Terpenes as Renewable Resources for Organic and Macromolecular Chemistry

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This work is dedicated to:

My parents: Djauhar Sanusi and Machmudah Bachrijah,

My wife: Ika Indah Maharoh,

and my beloved sons: Elrick Albrecht Firdaus and Finley Fadhil Firdaus

Abstract

With the goal to develop innovative science and technology to significantly reduce our dependence on fossil fuel and decrease carbon emissions, due to the deficiency of fossil fuel and global warming, the use of the renewable resources *via* green sustainable procedures are discussed. Implementation of efficient approaches, such as thiol-ene reactions and metal-free organocatalysis provides the potential to achieve sustainability and offer significant advantages in economical, environmental and scientific aspects. Thus, through sustainable and efficient approaches, a considerable amount of novel monomers and polymers (e.g. polyesters, polyamides, polyurethanes, polysulfides, and polysulfones) are prepared mainly from terpenes and/or few from vanillin in combination with fatty acid derivatives. Additionally, thermal properties of the synthesized polymers are studied in order to learn about the properties and possible applications for the future.

Kurzzusammenfassung

Die vorliegende Arbeit verfolgt als Hauptziel eine signifikante Reduzierung der Abhängigkeiten von fossilen Rohstoffen, sowie eine Reduzierung der Kohlendioxid-Emissionen. Aufgrund der stetigen Verknappung von fossilen Brennstoffen sowie der globalen Erderwärmung, wird die Verwendung erneuerbarer Rohstoffe über "grüne" und nachhaltige Methoden in der Chemie diskutiert. Die Anwendung von effizienten Verfahren, wie zum Beispiel Thiol-En-Reaktionen und metallfreie Organokatalyse, liefern das Potential zur Erfüllung der Nachhaltigkeit und bieten des Weiteren erhebliche Vorteile hinsichtlich ökonomischen, umweltfreundlichen und wissenschaftlichen Aspekten. Somit wurden durch nachhaltige und effiziente Methoden eine beträchtliche Anzahl von neuen Monomeren und Polymeren (z.B. Polyester, Polyamide, Polyurethane, Polysulfide und Polysulfone), hauptsächlich aus Terpenen, einige auch ausgehend von Vanillin, oft in Kombination mit Fettsäurederivaten, hergestellt. Zusätzlich wurden von allen synthetisierten Polymeren die thermischen Eigenschaften charakterisiert, um dadurch grundlegende Daten für mögliche zukünftige Anwendungen zu erhalten.

Contents

Chapter 1: Introduction 1

Chapter 2: Terpenes as Renewable Raw Materials for Polymers 6

Chapter 3: Efficient Approaches for Monomer Syntheses and Polymerization 22

Chapter 4: Terpene Based Renewable Monomers and Polymers *via* Thiol- Ene Additions 37

Chapter 5: Renewable Co-Polymers Derived from Vanillin and Fatty Acid Derivatives 63

Chapter 6: Renewable Polyamides and Polyurethanes Derived from Limonene 79

Chapter 7: Renewable Co-Polymers Derived from Limonene and Fatty Acid Derivatives 100

Chapter 8: Experimental Part 115

Chapter 9: Concluding Remarks and Outlook 167

List of Abbreviations 171

Curriculum Vitae 173

List of Publications and Conference Contributions 175

Acknowledgements 176

References 178

1

Introduction

Today, fossil resources are still widely used as transportation fuels, to produce electricity, and as raw materials for the production of many chemicals and other products that are involved in every level of life in our modern society. During the 20th century, the development of science and technology was mainly focused on the utilization of fossil resources, because during this era fossil resources were abundant and available at relatively low cost. As a result of the population explosion, the demand for food and the demand for other goods has also significantly grown. As a consequence, fossil resources are being exploited faster than they are being replenished, the price of oil and thereof derived products escalate, and hazardous materials are being released in large quantities into the environment. Many people have been discussing how to improve the way humans live and behave in order to enhance economic development and develop social welfare while still being concerned on the availability of fossil resources for present and future live and paying attention to the environmental impact. Thus, the term “sustainable development” was then introduced by the Brundtland Commission (1987), with the definition as

"development that meets the needs of the present without compromising the ability of future generations to meet their own needs".[1]

To achieve the goal of sustainable development, innovative science involving multi-disciplinary research about developing environmentally benign and fossil resources-independent methods is required. Green chemistry provides one such opportunity. Comprehensive and systematic guidelines, so called "12 principles of green chemistry", were thus introduced by Anastas and co-workers,[2,3] which are aiming to motivate chemists and others to minimize the use of materials that are hazardous to human health and the environment, to decrease energy and water usage, and to maximize efficiency. If possible, all 12 principles should be considered, although it will be difficult to maximize all at the same time. However, in order to bring the aims into reality, the following major concepts for chemistry can be pointed out from these twelve principles:

- Design more effective and environmentally benign chemical processes
- Design chemical products that are based on renewable resources
- Enhance reaction efficiency by using catalysts
- Minimize of used of toxic reagents and solvents
- Minimize waste and maximize energy savings

In line with the mentioned concepts, the present dissertation describes the development of new environmentally benign methods employing renewable resources, namely biomass, as alternative to fossil resources for the synthesis of polymers. It was estimated that over 120 billion tons carbon in biomass (equal to >80 billion tons of oil equivalents) exists in the biosphere and are generated annually by photosynthesis, of which approximately 5% is currently used by man.[4] Among of the

major classes of fossil-based feedstocks, compounds such as benzene and cyclohexane, provide hydrophobicity and rigidity to polymers derived from them. From the standpoint of cost and availability, terpenes and lignin are among valuable biomass containing rich cycloaliphatic and aromatic structures, which might be suitable substitutes. The presently available terpenes and their utilization for the synthesis of polymeric materials will be briefly discussed in **Chapter 2**.

The discussion of this dissertation will mainly focus on the introduction of new sustainable ways for value creation of terpenes (i.e. limonene) for the synthesis of, for example, polyesters in **Chapter 4** and polysulfides and polysulfones in **Chapter 7**. Furthermore, extensive investigations in utilizing a lignin derivative, vanillin, for the synthesis of aromatic polyesters through different synthetic approaches are described in **Chapter 5**. Apart from this, *via* different combinations with limonenes and/or vanillin, the use of fatty acid derivatives, which provide long flexible aliphatic chains, for polymer syntheses will also be investigated.

Another important key to achieve the aim of sustainable development is by designing environmentally benign and highly efficient reaction methods to guarantee the efficiency of the overall synthesis. Thus, to obtain high yields with high selectivity and to accomplish both economical and environmental benefits, the uses of catalysts, as selective as possible, in organic reactions are essential.[5] Nowadays, chemical transformations employing organic catalysts (organocatalysis) have gained attention due to their simplicity and potential for new synthetic possibilities. Furthermore, in addition to be metal-free and thus usually of lower toxicity, organocatalysts provide significant advantages in economical, environmental and scientific aspects. Among the available organic catalysts, the cyclic guanidine base, 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), represents a potent catalyst for enhancing the

performance of certain reactions which have been previously employed in many transformations for the synthesis of fine chemicals.[6] Moreover, the recently developed simple and technologically convenient synthesis of TBD using cheap and non-hazardous materials as well as the benefits in ease to handle and mildness of reaction conditions, make it a suitable choice for catalysis.[7] In this dissertation, **Chapter 3.2** will discuss TBD as efficient and promising catalyst. Nevertheless, minimizing toxic reagents should also be considered to achieve the goal of sustainability. Hence, environmentally benign method to synthesize dicarbamates and polyurethanes employing TBD catalyst avoiding phosgene and/or toxic isocyanate routes will be described in **Chapter 6**. Overall, the application of TBD for monomer and polymer syntheses will be discussed throughout the whole chapters. Especially in **Chapter 4**, investigations about the effect of a sulfur in β-position to an ester group on the reactivity towards TBD-catalyzed transesterification will be briefly described.

Beside TBD, Ruthenium-based catalysts are also considered as a potential "green" catalyst. Because of their discovery of a variety of highly efficient and selective Ruthenium-based catalysts for olefin synthesis, Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock were awarded the 2005 Nobel Prize in Chemistry.[8] In this dissertation, the knowledge of metathesis reactions as well as metathesis catalysts and a few contributions of their application as efficient catalyst for the preparation of monomer and polymers will be discussed in **Chapter 4** and **Chapter 5**.

The use of catalysts is not the only tool to achieve highly efficient reactions. In certain cases, thiol-ene reactions are generally a very useful approach for various transformations, which enable an efficient introduction of different functional groups to olefinic structures.[9,10] In addition, thiol-ene reactions are metal free, orthogonal,

regioselective, and usually provide high yields with simple or no chromatography separation techniques required.[11] In this dissertation, the knowledge of thiol-ene reactions and their application for material syntheses will be briefly discussed in **Chapter 3.1**. Throughout, the application of thiol-ene reactions for monomer syntheses and polymerizations will be discussed in all chapters. Moreover, limonene, the main terpene utilized in this work, naturally occurs in enantiomeric pure form. Thiol-ene addition at their endocyclic and exocyclic double bonds might present different reactivities. Thus, regioselectivity and/or stereoselectivity of limonenes toward thiol-ene reaction is described in **Chapter 4** and **Chapters 6**–**7**.

2

Terpenes as Renewable Raw Materials for Polymers

Terpenes are found in essential oils and are widely distributed in nature as secondary metabolite compounds, mainly synthesized by plants and a limited number of insects, marine microorganisms and fungi.[12] They can be classified as one of the largest families of naturally-occurring compounds, bearing enormous structural diversity.[12] In addition to play essential roles in nature and human life as, for example, pheromones, flavors, fragrances, and nutrients,[13] some terpenes showed important pharmacological functions for the treatment of many diseases, including cancer.[14,15] Most terpenes share units of five carbons, called isoprene (2-methyl-1,3-butadiene), ordered in a regular pattern, usually head-to-tail, as a common carbon skeleton building block and they can be classified associated with the number of isoprene units (n); for example: monoterpene (n=2), sesquiterpene (n=3), diterpene (n=4) and so on.[12,16] When terpenes are chemically modified, for example by oxidation or rearrangement of the carbon skeleton, the resulting compounds are generally

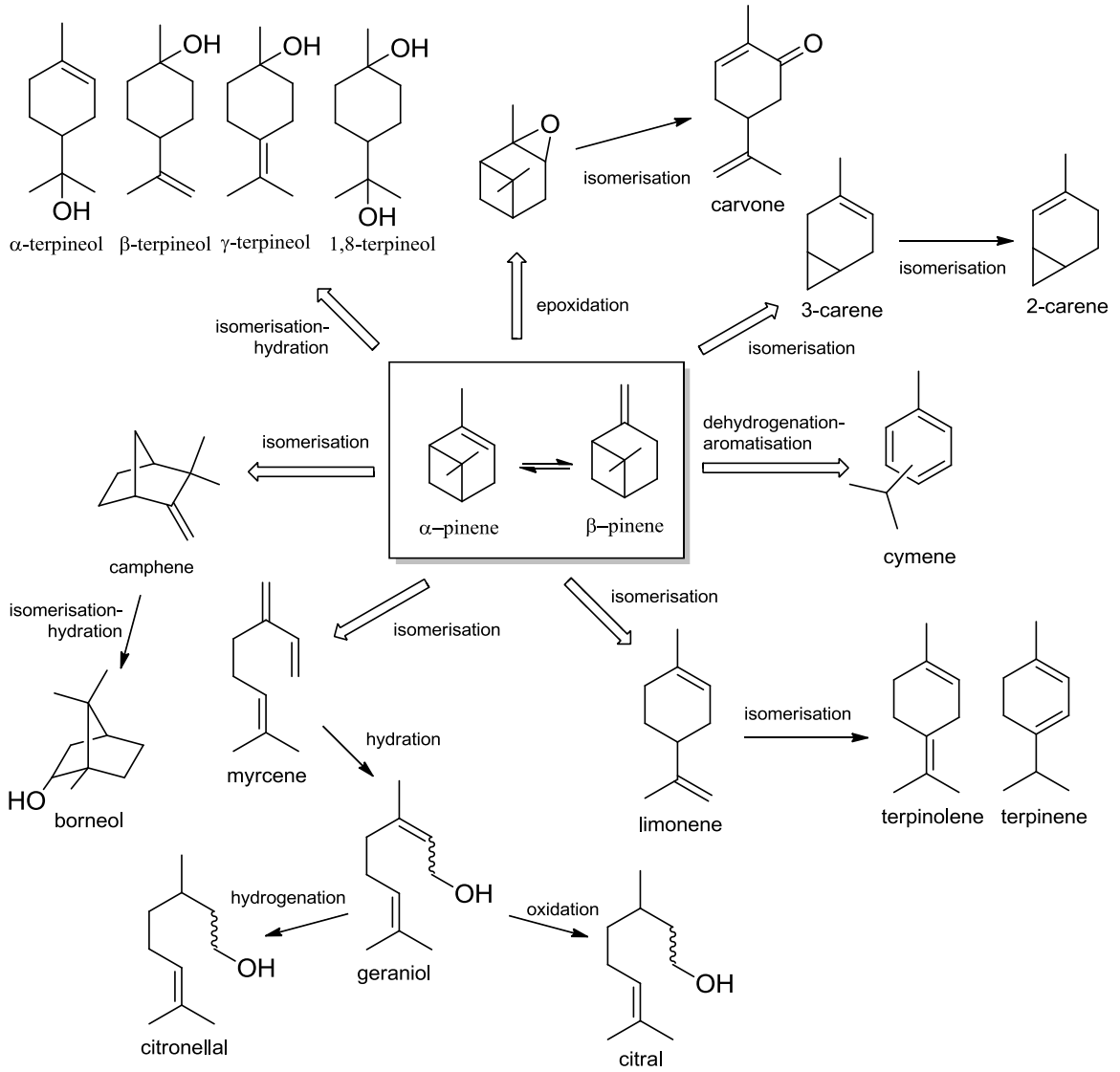
referred as terpenoids. The main terpenoid compounds found in some essential oils can be seen in Table 2.1.[16]

Table 2.1. Main terpenoid compound of some essential oils.[16]

Essential oil	Botanical Name	Main Constituents
Turpentine	*Pinus* spp.	Terpenes (pinenes, camphene)
Coriander	*Coriandrum sativum*	Linalool (65/80%)
Otto of rose	*Rosa* spp.	Geraniol, citronellol (>70%)
Geranium	*Pelargonium* spp.	Geraniol, citronellol
Lemon	*Citrus limon*	Limonene (90%)
Lemon grass	*Cymbopogon* spp.	Citral, citronellal (75/85%)
Citron scented	*Eucalyptus citriodora*	Citronellal (~70%)
Spearmint	*Mentha spicata* and *Menta cardiac*	Carvone (55/70%)
Peppermint	*Mentha piperita*	Menthol (45%)
Continental lavender	*Lavandula officinalis*	Linalool, linalyl acetate (much), ethyl penthyl ketone
Cinnamon bark	*Cinnamomum verum* Presl.	Cinnamic aldehyde (60/75%)
Cassia	*Cinnamomum cassia*	Cinnamic aldehyde (80%)
Cinnamon leaf Presl.	*Cinnamomum verum*	Eugenol (up to 80%)

The most representative and viable source of terpenes are the turpentine resins extracted from coniferous trees and terebinth (also called Chian, Scio, or Cyprian turpentine) and the essential oils obtained from citrics.[16] The world production of turpentine is estimated to be over 35×10^4 tons,[12] whereas citrus, which is the most abundant crop in the world, are produced worldwide over 88×10^6 tons.[17] Thus, from the standpoint of cost and availability, the major compounds isolated from them must be an ideal starting material for the synthesis of new important chemicals. Turpentine consists a few unsaturated hydrocarbon monoterpenes ($C_{10}H_{16}$), so called α-pinene (45–97%), β-pinene (0.5–28%), and smaller amounts of other monoterpenes,[12] and citrus peel oil contains limonene (90%) as major compound.[18]

Various (catalytic) chemical processes of terpenes have been developed for the production of valuable products *via* isomerization/rearrangement, hydrogenation, oxidation, hydration, hydroformylation, condensation, cyclization, ring contraction, etc. Chemical transformations of various terpenes were extensively reviewed by Corma *et al*.[16] Scheme 2.1 represents some possible products that can be obtained from pinene. The main terpenes and terpenoids, which can be considered as possible renewable platform chemicals, are pinene, limonene, carene, geraniol/nerol, citronellol, citral, and citronellal.[16]



Scheme 2.1. Some of possible products that can be obtained from pinene.[16]

Although terpenes can undergo various chemical transformations, only few of these compounds have been used as starting materials for polymer synthesis. Only α-pinene, β-pinene, limonene, and myrcene have been studied extensively as starting materials.[19] Nevertheless, efforts have been made to involve terpenes in the synthesis of polymeric materials. Since the middle of the last century, the application of terpenes in polymer chemistry has become an important research area with constant growth based on the basis following reason:

- Due to the availability of different functional groups on terpenes (i.e. double bonds, hydroxyl or carboxyl groups), which can be used to introduce new functionality and then further be modified, a wealth of possible polymers can be prepared from them.
- In addition to be abundant, terpenes might be used as an alternative in substituting the existing fossil resources based chemicals such as benzene, cyclohexene, and cyclohexane, minimizing the strong dependence of the polymer industry on fossil-derived raw materials.
- Polymers with certain desirable properties, such as biodegradability, hydrophobicity, bioactivity, and liquid crystallinity, can be derived from terpenes, and thus, might be useful for many applications.[20]

This chapter will summarize current knowledge and applications of terpenes derived from natural resources and discuss possible future applications/products as well as properties of these materials. The discussion will be focused on limonene, α-pinene, and β-pinene, the most abundant terpenes, which are also utilized in this work.

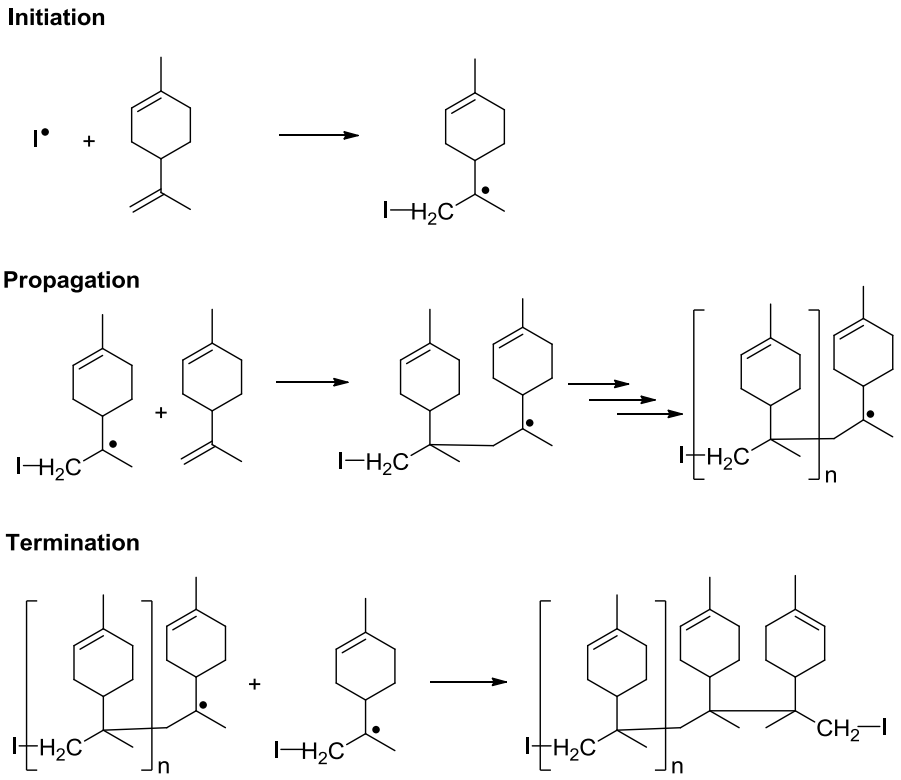
2.1. Polymers Derived from Limonene

Limonene is a chiral compound, as are most of the monoterpenoids made by plants. The (*R*) enantiomer is a cyclic diene responsible for the typical orange lemon like citrus smell. In contrast, pure (*S*)-(−)-limonene, the main constituent of the Silver Fir cone oil (*Abies alba*, synonym *A. pectinata* Mill.) has an odour more reminiscent of turpentine.[21] The earliest report on the polymerizations of limonene dates back to 1950.[22] In this report, Roberts and Day studied the polymerization of (*R*)-(+)-limonene employing Friedel-Crafts type catalyst ($AlCl_3$) resulting in low molecular weight polylimonenes. Further polymerization involving limonene was reported by Modena and co-workers in 1965.[23] The polymerizations were performed using a Ziegler-type catalyst (aluminium alkyl-metal halide in 1:1 molar ratio) and yielded almost completely racemized polylimonenes with low molecular weight. The cationic polymerization of limonene has also been reported employing Lewis acids $AlCl_3$ or $AlCl_3/SbCl_3$ as catalyst.[24] The result showed that using the binary system $AlCl_3/SbCl_3$ was advantageous in terms of reactivity and the obtained molecular weight.

Limonene contains exocyclic and endocyclic double bonds, which might be polymerized *via* a radical mechanism. In this case, radical co-polymerization has been the most suitable reaction tool to polymerize this monoterpene. Radical co-polymerization of (*R*)-(+)-limonene with maleic anhydride was reported using AIBN as initiator.[25] The obtained co-polymers were optically active with low molecular weight. The proposed mechanism described consistent participation of a charge-transfer complex of the comonomers in the propagation step *via* inter–intramolecular cyclopolymerization resulting a 1:2 alternating co-polymer.

Likewise, limonene has been radically co-polymerized by Sharma and Srivastava with styrene.[26] The co-polymerization was performed in xylene employing AIBN as

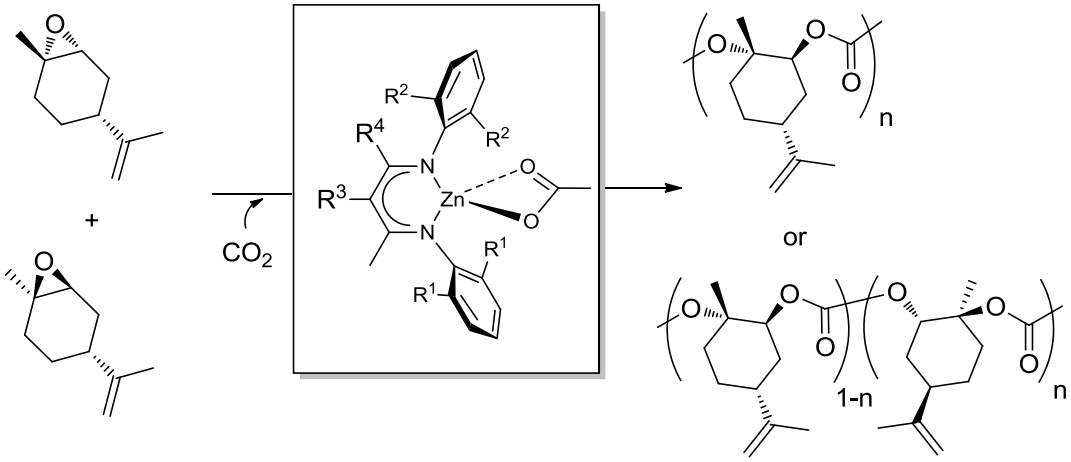
initiator under inert atmosphere of nitrogen for 2 h. It was proposed that the exocyclic double bond was susceptible to take part in polymerization. Under the same approach, the same author reported radical co-polymerization with other vinyl monomers, i.e. acrylonitrile (in DMF, benzoyl peroxide, 70 °C),[27] methyl methacrylate (in xylene, benzoyl peroxide, 80 °C),[28] *N*-vinyl pyrrolidone (in dioxane, AIBN, 80 °C),[29] and *N*-vinyl acetate (in dioxane, AIBN, 65 °C),[30] which always gave alternating co-polymers. More recently, without co-monomer, polylimonene was prepared by radical polymerization of limonene employing benzoyl peroxide as initiator in xylene at 85 °C under an inert atmosphere of nitrogen.[31] The proposed mechanism is depicted in Scheme 2.2. One of the two double bonds (the endocyclic one) is retained and it does not take part in the polymerization. Radical co-polymerization of limonene, methyl metacrylate, and styrene has been prepared using benzoyl peroxide as initiator in xylene at 80 °C to yield terpolymers.[32] Finally, a new series of liquid-crystalline polymers with limonene-co-methyl methacrylate as the backbone and a phenyl benzoate mesogenic group attached to the polymer backbone *via* a polymethylene spacer were reported.[33]



Scheme 2.2. Proposed mechanism of radical polymerization of limonene.[31]

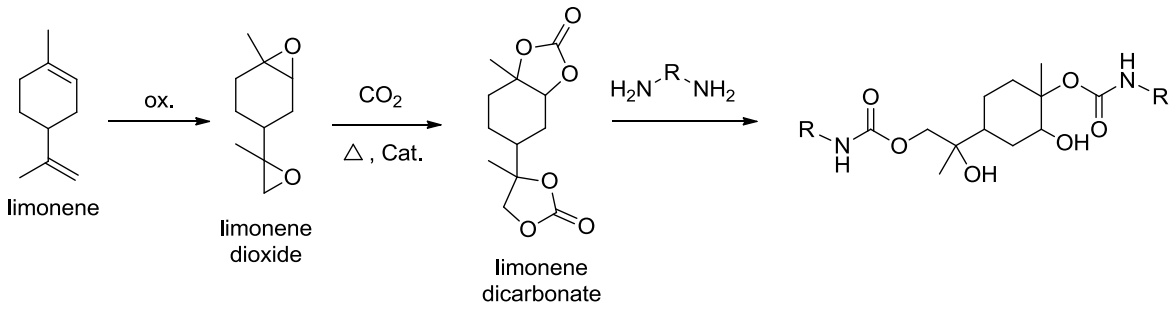
In the context of radical polymerizations, thiol-ene additions are considered as alternative and efficient processes, which contribute not only to a more feasible synthesis of limonene-based polymers, but also to broaden the application possibilities of limonene or other terpenes. Accordingly, thiol-ene polymerizations involving limonene or other monoterpenes will be described separately in **Chapter 3.** Through epoxidation of the unsaturated double bonds, the epoxidized product of limonene might result in monomers that can be utilized for the synthesis of polymers. Aikins and Williams reported the radiation-induced cationic polymerization of limonene oxide, α-pinene oxide, and β-pinene oxide.[34] The polymerization proceeds by the opening of the epoxide ring to yield a 1,2-trans polyether with low molecular weight and high monomer conversions. Coates and coworkers reported co-polymerization of limonene oxide and carbon dioxide using β-diiminate zinc complexes as catalyst (Scheme 2.3).[35] Highly regio- and stereoregular alternating

polycarbonate co-polymers were obtained in high molecular weight when the reaction was performed for longer reaction times and higher [epoxide]/[Zn] ratios.



Scheme 2.3. Co-polymerization of limonene and carbon dioxide.[35]

Another polymerization involving limonene oxide for the preparation of nonisocyanate polyurethanes was recently reported by Mülhaupt and co-workers.[36] Catalytic carbonation of limonene dioxide with carbon dioxide was performed in the presence of quaternary alkyl ammonium catalysts at 140 °C and 30 bar carbon dioxide pressure to produce a novel limonene dicarbonate as monomer. Polymerization of this limonene dicarbonate with diamines under solvent-free conditions without catalyst gave linear non isocyanate polyurethanes. This route (Scheme 2.4) shows not only an attractive "green" alternative to traditional isocyanate based polyurethanes avoiding the use of either phosgene or toxic isocyanate monomers, but also provides new polyurethanes derived from renewable resources minimizing the strong dependence on fossil-derived raw materials.

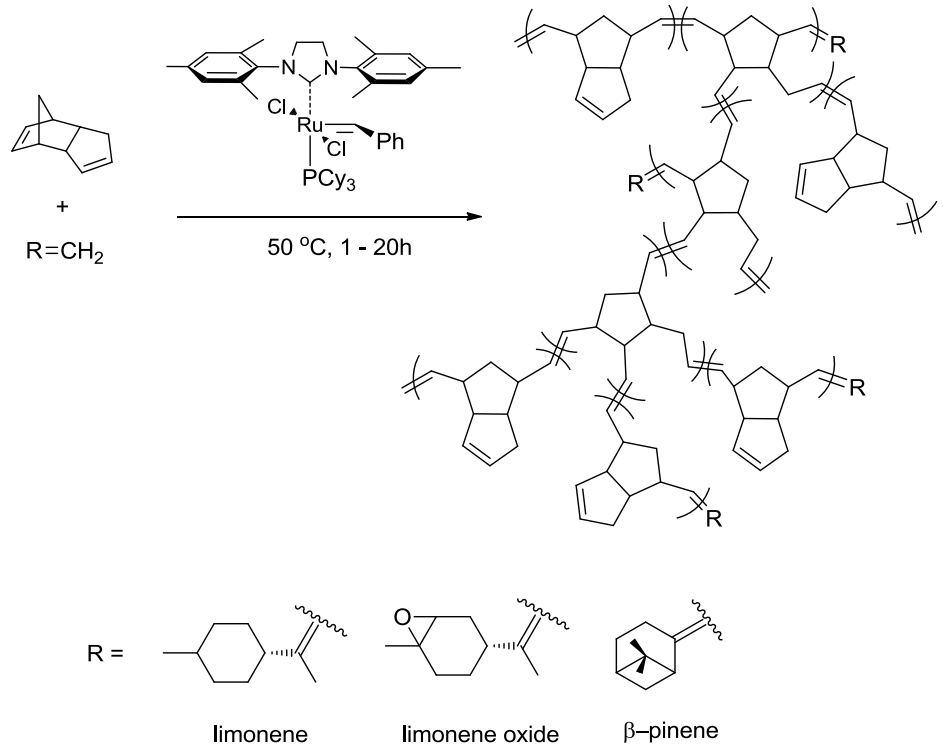


Scheme 2.4. Isocyanate free strategy from limonene to hydroxyurethane.[36]

Photoinitiated cationic ring-opening polymerization of limonene 1,2-oxide has recently been reported employing both diaryliodonium salt and triarylsufonium salt photoinitiators.[37] In addition to be polymerized, the limonene oxide undergoes a number of side reactions yielding a variety of nonpolymeric products. Nevertheless, the results indicate that limonene oxide, a potentially inexpensive and readily available biosourced epoxy monomer, may find considerable use in many applications as comonomers in photoinitiated cationic crosslinking polymerizations.

Ring Opening Metathesis Polymerization (ROMP) of dicyclopentadiene in monoterpenes (i.e. limonene, limonene oxide, and β-pinene) employing a second generation ruthenium initiator for the synthesis of functional hyperbranched polymers has also been reported (Scheme 2.5).[38] Chain transfer occurs when a monoterpene alkene reacts with the metathesis initiator. During ROMP, metathesis reactions between the growing polymer chain and monoterpenes produced soluble well-defined polymers. This approach not only converts the heterogenous ROMP of dicyclopentadiene into a homogenous process but this polymerization also provides a one-pot method for the synthesis of functional hyperbranched polymers. In a similar way, limonene has been utilized as a renewable solvent and chain transfer agent for the ROMP of various strained monomers, such as norbornene and 1,5-cyclooctadiene

and low strained monomers such as cyclopentene, *trans,trans,trans*-1,5,9-cyclododecatriene, and cycloheptene.[39]

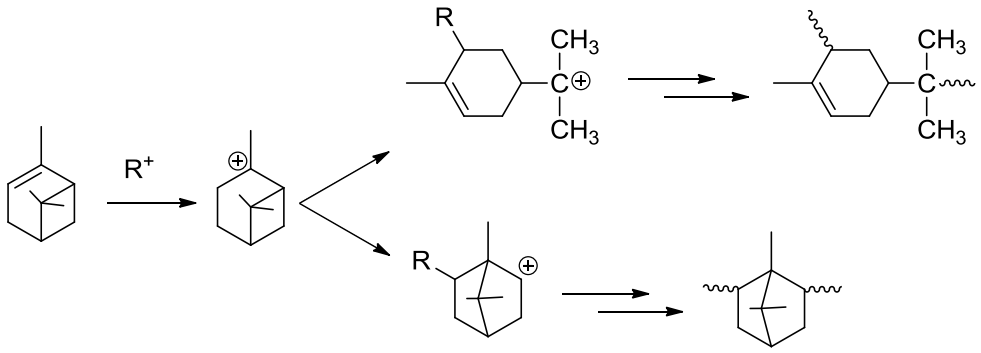


Scheme 2.5. Polymerization of dicyclopentadiene with monoterpenes using a second-generation Rhutenium initiator.[38]

2.2. Polymers Derived from Pinenes

Pinenes are the most abundant terpenes and thus represent the logical precursors to polyterpenic materials designed for bulk applications. The earliest study of the polymerization of α-pinene was reported in 1937, employing $AlCl_3$ as Friedel-Crafts catalyst in hydrocarbon solvent (i.e., benzene, toluene, xylene, or hexane).[40] Later on, investigation of the cationic polymerization of pinenes using various Lewis acid initiators showed that α-pinene was vastly less reactive than its β-isomer.[22] Due to the fact that α-pinene is abundant, a number of research has been conducted related to its cationic polymerization. For example, a series of metal halides such as $AlCl_3$,

$AlBr_3$, $AlEtCl_2$, $BF_3{\cdot}OEt_2$, $SnCl_4$, $TiCl_4$, and WCl_6 in conjunction with antimony trichloride ($SbCl_3$) were investigated as initiator for the cationic polymerization of α-pinene.[41,42] It was found that $AlCl_3$ was best suited to initiate the cationic polymerization. Cationic polymerization of α-pinene with Keggin silicotungstic acid (SiW_{12}) as homogenous catalyst was recently reported.[43] SiW_{12} is found not only as polymerization initiator but also as the counter-anion of the growing cationic center. Considering the cationic polymerization mechanism, it should be noted that, even though α-pinene is readily protonated to form a tertiary carbocation, which can then rearrange to an unsaturated *p*-menthane isomer (Scheme 2.6), the attack of the endocyclic double bond to the isopropenyl cationic site is limited by steric hindrance.[12] Thus, the vast majority of pinene polymerization involves the use of β-pinene instead of the α-homologue although the β-isomer is less abundant than the α-one.



Scheme 2.6. Alternative mechanism of α-pinene cationic polymerization.[12]

Likewise, the exocyclic double bond in β-pinene can also be polymerized by conventional cationic techniques. Earliest investigation was done in 1950 employing Friedel-Crafts type catalyst such as $AlCl_3$, $AlBr_3$, and $ZrCl_4$ as initiator.[22] Later on, other Lewis initiators i.e. $SnCl_4$, $TiCl_4$, BF_3, and Et_2AlCl, were also studied.[44] From these initiators, Et_2AlCl proved to be the most efficient catalyst. Cationic

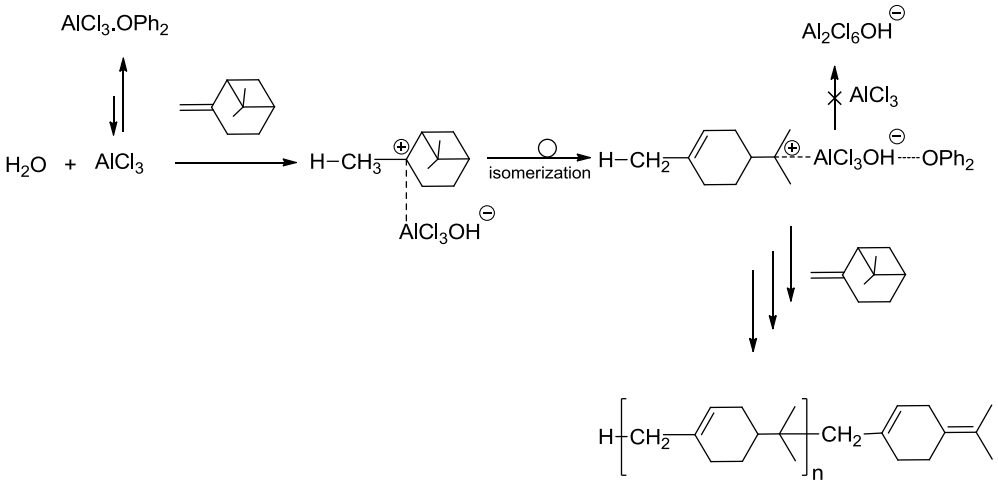
polymerization of β-pinene under microwave irradiation was recently reported using $AlCl_3$ as initiator, which was shown to proceed rather rapid and smoothly.[45] However, all of these conventional polymerization methods resulted in only low molecular weight ($M_n \leq 4000$ Da). The development of novel initiating systems capable of providing controlled cationic polymerizations in terms of living manner is then necessary.

The first successful study involving β-pinene on the living cationic polymerization systems were reported by Sawamoto *et al.* in 1997.[46,47,48] The proposed polymerization mechanism involves the addition of cationic initiator onto β-pinene to form a tertiary carbocation which then undergoes rearrangement of the pinane skeleton with the formation of a *p*-menthane type repeating unit.[47,48] Along with the high reactivity of the exocyclic double bond, the strain release resulting from the opening of the fused cyclobutane ring and the formation of a relatively stable tertiary carbenium ion are driving forces in the propagation mechanism.[12,19]

The possibility of controlling the cationic polymerizations of β-pinene using the living systems, allowed an opportunity to introduce reactive functional groups for the synthesis of block co-polymers with desirable properties. A number of papers have been reported to involve the synthesis of block co-polymers with, for example, styrene or *p*-methylstyrene,[48] isobutene,[49] and other co-monomers.[50,51] The combination of living cationic polymerization with atom transfer radical polymerization (ATRP) was also reported.[51,52]

Most homopolymers and block co-polymers prepared by living cationic polymerization resulted only in low molecular weight. High molecular weight of poly(β-pinene) with up to 40 KDa can be achieved by employing the $H_2O/EtAlCl_2$ system.[53,54] However, in order to achieve high molecular weight, the reaction must be

performed at very low temperature ~ 80 °C. In order to obtain high molecular, further optimization with an efficient and preferably with environmentally benign methods is then necessary. Kostjuk and co-workers reported an effective initiating system based for cationic polymerization of β-pinene using $AlCl_3$ etherates ($AlCl_3OPh_2$ or $AlCl_30.8EtOAc$) under industrially attractive experimental conditions (room temperature, low co-initiator concentration, and possibility to use non-chlorinated solvents).[55] Poly(β-pinene)s with relatively high molecular weight (M_n 9–14 KDa) and good thermal properties were obtained. Concerning the reaction mechanism (Scheme 2.7), it was proposed that the dissociation of the $AlCl_3{\times}OPh_2$ complex caused the formation of free Lewis acid. The *in situ* generation of a weakly nucleophilic counteranion through the interaction of $AlCl_3OH^-$ with diphenyl ether, which leads to the suppression of chain transfer reactions, could be the reason that high molecular weight poly(β-pinene) was achieved.[55]



Scheme 2.7. Proposed mechanism for β-pinene polymerization using $H_2O/AlCl_3{\cdot}OPh_2$ initiating system.[55]

It was already mentioned that the free radical mechanism is one of the most efficient tools to polymerize compounds containing double bonds. The radical

homopolymerization of β-pinene or other monoterpenes is an inefficient process which leads to oligomers with molecular weights below 1000 Da.[56] However, when pinenes and other monoterpenes are used as co-monomers in free radical co-polymerizations with monomers bearing structures other than theirs, high molecular weight can be achieved. Thus, β-pinene has been successfully co-polymerized with, for example, methyl methacrylate,[56] acrylonitrile,[57] maleimide,[58] other co-monomers.[45] Another radical polymerization technique involving β-pinene is Reversible Addition-Fragmentation Chain-Transfer (RAFT) polymerization. RAFT polymerization is one of the most promising synthetic methods to produce polymers with specific functionalities and very well controlled structures for specialized applications.[59] Co-polymerization of β-pinene *via* RAFT with fossil-based co-monomers i.e. methyl acrylate,[60] acrylonitrile,[57] *N*-substituted maleimides,[61] or *N*-butyl acrylate[62] (to only mention a few recent examples) was reported.

2.3. Application of Terpene-based Polymers

A brief overview of terpene-based polymers applications is given in the following section. The fact that most terpenes can be obtained from nature as pure enantiomers, the chiral polymers derived from them have potential application for chiral purification,[63] asymmetric catalysis,[64] in non-linear optics,[65] or as conducting materials.[66]

Poly(pinene)s and other commercially available polyterpene resins are low molecular weight hydrocarbon like polymers used as adhesive components to impart tack (to both solvent-based and hot-melt systems), provide high gloss, good moisture vapour transmission resistance and good flexibility for wax coating and ensure viscosity control and density increase to casting waxes.[12]

Thakur and co-workers reported the application of poly(β-pinene) as semi-conductive material.[67] Upon doping poly(β-pinene) with iodine, the formed nonconjugated polymer became electrically conductive. The same author also reported that at high doping level of iodine, the nonconjugated polymer exhibited a large quadratic electro-optic effect that would make useful for non-linear optics application.[68]

Beside poly(β-pinene), investigations of poly(α-pinene) for nonisothermal crystallization has been reported. Poly(α-pinene) was utilized in the nonisothermal crystallization of isotactic polypropylene blends containing up to 30 per cent of this polyterpene.[69,70,71]

During the last 20 years, an increased interest has been devoted to side-chain liquid-crystalline polymers because these types of polymers have great potential as new materials for electronic devices, nonlinear optic information storage, and display devices.[33] Thus, a new series of liquid-crystalline polymers with a polymer backbone of limonene-co-methyl methacrylate were prepared. The synthesized polymer was semicrystalline but formed a liquid-crystalline phase at temperatures above its glass transition temperatures and exhibited optical activity.[33]

2.4. Conclusion

In summary, due to their abundance in nature and desirable properties, there has been great interest in utilizing terpenes for producing polymers that could substitute, at least partially, for the fossil-based materials which are on the market today. Different synthetic approaches including a large variety of polymerization techniques could be efficiently used to exploit large-scale utilization of terpenes. Nevertheless,

aside from all of the achievement and improvement made in the synthesis of terpene-based polymers, there are still challenges in this field to open new discoveries and developments.

3

Efficient Approaches for Monomer Syntheses and Polymerization

An intense focus in developing innovative science and technology to significantly reduce our dependence on fossil fuel and decrease carbon emissions, due to the deficiency of fossil fuel and global warming, has gained attention from scientist, academia, and industry. This focus has directed researcher to substitute the existing fossil based feedstock and to develop more efficient and sustainable methodologies based on renewable resources. With regard to highly efficient reaction procedures, in 2001, Sharpless and co-workers introduced the concept of "click chemistry" to define a set of nearly perfect or ideal reactions.[9] To be considered as a "click" reaction certain strict criteria are required, such as simplicity, high reactivity, and broad variety of available reagents applicable in wide scope of reactions. Thus, thiol-ene reactions can be considered as click reaction since this reaction fulfills most of the click-criteria under certain conditions, e.g. being highly efficient, simple to execute, and proceeding rapidly to high yield.[10]

Another efficient strategy to achieve highly efficient reactions can be implemented by employing catalytic methods. Especially, transition metal catalyzed reactions gained

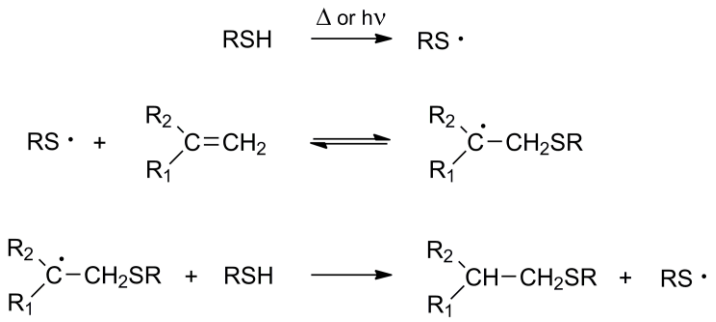
an increased attention in the recent past. Evidently, because of their influential contributions to this field, three Nobel Prizes in Chemistry for metal catalyzed procedures have been shared among nine individuals in 2001, 2005, and 2010. Although the impact of metal-based catalysts on synthetic organic chemistry cannot be understated, in certain cases, this type of catalysis can be expensive, toxic and/or sensitive to air and moisture.[72] Thus, organo-catalysts can be seen as valuable alternative for catalysis in organic synthesis. Organocatalysts might also offer environmental benefits by reducing the risk of reactions and creating unwanted waste products that may be harmful to the environment. Moreover, organocatalysts are usually cheap, easy to prepare, and insensitive to oxygen and moisture, so that there is no need for special reaction set ups, storage containers, experimental techniques or for ultra-dry reagents and solvents.[72]

The following sections will discuss about the application of the thiol-ene reaction and one organic catalyst, TBD, as efficient approaches for the synthesis of diverse monomers and polymers.

3.1. Thiol-ene Reaction

Thiol-ene reactions were already subject of intensive research more than 100 years ago[73] and have been studied throughout the years. These reactions proceed *via* a free radical chain mechanism and mainly lead to the anti-Markovnikov products.[74] First, the initially formed thiyl radical attacks the unsaturated substrate forming a carbon radical. Subsequently, the carbon radical reacts with a thiol molecule to give the final product and a new thiyl radical, thus propagating the radical chain (Scheme 3.1). Since this involves the cleavage of an S-H bond, the overall reaction rate will be strongly influenced by the structure of the thiol as well as the lifetime of the

intermediate carbon radical. Moreover, Walling and Helmreich reported that the C-S bond formation is a reversible process, which depends on the structure of the olefin.[75] This author also compared the relative reactivities of olefins towards dodecanethiol, and concluded that: the reactivity is increased when the radical is stabilized by resonance. If electron donating groups are linked to the olefin, the reactivity is also increased, cyclohexene is less reactive than cyclopentene, and terminal double bonds are generally more reactive than internal ones.



Scheme 3.1. Mechanism of radical thiol-ene additions.

With regard to the extremely-detailed kinetics and applications of thiol-ene chemistry in material science, an excellent review of thiol-ene chemistry was published in 2004 by Hoyle and co-workers.[76] It was reported that the overall kinetics of thiol-ene reactions depend on the olefin and thiol structures. Electron density of the olefins and the extent of substitution or location of the double bond in the alkene structures affected the reactivity of thiol-ene reactions. Concerning the electron density on olefins, this author compared the reactivities of the olefins against thiol-ene literature and their laboratory results by means of structure and the reactivity order. The results showed that in most cases, with an increasing electron density of the carbon–carbon double bond, the ene reactivity is increasing, leading to the following order: Norbornene > Vinyl ether > Propenyl > Alkene ≈ Vinyl ester > *N*-Vinyl amides > Allyl

ether ~ Allyltriazine ~ Allylisocyanurate > Acrylate > Unsaturated ester > *N*-substituted maleimide > Acrylonitrile ~ Methacrylate > Styrene > Conjugated dienes.[76]

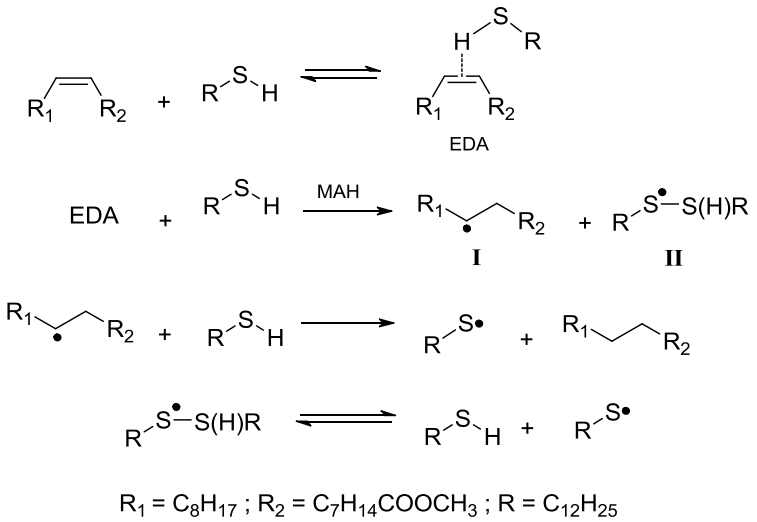
Moreover, the reactivity of the ene in a thiol-ene free radical chain reaction is also dependent on the location of the double bond. Model studies performed by Hoyle and co-workers have shown that highly substituted alkenes are less reactive than the non substitute ones.[76] For example, monofunctional thiol addition to 1-hexene was 8 times faster than to trans-2-hexene and 18 times faster than to trans-3-hexene.

Other kinetic studies reported about the influence of thiol structures with regard to the reactivity of thiol-ene reactions. Three types of multifunctional thiols, e.g. alkyl thiols, thiol glycolate esters, and thiol propionate esters, have been employed as thiol substrates in thiol-ene reactions. It has been reported that, because of a weakening of the sulfur-hydrogen bond by hydrogen bonding of the thiol hydrogen groups with the ester carbonyl, thiols based on propionate esters and glycolate esters result in higher reaction rates compared to alkyl thiols.[76] Thus, rates of addition almost 6 times greater have been found for the free-radical addition of methyl mercaptopropionate to 1-heptene than for 1-pentanethiol to 1-heptene (Scheme 3.2).

Scheme 3.2. Addition of methyl mercaptopropionate or 1-pentanethiol to 1-heptene.[76]

Thiol-ene additions can be performed under mild reaction conditions by simply mixing thiols and olefinic substrates without any radical initiator, if reactive olefins

i.e. terminal double bonds, are used. In this case, the reaction proceeds *via* self-initiation. Extensive investigations about the reaction mechanism of the self-initiated thiol-ene reaction was recently reported by Metzger *et. al*, who performed a kinetic study of the *cis-trans* isomerization of methyl oleate in the presence of dodecanethiol.[77] The initiation was found to be a complex reaction (Scheme 3.3) involving the formation of an electron-donor/-acceptor (EDA) complex formed by dodecanthiol and *cis*-methyl oleate in a pre-equilibrium step. The complex then reacts with another thiol to give a stearyl (**I**) and a sulfuranyl (**II**) radical through molecule-assisted homolysis (MAH) of the sulfur–hydrogen bond that subsequently dissociates to the thiyl radical catalyzing the *cis-trans* isomerization. Thus, the results clearly revealed that the thermal generation of thiyl radicals without any initiator is responsible for many well-known thermally initiated thiol-ene addition reactions and their respective polymerizations, as well as the low shelf-life stability of alkene and thiol mixtures.[77]



Scheme 3.3. Radical chain mechanism of the thermal isomerization of *cis*-methyl oleate catalyzed by dodecanethiol.[77]

On the other hand, for less reactive olefins, the thiol-ene addition can be thermally initiated by radical initiators, such as peroxides, azo compounds, etc. or by radical photo-initiators in presence of UV light irradiation. A recent study about the influence of type of initiator on thiol-ene reactions was reported by Yagci and co-workers.[78] Cleavage (Type I) and H-abstraction (Type II) type initiators, and the classical thermal radical initiation were used to investigate thiol-ene reactions between several ene groups such as allyl bromide, methyl acrylate, and methyl methacrylate with thiol end-functional polystyrene. The result clearly revealed that comparing to the thermal initiators and Type II photoinitiators, cleavage Type I photoinitiators such as (2,4,6-trimethylbenzoyl)diphenylphosphine oxide or 2,2-dimethoxy-2-phenyl acetophenone (DMPA) were found to induce thiol-ene reactions in higher efficiency.[78]

Generally, thiol-ene reactions have been extensively studied and several reviews were published; for example in 1970, Griesbaum reported reversibility, reaction rate, and reactant structure-reactivity in detail,[74] all aspect i.e. kinetics and applications of thiol-ene photopolymerization for material sciences was reviewed by Hoyle *et al*.,[76] the impact of thiol-ene chemistry on polymer and materials science was reported by Hawker *et al*.,[79] Hoyle and Bowman reviewed the radical-mediated thiol-ene reaction as click reaction,[10] and the latest, being in 2013, Türünç and Meier have published an overview on the development of thiol-ene (click) reaction for the syntheses of plant oils derived polymers.[80] Concerning thiol-ene reactions on plant oils and thereof derived products, these reactions have already been shown to be a unique tool for diverse transformation. For example, Boutevin *et al.* prepared mercaptoalcohols *via* the addition of mercaptoethyl ether to 10-undecen-1-ol for telechelics syntheses;[81] Galià *et al.* added mercaptopropionic acid to oleic and erucic acids to synthesize polyanhydride precursors;[82] Bromberg *et al*. synthesized ligands for silver and cobalt

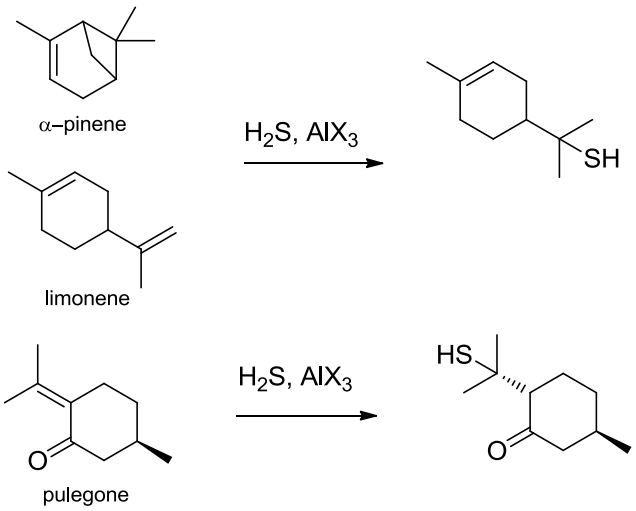
nanoparticles *via* thiol-ene reactions on oleic acid;[83] Cádiz and Cramail e*t al.* prepared polyols *via* the addition of mercaptoethanol to oleic and erucic acids for polyurethane synthesis;[84,85] Bantchev *et al.* modified corn and canola oils with 1-butanethiol for lubricants;[86] and Heise *et al.* coupled different thiol compounds to an unsaturated polyester.[87] Moreover, 10-undecenoic acid, a castor oil derivative, was widely utilized to prepare bio-based building blocks.[88,89]

The thiol-ene reaction is also a very versatile tool for the polymerization of α,ω-diene monomers bearing, for example, ester,[90,91] ether,[92] anhydride,[153] and amide[93] functional groups. Very recently, Du Prez *et al*. reported the synthesis of polythioethers with molar masses up to 40 kDa *via* UV- or thermal initiated thiol-ene polyaddition polymerization from an aliphatic α-olefinic ω-thiol, an AB-type monomer derived from 10-undecenoic acid.[94] Interestingly, an increased thermal stability and higher melting temperature were observed if the polysulfides were oxidized into polysulfones. Moreover, thiol-ene reactions were exploited for the preparation of dendrimers,[95] star-shaped polymers,[96] and shape memory polymers for medical applications.[97] Other publications on thiol-ene reactions described on the modification and functionalization of existing (polymer) structures and the design of new molecular architectures. Kolb and Meier recently modified the double bonds of poly(malonate)s for grafting onto reactions by either ruthenium-catalyzed cross-metathesis reactions with acrylates or thiol–ene addition reactions.[98]

Thiol-ene chemistry is also widely applied for medical applications,[97] dental application,[99,100] degradable polymeric structures for liquid crystalline compositions for optical applications,[101] biomedical application,[102] the preparation of low gas permeability membranes,[103] sealants,[104] stamps for lithography,[105] and polymer electrolytes for e.g. batteries.[106]

As already mentioned in **Chapter 2**, the presence of double bonds in monoterpenes (i.e. limonene and pinenes) can also undergo thiol-ene reactions. However, only very few examples have been reported on thiol-ene reactions involving these monoterpenes. This following paragraph intends to provide an overview on thiol-ene reactions of terpenes.

