Efficient Routes to Degradable and non-Degradable Renewable Polymers from Fatty Acids

Zur Erlangung des akademischen Grades eines

DOKTORS DER NATURWISSENSCHAFTEN

(Dr. rer. nat.)

Fakultät für Chemie und Biowissenschaften

Karlsruher Institut für Technologie (KIT) – Universitätsbereich

genehmigte

DISSERTATION

von

Oğuz Türünç

aus

Samandağ, Türkei

Dekan: Prof. Dr. M. Bastmeyer

Referent: Prof. Dr. M. A. R. Meier

Korreferent: Prof. Dr. C. Barner-Kowollik

Tag der mündlichen Prüfung: 16.07.2012

Die vorliegende Arbeit wurde von März 2009 bis Mai 2012 unter Anleitung von Prof. Dr. Michael A. R. Meier an der Hochschule Emden/Leer (von März 2009 bis August 2009), der Universität Potsdam (von September 2009 bis September 2010) und am Karlsruher Institut für Technologie (KIT, von Oktober 2010 bis Mai 2012) - Universitätsbereich angefertigt.

To my parents,

Ragibe and Behcet Türünç…

Abstract

With the goal to establish a sustainable pathway to plastics, exploitation of the renewable resources through green production procedures are discussed. First, the globally available renewable resources and the knowledge of their exploitation was briefly overlooked, and plant oils are highlighted as a valuable renewable resource for polymers. Second, thiol-ene addition and metathesis reactions, and their utilization in both renewable building blocks and polymers are discussed by means of efficiency, reaction conditions, and green chemistry parameters. Last but not least, a number of polymers, e.g. polyesters, polyanhydrides, (&their copolymers) polyethylenes, poly(thio/oxo)ethers, and polyamides are prepared from fatty acids in the form of linear, hyperbranched, and dendrimers. Finally, material properties of the thus prepared polymers are studied and discussed in order to show application possibilities of this call of renewable materials.

Kurzzusammenfassung

Diese Arbeit hat als Ziel, nachhaltige Wege zu Kunststoffen, durch die Verwendung von erneuerbaren Ressourcen und umweltfreundlichen Produktionsprozessen, aufzuzeigen. In einer kurzen Einführung werden zunächst global verfügbare, erneuerbare Ressourcen, deren Gewinnung und Nutzung diskutiert. In diesem Zusammenhang erweisen sich besonders Pflanzenöle als wertvolle nachwachsende Ressourcen zur Herstellung von Polymeren. Des Weiteren sollen die Thiol-En- und Olefin Metathese-Reaktion für die Synthese von nachwachsenden Materialien und Polymeren hinsichtlich ihrer Leistungsfähigkeit, Reaktionsbedingungen und Nachhaltigkeit erörtert werden. Schließlich wurden eine Reihe linearer oder hochverzweigter Polymere z.B. Polyester, Polyanhydride, Polyethylene, Poly(thio/oxo)ether und Polyamide aus Fettsäuren hergestellt. Zuletzt wurden die Materialeigenschaften der dargestellten erneuerbaren Polymere untersucht, um verschiedene Anwendungsmöglichkeiten dieser Polymerklassen aufzuzeigen.

Contents

1

Introduction

Since the global production of plastics has grown almost 5% per year over the last 20 years (even it increased by 6% to 265 million tonnes from 2009 to 2010),[1] it is hard to imagine a future without the use of plastics. Plastics can be produced in a number of different forms by means of mechanical strength and shape, and exhibit much lower density than ceramics, glass, or metal; the latter have of course been used as starting materials for the production of the tools of the daily life since a long time, but plastics can offer comparable mechanical and other properties. Considering the depletion of the petroleum resources and the accumulation of the plastics waste should be reason enough to encourage research on novel plastics that, for instance, secure food and water for a growing population, reduce materials weight, serve and protect household, and enable smarter packaging, coating, etc.

As the negative impact, namely fingerprint, of man on the planet is being discussed immensely in the last decade, reponsibles from academia, politics, industry, and most importantly from the public have emerged individually specific goals to sustain the life on the earth. The discussions brought the chemistry community to ask the question, “***Is the chemistry I am doing the most benign that I can make it?***”.[2] In order to bring these goals into reality *via* a more comprehensive and systematic guide line, Anastas and coworkers introduced the by noe well-known “12 Principles of Green Chemistry (or Engineering)”.[3,4] Those principles are:

1. **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
2. **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis**. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals**. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. **Safer Solvents and Auxiliaries**. The use of auxiliary substances (e.g., solvents, separation agents, and so forth) should be made unnecessary wherever possible and innocuous when used.
6. **Design for Energy Efficiency**. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks**. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. **Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation**. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11. **Real-Time Analysis for Pollution Prevention**. Analytical methodologies need to be developed further to allow for real-time in-process monitoring and control before the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention**. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

When these principles are evaluated by a polymer chemist, the majority of the principles seem to be related to the process design. However, the principle 7 is likely to be the most important one as a 'Life Cycle' of a product starts from the raw material (see Figure 1.1).

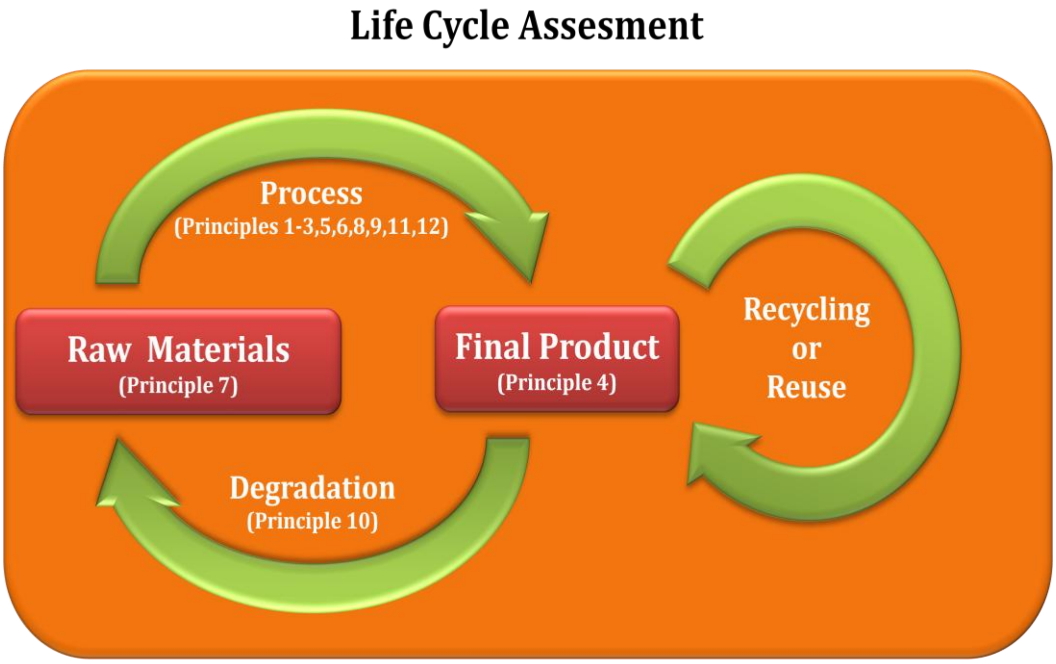


Figure 1.1: The evaluation of the 12 Principles of Green Chemistry for plastics design.

This principle dictates the use of available renewable resources. Since the majority of the plastic materials are organic, the biomass available on earth should be considered as a renewable resource for the chemical industry, with respect to the abundance. Indeed, it was estimated that about 120 billion tons carbon in biomass, equivalent to >80 billion tons of oil equivalents, are generated globally annually by photosynthesis, of which about 5% is presently used by man.[5] The currently available biomass and the knowledge on their exploitation in material science will be briefly discussed in **Chapter 2**. Moreover, use of particularly plant oils and the fatty acids in highly efficient reactions with atom economy, short reaction times, less and non-offensive waste will be discussed in **Chapter 3**. Throughout, this thesis will contribute to the use of plant oils as renewable raw materials for the synthesis of, for example, polyesters in **Chapter 4** and polyamides in **Chapter 8**.

The principles 4 and 10 may be ascribed to the toxicity issue of the plastics, their degradation properties, and the monomers used for their production. These parameters are especially important for the synthesis of biopolymers. Though the term 'biopolymers' is used in very different aspects, such as the origin, area of use, or degradability of the polymer, safer production technologies and desired biodegradation properties count for all; hence, **Chapter 5** and **Chapter 6** will contribute particularly to these issues.

The other principles dictate a sustainable production process, which should be non-hazardous, minimizing waste, energy, and material use and maximizing mass, energy, and time efficiency. Hence, highly efficient and non-hazardous reaction procedures must be applied to ensure the efficiency of the overall synthesis. These expectations often come along the issues 'green solvent', 'catalysis', and 'flow chemistry' to the table. Although reactions that can be carried out without solvents are best for a green reaction,[6] green solvents are still necessary for many other reactions. Green solvents may be approached via four directions:[7,8] i) substitution of hazardous solvents with ones that have a significantly reduced ecological footprint (better environmental, health, and safety properties); ii) use of bio-solvents, i.e. solvents produced with renewable resources such as ethanol. For example, biomass-derived 2-methyltetrahydrofuran was shown to exhibit superior solvent characteristics especially for organometallic reagents comparing to THF that requires highest production energy of >250 MJ / kg among other classical solvents,[9] and most importantly toxicological studies revealed the absence of genotoxicity and mutagenicity associated with exposure to this solvent;[10] iii) substitution of organic solvents either with supercritical fluids that are environmentally harmless;[11] or iv) with ionic liquids that show low vapour pressure, and thus less emission to air. In combination with supercritical fluid systems, continuous flow reactors are being introduced as alternative and even more sustainable or greener chemical processes.[12] For instance, hydrogenation reactions, which are of major importance, were carried out in a supercritical (CO_2) flow reactor for a wide range of organic compounds with good throughput (up to >1200 mL / h in favourable cases).[13] The issue of solvent use upon monomer synthesis and polymerization reactions is not devoted to any particular section in this thesis, yet will be discussed throughout the all chapters. On the other hand, the 12 principles outlined above should all be considered by addressing, for instance, overall yield, number of total synthetic steps, or selectivity. It will not be possible to maximize all, but optimizations should be considered for highest benefit. Environmental gains will not be realized if pollution is simply shifted from one step to another.[14] These considerations implement use of catalysts in organic reactions to achieve high yields with high selectivity and fulfil both economical and environmental benefits.[15] For instance in 2005, Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock were awarded with Nobel Prize for their development of the new and well-defined Ruthenium-based catalysts that made metathesis reactions be highly efficient and “green” processes for olefin synthesis.[16] Nevertheless Ei-chi Negishi, who was awarded with Nobel Prize together with Richard F. Heck and Akira Suzuki in 2010, strongly recommends even bimetallic systems to achieve highly selective organic reactions, which in turn reduce purification steps and the waste produced therefrom.[17],[18] In this thesis, **Chapter 3.2** will discuss metathesis reactions as well as metathesis catalysts, and **Chapter 5** and **Chapter 6** will contribute to the use of Ru-catalyzed metathesis reactions for the synthesis of plastics. While designing a production process for a desired product using the 12 Green Chemistry Principles in order to assess the whole system in order to achieve green and sustainable production level, it seems that one should consider a number of parameters in an iterative manner to come up with a final decision. Therefore, systematic and quantitative approaches are described to evaluate how green organic reactions and processes are via green metrics.[19] Among others, ‘atom efficiency’ is most commonly used.

Highly efficient reactions are not limited to the use of catalysts. For example, the radical initiated thiol-ene addition reaction is also considered to be robust, orthogonal, and efficient.[20] Its tolerance to a number of functional groups, mild reaction conditions, and readily available thiol compounds made this reaction to be used exclusively in the last decade for polymer synthesis. Thus, its applications for monomer syntheses from plant oils and polymerizations will be briefly discussed through green chemistry lines in **Chapter 3.1**, and all chapters will mainly contribute to the applications of this reaction. Moreover, **Chapter 7** will introduce thiol-alkyne addition as a novel polymerization method for the synthesis of linear functional polymers.

2

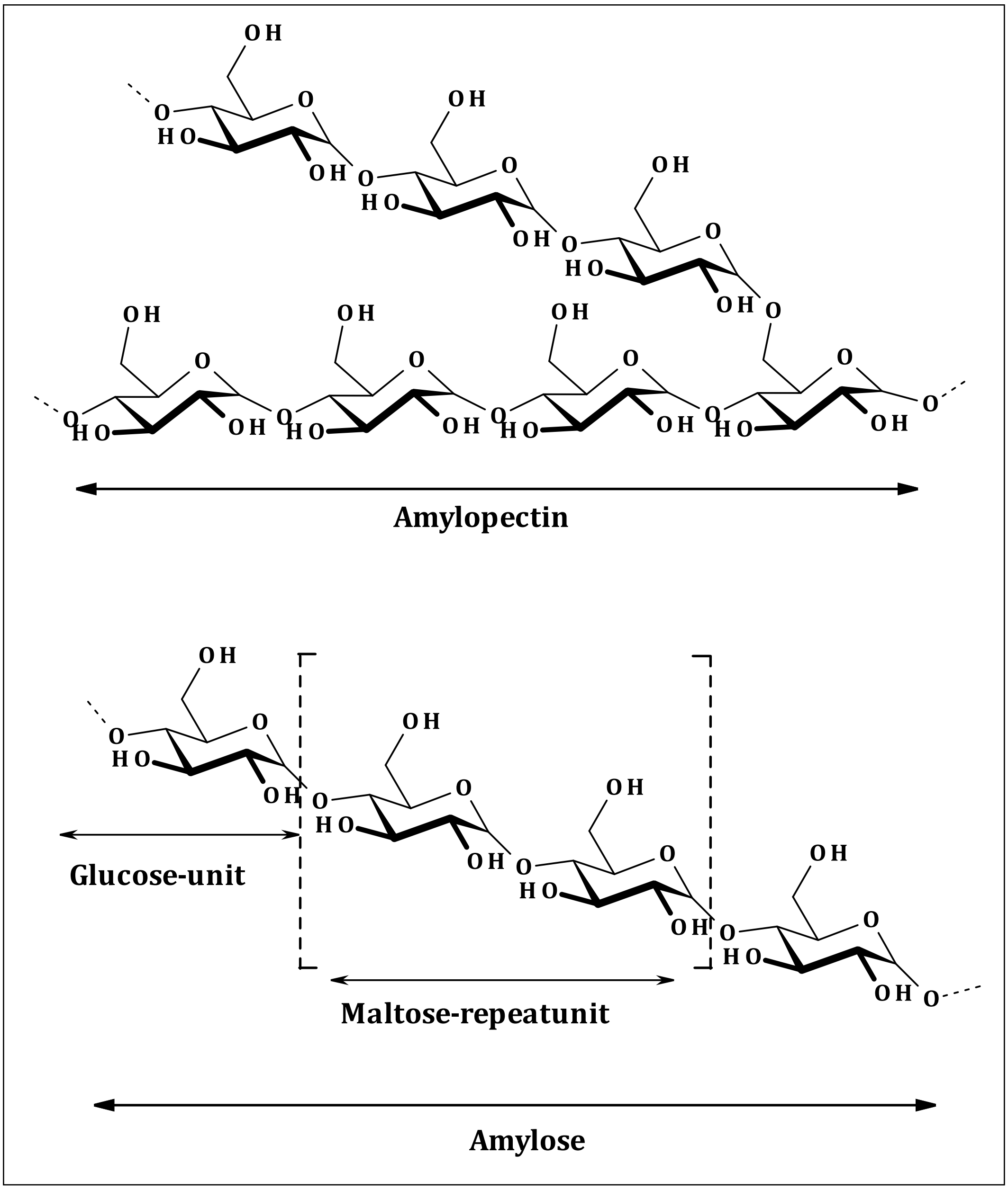
Renewable Resources as Raw Materials for Polymers[21]

