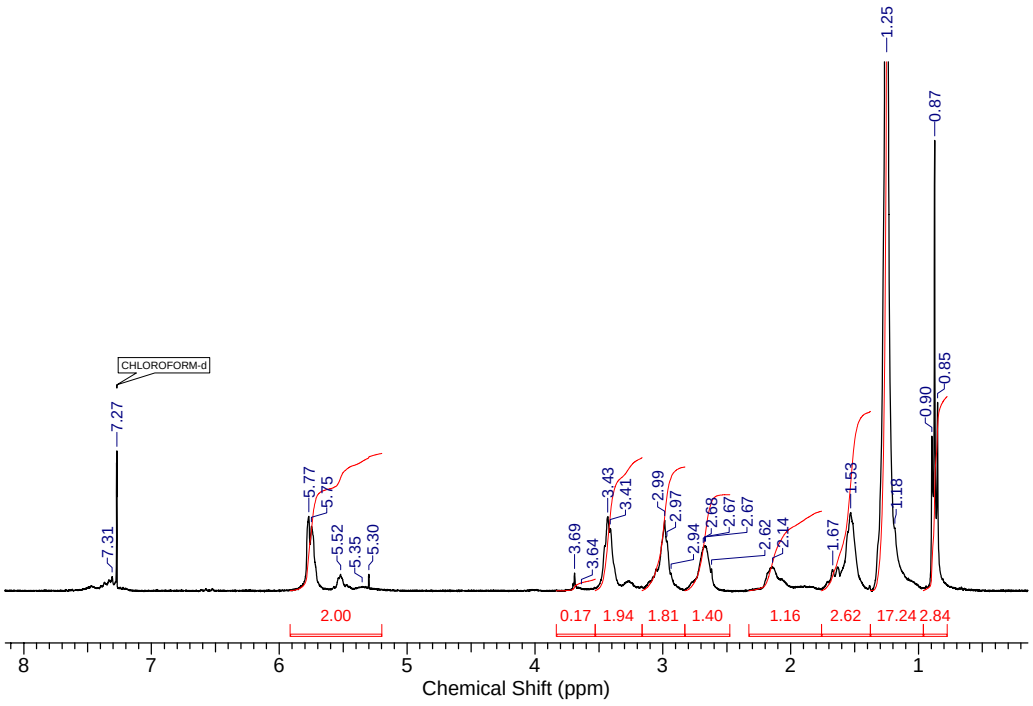
SI-1: Additional NMR spectra of the macromonomers.



^{1}H-NMR of polymer 8 before deprotection.

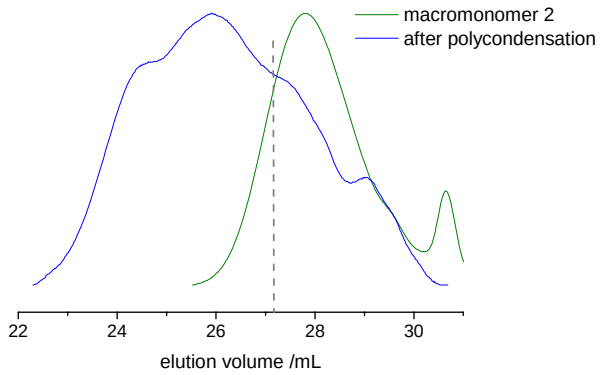


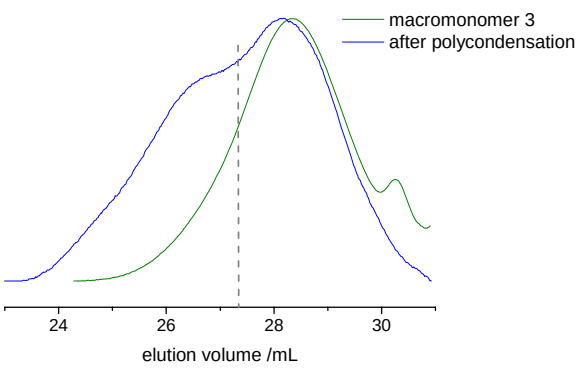
^{1}H-NMR of polymer 4 before deprotection.

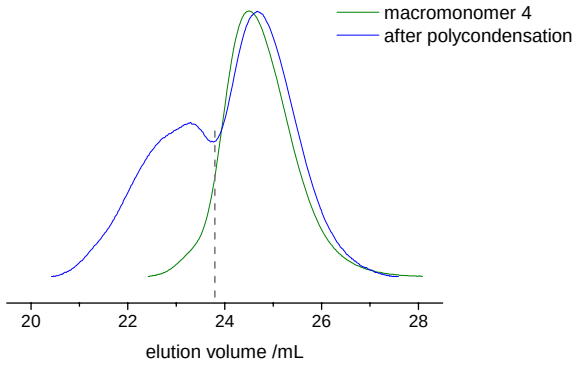


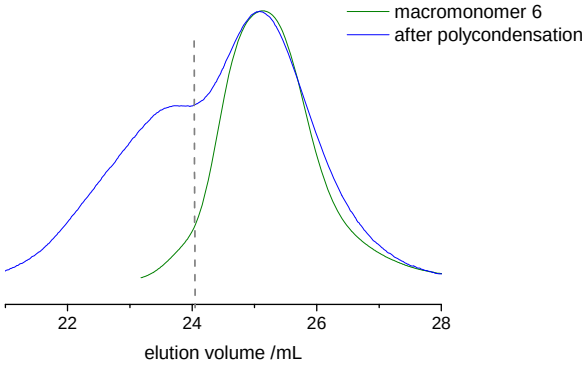
^{1}H-NMR of macromonomer 13

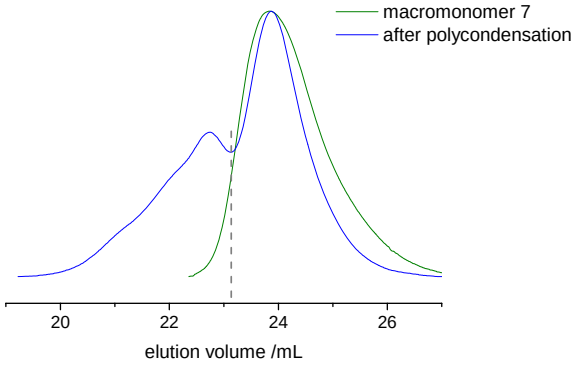
SI-2: SEC traces for the macromonomers and their polycondensation:

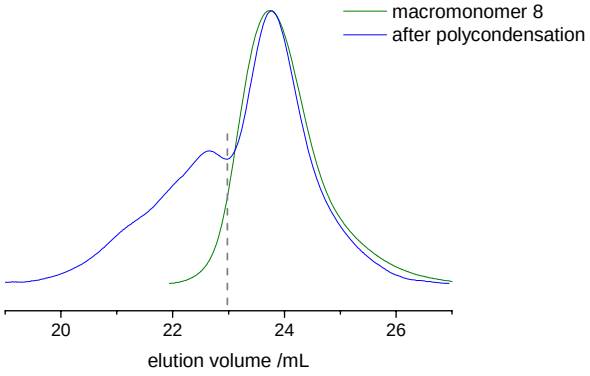


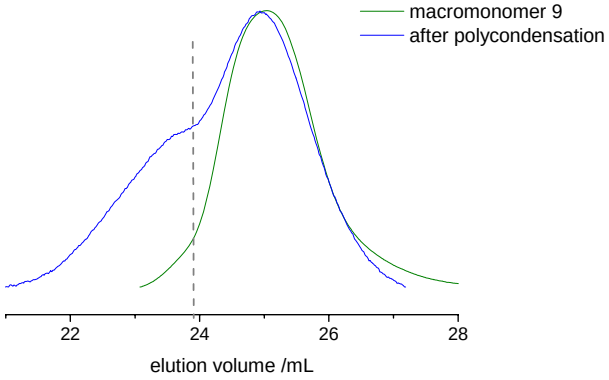


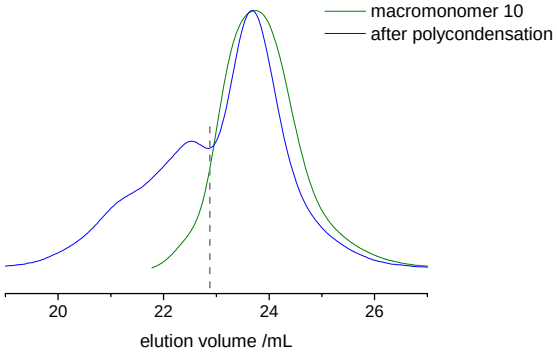


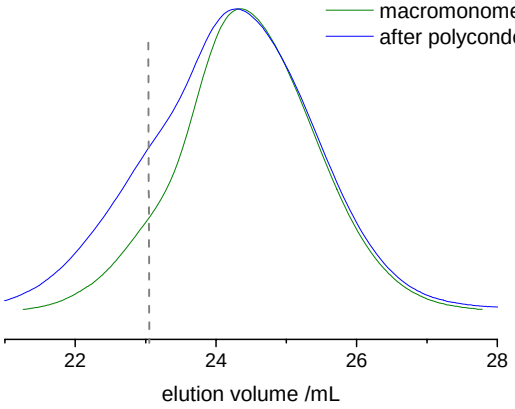


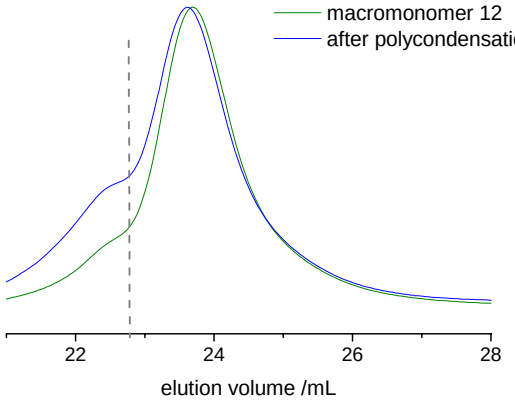


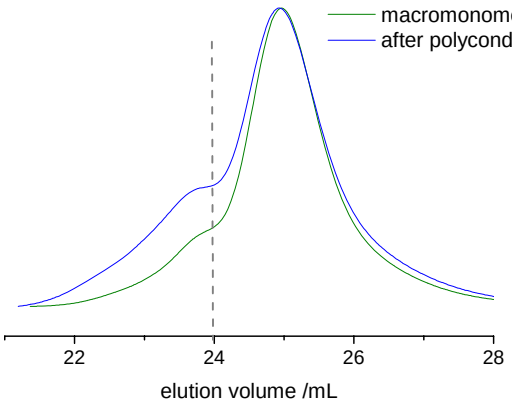



macromonomer 9
after polycondensation
22
24
26
28
elution volume /mL

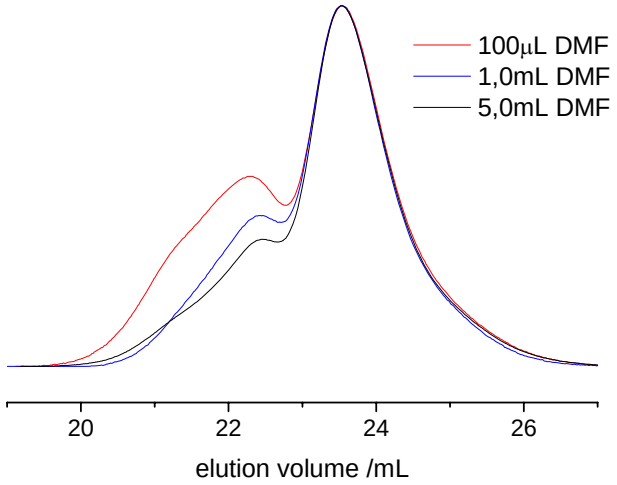

macromonomer 10
after polycondensation
20
22
24
26
elution volume /mL


macromonomer 11
after polycondensation
22
24
26
28
elution volume /mL


macromonomer 12
after polycondensation
22
24
26
28
elution volume /mL


macromonomer 13
after polycondensation
22
24
26
28
elution volume /mL

SI-3: polycondensation of macromonomer 5 dissolved in different amounts of DMF:



Chapter 4: Cooperation Projects

4.0: Preface

The cooperation projects contained in this chapter represent joint research efforts between the respective co-authors. The contributions by me shall be explained in this preface.

In Chapter 4.1, wich focuses on the utility of ruthenium carbenes for TEM staining and the Janus micelles induced by this staining, my contributions have focused on the general planning of the metathesis steps, kinetic measurements of the Fischer-carbene formation and assisting in sample preparations for the TEM.

In Chapter 4.2, where oligo(thiophene amide) oligomers are synthesized and polymerized, I have planned and synthesized the oligomers structures, polymerized them and characterized them by conventional analytic methods. The measurements focusing on the exploration of solution self-assembly and bulk phase separation were conducted in cooperation with Johannes Klos and our Korean collaborators.

In the project described in Chapter 4.3, which deals with the synthesis of hyperbranched PCS on electro-active poly(ferrocenyl silane)s, I supported the synthesis of PFS monomers and their polymerization t block-copolymers. The subsequent work on the hypergrafting of PCS and the analysis of the final polymers was conducted by Frederik Wurm.

4.1: Janus Micelles Induced by Olefin Metathesis

Frederik Wurm, Hannah M. König, Stefan Hilf, and Andreas F.M. Kilbinger

Published in: Journal of the American Chemical Society 2008, 130, 10

Supramolecular polymeric structures are frequently visualized using transmission electron microscopy (TEM). The differentiation between individual compartments or constituents of the supramolecular assembly can be difficult or even impossible due to lack of contrast. Often, heavy metal staining agents are employed to increase the image contrast between areas of different chemical composition. [1] The most common examples are osmium tetroxide which has been widely employed as a stain for unsaturated polymers,[1] ruthenium tetroxide for saturated and unsaturated polymers[1] or phosphotungstic acid which is especially useful for polyamide staining.[1]

To our surprise, the commercially available ruthenium carbene catalysts developed by Grubbs et al.[2] have to date not been employed in TEM staining of polymers. One advantage this catalyst might offer is its ability to covalently bind to the polymeric substrate in a regioselective and irreversible manner, forming a so-called Fischer carbene. Due to the catalyst's large size and hydrophobicity we were particularly interested in the effects of covalent catalyst attachment on solution self-assembly of block copolymers.

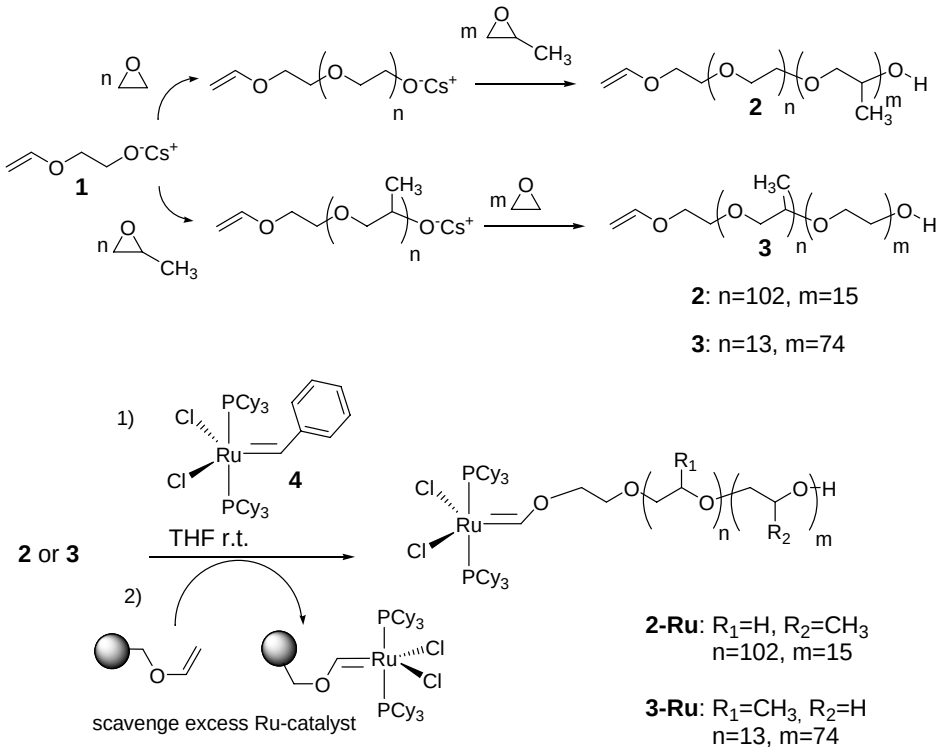
Here we report a facile one-step method allowing regiospecific covalent binding of Grubbs' 1st generation catalyst (Scheme 1, compound **4**) to polymeric architectures.

As proof of principle we synthesized poly(ethylene oxide)-*block*-poly(propylene oxide) (PEO-PPO) block copolymers which are known to form micelles in aqueous solution and for which the solution structures have been well investigated.[3] In order to be able to attach Grubbs' 1st generation catalyst to the diblock copolymer, we initiated the ring opening polymerization of ethylene oxide or propylene oxide using the cesium salt of 2-(vinyloxy)ethanol (**1**, Scheme 1). This approach allowed us to prepare two PEO-PPO diblock copolymers with the vinylether moiety attached to either the hydrophilic (**2,** PEO_{102}-PPO_{15}, M_n(THF)=5300 g mol^{-1}, PDI=1.06) or the hydrophobic (**3,** PPO_{13}-PEO_{74}, M_n(THF)=4200 g mol^{-1}, PDI=1.05) chain end.

Addition of an excess of **4** to the THF solutions of **2** and **3** initiated an olefin metathesis reaction at the vinylic chain ends of the block copolymers. This resulted in the formation of a Fischer-type carbene, covalently bound to the block copolymer chain end. The formation of the Fischer-type carbene, and thus polymers **2-Ru** and **3-Ru**, could be followed by additional ^{1}H-NMR kinetic studies, which were carried out in dichloromethane-d_2.

After a reaction time of 2.5 h at r.t. 80% of all polymer chains carried catalyst **4** covalently bound as a Fischer carbene. Excess **4** was removed by immobilization using a specially developed scavenger resin carrying vinyl ethers (Scheme 1). This technique removed virtually all catalyst **4** that was not covalently bound to the polymer, as could be shown by ^{1}H-NMR spectroscopy. The scavenging of excess catalyst **4** could also be followed with the naked eye, as the resin turned markedly darker over the reaction time.

After removal of the resin by filtration, the THF solutions of **2-Ru** and **3-Ru** were diluted with water (V_{THF}:V_{water} = 1:50) to induce micellation. After 0.5h and 3h of equilibration time, TEM images were recorded by drop casting the THF/water solutions onto carbon coated copper grids.



Scheme 1. Top: Synthesis of amphiphilic PEO-PPO diblock copolymers carrying the vinyl ether moiety at the hydrophilic (**2**) or the hydrophobic (**3**) chain end. Bottom: Attachment of Grubbs' 1st generation ruthenium catalyst **4** to the chain ends of polymers **2** and **3**. A newly developed scavenger resin was employed to remove excess **4** from polymers **2-Ru** and **3-Ru**.

Polymer **3-Ru** where the metathesis reaction occurred at the hydrophobic end of the copolymer, only showed dark spherical "classical" micelles. We believe that due to slower phase separation processes the Ru-complex is most likely kinetically trapped in the micellar PPO-core. Detailed investigations are part of ongoing studies.

Interestingly, the TEM images recorded of polymer **2-Ru** after 0.5h of equilibration time showed micellar objects which closely resembled the so-called Janus micelles reported by Nie et al. and others (Figure 1, A).[4] Similar to previously reported observations, these small micelles ($\varnothing_{av.}$ = 35 nm) co-exist with their supramolecular aggregates ($\varnothing_{av.}$ > 200 nm, Figure 1, B).[4]

Such unusual polymeric solution structures, particularly non-spherical micelles, have received increased attention over the last decade.[5,6,7] Since the first mention of Janus micelles,[8,4] Janus discs[9] and Janus cylinders[10] have also been reported and raised broad academic interest.[11]

Upon increasing the equilibration time from 0.5h to 3h before preparation of the TEM sample, much larger assemblies could be observed ($\varnothing_{av.}$ = 30-500 nm, Figure 1, C). We believe that addition of water to the THF solution of **2-Ru** induces formation of micelles in which the two hydrophobic segments, i.e. the Fischer carbene end-group and the PPO block, are phase separated. This gives rise to the peculiar anisotropic shape of the micelles (Figure 2) and allows for a high contrast differentiation when using electron microscopy. These Janus micelles can further aggregate and, depending on the equilibration time in solution, can be visualized as ill-defined clusters (Figure 1, B and Figure 2, B) or well-defined aggregates (Figure 1, C and Figure 2, C) for short and extended equilibration times, respectively.

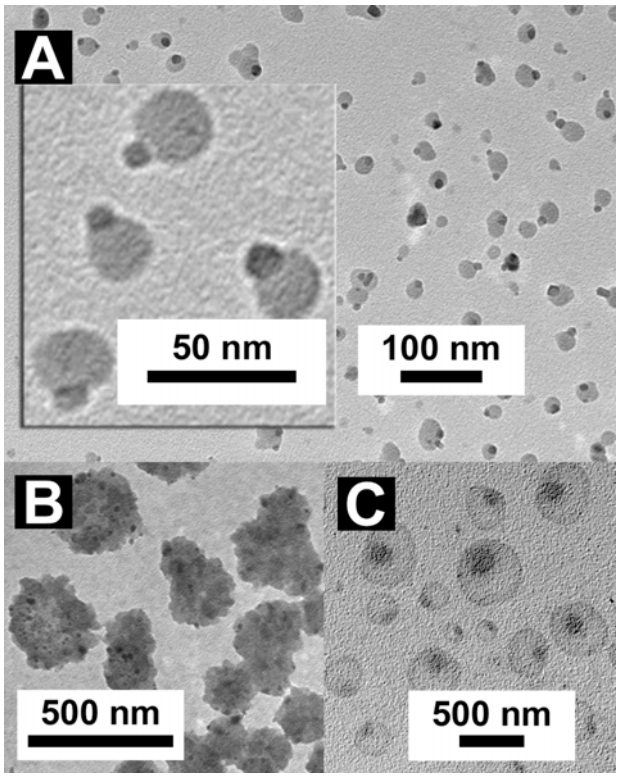


Figure 1. Transmission electron microscopy (TEM) images of block copolymer **2-Ru** drop cast from THF/water solution (c = 1 mg mL^{-1}). A) Janus micelles are observed after 0.5h of equilibration time B) Ill-defined aggregates of Janus micelles are observed after 0.5h of equilibration time C) after 3h of equilibration time, large well-defined assemblies (super-micelles) of the Janus micelles can be observed.

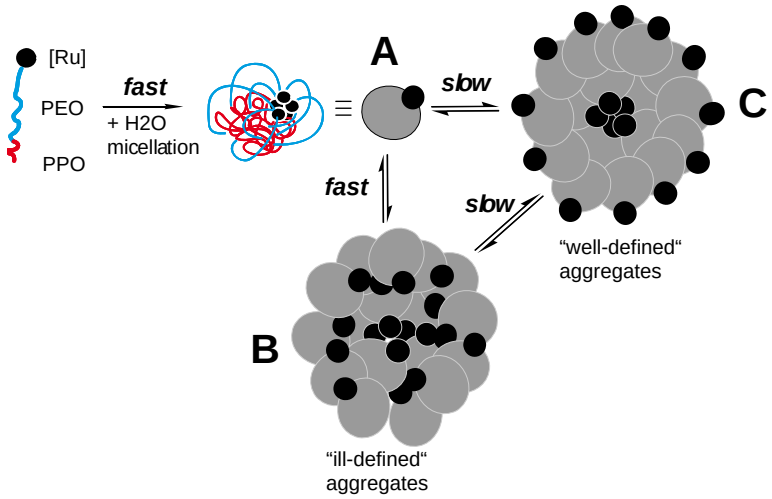


Figure 2. Cartoon representation showing the formation of Janus-type micelles from block copolymer **2-Ru** and their assembly into larger aggregates depending on equilibration time.

The formation of Janus micelles (Figure 1, A and Figure 2, A), i.e. the first stage of the hierarchical self-assembly, yields objects with a very narrow size distribution and an average diameter ($\varnothing_{av.}$ = 35nm) which is in good agreement with the molecular constitution of the copolymer **2-Ru**. As has been described earlier,[4] these Janus micelles can self-assemble into larger "ill-defined" clusters giving rise to an overall enhanced contrast in TEM (Figure 1, B and Figure 2, B). These aggregates then equilibrate into well-defined "super-micelles" as shown in Figure 2 C and Figure 1 C. Such a self-assembly of Janus micelles into super particles has recently been proposed based on calculations.[12] The "super-micelles" and the constituting Janus-micelles are self-similar. However, the "super-micelles" show a broad range of different sizes. A statistical analysis in which the diameter of the darker (ruthenium-containing) core of the well-defined "super-micelles" was plotted against the diameter of the entire super-micelle, gave a linear relationship (see supporting information). This is in good agreement with our model that the larger "super-micelles" are built from smaller well-defined building blocks, i.e. the Janus-micelles.

In conclusion, we have demonstrated that commercially available Grubbs 1st generation ruthenium catalyst offers a facile synthetic route for hydrophobic modification and TEM image contrast enhancements of block copolymers. Formation of a Fischer-type carbene allows the covalent attachment of the ruthenium complex to pre-defined sites on the polymer chain. The formation of Janus micelles in the case of the examined PEO-PPO block

copolymers as well as their self-assembly into higher well-defined aggregates could be shown.

This new technique of regio-selective hydrophobic modification of polymers in combination with a newly developed scavenger resin for ruthenium carbene complexes adds a valuable new instrument to the visualization toolkit for supramolecular polymeric architectures.

References

[1] Smith, R.W.; Bryg, V. *Rubber Chem. Technol*. **2006**, *79*, 520 and references within.

[2] Nguyen, S.T.; Johnson, L.K.; Grubbs, R.H. *J. Am. Chem. Soc*. **1992**, *114*, 3974. Nguyen, S.T.; Grubbs, R.H. *J. Am. Chem. Soc*. **1993**, *115*, 9858. Schwab, P.; Grubbs, R.H.; Ziller, J.W. *J. Am. Chem. Soc*. **1996**, *118*, 100. Chatterjee, A.K.; Morgan, J.P.; Scholl, M.; Grubbs, R.H. *J. Am. Chem. Soc*. **2000**, *122* ,3783. Scholl, M.; Ding, S.; Lee, C.W.; Grubbs, R.H. *Org. Lett*. **1999**, *1*, 953.

[3] a)Alexandridis, P. *Curr. Opin. Colloid Interface Sci*. **1997**, *2*, 478. b) Alexandridis, P.; Holzwarth, J.F.; Hatton, T.A. *Macromolecules* **1994**, *27*, 2414 c) Edens, M.W. Applications of Polyoxyethylene Block Copolymer Surfactants. In *Nonionic Surfactants. Polyoxyalkylene Block Copolymers*; Nace, V.N., Ed. Marcel Dekker: New York, **1996** d) Chu, B.; Zhou, Z. Physical Chemistry of Polyoxyalkylene Block Copolymer Surfactants. In *Nonionic Surfactants. Polyoxyalkylene Block Copolymers*; Nace, V.N., Ed. Marcel Dekker: New York, **1996**

[4] Nie, L.; Liu, S.; Shen, W.; Chen, D.; Jiang, M. *Angew. Chem*. **2007**, *46*, 6321.

[5] T.P.; Hillymer, M.A.; Zhou, Z. *Macromolecules* **2004**, *37*, 6680.

[6] Li, Z.; Hillmyer, M.A.; Lodge, T.P. *Macromolecules* **2006**, *39*, 765.

[7] Li, Z.; Kesselman, E.; Talmin, Y.; Hillmyer, M.A.; Lodge, T.P. *Science* **2004**, *306*, 98.

[8] Erhardt, R.; Böker, A.; Zettl, H.; Kaya, H.; Pyckhout-Hintzen, W.; Krausch, G.; Abetz, V.; Müller, A.H.E. *Macromolecules* **2001**, *34*, 1069.

[9] Walther, A.; André, X.; Drechsler, M.; Abetz, V.; Müller, A.H.E. *J. Am. Chem. Soc*. **2007**, *129*, 6187

[10] Liu, Y.; Abetz, V.; Müller, A.H.E. *Macromolecules* **2003**, *36*, 7894.

[11] a) Erhard, R.; Zhang, M.; Böker, A.; Zettl, H.; Abetz, C.; Frederik, P.; Krausch, G.; Abetz, V.; Müller, A.H.E. *J. Am. Chem. Soc.* **2003**, *125*, 3260 b) Xu, H.; Erhard, R.; Abetz, V.; Müller, A.H.E.; Goedel, W.A. *Langmuir*, **2001**, *17*, 6787 c) Glaser, N.; Adams, D.J.; Böker, A.; Krausch, G. *Langmuir*, **2006**, *22*, 5227 d) Perro, A.; Reculusa, S.; Pereira, F.; Delville, M.-H.; Mingotaud, C.; Duguet, E.; Bourgeat-Lami, E.; Ravaine, S. *Chem. Commun.* **2005**, 5542 e) Ma, R.; Wang, B.; Xu, Y.; An, Y.; Zhang, W.; Li, G.; Shi, L. *Macromol. Rapid. Commun.* **2007**, *28*, 1062.

[12] Vanakaras, A.G. *Langmuir* **2006**, *22*, 88.

Supporting Information for: Janus Micelles Induced by Olefin Metathesis

Frederik Wurm, Hannah M. König, Stefan Hilf, and Andreas F.M. Kilbinger

Experimental:

Instrumentation: ^{1}H-NMR spectra were recorded at 300 MHz on a Bruker AC and are referenced internally to residual proton signals of the deuterated solvent. ^{1}H-NMR spectra for kinetic measurements were recorded on a Bruker ARX400. Size exclusion chromatography (SEC) was performed on an instrument consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump and a set of three PSS-SDV 5µ columns with 100, 1 000, und 10 000 Å porosity. THF or chloroform was used as an eluent at 30 °C and at a flow rate of 1 mL min^{-1}. UV absorptions were detected by a SpectraSYSTEM UV2000. RI detection was measured at 30 °C on an Optilab DSP. Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service and performing a 3rd order polynomial fit. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-ToF) measurements were performed on a Shimadzu Axima CFR MALDI-TOF mass spectrometer equipped with a nitrogen laser delivering 3ns laser pulses at 337nm. α-cyano -4- hydroxy cinnamic acid (CHCA) was used as matrix. Samples were prepared by dissolving the polymer in $CHCl_3$ at a concentration of 10g/L. A 10µL aliquot of this solution was added to 210µL of a 10g/L solution of the matrix and 1µL of a solution of LiTFA (0.1M in methanol as cationization agent). A 1µL aliquot of the mixture was applied to a multistage target to evaporate CHCl3 and create a thin matrix/analyte film. The samples were measured in positive ion and in linear or reflection mode of the spectrometer. A Philips EM 420 transmission electron microscope using a LaB_6 cathode at an acceleration voltage of 120 kV was used to obtain TEM-images. TEM grids (carbon film on copper, 300 mesh) were obtained from Electron Microscopy Sciences, Hatfield, PA, USA.

