Reactive Polyphosphoesters via Acyclic Diene Metathesis Polymerization

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Herrn Dr. Frederik Wurm

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durchgeführt.

meinen Eltern und meinen Großeltern gewidmet

„Vollendet ist das große Werk, der Schöpfer sieht's und freuet sich."

Joseph Haydn: Die Schöpfung (1798)

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Contents

A Abstract

Telechelic (unsaturated) poly(phosphoester)s ((U)PPEs) have been prepared via acyclic diene metathesis polymerization with varying molecular weight and various end groups. The (U)PPEs were either functionalized during the polymerization to generate telechelic polymers or post modified at the double bonds along the polymer backbone. Telechelic UPPEs were synthesized in a one-step reaction introduced by adding a chain termination reactant (CTR) to the ADMET polymerization. The CTR is a monofunctional olefin, which acts as a chain stopper. Adjusting the ratio between the CTR and the monomer allows controlling the molecular weight obtained. Telechelic alcohols, acids, epoxides and bromides with molecular weights between 3,000 and ca. 30,000 g/mol have been prepared and are characterized in detail. A very high end group functionality (>99%) was found in all cases.

The phosphate monomers investigated in this thesis were synthesized from $POCl_3$ to alter (or adjust) the properties of resulting polymers with variable side chain and backbone. UPPEs are synthesized by the acyclic diene metathesis (ADMET) polymerization. This work introduced three new monomers bis-(undecen-10-yl) chlorophosphate, bis-(undecen-10-yl) phosphate and bis-(undecen-10-yl) methylphosphate.

Unmodified UPPEs, ranging from 5,000 to 20,000 $g \cdot mol^{-1}$ have been synthesized. Thermal properties of UPPEs were studied and their thermal degradation was evaluated. Those polymers were altered in post-polymerization modification reactions.

In addition to the main topic, this thesis also presents first results on polymerization attempts of a natural compound, namely a lactonic sophorolipid (LSL). It was modified by ring-opening metathesis (ROM) to obtain two terminal double bonds instead of the given internal one. Subsequently, modified LSL was polymerized by the ADMET approach to generate biometric polymers (this is a collaboration with R. Gross at the University NY).

To sum up, this thesis is focusing on broadening the spectrum of functionalized UPPEs synthesized by ADMET to more sophisticated polymers and introducing new functional end groups to these polymers.

1 Introduction

1.1 (Unsaturated) poly(phosphoester)s

Phosphorus-based polymers are a predominant class of materials in nature and are the source of life (DNA/RNA). In polymer science, however, they are scarcely investigated and only a few recent publications deal with much simpler poly(phosphoester)s (PPEs) in spite of their unique properties in bio-relevant, but also materials science applications.[1] On the other hand, poly(carboxylic ester)s are a typical example of synthetic polymers that are applied in biomedical applications due to their biocompatibility and degradability. However, when it comes to versatility, phosphoesters are in many cases superior to carboxylic acid esters due to the inherent capability of phosphates to form triesters, i.e. having a functional group at every repeating unit along the polymer backbone, but also as they possess three ester groups that can undergo hydrolysis. PPEs combine the excellent biocompatibility and biodegradability[2,3,4,5,6,7] (either by hydrolysis and/or by enzymatic degradation[8]) of conventional (carboxylic) polyesters, they are water-soluble in many cases and allow easy structural diversity with the chemical variability of the phosphorus center.[9]

Especially unsaturated polyesters are interesting, due to their double bonds in the material, which can be used for further functionalization or crosslinking. (U)PPEs are also used as flame-retardant materials.[10] These materials have received tremendous interest in recent decades[10]. Due to their biodegradability, biocompatibility and structural similarities to naturally occurring nucleic acids poly(phosphoester)s are interesting for biological and pharmaceutical applications[12,13], they were also used in the field of tissue engineering as scaffolds or as gene carriers.[14,15]

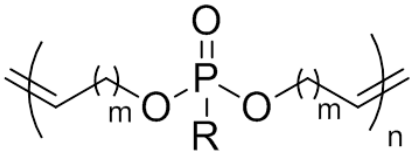


Figure 1-1: A usual UPPE

A major benefit of the UPPEs is their versatility. As mentioned above, phosphours' pentavalence allows great variation at all structural positions. Combined with modern metathesis chemistry this allows variation of backbone and side chain, for instance to control the thermal properties with tunable melting or glass transition temperatures for the different saturated and unsaturated PPEs which is an important feature for future applications or to attach labels, functionalities, etc.[16]

Recently, there have been interesting studies of poly(phosphoester)s used in biomedical applications.[5,6,7]

The chemical versatility of the monomeric phosphate (Figure 1-2) allows the design of functional materials of complex architectures and tunable properties for biomedical applications, such as drug delivery[17], gene delivery[15], pH/thermoresponsive materials[18,19], and tissue engineering.[20] Through the chemical versatility of the monomeric phosphate and the ability to alter the emerging internal and terminal double bonds by polymer modification reactions, there are various tunable positions on the polymer (Figure 1-2). Regenerative medicine requires scaffolds with tunable properties for tissue engineering applications, and unsaturated polyphosphoesters (UPPEs) with the phosphates being capable of binding calcium phosphates are advantageous in terms of cytocompatibility and good tissue compatibility.[20,21] The treatment of bone defects could benefit from biocompatible and degradable materials, which also assist in bone regeneration[22], and could be a valid substitute to the widely used poly(methylmethacrylate) (PMMA).[23] However, till now a major drawback is the restriction to a few monomer systems that often requires polymer modification reactions, resulting in demanding multistep approaches.[16,23]

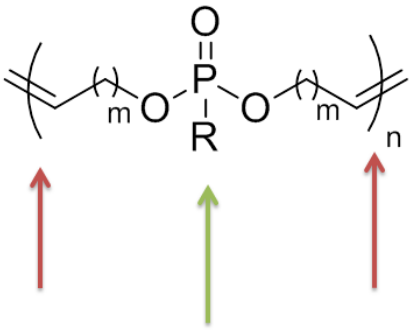


Figure 1-2: Tunable positions of a UPPE

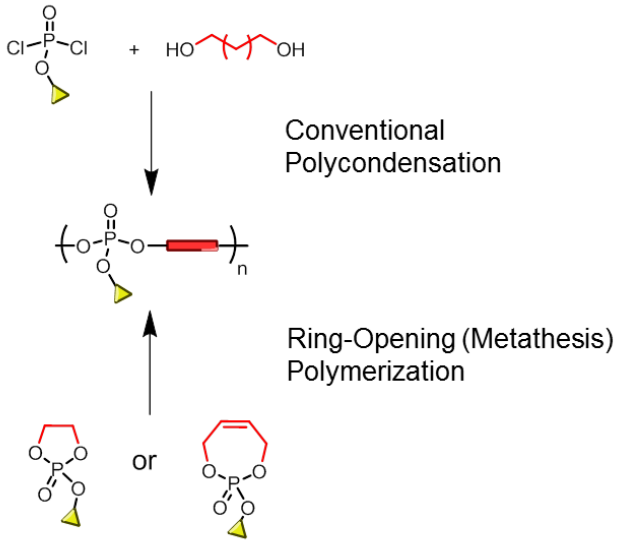
1.2 Synthesis of well-defined poly(phosphoester)s

1.2.1 Synthetic approaches to poly(phosphoester)s

In the early 1970s, seminal works carried out by Penczek and coworkers established the basis of the synthesis and pioneered their potential in biological applications for a series of PPEs.[24,25] These PPEs are prepared by classical polycondensation, transesterification or by ring-opening polymerization (ROP) of strained cyclic phosphates (Scheme 1-1).[13,23,26]

Polycondensation is the most widely used method for the preparation of PPEs due to readily available monomers. However, Vogt and Balasubramanian reported that the conventional polycondensation route is plagued by side reactions that prevent the formation of polymers with molecular weights higher than ca. 1,000 g·mol^{-1}.[27,28] Penczek and coworkers reported that the transesterification route yields polymers with molecular weights which are also higher than 10,000 g·mol^{-1} however functional group tolerance is very limited in the classical polycondensation approach.[23,29,30]

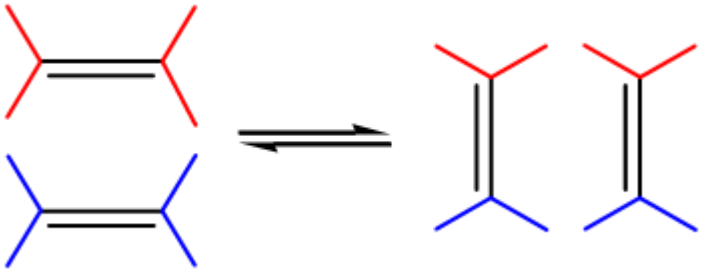
The second approach to PPEs is ROP that has been studied extensively for cyclic phosphate monomers in bulk, with enzymatic catalysis[31], or via cationic[32], anionic or coordinative polymerization[33]. Anionic polymerization allows high control over molecular weight and polydispersity, however functional group tolerance is limited. Thus most PPEs reported to date carry simple alkyl side chains and terminal, i.e. initiator-based, functionalities have to be protected.[34] A typical problem with cationic polymerization is that it produces exclusively colored products. Further problems here are low molecular weight materials, the need of high-purity monomers. In addition the five and six membered cyclic phosphates which are used in ROP are sensitive monomers, and special precautions have to be followed in handling these monomers, during the preparation, the purification (generally by distillation) and especially while conducting the ROP. Their sensitivity easily quenches the polymerization or unwanted initiation by water can occur. For the liability of these cyclic compounds, most of the ROPs are carried out on rather simple five membered, ethylene glycol-bridged cyclic phosphates and subsequent post-polymerization modification reactions are carried out.[23] Low monomer conversions can be problematic (usually ca. 70%) and the materials show polydispersities around 1.50 or lower in some cases.[23] Recently metathesis polymerization has been used to synthesize PPEs either by ROMP or ADMET (see below). The ROMP approach has similar limitations as the ROP approach, however due to functional group tolerance of the olefin metathesis functional side groups is possible.



Scheme 1-1: Polycondensation and Ring-Opening polymerization as methods to receive poly(phosphoester)

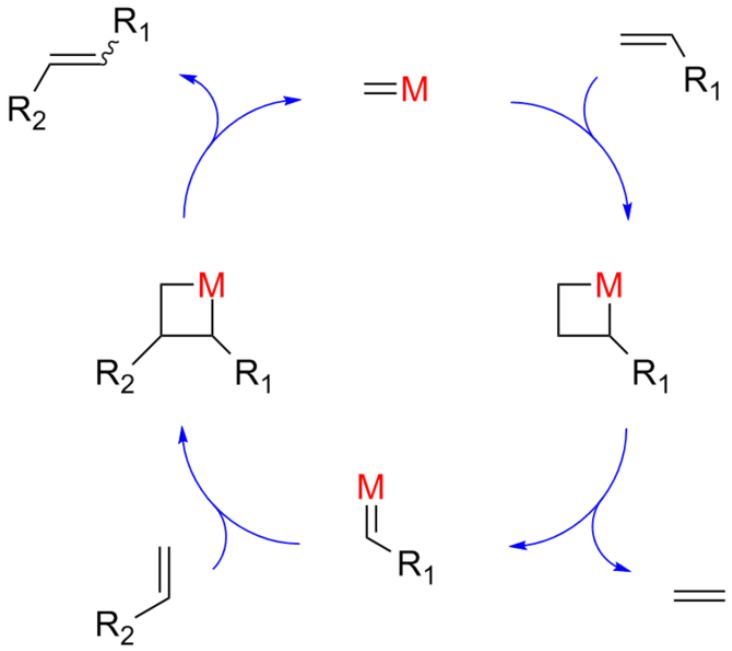
1.2.2 Olefin metathesis as a versatile tool in polymer chemistry

A metathesis reaction is defined as a chemical transformation in which atoms from different functional groups interchange with one another, resulting in the redistribution of functionality yielding similar bonding patterns for the functional groups. In olefin metathesis, two carbon-carbon double bonds react to form two new olefins (Scheme 1-2).[35]



Scheme 1-2: Ideal olefin metathesis reaction[36]

1971 Chauvin *et al.* suggested that olefin metathesis is initiated by a metal carbene. The metal carbene reacts with an olefin to form a metallacyclobutane intermediate that breaks apart to form a new olefin and a new metal carbene, which propagates the reaction (Scheme 1-3).[37]



Scheme 1-3: Chauvin mechanism[36]

The Chauvin mechanism resulted in the development of well-defined catalysts by Schrock and coworkers.[37] A number of achievements in the synthesis of both small molecules and polymers were made possible by the advent of Schrock's catalysts (Figure 1-3). However, these catalysts are sensitive to air and moisture and some protic or polar functional groups as to be expected of high oxidation state early-transition metal complexes due to the electrophilicity of the metal atom.[39] Complexes of the late-transition metals are typically less sensitive to air, moisture, and polar or protic functional groups than the early-transition metals because the metal atom is less electrophilic; therefore, there was a general desire to develop olefin metathesis catalysts based on late-transition metals.[39]

In the early 1990s, Grubbs and coworkers introduced well-defined carbene complexes of ruthenium that were active for olefin metathesis. These first-generation ruthenium compounds (Figure 1-3) were considerably less active than the early-transition metal catalysts, but they did not suffer as much from exposure to water, oxygen, and coordinating functional groups. Recent developments in the ligands have produced complexes with much higher activity than the initially developed ruthenium carbenes.[39]

Metathesis activity and functional group tolerance were substantially increased for the second-generation Grubbs catalyst (Figure 1-3). One of the trialkyl phosphine ligands of the first generation was exchanged for an *N*-heterocyclic carbene ligand. However, one major disadvantage which was only later discovered; is that the first and second-generation complex simultaneously catalyzed metathesis and olefin isomerization. Since then, cross metathesis studies have revealed isomerization occurring at the same time as metathesis, leading to a myriad of olefin products [35]

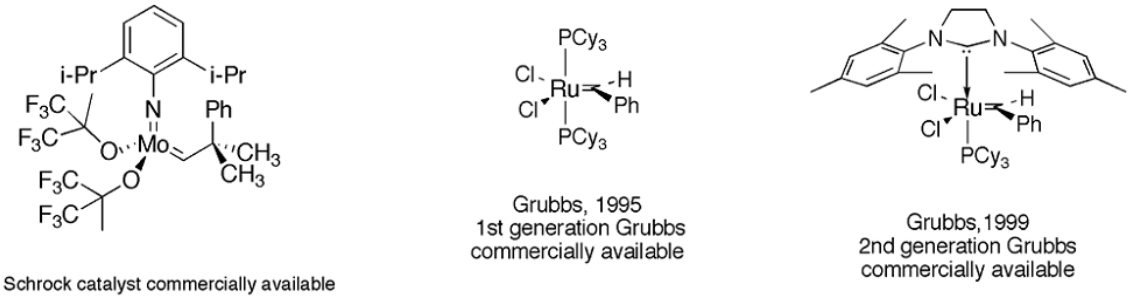


Figure 1-3: Some modern metathesis catalysts[39]

Macromolecular chemists have embraced olefin metathesis, as it allows the preparation of functionalized hydrocarbon polymers through ring-opening metathesis polymerization (ROMP; Scheme 1-4) and acyclic diene metathesis (ADMET; Scheme 1-5).[35]

Scheme 1-4: Ring-Opening Metathesis Polymerization (ROMP)[39]

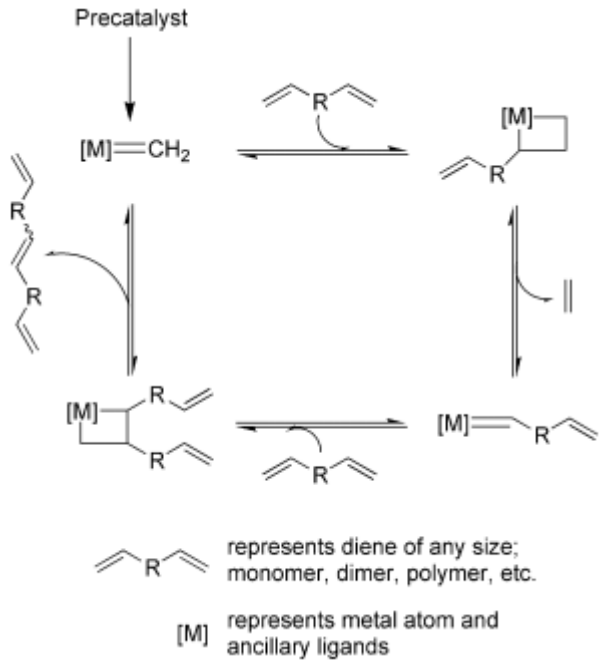
Scheme 1-5: Acyclic Diene Metathesis Polymerization (ADMET)[39]

ADMET polymerization uses *α,ω*-dienes to produce linear polymers with unsaturated backbones, as shown in Scheme 1-5. This step-growth polymerization is a thermally neutral process driven by the release of a small molecule condensate, ethylene. Ring-opening metathesis polymerization (ROMP; Scheme 1-4) is widely used to polymerize cyclic olefins and is performed with the same catalysts (Figure 1-3) as in ADMET polymerizations.[35] Ring-opening metathesis polymerization (ROMP) is driven by the release of ring strain in the starting olefin substrate.[39]

Due to the mild nature of the polymerization and the ease of monomer synthesis, ADMET polymers have been incorporated into various materials and functionalized hydrocarbon polymers.[35] Modeling industrial polymers has proven successful, and continues to be applied in order to study polyethylene structure-property relationships.[35]

1.2.3 The ADMET approach for UPPEs

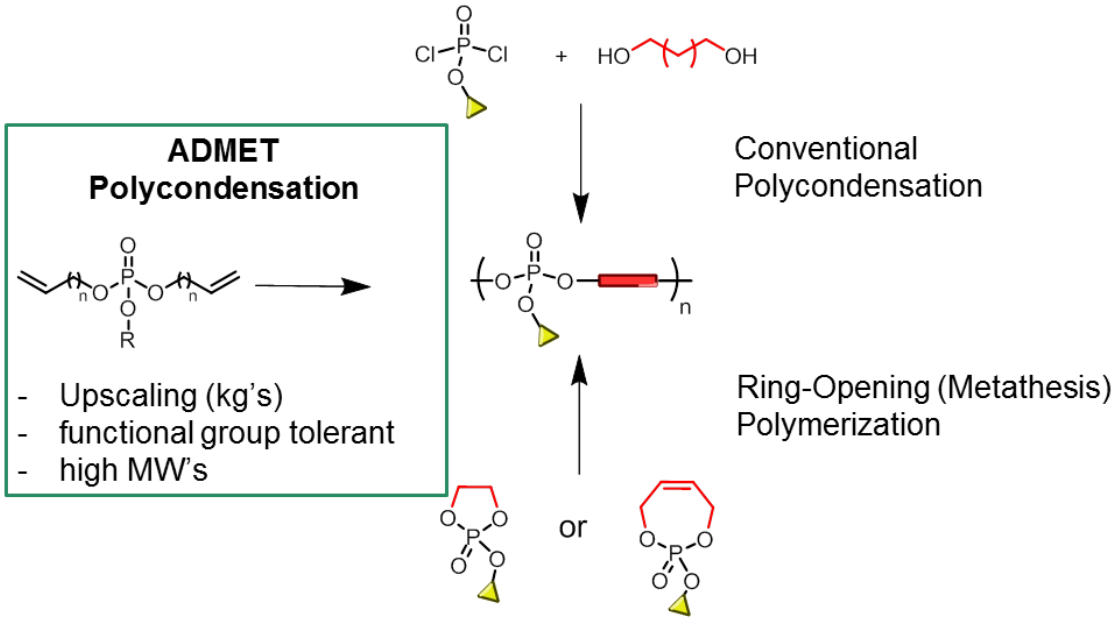
The acyclic diene metathesis polymerization (ADMET)[40] is a quantitative reaction tolerating many functional groups on the diene monomer and yields only linear polymer and ethylene as a byproduct. The mechanism is shown in Scheme 1-6. ADMET should be a perfect approach for the synthesis of linear UPPEs (Scheme 1-7), as it provides a tool for accessing linear polymeric structures in an efficient way from versatile starting materials[41], which is in case of PPEs, $POCl_3$.[23] Compared to classical polycondensations ADMET is not plagued by side reactions that prevent the formation of polymers with higher molecular weights. Moreover, in comparison of ROP there is no need of high-purity monomers which are sensitive to water and air. Further the ADMET polymerization can only produce polymers with high molecular weights and normally a dispersity of 2 is typical for a step-growth polymerization. Since the ADMET approach is carried out under mild conditions it is tolerating many functional groups. Hence there is the ability to use broad monomer variations (with different functional groups) directly in ADMET polymerizations. The need of subsequent post-polymerization modification reactions is not necessary as in ROP, where rather simple monomers are used.



Scheme 1-6: ADMET mechanism[39]

Generally, in ADMET, the polymerizability of a monomer is limited by the number of methylene spacers between the olefin and the phosphate moiety. For instance, allyl esters/ethers cannot be polymerized. This is attributed to the so-called ”negative neighboring group effect”. Because of the proximity of the coordinating ester, metathesis under ruthenium catalysis is slowed down or even prevented due to coordination of the

heteroatom lone pair to the metal center.[42] This lack of reactivity could alternatively justified by the formation of particular resting state of the carbene formed with the allyl substrate possible via coordination to the carbonyl or phosphate.[43] In order to avoid a negative neighboring group effect, the number of the methylene spacers between these functionalities has to be at least two for successful metathesis to occur.[42] Consequently, the acrylate functionality has always failed to (homo)polymerize. Hence, the smallest usable diene monomer is the bisbutenyl phosphate.[23]



Scheme 1-7: Principal polymerization techniques for the production of (U)PPEs

Consequently, the ADMET approach opens a great toolbox of a tremendous variety of substrates which are more stable and easily available from $POCl_3$.

1.3 Telechelic polymers

1.3.1 Defintion of telechelic polymer

By definition, a telechelic polymer is a di-end-functional polymer where both ends possess the same functionality. Polymers which have different end groups are termed di-end-functional polymers or heterotelechelic polymers.[44]

A telechelic polymer or oligomer is a prepolymer capable of entering into further polymerizations or other reactions through its reactive end-groups. It can be used for example to synthesize block copolymers.[44] Reactive end-groups in telechelic polymers can stem from the initiator or termination or chain-transfer agents in chain polymerizations, but not from monomers as in polycondensations and polyadditions.[45]

Other examples of telechelic polymers are the halato-telechelic polymers or halatopolymers. The end-groups of these polymers are ionic or ionizable like carboxylate or quaternary ammonium groups. The term halato-telechelic polymer is used to denote a polymer composed of macromolecules having stable (long-lived) ionic or ionizable groups, such as carboxylate or quaternary ammonium groups, as chain ends. It should not be used to describe a polymer composed of macromolecules having chain ends that are transient intermediates in ionic polymerizations initiated by difunctional initiators. In addition the term halatopolymer is used for a linear polymer formed by the coupling of halato-telechelic polymer molecules, for example, for the linear polymer formed by the coupling of carboxylate end-groups with divalent metal cations.[44]

1.3.2 Properties and applications of telechelic polymers

Since their first reference in 1960[46], telechelic polymers have been used widely, e.g. for post polymerization reactions such as gel formation or as macromonomers to generate complex macromolecular architectures.[47]

The chemical nature of the end-group functionalities dominates not only the material's solubility in organic solvents, but also thermal properties such as glass transitions temperature and melting temperature as well as crystallinity. Therefore, modification of these end groups is an important strategy for tuning the properties of known polymers and finding new applications. Nevertheless, functionalization of polymers is considerably more challenging than that of small molecules because it requires a clean and quantitative reaction to avoid the formation of mixtures along the chain. Consequently, it is desirable to

have a simple and convenient method for the post polymerization modification of polymers.[41]

As mentioned before, a polymer can be considered to be telechelic if it contains functional end groups (such as vinyl, hydroxyl, carboxyl, amine, ester groups, or other moieties) that selectively enable further reactions.[42] Various well-defined high molecular weight macromolecular architectures with enhanced thermal and mechanical properties can be obtained from telechelics, since they can be applied as cross-linkers, chain extenders, and precursors to building blocks for complex macromolecular structures, including block and graft copolymers, star, hyperbranched or dendritic polymers.[49,50] A very important requirement of telechelic polymers is their perfect end-group functionality (number of functional end groups per chain). Depending on the functionality, telechelics are classified as mono-, di-, tri-, and multifunctional telechelics. When the telechelics are bifunctional (for instance, α,ω-divinyl end groups) they can be used in polymerizations and such telechelics are considered as macromolecular monomers (macromonomers or macromers). Preparing telechelics with perfect difunctionality (2.0 functionality) has been a challenge for years. Different methods, including step growth, anionic, cationic, free radical procedures, ROMP, and ADMET depolymerization and polymerization methods have been used in the synthesis of telechelic oligomers.[49,50]

1.4 Poly(phosphoester) telechelics

Poly(phosphoester) telechelics combine the advantages of poly(phosphoester)s:

- Biodegradability[6,7,10]
- Biocompatibility[6,7,10]
- The chemical versatility of the monomeric phosphate[23]
- Design of functional materials with tunable and complex architectures[23]
- Phosphates being capable of binding calcium phosphates[20,21]
- Thermoresponsivity in aqueous media[5]
- Cytocompatibility and good tissue compatibility[20,21]

and telechelic material:

- Unique structures depend on the large number of terminal functional groups[51]
- Controllability of the solubility in organic solvents[48]
- Enhanced thermal and mechanical properties[48]

- Controllable thermal properties such as glass transitions temperature and crystallinity[48]
- Participate in polymerization (macromolecular monomers: macromonomers or macromers)[50]
- Building blocks for preparing polymer blends and hydrogels[5]
- Cross-linkers[49,50]
- Chain extenders[49,50]

Moreover, through its chemical versatility of the monomeric phosphate (side-chain functionality), the ability to alter the emerging internal double bonds (in-chain functionality) and the variety of functional chain-ends (end-chain functionality) by polymerization there are three tunable positions on the polymer (Figure 1-4). Hence it is one of the most versatile polymers in chemistry which opens a tremendous field of applications.

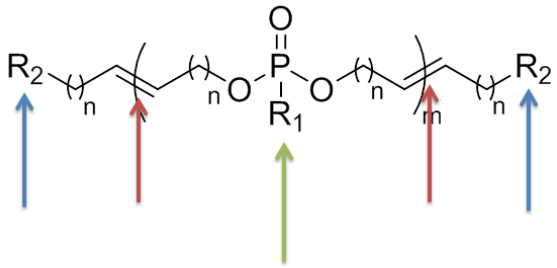


Figure 1-4: Tunable positions of a telechelic UPPE

This unique combination of the benefits of telechelic material and phosphorus chemistry is a highly versatile system for materials in many applications:

- Adhesives
- Biomaterials
- Biological and pharmaceutical applications
- Biomedical applications, as tissue engineering as scaffolds[5], drug delivery[17], gene delivery[11] and pH/thermoresponsive materials[18,19]
- The treatment of bone defects[22]
- Assist in bone regeneration[22]
- Biodegradable macroinitiator and macrocrosslinker[5]
- Building blocks for preparing polymer blends and hydrogels[5]
- Cross-linkers[49,50]
- Chain extenders[49,50]
- macromolecular monomers: macromonomers or macromers[50]
- Precursors as important building blocks for various macromolecular structures, including block and graft copolymers, star, hyperbranched or dendritic polymers[49]

2 Motivation and Aim

The chemistry of (U)PPEs is remarkable through the versatile phosphorus chemistry, which allows the generation of highly functional, reactive, bio-related, and degradable materials.[34]

The ADMET approach was proven to be a potent and mild method for the effective synthesis of (U)PPEs.[23]

Combination of ADMET with the previously mentioned versatility of the phosphorus chemistry results in a highly versatile and general protocol to design unsaturated biodegradable polyesters.