It has been a long time since human beings began using plant and animal products for purposes other than nutrition, such as paints or clothing. Since that time, the methods and knowledge-base used to produce these products from such resources have steadily developed. Eventually, the discovery of fossil oil and its consequent exploitation, including the improved knowledge about petroleum chemistry and chemical engineering, resulted in a “plastic revolution”, which first seemed to be very cheap, easily formed, and a long-lasting technology. However, due to the recent awareness of not only the greenhouse effect, but also due to accumulation of plastic waste in almost every part of the world as well as environmentally unsound production technologies, mankind has started to search for sustainable, environmentally-friendly feed-stocks and technologies to improve the ecological impact of the chemical industry. The fact that fossil oil is a limited feedstock only further clarifies the need to develop more sustainable alternatives. Today, carbohydrate- and plant oil-based polymers and synthesis technologies are being extensively researched and even commercialized to some extent. Therefore, this chapter will summarize current knowledge and applications of some carbohydrate- and plant oil-based biopolymers derived from natural resources and discuss possible future applications/products as well as properties of these materials.

2.1 Carbohydrate-based Polymers

2.1.1 Polymers from Starch

Starch is a highly abundant polysaccharide and is produced by plants to store energy. Starch is a semi-crystalline polymer composed of amylose and amylopectin. Amylose is an almost linear polymer consisting of $\alpha(1\rightarrow4)$ linked glucose molecules, whereas amylopectin has a similar (1–4)-linked polymer backbone with an additional ca. 5% $\alpha(1\rightarrow6)$ linkages with branches typically occurring every 24 to 30 glucose units (scheme 2.1).[22] The relative amounts of amylose and amylopectin depend on the plant source and affect the final properties of the material. Corn starch granules for instance contain approximately 70% amylopectin and 30% amylose.[23] Starch is one of the cheapest and most abundant natural polymers.[24] The abundance and degradability make starch interesting for several industrial applications.



Scheme 2.1: Chemical structure of starch.

Although starch can itself be a thermoplastic polymer (thermoplastic starch, TPS)[25] and can be processed *via* extrusion or molding with the aid of a plasticizer,[26] this natural polymer is a rapidly degrading material with minimal moisture-resistance. Application possibilities of TPS are as fillers or blends with other thermoplastics.[27,28] Chemical modification of starch, on the other hand,[29,30] can be used to adjust degradation properties as well as the water-stability of the resulting materials.

For instance, blends of starch with polyethylene or polyesters are manufactured by Novamont on a scale of ~36000 metric tons per year for packaging applications.[31] Moreover, foam materials of starch blends are also used in packaging applications. First, the blend is prepared *via* the extrusion of TPS and a biodegradable[32] or non-biodegradable polymer.[33,34] Subsequently, the blends are blown into foams in order to improve the hydrophobic character and mechanical properties of starch foams and films.[23,35] In 2006 Yoon *et al.* studied the effect of additives such as glycerol, succinic acid, malic acid, and tartaric acid on the physical properties of starch/PVA blend films and the results showed that the flexibility and strength of the films could be improved with alcohol and carboxylic acid functionalities.

Flieger *et al.*, in their review, classify starch composites according to their starch content: low (~10 – 20 %), medium (~ 40 – 60 %), and high amounts (~ 90 %) of starch, each class demonstrating distinct material properties.[36] Addition of low amounts of starch to, for example, polyethylene accelerates the disintegration of the polymer and the breaking apart of the material in such a way that the fast degradation of starch produces pores in the remaining plastic film, which leads to a better interaction between oxygen, microorganisms and the plastic molecules.[37] In some applications photo initiators, such as benzophenone derivatives, are used as pro-oxidants to speed up the degradation progress via generation of free radicals, which results in polymer oxidation and finally chain scission.[38]

Jansson *et al.* studied free films made of starch and PVA mixtures (produced by casting) with respect to their mechanical and moisture uptake in order to establish their potential as spray-dried powders.[39] The moisture uptake was substantially higher when glycerol was added and the glycerol-containing films had a lower failure stress under tension than the corresponding glycerol-free films. Nevertheless, the films containing

20% glycerol showed almost double the water uptake compared to the glycerol-free films. The observed swelling behavior indicated that some of the powders were good candidates for plastisol coatings, which are suspensions of polymer particles in a plasticizer commonly dioptyl adipate) used mainly in textile inks.[40]

Starch can also be chemically-modified *via* esterification with fatty acids to synthesize completely renewable and biodegradable materials. Sagar and Merrill esterified high-amylose starch with different chain length fatty acid chlorides in the presence of pyridine and then evaluated the rheological, thermal, and mechanical properties of the resulting materials.[41] It was shown that ester groups within the structure act as internal plasticizers, making the material more easily processible and more ductile. The starch esters of pentanoic and hexanoic acid were semi-crystalline. The report showed that fatty acid modified starch could be used for some applications where biodegradability is required, but mechanical property requirements are not too demanding. Moreover, it was shown that the degradation rate of starch could be controlled by the degree of acetylation.[42]

A great deal of attention has been given to the incorporation of polysaccharides into PU foams.[43] Attempts to form PUs from starch and its degradation products, polyol glucoside ethers, suitable for polyurethane were reported in the early 1960's.[44] Some methods for depolymerizing polysaccharides are well known. For instance, starch can be enzymatically degraded to yield saccharide mixtures (containing dextrin, maltose, maltotriose and glucose), high maltose syrups, or high glucose syrups via the use of α-amylase, pullulanase, and amyloglucosidase enzymes.[43] Polyethers were derived from starch degradation products by alkoxylation of the carbohydrate to a degree necessary to give a liquid of the desired viscosity and hydroxyl number. Ge *et al*. utilized starch and wattle tannin of the bark of *Acacia mearnsii* (a fast-growing tree native to Australia) and toluene diisocyanate to synthesize flexible PU foams for car cushions, which need a high cross-linking density to maintain a high-resilient property.[45] On the other hand, Kim *et al*. used starch as the main polyol component, with the amount of 30 – 50 wt%, for polyurethane film formation.[46] Two endothermic peaks were observed by DSC analysis, resulting from urethane and starch domains. From tensile testing, the stress at break and modulus were observed to increase significantly with the starch content and -NCO/-OH molar ratio. Much research has also been carried out to enhance the fire resistance of PU by the incorporation of phosphorus, halogens, or nitrogen-containing compounds, or by the use of rigid molecules either as polyol or as isocyanate. [43]

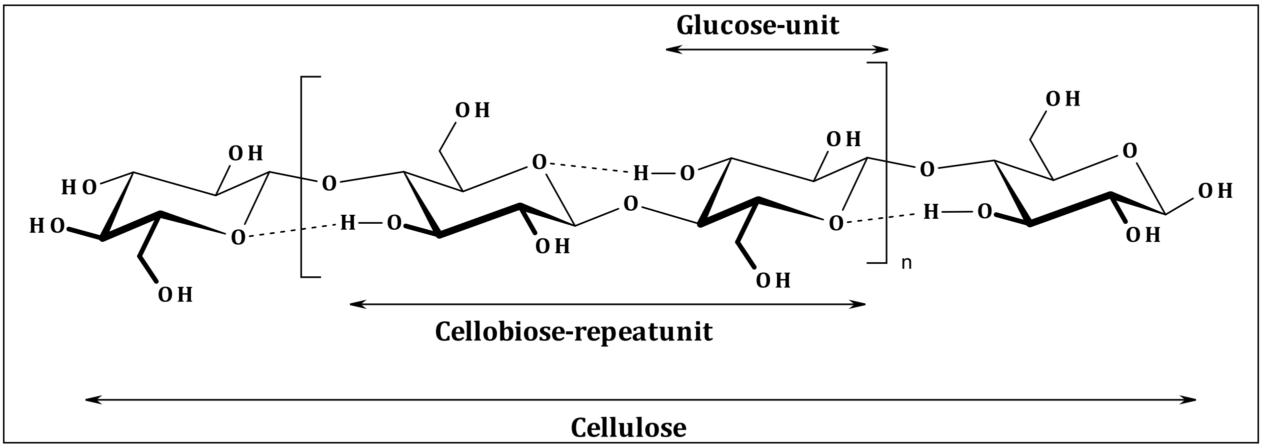
Because of their low immunogenic potential, potential bioactive behavior, capability of interacting with the host's tissue, chemical versatility, and almost unlimited source, starch-based polymers are considered to be ideal materials for tissue engineering.[47] Different degradable porous architectures have thus been developed using polymers based on blends of corn starch with poly(ethylene-co-vinyl alcohol)(SEVA-C, Novamont, Italy) and cellulose acetate (SCA, Novamont, Italy).[48] These materials present a non-cytotoxic behavior and are under consideration for a wide range of biomedical applications such as scaffolds for bone-tissue engineering.[49]

Another future application of starch might be in the field of electro-active polymers or polymer electrolytes. Although starch is an insulator and its proton mobility is low, upon doping with MX (NaCl, NaI, LiCl, LiI), it exhibits conductance between 10^{-5} and 10^{-6} S/cm (compared to 10^{-9} - 10^{-11} S/cm for starch which contains 30% water).[50] Recently, Khiar and Arof studied an electrolyte based on starch and different amounts of ammonium nitrate. The study revealed that the conductivity was increased from $6.28\text{x}10^{-10}$ to $2.83\text{x}10^{-5}$ upon addition of 25% ammonium nitrate at room temperature.[51]

One of the most recent and interesting application possibilities of starch are shape-memory materials. Non-modified starch has been shown to present very efficient shape-memory capabilities, with a recovery ratio of $R_r > 90\%$ for a fixed deformation of 200%, which was permanently shaped by extrusion and this shape was stabilized below T_g. A second shape was gained via thermo-molding above T_g and shape recovery was triggered by water sorption at 20 °C. The study stimulates the use of starch as environmentally friendly smart material.[52]

2.1.2 Polymers from Cellulose

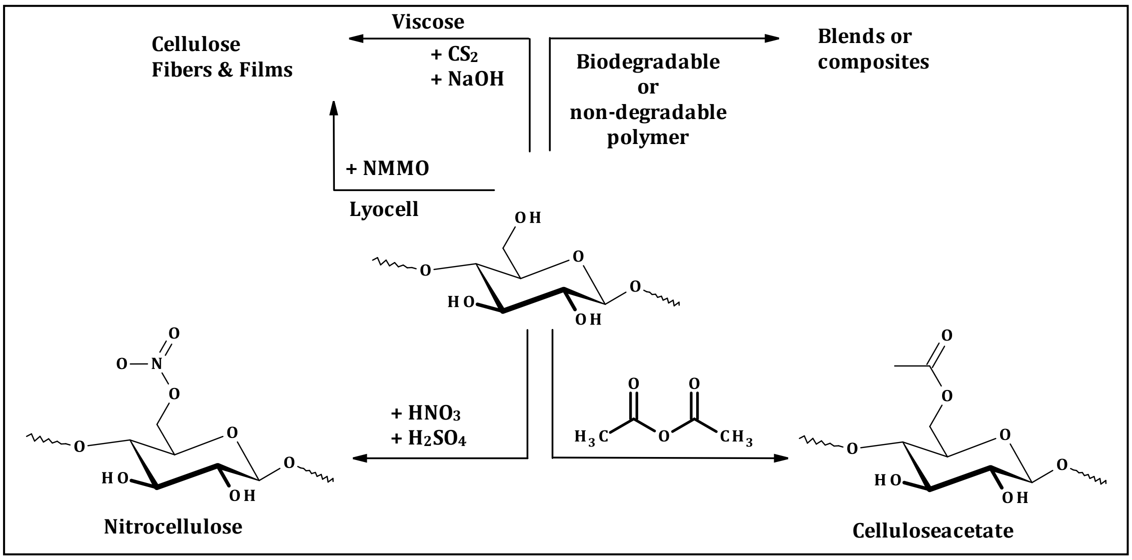
Cellulose is, next to chitin, the most abundant biopolymer on earth. It is the major constituent of plant cell walls and more than half of the organic carbon on earth is fixed in cellulose. It is composed of unbranched, linear chains of D-glucose molecules linked through 1,4-β-D glycosidic bonds (Scheme 2.1.2.1).



Scheme 2.1.2.1: Chemical structure of cellulose.