The earliest report involving limonene in a thiol-ene reaction dates back to 1905, when Posner reported the additions of mercaptans to limonene and 1,4-cyclopentadiene selectively resulting in only monoaddition products.[73] Later on, in 1957, Marvel and Olson prepared a dithiol by addition of thioacetic acid to (*R*)-(+)-limonene, which was subsequently polymerized with the initial (*R*)-(+)-limonene.[107] However, structure and thermal characterizations of the resulting polyalkylene sulfides, as well as their molecular weights were not reported. Tolstikov *et al*. reported the addition of hydrogen sulfide to limonene[108] and pinenes[109] catalyzed by Lewis acids. Likewise, Janes *et al.* prepared terpene-based thiols by reacting hydrogen sulfide with limonene, α-pinene, α- and γ-terpinene, terpinolene, 3-carene and pulegone in the presence of aluminium trichloride or tribromide leading to a mixture of thiols and sometimes additionally bridges *epi*-sulphides.[110] The main product from the reaction of limonene or α-pinene with hydrogen sulfide (Scheme 3.4) was *p*-menth-1-en-8-thiol, characteristic for the grapefruit flavor. Whereas, the main product from pulegone was 8-mercapto-trans-*p*-menth-3-one, an important component of Buchu leaf oil. Based on this short literature survey, the derivatization of terpenes *via* thiol-ene reaction is still limited.

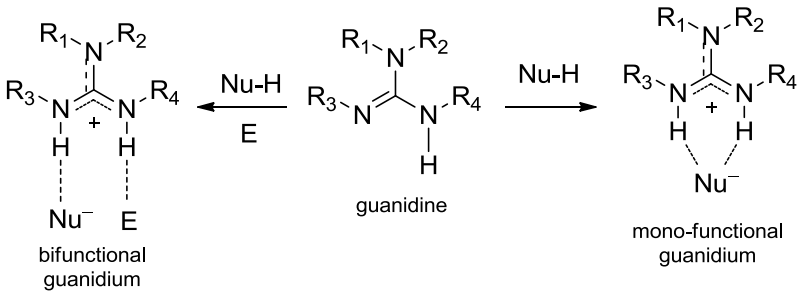


Scheme 3.4. Reaction of limonene, α-pinene, and pulegone with hydrogen sulfide.[110]

3.2. TBD as Efficient and Potent Organocatalyst

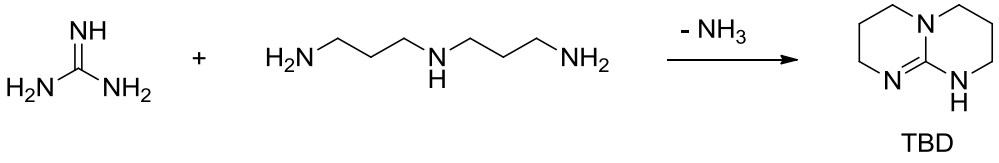
Historically, catalysis in synthetic organic chemistry has been dominated by transition metal catalysts.[111] Although the use of small organic molecules to catalyze organic transformations has already been known for more than a century, only in the past decade, organocatalysis has grown explosively to become one of the most exciting research areas in current synthetic organic chemistry.[112] Basically, there are four types of organocatalysts (i.e. Lewis bases, Lewis acids, Brønsted bases, and Brønsted acids).[113] These catalysts initiate their catalytic cycles by either providing or removing protons or electrons from a substrate or a transition state. Lewis base catalysts, such as amines and carbenes, are the most common catalyst exploited in organocatalysis, while Lewis acids such as carbonyl compounds are less frequently used.[113] Among of the most straightforward available Lewis base catalyst, guanidine type catalysts have recently drawn much attention.[6,114] The special interest in guanidine based catalysts arise from their activity as strong neutral organic base. Guanidines generally initiate a reaction by abstracting an acidic proton to form its conjugated acid, the guanidinium, which then participates in the reaction by utilizing

ion-pair interaction and/or hydrogen bonding to accelerate the reaction rate and/or provide chiral induction (Scheme 3.5).[115] Two possible modes of interactions could be possible. The guanidinium can activate only the nucleophile or both the electrophile and nucleophile in a bifunctional mode. In addition to their usual role as general base catalysts, guanidines have been found to act as nucleophilic catalyst.[114,115]



Scheme 3.5. Ion-pair interaction and hydrogen bonding of guanidinium.[115]

One of the family members of bicyclic guanidines and a widely used organocatalyst is TBD. Driven by an interest in the utilization of TBD for many applications, Usachev and Gridnev recently developed a convenient way to synthesize TBD.[7] Guanidine, cyanamide, or their derivatives were heated with *bis*-(3-aminopropyl)amine and a strong acid at 140–180 °C for 7–9 h to form TBD in 95–97% yield (Scheme 3.6). This synthetic route represents a very convenient method to replace the previously reported procedures,[116,117] avoiding the use of expensive and toxic starting materials, as well as the generation of toxic intermediates.

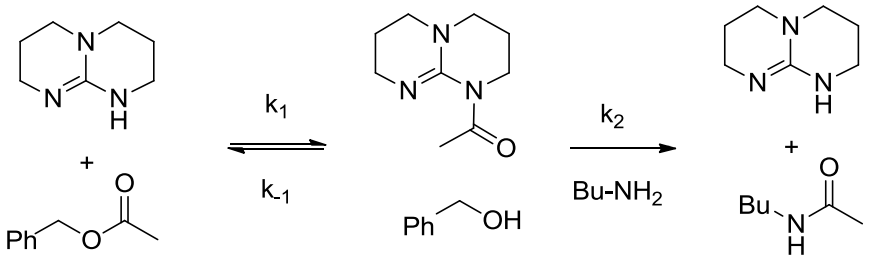


Scheme 3.6. New synthesis strategy of TBD.[7]

In addition to being cheap, TBD represents an effective organocatalyst, most widely used in many chemical transformations. Tan *et al.* used TBD as catalyst for Michael

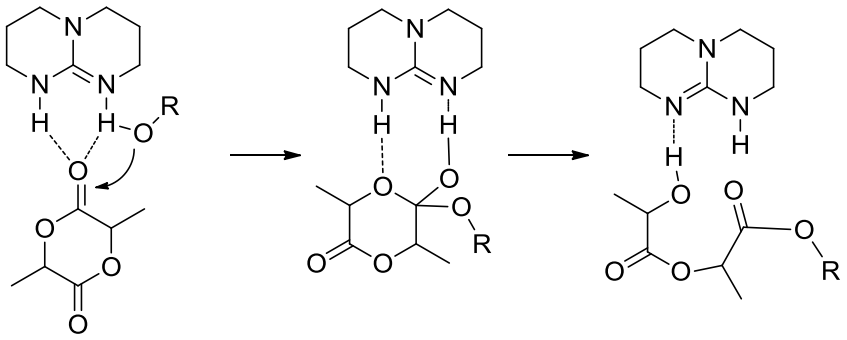
reactions of malonates to α,β-unsaturated ketenes, nitriles, and nitro groups.[118] Baati and co-workers demonstrated that TBD is an efficient organocatalyst for the direct intramolecular aldol reaction of ketoaldehydes, forming cyclic aldol products in reasonable yields with modest levels of diastereoselectivity.[119] It has been reported that TBD easily catalyzed the synthesis of biologically important 3,5-diarylpyrazolines from chalcones and acylhydrazines *via* a selective secondary amine alkylation.[120] Waymouth *et al*. have shown that TBD catalyzed the formation of secondary amides from vinyl, benzyl and ethyl esters, as well as primary amides.[121] In addition, this authors have also reported that TBD is an efficient catalyst for transesterifications and the ring-opening polymerization (ROP) of cyclic esters such as lactide, δ-valerolactone, and ε-caprolactone.[121]

Concerning the reaction mechanism, Waymouth *et al*. also performed mechanistic and kinetic investigations of TBD as transacylation catalyst, mediating both the formation of amides from esters and the transesterification of esters. The results revealed that TBD can act both as a nucleophile for transacylation reactions and as a bifunctional general base/H-bond donor. As a model for amidation reactions, benzyl acetate was reacted with 4 equiv. of *n*-butylamine employing 10 mol % of TBD in a toluene solution at 25 °C affording *n*-butylacetamide in quantitative yields after only 6 minutes. Mechanistic and kinetic investigations revealed a nucleophilic mechanism including a reversible reaction of TBD with the ester to generate a “twisted amide” acyl-TBD intermediate that acylates amines to generate the amides (Scheme 3.7).[121]



Scheme 3.7. Proposed mechanism of TBD-catalyzed synthesis of n-butylacetamide from benzyl acetate and butylamine.[121]

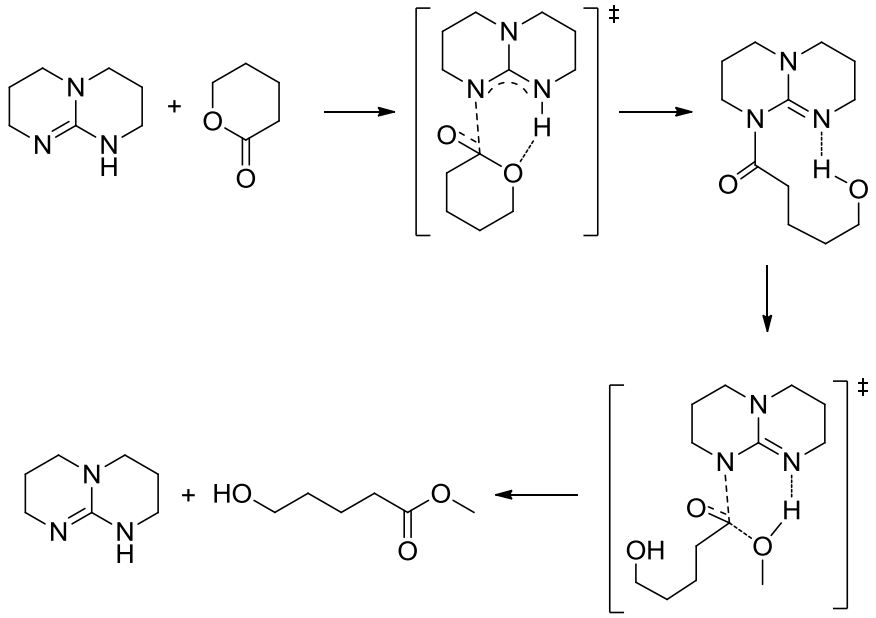
In case of transesterification reactions, detailed mechanistic and computational studies predicted that a nucleophilic mechanism was feasible, but had a considerably higher barrier than a mechanism *via* hydrogen bonding. Thus, a hydrogen-bonding mechanism is favored over nucleophilic catalysis. Through hydrogen bonding, TBD activates the carbonyl group of the *L*-lactide. The imine nitrogen simultaneously activates the alcohol by attracting the hydrogen of its hydroxyl group through a lone pair interaction, which then generates a guanidinium species that stabilizes the tetrahedral intermediate (Scheme 3.8).[121,122]



Scheme 3.8. Proposed mechanism for TBD-catalysis of the ROP of *L*-lactide (Hydrogen bonding mechanism).[121,122]

Beside TBD-catalyzed transesterification in ROP (based on entirely hydrogen bonding), a bifunctional nucleophilic mechanism was suggested as another mechanistic possibility (Scheme 3.9).[122] Nucleophilic attack of the TBD nitrogen at the carbonyl would generate the formation of a 6-membered transition between the TBD

nitrogen atoms and the ester function, resulting in the weakening of the ester bond, and consequently the insertion of another alcohol giving the transesterification product.



Scheme 3.9. Proposed mechanism for TBD-catalyzed in ROP of lactone (nucleophilic mechanism).[122]

Additionally, the sustainable aspects of TBD-promoted chemistry have been explored. The use of carbon dioxide as a feedstock to produce material is attracting considerable attention because CO_2 is known as one of the sources of global warming. Thus, Costa and co-workers demonstrated that TBD catalyses the reaction of acetylinic amines with CO_2 to yield 5-methylene-oxazolidin-2-ones.[123] Later on, Sun and co-workers reported the synthesis of propylene carbonate from propylene glycol and carbon dioxide in the presence of TBD.[124]

Moreover, sustainable methods involving TBD as catalyst were subject of numerous recent publications. For example, Saliu and Rindone reported the synthesis of 1,3-disubstituted symmetrical and unsymmetrical ureas from ethylene carbonate and the corresponding amines in good to excellent yields using TBD as catalyst under solvent-

less conditions.[125] Meier and co-workers reported about an eco-friendly method to synthesize unsymmetric and symmetric carbonates, as well as polycarbonates.[126] Under solvent-free conditions, direct condensation of an alcohol and dimethyl carbonate at 80 °C in the presence of TBD was performed to give carbonates with up to 98% yield. Both of these methods can be used as a valuable alternative to replace conventional procedures employing toxic phosgene. Another recent report has shown that TBD can be utilized for the synthesis of carbamates and amines *via* a catalytically performed Lossen rearrangement.[127]

In polymer chemistry, TBD was utilized as an excellent catalyst for polycondensation reactions thus leading to castor oil-based polyesters[88] and polyamides,[128] bio-based dihidroxyl-terminated aliphatic polyesters,[129] bio-based segmented polyureas,[130] and renewable polycarbonates.[126] Last but not least, the attachment of TBD onto a polymer support revealed high activity and possible reusability of the TBD based catalyst. During the past decade, polymer-supported catalysts have attracted much attention because of their inherent benefits in synthetic chemistry, for example, simplification of reaction procedures including easy recovery of the catalyst by filtration, application to automated systems, and recycling of the employed catalyst.[131] Styrene-based resins are the most widely used supports due to their easy availability and high loading capacity.[132] To only present a few recent examples, polystyrene-supported TBD has reported as an effective catalyst for cyanosilylation of aldehydes, ketones, and imines.[132] It was demonstrated that this catalyst could be easily recovered and reused without losing the catalytic activity after 5 runs. Matsukawa *et al.* reported ring-opening of *N*-tosylaziridines with silylated nucleophiles in the presence of polystyrene-supported TBD catalyst. Supported catalysts for Huisgen's cycloaddition have been prepared by immobilization of copper

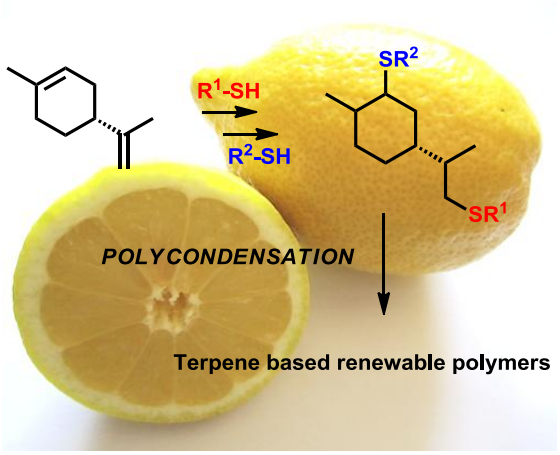
species on commercially available polymeric matrixes incorporating a TBD template.[133]

3.3. Conclusion

The use of thiol-ene reactions as non-catalytic carbon–heteroatom bond forming method can be considered as an efficient tool for the synthesis of fine chemicals and monomers, as well as for the synthesis and modification of polymers derived either from natural or fossil-based sources. Moreover, along the abovementioned benefits over common (transition)-metal catalysts, the ease of handling and mildness of reaction conditions, as well as the potential to perform reactions in a very economically and ecologically way certainly make TBD a convenient and highly interesting catalyst for many transformations (i.e. the synthesis of fine chemicals and the polymerizations of diverse monomers, either *via* polycondensation or ring-opening polymerization).

4

Terpene Based Renewable Monomers and Polymers *via* Thiol-Ene Additions[134]



4.1. Introduction

The utilization of renewable resources for the synthesis of new platform chemicals has been accepted as a great challenge in order to contribute to a sustainable development.[135,136] Among the wide variety of available renewable resources, terpenes are found in many essential oils and represent a versatile chemical feedstock.[16] α- and β-Pinene are the major components of wood turpentine, which

can be obtained from the resinous sap of pine trees by steam-distillation. It is also one of the main by-products of the Kraft process, which is used in the paper industry to extract lignin from wood in the production of pulp.[137] Limonene can be obtained as a by-product of the citrus industry and is a very common terpene, being produced by more than 300 plants.[138] The (*R*)-enantiomer represents 90-96% of citrus peel oil,[18] and its world production is over 70,000 tonnes per year.[139] In contrast to many other terpenes, pinenes and limonenes are abundant and inexpensive natural compounds that are real building blocks for the synthesis of new important chemicals for use as fragrances, flavors, pharmaceuticals, solvents, and chiral intermediates.[16,21]

Known chemical transformations of these renewables were extensively reviewed by Corma *et al*.,[16] including isomerization, epoxidation, hydration, or dehydrogenation reactions among others. The isomerization of terpenes provides a wide range of products such as camphene, which is produced industrially by isomerization of α-pinene and is used as an intermediate in the chemical industry for production of fragrance compounds, terpene-phenol resins, and other derivatives. The hydration of α-pinene or turpentine oil with aqueous mineral acids yields *cis*-terpin hydrate, which can be partially dehydrated into α-terpineol, the most important monocyclic monoterpenic alcohol and the one most used as a fragrance in soaps and cosmetics due to its typical lilac odor. The selective epoxidation of limonene leads to limonene oxide, which is found in natural sources and used in fragrances. It is also an active cycloaliphatic epoxide with low viscosity that can be used with other epoxides in applications including metal coatings, varnishes, and printing inks.

Thiol-ene chemistry, although already known for more than 100 years,[73] has not been studied in detail using terpenes as olefinic substrates. The mechanism and features of this reaction were briefly discussed in **Chapter 3.1**. Nowadays, thiol-ene additions

are widely used as very efficient transformations since in many cases they display click reaction features,[9] and are thus versatile tools for the preparation of value added chemical intermediates.[76,95] Even though thiol-ene reactions have been studied for a long time, covering different scientific fields from biochemistry to polymer science, only very few examples have been reported on thiol-ene additions with terpenes as olefinic substrates. As already discussed in **Chapter 3.1**, the knowledge about the reactivity of terpenes towards thiol additions is still limited. However, the high efficiency of thiol-ene additions, which permits the introduction of different functionalities to olefinic structures, makes it a suitable way to obtain terpene based monomers for the synthesis of renewable polymers.

Within this chapter, the aim is to extend the current knowledge on the reactivity of naturally occurring terpenes towards thiol additions and to establish the reaction conditions that maximize their efficiency. Furthermore, thiol-ene terpene modification as a suitable tool to obtain renewable monomers for the synthesis of polyesters is also described.

4.2. Results and Discussion

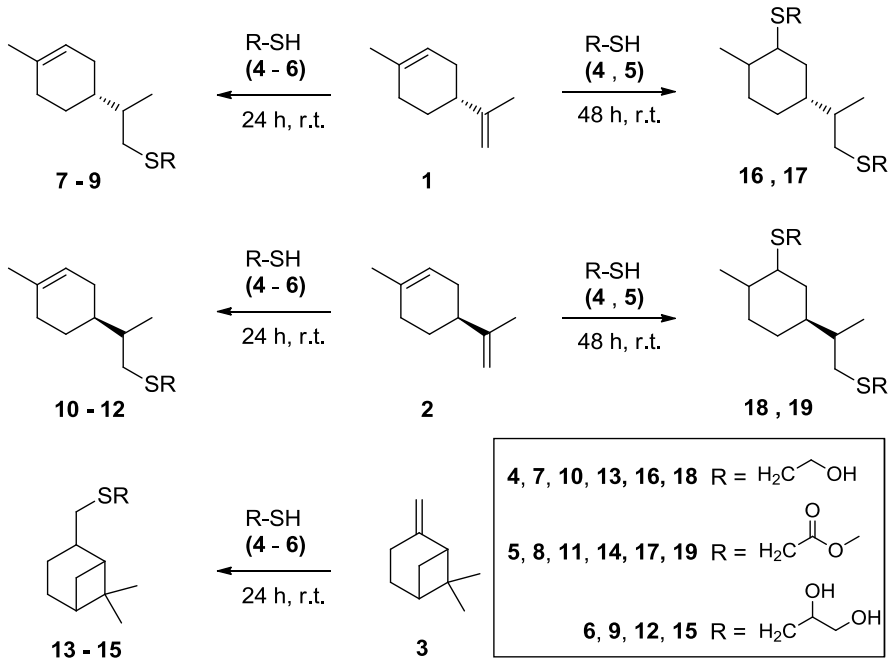
4.2.1. Syntheses of monomers

As discussed above, despite the large amount of work that has been done on the chemical transformation of terpenes for the synthesis of industrially valuable chemicals, building-blocks, or monomers for polymer synthesis, the thiol-ene reaction using limonene and pinene as olefinic substrates has not been fully explored yet, and only a few studies have been reported. The reaction of these abundantly available terpenes with functional thiols is attractive since it can provide chiral monomers in a one-step procedure directly from a renewable feedstock. More specifically, the

extensive reaction of both double bonds of limonene with hydroxyl or methyl ester functionalized thiols would lead to suitable monomers for polycondensation. On the other hand, the reaction of pinene with these functional thiols would lead to terpene-based building blocks that could be used for the synthesis of grafted polymers following a grafting-onto approach or for the synthesis of monomers of higher complexity. Furthermore, the different reactivity of the double bonds of limonene towards thiol additions can be exploited to selectively functionalize the more reactive exocyclic (terminal) double bond, leaving the endocyclic (internal) one unreacted for further transformations. It is worth to highlight the simplicity of these reactions, which can usually be performed by simply mixing thiol and olefin in absence of solvent and radical initiator, and at temperatures close to room temperature.[88]

Taking this information, we started by studying the solvent-free, radical initiator-free thiol-ene addition of 2-mercaptoethanol (**4**), methyl thioglycolate (**5**), and thioglycerol (**6**), to (*R*)-(+)-limonene (**1**), (*S*)-(−)-limonene (**2**), and (−)-β-pinene (**3**) at room temperature (Scheme 4.1). During the course of our investigations, we found that **5** shows a higher reactivity than **4** and **6**. For this reason, in the following discussion, the results of the thiol-ene additions using **5** will be addressed separately since a more thorough optimization of the reaction conditions was needed. The high reactivity of thiols based on glycolate esters has been already observed, and it has been ascribed to a weakening of the thiol bond by formation of a hydrogen bond with the carbonyl group.[76] With the exception of additions of **5**, the rest of the reactions were performed under vacuum (200 mbar) in order to remove oxygen,[88] which is an efficient radical scavenger in these reactions. First, the thiol-terpene ratio was optimized to maximize the efficiency of the monoaddition reactions. Initially, a 1:1 ratio was used for the addition of **4** and **6** to **1**, **2** and **3**. However, the conversion of

the double bonds was rather low (below 50%), even after 48 h. When the amount of thiol was increased to 1.2 equiv., the double bond conversions also increased, and 60 to 80 % isolated yields of monoaddition products were obtained after column chromatography (see Table 4.1). Interestingly, the addition of **4** and **6** to **1** and **2** took place exclusively at the exocyclic double bond and no diaddition products were observed. On the other hand, the addition of **5** to **1** and **2** showed a lower selectivity, giving additions both to the exocyclic and endocyclic double bonds when working in a 1:1 ratio. Moreover, low double bond conversions were obtained even after 24 h (below 75 %). Also for the addition of **5**, the use of a thiol excess (1.2 mol equiv.) provided better results, leading to yields ranging from 52 to 85% after column chromatography (Table 4.1), but also to a decrease in the regioselectivity (from 74 to 55%). A thiol-terpene ratio of 0.9:1 was then tried in order to favor monoaddition; although it gave a slight increase of regioselectivity (77 %), the isolated yield dropped ~10%. An increase of the temperature to 35 °C gave only a very slight increase in conversions (below 5% increase), and at the same time generally led to a drop of regioselectivity. All thiol-ene additions were also performed in the presence of AIBN at 70 °C. Adding a radical initiator resulted in faster conversion of the terpenes, however, it also resulted in lower regioselectivities and the conversion rates decreased at reaction times above 5 hours, which is about the half life time of AIBN. As a summary, Table 4.1 shows the results obtained after optimization of the reaction conditions for the thiol-ene monoadditions and clearly reveals that the exocyclic double bond of limonene can be addressed regioselectively in these radical additions.



Scheme 4.1. Mono- and diadditions of thiols **4**–**6** to terpenes **1**–**3.**

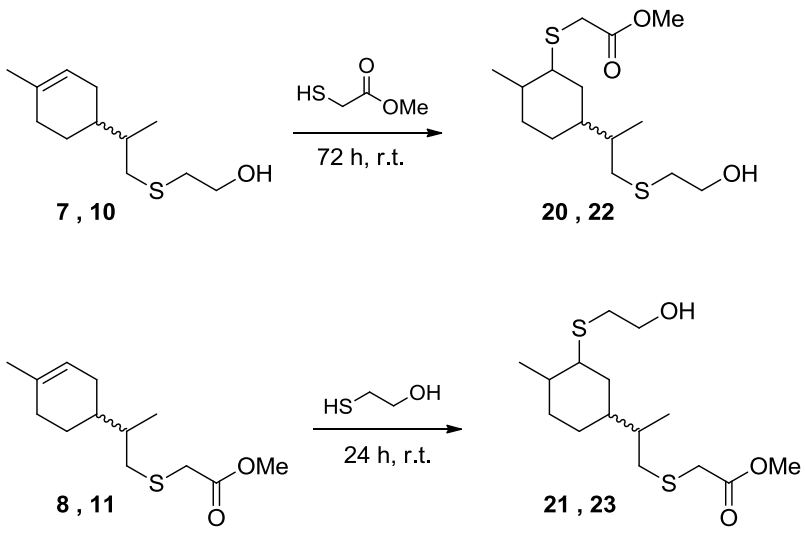
Table 4.1. Results of monoaddition of thiols **4** – **6** to terpenes **1** – **3**[a].

Terpene	Thiol	Product	Yield (%)[b]
1	**4**	**7**	85
1	**5**	**8**	55
1	**6**	**9**	80
2	**4**	**10**	82
2	**5**	**11**	52
2	**6**	**12**	61
3	**4**	**13**	81
3	**5**	**14**	60
3	**6**	**15**	76

[a] Reaction conditions: terpene:thiol ratio 1:1.2, r.t. for 24 h. [b] after column chromatography.

Once the thiol-terpene monoadditions were optimized, we focused on the synthesis of the diaddition products of thiols **4**, **5**, and **6** to terpenes **1** and **2** (Scheme 4.1), for which a thiol-terpene ratio of 2.5:1 was used. The addition of **6** to both **1** and **2** did

not give the diaddition products, and only the monoadditions to the exocyclic double bonds were observed, probably due to steric hindrance around the endocyclic double bonds. The additions of **4** and **5** led to a mixture of mono- and diaddition products with conversions over 97% (Table 4.2). As already mentioned, the monoaddition products from (*R*)-(+)- and (*S*)-(−)-limonene can undergo a second thiol addition with a different thiol to obtain heterodifunctional monomers. Thus, the alcohol functionalized products **7** and **10** were reacted with methyl thioglycolate, and the ester functionalized products **8** and **11** were reacted with 2-mercaptoethanol (Scheme 4.2). The reactions were conducted at room temperature, in absence of solvent and radical initiator, and using 2-fold and 1.2-fold excesses of methyl thioglycolate and 2-mercaptoethanol, respectively. In this way, difunctional monomers containing both ester and alcohol groups (**20**-**23**, Table 4.2) were obtained.



Scheme 4.2. Addition of thiols **4** or **5** to monoaddition products.

Table 4.2. Results of diadditions of thiols **4** - **6** to terpenes **1** and **2**, and additions of **4** and **5** to monoaddition products.

Terpene	Thiol (eq)	Product	Yield (%)[d]
1	**4** (2.5) [a]	**7** + **16**	36 (**7**); 62 (**16)**
1	**5** (2.5) [a]	**8** + **17**	5 (**8**); 93 (**17**)
1	**6** (2.5) [a]	[e]	-
2	**4** (2.5) [a]	**10** + **18**	11 (**10**); 82 (**18**)
2	**5** (2.5) [a]	**11** + **19**	4 (**11**); 93 (**19**)
2	**6** (2.5) [a]	[e]	-
7	**5** (2.0) [b]	**20**	83
8	**4** (1.2) [c]	**21**	92
10	**5** (2.0) [b]	**22**	81
11	**4** (1.2) [c]	**23**	90

[a] r.t. for 48 h. [b] r.t. for 72 h. [c] r.t. for 24 h. [d] after column chromatography. [e] only the monoaddition product was obtained.

4.2.2. Characterization of monomers

The terpenes used in this study are pure enantiomers. The addition of one molecule of thiol to the exocyclic double bond of **1** or **2**, or to the double bond of **3** generates a new stereogenic center, and thus, two different diastereomers of each product. The addition of a second thiol molecule to the endocyclic double bond of **1** or **2**, generates two additional stereogenic centers, increasing the number of possible diastereomer to eight. However, the cyclic and bicyclic structures of these terpenes, together with the fact that they are pure enantiomers, favor the formation of certain diastereomers over others as a result of preferential sides for the thiol approach during the hydrogen abstraction process. Nevertheless, complex NMR spectra were obtained for all addition products and conventional two dimensional NMR experiments (COSY, HSQC, and HMBC) were necessary for full assignment.

The presence of diastereomers, which could not be isolated by column chromatography, was also observed in the GC-MS chromatograms of the purified monoaddition products to **1**, **2**, and **3**, where (although not always) two peaks can be observed. For instance, the chromatogram of **14** shows two peaks with different intensities (Figure 4.1), indicating that after the initial thiol addition the approach of a second thiol to the carbon-centered radical, and thus the hydrogen abstraction, takes place preferably from one side. The GC chromatograms of the purified diaddition products to **1** and **2** present several peaks of different intensities as a result of the partial diastereoselectivity in the hydrogen abstraction (see Figure 4.1 for chromatograms of **17** and **19**).

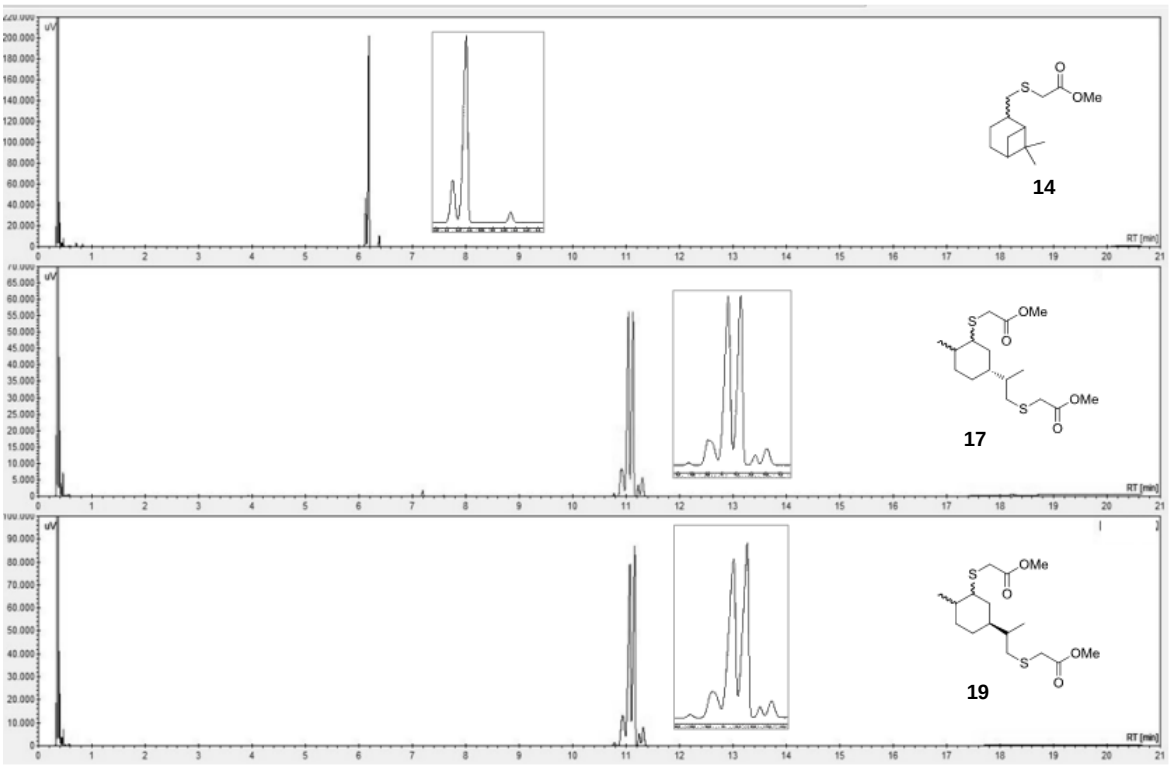


Figure 4.1. GC chromatograms of **14**, **17**, and **19**.

The analysis of the NMR spectra of these products further confirmed the presence of diastereomers. Moreover, in some cases, the integration of the ^{1}H NMR signals

allowed calculating the ratio of the diastereomers. For instance, Figure 4.2a shows the ^{1}H NMR spectrum of **7** (addition of 2-mercaptoethanol to *R*-(+)-limonene), in which the region of methyl groups bonded to the new stereogenic center is highlighted (for full assignment see experimental part). The methyl groups of both diastereomers appear as doublets of equal intensity, which merge in a false triplet, indicating a 1:1 ratio between both diastereomers. A different case can be observed in Figure 4.2b, which shows the ^{1}H NMR spectrum of **13** (addition of mercaptoethanol to (–)-β-pinene). As can be seen, the signals of the methyl groups attached to the bicyclic backbone present different chemical displacements in both diastereomers. The integration of these signals reveals a ratio of 5:1 between the diastereomers, which confirms that the hydrogen abstraction is stereoselective and controlled by the substrate.

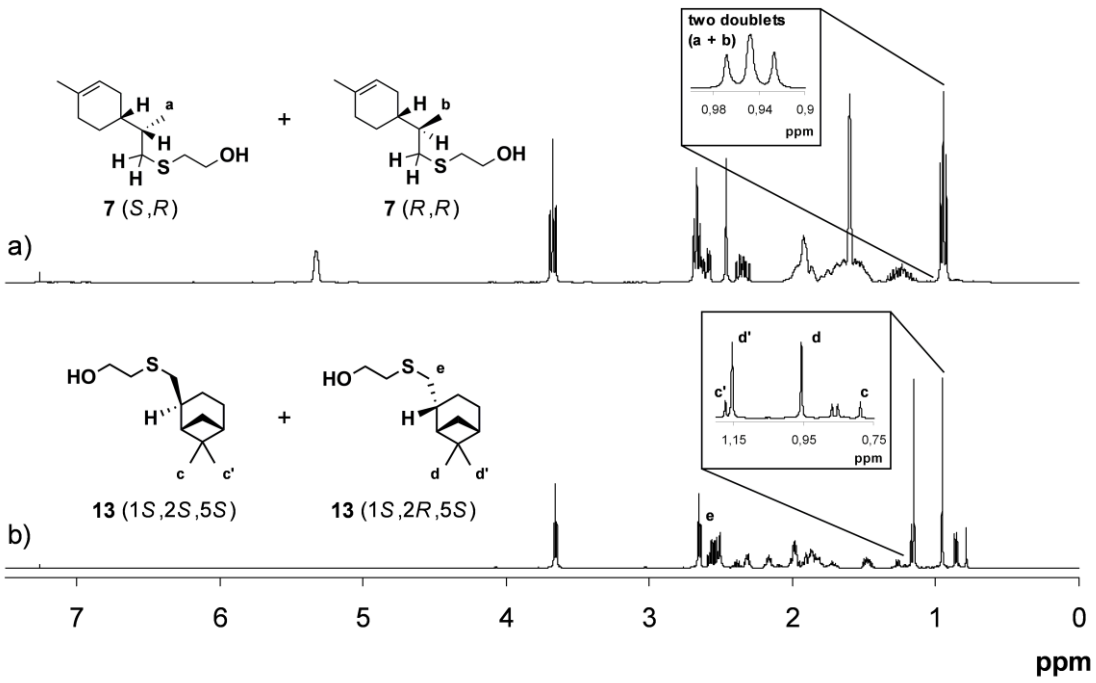


Figure 4.2. ^{1}H NMR spectra of a) **7** and b) **13**.

In order to determine which one of the two possible diastereomers is the major, we performed a NOE experiment (Figure 4.3), which showed correlation between the

protons H^e and H^d of the major diastereomer. This confirms that the approach of the second thiol, and thus the hydrogen abstraction, preferentially takes place from the opposite face to the methyl groups due to steric hindrance.

The ^{1}H NMR spectrum of **17** (diaddition of methyl thioglycolate to *R*-(+)-Limonene) shows a higher complexity due to the higher number of possible diastereomers (Figure 4.4). In this case, the analysis of the ^{13}C NMR is more helpful in order to determine the number of diastereomers present in the diaddition product, and to estimate their ratio. Figure 4.4b shows the region from 53 ppm to 51 ppm, in which four different signals are observed for C_a indicating that the product mainly consists of a mixture of four diastereomers.

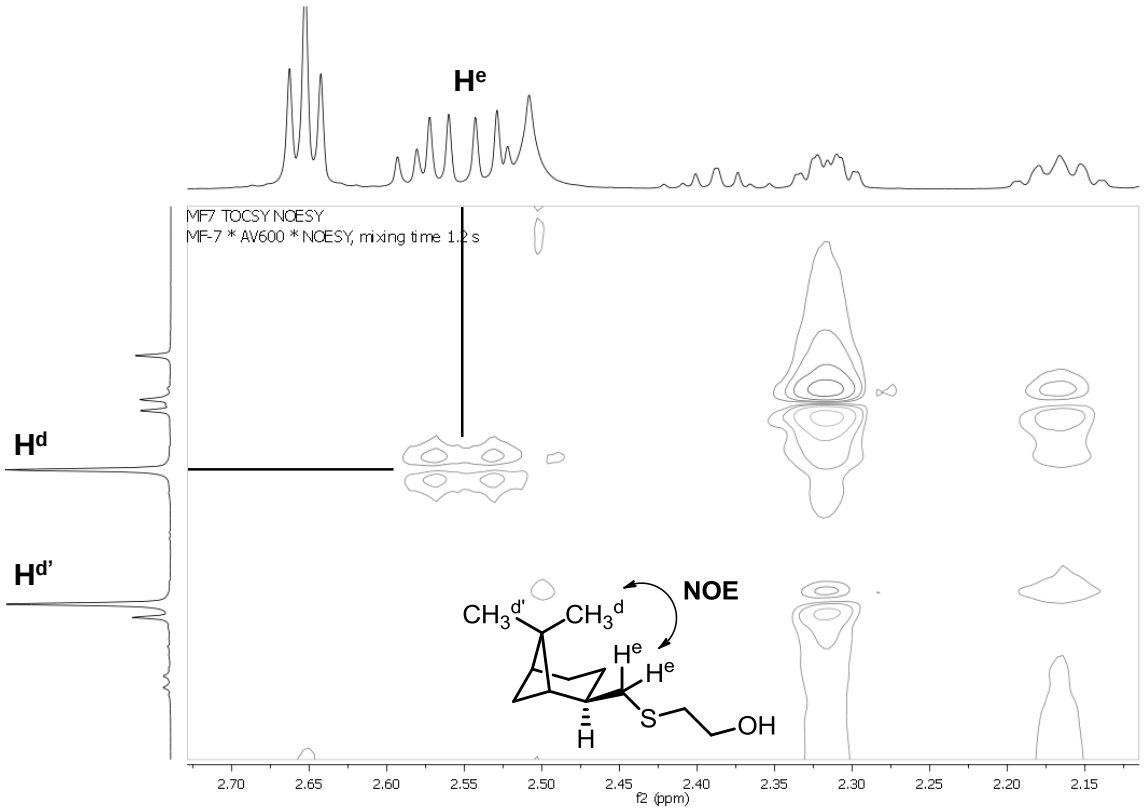


Figure 4.3. Ampliation of the NOE spectrum of **13**.

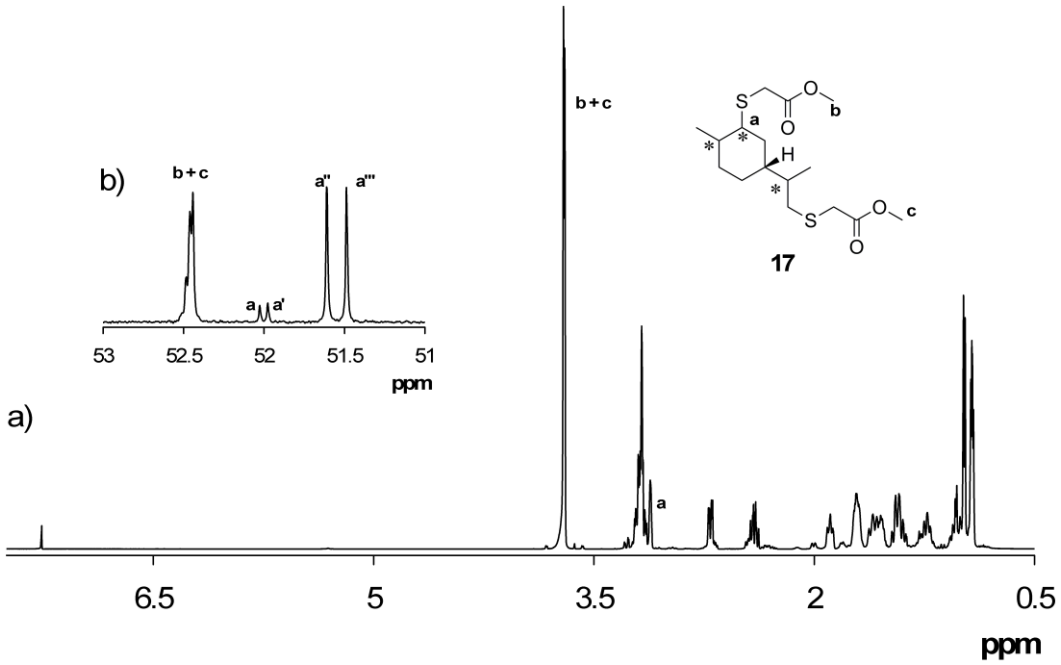
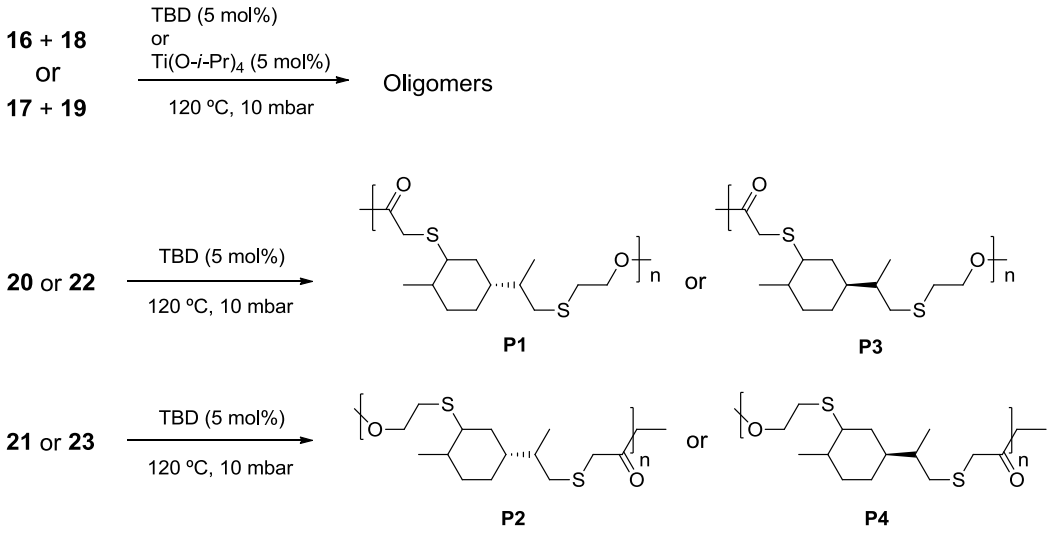


Figure 4.4. a) ^{1}H NMR and b) ^{13}C NMR (region 53-51 ppm) of **17**.

4.2.3. Polymerization studies

The difunctional monomers obtained by diaddition of 2-mercaptoethanol or methyl thioglycolate to (*R*)-(+)-limonene or (*S*)-(−)-limonene were subsequently used for polyester synthesis. The purity of these monomers was over 99.9% by GC analysis, ruling out the presence of monofunctional by-products that could act as chain-stoppers. TBD was chosen as polycondensation catalyst based on our own experience, and on previous reports on its high tranesterification activity.[140] The removal of methanol strongly determines the efficiency of TBD catalyzed transesterification and can be carried out applying a continuous stream of an inert gas such as nitrogen or constant vacuum in the case of polymerizations. Thus, we performed the polymerizations in presence of 5 mol% (related to ester groups) TBD at 100 and 120 °C under continuous vacuum for 7 h. Initially, diesters **17** and **19** were polymerized with diols **16** or **18** at 200 mbar for 7 h; however, only oligomers of 3 kDa were

obtained (Scheme 4.3), probably due to the bulky cyclic structures of both monomers, which could hinder the catalysts' approach and thus decreasing the polymerization efficiency. Moreover, longer reaction times did not lead to an increase of molecular weight. Titanium isopropoxide was also tried in an attempt to reach higher molecular weights. Titanium alkoxides are known to act as efficient trans-esterification catalysts and have been successfully used for polyester synthesis[141] being compatible with a variety of functional groups.[142] Moreover, titanates are recognized as extremely powerful for ester-exchange reactions.[143] However, using 5 mol% of titanium isopropoxide under continuous vacuum and 100 or 120 °C provided only slightly higher molecular weights (up to 4 kDa) after 7 h (longer reaction times did not lead to higher molecular weights). The polymerization of heterodifunctional monomers **20**-**23** was then attempted in presence of TBD (Scheme 4.3). Interestingly, despite having very similar structures to the above mentioned diesters and diols, the polycondensation of these monomers at 120 °C under continuous vacuum for 7 h led to homopolymers with higher molecular weights (M_n) between 8 and 10 kDa (see Table 4.3 for data of precipitated polymers). During polycondensations, little deviations from an ideal 1:1 ratio between monomers can substantially decrease molecular weights through a chain-stopper effect. Monomers **20**-**23**, which do not need comonomers, are thus more likely to reach high molecular weights. However, also here, the sterical hindrance caused by the terpene core might reduce the activity of the catalyst.



Scheme 4.3. Polymerization of difunctional monomers and homopolymerization of heterodifunctional monomers.

Table 4.3. Analytical data of synthesized limonene based polyesters.[a]

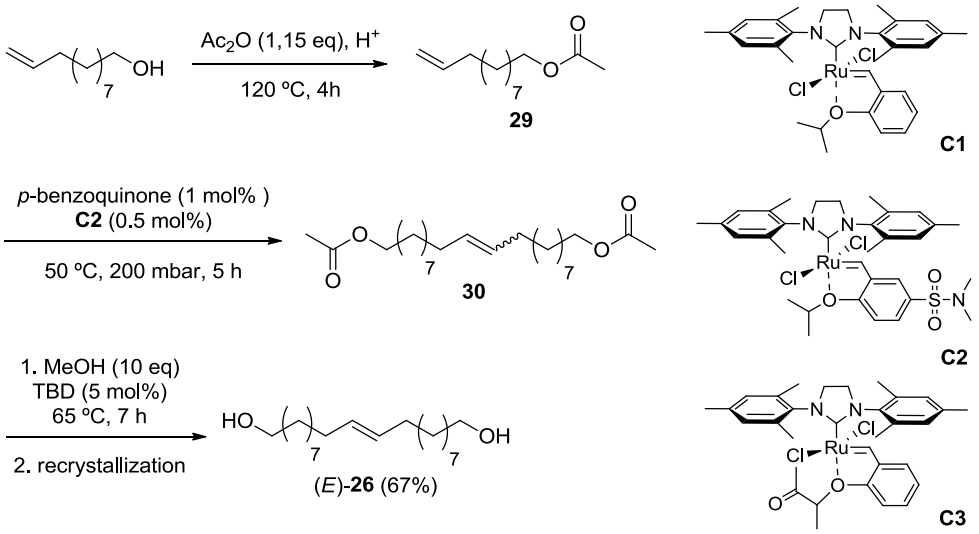
Polymer (monomer)	M_n (kDa)	PDI	T_g (°C)[b]
P1 (**20**)	9.3	1.79	-9.7
P2 (**21**)	7.7	1.66	-9.2
P3 (**22**)	10.5	1.89	-10.4
P4 (**23**)	8.2	1.65	-9.9

[a] GPC and DSC data of precipitated polymers, [b] DSC data recorded at 10 °C/min, results from the second heating scan.

From these results, it can be concluded that in order to obtain high molecular weight polyesters from limonene based diesters and diols, comonomers providing spacing between terpene units might be needed. First, diesters **17** and **19** were polymerized with 1,3-propanediol and 1,6-hexanediol in presence of 5 mol% of TBD. The polymerizations, which were also performed at 100 and 120 °C and 200 mbar vacuum, only yielded oligomers below 5 kDa. Moreover, substituting TBD by titanium isopropoxide (5 mol%) in the same reaction conditions provided only slightly higher molecular weights (up to 7 kDa) and broad polydispersities. All polymerizations were

run for 7 h since longer reaction times did not further increase the molecular weights. These results suggested that comonomers with longer alkyl chains between the reactive groups might be needed due to steric reasons. To prove this, suitable diester (**24** and **25**, Scheme 4.5) and diol (**26** and **27**, Scheme 4.5) monomers were prepared *via* self-metathesis or thiol-ene homocoupling of methyl-10-undecenoate and 10-undecen-1-ol. It is worth to mention that both platform chemicals are castor oil derived, and thus, the monomers obtained thereof are also renewable. The presence of double bonds affects both crystallinity and thermal stability of polymers, and for this reason, unsaturated diester **24** was reduced to its saturated counterpart (**28**, Scheme 4.5) in order to compare the thermal properties of the polyesters derived from them. Diesters **24**[144] and **25**,[88] and diol **27**[88] were prepared as previously reported. The synthesis of diol **26** was carried out *via* self-metathesis of 10-undecen-1-ol (Scheme 4.4). Olefins containing alcohol groups, such as 9-decen-1-ol,[145] have been reported to give moderate yields during metathesis reactions due to formation of side products and/or degradation of the catalyst.[146-148] In this regard, alcohol protection was shown to be helpful in overcoming this drawback.[149] Moreover, we have already shown that acetylation of oleyl alcohol and subsequent cross-metathesis reactions, were more efficient, both in terms of catalyst load and produced waste, than using oleyl alcohol directly.[150] Therefore, we followed the same strategy and protected 10-undecen-1-ol by reaction with acetic anhydride to obtain 10-undecenyl acetate (**29**, Scheme 4.4). After purification by simple filtration through silica gel, the behavior of **29** in self-metathesis was studied. Three different metathesis catalysts were tested (Scheme 4), namely Hoveyda-Grubbs 2nd generation (**C1**), Zhan (**C2**), and Umicore 5_1 (**C3**), to obtain the desired self-metathesis product **30** (Scheme 4.4). These catalysts have been shown to give high conversions at loadings as low as 0.05

mol% in self- and cross-metathesis reactions of fatty acid derivatives.[144] Moreover, the addition of 1 mol% of *p*-benzoquinone to these reactions efficiently prevents double bond isomerization,[151] which can drastically decrease the yield of the desired product.[144] Initially, catalyst loadings of 0.5 mol% were used, and the reactions were followed by GC-MS in order to identify the most active catalyst. Vacuum (200 mbar) was applied throughout the reaction to remove the released ethylene. Fast conversions were observed for all three catalysts within the first hour of reaction; however, the conversions did not further increase appreciably. **C1** gave the lowest conversion (48.12% after 5 h) with very low double bond isomerization (1.3%). **C2** and **C3** performed similarly leading to conversions over 80% with only slightly higher isomerization degrees around 2.5 % after 5 h reaction. Based on these results, **C2** was selected for further optimization. Thus, **C2** loadings of 0.2 and 1 mol% were also tested, however, using 0.2 mol% resulted in lower conversion after 5 h reaction, and using 1 mol% gave a higher isomerization degree despite an increase in conversion. From these results, we could conclude that around 0.5 mol% **C2** is a suitable choice for the self-metathesis of **29**. The deprotection of the hydroxyl groups was carried out by direct reaction of the metathesis reaction mixture with excess of methanol in presence of TBD at 65 °C, and the product (**26**) was purified by recrystallization from methanol. It is worth to highlight the simplicity of this synthetic route, which leads to **26** with an overall yield of 67%, without chromatographic purification steps (Scheme 4.4).