An additional benefit of the versatile phosphorus chemistry and the mild ADMET conditions is the ability of polymerizing even very reactive phosphate monomers such as acid chloride phosphate derivatives in a one-step synthesis.

Telechelic polymers have attracted considerable attention due to the unique structures caused by the large number of terminal functional groups.[51] Thus, with the same protocols, phosphate monomers and several reactive chain termination agents (CTRs) will be (co)polymerized in order to form telechelic poly(phosphoester)s that carry different kinds of end groups and polymer units. These compounds/polymers will be characterized in detail by conventional methods such as nuclear magnetic resonance (NMR) spectroscopy, Gel permeation chromatography (GPC; also: Size exclusion chromatography (SEC) analysis, mass spectrometry, etc.

The aim of the last part of this diploma thesis is to improve the already introduced ROMP method for the synthesis of poly lactonic sophorolipid (LSL) by using ring-opening metathesis (ROM) to convert the unsaturated cyclic sugar LSL in a diene with terminal double bonds in order to polymerize it via ADMET and to make copolymers with the above mentioned phosphates to generate biodegradable, amphiphilic polymers.

2.1 ADMET to UPPEs

2.1.1 ADMET

It was recently introduced that metathesis polymerizations lead to novel PPE structures that further increase the functional group tolerance during their production.[23,52,53] For many applications it is important that the PDI is as near as possible to two, when conversion reaches 100% at a step-growth-polymerization, in order to obtain linear polymers with exactly two functional end groups per chain, which is feasible with ADMET. Hence ADMET polymerization (Figure 2-1) is useful for the straightforward preparation of telechelics.[51,54]

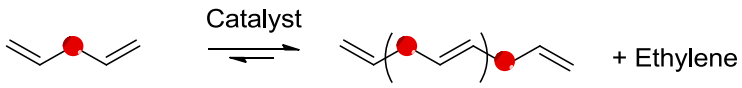


Figure 2-1: ADMET polymerization[23]

Herein, the versatility of PPEs will be further increased by acyclic diene metathesis (ADMET) polymerization by copolymerization of phosphate monomers with several reactive chain termination agents to produce perfect linear PPE telechelics with various functional end-groups.

Thus, with slightly altered procedures, different length of polymers will be polymerized to modify them in order to obtain different properties in contrast to the unmodified polymers. These compounds will be characterized in detail by conventional methods such as nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC).

2.1.2 UPPEs

Due to the pentavalence of phosphorus, three esters can be generated, from which two can be used to build up a linear polymer chain, while the third, pendant ester can be used to functionalize the repeat unit or to adjust its hydrophilicity.

These polymers can so be tailored at various positions: i) at the pendant phosphate ester, ii) at the internal double bonds that are inherent to the metathesis process, and iii) on the orthogonal end groups that are introduced by the chain termination agent in quantitative yield.

2.1.2.1 Side chain variation by alternation of the pendant group on the phosphate

In order to fulfill i) it will be introduced the monomers **2a** to **2f** (Figure 2-2 and Figure 2-3) to present various pedant groups. Additionally it will be possible to do post reactions on some of these pedant groups.

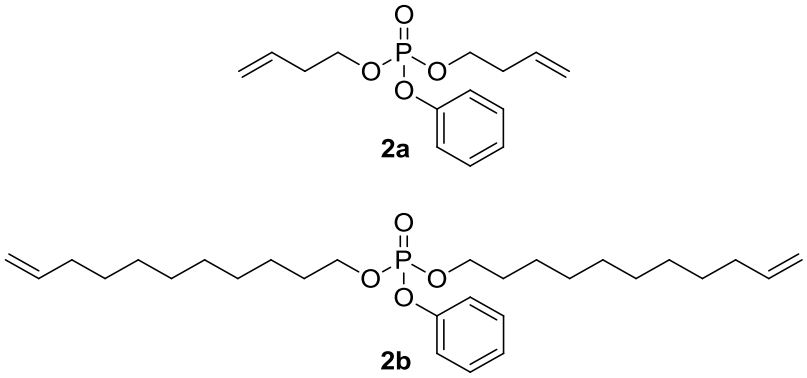


Figure 2-2: Monomers synthesized and examined by Marsico.[23]

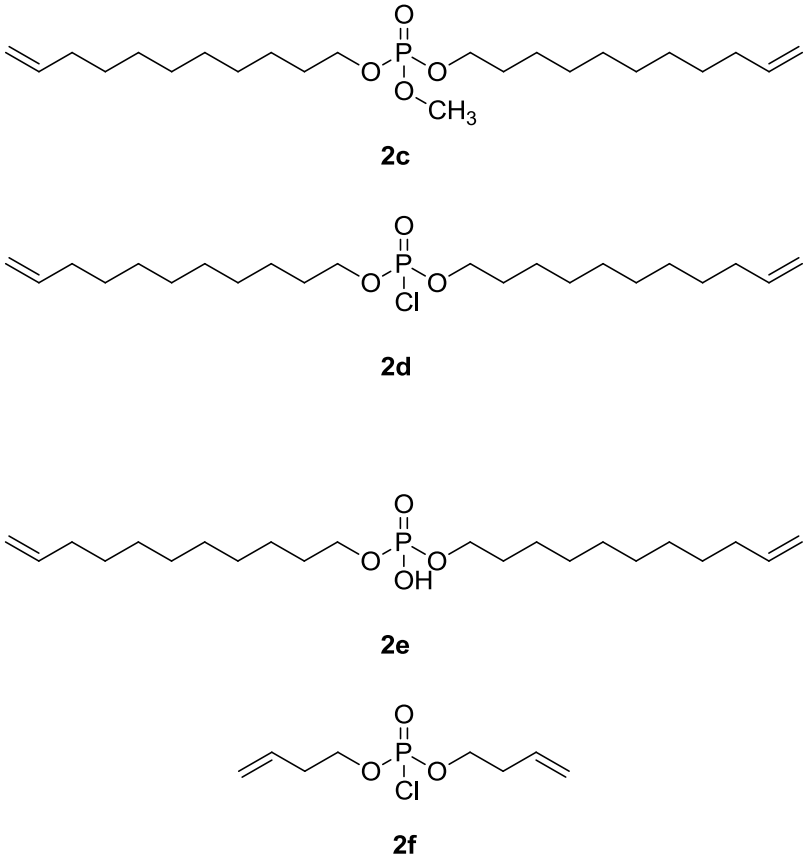


Figure 2-3: Novel monomers.

Thus one of the goals of this thesis will be the reproduction of monomer bis-(buten-3-yl)-phenyl-phosphate **2a** and bis-(undecen-10-yl)-phenylphosphate **2b** (Figure 2-2), which were already synthesized and examined by Marsico *et al.* [23], to introduce the phenyl group as a pedant group.

In addition, there will be the introduction of the synthesis of the proposed monomers bis-(undecen-10-yl) methylphosphate **2c**, bis-(undecen-10-yl) chlorophosphate **2d**, bis-(undecen-10-yl) phosphate **2e** and bis-(buten-3-yl) chlorophosphate **2f** (Figure 2-3). They will have enhanced/different properties in many respects compare to **2a** and **2b**.

Moreover the thermal properties of the polymer derived from monomer **2c** will be examined, as the less bulky methyl group as the pendant group at the phosphate instead of the phenyl group is expected to increase the crystallinity and consequently the melting point, which can be beneficial to receive nanoparticles from them. **2e** is supposed to have strong interaction between the phosphates by hydrogen bonding, which can lead to novel UPPEs with high crystallinity and high melting and glass transitions temperatures. Furthermore **2d** and **2f** are so important that it will be discussed in an additional chapter.

2.1.2.2 UPPE backbone variation by modification of the internal double bonds

Through the ADMET approach the double bonds of the monomer remain in the polymer and can be modified. Subsequently, post polymerization reactions can be carried out.

A thiol-ene reaction is supposed to link thiols at the double bonds in the polymers, which can be lead to higher hydrophilicity compare to the rather hydrophobic UPPEs with the proper thiol. Hydosilylation of the terminal double bonds might be a decent option to receive silyl end groups. An ATRP in order to link poly(ethylene glycol) methyl ether methacrylate ($PEGMA_{475}$) on both sides of the polymer could be realized to increase the water solubility as well.

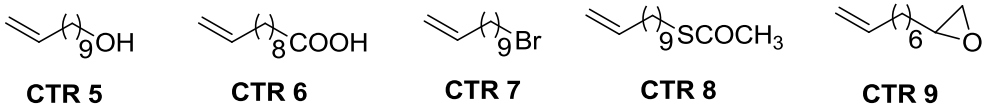
2.1.2.3 Modified end groups by using various CTRs

For the synthesis of telechelic UPPEs via ADMET polymerization two different approaches are conceivable, either polymers will be modified in a post polymerization reaction or the modifications will be introduced in a one-step reaction during the polymerization.

Advantages for the second approach as the high controllability of the molecular weight, the 2.0 functionality and the point that it is a one-step reaction seem to be appropriate to

develop this approach (introduced as direct-polymerization modification reaction by Wagener *et al.*)[51] further.

Telechelic UPPEs will be synthesized in a one-step reaction introduced by adding a chain termination reactant (CTR) to the ADMET polymerization. The CTR is a monofunctional olefin, which acts as a chain stopper. CTRs like alcohols, acids, epoxides and bromides (Figure 2-4) will be used in order to observe telechelic UPPEs. In addition, adjusting the ratio between the CTR and the monomer is supposed to allow controlling the molecular weight obtained.

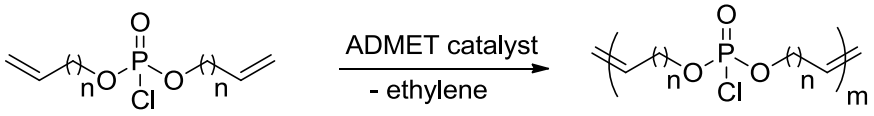


CTR 5 **CTR 6** **CTR 7** **CTR 8** **CTR 9**

Figure 2-4: CTRs for telechelic UPPEs

2.2 Reactive PPEs (poly[chlorophosphate]s)

In order to reach this goal the bis-(undecen-10-yl) chlorophosphate and the bis-(buten-3-yl) chlorophosphate were used to observe reactive UPPEs, which have the ability of post-polymerization modifications by the reactive acid chloride functionality. The proposed protocol of the ADMET polymerization of the chloro monomers **2d** and **2f** is shown in Scheme 2-1.



2d (n =9)
2f (n =2)

4d (n =9)
3f (n =2)

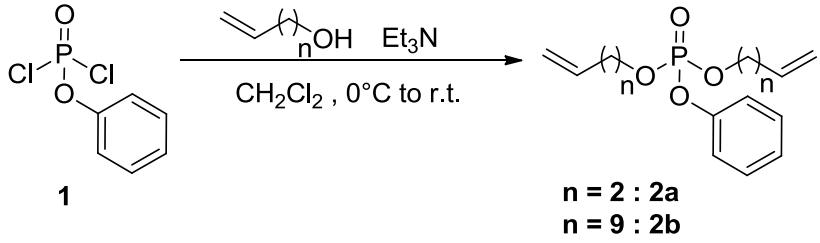
Scheme 2-1: ADMET polymerization of phosphate monomers **2d** and **2f**.

PDIs around 2.0 and a decent stability in the presence of water and air should be feasible. Furthermore it might be a possible substitution of poly(phosphazene) which possesses similar properties as the easily substituted chloride atoms on the phosphorous atom. By mixing it with nucleophiles it might be exchange the chloride in order to receive polymers with completely different properties. It would be then an entirely adjustable polymer.

3 Results and Discussion

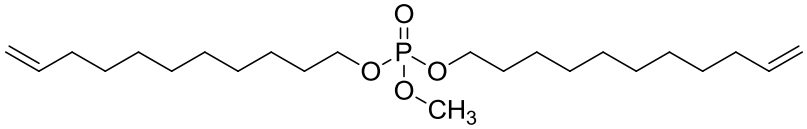
3.1 Monomers synthesis

For the ADMET polymerization towards UPPEs, unsaturated phosphate monomers were synthesized. Monomers **2a** and **2b** were synthesized using commercially available phenyl dichlorophosphate **1** which was esterified with the respective unsaturated alcohol (to adjust the length of the polymer backbone) in the presence of a base, triethylamine (Et_3N), in dichloromethane (CH_2Cl_2) as described in the following representative procedure (Scheme 3-1).[18]

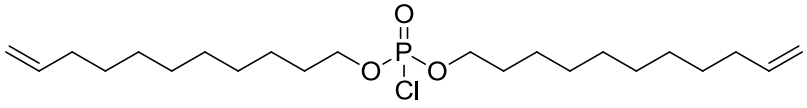


Scheme 3-1: General procedure for the synthesis of established phosphate monomers for ADMET.

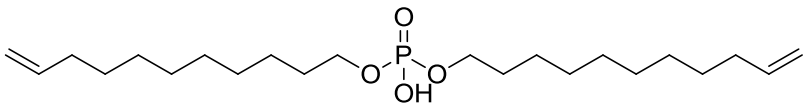
In addition to that, three new phosphorous monomers were synthesized, namely bis-(undecen-10-yl)-methyl-phosphate, bis-(undecen-10-yl) chlorophosphate, bis-(undecen-10-yl) phosphate and bis-(butenyl-3-yl) chlorophosphate **2c – 2f,** which are demonstrated as equally effective as the already proven monomers (Figure 3-1).



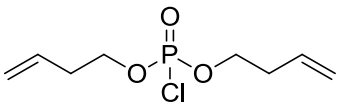
2c



2d



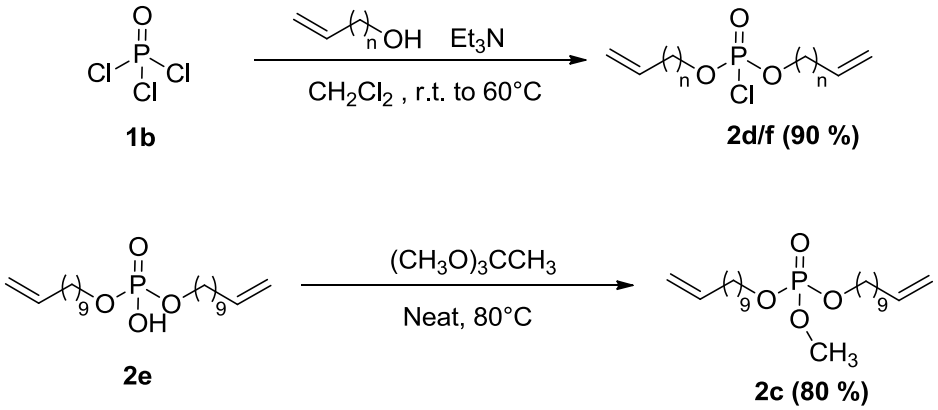
2e



2f

Figure 3-1: Novel monomers synthesized and examined in this study.

The synthesis of **2c** the bis-(undecen-10-yl)-methylphosphate requires a different protocol than the synthesis of monomers **2a** and **2b**. The methyl group causes unwanted transesterferication in the usual reaction and the following protocol was used. The first step of the synthesis of **2c,** the bis-(undecen-10-yl)-methylphosphate is the esterification of phosphoryl chloride **1b** with 10-undecen-1-ol. Also other unsaturated alcohols are suitable except allyalkohols because of the negative neighboring effect as mentioned before. The product of the first step is bis-(undecen-10-yl) chlorophosphate **2d** which is easily hydrolyzed to bis-(undecen-10-yl) phosphate **2e** (Scheme 3-2)**.** In a second step, **2e** was treated with trimethyl orthoacetate (Scheme 3-2).



Scheme 3-2: General procedure for the synthesis of the novel phosphate monomers for ADMET

These are the desired difunctional (diene) monomers which are able to polymerize on both sites leading to linear polymers with double bonds in the backbone and at the end to undergo subsequent post-polymerization modification reactions.

All these monomers were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Figure 3-2 to Figure 3-10 show the ^{1}H and ^{31}P NMR spectra in deuterated chloroform ($CDCl_3$). The signals are assigned to the hydrogen atoms in the compound. The ^{1}H NMR spectrum of monomer **2a** (Figure 3-2) shows the resonance signals of $C\boldsymbol{H_2}$=$CHCH_2$- protons (e) at 5.16-5.06 ppm, CH_2=$C\boldsymbol{H}CH_2$- protons (d) at 5.84-5.68 ppm, CH_2=$CHCH_2C\boldsymbol{H_2}OP$- protons (b) at 4.23-4.11 ppm, and CH_2=$CHC\boldsymbol{H_2}CH_2OP$- protons (c) at 2.48-2.39 ppm, and the phenyl- protons (a) at 7-36-7.12 ppm. The integration of the signals adds up to the expected amount of protons.

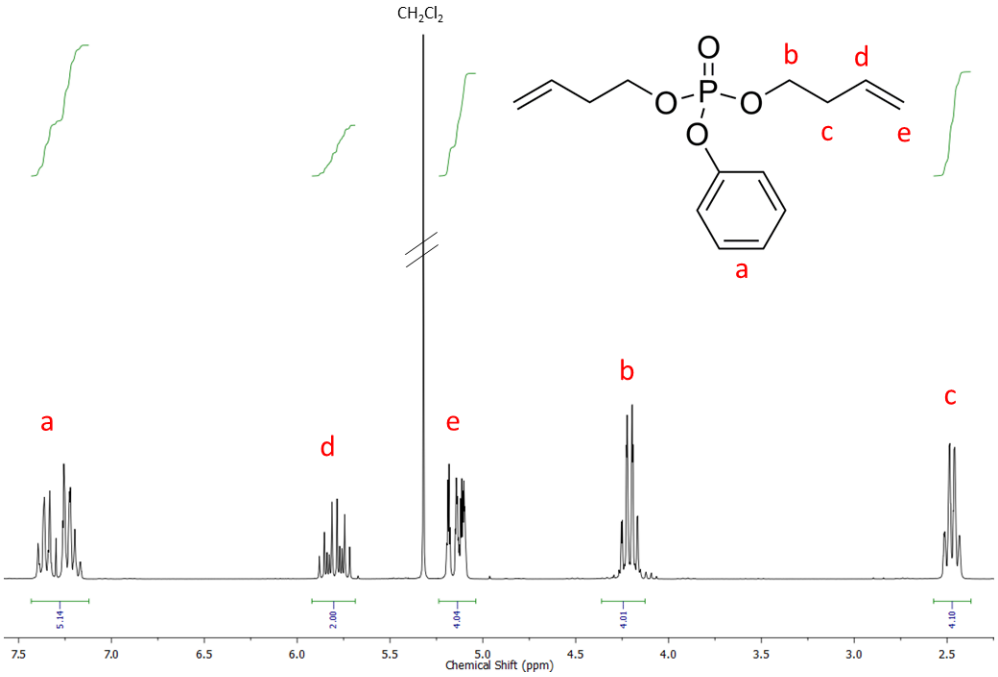


Figure 3-2: ^{1}H NMR spectrum (250 MHz in $CDCl_3$ at 25 °C) of monomer **2a**.

The ^{1}H NMR spectrum of monomer **2b** (Figure 3-3) shows the resonance signals of C***H*****$_2$**=CHCH$_2$- protons (g) at 5.06-4.92 ppm, CH$_2$=C***H***CH$_2$- protons (f) at 5.91-5.75 ppm, CH$_2$=CHC***H*****$_2$**- protons (e) at 2.10-2.10 ppm, - CH$_2$CH$_2$C***H*****$_2$**OP- protons (b) at 4.19-4.11 ppm, -CH$_2$C***H*****$_2$**CH$_2$OP- protons (c) at 1.75-1.62 ppm, and the phenyl- protons (a) at 7-38-7.15 ppm. The six methylene groups between the double bond and the phosphorus are one broad signal at 1.42-1.27 ppm. The integration over the signals confirmed the validity of the received monomer.

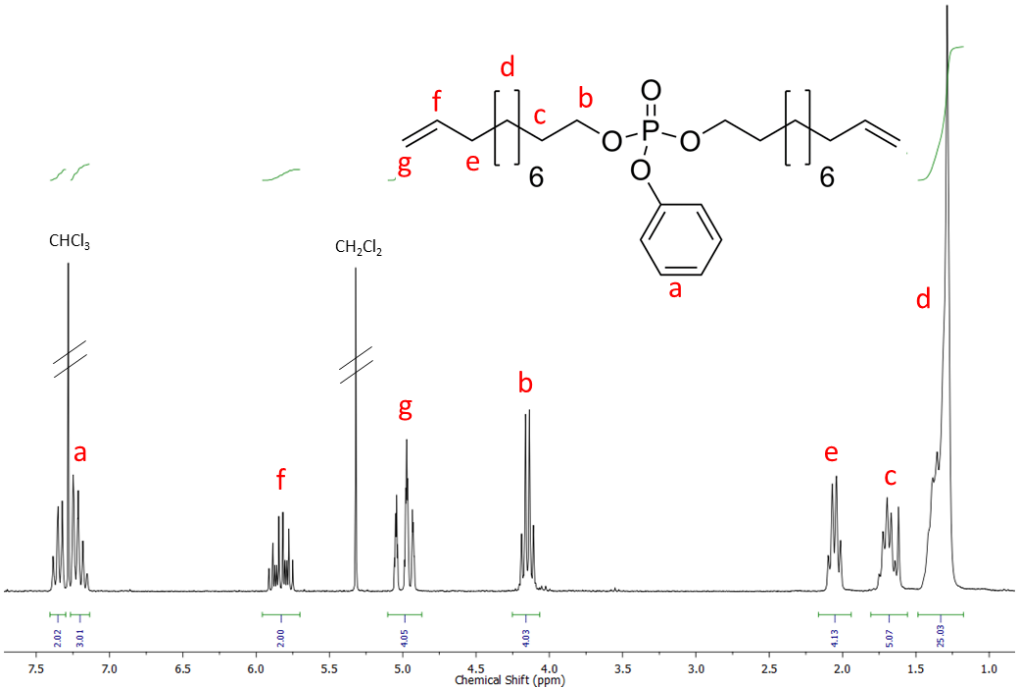


Figure 3-3: ^{1}H NMR spectrum (250 MHz in $CDCl_3$ at 25 °C) of monomer **2b**.

The ^{1}H NMR spectrum of monomer **2c** (Figure 3-4) described the same resonance signals as **2b** regarding the alkenyl substituents. The methyl-group is found at 3.78 ppm (a). Since the methyl-group has a different influence of the phosphate as the phenyl group the chemical shift of the - $CH_2CH_2C\boldsymbol{H_2}OP$- protons (b) are shifted to 4.00-3.92 ppm.

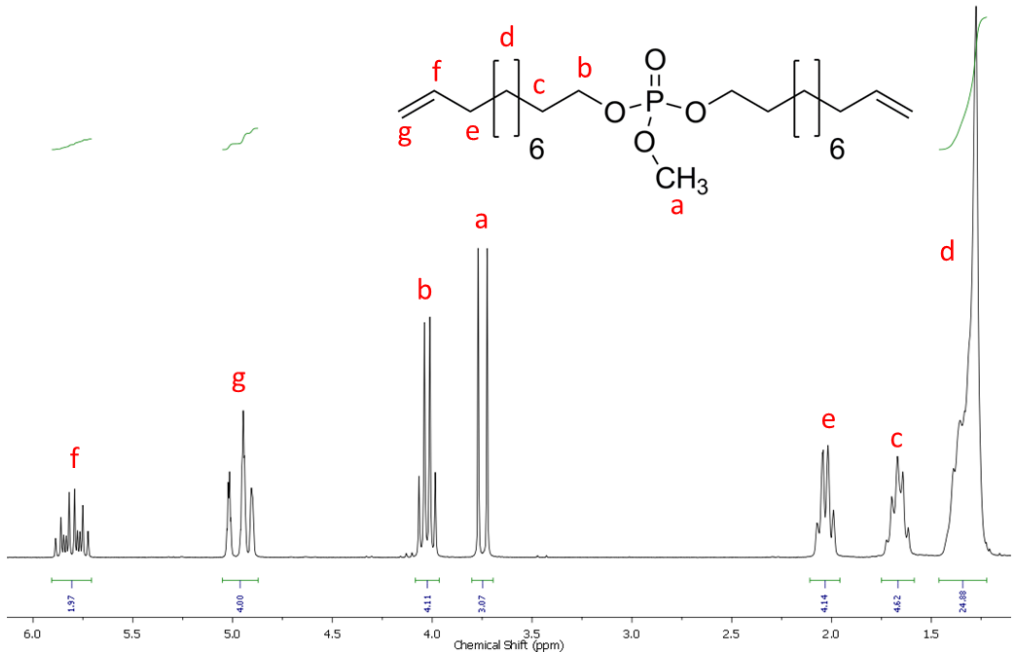


Figure 3-4: ^{1}H NMR spectrum (250 MHz in $CDCl_3$ at 25 °C) showing the monomer **2c**.

The signal of the methyl group at 3.78 ppm (a) is split to a doublet due to ^{3}J coupling with the phosphorous center; also the phenyl signals in the other monomers show an extended splitting due to coupling to phosphorous.

Furthermore it is interesting that the signal a (and b for **2c**) in **2d**, **2e** and **2c** (not to see in the spectra since it was purified by column chromatography but indicated in the unpurified spectrum in Figure 3-5) is actually not only one signal but two. That means there must be an isomer because of the phosphor atom. TLC results also prove that there must be a second compound.

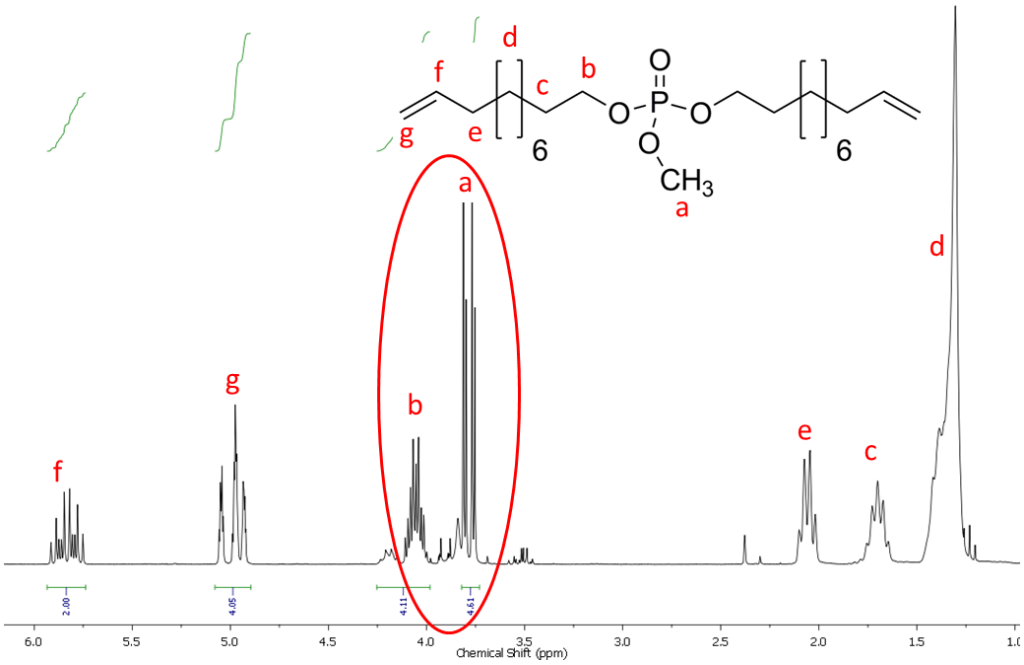


Figure 3-5: ^{1}H NMR spectrum (250 MHz in $CDCl_3$ at 25 °C) of the unpurified monomer **2c** to point out the signals a and b and its isomer signals.