Reagents & Materials:

Diglyme (99% Acros) and 2-(vinyloxy)ethanol (99% Acros), propylene oxide (99% Fluka) and 1,1,2,2-tetrafluoroethyl glycidyl ether for polymerizations were purified by distillation from CaH2 directly prior to use. ethylene oxide (99.5% Aldrich) was used without further purification. Cesium hydroxide monohydrate used as received. Deuterated chloroform-d1 and dichloromethane-d_2 were purchased from Deutero GmbH and dried and stored over molecular sieves. THF, chloroform, and other solvents and reagents were purchased from Acros and used as received as not otherwise mentioned. Merrifield resin was purchased from Iris Biotech GmbH and dried in a vacuum oven (40°C) before use.

General procedures:

Polymerizations: Cesium hydroxide monohydrate was suspended in benzene in a Schlenk flask and a stoichiometric amount of 2-(vinyloxy)ethanol was added under argon with a syringe. Stirring at 60°C for 30 minutes and evacuation at 90°C for two hours gave the cesium alkoxide, which was cooled to 0°C. Then ethylene oxide was cryo transferred to a graduated ampoule, diluted with diglyme (ca. 50 weight %) and added to the initiator via canula. The mixture was allowed to slowly warm up to room temperature and polymerization was performed for 2 days in vacuo. Subsequently the appropriate amount of propylene oxide or 1,1,2,2-tetrafluoroethyl glycidyl ether was added with a syringe and temperature was raised to 50°C for two more days. The polymerization was terminated by addition of methanol and acidic ion exchange resin. Filtration and precipitation into cold diethyl ether resulted in the pure block coplymer polymer. Polymerization with propylene oxide being the first monomer the procedure was carried out vice versa.

^{1}H-NMR data: Polymer **2**: ^{1}H NMR (400 MHz, CDCl3, δ ppm): 1.11 (br. m., CH3 (PPO) 50 H), 3.42-3.88 (m., br. backbone), 3.95 (dd, *J*=6.75, 2.05 Hz, 1 H) 4.13 (dd, *J*=14.28, 2.15 Hz, 1 H) 6.44 (dd, *J*=14.28, 6.85 Hz, 1 H). Polymer **3**: ^{1}H NMR (400 MHz, CDCl3, δ ppm): 1.08 (br. s., 40 H), 3.42-3.88 (m., br. backbone), 3.96 (dd, *J*=6.85, 2.15 Hz, 1 H), 4.13 (dd, *J*=14.38, 2.05 Hz, 1 H), 6.45 (dd, *J*=14.27, 6.85 Hz, 1 H).

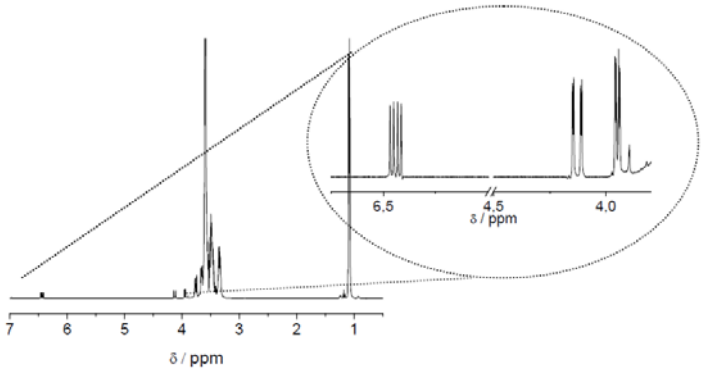
Scavenger Resin: 1 g Merrifield Resin (1,4 mmol loading) was added to a 10-fold excess of the cesium salt of 2-(vinyloxy)ethanol, which was synthesized analogues to the abovementioned procedure. 10 mL degassed, dry NMP was added and the mixture was allowed to react for 48 h at 80°C. The modified Merrifield resin was collected by filtration, washed first with THF, then acetone and finally methanol, dried and stored under argon at -20°C until use.

Staining and Micellization Using Grubbs' Catalyst: For staining with the 1st generation Grubbs' catalyst, the calculated amount of polymer (usually ca. 5 mg) was dissolved in degassed THF (concentration ca. 50 mg mL^{-1}) and 1.1 eq. Grubbs' catalyst was added. The mixture was placed on an orbital shaker for 2 hours.

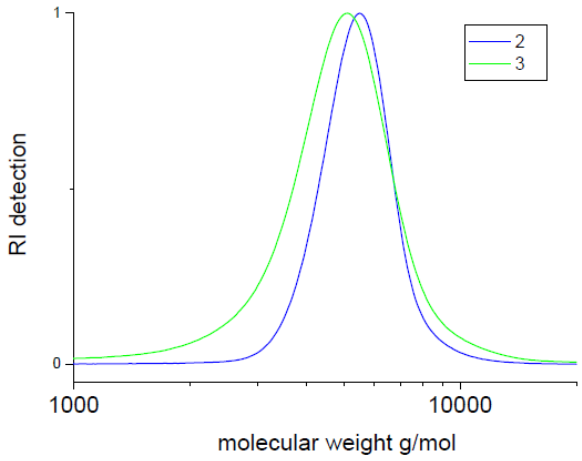
Without a scavenger resin: After degassed water (5 mL) was added to the polymer solution it was allowed to equilibrate at room temperature for 1 h and then ca. 2 µL were transferred on a TEM-copper grid and dried over night in vacuo.

With scavenger resin: The mixture was diluted with THF to approx. 10 mg mL-1, the calculated amount of scavenger resin (2 eq excess, at theor. 100% degree of functionalization) was added and the mixture was placed on an orbital shaker for an additional two hours. Finally, the resin was removed by filtration and the solution was concentrated again to approx 50 mg mL^{-1}, diluted with water (100-200 µL of THF solution was diluted with 5 mL of water), equilibrated for 0.5 - 3h at room temperature and then drop cast onto a TEM grid and dried over night in vacuo.

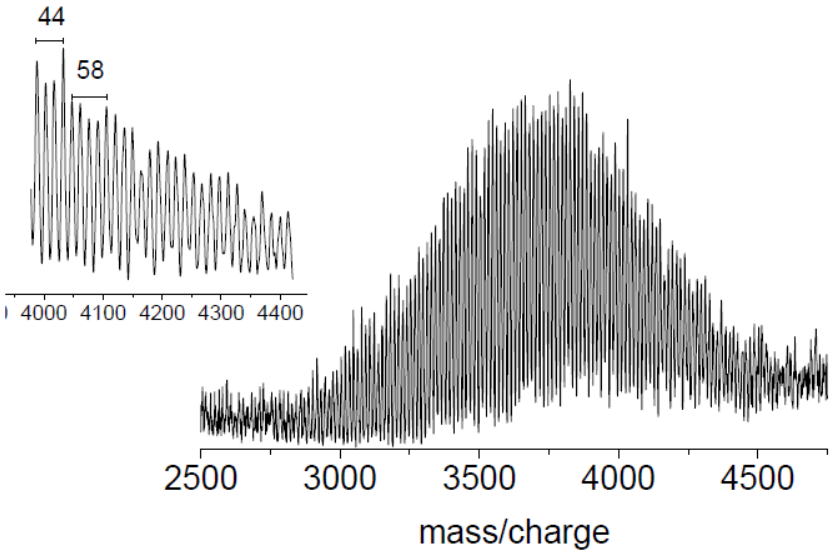
Additional spectra & pictures:



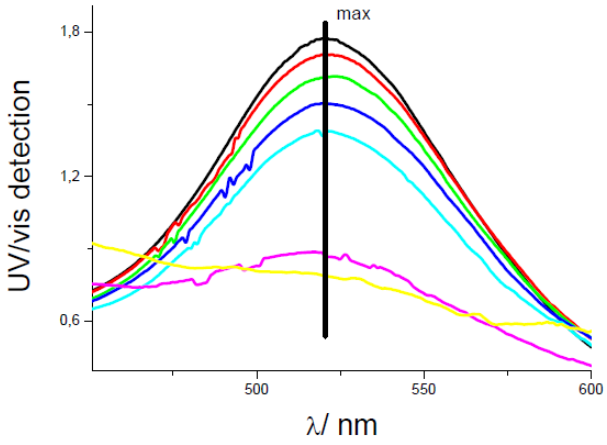
SI 1: ^{1}H-NMR (400 MHz, $CDCl_3$) for polymer **2**.



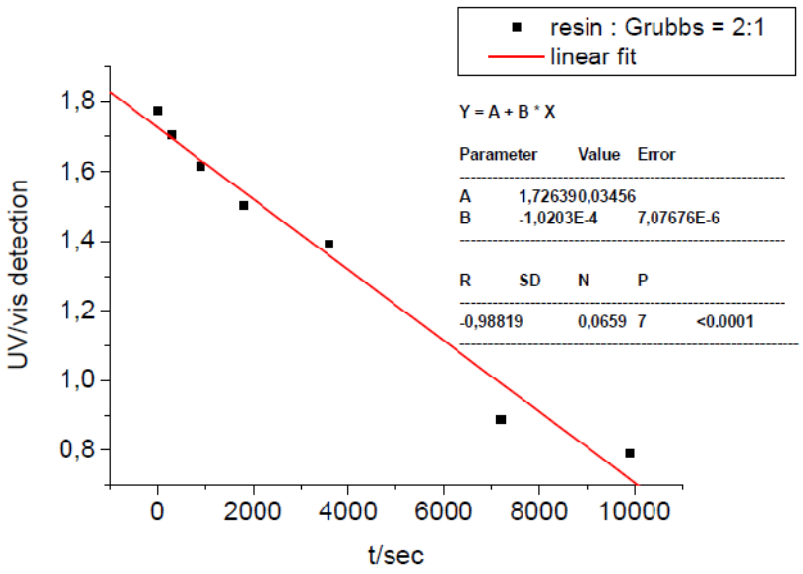
SI 2: SEC-traces of polymers **2** and **3** using THF as an eluent vs PS-standards.



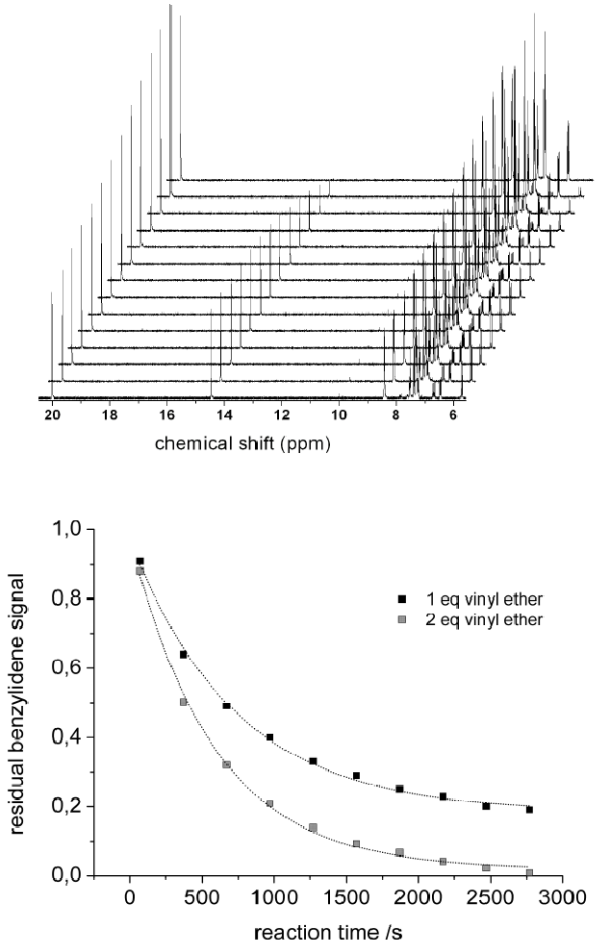
SI 3: MALDI-ToF spectrum of **2** (Li, CHCA)



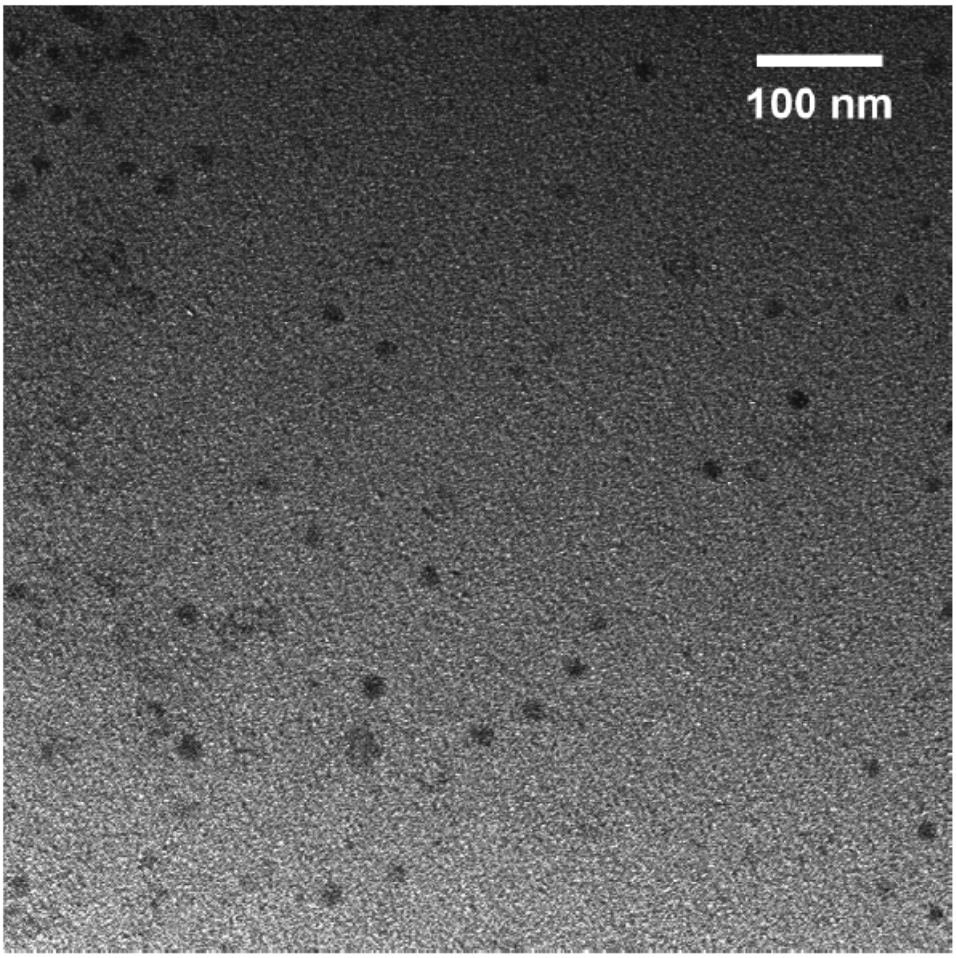
SI 4: UV/vis- detection of the metal carbene in a 1 g/L solution of Grubbs' 1st generation catalyst during reaction with the scavenger resin after several time intervals (cf. SI 5).



SI 5: UV/vis kinetic data showing a linear decrease of metal carbene concentration of Grubbs' 1st generation catalyst with time (reaction of catalyst with the scavenger resin).

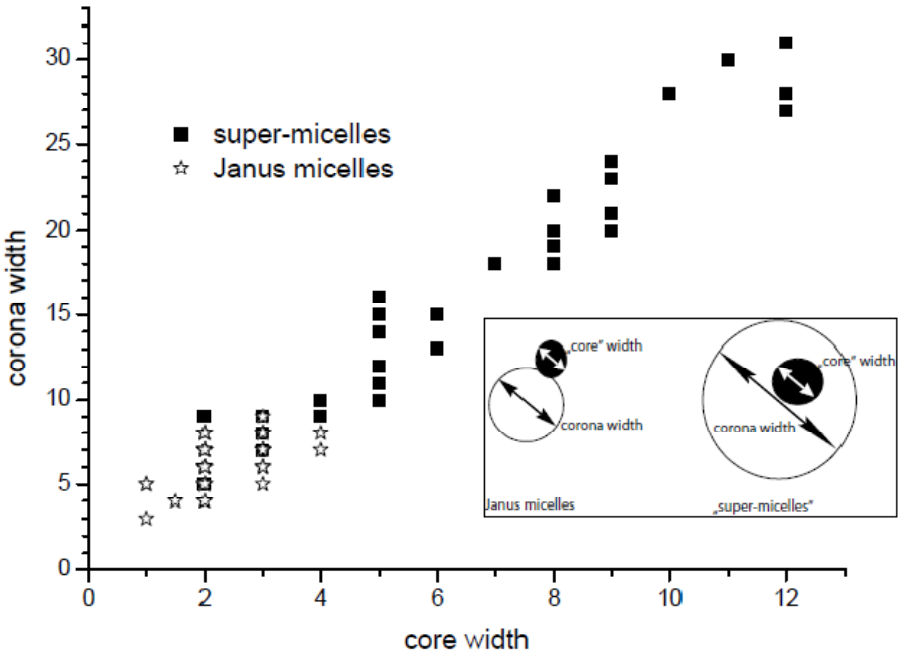


SI 6: Top: ^{1}H-NMR-spectra of **2** in CD_2Cl_2 (vinyl ether: Grubbs' 1st generation catalyst = 1:1). Bottom: Kinetic data for the formation of the Fischer carbene obtained from ^{1}H-NMR spectroscopic data.

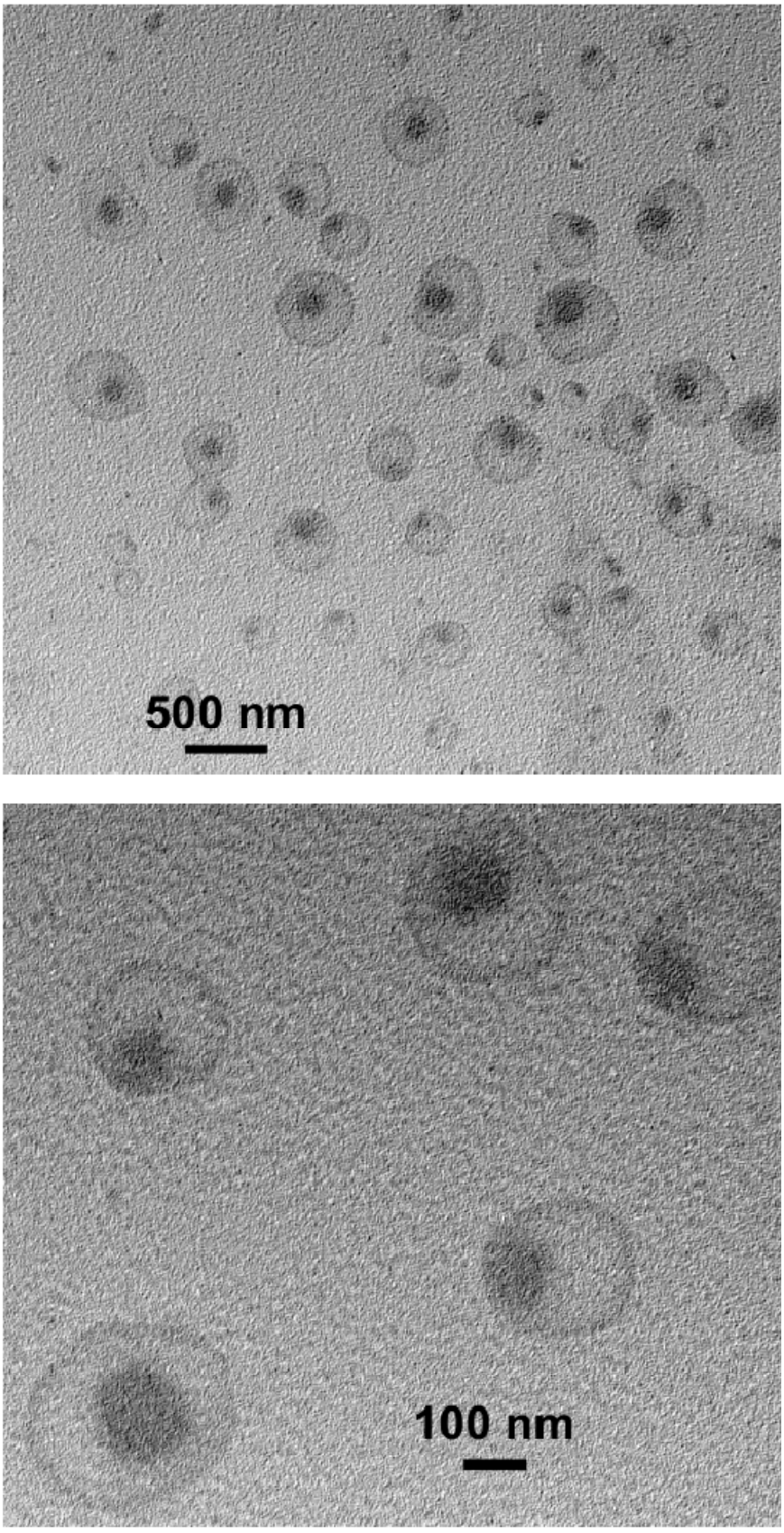


SI 7: TEM image of polymer **3-Ru**.

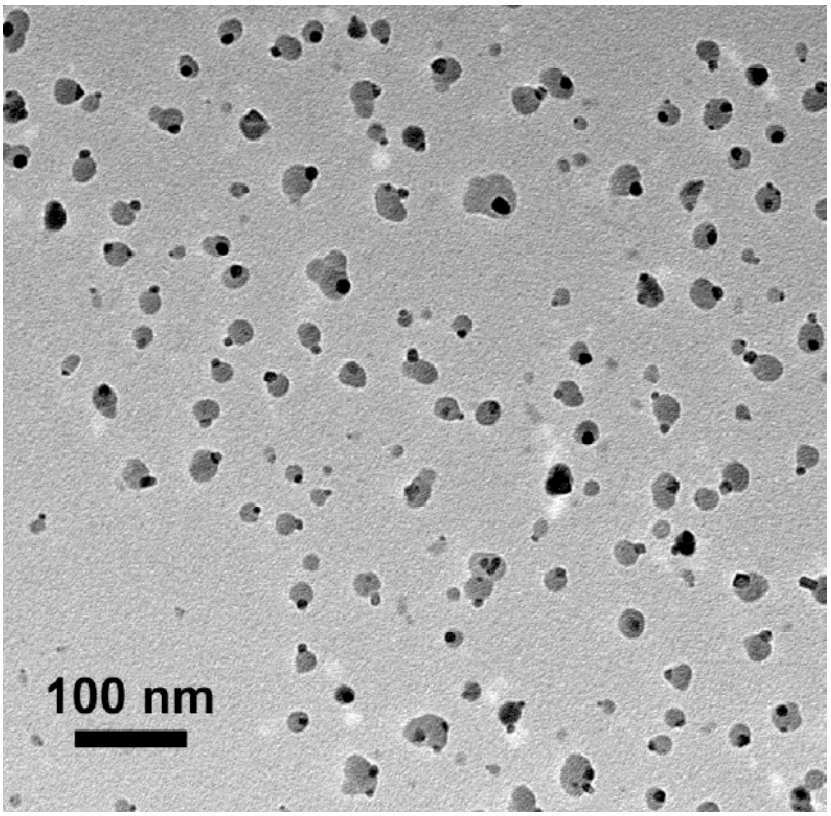
SI 8: Polymer (**2**) solutions in dichloromethane (DCM) with Grubbs' catalyst left: directly after mixing. Middle: after 2 h. Right: DCM solution of catalyst after reaction with scavenger resin for 2 h.



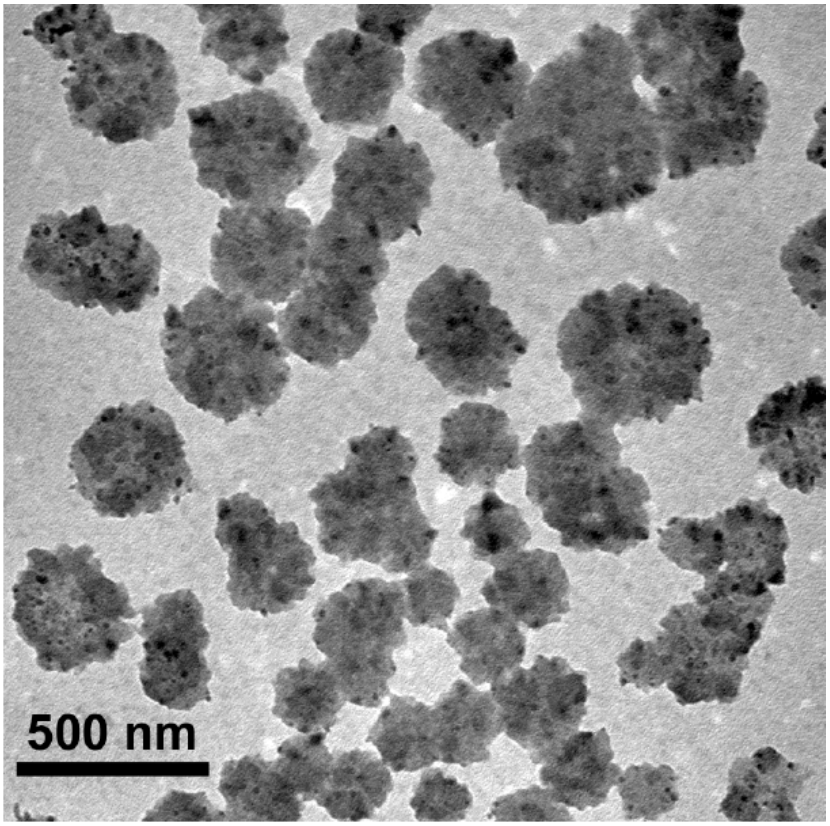
SI 9: Statistical analysis of 47 Janus micelles and 55 well-defined „super-micelles“ (several shown data points represent more than one micelle). The diameter of the dark part of the micelle is plotted against the diamter of the entire micelle (see cartoon inset). The graph shows the correlation of the two diameters.



SI 10: TEM images of super-micelles of **2-Ru** (top and bottom: different magnifications).



SI 11: TEM image of Janus micelles of **2-Ru** (0.5 h equilibration time in solution).



SI 12: TEM image of aggregates of Janus micelles of **2-Ru** (0.5 h equilibration time in solution).

4.2: Polymerizable well-defined oligo(thiophene amide)s and their ROMP block-copolymers

Stefan Hilf, Johannes Klos, Kookheon Char and Andreas F. M. Kilbinger

Manuscript prepared for publication in Macromolecular Rapid Communications

Abstract

Thiophene amides are a novel class of conjugated macromolecules. The electronical properties of the molecules are strongly dependant on the number of thiophene rings connected via amide bonds. Here we present the defined synthesis of metathesis-polymerizable thiophene amide oligomers on a norbornene core by conventional amide coupling and deprotection chemistry. The materials synthesized in this way are analyzed by UV/vis and fluorescence spectroscopy to prove the conjugation between the thiophene rings via the amide bond. By ring-opening metathesis polymerization, homopolymers and block-copolymers with solubilizing monomers are synthesized and analyzed. The successful transfer of the special electronic properties of the oligo(thiophene)s onto the polymers is dicussed. Also, the amphiphilic character of the block-copolymers is studied and used for the formation of heterogeneous materials which have potential for optoelectronic purposes.

Introduction

Thiophene and thiophene-based aromatic systems have attracted a large number of polymer scientists working on conjugated and semiconducting polymers over the last decade. Interesting approaches towards the applicability of various polythiopenes in the field of OLED and PLED, electronical conductor, transistor, photoresist, sensor and solar cell research have been made.[1] The conductivity of such polythiophene systems is caused by the conjugation of the aromatic thiophene moieties through a direct aromatic-aromatic linkage. The charge conduction along the polythiophene chains is based on a hole transport, i.e. positive charges induced by an oxidation step at the sulfur centers are transported via electron shifting along the aromatic polymer backbone.

The polymerization methods used in most application oriented syntheses represents an oxidative[2] polymerization, giving rather poorly defined polymers. Laboratory-scale metal organic polymerizations[3] such as the application of Grignard-reagents and alkali-metal coupling give much better[4] defined polymer materials.

An interesting class of thiophene monomers is available from the Gewald[5] synthesis. This reaction produces highly substituted thiophenes bearing a free amine and a protected carboxylic acid group. Here, the aromatic thiophene ring is synthesized from a β-ketoester, a cyanoacetic ester and sulfur under the influence of an organic base (e.g. morpholine) in a complex condensation reaction. This synthesis is highly variable in terms of substituents tolerated on the reaction components as a number of synthetic studies have shown.[6] The most comprehensive reaction scheme has been drawn by Vinogradoff et al.[7] A complete mechanism of this reaction, however, is hitherto unknown.

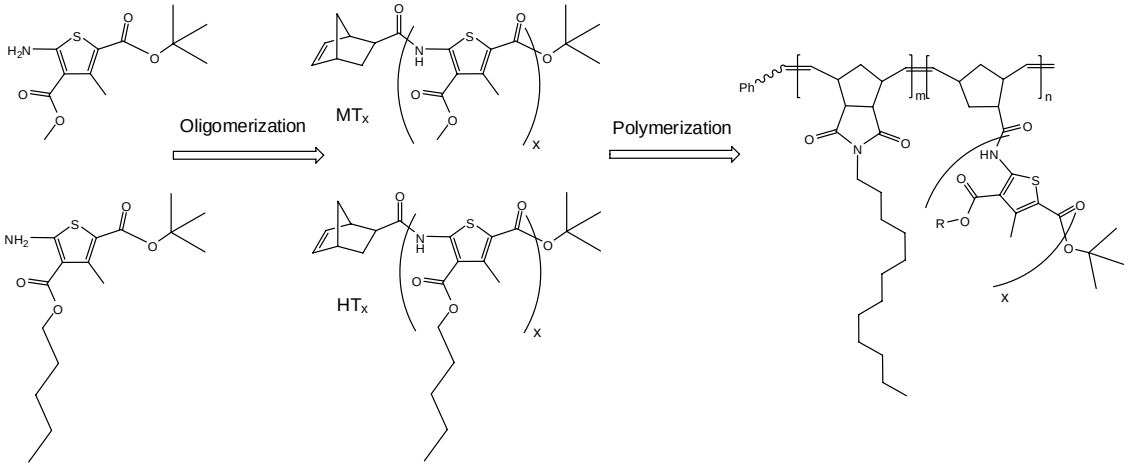


Figure 1. Protected thiophene amino acids and thiopheneamide oligomers synthesized and applied in this study.