Scheme 4.4. Synthesis of fatty acid derived 1,20-diol **26** and metathesis catalysts studied.

The polymerizations of limonene based monomers **16**-**19** were then performed with **24**, **25**, **26**, **27**, and **28** as fatty acid based comonomers, in presence of 5 mol% of TBD, and under continuous vacuum (10 mbar), leading to polyesters **P5**-**P14** (Scheme 4.5). Table 4.4 summarizes the results of these polymerizations at 120 °C for 7 h (data of precipitated polymers), and Figure 4.5 shows GPC traces of the (*R*)-(+)-limonene derived polyesters for comparison. As expected, higher molecular weight polymers (between 9 and 24 kDa and PDI between 1.75 and 2.47) could be obtained in all cases. This was further confirmed by NMR analysis. As a representative example, Figure 4.6 shows the ^{1}H NMR spectra of diester **17** and **P5**, revealing the transformation of methyl ester (H^{a}) to the backbone ester links (H^{c}).

Table 4.4. Analytical data of synthesized (*R*)- and (*S*)-limonene/fatty acid based polyesters.

Polymer (diester / diol)	M_n [a] /kDa	PDI [a]	T_g (°C)[b] / T_m (°C)[b]
P5 (**17** / **26**)	18.9	1.97	-46.9[c] / -15.4[c]
P6 (**19** / **26**)	21.3	2.00	-47.8[c] / -15.6[c]
P7 (**24** / **16**)	15.3	1.82	-46.6[d] / 17.1[d]
P8 (**24** / **18**)	15.5	1.75	-45.3[e] / 17.0[e]
P9 (**17** / **27**)	24.7	2.47	-45.4[f] / 28.2[f]
P10 (**19** / **27**)	23.1	2.47	-46.3[d] / 28.3[d]
P11 (**25** / **16**)	12.4	2.40	-41.9 [d] / 47.5 [d]
P12 (**25** / **18**)	14.0	2.06	-43.0 [g] / 47.2 [g]
P13 (**28** / **16**)	9.7	2.22	[f] / 50.8 [d]
P14 (**28** / **18**)	9.2	2.22	[f] / 50.3 [d]

[a] GPC data of precipitated polymers, [b] DSC data recorded at 10 °C/min, [c] 1 h annealing at -25 °C, [d] second heating scan, [e] 1 h annealing at 16 °C, [f] 1 h annealing at 20 °C, [g] 1 h annealing at 10 °C, [f] T_g not observable by DSC.

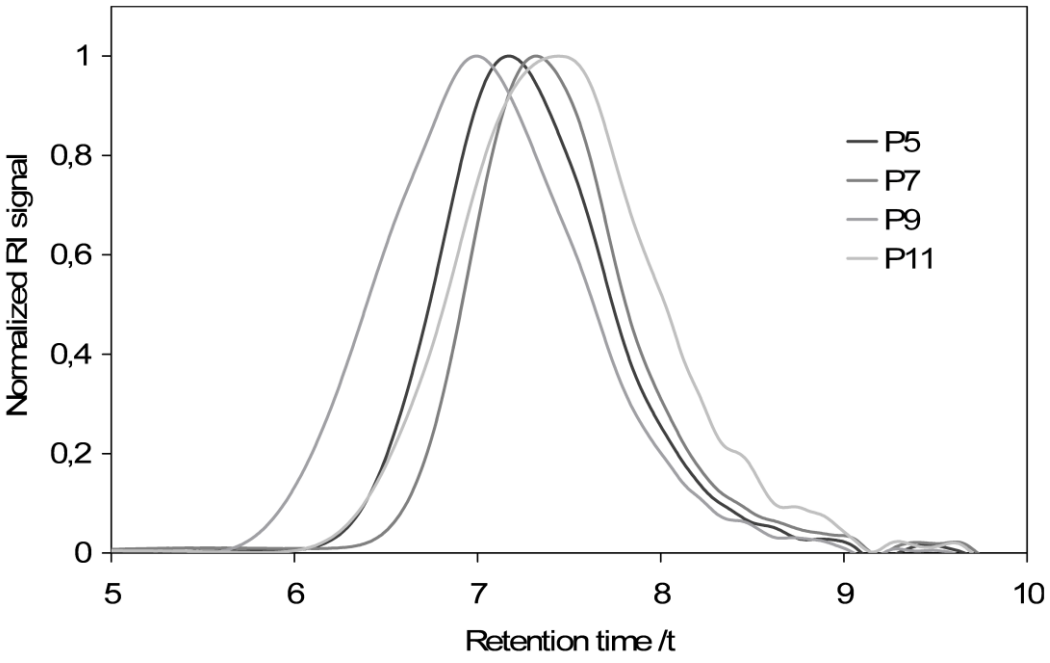
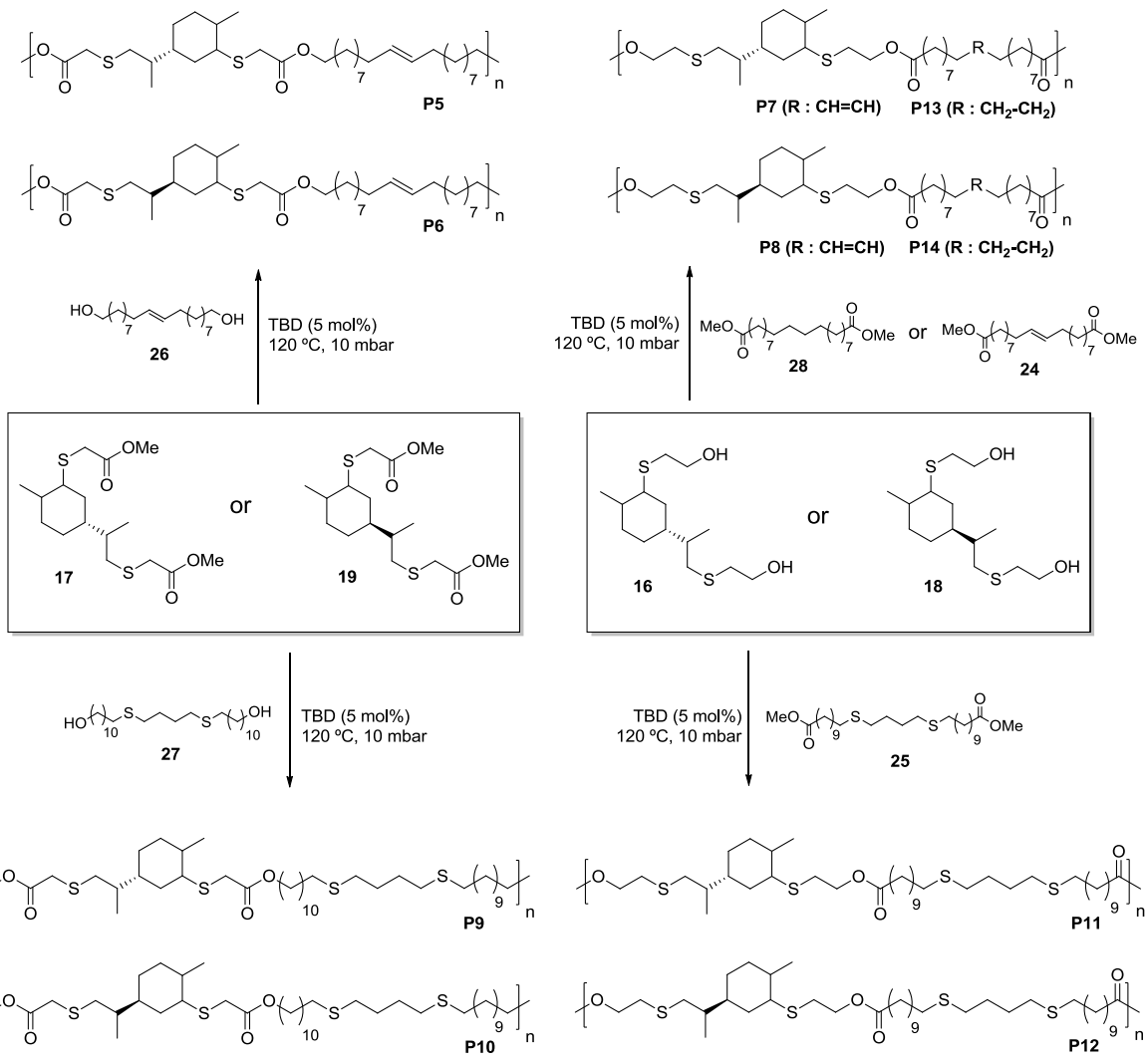


Figure 4.5. GPC traces of (*R*)-(+)-limonene based polyesters.



Scheme 4.5. Synthesis of (*R*)-(+)- and (*S*)-(–)-limonene/fatty acid based polyesters.

When short chain comonomers are used, the activity of the catalyst can be reduced due to the steric hindrance caused by the terpene rings. On the other hand, the introduction of long, flexible alkyl chains can reduce the steric hindrance around the terpene units, facilitating the approach of the catalyst. Interestingly, when comparing the polymerization results obtained with diesters **24** (unsaturated, **P7** and **P8**) and **28** (saturated, **P13** and **P14**), higher molecular weights are obtained with the unsaturated diester, probably due to a more flexible chain both in the monomers and the resulting polymer.

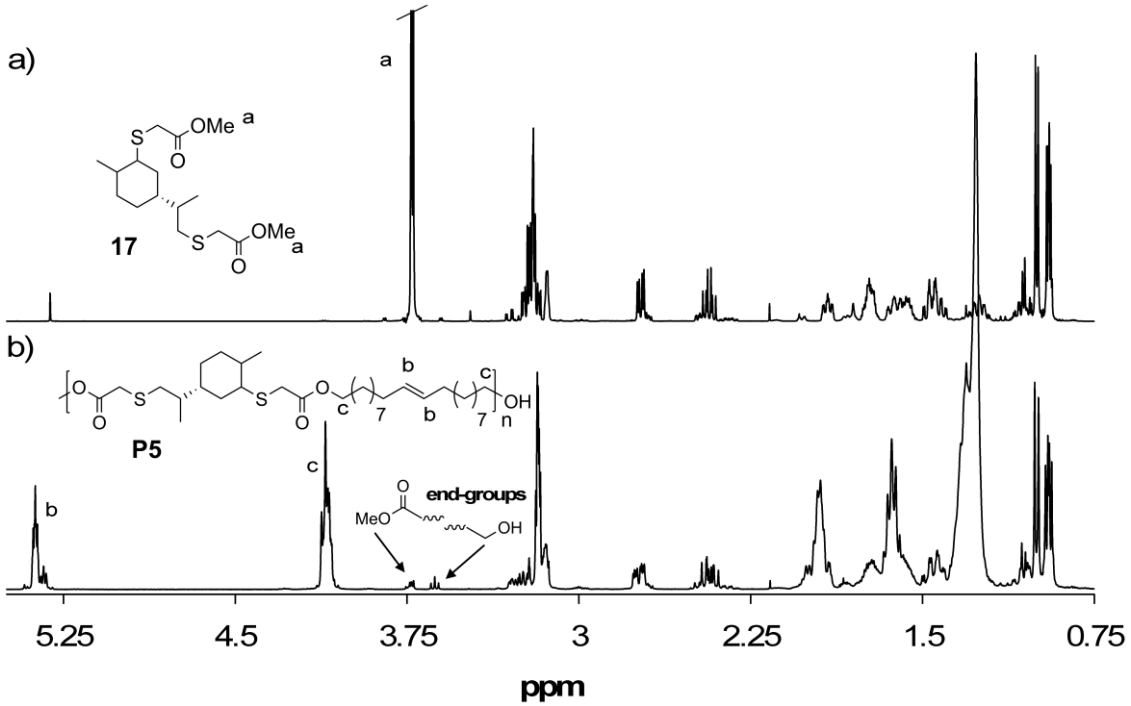


Figure 4.6. ^{1}H NMR spectra of a) monomer **17**, and b) product of polycondensation of **17** with diol **26** (**P5**).

Furthermore, a closer look at the polymerization results reveals an interesting fact regarding the obtained molecular weights. The molecular weights reached with diester monomers containing the methyl thioglycolate moiety (**17** and **19**) are clearly higher than those obtained with diesters, which do not have the sulfur in β-position to the carbonyl group (**24** and **25**). In order to establish whether the sulfur atom has an effect on the course of the esterification reaction, we performed a simple kinetic study, in which 10-undecen-1-ol was reacted with diester (**31**) containing both a methyl β-thioester and a methyl ester (Figure 4.7). The reaction was performed under polymerization conditions (5 mol% TBD related to ester groups, 120 °C, and 10 mbar) with a 1:1 molar ratio of the reactants, and the consumption of both ester groups was monitored in time by integration of characteristic ^{1}H NMR signals (Figure 4.8). The results of this competitive study, which are shown in Figure 4.7 as a plot of

ester conversion against time, confirm the higher reactivity of the methyl β-thioester compared to the unsubstituted one.

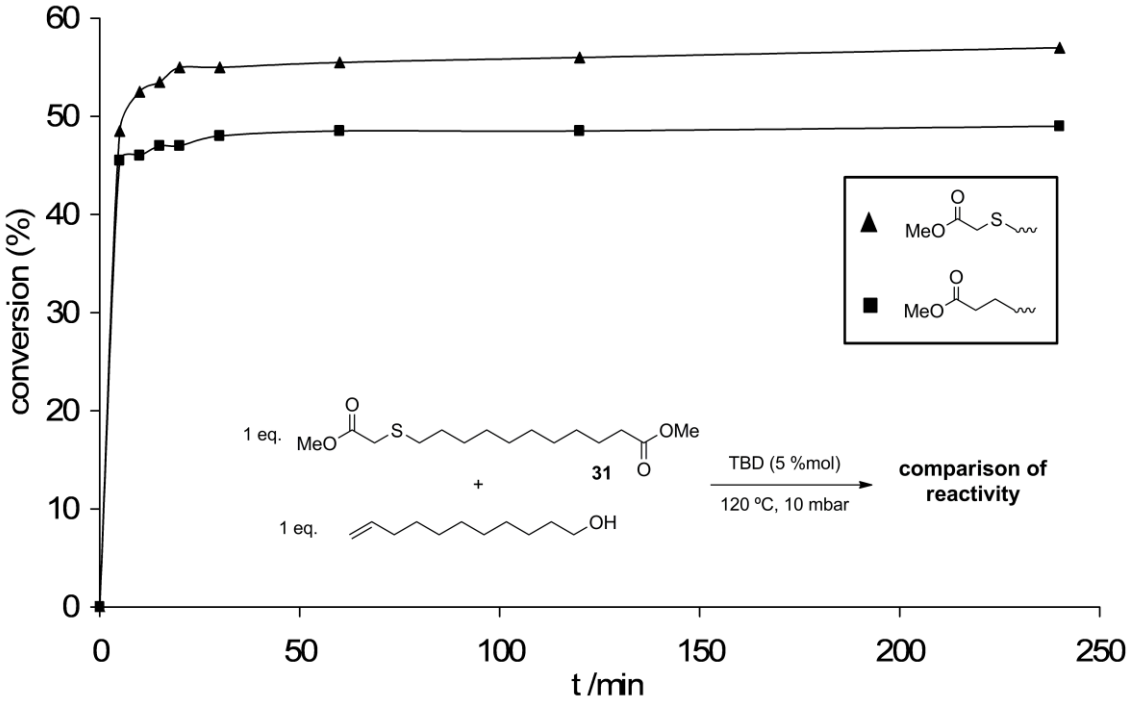


Figure 4.7. Study of the effect of sulfur in β-position to ester group on the reactivity towards transesterification with 10-undecen-1-ol.

The effect of sulfur on the reactivity of the ester group might be explained on the basis of the mechanism through which TBD catalyzes transesterification reactions. It has been proposed that in a first step, a reversible amidation occurs by formation of a six-membered ring intermediate between TBD and the ester group followed by release of methanol (see Scheme 3.9).[122] In a second step, a hydrogen bond is established between the TBD moiety and the approaching alcohol, favoring its approach, and weakening the O-H bond. In this second step, the sulfur atom might establish a hydrogen bond with the alcohol, thus assisting the process.

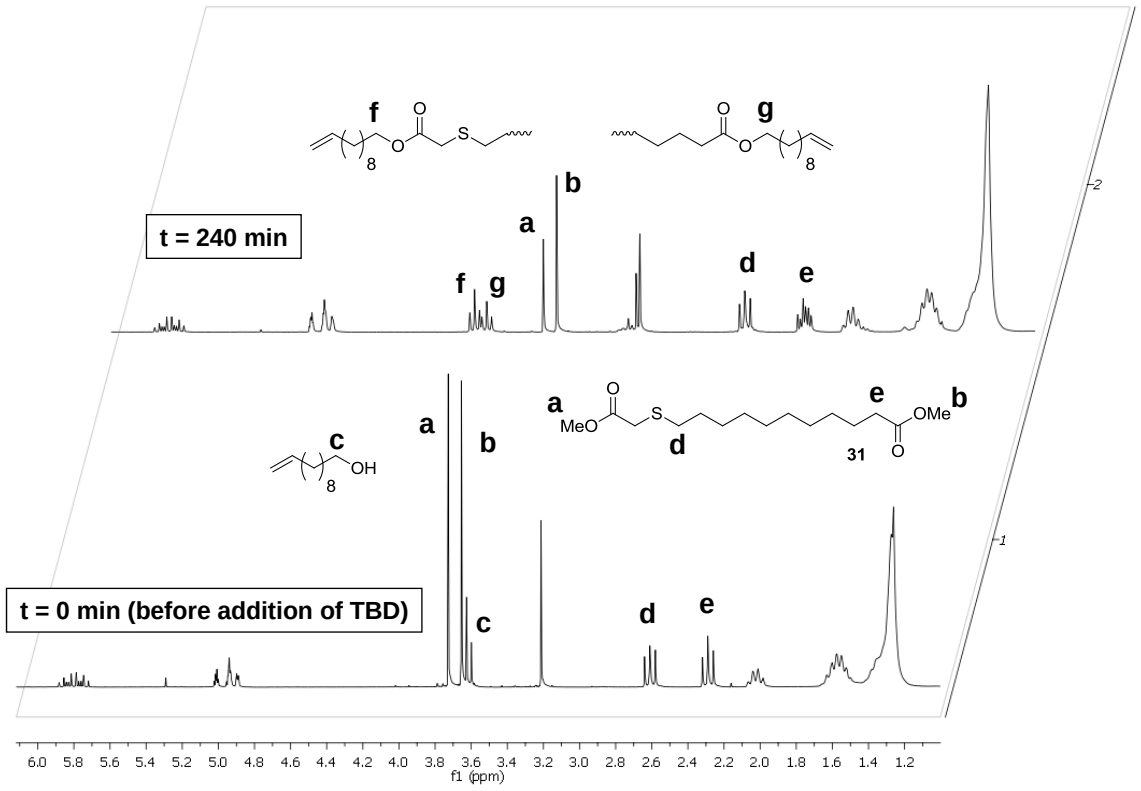


Figure 4.8. Representative ^{1}H NMR spectra of the kinetic study; t = 0 min (before addition of TBD), and t = 240 min.

4.2.4. Thermal analysis

Polyesters obtained from limonene based monomers **20**-**23** (**P1**-**P4**) consist of bulky 1,3,6-trisubstituted cyclohexane units connected by very short segments. Crystallization is thus very unlikely, and DSC analysis reveals amorphous structures for all of them (see Figure 4.9) with glass transition temperatures around -10 °C.

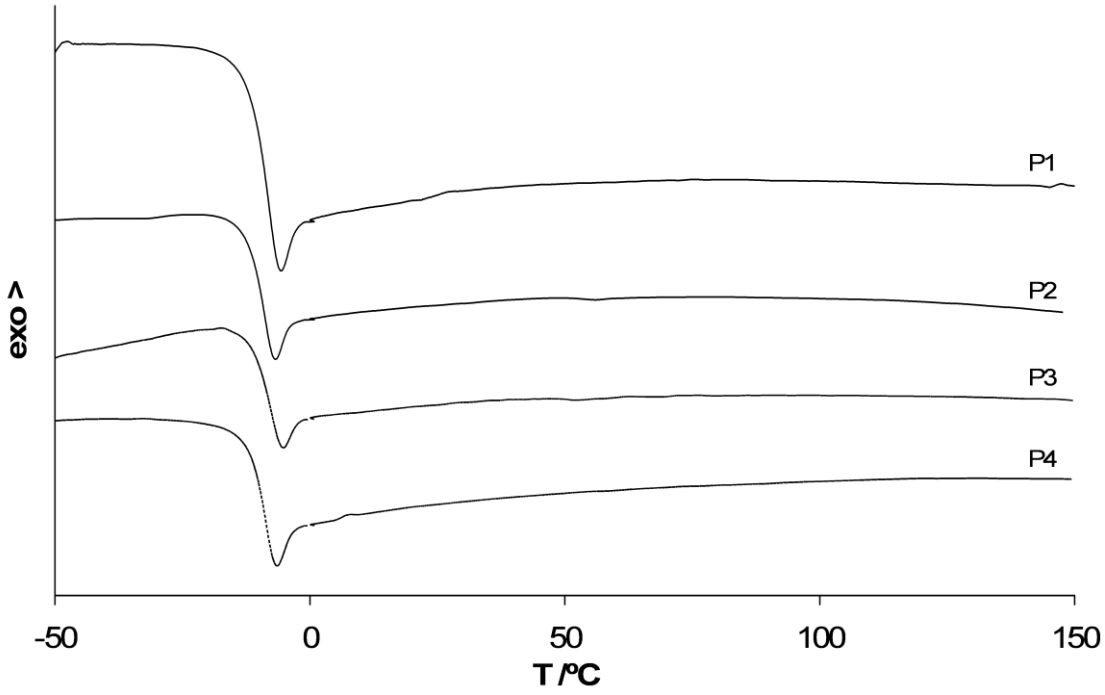


Figure 4.9. DSC traces of terpene based polyesters **P1**-**P4** (second heating scan).

Limonene/fatty acid based polyesters **P5**-**P14** (Scheme 4.5) display as a common structural feature the alternation of relatively long aliphatic segments (18 and 20 carbon atoms), and substituted cycloalkanes. On one hand, the aliphatic chains are able to crystallize, but on the other hand, the 1,3,6-trisubstituted cyclohexane units are too bulky to crystallize. DSC traces obtained for polyesters **P5**-**P12** are shown in Figure 4.10 and the extracted analytical data is summarized in Table 4.4. With the exception of **P7**, **P10**, **P13**, and **P14**, the studied polyesters displayed multiple melting transitions on the second heating scan. Annealing studies were thus performed to determine whether these multiple melting transitions were due to the presence of metastable crystalline phases, or actual crystalline structures (see Table 4.4 for experimental details). Appropriate annealing conditions could be found for **P5**, **P6**, **P8** and **P12**, which led to one, more or less broad, melting peak. However, annealing studies performed on **P9** and **P11** did not lead to single melting transitions, suggesting polymorphism. A first look at the thermal data in Table 4.4 reveals that all

the studied polyesters are semicrystalline, displaying both glass transition (T_g) and melting (T_m). Especially noteworthy is the fact that all studied polyesters (except **P13** and **P14**, for which the T_g could not be observed by DSC) have basically the same glass transition temperature despite of their clearly differentiated T_m values. This data could suggest that the polyester chains might crystallize independently of the cyclic moieties (common in all polyesters), letting them out of the crystallites as amorphous regions. The melting behavior of polyesters **P5**-**P14** can be explained attending to the factors that enhance or hinder interchain interactions and to their different chain-packing abilities. **P5** (T_m = -15.4 °C) and **P7** (T_m = 17.1 °C) present well differentiated melting points despite having relatively similar structures. Both present bulky main-chain groups that can impede crystallization, but in this case, the spacing between the ester groups and the bulky limonene rings, which is longer in **P7**, seems to favor interchain-interactions and/or chain packing compared to **P5**. The same applies for the pairs **P6**/**P8**, **P9**/**P11**, and **P10**/**P12**. On the other hand, the introduction of fatty acid based comonomers containing sulfur atoms leads to an increase of the melting temperatures. Thus, polyesters **P9-P12** display melting temperatures, which are up to 43 °C higher than for polyesters **P5-P8** (see e.g. **P5** vs. **P9**). The effect of sulfur on the T_m of these polyesters can be correlated with a higher cohesion energy due to stronger interchain interactions.[152] Finally, saturated polyesters **P13** and **P14** display sharp melting endotherms, which are around 35 °C higher than those of their unsaturated counterparts (**P7** and **P8**). This effect is due to the higher packing ability of the saturated alkyl chains and to the higher flexibility of the unsaturated ones, which results in the observed higher melting points. No glass transition could be detected for these polyesters, which also supports their higher crystallinity compared to **P7** and **P8**.

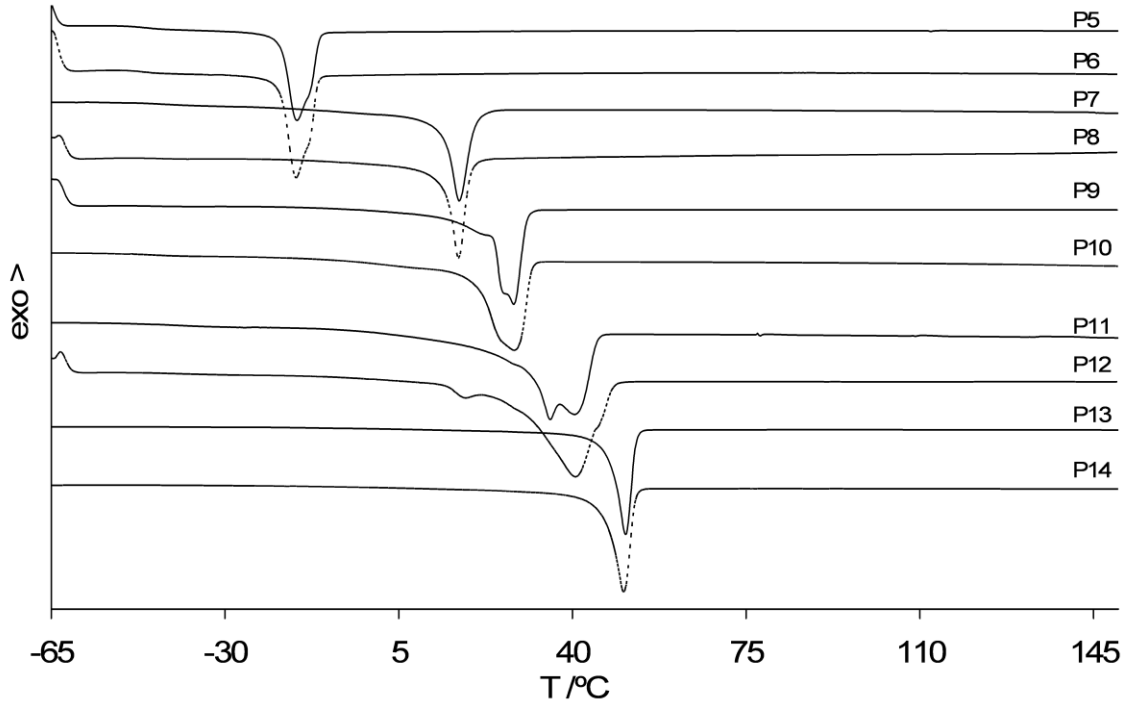


Figure 4.10. DSC traces of (R)-(+)- (—) and (S)-(−)- (····) limonene based polyesters **P5**-**P14** (see table 4.4 for experimental conditions).

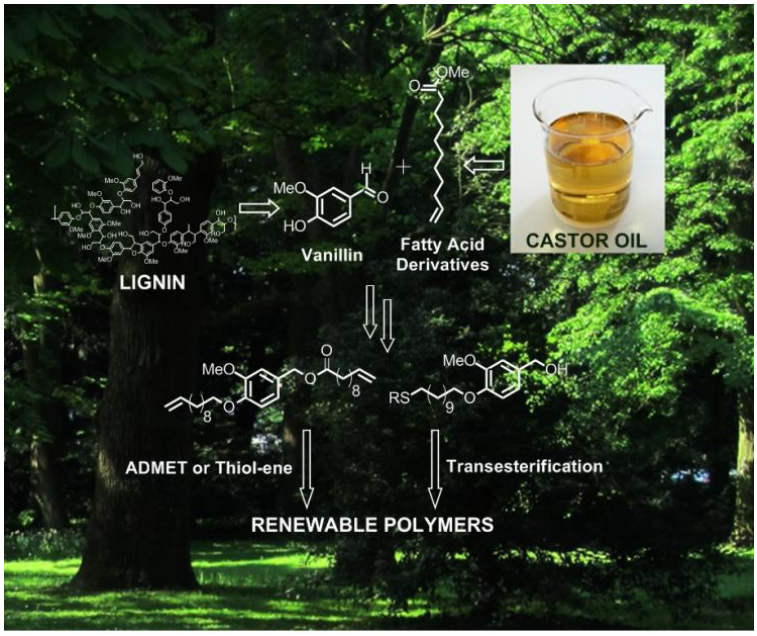
4.3. Conclusion

Addition of alcohol and ester functionalized thiols to terpenes takes place at room temperature in absence of solvent and radical initiator. These reactions are regioselective, and can thus be controlled to yield monofunctional, difunctional, or hetero-difunctional monomers, which are interesting renewable building blocks. Moreover, it was found that the addition of thiols to terpenes is also diastereoselective, reaching a ratio of 5:1 for this radical reaction in the addition of 2-mercaptoethanol to (−)-β-pinene. This effect was related to steric effects making hydrogen abstraction more favorable from one of both terpene faces. Difunctional monomers prepared from (*R*)-(+)-limonene (**1**) and (*S*)-(−)-limonene (**2**) have been subjected to polycondensation. Oligomers, or low molecular weight polyesters were obtained when these terpene based monomers were homopolymerized or

copolymerized with short chain diols. However, when long chain fatty acid based diesters and diols were used as comonomers, polyesters with number average molecular weights up to 25 kDa (M_n) were obtained. Most polyesters synthesized are semicrystalline with a common T_g around -45 °C, and melting points ranging from -15 to 50 °C.

5

Renewable Co-Polymers Derived from Vanillin and Fatty Acid Derivatives[153]



5.1. Introduction

The synthesis of new platform chemicals that are based on renewable resources has been accepted as a strategy to contribute to a sustainable development.[135,136] Vanillin,

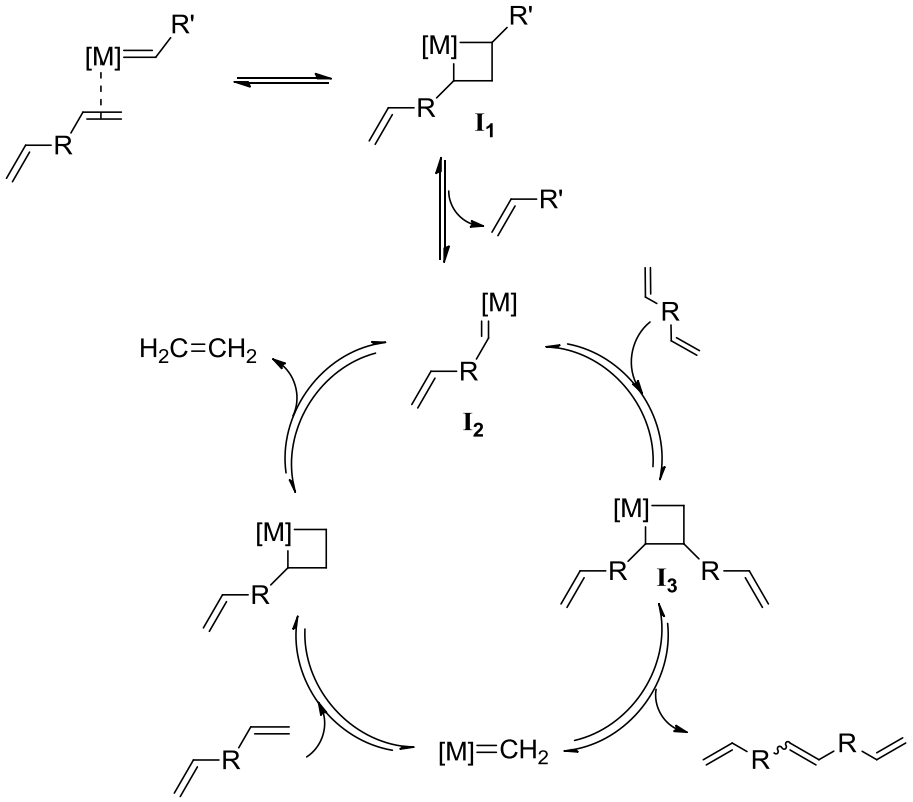
an important aromatic flavor compound used in foods, beverages, perfumes, and pharmaceuticals,[154] represents a sustainable and valuable chemical feedstock.[155,156,157] Industrially, vanillin is produced either from lignin or from petroleum-derived phenol. Due to the high abundance of lignin (over 3×10^{11} tons of lignin exists in the biosphere with approximately 2×10^{10} tons generated annually), new benign synthetic methods have been developed to obtain larger quantities of vanillin from lignin.[154,156,157] The global demand for synthetic vanillin is currently estimated to be around 16,000 tons per year, wherein the major quantities are used as flavoring and fragrance ingredients.[155]

Due to its functional groups, vanillin offers versatile possibilities for various chemical transformations, enabling the synthesis of bio-based renewable monomers and polymers for the chemical industry. Renbutsu *et al*. have successfully prepared UV-curable palladium-chelating chitosan derivatives employing methacrylated vanillin as photosensitive aldehydes, which are utilized as coating materials for electroless plating on non-conductive substrates.[158] Aromatic/aliphatic polyester poly(dihydroferulic acid), which exhibits thermal properties similar to those of polyethylene terephthalate (PET), was synthesized from vanillin and acetic anhydride.[159] Moreover, Wool *et al*. successfully employed methacrylated vanillin and cross-linked it with glycerol dimethacrylate to prepare vanillin-based resins intended for commercial polymer composites.[157] Interestingly, thermo-gravimetric and thermo-mechanical properties of the composites were comparable to commercial vinyl ester-based thermosets.

Even though extensive research has been performed to obtain commercial vanillin derived renewable polymers, only very few examples have been reported on acyclic diene metathesis (ADMET) polymerizations with vanillin derivatives as diene

substrates. For example eugenol and isoeugenol derivates, both vanillin precursors, were applied in ADMET polymerizations to obtain unsaturated polyethers and polycarbonates with molecular weights ranging from 2.700 to 32.000 g/mol.[160] Later on, Meier and co-workers reported on the copolymerization of ferulic acid (a precursor of vanillin) derivatives with α,ω-dienes derived from oleic and erucic acid *via* ADMET and thiol-ene addition polymerization, demonstrating a potentially new application for these renewable resources.[161]

ADMET polymerization is a step-growth polymerization driven by condensate release (typically ethylene).[162] This type of polymerization is usually performed on α,ω-dienes to give well-defined and strictly linear polymers with unsaturated often polyethylene like backbones. The mechanism of the ADMET polymerization cycle is well established (Scheme 5.1).[163,164] The mechanism involves coordination of an alkene double bond to a transition metal alkylidene to form metallacyclobutane intermediate (**I_1**). At this step, the productive cleavage of **I_1** leads to the metathesis active alkylidene complex (**I_2**). This complex then reacts with another monomer double bond to yield the metallacyclobutane ring (**I_3**), which subsequently leads to polymer formation. The cycle continues with coordination of another diene or growing polymer, followed by productive cleavage, and ethylene release. Nowadays, ADMET is a very useful approach for the construction of defined polymer architectures including highly improved activity and functional group tolerance.[164] Based on this method, renewable polyesters, polyethers, polyamides, and many other polymers were synthesized.[92,128,161,162,164,165]



Scheme 5.1. Generally accepted mechanism of ADMET polymerization.[163, 164]

Moreover, thiol-ene addition, although already discovered in 1905,[73] has not been studied in detail using vanillin derivates as olefinic substrates. Thiol-ene additions often display click reaction features and are widely employed for various highly efficient transformations.[9] In **Chapter 4**, it has been showed that the high efficiency of thiol-ene additions permits the introduction of different functionalities to olefinic structures, which makes it a suitable way to obtain terpene based monomers for the synthesis of renewable polyesters *via* polycondensation.[134]

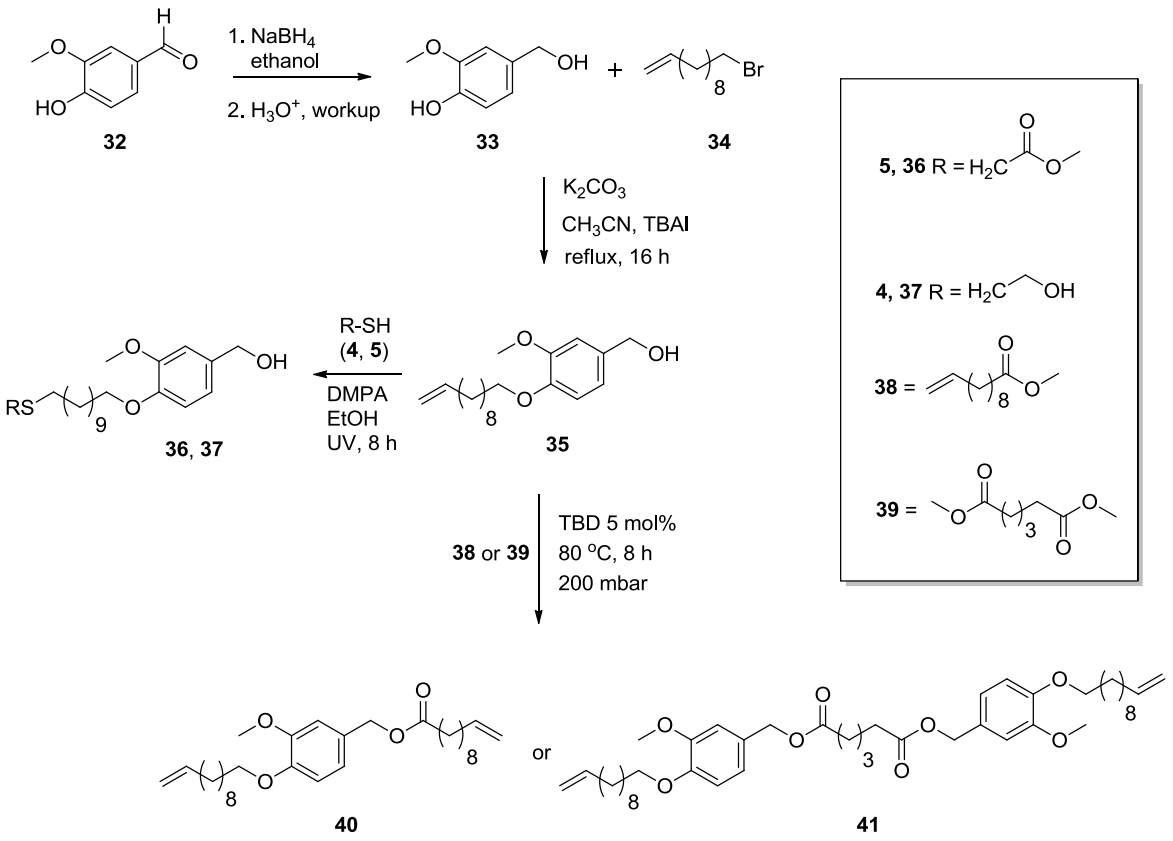
In this chapter, vanillin and different fatty acid derivatives were used to prepare α,ω-dienes and difunctional monomers containing ester and/or alcohol moieties. Then ADMET, thiol-ene polymerization, and/or classic polycondensation were used as different polymerization techniques for these monomers. Within these investigations, we present vanillin and fatty acid modification as a suitable tool to obtain renewable

monomers for the synthesis of aromatic polyesters. Additionally, the thermal properties of the synthesized polymers were studied in order to learn about the properties and possible applications for the future.

5.2. Results and Discussion

5.2.1. Syntheses of monomers

We started our study with the synthesis of the monomers using vanillin (**32**) as starting material. The first step involved the reduction of vanillin[166] using sodium borohydride followed by etherification of the obtained alcohol **33** with **34** (Scheme 5.2), which led to the formation of the aromatic ether **35** in good yield. Compound **34** is a commercially available undecenoic acid derivative, which can be obtained by simple pyrolysis of castor oil.[167] In order to synthesize α,ω-diene derivatives from vanillin, alcohol **35** was transesterified with **38** or commercially available diester **39** using TBD as catalyst. It is worth to mention that both **38** and **39** can be obtained from renewable resources. Ester **38** is also derived from castor oil. Previous work suggested that γ-valerolactone, a bio-based levulinic acid derivative, can be transformed to methyl pentenoate, which can be further converted to nylon intermediates such as adipic acid, caprolactam, or diester **39**.[168] Continuous vacuum (~ 200 mbar) was applied in order to force product formation by efficient removal of methanol from the reaction mixture. Good yields (≥89%) of the α,ω-diene **40** and **41** were obtained after 8 h reaction. Both α,ω-dienes **40** and **41** were suitable substrates for ADMET and thiol-ene polymerizations.



Scheme 5.2. Reaction pathways for the synthesis of the monomers from vanillin.

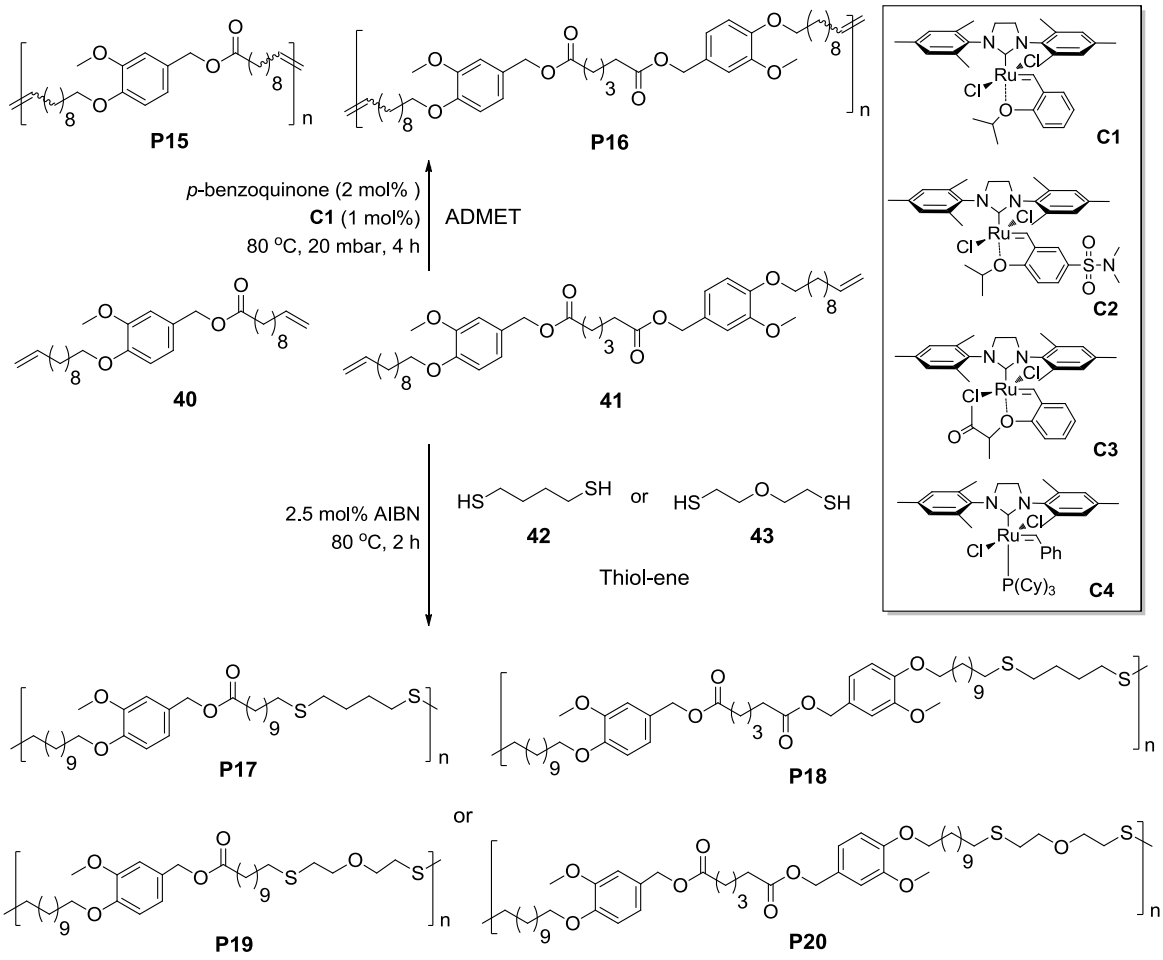
Another possible efficient modification of compound **35** would be to use its terminal double bond for thiol-ene addition. In previous reports, additions of hydroxyl or methyl ester functionalized thiols to terminal double bonds led to suitable monomers for polycondensation.[88,134] The simplicity of thiol-ene additions, which can be performed by simply mixing thiol and terminal olefin in absence of solvent and radical initiator, and at temperatures close to room temperature, makes it a useful tool for various chemical transformations. Unfortunately, within the current study, applying the same method to **35** did not work due to solubility problems. In order to solve this problem, the thiol-ene additions of thiol **4** or **5** to **35** were performed under UV irradiation, using a small amount of ethanol as solvent, and DMPA as a photoinitiator. Initially, 5 mol% DMPA and a 1:1 ratio was used for the addition reaction. However, based on ^{1}H-NMR analyses, the conversion of the double bond was

not complete (90%) even after 24 h. The amount of the thiol compounds was then increased to 1.1 equiv. and full conversion was achieved after 8 h. Further attempts were carried out to decrease the amount of DMPA. Using a 1:1.1 ratio of compound **35** to the employed thiols and 2 mol% DMPA, only the addition of methyl thioglycolate achieved complete double bond conversion after 8 h, whereas 90% conversion was obtained in case of 2-mercaptoethanol addition. After purification by column chromatography **36** and **37** were obtained in good yields (93 and 87%, respectively).

5.2.2. ADMET and thiol-ene polymerizations

Having different vanillin- and fatty acid-derived monomers in hand, we started our investigation on the polymerization behavior of the monomers in ADMET and thiol-ene polymerizations (Scheme 5.3). The first step of this study focuses on the reactivity of the diene to ruthenium-based olefin metathesis catalysts. Optimization studies were performed involving a catalyst screening. In order to guarantee a more efficient removal of ethylene, continuous vacuum (~ 20 mbar) was applied for all ADMET polymerizations. Additionally, the reactions were carried out without solvent, since under bulk conditions, polymer formation is favored.[169] It has been reported that olefin isomerization side reactions (double bond migration) can be observed in ADMET polymerization when using ruthenium-based olefin metathesis catalysts. However, such a double bond isomerization can be suppressed by using quinone-type compounds.[170,171] Therefore, 1,4-benzoquinone was used as additive to suppress olefin isomerization. Diene **40** was chosen for an optimization study of the ADMET polymerization. Four different metathesis catalysts were tested (Scheme 5.3), namely Hoveyda-Grubbs 2nd generation (**C1**), Zhan (**C2**), Umicore 5_1 (**C3**), and Grubbs 2nd

(**C4**). The reactions were performed at 80 °C, under continuous vacuum (~ 20 mbar), solvent-free, and with 2 equiv. 1,4-benzoquinone relative to the catalyst. Initially, catalyst loadings of 1.0 mol% were used, and the reactions were followed by GPC in order to identify the most active catalyst. After 4 h reaction time, the highest molecular weight was achieved by using catalyst **C1** (Table 5.1).



Scheme 5.3. ADMET and thiol-ene polymerization of dienes derived from vanillin and metathesis catalyst studied.

Table 5.1. Performed ADMET polymerization of monomer **40.**

Entry[a]	Catalyst (mol%)	M_n (kDa)[b]	PDI[b]	*DP*
1	**C1** [0.1]	7.6	1.73	16
2	**C1** [0.2]	28.9	1.88	61
3	**C1** [0.5]	30.5	1.95	64
4	**C1** [1.0]	45.4	1.96	96
5	**C2** [1.0]	21.3	2.72	45
6	**C3** [1.0]	40.8	1.98	86
7	**C4** [1.0]	4.3	1.77	9

[a] Reaction conditions: neat, 1,4 benzoquinone (2 equiv. per catalyst), 4 h reaction time, vacuum (~ 20 mbar), 80 °C. [b] GPC data of crude reaction samples.

Based on these results, **C1** was selected for further optimization studies. The use of lower catalyst loading e.g. 0.1 – 0.5 mol% did not lead to higher molecular weight. Furthermore, performing ADMET polymerization for longer reaction times also did not lead to increased molecular weights. Based on these results, we concluded that around 1.0 mol% **C1** is a suitable choice for the ADMET polymerization of **40**. Noteworthy, after precipitation into cold methanol, aromatic polyester derived from vanillin **P15** were obtained in high molecular weight (49.6 kDa). High molecular weight of **P16** (25.6 kDa) could also be obtained by applying the same method to monomer **41**. Table 5.2 summarizes the results of these polymerizations, and Figure 5.1 shows some GPC traces of the vanillin derived polyesters *via* ADMET and thiol-ene polymerization. The polymers were further characterized by NMR analysis. As a representative example, Figure 5.2 shows the ^{1}H NMR spectra of diene **40** and **P15**, revealing that the signals at 5.85-5.75 and 4.96 ppm corresponding to the terminal double bond disappeared and a new signal at 5.26 ppm corresponding to the internal double bond protons were formed.

Table 5.2. Analytical data of the synthesized polymers *via* ADMET and thiol-ene polymerization.

Polymer	Monomers	Polymerization Method	M_n (kDa)[a]	PDI[a]	*DP*	T_g (°C)[b]	T_m (°C)[b]
P15	**40**	ADMET	49.6	1.96	105	-31.29[c]	-
P16	**41**	ADMET	25.6	1.88	35	-17.89[c]	-
P17	**40** & **42**	Thiol-ene	15.4	1.77	26	-32.26[d]	57.65[d]
P18	**41** & **42**	Thiol-ene	12.1	1.94	14	-22.44[e]	68.75[e]
P19	**40** & **43**	Thiol-ene	16.1	1.87	26	-37.05[e]	36.07[e]
P20	**41** & **43**	Thiol-ene	9.6	1.76	11	-25.48[f]	45.64[f]

[a] GPC data of precipitated polymers [b] DSC data recorded at 10 °C/min, [c] second heating scan, [d] 30 min. annealing at 40 °C, [e] first heating scan, [f] 1 h annealing at 20 °C.