The ^{1}H NMR spectrum of monomer **2d** (Figure 3-6) indicates the same resonance signals as **2b** except the signal of the - $CH_2CH_2C\boldsymbol{H_2}OP$- protons (a) is shifted to 4.37-4.11 ppm, because of the effect of the chloride substituent.

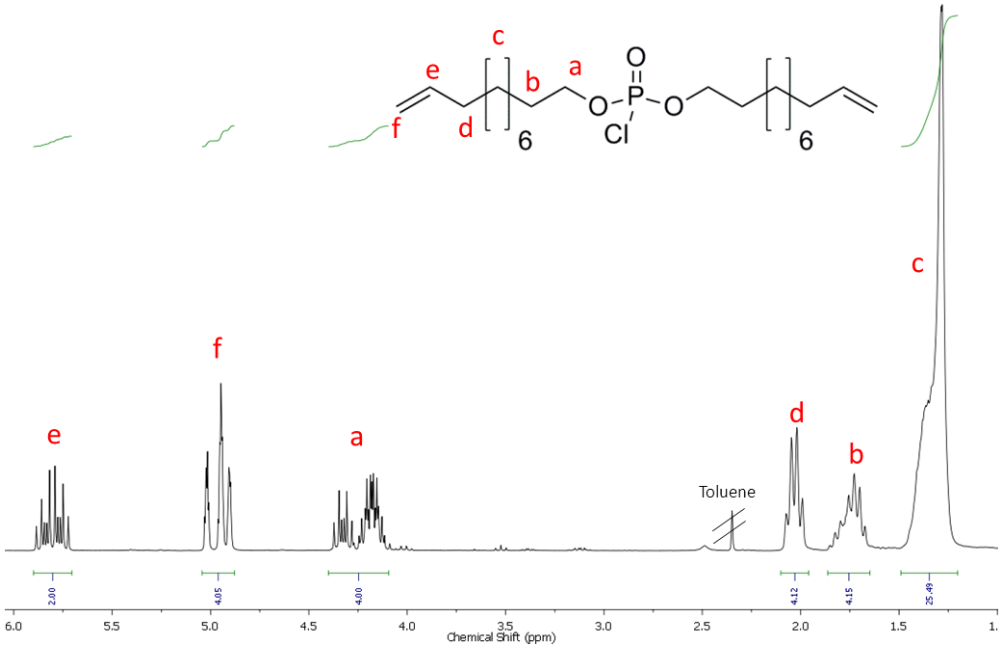


Figure 3-6: ^{1}H NMR spectrum (250 MHz in $CDCl_3$ at 25 °C) of monomer **2d**.

The ^{1}H NMR spectrum of monomer **2f** (Figure 3-7) point out the same resonance signals as **2a** except the signal of the - $CH_2CH_2C\boldsymbol{H_2}OP$- protons (a) is shifted to 4.37-4.11 ppm, because of the effect of the chloride substituent.

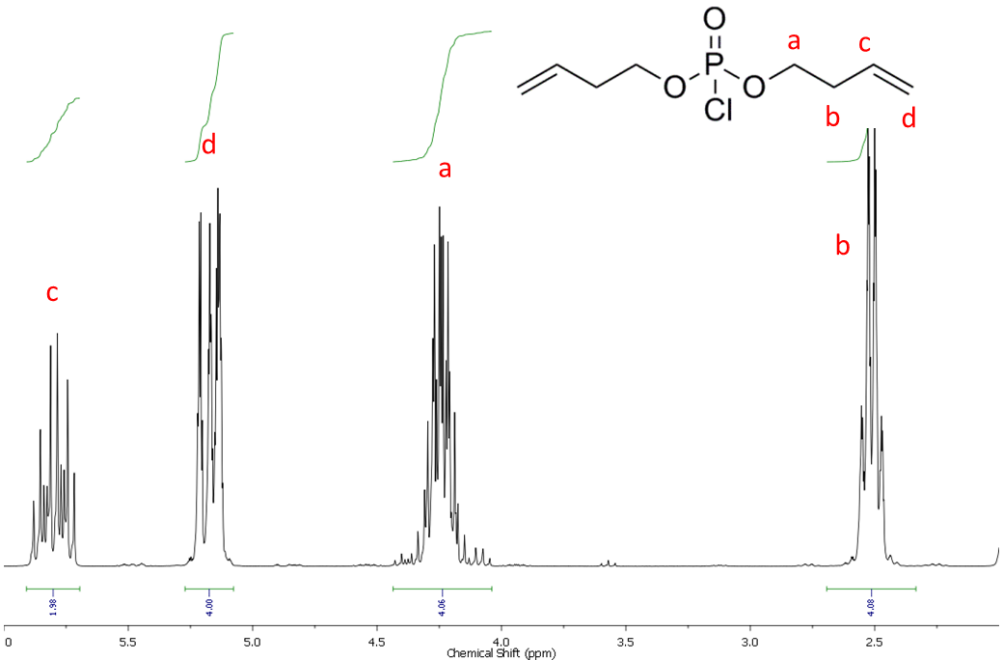


Figure 3-7: ^{1}H NMR spectrum (250 MHz in $CDCl_3$ at 25 °C) of **2f**.

The ^{1}H NMR spectrum of monomer **2e** (Figure 3-8) displays the same resonance signals as **2b** except the signal of the -$CH_2CH_2C\boldsymbol{H_2}$OP- protons (a) is shifted to 4.21-3.98 ppm because of effect of the hydroxyl-group.

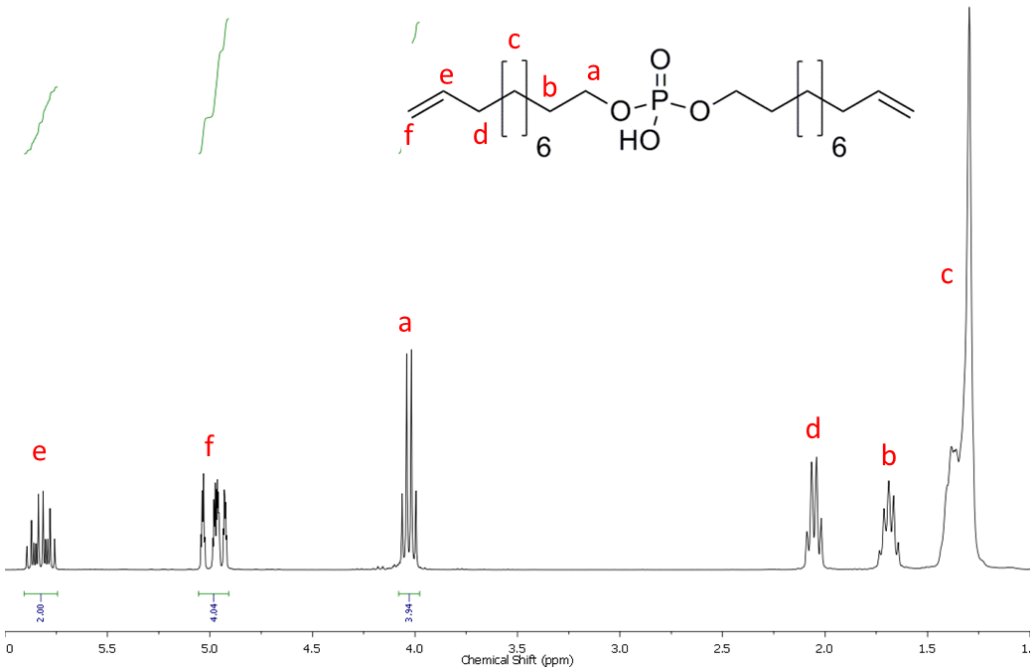


Figure 3-8: ^{1}H NMR spectrum (250 MHz in $CDCl_3$ at 25 °C) of monomer **2e**.

Figure 3-9 and Figure 3-10 show the different chemical shifts of the phosphorus atoms of the monomers. Observable is the increasing chemical shift in the row from the phenyl monomer (**2a** or **2b**) over the methyl (**2c**) and hydroxyl monomer (**2e**) to the chloro monomer (**2d** or **2f**). It indicates that the phosphorus has higher electron density in **2a** (**2b**) as in **2c** and much more as in **2e** or even in **2d** (**2f**), which confirms that the phenyl group is pushing more electrons to the phosphorus atom as the methyl group or the hydroxyl group, which are not as electronegative as the chloride substituent.

^{31}P NMR measurements revealed only a single peak for all monomers, excluding the presence of di-substituted or mono-substituted phosphate in the material isolated. The small peak in the **2d** and **2f** spectra is probably caused by the hydrolysis of the chloride into a hydroxyl group from residual water in the NMR solvent. In the spectrum of **2e** is also a small second signal visible which can be assigned to unconverted chloro monomer.

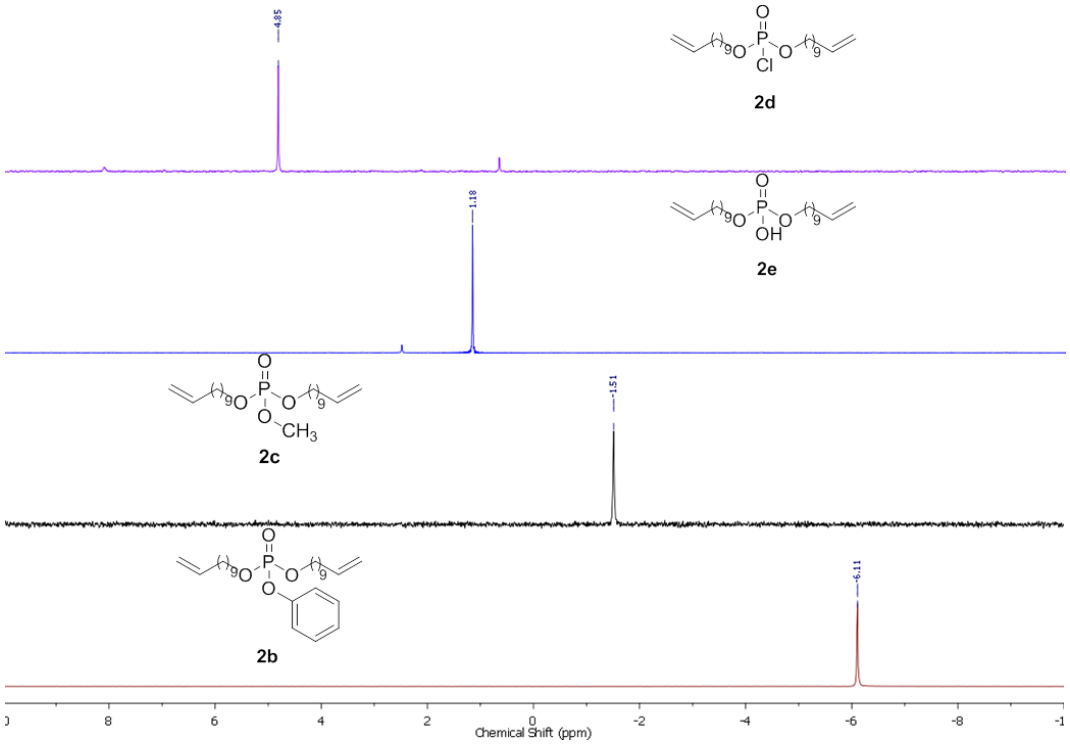


Figure 3-9: ^{31}P NMR spectra of monomers **2b** (bottom)**, 2c, 2e** and **2d** (top) (700 MHz in $CDCl_3$ at 25 °C).

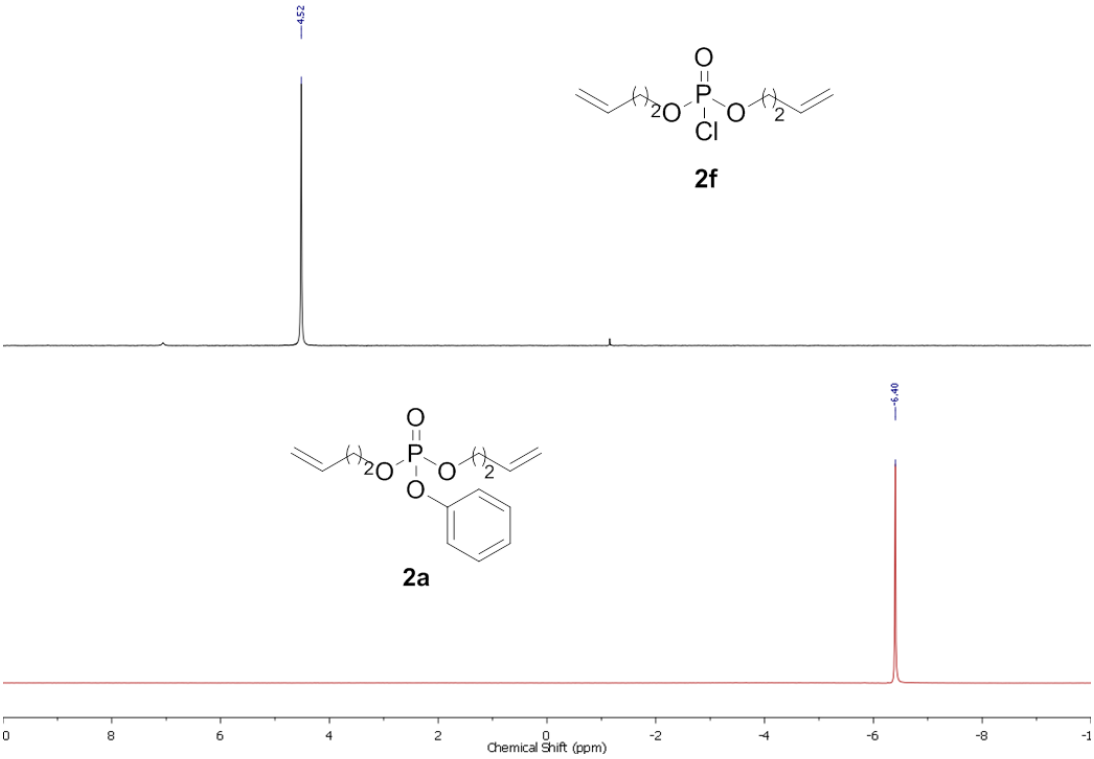


Figure 3-10: ^{31}P NMR spectra of monomers **2a** (bottom) and **2f** (top) (700 MHz in $CDCl_3$ at 25 °C).

In order to complete the NMR results the ^{13}C NMR spectra of monomers **2a** to **2f** are listed in chapter 5 (experimental part).

3.1.1 ESI-MS of Monomers

Furthermore, the molecular weights of **2a** to **2f** obtained from Electrospray ion trap mass spectrometric (ESI-MS) analysis were in good accordance with the theoretical value. Figure 3-11 and Figure 3-12 show representative typical obtained ESI-MS spectra.

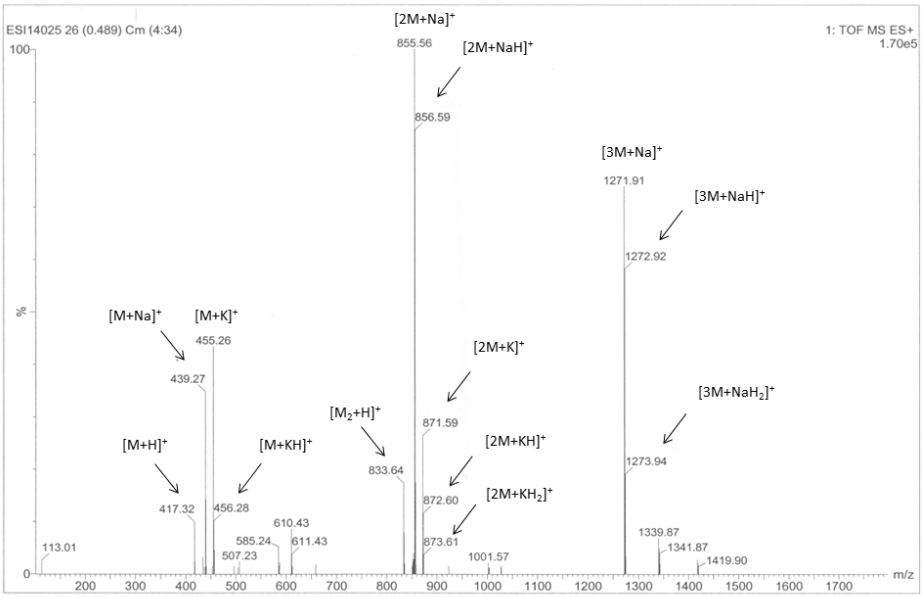


Figure 3-11: Positive ionization mode ESI-MS spectra of monomer **2c** in acetonitrile.

In acetonitrile as a solvent, the monomer **2c** was found as the protonated ion at m/z 417.32 alongside with the sodium adduct at m/z 439.27 and the potassium adduct at m/z 455.26.

The most intense signal was assigned to $[2M+Na]^+$ ion (m/z 855.56), the potassium adduct of the dimer is located at m/z 871.59 and the protonated dimer at m/z 833.64. The trimer of **2c** as well as the corresponding adducts with potassium and sodium ions were also present; however, their intensities were much lower, as expected from ESI mass spectrometry.

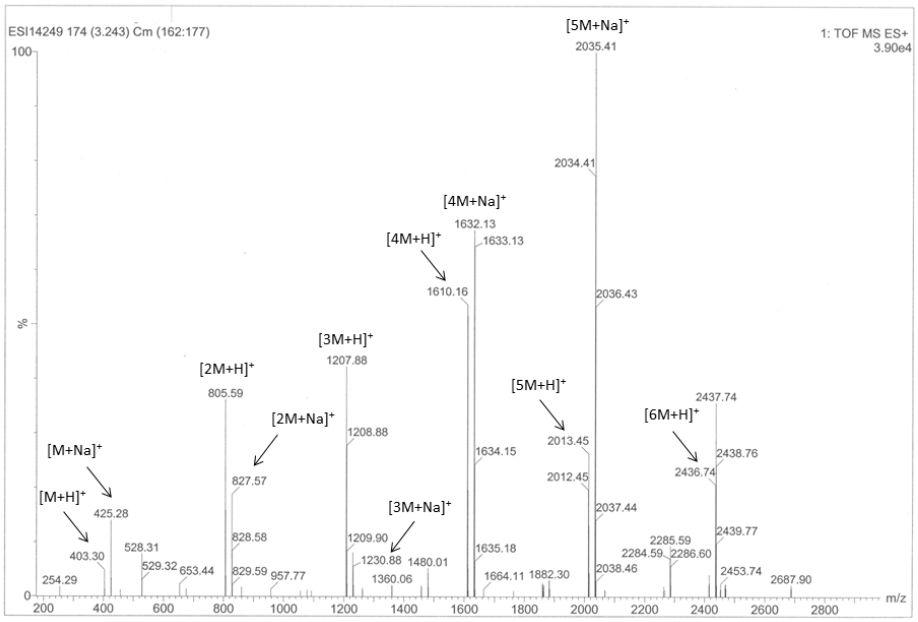


Figure 3-12: Positive ionization mode ESI-MS spectra of monomer **2e** in methanol.

Figure 3-12 indicates the obtained ESI mass spectra of **2e**. The important signals are assigned to the molecular unit which is responsible for the particular peak. Noticeable here is that monomer adducts of six monomers are identifiable, which is an evidence of the strong interaction between the phosphates by hydrogen bonding.

Additional ESI-MS results, which are not shown in this section, are listed in chapter 5 (experimental part).

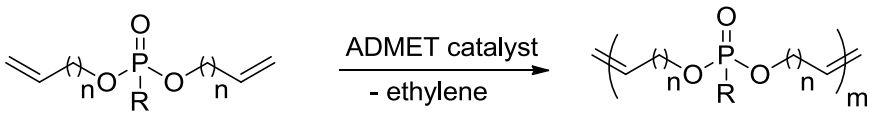
The monomers have a high purity as shown by TLC analysis, NMR spectroscopy and ESI-MS analysis. All of these methods confirmed the successful preparation of **2a-f** with the expected structures.

3.2 Polymerization techniques

3.2.1 Polycondensation via ADMET

Motivated by the high functional group tolerance of the Grubbs-type catalysts, the ADMET polymerization of the monomers **2a**-**e** (except **2d** and **2f**, which will be investigated in chapter 6.2) has been investigated in this thesis (Scheme 3-3). Investigations of the influence of various reaction conditions on the molecular weight and the polydispersity of the polymers have been made. The catalysts used in this study were the Grubbs catalyst 1st generation (**C1**; Figure 3-13) or the Hoveyda-Grubbs catalyst 2nd generation (**C2**; Figure 3-13). Molecular weights between 3,000 and 10,000 g·mol^{-1} were targeted (this is not a molecular weight limit, but allows easy quantification of the endgroups by mass spectrometry and NMR spectroscopy, see below). ADMET is a polycondensation and not a living chain growth, it was necessary to screen the reaction conditions empirically, such as temperature, pressure or the reaction time. Since the monomers described herein are liquids, a bulk polymerization is feasible and maximizing of the molar concentration of the olefin and appropriate shifting of the reaction equilibrium can be obtained to observe high molecular weights. Nevertheless for lower molecular weight materials the presence of a solvent was essential.

The protocol of the ADMET polymerization is simple: direct mixing of the monomer with Grubbs catalyst 1st or Hoveyda-Grubbs catalyst 2nd generation in solution or in bulk and applying the reaction conditions produces the pure polymer. This work has already introduced three completely new monomers bis-(undecen-10-yl) chlorophosphate, bis-(undecen-10-yl) phosphate and bis-(undecen-10-yl) methylphosphate. The respective polymers are poly[bis-(undecen-10-yl) chlorophosphate] and poly[bis-(undecen-10-yl) methylphosphate]. Since the hydroxyl group of bis-(undecen-10-yl) phosphate has strong hydrogen bonds the polymerization yields in an unsoluble polymer. Hence copolymers of bis-(undecen-10-yl) phosphate and bis-(undecen-10-yl) phenylphosphate were synthesized.



2a (R = Phenyl; n =2)
2b (R = Phenyl; n =9)
2c (R = OCH_3; n =9)

3a (R = Phenyl; n =2)
4b (R = Phenyl; n =9)
4c (R = OCH_3; n =9)

Scheme 3-3: ADMET polymerization of phosphate monomers **2a-f**.

C1

Grubbs Catalyst 1st Gen.

C2

Hoveyda-Grubbs Catalyst 2nd Gen.

Figure 3-13: Ruthenium-based olefin metathesis catalysts used in this study.

The first reactions were carried out between room temperature and 60 °C. A sudden color change from purple (**C1**) to red, evolution of ethylene, and a rapid increase in the viscosity of the reaction mixture was observed, which indicated the reaction progress. Table 3-1 lists the reaction conditions and the results of the polymerizations by Scheme 3-1.

Table 3-1: Conditions for the ADMET polycondensation (general representative procedure) of **2a-f** and molecular weight data of the resulting polymers.

Run	Catalyst [mol%]	Monomer	Reaction time [h]	Temperature [°C], solvent	Mw[(a)] [g·mol^{-1}]	Mn[(a)] [g·mol^{-1}]	PDI[(a)]	Mn[(b)] [g·mol^{-1}]
1	3.0 (C1)	2b	16	**r.t., CH_2Cl_2[(c)]**	4,100	2,700	1.53	1,800
2	3.0 (C1)	2b	60	**r.t., CH_2Cl_2[(c)]**	6,900	4,400	1.58	2,700
3	1.2 (C1)	2b	60	**r.t., CH_2Cl_2[(c)]**	6,500	3,800	1.71	2,700
4	1.0 (C1)	2b	60	**r.t., CH_2Cl_2[(c)]**	8,500	4,700	1.80	3,400
5	1.0 (C2)	2b	60	**r.t., CH_2Cl_2[(c)]**	2,100	1,800	1.19	600
6	1.0 (C2)	2b	16	**40°C, CH_2Cl_2[(c)]**	12,990	5,400	2.24	8,600
7	1.0 (C2)	2b	16	**r.t., none[(d)]**	21,500	8,100	2.64	-
8	1.0 (C2)	2b	16	**60°C, none[(d)]**	27,000	13,600	1.98	-
9	1.0 (C1)	2b	60	**r.t., THF[(c)]**	2,000	1,800	1.15	500
10	3.0 (C1)	2b	16	**60°C, THF[(c)]**	Oligomers	1,800	1.29	2700
11	1,2 (C1)	2b	16	**r.t., none[(d)]**	17,900	8,200	2.19	6,300
12	1,2 (C1)	2b	16	**60°C, none[(d)]**	54,300	17,700	3.07	-
13	3.0 (C1)	2a	16	**r.t., CH_2Cl_2[(c)]**	2,200	1,500	1.44	1,300
14	3.0 (C1)	2a	60	**r.t., CH_2Cl_2[(c)]**	2,000	1,200	1.61	1,300
15	1,2 (C1)	2a	16	**r.t., none[(d)]**	Oligomers	1000	1.13	800
16	3.0 (C1)	2a	16	**60°C, none[(d)]**	5,200	2,700	1.95	4100
17	1,0 (C1)	2c	16	**40°C, none[(d)]**	37,000	20,000	1.85	11,700
18	1,0 (C1)	2c	16	**r.t, none[(d)]**	11,900	4,900	2.42	8,600

[a] Determined by gel permeation chromatography (GPC) in THF vs. polystyrene standards.
[b] Determined by NMR.
[c] Performed using solution based ADMET as described in the experimental section.
[d] Performed using bulk based ADMET as described in the experimental section.

From Table 3-1 it is obvious that both monomers produce oligomeric PPEs when the ADMET is performed in solution, while bulk polymerization leads to high molecular weight materials as reported earlier.[23] From entries 1-12 one can adjust the molecular weight of the oligomer by variation of the reaction conditions. Missing NMR data can be explained by polymers with a really high molecular weight, where the end groups are not detectible anymore because of small noise to end group signal ratio.

3.2.1.1 Poly[bis-(undecen-10-yl) phenylphosphate] (4b)

The comparison of entries 1 and 2 on Table 3-1 shows that a shorter reaction time leads to a lower molecular weight which is important especially to the ADMET solution polymerization since those polymerizations are much slower as bulk polymerization by ADMET. The great advantage of these ADMET solution polymerizations compared to bulk polymerizations is the high controllability of the molecular weight of the polymers, since the viscosity increases radical in bulk that a decent stirring is not ensured anymore.

Entries 2 to 4 show that the amount of Grubbs catalyst 1st generation used did not affect the molecular weights obtained. Furthermore Table 3-1 indicates that also reactions (Entries: 5 – 8) by Hoveyda-Grubbs catalyst 2nd generation (**C2**) lead to the desired polymers and this faster with higher molecular weights but not as well controllable as reactions by Grubbs catalyst 1st generation. Observable is the exception of entry 5 which was not successfully feasible since the catalyst was not stable enough over 60 h.

After addition of the Grubbs catalyst 1st generation, the mixtures immediately turned red, with a gradual increase of the viscosity (only visible at bulk polymerizations) to give polymers with a broad range of molecular weights depending on the reaction conditions (Table 3-1). The same holds true for Hoveyda-Grubbs catalyst 2nd generation except there is no color change. It remains green until the catalyst is destroyed (brown color). The polymeric materials isolated were in the range of 1,000-20,000 (M_n) g·mol^{-1}, which included the target area of 3,000 to 10,000 g·mol^{-1} perfectly.

Since tetrahydrofuran (THF) is a coordinating solvent the polymerizations in the presence of THF under the usual reaction conditions (entries 9 and 10) were not able to polymerize the monomer.