By using the tertbutyl cyanoacetate, a thiophene moiety is generated that bears a tertbutyl ester, a protective group well known from peptide synthesis. For such protected amino acids, conventional deprotection - coupling chemistry can be applied for the construction of defined oligomers. Such oligomers, especially the defined oligomers of aromatic amides (aramides) have been studied in the case of *p*-benzamides in detail by our group.[8] There, we have focused on the length dependence of the properties of such oligo(*p*-benzamide)s (OPBA) in terms of e.g. solubility, chain stiffness and aggregation behavior.[9] Different synthetic strategies have been followed for the defined synthesis of those OPBA's ranging from manual[10] and automatized[11] solid-supported synthesis to solution coupling of soluble imidoyl chlorides[12] or *N*-sulfinyl amines[13].

Many of the length dependant properties are caused or enhanced by the conjugation between the aromatic rings across the amide linkages, which represent partial double bonds. A similar chain length dependence and conjugation can be expected for thiophene aramides, which render them particularly interesting, especially when the special electronic structure of thiophenes are taken into account.

In a first step towards the understanding of these new materials, the oligomer chain length dependence on molecule properties is investigated on defined oligomers in this study. Moreover, the molecule properties are then transferred onto a polymer material by grafting them along a polymer chain. Using *exo*-norbornene-carboxylic acid as a core group on which the oligomer is built (c.f. Figure 1), produces an easily polymerizable functionality for the ring-opening metathesis polymerization (ROMP). This method is especially suited for the formation of such graft-copolymers as it has proven compatibility with both, thiophene containing monomers[14] as well as amides and peptides.[15]

The incorporation of a highly hydrophobic monomer, *N*-dodecyl-2,3-norbornene dicarboximide (DNI), gives rise to materials with self-assembling characteristics by forming a block-copolymer. As the ROMP of norbornene polymers performs in a living manner, this block-copolymerization is particularly versatile and gives rise for future development of chain-end functionalized polymers[16] which can be used in the construction of more complex structures[17] or the precise attachment of single tracer molecules.[18]

Experimental

General. ^{1}H-NMR spectra were recorded at 300 MHz on a Bruker AC300 or at 400MHz on a Bruker ARX400. ^{13}C-NMR (at 100.15MHz) and 2D measurements were conducted on a Bruker ARX 400 or a Bruker AMX 400. All spectra were referenced internally to signals of the deuterated solvent. NMR solvents were purchased from Deutero GmbH. Gel permeation chromatography in chloroform was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P100 pump and a set of three PSS SDV columns ($10^5/10^3/10^2$ Å). Signal detection occurred by use of a TSP Spectra System UV2000 (UV at 254 nm) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by PSS. UV/vis spectroscopy was performed on a JASCO V630 spectrophotometer, Fluorescence was measured on a JASCO PL6200 spectrofluorometer. Field-desorption mass-spectra were recorded on a Finnigan MAT 95.

Grubbs' 1st generation catalyst was obtained from Materia, inc. All solvents and other reagents were purchased from Aldrich or Acros. All polymerization reactions were carried out under argon using Schlenk techniques. Dichloromethane was dried over P_2O_5 and distilled under nitrogen. *Exo*-5-norbornene-carboxylic acid and *N*-dodecyl-norbornene-2,3-dicvarboximide (DNI) were synthesized as described in earlier publications.[19]

Synthesis of ^{t}butyl-5-amino-4-(methoxycarbonyl)-3-methyl-thiophene-2-caboxylate (MT):

To a mixture of 6.4 g (0.2 mol) sulfur, 31.2 g (0.2 mol) tertbutyl-acetoacetate, 19.8 mL methyl-cyanoacetate and 60 mL methanol stirred at 60°C in a three-necked round-bottom flask was added 16 mL (0.2 mol) of morpholine dropwise over 1 hour. After dissolution of sulfur had stopped and the mixture had been heated for another hour, residual sulfur was removed by filtration of the hot solution. Upon cooling, crystallization occurred to give yellow crystals. After recrystallization from methanol, colorless crystals were obtained in 88% (48.2 g) yield.

^{1}H-NMR [$CDCl_3$, 300 MHz] δ(ppm): 1.54 (s, 9H, ^{t}Bu); 2.66 (s, 3H, Ar-CH_3); 3.85 (s, 3H, $COOCH_3$); 6.44 (br, 2H, NH_2). ^{13}C-NMR [$CDCl_3$, 100.15 MHz] δ(ppm): 15.83 (Ar-*C*H_3); 28.29 (O-C-(*C*H_3)$_3$); 50.94 (COO*C*H_3); 81.12 (O-*C*-(CH_3)$_3$); 108.15 (thiophene C^3); 110.18 (thiophene C^2); 146.75 (thiophene C^2); 162.27(*C*OOCH_2); 165.89(*C*OO^{t}Bu); 166.51 (*C*-N). FD-MS: 270.9 m/z (calc: 271.08 g/mol).

Synthesis of ^{t}butyl-5-amino-4-(hexthoxycarbonyl)-3-methyl-thiophene-2-caboxylate (HT):

To 90 g hexyl-cyanoacetate (synthesized in quantitative yield from n-hexanol and acetoacetic acid under Dean-Stark conditions) were mixed with 17.7 g (0.5 mol) sulfur, 86.9 g (0.5 mol) tertbutyl-acetoacetate, and 400 mL n-hexanol. The mixture was stirred at 60°C in a three-necked round-bottom flask while 48 mL (0.5 mol) of morpholine were added dropwise over 1.5 hours. After dissolution of sulfur had stopped and the mixture had been heated for another hour, residual sulfur was removed by filtration of the hot solution. Upon cooling, the product crystallized as yellow needles. After recrystallization from methanol, a colorless product was obtained in 75% (127 g) yield.

^{1}H-NMR [$CDCl_3$, 300 MHz] δ(ppm): 0.9 (m, 3H, C_5-CH_3); 1.3-1.5 (m, 6H, COO-C-$(CH_2)_3$); 1.7-1.8 (m, 2H, COO-C-CH_2); 1.54 (s, 9H, ^{t}Bu); 2.67 (s, 3H, Ar-CH_3); 4.25 (t, 3H, $COOCH_2$, ^{3}J=8.0 Hz); 6.46 (br, 2H, NH_2). ^{13}C-NMR [$CDCl_3$, 100.15 MHz] δ(ppm): 13.94 (C_5-*C*H_3); 15.97 (Ar-*C*H_3); 22.48 (C_4-*C*H_2-CH_3); 25.78 (C_3-*C*H_2-C-CH_3); 28.32 (O-C-(*C*H_3)$_3$); 28.62 (C_2-*C*H_2-C_2-CH_3); 31.36 (C-*C*H_2-C_3-CH_3); 64.21 (COO*C*H_2); 81.12 (O-*C*-$(CH_3)_3$); 108.4 (thiophene C^3); 110.21 (thiophene C^2); 146.77 (thiophene C^2); 162.31(*C*OOCH_2); 165.83(*C*OO^{t}Bu); 166.33 (*C*-N). FD-MS: 340.9 m/z (calc: 341.16 g/mol).

Synthesis of ^{t}Bu-MT-norbornenamide:

Exo-5-norbornene-carboxylic acid (4.9 g, 0.036 mol), MT (10g, 0.036 mol), *N,N'*-dicyclohexylcarbodiimide (DCC) (8.5 g, 0.04 mol) and *N,N*-dimethylaminopyridine (DMAP) (4.4 g, 0.036 mol) were dissolved in 100 mL dry dichloromethane and allowed to stir for 6 hours. Precipitating dicyclohexyl urea (DCU) was removed by filtration. The solvent was removed under reduced pressure and the resulting solids were recrystallized twice from acetone to give 8.6 g (82%) of colorless crystals.

^{1}H-NMR [$CDCl_3$, 400 MHz] δ(ppm): 1.0-1.2 (m, 1H, C(O)-CH-C$H_{2\ endo}$); 1.3-1.45 (m, 2H, CH_2-bridge); 1.55 (s, 9H, ^{t}Bu); 1.65-1.75 (m, 1H, C(O)-CH-C$H_{2\ exo}$);1.9-2.4 (m, 1H, CH-C(O)); 2.73 (s, 3H, Ar-CH_3); 3.00 (s, 1H, bridge head CH_2-side); 3.12 (s, 1H, bridge head amide side); 3.93 (s, 3H, $COOCH_3$); 5.9-6.3 (s, 2H, double bond). ^{13}C-NMR [$CDCl_3$, 100.15 MHz] δ(ppm): 15.21 (Ar-*C*H_3); 28.31 (O-C-(*C*H_3)$_3$); 30.67 (norbornene C^3); 33.91(norbornene C^2); 41.66 (norbornene bridge head unsubstituted side); 46.36 (norbornene *C*H_2-bridge); 47.17(norbornene bridge head amide side); 51.80 (COO*C*H_3); 81.6 (O-*C*-$(CH_3)_3$); 113.46 (thiophene C^3); 118.8(thiophene C^2); 135.63 (norbornene C^4); 138.57(norbornene C^5); 143.70 (thiophene C^2);

152.67(*C*OOCH$_3$); 162.28(*C*OO^{t}Bu); 167.15 (*C*-N); 173.74(*C*OONH). FD-MS: 391.5 m/z (calc. 291.15 g/mol).

Synthesis of ^{t}Bu-HT-norbornenamide:

Exo-5-norbornene-carboxylic acid (4.9 g, 0.036 mol), MT (10g, 0.036 mol), *N,N'*-dicyclohexylcarbodiimide (DCC) (8.5 g, 0.04 mol) and *N,N*-dimethylaminopyridine (DMAP) (4.4 g, 0.036 mol) were dissolved in 100 mL dry dichloromethane and allowed to stir for 6 hours. Precipitating dicyclohexyl urea (DCU) was removed by filtration. The solvent was removed under reduced pressure and the resulting solids were recrystallized twice from acetone to give 8.6 g (82%) of colorless crystals.

^{1}H-NMR [CDCl$_3$, 400MHz] δ(ppm): 0.9 (m, 3H, C$_5$-CH$_3$); 1.0-1.2 (m, 1H, C(O)-CH-C*H*$_{2\ endo}$); 1.3-1.5 (m, 8H, COO-C-(CH$_2$)$_3$ + norbornene CH$_2$-bridge); 1.55 (s, 9H, ^{t}Bu); 1.65-1.75 (m, 1H, C(O)-CH-C*H*$_{2\ exo}$); 1.7-1.8 (m, 2H, COO-C-CH$_2$); 1.9-2.4 (m, 1H, CH-C(O)); 2.75 (s, 3H, Ar-CH$_3$); 3.00 (s, 1H, bridge head CH$_2$-side); 3.12 (s, 1H, bridge head amide side); 4.32 (t, 3H, COOCH)$_2$ 6.1-6.3 (s, 2H, double bond); 11.68 (s, 1H, CONH). ^{13}C-NMR [CDCl$_3$, 100.15 MHz] δ(ppm): 13.94 (C$_5$-*C*H$_3$); 15.32 (Ar-*C*H$_3$); 22.47 (C$_4$-*C*H$_2$-CH$_3$); 25.73 (C$_3$-*C*H$_2$-C-CH$_3$); 28.31 (O-C-(*C*H$_3$)$_3$); 28.47 (C$_2$-*C*H$_2$-C$_2$-CH$_3$); 30.67 (norbornene *C*^{3}); 31.30 (C-*C*H$_2$-C$_3$-CH$_3$); 33.91(norbornene *C*^{2}); 41.65 (norbornene bridge head non-substituted side); 46.36 (norbornene *C*H$_2$-bridge); 47.19(norbornene bridge head amide side); 65.24 (COO*C*H$_2$); 81.55 (O-*C*-(CH$_3$)$_3$); 113.68 (thiophene *C*^{3}); 118.79 (thiophene *C*^{2}); 135.64 (norbornene *C*^{4}); 138.57(norbornene *C*^{5}); 143.77 (thiophene *C*^{2}); 152.56(*C*OOCH$_3$); 162.31 (*C*OO^{t}Bu); 166.79 (*C*-N); 173.71 (*C*OONH). FD-MS: 641.6 m/z (calc. 641.22 g/mol).

General Procedure for the deprotection of ^{t}Bu-esters of norbornenyl-oligo(thiophenamide)s.:

The ^{t}Bu-ester was placed in a flask and flushed with argon. 1 mL water was added before trifluoroacetic acid (TFA) was added under a constant stream of argon and cooling with a water bath until all starting material had dissolved. After 15 minutes, a large excess of water was added in order to precipitate the product. The resulting colorless solid was isolated by filtration, washed with further cold water and dried in vacuo before it was recrystallized (methanol for HT-oligomers and acetone for MT-oligomers) yields varied around 75-85%. Removal of the t-Bu group was checked by ^{1}H-NMR.

General Procedure for the coupling of MT or HT to deprotected norbornenyl-oligo(thiopheneamide)s:

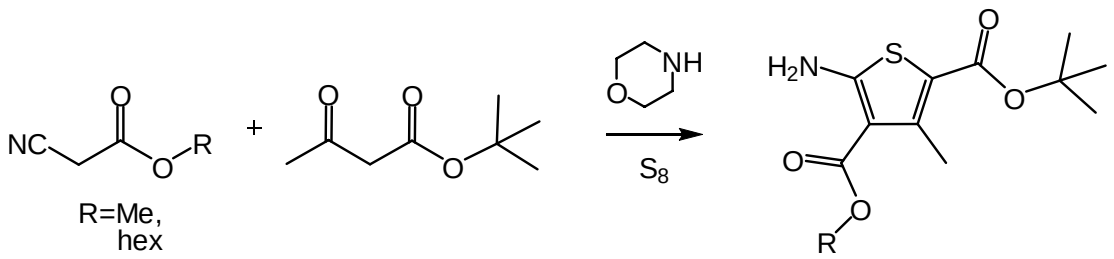
The deprotected thiopheneamide (3 g) was dissolved in dry dichloromethane, 1.0 equivalents of the respective tBu-protected thiophene amino acid and DMAP, as well as 1.2 equivalents of DCC were added. The mixture was stirred for 14 hours at r.t. before DCU was filtered off and the solvent was removed. The residue was recrystallized from acetone (MT-oligomers) or acetone (HT-oligomers) twice to give colorless or pale yellow (trimer) products in good yield (70-90%). Characterization data for these compounds can be found in the Supporting Information.

General Procedure for the synthesis of poly(DNI-b- oligo(thiopheneamide))s 6:1:

17 mg Grubbs' 1st generation catalyst were dissolved in 1 mL DCM. To this stirred catalyst solution was added 240 mg DNI dissolved in 4 mL DCM and allowed to react for 2 hours before a solution of 40 mg of the respective oligo(thiophenamide) was added in 5 mL dichloromethane. After another 2 hours, 100 µL ethyl vinyl ether was added to terminate the reaction. The polymer was precipitated by adding excess methanol. The collected solids were dried to give a colored polymer in 70-85% wield. The characterization data of all products are given in the Supporting Information.

Results and Discussion

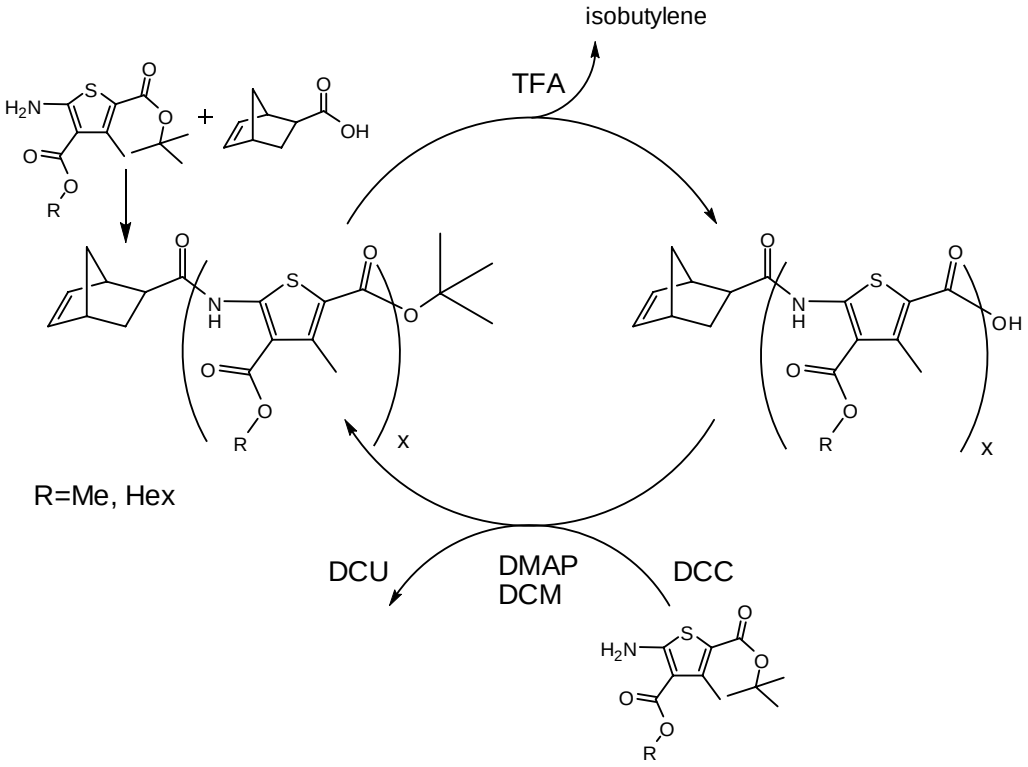
The Gewald reaction delivers protected thiophene amino acids in a one-pot reaction (Scheme 1). Starting from tertbutyl acetoacetate, sulfur and two cyanoacetic acid esters, MT and HT were synthesized under the influence of morpholine as a base. Those two compounds are especially suited for a conjugate construction since the tertbutyl ester can be removed under conditions in which the other ester bonds are not affected, thus enabling the sequential formation of defined oligomer structures.



Scheme 1. Gewald synthesis of protected thiophene amino acid building blocks.

For the formation of exactly defined oligomers, optimum coupling and subsequent deprotection reactions had to be found (Scheme 2). The amide formation between the norbornene core and the HT and MT thiopheneamine building blocks proved to perform smoothly under standard dicyclohexyl carbodiimide (DCC) / *N,N*-dimethylamino pyridine (DMAP) peptide coupling conditions employing 1 equivalent of DMAP. High degrees of conversion were found for all reactions in dry dichloromethane after 14 h reaction time. The products were purified by recrystallization and analyzed by ^{1}H-NMR and FD-MS which could prove the attachment of an additional thiophene ring.

The deprotection step, however, failed under aqueous acidic conditions, under the influence of formic acid in high concentrations as well as under catalysis by toluenesulfonic acid. Typically, decomposition of the substrate either by decarboxylation of the liberated acid group or direct destruction of the thiophene moiety was identified as the major side reactions caused in those approaches. Wet trifluoroacetic acid gave best results at r.t. under an inert argon atmosphere. TFA treatment under oxygen led to partial oxidation of the thiophene rings indicated by massive discoloration of the product. Unnecessarily long reaction times or heating of the reaction also can lead to partial decarboxylation.



Scheme 2. Synthesis of Norbornene-oligo(thiopheneamide)s.

A number of norbornene-oligo(thiopeneamide)s were synthesized by the procedures described above. The structures of the oligomers synthesized in this study are given in Scheme 3. The solution structure of the oligomers was investigated by NMR. The ^{1}H-NMR (given in Figure 2) of NHT_2-$COO^{t}Bu$, i.e. a norbornene bearing a thiophene amide dimer contains information on the orientation of the amide bond between the two thiophene rings. This NH-proton is shifted downfield of the second amide bond, the formation of a hydrogen-bond between the amide proton and the neighboring carboxyl-group of the hexyl ester is strongly indicated. In addition, an NOESY measurement showed a spatial proximity of this particular proton to the methyl group adjacent to the next thiophene ring. This conformation can only be taken in when the amide bond is locked in a *trans*-configuration, an observation which was also made on the oligo(*p*-benzamide)s reported by our group.[10] In the spectra of the thiophene trimer-carrying norbornenes, the third amide proton can be found in the same signal as the other inter-thiophene amide proton, therefore a similar configuration for all thiophene amides can be expected.

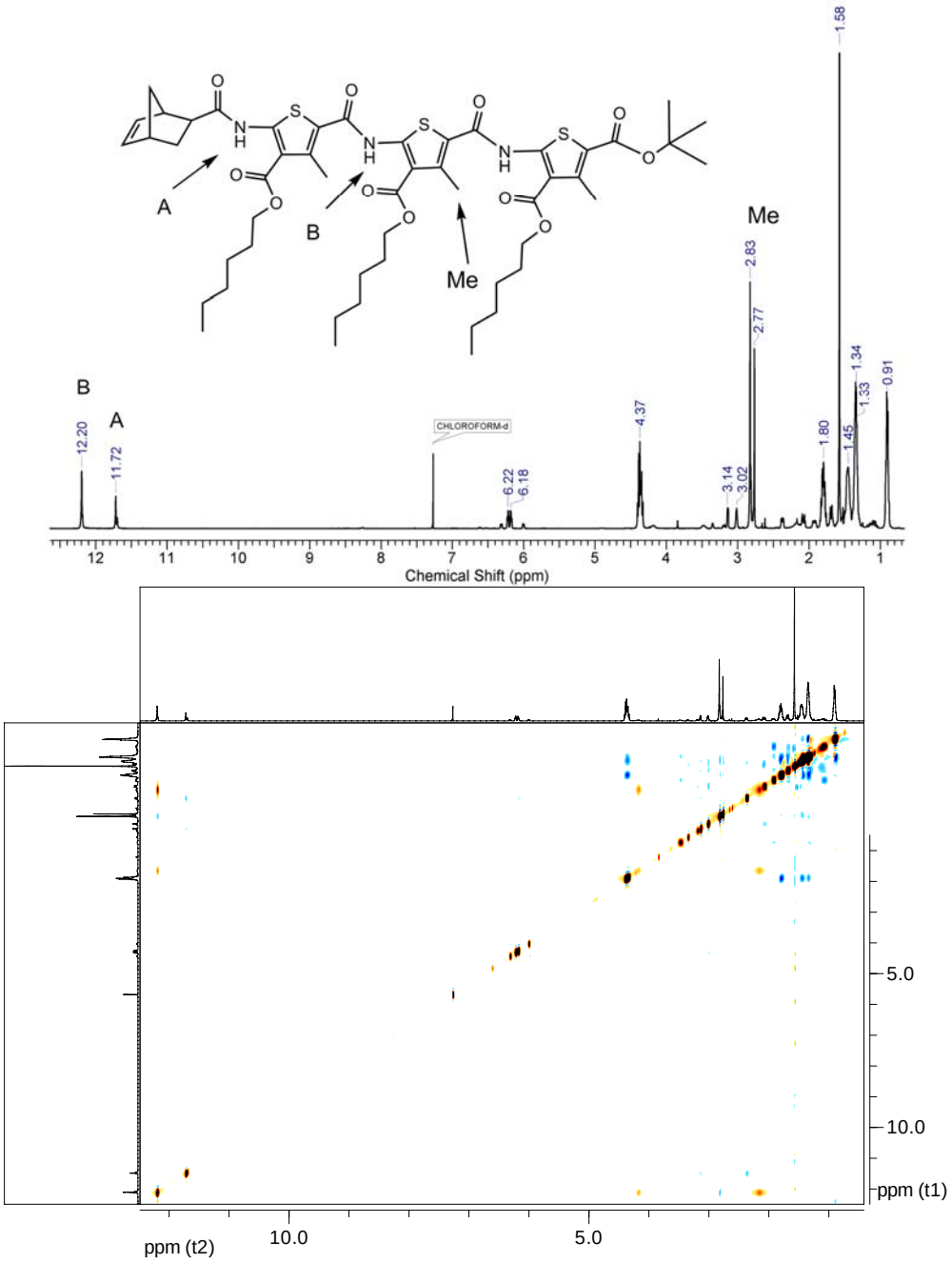
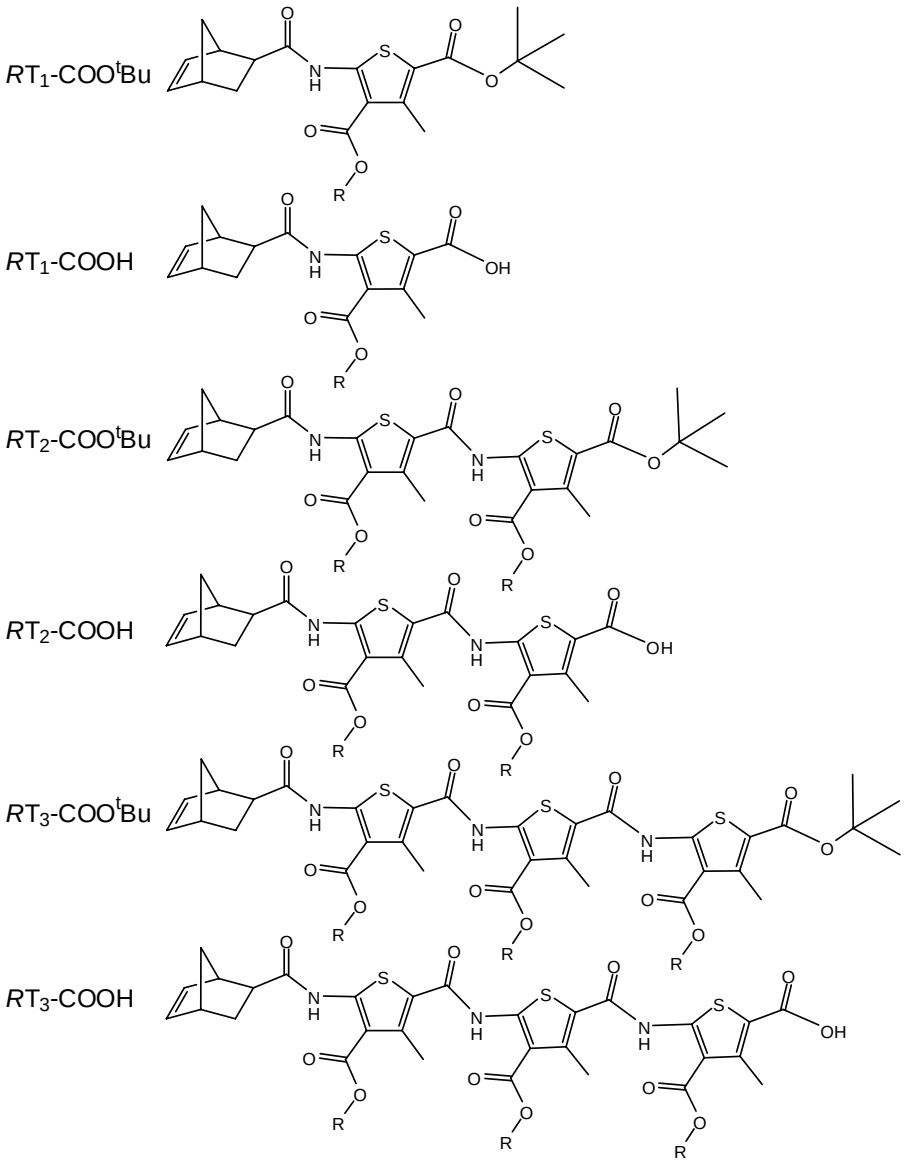


Figure 2: ^{1}H-NMR (*top*) and NOESY (*bottom*) spectra of HT_3-COO^tBu.



Scheme 3: Thiophene amide Oligomers synthesized in this study. *R*: M=Me, H=hexyl

Interestingly, an intensive fluorescence under UV light (365 nm) commenced as soon as the second thiophene amino acid had been coupled to the norbornene core. A study of the UV-absorption behavior proved major changes in the electronic structure of the aromatic system with every coupling step (Figure 3).

Every attachment of an additional thiophene unit caused the wavelength of maximum UV-absorption to increase (*c.f.* Figure 2, *left*). This absorption change indicates both narrowing of the HOMO-LUMO gap and thereby proves an enlargement of the conjugated system. The extent of maximum absorption increase with growing degrees of oligomerization follows the trend of directly bound oligothiophenes which also approximate a maximum wavelength

plateau after a few coupling steps. In fact, the absorption maxima can be found at almost the same wavelengths as completely unsubstituted oligothiophenes. The heavy substitution of the thiophenamides synthesized from Gewald-thiophene amino acids has only minor influence on the electronic structure of the total oligomer.

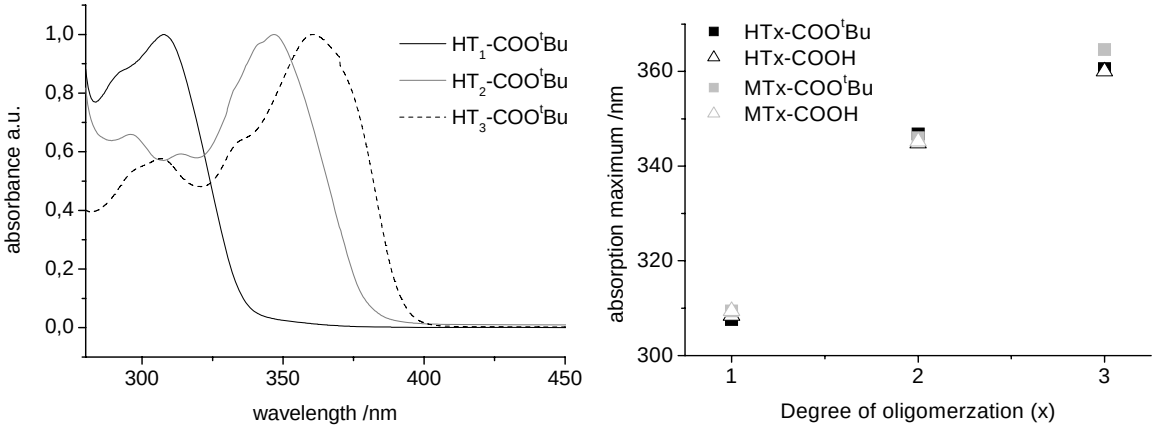


Figure 3. UV/vis spectra of three norbornene-oligo(thiopheneamide)s.

The molar absorbance parameters increase with higher degrees of oligomerization (c.f. Figure 4). This behavior could be monitored for all types of oligomers involved in this study in a similar trend. Also, the general extent of the ε–values for the different species with the same degree of oligomerizations ranges in the same area, which demonstrates that the thiophene system alone is responsible for the overall UV light absorption and the influence of the appending ester is minor. The reason for the increase of the ε–values with a rising number of thiophene rings involved can be explained by the rising cross section of the molecules which causes a higher probability of quantum absorption by every single molecule.