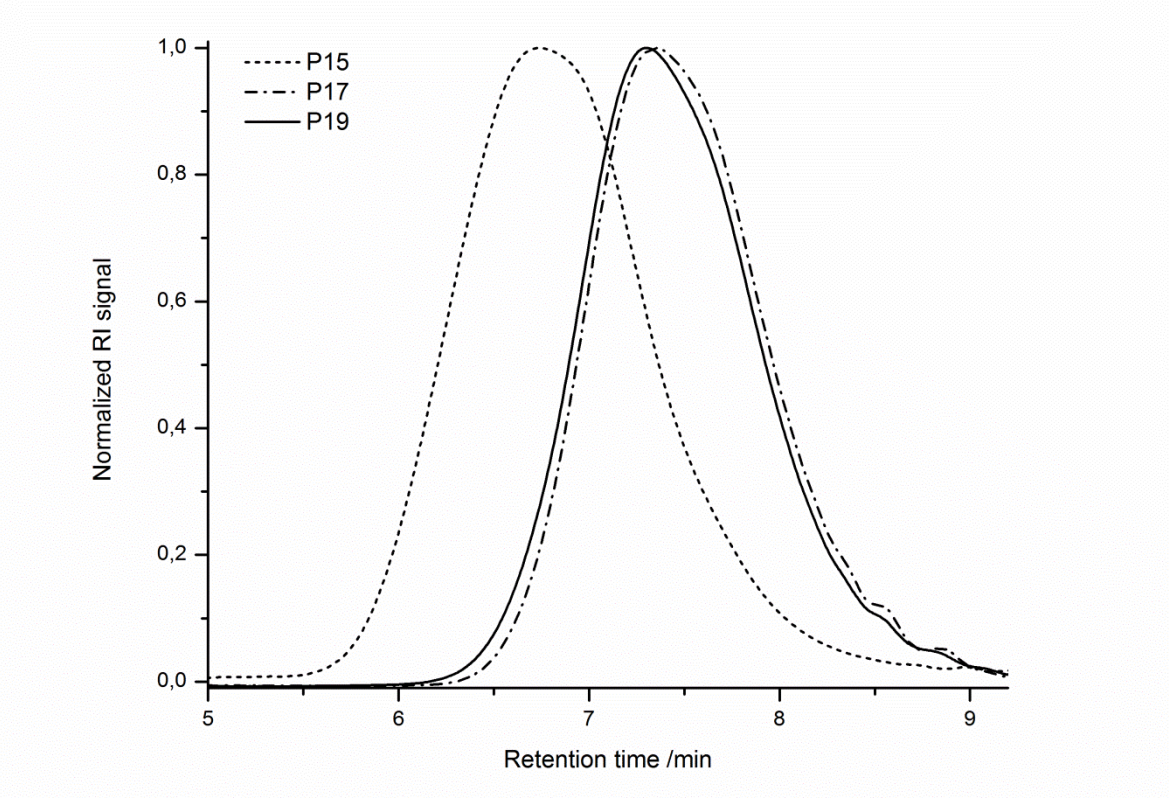


Figure 5.1. GPC traces of some polymers synthesized ADMET and thiol-ene polymerization.

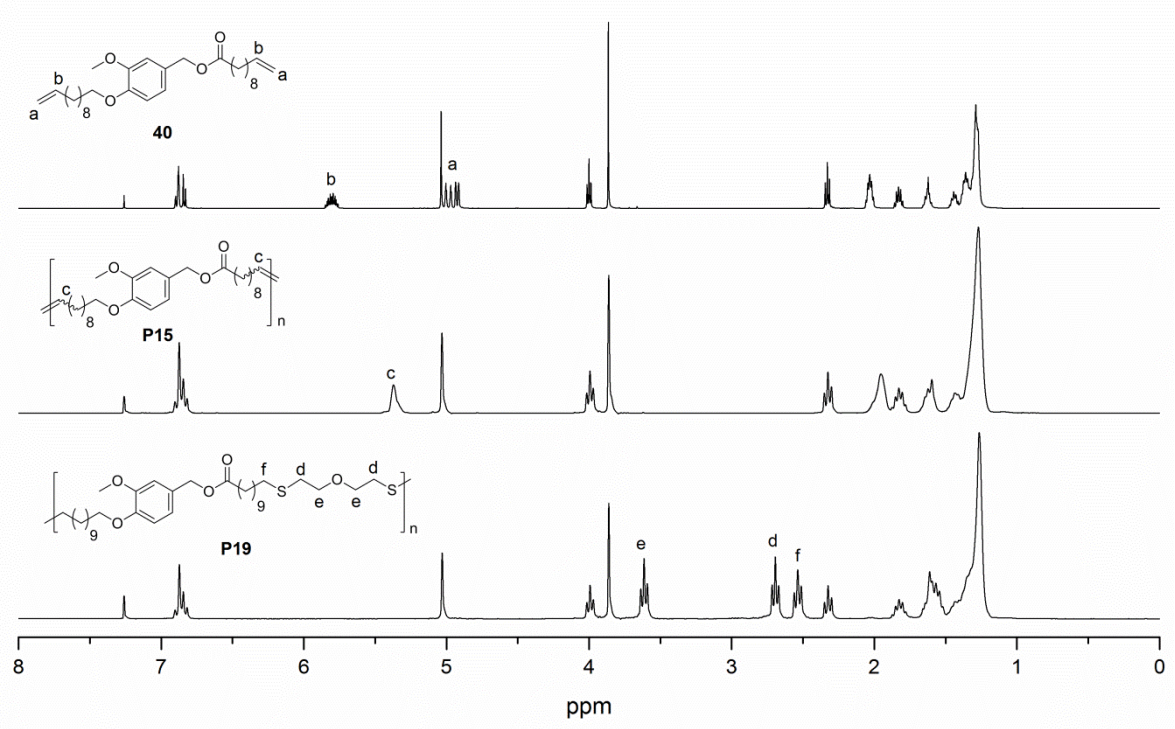


Figure 5.2. ^{1}H NMR spectra of monomer **40** (top), and the thereof derived ADMET **P15** (middle) and thiol-ene **P19** (bottom) polymers.

Beside ADMET polymerization, thiol-ene addition is also known to be a powerful tool for the polymerization of α,ω-dienes.[90,92,161] Since the dienes **40** and **41** are also perfectly suited to be polymerized with a dithiol *via* thiol-ene addition, this route was investigated as an alternative approach to the previously employed ADMET polymerization. Two dithiols **42** and **43**, which are commercially available, were chosen as representative dithiol compounds. AIBN (2.5 mol%) was used as radical initiator using the same conditions as previously reported.[90] The polymerization mixtures were degassed in order to remove oxygen,[88] which is a radical scavenger in these reactions. After performing thiol-ene additions at 80 °C for 2 h, the polymerization was completed and longer reaction times did not lead to higher molecular weights. GPC results of these polymerizations showed that vanillin based polyester with molecular weights (between 9 and 16 kDa and PDIs between 1.76 and

1.94) could be efficiently synthesized *via* thiol-ene polymerization (Table 5.2 and Figure 5.1). ^{1}H-NMR analysis confirmed the expected structure of these polymers. As an example, ^{1}H NMR spectra of **40** and **P19** (Figure 5.2), showed almost full conversion of the double bond and reveals the corresponding thio/oxo ether functionalities on the polymer backbone. This is evidenced by an almost complete disappearance of the signal of double bonds at 5.85-5.75 and 4.96 ppm and newly emerged signals of thio/oxo ether at 3.61, 2.69, and 2.54 ppm.

The thermal properties of the polymers synthesized *via* ADMET and thiol-ene were analyzed by DSC. The studied polymers displayed melting transitions (T_m) and glass transition temperatures (T_g) with the exception of **P15** & **P16**, which showed only a T_g (Table 5.2). Figure 5.3 shows representative example of DSC traces of the synthesized polymers. In case of **P17**–**20**, crystallization took place closely to its melting transition and displayed multiple melting transitions on the second heating scan. Therefore, annealing studies were performed to determine whether these crystallization and/or multiple melting transitions were due to the presence of metastable crystalline phases, or actual crystalline structures. Suitable annealing conditions could be found for **P17** and **P20**, which led to one melting peak. However, annealing studies conducted on **P18** and **P19** did not lead to single melting transitions and thus we report the T_m from the first heating scan. With the same dithiol, polyesters derived from monomer **41** (**P18** and **P20**) display melting temperatures higher than polyesters from monomer **40** (**P17** and **P19**). On the other hand, if dithiol **42** was used instead of dithiol **43**, somewhat higher melting points were observed.

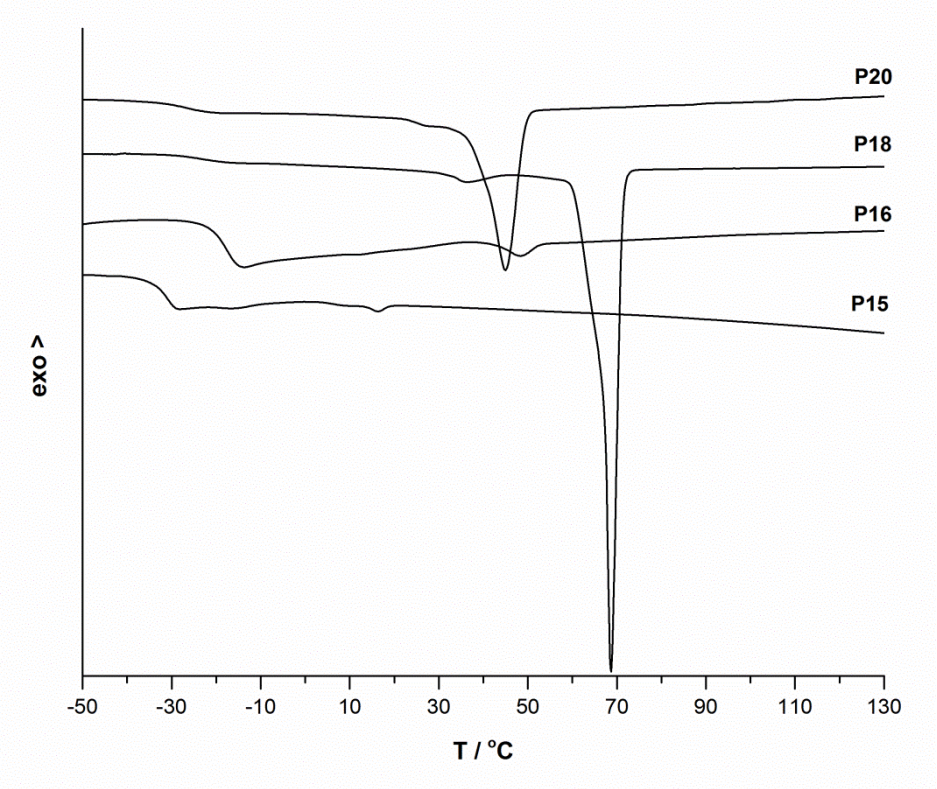
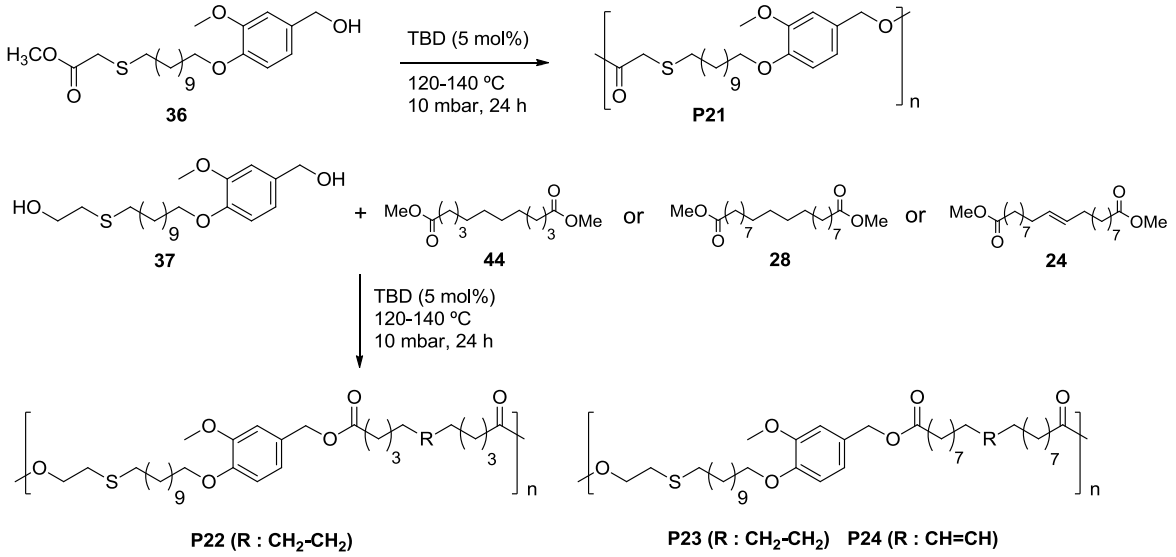


Figure 5.3. DSC traces of the vanillin based polyesters **P15, P16, P18, P20** (see Table 5.2 for experimental conditions).

5.2.3. Transesterification polymerization (polycondensation)

The difunctional monomers obtained by addition of 2-mercaptoethanol or methyl thioglycolate to alkene **35** were subsequently used for polyester synthesis (Scheme 5.4). Based on our experience and on previous reports,[140] the use of TBD as catalyst shows high transesterification activity. Therefore, these polycondensations were carried out using TBD as a catalyst. Constant vacuum (~ 10 mbar) was applied in order to remove methanol and force the product formation. Three diester (**24**, **28**, and **44**) monomers were prepared from methyl-10-undecenoate for these polycondensation studies. It is worth to point out that the monomers are castor oil derived, and thus, the polymers obtained thereof are also renewable. Monomer **24**[144] was synthesized *via* self-metathesis of methyl-10-undecenoate and diester **28**[134] was

prepared by reduction of **24** as previously reported. Monomer **44** was synthesized by hydrogenation of 1,12-dimethyl-(*E*)-dodec-2-enedioate.



Scheme 5.4. Synthesis of the vanillin/fatty acid based polyesters.

Thus, we performed the polymerizations using 5 mol% (related to ester groups) TBD at 120–140 °C under continuous vacuum for 24 h. Initially, homopolymerization of heterodifunctional **36** led to homopolymer **P21** with relatively high molecular weight (16.6 kDa, PDI 1.81). Performing the reaction for longer reaction times did not lead to higher molecular weights. Thus, under the same polymerization conditions, diol **37** was polymerized with the prepared diester **24**, **28**, or **44**. GPC analysis of the precipitated polymers (Table 5.3, Figure 5.4) showed molecular weight in the range of 16.8-17.3 kDa and PDIs around 1.7. ^{1}H NMR analysis of the synthesized polymers revealed the successful polymer formation. As a representative example (Figure 5.5), the ^{1}H NMR spectra of diester **44**, diol **37** and its derived polymer **P22**, showed almost full disappearance of the singlet peak at 3.65 ppm corresponding to methyl ester (H^{a}) transformed to the backbone ester link (H^{c}).

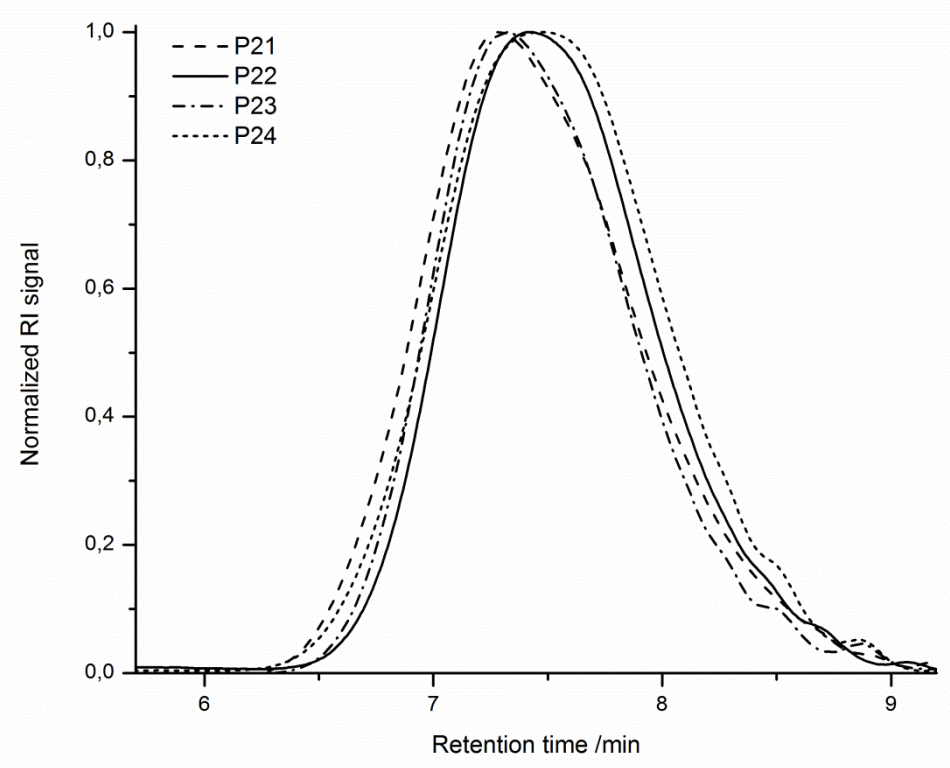


Figure 5.4. GPC traces of the synthesized polymers *via* polycondensation.

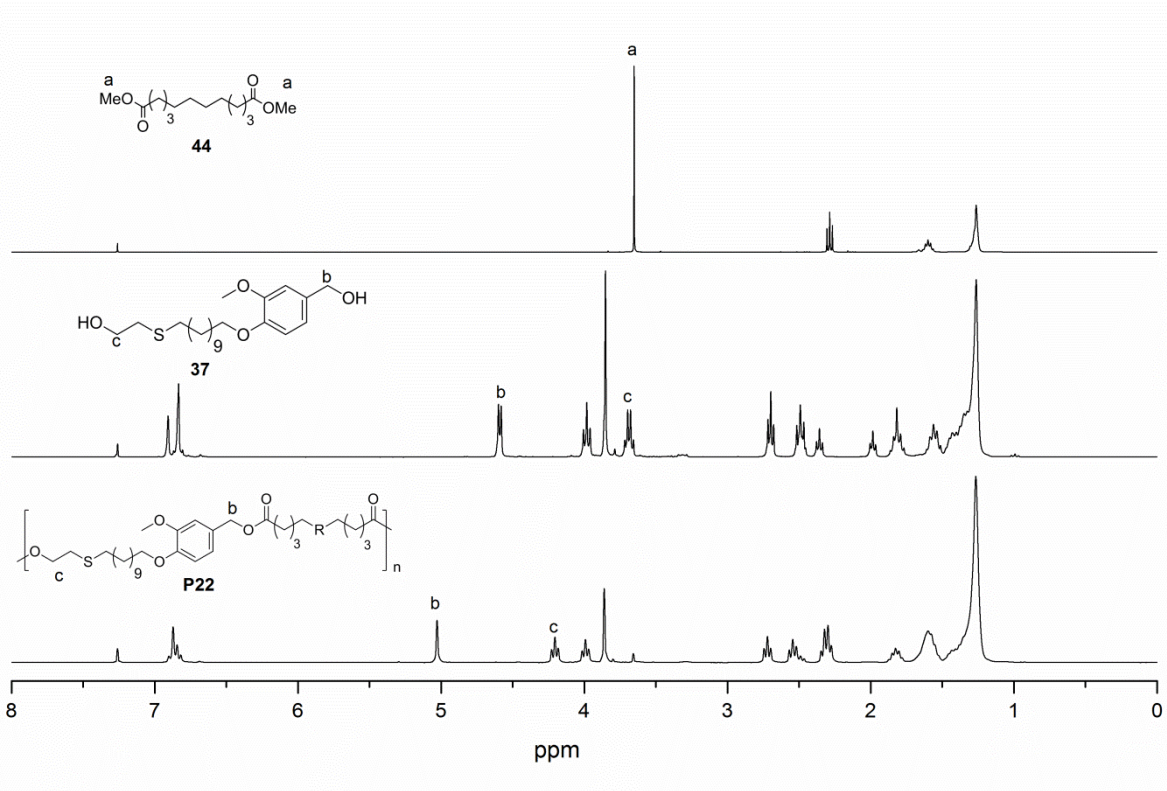


Figure 5.5. ^{1}H NMR spectra of diester **44** (top), diol **37** (middle) and its derived polymer **P22** (bottom).

DSC analysis of vanillin/fatty acid derived polymers (Table 5.3) displayed multiple melting transitions on the second heating scan with the exception of **P21**. However, annealing studies performed on **P22**, **P23**, and **P24** did not lead to single melting transitions, suggesting polymorphism.[134] The melting transition of the polymers increased, if longer diester were introduced. Finally, the T_m of saturated polyester **P23** is higher than its unsaturated counterpart **P24** due to the higher packing capability of the saturated alkyl chains and to the higher flexibility of the unsaturated ones, which results in the observed higher melting points.

Table 5.3. Analytical data of the synthesized polymers *via* polycondensation.

Polymer	Monomers	M_n (kDa)[a]	PDI[a]	*DP*	T_g (°C)[b]	T_m (°C)[b]
P21	**36**	16.6	1.81	43	-13.58[c]	77.81[c]
P22	**37** & **44**	15.8	1.71	27	-27.18[d]	15.79[d]; 34.75[d]
P23	**37** & **28**	17.3	1.75	25	-	46.21[e]; 60.99[e]
P24	**37** & **24**	16.2	1.78	23	-	18.49[f]; 32.71[f]

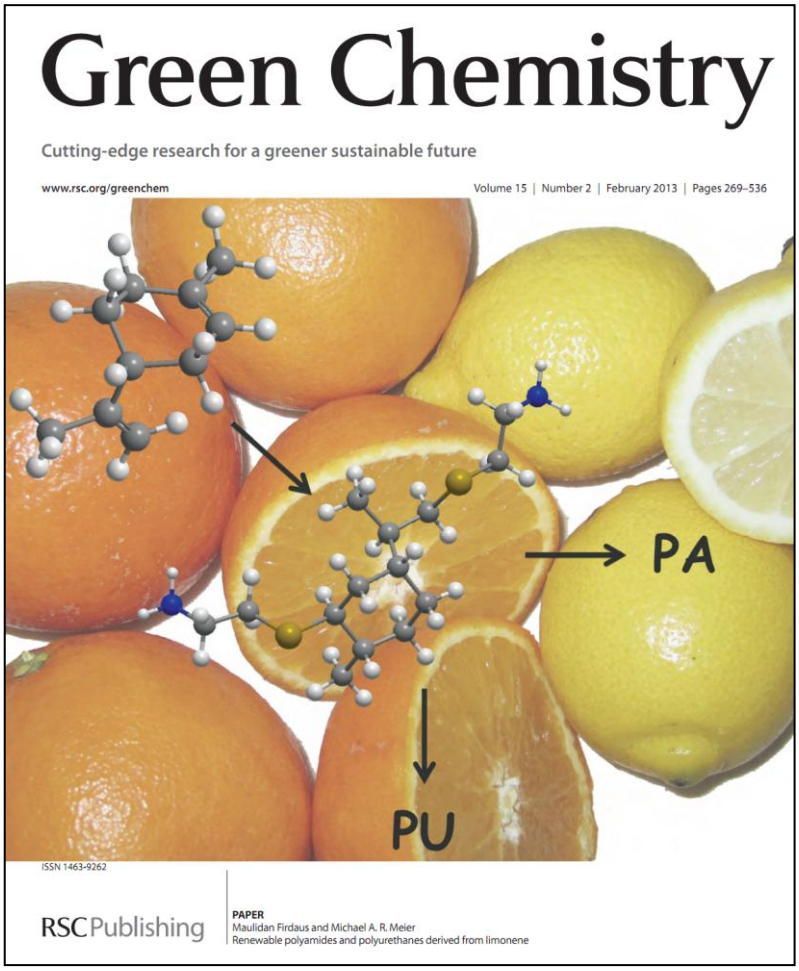
[a] GPC data of precipitated polymers, [b] DSC data recorded at 10 °C/min, [c] second heating scan, [d] 1 h annealing at 5 °C, [e] first heating scan, [f] 30 min. annealing at 10 °C.

5.3. Conclusion

In summary, a number of aromatic polyesters *via* three different pathways, ADMET, thiol-ene addition, and polycondensation were synthesized. These polymers were prepared from renewable feedstock (vanillin and fatty acids), which might eventually be used to substitute polymers from conventional petroleum-based monomers. ADMET polymerizations led to remarkably higher molecular weights (up to 49.6 kDa) than thiol-ene polyaddition and polycondensation. Finally, the synthesized polymers were characterized and their thermal properties were studied.

6

Renewable Polyamides and Polyurethanes Derived from Limonene[172]



6.1. Introduction

Polyamides and polyurethanes are among the most important polymeric materials, and since they display versatile properties, they can be used for many applications, such as tubings, footwear, industrial machinery, coatings and paints, elastic fibers, rigid insulations, soft flexible foam, medical devices, and many others.[173,174] Both polyamides and polyurethanes can be produced from petroleum resources or renewable feedstocks. However, due to the depletion of petroleum resources and their escalating prices as well as environmental impact, more research on alternative, preferably renewable, resources as well as the design of synthetic pathways that are more sustainable and environmentally benign, is urgently needed.

Terpenes, which are readily available in large scale, have a great potential to substitute currently used petrochemicals. A very common terpene, limonene, is an inexpensive natural compound and is considered as an economically feasible renewable feedstock. Limonene can, for instance, be obtained as a by-product of the citrus fruit industry.[138] As a result of citrus fruit processing and other minor contributors, more than 15 million tons of citrus waste accumulate annually.[17] The world production of limonene is estimated to be over 70,000 tons per year.[139] In addition to be abundant, the chemical structure, having two naturally occurring double bonds and a chiral center, and its ability to be readily obtained stereochemically pure, make limonene a very useful feedstock for the synthesis of new important chemicals for use as renewable solvent (replacing aromatic, mineral oils, etc.), fragrances, flavours, pharmaceuticals, and chiral intermediates, which can be further modified into diverse compounds *via* isomerization, addition, epoxidation, or hydration-dehydration reactions.[16,21]

Limonene has also been successfully incorporated into novel polymers as a bio-based monomer or monomer precursor. For example, Sharma and Srivastava reported on the radical copolymerization of limonene with styrene,[26] methyl methacrylate,[28] acrylonitrile,[27] *N*-vinyl pyrrolidone,[29] and other co-monomers.[12] Alternating polycarbonate copolymers were synthesized from (*R*)-limonene oxide and carbon dioxide using β-diiminate zinc complexes.[35] Aikins and Williams reported the radiation-induced cationic polymerization of α-pinene oxide, β-pinene oxide, and limonene oxide resulting in low molecular weight polyethers with high monomer conversions.[34] We recently described a simple approach to obtain a wide range of alcohol and/or ester functionalized renewable monomers from (*R*)-(+)- and (*S*)-(–)-limonene, as well as (–)-β-pinene *via* thiol-ene additions.[134] Polycondensation of the resulting monomers gave polyesters with molecular weights up to 25 kDa. However, only very few examples have been reported on employing limonene derivatives as a monomer for the synthesis of polyamides or polyurethanes. Polyamides based on 1,8-diamino-*p*-menthane, a readily available limonene derivative, have been synthesized *via* interfacial condensation with various diacid chlorides, which led to low molecular weight polymers.[175] Polyurethane-urea microcapsules utilizing limonene oil were synthesized by interfacial polymerization for textile applications.[176] However, in this report, limonene was used as active agent and not as monomer. More recently, Mülhaupt and co-workers developed a versatile route to linear as well as cross-linked terpene-based non-isocyanate poly(hydroxyurethanes) and prepolymers derived from a cyclic limonene dicarbonate monomer.[36]

Considering the olefin functional groups of limonene, introducing amine functional groups with a simple and efficient methodology would be highly desirable. In this

case, thiol-ene additions are a suitable tool since these reactions often display click reaction features and are a very useful approach for various transformations.[9,10] The high efficiency of thiol-ene additions allows the introduction of different functional groups, which can be employed to obtain polyesters,[88,134] polyurethanes,[84,85] polyamides,[177] and other polymers.[178,179] In a previous report, we successfully introduced an amine functionality to fatty acids *via* thiol-ene addition.[177] Since the introduction of an amine functional group to limonene *via* thiol-ene addition was not yet reported, we wanted to employ the same methodology to obtain limonene derived diamines, which are suitable AA-type monomers for polyamide synthesis.

With respect to polyurethane synthesis, a green route without using diisocyanates is preferable since diisocyanates are usually very toxic.[180] Several non-isocyanate routes for preparing polyurethanes have been reported including the use of di-*tert*-butyltricarbonate,[181] carbonylbiscaprolactam,[182] cyclocarbonates,[36,183] and carbamates.[130,184] Along with the idea to synthesize a diamine from limonene, the introduction of carbamate functional groups to this terpene would be also of great interest. To the best of our knowledge, the introduction of dicarbamate functions to limonene and subsequent preparation of non-isocyanate derived polyurethanes was not yet reported.

Thus, in this study, we synthesized new renewable diamine monomers from (*R*)-(+)- and (*S*)-(–)-limonene *via* thiol-ene addition. In order to obtain renewable polyamides, we copolymerized the synthesized diamines with different renewable diesters *via* polycondensation. Copolymers of Nylon 6,6 were also prepared to show the possible use of these new monomers as co-monomers for common Nylons. Moreover, the transformation of the resulting diamines into dicarbamates

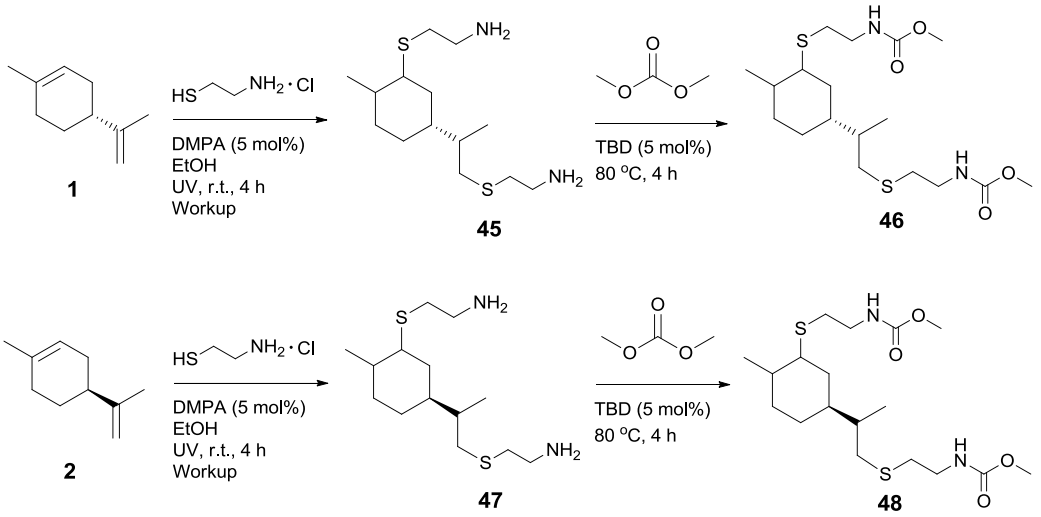
was accomplished *via* a phosgene-free route and the obtained AA-type monomers were employed in polycondensation with different diols in order to prepare a number of linear renewable polyurethanes *via* this non-isocyanate and phosgene-free route. All polymers were characterized by DSC and GPC to compare the molecular weights and thermal properties of the different polyamides and polyurethanes.

6.2. Results and Discussion

6.2.1. Syntheses of monomers

In **Chapter 4**, the reaction of both double bonds of limonene with hydroxyl or methyl ester functionalized thiols led to suitable monomers for polycondensation.[134] The reaction of limonene with functional thiols is attractive, since it can provide chiral monomers in a one-step procedure directly from a renewable feedstock. Taking this into account, we used an amine functionalized thiol, cysteamine hydrochloride, to perform a thiol-ene addition reaction employing (*R*)-(+)-limonene and its (*S*)-enantiomer as substrates. Instead of cysteamine in the pure form, the hydrochloride salt form was chosen since it is cheaper and gave better yields compared to the pure form in previous studies.[177] It was also reported that the salt form is more stable, which prevents side-reactions.[179,185] Initially, the thiol-ene addition was performed under solvent-free conditions at room temperature. Unfortunately, employing this method did not work here due to a lack of solubility of both reactants. In a previous report, the addition of cysteamine hydrochloride to fatty acid methyl esters worked well when the reactions were performed under UV irradiation.[177] Therefore, we

performed the addition of cysteamine hydrochloride to (*R*)-(+)-limonene (**1**) or (*S*)-(−)-limonene (**2**) under UV irradiation, using a small amount of ethanol as solvent, and DMPA as photoinitiator following the same previous method (Scheme 6.1).



Scheme 6.1. Synthesis of monomers from **1** and **2**.

First, the study was focused on optimizing the reaction conditions, in order to obtain complete conversion with small amounts of the thiol compound and DMPA. Initially, 3.0 equiv. of cysteamine (1.5 equiv. per double bond) and 0.01 equiv. DMPA was added to 1.0 equiv. of (*R*)-(+)-limonene. Based on ^{1}H NMR analyses, after 4 h reaction, 35% of the monoaddition product was detected and longer reaction time (24 h) did not lead to the diaddition product efficiently. Further attempts were carried out with an increased amount of DMPA and cysteamine to selectively obtain the diaddition product. When 0.02 equiv. of DMPA and 3.0 equiv. of cysteamine were used, the monoaddition product was still observed in rather large amounts of 21%, even after 24 hours of reaction time. However, when DMPA was increased up to 0.05 equiv. and 3.0 or 6.0 equiv. of cysteamine were used,

complete conversion to the final product was obtained in only 4 hours at ambient temperature. Based on these studies, we concluded that around 3.0 equiv. of cysteamine and 0.05 equiv. of DMPA provided the best results of the thiol-ene addition reaction employing the least of the thiol-compound and photoinitiator to obtain the diamine functional limonene in high yields and selectivity. Purification using column chromatography yielded the pure expected products in 84 and 81% for the (*R*)- and (*S*)-isomer, respectively.

The limonenes used in this study are pure enantiomers. The additions of molecules to the endocyclic and exocyclic double bonds of limonenes generate three additional stereogenic centers. Thus, eight possible diastereomers can be formed in these thiol-ene addition reactions. However, in our previous report, diaddition of thiols to the double bonds of limonenes generated products consisting mainly of a mixture of four diastereomers.[134] Thus, due to the high number of possible diastereomers, complex ^{1}H and ^{13}C NMR spectra of the products were obtained. Two-dimensional NMR experiments (COSY, HSQC, and HMBC) were then necessary for structure elucidation. The complete transformation was evidenced by the ^{1}H NMR spectrum of **47**, at which no exocyclic and endocyclic double bond signals were observed and the new peaks at 2.86–2.75 (H^{b}) and 2.61–2.50 (H^{a}) ppm corresponding to the protons at the α- and β-positions to thioether appeared (Figure 6.1B). The analysis of the ^{13}C NMR spectra confirmed the presence of diastereomers. As a representative example, ^{13}C NMR spectra of **47** (Figure 6.1A), showed four different signals of C^{d} (two peaks with higher intensities refer to major diastereomers and two peaks with lower intensities merge as one refer to minor diastereomers) in the region from 53 ppm to 50 ppm, indicating that the product mainly consists of a mixture of four diastereomers.

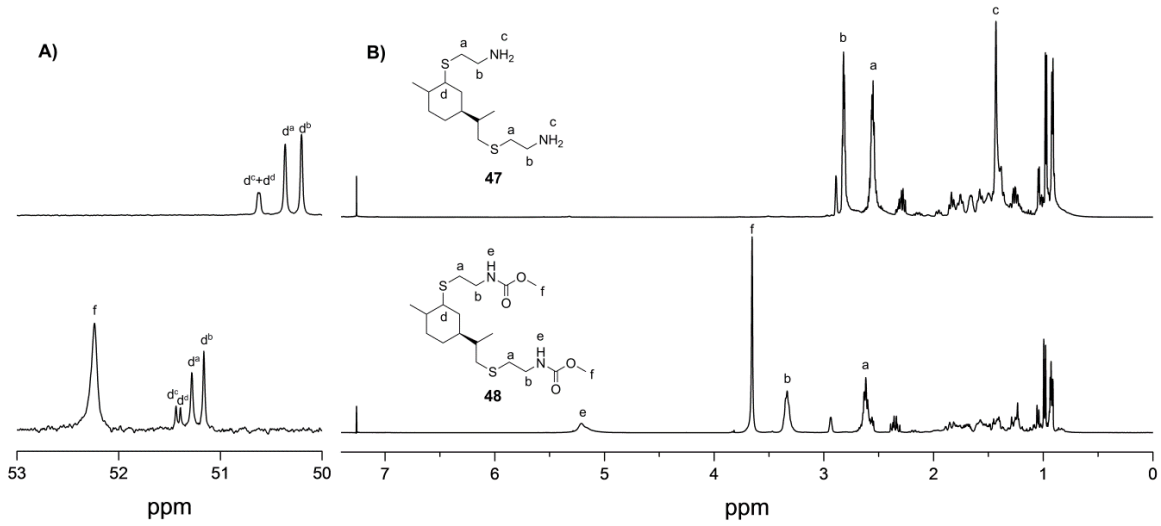


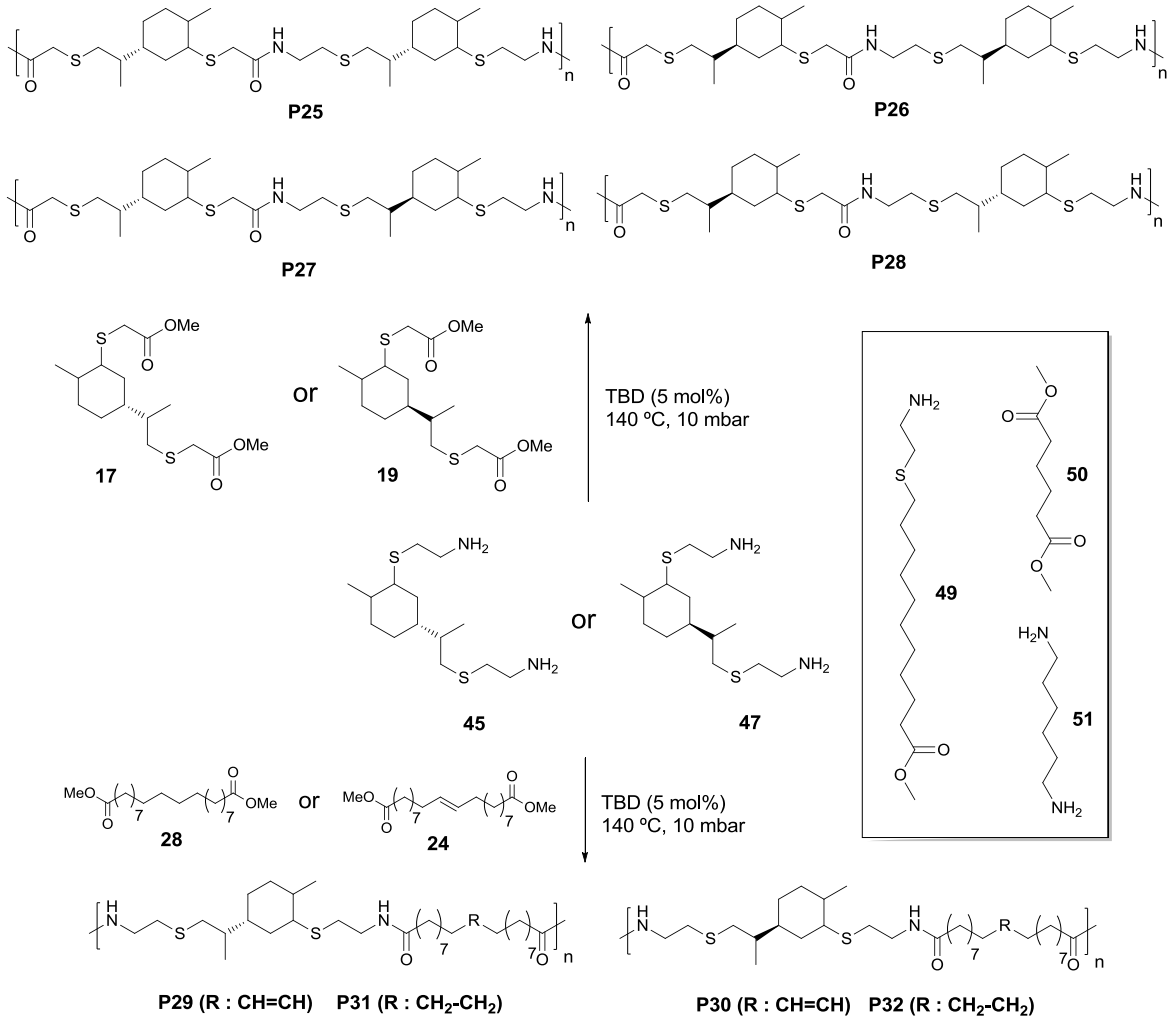
Figure 6.1. A) ^{13}C NMR (region 53–50 ppm) and B) ^{1}H NMR of **47** (top) and **48** (bottom).

Having the diamine compounds derived from (*R*)-(+)-limonene and (*S*)-(–)-limonene, further transformation was performed in order to introduce carbamate functional groups. With regard to a sustainable method, the preparation of dicarbamates from non-toxic reagents with low price and environmentally benign catalyst is highly desirable. Instead of using toxic phosgene or chloroformates, the use of dialkyl carbonate represents a good alternative, because the only by-product of this reaction is an alcohol that can be easily removed from the reaction mixture.[186] For the synthesis of carbamates from dialkyl carbonates and amines, the cyclic guanidine TBD proved to be an alternative potent organocatalyst[187]. Although several metal catalysts such as $Yb(OTf)_3$ hydrate,[186] $Zn(OAc)_2$,[188] and $Zn(OAc)_2$/activated carbon[189] have been successfully used in the synthesis of carbamates, such metal catalysts may cause problems in product separation or are environmentally hazardous and toxic. Thus, methoxycarbonylation of **45** and **47** with dimethyl carbonate were performed using TBD as catalyst (Scheme 6.1). The reaction was carried out at 80 °C for 4 h under solvent-free conditions and

dicarbamates **46** and **48** were obtained in good yields of 82 and 79%, respectively. After purification using column chromatography, the ^{1}H NMR spectra of **48** (Figure 6.1B) reveals the formation of the expected carbamate. This can be followed by disappearance of the signal at around 1.43 ppm corresponding to the protons from the amine functionality (H^{c}) and the two newly emerged signals at 5.39–4.93 and 3.65 ppm corresponding to NH (H^{e}) and methoxy carbamate (H^{f}), respectively. Since the reaction did not change the chiralilty of the compound, based on ^{13}C NMR analysis, a mixture of four diastereomers of **48** (C^{d}) was still observed (Figure 6.1A).

6.2.2. Synthesis of polyamides

The diamines obtained by double addition of cysteamine hydrocholoride to (*R*)-(+)-limonene or (*S*)-(–)-limonene were subsequently polymerized in order to obtain renewable polyamides (Scheme 6.2). **45** and **47** monomers were copolymerized with the monomers **17** and **19** (terpene-derived diester) and **24** and **28** (fatty acid-derived diester), which are renewable diester compounds that were already prepared in our previous studies.[134] Moreover, the monomers prepared within this report were also copolymerized with **49** and/or **50** and **51** to study how the thermal properties of Nylon 6,6 could be tuned when copolymerized with the renewable monomers bearing cycloaliphatic moieties. The cyclic guanidine TBD was chosen as organocatalyst, because it was reported to successfully catalyze the synthesis of amides from esters and primary amines,[121] and based on our experience for the synthesis of polyamides.[128,177] All polymerizations were carried out without solvent and under continuous vacuum (~10 mbar) to efficiently remove methanol.



Scheme 6.2. Synthesis of (*R*)-(+)- and (*S*)-(–)-limonene based polyamides and the structures of the other monomers utilized (**49**, **50**, **51**).

We started our investigation by copolymerizing **45** and **47** with **17** and **19** with 0.05 equiv. of TBD per ester group at 120, 140, and 160 °C for 24 h. Based on GPC analysis, the best result was obtained at 140 °C. Thus, the following polymerizations were performed using these conditions. The polyamides obtained from the combinations **45** or **47** and **17** or **19** exhibited molecular weights (M_n) between 6500–8000 Da (Table 6.1).

Table 6.1. Analytical data of the synthesized polyamides.

Polymer	M1 (equiv.)	M2 (equiv.)	M3 (equiv.)	M_n (Da)[a]	PDI[a]	T_m (°C)[b]	T_g (°C)[b]	Polymer Type
P25	**45** (1)	**17** (1)		6430	2.10		41.4[c]	Limonene
P26	**47** (1)	**19** (1)		7870	1.97		41.5[c]	
P27	**45** (1)	**19** (1)		7430	2.28		41.5[c]	
P28	**47** (1)	**17** (1)		6740	1.98		41.5[c]	
P29	**45** (1)	**24** (1)		9330	1.96	57.7; 84.0[d]		Limonene/ Linier diester
P30	**47** (1)	**24** (1)		10630	1.95	57.6; 83.4[d]		
P31	**45** (1)	**28** (1)		5500	1.97	102.0[e]		
P32	**47** (1)	**28** (1)		5870	1.86	101.5[e]		
P33	**45** (1)	**50** (2)	**51** (1)	8960	1.97	150–215[f]	40.9[f]	Limonene/ Nylon 6,6
P34	**47** (1)	**50** (2)	**51** (1)	9150	1.69	150–215[f]	42.4[f]	
P35	**47** (3)	**50** (4)	**51** (1)	12020	1.46	120–170[g]	41.9[g]	
P36	**47** (1)	**50** (4)	**51** (3)	9850	1.46	204–238[h]	41.7[h]	
P37	**45** (1)	**50** (1)	**49** (2)	9480	2.35		5.9[c]	Limonene/ Fatty acid
P38	**47** (1)	**50** (1)	**49** (2)	10200	2.03		7.7[c]	

[a] GPC data of precipitated polymers, [b] DSC data recorded at 10 °C/min, [c] second heating scan, [d] 0.5 h annealing at 45 °C, [e] 1 h annealing at 90 °C, [f] 0.5 h annealing at 150 °C, [g] 3 h annealing at 115 °C, [h] 1 h annealing at 200 °C.

The polymerization of the **17** and **19** is catalyzed less efficiently by TBD, most likely because of the steric hindrance caused by the cycloaliphatic ring. Thus, rather low molecular weight polyamides were obtained in this case. The introduction of long and flexible alkyl chains was thus investigated in order to decrease the steric hindrance and to obtain higher molecular weight polymers. Therefore, we copolymerized **45** and **47** with **24** and **28** (Table 6.1, entries **P29–P32**), which are the linear diester monomers synthesized from the self-metathesis of methyl 10-undecenoate and its hydrogenation product, respectively. It is worth to point out that these diesters are castor oil derived, and thus, the polymers obtained thereof are also renewable. GPC analysis showed that **P29** and **P30**

exhibited molecular weights of about 9300 and 10600 Da, which are higher than for **P25–28**, clearly indicating that the lower molecular weights do not result from the lower reactivity of **45** and **47**, but are due to steric hindrance. However, **P31** and **P32** exhibited much lower molecular weights, i.e. 5500 and 5870 Da, respectively, most probably because of the fact that the saturated C-20 linear structure of **28** gives rise to very high crystallinity that hinders the further growth of the chains in the polymerization conditions. It should be noted that **P29** and **P30** are unsaturated stereospecific polyamides, which can be further modified e.g. by a grafting-to approach *via* thiol-ene addition reaction to synthesize tailor-made polymers.[87]

These polymerizations were also investigated using ^{1}H NMR and confirmed the expected structure of the polymers. As an example for this investigation, ^{1}H NMR spectra of monomers **47** and **24** and the thereof derived polymer, **P30** (Figure 6.2), showed almost quantitative disappearance of the signal at 3.66 and at 1.43 ppm corresponding to the methyl ester (H^a) and the amine (H^c), respectively, which were transformed to the backbone amide link (H^d). Since most of the polymers are not soluble in conventional solvents, the NMR analyses of these polymers were conducted using a $CDCl_3$/TFAA solvent mixture. While TFAA was added dropwise under continuous shaking, a homogenous solution was obtained and the polymers were readily dissolved, because of the *N*-acylation of the amide groups, which leads to a break-up of the hydrogen bonding.[190] Therefore, the NH group could not anymore be observed in the ^{1}H NMR spectra.

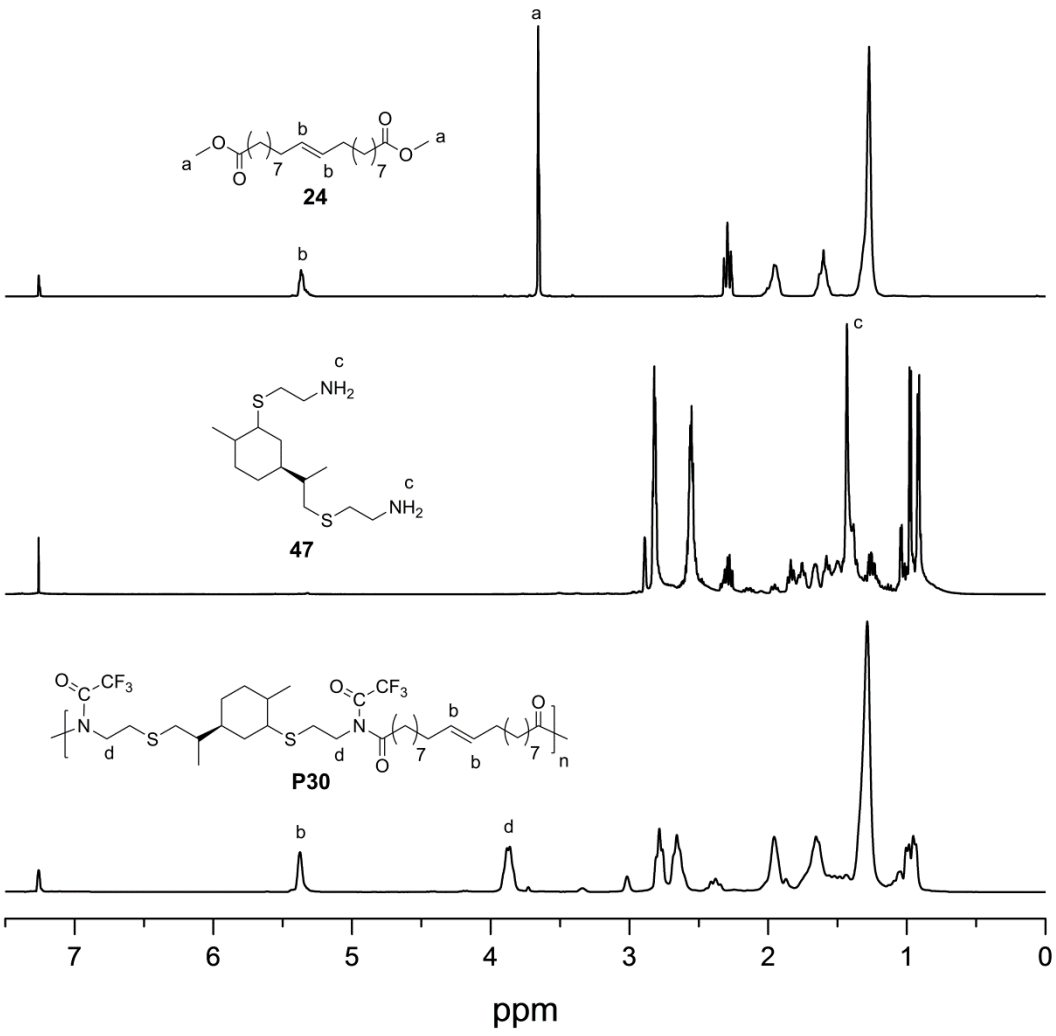


Figure 6.2. ^{1}H NMR spectra of diester **24** (top), diamine **47** (middle) and their derived polymer **P30** (bottom).

Based on our previous report, copolymerization of **50** and **51** for Nylon 6,6 formation worked well with TBD-catalyzed polymerization.[177] Therefore, copolymerizations of the monomer **45** and **47** with Nylon 6,6 were also performed to see if the properties of Nylon 6,6 can be modified with a monomer bearing a cycloaliphatic ring (see entries **P33–36**). It can be seen that increasing the ratio of diamine derived from limonene results in an increase of molecular weight. In order to show the diversity of the polyamides that can be obtained from fatty acids and limonene derivatives, we also successfully copolymerized **45** and **47** with **49**

in the presence of **50** to balance the functional group stoichiometry. GPC analysis of **P37** and **P38** revealed molecular weights about 9500 and 10200 Da and a polydispersity of 2.35 and 2.03, respectively. Although somewhat low molecular weights were obtained in some cases, this result shows that cysteamine-functionalized monomers derived from limonene can be used for TBD-catalyzed polyamide synthesis. Depending on the used co-monomer higher molecular weights could be achieved, revealing the significant impact of steric hindrance on the polymerization behaviour. Most importantly however, the thermal properties, also of commercially available polyamides, can be tuned by choosing appropriate co-monomer ratios, as will be discussed below.

The thermal properties of the synthesized polyamides were analyzed by DSC. Table 6.1 summarizes the thermal properties of these polymerizations and Figure 6.3 shows DSC thermograms of some of the synthesized polymers. Because of the cyclic moieties, terpene-derived polyamides showed completely different properties compared to conventional polyamides. The cycloaliphatic bulky groups prevented intermolecular interactions and the polyamides prepared thereof were amorphous polymers that exhibited a T_g value of about 41.5 °C, independent of the composition. The combinations of **45** or **47** and **17** or **19** (compare **P25–28**) did not show any effect on the thermal behavior of the polymers. This result reveals that the chirality of the monomers used does not have an effect on the thermal properties of the derived polyamides. However, when terpenes are copolymerized with fatty acids or Nylon 6,6, significant changes of the thermal properties are observed and a wide range of thermal characteristics, depending on the structure, can be obtained. For example, when **45** and **47** are polymerized with **24** and **28**, semicrystalline polyamides were obtained. Interestingly, the copolymers from **24**

exhibited two melting endotherms, i.e. $T_{m\text{-}1}$ = 57.7 and 57.6 °C, and $T_{m\text{-}2}$ = 84.0 and 83.4 °C for **P29** and **P30**, respectively. Nonetheless, when **28** instead of **24** was used, an increase of more than 20 degrees in the melting temperature and a single endotherm, which is about 102 °C for **P31** and 101.5 °C for **P32**, was obtained after an annealing pre-treatment at 90 °C for both **P31** and **P32**. Thus, the higher packing capability of the saturated alkyl chains and the higher flexibility of the unsaturated ones caused higher melting points on polyamides bearing saturated chain.