Interestingly, no vertebrate has the capacity to digest cellulose enzymatically. Herbivores subsist largely on cellulose, not because they can digest it themselves, but because their digestive tracks contain microbes that produce cellulose-hydrolyzing cellulases; various cellulase types are also synthesized by fungi. When compared to starch, cellulose is relatively resistant to biodegradation. Each cellulose molecule is an unbranched polymer of 10^3 – 10^6 D-glucose units.[36]

Although paper has been known for more than 2000 years, the sensitivity of the mechanical properties towards water limits the use of cellulose as a material in many applications. Moreover, cellulose cannot be thermally processed into plastics because of its hydrogen-bonded structure. However, micro fibrils with diameters ranging from 2 to 10 nm and lengths reaching several micrometers can be isolated from native cellulose fibers through a combination of chemical and mechanical methods. The viscose process has been known for more than 100 years and although it is far from being environmentally friendly (Scheme 2.1.2.2) it dominates other methods for isolating cellulose fibers. Cellulose processed in this way finds applications from textile fibers to technical fibers for cords of high-performance tires (rayon) or for film (cellophane) production, which is suitable for food packaging.[53] An environmentally friendlier method, the Lyocell process, was developed in the 1980s as an alternative to the viscose process, in which *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate is used as a more convenient solvent system, resulting in a process practically free from emissions since solvent recovery is almost complete.[54]



Scheme 2.1.2.2: Modification pathways of cellulose.

Their mechanical properties, with a Young's modulus of ~140 GPa, close to that of Kevlar, make cellulose fibers ideally suited as reinforcing elements in composite materials.[29] Moreover, cellulose ultrathin films are also of great interest for their extreme wetting behavior with aqueous systems and for being extremely stable against oxidation and thermal degradation.[55,56] These features make cellulose interesting for two distinct types of materials, cellulose composites and thermoplastically processable cellulose derivatives.

The introduction of cellulose into a graft-copolymer matrix and common thermoset polymers[57] was shown to improve the mechanical properties of the composite materials.[58] Fiber surface modification by physical and chemical means,[59] and the use of coupling agents in order to overcome the incompatibility between cellulose and a hydrocarbon polymer matrix as well as to improve interfacial interactions were applied.[60] When cellulose is used as a natural fiber in a biodegradable polymer matrix, so called eco-composite materials are formed that have drawn increasing attention due to environmental considerations. The processes required to prepare eco-composites are very similar to fiber glass composites and are reviewed by Bogoeva-Gaceva *et al.*[61] A brief review covering composites of biodegradable and nondegradable polymers with natural fibers was reported by Netravali and Chabba in 2003.[62]

Chemical modification of cellulose is another important research topic as well as industrial application area. The high number of hydroxyl groups present on each repeating unit of cellulose gives potential to be chemically modified through all possible alcohol-involved organic reactions, typically esterifications and etherifications. Moreover, click chemistry is currently being investigated to functionalize cellulose.[63,64] Cellulose acetate (Scheme 2.1.2.2) is the most widely known and used example of esterified cellulose derivatives. It is used for potentially biodegradable fibers and films. The degradation rates of cellulose acetate can be controlled with the degree of substitution.[65] Parkesin™, a moldable nitro derivative of cellulose (scheme 2.1.2.2), has been used as a replacement of ivory. Moreover celluloid, invented in the 1860s, is a nitro-cellulose derivative that uses camphor as a softener in order to improve its flexibility.[31]

The crystal structure and three-dimensional network prevent cellulose from behaving as a polyol for PU syntheses. To overcome this problem a liquefaction process in the presence of organic solvents was developed and resulted in products suitable for PU synthesis. Yan *et al*. liquefied cornstalk, an agricultural by-product, and tested it for the synthesis of PU foams blown by water.[66] The report revealed that such polyurethane foams had excellent mechanical properties and thermal properties and could be used as heat-insulating materials.

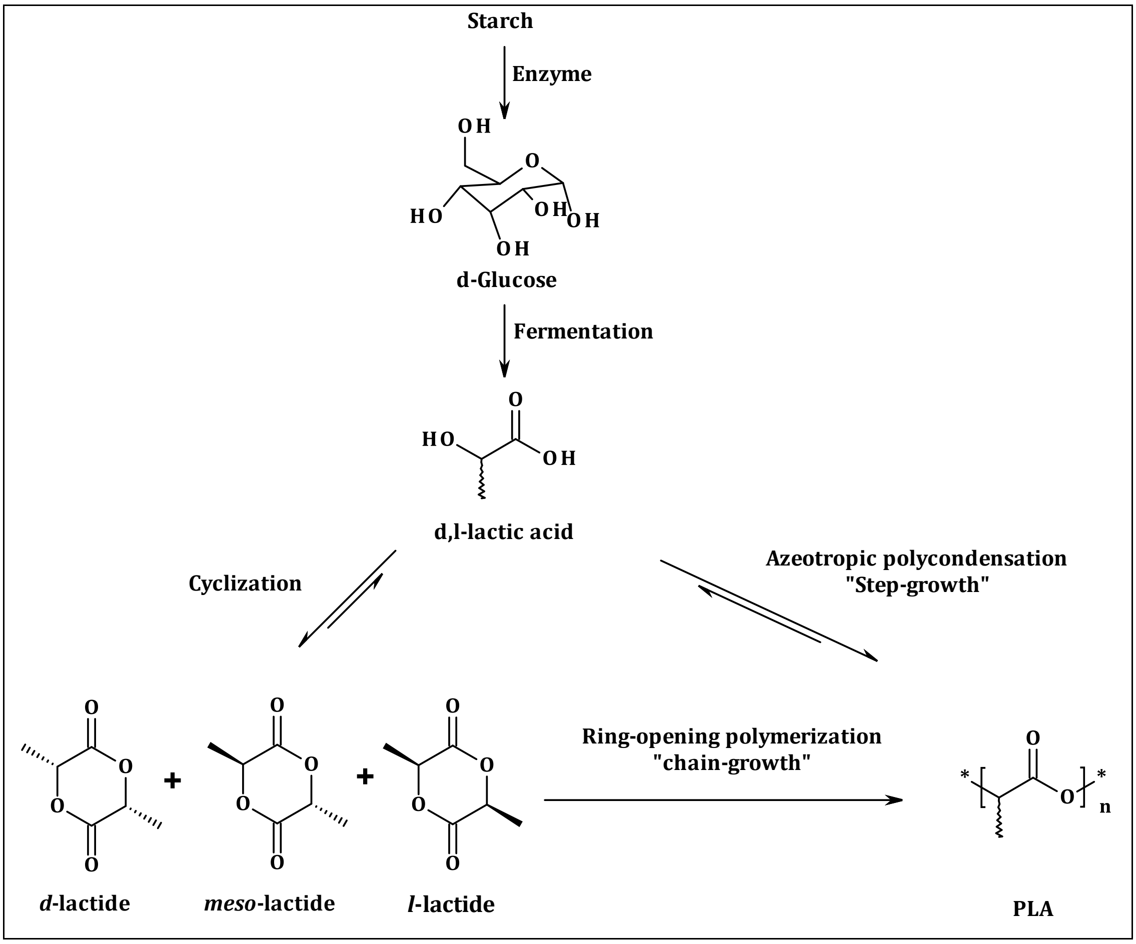
In addition to its renewability and satisfactory mechanical properties, cellulose presents biocompatibility, which makes it possible to use in some pharmaceutical applications. Different chemical modifications allow different applications of cellulose, such as oxycellulose for controlled drug delivery matrices, sodium carboxymethyl cellulose as emulsifying agents, and cellulose acetate phthalate for tablet coatings.[67]

Just like starch, cellulose has also been shown to exhibit some important electro-active properties. For instance, cellophane was found to be a piezoelectric material that transforms electrical energy into mechanical energy. Moreover, some cellulosic blends, e.g. the blend of cellulose xanthate and propylene oxide-grafted hydroxyethyl cellulose with PEG, showed conductivities around 10^{-5} and 10^{-4} S/cm.[50]

2.1.3 Polymers from lactic acid and lactide

An important feature of starch is its potential enzymatic hydrolysis into glucose and subsequent fermentation into lactic acid. Poly(lactic acid, PLA) can be obtained from this fermentation product via direct condensation or via its cyclic lactide form (L-, D-, or meso-lactide) (Scheme 2.1.3.1).[24,68] PLA chemistry was already investigated by Carothers in 1932 and since then it has been extensively studied by means of efficient glucose fermentation, enantiomerically pure monomer and polymer synthesis, wide range of catalyst systems, and final product properties and enhancements.

PLAs have been industrially fabricated into fibers, films, and surgical implants and sutures. Currently, most PLA is produced by Natureworks® (Dow – Cargill) in an amount of 136000 ton per year in their plant in Nebraska, USA.[31] The advantageous properties of PLA include being renewable, biodegradable, recyclable, compostable, biocompatible, processible, and energy saving. Nevertheless, PLA has poor toughness, slow degradation, hydrophobicity, and lack of reactive side-chain groups, which need to be improved.[69]



Scheme 2.1.3.1: Synthesis of lactic acid, lactide and poly(lactic acid).

Currently PLA is industrially synthesized *via* chemical pathways (e.g. ring opening polymerization of lactide or solvent-based azeotropic condensation). Although azeotrotopic distillation overcomes the limitation of the molecular weight, a typical drawback of step-growth polymerization kinetics, to some extent, the ring-opening polymerization of lactide allows better control of the polymerization and remains by far the most widely used method for the synthesis of well-defined materials.[70] In contrast, Yang and coworkers studied one-step fermentative *in vivo* production of PLA in *E. coli*.[71] The results led to the biosynthesis of PLA and its copolymers with 3-hydroxybutyrate containing various lactate fractions within the range of 8.7 to 64.4 mol%.

The polymerization rate, molecular weight control, and stereo-control are the key parameters for PLA synthesis.[72] The physical, mechanical, and degradation properties of

PLAs are strongly dependent on the chain stereochemistry. Isotactic PLLA is a highly crystalline polymer with a T_m of 170 °C.[73] It has excellent mechanical properties and degrades rather slowly. Atactic poly(*rac*-lactic acid) is amorphous and degrades faster. Therefore, it is very important to control the chain stereochemistry for PLA homopolymers and copolymers. Much effort has focused on the development of new catalysts for the controlled polymerization of lactide including chiral aluminum isopropoxides based on enantiopure or racemic cyclohexylsalen ligands (Jacobsen ligand), imidazole,[74] aluminum-methyl complexes supported by tetradentate phenoxy-amine ligands,[75] group 3 metal complexes supported by dianionic alkoxy-amino-bisphenolate ligands,[76] primary and secondary alcohol adducts of 1,3-dimesitylimidazolin-2-ylidene,[77] as well as tin(II) complexes supported by β-diketiminate ligands.[78] Moreover, Lohmeijer *et al*. reported some guanidine and amidine organocatalysts for ring opening polymerization of lactide, which avoid heavy metal contaminants from catalyst residues in the polymer.[79] It was shown that 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), *N*-methyl-TBD (MTBD), and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) are very efficient catalysts for ring opening polymerization with excellent control of molecular weight and polydispersity.

Since PLAs are generally very brittle and exhibit lower elongation at break, they need to be toughened for some applications. Anderson *et al*. reviewed the toughening methods as adjusting stereochemistry, crystallinity, and processing, plasticization, and blending with other degradable or non-degradable polymers.[80] For instance, when poly(l-lactic acid)(PLLA) is toughened with polymerized soybean oil, the blends exhibit a tensile toughness as high as 4 times and strain at break values as high as 6 times greater than those of unmodified PLLA.[81]

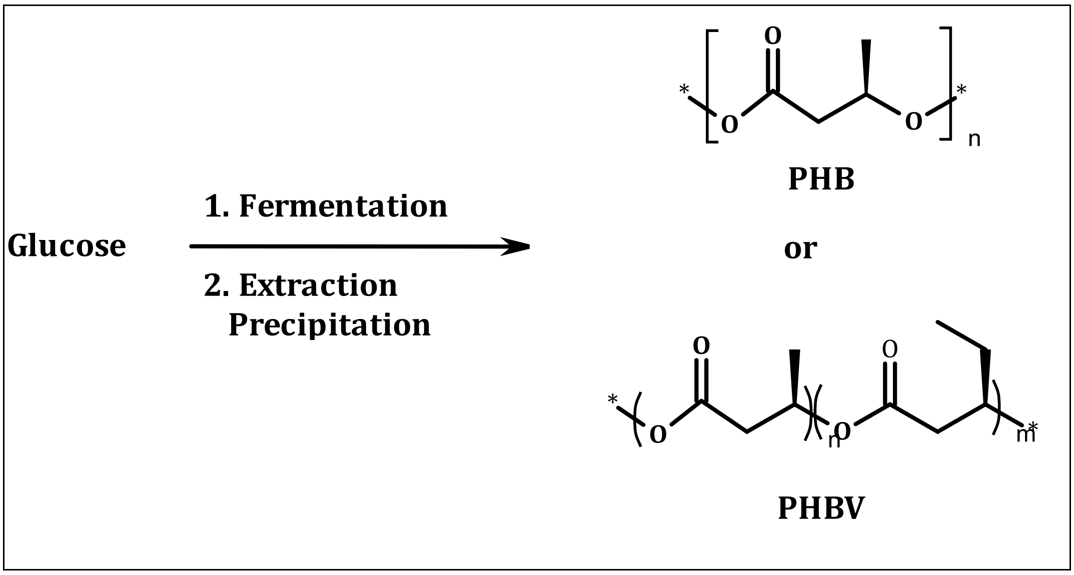
In 2008, Pounder *et al.* took advantage of thiol – ene reactions, which are considered to be one of the click reactions, and used a furan protected alcohol functional maleimide as an initiator for the polymerization of lactide.[82] After polymerization and deprotection, some aromatic and aliphatic thiol compounds with various functionalities were reacted to yield PLAs with different chain-end functionalities under very mild conditions without any degradation. Another interesting approach to synthesize PLA grafted with poly(ethylene oxide)(PEO), containing various repeating ethylene oxide units, was reported by Jiang *et al*. in 2008.[83] Mono-methoxy PEGs were functionalized with a lactic acid moiety through a three-step process and the subsequent cyclization of these lactic acid moieties into lactide was carried out with the aid of an organic acid. Finally this adduct was subjected to ring opening polymerization using Sn(2-ethylhexanoate)$_2$, a very common catalyst for PLA synthesis. The resulting polymers containing one and two PEO repeat units in the pendant chain were hydrophilic, but not water-soluble. Those having longer PEO chains were water-soluble. Moreover, a lower critical solution temperature was detected for the two polymers (19 and 37 °C, respectively) indicating their thermo responsive behavior.