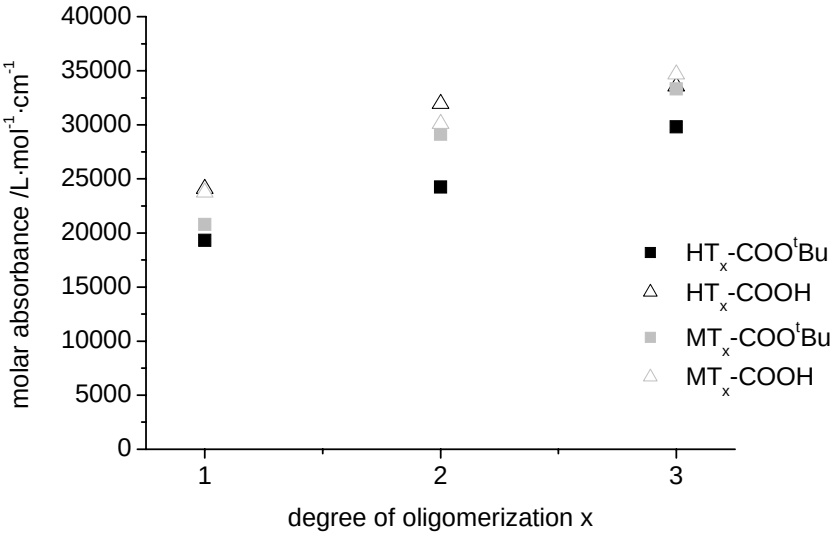


Figure 4. Molar absorbance values for the different oligomers in dependence of the degree of oligomerization.

The fluorescence spectra of the oligomers followed a similar trend. The norbornene conjugates with a single thiophene ring did not show a significant fluorescence over in the range of 220-400 nm extinction. The higher oligomers, however, did show fluorescent behavior in this range which was also dependant on the number of thiophenamide units attached. While all compounds containing two connected thiophene moieties fluoresced in the range of 407-417 nm when extinct at ca. 385 nm, the fluorescence of the trimer-containing conjugates peaked at 474-479 nm when extinct at ca. 395 nm. The exact maxima of the respective extinction and emission spectra are summarized in Table 1. The full spectra can be found in the Supporting Information. Again, the influence of the tertbutyl ester at the oligomers chain end on their electronic structure is negligible as the maximum wavelengths are not shifted between the ester-carrying compounds and their deprotected counterparts.

Table 1: UV/vis and Fluorescence spectroscopy data of the oligomers synthesized.

	UV/vis		Fluorescence	
Compound	λ_{abs} /nm	ε /L mol^{-1} s^{-1}	λ_{ex} /nm	λ_{em} /nm
NHT_1-COO^tBu	307.6	19330	--[a]	--[a]
HT_1-COOH	308.4	24080	--[a]	--[a]
HT_2-COO^tBu	309.4	24250	381	417
HT_2-COOH	309.4	31950	380	411
HT_3-COO^tBu	346.8	29810	395	479
HT_3-COOH	344.8	33560	396	474
MT_1-COO^tBu	346.0	20790	--[a]	--[a]
MT_1-COOH	345.2	23740	--[a]	--[a]
MT_2-COO^tBu	360.6	29120	386	414
MT_2-COOH	360.0	30110	386	407
MT_3-COO^tBu	354.6	33330	395	477
MT_3-COOH	362.4	34670	394	475

[a]no significant fluorescence observed

Polymerization of the norbornene groups on the oligomers was performed on the terbutyl-protected monomers. As illustrated in Figure 4, polymerization was initiated by Grubbs 1st generation catalyst. Some graft-copolymers exhibited lower solubility in dichloromethane than the monomers, thus leading to encapsulation of the active chain end and stopping the polymerization process at an early stage. The UV-absorption spectra of the grafted oligomers remained unchanged compared to the starting material. The SEC-characterization data of the homopolymers are given in Table 2. In general, the molecular weights of the polymers which did form a complete homopolymer was drastically underestimated, which indicates a very compact and stiff structure of the polymer chain as expected.

Table 2: SEC data of the homopolymers formed from *R*T$_x$-COO^{t}Bu monomers.

Entry	Monomer	DP$_{calc}$	Mn$_{calc}$	Mn$_{SEC}$ (RI)	PDI
1	HT$_1$-COO^{t}Bu	60	29000	500	--[b]
2	HT$_2$-COO^{t}Bu	40	29000	800	--[b]
3	HT$_3$-COO^{t}Bu	29	29000	18400	1.21
4	MT$_1$-COO^{t}Bu	40	15000	9500	1.13
5	MT$_2$-COO^{t}Bu	26	15000	5700	1.23
6	MT$_3$-COO^{t}Bu	20	15000	400	--[b]

[b] a minor fraction (<2%) of oligo(*R*T$_x$-COO^{t}Bu) could be observed in the UV trace

Interestingly, the oligomers bearing MT-units of the degree of oligomerization=3 aggregated, whereas uni- and dimers formed a homopolymers, while the opposite was observed on oligomers consisting of HT-units. This strongly supports two different aggregation mechanisms for the respective thiophene amides. While the reason for the aggregation of oligo(MT) molecules can be reasoned due to its stiff rod-like structure which lacks efficient solubilization by the alkyl chain appendant to the ester function on every ring, the higher number of hexyl chains appears to prevent the HT$_3$-COO^{t}Bu trimer from aggregating. The reason for the aggregation of the shorter oligomers of this type, however, remains unclear. A possible sterical blocking of the catalyst by the large residues and the comparably close proximity of the tertbutyl ester can be speculated on.

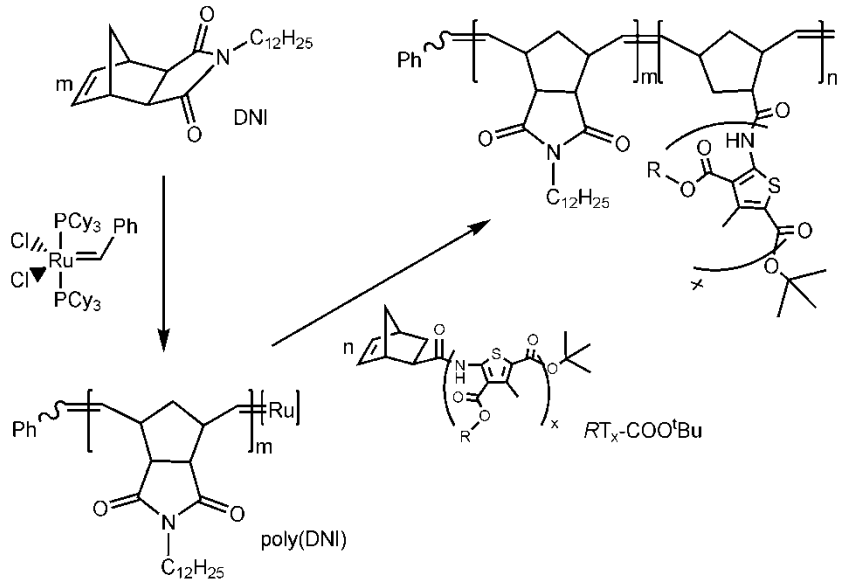


Figure 4. Formation of DNI-oligo(thiophene amide) block-copolymers by ROMP.

By addition of a solubilizing block of linear polymer, this encapsulation was avoided. *Exo*-*N*-dodecyl-norbornene-2,3-dicarboximide (DNI) was chosen for this polymer block as it is a clear, low T_g polymer that is highly soluble in most organic solvents. The DNI block was polymerized as the first block in order to take advantage of its solubilizing properties. Block copolymers of grafted oligomers with DNI (block rates 1:2 and 1:6) were synthesized of all oligo(thiophene amide)s. (c.f. Figure 4). All block-copolymers exhibited narrow molecular weight distributions (~1.2) and full oligomer incorporation into the polymer chain.

Table 3: Polymerization results

Entry	Monomer	Block rate	Mn_{SEC} (RI)	PDI
7	HT_1-COO^tBu	1:2	9300	1.41
8	HT_1-COO^tBu	1:6	11600	1.37
9	HT_2-COO^tBu	1:2	11600	1.26
10	HT_2-COO^tBu	1:6	10900	1.32
11	HT_3-COO^tBu	1:2	13300	1.29
12	HT_3-COO^tBu	1:6	9200	1.29
13	MT_1-COO^tBu	1:2	9000	1.29
14	MT_1-COO^tBu	1:6	13700	1.22
15	MT_2-COO^tBu	1:2	9300	1.27
16	MT_2-COO^tBu	1:6	13600	1.24
17	MT_3-COO^tBu	1:2	8700	1.28
18	MT_3-COO^tBu	1:6	13000	1.17

As indicated by the SEC characterization results, the incorporation of the oligo(thiophene amide) monomers was more successful than their homopolymerization. Slight aggregation broadening of the polymer molecular weight distribution could be monitored in the HT monomer bearing polymers, especially when a larger block of this monomer was polymerized (c.f. entry 7 and 8, Table 3). The same tendency can be seen on the MT_3-COO^tBu

bearing polymer samples, where the larger block (entry 17) did not reach complete polymerization. The general difference of the apparent molecular weight between polymers synthesized with a 1:6 block ratio compared to those with a 1:2 ratio can be explained by the extremely different solution behavior of the respective blocks. While DNI is very soluble and is typically appear slightly larger in hydrodynamic volume compared to poly(styrene) standards, the stiff oligomers a are generally underestimated (*vide infra*).

The UV/vis absorbance characteristics are not significantly shifted due to the presence of the polymer or the vicinity of the oligo(thiophene amide) units due to their attachment to a single polymer backbone. A comparison of a polymer spectrum with the respective monomer spectrum is given in Figure 5, further spectra are given in the Supporting Information. Therefore, the single oligomers units along the polymer chain do not form aggregates or an otherwise ordered phase which would lead to a shift of the absorption maximum. Measurements of the UV/vis absorption of the polymers in a non-solvent for the oligomer block could not be conducted due to massive light-scattering.

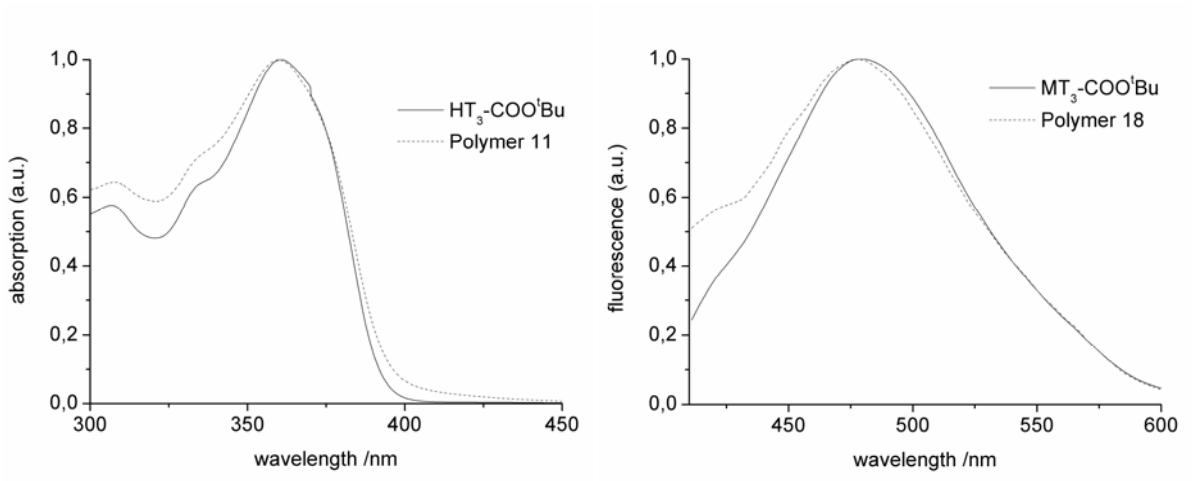


Figure 5: UV/vis (*left*) and fluorescence (*right*) spectroscopic comparison of monomeric and co-polymerized *R*T$_3$-COO^{t}Bu.

Fluorescence spectroscopy was conducted on all polymers containing fluorescent oligomers. The spectra obtained were similar to those for the monomers, which proves that the electronic structure of the oligomers is not influenced by the polymerization. An overlay of spectra of the monomer MT_3-COO^tBu and a co-polymer formed from it is shown in Figure 5 (*right*), additional spectra can be found in the Supporting Information. Also, on semi-aggregated samples (e.g. polymer 17 in dichloromethane, a polymer which showed scattering peaks much higher than the fluorescence) no shift in the maximum fluorescence wavelength was observed.

The block copolymers exhibited amphiphilic characteristics, showing aggregation of the polar oligomer portions in n-hexane which is a selective solvent for the DNI block. Here, islands of small nano-objects could be found in the TEM image (Figure 6, *top*). The regions of higher contrast can be expected to consist of the oligo(thiophene amide)s, which contain the denser material and sulfure hetero atoms. Poly(DNI), which is almost a pure hydrocarbon, is likely to induce little TEM contrast. The objects are ca. 10-15 nm large, which lies in the same order of magnitude as the object sizes of oligo(*p*-benzamide) hockey-puck micelles reported by our group.[12] the separation of the objects is given by a poly(DNI) layer surrounding the particles.

A phase separation of poly(DNI) and the oligo(thiophenamide) blocks can also be observed in the bulk phase. Drop-cast from dilute solution onto a TEM grid, regions of different fil thickness were found which demonstrate the phase separation progress during tempering. Within thinner areas, pre-oriented globular oligo(thiophene amide)-phases can be found. In regions of intermediate film thickness, the material starts to form lamellar phases around nucleation spots. In thicker areas, the structure is dominated by partly ordered lamellar phases. A deeper insight into the phase separation processes and a more precise study of the ordering of the bulk phases will be subject to further studies.

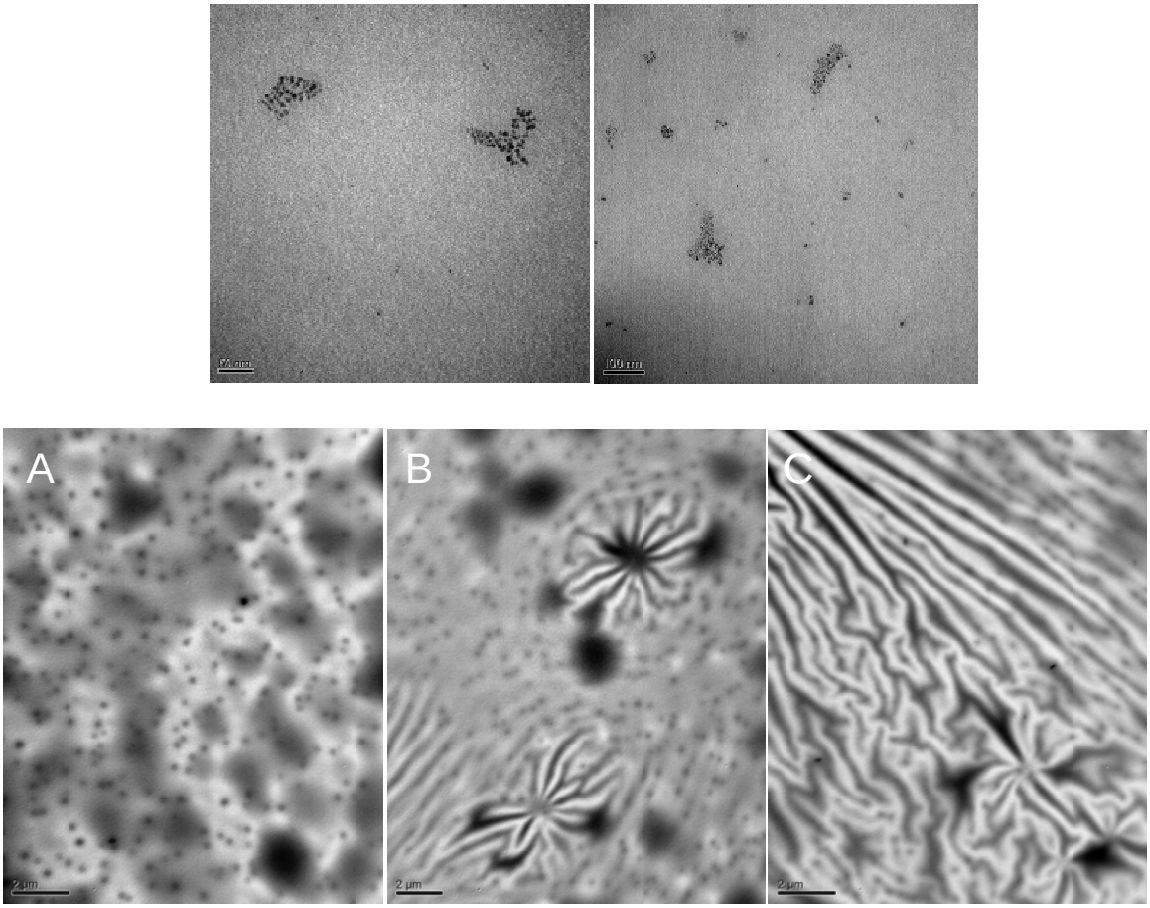


Figure 6. *Top*: TEM images of poly(DNI-*b*-HT_3-COO^tBu) block ratio 6:1, Mn=9200 drop-cast from n-hexane. *Bottom*: Phase separation in the bulk phase of polymer 12 drop-cast from a 1 g/L solution in dichloromethane after tempering at 60°C for 10 h A: thin area, B: intermediate area, C: thicker area.

Conclusions

Oligo(thiopheneamide)s were successfully synthesized based on norbornene cores. Classical coupling – deprotection chemistry could be applied to oligomerize the protected thiophene amino acids obtained from *Gewald* synthesis up to a degree of oligomerization of three in good purity and definition. As side reactions during the deprotection step with an increasing number of thiophene moieties, different synthetic strategies have to be found for the clean formation of longer oligomers.

The conjugation of these well-defined molecules was proven by their UV/vis absorption maxima, which changed significantly in wavelength, thus indicating expansion of the conjugated system with every coupling step and by the fluorescence of the molecules, which

commenced as soon as two thiophene rings had been connected via an amide bond. Furthermore, the UV/vis absorption maxima, as well as their fluorescence maximum were shifted to higher wavelengths with an increasing degree of oligomerization which also demonstrates the extension of the conjugated system.

These defined electronical properties were successfully transferred to polymer materials by formation of the homo-polymers of the defined oligo(thiophene amide)s and block-copolymers with DNI. The persistence of the electronic structure of these materials was proven by spectroscopic methods, which showed no significant changes due to the polymerization.

In addition, the block-copolymers with DNI exhibited amphiphilic properties in solution and in the bulk state. Nanoobjects were observed in a selective solvent for the DNI block. Bulk samples show a complex phase separation between the oligo(thiophene amide) and the poly(DNI) block towards a lamellar heterostructure. A more detailed investigation of the self-assembling properties of these hybrid compounds and their influence on possible semiconducting properties of the oligo(thiophene amide)s will be subject to further studies.

References:

[1] D. Fichou *Handbook of Oligo- and Polythiophenes*; Wiley-VCH: Weinheim, 1999.

[2] R. Sugimoto,S. Takeda, H. B. Gu, K. Yoshino *Chem. Express* **1986**, *1*, 635.

[3] R. L. Elsenbaumer, K. Y. Jen, R. Oboodi *Synthetic Met* **1986**, *15*, 169-174. R. L. Elsenbaumer, G. G. Miller, K. Y. Jen, *J. Chem. Soc., Chem. Commun.* **1986**, 1346-1347.

[4] R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson *J Org Chem* **1993**, *58*, 904-912. T. A. Chen, R. D. Rieke *J. Am. Chem. Soc.* **1992**, *114*, 10087-10088.

[5] K. Gewald *Chem. Ber.* **1965**, *98*, 3571-3577.

[6] K. Gewald, E. Schinke, H. Böttcher, *Chem. Ber.* **1966**, *99*, 94-100. K. Gewald *J. Prakt. Chem.* **1966**, *32*, 26-30. K. Gewald *Chem. Ber.* **1966**, *99*, 1002-1007.

[7] N. P. Peet, S. Sunder, R. J. Barbuch, A. P. Vinogradoff *J. Heterocyc. Chem.* **1986**, *23*, 129-134.

[8] R. Abbel, H. Frey, D. Schollmeyer, A. F. M. Kilbinger *Chem. – Eur. J.* **2005**, *11*, 2170-2176.

[9] R. Abbel, T. W. Schleuss, H. Frey, A. F. M. Kilbinger *Macromol. Chem. Phys.* **2005**, *206*, 2067-2074.

[10] H. M. Koenig, R. Abbel, D. Schollmeyer, A. F. M. Kilbinger *Org. Lett.* **2006**, *8*, 1819-1822.

[11] H. M. Koenig, T. Gorelik, U. Kolb, A. F. M. Kilbinger *J. Am. Chem. Soc.* **2007**, *129*, 704-708.

[12] T. W. Schleuss, R. Abbel, M. Gross, D. Schollmeyer, H. Frey, M. Maskos, R. Berger, A. F. M. Kilbinger *Angew. Chem. Int. Ed.* **2006**, *45*, 2969-2975.

[13] J. Klos, F. Wurm, A. F. M. Kilbinger *Macromolecules* **2007**, *40*, 7827-7833.

[14] H. A. Kang, H. E. Bronstein, T. M. Swager *Macromolecules* **2008**, *41*, 5540–5547.

[15] R. B. Breitenkamp, Z. Ou, K. Breitenkamp, M. Muthukumar, T. Emrick, *Macromolecules* **2007**, *40*, 7617-7624.

[16] S. Hilf, E. Berger-Nicoletti, R. H. Grubbs, A. F. M. Kilbinger, *Angew. Chem*. **2006**, *118*, 8214-8217; *Angew. Chem. Int. Ed.* **2006**, *45*, 8045-8048. S. Perrier, X Wang, *Nature* **2007**, *445*, 271. S. Hilf, R. H. Grubbs, A. F. M. Kilbinger, *Macromolecules* **2008**, *41*, 6006-6011.

[16] S. Hilf, R. H. Grubbs, A. F. M Kilbinger *J. Am. Chem. Soc.* **2008**, *130*, 11040-11048.

[17] S. Hilf, N. Hanik, A. F. M. Kilbinger *J. Polym. Sci. A* **2008**, *46*, 2913-2921. S. Hilf, A. F. M. Kilbinger *Macromol. Rapid Commun*. **2007**, *28*, 1225-1230.

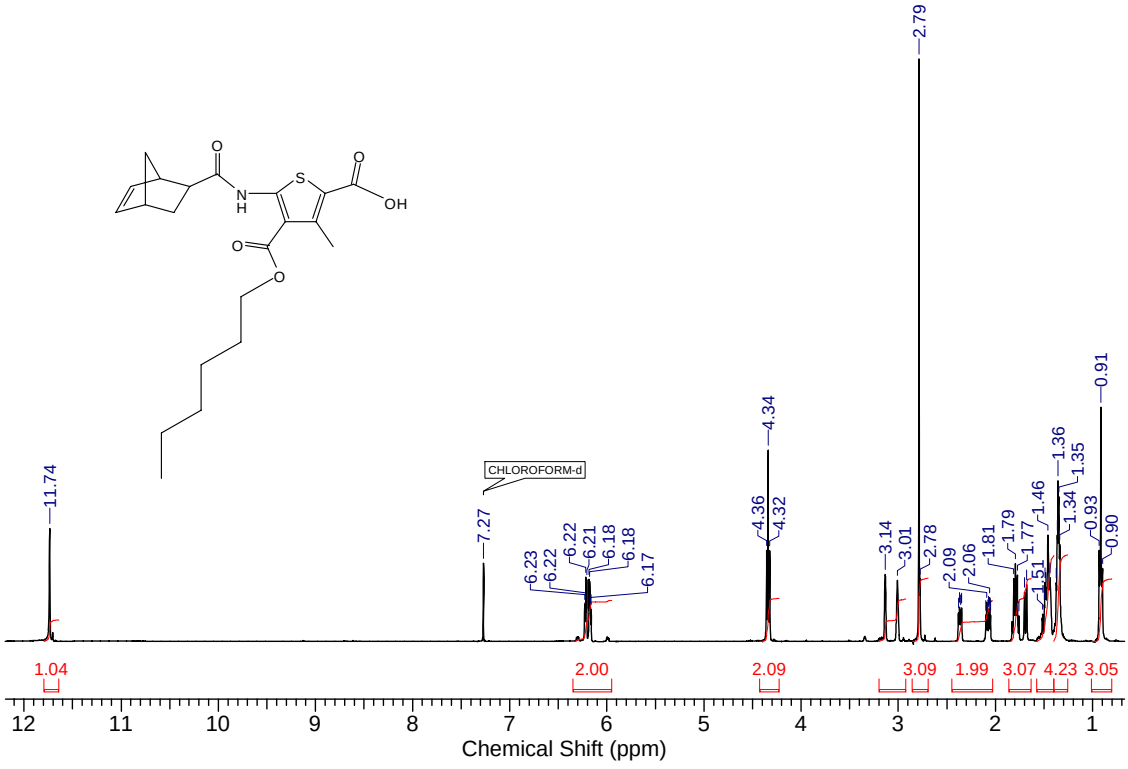
[18] S. Hilf, A. F. M. Kilbinger *Macromolecules* **2009**, *42,* 1099-1106.

[19] S. Hilf, A. F. M. Kilbinger *Macromol. Rapid Commun*. **2007**, *28*, 1225-1230.

Supporting Information for: Polymerizable well-defined oligo(thiophene amide)s and their ROMP block-copolymers

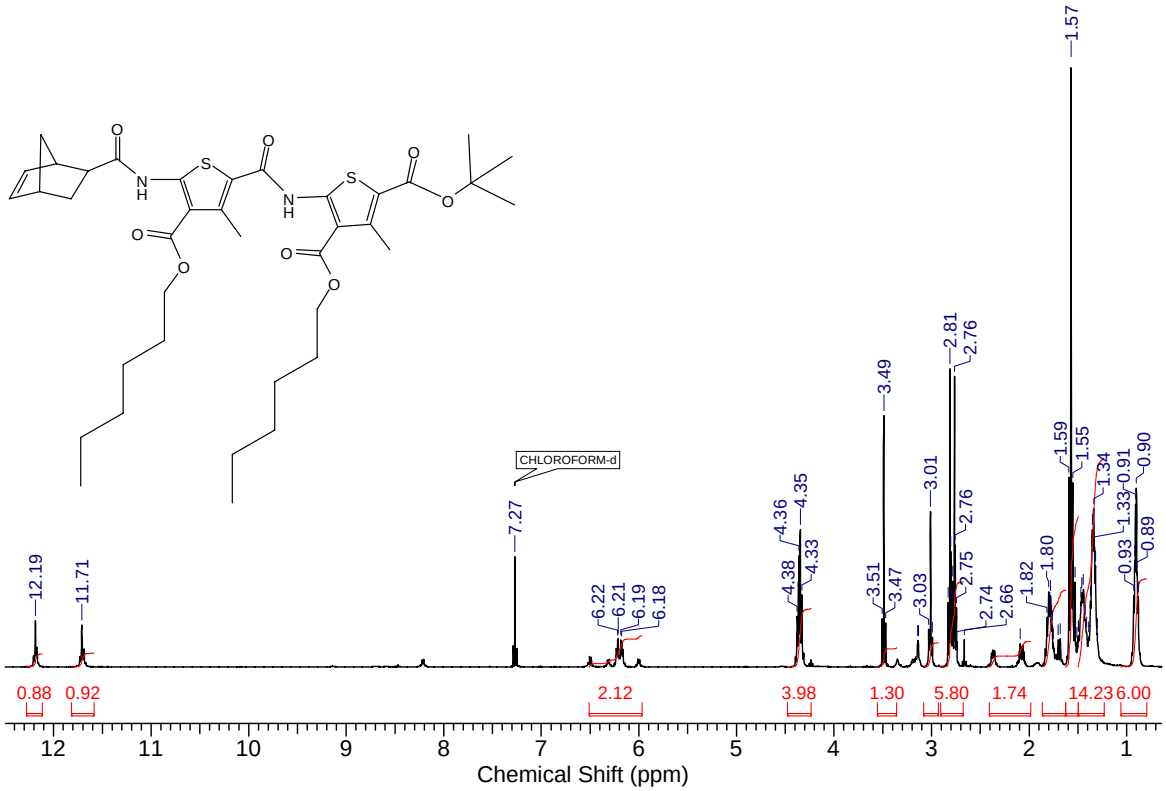
Stefan Hilf, Johannes Klos, Kookheon Char and Andreas F. M. Kilbinger

SI-1: Additional characterization data for the oligomers:



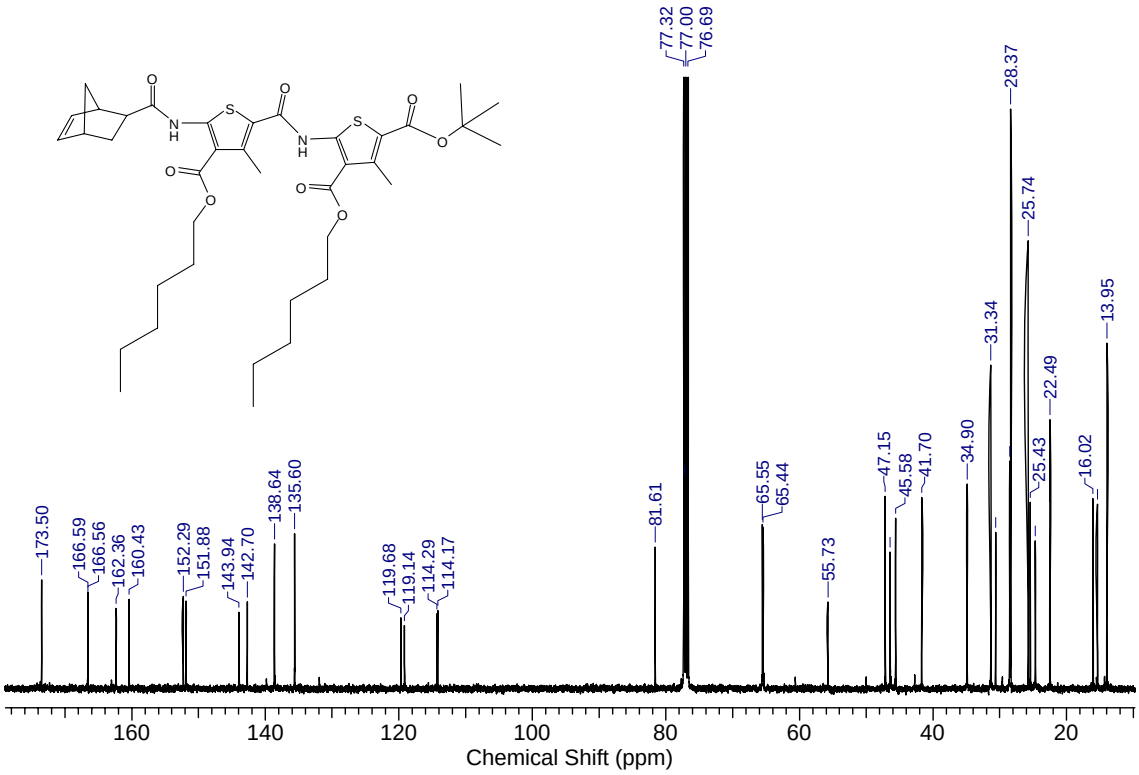
^{1}H spectrum of HT_1-COOH.