In case of Nylon 6,6 copolymers, different ratios of **45** or **47** were incorporated into Nylon 6,6 (compare **P33–36**) in order to see if their thermal properties can be tuned. The DSC thermograms of all these copolymers displayed clear T_gs in the range of 40.9–42.4 °C. However, concerning the T_m values of the polymers, somewhat multiple endothermic peaks in broad range with lack of a clear baseline were obtained even after annealing. However, decreasing the **47** ratio to the Nylon 6,6 would increase the melting transition (compare **P35** and **P36** in Figure 6.3). In **P35** it seems that the crystallization of Nylon 6,6 is completely changed (and hindered) due to the steric bulk, whereas in **P36** with higher content of Nylon 6,6, a higher melting range is observed; some part of this polymer behaves as copolymer with lower melting point, whereas most of the polymer still behaves as Nylon 6,6, with melting at ~230 °C. These results clearly show that the copolymerisation of limonene derived monomers can be used to adjust the properties of commercial polyamides.

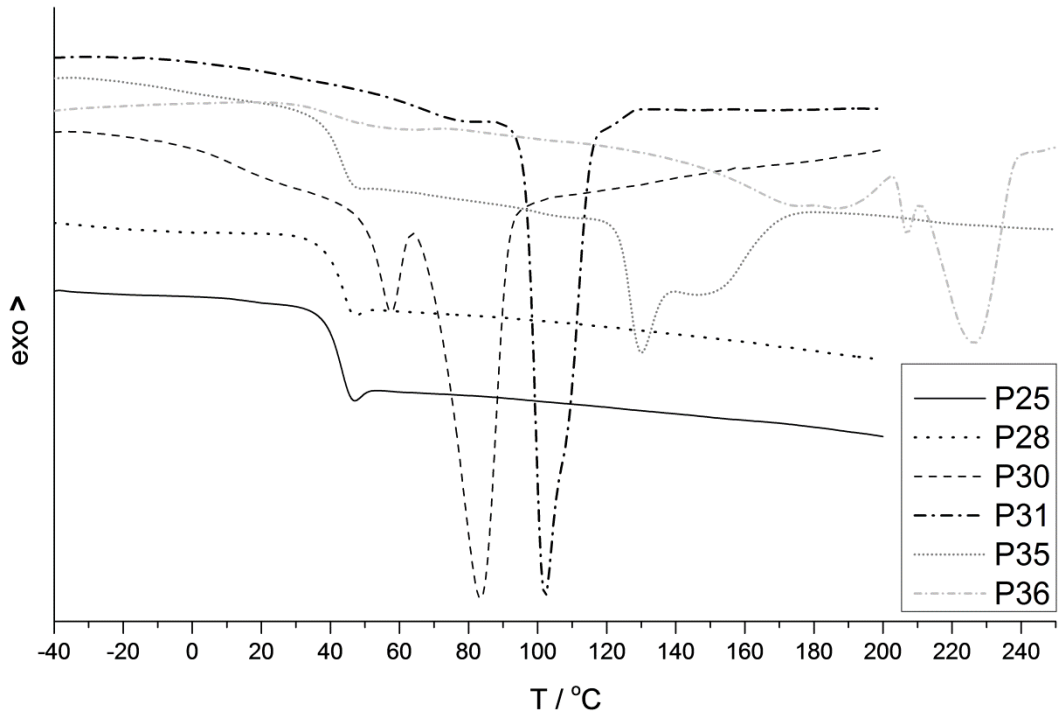
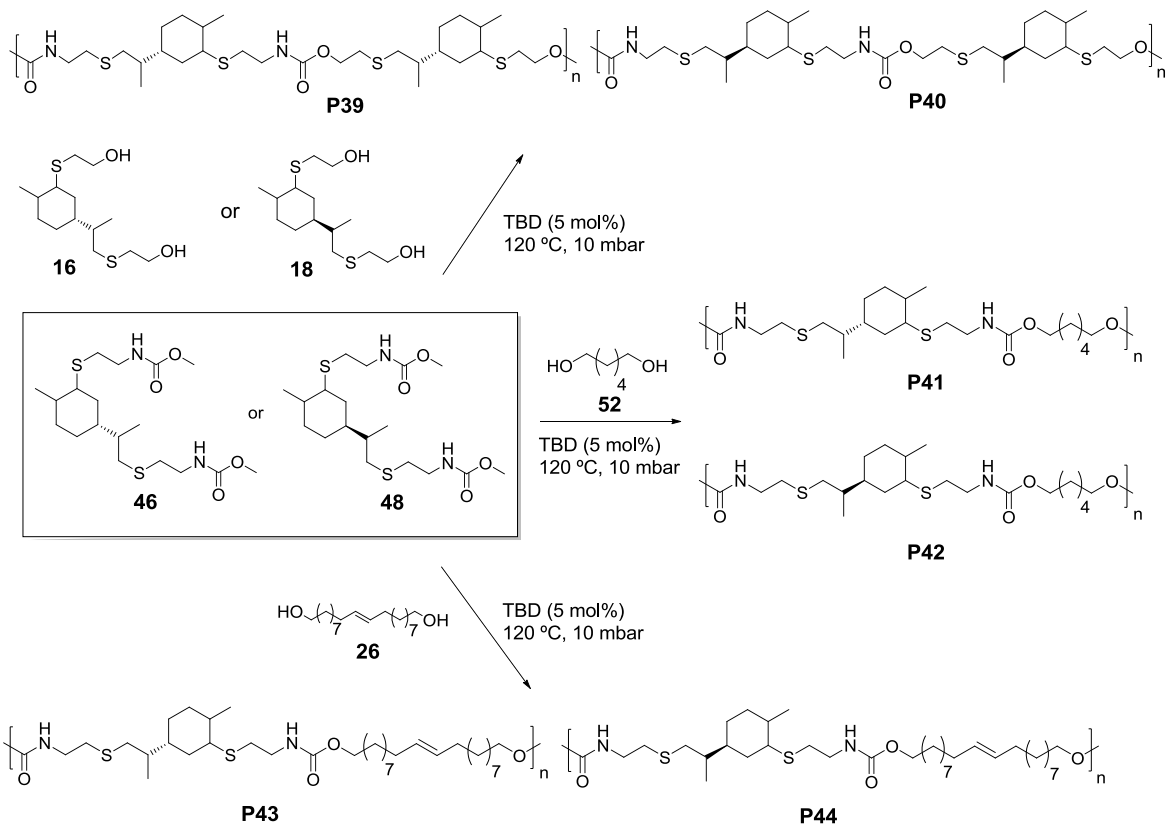


Figure 6.3. DSC traces of some synthesized polyamides (see Table 6.1 for experimental conditions).

6.2.3. Synthesis of polyurethanes

Besides our study of limonene based polyamides, we had a great interest in renewable polyurethanes synthesized *via* an isocyanate-free methodology. Thus, the dicarbamate AA-type monomers (**46** & **48)** derived from limonene were employed in a transesterification like polymerization with selected diols. Different renewable diols, which we prepared in our previous study [i.e. **16** & **18** (limonene-derived), **26** (fatty acid-derived)],[134] and commercial diol **52** were copolymerized with monomers **46** & **48** (Scheme 6.3). All polymerizations were carried out using TBD as catalyst, without solvent, and under continuous vacuum (~10 mbar) for an efficient methanol removal. Noteworthy, along with the use of renewable monomers, the polyurethanes were obtained *via* an isocyanate-free route.



Scheme 6.3. Synthesis of (*R*)-(+)- and (*S*)-(–)-limonene based polyurethanes.

Initially, optimization reactions were carried out for the polymerizations of **46** or **48** with **16** or **18** and the best results were obtained at 120 °C with 0.05 equiv. (related to carbamate groups) of TBD, the conditions that were used for all further polymerization reactions. Polyurethanes **P39** and **P40** were obtained after 16 h with molecular weights of 7900 and 6150 Da, respectively. Performing the reaction for longer reaction times (24 h) did not lead to higher molecular weights. Thus, under the same reaction conditions, the polymerizations were performed using long chain diols **52** and **26**. As expected and similar to the results discussed above for polyamide synthesis, **P41**–**44** were obtained with higher molecular weights in the range of 8660–12600 Da (Table 6.2, Figure 6.4). ^{1}H NMR analyses of the synthesized polymers revealed the successful polymerizations. As a representative example (Figure 6.5), the ^{1}H NMR spectra of dicarbamate **48**, diol **26** and the thereof derived polymer **P44**,

showed almost complete disappearance of the singlet peak at 3.65 ppm corresponding to the methyl carbamate (H^b) transformed to the backbone urethane link (H^e).

Table 6.2. Analytic data of the synthesized polyurethanes.

Polymer (dicarbamate/diol)	M_n (Da)[a]	PDI[a]	T_m (°C)[b]	T_g (°C)[b]
P39 (**46** / **16**)	7900	1.87		18.5[c]
P40 (**48** / **18**)	6150	1.79		18.3[c]
P41 (**46** / **52**)	8660	2.15		15.9[c]
P42 (**48** / **52**)	9480	2.03		14.6[c]
P43 (**46** / **26**)	11620	1.81	69.2[d]	na[f]
P44 (**48** / **26**)	12600	1.84	62.9[e]	na[f]

[a] GPC data of precipitated polymers, [b] DSC data recorded at 10 °C/min, [c] second heating scan, [d] 1 h annealing at 50 °C, [e] 1 h annealing at 55 °C, [f] T_g not observable by DSC.

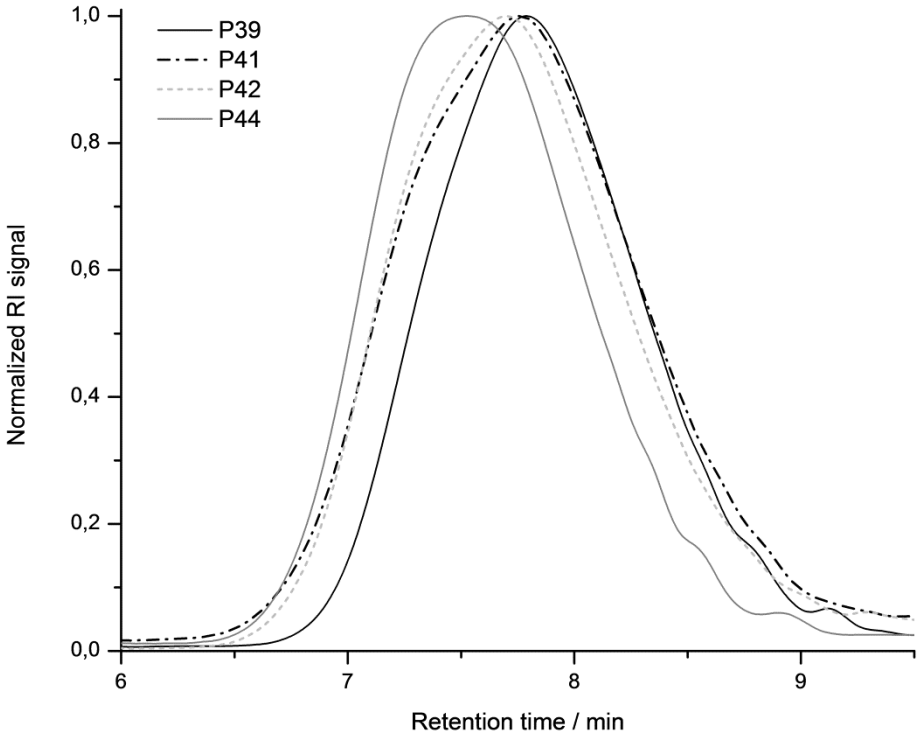


Figure 6.4. GPC traces of selected synthesized polyurethanes.

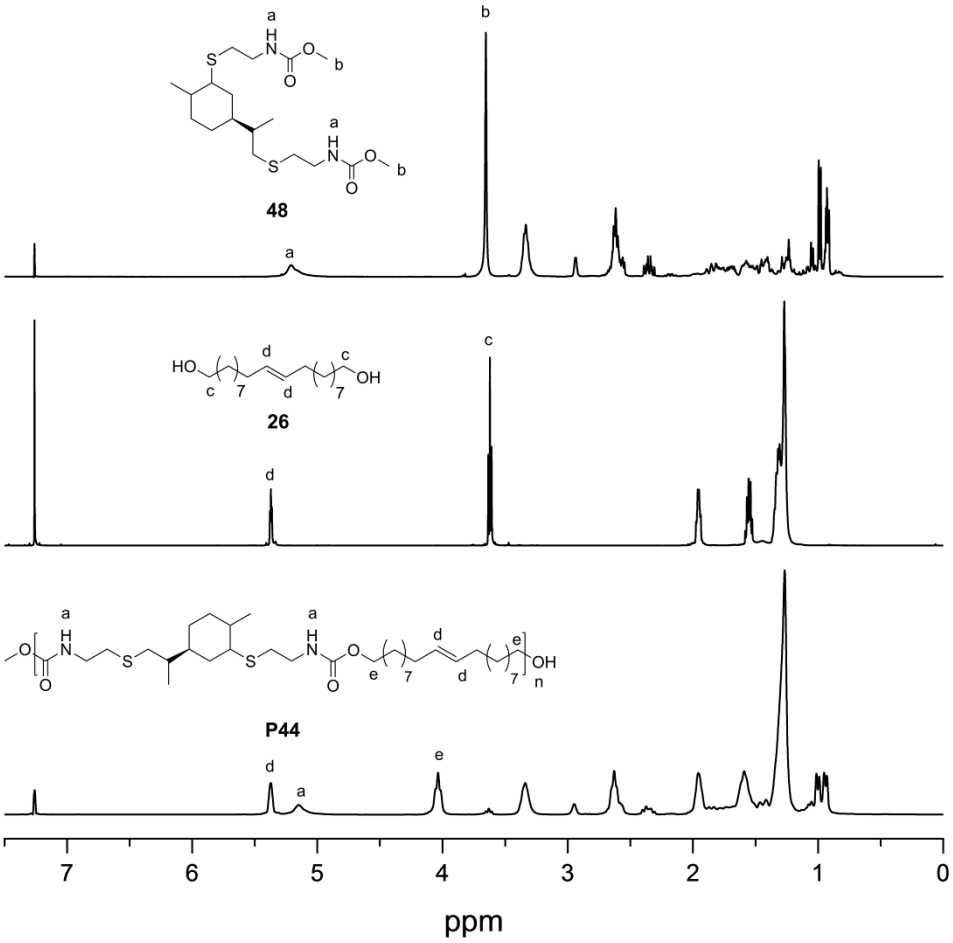


Figure 6.5. ^{1}H NMR spectra of dicarbamate **48** (top), diol **26** (middle) and their derived polymer **P44** (bottom).

The prepared polyurethanes (**P39–42**) consist of bulky cycloaliphatic units linked with very short segments, which prevent crystallization and should lead to characteristic thermal properties. DSC analyses display amorphous structures for all of them (see Figure 6.6) with glass transition temperatures in the range of 14.6–18.5 °C. However, when the long chain diol **26** was copolymerized with **46** or **48**, crystallization occurred. On the second heating scan, the synthesized polyurethanes (**P43** and **P44**) displayed multiple melting transitions. Thus, annealing was necessary to verify whether these multiple melting transitions were due to the occurrence of metastable crystalline phases or actual crystalline

structures. After an annealing pre-treatment, DSC analysis exhibited melting transition at 69.2 and 62.9 °C for **P43** and **P44**, respectively. In this study, the T_g could not be observed for these two polymers by DSC.

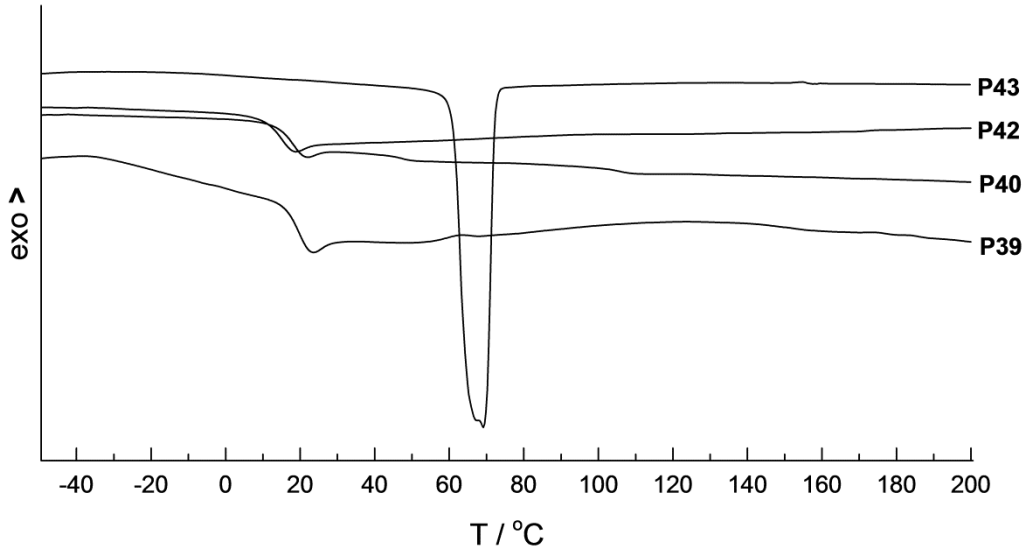


Figure 6.6. DSC traces of some synthesized polyurethanes (see Table 6.2 for experimental conditions).

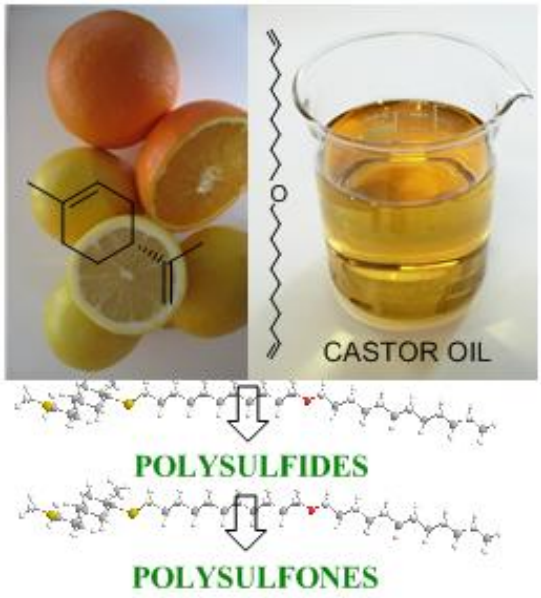
6.3. Conclusion

In summary, we have shown that thiol-ene additions offer a versatile and effective way to introduce primary amine functional groups into (*R*)-(+)- and (*S*)-(–)-limonene to produce new renewable monomers for polyamides synthesis. The GPC results and intensive DSC analysis of the resulting polymers revealed that renewable polyamides from amorphous to high-melting semicrystalline polymers with molecular weights up to 12 kDa can be obtained *via* the selective combination of the abovementioned monomers. Moreover, Nylon 6,6 copolymers were successfully prepared. In addition, the synthesized diamines derived from limonenes have been efficiently transformed into dicarbamates *via* a phosgene-free route, and subsequently employed in polycondensations with several

renewable diols. A number of linear renewable polyurethanes were obtained *via* an isocyanates-free route with molecular weights up to 12.6 kDa. Finally, DSC analysis of these polyurethanes showed amorphous to semicrystalline structures. Overall, the great potential of these renewable resources for polyamide and polyurethane synthesis was demonstrated.

7

Renewable Co-Polymers Derived from Limonene and Fatty Acid Derivatives *



* In collaboration with Prof. Jürgen O. Metzger (University of Oldenburg, Germany) and co-workers, some part of this chapter is currently being prepared for publication.

7.1. Introduction

The limited availability of petroleum resources and their escalating prices led to an increased interest in the development of new platform chemicals from renewable resources. From the standpoint of cost and availability, (*R*)-(+)-limonene (**1**) is among valuable renewable raw materials of great promise that might be utilized for polymer synthesis. Considering the chemical structure bearing two double bonds, **1** can be transformed and derivatized into novel polymers such as polyalkylene sulfides,[107] polyethers,[34] polycarbonates,[35] polyesters,[134] polyamides,[172] polyurethanes,[36,172] and other polymers.[12,26–30] Potential application of **1** is still limited and not significant. However, **1** is a common daily life component for cleaning and has been mainly used as a solvent and as a fragrance.[138] Therefore, transformation of **1** with simple and efficient processes would be highly desirable.

As already discussed in **Chapter 3.1**, thiol-ene reactions are considered as a versatile and widely applicable tool in polymer science. Thiol-ene reactions have recently been used to prepare renewable monomers,[88,134] to polymerize dithiols and diolefins,[153] to modify the side chains of polymers,[98] and many others.[191,192] However, only very few example have been reported on thiol-ene polyaddition employing **1** as olefinic substrate.

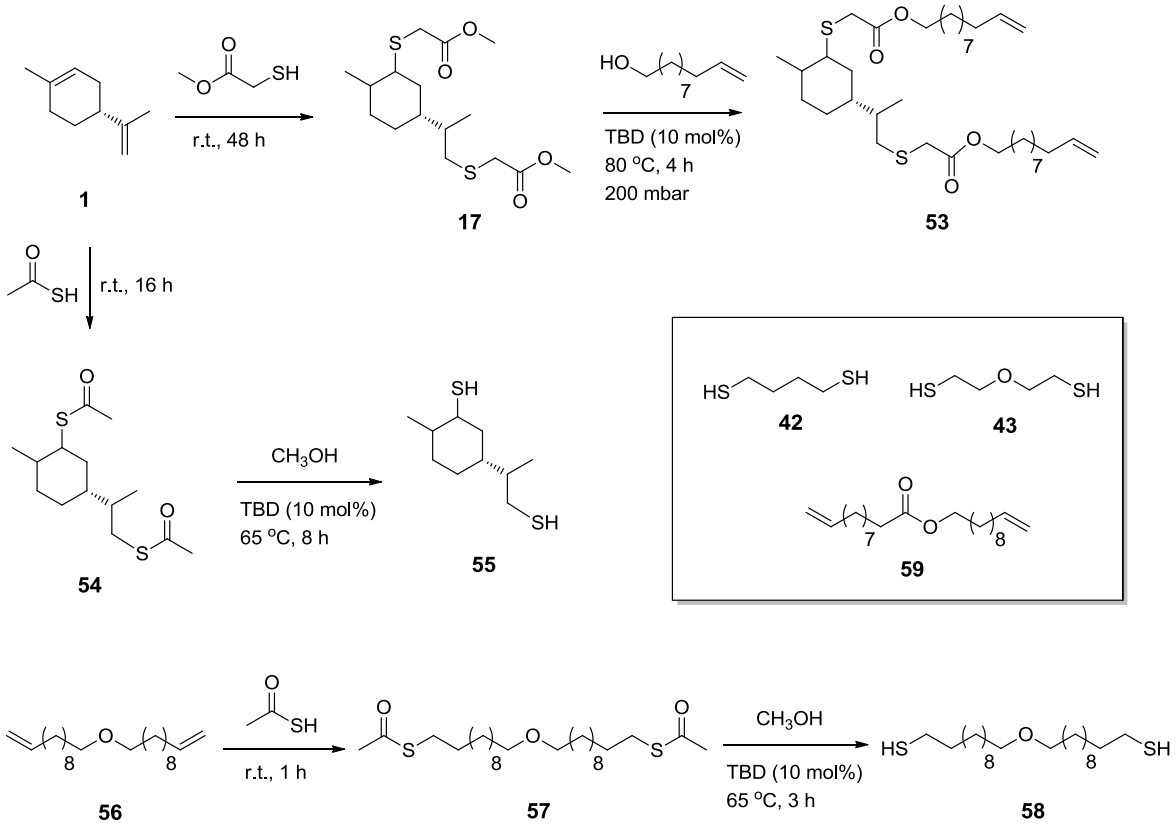
In this chapter, **1** and different fatty acid derivatives were used to prepare renewable dithiols and diolefins, which were then employed in thiol-ene polymerizations. The combination of **1**, bearing a cycloaliphatic ring, and fatty acid derived monomers, containing linier flexible structure, might open an access to new polymers derived from these renewable resources. In collaboration with Metzger and co-workers, one of the monomers utilized in this study, 11-(undec-

10-en-1-yloxy)undec-1-ene (**56**), was prepared by this group *via* catalytic reduction of undec-10-enyl undec-10-enoate (**59**). Moreover, some of the synthesized polymers were finally oxidized to convert the sulfide ether groups into sulfone linkages. Additionally, the thermal properties of the synthesized polymers were studied. Within this contribution, we present an efficient and sustainable entry to renewable raw materials derived from **1**. The presented results offer new insights into the derivatization of **1** and constitute an important completion of our recently reported results.[134,172]

7.2. Results and Discussion

7.2.1. Syntheses of monomers

We started our investigation by synthesizing our dithiol monomers from **1** and **56** as a model compound (Scheme 7.1). Although the synthesis of dithiol **55** from **1,** was already reported by Marvel and Olson in 1950,[107] until now a detailed characterization of **55** by MS and/or NMR was not yet reported. Dithiol **55** was prepared by thiol-ene addition of thioacetic acid to **1** under UV irradiation followed by basic hydrolysis of the resulting thioester **54**. In this study, we slightly modified the already reported methodology and performed further investigations in order to determine the chemical structure of **55**.



Scheme 7.1. Synthesis of monomers from **1** and fatty acid derivative, and the structures of the other monomers utilized (**42**, **43**, **59**).

First, the thiol-ene addition of thioacetic acid to **1** or **56** was performed at room temperature under solvent-free conditions without any initiator. Full conversion of **1** was achieved after 16 h, which led to the formation of the dithioester **54**. In case of the addition of thioacetic acid to **56**, the reaction proceeds rather fast, forming the white solid of **57** after 1 h indicating the completion of the reaction, which was also confirmed by NMR spectroscopy. The resulting dithioesters were then cleaved to obtain the corresponding dithiol. The reactions were performed under Argon atmosphere to avoid the formation of disulfides. Initially, basic hydrolysis of **54** using a sodium hydroxide solution or acid catalyzed saponification was performed in order to cleave the dithioester as reported by Marvel and Olson.[107] However, these

procedures required longer reaction times (48 h), thus further attempts were carried out in order to find a suitable method to significantly decrease the reaction time. As an alternative the cyclic guanidine base catalyst, TBD, in methanol was examined. Thus, complete conversion was reached after 16 h. The excess of methanol and the formed methyl acetate can be easily removed under reduced pressure. After purification by column chromatography, a colorless liquid of **55** was obtained in high yield (90%). Employing the same method, the thioester cleavage of **57** was achieved in only 3 h. The product was purified by recrystallization in methanol to afford a white solid **58** in 93% yield.

Complete transformation of the diolefins to dithiols was evidenced by ^{1}H NMR analyses. As a representative example, the ^{1}H NMR of **58** (Figure 7.1) showed no double bond signals and a new signal at 2.52 ppm (H^{c}) corresponding to a methylene proton next to –SH group appeared. When thioacetic acid is added to the double bonds of **1**, eight possible diastereomers can be formed. Due to the presence of diastereomers, complex ^{1}H NMR spectra of **55** (Figure 5.1) were obtained. Conventional DEPT and two-dimensional NMR (COSY, HSQC, and HMBC) experiments were employed for the determination of the exact structure. The occurrence of diastereomers, which could not be isolated by column chromatography, can be observed by ^{13}C NMR. Figure 5.1 (in the rectangle) depicted ^{13}C NMR spectra of **55** in the region from 21 ppm to 20 ppm, in which four different signals of C^{a} are observed indicating that the product mainly consists of a mixture of four diastereomers. Two peaks with higher intensities refer to major diastereomers and two peaks with lower intensities refer to the minor ones.

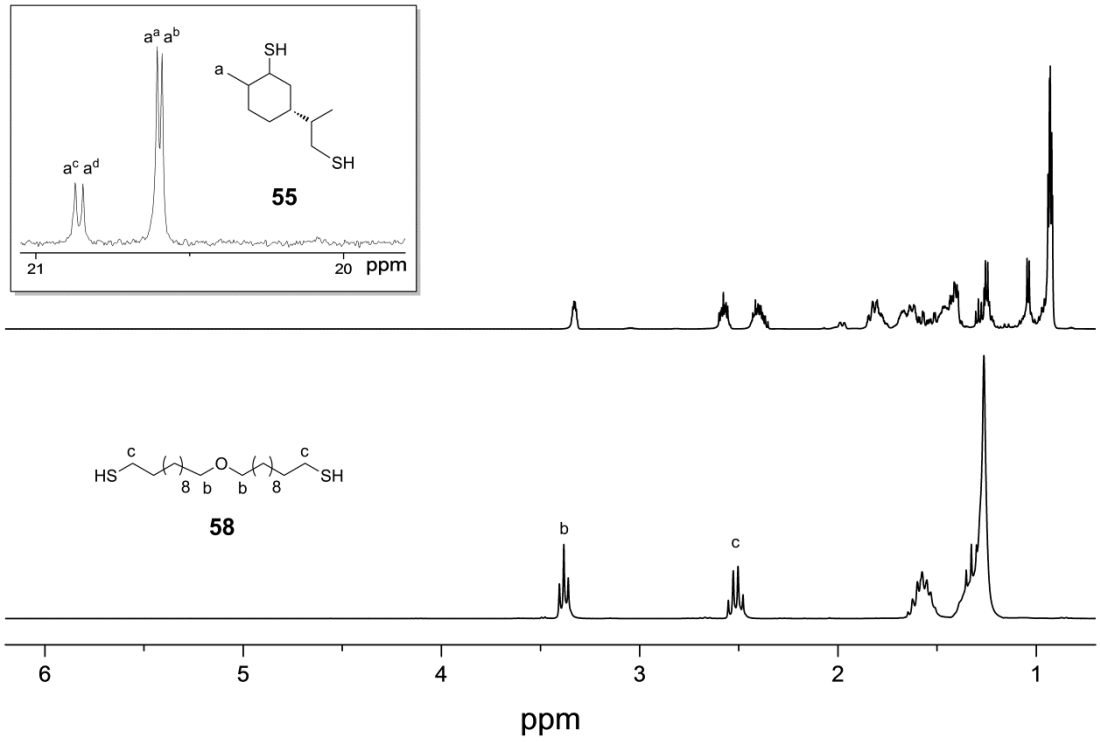


Figure 7.1. ^{1}H NMR of **55** (top) and **58** (bottom), and ^{13}C NMR spectra of **55** (in the rectangle).

Both the synthesized dithiols are renewable and suitable substrates for thiol-ene polymerization. Also, due to the odorless characteristic of **58**, it might be applied in organic synthesis as dealkylation agent[193,194,195] or for the reduction of azides,[196] replacing foul-smelling thiol compounds.

We have also prepared a diene, which can be derived from **1** and a fatty acid derivative. In **Chapter 4**, di-addition of methyl thioglycolate to **1** resulted in the renewable monomer **17**, which was employed for the synthesis polyesters. Furthermore, the two available ester groups in **17** offer the possibility to introduce other desired functional groups. Thus, we performed a transesterification reaction of **17** with 10-undecen-1-ol to obtain a α,ω-diene. Herein, TBD was used as efficient transesterification catalyst. Full conversion was achieved after 4 h and purification of the product by column chromatography yielded the desired diene **53** in 93%.

7.2.2. Syntheses of polymers

Having different monomers in hand, we started to study their behavior in thiol-ene polyadditions. Initially, diolefin **53** was polymerized employing AIBN (2.5 mol%) as radical initiator under the same conditions as previously reported.[153] Dithiols **42** and **43**, which are commercially available, were chosen as dithiol compounds. The polymerizations were completed after 2 h and GPC analyses of the resulting polymer showed polysulfides **P45** and **P46** with molecular weights of 11.8 and 14.5 kDa, respectively. Table 7.1 summarizes analytical data of the synthesized polysulfides and Figure 7.2 shows GPC traces of selected polysulfides for comparison. ^{1}H NMR analysis verified the expected structure of these polymers. As an example, ^{1}H NMR spectra of **53** and **P46** (Figure 7.3), showed almost quantitative disappearance of the double bond signals at 5.80 and 4.95 ppm (H^a and H^b) and the appearance of triplet signals at 3.61, 2.69, and 2.54 ppm (H^e, H^f, and H^g, respectively) corresponding thio/oxo ether functionalities on the polymer backbone.

Table 7.1. Analytical data of the synthesized polysulfides.

Entry	Initiator	Reaction Times (h)	Polymer	Monomer Ratio (Equiv.)	M_n (kDa)[a]	PDI[a]	T_m (°C)[b]	T_g (°C)[b]
1	AIBN	2	**P45**	**53**:**42** = 1:1	11.8	1.78	25.8	–[c]
2	AIBN	2	**P46**	**53**:**43** = 1:1	14.5	2.17	-18.9	-48.9
3	AIBN	4	**P47**	**56**:**58** = 1:1	–[d]	–[d]	84.7	–
4	DMPA	16	**P48**	**1**:**42** = 1:1	12.3	1.76	–	-22.9
5	DMPA	16	**P49**	**1**:**43** = 1:1	10.9	1.96	–	-21.6
6	DMPA	4	**P50**	**55**:**56** = 1:1	31.8	2.20	24.1	–
7	DMPA	16	**P51**	**59**:**55** = 1:1	16.2	1.84	12.4	–
8	DMPA	16	**P52**	**1**:**59**:**55** = 1:4:5	12.3	1.94	8.3	–
9	DMPA	16	**P53**	**1**:**59**:**55** = 4:1:5	6.0	1.88	-6.53	-34.4

[a] GPC data in THF system of precipitated polymers, [b] DSC data second heating scan recorded at 10 °C/min, [c] T_g not observable by DSC, [d] insoluble in THF.

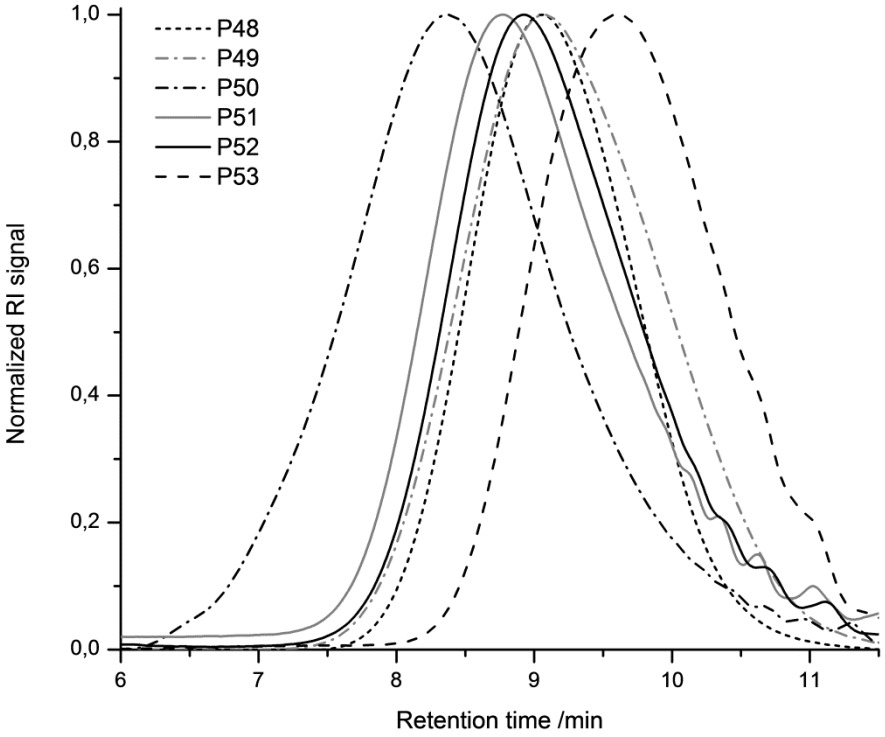


Figure 7.2. GPC traces of some synthesized polysulfides.

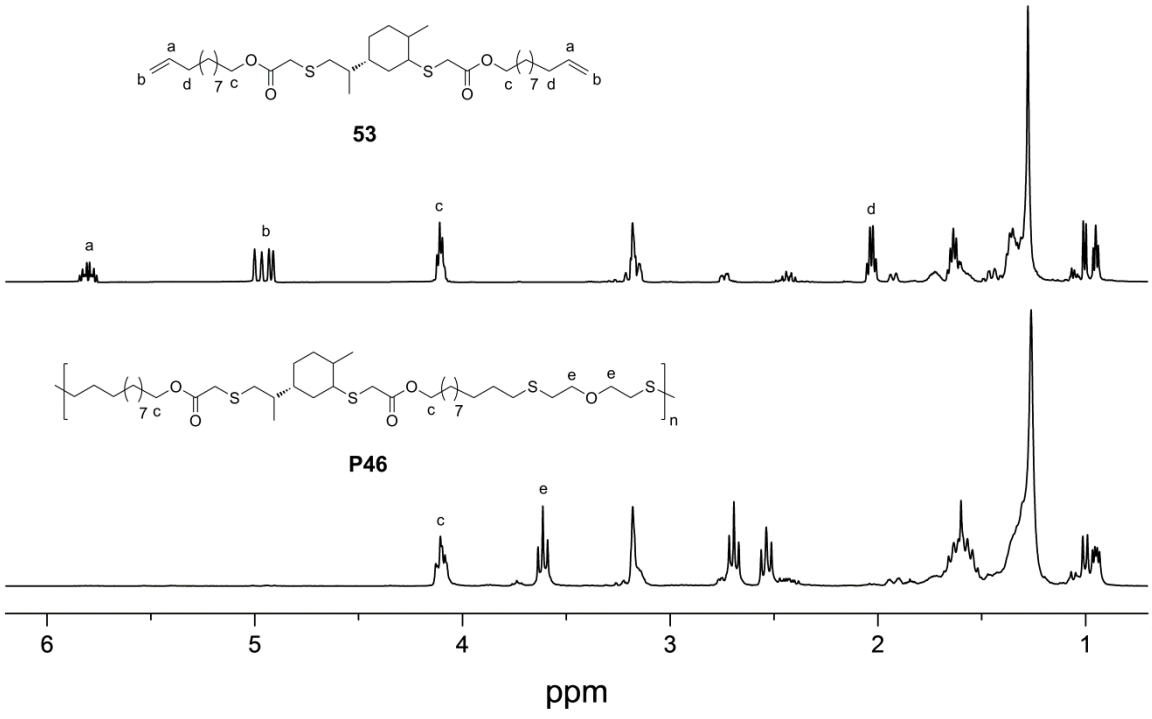


Figure 7.3. ^{1}H NMR spectra of **53** (top) and **P46** (bottom).

The synthesized dithiols **55** and **58** were then subjected to thiol-ene (co)-polymerizations. Dithiol **55** was polymerized with **1** under the same previous condition. However, this polymerization did not work and only tetramers were obtained. Performing these thiol-ene polymerization employing DMPA as radical photoinitiator under UV irradiation did not significantly increase the molecular weight of the product and only tetramers were observed. Most likely, the steric hindrance caused by the cycloaliphatic ring and the relatively low reactivity of the endocyclic double bond prevent an efficient polymerization. Thus, co-monomers providing space between the cycloaliphatic units are needed to decrease the steric hindrance. To prove this, **1** was polymerized with short chain dithiols **42** or **43** using AIBN as thermal radical initiator. However, only oligomer were obtained. Photo-initiated thiol-ene polymerizations performed in bulk, employing DMPA (5 mol%) and UV irradiation on the other hand led to efficient polymer formation after 16 h at ambient temperature. GPC analysis of thiol-ene polymerization of **1** with **42** or **43** revealed the formation of polymer **P48** and **P49** with molecular weights of 12.3 and 10.9 kDa, respectively (see entry 4 and 5, Table 7.1). Based on these results, photo-polymerizations using DMPA were chosen as the reaction condition for further thiol-ene polymerizations involving **1** or **55** as co-monomers (see entries 4–9 in Table 7.1). In order to obtain high molecular weight polysulfides, the introduction of long linear and flexible alkyl chains were also investigated. Under the same condition, fatty acid based co-monomers **56** and **59** were selected as diolefins substrates for thiol-ene polymerization with **55**. As expected, polymers **P50** and **P51** (31.8 and 16.2 kDa, respectively) of higher molecular weight could be obtained (see entries 6 and 7 in Table 7.1). The combination of monomers bearing an cycloaliphatic ring (**1** and **55**)

and the long chain fatty acid based monomer **59** in different ratio was subject of further studies (compare entry 7–8 in Table 7.1). It can be seen that increasing the ratio of long chain fatty acid based **59** results in an increase of the molecular weight. When short chain co-monomers are used, the propagation of the monomers can be reduced due to the steric hindrance caused by the cycloaliphatic rings. On the other hand, the introduction of long and flexible alkyl chains can avoid the steric hindrance around the cycloaliphatic units, facilitating the polymerization of the monomers. In the case of the thiol-ene polymerization of **56** and **58** solubility problems did not allow us to perform a photo-polymerization under the established conditions. Thus, thermal polymerization using AIBN was then performed. Unfortunately, the resulting product is insoluble in common GPC or NMR solvents and the determination molecular weight was not possible. It is worth to mention that monomer **59**,[197] which can be synthesized by esterification of 10-undecenoic acid and 10-undecen-1-ol is also renewable. Therefore, polysulfides derived from them (**P47** and **P50–53)** are 100% renewable.

To study the thermal properties of the synthesized polysulfides, DSC analyses were performed. Table 7.1 summarizes the thermal properties of the prepared polymers and Figure 7.4 shows DSC thermograms of selected polymers. All of the studied polymers displayed melting transitions with the exception of **P48** and **P49**, which showed glass transition temperatures (-22.9 and -21.6 °C, respectively). **P48** and **P49** contain bulky cycloaliphatic units linked with very short segments. The cycloaliphatic rings prevent crystallization and DSC analysis reveals amorphous structures for both of them. **P45** and **P46** display an alternation of relatively long aliphatic segments and substituted cycloaliphatic units. On the one hand, the aliphatic chains are able to

crystallize, and on the other hand the cycloaliphatic cannot crystallize. The DSC thermogram exhibits semicrystalline structures with T_m = 25.8 °C for **P45** and T_m = 25.8 °C & T_g = -48.9 °C for **P46**. In this case, the T_g of **P45** could not be observed by DSC and interestingly, if dithiol **42** was used instead of dithiol **43**, somewhat higher melting point was observed.

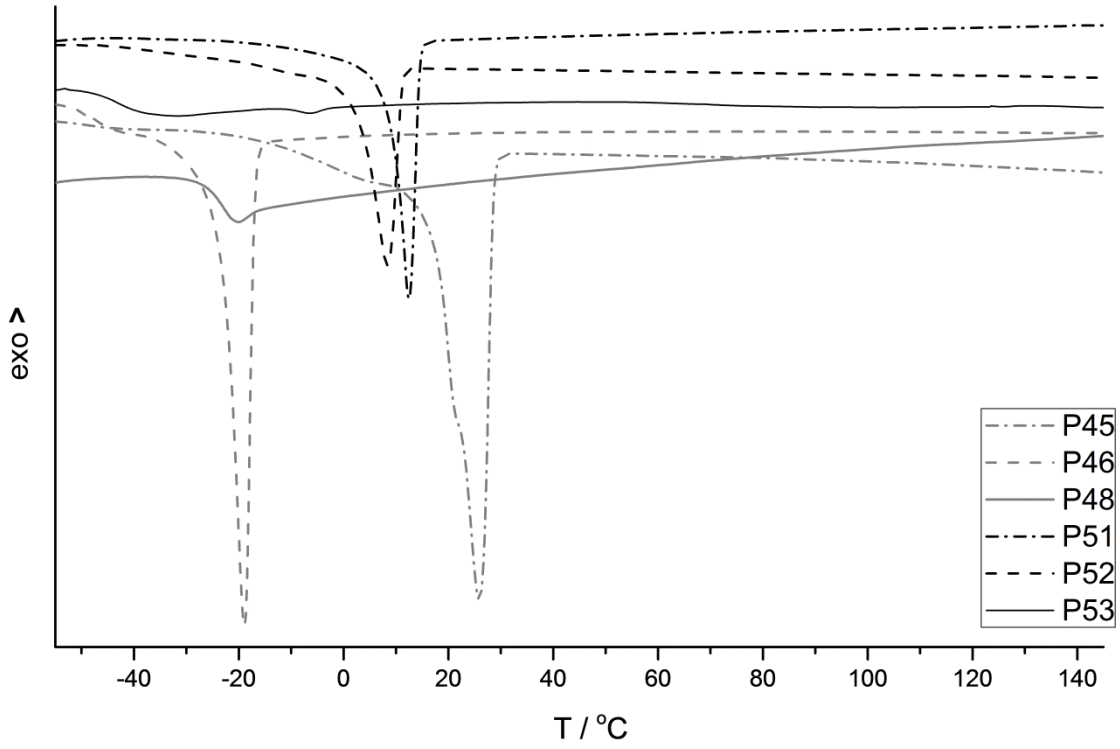


Figure 7.4. DSC traces of some synthesized polysulfides.

As previously mentioned, the combination of monomers bearing cycloaliphatic ring and long chain fatty acid based monomer in different ratios resulted in different molecular weights. The different ratios also had an effect on their thermal properties (compare P**51**–**53** in Table 7.1 and Figure 7.4). Increasing the ratio of long chain fatty acid based **59** leads to an increase of the melting temperatures. Polysulfide **P51** contains long aliphatic chains and cycloaliphatic rings in the same ratio and displays only melting transition (no T_g), which is up to 24 °C higher than for polysulfides **P52**

and **P53**. Contrary, **P53,** which contains more cycloaliphatic units and less long aliphatic units showed almost no melting transition (only a weak endotherm signal appeared at -6.53 °C) and displayed a T_g of -34.4 °C. Thus, the cycloaliphatic units most likely avoid crystallization. Moreover, employing the same dithiol, the polysulfide bearing ether groups (**P50**) exhibits melting temperatures higher than polysulfide contain ester units (**P51**). Finally, **P47** which is no cycloaliphatic units displays sharp melting endotherms (T_m = 84.7 °C) higher than those of all of polysulfides bearing cycloaliphatic ring.

7.2.3. Oxidation to polysulfones

The synthesized polysulfides were selected to be modified into polysulfones by oxidation with hydrogen peroxide. Polysulfides **P47**–**50** were selected as a model for the oxidation. The oxidations were performed using 35% hydrogen peroxide solution (5 equiv. to sulfur atom) in THF at 65 °C for 24 h. Table 7.2 summarizes the analytical data of the synthesized polysulfones. In general, GPC (in HFIP system) analyses showed an increase of the molecular weights of the prepared polysulfones. FT-IR analyses of the synthesized polymers also revealed the successful oxidations. As a representative example (Figure 7.5), the FT-IR spectra of polysulfide **P50** and the thereof oxidized polymer **P57**, showed the appearance of two strong and sharp characteristic absorption peaks for sulfone at 1285 and 1102 cm^{-1}.

Table 7.2. Analytical data of synthesized polysulfones and polysulfides for comparison.

Entry	Polymer	M_n (kDa)[a]	PDI[a]	T_m (°C)[b]	T_g (°C)[b]
1	**P47**	–[c]	–[c]	84.7[d]	–
2	**P48**	11.0	1.68	–	-22.9[d]
3	**P49**	11.2	1.72	–	-21.6[d]
4	**P50**	–[c]	–[c]	24.1[d]	–
5	**P54**	15.5	1.41	–	72.3[d]
6	**P55**	13.3	1.53	–	96.1[e]
7	**P56**	–[c]	–[c]	130.8[d]	–
8	**P57**	–[c]	–[c]	65.2[d]	–

[a] GPC data in HFIP system of precipitated polymers, [b] DSC data recorded at 10 °C/min, [c] insoluble in HFIP, [d] second heating scan, [e] 30 min. annealing at 123 °C.

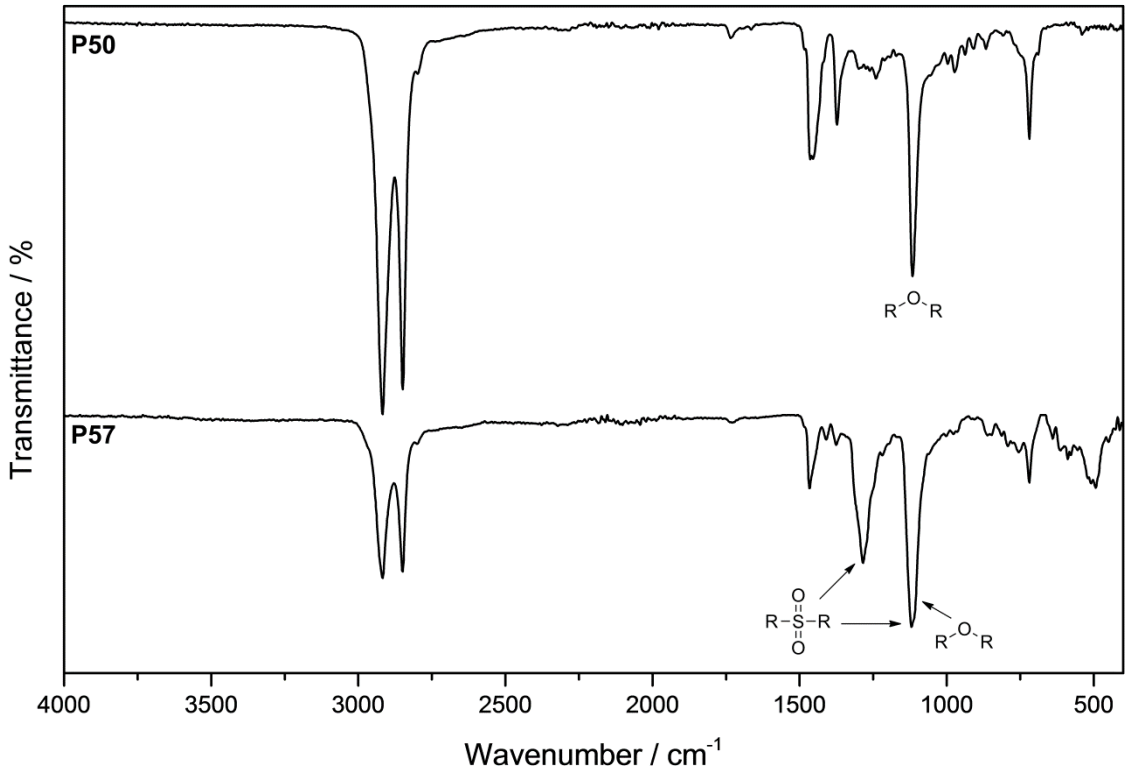


Figure 7.5. FT-IR spectra of **P50** (top) and **P57** (bottom).

Interestingly, enormous changes in thermal properties are observed if the polysulfides are oxidized into polysulfones.[94] For example, if **P50** was oxidized to

P57, an increase of 40 °C in melting transition was observed (Table 7.2 and Figure 7.6). An even more pronounced increase is observed for the oxidation from **P47** to **P56**, making **P56** an interesting plant oil derived material with high melting point. A reason for the observed increases might be the polarity of the introduced sulfone moieties that introduce intermolecular dipole-dipole interactions to the polymer chains.

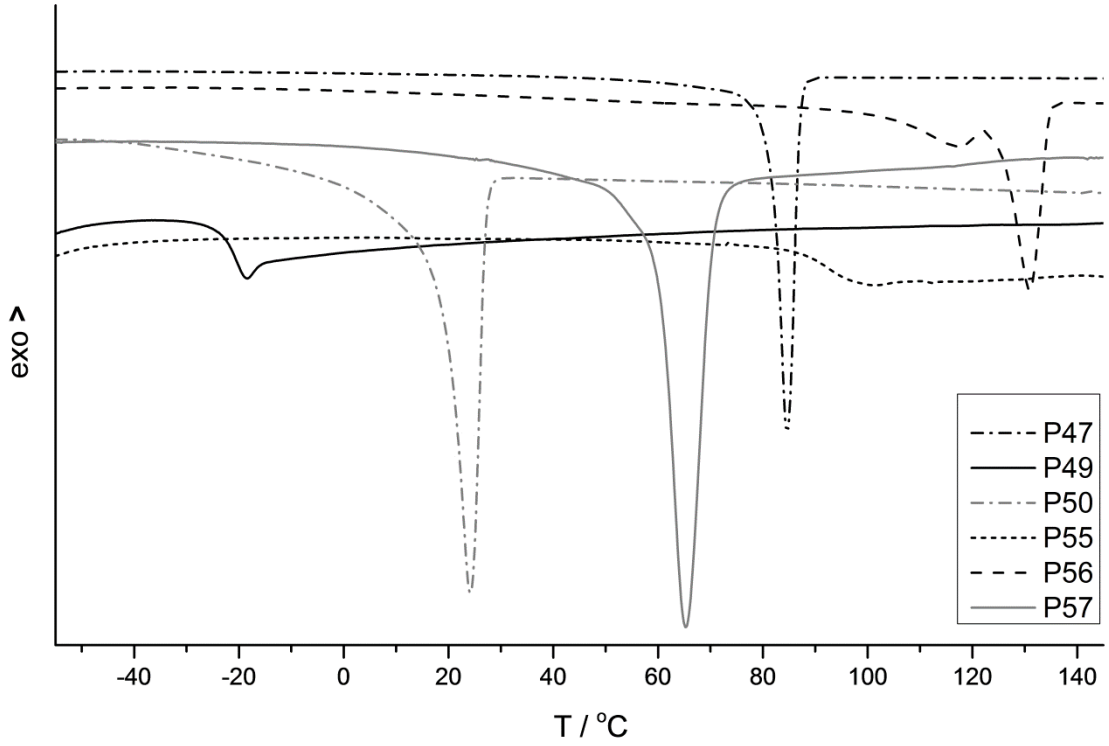


Figure 7.6. DSC traces of synthesized polysulfones and some of polysulfides for comparison.