PLA can also be used for medical applications owing to its biocompatibility and biodegradability. PLA was shown to degrade *via* hydrolytic erosion,[84] in which the mechanical properties remain similar during the degradation progress. The degradation rate and mechanism, as well as other properties of PLA, depend on molecular weight & distribution, pH, T_g, crystallinity, and temperature. For further enhancement of the physical and mechanical properties, PLA was copolymerized with glycolic acid resulting in a more hydrophilic and highly crystalline polymer. Interestingly, no linear relationship between the composition and degradability was reported; hence, copolymers with high or low comonomer ratios are less sensitive to hydrolysis than copolymers with equal ratio, due to their greater crystallinity.[85] Another medical application of PLA and its copolymers, owing to their tissue compatibility, is the preparation of scaffolds for tissue engineering.[86]

2.1.4 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA) are a form of carbon and energy storage in the cytoplasm of most of the bacteria belonging to the Halobacteriaceae family.[87,36] After the destruction of the cell walls, up to 90 % poly(3-hydroxybutyrate) (PHB) polymer, the most known class of PHAs, can be isolated (Scheme 2.1.4.1).24 These polymers are biodegraded by microbes within 5 to 6 weeks. During this period of time they can be metabolized, both in the presence and absence of oxygen, into carbon dioxide and water or methane, respectively.[88]

PHAs can be used for the manufacture of films, coated paper, compost bags and can also be molded into bottles and razors.[31] Additionally, since they are biocompatible they can also be used as implants without causing inflammation.[89]



Scheme 2.1.4.1 Examples for the synthesis of PHAs.

Copolymers of PHAs are more useful for the industry, since they exhibit lower crytallinity, easy processibility, and more flexible final product properties. The final PHA polymer properties can thus be adjusted from semi-crystalline to elastomeric plastics. The most common instance is poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). The relative content of hydroxybutyrate and hydroxyvalerate monomers can be adjusted by the amount of the valine added to the glucose-based culture medium.[90] The melting point of PHB (180 °C) is lowered to 137 °C by 25 mol% of hydroxyvalerate units.[24] PHBV was first commercialized by ICI (Imperial Chemical Industries) in the late 1980s as Biopol® and its production was stopped in 1998 after it was sold to Monsanto in 1996. Currently, the Biomer company in Münich, Germany produces about 100 kg of PHB per m^3 of fermentation medium and a white powder with 98 % purity can be collected after extraction.

PHAs require expensive bacterial fermentation and isolation processes resulting in more expensive production costs if compared to other petroleum-derived polymers. Thus, in the beginning of the 2000s, an alternative strategy for lowering the production costs proposed to develop transgenic plants (genetically modified plants) that produce PHAs.[91,92] Presently, a variety of PHAs can be synthesized in many transgenic plants such as tobacco, rapeseed, cotton, alfalfa, flax, and oil palm.[93]

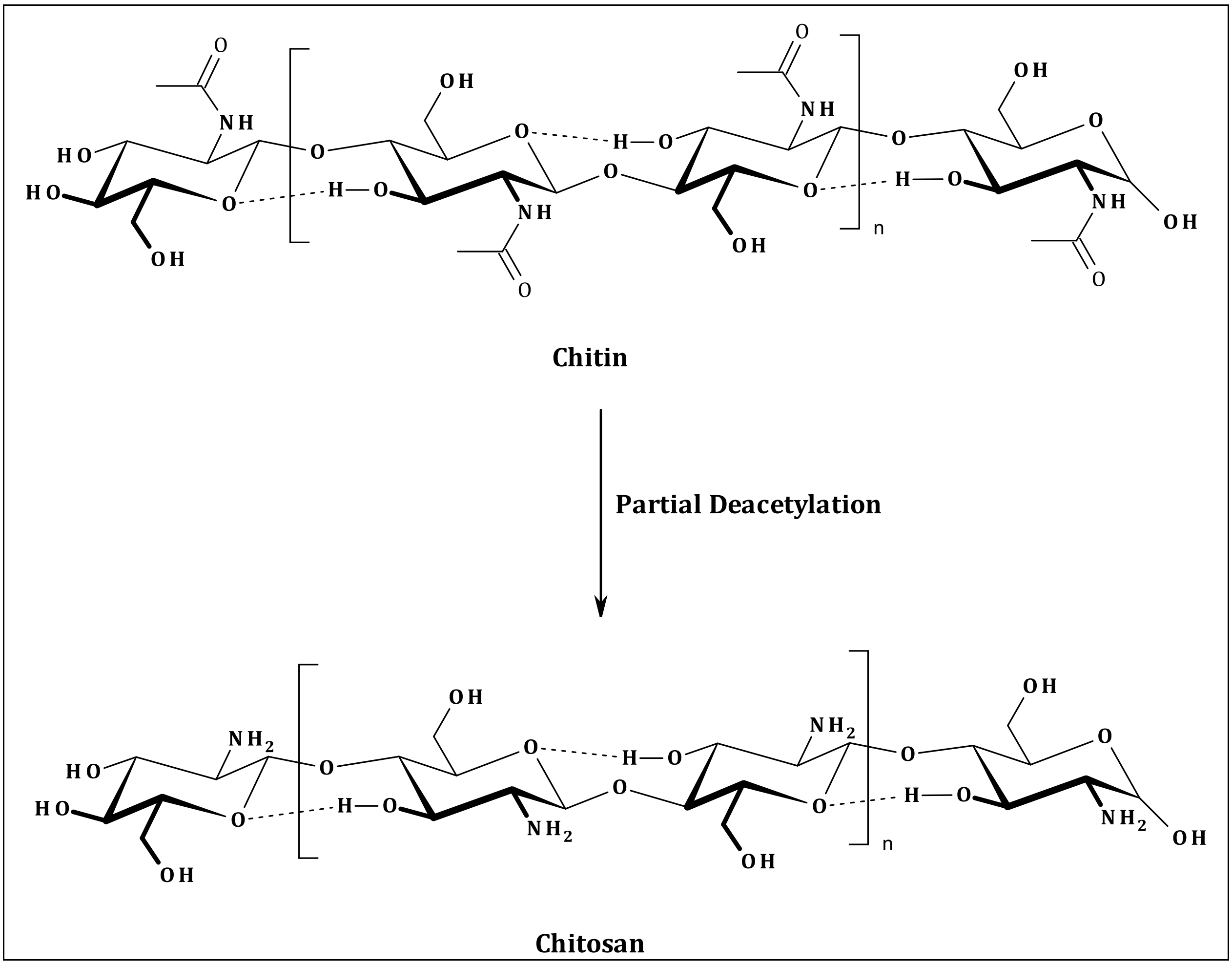
Moreover, alternative carbon sources for bacterial fermentations in order to synthesize PHAs are also under investigation. These include fatty acids[94,95] and glycerol.[96] With the aid of genetically-modified bacterial strains a direct utilization of plant oils, e.g. bacterias with lipase activity to utilize triacylglycerols, is also described.[97] Moreover, it was shown that by varying the fatty acid feed composition the properties of the plastic material can be tuned.[98] Additionally, low-rank coal liquefaction products could also be used as carbon source, since low-rank coal exists in high amount and is rather worthless for common industrial processes.[99]

2.1.5 Polymers from Chitin – Chitosan

Chitin is a polysaccharide found in the outer skeleton of crustaceans, insects, crabs, shrimp, lobsters, in the internal structures of other invertebrates, and in the cell walls of fungi. Chitin (poly-N-acetyl-d-glucosamine, 2-acetamido-2-deoxy-1,4-β-d-glucan) (Scheme 2.1.5.1) is one of the three most abundant polysaccharides in nature, is biodegradable, nontoxic, and readily biocompatible.

Chitosan is also a natural product and can be obtained *via* (partial) deacetylation of chitin, most commonly by aqueous alkali, although this N-deacetylation is almost never complete (Scheme 2.1.5.1). Chitin is insoluble in aqueous solutions at neutral pH, but *N*-deacetylation increases the aqueous solubility of the polymer while also providing reactive primary amines for chemical modification, whilst the molecular weight reduces from 1000–2500 kDa to 100–500 kDa during the deacetylation process.

The improved solubility of chitosan enables the synthesis of biomaterial conjugates by grafting of synthetic hydrophobic polymers, which induce amphiphilic pH-sensitive and thermally sensitive properties.[100]



Scheme 2.1.5.1: Chemical structure of chitin and chitosan.

Preparation methods, physicochemical properties, and applications of chitosan are reviewed by Wani *et al.*[101] Moreover, chitooligosaccharides, which are chemically or enzymatically derived chitosan oligomers, have been found to exhibit various bioactivities, although the mechanisms remain poorly understood.[102] Chitin is degraded into its monomer, *N*-acetyl glucosamine, by chitinase enzymes, which are derived from plants, fungi, bacteria, insects, and fish.[36] The production of microbial chitinases, e.g. the production of chitinases by genetically engineered organisms and by incorporating modern fermentation techniques, were summarized by Felse and Panda.[103] Very recently, Sahoo *et al.* reviewed the chemical modification, depolymerization processes, and the use of chitin and chitosan in biomedical, food/nutritional, material, microbiological, immunological, and other miscellaneous applications.[104] In addition, just like the aforementioned carbohydrates, chitosan films also show electro-activity when doped with $NaClO_4$, NaI, $LiCF_3SO_3$, and $LiCH_3CO_2$ between 10^{-5} – 10^{-6}, depending on salt type and amount, and hydrated films achieve 10^{-4} S/cm conductance.[50] On the other hand, the potential of chitin and chitosan for arsenic (As) removal from groundwater and the use of these natural polymers for arsenic trioxide delivery in tumor therapy were described and attributed to the hydoroxyl- and amine-functional groups, which are acting as metal scavengers.[105]

2.2 Fat- and Oil-based Polymers

The relatively low cost, ready availability, renewability, and the potential biodegradability of materials derived from plant oils make vegetable oils advantageous starting materials for many applications. This class of renewable raw materials possess great potential as sustainable resources for the polymer industry, since the synthetic potential of naturally occurring fatty acids can be exploited for monomer and polymer synthesis without many reaction steps. The possibility to use the plant oil directly, without chemical modification or further functionalization, most often leads to cross-linked structures (thermosets, coatings, resins, …). Moreover, thermoplastic materials can be prepared from fatty acids and their derivatives (obtained by transesterification of the triglycerides) having linear and hyperbranched architectures and resulting in polymers with tunable properties.

2.2.1 Polymers from Triglycerides

Plant oils are mainly constituted by triglycerides that can be used directly for the synthesis of a variety of polymers. For instance, they have been used in the synthesis of coatings,[106] often avoiding additional costs and time associated with the modification of the starting materials. A wide range of polymerization methods, including condensation, radical, cationic, and metathesis procedures have been applied. The scope, limitations, and possibility of utilizing such methods on triglycerides for various applications have recently been highlighted by Güner *et al*.[107]

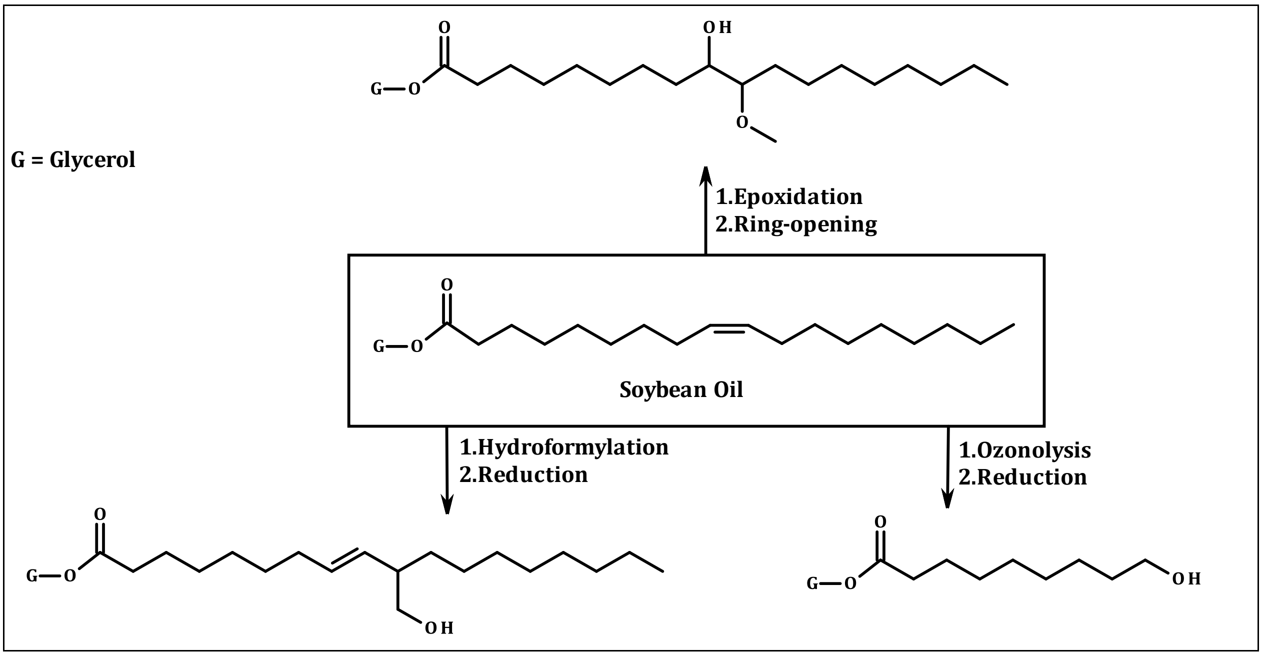
i. Polymers from Soybean Oil

Soybean oil is a vegetable oil dominating today's food oil market. About 80% of the soybean oil produced each year is used for human food; another 6% is used for animal feed, while the remainder (14%) serves nonfood uses (soaps, fatty acids, lubricants, coatings, etc.).[108] Another increasingly important nonfood use of soybean oil is biodiesel production (~80% of the vegetable oil used to produce biodiesel in the USA in 2007 was soybean oil).

Soybean oil is less expensive than corn, safflower, and sunflower oils. It also has a higher level of unsaturation (typical composition: 53% linoleic, 21% oleic, 8% linolenic, 10% palmitic, and 5% stearic) compared to some other vegetable oils.[109] Crude soybean oil contains approximately 95–97% triglycerides making soybean oil a potential candidate to be used as a renewable macromonomer for the polymer industry.