FD-MS: 405.6 m/z (calc. 405.51 g/mol)

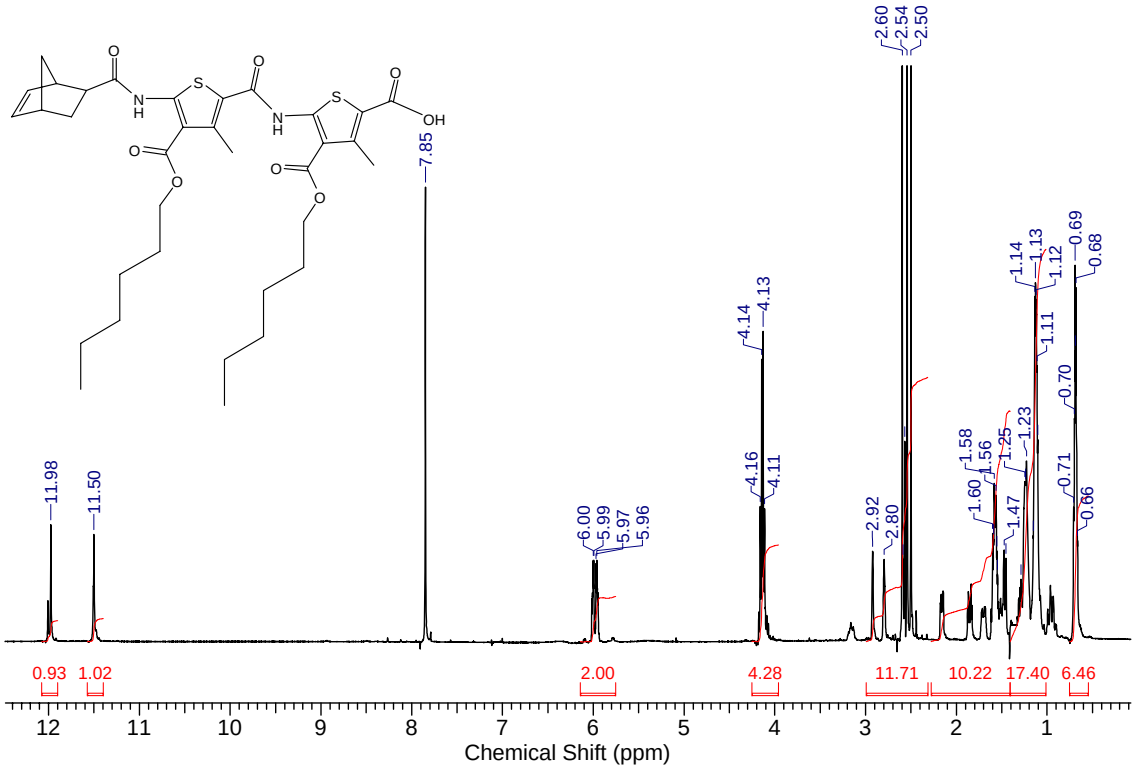


^{1}H spectrum of HT_2-COO^{t}Bu.

FD-MS: 729.1 m/z (calc. 728.96 g/mol)

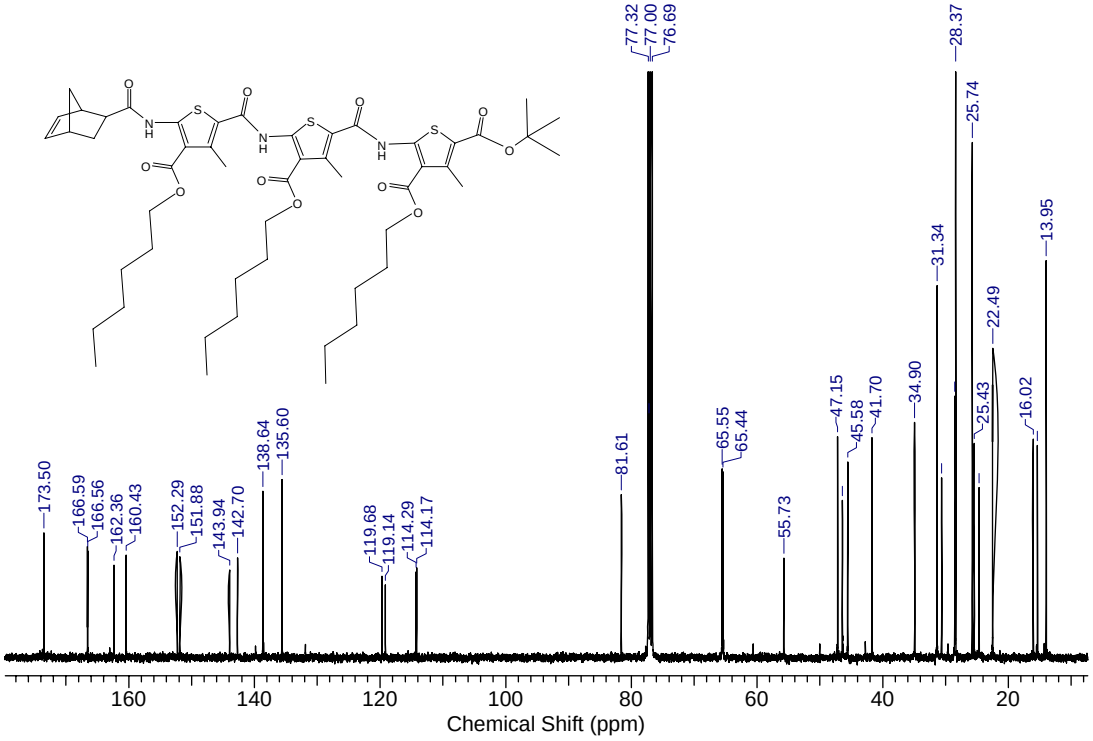


^{13}C spectrum of HT_2-COO^{t}Bu.



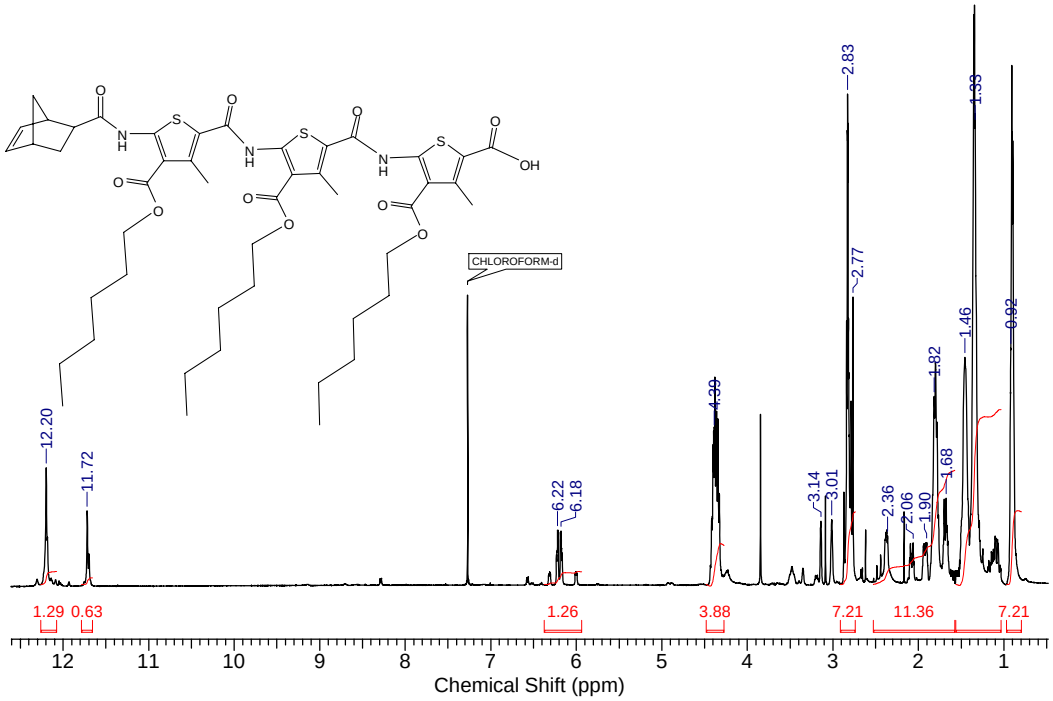
^{1}H spectrum of HT_2-COOH.

FD-MS: 673.1 m/z (calc. 672.85 g/mol).



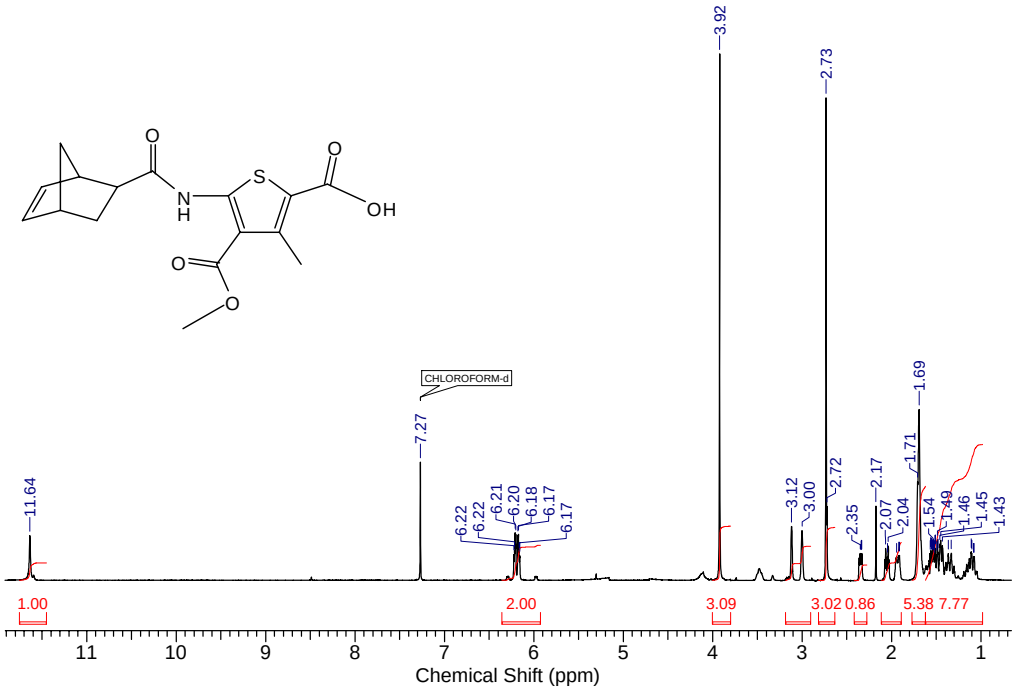
^{13}C spectrum of HT_3-COO^{t}Bu.

FD-MS: 996.7 m/z (calc. 996.30 g/mol).



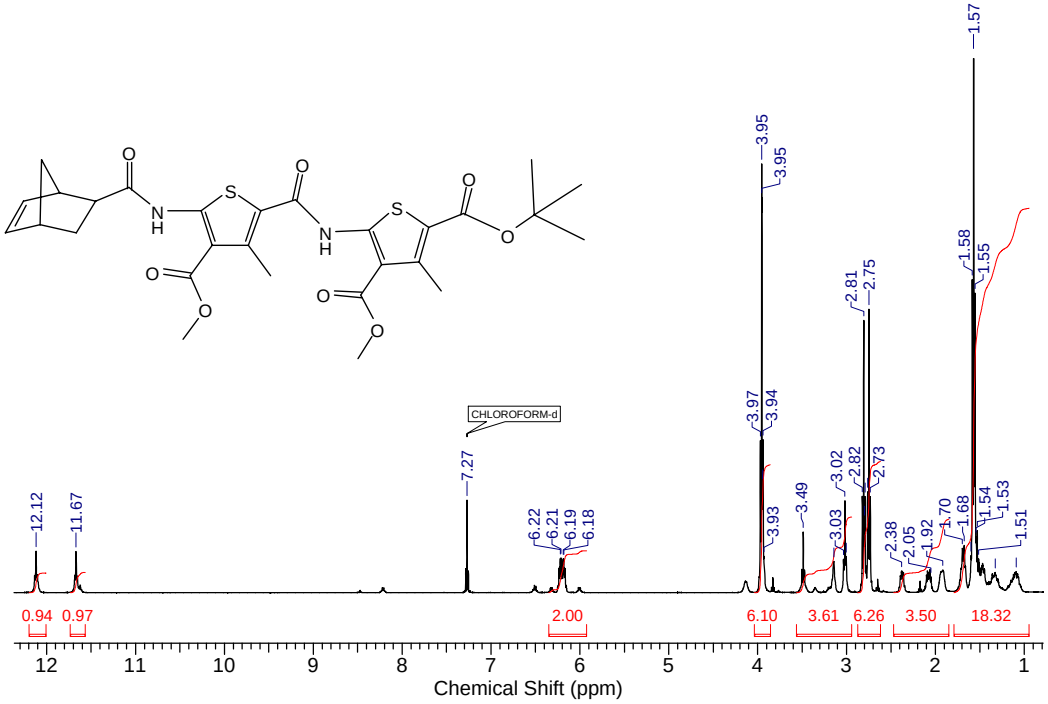
^{1}H spectrum of HT_3-COOH.

FD-MS: 940.6 m/z (calc. 940.20 g/mol).



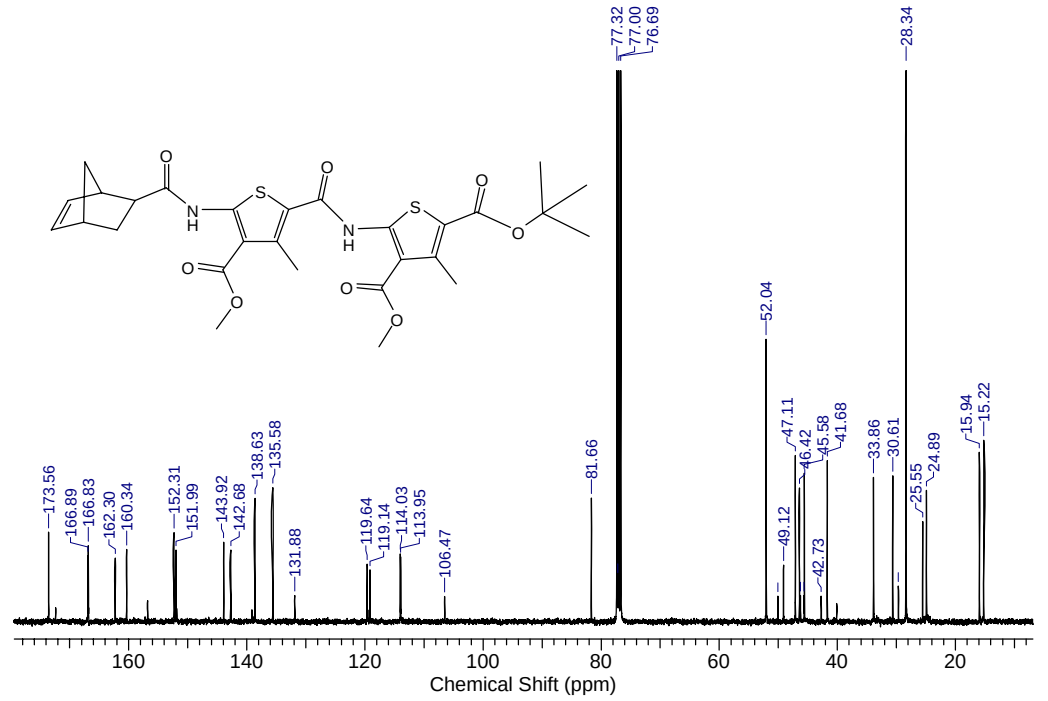
^{1}H spectrum of MT_1-COOH.

FD-MS: 335.3 m/z (calc. 335.37 g/mol).

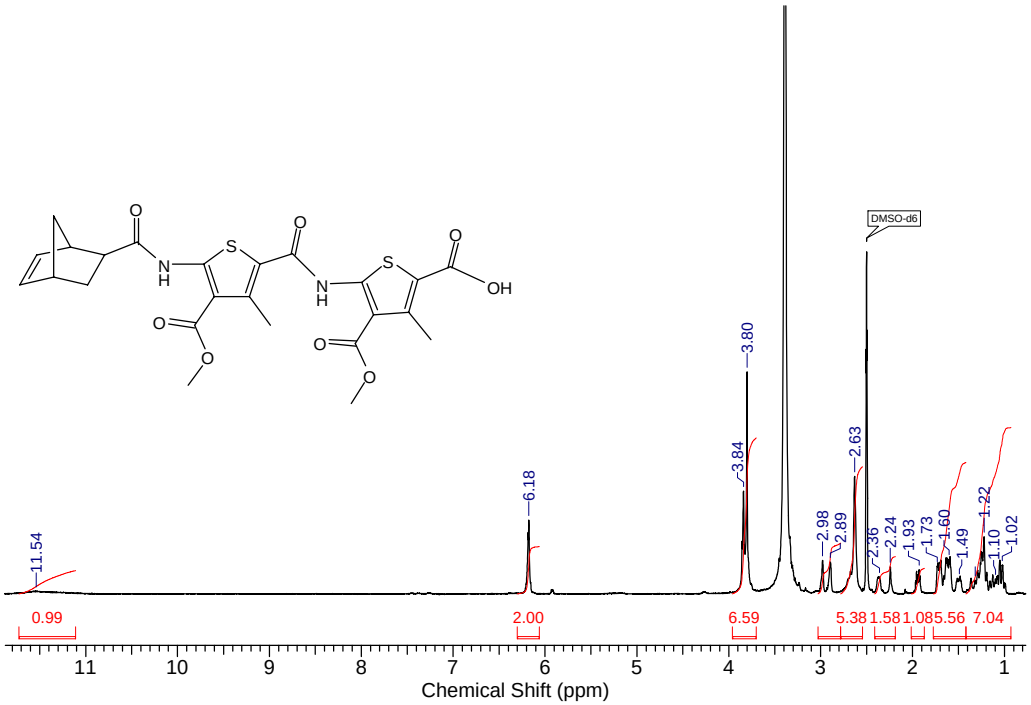


^{1}H spectrum of MT_2-COO^{t}Bu.

FD-MS: 588.8 m/z (calc. 588.69 g/mol).

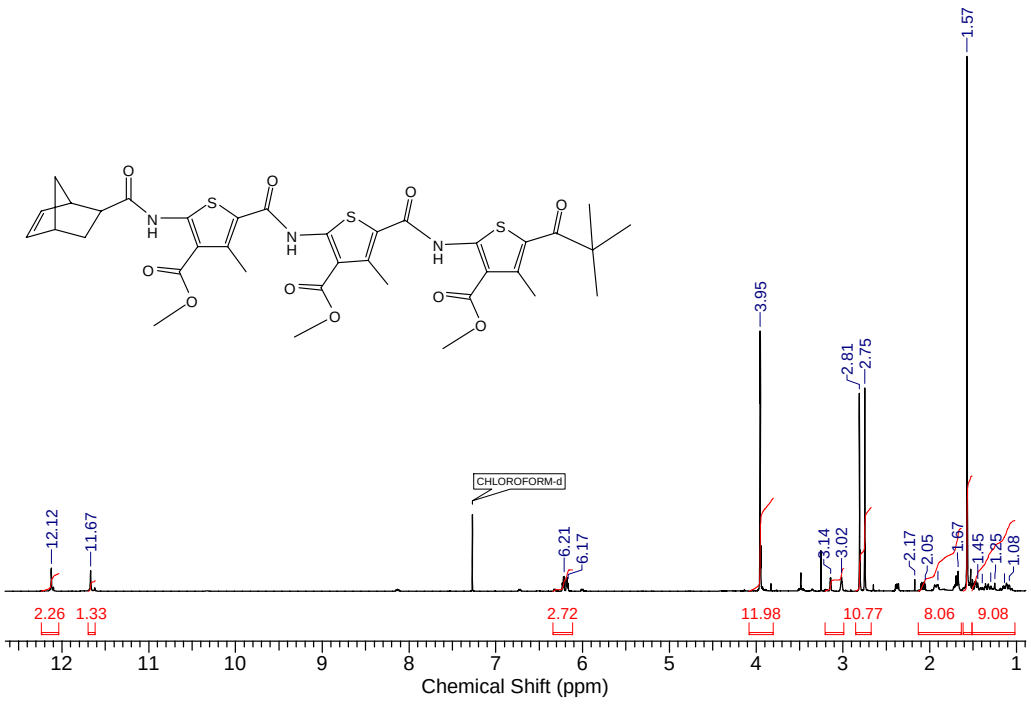


^{13}C spectrum of MT_2-COO^{t}Bu.

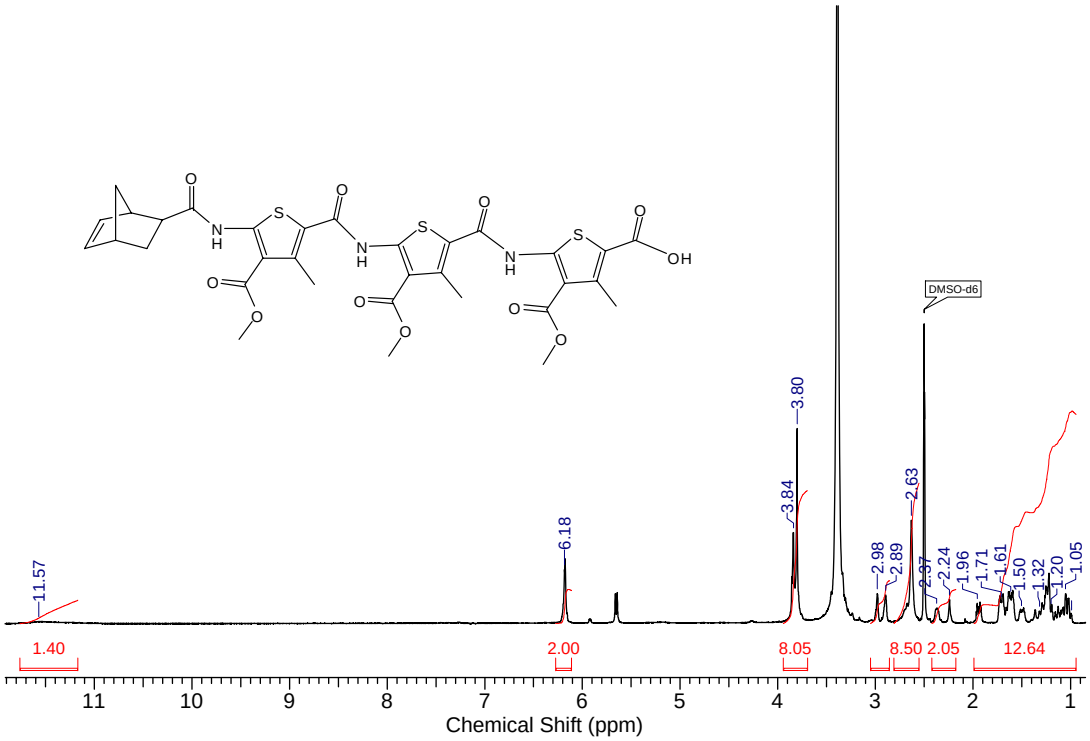


^{1}H spectrum of MT_2-COOH.

FD-MS: 532.7 m/z (calc. 532.59 g/mol).

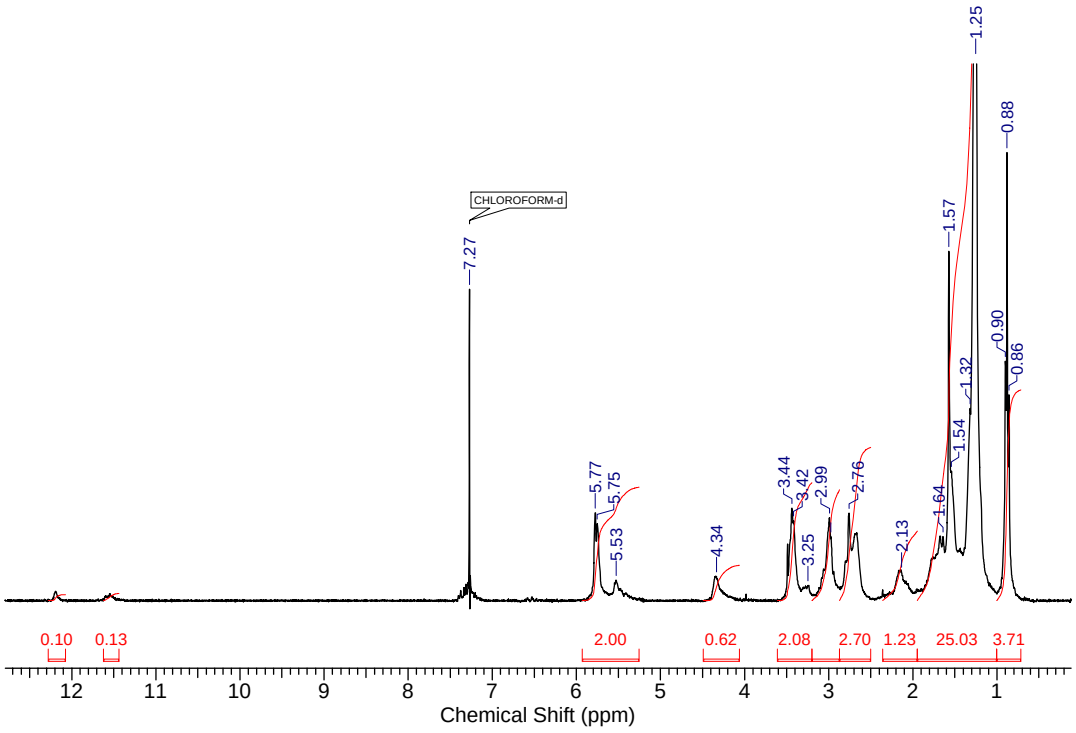


^{1}H spectrum of MT_3-COO^{t}Bu.

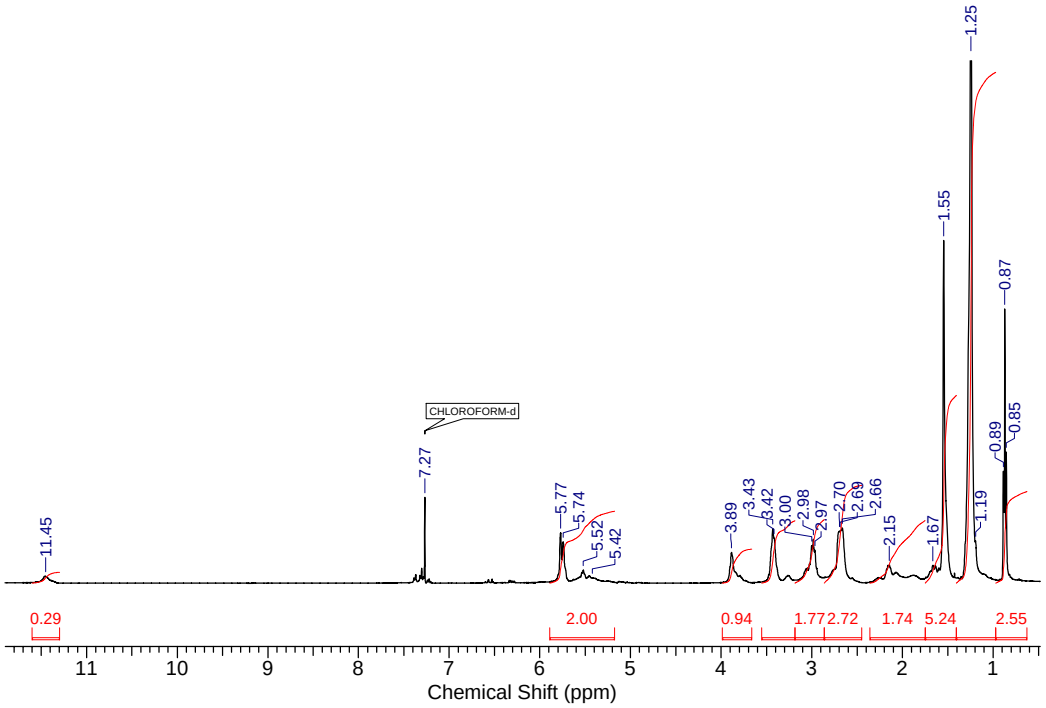


^{1}H spectrum of MT_3-COOH.

SI-2. Exemplary 1H-NMR spectra of the copolymers.

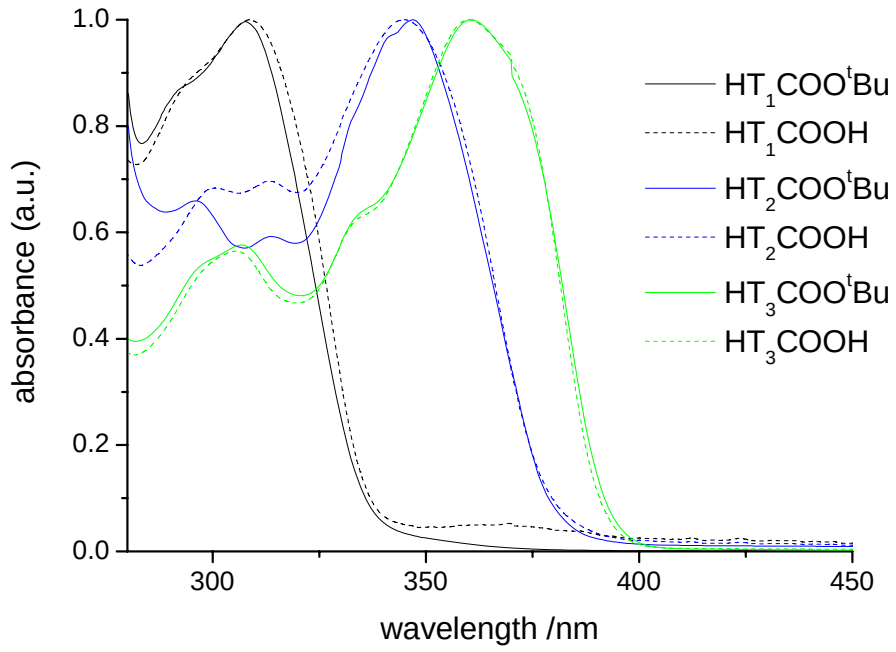


^{1}H spectrum of polymer 12 (ca 12% HT_3-COO^tBu by NMR).