7.3. Conclusion

In conclusion, we have shown that thiol-ene reactions offer a versatile and efficient way to synthesize renewable diolefin and dithiols derived from (*R*)-(+)-limonene and/or fatty acid derivatives. In addition, polysulfides were successfully prepared by thermal and/or photochemical thiol-ene polyaddition. The GPC results and

comprehensive DSC analysis of the resulting polymers revealed that renewable polysulfides from amorphous to high-melting crystalline polymers with molecular weights up to 31.8 kDa can be obtained *via* different ratio combination of the aforementioned monomers. Moreover, polysulfones were also prepared by oxidation of corresponding polysulfides with hydrogen peroxide solution. Surprisingly, enormous changes in thermal properties are observed if the polysulfides are oxidized to polysulfone, which allowed for an interesting modification of the polymers prepared by the thiol-ene polymerization technique. Overall, the great potential of these renewable resources for polysulfide and polysulfone synthesis was demonstrated.

8

Experimental Part

8.1. General Methods

Thin layer chromatography (TLC) was performed on silica gel TLC-cards (layer thickness 0.20 mm, Fluka). Permanganate reagents were used as developing solutions. Column chromatography was carried out using Silica Gel 60 (0.035-0.070 mm, Fluka) and all solvents used as mobile phase were technical grade, unless otherwise indicated.

8.2. Analytical Instruments

Nuclear Magnetic Resonance Spectroscopy (NMR).

^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker Avance spectrometers operating at 300, 400, 500, or 600 MHz. ^{1}H-NMR spectra were reported in ppm relative to TMS or to the solvent signal for $CDCl_3$ at 7.26 ppm, and ^{13}C-NMR spectra were reported in ppm relative to the central line of the triplet for $CDCl_3$ at 77.00 ppm. The relaxation time (d1) was set to 5 seconds for the analyses of the polymers. Where necessary, NMR analyses of the polymers were conducted after trifluoacetic anhydride treatment, likewise: the necessary amount of the polymer and deutorated

solvent were placed into a NMR tube and trifluoroacetic anhydride was added dropwise with continuous shaking until a homogenous solution was obtained.

Mass Spectrocopy (MS).

Fast atom bombardment mass spectra (FAB-MS) were recorded on a Micromass Q-TOF instrument and high resolution mass spectra (HRMS) with electron impact ionization (EI) were recorded on a GC-TOF. Electro-spray ionization mass spectra (ESI-MS) were recorded using:

1) Varian 500-MS ion trap mass spectrometer with the TurboDDS™ option installed. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the drying gas. Helium served as cooling gas for the ion trap and collision gas for MS. Nitrogen was generated by a nitrogen generator Nitrox from Dominick Hunter.
2) Micromass Q-TOF_{MICRO} instrument.

Gas Chromatography (GC).

Analytical GC characterization was carried out with a Bruker 430 GC instrument equipped with a capillary column FactorFour™ VF-5 ms (30 m × 0.25 mm × 0.25 μm), using flame ionization detection. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C × min^{-1} to 220 °C, hold for 4 min, ramp at 15 °C × min^{-1} to 300 °C, hold for 2 min. The injector transfer line temperature was set to 220 °C. Measurements were performed in split-split mode using hydrogen as the carrier gas (flow rate 30 mL min^{-1}).

GC-MS (EI) chromatograms were recorded using:

1) GC-MS (EI) chromatograms were recorded using a Varian 431 GC instrument with a capillary column FactorFour™ VF-5 ms (30 m × 0.25 mm × 0.25 μm) and a

Varian 210 ion trap mass detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scan × s^{-1}. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C × min^{-1} to 200 °C, hold for 2 min, ramp at 15 °C × min^{-1} to 325 °C, hold for 5 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in split-split mode (split ratio 50 : 1) using helium as the carrier gas (flow rate 1.0 mL × min^{-1}).

2) Varian 3900 GC instrument with a capillary column FactorFourTM VF- 5ms (30 m × 0.25 mm × 0.25 μm) and a Saturn 2100T ion trap mass detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scans×s^{-1}. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C × min^{-1} to 200 °C, hold for 2 min, ramp at 15 °C × min^{-1} to 325 °C, hold for 5 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in the split–split mode (split ratio 50:1) using helium as carrier gas (flow rate 1.0 mL × min^{-1}).
3) HP 5890 Series II instrument with a capillary column (30 m × 0.25 mm × 0.25 μm) and a HP 5971A Mass Selective Detector. The oven temperature program was: initial temperature 70 °C, ramp at 25 °C × min^{-1} to 280 °C, hold for 5 min. The injector temperature was set to 250 °C. Measurements were performed in the split-split mode (split ratio 1:1) using He as carrier gas (flow rate 0.8 mL × min^{-1}).

Gel Permeation Chromatography (GPC).

Polymer analyses were performed using:

1) THF system: GPC System LC-20 A from Shimadzu equipped with a SIL-20A auto sampler, PL gel 5 mm MIXED-D column (Polymer Laboratories, 300 mm × 7.5 mm, 100 Å, 1000 Å, 10000 Å) and a RID-10A refractive index detector in THF (flow

rate 1 mL × min^{-1}) at 50 °C. All determinations of molar mass were performed relative to PMMA standards (Polymer Standards Service, Mp 1100–981000 Da).

2) HFIP system: a Tosoh EcoSEC HLC-8320 GPC system with Hexafluoroisopropanol (HFIP, Chempur, 99.9%) containing 0.1 wt% potassium trifluoroacetate (Sigma Aldrich, 98%) as the solvent. The solvent flow was 0.40 mL/min at 30.0 °C. The analysis was performed on a 3-column system: PSS PFG Micro precolumn (3.0 × 0.46 cm, 10.000 Å), PSS PFG Micro (25.0 × 0.46 cm, 1000 Å) and PSS PFG Mirco (25.0 × 0.46 cm, 100 Å). The system was calibrated with linear poly(methyl methacrylate) standards (Polymer Standard Service, M_P 102 – 981 000 Da).

Differential Scanning Calorimetry (DSC).

Thermal experiments were carried out with a DSC821e (Mettler Toledo) calorimeter, under nitrogen atmosphere. Heating rates and maximal temperatures are indicated where necessary (see sections for details). A sample mass of between 4–7 mg were taken into Aluminium crucibles. Data from second heating scans are reported unless special heating treatments were applied (see sections for details). The glass transition temperature, T_g, is reported as the midpoint of the heat capacity change. The melting temperature, T_m, is recorded as the minimum (endothermic transitions are represented downwards) of the endothermic melting peak.

Infra Red Spectroscopy (IR).

Infrared spectroscopy was recorded on a FT-IR Bruker alpha.

8.3. Terpene Based Renewable Monomers and Polymers *via* Thiol-Ene Additions

8.3.1. Materials

(*R*)-(+)-Limonene (**1**, Sigma, 97%), (*S*)-(–)-limonene (**2**, Aldrich, 96%), (–)-β-pinene (**3**, Aldrich, 99%), 2-mercaptoethanol (**4**, Aldrich, >99%), methyl thioglycolate (**5**, Aldrich, >97%), 1-thioglycerol (**6**, Aldrich, >99%), tetradecane (Aldrich, 99,5%), 10-undecen-1-ol (Aldrich, 98%), acetic anhydride (Aldrich), sulfuric acid (Fluka, 95–97%), $NaHCO_3$ (Fisher Scientific), Na_2SO_4 (≥ 99%, Fluka), silica gel 60 (0.035 – 0.070 mm, Aldrich), chloroform-d (99.8 atom-% D, Armar Chemicals), 1,4-benzoquinone (>99%, Aldrich), (1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(*o*-isopropoxyphenylmethylene) ruthenium (**C1**, Hoveyda–Grubbs Catalyst 2nd Generation, Aldrich), 1,3-*bis*-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-yliden[2-(isopropoxy)-5*N*,*N*-dimethylaminosulfonyl)phenyl]methylene ruthenium (II) dichloride (**C2**, Zhan catalyst, 96%, ABCR), [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro [2-(1-methylacetoxy)phenyl]methylene ruthenium(II) (**C3**, Umicore $M5_1$), ethyl vinyl ether (99%, Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene, (TBD, Aldrich, 98%), palladium on activated carbon (Pd/C, 10% Pd, Acros Organics), 1,3-propanediol (Aldrich, >99%), 1,6-hexanediol (Acros Organics, 97%), titanium (IV) isopropoxide ($Ti(O\text{-}i\text{-}Pr)_4$, Acros Organics, 98%) were used as received. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%) was used after recrystallization from methanol. All solvents (technical grade) were used without purification. Diester (*E*)-dimethyl icos-10-enedioate (**24**),[144] dimethyl 11,11'-(butane-1,4-diylbis(sulfanediyl))diundecanoate (**25**),[88] methyl 11-((2-methoxy-2-oxoethyl)-thio)undecanoate (**31**),[88] and diol 11,11'-(butane-1,4-diylbis(sulfanediyl))-*bis*(undecan-1-ol) (**27**)[88] were prepared as previously reported.

8.3.2. Syntheses of monomers

General procedure for monoadditions of thiols to (*R*)-(+)-limonene, (*S*)-(–)-limonene, and (–)-β-pinene.

The thiol-ene reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). A mixture of terpene **1**, **2**, or **3** (0.5 mL), tetradecane (internal standart, 10% volume of terpene), and thiol **4**, **5**, or **6** (1.2 equiv.) was added to the carousel tube. After taking a t = 0 min sample, the reaction mixture was degassed under vacuum (200 mbar) for 5 minutes. The mixture was then stirred magnetically at room temperature. Samples were taken periodically for conversion analysis using GC and or GC-MS. The reactions were also scaled up to 2.4 mL of terpenes following the same procedure. The products **7**–**15** were purified by column chromatography on silica gel with hexane–ethyl acetate (9:1) as eluent.

General procedure for diadditions of thiols to (*R*)-(+)-limonene, (*S*)-(–)-limonene.

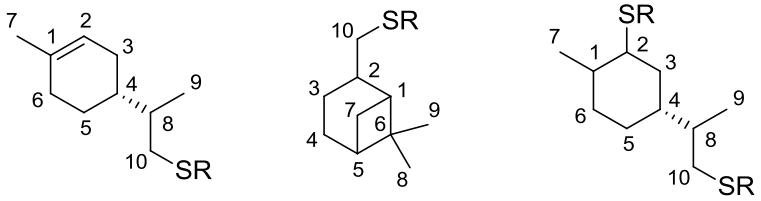
The thiol-ene reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). Example of procedure: In a carousel tube, **1** (0.50 mL, 3.09 mmol), was mixed with 2.5 equiv. of **4** (0.54 mL, 7.72 mmol), and tetradecane (0.05 mL) as internal standart. After taking a t = 0 min sample, the reaction mixture was degassed under vacuum (200 mbar) for 5 minutes. The mixture was then stirred magnetically at room temperature. Samples were taken periodically for conversion analysis using GC and/or GC-MS. The thiol-ene diadditions were scaled up to 1.4 mL of terpene following the same procedure. The resulting products **16**-**19** were purified by column chromatography on silica gel with hexane-ethyl acetate (7:3) as eluent.

General procedure for additions of thiols 4 and 5 to 7, 8, 10, and 11.

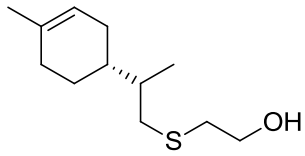
A mixture of monoaddition product **8** or **11** (0.50 g, 2.06 mmol) and thiol **4** (0.23 mL, 2.47 mmol) was degassed under vacuum (200 mbar) for 5 minutes. The mixture was then stirred magnetically at room temperature. The reaction were monitored by TLC until completion using hexane-ethyl acetate (7:3). The same procedure was applied for the addition of **5** to **7** or **10**, but without applying vacuum. The products **20**-**23** were purified by column chromatography with hexane-ethyl acetate (7:3) as eluent.

Characterization of thiol-ene addition products.

When possible, " ´ " is used to differentiate between different diastereomers. In the ^{1}H NMR spectra, " $_{A}$ " and " $_{B}$ " differentiates between two protons connected to the same carbon. The thioglycerol used is a mixture of enantiomers, and thus leads to an additional stereocenter in the addition products. The ^{13}C assignment is unambiguous with respect to each nucleus, but laborious when it comes to differentiate between a particular carbon atom belonging to different diastereomers. In the diaddition products, the two major diastereomers are marked with " " and " ´ ", and the minor ones with " ´´ " and " ´´´ ". The assignment of ^{1}H and ^{13}C NMR spectra has been done using the following number codes for each nucleus in the mono- and diaddition products:



2-(((*R,S*)-1´´-((*R*)-4´´-Methylcyclohex-3´´-en-1´´-yl)propyl)thio)ethanol (**7**).



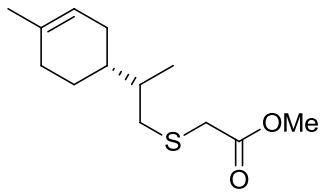
Colorless liquid (yield 85%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 5.36-5.29 (m, 1H, C=CH), 3.67 (t, *J* = 6.0 Hz, 2H, C*H*$_2$-OH), 2.67 (t, *J* = 6.0 Hz, 2H, S-CH_2), 2.61 (dd, *J* = 12.4, 5.0 Hz, 1H, CH_2-S), 2.46 (s, 1H, OH), 2.35 (dd, *J* = 12.4, 8.1, 6.7 Hz, 1H, CH_2-S), 2.06-1.82 (m, 3H, C*H*$_2$-C(CH_3)= and C*H*$_A$H$_B$-CH=), 1.82-1.42 (m, 4H, C*H*$_A$H$_B$-CH_2-C(CH_3)=, CH_A*H*$_B$-CH=, C*H*-CH-CH_3 and C*H*-CH_3), 1.60 (s, 3H, C-CH_3), 1.34–1.14 (m, 1H, CH_A*H*$_B$-CH_2-C(CH_3)=), 0.94 (t, *J* = 6.2 Hz, 3H, CH-C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 134.12 (C_1), 134.08 (C_1´), 120.67 (C_2), 120.62 (C_2´), 60.43 (CH_2OH), 37.92 (C_4), 37.83 (C_4´), 37.80 (C_8), 37.65 (C_8´), 37.31 (C_{10}), 37.22 (C_{10}´), 36.00 (CH_2S), 35.95 (C´H_2S), 30.87 (C_6), 30.73 (C_6´), 29.66 (C_5), 27.50 (C_3), 27.25 (C_3´), 25.41 (C_5´), 23.53 (C_7, C_7´), 16.27 (C_9), 15.82 (C_9´).

HRMS of $C_{12}H_{22}OS$ (M+H$^+$ = 215.1478, calc. 215.1470).

Methyl 2-(((*R,S*)-1´´-((*R*)-4´´-methylcyclohex-3´´-en-1´´-yl)propyl)thio)acetate (8).



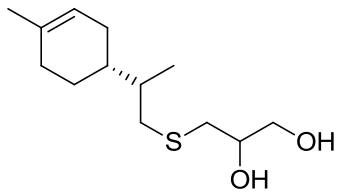
Colorless liquid (55%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 5.38-5.30 (m, 1H, C=CH), 3.72 (s, 3H, OCH_3), 3.18 (s, 2H, CO-CH_2), 2.75 (dd, *J* = 12.4, 4.9 Hz, 1H, C*H*$_A$H$_B$-S), 2.74 (dd, *J* = 12.4, 5.1 Hz, 1H, C*H*´$_A$H´$_B$-S), 2.47 (dd, *J* = 12.4, 5.8 Hz, 1H, CH$_A$*H*$_B$ -S), 2.45 (dd, *J* = 12.4, 5.8 Hz, 1H, CH´$_A$*H*´$_B$-S), 2.07-1.84 (m, 3H, C*H*$_2$-C(CH$_3$)= and C*H*$_A$H$_B$-CH=), 1.84-1.42 (m, 4H, C*H*$_A$H$_B$-CH$_2$-C(CH$_3$)=, CH$_A$*H*$_B$-CH=, C*H*-CH-CH$_3$ and C*H*-CH$_3$), 1.62 (s, 3H, C-CH$_3$), 1.36–1.15 (m, 1H, CH$_A$*H*$_B$-CH$_2$-C(CH$_3$)=), 0.97 (d, *J* = 5.7 Hz, 3H, CH-C*H*$_3$), 0.95 (d, *J* = 5.7 Hz, 3H, CH-C*H*$_3$´).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 171.20 (CO), 134.16 (C$_1$, C$_1$´), 120.74 (C$_2$), 120.67 (C$_2$´), 52.48 (OCH_3), 38.30 (C$_{10}$), 38.22 (C$_{10}$´), 37.87 (C$_4$), 37.66 (C$_4$´), 37.35 (C$_8$), 37.25 (C$_8$´), 34.13 (CH_2CO), 34.08 (C´H_2CO), 30.91 (C$_6$), 30.77 (C$_6$´), 29.63 (C$_5$), 27.53 (C$_3$), 27.23 (C$_3$´), 25.43 (C$_5$´), 23.59 (C$_7$, C$_7$´), 16.25 (C$_9$), 15.83 (C$_9$´).

HRMS of $C_{13}H_{22}O_2S$ ($M+H^+$ = 243.1411, calc. 243.1419).

3-(((*R,S*)-1´´-((*R*)-4´´-Methylcyclohex-3´´-en-1´´-yl)propyl)thio)propane-1,2-diol (9).



Colorless viscous liquid (80%).

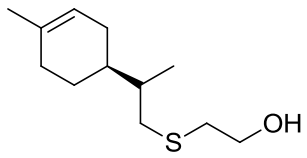
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 5.39-5.29 (m, 1H, C=CH), 3.82 – 3.68 (m, 2H, C*H*-OH and C*H*$_A$H$_B$-OH), 3.53 (dd, *J* = 11.2, 6.0 Hz, 1H, CH$_A$*H*$_B$-OH), 3.02 (s, broad, OH), 2.71-2.50 (m, 3H, CH-C*H*$_A$H$_B$-S and CH$_2$-S), 2.44-2.32 (m, 1H, CH-CH$_A$*H*$_B$-S), 2.08-1.84 (m, 3H, C*H*$_2$-C(CH$_3$)= and C*H*$_A$H$_B$-CH=), 1.84-1.43 (m, 4H, C*H*$_A$H$_B$-CH$_2$-C(CH$_3$)=, CH$_A$*H*$_B$-CH=, C*H*-CH-CH$_3$ and C*H*-CH$_3$), 1.61 (s, 3H, C-CH$_3$), 1.35-1.14 (m, 1H, CH$_A$*H*$_B$-CH$_2$-

C(CH_3)=), 1.012 (d, *J* = 6.4 Hz, 3H, CH-C*H*$_3$), 1.007 (d, *J* = 6.1 Hz, 3H, CH-C*H*$_3$′), 0.991 (d, *J* = 6.4 Hz, 3H, CH-C*H*$_3$′′), 0.987 (d, *J* = 6.5 Hz, 3H, CH-C*H*$_3$′′′).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 134.20 (C_1 and C_1′), 134.17 (C_1′′ and C_1′′′), 120.71 (C_2), 120.68 (C_2′), 120.64 (C_2′′ and C_2′′′), 70.38 (CH-OH), 70.37 (C′H-OH), 70.15 (C′′H-OH), 70.13 (C′′′H-OH), 65.58 (CH_2OH), 38.24 (C_{10}), 38.18 (C′$_{10}$), 37.95 (C′′$_{10}$), 37.84 (C′′′$_{10}$), (37.95, 37.82, 37.77, 37.71 and 37.60: C_4 and C_8), 36.64 (CH_2-S), 36.59 (C′H_2-S), 36.43 (C′′H_2-S), 36.38 (C′′′H_2-S), 30.91 (C_6, C_6′), 30.76 (C_6′′, C_6′′′), 29.73 (C_5), 29.68 (C_5′), 27.60 (C_3), 27.45 (C_3′), 27.32 (C_3′′), 27.26 (C_3′′′), 25.50 (C_5′′), 25.38 (C_5′′′), 23.58 (C_7), 16.32 (C_9), 16.31 (C_9′), 15.86 (C_9′′), 15.85 (C_9′′′).

HRMS of $C_{13}H_{24}O_2S$ (M+H^+ = 245.1573, calc. 245.1575).

2-(((*R,S*)-1′′-((*S*)-4′′-methylcyclohex-3′′-en-1′′-yl)propyl)thio)ethanol (10).



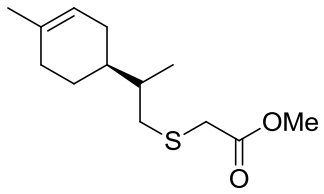
Colorless liquid (yield 82%).

^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm) 5.34-5.30 (m, 1H, C=CH), 3.67 (t, *J* = 6.0 Hz, 2H, C*H*$_2$-OH), 2.67 (t, *J* = 5.9 Hz, 2H, S-CH_2), 2.66 (t, *J* = 6.1 Hz, 2H, S-CH_2′), 2.602 (dd, *J* = 12.4, 4.8 Hz, 1H, C*H*$_A$H$_B$-S), 2.598 (dd, *J* = 12.4, 5.1 Hz, 1H, C*H*$_A$′H$_B$′-S), 2.53 (s, broad, OH), 2.35 (dd, *J* = 12.4, 8.3 Hz, 1H, CH$_A$*H*$_B$-S), 2.33 (dd, *J* = 12.4, 8.4 Hz, 1H, CH$_A$′*H*$_B$′-S), 2.02-1.85 (m, 3H, C*H*$_2$-C(CH_3)= and C*H*$_A$H$_B$-CH=), 1.79-1.69 (m, 1H, C*H*$_A$H$_B$-CH_2-C(CH_3)=), 1.69-1.62 (m, 1H, CH$_A$*H*$_B$-CH=), 1.60 (s, 3H, C-CH_3), 1.60-1.45 (m, 2H, C*H*-CH_3 and C*H*-CH_3), 1.31–1.16 (m, 1H, CH$_A$*H*$_B$-CH_2-C(CH_3)=), 0.95 (t, *J* = 6.7 Hz, 3H, CH-C*H*$_3$), 0.93 (t, *J* = 6.8 Hz, 3H, CH-C*H*$_3$′).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 134.10 (C_1), 134.06 (C_1'), 120.65 (C_2), 120.60 (C_2'), 60.38 (CH_2OH), 37.87 (C_4), 37.78 (C_4'), 37.75 (C_8), 37.60 (C_8'), 37.24 (C_{10}), 37.16 (C_{10}'), 35.93 (CH_2S), 35.88 ($C'H_2S$), 30.84 (C_6), 30.70 (C_6'), 29.63 (C_5), 27.44 (C_3), 27.22 (C_3'), 25.36 (C_5'), 23.53 (C_7, C_7'), 16.24 (C_9), 15.78 (C_9').

HRMS of $C_{12}H_{22}OS$ ($M+H^+$ = 215.1451, calc. 215.1470).

Methyl 2-(((*R,S*)-1´´-((*S*)-4´´-methylcyclohex-3´´-en-1´´-yl)propyl)thio)acetate (11).



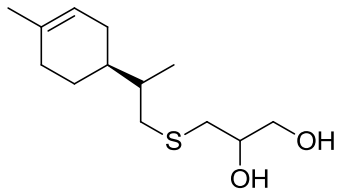
Colorless liquid (52%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 5.37-5.27 (m, 1H, C=CH), 3.69 (s, 3H, OCH_3), 3.16 (s, 2H, CO-CH_2), 2.73 (dd, *J* = 12.5, 4.8 Hz, 1H, C$H_A$$H_B$-S), 2.72 (dd, *J* = 12.4, 5.1 Hz, 1H, CH'_AH'$_B$-S), 2.45 (dd, *J* = 12.4, 5.7 Hz, 1H, CH$_A$$H_B$ -S), 2.42 (dd, *J* = 12.5, 5.7 Hz, 1H, CH'$_A$$H'_B$-S), 2.05-1.82 (m, 3H, C$H_2$-C($CH_3$)= and C$H_AH_B$-CH=), 1.82-1.41 (m, 4H, CH_AH$_B$-CH_2-C(CH_3)=, CH$_A$$H_B$-CH=, C*H*-CH-$CH_3$ and C*H*-CH_3), 1.59 (s, 3H, C-CH_3), 1.33–1.13 (m, 1H, CH$_A$$H_B$-$CH_2$-C($CH_3$)=), 0.94 (d, *J* = 5.7 Hz, 3H, CH-CH_3), 0.92 (d, *J* = 5.8 Hz, 3H, CH-CH_3').

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 171.08 (CO), 134.03 (C_1, C_1'), 120.68 (C_2), 120.61 (C_2'), 52.36 (OCH_3), 38.22 (C_{10}), 38.14 (C_{10}'), 37.81 (C_4), 37.60 (C_4'), 37.28 (C_8), 37.18 (C_8'), 34.03 (CH_2CO), 33.98 ($C'H_2CO$), 30.84 (C_6), 30.70 (C_6'), 29.56 (C_5), 27.48 (C_3), 27.16 (C_3'), 25.37 (C_5'), 23.50 (C_7, C_7'), 16.18 (C_9), 15.76 (C_9').

HRMS of $C_{13}H_{22}O_2S$ ($M+H^+$ = 243.1404, calc. 243.1419).

3-(((*R,S*)-1´´-((*S*)-4´´-Methylcyclohex-3´´-en-1´´-yl)propyl)thio)propane-1,2-diol (12).



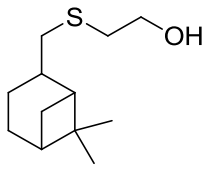
Colorless viscous liquid (61%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 5.36-5.26 (m, 1H, C=CH), 3.81-3.59 (m, 2H, C*H*-OH and C$H_A$$H_B$-OH), 3.49 (dd, *J* = 11.4, 6.3 Hz, 1H, $CH_A$$H_B$-OH), 3.02 (s, broad, OH), 2.66-2.48 (m, 3H, CH-C$H_A$$H_B$-S and CH_2-S), 2.40-2.29 (m, 1H, CH-$CH_A$$H_B$-S), 2.04-1.80 (m, 3H, C$H_2$-C($CH_3$)= and C$H_A$$H_B$-CH=), 1.80-1.40 (m, 4H, C$H_A$$H_B$-$CH_2$-C($CH_3$)=, $CH_A$$H_B$-CH=, C*H*-CH-$CH_3$ and C*H*-CH_3), 1.58 (s, 3H, C-CH_3), 1.32-1.11 (m, 1H, $CH_A$$H_B$-$CH_2$-C($CH_3$)=), 0.933 (d, *J* = 5.8 Hz, 3H, CH-CH_3), 0.930 (d, *J* = 5.8 Hz, 3H, CH-CH_3´), 0.910 (d, *J* = 5.9 Hz, 3H, CH-CH_3´´), 0.907 (d, *J* = 5.9 Hz, 3H, CH-CH_3´´´).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 134.00 (C_1 and C_1´), 133.97 (C_1´´ and C_1´´´), 120.64 (C_2), 120.62 (C_2´), 120.57 (C_2´´ and C_2´´´), 70.73 (CH-OH), 70.71 (C´H-OH), 70.53 (C´´H-OH), 70.51 (C´´´H-OH), 65.43 (CH_2OH), 38.21 (C_{10}), 38.15 (C´$_{10}$), 38.01 (C´´$_{10}$), 37.90 (C´´´$_{10}$), (37.82, 37.72, 37.64, 37.62 and 37.52: C_4 and C_8), 36.29 (CH_2-S), 36.23 (C´H_2-S), 36.17 (C´´H_2-S), 36.11 (C´´´H_2-S), 30.81 (C_6, C_6´), 30.67 (C_6´´, C_6´´´), 29.62 (C_5), 29.58 (C_5´), 27.46 (C_3), 27.36 (C_3´), 27.20 (C_3´´), 27.16 (C_3´´´), 25.37 (C_5´´), 25.28 (C_5´´´), 23.48 (C_7), 16.21 (C_9, C_9´), 15.74 (C_9´´, C_9´´´).

HRMS of $C_{13}H_{24}O_2S$ ($M+H^+$ = 245.1561, calc. 245.1575).

2-(((6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)thio)ethanol (13).



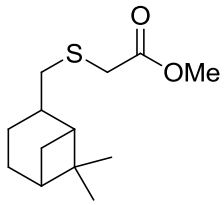
Colorless viscous liquid (81%).

^{1}H NMR (600 MHz, $CDCl_3$, δ in ppm) 3.66 (t, *J* = 6.1 Hz, C*H*$_2$-OH, C*H*$_2$´-OH), 2.65 (t, *J* = 6.1 Hz, CH_2-S, CH_2´-S), 2.59-2.51 (m, H_{10}), 2.51 (s, broad, OH), 2.42-2.45 (m, H_{10}´), 2.34-2.30 (m, H_{7e}), 2.20-2.14 (m, H_2), 2.11-2.06 (m, H_2´), 2.04-1.95 (m, H_1, H_{4a}, H_{7a}´, H_{7e}´, H_{4a}´), 1.94-1.78 (m, H_5, H_{3a}, H_{3e}, H_1´, H_5´, H_{3a}´), 1.77-1.67 (H_{3e}´), 1.51-1.45 (m, H_{4e}), 1.30-1.24 (m, H_{4e}´), 1,17 (s, H_8´), 1.15 (s, H_8), 0.96 (s, H_9), 0.86 (d, *J* = 9.7 Hz, H_{7a}), 0.79 (s, H_9´).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 60.46 (C*H*$_2$-OH), 45.56 (C_1), 44.99 (C_1´), 41.33 (C_2), 41.18 (C_5), 40.89 (C_5´), 39.48 (C_6´), 39.08 (C_{10}), 38.68 (C_6), 38.40 (C_{10}´), 35.64 (C´H_2-S), 35.32 (CH_2-S), 35.14 (C_2´), 33.38 (C_7), 28.03 (C_8), 26.72 (C_8´), 26.18 (C_3), 24.31 (C_3´), 23.35 (C_4´), 23.29 (C_9), 22.24 (C_7´), 22.14 (C_4), 20.12 (C_9´).

HRMS of $C_{12}H_{22}OS$ ($M+H^+$ = 215.1476, calc. 215.1470).

Methyl 2-(((6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)thio)acetate (14).



Colorless viscous liquid (60%).

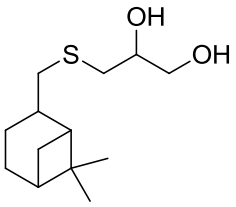
^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 3.67 (s, OCH_3), 3.13 (s, CO-CH_2), 2.71-2.58 (m, H_{10}), 2.53-2.42 (m, H_{10}´), 2.33-2.25 (m, H_{7e}), 2.23-2.04 (m, H_2, H_2´), 2.03-1.91 (m, H_1,

H_{4a}, H_{7a}′, H_{7e}′, H_{4a}′), 1.91-1.76 (m, H_5, H_{3a}, H_{3e}, H_1′, H_5′, H_{3a}′), 1.76-1.62 (H_{3e}′), 1.53-1.40 (m, H_{4e}), 1.29-1.17 (m, H_{4e}′), 1,15 (s, H_8′), 1.13 (s, H_8), 0.94 (s, H_9), 0.84 (d, *J* = 9.8 Hz, H_{7a}), 0.76 (s, H_9′).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 171.03 (CO), 52.29 (OCH_3), 45.50 (C_1), 44.96 (C_1′), 41.34 (C_5), 40.89 (C_5′), 40.52 (C_2), 39.97 (C_{10}), 39.51 (C_6′), 39.36 (C_{10}′), 38.70 (C_6), 34.59 (CO-*C*′H_2), 33.96 (C_2′), 33.60 (CO-*C*H_2), 33.37 (C_7), 28.02 (C_8), 26.72 (C_8′), 26.19 (C_3), 24.31 (C_3′), 23.37 (C_4′), 23.23 (C_9), 22.14 (C_7′), 22.03 (C_4), 20.12 (C_9′).

HRMS of $C_{13}H_{22}O_2S$ ($M+H^+$ = 243.1439, calc. 243.1419).

3-(((6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)thio)propane-1,2-diol (15).



Colorless viscous liquid (76%).

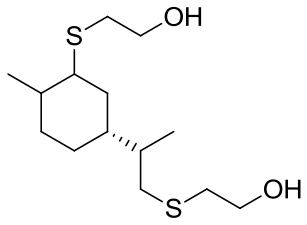
^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 3.78-3.75 (m, C*H*-OH and CH_AH_B-OH), 3.50 (dd, *J* = 11.3, 6.1 Hz, CH_A*H*$_B$-OH), 3.43 (s, broad, OH), 2.64-2.49 (m, CH_2-S and H_{10}), 2.43-2.39 (m, 2H, H_{10}′), 2.36-2.28 (m, H_{7e}), 2.23-2.06 (m, H_2, H_2′), 2.04-1.94 (m, H_1, H_{4a}, H_{7a}′, H_{7e}′, H_{4a}′), 1.94-1.80 (m, H_5, H_{3a}, H_{3e}, H_1′, H_5′, H_{3a}′), 1.80-1.67 (H_{3e}′), 1.54-1.41 (m, H_{4e}), 1.28-1.19 (m, H_{4e}′), 1,17 (s, H_8′), 1.15 (s, H_8), 0.95 (s, H_9), 0.86 (d, *J* = 9.6 Hz, H_{7a}), 0.79 (s, H_9′).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 70.53 (CH-OH), 70.51 (C′′H-OH, C′′′H-OH), 70.42 (C′H-OH), 65.49 (CH_2-OH, C′H_2-OH, C′′H_2-OH, C′′′H_2-OH), 45.71 (C_1), 45.57 (C_1′), 45.13 (C_1′′), 45.03 (C_1′′′), 41.38 (C_5, C_5′), 41.17 (C_2), 41.11 (C_2′), 40.95 (C_5′′, C_5′′′), 39.92 (C_{10}), 39.81 (C_{10}′), 39.59 (C_6′′), 39.56 (C_6′′′), 39.26 (C_{10}′′), 39.19 (C_{10}′′′), 38.76 (C_6,

C_6'), 36.19 ($C''H_2$-S, $C'''H_2$-S), 35.86 (CH_2-S), 35.79 ($C'H_2$-S), 35.16 (C_2''), 35.14 (C_2'''), 33.46 (C_7), 33.44 (C_7'), 28.10 (C_8, C_8'), 26.79 (C_8'', C_8'''), 26.23 (C_3, C_3'), 24.37 (C_3'', C_3'''), 23.45 (C_4''), 23.43 (C_4'''), 23.37 (C_9, C_9'), 22.32 (C_7''), 22.28 (C_7'''), 22.22 (C_4), 22.14 (C_4'), 20.21 (C_9'', C_9''').

HRMS of $C_{13}H_{24}O_2S$ ($M+H^+$ = 245.1576, calc. 245.1575).

2-[2′-((1′′*R*)-3′′-((2′′′-hydroxyethyl)thio)-4′′-methylcyclohexyl)propyl)thio]-ethanol (16).



Colorless viscous liquid (62%).

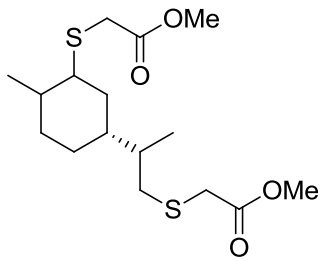
^{1}H NMR (600 MHz, $CDCl_3$, δ in ppm): 3.73-3.64 (CH_2-OH), 2.95-2.91 (H^2, $H^{2'}$), 2.83-2.64 (S-C*H*$_2$-CH_2-OH), 2.60 (dd, *J* = 12.0, 7.0 Hz, H_A^{10}), 2.58 (dd, *J* = 12.0, 4.4 Hz, $H_A^{10'}$), 2.45 (dd, *J* = 12.0, 7.6 Hz, $H_B^{10'}$), 2.42-2.34 (m, $H^{10''}$, $H^{10'''}$), 2.37 (dd, *J* = 12.0, 7.5 Hz, H_B^{10}), 2.24-2.16 (m, $H^{2''}$, $H^{2'''}$), 2.04-1.97 (m, $H_A^{3''}$, $H_A^{3'''}$), 1.93-1.87 (m, H_A^3, $H_A^{3'}$), 1.87-1.77 (H^4, $H^{4'}$), 1.73-1.67 (m, H^1, $H^{1'}$), 1.65-1.50 (m, H_A^5, $H_A^{5'}$, H^8, $H^{8'}$, $H_A^{5''}$, $H_A^{5'''}$), 1.49-1.39 (m, H_B^3, $H_B^{3'}$, H_A^6, $H_A^{6'}$, $H_A^{6''}$, $H_A^{6'''}$, $H^{8''}$, $H^{8'''}$), 1.37-1.22 (m, H_B^6, $H_B^{6'}$, $H_B^{6''}$, $H_B^{6'''}$, $H^{1''}$, $H^{1'''}$), 1.20-1.03 (m, H_B^5, $H_B^{5''}$, $H_B^{3''}$, $H_B^{3'''}$), 1.07 (d, *J* = 6.4 Hz, $H^{7''}$, $H^{7'''}$), 1.01 (d, *J* = 6.7 Hz, H^7, $H^{7'}$), 0.96 (d, *J* = 6.8 Hz, H^9), 0.98-0.94 (m, $H_B^{5'}$, $H_B^{5'''}$, $H^{9''}$, $H^{9'''}$), 0.92 (d, *J* = 6.9 Hz, $H^{9'}$).

^{13}C NMR (151 MHz, $CDCl_3$, δ in ppm): δ 61.12 (CH_2-OH), 61.09 (CH_2-OH), 60.82 (CH_2-OH), 60.58 (CH_2-OH), 60.52 (CH_2-OH), 60.42 (CH_2-OH), 60.30 (CH_2-OH), 60.20 (CH_2-OH), 51.50 (C^2, $C^{2'}$), 51.38 ($C^{2''}$), 51.35 ($C^{2'''}$), 42.05 ($C^{8''}$), 41.97 ($C^{8'''}$), 39.73 ($C^{3''}$,

$C^{3\prime\prime\prime}$), 38.36 ($C_{minor\ diast}$), 38.20 ($C_{minor\ diast}$), 38.16 ($C_{minor\ diast}$), 38.09 ($C_{minor\ diast}$), 38.07 ($C_{minor\ diast}$), 38.00 (C^{3}), 37.92 (C^{8}), 37.79 ($C^{8\prime}$), 37.57 ($C^{3\prime}$), 37.25 C^{10}), 37.12 (C^{1}), 37.05 ($C_{minor\ diast}$), 36.98 ($C^{1\prime}$), 36.87 ($C^{10\prime}$), 36.70 (S-*C*H_2-CH_2-OH), 36.30 (S-*C*H_2-CH_2-OH), 36.21(S-*C*H_2-CH_2-OH), 36.00 ($C_{minor\ diast}$), 35.96 ($C_{minor\ diast}$), 35.83 ($C_{minor\ diast}$), 35.70 ($C_{minor\ diast}$), 35.40 (C^{4}), 35.06 ($C^{4\prime}$), 34.88 (S-*C*H_2-CH_2-OH), 33.82 (S-*C*H_2-CH_2-OH), 30.62 (C^{5}), 30.19 (C^{6}, $C^{6\prime\prime}$), 30.08 ($C^{5\prime\prime}$), 29.96 ($C^{6\prime}$, $C^{6\prime\prime\prime}$), 28.35 ($C^{5\prime}$), 27.63 ($C^{5\prime\prime\prime}$), 21.05 ($C^{7\prime\prime}$), 21.02 ($C^{7\prime\prime\prime}$), 20.60 (C^{7}), 20.55 ($C^{7\prime}$), 16.30 (C^{9}), 16.17 ($C^{9\prime\prime}$), 16.03 ($C^{9\prime\prime\prime}$), 15.99 ($C^{9\prime}$).

ESI-MS of $C_{14}H_{28}O_2S_2$ ($M+Na^+$ = 315.177, calc. 315.142; $M+K^+$ = 331.134, calc. 331.116). HRMS of $C_{14}H_{28}O_2S_2$ ($M+H^+$ = 293.1634, calc. 293.1609).

Methyl 2-[2′-((1′′*R*)-3′′-((2′′′-methoxycarbonylethyl)thio)-4′′-methylcyclohexyl)propyl)thio]acetate (17).



Colorless viscous liquid (93%).

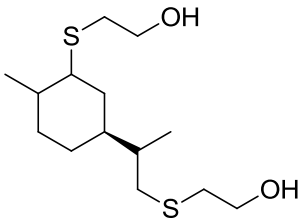
^{1}H NMR (600 MHz, $CDCl_3$, δ in ppm): 3.70-3.69 (group of singlets, OCH_3), 3.29-3.13 (m, CO-CH_2), 3.12-3.09 (m, CH^2, $CH^{2\prime}$), 2.70 (dd, *J* = 12.5, 4.8 Hz, H_A^{10}, $H_A^{10\prime}$), 2.68-2.65 (m, $H_A^{10\prime\prime}$, $H_A^{10\prime\prime\prime}$), 2.46-2.42 (m, $H_B^{10\prime\prime}$, $H_B^{10\prime\prime\prime}$), 2.41 (dd, *J* = 12.5, 8.8 Hz, H_B^{10}), 2.39 (dd, *J* = 12.5, 8.8 Hz, $H_B^{10\prime}$), 2.35-2.28 (m, $CH^{2\prime\prime}$, $CH^{2\prime\prime\prime}$), 2.02-1.97 (m, $H_A^{3\prime\prime}$, $H_A^{3\prime\prime\prime}$), 1.91-1.85 (m, H_A^3, $H_A^{3\prime}$), 1.82-1.75 (m, $H_A^{6\prime\prime}$, $H_A^{6\prime\prime\prime}$, $H_B^{6\prime\prime}$, $H_B^{6\prime\prime\prime}$), 1.73-1.66 (m, H^4, $H^{4\prime}$, $H^{4\prime\prime}$, $H^{4\prime\prime\prime}$, H^1, $H^{1\prime}$), 1.63-1.50 (m, H_A^5, $H_A^{5\prime}$, $H_A^{5\prime\prime}$, $H_A^{5\prime\prime\prime}$, H^8, $H^{8\prime}$), 1.46-1.36 (m, H_A^6, $H_A^{6\prime}$, H_B^3, $H_B^{3\prime}$, $H^{8\prime\prime}$, $H^{8\prime\prime\prime}$), 1.29-1.17 (m, $H^{1\prime\prime}$, $H^{1\prime\prime\prime}$, H_B^6, $H_B^{6\prime}$, $H_B^{3\prime\prime}$), 1.15-1.09 ($H_B^{3\prime\prime\prime}$), 1.09-

0.99 (m, H_B^5, $H_B^{5'}$, $H_B^{5''}$, $H_B^{5'''}$), 0.97 (s, H^7), 0.96 (s, $H^{7'}$), 0.97-0.96 (two singlets, $H^{7''}$ and $H^{7'''}$), 0.93-0.90 (m, H^9, $H^{9'}$, $H^{9''}$, $H^{9'''}$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 171.45 (CO), 171.35 (CO), 171.09 (CO), 171.02 (CO), 52.38 (OCH_3), 52.04 ($C^{2''}$), 52.00 ($C^{2'''}$), 51.61 (C^2), 51.50 ($C^{2'}$), 42.04 ($C^{8''}$), 41.94 ($C^{8'''}$), 38.75 ($C^{3''}$), 38.19 (C^{10}), 38.10 ($C^{10''}$), 38.02 ($C^{10'''}$), 37.96 ($C^{10'}$), 37.64 ($C^{1''}$, $C^{1'''}$), 37.48 (C^8), 37.44 ($C^{8'}$), 36.88 (C^1, $C^{1'}$), 36.56 (C^3, $C^{3'''}$), 35.77 (C^4, $C^{4'}$), 35.63 ($C^{6''}$), 34.79 ($C^{3'}$), 34.02 and 33.99 (CH-S-CH$_2$, CH$_2$-S-CH$_2$, CH-S-C'H$_2$, CH$_2$-S-C'H$_2$), 32.33 (CH$_2$-S-C''H$_2$), 32.30 (CH$_2$-S-C'''H$_2$), 32.06 (CH-S-C''H$_2$), 32.02 (CH-S-C'''H$_2$), 30.05 (C^6), 30.02 ($C^{6'}$, $C^{5''}$), 29.98 ($C^{5'''}$), 29.92 (C^5), 28.10 ($C^{5'}$), 21.11 ($C^{7''}$), 20.68 ($C^{7'''}$), 20.17 (C^7, $C^{7'}$), 16.15 (C^9), 16.01 ($C^{9'}$), 15.92 ($C^{9''}$), 15.77 ($C^{9'''}$).

ESI-MS of $C_{16}H_{28}O_4S_2$ (M+Na$^+$ = 371.172, calc. 371.132; M+K$^+$ = 387.102, calc. 387.106). HRMS of $C_{16}H_{28}O_4S_2$ (M+H$^+$ = 349.1475, calc. 349.1507).

2-[2′-((1′′*S*)-3′′-((2′′′-hydroxyethyl)thio)-4′′-methylcyclohexyl)propyl)thio]-ethanol (18).



Colorless viscous liquid (82%).

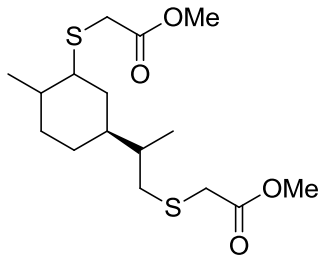
^{1}H NMR (600 MHz, $CDCl_3$, δ in ppm): 3.73-3.63 (CH$_2$-OH), 2.94-2.91 (H^2, $H^{2'}$), 2.88-2.63 (S-CH_2-CH$_2$-OH), 2.59 (dd, J = 12.0, 7.0 Hz, H_A^{10}), 2.57 (dd, J = 12.2, 4.9 Hz, $H_A^{10'}$), 2.44 (dd, J = 12.2, 7.7 Hz, $H_B^{10'}$), 2.41-2.35 (m, $H^{10''}$, $H^{10'''}$), 2.36 (dd, J = 12.0, 7.5 Hz, H_B^{10}), 2.23-2.16 (m, $H^{2''}$, $H^{2'''}$), 2.02-1.97 (m, $H_A^{3''}$, $H_A^{3'''}$), 1.93-1.86 (m, H_A^3, $H_A^{3'}$), 1.86-1.76 (H^4, $H^{4'}$), 1.73-1.66 (m, H^1, $H^{1'}$), 1.65-1.49 (m, H_A^5, $H_A^{5'}$, H^8, $H^{8'}$, $H_A^{5''}$, $H_A^{5'''}$),

1.48-1.38 (m, H_B^3, $H_B^{3'}$, H_A^6, $H_A^{6'}$, $H_A^{6''}$, $H_A^{6'''}$, $H^{8''}$, $H^{8'''}$), 1.37-1.22 (m, H_B^6, $H_B^{6'}$, $H_B^{6''}$, $H_B^{6'''}$, $H^{1''}$, $H^{1'''}$), 1.20-1.03 (m, H_B^5, $H_B^{5''}$, $H_B^{3''}$, $H_B^{3'''}$), 1.07 (d, *J* = 6.4 Hz, $H^{7''}$, $H^{7'''}$), 1.01 (d, *J* = 6.7 Hz, H^7, $H^{7'}$), 0.95 (d, *J* = 6.8 Hz, H^9), 0.98-0.92 (m, $H_B^{5'}$, $H_B^{5'''}$, $H^{9''}$, $H^{9'''}$), 0.92 (d, *J* = 6.9 Hz, $H^{9'}$).

^{13}C NMR (151 MHz, $CDCl_3$, δ in ppm): δ 61.14 (CH_2-OH), 61.11 (CH_2-OH), 60.85 (CH_2-OH), 60.60 (CH_2-OH), 60.54 (CH_2-OH), 60.45 (CH_2-OH), 60.33 (CH_2-OH), 60.23 (CH_2-OH), 51.47 (C^2, $C^{2'}$), 51.36 ($C^{2''}$), 51.33 ($C^{2'''}$), 42.02 ($C^{8''}$), 41.95 ($C^{8'''}$), 39.69 ($C^{3''}$, $C^{3'''}$), 38.34 ($C_{minor\ diast}$), 38.18 ($C_{minor\ diast}$), 38.14 ($C_{minor\ diast}$), 38.06 ($C_{minor\ diast}$), 38.05 ($C_{minor\ diast}$), 37.95 (C^3), 37.90 (C^8), 37.78 ($C^{8'}$), 37.56 ($C^{3'}$), 37.24 (C^{10}), 37.19 ($C_{minor\ diast}$), 37.09 (C^1), 36.95 ($C^{1'}$), 36.78 ($C^{10'}$), 36.61 (S-*C*H_2-CH_2-OH), 36.23 (S-*C*H_2-CH_2-OH), 36.15 (S-*C*H_2-CH_2-OH), 35.93 ($C_{minor\ diast}$), 35.90 ($C_{minor\ diast}$), 35.81 ($C_{minor\ diast}$), 35.68 ($C_{minor\ diast}$), 35.38 (C^4), 35.05 ($C^{4'}$), 34.87 (S-*C*H_2-CH_2-OH), 33.75 (S-*C*H_2-CH_2-OH), 30.59 (C^5), 30.16 (C^6, $C^{6''}$), 30.06 ($C^{5''}$), 29.94 ($C^{6'}$, $C^{6'''}$), 28.31 ($C^{5'}$), 27.62 ($C^{5'''}$), 21.03 ($C^{7''}$), 21.00 ($C^{7'''}$), 20.58 (C^7), 20.52 ($C^{7'}$), 16.27 (C^9), 16.14 ($C^{9''}$), 16.01 ($C^{9'''}$), 15.97 ($C^{9'}$).

ESI-MS of $C_{14}H_{28}O_2S_2$ ($M+Na^+$ = 315.177, calc. 315.142). HRMS of $C_{14}H_{28}O_2S_2$ ($M+H^+$ = 293.1581, calc. 293.1609).

Methyl 2-[2′-((1′′*S*)-3′′-((2′′′-methoxycarbonylethyl)thio)-4′′-methylcyclohexyl)propyl)thio]acetate (19).



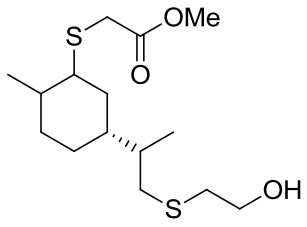
Colorless viscous liquid (93%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 3.64-3.63 (group of singlets, OCH_3), 3.20-3.09 (m, CO-CH_2), 3.08-3.03 (m, CH^{2}, $CH^{2'}$), 2.65 (dd, *J* = 12.5, 4.9 Hz, H_A^{10}, $H_A^{10'}$), 2.65-2.59 (m, $H_A^{10''}$, $H_A^{10'''}$), 2.42-2.34 (m, $H_B^{10''}$, $H_B^{10'''}$), 2.35 (dd, *J* = 12.5, 8.7 Hz, H_B^{10}), 2.33 (dd, *J* = 12.5, 8.7 Hz, $H_B^{10'}$), 2.30-2.20 (m, $CH^{2''}$, $CH^{2'''}$), 1.99-1.89 (m, $H_A^{3''}$, $H_A^{3'''}$), 1.89-1.78 (m, H_A^{3}, $H_A^{3'}$), 1.78-1.71 (m, $H_A^{6''}$, $H_A^{6'''}$, $H_B^{6''}$, $H_B^{6'''}$), 1.72-1.58 (m, H^{4}, $H^{4'}$, $H^{4''}$, $H^{4'''}$, H^{1}, $H^{1'}$), 1.58-1.44 (m, H_A^{5}, $H_A^{5'}$, $H_A^{5''}$, $H_A^{5'''}$, H^{8}, $H^{8'}$), 1.43-1.28 (m, H_A^{6}, $H_A^{6'}$, H_B^{3}, $H_B^{3'}$, $H^{8''}$, $H^{8'''}$), 1.25-1.08 (m, $H^{1''}$, $H^{1'''}$, H_B^{6}, $H_B^{6'}$, $H_B^{3''}$, $H_B^{3'''}$), 1.05-0.94 (m, H_B^{5}, $H_B^{5'}$, $H_B^{5''}$, $H_B^{5'''}$), 0.93 (s, H^{7}), 0.90 (s, $H^{7'}$), 0.93-0.90 (two singlets, $H^{7''}$ and $H^{7'''}$), 0.88-0.85 (m, H^{9}, $H^{9'}$, $H^{9''}$, $H^{9'''}$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 171.29 (CO), 171.19 (CO), 171.10 (CO), 170.93 (CO), 170.87 (CO), 52.25 (OCH_3), 51.90 ($C^{2''}$), 51.85 ($C^{2'''}$), 51.47 (C^{2}), 51.36 ($C^{2'}$), 41.91 ($C^{8''}$), 41.81 ($C^{8'''}$), 38.62 ($C^{3''}$), 38.05 (C^{10}), 37.95 ($C^{10''}$), 37.87 ($C^{10'''}$), 37.82 ($C^{10'}$), 37.50 ($C^{1''}$, $C^{1'''}$), 37.34 (C^{8}), 37.31 ($C^{8'}$), 36.75 (C^{1}, $C^{1'}$), 36.43 (C^{3}, $C^{3'''}$), 35.63 (C^{4}, $C^{4'}$), 35.51 ($C^{6''}$), 34.64 ($C^{3'}$), 33.87 and 33.84 (CH-S-*C*H_2, CH_2-S-*C*H_2, CH-S-*C*′H_2, CH_2-S-*C*′H_2), 32.21 (CH_2-S-*C*″H_2), 32.16 (CH_2-S-*C*‴H_2), 31.91 (CH-S-*C*″H_2), 31.87 (CH-S-*C*‴H_2), 29.94 (C^{6}), 29.91 ($C^{6'}$, $C^{5''}$), 29.85 ($C^{5'''}$), 29.80 (C^{5}), 27.99 ($C^{5'}$), 20.59 ($C^{7''}$), 20.57 ($C^{7'''}$), 20.05 (C^{7}, $C^{7'}$), 16.02 (C^{9}), 15.89 ($C^{9'}$), 15.81 ($C^{9''}$), 15.67 ($C^{9'''}$).