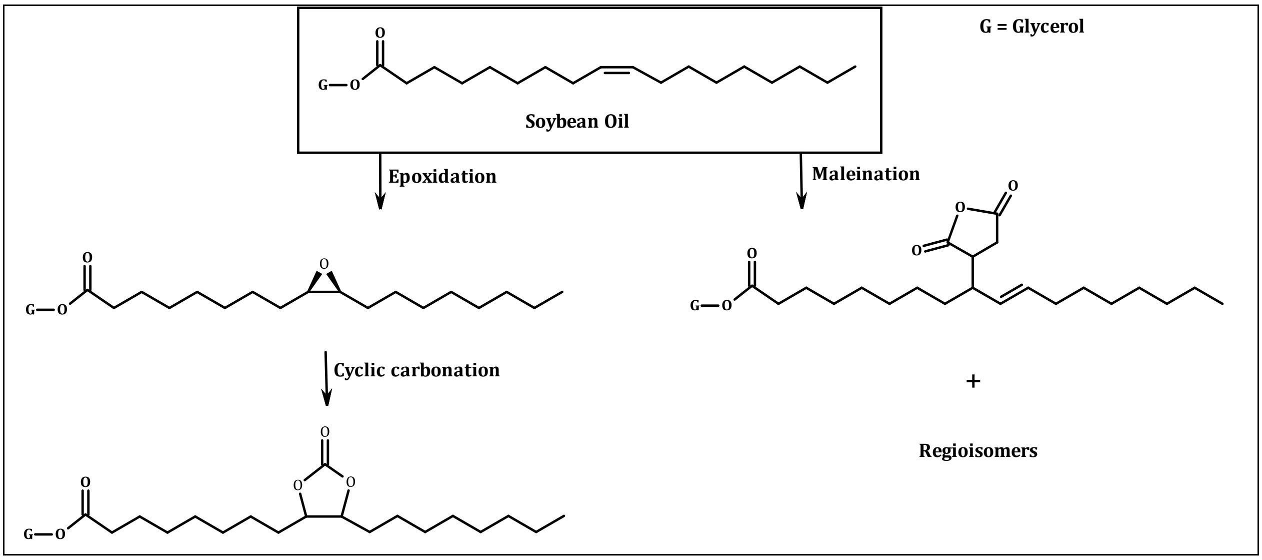
The double bonds present on the fatty acid chains can undergo cationic or radical polymerization processes. The reactivity towards different polymerization techniques depends on the number and position of the double bonds; hence conjugated double bonds are more reactive. Henna *et al*. prepared a copolymer of conjugated low-saturation soybean oil, acrylonitrile, and either divinylbenzene or dicyclopentadiene *via* free-radical polymerization.[110] The resulting transparent yellow polymers exhibited 10% weight loss for the dicyclopentadiene and divinylbenzene between 402 – 428 and 370 – 391 °C, respectively. Complete conversion of conjugated low-saturation soybean oil was achieved when the content was kept between 40 – 65 %.

An important application of soybean oil is its conversion to polyols and use for PU foam synthesis (Scheme 2.2.1.1).



Scheme 2.2.1.1: Different ways to prepare polyols for PU synthesis from soybean oil; G: Glycerol moiety with two more fatty acid derivatives attached.

John *et al*. used three different polyols made from soybean oil triglycerides for PU synthesis with TDI and MDI and studied the reactivities upon PU foam formation and material properties.[111] The results revealed that soy polyols react similarly to synthetic polyols, and the foams prepared with MDI were more rigid than those synthesized with TDI. Modification of soybean oil into polyols in order to react with an isocyanate and finally synthesize PUs was also achieved via hydroformylation and subsequent hydrogenation reactions. Guo *et al.* reported that the rhodium-catalyzed hydroformylation afforded a polyol with 95% conversion, giving rise to a rigid polyurethane, while the cobalt-catalyzed reaction gave a polyol with 67% conversion, leading to a material with lower mechanical strengths.[112] Recently, a similar route, but with partial esterification of the hydroxyl groups with formic acid, was also applied.[113] In addition to hydroformylation, epoxidation followed by ring opening with methanol[114,115] or phosphoric acid[116] and ozonolysis[117] are other tools for synthesizing polyols. The soybean oil-based polyols were studied in detail in order to establish structure-property relationships of the polyurethanes produced thereof. The polyols synthesized through hydroformylation, bearing primary alcohols, showed higher reactivity towards PU formation and resulted in less rigid PU materials than those obtained through epoxidation. On the other hand, the polyols synthesized from soybean oil *via* ozonolysis, free from long pendant alkyl chains, resulted in PUs which displayed the best mechanical properties and highest T_g. A different approach to synthesize PUs from soybean oil excluding isocyanates is the cyclic carbonation of epoxidized soybean oil (ESBO)(Scheme 1.2.1.2),[118] a very successfully commercialized soybean oil product, and curing with primary amines to yield β-hydroxy urethanes.[119,120] Additionally, thermal and mechanical properties of these polyurethanes were enhanced by incorporation of silica nano-particles *via* nano-composite formation.[118]



Scheme 2.2.1.2: Modification possibilities of soybean oil; G: Glycerol moiety with two more fatty acid derivatives attached.

Eren *et al.* modified soybean oil via anhydride functionalization of the double bonds and polymerized the resulting monomers by polycondensation with low molecular weight polyols and long diols (Scheme 2.2.1.2).[121] The polyesters were resilient and soft rubbers at room temperature that could find application as adhesives, film formers, textile and paper sizes, and tackifiers.

In 2008 Biswas *et al.* reviewed nitrogen containing monomers, e.g. fatty amines, fatty amides, fatty imidazolines, and polymers (PUs) made from soybean oil-based triglyceride oils, fatty acid esters, and methyl esters of triglyceride oils in all aspects.[122] Among them, fatty amines and amides are industrially significant and widely used.

ii. Polymers from Castor Oil

The castor oil plant (*Ricinus communis)* is a native of tropical Asia and Africa. The gathering and refining processes of castor oil from the plant is reviewed by Ogunniyi[123] and more recently by Mutlu and Meier.[124] The fatty acids generally consist of up to 90%

ricinoleic, 4% linoleic, 3% oleic, 1% stearic, and less than 1% linolenic acids. The high content of ricinoleic acid is the reason for the high value of castor oil and its versatile application possibilities in the chemical industry. Moreover, the hydroxyl functionality of ricinoleic acid, which makes castor oil a natural polyol, provides oxidative stability to the oil, and a relatively high shelf life compared to other oils, by preventing the formation of peroxides. Furthermore, the hydroxyl group allows a variety of chemical reactions to be performed on ricinoleic acid and its derivatives including, dehydration, halogenation, alkoxylation, esterification, and sulfation. Castor oil is already widely used for industrial chemical products, like paints, coatings, inks, lubricants, etc.

Castor oil is often used as a polyol and reacted with various diisocyanates in order to produce PU products, ranging from coatings, cast elastomers, thermoplastic elastomers, rigid foams, semi-rigid foams, sealants, and adhesives to flexible foams. Moreover, Moeini reported novel green poly(ether-ester urethane) insulating coatings based on polyols derived from glycolyzed poly(ethylene terephtalate) (PET), castor oil, and adipic acid, which exhibited the combination of excellent mechanical properties and electrical insulation characteristics.[125] Since castor oil has a low hydroxy functionality, transesterification with glycerol can improve the properties and yield rigid PU foams with good physico-mechanical properties.[126] Moreover, with trimethylol propane and pentaerythritol[127] an even higher thermal stability was achieved. Karak *et al*. reported on the synthesis of castor oil-modified hyperbranched thermoplastic PU.[128] These materials were derived from castor oil, a macroglycol [*e.g.* poly(ε-caprolactone) (PCL)-diol or PEG], and MDI, with or without chain extender. Castor oil-derived PUs are also of interest for composite materials. For instance, castor oil / graphite composites were studied as electrode materials.[129] Moreover, when doped with sulfonated polyaniline, electrically conductive PUs were synthesized from castor oil.[130]

Castor oil has found application in the synthesis of interpenetrating polymer networks (IPNs). These materials can be defined as a combination of two polymer networks, at least one of which is synthesized and/or cross-linked in the immediate presence of the other. They are called semi-IPN if just one of the polymers is a network.[131] Early reports on castor oil IPNs appeared in 1977 by Yenwo *et al*.[132] The report discussed the synthesis possibilities via cross-linking of double bonds with sulfur, reaction of hydroxyl groups with diisocyanates, and emulsion polymerizations with saponified ricinoleic acids as emulsifier. Moreover, the IPNs from acrylic polymers, such as poly(methyl methacrylate) and poly(2-ethoxyethyl methacrylate), and castor oil-based polyurethanes were reported to contribute to the final properties of the material.[133,134] Incorporation of acrylic moieties into the PU networks increased toughness and thermal properties. In contrast, IPN polyesters derived from castor oil and dibasic acids (e.g. malonic, succinic, glutaric, adipic, suberic, and sebacic acid) were obtained as soft and opaque elastomers.[135] Mohapatra *et al*. synthesized a castor-oil based PU via isocyanates and a novolac resin to produce semi-IPNs.[136] Various PUs from diphenylmethane diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate, and novolac resins from cardanol, furfural, and *p*-aminobenzoic acid were copolymerized to yield thermally stable semi-IPNs. It was shown that the stability of the networks increased with the increase of the novolac resin content. The semi-IPNs prepared from castor oil-based PUs from iso-phorone as well as diphenylmethane diisocyanates and the cardanol based resins were reported to withstand very high temperatures before decomposition.

The double bonds present on ricinoleic acid triglycerides are inactive to free-radical polymerization. To overcome this, Wang *et al*. prepared a half-ester of castor oil *via* maleation and copolymerized this monomer with styrene as reactive diluent and a free-radical initiator. [137] Polymers with different castor oil / styrene ratio and curing methods were prepared and optimized in order to yield biodegradable plastic foams with tuned rigidity. In addition to being more cost-effective and bio-friendly, the foam plastics synthesized were softer and tougher with comparable compressive stress at 25% strain as commercial semi-rigid PU foams based on fossil oil. The results revealed that higher styrene content resulted in higher compressive stress but decreased biodegradation rate.

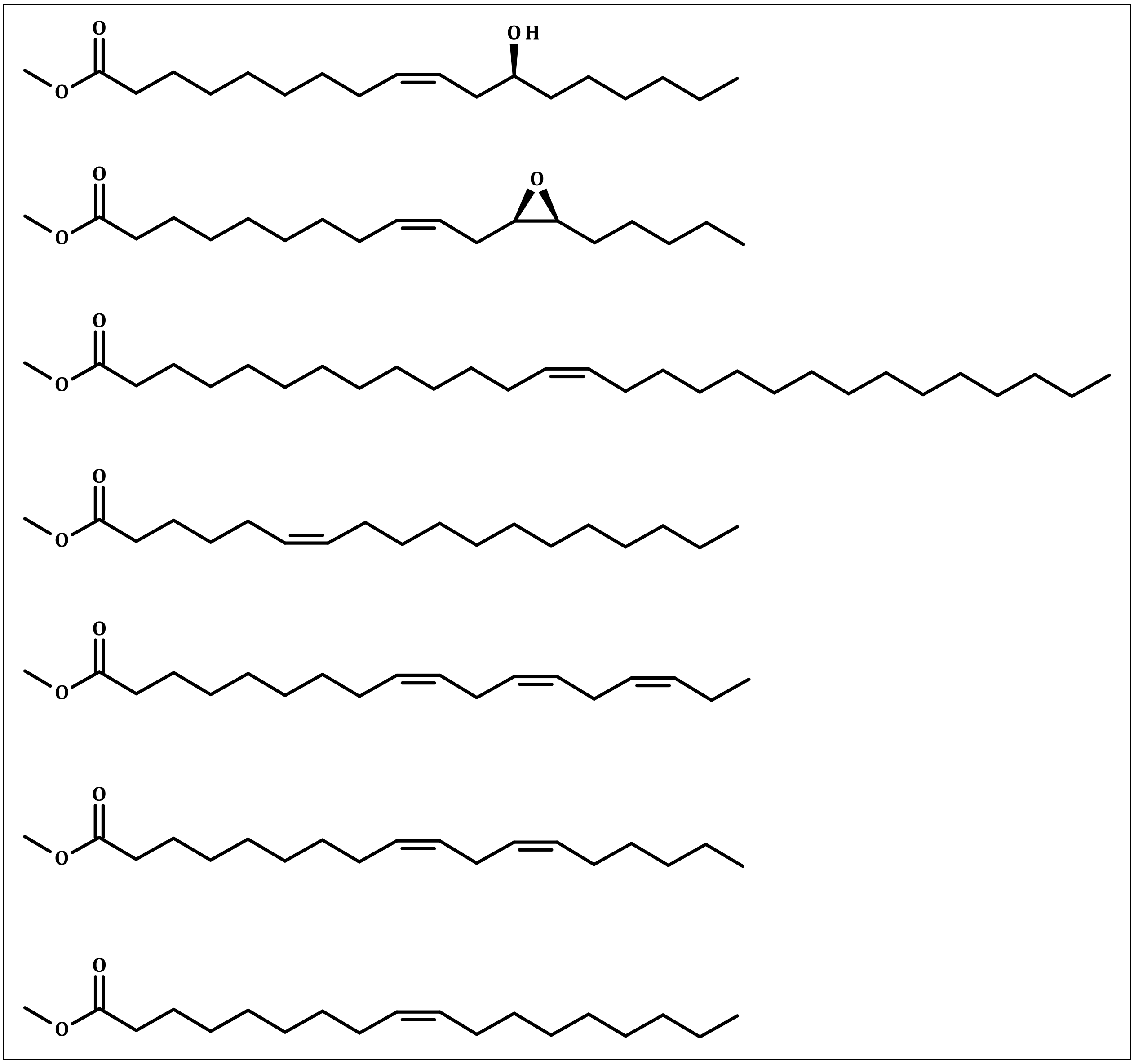
iii. Polymers from other oils

Although plant oil-based polymers are mainly derived from soybean and castor oil, an ever increasing number of publications are devoted to the use of other plant oils, such as linseed oil, tung oil, canola oil, high oleic sunflower oil, and many others.