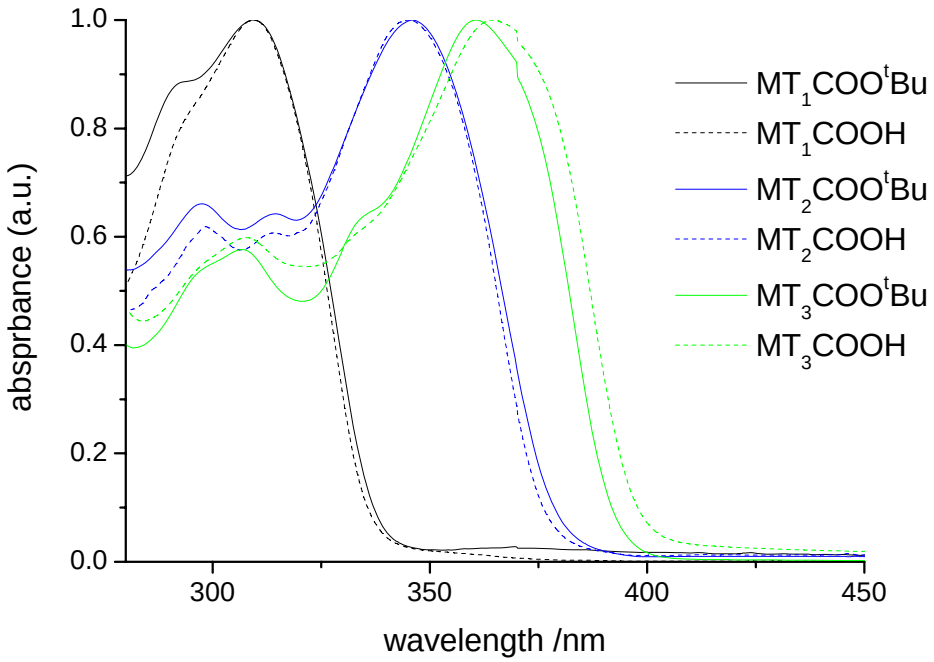


^{1}H spectrum of polymer 13 (ca 32% NT_1-COO^tBu by NMR).

SI-3. UV/vis spectra of oligo(thiophene amide) monomers and copolymers.

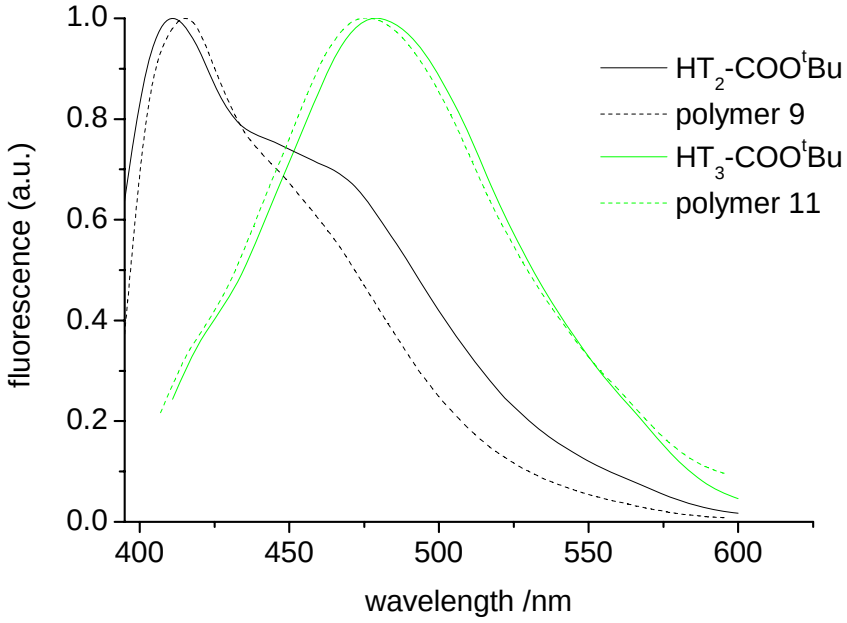


UV/vis spectra of HT-oligomers

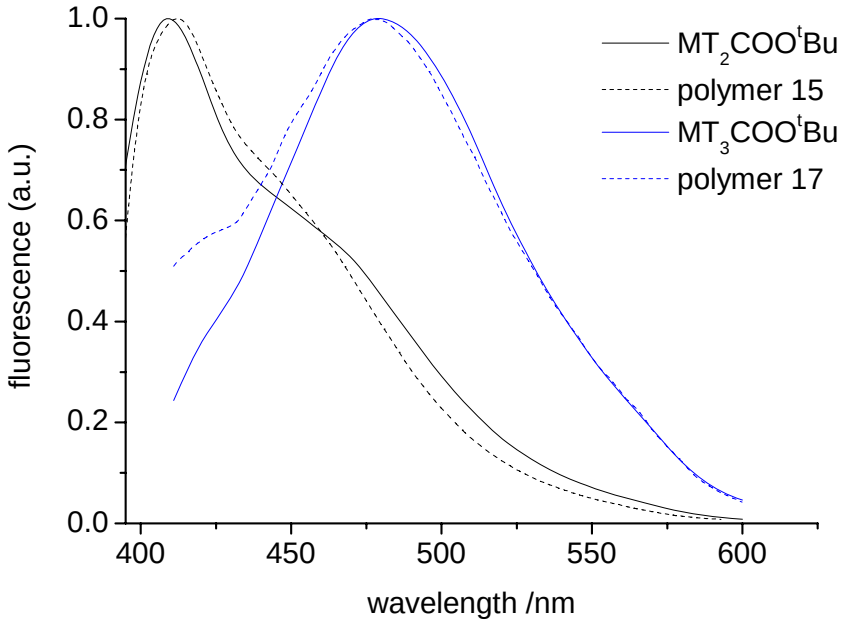


UV/vis spectra of MT-oligomers

SI-4. Fluorescence spectra of oligo(thiophene amide) monomers and copolymers.



Fluorescence spectra of HT oligomers and co-polymers.



Fluorescence spectra of MT oligomers and co-polymers.

4.3: Electroactive Linear-Hyperbranched Block Copolymers based on Linear Poly(ferrocenylsilane)s and Hyperbranched Poly(carbosilane)s

Frederik Wurm, Stefan Hilf and Holger Frey

Submitted for publication in: Chemistry – A European Journal.

Abstract: A convenient 2-step protocol for the synthesis of linear-hyperbranched diblock copolymers consisting of a linear, organometallic poly(ferrocenylsilane) (PFS) block and hyperbranched poly(carbosilane) (hbPCS) segments is presented. Linear PFS diblock copolymers were synthesized via the photolytic ring opening polymerization of dimethyl-[1]silaferrocenophane as the first and methylvinyl-[1]silaferrocenophane as the second block. These block copolymers serve as polyfunctional cores in a subsequent hydrosilylation polyaddition of different silane-based AB_2-monomers. Three different AB_2 monomers were investigated: i) methyldiallylsilane; ii) methyldiundecenylsilane and iii) ferrocenyldiallylsilane. These monomers introduce a structural diversity into the hyperbranched block and show variable reactivity for the hydrosilylation reaction. In case of the additional ferrocene moiety in the latter monomer an electroactive hyperbranched block is generated. No slow monomer addition was necessary for molecular weight control of the hyperbranching polyaddition, as the core possesses a much higher functionality and reactivity compared to the monomers. Different block ratios were targeted and hybrid block copolymers with narrow polydispersity (<1.2) were obtained. All resulting polymers were investigated and characterized via size exclusion chromatography, NMR-spectroscopy, cyclic voltammetry and transmission electron microscopy.

Introduction

Metal-containing polymers have found increased attention during the last decades due to their unique properties arising from the presence of (transition) metals in the macromolecular structure.[1] In such materials, metals can be incorporated as side groups (e.g. poly(vinyl ferrocene)[2]) or in the main chain. One of the most thoroughly investigated systems featuring a transition metal in the main chain is poly(ferrocenyl silane) (PFS).[3] Interesting properties of PFSs, such as redox activity, semiconductivity, and the ability to function as precursors to catalysts for the growth of carbon nanotubes have been studied.[3,4] PFSs have also attracted attention as redox-active matrices for color-tunable photonic crystals,[5] etch resists,[6] charge dissipation coatings,[7] photoconductive materials,[8] as precursors to magnetic[9] or catalytically active nanoparticles,[10] and as materials with high refractive index.[11]Since the discovery of thermal ring-opening polymerization of strained [1]-silaferrocenophanes,[12] various other polymerization techniques such as transition-metal-catalyzed, living anionic, and photolytic ring-opening polymerization (PROP) have been developed.[3,13] Among these mechanisms, the transition-metal-catalyzed and the PROP polymerization are of special interest due to their tolerance to several functional groups that are present in the monomers; these would not endure, e.g. the strongly basic conditions of a living anionic polymerization initiated with strong bases such as butyl lithium (for n-butyl lithium, pk_B ca. 42). PROP of [1]-silaferrocenophanes is initiated with weak bases such as sodium cyclopentadienide (pK_B ca. 16) under irradiation, thus tolerating functional groups such as alkenes, alkynes, amines, etc.. Furthermore, in contrast to the transition-metal-catalyzed polymerization, PROP proceeds in a living manner and thus permits the synthesis of block copolymers or other macromolecular architectures. Such block copolymers (previously synthesized via living anionic ROP) have shown impressive self-assembly properties as a result of phase separation to give well-defined nanostructures.[3,14]

Dendrimers are believed to be interesting candidates for the incorporation in polymeric architectures due to their globular structure, low viscosity and the high number of terminal (in many cases functional) end groups. However, due to the demanding multi-step synthesis and the need for high-conversion transformations, dendrimers are accessible only in limited quantities via time-consuming multi-step processes, often followed by tedious purification steps.[15] In contrast, statistically branched, i.e. hyperbranched, materials can be synthesized

usually in one polymerization step. By adjusting the monomer / initiator (or core) ratio even elevated molecular weights can be achieved in one step. Nevertheless, investigations on hyperbranched materials showed physical properties comparable to their perfect dendrimer analogues. A drawback of hyperbranched polymers is often their broad molecular weight distribution and imperfect structure, making further reactions or supramolecular assembly difficult. Furthermore, different functional end groups may be present due to random branching, i.e. linear, dendritic and terminal units. Thus, polymer chemists were challenged to realize control over molecular weight and branching during the synthesis of nonlinear macromolecules. Several works describe the synthesis of dendrimer segments attached to a linear polymer chain;[16] the resulting hybrids show interesting properties in solution and in bulk that are currently under investigation. Only a few papers, however, have detailed the synthesis of linear-hyperbranched block copolymers with promising properties similar to perfect dendrimer blocks, but based on a feasible synthetic pathway.[17] Our group has developed the hypergrafting concept, e.g., for the formation of hyperbranched poly(carbosilane)s (hbPCS) connected to a linear polymeric core via hydrosilylation polyaddition of a suitable AB_2-monomer. In this manner, poly(styrene)-*b*-hb-poly(carbosilane)[17a] and poly(ethylene oxide)-*b*-hb-poly(carbosilane)s[17d] have been realized. The basic idea guaranteeing molecular weight control is the use of a polyfunctional core, whose incorporation is favored compared to homopolymerization of the AB_2-monomer ,yielding narrowly distributed linear- hyperbranched block copolymers.

Here we report on the first synthesis of linear- hyperbranched diblock copolymers based on PFS and hbPCS with narrow molecular weight distributions and different chemical composition. The synthesis relies on a straightforward two-step method, combining PROP of [1]-silaferrocenophanes for the generation of linear block copolymer cores with subsequent hydrosilylation polyaddition of suitable AB_2-monomers for the construction of the hyperbranched block. Both the molecular weights of the linear precursors as well as the molecular weights of the hyperbranched blocks were varied. The linear block copolymers are based on poly(dimethylferrocenylsilane) (PFDMS) and poly(methylvinylferrocenylsilane) (PFMVS). The polyfunctionality of the core with several Si-vinyl bonds was believed to favor the hypergrafting reaction compared to the homopolymerization of the AB_2-monomer. A previous work investigated the activity of double bonds in PFSs in hydrosilylation reactions with monofunctional silanes.[18] It was found that Si-vinyl bonds show a high reactivity in

hydrosilylation reactions, in fact the highest compared to allyls or oxyallyls.[19] Highly reactive core molecules have been employed in hyperbranching reactions in several other works.[17d,20]

This paper presents the synthesis of several linear-hyperbranched block copolymers and their detailed characterization via NMR-spectroscopy and size exclusion chromatography (SEC). The electrochemistry was studied with cyclic voltammetry (CV) and supramolecular assembly was investigated via transition electron microscopy (TEM). A schematic picture of the block copolymers presented here is shown in Scheme 1.

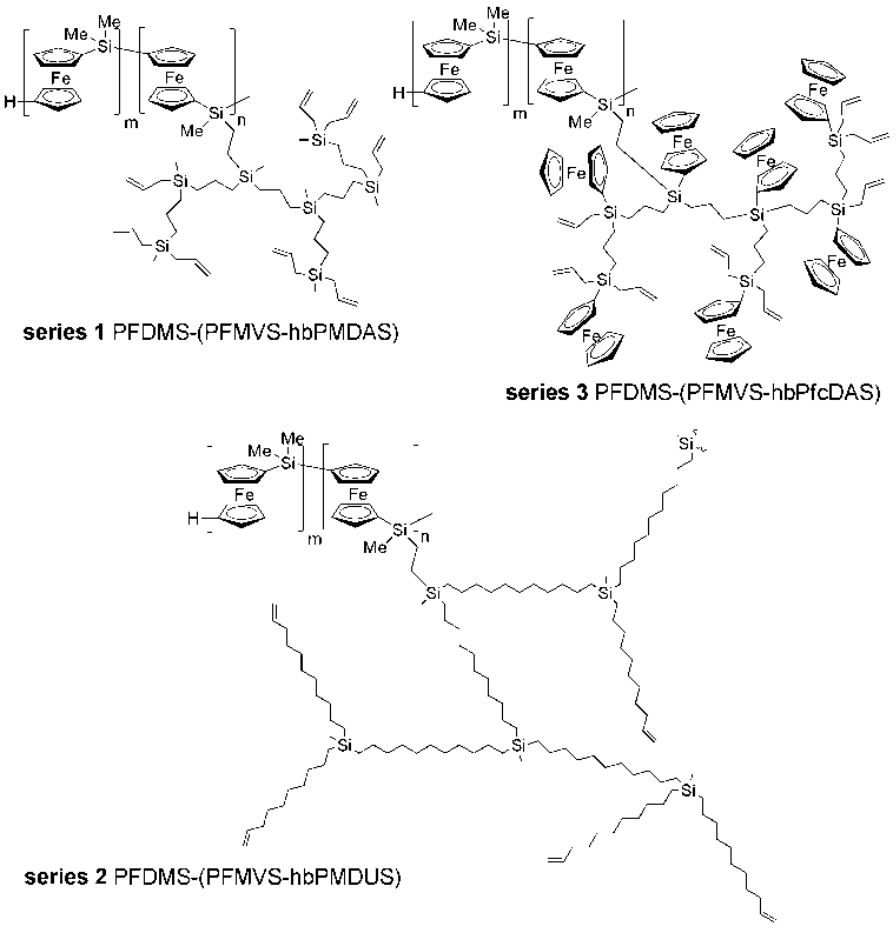
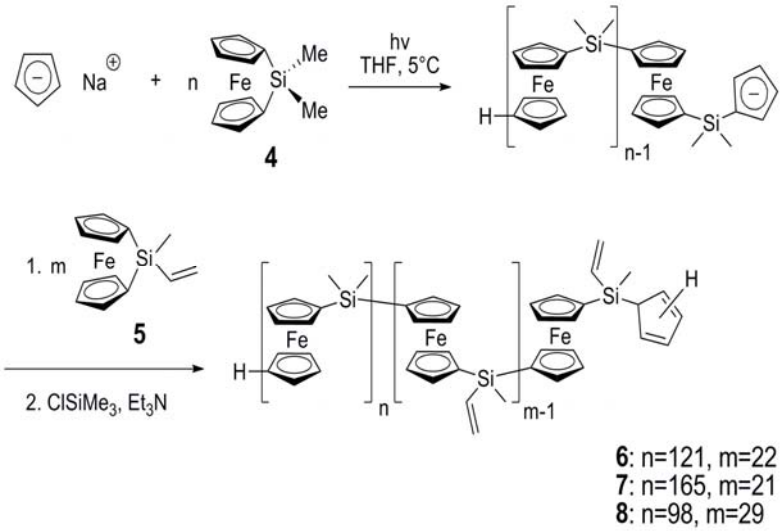


Figure 1: Schematic representation of the linear-hyperbranched block copolymers based on poly(dimethylferrocenylsilane)-*b*-poly(methylvinyl-ferrocenylsilane) (PFDMS-*b*-PFMVS) after hypergrafting of the AB_2-monomers (abbreveations: series 1: methyl diallyl silane (**MDAS**) (**1**); series 2: methyl diundecenyl silane (**MDUS**) (**2**); series 3: ferrocenyl diallyl silane (**fcDAS**) (**3**)).

Results and Discussion

Synthesis. Two different [1]-silaferrocenophanes were synthesized using literature methods: dimethyl-[1]-silaferrocenophane (**4**) and methylvinyl-[1]-silaferrocenophane (**5**).[13] Polymerization was conducted by consecutive PROP of **4** (as first block) and **5** (as second block) in tetrahydrofuran (THF) as solvent at 5°C using sodium cyclopentadienide (NaCp) as the initiator (Scheme 1, molecular weight data can be found in Table 1).



Scheme 1. Photolytic anionic ring-opening polymerization of dimethyl-[1]-silaferrocenylsilane and methylvinyl-[1]-silaferrocenylsilane.

After workup, these linear diblock copolymers serve as macromolecular cores for the ensuing hyperbranching hydrosilylation polyaddition of **1**, **2** and **3** to generate the linear-hyperbranched block copolymers. A higher reactivity of the core molecule compared to the monomers is desirable to achieve full incorporation of the core and to prevent homopolymerization of the monomer without core. In a previous report[17d] the use of highly reactive double bonds in block copolymers containing poly(allyl glycidyl ether) (PAGE) proved the redundancy of the slow monomer addition technique in this special case. Usually this strategy is necessary to gain molecular weight control, when a core with aliphatic double bonds is applied, e.g., for poly(butadiene).[17a] As it is well-known from literature, vinyl silanes show even higher reactivity in hydrosilylation reactions compared to the aforementioned oxy-allyl groups.[19] Thus, we believed that using such highly reactive cores slow monomer addition can also be avoided. Detailed studies demonstrated that the highly reactive vinyl

silane groups of the core permit simultaneous copolymerization, avoiding slow monomer addition. Moreover, the vinyl silane groups are fully incorporated, even when the sterically demanding monomer **2** is polymerized. In the case of the PAGE core we found unreacted core double bonds and ascribed this finding to steric reasons. Moreover, the Si-vinyl bonds cannot be isomerized, in contrast to allyl groups that can be rearranged to propenyls, which are unreactive in hydrosilylation.

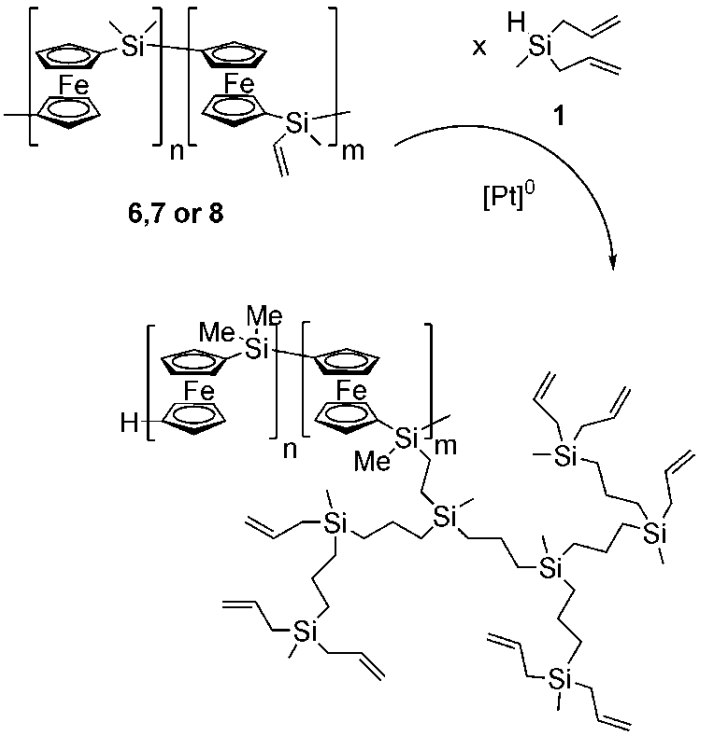
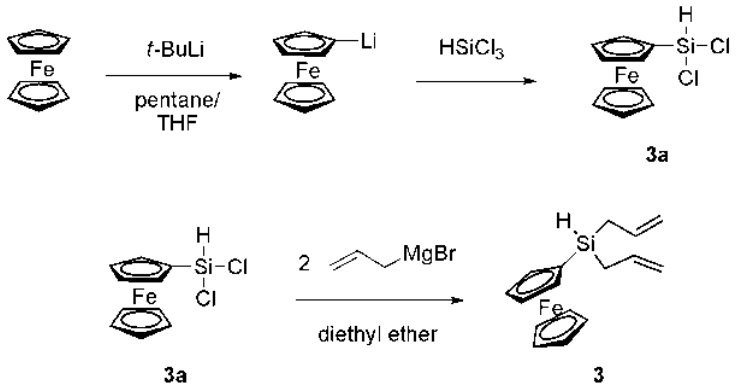


Figure 2. Hypergrafting of methyl diallyl silane (**1**) via hydrosilylation polyaddition onto linear diblock copolymer precursors.

Different equivalents of the AB_2-monomer were added to the core and polyaddition was started by the addition of one droplet of Karstedt's catalyst (Figure 1 shows a scheme for polyaddition with monomer **1**). As a side reaction, homopolymerization of the AB_2-monomer is still observed, as reported previously.[17] The undesired low molecular weight homopolymer side product can be conveniently separated from the block copolymers in different ways: 1.) preparative SEC in THF by cutting off the lower molecular masses (<10,000 g/mol). 2.) Dialysis in THF using a dialysis tube with a molecular weight cut-off of ca. 8,000 g/mol. 3.) repetitive precipitation of the crude reaction mixture from THF into hexanes/methanol (9:1).

After separation of the broadly distributed homopolymer (PDI>3) the desired narrowly distributed linear-hyperbranched block copolymer is obtained in reasonable yields (50-80%).

Different AB_2-monomers have been employed: **1** and **2** were previously investigated in polyaddition reactions. A third novel AB_2-monomer was synthesized, containing a ferrocenyl moiety to introduce electroactivity into the hyperbranched poly(carbosilane). Ferrocenyldiallylsilane (**3**) is synthesized in two steps, starting from ferrocene via dichloroferrocenylsilane (**3a**); the synthesis is shown in Scheme 2.



Scheme 2. Synthesis of diallylferrocenylsilane (**3)**.

Characterization. The linear-hyperbranched block copolymers were investigated via SEC measurements and NMR-spectroscopy. Molecular weights determined via SEC are underestimated, as expected for branched polymers. As the tabulated data shows, underestimation of molecular weight is more pronounced, when the degree of polymerization of the hyperbranched block increases. Thus, determination of absolute molecular weights of the block copolymers cannot be conducted via SEC experiments. Due to the high molecular weights of the polymers and the absence of a well-detectable end group in the linear block copolymers, determination of the absolute molecular weights by NMR spectroscopy is not applicable or would cause a large error. Thus, molecular weights were determined as follows: i) ^{1}H-NMR of the linear block copolymers (**6**-**8**) provides the block ratio PFDMS:PFMVS due to distinct signals for the methyl group in PFMVS at δ = 0.61 ppm (methyl shifts in PFDMS are detected at δ = 0.54 ppm) and the signals for the vinyl group (δ = 6.52-5.76 ppm; compare Supporting Information). ii) Synthesis of PFDMS homopolymers with an end group[21]having distinct NMR resonances and comparison of the molecular weights determined via ^{1}H-NMR and SEC showed that SEC values vs. PS-standards

give reliable molecular weights with an estimated error of ca. 5%. Thus, we used the molecular weights from the SEC-experiments for **6**-**8** as a reference in the ^{1}H-NMR spectra and by knowledge of the block ratio the absolute molecular weight was determined. After hydrosilylation polyaddition the additional signals for the PCS-block can be integrated in the ^{1}H-NMR spectra separately and the DP_n of the AB_2-monomers can be calculated (cf. Table 1 and Figure 3).

Table 1. Molecular weight data and polydispersity indices for linear and linear-hyperbranched block copolymers. Abbreviations: PFDMS: poly (dimethylferrocenylsilane); PFMVS: poly(methylvinylferrocenylsilane); PMDAS: poly(methyl diallyl silane); PMDUS: poly(methyl diundecenyl silane); PfcDAS: poly(ferrocenyl diallyl silane).

#	sample	M_n[a]	PDI[a]	M_n[b]
6	$PFDMS_{121}$-$PFMVS_{22}$	35,600	1.09	-
7	$PFDMS_{165}$- $PFMVS_{21}$	45,400	1.09	-
8	$PFDMS_{98}$- $PFMVS_{29}$	31,000	1.11	-
9	$PFDMS_{121}$-($PFMVS_{22}$-$hbPMDAS_{60}$)	38,000	1.16	43,200
10	$PFDMS_{121}$-($PFMVS_{22}$-$hbPMDAS_{88}$)	41,400	1.06	46,800
11	$PFDMS_{121}$-($PFMVS_{22}$-$hbPMDAS_{235}$)	44,500	1.07	65,300
12	$PFDMS_{165}$-($PFMVS_{21}$-$hbPMDAS_{85}$)	49,000	1.19	56,200
13	$PFDMS_{121}$-($PFMVS_{22}$-$hbPMDUS_{25}$)	37,300	1.09	44,200
14	$PFDMS_{121}$-($PFMVS_{22}$-$hbPMDUS_{30}$)	43,400	1.08	46,100
15	$PFDMS_{121}$-($PFMVS_{22}$-$hbPMDUS_{35}$)	47,800	1.20	48,900
16	$PFDMS_{98}$-($PFMVS_{29}$-$hbPfcDAS_{35}$)	34,200	1.05	41,500
17	$PFDMS_{98}$-($PFMVS_{29}$-$hbPfcDAS_{60}$)	36,600	1.15	48,900
18	$PFDMS_{98}$-($PFMVS_{29}$-$hbPfcDAS_{76}$)	38,700	1.07	53,900
19	$PFDMS_{98}$-($PFMVS_{29}$-$hbPfcDAS_{110}$)	37,500	1.06	66,800

[a] determined via size exclusion chromatography in tetrahydrofuran. [b] determined via ^{1}H-NMR.

NMR-Analysis As mentioned previously, ^{1}H-NMR spectroscopy was used to determine absolute molecular weights of the block copolymers. Figure 3 shows three representative ^{1}H-NMR spectra for linear-hyperbranched block copolymers based on all three AB_2-monomers. The ^{1}H-NMR spectra for the linear precursors can be found in the Supporting Information. In the case of **2** as the respective monomer, the DP_n can be determined by integration of the distinct methyl-signals of the hbPCS block (δ = 0-0.2 ppm). Additionally, one can distinguish between monomers that are directly linked to the core (ca. δ = 0.1 ppm) and monomers in the periphery (ca. δ = 0.18 ppm). The double bonds of hbPCS can be detected at lower field (δ = 5-6 ppm); partial isomerization of the double bonds during hydrosilylation is also detected (Figure 3B).

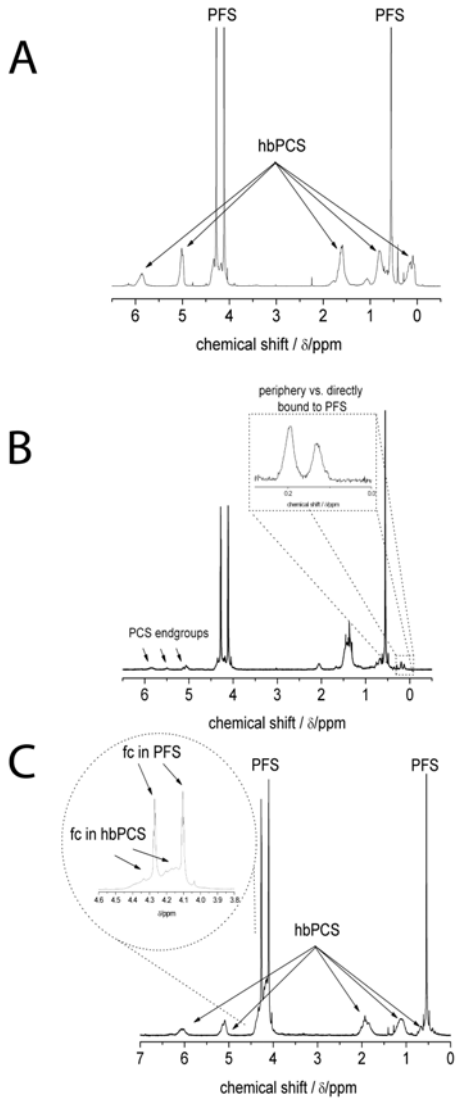


Figure 3. ^{1}H-NMR (benzene-d_6) of different linear-hyperbranched block copolymers:

A) **PFDMS$_{121}$-(PFMVS$_{22}$-hbPMDAS$_{88}$)** (**10**);

B) **PFDMS$_{121}$-(PFMVS$_{22}$-hbPMDUS$_{25}$)** (**13**);

C) **PFDMS$_{98}$-(PFMVS$_{29}$-hbPfcDAS$_{76}$)** (**18**).

For polymers with **3** as the branching monomer additional broad ferrocenyl signals can be detected between δ = 4.0-4.4 ppm overlapping with the signals representing the PFS-backbone that gives much sharper signals (Figure 3C). Polymers with **1** as the AB_2-monomer show several signals in the silane region (δ = 0-1 ppm) of the ^{1}H-NMR spectrum for the methyl group, indicating the branched structure of the PCS segment. An analysis by ^{13}C-NMR and ^{29}Si-NMR spectroscopy (Figure 4) supports the complete reaction of the core vinyl bonds and evidences the hyperbranched nature of the PCS block. Separate signals for dendritic (δ = 1.2 ppm), linear (δ = 0.8 ppm) and terminal (δ = 0.23 ppm) silane signals in the ^{29}Si spectra of the polymers for polymers with **1** as the AB_2-monomer are observed. In addition, the signal for the core Si-vinyl bonds (δ = -13 ppm) vanishes after hydrosilylation and is shifted to lower field (δ = -3.8 ppm), due to the presence of the attached carbosilane moiety. Interestingly, the ^{29}Si shifts for copolymers with **3** as a monomer differ significantly from the abovementioned spectra: the dendritic Si-centres can be detected at δ = 2.6 ppm, the linear at δ = -3.6 ppm and the terminal ^{29}Si centers at δ = -4.7 ppm. Furthermore, the signal for the reacted core vinyl bonds is shifted to higher field (δ = -21 ppm). In the ^{13}C-NMR spectrum of polymers **16**-**19** additional broad signals for ferrocenes in the hbPCS compartment can be assigned at (δ = 68.2 and 70.7 ppm) separate from the signals for ferrocene-carbons of the PFDMS-backbone (δ = 73.2 and 71.3 ppm) and the reacted PFMVS-core (δ = 73.4 and 71.4 ppm). (For spectra see Supporting Information).