ESI-MS of $C_{16}H_{28}O_4S_2$ ($M+Na^+$ = 371.176, calc. 371.132). HRMS of $C_{16}H_{28}O_4S_2$ ($M+H^+$ = 349.1480, calc. 349.1507).

Methyl 2-(2′-((1′′*R*)-3′′-((2′′′-hydroxyethyl)thio)propan-2′′-yl)-4′′-methylcyclohexyl)thio)acetate (20).



Colorless viscous liquid (83%).

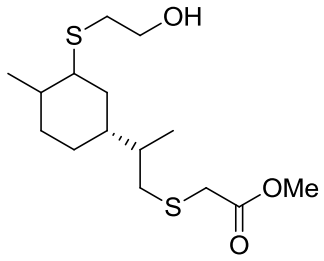
^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.71 (s, OMe), 3.69 (t, *J* = 5.9 Hz, CH_2-OH), 3.31-3.16 (m, CO-CH_2), 3.14-3.09 (m, H^2, $H^{2'}$), 2.73-2.66 (m, S-C*H*$_2$-CH_2-OH), 2.61-2.56 (m, $H_A{}^{10}$, $H_A{}^{10'}$, $H_A{}^{10''}$, $H_A{}^{10'''}$), 2.40-2.30 (m, $H_B{}^{10}$, $H_B{}^{10'}$, $H_B{}^{10''}$, $H_B{}^{10'''}$), 2.27-2.21 (broad, OH), 2.07-1.98 (m, $H_A{}^{3''}$, $H_A{}^{3'''}$), 1.94-1.86 (m, $H_A{}^{3}$, $H_A{}^{3'}$), 1.85-1.79 (m, $H_A{}^{6''}$, $H_A{}^{6'''}$, $H_B{}^{6''}$, $H_B{}^{6'''}$), 1.79-1.65 (m, H^1, $H^{1'}$, H^4, $H^{4'}$), 1.65-1.49 (m, $H_A{}^{5}$, $H_A{}^{5'}$, H^8, $H^{8'}$, $H_A{}^{5''}$, $H_A{}^{5'''}$, $H^{4''}$, $H^{4'''}$, $H^{8''}$, $H^{8'''}$), 1.49-1.36 (m, $H_B{}^{3}$, $H_B{}^{3'}$, $H_A{}^{6}$, $H_A{}^{6'}$), 1.31-1.18 (m, $H_B{}^{6}$, $H_B{}^{6'}$, $H^{1''}$, $H^{1'''}$), 1.16-1.02 (m, $H_B{}^{3''}$, $H_B{}^{3'''}$, $H_B{}^{5}$, $H_B{}^{5'}$, $H_B{}^{5''}$, $H_B{}^{5'''}$), 1.04 (d, *J* = 6.4 Hz, $H^{7''}$), 0.99 (d, *J* = 6.8 Hz, H^7, $H^{7'}$), 0.94 (d, *J* = 6.8 Hz, H^9, $H^{9'}$), 1.01-0.94 (m, $H^{7'''}$, $H^{9''}$, $H^{9'''}$).

^{13}C NMR (101 MHz, $CDCl_3$, δ in ppm): δ 171.67 (C′′O), 171.65 (C′′′O), 171.56 (CO), 171.52 (C′O), 60.48 (CH_2′′-OH), 60.46 (CH_2′′′-OH), 60.43 (CH_2-OH), 60.40 (CH_2′-OH), 52.57 (OC′′H_3), 52.56 (OC′′′H_3), 52.52 (OCH_3), 52.51 (OC′H_3), 52.12 ($C^{2''}$), 52.09 ($C^{2'''}$), 51.77 (C^2), 51.67 ($C^{2'}$), 41.99 ($C^{8''}$, $C^{8'''}$), 38.89 ($CH_{2\text{minor diast}}$), 38.31 ($CH_{\text{minor diast}}$), 38.20 ($CH_{\text{minor diast}}$), 38.10 (C^8), 38.07 ($C^{8'}$), 37.72 ($CH_{\text{minor diast}}$), 37.71 ($CH_{\text{minor diast}}$), 37.38 (C^{10}), 37.23 ($CH_{2\text{minor diast}}$), 37.12 ($C^{10'}$), 37.07 ($CH_{2\text{minor diast}}$), 36.99 (C^1), 36.94 ($C^{1'}$), 36.87 (C^3), 36.50 ($CH_{2\text{minor diast}}$), 36.06 (S-*C*H_2-CH_2-OH), 36.02 ($CH_{2\text{minor diast}}$), 35.79 (C^4), 35.77 ($C^{4'}$), 35.68 ($CH_{2\text{minor diast}}$), 34.70 ($C^{3'}$), 34.21 (S-*C*H_2-CO), 34.17 (S-*C*′H_2-CO), 32.16 (S-*C*′′H_2-CO), 32.14 (S-*C*′′′H_2-CO), 30.30 (C^5), 30.13 (C^6, $C^{6''}$), 30.06

($C^{5''}$), 29.97 ($C^{6'}$, $C^{6'''}$), 28.09 ($C^{5'}$), 27.65 ($C^{5'''}$), 20.77 ($C^{7''}$), 20.75 ($C^{7'''}$), 20.24 (C^{7}), 20.22 ($C^{7'}$), 16.12 (C^{9}, $C^{9''}$), 15.99 ($C^{9'}$, $C^{9'''}$).

ESI-MS of $C_{15}H_{28}O_3S_2$ ($M+Na^+$ = 343.190, calc. 343.137).

Methyl 2-[2′-((1′′*R*)-3′′-((2′′′-hydroxyethyl)thio)-4′′-methylcyclohexyl)propyl)-thio)acetate (21).



Colorless viscous liquid (92%).

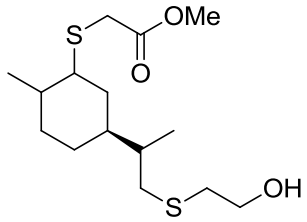
^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.71 (s, OMe), 3.66 (t, *J* = 6.0 Hz, CH_2-OH), 3.23-3.14 (m, CO-CH_2), 2.95-2.91 (m, H^2, $H^{2'}$), 2.76-2.61 (m, S-C*H*$_2$-CH_2-OH, H_A^{10}, $H_A^{10'}$, $H_A^{10''}$, $H_A^{10'''}$), 2.49-2.39 (m, H_B^{10}, $H_B^{10'}$, $H_B^{10''}$, $H_B^{10'''}$), 2.35-2.25 (broad, OH), 2.25-2.14 ($H^{2''}$, $H^{2'''}$), 2.03-1.94 (m, $H_A^{3''}$, $H_A^{3'''}$), 1.90-1.82 (m, H_A^3, $H_A^{3'}$), 1.81-1.73 (m, H^4, $H^{4'}$), 1.73-1.64 (m, H^1, $H^{1'}$), 1.64-1.49 (m, H_A^5, $H_A^{5'}$, H^8, $H^{8'}$, $H_A^{5''}$, $H_A^{5'''}$, $H^{4''}$, $H^{4'''}$), 1.49-1.37 (m, H_A^6, $H_A^{6'}$, H_B^3, $H_B^{3'}$, $H_A^{6''}$, $H_A^{6'''}$, $H^{8''}$, $H^{8'''}$), 1.34-1.18 (m, H_B^6, $H_B^{6'}$, $H_B^{3''}$, $H_B^{3'''}$, $H^{1''}$, $H^{1'''}$, $H_B^{6''}$, $H_B^{6'''}$), 1.15-0.96 (m, H_B^5, $H_B^{5'}$, $H_B^{5''}$, $H_B^{5'''}$), 1.05 (d, *J* = 7.4 Hz, $H^{7''}$), 0.99 (d, *J* = 6.7 Hz, H^7, $H^{7'}$), 0.93 (d, *J* = 6.8 Hz, H^9, $H^{9'}$), 0.98-0.90 (m, $H^{7'''}$, $H^{9''}$, $H^{9'''}$).

^{13}C NMR (101 MHz, $CDCl_3$, δ in ppm): 171.28 (CO), 171.25 (C′O), 171.22 (C′′O), 171.21 (C′′′O), 61.18 (CH_2′′-OH), 61.16 (CH_2′′′-OH), 60.69 (CH_2-OH), 60.63 (CH_2′-OH), 52.51 (OCH_3, $OC'H_3$, $OC''H_3$, $OC'''H_3$), 52.33 ($C^{2''}$), 51.28 ($C^{2'''}$), 51.02 (C^2), 50.98 ($C^{2'}$), 42.02 ($C^{8''}$), 41.93 ($C^{8'''}$), 39.59 ($C^{3''}$), 38.29 (C^{10}), 38.17 ($CH_{2\text{minor diast}}$), 38.04 ($CH_{\text{minor diast}}$),

38.01 ($C^{10'}$, $CH_{minor\ diast}$), 37.60 ($CH_{minor\ diast}$), 37.55 ($CH_{minor\ diast}$), 37.49 (C^{8}), 37.48 ($C^{8'}$), 37.41 (C^{3}), 37.15 ($CH_{2minor\ diast}$), 36.97 (C^{1}), 36.91 ($C^{1'}$), 36.24 (S-*C*H_2-CH_2-OH), 36.14 (S-*C'*H_2-CH_2-OH), 35.80 ($CH_{2minor\ diast}$), 35.66 (C^{4}), 35.56 ($C^{4'}$), 35.37 ($C^{3'}$), 34.06 (S-*C*H_2-CO), 34.05 (S-*C*H_2-CO), 33.72 ($CH_{2minor\ diast}$), 30.18 (C^{5}), 30.05 (C^{6}, $C^{6''}$, $C^{5''}$), 29.88 ($C^{6'}$, $C^{6'''}$), 28.24 ($C^{5'}$), 27.54 ($C^{5'''}$), 21.01 ($C^{7''}$), 20.97 ($C^{7'''}$), 20.53 (C^{7}), 20.50 ($C^{7'}$), 16.15 (C^{9}, $C^{9''}$), 16.06 ($C^{9'}$), 15.89 ($C^{9'''}$).

ESI-MS of $C_{15}H_{28}O_3S_2$ (M+Na^+ = 343.192, calc. 343.137).

Methyl 2-(2′-((1′′*S*)-3′′-((2′′′-hydroxyethyl)thio)propan-2′′-yl)-4′′-methylcyclohexyl)thio)acetate (22).



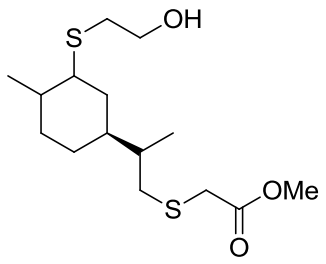
Colorless viscous liquid (81%).

^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 3.72 (s, OMe), 3.71 (s, OMe), 3.69 (t, *J* = 6.0 Hz, CH_2-OH), 3.31-3.16 (m, CO-CH_2), 3.13-3.10 (m, H^2, $H^{2'}$), 2.74-2.65 (m, S-C*H*$_2$-CH_2-OH), 2.61-2.55 (m, H_A^{10}, $H_A^{10'}$, $H_A^{10''}$, $H_A^{10'''}$), 2.40-2.30 (m, H_B^{10}, $H_B^{10'}$, $H_B^{10''}$, $H_B^{10'''}$), 2.27-2.16 (broad, OH), 2.06-1.99 (m, $H_A^{3''}$, $H_A^{3'''}$), 1.94-1.87 (m, H_A^{3}, $H_A^{3'}$), 1.85-1.79 (m, $H_A^{6''}$, $H_A^{6'''}$, $H_B^{6''}$, $H_B^{6'''}$), 1.79-1.66 (m, H^1, $H^{1'}$, H^4, $H^{4'}$), 1.64-1.50 (m, H_A^{5}, $H_A^{5'}$, H^8, $H^{8'}$, $H_A^{5''}$, $H_A^{5'''}$, $H^{4''}$, $H^{4'''}$, $H^{8''}$, $H^{8'''}$), 1.49-1.37 (m, H_B^{3}, $H_B^{3'}$, H_A^{6}, $H_A^{6'}$), 1.31-1.19 (m, H_B^{6}, $H_B^{6'}$, $H^{1''}$, $H^{1'''}$), 1.17-1.02 (m, $H_B^{3''}$, $H_B^{3'''}$, H_B^{5}, $H_B^{5'}$, $H_B^{5''}$, $H_B^{5'''}$), 1.05 (d, *J* = 6.5 Hz, $H^{7''}$), 0.99 (d, *J* = 6.7 Hz, H^{7}, $H^{7'}$), 0.94 (d, *J* = 6.8 Hz, H^{9}, $H^{9'}$), 1.01-0.94 (m, $H^{7'''}$, $H^{9''}$, $H^{9'''}$).

^{13}C NMR (126 MHz, $CDCl_3$, δ in ppm): 171.67 (C´´O), 171.65 (C´´´O), 171.56 (CO), 171.52 (C´O), 60.47 (CH_2´´-OH), 60.45 (CH_2´´´-OH), 60.42 (CH_2-OH), 60.38 (CH_2´-OH), 52.57 (OC´´H_3), 52.56 (OC´´´H_3), 52.53 (OCH_3), 52.51 (OC´H_3), 52.11 ($C^{2´´}$), 52.08 ($C^{2´´´}$), 51.76 (C^2), 51.66 ($C^{2´}$), 41.98 ($C^{8´´}$, $C^{8´´´}$), 38.88 ($CH_{2\text{minor diast}}$), 38.30 ($CH_{\text{minor diast}}$), 38.20 ($CH_{\text{minor diast}}$), 38.09 (C^8), 38.07 ($C^{8´}$), 37.71 ($CH_{\text{minor diast}}$), 37.70 ($CH_{\text{minor diast}}$), 37.36 (C^{10}), 37.22 ($CH_{2\text{minor diast}}$), 37.11 ($C^{10´}$), 37.06 ($CH_{2\text{minor diast}}$), 36.99 (C^1), 36.94 ($C^{1´}$), 36.86 (C^3), 36.49 ($CH_{2\text{minor diast}}$), 36.06 (S-*C*H_2-CH_2-OH), 36.02 ($CH_{2\text{minor diast}}$), 35.78 (C^4), 35.77 ($C^{4´}$), 35.68 ($CH_{2\text{minor diast}}$), 34.70 ($C^{3´}$), 34.20 (S-*C*H_2-CO), 34.16(S-*C*´H_2-CO), 32.16 (S-*C*´´H_2-CO), 32.13 (S-*C*´´´H_2-CO), 30.29 (C^5), 30.13 (C^6, $C^{6´´}$), 30.05 ($C^{5´´}$), 29.96 ($C^{6´}$, $C^{6´´´}$), 28.08 ($C^{5´}$), 27.64 ($C^{5´´´}$), 20.77 ($C^{7´´}$), 20.75 ($C^{7´´´}$), 20.25 (C^7), 20.22 ($C^{7´}$), 16.12 (C^9, $C^{9´´}$), 15.98 ($C^{9´}$, $C^{9´´´}$).

ESI-MS of $C_{15}H_{28}O_3S_2$ ($M+Na^+$ = 343.177, calc. 343.137).

Methyl 2-(2´-((1´´*S*)-3´´-((2´´´-hydroxyethyl)thio)-4´´-methylcyclohexyl)propyl)-thio)acetate (23).



Colorless viscous liquid (90%).

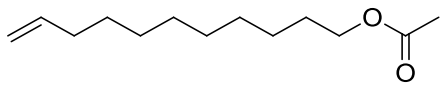
^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 3.70 (s, OMe), 3.66 (t, *J* = 6.0 Hz, CH_2-OH), 3.22-3.13 (m, CO-CH_2), 2.95-2.90 (m, H^2, $H^{2´}$), 2.75-2.61 (m, S-C*H*$_2$-CH_2-OH, $H_A{}^{10}$, $H_A{}^{10´}$, $H_A{}^{10´´}$, $H_A{}^{10´´´}$), 2.49-2.37 (m, $H_B{}^{10}$, $H_B{}^{10´}$, $H_B{}^{10´´}$, $H_B{}^{10´´´}$), 2.41-2.30 (broad, OH), 2.23-2.13 ($H^{2´´}$, $H^{2´´´}$), 2.03-1.94 (m, $H_A{}^{3´´}$, $H_A{}^{3´´´}$), 1.90-1.81 (m, $H_A{}^3$, $H_A{}^{3´}$), 1.81-1.72 (m, H^4, $H^{4´}$), 1.72-1.64 (m, H^1, $H^{1´}$), 1.64-1.50 (m, $H_A{}^5$, $H_A{}^{5´}$, H^8, $H^{8´}$, $H_A{}^{5´´}$, $H_A{}^{5´´´}$, $H^{4´´}$, $H^{4´´´}$),

1.50-1.36 (m, H_A^6, $H_A^{6'}$, H_B^3, $H_B^{3'}$, $H_A^{6''}$, $H_A^{6'''}$, $H^{8''}$, $H^{8'''}$), 1.32-1.19 (m, H_B^6, $H_B^{6'}$, $H_B^{3''}$, $H_B^{3'''}$, $H^{1''}$, $H^{1'''}$, $H_B^{6''}$, $H_B^{6'''}$), 1.16-0.96 (m, H_B^5, $H_B^{5'}$, $H_B^{5''}$, $H_B^{5'''}$), 1.05 (d, *J* = 6.5 Hz, $H^{7''}$), 0.98 (d, *J* = 6.7 Hz, H^7, $H^{7'}$), 0.920 (d, *J* = 6.8 Hz, H^9), 0.916 (d, *J* = 6.8 Hz, $H^{9'}$), 0.98-0.90 (m, $H^{7'''}$, $H^{9''}$, $H^{9'''}$).

^{13}C NMR (126 MHz, $CDCl_3$, δ in ppm): 171.25 (CO), 171.22 (C′O), 171.19 (C′′O), 171.18 (C′′′O), 61.19 (CH_2′′-OH), 61.16 (CH_2′′′-OH), 60.70 (CH_2-OH), 60.64 (CH_2′-OH), 52.48 (OCH_3, OC′H_3, OC′′H_3, OC′′′H_3), 51.31 ($C^{2''}$), 51.25 ($C^{2'''}$), 51.00 (C^2), 50.96 ($C^{2'}$), 42.00 ($C^{8''}$), 41.91 ($C^{8'''}$), 39.56 ($C^{3''}$), 38.26 (C^{10}), 38.14 ($CH_{2\text{minor diast}}$), 38.01 ($CH_{\text{minor diast}}$), 37.98 ($C^{10'}$, $CH_{\text{minor diast}}$), 37.58 ($CH_{\text{minor diast}}$), 37.52 ($CH_{\text{minor diast}}$), 37.46 (C^8), 37.45 ($C^{8'}$), 37.38 (C^3), 37.13 ($CH_{2\text{minor diast}}$), 36.94 (C^1), 36.89 ($C^{1'}$), 36.19 (S-*C*H_2-CH_2-OH), 36.09 (S-*C*′H_2-CH_2-OH), 35.77 ($CH_{2\text{minor diast}}$), 35.63 (C^4), 35.54 ($C^{4'}$), 35.35 ($C^{3'}$), 34.03 (S-*C*H_2-CO), 34.02 (S-*C*H_2-CO), 33.97 (S-*C*H_2-CO), 33.66 ($CH_{2\text{minor diast}}$), 30.15 (C^5), 30.02 (C^6, $C^{6''}$, $C^{5''}$), 29.86 ($C^{6'}$, $C^{6'''}$), 28.21 ($C^{5'}$), 27.52 ($C^{5'''}$), 20.98 ($C^{7''}$), 20.95 ($C^{7'''}$), 20.51 (C^7), 20.47 ($C^{7'}$), 16.13 (C^9, $C^{9''}$), 16.03 ($C^{9'}$), 15.86 ($C^{9'''}$).

ESI-MS of $C_{15}H_{28}O_3S_2$ ($M+Na^+$ = 343.183, calc. 343.137).

Synthesis of undec-10-en-1-yl acetate (29).



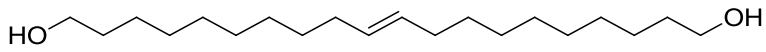
10-undecen-1-ol (30.00 g, 0.176 mol), acetic anhydride (20.00 g, 0.196 mol), and 15 drops of concentrated sulfuric acid were added into a 100 mL round bottom. The mixture was refluxed for 4 h, and then poured into 100 mL ice water and stirred for 30 minutes. The organic layer was separated and the water layer was extracted with 2 x 100 mL ethyl acetate. The combined organic layers were washed with 2 x 100 mL $NaHCO_3$ (10% solution), and 100 mL water. The organic layer was dried over

anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulting product was filtered through a short pad of silica gel and obtained as a light yellow liquid (34,59 g, 93 %). This compound was then used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H, =CH–), 4.96 (m, 2H, CH_2=), 4.05 (t, *J* = 6.7 Hz, 2H, –OCH_2–), 2.14 – 1.96 (m, 5H, –CH_3 and =CH–C*H*$_2$–), 1.72 – 1.53 (m, 2H, –OCH_2–C*H*$_2$–), 1.46 – 1.22 (m, 12H, hydrocarbon).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.18 (s,>C=O), 139.14 (s, =CH–), 114.10 (s, CH_2=), 64.61 (s, –OCH_2–), 33.77 (s), 29.42 (s), 29.36 (s), 29.21 (s), 29.07 (s), 28.89 (s), 28.58 (s), 25.88 (s) (hydrocarbon), 20.97 (s, –CH_3).

Synthesis of (*E*)-icos-10-ene-1,20-diol (26) *via* self-metathesis of 29 and alcohol deprotection.



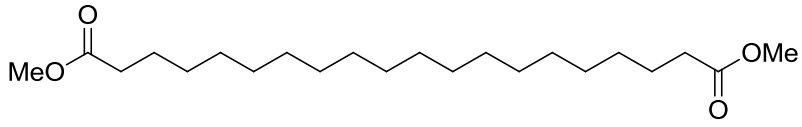
The general procedure for self-metatheses is as follows. Reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). To a stirred mixture of 10-undecen-1-yl acetate (0.40 g, 1.90 mmol) and 0,60 mL of tetradecane (internal standard), 2.00 mg of 1,4-benzoquinone (1.0 mol% to monomer) were added. The mixture was stirred 5 minutes at 50 °C and then, the desired metathesis catalyst (**C1**, **C2**, or **C3**, 0.5 mol% to monomer) was added. The reactions were carried out at 50 °C under continuous vacuum (200 mbar). For the optimization study, samples were taken before catalyst addition and at different reaction times, quenched with an excess of ethyl vinyl ether, and analyzed by GC. Once the reaction conditions were optimized (0.5 mol% **C2**, 50 °C, 1 mol% 1,4-

benzoquinone), the reaction was scaled-up to 3.00 g of 10-undecen-1-yl acetate, and the work-up was carried out as follows: The reaction was quenched by addition of a 50-fold excess (to catalyst) of ethyl vinyl ether and stirring 20 min at room temperature. The excess of ethyl vinyl ether was removed at reduced pressure, and the product was dissolved in hexane, filtered through a short pad of silica using hexane as eluent, and concentrated under reduced pressure. The product (**30**) was used in the deprotection step without further purification. In a 25 mL round bottom flask, **30** (2.08 g), methanol (0.22 mL), and TBD (0.09 g, 10 mol%) were heated to 65 °C for 7 h. Then, the formed methyl acetate and the excess of methanol were removed at reduced pressure. The product was recrystallized twice from methanol. (*E*) icos-10-ene-1,20-diol (**26**) was obtained as white crystals (1.48 g, 67%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 – 5.34 (m, 1H, =CH–), 3.65 (t, *J* = 6.6 Hz, 2H, –C*H*$_2$OH), 2.06 – 1.90 (m, 2H, =CH–C*H*$_2$–), 1.65 – 1.51 (m, 2H, –C*H*$_2$CH$_2$OH), 1.41 – 1.19 (m, 12H, hydrocarbon).

^{13}C NMR (126 MHz, $CDCl_3$) δ 130.39 (s, =CH–), 62.95 (s, –CH_2OH), 32.77 (s), 32.60 (s), 29.61 (d, *J* = 3.2 Hz), 29.45 (s), 29.12 (s), 25.77 (s) (hydrocarbon).

Dimethyl icosanedioate (28).



A mixture of **24** (0.50 g , 1.36 mmol), 5 mL of ethyl acetate, and Pd/C (0.05 g, 10 wt% of **24**) was added to a 10 mL round bottom flask which was sealed with septum. After two vacuum/H_2 cycles to replace the air inside with hydrogen, the mixture was vigorously stirred at room temperature under hydrogen pressure (balloon) for 16 h.

The catalyst was then filtered off and the solvent was removed at reduced pressure to obtain the product (**28**) quantitatively as white crystalline powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 6H, –OCH_3), 2.32 (t, *J* = 7.6 Hz, 4H, –CO–CH_2), 1.70-1.56 (m, 4H, –CO–CH_2–CH_2), 1.28 (m, 28H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.34 (s, >C=O), 51.42 (s, –OCH_3), 34.12 (s, –CO–CH_2), 29.86-28.98 (m, CH_2), 24.96 (s, –CO–CH_2–CH_2).

8.3.3. Synthesis of polymers

General procedure for polycondensation reactions.

All polycondensation reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK) at 120°C applying continuous vacuum (10±5 mbar). 5 mol% (relative to ester groups) of TBD was used as catalyst.

P1-P4

Monomer **20**, **21**, **22**, or **23** (250.0 mg, 0.78 mmol) was polymerized with TBD (5.4 mg, 0.04 mmol) for 7 h. The polymers were purified by precipitation of a concentrated THF solution of the reaction products into ethanol at room temperature. Yields: **P1** (190 mg, 85%), **P2** (160 mg, 70%), **P3** (190 mg, 82%), **P4** (160 mg, 71%).

P5, **P6**

Monomer **17** or **19** (150.0 mg, 0.43 mmol) and diol **26** (134.5 mg, 0.43 mmol) were polymerized with TBD (6.0 mg, 0.04 mmol) for 7 h. The polymers were purified by precipitation of a concentrated THF solution of the reaction products into ethanol at room temperature. Yields: **P5** (215 mg, 84%), **P6** (220 mg, 86%).

P7, **P8**

Diol **16** or **18** (150.0 mg, 0.51 mmol) and diester **24** (189.0 mg. 0.51 mmol) were polymerized with TBD (7.1 mg, 0.05 mmol) for 7 h. The polymers were purified by precipitation of a concentrated THF solution of the reaction products into ethanol at room temperature. Yields: **P7** (227 mg, 74%), **P8** (240 mg, 78%).

P9, **P10**

Diester **17** or **19** (150.0 mg, 0.43 mmol) and diol **27** (199.2 mg, 0.43 mmol) were polymerized with TBD (6.0 mg, 0.04 mmol) for 7 h. The polymers were purified by precipitation of a concentrated THF solution of the reaction products into ethanol at room temperature. Yields: **P9** (275 mg, 85%), **P10** (269 mg, 83%).

P11, **P12**

Diol **16** or **18** (150.0 mg, 0.51 mmol) and diester **25** (266.0 mg. 0.51 mmol) were polymerized with TBD (7.1 mg, 0.05 mmol) for 7 h. The polymers were purified by precipitation of a concentrated THF solution of the reaction products into ethanol at room temperature. Yields: **P11** (241 mg, 63%), **P12** (289 mg, 75%).

P13, **P14**

Diol **16** or **18** (150.0 mg, 0.51 mmol) and diester **28** (190.0 mg. 0.51 mmol) were polymerized with TBD (7.1 mg, 0.05 mmol) for 7 h. The polymers were purified by precipitation of a concentrated THF solution of the reaction products into ethanol at room temperature. Yields: **P13** (196 mg, 64%), **P14** (195 mg, 63%).

8.3.4. ^{1}H NMR kinetic study: reaction between 31 and 10-undecen-1-ol

The reaction was performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). In a carousel tube, diester **31** (500.0 mg, 1.64 mmol)

was mixed with 10-undecen-1-ol (280.0 mg, 1.64 mmol). After taking an initial sample t = 0 min, TBD (22.8 mg, 0.16 mmol) was added. The reaction mixture was then stirred magnetically at 120 °C under continuous vacuum at 10±5 mbar. Samples were taken at 5, 10, 15, 20, 60, 120, and 240 minutes for conversion analysis using ^{1}H-NMR. The conversion of the ester groups was calculated, at each step of the reaction, taking the integrals of a) a characteristic signal of **31** which is not affected during the reaction (H^{d}, see figure 4.8), and b) characteristic signals of the products of esterification (H^{f} and H^{g}, see figure 4.8). A relaxation time (d1) of 5 s was used in the ^{1}H NMR analyses in order to obtain reliable integral values.

8.4. Renewable Co-Polymers derived from Vanillin and Fatty Acid Derivatives

8.4.1. Materials

Vanillyl alcohol (**33**),[166] methyl 10-undecenoate (**38**),[144] 1,12-dimethyl-(*E*)-dodec-2-enedioate,[144] dimethyl icosanedioate (**28**),[134] (*E*)-dimethyl icos-10-enedioate (**24**),[144] were prepared as previously reported. Vanillin (**32**, Sigma-Aldrich, 99%), 11-bromo-1-undecene (**34**, Aldrich, 98%), 10-undecen-1-ol (Aldrich, 98%), tetrabutylammonium iodide (TBAI, Acros Organics, 98%), K_2CO_3 (Sigma-Aldrich, 99%), acetonitrile (Carl-Roth, ≥99.9%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), methyl thioglycolate (**5**, Aldrich, >97%), 2-mercaptoethanol (**4**, Aldrich, >99%), dimethyl adipate (**39**, Aldrich, ≥99%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene, (TBD, Aldrich, 98%), silica gel 60 (0.035–0.070 mm, Aldrich), 1,4-benzoquinone (>99%, Aldrich), (1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(*o*-isopropoxyphenylmethylene)ruthenium (**C1**, Hoveyda–Grubbs Catalyst 2nd Generation, Aldrich), benzylidene[1,3-*bis*-(2,4,6-trimethylphenyl)imidazolidinylidene]dichloro(tricyclohe-xylphosphine)ruthenium

(**C4**, second generation Grubbs catalyst, Aldrich), [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro [2-(1-methylacetoxy)phenyl]methylene ruthenium(II) (**C3**, Umicore $M5_1$), 1,3-*bis*-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-yliden[2-(isopropoxy)-5*N*,*N*-dimethylaminosulfonyl)phenyl]me-thylene ruthenium (II) dichloride (**C2**, Zhan catalyst, 96%, ABCR), ethyl vinyl ether (99%, Aldrich), palladium on activated carbon (Pd/C, 10% Pd, Acros Organics), 1,4-butanedithiol (**42**, >97%, Aldrich), and 2-mercaptoethyl ether (**43**, >95%, Aldrich), were used as received. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%) was recrystallized from methanol. All solvents (technical grade) were used without further purification.

8.4.2. Syntheses of monomers

(3-methoxy-4-(undec-10-en-1-yloxy)phenyl)methanol (35).

Into a 25 mL round bottom flask equipped with a reflux condenser was added **33** (1.54 g, 10.0 mmol), **34** (3.03 g, 13.0 mmol), acetonitrile (5 mL), tetrabutylammonium iodide (TBAI, 0.06 g) and K_2CO_3 (1.93 g, 14.0 mmol). The mixture was refluxed for 16 h. The mixture was then filtered and washed with acetone. After concentration under vacuum the product was obtained by precipitation in hexane to afford white crystals in quantitative yield.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.95-6.80 (m, 3H, aromatic -CH=), 5.83 (ddt, *J* = 16.9, 10.0, 6.7 Hz, 1H, -CH=), 5.10-4.85 (m, 2H, $-CH_2$), 4.65-4.56 (2H, $-CH_2OH$), 4.01 (t, *J* = 6.9 Hz, 2H, $-CH_2-CH_2-O-$), 3.88 (s, 3H, $-OCH_3$), 2.10-2.00 (m, 2H, $-CH_2-CH_2-$), 1.92-1.79 (m, 2H, $-CH_2-CH_2-O-$), 1.75 (1H, $-CH_2OH$), 1.54-1.21 (m, 12H, $-CH_2$-aliphatic).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) δ 149.63 (aromatic $-C-OCH_3$), 148.23 (aromatic $-C-OCH_2-$), 139.29 (-CH=), 133.68 (aromatic $-C-CH_2-$), 119.51 (aromatic -CH-), 114.21 (aromatic -CH-), 112.97 ($-CH_2$), 111.05 (aromatic -CH-), 69.25 ($-CH_2-CH_2-O-$), 65.35

(-CH_2OH), 56.03 (-OCH_3), 33.88 (-CH_2-*C*H_2-), 29.57 (aliphatic -CH_2-), 29.49 (aliphatic -CH_2-), 29.45 (aliphatic -CH_2-), 29.25 (aliphatic -CH_2-), 29.19 (aliphatic -CH_2-), 29.00 (aliphatic -CH_2-), 26.03 (aliphatic -CH_2-).

FAB of $C_{19}H_{30}O_3$ (M^+ = 306.3), HRMS (FAB) of $C_{19}H_{30}O_3$ [M^+] calc. 306.2195, found 306.2193).

General procedure for transesterification of 35 with 38 or 39.

The transesterification reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). A mixture of alcohol **35** (2.00 g, 6.52 mmol), ester **38** (1.18 g, 5.93 mmol), and TBD catalyst (0.042 g, 0.30 mmol) was added to the carousel tube. The mixture was stirred magnetically at 80 °C under continuous vacuum (~ 200 mbar). The reaction was monitored by TLC (hexane-ethyl acetate 9:1) until completion was achieved. The crude product was purified by column chromatography on silica gel (hexane–ethyl acetate 9:1). Transesterifications of 2.5 equiv. **35** with 1 equiv. diester **39** was also carried out following the same procedure.

3-Methoxy-4-(undec-10-en-1-yloxy)benzyl undec-10-enoate (40).

White crystal (yield 91%).

^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm) δ 6.91-6.81 (m, 3H, aromatic -CH=), 5.85-5.75 (m, 2H, -CH=), 5.04 (s, 2H, -$COOCH_2$-), 4.96 (dd, *J* = 30.6, 13.7 Hz, 4H, -CH_2), 4.00 (t, *J* = 6.9 Hz, 2H, -OC*H*$_2$-CH_2-CH_2-), 3.87 (s, 3H, -OCH_3), 2.33 (t, *J* = 7.5 Hz, 2H, -CO-C*H*$_2$-CH_2-), 2.07-1.99 (m, 4H, -CH_2-C*H*$_2$-), 1.87-1.78 (m, 2H, -OCH_2-C*H*$_2$-CH_2-), 1.67-1.58 (m, 2H, -CO-CH_2-C*H*$_2$-), 1.49-1.40 (m, 2H, -OCH_2-CH_2-C*H*$_2$-), 1.40-1.21 (m, 20H, aliphatic -CH_2-).

^{13}C NMR (126 MHz, $CDCl_3$, δ in ppm) δ 173.87 (CO), 149.51 (aromatic -*C*-OCH_3), 148.79 (aromatic -*C*-OCH_2-), 139.32 (-CH=), 139.27 (-CH=), 128.67 (aromatic -*C*-CH_2-), 121.31 (aromatic -CH-), 114.27 (CH_2=), 114.24 (CH_2=), 112.79 (aromatic -CH-), 112.35 (aromatic -CH-), 69.19 (-CH_2-*C*H_2-O-), 66.30 (-COO*C*H_2-), 56.12 (-OCH_3), 34.50 (-CO-*C*H_2-CH_2-), 33.92 (=CH-*C*H_2-), 33.89 (=CH-*C*H_2-), 29.61 (aliphatic –CH_2-), 29.53 (aliphatic –CH_2-), 29.49 (aliphatic –CH_2-), 29.39 (aliphatic –CH_2-), 29.31 (aliphatic –CH_2-), 29.25 (aliphatic –CH_2-), 29.23 (aliphatic –CH_2-), 29.16 (aliphatic –CH_2-), 29.04 (aliphatic –CH_2-), 29.01 (aliphatic –CH_2-), 26.06 (aliphatic –CH_2-), 25.08 (-CO-CH_2-C*H*$_2$-).

FAB of $C_{30}H_{48}O_4$ (M^+ = 472.3), HRMS (FAB) of $C_{30}H_{48}O_4$ [M^+] calc. 472.3553, found 472.3550.

***Bis*(3-methoxy-4-(undec-10-en-1-yloxy)benzyl) adipate (41).**

White crystal (yield 89%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.92-6.78 (m, 6H, aromatic =CH-), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 2H, alkene =CH-), 5.03 (s, 4H, -CH_2-O-CO), 5.03-4.86 (m, 4H, CH_2=), 4.00 (t, *J* = 6.8 Hz, 4H, -CH_2-O-), 3.86 (s, 6H, -OCH_3), 2.34 (t, *J* = 6.1 Hz, 4H, -CH_2-CO-), 2.09-1.96 (m, 4H, =CH-C*H*$_2$-), 1.90-1.75 (m, 4H, aliphatic –CH_2-), 1.71-1.60 (m, 4H, aliphatic –CH_2-), 1.52-1.21 (m, 24H, aliphatic –CH_2-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) δ 173.29 (CO), 149.53 (aromatic -*C*-OCH_3), 148.85 (aromatic -*C*-OCH_2-), 139.32 (-CH=), 128.49 (aromatic -*C*-CH_2-), 121.37 (aromatic -CH-), 114.24 (CH_2=), 112.82 (aromatic -CH-), 112.41 (aromatic -CH-), 69.20 (-CH_2-O-), 66.47 (-COO*C*H_2-), 56.14 (-OCH_3), 34.05 (-CO-*C*H_2-), 33.90 (=CH-*C*H_2-), 29.60 (aliphatic –CH_2-), 29.52 (aliphatic –CH_2-), 29.48 (aliphatic –CH_2-), 29.25 (aliphatic –

CH_2-), 29.22 (aliphatic –CH_2-), 29.04 (aliphatic –CH_2-), 26.06 (aliphatic –CH_2-), 24.48 (aliphatic –CH_2-).

FAB of $C_{44}H_{66}O_8$ (M^+ = 722.3), HRMS (FAB) of $C_{44}H_{66}O_8$ [M^+] calc. 722.4758, found 722.4756.

General procedure for additions of thiols 5 or 4 to 35.

A mixture of **35** (0.40 g, 1.3 mmol), the corresponding amount of thiol (1.0–1.1 equiv.), and DMPA (0.02–0.05 equiv.) was dissolved in a minimal amount of ethanol. The mixture was exposed to a hand-held UV-lamp (λ_{exc} = 365nm). Samples were taken periodically for conversion analysis using ^{1}H-NMR. The reactions were also scaled up to 2.0 g of **35** following the same procedure. The crude products were purified by column chromatography on silica gel with hexane–ethyl acetate (9:1) as eluent.

Methyl 2-((11-(4-(hydroxymethyl)-2-methoxyphenoxy)undecyl)thio)acetate (36).

White crystal (yield 93%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.93-6.78 (m, 3H, aromatic -CH=), 4.63-4.54 (2H, -C*H*$_2$OH), 4.00 (t, *J* = 6.9 Hz, 2H, -CH_2-C*H*$_2$-O-), 3.86 (s, 3H, -OCH_3), 3.73 (s, 3H, -$COOCH_3$), 3.22 (s, 2H, -S-CH_2-CO), 2.62 (t, *J* = 7.2 Hz, 2H, -S-C*H*$_2$-CH_2-), 1.91-1.75 (m, 2H, -C*H*$_2$-CH_2-O-), 1.66-1.51 (m, 2H, -S-CH_2-C*H*$_2$-), 1.50-1.18 (m, 14H, aliphatic –CH_2-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) δ 171.21 (CO), 149.66 (aromatic -*C*-OCH_3), 148.27 (aromatic -*C*-OCH_2-), 133.66 (aromatic -*C*-CH_2-), 119.54 (aromatic -CH-), 113.02 (aromatic -CH-), 111.10 (aromatic -CH-), 69.27 (-CH_2-*C*H_2-O-), 65.38 (-CH_2OH), 56.06 (-OCH_3), 52.43 (-COO*C*H_3), 33.59 (-S-*C*H_2-CO), 32.85 (-S-*C*H_2-CH_2-), 29.55 (aliphatic -

CH_2-), 29.45 (aliphatic -CH_2-), 29.25 (aliphatic -CH_2-), 29.07 (aliphatic –CH_2-), 28.82 (aliphatic -CH_2-), 26.03 (aliphatic -CH_2-).

FAB of $C_{22}H_{36}O_5S$ (M^+ = 412.2), HRMS (FAB) of $C_{22}H_{36}O_5S$ [M^+] calc. 412.2283, found 412.2282.

2-((11-(4-(hydroxymethyl)-2-methoxyphenoxy)undecyl)thio)ethanol (37).

White crystal (yield 87%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.97 – 6.74 (m, 3H, aromatic -CH=), 4.65-4.55 (d, *J* = 5.7 Hz, 2H -C*H*$_2$OH), 3.98 (t, *J* = 6.9 Hz, 2H, -CH_2-C*H*$_2$-O-), 3.85 (s, 3H, -OCH_3), 3.69 (q, *J* = 6.0 Hz, 2H, -S-CH_2-C*H*$_2$-OH), 2.70 (t, *J* = 6.0 Hz, 2H, -S-C*H*$_2$-CH_2-OH), 2.49 (t, *J* = 7.4 Hz, 2H, -S-C*H*$_2$-CH_2-), 2.36 (t, *J* = 6.1 Hz, 1H, -S-CH_2-CH_2-O*H*), 1.98 (t, *J* = 5.8 Hz, 1H, -CH_2O*H*), 1.82 (p, *J* = 6.9 Hz, 2H, -C*H*$_2$-CH_2-O-), 1.64-1.50 (m, 2H, -S-CH_2-C*H*$_2$-), 1.49-1.17 (m, 14H, aliphatic –CH_2-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) δ 149.70 (aromatic -*C*-OCH_3), 148.31 (aromatic -*C*-OCH_2-), 133.70 (aromatic -*C*-CH_2-), 119.57 (aromatic -CH-), 113.03 (aromatic -CH-), 111.11 (aromatic -CH-), 69.29 (-CH_2-*C*H_2-O-), 65.46 (-CH_2OH), 60.32 (-S-CH_2-*C*H_2-OH), 56.10 (-OCH_3), 35.44 (-S-*C*H_2-CH_2-OH), 31.77 (-S-*C*H_2-CH_2-), 29.87 (aliphatic -CH_2-), 29.58 (aliphatic -CH_2-), 29.47 (aliphatic -CH_2-), 29.29 (aliphatic -CH_2-), 28.95 (aliphatic -CH_2-), 26.05 (aliphatic -CH_2-).

FAB of $C_{21}H_{36}O_4S$ (M^+ = 384.1), HRMS (FAB) of $C_{21}H_{36}O_4S$ [M^+] calc. 384.2334, found 384.2332.

Reduction of 1,12-dimethyl-(*E*)-dodec-2-enedioate.

The reduction of 1,12-dimethyl-(*E*)-dodec-2-enedioate was conducted according to a previously reported method.[134] A mixture of 1,12-dimethyl-(*E*)-dodec-2-enedioate

(0.50 g , 1.95 mmol), 5 mL of ethyl acetate, and Pd/C (0.05 g, 10 wt% of 1,12-dimethyl-(*E*)-dodec-2-enedioate) was added to a 10 mL round bottom flask which was sealed with a rubber septum. After two vacuum/H_2 cycles, the mixture was vigorously stirred at room temperature under hydrogen pressure (balloon) for 16 h. The catalyst was then filtered off and the solvent was removed under reduced pressure to obtain dimethyl dodecanedioate (**44**) in quantitative yield as clear crystal.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) δ 3.65 (s, 6H, -OCH_3), 2.29 (t, *J* = 7.6 Hz, 4H, -CO-CH_2-CH_2-), 1.65-1.54 (m, 4H, -CO-CH_2-CH_2-), 1.35-1.21 (m, 12H, aliphatic –CH_2-).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) δ 174.45 (CO), 51.56 (-OCH_3), 34.23 (-CO-*C*H_2-), 29.47 (aliphatic -*C*H_2-), 29.33 (aliphatic -*C*H_2-), 29.25 (aliphatic -*C*H_2-), 25.07 (aliphatic -*C*H_2-).

FAB of $C_{14}H_{26}O_4$ ($M+H^+$ = 259.4), HRMS (FAB) of $C_{14}H_{26}O_4$ [$M-H^+$] calc. 257.1758, found 257.1752.

8.4.3. Syntheses of polymers

General procedure for ADMET polymerization.

Reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). In a carousel tube was added **40** (0.25 g, 0.53 mmol) and 1.10 mg of 1,4-benzoquinone (2.0 mol% to monomer). The mixture was stirred for 5 minutes at 80 °C and afterwards the desired metathesis catalyst (**C1**, **C2**, or **C3**, **C4**, 1 mol% to monomer) was added. The reactions were carried out at 80 °C under continuous vacuum (~ 20 mbar). For the catalyst screening, samples were taken after 4 h, dissolved in 1 mL THF and an excess of ethyl vinyl ether to quench the reaction, and analyzed by GPC. Once the best catalyst was determined (1 mol% **C1**, 80 °C, 2

mol% 1,4-benzoquinone), the amount of **C1** was varied in order to optimize the polymerization conditions.

ADMET polymerization of **41** was also conducted using 1 mol% **C1** and 2 mol% 1,4-benzoquinone (both relative to the monomer) following the same method. All polymers were purified by precipitation in cold Methanol.

P15 (yield 95%) : ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.95–6.77 (m, aromatic -CH=), 5.46–5.26 (m, alkene -CH=), 5.03 (s, -$COOCH_2$-), 3.99 (t, *J* = 6.8 Hz, -OCH_2-CH_2-), 3.86 (s, -OCH_3), 2.33 (t, *J* = 7.4 Hz, -CO-CH_2-CH_2-), 2.09–1.89 (m, -CH_2-CH_2-), 1.89–1.75 (m, -OCH_2-CH_2-), 1.70–1.52 (m, -CO-CH_2-CH_2-), 1.51–1.15 (m, aliphatic –CH_2-).

P16 (yield 89%) : ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.94–6.76 (m, aromatic =CH-), 5.46–5.29 (m, alkene =CH-), 5.02 (s, -CH_2-O-CO), 3.99 (t, -CH_2-O-), 3.86 (s, -OCH_3), 2.43–2.25 (m, -CH_2-CO-), 2.08–1.90 (m, =CH-CH_2-), 1.90–1.75 (m, aliphatic -CH_2-), 1.75–1.62 (m, aliphatic -CH_2-), 1.62–1.51 (m, aliphatic -CH_2-), 1.51–1.14 (m, aliphatic -CH_2-).

General procedure for thiol-ene polymerizations.

The thiol-ene polymerizations were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). In a carousel tube, **40** (0.25 g, 0.53 mmol), dithiols **42** or **43** (1 eq), and AIBN (2.2 mg, 2.5 mol% to **40**) was added and degassed *via* 3 times 200 mbar vacuum and subsequent Argon purge. The mixture was then stirred magnetically at 80°C for 2 h. The polymers were dissolved in THF and precipitated in cold methanol. The thiol-ene polymerizations of **41** with dithiols **42** or **43** were carried out following the same procedure.

P17 (yield 83%) ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.93–6.78 (m, aromatic -CH=), 5.03 (s, -$COOCH_2$-), 3.99 (t, *J* = 6.8 Hz, -OCH_2-CH_2-), 3.86 (s, -OCH_3), 2.59–2.40 (m, -S-

CH_2-), 2.33 (t, *J* = 7.5 Hz, -CO-C*H*$_2$-CH_2-), 1.92–1.75 (m, -OCH_2-C*H*$_2$-), 1.75–1.63 (m, -CO-CH_2-C*H*$_2$-), 1.63–1.49 (m, aliphatic –CH_2-), 1.49–1.12 (m, aliphatic –CH_2-).

P18 (yield 72%) ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.92–6.77 (m, aromatic =CH-), 5.02 (s, -CH_2-O-CO), 3.99 (t, *J* = 6.8 Hz, -CH_2-O-), 3.86 (s, -OCH_3), 2.58–2.42 (m, -S-CH_2-), 2.41–2.26 (m, -CH_2-CO-), 1.91–1.75 (m, aliphatic -CH_2-), 1.75–1.63 (m, aliphatic -CH_2-), 1.63–1.49 (m, aliphatic -CH_2-), 1.49–1.15 (m, aliphatic -CH_2-).

P19 (yield 78%) ^{1}H NMR (300 MHz, $CDCl_3$ δ in ppm) δ 6.93–6.79 (m, aromatic =CH-), 5.03 (s, -CH_2-O-CO), 3.99 (t, *J* = 6.8 Hz, -CH_2-O-), 3.86 (s, -OCH_3), 3.61 (t, *J* = 6.9 Hz, -S-CH_2-C*H*$_2$-O-), 2.69 (t, *J* = 6.9 Hz, -S-C*H*$_2$-CH_2-O-), 2.54 (t, *J* = 7.3 Hz, -S-CH_2-), 2.32 (t, *J* = 7.5 Hz, -CH_2-CO-), 1.90–1.73 (m, aliphatic -CH_2-), 1.71–1.50 (m, aliphatic -CH_2-), 1.50–1.17 (m, aliphatic -CH_2-).

P20 (yield 67%) ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.94–6.76 (m, aromatic =CH-), 5.02 (s, -CH_2-O-CO), 3.99 (t, *J* = 6.8 Hz, -CH_2-O-), 3.86 (s, -OCH_3), 3.62 (t, *J* = 6.9 Hz, -S-CH_2-C*H*$_2$-O-), 2.70 (t, *J* = 6.9 Hz, -S-C*H*$_2$-CH_2-O-), 2.54 (t, *J* = 7.3 Hz, -S-CH_2-), 2.43–2.25 (m, *J* = 5.6 Hz, -CH_2-CO-), 1.90–1.74 (m, aliphatic -CH_2-), 1.74–1.63 (m, *J* = 14.5 Hz, aliphatic -CH_2-), 1.63–1.50 (m, *J* = 7.4 Hz, aliphatic -CH_2-), 1.50–1.15 (m, aliphatic -CH_2-).

General procedure for polycondensation reaction.

All polycondensation reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK) by applying continuous vacuum (~ 10 mbar). 5 mol% (relative to ester groups) of TBD was used as catalyst. The reactions were carried out at 120°C and the reaction temperature was increased to 140°C when the reactions could not be stirred anymore and/or the obvious release of methanol (“bubble formation”) stopped.

Synthesis of polymer P21.

Ester **36** (0.25 g, 0.60 mmol) was homopolymerized with TBD (4.2 mg, 0.03 mmol) for 24 h. The polymer was purified by precipitation in cold methanol.

P21 (yield 91%) : ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.96–6.77 (m, aromatic -CH=), 5.09 (s, -C*H*$_2$-O-CO-), 3.99 (t, *J* = 6.8 Hz, -CH$_2$-C*H*$_2$-O-), 3.86 (s, -OCH$_3$), 3.23 (s, -S-CH$_2$-CO), 2.60 (t, *J* = 7.3 Hz, -S-C*H*$_2$-CH$_2$-), 1.91–1.75 (m, -C*H*$_2$-CH$_2$-O-), 1.70 (m, aliphatic -CH$_2$-), 1.63–1.48 (m, aliphatic -CH$_2$-), 1.49–1.12 (m, aliphatic -CH$_2$-).

Synthesis of polymers P22–P24.

Diol **37** (0.15 g, 0.39 mmol) and diester **24** or **28** or **44** (1 equiv. to the diol) were polymerized with TBD (5.43 mg, 0.039 mmol) for 24h. The polymers were purified by precipitation in cold methanol.