Kundu and Larock used conjugated (87%) linseed oil, since it is more reactive towards free-radical reactions and copolymerized it with styrene and divinyl benzene (3 to 5%) by gradually heating for some time.[138] Soxhlet extractions showed that only 35 – 85% of the oil could be incorporated into the cross-linked thermosets. The dynamic mechanical analysis of these polymers indicated that they were phase separated as two separate T_gs appeared; these materials presented a soft rubbery phase with a sharp T_g at -50 °C and a hard brittle plastic phase with a broadened T_g at 70-120 °C. Thus, different types of polymers ranging from soft rubbers to hard plastics were prepared, which were shown to be stable below 350 °C. Moreover, the same group used 100% conjugated linseed oil and copolymerized it with acrylonitrile and DVB using the thermal initiator, 2,2'-azobis isobutyronitrile (AIBN).[139] Much better oil incorporation, e.g. 61 – 96%, was revealed by the soxhlet extractions. Carter *et al.* investigated commercially available epoxidized linseed oil (ELO) as an attractive alternative to polyvinyl-chloride (PVC) flooring products in some applications.[140] Upon screening of the process parameters and extensive flooring investigations, it was shown that the ELO system fits for the purpose of providing a flooring surface and thus, altering processing parameters of this system can be effective in changing material properties. The system was shown to be competitive with regards to performance against PVC when used as a flooring material. On the other hand, ring opening metathesis was also applied to vegetable oil derivatives. When linseed oil is subjected to high temperature and pressure, Diels-Alder reactions with cyclopentadiene can take place resulting in the commercially available monomer Dilulin from Cargill bearing a 5-membered cyclic mono-ene structure. Recently, Henna *et al*. performed the ring opening metathesis-copolymerization of Dilulin with dicyclopentadiene with the aid of Grubbs 2nd generation catalyst.[141] The resulting bio-based polymers offer unique and promising properties encouraging the replacement of petrochemical-based materials in some applications, although sometimes fiber reinforcement or other fillers are needed to further enhance the mechanical properties. Casado *et al.* utilized tung oil via epoxidation-ring opening and increased hydroxyl functionality with triethanol amine insertion, yielding a highly reactive tung oil-based polyol for PU synthesis.[142] Incorporation of 10 - 15% pine wood flour to prepare PU composites led to a stronger material that not only showed improved tensile strength, but also improved impact behavior, attributed to very good interfacial adhesion. A different approach to synthesize polyols for PU synthesis from canola oil was utilized by Petrović *et al.*[143] Ozonolysis of canola oil yielded polyols with terminal primary hydroxyl functionalities in a similar fashion as already discussed for soybean oil (see above).

2.2.2 Polymers from fatty acids

Today, plant oils represent the major renewable resource of the chemical industry, offering widespread possibilities for material uses of this sustainable feedstock.[144] Plant oils offer a number of fatty acids with different chain lengths and functional groups as well as different numbers and positions of C=C double bonds when transesterified with an alcohol, mainly methanol (Scheme 2.2.2.1).

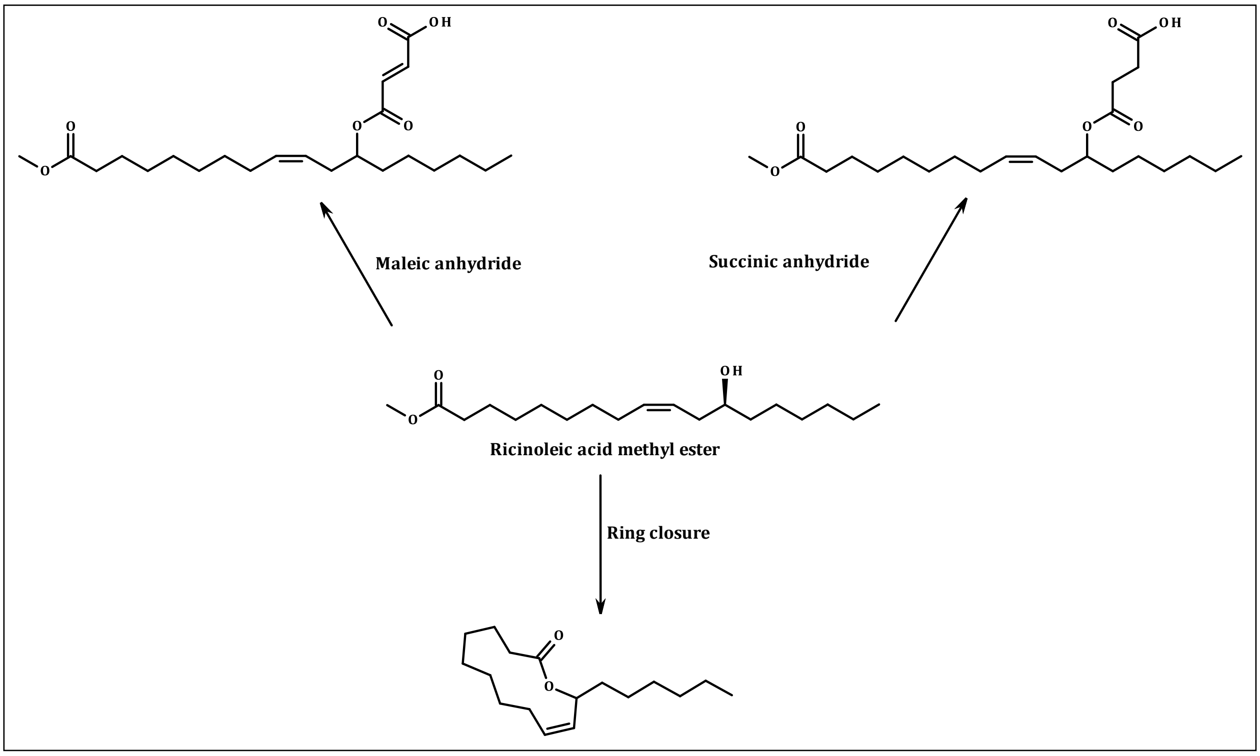


Scheme 2.2.2.1: Chemical structure of the most widely applied fatty acid methyl esters.

Since plant oils consist mainly of triglycerides of various saturated and unsaturated fatty acids, it is difficult to synthesize structurally well-defined and property-tailored polymers. As a result fatty acids serve as valuable monomers in the formation of linear monomers and (co)polymers, and cross-linked and interpenetrating polymer and composite materials for the chemical industry.

Fatty acids and fatty acid methyl esters (FAME) can be used directly or after functionalization as monomers for the synthesis of a variety of polymeric materials. The most important functionalization possibilities of the double bonds and the ester groups are extensively reviewed in the literature.[145,146,147]

In the case of ricinoleic acid, which has a hydroxyl functionality on the aliphatic chain, it is easily possible to introduce functional groups suitable for polymerization leading to fatty acid-based biodegradable polymers. Domb and Nudelman utilized succinic and maleic anhydride (Scheme 2.2.2.2) to modify ricinoleic acid and subsequently copolymerized the obtained monomers with sebacic acid to yield a polyanhydride via condensation with acetic anhydride.[148] These polymers were shown to be useful as drug carriers, are biocompatible and degrade within 4-6 weeks both *in vivo* and *in vitro*. On the other hand, ricinoleic acid was also used for macrolactone formation, but subsequent ring-opening co-polymerization with lactide to produce 100% renewable polyesters was found to be difficult, yielding low molecular weight polymers and oligomers (Scheme 2.2.2.2). This behavior was attributed to the low reactivity of ricinoleic acid macrolactones.[149]



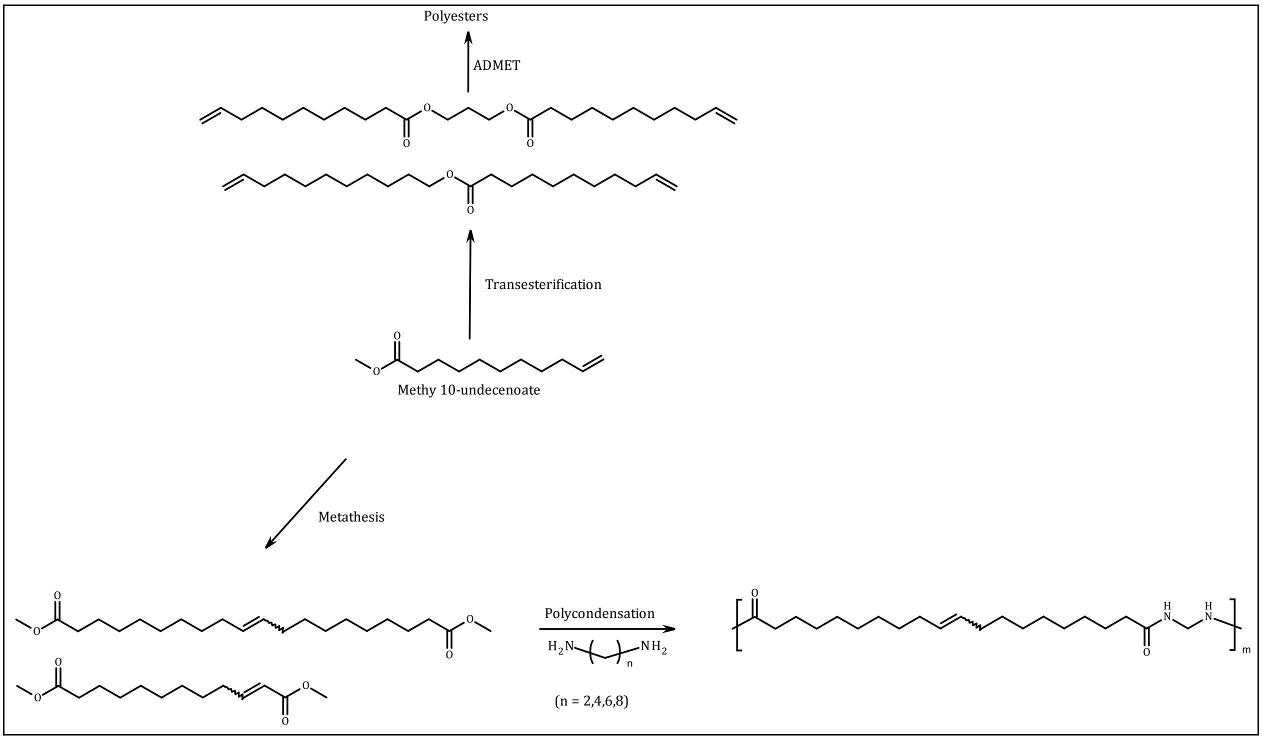
Scheme 2.2.2.2: Modification possibilities of ricinoleic acid.

In 2008 Sokolsky-Papkov *et al.* prepared copolymers of ricinoleic acid lactones and lactide, which were then evaluated as biomaterials for the *in situ* formation of injectable gels.[150] However, copolymerization with lactide resulted in molecular weights in the range of 5-16 kDa with melting temperatures between 100-130 °C for copolymers containing 10-50% ricinoleic acid.

Since fatty acids have only one carboxylic acid functionality, different functionalization or polymerization routes were studied. Warwel *et al.* synthesized ω-olefinic fatty acids *via* cross-metathesis of ethylene and FAME catalyzed by heterogeneous rhenium or homogeneous ruthenium catalysts.[151] These ω-olefinic fatty acids were then converted to various polymers including polyolefins, polyesters, polyethers, and polyamides. Moreover, a number of metathesis catalysts and reaction conditions were investigated in order to optimize the cross-metathesis of FAMEs for high-conversion and selectivity with the goal to synthesize new polycondesation monomers from FAMEs.[152,153,154] Furthermore, dimers of fatty acids have been exploited as renewable di-functional monomers for linear polymer synthesis and have become commercially available products, although they are ill-defined and also contain monomers and trimers to some extent. A class of those polymers is dimer-acid derived polyamides. Wang *et al*. polymerized a commercial dimer acid synthesized from C-18 fatty acids and different aromatic diamines *via* melt polycondensation.[155] The physical and mechanical properties of the resulting polyamides were found to be similar. The heat resistance and mechanical properties of poly (4,4'-diphenylsulfone dimeramide) and poly(4,4'-diphenyl dimeramide) were found to be comparable to those of PA 12,12. Moreover, modified FAMEs were also used as reactive diluents for the replacement of fossil-originated compounds. Campanella *et al.* acrylated an epoxidized FAME (AFAME) and utilized this compound as a replacement of styrene and studied the thermo-mechanical properties of the resulting materials.[156] The study revealed that the use of AFAME introduced the advantage of reducing hazardous air pollutants (HAPs) and volatile organic compounds (VOCs), but is not industrially applicable due to cost issues, viscosity, and thermo-mechanical properties. Instead, blends of styrene and AFAME (17.5% of each) resulted in viscosities that meet the industry requirements for composites, T_g (~100 °C), and storage modulus (at 30 °C ~1200 MPa), comparable with petroleum-based commercial resins.

Furthermore, 10-undecenoic acid (10-UA), a platform chemical obtained *via* pyrolysis of ricinoleic acid,[124] offers various ways to utilize fatty acids as polymer building blocks. The terminal double bond is successfully used for thiol-ene addition reactions[20] as well as acyclic diene metathesis (ADMET) reactions.[157] Recently, Lluch *et al*. synthesized the allyl ester of undecenoic acid and polymerized it via UV-initiated thiol-ene addition reactions.[158] The one-pot reaction yielded a series of well-defined telechelics with molecular weights in the range of 1000–3000 g/mol and hydroxyl, carboxyl, or trimethoxysilyl end-groups. The telechelics with hydroxy end-groups were then reacted with a diisocyanate compound, resulting in a bio-based multi-block poly(ester-urethane)s.

Moreover, the use of metathesis reactions as a versatile tool in fatty acid-based monomer synthesis was studied in detail by Meier's group (Scheme 2.2.2.3).[159,152] A comparative study of dimerization of methyl 10-undecenoate via self-metathesis[160] and subsequent polycondensation with different diamines was reported by Mutlu and Meier in 2009.[161]



Scheme 2.2.2.3: Use of methyl 10-undecenoate as a sustainable building block for the polymer industry.

The synthesis of α,ω-diene monomers is suitable for the synthesis of fatty acid-based biodegradable polyesters via ADMET polymerization.[162,163,164] These reports showed the possibility of producing a series of polymeric materials from fatty acids *via* different routes. Since the material properties of the polymers strongly depend on the polymer structure, it is important to establish and suppress the olefin isomerization trend observed during ADMET polymerizations. Recently, an α,ω-diene monomer from methyl 10-undecenoate and 1,3-propanediol was first ADMET polymerized and the trans-esterification (with MeOH) products of this polymer were analyzed by GC-MS to establish the degree of isomerisation. The report revealed that the use of benzoquinone can prevent olefin isomerization efficiently, leading to the preparation of polymers with well-defined repeating units *via* ADMET of functional group containing monomers. Moreover, ADMET polymerization of fatty acid-derived dienes is also applicable to phosphorous containing monomers leading to flame retardant renewable polymers.[165,166] Linear polymers with different phosphorous contents were prepared by copolymerization of a phosphorous and a non-phosphorous containing monomer revealing that approximately 3% phosphorous content resulted in a limiting oxygen index (LOI) of 23.5, whereas an LOI of 19.0 was obtained for the polymer without phosphorous. Thus the flame retardancy was significantly increased. In case of the cross-linked polymers, the LOI values increased from 18.4 to 25.7 with increasing phosphorous content from 0 to 3.8%.