Figure 4 right shows a zoom into the ^{13}C-NMR spectrum of **10** in the region from δ = 145 to 105 ppm. Here, the same observation as mentioned before for the Si centers is made: the signals for the carbon atoms of the vinyl bonds at δ = 138 ppm and 132 ppm are not detected after hypergrafting of **1**. The spectrum shows the terminal and linear allyl groups and only a small amount of isomerization to the respective propenyl signals (δ = 142.4 and 144.3 ppm) is observed. This isomerization can be prevented, when the reaction time is reduced, however, complete conversion can be maintained in this case (samples taken for IR-control: disappearance of Si-H vibration at ca. 2100 cm^{-1}).

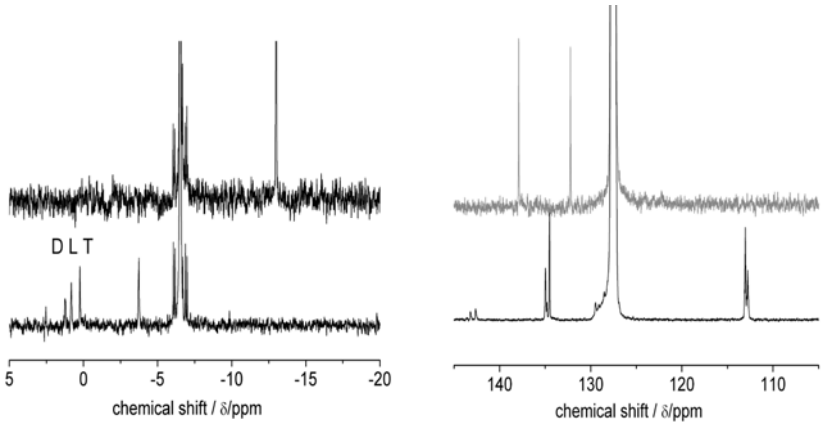


Figure 4. left: ^{29}Si-NMR spectra of 6 (top) and 10 (bottom). Right: ^{13}C-NMR spectra of 6 (top) and 10 (bottom) *NB*: benzene-d_6 = 128 ppm.

SEC-Analysis A crucial aspect for the preparation of complex macromolecular architectures is control over molecular weights and polydispersity of the resulting materials. In hyperbranched polymers, not only polydispersity with respect to molecular weight is present (as in any other synthetic polymer), but in addition, due to the randomly branched architecture, structural polydispersity has to be considered due to the large number of configurational isomers for one distinct molecular weight. SEC experiments, however, usually give an apparent molecular weight distribution. Samples that were analyzed via SEC directly after the hypergrafting step showed a multimodal SEC elugram (see Supporting Information). In addition to the desired linear-hyperbranched block copolymer, low molecular weight hbPCS are present in the mixture. After separation from the broadly distributed homopolymer by preparative SEC, dialysis in THF or repetitive precipitation, all materials exhibit a monomodal narrow apparent molecular weight distribution in SEC (compare Figure 5 and Supporting Information) with low polydispersities below 1.15 in most cases. We observed undesired coupling only after prolonged reaction time with Karstedt's catalyst, resulting in a second mode in SEC elugrams (entry 18). These high molecular weight shoulders were removed during preparative SEC, but can be prevented if the catalyst is removed from the crude reaction mixture by addition of charcoal, followed by filtration over celite (c.f. experimental section) directly after disappearance of the Si-H functionality in the IR spectrum).

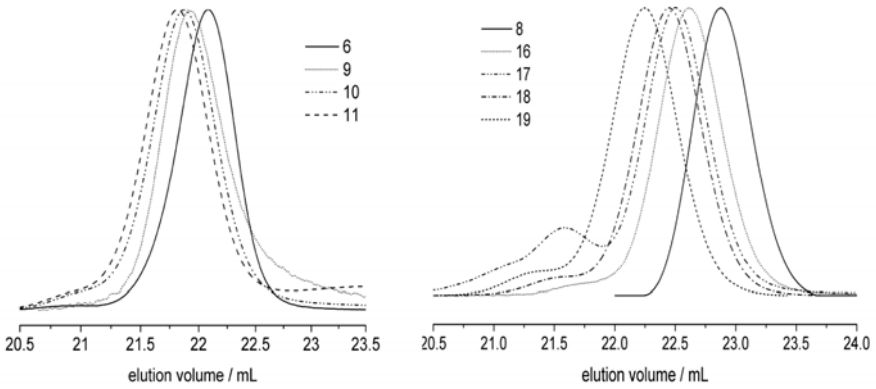


Figure 5. SEC elugrams in THF for: left: series 1 right: series 3.

Electrochemistry – A significant issue related to the synthesis of the linear-hyperbranched block copolymers was their electroactivity. Specifically, the following questions were intriguing: (i) does the electroactivity change after polyaddition of an electrochemically inactive species? and (ii) Is it possible to tune the electroactivity of the polymers by polyaddition of a novel electroactive monomer (**3**)? This is a crucial aspect for future application of such materials, e.g., for tunable (bio)sensors.

As it is well-known from the literature,[1] PFSs show two single oxidation waves in a CV-experiment, resulting from stepwise oxidation (or reduction) of the iron centers along the backbone. The first oxidation wave arises from oxidation of every second ferrocenyl moiety (Fe^{2+}) into the respective ferrocenium (Fe^{3+}) ion. The second oxidation wave at higher voltage oxidizes the remaining ferrocenes ("communicating ferrocenes"). When the voltage is reduced, the opposite devolution can be observed. The block copolymers were dissolved in dichloromethane (conc. ca. 2 g/L), containing 0.1 M Bu_4NPF_6 as conducting salt and degassed before measurements. Figure 6 shows four different CVs at different scan rates (from 0.1 V/s to 0.9 V/s): A and B represent two different linear- hyperbranched block copolymers based on the electro-inactive monomers **1** (A) (Table 1, entry **11**) and **2** (B) (Table 1, entry **14**). The resulting CVs do not differ from each other, thus their electrochemical properties are determined by the PFS backbone only and no change in their behavior is observed after hypergrafting. The additional functional groups still offer potential for further application of these materials for electrochemical devices.

If **3** is used as the respective AB_2-monomer, the electrochemical properties of the linear block are clearly affected: The first oxidation wave is shifted to higher voltages and more pronounced compared to the abovementioned samples (Figure 6 C, table 1, entry **18**); this indicates oxidation of every second ferrocenyl moiety in the PFS-chain and oxidation of the ferrocenes in the hyperbranched periphery (which are not communicating with each other due to a lack of conjugation between them). The second oxidation wave remains unchanged. For comparison Figure 6 D shows the CV measurement of a homopolymer of **3** ($M_{n(SEC)}$=1,200 g/mol, $M_{n(MALLS)}$=4,500, PDI=1.5) (separated from the crude reaction mixture from **18**), exhibiting only one single oxidation wave and no communicating ferrocenes. Polymers based on **3** might therefore be of considerable interest when oxidative or reductive activity is required at different potentials and with different intensity.

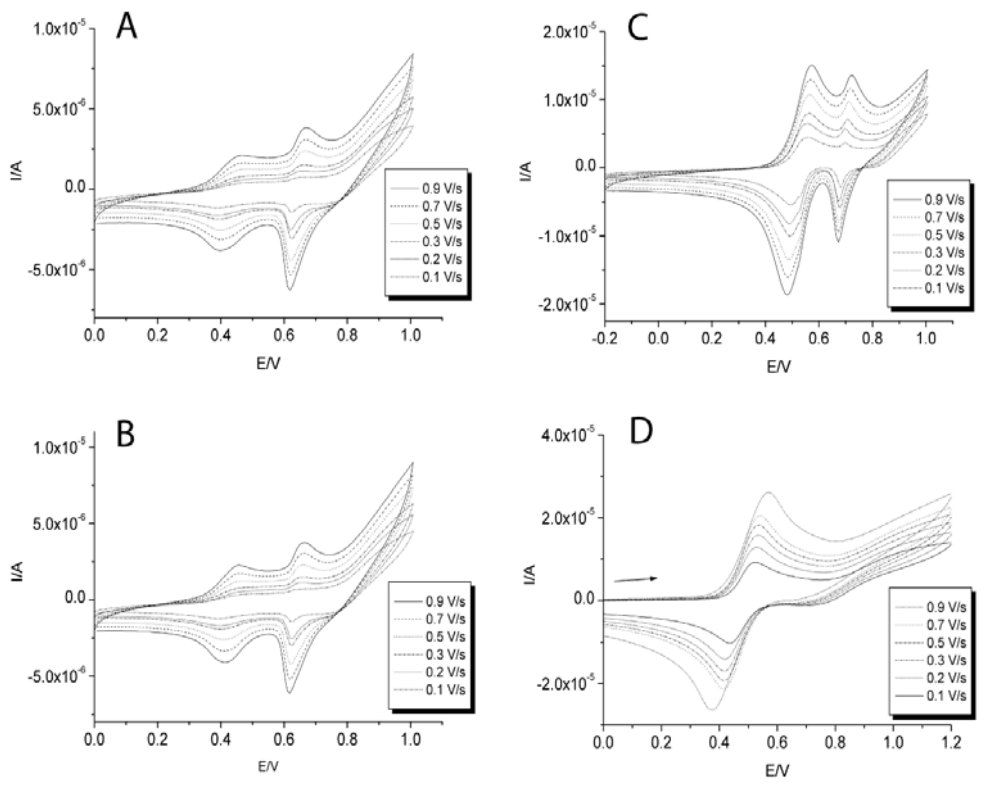


Figure 6. Cyclic voltammograms of different linear-hyperbranched block copolymers.

A = $PFDMS_{121}$-($PFMVS_{22}$-$hbPMDAS_{235}$) (**11**), B= $PFDMS_{121}$-($PFMVS_{22}$-$hbPMDUS_{30}$) (**14**), C=$PFDMS_{98}$-($PFMVS_{29}$-$hbPfcDAS_{76}$) (***18***), D= oligomers separated from the crude reaction mixture for **18**.

Transmission Electron Microscopy (TEM) An investigation concerning the self-assembly of the novel linear-hyperbranched block copolymers in solution was conducted via TEM measurements. In a previous report on PEO-*b*-hbPCS copolymers, interesting, rod-like micelles were detected in different solvents. The observed rodlike structures are believed to be a consequence of the crystallization of the linear PEO chains and the constraints resulting from the hyperbranched structure at the junction point between both blocks. Motivated by such findings, we investigated self-assembly for the novel series of block copolymers in decane, which is a non-solvent for the crystalline PFDMS-block, but a good solvent for the highly apolar hbPCS segment.

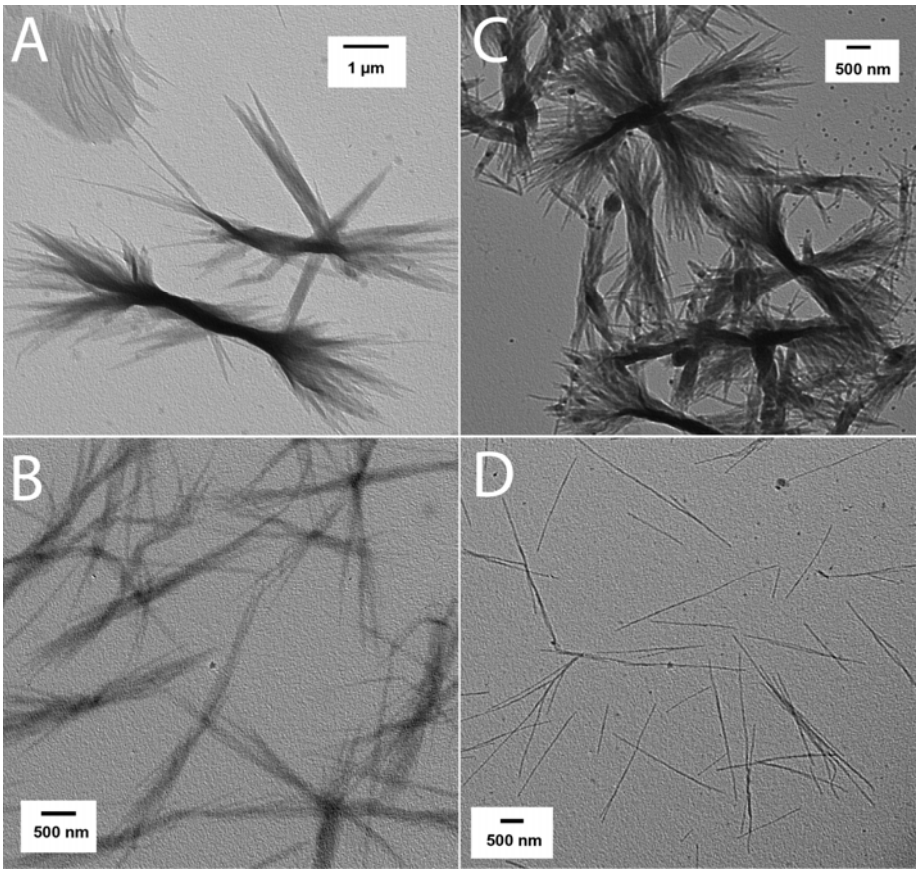


Figure 7: Transmission Electron Microscopy pictures of a decane/THF (9:1) solution (1 mg/mL) drop-cast onto copper grids A: $PFDMS_{121}$-($PFMVS_{22}$-$hbPMDAS_{60}$) (**9**); B: $PFDMS_{165}$-($PFMVS_{21}$-$hbPMDAS_{85}$) (**12**); C: $PFDMS_{121}$-($PFMVS_{22}$-$hbPMDUS_{25}$) (**13**); D: $PFDMS_{121}$-($PFMVS_{22}$-$hbPMDUS_{35}$) (**15**).

Figure 7 shows TEM pictures of block copolymers solutions in decane/THF mixtures (9:1) with a concentration of ca. 1 mg/mL, drop-cast onto a carbon-coated copper grid. Generally, large, bundled aggregates with high aspect ratio are detected for block copolymers with different hbPCS blocks. The density of these bundles varies with the DP_n of the hbPCS in the following manner: As it can be seen in Figure 7 A and C, block copolymers based on **1** and **2** as the respective AB_2-monomer form highly bundled structures at a molecular weight of ca. 8,000 g/mol for both hbPCS structures. As the molecular weight of hbPCS increases, the solubility of the block copolymers rises and less bundled aggregates are detected (Figure 7, B, M_w(hbPCS)=10,500 g/mol) or even almost distinct, single rods with a length of several micrometers (5-10 µm) are obtained (Figure 7, D, M_w(hbPCS)=12,500 g/mol). A key mechanisms for the formation of these impressive aggregates is most probably epitaxial growth. A solution of **15** was investigated 30 min after addition of decane, and shorter rods were detected (length between 250 nm and few micrometers). Solutions that had been allowed to equilibrate over a period of several hours showed cylindrical aggregates with lengths exceeding several micrometers. To gain further insight into the aggregation behavior of the materials, a micellar solution of **15** was sonicated for 30 min to destroy the long aggregates and to obtain small rods (compare Figure 8A). After addition of a unimer solution of **15** or of **12** in THF to the shortened cylindrical micelles the aspect ratio of the resulting aggregates rises and very long entangled rods can be detected via TEM investigations (Figure 8 C & D) that display several bends and crossovers. This indicates epitaxial growth of the unimer block copolymers onto the previously formed short rods that act as nuclei for a supramolecular aggregation in the nonsolvent decane (> 10 µm). Interestingly, the micellar solutions of these highly entagled aggregates stays clear over days without any precipitation indicating a very stable solution.

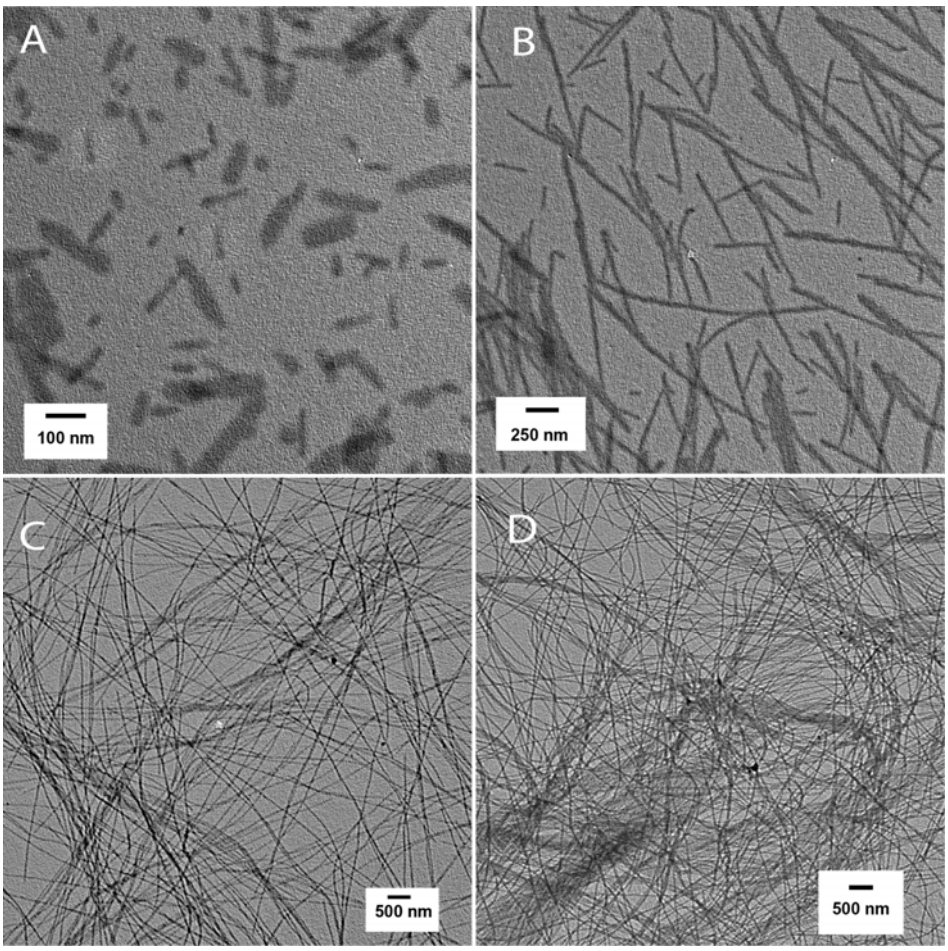


Figure 8: Transmission Electron Microscopy images of a decane/THF (9:1) solution (1 mg/mL) drop cast onto copper grids $PFDFS_{121}$-($PFMVS_{22}$-$hbPMDUS_{35}$) (**15**): (A) micellar solution after sonification for 30 min. (B) Micellar solution after 1 hour equilibration time. (C) Micellar solution of 15 sonicated for 30 min and addition of an unimer solution of $PFDMS_{165}$-($PFMVS_{21}$-$hbPMDAS_{85}$) (**12**).

Conclusion & Outlook

In summary, a straightforward two-step approach for the synthesis of linear-hyperbranched block copolymers with an organometallic linear polyferrocenylsilane block is presented. The molecular weights of the polymers can be tailored in two ways: a) the molecular weight of the linear block can be adjusted via the living anionic polymerization of ferrocenophanes very accurately; b) the molecular weight of the hyperbranched block can be controlled by the amount of AB_2-monomer employed. Narrowly distributed block copolymers are obtained in reasonable yields. It was demonstrated that different AB_2-

monomer structures can be used for the synthesis of structurally different and functional materials. Three different AB_2-monomers have been investigated: i) methyl diallyl silane (**MDAS**) (**1**) ii) methyl di(undecenyl) silane (**MDUS**) (**2**) and iii) ferrocenyl diallyl silane (**fcDAS**) (**3**). By applying these monomers in the hypergrafting step, the architecture of the hyperbranched block was varied from a high density branched material with **1** as the respective AB_2-monomer to a low density branched material, when monomer **2** is polymerized. The highly flexible hyperbranched segments based on **2** can be viewed as an analogue to low-density polyethylene. By the introduction of an additional ferrocene moiety into the hyperbranched block using **3** as a novel AB_2 monomer, the electroactivity of the resulting block copolymers can be tailored.

The electrochemical properties of the block copolymers have also been studied. Clearly, by the use of an electrochemically active AB_2-monomer one can tune the electrochemical response of the polymers, e.g., for application in sensors. Furthermore, aggregation of the block copolymers in solution has been studied. A nonsolvent (decane) for the linear crystalline poly(dimethylferrocenylsilane) block was slowly added to the block copolymer solution in THF to induce micellization. Anisotropic rod-like aggregates with varying structures and sizes depending on the molecular weight of the hyperbranched block were visualized via TEM.

Further detailed studies are currently in progress, such as variation of the core polymer to an amorphous structure and the generation of different functional groups at the polymer backbone and more detailed investigation concerning the aggregation behavior ,including light scattering techniques. The complex materials introduced here may find application as electrode material or precursors for nanostructured ferromagnetic ceramics.

Experimental Section

Instrumentation & General Procedures. Most reactions and manipulations were performed under an atmosphere of pre-purified nitrogen or argon using Schlenk techniques, or in a nitrogen-filled glovebox. The air- and moisture-stable polymers were handled in air with p.a. grade solvents after workup. ^{1}H, ^{13}C and ^{29}Si nuclear magnetic resonance spectra were recorded using a Bruker AC 300 or on a Bruker AMX 400 spectrometer, operated at 400 MHz for ^{1}H, employing deuterated chloroform as a solvent. ^{13}C-NMR spectra (referenced internally to solvent signals) at 100.15 MHz and ^{29}Si-NMR spectra (referenced externally to

TMS) at 79.49 MHz. FT-IR spectra were recorded on a Nicolet SDXC FT-IR spectrometer equipped with an ATR unit. Size exclusion chromatography (SEC) was performed with an instrument consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump and a set of three PSS-SDV 5A columns with 100, 1 000, und 100 000 Å porosity. Tetrahydrofuran was used as an eluent at 30°C and at a flow rate of 1 mL min^{-1}. UV absorptions were detected by a SpectraSYSTEM UV2000. An Optilab DSP was used as the RI detector. Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service and performing a 3rd order polynomial fit. Photocontrolled ring-opening polymerization reactions were performed with a Philips 125 W high pressure mercury arc lamp. A Pyrex filter was placed inside the quartz immersion well to filter out wavelengths below 310 nm, and a thermostated water bath was used to maintain the reaction temperature at 5 °C. Cyclic voltammetry (CV) was performed using a BAS CV-50W potentiostat using dichloromethane as a solvent under an inert atmosphere (N_2). The supporting electrolyte was tetra-n-butylammonium hexafluorophosphate (TBAH [0.1 M]. All experiments were performed at 25 °C, in a conventional three-electrode cell using a platinum working electrode (A=0.02 cm^2). All potentials are referred to a saturated calomel reference electrode (SCE). A coiled platinum wire was used as counter electrode. A Philips EM420 transmission electron microscope (TEM) using a LaB_6 cathode at an acceleration voltage of 120 kV was used to obtain TEM images. TEM grids (carbon film on copper, 300 mesh) were obtained from Electron Microscopy Sciences Hatfield, PA, USA.

Materials. Allyl bromide, 11-bromoundec-1-ene, dichloromethylsilane, chlorodimethylsilane, ferrocene, trichlorosilane, *t*-butyl lithium (1.5M in pentane) were used as received. Pentane and diethyl ether were dried by refluxing them over sodium/benzophenone and were distilled prior to use. Platinumdivinyltetramethyldisiloxane complex (Karstedt catalyst) in xylene with 2.1-2.4% platinum concentration was purchased from Gelest. Deuterated chloroform and benzene were purchased from Deutero GmbH, dried and stored over molecular sieves. 1,1'-dilithioferrocene ($fcLi_2$*2/3TMEDA) was prepared by a literature method.[22]

Diallylmethylsilane (1). The monomer was synthesized according to literature procedures[23] using 68.96g (0.57mol) allylbromide, 69.28g (2.85mol) magnesium and 21.86g (0.19mol) dichloromethylsilane. Yield: 13.82g (57%); bp 123°C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm]: 5.78 (m, 2H, -CH=CH_2); 4.95-4.83 (m, 4H, -CH=CH_2); 3.79 (m, 1H, Si-H); 1.68-1.52 (m, 4H, -CH_2-CH=CH_2); 0.09 (d, J=3.67Hz, 3H, Si-CH_3).

Methyldi(undec-10-enyl)silane (2). The monomer was synthesized according to literature procedures[23] using 50g (21.4mmol) 11-bromoundec-1-ene, 26.1g (1,1mol) magnesium and 8.21g (7,1mmol) dichloromethylsilane. Yield: 17,4g (75%); bp 144-149°C, 0,2mbar. ^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm]: 5.83 (m, 2H, -CH=CH_2); 4.97 (dd, 4H, -CH=CH_2); 3.77 (m, 1H, Si-H); 2.05 (m, 4H, -CH_2-CH=CH_2); 1.47-1.14 (m, 28H, CH_2); 0.58 (m, 4H, Si-CH_2); 0.05 (d, J=3.68Hz, 3H, Si-CH3).

Dichloroferrocenylsilane (3a). An amount of 13.02 g of ferrocene (70mmol) was suspended in 75 mL freshly distilled pentane/THF (1:1) under N_2 atmosphere, cooled to 0°C and stirred for 15 min. A volume of 50ml of a 1.5M solution of *t*-butyllithium in pentane (75mmol) was added over 60 min. The mixture was stirred for an additional 30 min at 0°C and was then cooled to -78°C. The mixture was treated with 11.38 g $HSiCl_3$ (84mmol) via syringe. The mixture was allowed to warm to room temperature and stirred over night. The precipitate was removed by filtration and the filtrate was concentrated by evaporation of the solvent. The residue was diluted with 30ml of pentane and filtered once again. Pentane was removed and the product was purified by vacuum distillation (bp. 77-80°C/4x10^{-3}mbar). Yield: 6.14g (31%) of a viscous red oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm]: 6.03 (s, 1H, Si-H); 4.56 (t, J = 1.47 Hz, 2H, η-

C_5H_4); 4.39 (t, J = 1.47 Hz, 2H, η-C_5H_4); 4.28 (s, 5H, η-C_5H_5).

Diallylferrocenylsilane (3). A solution of 6.00 g dichloroferrocenylsilane (**3a**) (21 mmol) in 10 mL dry diethyl ether was slowly added to 90 mL of a freshly prepared solution of allylmagnesiumbromid (0.9 M; 81 mmol) in diethyl ether. For completion of the reaction the mixture was stirred for 12h under reflux. At 0°C 10ml of a sat. solution of NH_4Cl were added, followed by 15ml H_2O. The organic layer was separated and washed twice with a sat.

Na_2CO_3-solution. The diethyl ether layer was washed with water until neutral reaction of the aqueous layer. The organic layer was dried with $MgSO_4$ and 5.9 g of the crude product were obtained by removal of the solvent. The product was purified by column chromatography (PE, R_f=0.22). Yield: 4.6g (74%) of a red oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm]: 5.92 (m, 2H, -CH=CH_2); 5.09-4.85 (m, 4H, -CH=CH_2); 4.38 (m, 2H, η-C_5H_4); 4.32 (m, 1H, Si-H); 4.19 (m, 2H, η-C_5H_4); 4.17 (s, 5H, η-C_5H_5); 1.91-1.81 (m, 4H, CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$) δ [ppm]: 134.56 (-CH=CH_2); 114.05 (-CH=CH_2); 73.75 (η-C_5H_4(CH)); 71.13 (η−C_5H_4(CH)); 68.51 (η- C_5H_5); 64.57 (η-C_5H_4(C); 19.84 (CH_2). ^{29}Si-NMR (60 MHz, $CDCl_3$) δ [ppm]: -4.20. IR ν [cm^{-1}]: 3075 (stretching C-H); 2954, 2922, 2853 (stretching C-H), 2117 (stretching Si-H); 1630 (stretching C=C). FD-MS: 295.9 (calc. for $C_{16}H_{20}FeSi$: 296.3). Elemental Analysis: C, 64.85%; 6.80% (cal. for $C_{16}H_{20}FeSi$: C, 64.87%; H, 6.80%).

Dimethyl-[1]-silaferrocenophane (4). Over a period of 5 min, 4.6 mL of Me_2SiCl_2 (38 mmol) was added dropwise to a suspension of 10.0 g of $fcLi_2$*2/3TMEDA (36.4 mmol) in 500 mL of diethyl ether at -60°C. The reaction mixture was then slowly allowed to warm to 20 °C over 4 h, during which the reaction mixture changed from orange-yellow to red. The solvent and excess Me_2SiCl_2 were removed in vacuo. The crude product was redissolved in dry hexane, filtered and concentrated in vacuo. Crystallization of the crude product from hexanes (-20°C) and repetitive sublimation (3x, 0.005 mm,) at room temperature onto a cold probe afforded 6.98 g (79%) of red crystalline [1]ferrocenophane **4.** ^{1}H-NMR (300 MHz,C_6D_6) δ [ppm]: 0.51 (s, 6H, Me), 4.08 (t, *J*H-H) 1.7 Hz, 4H, Cp), 4.48 (t, *J*H-H) 1.7 Hz, 4H, Cp).

Methylvinyl-[1]-silaferrocenophane (5). The synthesis and purification is analogues to 4, instead of Me_2Cl_2, (CH_2=CH)$MeSiCl_2$ was used as the respective silane (4.97 mL, 38 mmol). Yield: 6.5 g (70%).

^{1}H-NMR (300 MHz,C_6D_6) δ [ppm]: 0.61 (s, 3H, Me), 4.08 (t, *J*H-H) 1.7 Hz, 4H, Cp), 4.48 (t, *J*H-H) 1.7 Hz, 4H, Cp), 5.98 (dd, 2H, J=20 Hz, J=80Hz), 6,54 (t, 1H, J=16Hz).