P22 (yield 81%) ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.93–6.78 (m, aromatic -CH=), 5.03 (s, -C*H*$_2$-O-CO-), 4.21 (t, *J* = 6.9 Hz, -S-CH$_2$-C*H*$_2$-O-), 3.99 (t, *J* = 6.7 Hz, -CH$_2$-C*H*$_2$-O-), 3.86 (s, -OCH$_3$), 2.72 (t, *J* = 6.9 Hz, -S-C*H*$_2$-CH$_2$-O-), 2.54 (t, *J* = 7.4 Hz, -S-C*H*$_2$-CH$_2$-), 2.37–2.23 (m, -CH$_2$-CO-), 1.93–1.75 (m, aliphatic –CH$_2$-), 1.73–1.50 (m, aliphatic –CH$_2$-), 1.49–1.12 (m, aliphatic –CH$_2$-).

P23 (yield 85%) ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) δ 6.93–6.79 (m, aromatic -CH=), 5.03 (s, -C*H*$_2$-O-CO-), 4.21 (t, *J* = 6.9 Hz, -S-CH$_2$-C*H*$_2$-O-), 3.99 (t, *J* = 6.8 Hz, -CH$_2$-C*H*$_2$-O-), 3.86 (s, *J* = 3.9 Hz, -OCH$_3$), 2.72 (t, *J* = 6.9 Hz, -S-C*H*$_2$-CH$_2$-O-), 2.55 (t, *J* = 7.4 Hz, -S-C*H*$_2$-CH$_2$-), 2.37–2.24 (m, -CH$_2$-CO-), 1.90–1.75 (m, aliphatic –CH$_2$-), 1.71–1.50 (m, aliphatic –CH$_2$-), 1.49–1.16 (m, aliphatic –CH$_2$-).

P24 (yield 83%) ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) : δ 6.94–6.79 (m, *J* = 7.9 Hz, aromatic -CH=), 5.45–5.28 (m, alkene -CH=), 5.03 (s, -C*H*$_2$-O-CO-), 4.21 (t, *J* = 6.7 Hz, -

S-CH_2-CH_2-O-), 3.99 (t, *J* = 6.6 Hz, -CH_2-CH_2-O-), 3.86 (s, -OCH_3), 2.72 (t, *J* = 6.8 Hz, -S-CH_2-CH_2-O-), 2.54 (t, *J* = 7.4 Hz, -S-CH_2-CH_2-), 2.39–2.24 (m, -CH_2-CO-), 2.06–1.89 (m, =CH-CH_2-), 1.87–1.76 (m, aliphatic –CH_2-), 1.72–1.49 (m, aliphatic –CH_2-), 1.50–1.12 (m, aliphatic –CH_2-).

8.5. Renewable Polyamides and Polyurethanes Derived from Limonene

8.5.1. Materials

Methyl 2-[2′-((1′′*R*)-3′′-((2′′′-methoxycarbonylethyl)thio)-4′′-methylcyclohexyl)-propyl)thio]acetate (**17**),[134] methyl 2-[2′-((1′′*S*)-3′′-((2′′′-methoxycarbonylethyl)-thio)-4′′-methylcyclohexyl)propyl)thio]acetate (**19**),[134] 2-[2′-((1′′*R*)-3′′-((2′′′-hydroxyethyl)thio)-4′′-methylcyclohexyl)propyl)thio]ethanol (**16**),[134] 2-[2′-((1′′*S*)-3′′-((2′′′-hydroxyethyl)thio)-4′′-methylcyclohexyl)propyl)thio]ethanol (**18**),[134] dimethyl icosanedioate (**28**),[134] (*E*)-dimethyl icos-10-enedioate (**24**),[144] methyl 11-(2-aminoethylthio)undecanoate (**49**),[177] (*E*)-icos-10-ene-1,20-diol (**26**),[134] were prepared as previously reported. (*R*)-(+)-Limonene (**1**, Sigma, 97%), (*S*)-(–)-limonene (**2**, Aldrich, 96%), cysteamine hydrochloride (Fluka, >97%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), K_2CO_3 (Aldrich, 99%), Na_2SO_4 anhydrous (Acros Organics, 99%), dimethyl carbonate (Aldrich, 99%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene, (TBD, Aldrich, 98%), silica gel 60 (0.035–0.070 mm, Aldrich), dimethyl adipate (**50**, Aldrich, ≥99%), hexamethylenediamine (**51**, Aldrich, 98%,), 1,6-hexanediol (**52**, Acros Organics, 97%), and trifluoroacetic anhydride (TFAA, Aldrich), were used as received. All solvents (technical grade) were used without further purification.

8.5.2. Syntheses of the monomers

General procedure for additions of cysteamine hydrochloride to (*R*)-(+)-limonene or (*S*)-(−)-limonene.

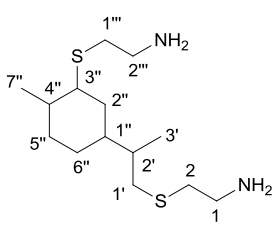
A mixture of (*R*)-(+)-Limonene or (*S*)-(−)-limonene (1.00 g, 7.30 mmol), cysteamine hydrochloride (3.0–6.0 equiv.), and DMPA (0.01–0.2 equiv.) was dissolved in a minimal amount of ethanol. The mixture was exposed to a hand-held UV-lamp (2 × 4 W, λ = 365 nm). Samples were taken periodically to test for conversion of the double bonds using ^{1}H NMR. Ethanol was then removed and the mixture was dissolved in dichloromethane and washed with K_2CO_3 solution until the pH of the solution became 10 (to neutralize the hydrochloride salt and obtain free amines) and washed two times with water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The products **45** and **47** were purified by column chromatography on silica gel with hexane-ethyl acetate (1:1) followed by methanol as eluents.

Methoxycarbonylation of 45 or 47 with dimethyl carbonate.

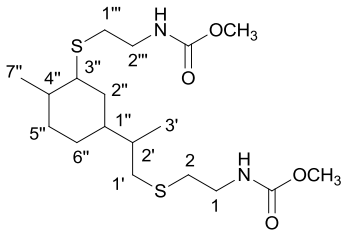
Reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). In a carousel tube was added **45** or **47** (1.27 g, 4.37 mmol), dimethyl carbonate (3.94 g, 43.7 mmol), and TBD (60.8 mg, 0.43 mmol). The mixture was stirred magnetically at 80 °C. The reactions were monitored by TLC until completion using hexane-ethyl acetate (6:4) as eluent. Excess of dimethyl carbonate was then removed by vacuum evaporation. The crude reaction mixture was purified by column chromatography with hexane-ethyl acetate (6:4) as eluent to obtain pure products **46** and **48.**

Characterization of monomers.

When possible, " a, b, c, or d " is used to differentiate between different diastereomers. In the ^{1}H NMR spectra, " A " and " B " differentiates between two protons connected to the same carbon. The ^{13}C NMR assignment is unambiguous with respect to each nucleus, but laborious when it comes to differentiate between a particular carbon atom belonging to different diastereomers. The two major diastereomers are marked with " a " and " b ", and the minor ones with " c " and " d ". The assignment of ^{1}H and ^{13}C NMR spectra has been done using the following number codes for each nucleus in the diamine and dicarbamate products:



(**45** or **47**)



(**46** or **48**)

2-[2′-((1′′*R*)-3′′-((2′′′-aminoethyl)thio)-4′′-methylcyclohexyl)propyl)thio]-ethanamine (45).

Slightly yellow viscous liquid (84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.90–2.85 ($H^{3''a}$, $H^{3''b}$), 2.84–2.75 (m, -S-CH_2-CH_2-NH_2), 2.62–2.46 (m, -S-CH_2-CH_2-NH_2), 2.29 (dt, *J* = 21.8, 13.0 Hz, $H_A{}^{1'a}$, $H_A{}^{1'b}$, $H^{1'c}$, $H^{1'd}$, $H_B{}^{1'a}$, $H_B{}^{1'b}$), 2.18–2.07 (m, $H^{3''c}$, $H^{3''d}$), 1.93 (dd, *J* = 24.2, 8.5 Hz, $H_A{}^{2''c}$, $H_A{}^{2''d}$), 1.87–1.78 (m, $H_A{}^{2''a}$, $H_A{}^{2''b}$), 1.78–1.69 (m, $H^{1''a}$, $H^{1''b}$), 1.69–1.61 (m, $H^{4''a}$, $H^{4''b}$), 1.61–1.44 (m, -NH_2, $H_A{}^{6''a}$, $H_A{}^{6''b}$, $H^{2'a}$, $H^{2'b}$, $H_A{}^{6''c}$, $H_A{}^{6''d}$), 1.44–1.30 (m, $H_B{}^{2''a}$, $H_B{}^{2''b}$, $H_A{}^{5''a}$, $H_A{}^{5''b}$, $H_A{}^{5''c}$, $H_A{}^{5''d}$, $H^{2'c}$, $H^{2'd}$), 1.30–1.17 (m, $H_B{}^{5''a}$, $H_B{}^{5''b}$, $H_B{}^{5''c}$, $H_B{}^{5''d}$, $H^{4''c}$, $H^{4''d}$), 1.17–1.07 (m, $H_B{}^{6''a}$, $H_B{}^{6''c}$, $H_B{}^{2''c}$, $H_B{}^{2''d}$), 1.03 (d, *J* = 5.6

Hz, $H^{7''c}$, $H^{7''d}$), 0.96 (d, *J* = 6.5 Hz, $H^{7''a}$, $H^{7''b}$), 0.95–0.90 (m, $H_B{}^{6''b}$, $H_B{}^{6''d}$, $H^{3'c}$, $H^{3'd}$), 0.90 (d, *J* = 6.4 Hz, $H^{3'a}$, $H^{3'b}$).

^{13}C NMR (101 MHz, $CDCl_3$, δ in ppm): δ 50.84 ($C^{3''c}$, $C^{3''d}$), 50.58 ($C^{3''a}$), 50.42 ($C^{3''b}$), 42.14 ($C_{minor\ diast}$), 41.98 ($C_{minor\ diast}$), 41.90 ($C_{minor\ diast}$), 41.67 ($C^{2'c}$), 41.52 ($C^{2'd}$), 41.45 (-S-CH_2-*C*H_2-NH_2), 41.14 (-S-CH_2-*C*H_2-NH_2), 41.12 (-S-CH_2-*C*H_2-NH_2), 40.77 (-S-CH_2-*C*H_2-NH_2), 40.75 (-S-CH_2-*C*H_2-NH_2), 39.17 (-S-CH_2-*C*H_2-NH_2), 37.90 ($C_{minor\ diast}$), 37.84 ($C_{minor\ diast}$), 37.81 ($C_{minor\ diast}$), 37.68 ($C^{4''c}$), 37.57 ($C^{2'a}$, $C^{2'd}$), 37.49 ($C^{4''d}$), 37.06 ($C^{2''a}$), 36.97 ($C^{1'a}$), 36.82 ($C^{1'c}$), 36.81 ($C^{1'd}$), 36.76 ($C^{1'b}$), 36.73 (-S-*C*H_2-CH_2-NH_2), 36.63 ($C_{minor\ diast}$), 36.53 (-S-*C*H_2-CH_2-NH_2), 36.50 (-S-*C*H_2-CH_2-NH_2), 36.48 ($C^{4''a}$, $C^{4''b}$), 35.33 ($C^{2''c}$), 35.24 ($C^{1''a}$), 35.21 ($C^{1''b}$), 34.96 ($C^{2''b}$), 34.55 ($C_{minor\ diast}$), 34.12 ($C^{2''d}$), 32.42 ($C_{minor\ diast}$), 32.32 ($C_{minor\ diast}$), 31.60 ($C_{minor\ diast}$), 31.48 ($C_{minor\ diast}$), 31.43 ($C_{minor\ diast}$), 31.40 ($C_{minor\ diast}$), 31.16 ($C_{minor\ diast}$), 29.77 ($C^{6''a}$, $C^{6''c}$), 29.59 ($^{5''a}$, $C^{5''c}$), 29.44 ($C^{5''b}$, $C^{5''d}$), 29.27 ($C_{minor\ diast}$), 27.64 ($C^{6''b}$), 27.02 ($C^{6''d}$), 20.55 ($C^{7''c}$), 20.52 ($C^{7''d}$), 20.06 ($C^{7''a}$, $C^{7''b}$), 15.67 ($C^{3'a}$), 15.64 ($C^{3'c}$) 15.50 ($C^{3'b}$), 15.43 ($C^{3'd}$).

FAB-MS of $C_{14}H_{30}N_2S_2$ ($M+H^+$ = 291.2). HRMS (FAB) of $C_{14}H_{30}N_2S_2$ [$M+H^+$] calc. 291.1923, found 291.1926.

2-[2′-((1′′*S*)-3′′-((2′′′-aminoethyl)thio)-4′′-methylcyclohexyl)propyl)thio]-ethanamine (47).

Slightly yellow viscous liquid (81%).

^1H NMR (600 MHz, $CDCl_3$, δ in ppm): δ 2.91–2.87 ($H^{3''a}$, $H^{3''b}$), 2.86–2.75 (m, -S-CH_2-C*H*$_2$-NH_2), 2.61–2.50 (m, -S-C*H*$_2$-CH_2-NH_2), 2.66–2.39 (m, $H_A{}^{1'a}$, $H_A{}^{1'b}$), 2.33 (dd, *J* = 8.3, 3.4 Hz, $H^{1'c}$, $H^{1'd}$), 2.31 (dd, *J* = 8.7, 2.0 Hz, $H_B{}^{1'a}$), 2.27 (dd, *J* = 13.1, 8.8 Hz, $H_B{}^{1'b}$), 2.19–2.08 (m, $H^{3''c}$, $H^{3''d}$), 2.00–1.89 (m, $H_A{}^{2''c}$, $H_A{}^{2''d}$), 1.88–1.80 (m,

$H_A{}^{2''a}$, $H_A{}^{2''b}$), 1.76 (ddd, *J* = 12.2, 10.3, 3.6 Hz, $H^{1''a}$, $H^{1''b}$), 1.71–1.62 (m, $H^{4''a}$, $H^{4''b}$), 1.62–1.47 (m, $H_A{}^{6''a}$, $H_A{}^{6''b}$, $H^{2'a}$, $H^{2'b}$, $H_A{}^{6''c}$, $H_A{}^{6''d}$), 1.47–1.31 (m, $-NH_2$, $H_B{}^{2''a}$, $H_B{}^{2''b}$, $H_A{}^{5''a}$, $H_A{}^{5''b}$, $H_A{}^{5''c}$, $H_A{}^{5''d}$, $H^{2'c}$, $H^{2'd}$), 1.31–1.17 (m, $H_B{}^{5''a}$, $H_B{}^{5''b}$, $H_B{}^{5''c}$, $H_B{}^{5''d}$, $H^{4''c}$, $H^{4''d}$), 1.17–1.01 (m, $H_B{}^{6''a}$, $H_B{}^{6''c}$, $H_B{}^{2''c}$, $H_B{}^{2''d}$), 1.04 (d, *J* = 6.3 Hz, $H^{7''c}$, $H^{7''d}$), 0.97 (d, *J* = 6.7 Hz, $H^{7''a}$, $H^{7''b}$), 0.95–0.88 (m, $H_B{}^{6''b}$, $H_B{}^{6''d}$, $H^{3'c}$, $H^{3'd}$), 0.92 (d, *J* = 6.8 Hz, $H^{3'a}$, $H^{3'b}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 50.63 ($C^{3''c}$, $C^{3''d}$), 50.36 ($C^{3''a}$), 50.20 ($C^{3''b}$), 41.78 ($C_{minor\ diast}$), 41.70 ($C_{minor\ diast}$), 41.47 ($C^{2'c}$), 41.33 ($C^{2'd}$), 41.28 (-S-CH_2-*C*H_2-NH_2), 40.96 (-S-CH_2-*C*H_2-NH_2), 40.94 (-S-CH_2-*C*H_2-NH_2), 40.60 (-S-CH_2-*C*H_2-NH_2), 40.57 (-S-CH_2-*C*H_2-NH_2), 38.98 (-S-CH_2-*C*H_2-NH_2), 37.70 ($C_{minor\ diast}$), 37.64 ($C_{minor\ diast}$), 37.61 ($C_{minor\ diast}$), 37.48 ($C^{4''c}$), 37.36 ($C^{2'a}$, $C^{2'b}$), 37.28 ($C^{4''d}$), 36.86 ($C^{2''a}$), 36.76 ($C^{1'a}$), 36.62 ($C^{1'c}$, $C^{1'd}$), 36.56 ($C^{1'b}$), 36.52 (-S-*C*H_2-CH_2-NH_2), 36.42 ($C_{minor\ diast}$), 36.29 (-S-*C*H_2-CH_2-NH_2, $C^{4''a}$, $C^{4''b}$), 35.14 ($C^{2''c}$, $C^{2''d}$), 35.03 ($C^{1''a}$), 35.00 ($C^{1''b}$), 34.75 ($C^{2''b}$), 34.34 ($C_{minor\ diast}$), 33.91 ($C^{2''d}$), 32.22 ($C_{minor\ diast}$), 32.12 ($C_{minor\ diast}$), 31.40 ($C_{minor\ diast}$), 31.28 ($C_{minor\ diast}$), 31.22 ($C_{minor\ diast}$), 30.96 ($C_{minor\ diast}$), 29.59 ($C^{6''a}$, $C^{6''c}$), 29.40 ($C^{5''a}$, $C^{5''c}$), 29.25 ($C^{5''b}$, $C^{5''d}$), 29.08 ($C_{minor\ diast}$), 27.46 ($C^{6''b}$), 26.84 ($C^{6''d}$), 20.37 ($C^{7''c}$), 20.34 ($C^{7''d}$), 19.88 ($C^{7''a}$, $C^{7''b}$), 15.60 ($C^{3'a}$), 15.48 ($C^{3'c}$), 15.32 ($C^{3'b}$), 15.24 ($C^{3'd}$).

FAB-MS of $C_{14}H_{30}N_2S_2$ ($M+H^+$ = 291.3). HRMS (FAB) of $C_{14}H_{30}N_2S_2$ [$M+H^+$] calc. 291.1923, found 291.1927.

N^1,$N^{2'''}$-dimethoxy-carbonyl-2-[2′-((1′′*R*)-3′′-((2′′′-aminoethyl)thio)-4′′-methylcyclohexyl)propyl)thio]ethanamine (46).

Colourless viscous liquid (82%).

^1H NMR (500 MHz, $CDCl_3$, δ in ppm) δ 5.38–5.03 (m, NH), 3.66 (s, OCH_3), 3.38–3.22

(m, -S-CH_2-C*H*$_2$-NH), 2.95–2.89 ($H^{3''a}$, $H^{3''b}$), 2.69–2.57 (m, -S-C*H*$_2$-CH_2-NH), 2.55 (dd, *J* = 8.5, 3.8 Hz, $H^{1'a}$), 2.33 (ddd, *J* = 15.3, 12.4, 8.3 Hz, $H^{1'b}$), 2.38–2.29 (m, $H^{1'c}$, $H^{1'd}$), 2.22–2.11 (m, $H^{3''c}$, $H^{3''d}$), 2.01–1.93 (m, $H_A{}^{2''c}$, $H_A{}^{2''d}$), 1.92–1.72 (m, $H_A{}^{2''a}$, $H_A{}^{2''b}$, $H^{1''a}$, $H^{1''b}$), 1.72–1.63 (m, $H^{4''a}$, $H^{4''b}$), 1.62–1.50 (m, $H_A{}^{6''a}$, $H_A{}^{6''b}$, $H^{2'a}$, $H^{2'b}$, $H_A{}^{6''c}$, $H_A{}^{6''d}$), 1.50–1.34 (m, $H_B{}^{2''a}$, $H_B{}^{2''b}$, $H_A{}^{5''a}$, $H_A{}^{5''b}$, $H_A{}^{5''c}$, $H_A{}^{5''d}$, $H^{2'c}$, $H^{2'd}$), 1.33–1.17 (m, $H_B{}^{5''a}$, $H_B{}^{5''b}$, $H_B{}^{5''c}$, $H_B{}^{5''d}$, $H^{4''c}$, $H^{4''d}$), 1.17–1.01 (m, $H_B{}^{6''a}$, $H_B{}^{6''c}$, $H_B{}^{2''c}$, $H_B{}^{2''d}$), 1.03 (d, *J* = 6.4 Hz, $H^{7''c}$, $H^{7''d}$), 0.97 (d, *J* = 6.7 Hz, $H^{7''a}$, $H^{7''b}$), 0.92 (d, *J* = 3.9 Hz, $H^{3'a}$), 0.96–0.91 (m, $H_B{}^{6''b}$, $H_B{}^{6''d}$, $H^{3'c}$, $H^{3'd}$), 0.90 (d, *J* = 3.9 Hz, $H^{3'b}$).

^{13}C NMR (126 MHz, $CDCl_3$, δ in ppm) δ 157.04 (CO), 52.36–52.04 (group of singlets, OCH_3), 51.38 ($C^{3''c}$), 51.34 ($C^{3''d}$), 51.22 ($C^{3''a}$), 51.10 ($C^{3''b}$), 42.03 ($C^{2'c}$), 41.91 ($C^{2'd}$), 40.96 (-S-CH_2-*C*H$_2$-NH), 40.67 (-S-CH_2-*C*H$_2$-NH), 40.28 (-S-CH_2-*C*H$_2$-NH), 38.25 ($C_{minor\ diast}$), 38.20 ($C_{minor\ diast}$), 38.15 ($C_{minor\ diast}$), 38.05 ($C^{4''c}$), 37.97 ($C^{4''d}$), 37.87 ($C^{2'a}$), 37.77 ($C^{2'b}$), 37.50 ($C^{2''a}$), 37.44 ($C^{1'a}$), 37.30 ($C^{1'c}$), 37.20 ($C^{1'b}$), 37.11 ($C_{minor\ diast}$) 37.03 ($C^{1'd}$), 36.93 ($C^{4''a}$), 36.87 ($C^{4''b}$), 35.72 ($C^{2''c}$), 35.60 ($C^{2''d}$), 35.44 ($C^{1''a}$), 35.37 ($C^{1''b}$), 34.96 ($C^{2''b}$), 32.97 (-S-*C*H$_2$-CH_2-NH), 32.91 (-S-*C*H$_2$-CH_2-NH), 32.80 (-S-*C*H$_2$-CH_2-NH), 30.39 ($C^{6''c}$), 30.28 ($C^{6''a}$), 30.00 ($C^{5''a}$), 29.95 ($C^{5''c}$), 29.83 ($C^{5''b}$), 29.75 ($C^{5''d}$), 28.07 ($C^{6''b}$), 27.48 ($C^{6''d}$), 20.88 ($C^{7''c}$, $C^{7''d}$), 20.43 ($C^{7''a}$, $C^{7''b}$), 16.04 ($C^{3'c}$), 15.97 ($C^{3'a}$, $C^{3'b}$), 15.85 ($C^{3'd}$).

FAB-MS of $C_{18}H_{35}N_2S_2O_4$ ($M+H^+$ = 407.2). HRMS (FAB) of $C_{18}H_{35}N_2S_2O_4$ [$M+H^+$] calc. 407.2033, found 407.2036.

N^1,$N^{2'''}$-dimethoxy-carbonyl-2-[2′-((1′′*S*)-3′′-((2′′′-aminoethyl)thio)-4′′-methylcyclohexyl)propyl)thio]ethanamine (48).

Colourless viscous liquid (79%).

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 5.39–4.93 (m, NH), 3.65 (s, OCH_3), 3.42–3.23

(m, -S-CH_2-C*H*$_2$-NH), 2.97–2.90 ($H^{3''a}$, $H^{3''b}$), 2.70–2.58 (m, -S-C*H*$_2$-CH_2-NH), 2.56 (dd, *J* = 7.8, 4.7 Hz, $H^{1'a}$), 2.35 (td, *J* = 12.6, 8.3 Hz, $H^{1'b}$), 2.41–2.28 (m, $H^{1'c}$, $H^{1'd}$), 2.18 (ddd, *J* = 21.6, 10.6, 3.2 Hz, $H^{3''c}$, $H^{3''d}$), 2.02–1.94 (m, $H_A^{2''c}$, $H_A^{2''d}$), 1.93–1.75 (m, $H_A^{2''a}$, $H_A^{2''b}$, $H^{1''a}$, $H^{1''b}$), 1.75–1.63 (m, $H^{4''a}$, $H^{4''b}$), 1.64–1.50 (m, $H_A^{6''a}$, $H_A^{6''b}$, $H^{2'a}$, $H^{2'b}$, $H_A^{6''c}$, $H_A^{6''d}$), 1.50–1.35 (m, $H_B^{2''a}$, $H_B^{2''b}$, $H_A^{5''a}$, $H_A^{5''b}$, $H_A^{5''c}$, $H_A^{5''d}$, $H^{2'c}$, $H^{2'd}$), 1.34–1.17 (m, $H_B^{5''a}$, $H_B^{5''b}$, $H_B^{5''c}$, $H_B^{5''d}$, $H^{4''c}$, $H^{4''d}$), 1.17–1.01 (m, $H_B^{6''a}$, $H_B^{6''c}$, $H_B^{2''c}$, $H_B^{2''d}$), 1.05 (d, *J* = 6.5 Hz, $H^{7''c}$, $H^{7''d}$), 0.99 (d, *J* = 6.7 Hz, $H^{7''a}$, $H^{7''b}$), 0.93 (d, *J* = 3.3 Hz, $H^{3'a}$), 0.96-0.92 (m, $H_B^{6''b}$, $H_B^{6''d}$, $H^{3'c}$, $H^{3'd}$), 0.92 (d, *J* = 3.3 Hz, $H^{3'b}$).

^{13}C NMR (101 MHz, $CDCl_3$, δ in ppm): δ 157.06 (CO), 52.48–52.07 (group of singlets, OCH_3), 51.44 ($C^{3''c}$), 51.39 ($C^{3''d}$), 51.28 ($C^{3''a}$), 51.16 ($C^{3''b}$), 42.08 ($C^{2'c}$), 41.96 ($C^{2'd}$), 40.72 (-S-CH_2-*C*H_2-NH), 40.32 (-S-CH_2-*C*H_2-NH), 39.51 (-S-CH_2-*C*H_2-NH), 38.30 ($C_{minor\ diast}$), 38.25 ($C_{minor\ diast}$), 38.21 ($C_{minor\ diast}$), 38.19 ($C_{minor\ diast}$), 38.10 ($C^{4''c}$), 38.02 ($C^{4''d}$), 37.92 ($C^{2'a}$), 37.81 ($C^{2'b}$), 37.55 ($C^{2''a}$), 37.50 ($C^{1'a}$), 37.35 ($C^{1'c}$), 37.25 ($C^{1'b}$), 37.17 ($C_{minor\ diast}$), 37.08 ($C^{1'd}$), 36.98 ($C^{4''a}$), 36.92 ($C^{4''b}$), 35.77 ($C^{2''c}$), 35.64 ($C^{2''d}$), 35.49 ($C^{1''a}$), 35.41 ($C^{1''b}$), 35.00 ($C^{2''b}$), 33.05 (-S-*C*H_2-CH_2-NH), 32.99 (-S-*C*H_2-CH_2-NH), 32.89 (-S-*C*H_2-CH_2-NH), 32.86 (-S-*C*H_2-CH_2-NH), 30.47 ($C^{6''c}$), 30.33 ($C^{6''a}$), 30.05 ($C^{5''a}$), 29.98 ($C^{5''c}$), 29.87 ($C^{5''b}$), 29.79 ($C^{5''d}$), 28.12 ($C^{6''b}$), 27.52 ($C^{6''d}$), 20.94 ($C^{7''c}$), 20.91 ($C^{7''d}$), 20.49 ($C^{7''a}$), 20.45 ($C^{7''b}$), 16.07 ($C^{3'c}$), 16.01 ($C^{3'a}$, $C^{3'b}$), 15.90 ($C^{3'd}$).

FAB-MS of $C_{18}H_{35}N_2S_2O_4$ ($M+H^+$ = 407.1). HRMS (FAB) of $C_{18}H_{35}N_2S_2O_4$ [$M+H^+$] calc. 407.2033, found 407.2036.

8.5.3. Syntheses of the polymers

General procedure for synthesis of polyamides.

All polycondensation reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). The corresponding monomers (see the entries in Table 6.1) and 0.05 equiv. (relative to ester groups) of TBD were added to the carousel tube and placed in the reactor system. The polymerization was performed at 140 °C for 24 h by applying continuous vacuum (10±5 mbar). When low boiling point monomers were used, the polymerization was started at lower temperatures and the temperature was gradually increased to 140 °C. The polymers (**P25–28**) were purified by precipitation of a concentrated THF solution of the reaction products into cold methanol. The polymers (**P29–38**) were purified by precipitation of a concentrated HFIP solution of the reaction products into cold methanol. TFAA treatment was applied prior to the NMR analysis.

General procedure for synthesis of polyurethanes.

The polymerizations were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK) at 120 °C applying continuous vacuum (10±5 mbar). TBD (0.05 equiv. relative to carbamate groups) was used as catalyst. Monomer **46** or **48** (150 mg, 0.37 mmol) and the corresponding diols (1.0 equiv.) were polymerized with TBD (5.00 mg, 0.04 mmol) for 16 h. The polymers (**P39–44**) were purified by precipitation of a concentrated THF solution of the reaction products into cold hexane-ethanol (9:1).

8.6. Renewable Co-polymers Derived from Limonene and Fatty Acid Derivatives

8.6.1. Materials

Undec-10-enyl undec-10-enoate (**59**),[197] and methyl 2-[2´-((1´´*R*)-3´´-((2´´´-methoxycarbonylethyl)thio)-4´´-methylcyclohexyl)propyl)thio]acetate (**17**),[134] were prepared as previously reported. (*R*)-(+)-Limonene (**1**, Sigma, 97%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), Na_2SO_4 anhydrous (Acros Organics, 99%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene, (TBD, Aldrich, 98%), silica gel 60 (0.035–0.070 mm, Aldrich), 1,4-butanedithiol (**42**, >97%, Aldrich), thioacetic acid (Aldrich, 96%), 10-undecen-1-ol (Aldrich, 98%), hydrogen peroxide solution (Sigma, 35 wt. %), and 2-mercaptoethyl ether (**43**, >95%, Aldrich), were used as received. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%) was recrystallized from methanol. 11-(Undec-10-en-1-yloxy)undec-1-ene (**56**) was prepared by Metzger and co-workers *via* catalytic reduction of **59**. All solvents (technical grade) were used without further purification.

8.6.2. Syntheses of the monomers

Transesterification of 17.

The transesterification reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). A mixture of **17** (1.00 g, 2.87 mmol), 10-undecen-1-ol (1.22 g, 7.16 mmol), and TBD catalyst (0.04 g, 0.28 mmol) was added to the carousel tube. The mixture was stirred magnetically at 80 °C under continuous vacuum (~ 200 mbar). The reaction was monitored by TLC (hexane-ethyl acetate 9:1) until completion was achieved. The product (**53**) was purified by column chromatography on silica gel (hexane–ethyl acetate 9:1).

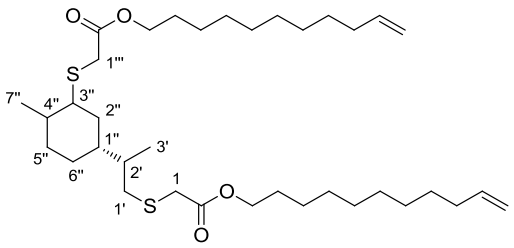
General procedure for the synthesis of dithiols.

The synthesis of dithiols were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). A mixture of diene **1** or **56** (1.00 g) and thioacetic acid (2.5 equiv.) was added to the carousel tube. The mixture was then stirred magnetically at room temperature. Samples were taken periodically and analyzed by ^{1}H NMR spectroscopy. After the reactions had been completed, the excess of thioacetic acid was removed under reduced pressure. The products (**54** and **57**) were then used for the next reaction step without further purification.

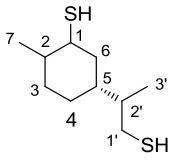
Dithioacetic ester **54** or **57** (1.5 g), methanol (20 equiv.), and TBD catalyst (0.1 equiv.) were added to the carousel tube. The reaction mixture was then refluxed under Argon atmosphere and the reaction progress was monitored *via* ^{1}H NMR. The formed methyl acetate and the excess of methanol were removed at reduced pressure. The crude product was purified by column chromatography on silica gel (hexane–ethyl acetate 19:1) to give colorless liquid **55**. In case dithioester cleavage of **57**, the product (**58**) was recrystallized from methanol.

Characterization of monomers.

In order to distinguish between the different diastereomers, the descriptors " $^{a, b, c, or\ d}$ " are used. " $_{A}$ " and " $_{B}$ " in the ^{1}H NMR spectra differentiates between two protons connected to the same carbon. The ^{13}C NMR assignment is unambiguous related to each nucleus, but laborious when it comes to distinguish between a particular carbon atom belonging to different diastereomers. The two major diastereomers are marked with " ^{a} " and " ^{b} ", and the minor ones with " ^{c} " and " ^{d} ". The assignment of ^{1}H and ^{13}C NMR spectra has been done using the following number codes:



53



55

Undec-10-en-1-yl 2-[2'-((1''R)-4''-methyl-3''-((2'''-oxo-2'''-(undec-10'''-en-1'''-yloxy)-ethyl)thio)cyclohexyl)propyl)thio]acetate (53).

Colorless viscous liquid (94%).

^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): δ 5.80 (ddt, *J* = 16.9, 10.1, 6.7 Hz, =CH), 4.95 (dd, *J* = 30.9, 13.6 Hz, CH_2=), 4.11 (t, *J* = 6.4 Hz, OCH_2), 3.25–3.11 (m, CO-CH_2, $CH^{3''a}$, $CH^{3''b}$), 2.74 (dd, *J* = 12.5, 4.6 Hz, $H_A{}^{1'a}$, $H_A{}^{1'b}$), 2.71–2.68 (m, $H_A{}^{1'c}$, $H_A{}^{1'd}$), 2.50–2.47 (m, $H_B{}^{1'c}$, $H_B{}^{1'd}$), 2.45 (dd, *J* = 8.8, 3.7 Hz, $H_B{}^{1'a}$), 2.41 (dd, *J* = 8.8, 3.7 Hz, $H_B{}^{1'b}$), 2.31–2.38 (m, $CH^{3''c}$, $CH^{3''d}$), 2.07–1.99 (m, =CH-C*H* , $H_A{}^{2''c}$, $H_A{}^{2''d}$), 1.96–1.89 (m, $H_A{}^{2''a}$, $H_A{}^{2''b}$), 1.86–1.80 (m, $H_A{}^{5''a}$, $H_A{}^{5''b}$, $H_B{}^{5''c}$, $H_B{}^{5''d}$), 1.79–1.68 (m, aliphatic, $H^{1''a}$, $H^{1''b}$, $H^{1''c}$, $H^{1''d}$, $H^{4''a}$, $H^{4''b}$), 1.68–1.52(m, aliphatic, $H_A{}^{6''a}$, $H_A{}^{6''b}$, $H_A{}^{6''c}$, $H_A{}^{6''d}$, $H^{2'a}$, $H^{2'b}$), 1.50–1.39 (m, $H_A{}^{5''a}$, $H_A{}^{5''b}$, $H_B{}^{2''a}$, $H_B{}^{2''b}$, $H^{2'c}$, $H^{2'd}$), 1.39–1.19 (m, aliphatic, $H^{4''c}$, $H^{4''d}$, $H_B{}^{5''a}$, $H_B{}^{5''b}$, $H_B{}^{2''c}$), 1.17–1.11 ($H_B{}^{2''d}$), 1.11–1.02 (m, $H_B{}^{6'a}$, $H_B{}^{6''b}$, $H_B{}^{6''c}$, $H_B{}^{6''d}$), 1.01 (s, $H^{7''a}$), 0.98 (s, $H^{7''b}$), 1.01-0.98 (two singlets, $H^{7''c}$ and $H^{7''d}$), 0.98–0.91 (m, $H^{3'a}$, $H^{3'b}$, $H^{3'c}$, $H^{3'd}$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): δ 171.05 (CO), 170.98 (CO), 170.74 (CO), 170.67 (CO), 139.20 (=CH), 114.22 (=CH_2), 65.48 (OCH_2), 65.45 (OCH_2), 51.84 ($C^{3''c}$), 51.74 $C^{3''d}$), 51.35 ($C^{3''a}$), 51.21 ($C^{3''b}$), 42.11 ($C^{2'c}$), 41.94 ($C^{2'd}$), 38.66 ($C^{2''c}$), 38.11 ($C^{1'a}$), 38.02 ($C^{1'c}$), 37.96 ($C^{1'd}$), 37.93 ($C^{1'b}$), 37.64 ($C^{4''c}$), 37.61 ($C^{4''d}$), 37.47 ($C^{2'a}$), 37.42 ($C^{2'b}$), 36.87 ($C^{4''a}$, $C^{4''d}$), 36.43 ($C^{2''c}$, $C^{2''d}$), 35.81 ($C^{1''a}$), 35.79 ($C^{1''b}$), 35.64 ($C^{5''c}$),

34.83 ($C^{2''b}$), 34.26, 34.20, and 34.13 (CH-S-$C^{a}H_2$, CH_2-S-$C^{a}H_2$, CH-S-$C^{b}H_2$, CH_2-S-$C^{b}H_2$), 33.86 (=CH-*C*H), 32.55 (CH_2-S-$C^{c}H_2$), 32.52 (CH_2-S-$C^{d}H_2$), 32.20 (CH-S-$C^{c}H_2$, CH-S-$C^{d}H_2$), 30.01 ($C^{5''a}$, $C^{5''b}$), 29.90 ($C^{6''a}$, $C^{6''c}$, $C^{6''}$d), 29.53–28.67(aliphatic) 28.09 ($C^{6''b}$), 25.95 (aliphatic), 20.71 ($C^{7''c}$), 20.63 ($C^{7''d}$), 20.18 ($C^{7''a}$, $C^{7''b}$), 16.20 ($C^{3'a}$), 16.09 ($C^{3'c}$), 15.90 ($C^{3'b}$), 15.73 ($C^{3'd}$).

FAB-MS of $C_{36}H_{65}O_4S_2$ ($M+H^+$ = 625.2). HRMS (FAB) of $C_{36}H_{65}O_4S_2$ [$M+H^+$] calc. 625.4319, found 625.4327.

5-((*R*)-1´-mercaptopropan-2´-yl)-2-methylcyclohexanethiol (55).

Colorless liquid (90%).

^{1}H NMR (600 MHz, $CDCl_3$, δ in ppm): δ 3.33 (dd, *J* = 6.8, 3.4 Hz, H^{1a}, H^{1b}), 2.62–2.54 (m, $H^{1'a}$, $H^{1'c}$, $H^{1'd}$), 2.45–2.34 (m, H^{1c}, H^{1d}, $H^{1'b}$), 2.00 (dd, *J* = 21.3, 8.3 Hz, H^{3c}, H^{3d}), 1.88–1.73 (m, H^{2a}, H^{2b}, $H_A{}^{3a}$, $H_A{}^{3b}$), 1.73–1.60 (m, H^{5a}, H^{5b}, $H_A{}^{6a}$, $H_A{}^{6b}$, H^{6c}, H^{6d}), 1.60–1.50 ($H_B{}^{3a}$, $H_B{}^{3b}$), 1.50–1.36 (m, $H^{2'a}$, $H^{2'b}$, $H_A{}^{4a}$, $H_A{}^{4b}$), 1.32–1.20 (m, SH, $H_A{}^{4c}$, $H_A{}^{4d}$), 1.20–1.00 (H^{2c}, H^{2d}, $H_B{}^{4c}$, $H_B{}^{4d}$, H^{5c}, H^{5d}, $H_B{}^{6a}$, $H_B{}^{6b}$), 1.04 (d, *J* = 6.4 Hz, H^{7c}, H^{7d}), 1.00–0.90 (m, $H_B{}^{4a}$, $H_B{}^{4d}$, H^{7a}, H^{7b}, $H^{2'c}$, $H^{2'd}$, $H^{3'a}$, $H^{3'b}$, $H^{3'c}$, $H^{3'd}$).

^{13}C NMR (151 MHz, $CDCl_3$, δ in ppm): δ 46.25 (C^{1c}), 46.24 (C^{1d}), 44.00 (C^{1a}), 43.89 (C^{1b}), 43.20 (C^{3c}), 42.51 ($C_{\text{minor diast}}$), 42.48 ($C_{\text{minor diast}}$), 41.99 ($C_{\text{minor diast}}$), 41.70 ($C^{2'c}$), 41.65 ($C^{2'd}$), 41.33 (C^{5c}, C^{5d}), 41.11 ($C_{\text{minor diast}}$), 41.09 ($C_{\text{minor diast}}$), 40.96 (C^{3d}), 40.94 (C^{2c}), 40.92 (C^{2d}), 40.75 ($C^{2'a}$), 40.68 ($C^{2'b}$), 39.35 (C^{3a}), 37.14 (C^{3b}), 36.27 (C^{5a}), 36.24 (C^{5b}), 35.93 ($C_{\text{minor diast}}$), 35.42 (C^{4c}), 35.32 (C^{4d}), 34.43 ($C_{\text{minor diast}}$), 34.41($C_{\text{minor diast}}$), 33.93 (C^{2a}), 33.77 (C^{2b}), 33.06 ($C_{\text{minor diast}}$), 32.98 ($C_{\text{minor diast}}$), 30.46 (C^{6a}), 30.34 (C^{6c}), 29.63 ($C^{1'a}$), 29.45 ($C^{1'b}$), 29.40 ($C^{1'c}$, $C^{1'd}$), 28.32 (C^{4a}), 28.24 (C^{4b}), 28.10 (C^{6b}), 27.91 (C^{6d}), 20.85 (C^{7c}), 20.82 (C^{7d}), 20.58 (C^{7a}), 20.56 (C^{7b}), 15.44 ($C^{3'a}$, $C^{3'c}$), 15.37 ($C^{3'd}$), 15.34 ($C^{3'b}$).

FAB-MS of $C_{10}H_{20}S_2$ ($M\text{-}H^+$ = 203.1). HRMS (FAB) of $C_{10}H_{20}S_2$ [M^+] calc. 204.1006, found 204.1003.

11,11'-oxybis(undecane-1-thiol) (58).

White solid (93%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): δ 3.38 (t, *J* = 6.7 Hz, 4H, -OC*H*$_2$-CH$_2$-), 2.52 (dd, *J* = 14.7, 7.5 Hz, 4H, -CH$_2$-C*H*$_2$SH), 1.67–1.48 (m, 8H, -OCH$_2$-C*H*$_2$-, -C*H*$_2$-CH$_2$SH), 1.43–1.16 (m, aliphatic, -SH, 30H).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): δ 71.07 (-OCH$_2$-), 34.17–26.31 (aliphatic), 24.78 (-CH$_2$SH).

FAB-MS of $C_{22}H_{46}OS_2$ ($M+H^+$ = 391.3). HRMS (FAB) of $C_{22}H_{46}OS_2$ [$M+H^+$] calc. 391.3063, found 391.3064.

8.6.3. Syntheses of the polymers

General procedure for thiol-ene polymerizations.

Thermal initiated polymerization using AIBN.

The polymerization reactions were performed in a carousel reaction station RR98072 (Radleys Discovery Technologies, U.K.). Into a carousel tube 0.20 g of the diene, the corresponding dithiol compound (see entries 1–3 in Table 7.1), and AIBN (2.5 mol%) were introduced and degassed *via* 3 times 200 mbar vacuum and subsequent purging with argon. The reaction mixture was stirred magnetically at 80 °C until the reaction could not be stirred anymore. The polymers (**P45**–**47**) were dissolved in THF and precipitated in cold methanol.

Photo initiated polymerization using DMPA.

A mixture of diene (0.20 g), the corresponding dithiol compound (see entries 4–9 in Table 7.1), and DMPA (5 mol%) was added into a reaction vessel. The mixture was stirred and exposed to a hand-held UV-lamp (2 × 4 W, λ = 365 nm) until the reaction became very viscous and could not be stirred anymore. The polymers (**P48–53**) were purified by precipitation of a concentrated THF solution of the reaction products into cold methanol.

General procedure for oxidation to polysulfone.

The polysulfide (0.15 g, see the entry in Table 7.2) was dissolved in THF (2 mL) and subsequently 35% hydrogen peroxide solution (5 equiv. to sulfur atom) was added. Afterwards, the reaction mixture was stirred at 65 °C for 24 h. The obtained polymers (**P54–57**) were purified by precipitation in a methanol-water (70:30) mixture.

9

Concluding Remarks and Outlook

The purpose of this dissertation is to present a brief assessment of the state of the art related to the realm of monomers and macromonomers from renewable resources and their polymerization through efficient pathways. Special attention has been given to terpenes, especially limonene, as renewable resources, since these compounds can be readily obtained from nature as pure enantiomer and contain rich cycloaliphatic ring, which might be eventually used to develop diverse organic building blocks as well as polymers with certain desirable properties, such as biodegradability, hydrophobicity, bioactivity, and liquid crystallinity. To offer some considerations about the prospective of terpenes as renewable resources for polymeric materials, the currently available terpenes and the knowledge on their exploitation in material science were briefly discussed in **Chapter 2**. Moreover, the application of highly efficient and green procedures are needed to achieve sustainable development. For this purpose, in **Chapter 3**, the use of thiol-ene reactions as non-catalytic carbon–heteroatom bond forming method and the use of TBD catalyst in organic reactions were described as an efficient tool for the synthesis of fine chemicals and monomers, as well as for the synthesis and modification of polymers derived either from natural or fossil-based sources.

In **Chapter 4**, addition of thiols to terpenes (i.e. (*R*)-(+)- and (*S*)-(–)-limonene, and (–)-β-pinene) were described as a simple approach to obtain a wide range of alcohol and/or ester functionalized renewable monomers. Solvent and radical initiator-free additions of alcohol and ester functional thiols to limonenes presenting different reactivity at the endocyclic and exocyclic double bonds can be regioselective, and can thus be controlled to yield monofunctional, difunctional, or hetero-difunctional monomers by simple variation of the thiol feed ratio. In the same manner, (–)-β-pinene derived alcohol and ester monomers have been prepared. It was found that the addition of thiols to terpenes is also diastereoselective, reaching a ratio of 5:1 for this radical reaction in the addition of 2 mercaptoethanol to (–)-β-pinene. Moreover, the monomers, which are interesting renewable building blocks, have been characterized and their behavior in polycondensation reactions has been studied. It has been found that long chain diesters or diols, which were synthesized from a castor oil derived platform chemical, are suitable comonomers and result in polycondensates with number average molecular weights of up to 25 kDa. Thus, terpene/fatty acid based polyesters were prepared and their structure-thermal property relationships were studied.

In **Chapter 5**, a number of aromatic polyesters can be synthesized from monomers that are derived from vanillin and fatty acid derivatives. Different efficient approaches were employed to prepare α,ω-dienes and difunctional monomers containing ester and/or alcohol moieties, which were then used to synthesize polyesters. Thus, thermoplastic polymeric materials with high molecular weight (up to 50 kDa) were obtained *via* three different pathways, i.e. ADMET, thiol-ene addition, and polycondensation. Within these investigations, we present vanillin and fatty acid

modification as a suitable tool to obtain renewable monomers for the synthesis of aromatic polyesters which might eventually be used to substitute polymers from conventional petroleum-based monomers.

In **Chapter 6**, the addition of cysteamine hydrochloride to (*R*)-(+)- and (*S*)-(–)-limonene was described as a versatile and effective way to obtain new amine functionalized renewable monomers for polyamide and polyurethane synthesis. Thus, through different combinations, limonene, fatty acid, as well as Nylon 6,6 copolymers were prepared and their structure-thermal property relationships were studied. GPC and DSC characterization revealed that these monomers can be used to synthesize polyamides with good and adjustable thermal properties. Moreover, the synthesized diamines have successfully been transformed into dicarbamates *via* a phosgene-free route and their behavior in polycondensation was studied. A number of linear renewable polyurethanes, from amorphous to semi-crystalline, were thus obtained *via* an isocyanate-free route, demonstrating new potential uses for these renewable resources.

Last but not least, renewable dithiols and diolefins from (*R*)-(+)-limonene and/or fatty acid were prepared and were used for the thiol-ene polyaddition, yielding a fully renewable thiol-ene polymers with good thermal properties. Thus, in **Chapter 7**, through different combinations, (*R*)-(+)-limonene and fatty acid derivatives copolymers were prepared and their thermal properties were studied. GPC results and intensive DSC analysis of the resulting polymers revealed that renewable polysulfides from amorphous to high-melting crystalline polymers with molecular weights up to 31.8 kDa can be obtained. In addition, polysulfones were prepared by oxidation of the corresponding polysulfides with a hydrogen peroxide solution.

Interestingly, DSC analysis revealed significant higher T_g or T_m values, when the polysulfides are oxidized into polysulfones. Overall, the combination of (*R*)-(+)-limonene and fatty acid derived monomers might open an entry to new polymers derived from these renewable resources.

Summarizing, a considerable amount of novel monomers and polymers, mainly from terpenes, as well as highly efficient synthetic procedures were introduced within this dissertation. The aforementioned results demonstrate the achievement devoted in the development of environmentally benign methodologies for the production of organic building blocks and polymers, which might be used as alternative in substituting, at least partially, the existing fossil resource based materials. In line with green chemistry concepts, all procedures exhibit some interesting advantages over the traditional synthetic routes.

List of Abbreviations

ADMET : Acyclic diene metathesis polymerization

AIBN : 2,2'-azobisisobutyronitrile

ATRP : Atom Transfer Radical Polymerization

COSY : Correlation Spectroscopy

DEPT : Distortionless Enhancement by Polarization Transfer

DMF : Dimethylformamide

DP : Degree of Polymerization

DSC : Differential Scanning Calorimetry

DMPA : 2,2-dimethoxy-2-phenyl acetophenone

EDA : Electron Donor Acceptor

EI : Electron Impact

ESI : Electro-spray Ionization

FAB : Fast Atom Bombardment

GC : Gas Chromatography

GC-MS : Gas Chromatography – Mass Spectroscopy

GPC : Gel Permiation Chromatography

HFIP : Hexafluoroisopropanol

HMBC : Heteronuclear Multiple Bond Correlation

HRMS : High Resolution Mass Spectrometry

HSQC : Heteronuclear Single Quantum Correlation

IR : Infra Red (Spectroscopy)

MAH : Molecule-Assisted Homolysis

M_n **:** Number average molecular weight

MS **:** Mass Spectroscopy

NOE **:** Nuclear Overhauser Effect

NMR **:** Nuclear Magnetic Resonance Spectroscopy

PDI **:** Polydispersity Index

PET **:** Polyethylene Terephthalate

RAFT **:** Reversible Addition-Fragmentation chain Transfer

ROMP **:** Ring Opening Metathesis Polymerization

ROP **:** Ring Opening Polymerization

TBAI **:** Tetrabutylammonium Iodide

TBD **:** 1,5,7-Triazabicyclo[4.4.0]dec-5-ene

TFAA **:** Trifluoroacetic Anhydride

T_g **:** Glass Transition Temperature

THF **:** Tetrahydrofuran

TLC **:** Thin Layer Chromatography

T_m **:** Melting Transition Temperature

UV **:** Ultra Violet

Curriculum Vitae

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2013: - Journal inside front cover at Green Chemistry (*Green Chem.,* **2013**, 15, 370–380).

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- Competitive research grant funded by Indonesian Directorate General of Higher Education (2 years, member).

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List of Publications and Conference Contributions

Refereed Journal Publications:

M. Firdaus, M. A. R. Meier, Renewable polyamides and polyurethanes derived from limonene, *Green Chem.,* 2013, 15, 370–380.

M. Firdaus, M. A. R. Meier, Renewable co-polymers derived from vanillin and fatty acid derivatives, *Eur. Polym. J.*, **2013**, 49, 156–166.

O. Türünç, *M. Firdaus*, G. Klein, M. A. R. Meier, Fatty acid derived renewable polyamides *via* thiol-ene additions, *Green Chem.*, **2012**, 14, 2577–2583.

M. Firdaus, L. Montero de Espinosa, M. A. R. Meier, Terpene-based renewable monomers and polymers *via* thiol–ene additions, *Macromolecules*, **2011**, 44, 7253–7262.

Poster and Oral Presentations:

M. Firdaus, M. A. R. Meier, Renewable co-polymers derived from limonene and fatty acid derivatives, 6th workshop on fats and oils as renewable feedstock for the chemical industry, March 17–19, **2013**, Karlsruhe, Germany, poster presenter.

M. Firdaus, L. Montero de Espinosa, M. A. R. Meier, Renewable monomers and polymers derived from terpenes *via* thiol-ene additions, 5th Workshop on fats and oils as renewable feedstock for the chemical industry, March 18–20, **2012**, Karlsruhe, Germany, poster presenter.

M. Firdaus, M. A. R. Meier, Clicking renewable resources: thiol-ene additions as a versatile tool for terpene modification, 3rd workshop on fats and oils as renewable feedstock for the chemical industry, March 14–15, **2010**, Emden, Germany, poster presenter.

M. Firdaus, Jumina, C. Anwar, Green synthesis of *C*-4-hydroxy-3-methoxyphenyl calix[4]resorcinarene, and *C*-4-methoxyphenylcalix[4]resorcinarene, International Seminar on Chemistry, October 30 – 31, **2008**, Bandung, Indonesia, oral presenter.

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