Additionally, entries 11 and 12 realize the polymerization with Grubbs catalyst 1st generation catalyst by typical conditions for ADMET polymerizations, namely reduced pressure and 60 °C, which can be compared with entries 7 and 8 with Hoveyda-Grubbs catalyst 2nd generation catalyst. As mentioned before the molecular weight is higher by using Hoveyda-Grubbs catalyst 2nd generation catalyst.

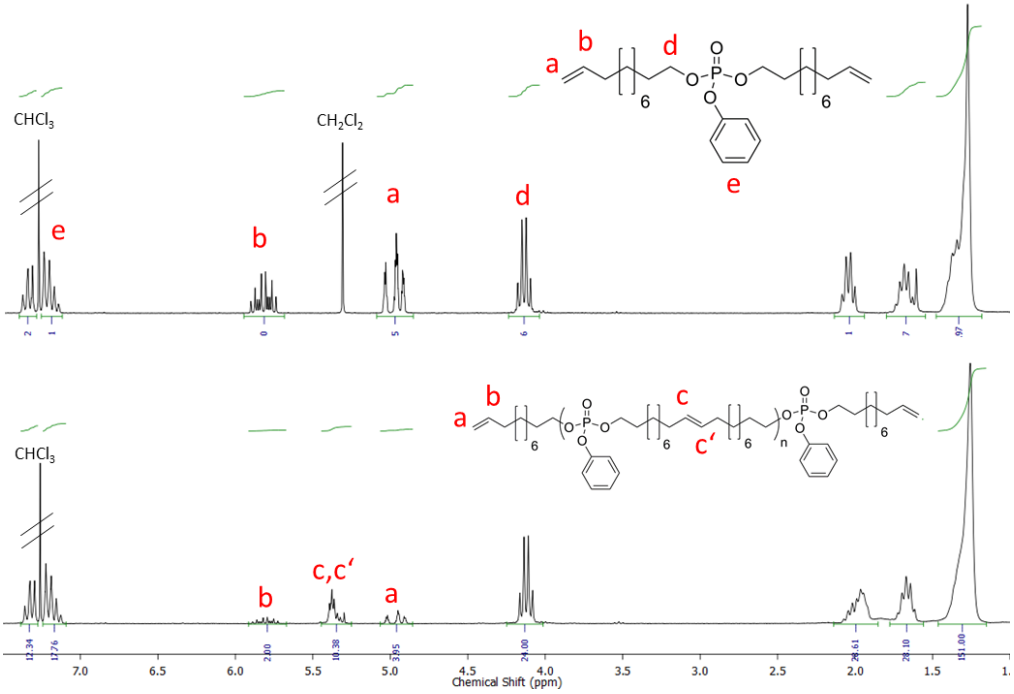


Figure 3-14: ^{1}H NMR spectrum of monomer **2b** (top) and the respective polymer **4b** proving the formation of internal double bonds at 5.4 ppm (250 MHz in $CDCl_3$ at 25 °C).

The resonances of the ^{1}H NMR spectrum of polymer **4b** (Figure 3-14) labeled belong respectively to the phenyl pendant group (7.2 ppm), the terminal groups (a: 5.1 ppm, b: 5.8 ppm) and internal (c,c: 5.4 ppm) olefinic protons. The polymerization of monomer **2a** is easily monitored by ^{1}H NMR spectroscopy. Figure 3-14 shows the ^{1}H NMR spectrum of the resulting polymer **3a** compared to the respective monomer **2a**. It can be seen that the terminal double bond protons (a and b) at 5.1 and 5.8 ppm are smaller after polymerization. Moreover, as expected, a new peak (c,c) appeared at 5.4 ppm due to formation of internal double bonds. As no additional resonances can be detected in the spectrum, the formation of a perfect telechelic diolefinic PPE without isomerization was produced. In general, butenyl groups are unlikely to isomerize as they would produce allylic double bonds.[23]

In addition, ADMET produces only linear polymers that possess terminal double bonds as the respective end groups which are accessible for further reactions. NMR spectroscopy allows the calculation of the absolute molecular weight. For instance the integration of all signals of UPPE **3a** and monomer **2a** are shown in Figure 3-14. By integration of the terminal olefinic signals in comparison with the internal double bonds the determination of the molecular

weight of the polymers is possible. The results are listed in Table 3-1. For high molecular weights the method is limited of course, as the noise to end group signal ratio decreases.

Figure 3-15 of polymer **4b** proves the presence of terminal double bond signals in ^{13}C NMR spectrum in Figure 3-15. The two signals of the terminal double bonds in the ^{13}C NMR spectrum of polymer **4b** are highlighted.

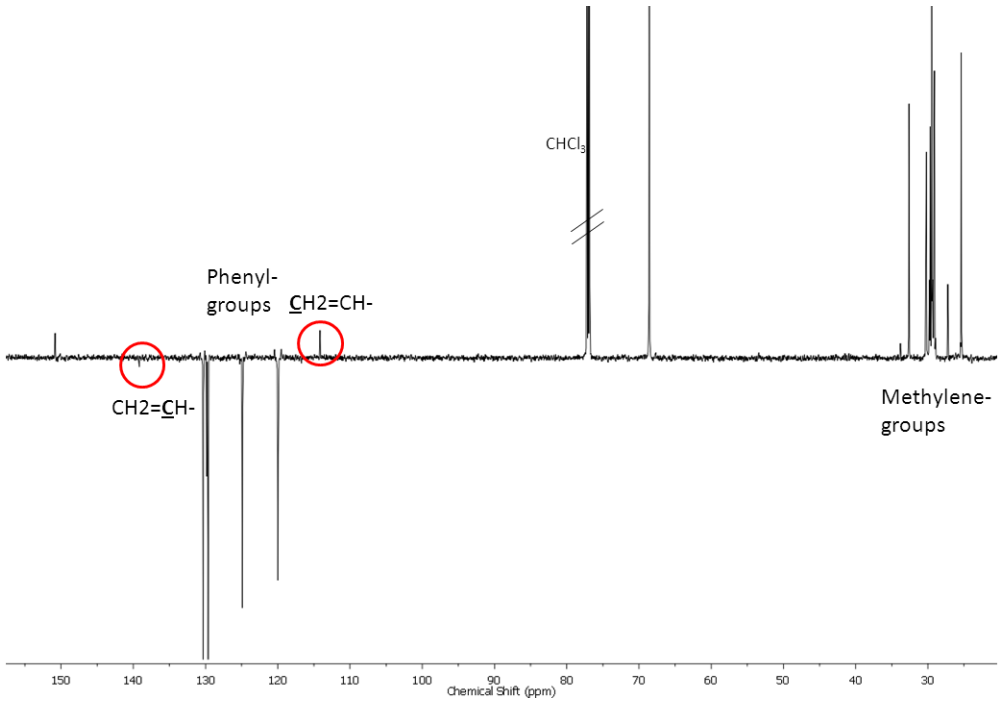


Figure 3-15: ^{13}C NMR spectrum of polymer 4b shows the presence of the terminal double bond signals at 114.2 and 139,2 ppm (700 MHz in $CDCl_3$ at 25 °C).

GPC analyses have been made and some representative curves are discussed below. The UPPE **4a** with $M_{n,GPC}$ = 4,400 g·mol^{-1} and a PDI of 1.58 was formed by solution polymerization. This observation clearly illustrates that the monomer has been converted into a polymer with relatively low molecular weights via ADMET polymerization. For verification reasons a polymerization under the exact same conditions like the polymer above is realized (4,700 g·mol^{-1}) and it is also displayed in Figure 3-16. As seen in Figure 3-16 the curves are almost identical indicating an empirical molecular weight control by variation of the reaction conditions.

With a bulk ADMET polymerization at 25 °C, the peaks at low molecular weights positions decreased, the elution curve of the 4,700 g·mol^{-1} UPPE was gradually shifted to higher molecular weight region (M_n = 8,200 g·mol^{-1}), and molecular weight distribution became broader (PDI = 2.19). The same is applied for the bulk polymerization at 60°C with a M_n of 17,700 g·mol^{-1}. Also, PDIs for all UPPEs became broader with increasing molecular weight, indicating shorter polymerization time with less homogenous reaction mixture because of

the higher viscosity resulted in higher molecular weights but broader molecular weight distributions, which is in accordance with the mechanism of ADMET polymerization.

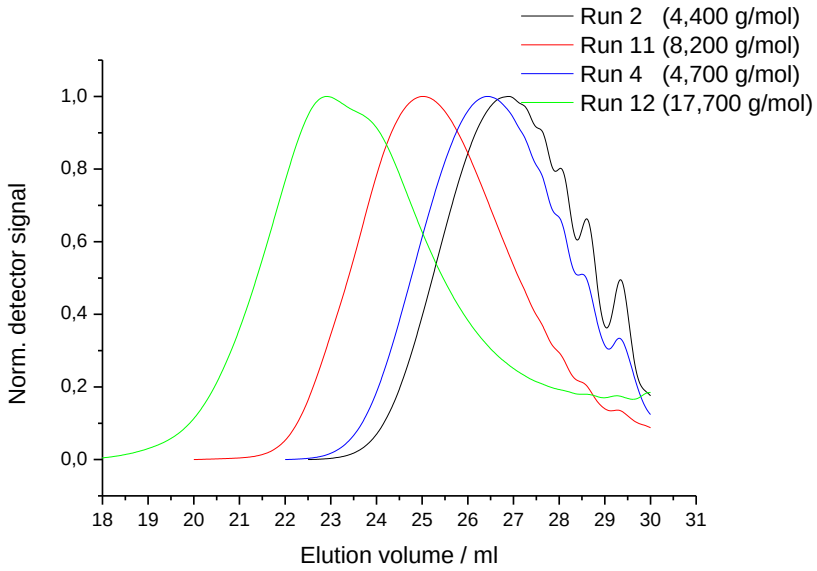


Figure 3-16: GPC-elugram of polymer **4b** (4,400 and 4,800 g·mol^{-1} by solution and 8,200 and 17,700 g·mol^{-1} by bulk polymerization, respectively) vs. polystyrene standards in THF measured by RI-detector. The presence of oligomers can be clearly detected for low molecular weight polymers 4,400 and 4,800 g·mol^{-1}.

Figure 3-16 shows a representative GPC elugram of a polymer from monomer **2b** synthesized in bulk (8,200 and 17,700 g·mol^{-1}), in comparison to the diluted synthesis performed in solution (4,400 and 4,700 g·mol^{-1}). The polymers of 4,400 and 4,700 g·mol^{-1} were also injected to the GPC and it can be observed, that the polymers from solution polymerization still contain smaller oligomers fractions (peaks, which elute between 30 and 28 mL).

Subsequently, post-polymerization reactions could be carried out. For instance a thiol-ene reaction could be realized to link thiols at the double bonds in the polymers. Hydosilylation of the terminal double bonds might be a decent option to receive silyl end groups. An ATRP in order to link poly(ethylene glycol) methyl ether methacrylate ($PEGMA_{475}$) on both sides of the polymer to observe water solubility could be realized as well.

In order to discuss the thermal properties polymer **4b** was hydrogenated. Figure 3-17 shows the ^{1}H NMR spectrum of polymer **4b** (bottom) and the hydrogenated version **4b$_h$**. The saturated PPEs **4b$_h$** were synthesized from **2b** via catalytic hydrogenation. ^{1}H NMR and ^{13}C NMR spectroscopy proves complete reduction of all double bonds (Figure 3-17).

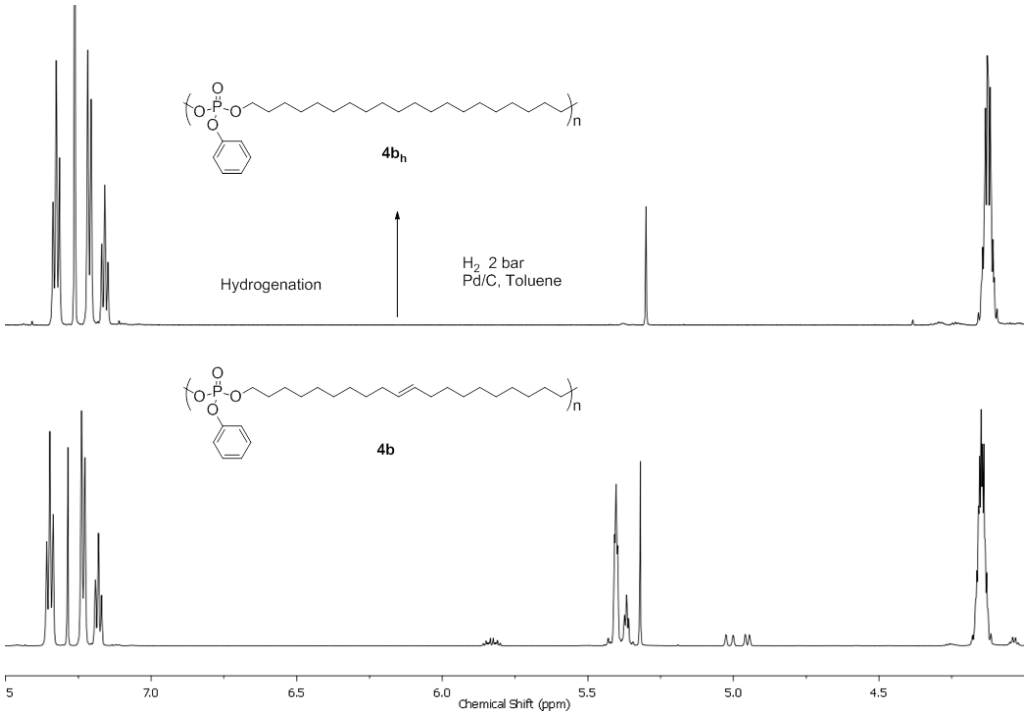


Figure 3-17: ^{1}H NMR investigation (700 MHz in $CDCl_3$ at 25 °C) showing the aromatic and olefinic region of the spectra of polymer and hydrogenated polymer (**4b** and **4b$_h$**).

The UPPEs synthesized in this study range from oils to rubbery material depend on the crystallinity, which are soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2 and toluene. The flexible P-O-C groups in the backbone commonly result in PPEs with low glass transitions temperatures (-40 °C).[55, 56] The Fox equation for these polymeric systems estimates the T_g at -30 °C for a PPE homopolymer dependent on the length of the polymer, which is consistent with the role of an internal plasticizer of the phosphoester monomer itself.

The glass transition temperatures (T_g) and the melting points (T_m) were determined by differential scanning calorimetry (DSC) under nitrogen atmosphere (Figure 3-18). The materials synthesized showed the typical low temperature glass transitions of PPEs.

In addition, the melting temperatures of the polymers **4b** (here **6**) and **4b$_h$** (here **7**) (50,000 g·mol^{-1}[23]) change as the unsaturated backbone is hydrogenated. Even polymer **6** exhibits a melting temperature at -7 °C with dH_m (molar heat of fusion) = 24.79 J·g^{-1}[23] upon heating and cooling, while the equivalent hydrogenated polymer **7** melts at 44 - 45 °C with a dH_m of 61.66 J·g^{-1}[23] due to the disappearance of the double bonds which act as a defect during the crystallization of the polymer (Figure 3-18). All the other unsaturated polymers exhibit different glass transitions at -32 °C for “lower” molecular weight (14,000 g·mol^{-1}[23]) and -53 °C for a “medium” molecular weight (20,000 g·mol^{-1}[23]).

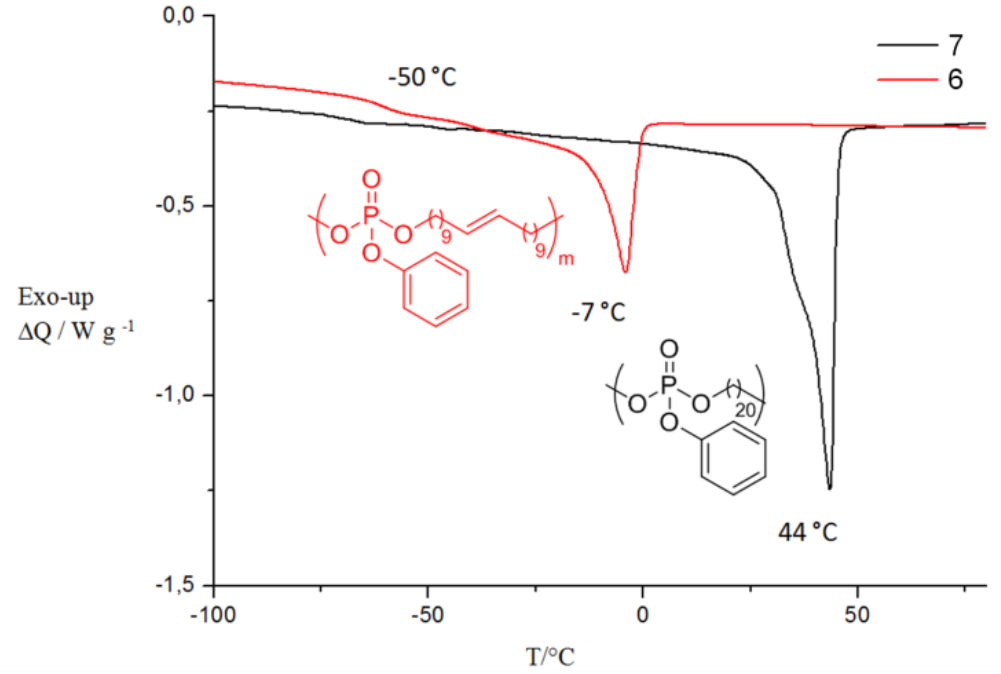


Figure 3-18: DSC thermograms of **4b** (red) and **4b**$_h$ (black).

3.2.1.2 Poly[bis-(buten-3-yl) phenylphosphate] (4a)

Entries 13-16 show the ADMET polymerization of monomer **2a**. The reactions of **2a** proceed in the same manner as for **2b,** except that the molecular weights are lower because of the lower molecular weight of the monomer. Figure 3-19 shows the ^{1}H NMR of resulting polymer **4a**.

Figure 3-19 shows the ^{1}H NMR spectra of polymer **4a** (top) and of monomer **2a** (bottom) respectively with the terminal double bonds at 5.8 ppm and 4.9 ppm and the formation of internal double bonds at 5.4 ppm. The integration of the region of the terminal double bonds in comparison with the internal double bonds allows the determination of the molecular weight of the polymers.

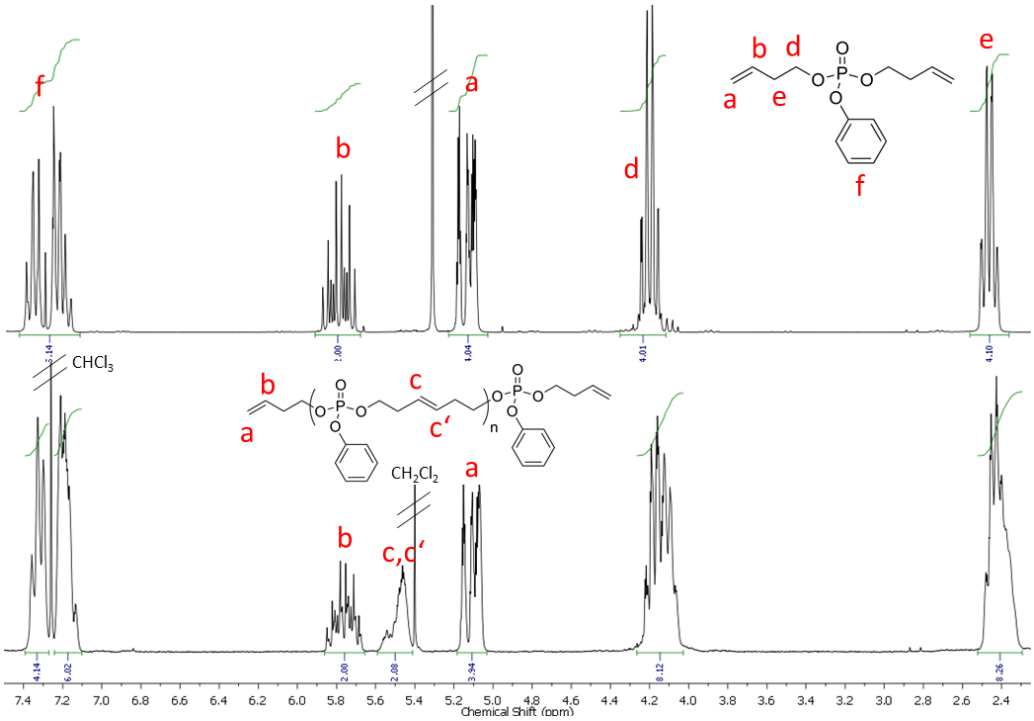


Figure 3-19: ^{1}H NMR spectrum of monomer **2a** (top) and the respective polymer **3a** proving the formation of internal double bonds at 5.4 ppm (250 MHz in $CDCl_3$ at 25 °C).

3.2.1.3 Poly[bis-(undecen-10-yl) methylphosphate] (4c)

Entry 17 and 18 used the novel monomer **2c. 2c** was successfully polymerized in entry 17 and 18 at different temperatures to **4c**. The reactions of **2c** proceed in the same manner as for the other monomers **2a** and **2b**. NMR results are shown in Figure 3-20. The resonances in Figure 3-20 labeled belong respectively to the methyl pendant group (3.7 ppm), the terminal groups (a: 4.9 ppm, b: 5.7 ppm) and internal (c,c': 5.4 ppm) olefinic protons. In the spectra on the bottom in Figure 3-20 the absence of the terminal olefinic signal is not visible because the molecular weight is too high to receive a decent signal to noise ratio.

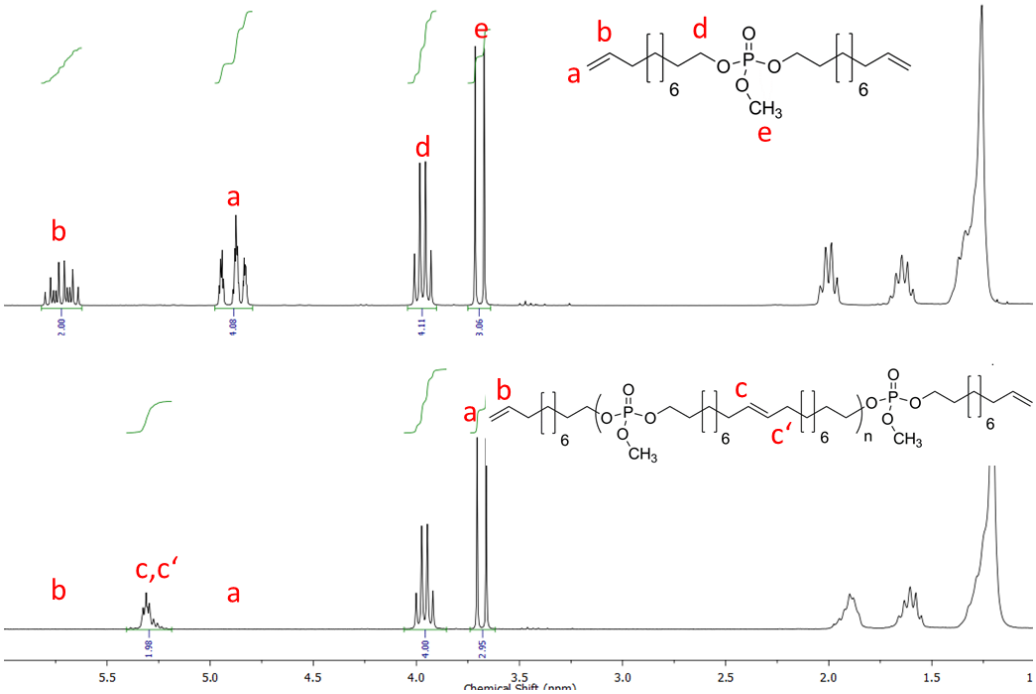


Figure 3-20: ^{1}H NMR spectrum of monomer **2c** (top) and the respective polymer **4c** proving the formation of internal double bonds at 5.4 ppm (250 MHz in $CDCl_3$ at 25 °C).

In order to discuss the thermal properties polymer **4c** was hydrogenated. Figure 3-21 shows the ^{1}H NMR spectrum of polymer **4c** (bottom) and the hydrogenated version **4c$_h$**. The saturated PPE (**4c$_h$**) was synthesized from **2c** via catalytic hydrogenation.

Hydrogenation of UPPEs broadens the range of accessible materials by this synthetic strategy. Metathesis chemistry, in fact, is giving promising results in the preparation of degradable materials from renewable resources.[57] Polymers **4b$_h$** (Figure 3-17) and **4c$_h$** (Figure 3-21) can be regarded as a degradable polyethylene with predetermined breaking points inside the backbone. ^{1}H NMR and ^{13}C NMR spectroscopy proves complete reduction of all double bonds (Figure 3-17; Figure 3-21).

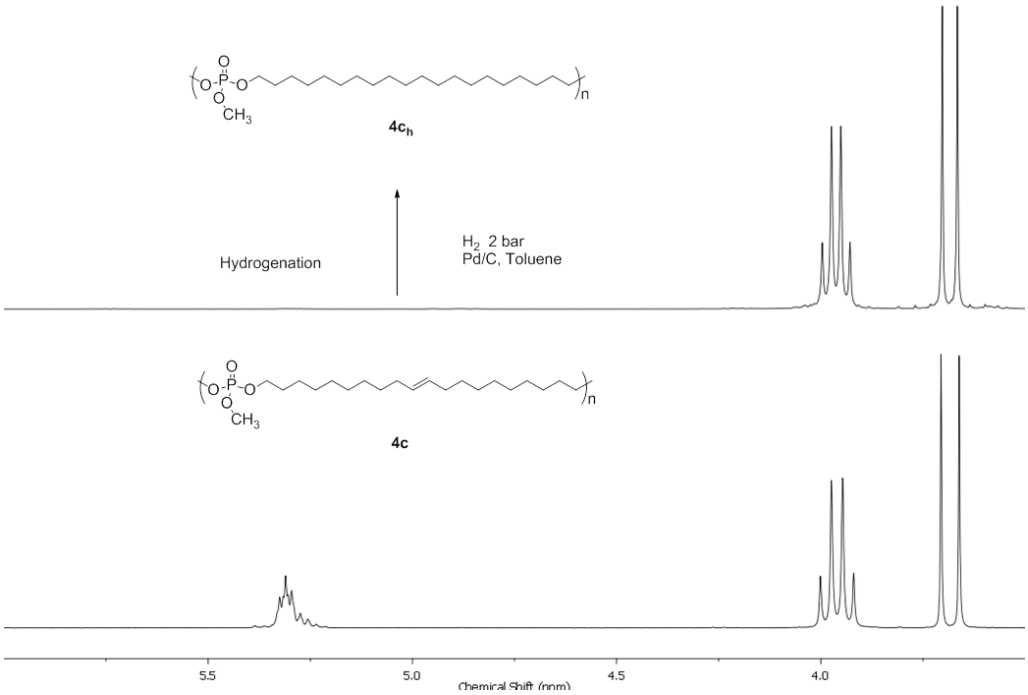


Figure 3-21: ^{1}H NMR investigation (250 MHz in $CDCl_3$ at 25 °C) showing the aromatic and olefinic region of the spectra of polymer and hydrogenated polymer (**4c** and **4c$_h$**).

The thermal stability of the polymers **4c** was examined by thermal gravimetric analysis (TGA; Figure 3-23) while the glass transition temperatures (T_g) and the melting points (T_m) were determined by differential scanning calorimetry (DSC) under nitrogen atmosphere (Figure 3-22). The materials synthesized showed the typical low temperature glass transitions of PPEs.

The polymer of monomer **2c** fulfilled the requirements of an increased melting point compare to the phenyl equivalent the melting point for the unsaturated polymer is at 17 °C (dH_m = 26.42 J·g^{-1}) instead of -7 °C (dH_m = 24.79 J·g^{-1}). The saturated polymer got an increased melting point of 63 °C (dH_m = 72.49 J·g^{-1}) instead of 44 – 45 °C (dH_m = 61.66 J·g^{-1}) for the diene phenyl phosphate.