General procedure for photocontrolled polymerization of 4 and 5. In an inert atmosphere glove box a Schlenk tube was charge with 4 (500 mg, 2.06 mmol) dissolved in THF (ca. 4 mL) and Na[C_5H_5] (0.021 mmol, 21µL of a 1M solution in THF) was added to the dark red solution in the absence of light. The mixture was photolyzed for 4 h at 5 °C. The reaction vessel containing an orange solution was introduced into the glove box and the calculated amount of **5** (160mg, 0.63 mmol for entry 8, table 1) was added in absence of light. Photolysis was continued for 2 h and the reaction was quenched with 10 drops of freshly distilled Me_3SiCl. The solvents were removed in vacuo to give an orange film. The film was redissolved in THF and precipitated into MeOH to give an orange powder that was dried in vacuo at 40°C for 48 h and stored under argon at 5°C. Molecular weight data can be found in table 1 (entries 6-8).

^{1}H-NMR (300 MHz, C_6D_6) δ [ppm]: 6,54 (t, *J*=16Hz), 5.98 (dd, *J*=20 Hz, *J*=80Hz), 4.31-4.00 (br, m, Cp), 0.62 (s), 0.54(s). ^{13}C-NMR (100.15 MHz, C_6D_6) δ [ppm]: 137.9 (Si-*C*H=CH_2), 132.2 (Si-CH=*C*H_2), 73.5-71.3 (Cp), -1.0 (Si*Me*$_2$), -3.3 (Si*Me*Vi). ^{29}Si-NMR (79.49 MHz, C_6D_6) δ [ppm]: -6.5 (*Si*Me_2), -13.0 (*Si*MeVi).

General Procedure for hypergrafting of AB_2-monomers (1, 2, 3) to linear PFS-block copolymers (6, 7, 8). 100 mg of the polymer core was placed in a Schlenk tube under argon. The polymer was dissolved in dry chlorobenzene (ca 200 µL) and the calculated amount of AB_2-monomer was added. The mixture was heated to 60°C and 2µL (0.25 µmol Pt) of Karstedt's catalyst (2.4% in xylene) was added to start the reaction. The tube was closed by a Teflon tap and hydrosilylation was continued for ca. 10 h (until absence of Si-H (at ca. 2100 cm^{-1}) vibration in the IR spectrum). The sludge was diluted with 5 mL THF, 1 mL MeOH and allowed to stir in the presence of an excess of active charcoal to bind most of the platinum. The solution was filtrated over celite to remove charcoal, concentrated in vacuo and precipitated into MeOH. After drying in vacuo the mixture of hyperbranched homopolymer and desired block copolymer was either purified by a) dialysis in THF using a dialysis tube with a molecular weight cut-off of ca. 8 kg/mol to remove the hbPCS. b) repetitive precipitation into hexanes to remove the hexane-soluble hbPCS (only applicable for block copolymers with a low DP_n of the hypergrafted hbPCS). c) Preparative SEC in THF to remove all low molecular material. Yields vary between 40-90%. Molecular weight data can be found in table 1 (entries 9-19).

NMR characterization for block copolymers based on **1**: ^{1}H-NMR (300 MHz, C_6D_6): 5.85 (m, C*H*=CH_2), 4.98 (m, CH=C*H*$_2$), 4.31-4.00 (br, m, Cp), 1.83-1.31 (br, m, SiC*H*$_2$), 1.10-0.62 (br, m, SiC*H*$_2$), 0.54 (s, Si*Me (PFS)*), 0.24-0.01(br, m, Si*Me (PCS)*). ^{13}C-NMR (100.15 MHz, C_6D_6) δ [ppm]: 134.9 *(linear),* 134.5 (*terminal*) (*C*H=CH_2), 113.1*(linear),* 112.8 (*terminal*) (CH=*C*H$_2$), 73.5-71.0 (Cp), 21.9-18.0 (different *C*H$_2$), -1.0 (Si*Me$_2$ (PFS)*), -4- (-6.4) (different Si*Me*). ^{29}Si-NMR (79.49 MHz, C_6D_6) δ [ppm]: 1.2 (dendritic PCS), 0.8 (linear PCS), 0.2 (terminal PCS), -3.5 (*Si*Me (*PFS*)), -6.5 (*Si*Me$_2$ (*PFS*)).

NMR characterization for block copolymers based on **2**: ^{1}H-NMR (300 MHz, C_6D_6): 5.85 (br, m, C*H*=CH_2), 5.10 (br, m, CH=C*H*$_2$), 4.31-4.00 (br, m, Cp), 2.06 (br, CH_2), 1.83-1.31 (br, m, SiC*H*$_2$), 1.40 (br, C*H*$_2$), 0.70-0.56 (br, Si*Me (PFS)*), 0.18 (br, Si*Me (PCS directly bound to PFS)*), 0.10 (br, Si*Me (PCS periphery)*). ^{13}C-NMR (100.15 MHz, C_6D_6) δ [ppm]: 134.9, 134.5 (*C*H=CH_2), 113.1, 112.8 (CH=*C*H$_2$), 73.5-71.0 (Cp), 21.9-18.0 (different *C*H$_2$), -1.0 (Si*Me$_2$ (PFS)*), -4.2 (different Si*Me*).

NMR characterization for block copolymers based on **3**: ^{1}H-NMR (300 MHz, C_6D_6): 6.04 (m, C*H*=CH_2), 5.14 (m, CH=C*H*$_2$), 4.35-4.01 (br, m, Cp), 1.96-0.92 (br, m, SiC*H*$_2$), 0.55 (s, Si*Me$_2$ (PFS)*), 0.28(s, Si*Me (PFS)*). ^{13}C-NMR (100.15 MHz, C_6D_6) δ [ppm]: 135.3 (*linear*), 134.9 (*terminal*) (*C*H=CH_2), 113.5 (*linear*), 113.2 (*terminal*) (CH=*C*H$_2$), 73.5-71.0 (Cp (PFS)), 70.7, 68.2 (br, *Cp* (*PCS*)), 21.9-18.0 (different *C*H$_2$), 0.9 (Si*Me* (*PFS*), -1.0 (Si*Me$_2$ (PFS)*). ^{29}Si-NMR (79.49 MHz, C_6D_6) δ [ppm]: -2.6 (dendritic PCS), -3.6 (linear PCS), -4.6 (terminal PCS), -6.5 (*Si*Me$_2$ (*PFS*)), -21.5 (*Si*Me (*PFS*)).

Preparation of TEM samples. 1 mg block copolymer was dissolved in 50 µL of THF. Then decane was added drop wise to the mixture to give a 9:1 mixture of decane: THF. The opaque solutions were allowed to stabilize for 12 h and were drop cast onto copper TEM grids and dried over night to remove the solvents.

References:

[1] (a) R. D. Archer *Inorganic and Organometallic Polymers*; John Wiley & Sons: New York, **2001**. (b) A. S. Abd-El-Aziz *Macromol. Rapid. Comm.* **2002**, *23*, 995-1031. (c) Whittell, G.R.; Manners, I. *Adv. Mater.* **2007**, *19*, 3439-3468. (d) I. Manners *Science* **2001**, *294*, 1664-1666.

[2] a) C. Simionescu, T. Lixandru, I. Negulescu, I. Mazilu, L. Tataru, *Makromol. Chem.* **1973**, *163*, 59-74. b) M. Baumert, J. Fröhlich, M. Stieger, H. Frey, R. Mülhaupt, H. Plenio **Macromol. Rapid Commun. 1999**, **20**, 203-209.

[3] K. Kulbaba, I. Manners, *Macromol. Rapid Commun.* **2001**, *22*, 711-724.

[4] (a) C. Kloninger, M. Rehahn *Macromolecules* **2004**, *37*, 1720-1727. (b) J.Y. Cheng, C.A. Ross, V. Z.-H. Chan, E.L. Thomas, R. G. H. Lammertink, G.J. Vancso *Adv. Mater.* **2001**, *13*, 1174-1178. (c) H.B. Eitouni, N.P. Balsara *J. Am. Chem. Soc.* **2004**, *126*, 7446-7447. (d) S. Lastella, Y.J. Jung, H. Yang, R. Vajtai, P.M. Ajayan, C.Y. Ryu, D.A. Rider, I. Manners *J. Mater. Chem.* **2004**, *14*, 1791-1794. (e) C. Hinderling, Y. Keles, T. Stöckli, H.F. Knapp, T. de los Acros, P. Oelhafen, I. Korczagin, M.A. Hempenius, G.J. Vancso, R. Pugin, H. Heinzelmann *Adv. Mater.* **2004**, *16*, 876- 879. (f) Rider, D.A.; Liu, K.; Eloi, J-C.; Vanderark, L.; Yang, L.; Wang, J-Y.; Grozea, D.; Lu, Z-H.; Russell, T.P.; Manners, I. *ACS Nano* **2008**, *2*, 263-270. (g) K.T. Kim, G.W.M. Vandermeulen, M.A. Winnik, I. Manners *Macromolecules* **2005**, *38*, 4958-4961. (h) K.T. Kim, C. Park, G.W.M. Vandermeulen, D.A. Rider, C. Kim, M.A. Winnik, I. Manners *Angew. Chem., Int. Ed.* **2005**, *44*, 7964-7968.

[5] Arsenault, A.C.; Puzzo, D.P.; Manners, I.; Ozin, G.A. *Nature Photonics* **2007**, *1*, 468-472.

[6] a) R. G. H. Lammertink, M. A. Hempenius, J. van den Enk, V. Z.-H. Chan, E. L. Thomas, G. J. Vancso, *Adv. Mater.* **2000**, *12*, 98-103. b) S. B. Clendenning, S. Aouba, M. S. Rayat, D. Grozea, J. B. Sorge, P. M. Broderson, R. N. S. Sodhi, Z.-H. Lu, C. M. Yip, M. R. Freeman, H. E. Ruda, I. Manners, *Adv. Mater.* **2004**,*16*, 215-219.

[7] R. Resendes, A. Berenbaum, G. Stojevic, F. Jäkle, A. Bartole, F. Zamanian, G. Dubois, C. Hersom, K. Balmain, I. Manners, *Adv. Mater.* **2000**, *12*, 327-330.

[8] P.W. Cyr, M. Tzolov, I. Manners, E. H. Sargent, *Macromol. Chem. Phys.* **2003**, *204*, 915-921.

[9] M. J. MacLachlan, M. Ginzburg, N. Coombs, T. W. Coyle, N. P. Raju, J. E. Greedan, G. A. Ozin, I. Manners, *Science* **2000**, *287*, 1460-1463.

[10] a) S. Lastella, Y. J. Jung, H. C. Yang, R. Vajtai, P. M. Ajayan, C. Y. Ryu, D. A. Rider, I. Manners, *J. Mater. Chem.* **2004**, *14*, 1791-1794. b) C. Hinderling, Y. Keles, T. Stöckli, H. F. Knapp, T. de los Arcos, P. Oelhafen, I. Korczagin, M. A. Hempenius, G. J. Vancso, R. Pugin, H. Heinzelmann, *Adv. Mater.* **2004**, *16*, 876-879.

[11] a) C. Paquet, P. W. Cyr, E. Kumacheva, I. Manners, *Chem. Mater.* **2004**, *16*, 5205-5211. b) L. I. Espada, M. Shadaram, J. Robillard, K. H. Pannell*, J. Inorg. Organomet. Polym.* **2000**, *10*, 169-176.

[12] D.A. Foucher, B.-Z. Tang, I. Manners *J. Am. Chem. Soc.* **1992**, *114*, 6246-6248.

[13] (a) M. Tanabe, I. Manners *J. Am. Chem. Soc.* **2004**, *126*, 11434- 11435. (b) M. Tanabe, G.W.M. Vandermeulen, W.Y. Chan, P.W: Cyr, L. Vanderark, D.A. Rider, I. Manners *Nat. Mater.* **2006**, *5*, 467-470.

[14] a) J. A. Massey, K. N. Power, M. A. Winnik, I. Manners, *Adv. Mater.* **1998**, 10, 1559-1562. b) R. G. H. Lammertink, M. A. Hempenius, E. L. Thomas, G. J. Vancso, *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1009-1021. c) U. Datta, M. Rehahn, *Macromol. Rapid Commun.* **2004**, *25*, 1615-1622. d) H. B. Eitouni, N. P. Balsara, *J. Am. Chem. Soc.* **2004**, *126*, 7446-7447.

[15] J.M.J. Fréchet, D.A. Tomalia *Dendrimers and other Dendritic Polymers*; John Wiley & Sons: New York, **2001**.

[16] a) J.C.M. Van Hest, D.A.P. Delnoye, M.W.P.L. Baars, C. Elissen-Román, M.H.P. van Genderen, E.W. Meijer *Chem. Eur. J.* **1996**, *2*, 1616-1626. b) I. Gitsov, J.M.J. Fréchet *Macromolecules* **1993**, *26*, 6536–6546. c) I. Gitsov, K.L. Wooley, C.J. Hawker, P.T. Ivaova, J.M.J. Fréchet, *Macromolecules* **1993**, *26*, 5621-5627. d) P.M. Nguyen, P.T. Hammond *Langmuir* **2006,** *22,* 7825-7832. e) C.M.B. Santini, M.A. Johnson, J.Q. Boedicker, T.A. Hatton, P.T. Hammond *Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2784-2814.

[17] a) A. G. Marcos, T.M. Pusel, R. Thomann T. Pakula, L. Okrasa, S. Geppert, W. Gronski, H. Frey *Macromolecules* **2006,** *39,* 971-977. b) E. Barriau, A.G. Marcos, H. Kautz, H. Frey *Macromol. Rapid Commun.* **2005**, *26*, 862–867. c) F. Wurm, J. Nieberle, H. Frey *Macromolecules* **2008**, *41*, 1184-1188.d) F. Wurm, H. Schüle, H. Frey *Macromolecules* **2008**, *41,* 9602-9611.

[18] S. Hilf, P.W. Cyr, D.A. Rider, I. Manners, T. Ishida, Y. Chujo, *Macromol. Rapid. Comm.* **2005**, *26*, 950–954.

[19] B. Marciniec, *''Comprehensive Handbook on Hydrosilylation''*, Pergamon Press, New York **1992**.

[20] a) R. Hanselmann, D. Hölter, H. Frey *Macromolecules* **1998**, *31*, 3790-3801. b) D.P. Bernal, L. Bedrossian, K. Collins, E. Fossum *Macromolecules* **2003**, *36*, 333-338. c) L. Pastor-Pérez, E. Barriau, E. Berger-Nicoletti, A.F.M. Kilbinger, J. Pérez-Prieto, H. Frey S.-E. Stiriba *Macromolecules* **2008**, *41*, 1189-1195.

[21] PFDMS-homopolymers were synthesized with OH-endgroup according to: I. Korczagin, M.A. Hempenius, G.J. Vancso *Macromolecules* **2004**, *37,* 1686-1690.

[22] M.S. Wrighton, M.C. Palazzotto, A.B. Bocarsly, J.M. Bolts, A.B. Fischer, L. Nadjo *J. Am. Chem. Soc.* **1978**, *100*, 7264-7271.

[23] a) C. Drohmann, M. Möller, O.B. Gorbatsevich, A.M. Muzafarov *J. Polym. Sci. Pol. Chem.* **2000**, *38*, 741-751. b) A.G. Marcos, *Dissertation*, University of Mainz **2006.**

Supporting Information for: Electroactive Linear-Hyperbranched Block Copolymers based on Linear Poly(ferrocenylsilane)s and Hyperbranched Poly(carbosilane)s

Frederik Wurm, Stefan Hilf, Ian Manners and Holger Frey

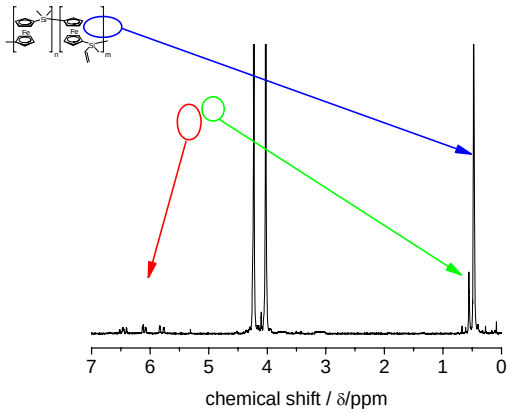


Figure S1: ^{1}H-NMR (C_6D_6) of 6

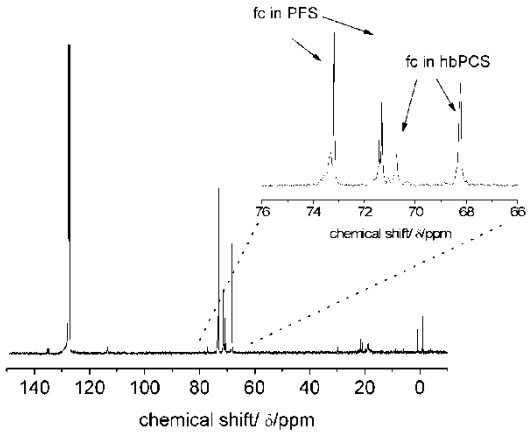


Figure S2: ^{13}C-NMR of 17 in C_6D_6 showing additional broad signals for ferrocenes in the hbPCS compartment that can be assigned at (δ = 68.2 and 70.7 ppm) separately from the signals for ferrocene-carbons of the PDMFS-backbone (δ = 73.2 and 71.3 ppm) and the reacted PMVFS-core (δ = 73.4 and 71.4 ppm).

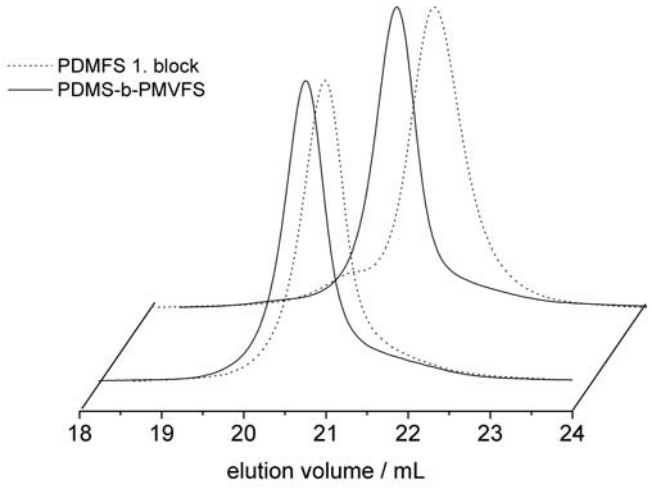


Figure S3: SEC elugrams of linear precursors 6 (top) & 7 (bottom).

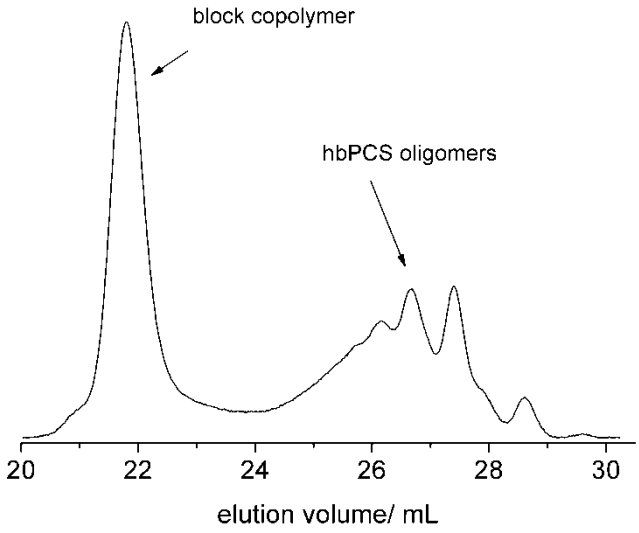


Figure S4: SEC elugram of the raw reaction mixture of 19.

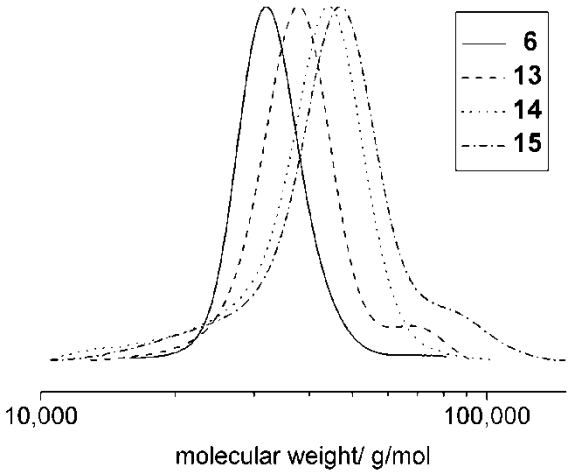


Figure S5: Molecular weight distributions obtained via SEC in THF of series 2.

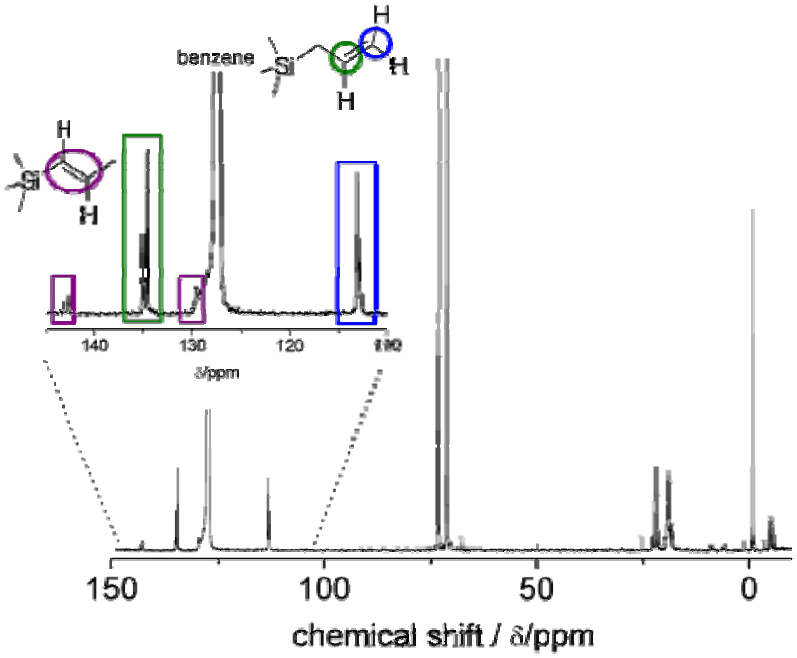


Figure S6: ^{13}C-NMR of 10 in C_6D_6.

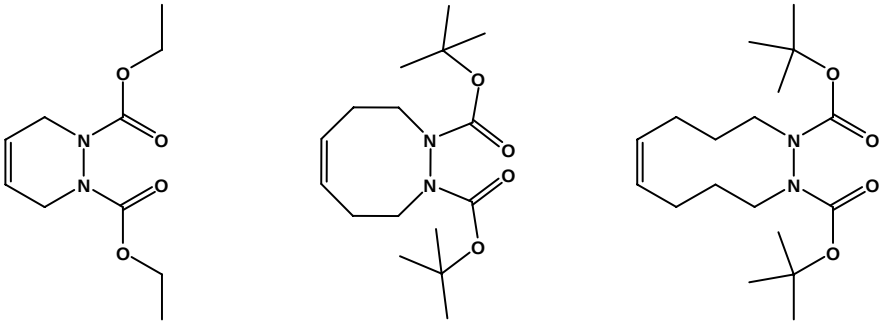
Appendix

A.1: Future Work

Several projects have not been tackled during the last years. Starting from the functionalized polymers developed in this thesis, a huge number of applications can imagined such as labeled polymers with a specific function in bio-, materials-, medical- and life sciences. Some planned projects which have been tested for feasibility are listed below.

Amine functionalized ROMP polymers

For the synthesis of amine end-capped ROMP polymers, three different possible monomers for an approach based of the Sacrificial Synthesis strategy have been synthesized and tested for polymerization and subsequent cleaving characteristics. The hydrazine N-N bond was chosen as the cleavable site since all attempts to synthesize cyclic aminoacetals have failed. Six-, eight- and ten-membered rings containing acyl protected hydrazines have been synthesized either by cycloaadition of 1,3-butadiene to diethyl-azo-diformate (DEAD) (six-membered ring) or by alkylation of terbutyl-hydrazodieformate with the respective alkenes followed by ring-closing metathesis under high dilution (eight- and ten-membered ring). The structures are given below.

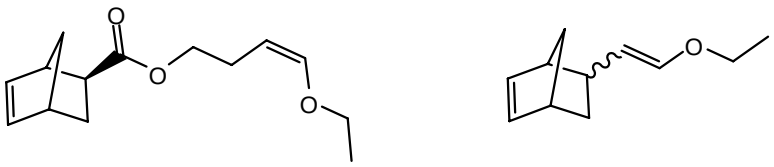


Presumably due to insufficient ring-strain and steric hindrance of the bulky acyl protective groups, the six- and the eight-membered rings did not show any initiation under the influence of both 1st generation and the 3rd generation of Grubbs' catalysts. The ten-membered ring did polymerize under catalysis of the 3rd generation catalyst, however, removal of the BOC protective groups or direct hydrogenation of the hydrazone bond failed.

The next step of this sacrificial approach should focus on the development of non-protected cyclic hydrazines. Alternatively, a Lactone Termination-based approach via oxazolines seems promising and worth testing.

Termimers

For the synthesis of branched polymers, two types of convergent strategies are possible. The first pathway, the polymerization of macromonomers, has been described in Chaper 3.3. Another way to connect polymer chains in a branching manner is given by the application of monomers that also carry a termination site, i.e. a termimer. This termination site can comprise of a vinyl ether or a lactone, while the monomer unit can be a classical ROMP monomer structure, e.g. a norbornene.



Such structures can be synthesized either by coupling of the two compartments via an ester or by direct introduction of the vinyl ester in a Wittig-Horner reaction starting from the norbornene aldehyde.

Sacrificial micelles for emulsion polymerization

The synthesis of a triblock-copolymer which consists of a hydrophobic section followed by a sacrificial section and by a hydrophilic section would enable an emulsion polymerization of e.g. styrene with the triblock acting as the emulsifier. After the radical polymerization is finished, the sacrificial block of the emulsifier could be cleaved leaving functional groups on the surface of the latex particle behind. A group that can be polymerized in a radical polymerization, such as a methacrylate, along the hydrophobic block of the emulsifying polymer would guarantee its attachment to the particle.

Light-responsive monomers

Aza-bridged benzenes are responsive to light. The conformation of the N-N double bond can be switched from *cis* to *trans* upon irradiation with a certain wavelength and vice versa. A cyclic ROMP monomer containing such a structure should experience a major change in ring strain by this switching. In fact, polymerization of this monomer may be triggered or even controlled by irradiation with the respective wavelength. Also, the control over polymerization and depolymerization, as well as the conformation of the N-N double bonds along the polymer chains of the material could give rise to materials which vary in viscosity and thermal behavior upon irradiation.

Additional vinyl lactones

The exceptional versatility of Lactone Quenching is inspirational for the development of further functional groups incorporated in such termination agents. One direction, in which further developments should direct, is the covalent attachment of further structures to the lactones which would therefore be left on the polymer chain end during the termination process. The advantage of these termination agents over substituted vinyl ethers is clearly that vinyl lactones do not suffer from complicated termination kinetics due to the presence of cis- and trans-conformational double bonds.

Another direction would be the introduction of different acids which form the lactone. Carboxylic acids and carbonic acids have been contained in the first report which gave acids and aldehydes. Other acids could be carbamic acid, giving imines after decarboxylation, sulfonic acids, phosphoric or phosphonic acids and many more.

Non-covalent ugly-star formation

Apart form the covalent branching of macromonomers as reported in Chapter 3.3, also non-covalent formation of branching points is of considerable interest. By attaching orthogonal binding motives along the chain and at the chain end, such macromonomers could be formed. One advantage of non-covalent branching would be reversibility, whereby responsivity of the systems could also be realized, and little chance for a deactivation of the single sites due to side reactions caused during the coupling reaction. Also, metal-mediated coupling via coordinative binding can be imagined which might introduce catalytically active sites within the branched polymer.

Aramide - ROMP polymer conjugates

First attempts towards such materials have been made starting from hydroxyl-functionalized ROMP polymers. The reaction with soluble imidoyl chloride building blocks gave conjugates with tri- and tetra-*p*-benzamides. Also, a click-approach has been explored based on alkyne functionalized OPBAs synthesized on solid support. The conjugation to azide-functionalized ROMP polymers (synthesized from the hydroxyl-functionalized materials obtained by Sacrificial Synthesis) is described in the thesis of Dr. Hannah M. König.

ROMP in microstructures reactors

An interesting feature of carrying out polymerizations in a microstructured reactor is the extreme flexibility of the experimental setup. Furthermore, reactions can be carried out under conditions inaccessible in conventional glass reaction devices. First trials of the applicability of ROMP polymerizations in such a reactor employing the very fast polymerization of norbornene with Grubbs

1st generation catalyst gave bimodal molecular weight distributions. The polymerization reaction, however, proved to finish extremely fast. It should therefore be tested in future experiments, how experimental conditions, i.e. dilution of the reagents and choice of catalyst, influence the polymerization results.

ROMP polymer – Poly(lactide) block-copolymers, quasi-triblock-copolymers

Based on hydroxyl-functionalized ROMP polymers, the ring-opening polymerization of lactides has been tested. First results showed promising degrees of incorporation of the ROMP polymer into the resulting block-copolymers when the ROP was promoted with DBU or $Sn(Oct)_2$. The aim of this project was to synthesize block-copolymers of various hydroxyl-functionalized polymers synthesized by different polymerization techniques and different lactides, especially D- and L-lactides. The formation of stereocomplexes of PLLA and PDLA was to be exploited to form quasi-triblock colpolymer behavior in the solid phase of adequate polymer blends.

Polymerization to and from solid support

Polymerizations from solid support by ROMP have been reported from silicon surfaces. The utility of polymerization fixed to solid support, however, offers particularly interesting and unique features when exactly one monomer unit is to be added to a polymer chain without deactivating it. The spatial remoteness of two reactive sites on solid supports such as styrene lattices typically used in SPPS avoid the polymerization of the attached monomer sites when a living ROMP polymer chain is added to such a latex particle, it would propagate once with the monomers bound to the surface of the particle while maintaining its living character and activity. Addition of fresh monomer would therefore lead to further polymerization at this site. After cleaving the resulting polymer off the solid phase substrate, a polymer material would be obtained that bears precisely one functional group in the middle of the chain.

First experiments showed that binding of exo-norbornene-5-carboxylic acid to Wang's resin can be conducted using the acid-chloride strategy. Addition of Grubbs 3rd generation catalyst resulted in the initiation of the monomer units on the resin. However, it has to be taken care of efficient shaking of the reaction vessel in order to avoid polymerization of norbornene moieties on different particles which results in agglomeration of the latex particles. Also, use of less densely functionalized resins seems promising (resins carrying 1.3 mmol/g active sites were used).

A.2. Curriculum Vitae Stefan Hilf

A.2. List of Publications and Conference Contributions