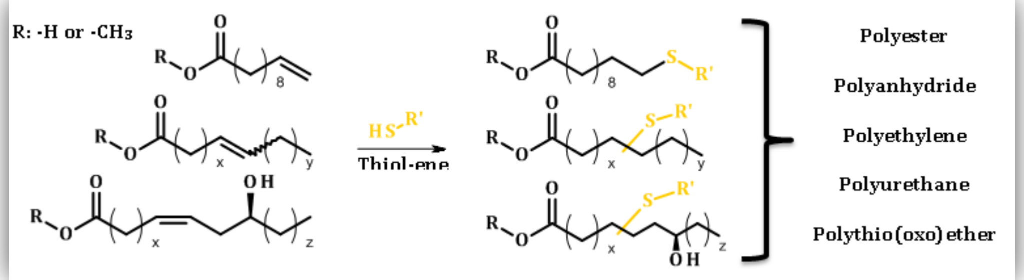
2.3 Conclusion

As can be seen from this literature review, there are encouraging carbohydrate- and plant oil-based polymers that could substitute, at least partially, for the mineral oil-based materials which are on the market today. Although some renewable polymeric materials are already commercialized, others are still too expensive. However, the declining fossil oil reserves might change this situation soon. Moreover, the improvement of pure scientific and engineering knowledge on generating platform chemicals, polymer building blocks, and plastic materials from renewable resources will certainly help in the future to switch to sustainable resources globally. This switch actually has to be considered as a must, which should force universities, industrial R&D departments, and politics, away from depleting fossil fuel reservoirs.

3

Efficient Reactions for Monomer Syntheses and Polymerization

3.1 The Thiol-Ene (Click) Reaction for the Synthesis of Plant Oil derived Polymers[167]



3.1.1 Discovery and Development

The earliest report on the addition of mercaptans to unsaturated compounds dates back to 1905.[168] In this report, Posner discussed that mercaptans add to double bonds in an anti-Markovnikov manner and that the structure of the unsaturated compounds strongly influences the outcome of the thioether products. Interestingly, two diunsaturated compounds, limonene and 1,4-cyclopentadiene were also utilized and only monoaddition products were observed. In the following decades, a number of papers reported non-distillable liquid residues upon allyl mercaptan synthesis and later on, the utilization of diolefins and dithiols to yield polymeric alkylene sulphides with molecular weights of up to about 1300 Da; subsequently, Marvel and Chambers extended the concept of this reaction in order to obtain higher molecular weight polymers in 1948.[169] After optimization, the UV-initiated polymerizations of hexamethylenedithiol and 1,5-hexadiene resulted in polymers with up to 12 – 14 kDa molecular weight and a melting range of 74 – 76 °C. X-ray analysis of some of the polymers was conducted to show the crystalline nature of the polymers, which agreed with the sharp melting peaks of the polymers and, therefore, with the anti-Markovnikov selectivity of this new addition polymerization.

It was already known in the 1950s that thiols add to a double bond in the form of thiyl radicals and that the reaction involves radical chain propagation steps, when Walling and Helmreich reported on the overall mechanism and the reversibility of some of the reactions involved in 1959.[170] The mechanism comprises the *in situ* formation of thiyl radicals, which add to the double bond and yield a carbon radical, which subsequently abstracts a hydrogen atom from another thiol compound resulting in the final addition product. A new thiyl radical is generated during this last step allowing the radical chain mechanism to propagate. (Eq. 1-4)

$$\text{R-SH} \quad (+\ \text{I}\bullet) \quad \rightarrow \quad \text{R-S}\bullet\ (+\ \text{IH}) \tag{1}$$

$$\text{R-S}\bullet + \text{H}_2\text{C=CHR} \quad \rightleftarrows \quad \text{R-S-CH}_2\text{-C}\bullet\text{HR} \tag{2}$$

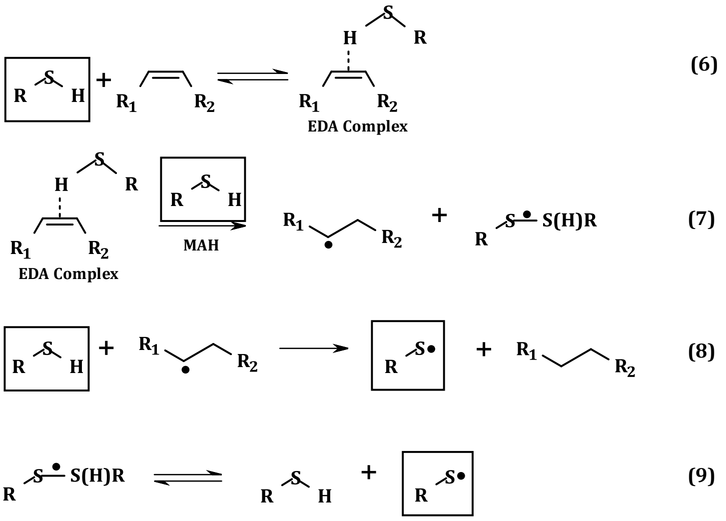
$$\text{R-S-CH}_2\text{-C}\bullet\text{HR} + \text{R-SH} \quad \rightarrow \quad \text{R-S-CH}_2\text{-CH}_2\text{R} + \text{R-S}\bullet \tag{3}$$

$$2\ \text{R-S-C H}_2\text{-C}\bullet\text{HR} \quad \rightarrow \quad \text{R-S-C H}_2\text{-C(HR)-C(RH)-CH}_2\text{-S-R} \tag{4}$$

$$2\ \text{R-S}\bullet \quad \rightarrow \quad \text{R-S-S-R} \tag{5}$$

Their earlier experiments, which demonstrated a rapid *cis* - *trans* isomerization of olefins during the addition of methanethiol to cis- and trans-2-butene at 60 °C, made them conclude that the addition reaction (2) is reversible. Additionally, the experiments confirmed that the addition to α-olefins is generally more rapid, more exothermic, and less reversible than the addition to 1,2-disubstituted olefins. Moreover, from their additional experiments about the relative reactivities of olefins towards dodecanethiol, the authors concluded from their data that: 1. the reactivity is increased if the radical is stabilized by resonance, 2. electron-dionating groups on the olefin increase the rate, 3. cyclopentene is more reactive than cyclohexene, and 4. terminal double bonds are more reactive than internal ones. In 1964, Testa transferred this last feature to oleochemistry and utilizied thiol-ene reaction as a cis-trans isomerization tool for unsaturated fatty acids, e.g. methyl oleate.[171] The experiments showed that methyl oleate isomerizes to methyl elaidate with the ratio of 1 to 3, respectively, when the reaction is initiated by benzophenone at 25 °C. Hoyle *et al.* compared the reactivities of the alkene compounds against thiol-ene literature and their laboratory results by means of structure and the reactivity order was given as follows: 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.[20] In addition, 1-hexene was found to be 8 times more reactive than trans-2-hexene and 18 times more reactive than trans-3-hexene against monofunctional thiol addition, revealing the strong effect of the position of the double bond in the alkene compound.

In the following decades, the addition of thiol compounds to unsaturations took its place among the most common organic reactions and a number of reviews were published; for example, in 1970 Griesbaum reviewed reversibility, reaction rate, and reactant structure-reactivity in detail.[172] Until the beginning of the 90s, the mechanism of the free radical addition of thiols to unsaturations was clear: formation of a thiyl radical with the help of a radical initiator, e.g. the addition of peroxides, azo compounds, etc. or exposure to UV irradiation; addition of the thiyl radical to the unsaturated substrate to form a carbon radical, which is reversible; abstraction of an hydrogen from another thiol compound by the carbon radical to form the final product (Eq. 1-4). Nevertheless, for the primary radical formation reactions, it was also reported that apart from an external radical initiator, this reaction can also precede UV-&thermal-initiator-free and under dark conditions, though the initiation mechanism for these reactions remained unclear. Two postulations were earlier discussed in the literature in order to give an explanation to this phenomenon, one of them being a "Molecule-Assisted Homolysis" (MAH), as first suggested by Pryor *et al.* in 1974.[173] Nuyken and Völkel, in 1990, reported the synthesis of telechelics from aromatic and/or aliphatic dithiols and diolefins *via* spontaneous addition under UV radiation, citing Pryor's work (MAH) as the mechanism.[174] In their following report, the high thermal stability of the telechelics synthesized in this way was measured and 5% weight loss-temperature ($T_{5\%}$) was detected from 190 up to 390 °C in the case of norbornadiene and 1,3-benzenedithiol, depending on the molecular weight.[175] In 1991, Klemm *et al.* designed some reactions in order to clarify the self-initiation mechanism of thiol-ene polymerization, shortly after their report on the linear photopolymerization of dithiols and diolefins, and to find a potential inhibitor against the high reactivity of the homogenous thiol-ene mixtures.[176,177] In their setup, Klemm and coworkers measured the UV-absorption spectra of a dithiol and diolefins, and compared them to the spectra taken after 1 minute and 2 hours after mixing these substances. A new batochromicly shifted absorption band, which was attributed to a complex, formed between the dithiols and diolefins. This complex was described as an “Electron-Donor-Acceptor Complex” (EDA), whose formation was not detected in the presence of DABCO as an inhibitor. Very recently, the mechanism of the self-initiated thiol-ene reaction was clarified by Metzger *et al.*[178] The kinetic study of the *cis-trans* isomerization of methyl oleate in the presence of dodecanethiol was conducted, focusing on the initiation of the radical chain mechanism. The initiation was found to be a complex reaction: the EDA complex of the thiol and ene forms in a pre-equilibrium (6) and then reacts with another thiol to give, in a MAH of the sulphur-hydrogen bond, an alkyl radical (7) and a sulfuranyl radical (8) that subsequently dissociates to the thiyl radical and thiol (9), catalyzing the *cis-trans* isomerization. The experimentally found activation energy of the isomerization, in good agreement with the computational calculations carried out, is 82 kJ×M^{-1}. The results thus clearly revealed the thermal generation of thiyl radicals. Therefore, many well-known thermally initiated thiol-ene addition reactions as well as the low shelf-life stability of alkene and thiol mixtures can now be explained.



Apart from the discussion of the self-initiation mechanism, the thiol-ene addition reaction was already exploited for diverse functionalization protocols. For example, in 1998, Boutevin and coworkers employed this chemistry in order to introduce thiol functionality to phosphorous compounds.[179] The terminal alkene of the phosphorous containing compounds was transformed into thiols *via* the addition of thioacetic acid and subsequent transesterification with methanol; the resulting compound was grafted onto polybutadiene telechelics in the presence of AIBN. Another interesting application of this reaction in organic chemistry came from de Meijere *et al.* in 1998: the thiophenol addition to the double bonds of bicyclopropylidene, methylenespiropentane, and some others in deuterobenzene occurred at room temperature in the dark and exothermally, and completed within 1 hour.[180] Bicyclopropylidene and methylenespiropentane reacted with complete retention of both three-membered rings; methylenespiropentane gave exclusively the anti-Markovnikov type adducts and methylenecyclopropane gave 91% of the anti-Markovnikov product. Aliphatic and functionally substituted thiols added also quantitatively onto bicyclopropylidene, but heating and longer reaction times (2 to 4 hours) were necessary. Last but not least, Johansson *et al.* studied the coupling of mercapto acetate and propionate esters to methyl oleate and linoleate; mercapto acetates showed higher reaction rates than mercapto propionates for both alkenes. In addition, compared with those of linoleate, the higher isomerisation rate of oleate was attributed to a somewhat more restricted rotation along the unreacted linoleate C=C bond, which would have an effect on the overall addition rate of thiols because of the fact that *trans*- is more reactive than a *cis*-alkene.[181]

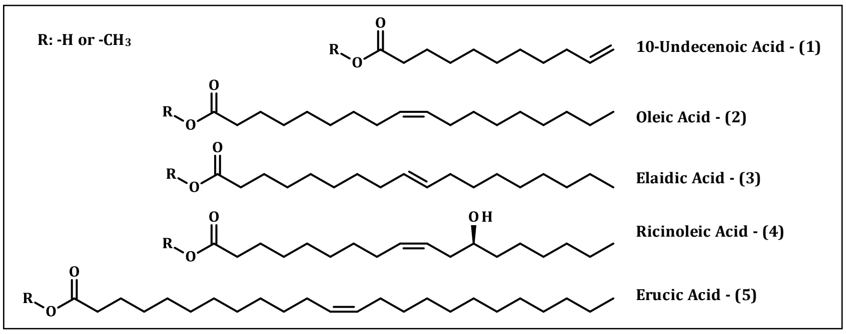
Not only the structure of the thiols and the unsaturated compounds, but also the reaction conditions play an important role in the overall success of this reaction. For instance, Lin *et al.* studied the addition of thiols to vinyl ethers and the reactions were optimized by means of temperature and solvent under initiator-free conditions.[182] Interestingly, the reaction was found to be very "sluggish" in common organic solvents and moderate in neutral ionic liquids, but good yields were obtained under the solvent-free conditions in 5 hours. In addition, a temperature value of 40 °C resulted in the best yields for both aromatic and aliphatic thiol compounds; lower and higher temperatures somewhat lowered the reaction yields. On the other hand, the first systematic study on the efficiency of the initiation reaction depending on the type of initiation was reported by Yagci's group in 2010.[183] The thiol-ene reactions between a library of several ene groups such as allyl bromide, methyl acrylate, and methyl methacrylate with thiol end-functional polystyrene using both cleavage (Type I) and H-abstraction (Type II) type initiators, and the classical thermal radical initiation was studied. From the results the authors concluded that the thiol-ene coupling reactions have the characteristics of a ''click'' reaction and when the reactions are initiated using the photochemical and thermal radical initiators, the use of Type I photoinitiators, such as (2,4,6-trimethylbenzoyl)diphenylphosphine oxide or 2,2-dimethoxy-2-phenyl acetophenone (DMPA), leads to highest efficiencies.