These properties might have positive effects of the features of making nanoparticles out of it, since they are solid at room temperature and hence the nanoparticles are more stable. On the other side, the methyl group is harder to cleave than the phenyl group. In order to know whether the methyl polyphosphate has improved properties compared to the phenyl polymer more experiments are essential.

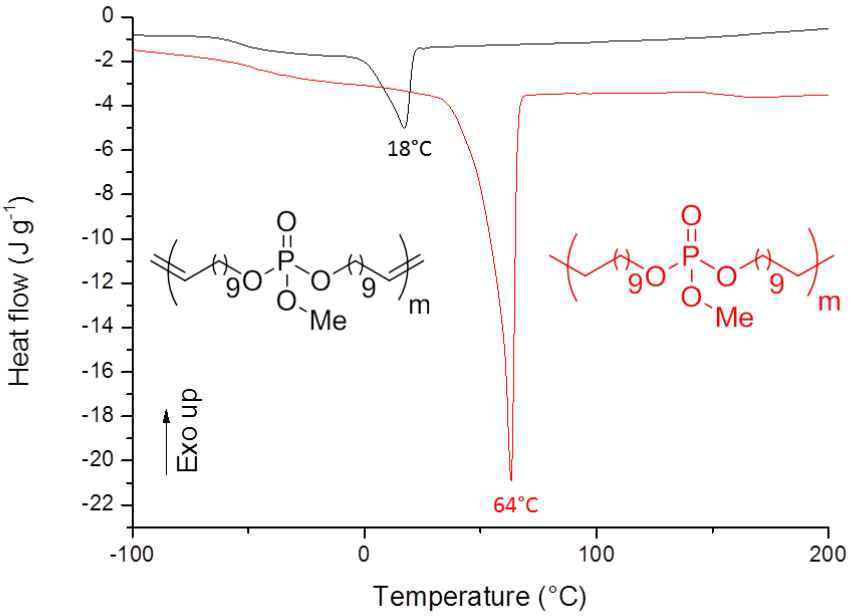


Figure 3-22: DSC thermograms of **4c** (black) and **4c$_h$** (red).

TGA curves in Figure 3-23 exhibit a one-step degradation process, and the temperature range of 50% weight loss was determined to lie between 250 and 350 °C, demonstrating the good thermal stability of these polymers compare to polymers like Poly-L-lactide (PLLA) which is decomposing between 187 and 384 °C[58] or polystyrene (PS) with a decomposition range between 400 and 475 °C[59] or PEG with 340 to 420 °C[60] as decomposition range. The curve of **4c** displayed a small increase of weight at low temperatures, which can be explained by oxidation of the double bonds. Moreover, the thermal degradation of UPPEs leads to the formation of a phosphate char with a theoretical value of 23,0 %. In fact, the residues obtained at 400 (**4c**) and 700 °C (**4c$_h$**) are at 22,0 % and 25 % which is within the error range of the TGA analysis.

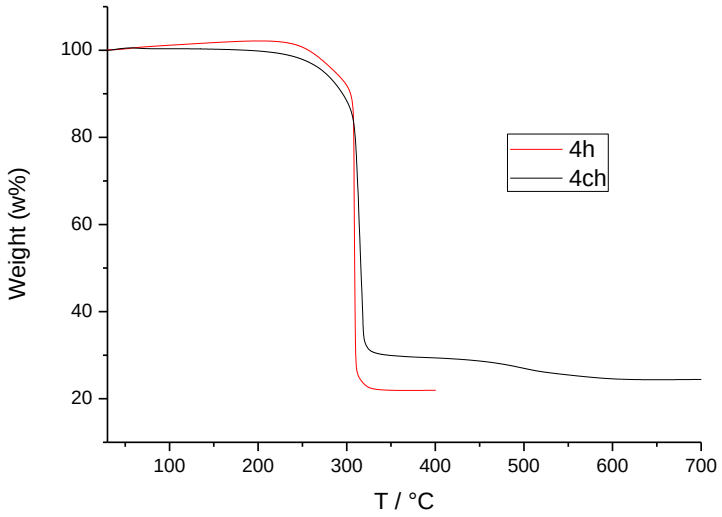


Figure 3-23: TGA thermograms of **4c** and **4c**$_h$.

The systematic process of the polymerization allows the study of ideal models of functionalized UPPEs with precisely placed substituents (see below) simply by choosing the proper catalyst and monomer, in the presence or absence of solvent and under atmospheric or reduced pressure, leads to quantitative yield of the desired polymer.[23] Only polymers of **2b** were applied for post-polymerization modification reactions, since the molecular weight is higher, but its reaction behavior is related to **2a**.

3.2.1.4 Copolymer of bis-(undecen-10-yl) phenylphosphate and bis-(undecen-10-yl) phosphate

Moreover, it was shown that monomer **2e** can be polymerized but characterization proved difficult, since the strong interactions between the hydroxyl group lowers its solubility. Hence a copolymerization was realized with monomer **2e** and **2b** in a ratio of 1 to 4. ^{1}H, ^{13}C, H-DOSY NMR as well as GPC are confirming the copolymerization. The reaction conditions were the same as described at the beginning of the chapter. Figure 3-24 displayed the ^{1}H NMR of the copolymer of monomer **2e** and **2b** and the two monomers itself to compare with. As mentioned above the ratio between them are 1 to 4 as seen by the signals of the methylene group next to the phosphate, which are different for both kinds of monomers and both signals are coexistent in the copolymer. Together with ^{13}C, H-DOSY NMR as well as GPC results (listed in Experimental part) the synthesis of the copolymer is confirmed.

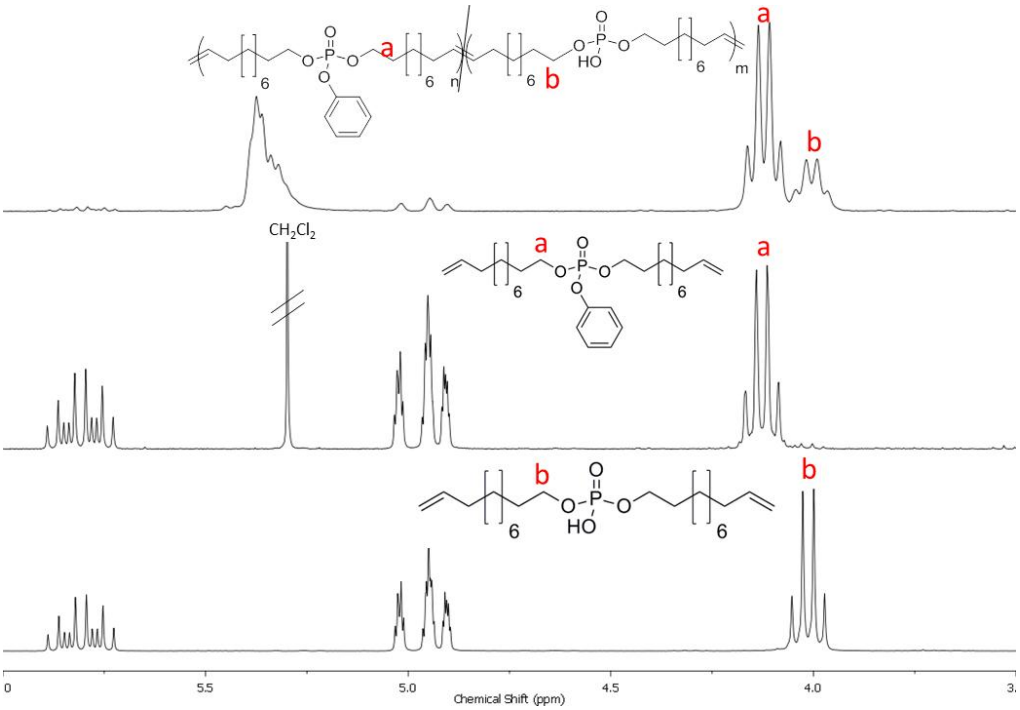
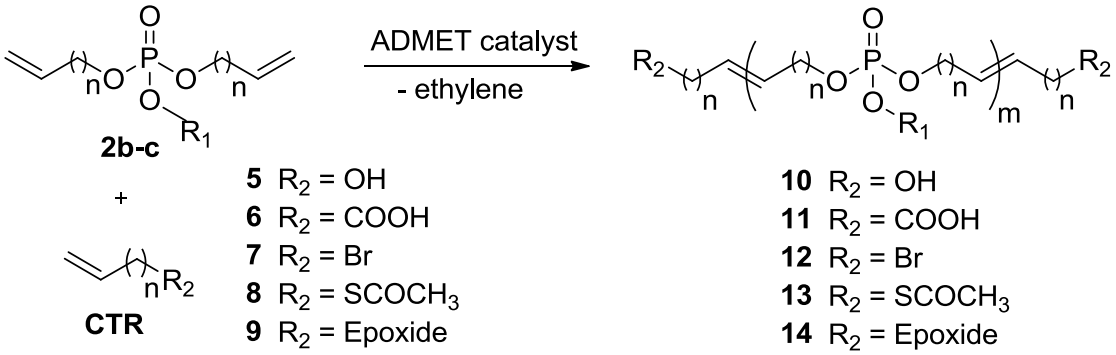


Figure 3-24: ^{1}H NMR spectra of monomer **2e** (bottom) and **2b** (middle) vs copolymer of **2e** and **2b** with a ratio of 1 to 4 shows the presence of both kinds of signals of the methylene group next to the phosphate (250 MHz in $CDCl_3$ at 25 °C).

3.2.2 Polycondensation with CTR via ADMET

This chapter describes the ADMET synthesis to telechelic UPPEs. The backbone is based on UPPEs, made by the ADMET polymerization of monomers **2b** and **2c**, respectively. Furthermore a chain termination reactant (CTR) was added to the reaction mixture. A CTR is a chain stopper with only one double bond in the structure and having a particular number of methylene groups, between their olefin and precursor. It was used to cap the polymer chain ends to yield difunctional telechelic material. The CTRs with nine methylene groups have two advantages i) the lengths is the same as the lengths of the methylene groups between the phosphates ii) the molecular weight of the CTR allows to work under vacuum without losing the CTR due to a high boiling point.



Scheme 3-4: ADMET polymerization of phosphate monomer **2b-c** and CTR **5-9**.

By variation of the reaction conditions, the molecular weight of ADMET polymers can be empirically controlled; however in the presence of a chain stopper, the molecular weights can be adjusted very accurately. In the next experiments, 10-undecen-1-ol, 11-bromo-1-undecene, 1,2-epoxy-9-decene, *S*-10-Undecen-1-yl thioacetic acid ester, and 10-undecenoic acid were used as the respective CTRs to generate, PPEs carrying two alcohol-, bromide-, epoxy-, thioacetate, and carboxylic acid groups (Scheme 3-4). In all cases no interference with the catalyst activity was observed and perfect matching between theoretical and experimentally determined molecular weights was detected (compare Table 3-1). Molecular weight distributions are typically around 2 as expected for a linear polycondensation. Table 3-2 lists the molecular weight data of the resulting materials and the CTRs as well as **2b/c** to CTR ratios of the polymerizations by Scheme 3-4.

Table 3-2: Metathesis polymerization of **2b** and **2c** and CTR, molecular weight data of the resulting materials and the **2b/c** to CTR ratios.

Product[(c)]	CTR	Ratio 2b-c:CTR	Mw[(a)] [g/mol]	Mn[(a)] [g/mol]	PDI[(a)]	Mn[(b)] [g/mol]	Mn (cal)[(d)] [g/mol]
10b	**5**	7.8:2	8,500	4,300	1.96	3,900	3,900
10b	**5**	15:2	4,800	2,900	1.68	6,800	7,100
10b	**5**	20:2	19,800	9,100	2.17	9,300	9,300
10c	**5**	10:2	11,100	5,100	2.16	4,200	4,200
10c	**5**	20:2	17,600	7,300	2.42	8,100	8,100
11b	**6**	7.5:2	5,900	2,900	2.06	2,200	3,700
11b	**6**	15:2	14,800	8,400	1.75	4,300	6,900
11b	**6**	20:2	23,900	12,400	1.92	9,400	8,000
12b	**7**	7.5:2	11,800	6,400	1.84	3,600	3,600
12b	**7**	15:2	18,700	10,100	1.87	6,100	7,200
12b	**7**	20:2	23,500	12,200	1.93	10,400	9,500
13b	**8**	7.5:2	9,900	5,300	1.85	3,400	3,600
13b	**8**	15:2	20,300	11,700	1.74	4,000	7,200
13b	**8**	20:2	28,600	14,300	2.00	9,400	13,100
14b	**9**	7.5:2	14,600	6,800	2.16	6,800	3,700
14b	**9**	15:2	25,100	9,800	2.56	21,000	7,000
14b	**9**	20:2	29,200	11,300	2.59	38,600	9,300

[(a)] Determined by gel permeation chromatography (GPC) in THF vs. polystyrene standards.
[(b)] Determined by NMR.
[(c)] Reaction conditions as described in the experimental section.
[(d)] Determined by calculation.

3.2.2.1 Unsaturated telechelic UPPE diol (10b)

By using Grubbs catalyst 1st generation in a direct polymerization of monomer **2b** and CTR (**5**) polymer **10b** (**b** for polymer of monomer **2b**) was obtained as product (Scheme 3-4). A monomer to CTR ratio of 7.8:2 was used for a targeted molecular weight of the unsaturated telechelic diol of 3,900 g·mol^{-1}. The ^{1}H NMR spectrum indicated a M_n of 3,900 g·mol^{-1} (7.8 average number of repeat units; Table 3-2), which was precisely the target of 3,900 g·mol^{-1}. GPC analysis resulted in a PDI of 1.96 of this telechelic polymer, which means the conversion reaches practically 100% (see above).[61]

Product **10c** attempted to do the same telechelic modifications with the monomer **2c**. Table 3-2 shows the results of monomer **2b** and **2c**.

10b was characterized by ^{1}H, ^{13}C, C,H-COSY and DOSY NMR spectroscopy. Figure 3-25 to Figure 3-29 show the obtained NMR spectra in deuterated chloroform ($CDCl_3$). The important signals are assigned to the hydrogen atoms in the compound.

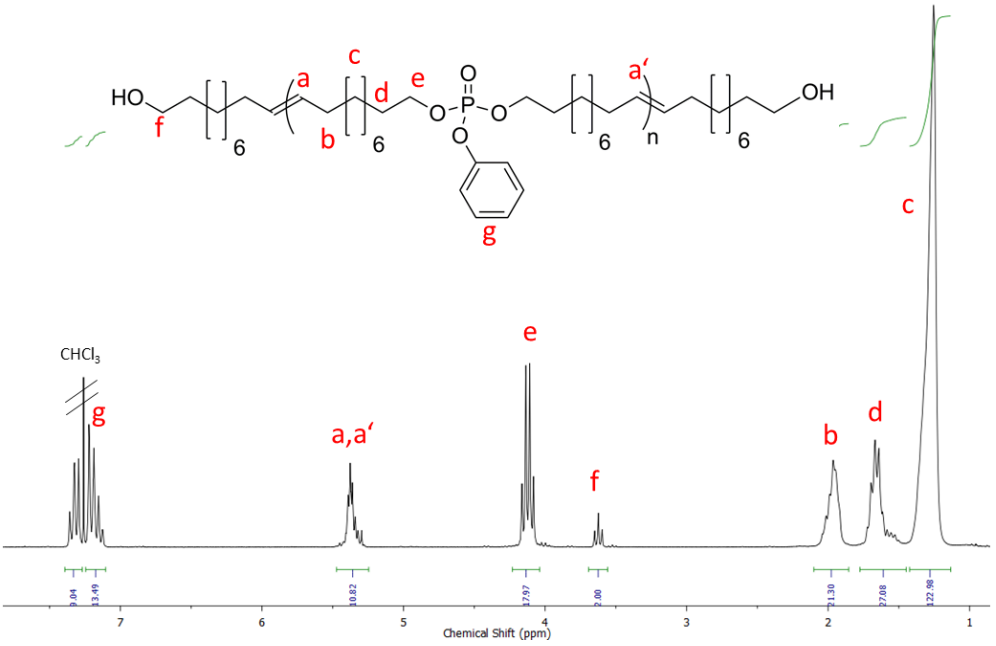


Figure 3-25: ^{1}H NMR spectrum (250 MHz in $CDCl_3$ at 25 °C) of the telechelic diol **10b**.

Figure 3-25 shows a first proof for observing the telechelic diol (**10b**) by ^{1}H NMR. Since all signals are assigned to the hydrogen atoms in the structure because the chemical shifts are suitable and the integration of those signals confirming the successful synthesis of the diol. The resonances labeled belong respectively to the phenyl pendant group (g: 7.2 ppm), the internal olefinic protons (c,c: 5.4 ppm) and the signal of the methylene group next to the phosphate (f: 3.6 ppm). Moreover, the ^{1}H NMR spectra indicated that the unsaturated telechelic diol (**10b**) was completely difunctional within the limits of detection of a 700 MHz ^{1}H NMR spectrometer. Thus the ^{1}H NMR spectra clearly prove that no terminal olefins are present within the sample.

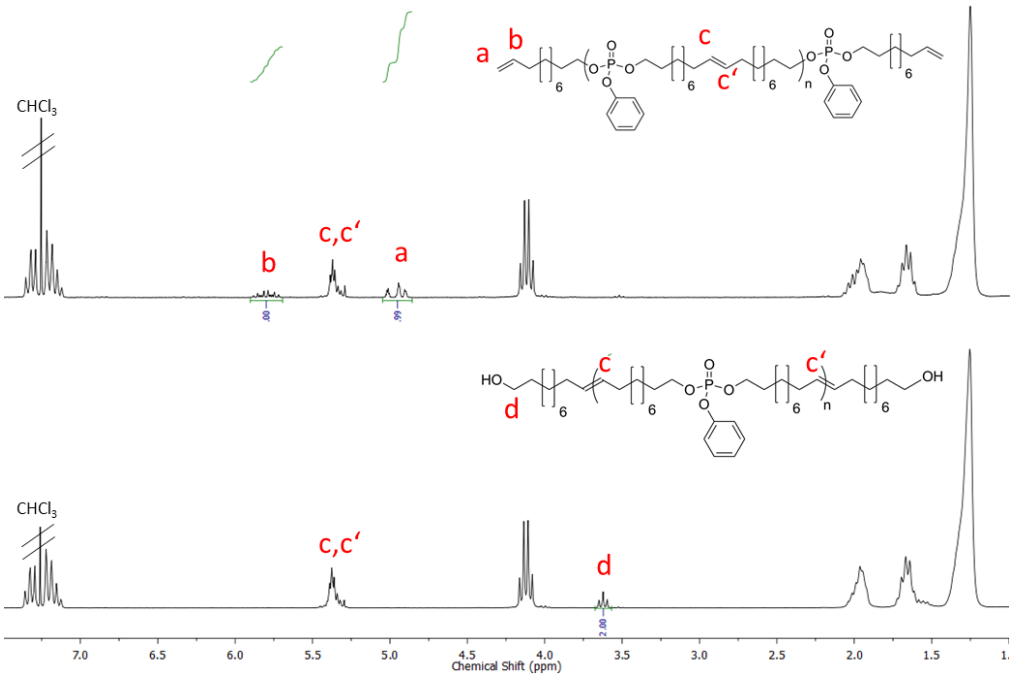


Figure 3-26: ^{1}H NMR spectrum of polymer **4b** (top) and the telechelic polymer **10b** proving the complete disappearance of the terminal double bonds at 5.8 ppm and 4.9 ppm (250 MHz in $CDCl_3$ at 25 °C).

The ^{1}H NMR spectra shown in Figure 3-26 compare a usual UPPE (**4b**; top) without any modifications with a telechelic UPPE (**10b**; bottom). It indicates the appearance of the signals for the terminal double bonds at 5.8 and 4.9 ppm and the appearance of a new signal for the methylene group next to the functional end group in this case the hydroxyl group.

The resonances for the internal double bonds and for the methylene group next to the hydroxyl group can be detected, allowing the determination of the degree of polymerization, equally as explained before. As no additional resonances can be detected in the spectrum, the formation of a perfect telechelic diolic PPE without isomerization was produced.

Figure 3-27 illustrate the comparison of ^{13}C NMR spectra of a usual UPPE (top) with a chemical shift of 114.2 and 139.2 ppm for the terminal double bonds and the corresponding peak assignments to the respective group and the telechelic diol with a chemical shift of the methylene group next to the hydroxyl group at 63.0 ppm. The appearance of the resonance signal of the methylene group next to hydroxyl group along with the disappearance of the two signals for the terminal olefinic region strongly suggests the complete transformation of terminal double bonds into hydroxyl groups.

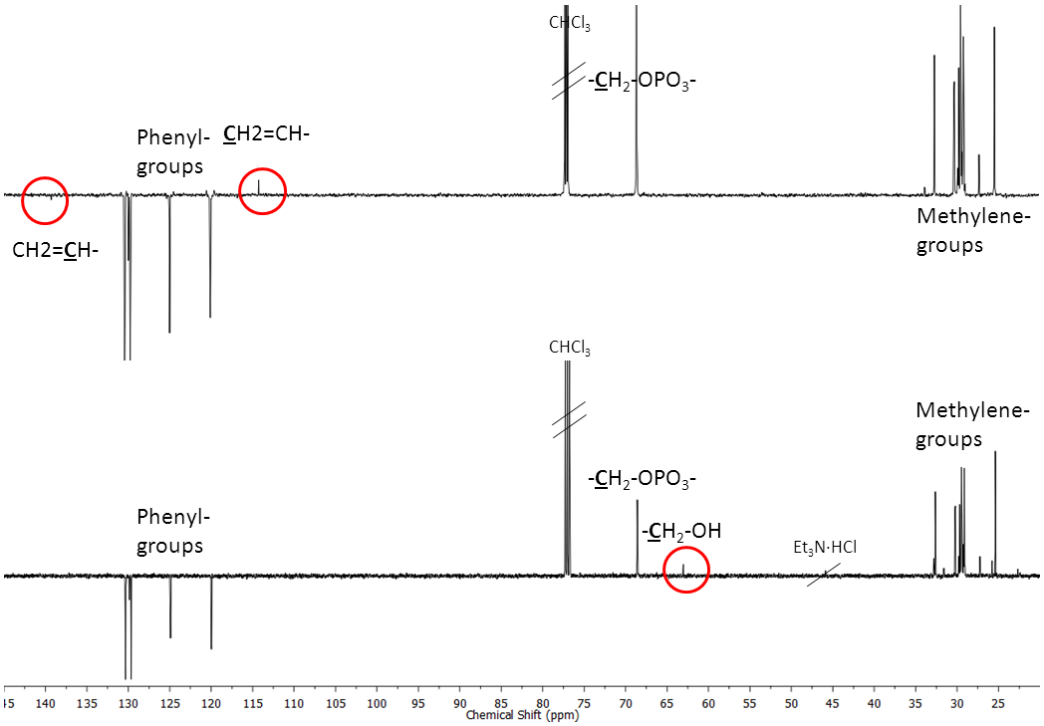


Figure 3-27: ^{13}C NMR spectrum of polymer **4b** (top) and the telechelic polymer **10b** proving the complete disappearance of the terminal double bonds at 114.2 ppm and at 139,2 ppm as well as the appearance of the methylene group next to hydroxyl group at 63.0 ppm (700 MHz in $CDCl_3$ at 25 °C).

^{13}C-^{1}H COSY of polymer **10b** (Figure 3-28) assign the presence of methylene group next to the hydroxyl group signals in ^{13}C NMR spectrum in Figure 3-27 to the terminal olefinic signals in ^{1}H NMR. The red circled signal is the peaks for the methylene group next to the hydroxyl group of the telechelic UPPE.

Another certain proof for covalent modification of the polymer with the functional groups (for all CTRs) can be obtained from the ^{1}H-DOSY NMR spectra. For all telechelic polymers the resonances for the methylene groups next to the endgroups can be detected at the same diffusion value as the other polymer signals proving the formation of telechelic materials (Figure 3-29 shows the ^{1}H DOSY NMR of the telechelic diol, which is representative for the other telechelic material).

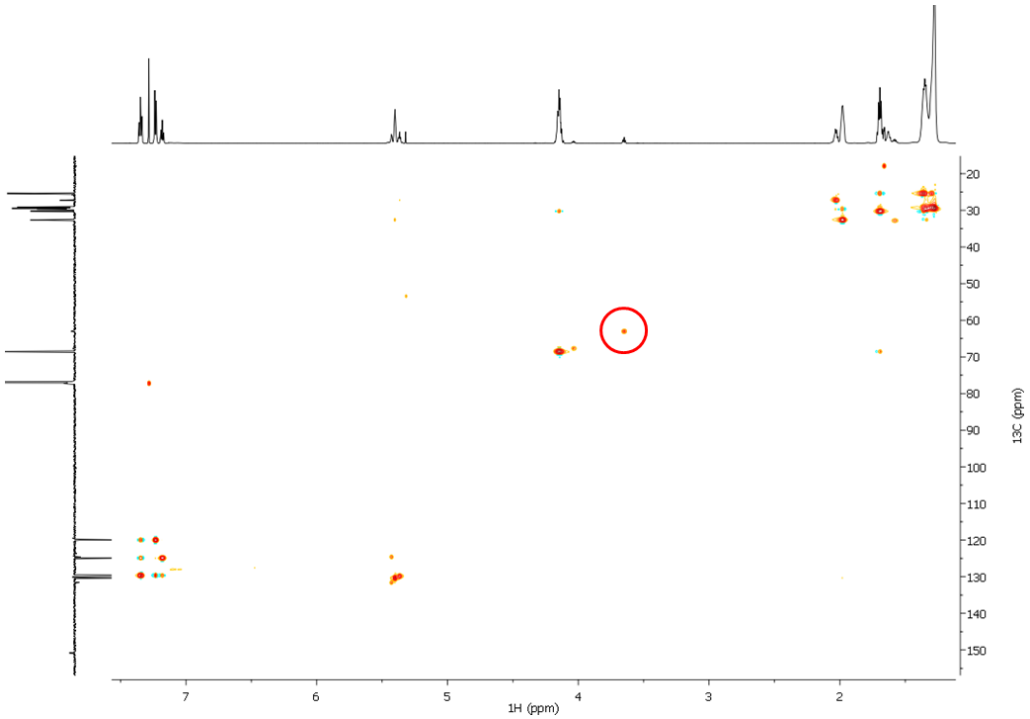


Figure 3-28: ^{1}H-^{13}C-2D-NMR spectrum of polymer **10b** proving the correlation of the signal at 63.0 ppm (^{13}C-NMR) to the methylene group next to the hydroxyl group at 3.6 ppm (^{1}H-NMR) (500 MHz in $CDCl_3$ at 25 °C).

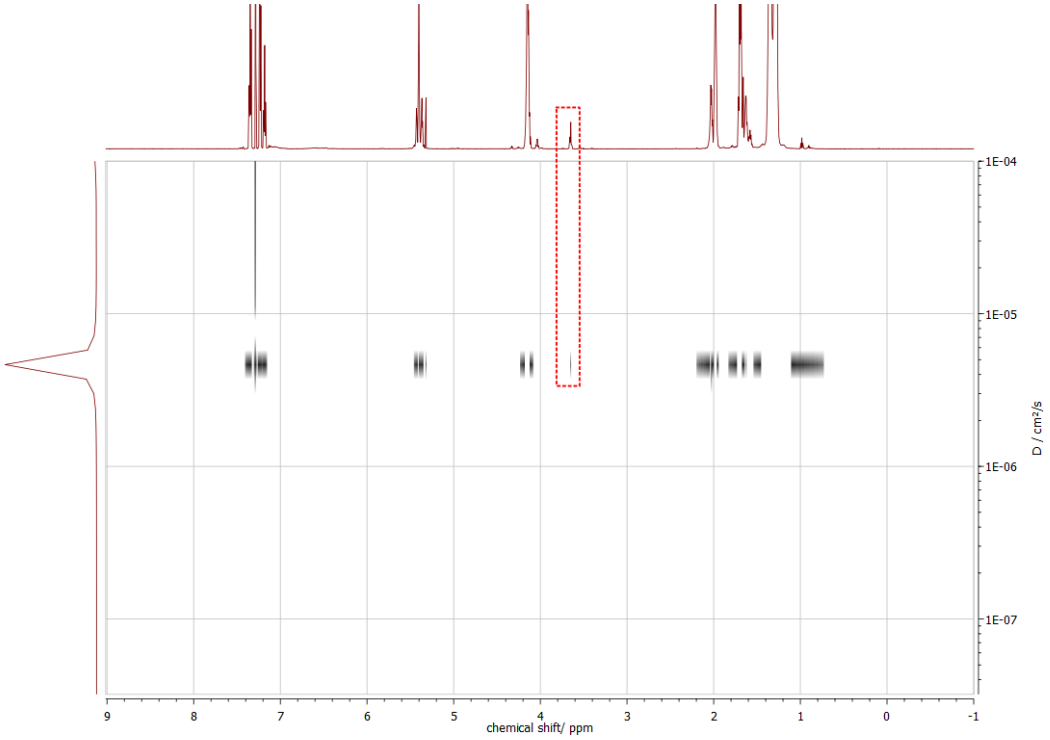


Figure 3-29: ^{1}H-DOSY NMR spectrum of the telechelic diol proving the formation of telechelic material (700 MHz in $CDCl_3$ at 25 °C).

The GPC method is used to trace the polymerization of monomer **2b** with a CTR, and the results are listed in Table 3-2. The GPC curve of **10b** the telechelic UPPE with the three different chain length are displayed in Figure 3-30.

It has to be mentioned again that although GPC is well known to determine the molecular weight and molecular weight distribution for linear polymers by using calibration with linear poly(styrene), for UPPEs, its size smaller than that of linear once with the same molecular weight because of the difference in hydrodynamic volume. For exact results it has to be the same standard as the sample. In order to observe such information the method has to be changed to absolute GPC by for instance using a viscosity detector. Here it is an approximation.

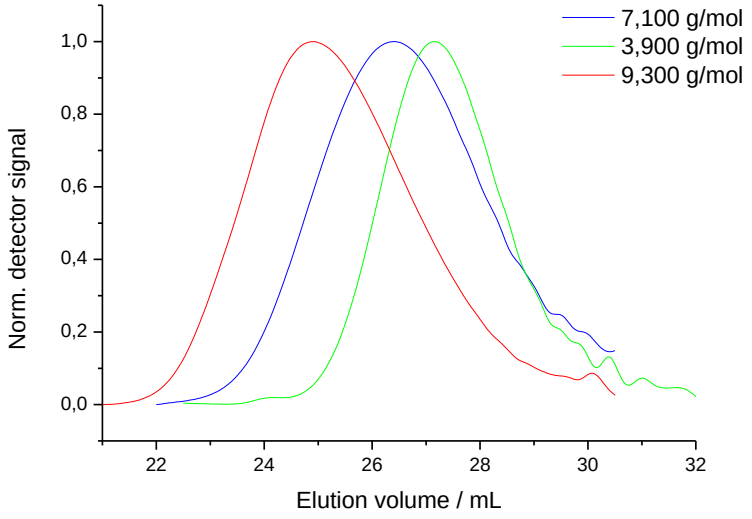


Figure 3-30: GPC-elugram of polymer **10b** vs. polystyrene standards in THF. The presence of oligomers can be clearly detected for low molecular weight polymers (the MW's are observed by NMR).

Figure 3-30 shows a representative GPC elugram of three different molecular weights of polymer **10b** synthesized by direct-polymerization modification reaction. The polymer traces still contain smaller oligomers fractions (peaks, which eluate between 32 and 29 mL). The curves are as expected. The molecular weights written in the Figure 3-30 are observed by NMR just to indicate that while the molecular weight obtained by GPC analysis is wrong, the overall trend is correct. Reasons why results by NMR and GPC are not fitting together are listed above.

3.2.2.2 Unsaturated telechelic UPPEs (11b, 12b, 13b, 14b)

Similar reaction conditions were used in the direct-polymerization modification reaction of the monomer **2b** and CTR **6, 7** and **8** in different ratios. The resulting unsaturated telechelic UPPEs (**11b, 12b** and **13b**) were difunctional within the detection limits of the 700 MHz ^{1}H NMR spectrometer. The GPC analysis of these telechelic polymers gave a PDI between of 1.7 and 2.0 (Table 3-2). Reasons for those results were already discussed in chapter 3.2.1.

Different was just the telechelic diepoxide (**14b**) since the CTR **9** had a too high vapor pressure so that a part evaporated before it could react.

Table 3-2 shows that in general all molecular weights of **10b** and **10c** in excellent accordance with the expected molecular weight. The same results can be shown on the molecular weights of polymer **11b**, **12b**, and **13b** except **14b** because of the reasons listed above.

Moreover, Table 3-2 shows partly big differences between the GPC results and the NMR results for the molecular weight. A reason might be that the data was determined by GPC in THF vs. polystyrene standards. In order to receive exact results it has to be the same standard as the sample (see above).

The molecular structures of the five telechelic polymers (**10b - 14b**) differ by the group at the chain ends, which is a direct result of the identity of the CTR used to end-cap the polymer chains during the ADMET reaction. The CTR serves to limit the molecular weight of the polymer and to cap the chain-ends with a desired functional group. The use of the CTR directly in polymerization reaction allows synthesizing telechelic UPPEs with almost perfect molecular weight control (Table 3-2).

All telechelic polymers were characterized by ^{1}H, ^{13}C, C,H-COSY and DOSY NMR spectroscopy. ^{1}H NMR in Figure 3-31 and Figure 3-32 pointed out the region of the methylene group next to the functional group to compare the different NMR spectra of all telechelic polymers.

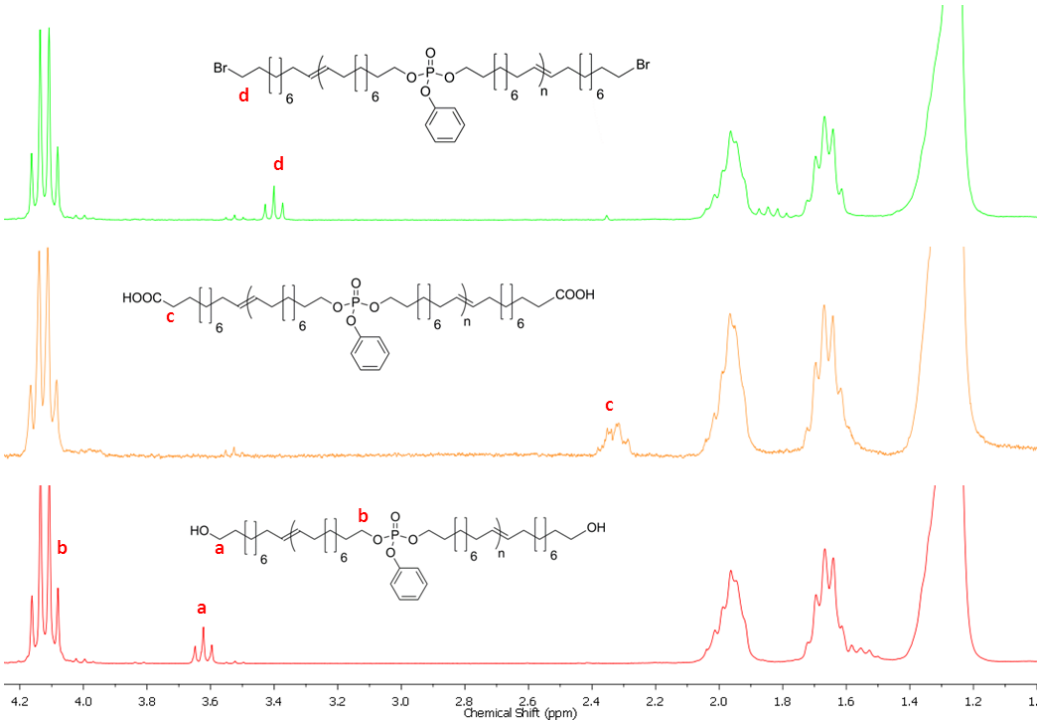


Figure 3-31: Shows the ^{1}H NMR spectra of all telechelic polymers (**12b** (top) and **11b** (middle) compare to **10b** (bottom)) pointing out the chemical shifting of the methylene group next to the functional end group (3.4 ppm (**12b**), 2.3 ppm (**11b**) and 3.6 ppm (**10b**)) (250 MHz in $CDCl_3$ at 25 °C).

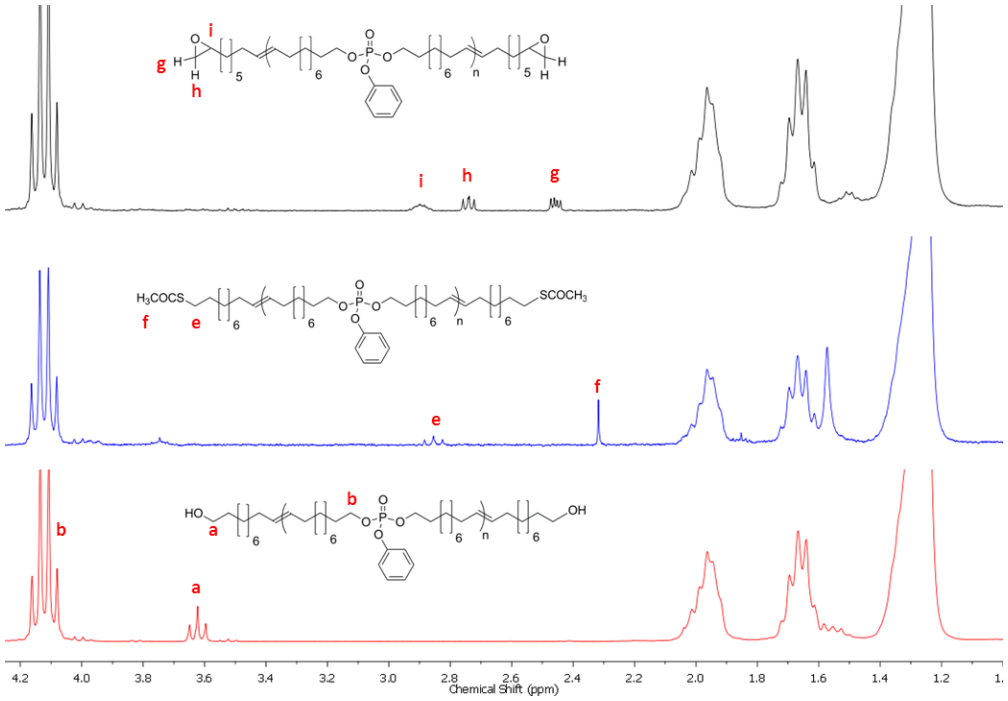


Figure 3-32: Shows the ^{1}H NMR spectra of all telechelic polymers (**14b** (top) and **13b** (middle) compare to **10b** (bottom)) pointing out the chemical shifting of the methylene group next to the functional end group (2.9 + 2.7 + 2.5 ppm (**14b**), 2.9 ppm (**13b**) and 3.6 ppm (**10b**)) (250 MHz in $CDCl_3$ at 25 °C).

All telechelic polymers were characterized by GPC analysis. Figure 3-33 to Figure 3-36 show the obtained GPC elugrams in THF vs. poly(styrene) standards.

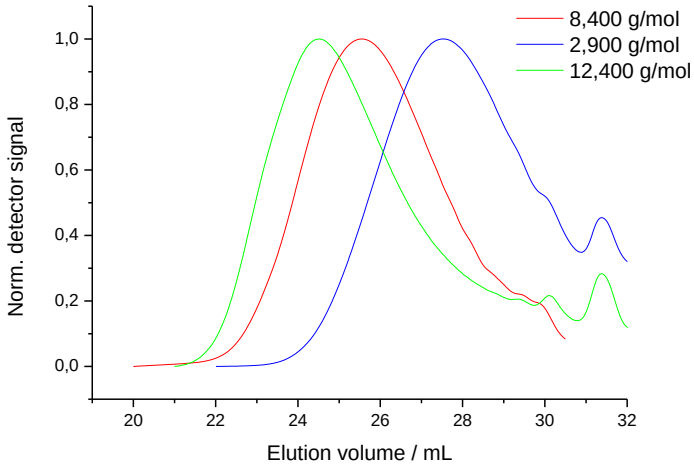


Figure 3-33: GPC-elugram of polymer **11b** vs. polystyrene standards in THF. The presence of oligomers can be clearly detected for low molecular weight polymers.

Figure 3-33 displayed a representative GPC elugram of the three different molecular weights of polymer **11b** synthesized by direct-polymerization modification reaction. The curves are as expected. The molecular weights shown in the figure are observed by GPC as well as for the following spectra. The molecular weights by NMR are 2,200, 4,300 and 9,400 g·mol^{-1}. The GPC results are usually a bit higher as the values by NMR. Reasons for that are explained above.

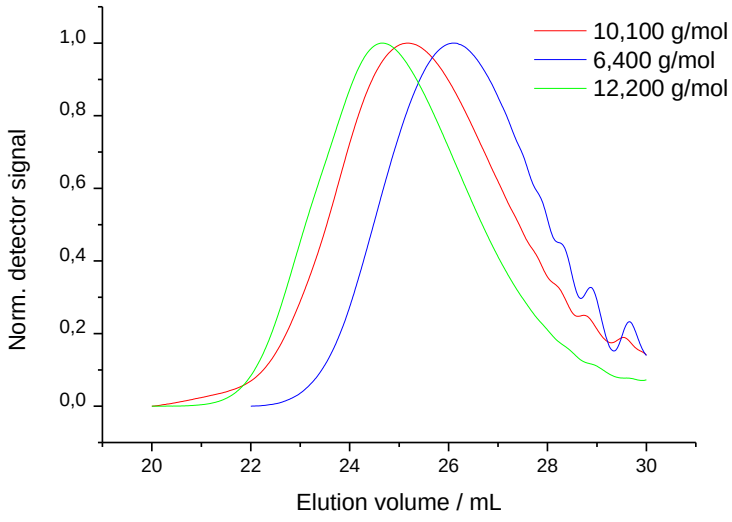


Figure 3-34: GPC-elugram of polymer **12b** vs. polystyrene standards in THF. The presence of oligomers can be clearly detected for low molecular weight polymers.

Figure 3-34 to Figure 3-36 exhibit representative GPC elugrams of the three different length of polymer **12b, 13b** and **14b** synthesized by direct-polymerization modification reaction. The curves are as expected.

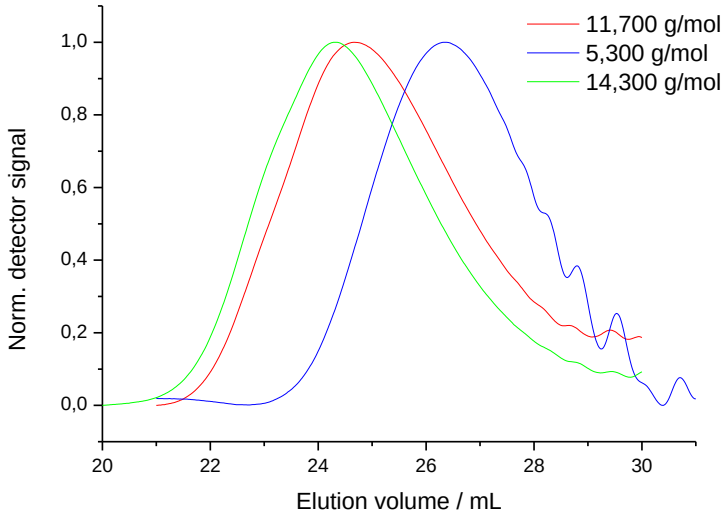


Figure 3-35: GPC-elugram of polymer **13b** vs. polystyrene standards in THF. The presence of oligomers can be clearly detected for low molecular weight polymers.

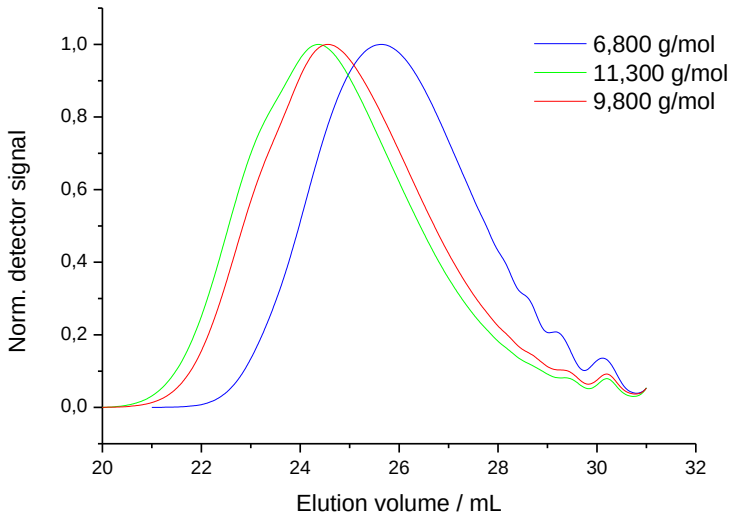


Figure 3-36: GPC-elugram of polymer **14b** vs. polystyrene standards in THF. The presence of oligomers can be clearly detected for low molecular weight polymers.

Figure 3-37 depicts also a MALDI-TOF spectrum of **13b**. The main peaks in the MALDI-Tof spectrum in Figure 3-37 correspond to the oligomers, ranging from dimers to undecamers (for example: the peak at 4069.8 g·mol^{-1} in Figure 3-37 corresponds to the molecular ion of [8 M + K + 2 CTR – (8 + 1) CH_2=CH_2]$^+$] observed for **13b**, while the neighboring peaks exhibit an interval of 450 g·mol^{-1} which is most likely attributed to a monomer (M) unit minus ethylene. Unfortunately this is the only spectrum where the signals can be assigned to the respective oligomers.

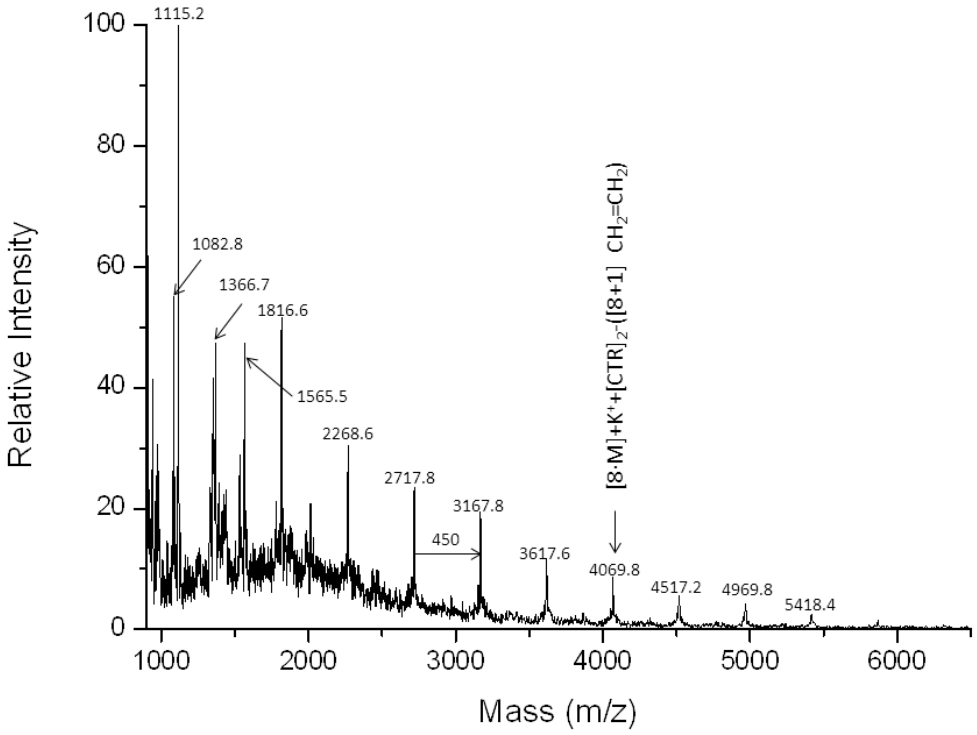


Figure 3-37: MALDI-ToF spectrum of **13b**

3.3 Modifications on poly(dialkylene chlorophosphate)

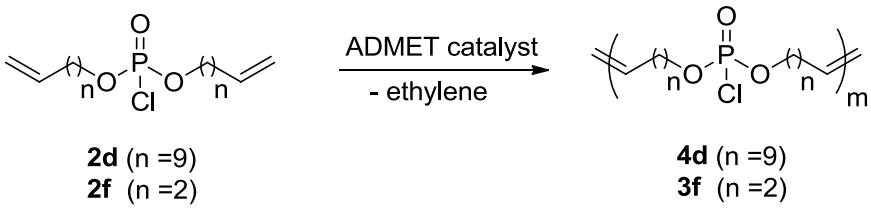
Reactive polymers and reactions on/with polymers have a long history ranging back to Schönbein's nitration[62] of cellulose or the vulcanization process of natural rubbers.[63] Today, modern polymer chemistry offers a large toolbox to design novel and (poly)functional materials. Controlled radical polymerization methods[64] or very tolerant catalytic polymerization techniques allow the introduction of a variety of functional groups that used to be impossible with "classical" methods such as polycondensation[23,26] or living ionic polymerization[65]. The direct polymerization of functional monomers is clearly an attractive strategy, is however often hampered due to interference with the polymerization conditions or -in copolymerizations- due to incompatible copolymerization parameters, especially in radical polymerization. These factors limit the synthesis of functional polymers, and moreover the access to materials having a precisely defined molecular weight, composition and architecture. Especially when several functional materials should be compared to establish structure-property relationships, the influences of the degree of polymerization or molecular weight distribution in different batches of the material are dominating problems. To overcome these issues reactive polymers have been studied intensively in recent years.[66] These materials can be generated with conventional polymerization techniques and subsequently post-modified to generate the functional material of choice. The precursor polymers are soluble and the activated group is inert towards the polymerization conditions. This allows the facile generation of a diverse library of functional polymers with identical average chain length and architecture (e.g. degree of branching).[66]

Post-polymerization modification has been applied to almost every polymer class, however, degradable polymers have been only investigated rarely.[67] This is probably attributed to their synthesis via ring-opening polymerization[31,32,33]: here it is rather challenging to synthesize a functional lactone, regardless if it should carry the final functionality or a reactive intermediate.

This chapter fills this gap and will present an approach for the synthesis of diverse functional and degradable polyesters. These approaches utilize metathesis polymerization to generate reactive and degradable poly(phosphoester)s that can be modified to generate highly functional materials which are only accessible via post-modification. The metathesis approach already tolerates many functional groups, such as acid chlorides, however highly nucleophilic groups (and others) are difficult to introduce or hamper the removal of the catalyst. With the approaches presented herein, also water-soluble and biocompatible materials will be accessible that may find applications in polymer-therapeutics or adhesives.

3.3.1 Synthesis of poly[dialkenyl chlorophosphate]

In order to reach this goal the bis-(undecen-10-yl) chlorophosphate and the bis-(buten-3-yl) chlorophosphate were used to observe reactive UPPEs, which have the ability of post-polymerization modifications by the reactive acid chloride functionality. The protocol of the ADMET polymerization of the chloro monomers **2d** and **2f** are the same as in chapter 3.2.1 described (Scheme 3-5): Direct mixing of the monomer with Grubbs catalyst 1st catalyst in bulk and applying the reaction conditions in Table 3-3 produces the pure polymer.



Scheme 3-5: ADMET polymerization of phosphate monomers **2d** and **2f**.

Table 3-3 lists the reaction conditions and the results of the polymerizations by Scheme 3-5.

Table 3-3: Conditions for the ADMET polycondensation (general representative procedure) of **2d** and **2f** and molecular weight data of the resulting polymers.

Run	Catalyst [mol%]	Monomer	Reaction time [h]	Temperature [°C], solvent	Mw[(a)] [g·mol^{-1}]	Mn[(a)] [g·mol^{-1}]	PDI[(a)]	Mn[(b)] [g·mol^{-1}]
19	1,0 (C1)	2d	16	**r.t, none**[(d)]	No	data	available	5,300
20	1,0 (C1)	2f	16	**r.t, none**[(d)]	No	data	available	3,000

[(a)] Determined by gel permeation chromatography (GPC) in THF vs. polystyrene standards.
[(b)] Determined by NMR.
[(c)] Performed using solution based ADMET as described in the experimental section.
[(d)] Performed using bulk based ADMET as described in the experimental section.

A first polymer of **2d** is shown in entry 19 and for monomer **2f** in entry 20. On the basis of GPC analysis and NMR results the aim is reached. That included the highly stable catalyst system which is even stable in presence of phosphoric acid chloride. In order to complete the investigation Figure 3-38 and Figure 3-39 show the ^{1}H NMR of polymers **4d** and **3f** as well as monomers **2d** and **2f**, respectively. All polymers show similar behavior as the polymers **3a**, **4b** and **4c** before.

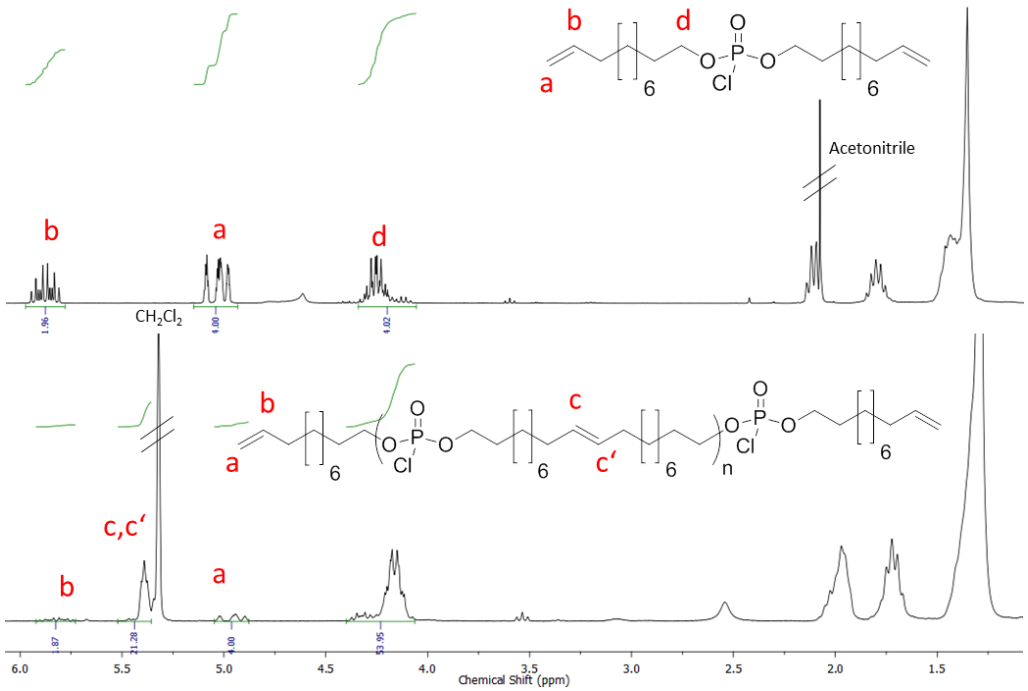


Figure 3-38: ^{1}H NMR spectrum of monomer **2d** (top) and the respective polymer **4d** proving the formation of internal double bonds at 5.4 ppm (250 MHz in $CDCl_3$ at 25 °C).

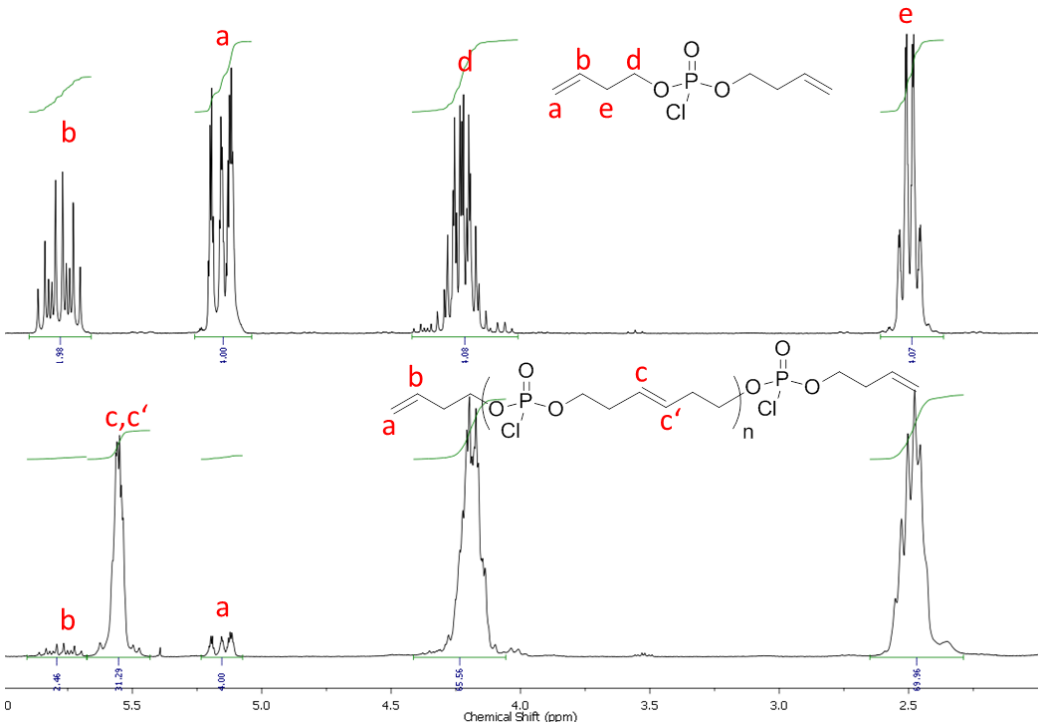


Figure 3-39: ^{1}H NMR spectrum of monomer **2f** (top) and the respective polymer **3f** proving the formation of internal double bonds at 5.4 ppm (250 MHz in $CDCl_3$ at 25 °C).

The approach to alter the poly(dialkylene chlorophosphate)s by reaction of the phosphoric acid chloride though the nucleophilic attack of an nucleophile at the chloride on the backbone of the telechelic UPPE are listed. In Figure 3-40 and Figure 3-41 depict the two potential chlorophosphates to modify.

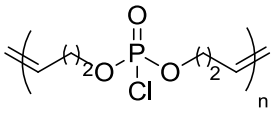


Figure 3-40: Structure of polymer **3f**.

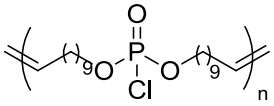
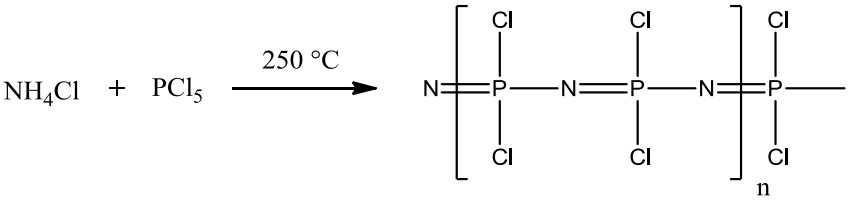


Figure 3-41: Structure of polymer **4d**.

These polymers might be a potential upgrade/replacement of poly(phosphazene) which can be synthesized by heating up ammonium chloride with phosphorous pentachloride at 250 °C (Scheme 3-6).[68]



Scheme 3-6: Synthesis of polyphospazene

There are some disadvantages about poly(phosphazene)s such as it is extremely hydrolysis sensitive and the polymerization is hard to control. It usually leads to high molecular weights but with a high PDI.[68]

3.3.2 Modification of poly[dialkenyl chlorophosphate]

Motivated by those facts it was feasible to synthesize a similar product (chapter 3.2.1) which has a PDI around 2.0 and it is decent stable in the presence of water and air. Furthermore it possesses similar properties as poly(phosphazene) as the easily sustituated chloride atoms on the phosphate. In order to confirm these properties the poly(dialkylene chlorophosphate)s were exposed to different nucleophiles such as benzyl alcohol (BzOH), as well as poly ethylene glycol methyl ether (PEG_{750}-OH) with a molecular weight of 750 $g \cdot mol^{-1}$ and Hydroxyethylmethacrylate (HEMA) in the presence of the base Et_3N. All reagents are shown in Figure 3-42.

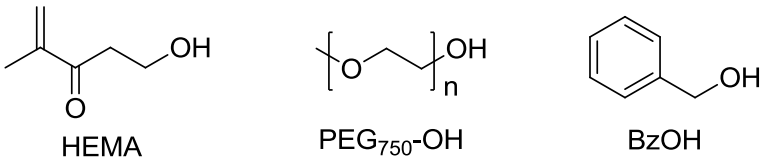
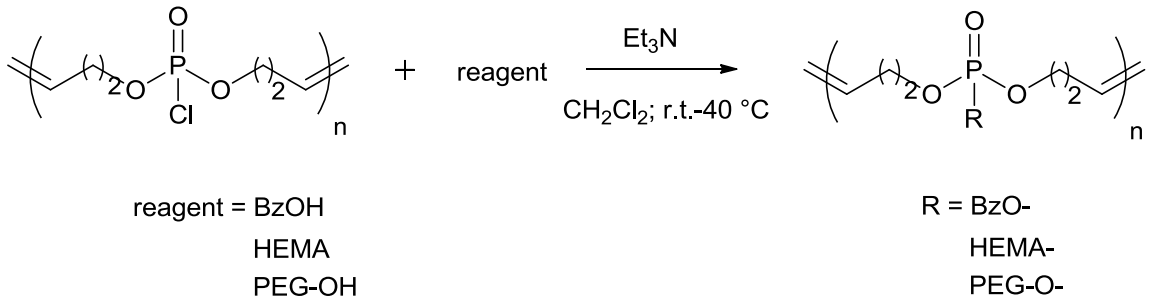


Figure 3-42: Nucleophiles for the modification of poly(dialkylene chlorophosphate)s

The post modification reaction according to the procedure described above is depicted in Scheme 3-7 for the polymer of monomer **2f**. The altered poly(dialkylene chlorophosphate)s were synthesized by adding the respective reagent (Figure 3-42) to polymer **3f** dissolved in dichloromethane (CH_2Cl_2) in the presence of trimethylamine (Et_3N) in order to remove the occurred hydrogen chloride as described in the following representative procedure.

Reactions were limited to polymer **4d**, as it has a higher density of substitutable chloride atoms at the same length as the polymer **4d** so it has more potential functionalization points per length unit.



Scheme 3-7: Post modification reactions of poly(dialkylene chlorophosphate) 2b-c and CTR 5-8.

^{31}P NMR was used to proof the complete conversion of the polymer **3f** since it is known that the ^{31}P NMR signal appears at 4.52 ppm. But unfortunately the chloride atom on the phosphate is too stable to exchange with one of the stated nucleophiles. Hence the reaction was carried out again with much stronger nucleophiles such as potassium ethanolate, but unfortunately even this strong nucleophile was not able to exchange the chloride on the phosphate under these conditions. These experiments are still under investigations.

Potential applications are large since it is able to transform the poly(dialkylene chlorophosphate)s into almost every functional polymer. Applications like to use it as main chain adhesive or other applications according to the high variety of the functional groups are imaginable.

3.4 Sugar-containing PPEs via ADMET

A side project was to improve the synthesis of poly lactonic sophorolipid (LSL; structure in Figure 3-42) by using ring opening metathesis (ROM) to convert the unsaturated cyclic sugar LSL in a diene with terminal double bonds in order to polymerize it via ADMET and to make copolymers with the above mentioned phosphates to generate biodegradable, amphiphilic polymers.

According to R. Gross *et. al.* it was described the ROMP of a 26-membered ring glycolipid monomer (LSL) by using a ruthenium catalyst.[69] The glycolipid monomer is the natural lactonic form of sophorolipids, a microbial biosurfactant. Sophorolipids are most often constructed from the disaccharide sophorose that is glycosidically linked to the hydroxyl group at the penultimate carbon of a mono-unsaturated C18 chain-length fatty acid. They are fermentatively produced by yeasts such as *Candida bombicola*. Sophorolipids have shown great promise in a wide range of therapeutic functions that include (i) septic shock antagonists, (ii) antibacterial, (iii) antifungal, (iv) antiviral (HIV-1), (v) antispermicidal, and (vi) anticancer agents.[70] Chemoenzymatic methods have been developed to synthesize a range of pure sophorolipid analogues from the microbially produced natural mixture.[69]

Natural lactonic sophorolipids, highly abundant within the mixture of products formed by *Candida bombicola*, were directly polymerized. The resulting polymers were prepared in high molecular weights and are soluble in common organic media. Furthermore, the polymer is designed to bioresorb in biologically active milieus due to the regular occurrence of disaccharide and ester links along chains.[69]

According to Gross *et. al.* they were able to observe poly LSL by using the ROMP approach but there are disadvantages compare to the ADMET approach. E.g. ADMET allows the copolymerization of other monomers, which do not feature ring strain, since ADMET is working with dienes without ring strain. Hence in this thesis the ADMET approach was used to try the benefits of an ADMET polymerization.

3.4.1 ROM of LSL

First it was necessary to cleave the double bond in LSL (^{1}H NMR of LSL in Figure 3-43) via ROM.

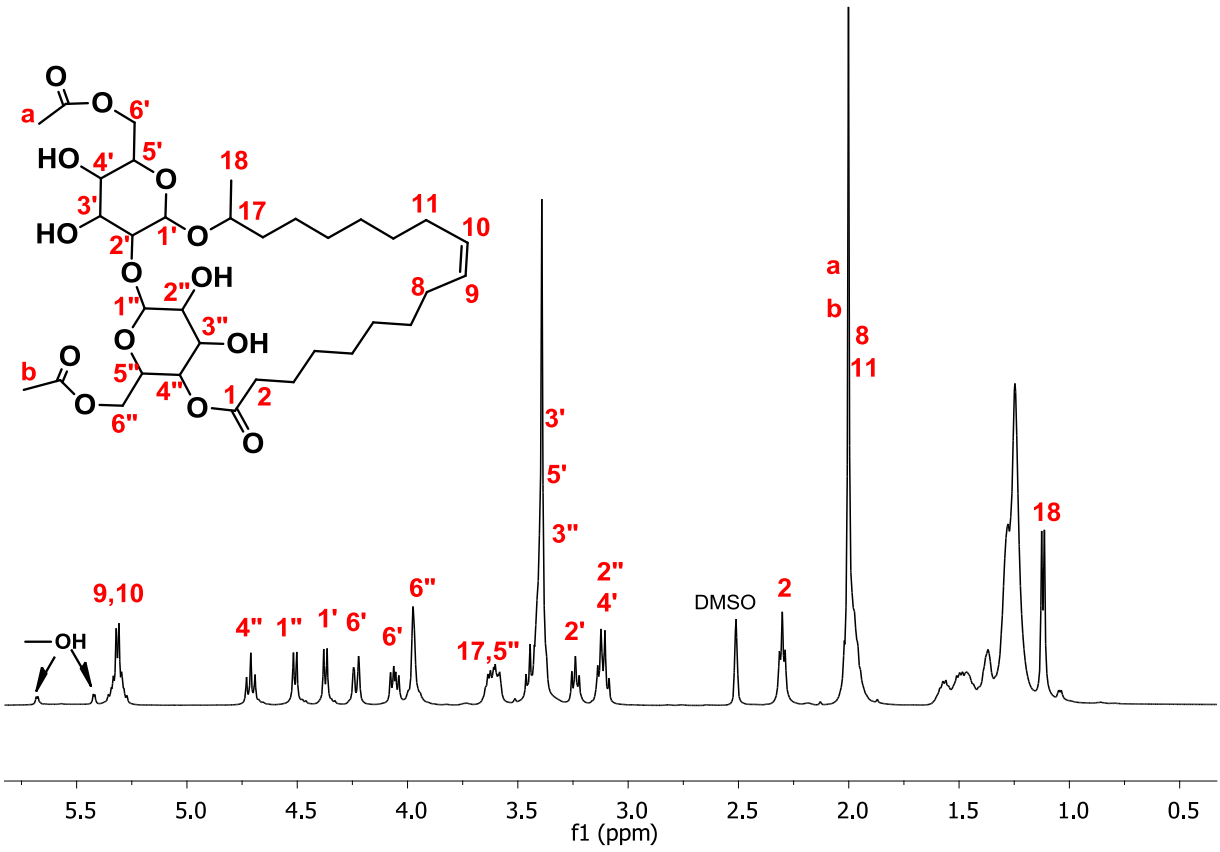
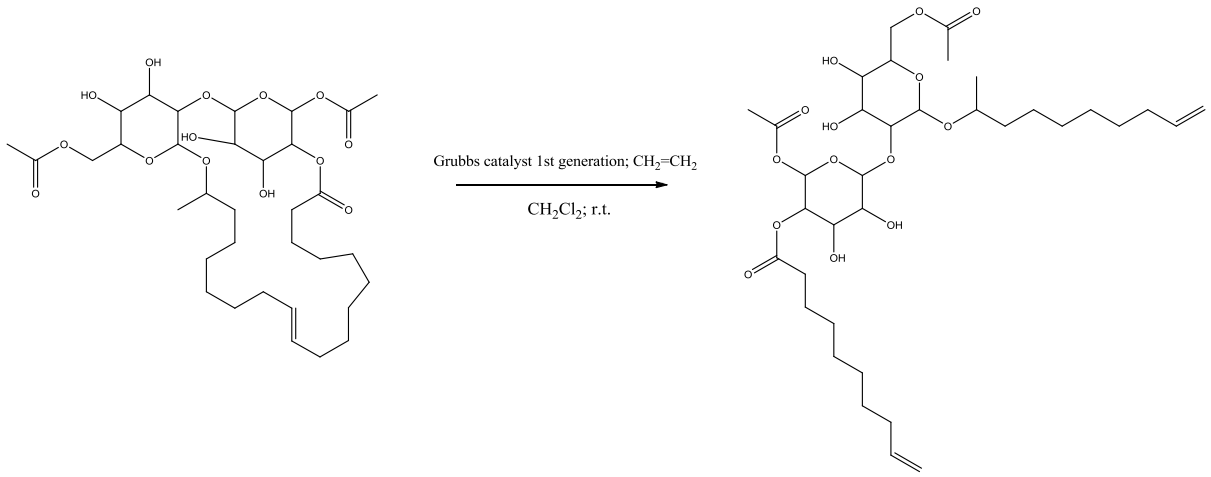


Figure 3-43: ^{1}H NMR of LSL (400 MHz in DMSO-d_6 at 25 °C)

The modified LSL was synthesized by the exposure of LSL with ethylene (CH_2=CH_2) gas under a pressure of 3 bar. The reaction was carried out in a high pressure reactor (Figure 5-1). LSL as well as the Grubbs catalyst 1st generation were dissolved in dichloromethane (CH_2Cl_2) as described in the following representative procedure (Scheme 3-8).



Scheme 3-8: ROM of LSL.

Figure 3-44 depicts the NMR spectrum before and after the successfully realized ROM. In this spectrum the signal for the internal double bond has almost disappeared for the modified LSL is contrast to the unmodified LSL. To be featured is also the appearance of the signals for the terminal double bonds in the NMR spectrum of the modified LSL.

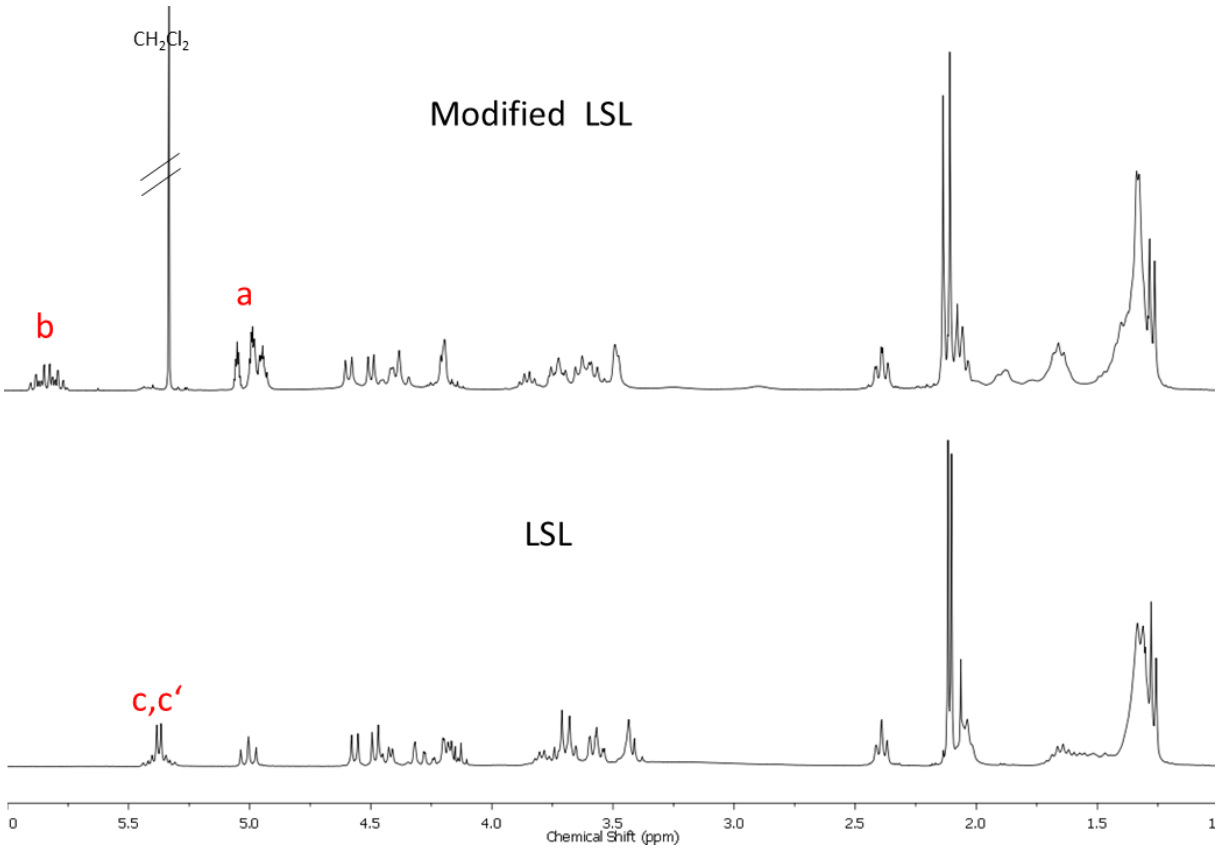


Figure 3-44: ^{1}H NMR spectra of LSL (bottom) and the modified LSL (top), proving the disappearance of the internal double bond signal at c,c' and appearance of the terminal double bond signals at a and b (250 MHz in $CDCl_3$ at 25 °C).

3.4.2 ADMET polymerization of modified LSL

Further steps to polymerize the compound via ADMET were unsuccessful neither in a solution polymerization nor in a copolymerization with monomer **2b**. Next steps will be the removal of residual catalyst in the product with particular designed resin to make sure this is not the reason for the unsuccessful steps after the cleavage of LSL.

4 Conclusion and Outlook

4.1 Conclusion

In this work, a robust approach for the synthesis of novel monomers and the respective (telechelic) UPPEs with variable reactive (end) groups (double bonds, hydroxyl, carboxy, thioacetate, bromide, expoxy groups) were developed. The polymerizations were carried out through the ADMET polymerization method. The presence of phosphorus in the structure of the monomers did not affect the activity of the catalysts as well as the third functional group at the phosphate and obtained UPPEs with reasonably high molecular weight of 1,000 – 20,000 $g \cdot mol^{-1}$ in order to have a descent molecular weight to establish post-polymerization modifications.

The first part was described a novel approach of synthesizing newly phosphate-containing monomers and polymers having functional groups along the main chain and at the chain termini.

The second part of this thesis was devoted to the synthesis of different UPPEs, which can be used in post-polymerization reaction. The novel approach to several UPPEs was reported based on bulk and solution polymerization using Grubbs-type metathesis catalysts. The molecular weights vary for the different reaction conditions, which were applied but in all cases the desired polymers were obtained and thus empirically the molecular weight can be adjusted. The UPPEs were synthesized with high yield (between 70 and 90 %) and high purity confirmed by ^{1}H, ^{13}C NMR spectroscopy, GPC analysis and mass spectrometry.

With phosphate linkages along the unsaturated backbone many properties of these unsaturated polyesters could be altered, which was a part of this study and it is still under investigation.

The main part was dedicated to the approach of making telechelic UPPEs in a one-step reaction. Polymers with different end groups, like hydroxyl groups, which can be applied to manufacture poly(urethanes), carboxylate groups, bromides or thioacetate groups in order to cleave them to thiols, from the appropriate CTR were synthesized from the monomer – bis-(undec-10-en-1-yl) phenylphosphate. The molecular weights of the materials was adjusted by the ratio between monomer and CTR and in all cases a perfect match between theoretical molecular weights and experimentally determined values was found. The end groups' functionality was almost 100% as proven by ^{1}H NMR and H-DOSY NMR spectroscopy for all chain termination agents investigated herein. Also mass spectrometry proved an efficient capping of the polymers. The success of this approach can be pointed out though the absence of terminal olefin, which was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy.

Characterization of the obtained polymers by GPC confirmed the achievement of reliable results since the measured PDI is in fact close to two.

The forth part was a closer look of the poly(dialkylene chlorophosphate)s. These polymers might be a potential replacement of poly(phosphazene). It was feasible to synthesize a similar product which has a PDI around 2.0 and it is decently stable in the presence of water and air. Furthermore, it possesses similar properties as poly(phosphazene) as relatively easy cleavable chloride atoms on the phosphate. In preliminary experiments, however, no successful functionalization was achieved but is still under investigation. Applications like main chain adhesives or other possibilities according to the high variety of the functional groups are imaginable for these materials.

The last part was dedicated to improve the synthesis of poly lactonic sophorolipid (LSL) by using ring opening metathesis (ROM) to convert the unsaturated cyclic sugar LSL in a diene with terminal double bonds in order to polymerize it via ADMET. Through the ROM of LSL it was received the LSL with terminal double bonds but further experiments are still under investigations.

In summary the polymerizations are giving promising results in the preparation of degradable materials from renewable resources. The polymer can be regarded as a degradable polyethylene with predetermined breaking points inside the backbone. This thesis was focusing on broadening the spectrum of UPPEs synthesized by ADMET to more sophisticated polymer architectures, investigate and tailor physical properties and introducing new functional (end) groups.

4.2 Outlook

The syntheses of the UPPEs based on ADMET polymerizations were found to be an effective tool to develop novel materials. Other projects, outside the area of ADMET polymerizations, relying on the functional group reactivity and selectivity are imaginable, like post polymerization reactions on these polymers. For example the synthesis of triblock copolymers might be an interesting approach to generate amphiphilic degradable materials, e.g. by ROP of strained phosphates. Telechelic diols presented in this work would serve as a macro monomer lead to poly(urethane)s (PU) with novel interesting features. Furthermore any chosen telechelic macro monomer could be polymerized to yield innovative polymers with new properties depending on the architecture and degree of polymerization of the introduced polymer chains, such as poly(ester)s by telechelic dicarboxylates.

Improvement of the presented direct-polymerization modification reaction to obtain telechelic UPPEs in an only one-step reaction might be optimized by achieving ideal reaction conditions, such as mixable reaction suspensions during the synthesis. An appropriate method to stir well has to be found to guarantee a fluently mixing to ensure a homogenous reaction system even for high molecular weights.

Other functional groups, such as amines, will be an interesting challenge to conduct ADMET from modified CTRs.

With phosphate linkages along the unsaturated backbone many properties of these unsaturated polyesters could be altered, which is still under investigation. Many post-polymerization reactions might be carried out in order to link thiols on the internal double bonds, silyl groups on the terminal double bonds as well as poly(ethylene glycol) methyl ether methacrylate ($PEGMA_{475}$) via atom transfer radical polymerization (ATRP).

One interesting aim will be the application of a difunctional atom transfer radical polymerization (ATRP) initiator based on the telechelic diol. The hydroxyl functionality will be esterified by 2-bromoisobutyryl bromide (BIBB) leading to the desired difunctional ATRP initiator which should be able to polymerize poly(ethylene glycol) methyl ether methacrylate (PEGMA) to synthesize surfactants based on PPEs. Different architectures of the telechelic polymer should significantly affect the observed water solubility and finally provide self-assembly of micelles or vesicles for drug delivery applications.

The UPPEs are also interesting candidates for biomedical applications and as potential tissue engineering scaffold materials but also in materials science and concerning their flame-retardant properties.

5 Experimental Part

5.1 General Remarks

All chemicals and solvents were purchased from customary suppliers (*Acros, Sigma-Aldrich, Fluka, etc.)* and used without purification, unless otherwise indicated. Grubbs catalyst 1st generation and Hoveyda-Grubbs catalyst 2nd generation were purchased from Sigma Aldrich and stored under argon atmosphere. Tris (hydroxymethyl) phosphine was synthesized according to literature.[71] *S*-10-Undecen-1-yl thioacetic acid ester was synthesized according to literature.[72]

5.2 Analytics

5.2.1 GPC/SEC

Gel-permeation chromatography (GPC) measurements were carried out in THF, with samples of the concentration of 1 g L^{-1}. Sample injection was performed by a 1260-ALS auto sampler (Waters) at 30 °C (THF). The flow was 1 mL min^{-1}. In THF, three SDV columns (PSS) with dimensions of 300 × 80 mm, 10 µm particle size and pore sizes of 106, 104 und 500 Å were employed. Detection was accomplished with a DRI Shodex RI-101 detector (ERC) and UV-Vis 1260-VWD detector (Agilent). Calibration was achieved using poly(styrene) standards provided by Polymer Standards Service.

5.2.2 MALDI-ToF Mass Spectrometry

Matrix-assisted laser desorption and ionization time-of-flight (MALDI-ToF) measurements were obtained with a Shimadzu Axima CFR MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. Dithranol (1,8,9-tris-hydroxy-anthracene) was used as a matrix. Samples were prepared by dissolving the analyte in $CHCl_3$ at a concentration of 10 g L^{-1}. A 10 mL aliquot of this solution was added to 10 mL of a 10 g L^{-1} matrix solution and 1 mL of a potassium trifluoroacetic acid (KTFA) solution (0.1 M in methanol as cationization agent). A 1 mL aliquot of the resulting mixture was applied to a multistage target, the thin matrix/analyte film was obtained by evaporation of the solvent. The samples were measured in positive ion- and in linear mode of the spectrometer.

5.2.3 NMR-Spectroscopy

^{1}H NMR spectra were recorded on a Bruker avance 250 MHz, 300 MHz, 500 MHz or 700 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker avance 500. All spectra were recorded at room temperature. The proton, carbon and phosphorous spectra were measured in $CDCl_3$ at 298.3K and the spectra were referenced as follows: for the residual $CHCl_3$ at δ (^{1}H) = 7.26 ppm, $CDCl_3$ δ (^{13}C triplett) = 77,0 ppm and triphenylphosphine (TPP) δ (^{31}P) = -6 ppm.

5.2.4 DSC

The glass transition temperature was measured by differential scanning calorimetry (DSC) on a Mettler Toledo DSC 823 calorimeter. Three scanning cycles of heating–cooling were performed (in a N_2 atmosphere 30 mL min^{-1}) with a heating rate of 10 °C min^{-1}.

5.3 Synthesis

5.3.1 Synthesis of Monomers

*Representative procedure for the synthesis of monomer **2a** and **2b***

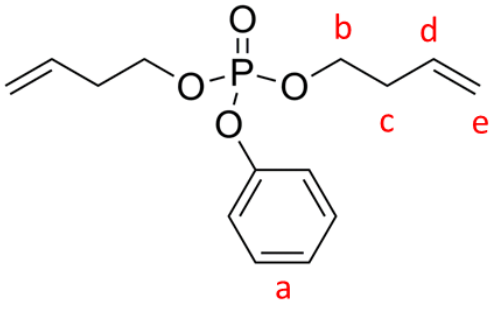
In a dried two-necked, 250 mL round bottom flask 5 mL (7.05 g, 33.4 mmol) of **1** were dissolved in 50 mL of dry CH_2Cl_2 under an argon atmosphere. The solution was cooled to 0 °C and 2 equivalents of the appropriate alcohol and 2 equivalents of triethylamine (Et_3N) were added to the solution via a syringe. The reaction was stirred overnight at room temperature. The crude mixture was concentrated under reduced pressure, dissolved in diethyl ether and filtered. The organic phase was washed twice with brine and once with aqueous 10% hydrochloric acid (HCl). The organic layer was dried over sodium sulfate, filtered, concentrated under reduced pressure, and purified by flush chromatography over neural alumina using dichloromethane as eluent to give a clear colorless liquid in 60-80 % yield. The structures were determined by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectroscopies as well as Electrospray Ionization Mass Spectrometry (ESI-MS).

*Representative procedure for the synthesis of monomer **2c** to **2f***

To a stirred solution of $POCl_3$ (6.57 g, 4.00 mL, 42.78 mmol) in toluene or CH_2Cl_2 (20 mL) at 0 °C was added a mixture of the appropriate alcohol (77.01 mmol) and Et_3N (7.79 g, 10.74 mL, 77.01 mmol). After stirring overnight, $Et_3N{\cdot}HCl$ was removed as a white solid by filtration. The filtrate containing the dialkylene chlorophosphate in toluene or CH_2Cl_2 was stirred vigorously while adding an excess of water to the mixture. After stirring overnight, the organic layer was separated, dried ($NaSO_4$), and concentrated under reduced pressure to give dialkylene phosphate. 2 equivalents of trimethyl orthoacetate were added to the dialkylene phosphate and the mixture was heated at 80 °C under an argon atmosphere. The reaction was monitored by TLC until the starting material had disappeared. After 2.5 h, the mixture was extracted with Et_2O (3 x 10 mL). The combined organic extracts were purified by column chromatography on silica gel (eluent: petrolether (PE)/ethylacetate (EtOAc), 8:2) to give the product as a clear colorless liquid of dialkylene methyl phosphate in 60-80 % yield. The structures were determined by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectroscopies as well as Electrospray Ionization Mass Spectrometry (ESI-MS).

*Synthesis of bis-(but-3-en-1-yl) phenyl phosphate (**2a**)*

Following the general procedure described above and using 3-buten-1-ol, **2a** was obtained as a clear oil (yield: 70 %; R_f: 0.3 (CH_2Cl_2)).



2a

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ 7.33-7.31 (m, 2H, **a**), 7.20 (d, J = 7.7 Hz, 2H, **a**), 7.16(t, J = 7.7 Hz, 1H, **a**), 5.79-5.73 (ddt, J_1 = 16.8 Hz, J_1 = 10 Hz, J_3 = 3.5 Hz, 2H, **d**), 5.11 (ddt, J_1 = 16.8 Hz, J_2 = 1.4 Hz, 2H, **e**), 5.08 (d, J = 10 Hz, 2H, **e**), 4.20-4.13 (m, 4H, **b**), 2.44-2.42 (m, 4H, **c**).

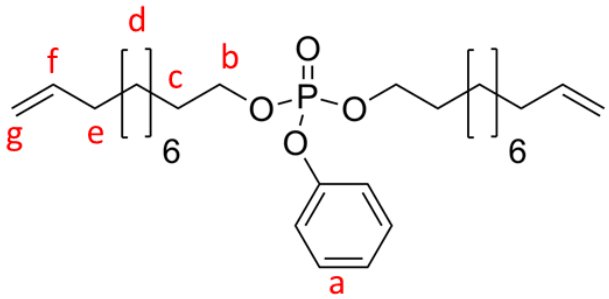
^{13}C NMR (176 MHz, $CDCl_3$, ppm): δ 150.69, 150.65, 133.12, 129.70, 125.05, 120.04, 120.01, 117.91, 67.54, 67.50, 34.60, 34.56.

^{31}P NMR (283 MHz, $CDCl_3$, ppm): δ -6.40.

ESI-MS *m/z* 305.07 $[M+Na]^+$, 587.18.30 $[2M+Na]^+$ (Calculated for $C_{14}H_{19}O_4P$: 282.10).

*Synthesis of bis-(undec-10-en-1-yl) phenylphosphate (**2b**)*

Following the general procedure described above and using 10-undecen-1-ol, **2b** was obtained as a clear oil (yield: 80 %; R_f: 0.5 (CH_2Cl_2)).



2b

^{1}H NMR (700 MHz, $CDCl_3$, ppm): δ 7.32 (t, *J* = 7.7 Hz, 2H, **a**), 7.21(d, *J* = 7.7 Hz, 2H, **a**), 7.16(t, *J* = 7.7 Hz, 1H, **a**), 5.83-5.77 (ddt, J_1 = 16.8Hz, J_2 = 10 Hz, J_3 = 3.5 Hz, 2H, **f**), 5.00-4.97 (ddt, J_1 = 10 Hz, J_2 = 3.5 Hz, J_3 = 1.4 Hz, 2H, **g**), 4.93-4.91 (ddt, J_1 = 10 Hz, J_2 = 1.4 Hz, 2H, **g**),4.16-4.09 (m, 4H, **b**), 2.04-2.01 (m, 4H, **e**), 1.69-1.65 (m, 4H, **c**), 1.39-1.32 (m, 8H, **d**), 1.26 (m, 16H, **d**).

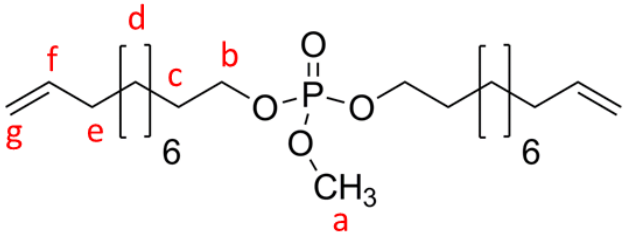
^{13}C NMR (176 MHz, $CDCl_3$, ppm): δ 150.98, 150.94, 139.29, 129.77, 125.02, 120.10, 114.27, 68.69, 68.66, 33.93, 30.37, 30.33, 29.55, 29.04.

^{31}P NMR (283 MHz, $CDCl_3$, ppm): δ -6.11.

ESI-MS *m/z* 501.33 $[M+Na]^+$, 979.67 $[2M+Na]^+$, 1458.00 $[3M+Na]^+$ (Calculated for $C_{28}H_{47}O_4P$: 478.32).

*Synthesis of bis-(undec-10-en-1-yl) methyl phosphate (**2c**)*

Following the general procedure described above and using 10-undecen-1-ol, **2c** was obtained as a clear oil (yield: 60 %; R_f: 0.4 (PE/EtOAc 8:2)).



2c

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.82-5.66 (ddt, J_1 = 16.8 Hz, J_2 = 10 Hz, J_3 = 3.5 Hz, 2H, **f**), 5.00-4.97 (ddt, J_1 = 10 Hz, J_2 = 3.5 Hz, J_3 = 1.4 Hz, 2H, **g**), 4.93-4.91 (ddt, J_1 = 10 Hz, J_2 = 1.4 Hz, 2H, **g**), 4.00-3.92 (m, 4H, **b**), 3.70-3.66 (d, J = 10 Hz, 3H, **a**), 2.01-1.92 (m, 4H, **e**), 1.66-1.55 (m, 4H, **c**), 1.30-1.21 (m, 24H, **d**).

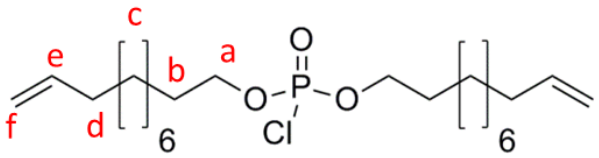
^{13}C NMR (176 MHz, $CDCl_3$, ppm): δ 137.20, 112.20, 66.92, 66.87, 43.21, 31.86, 30.71, 28.38, 28.33, 27.52, 27.45, 27.19, 27.16, 26.98, 24.94, 23.49.

^{31}P NMR (283 MHz, $CDCl_3$, ppm): δ -1.51.

ESI-MS *m/z* 417.32 $[M+H]^+$, 439.27 $[M+Na]^+$, 455.26 $[M+K]^+$, 833.64 $[2M+H]^+$ 855.56 $[2M+Na]^+$, 871.59 $[2M+K]^+$ (Calculated for $C_{23}H_{45}O_4P$: 416.31).

*Synthesis of bis-(undec-10-en-1-yl) chlorophosphate (**2d**)*

Following the general procedure described above using 10-undecen-1-ol in CH_2Cl_2, **2d** and its isomer were obtained as clear oil after filtration of $Et_3N{\cdot}HCl$ and evaporating the solvent (yield: 90 %).



2d

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.89-5.72 (ddt, J_1 = 16.8 Hz, J_2 = 10 Hz, J_3 = 3.5 Hz, 2H, **e**), 5.08-4.89 (ddt, J_1 = 10 Hz, J_2 = 3.5 Hz, J_3 = 1.4 Hz, 2H, **f**), 4.93-4.91 (ddt, J_1 = 10 Hz, J_2 = 1.4 Hz, 2H, **f**), 4.25-3.90 (m, 4H, **a**), 2.08-1.92 (m, 4H, **d**), 1.79-1.64 (m, 4H, **b**), 1.42-1.23 (m, 24H, **d**).

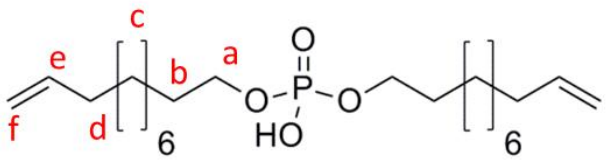
^{13}C NMR (176 MHz, $CDCl_3$, ppm): δ 139.15, 114.15, 114.13, 69.79, 69.74, 29.83, 29.77, 29.47, 29.39, 29.36, 29.14, 29.11, 29.07, 29.01, 28.92, 28.90, 28.87, 26.88, 25.46, 25.31.

^{31}P NMR (283 MHz, $CDCl_3$, ppm): δ 4.85.

ESI-MS *m/z* 443.26 $[M+Na]^+$, 459.24 $[M+K]^+$, 863.52 $[2M+Na]^+$ (Calculated for $C_{22}H_{42}ClO_3P$: 420.26).

*Synthesis of bis-(undec-10-en-1-yl) phosphate (**2e**)*

Following the general procedure described above and using 10-undecen-1-ol in toluene, **2e** was obtained as clear oil after the organic layer was separated from water, dried ($NaSO_4$), and the toluene evaporated (yield: 80 %).



2e

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.92-5.76 (ddt, J_1 = 16.8 Hz, J_2 = 10 Hz, J_3 = 3.5 Hz, 2H, **e**), 5.06-4.93 (ddt, J_1 = 10 Hz, J_2 = 3.5 Hz, J_3 = 1.4 Hz, 2H, **f**), 4.93-4.91 (ddt, J_1 = 10 Hz, J_2 = 1.4 Hz, 2H, **f**), 4.08-4.00 (m, 4H, **a**), 2.11-2.02 (m, 4H, **d**), 1.76-1.65 (m, 4H, **b**), 1.40-1.30 (m, 24H, **d**).

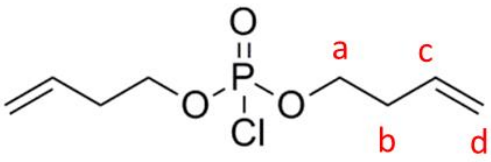
^{13}C NMR (176 MHz, $CDCl_3$, ppm): δ 139.16, 114.13, 67.74, 67.71, 33.80, 31.59, 30.20, 30.16, 29.47, 29.42, 29.16, 29.11, 29, 27.06, 28.93, 25.43, 25.37, 22.65.

^{31}P NMR (283 MHz, $CDCl_3$, ppm): δ 1.18.

ESI-MS *m/z* 403.30 $[M+H]^+$, 425.28 $[M+Na]^+$, 805.59 $[2M+H]^+$ 827.57 $[2M+Na]^+$ (Calculated for $C_{23}H_{45}O_4P$: 402.29).

*Synthesis of bis-(but-3-en-1-yl) chlorophosphate (**2f**)*

Following the general procedure described above using 3-buten-1-ol in CH_2Cl_2, **2f** was obtained as clear oil after filtration of $Et_3N{\cdot}HCl$ and distillation of the product at 90°C under a pressure of $5{\cdot}10^{-2}$ mbar (yield: 90 %).



2f

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.89-5.72 (ddt, J_1 = 16.8 Hz, J_2 = 10 Hz, J_3 = 3.5 Hz, 2H, **c**), 5.08-4.89 (ddt, J_1 = 10 Hz, J_2 = 3.5 Hz, J_3 = 1.4 Hz, 2H, **d**), 4.93-4.91 (ddt, J_1 = 10 Hz, J_2 = 1.4 Hz, 2H, **d**), 4.43-4.05 (m, 4H, **a**), 2.56-2.47 (m, 4H, **b**).

^{13}C NMR (176 MHz, $CDCl_3$, ppm): δ 132.52, 118.29, 68.61, 68.59, 34.13, 34.07.

^{31}P NMR (283 MHz, $CDCl_3$, ppm): δ 4.52.

5.3.2 Synthesis of Polymers

Representative procedure for ADMET bulk polymerization for UPPEs

In a glass Schlenk tube the respective monomer (200 mg) and the Grubbs catalyst 1st generation (1-3 mol%) or Hoveyda-Grubbs catalyst 2nd generation were mixed under an argon atmosphere. Polymerization was carried out under reduced pressure to remove ethylene gas evolving during the metathesis reaction, at temperatures between room temperature and 80 °C for 16-18 h. The crude mixture was dissolved in CH_2Cl_2, treated with tris (hydroxymethyl) phosphine (50 eq with respect to the catalyst) and washed twice with aqueous 10% HCl and water. The organic layer was dried over sodium sulfate ($NaSO_4$), filtered and concentrated under reduced pressure. The polymers were precipitated in hexane collected after decanting the supernatant, and finally dried (yields typically: 90-95 %).

Representative procedure for ADMET solution polymerization for UPPEs

The monomer (200 mg) and Grubbs catalyst 1st generation (1-3 mol%) were dissolved in CH_2Cl_2 for polymerization in an argon atmosphere and stirred at room temperature to 60 °C for 1-4 d. The work up procedure described for ADMET bulk polymerization was used (yields typically: 90-95 %).

Representative procedure for ADMET bulk polymerization for the telechelic UPPEs

In an argon atmosphere the monomer (200 mg), appropriate CTR (amount depend on the ratio between monomer and CTR) and Grubbs catalyst 1st generation (0.4 mol%) were placed in a glass Schlenk tube equipped with a magnetic stir bar. The reaction was carried out under intermittent vacuum (~10^{-1} mbar) at room temperature for the 24 h or until gas evolution decreased. From then on high vacuum (<10^{-3} mbar) was applied. The temperature was increased to 45 °C on the 2nd day and 50 °C for further 2 days. The mixture gradually became more viscous. The reaction was removed from the Schlenk line on the fourth day. The work up procedure described for ADMET bulk polymerization was used (yield: 90-95 %).

Procedure for catalytic hydrogenation

A high pressure reactor (Figure 5-1) was charged with 200 mg of an (telechelic) UPPE, 5 mL of toluene and 10 mg of 5% Pd/C catalyst and flushed with nitrogen. Hydrogenation was then performed with vigorous stirring under a hydrogen pressure of 2 bar at room temperature for 16-18 h. The solution was filtered over celite and the polymer was obtained as a solid after solvent evaporation in quantitative yield.

Figure 5-1: High pressure reactor structurally identical to the reactor which was used.[67]

*Poly [bis-(but-3-en-1-yl) phenyl phosphate] (**3a**)*

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.47-5.44 (m, -CH=CH-), 4.10-4.08 (m, -OPO_3-$\underline{CH_2}$-CH_2-), 2.40-2.35 (m, -OPO_3-$\underline{CH_2}$-$\underline{CH_2}$=CH_2).

^{13}C NMR (176 MHz, $CDCl_3$, ppm): δ 150.79, 150.75, 129.86, 128.18, 127.23, 125.23, 120.10, 120.08, 67.83, 67.80, 67.59, 33.64, 33.60.

^{31}P NMR (283 MHz, $CDCl_3$, ppm): δ-6.38.

*Poly [bis-(undec-10-en-1-yl) phenyl phosphate] (**4b**).*

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.34-7.15 (m, phenyl), 5.41-5.34 (m, -CH=CH-), 4.15-4.09 (m, -OPO_3-$\underline{CH_2}$-CH_2-), 2.02-1.96 (m, =CH-$\underline{CH_2}$-), 1.69-1.65 (m, -OPO_3-CH_2-$\underline{CH_2}$-), 1.38-1.21 (m).

^{13}C NMR (176 MHz, $CDCl_3$, ppm): δ 151.00, 150.96, 130.48, 129.80, 125.05, 120.14, 120.11, 68.73, 68.69, 32.77, 30.40, 30.36, 29.82, 29.62, 29.57, 29.33, 29.26, 25.53.

^{31}P NMR (283 MHz, $CDCl_3$, ppm): δ-6.11.

*Poly [bis-(undec-10-en-1-yl) methyl phosphate] (**4c**).*

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.33-5.26 (m, -CH=CH-), 4.00-3.92 (m, -OPO_3-$\underline{CH_2}$-CH_2-), 3.71-3.66 (m, P-O-$\underline{CH_3}$), 1.95-1.85 (m, =CH-$\underline{CH_2}$-), 1.66-1.55 (m, -OPO_3-CH_2-$\underline{CH_2}$-), 1.32-1.20 (m).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 139.15, 130.31, 129.85, 114.13, 67.84, 54.05, 33.78, 32.60, 32.06, 30.27, 29.76, 29.66, 29.48, 29.42, 29.15, 28.15, 27.21, 25.77, 25.43.

^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ0.38.

*Poly [bis-(but-3-en-1-yl) chlorophosphate] (**3f**)*

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ5.83-5.72 (m, -$\underline{CH}$=CH_2), 5.62-5.55 (m, -CH=CH-), 5.20-5.11 (m, -CH=$\underline{CH_2}$), 4.28-4.10 (m, $ClPO_3$-$\underline{CH_2}$-CH_2-), 2.55-2.35 (m, $ClPO_3$-$\underline{CH_2}$-$\underline{CH_2}$=CH_2).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 132.52, 128.03, 127.06, 118.33, 68.79, 66.54, 34.13, 33.09, 33.03, 28.18, 28.11.

^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ4.57.

*Copolymer of monomer **2e** and **2b***

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ7.36-7.13 (m, Phenyl), 5.88-5.72 (m, -$\underline{CH}$=CH_2), 5.39-5.30 (m, -CH=CH-), 5.02-4.91 (m, -CH=$\underline{CH_2}$), 4.16-4.08 (m, Ph-OPO_3-$\underline{CH_2}$-CH_2-), 4.04-3.96 (m, $HOPO_3$-$\underline{CH_2}$-CH_2-), 2.04-1.95 (m, =CH-$\underline{CH_2}$-), 1.72-1.61 (m, -OPO_3-CH_2-$\underline{CH_2}$-), 1.36-1.25 (m).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 150.86, 150.81, 130.31, 129.85, 129.63, 124.88, 119.99, 119.95, 114.13, 68.58, 68.53, 33.61, 30.25, 30.20, 29.77, 29.66, 29.46, 29.41, 29.17, 29.08. 27.23, 25.38.

^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ 1.23, -6.13.

*Unsaturated telechelic UPPE diol (**10b**)*

No terminal olefin was detected by NMR. The following spectral properties were observed:

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.36-7.13 (m, Phenyl), 5.39-5.36 (m, -CH=CH-), 4.16-4.08 (m, $-OPO_3-\underline{CH_2}-CH_2-$), 3.67-3.64 (m, $-CH_2-OH$), 2.02-1.92 (m, $=CH-\underline{CH_2}-$), 1.70-1.57 (m, $-OPO_3-CH_2-\underline{CH_2}-$), 1.34-1.25 (m).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 150.94, 130.46, 130.00, 129.79, 124.04, 120.13, 68.73, 68.68, 46.01, 32.96, 32.77, 31.74, 30.40, 30.35, 29.82, 29.62, 29.57, 29.33, 29.26, 25.53, 22.81, 14.27.

^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ -6.10.

*Unsaturated telechelic UPPE dicarboxylic acid (**11b**)*

No terminal olefin was detected by NMR. The following spectral properties were observed:
^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.36-7.13 (m, Phenyl), 5.39-5.36 (m, -CH=CH-), 4.16-4.08 (m, $-OPO_3-\underline{CH_2}-CH_2-$), 2.31-2.28 (m, $-\underline{CH_2}-COOH$), 2.02-1.92 (m, $=CH-\underline{CH_2}-$), 1.70-1.57 (m, $-OPO_3-CH_2-\underline{CH_2}-$), 1.34-1.25 (m).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 150.81, 130.32, 129.86, 129.65, 124.90, 119.99, 66.60, 32.63, 32.52, 30.25, 30.21, 29.78, 29.62, 29.57, 29.33, 29.11, 27.24, 25.39, 24.86.

^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ -6.12.

*Unsaturated telechelic UPPE dibromide (**12b**)*

No terminal olefin was detected by NMR. The following spectral properties were observed:

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.36-7.13 (m, Phenyl), 5.39-5.36 (m, -CH=CH-), 4.16-4.08 (m, $-OPO_3-\underline{CH_2}-CH_2-$), 3.43-3.37 (m, $-CH_2-Br$), 2.02-1.92 (m, $=CH-\underline{CH_2}-$), 1.70-1.57 (m, $-OPO_3-CH_2-\underline{CH_2}-$), 1.34-1.25 (m).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 150.81, 130.32, 129.86, 129.65, 124.90, 119.99, 68.60, 34.06, 32.63, 30.25, 30.21, 29.78, 29.62, 29.57, 29.33, 29.11, 27.24, 25.39.

^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ -6.10.

*Unsaturated telechelic UPPE dithioacetic acid ester (**13b**)*

No terminal olefin was detected by NMR. The following spectral properties were observed:

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.36-7.13 (m, Phenyl), 5.39-5.36 (m, -CH=CH-), 4.16-4.08 (m, -OPO_3-$\underline{CH_2}$-CH_2-), 2.88-2.83 (m, -CH_2-SCO-), 2.32 (m, -CH_3), 2.02-1.92 (m, =CH-$\underline{CH_2}$-), 1.70-1.57 (m, -OPO_3-CH_2-$\underline{CH_2}$-), 1.34-1.25 (m).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 150.81, 130.32, 129.86, 129.65, 124.90, 119.99, 66.60, 32.63, 30.25, 30.21, 29.78, 29.62, 29.57, 29.33, 29.11, 27.24, 25.39.

^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ -6.11.

*Unsaturated telechelic UPPE diepoxide (**14b**)*

No terminal olefin was detected by NMR. The following spectral properties were observed:

^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.36-7.12 (m, Phenyl), 5.40-5.32 (m, -CH=CH-), 4.16-4.08 (m, -OPO_3-$\underline{CH_2}$-CH_2-), 2.94-2.87 (m, epoxide), 2.76-2.72 (m, epoxide), 2.47-2.44 (m, epoxide), 2.02-1.92 (m, =CH-$\underline{CH_2}$-), 1.73-1.62 (m, -OPO_3-CH_2-$\underline{CH_2}$-), 1.37-1.25 (m).

^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 150.81, 130.32, 129.86, 129.65, 124.90, 119.99, 66.60, 32.63, 32.52, 30.25, 30.21, 29.78, 29.62, 29.57, 29.33, 29.11, 27.24, 25.39.

^{31}P NMR (202 MHz, $CDCl_3$, ppm): δ -6.11.

5.3.3 ROM

Procedure for the ring-opening metathesis reaction of LSL

To a solution of LSL (1023 mg, 1.5 mmol) in CH_2Cl_2 solution was added Grubbs catalyst 1st generation (123 mg, 0.15 mmol). The solution was degassed by freeze-pump-thaw cycle, and stirred at room temperature under an atmosphere of ethylene at 3 bar for 5 h. To this solution an excess of ethyl vinyl ether was added. After the solvent was removed, brown colored sediment was observed (yield: 95 %). The removal of the catalyst is still under investigation.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.89-5.75 (m, -CH=CH_2, 2H), 5.05-4.91 (m, -CH=CH_2, 4H) 4.64-4.33 (m, 5H), 4.20-4.17 (m, 2H), 3.87-3.43 (m, 8H), 2.43-2.35 (m, 2H), 2.13-2.02 (m, 10H), 1.90-1.85 (m, 2H), 1.67-1.60 (m, 4H), 1.48-1.25 (m, 22H).

6 List of Abbreviations

ADMET	Acyclic Diene Metathesis Polymerization
ATRP	Atom Transfer Radical Polymerization
BIBB	2-Bromoisobutyryl Bromide
$CH(D)Cl_3$	(deuterated) Chloroform
CH_2Cl_2	Dichloromethane
COSY	Correlation Spectroscopy
CTR	Chain Termination Reactant
dH_m	Molar heat of fusion
DOSY	Diffusion Ordered Spectroscopy
DSC	Differential Scanning Calorimetry
Et_3N	Triethylamine
ESI-MS	Electrospray Ionization Mass Spectrometry
GPC	Gel Permeation Chromatography
HCl	Hydrochloric acid
LCST	Lower Critical Solution Temperature
LSL	Lactonic Sophorolipid
MeOH	Methanol
M_w	Weight average molecular weight
M_n	Number average molecular weight
NMR	Nuclear Magnetic Resonance
PCL	Poly (ε-caprolactone)
PDI	Polydispersity Index
PEG	Polyethylene Glycol

PEGMA	poly(ethylene glycol) methyl ether methacrylate
PLA	Polylactide
PLLA	Poly-L-lactide
PMMA	Poly(methylmethacrylate)
PS	Polystyrene
PU	Polyurethane
ROM	Ring Opening Metathesis
ROMP	Ring Opening Metathesis Polymerization
ROP	Ring Opening Polymerization
r.t.	Room Temperature
SEC	Size-Exclusion Chromatography
T_g	Glass transitions temperature
T_m	Melting point
TGA	Thermal Gravimetric Analysis
THF	Tetrahydrofuran
TPP	Triphenylphosphine
(U)PPE	(Unsaturated) Polyphosphorester

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