Easy post polymerization modification of polymer backbones is an important and challenging concept in polymer science. Thiol-ene addition reactions helped polymer chemists to perform such modifications in a highly efficient manner. A number of thiol compounds bearing diverse functional groups can be introduced onto a polymer chain that bears non-activated mono-substituted double bonds as functional groups. In 2008, Schlaad´s group applied this chemistry also for the modification of polybutadiene that bears vinyl side-groups with different monothiol compounds.[184] The ^{1}H-NMR analysis of the final polymers showed that up to about 80% functionalization with complete double bond conversion could be achieved when a 2-fold excess of corresponding thiol compound with respect to the double bonds was used under irradiation with UV (303 nm). They observed that the intermediate carbon radical may add, prior to proton transfer, to an adjacent double bond under the formation of a six- or five-membered cyclic unit. Interestingly, this side reaction was partially suppressed when solely UV light was used and similar results were obtained when sun light was used as UV source. In order to provide spacing between the vinyl groups and to avoid this side reaction, Schlaad's group also applied this chemistry to poly[2-(3-butenyl)-2-oxazoline]s, which was obtained *via* living/controlled cationic ring opening polymerization.[185] The reactions proceeded smoothly with 1.2-1.5 equivalents of mercaptan with respect to double bonds under UV light. In the following years, the same group reported on the side-chain modification of vinyl-functional peptide homo and copolymers[186] as well as on the surface-modifications of glass[187] and gold&silicone substrates[188] *via* thiol-ene chemistry.

Thiol-ene chemistry was not only exploited in the construction of linear polymers, but also for the synthesis of dendrimers, which generally requires highly efficient linking reactions. Rissing and Son, for instance, used tetravinyl silane and a number of thiol compounds in order to synthesize a series of multifunctional organosilicon thioethers under UV light.[189] High yields were obtained in 2-4 hours reaction time. Perhaps the most famous application of the thiol-ene chemistry is the synthesis of dendrimers by Hawker in 2008. In their report, Hawker and co-workers utilized this chemistry for the synthesis of up to 4th generation dendrimers with diverse peripheral functionalities.[190] This reaction was classified as one of the click reactions by the authors, the concept of which was introduced by Sharpless *et al.* in 2001 for highly efficient and orthogonal reactions. [191] Subsequently, a large number of articles were published utilizing thiol-ene reactions in the scope of click chemistry[192,193,194] although not all of the described procedures actually fulfilled the requirements. In 2010, Koo and co-workers briefly studied the efficiency of both thermal and UV initiated thiol-ene addition reactions as a polymer-polymer conjugation tool for star-shaped polymer synthesis.[195] The authors prepared macromonomers bearing single thiol or alkene end-groups, employing thermally decomposing initiators. The ESI-MS studies revealed that conjugation of a polymer with a small molecule proceeded quite well, whereas the polymer-polymer conjugations were mostly unsuccessful as the starting materials were taken close to equimolar. The reason for the failure was ascribed to head-to-head couplings that result from Eq. 4 and 5, which interrupt the propagation cycle of the thiol-ene process and lowers the overall coupling efficiency. Nevertheless, it was also found that the thermal and photochemical initiation showed similar results.

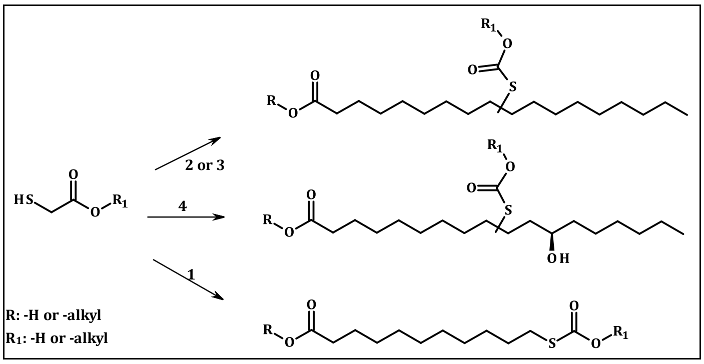
3.1.2 Applications of Thiol-ene Reactions to Plant Oils and Fatty Acid Derivatives

The relatively low cost, ready availability, renewability, and the potential biodegradability of materials derived from plant oils make vegetable oils advantageous starting materials for many applications (Scheme 3.1).[5,144] This class of renewable raw materials possesses great potential as sustainable resource for the polymer industry, since the synthetic potential of naturally occurring fatty acids can be exploited for monomer and polymer synthesis without many reaction steps.[21,109] The possibility to use the plant oil directly, without chemical modification or further functionalization, most often leads to cross-linked structures (thermosets, coatings, resins ...). Moreover, thermoplastic materials can be prepared from fatty acids and their derivatives, resulting in polymers with tuneable properties and linear or hyperbranched architectures.



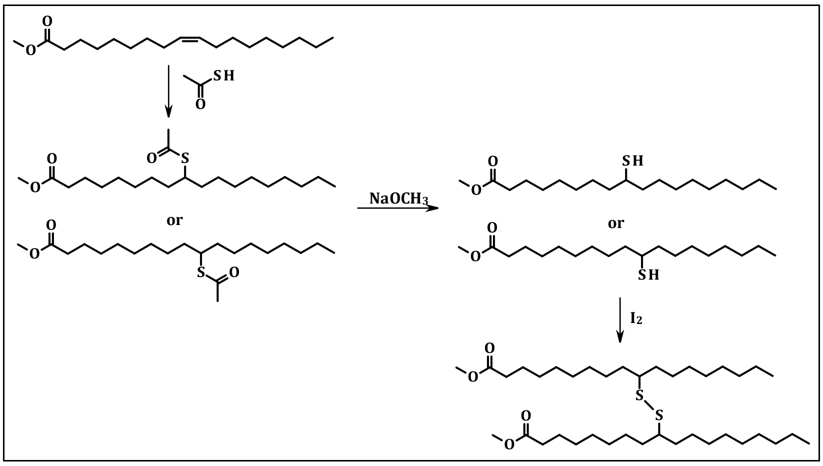
Scheme 3.1: The chemical structures of the common fatty acids utilized for polymer synthesis.[31-34]

The functionalization of fatty acids and their esters *via* the addition of sulphur, phosphor but also carbon radicals onto a C=C bonds has been known for long time.[6] This chapter intends to provide an overview on the radical addition of thiols to plant oil derivatives, since this reaction received increased interest in the recent years. Although the reactions of unsaturated fats and oils were known, the first systematic investigations were reported by Koenig and co-workers in the 50s.[196] In their first report, mercaptoacetate was added to undecenoate **1**, oleate **2**, elaidate **3**, and ricinoleate **4**, all both in the acid and ester form, yielding diverse diester and (or) diacid compounds (Scheme 3.2). It was also shown that Lauroyl peroxide enhanced the rate of the addition reaction.



Scheme 3.2: Modification of fatty acids with mercapto acetate.[32]

In addition, this reaction was extended to include both aliphatic and aromatic thiols: the resulting (alkylthio)- and (arylthio)-undecanoic acids were converted to, for example, sulfoxides, sulfones, and esters in the presence of peracetic acid.[197] Noteworthy, the authors were able to synthesize fatty thiol compounds with addition of thioacetic acid to **2**; the obtained thioacetate was later hydrolyzed to mercaptans and further functionalized to disulfide products by iodine oxidation (Scheme 3.3).[198] In contrast to Koenig´s method to couple **2**, which yields a diester, Schwab and co-workers used 1,6-hexanedithiol under UV irradiation, but the isolated diester yield was less than 20% (by weight).[199] In the same study, hydrogen sulphide (H_2S) was added to linseed oil, and the alkali-resistance and pencil hardness of the films prepared therefrom were found to increase with the sulphur content. Shortly after, the authors reported on the kinetics of the addition of H_2S to conjugated and nonconjugated fatty acid methyl esters and the reactivity order given was as: methyl oleate ≅ methyl linoleate **5** ≅ methyl linolenate **6** ≫ methyl 9,11-*trans,trans*-octadecanedienoate > methyl β-eleosteorate.[200]



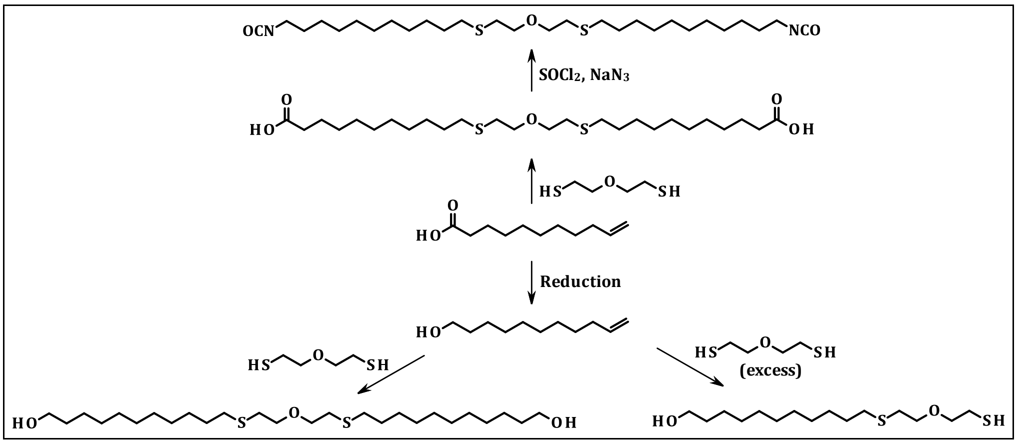
Scheme 3.3: Modification of oleic acid with thioacetate.[34]

The use of fatty acids or plant oils is not only interesting for the synthesis of polymeric materials, but also some other application possibilities of thiol-ene modified plant oil derivatives were reported. For instance, the pre-treatment of Aluminium metal sheets with a special linseed oil (high in **5**-content; 70.6 %) was applied as an environmentally friendly alternative to the toxic and carcinogenic chromium-based surface pre-treatments.[201] For this purpose, Aluminium substrates were treated with γ-mercaptopropyltrimethoxysilane in buffer solution prior to the plant oil solution with 4 wt% benzophenone, as photoinitiator, under UV light. The Tof-MS[202] and XPS[203] spectra of the substrates as well as the wash solutions, respectively, revealed that the unsaturated fatty acids reacted and were bound onto the metal surface. The same group reported on the kinetics of thiol-ene addition reactions of mono- and poly-unsaturated fatty acids, e.g. **2** and **5**, and two different tri-functional thiol compounds, trimethylolpropane trimercaptoacetate and trimethylolpropane trimercaptopropionate, under UV conditions. The important result of this study for the application of thiol-ene reactions on plat oils is that *trans* isomers result in higher reaction rates, which is not the case for the natural plant oils. Thus, some additional driving force should be applied for these applications. For instance, Bantchev *et al.* modified corn and canola oils with butanethiol. In order to better understand how the reaction parameters influence this reaction, the temperature, oil/butanethiol ratio, presence of photoinitiator, and type of oil were varied.[204] The conversion of double bonds and the yields were quantified by NMR and GC. The results revealed that the double bond conversion was higher at lower temperatures. This phenomenon was attributed to the entropically favoured dissociation of the carbon radical (back reaction of (2)). The presence of DMPA as photoinitiator did not have an extraordinary effect on the double bond conversion, but an increase of the initial thiol to double bond ratio from 1:1 to 6:1 ratio resulted in threefold increase in the formation of sulfide modified vegetable oil.

UV-curable coatings, which are typically aimed to be volatile organic compound (VOC)-free systems, offer rapid ambient crosslinking as well as reduced energy consumption. However, and even though superior properties are often obtained for thiol-ene resins (i.e. a lack of oxygen inhibition, uniform networks, delayed gel points, reduced polymerization shrinkage and stress, lack of toxicity concerns that are typically associated with low molecular weight acrylates) the unpleasant smell of low molecular weight thiols limits the commercial utilization. Nonetheless, Black and Rawlings utilized castor oil in a thiol-ene UV curable coating formulation for the benefits of renewable resource utilization, fatty acid plasticization, for VOC-free coalescence, and the opportunity of dried films *via* auto-oxidation.[205] To achieve this, the authors prepared allyl, acrylate, and vinyl ether derivatives of castor oil and blended them with multifunctional thiols to yield films with about 40% vegetable oil content without VOCs. The prepared films were evaluated for their gel content and by dynamic mechanical thermal analyses (DMTA). The results showed that each bio-based monomer exhibited excellent thin film performance, high solvent, resistance and hardness with adhesion and flexibility regardless of functionality. In addition, FT-IR spectroscopy was used to delineate between homopolymerization and thiol-ene reactions, and it was found that acrylates gave significant homopolymerization together with thiol-ene, whereas vinyl and allyl ethers copolymerized with *cis*-unsatuations and thiols.

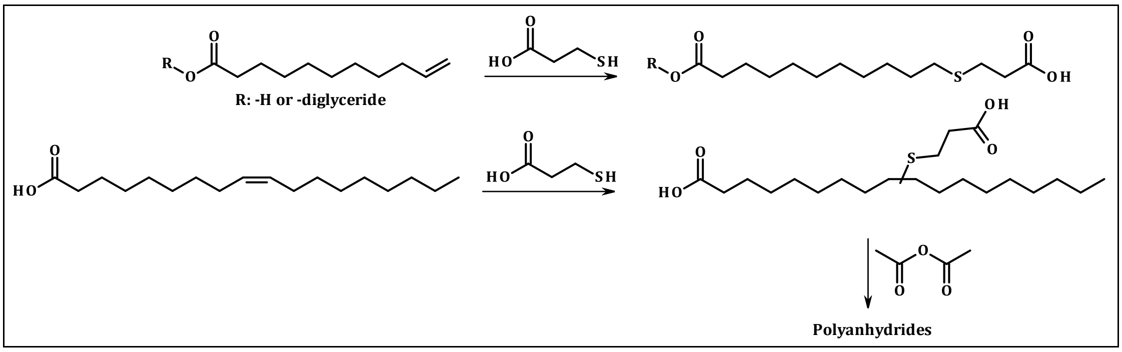
In contrast to Black and Rawlings' work, for which commercial thiol compounds were used in order to cure functionalized triglycerides, Webster and co-workers synthesized their own multifunctional thiol as well as mono-substituted ene compounds *via* BF_3-catalyzed ring opening reaction of epoxidized soy bean oil by appropriate thiols and alcohols, respectively.[206] Due to the very low T_gs, the UV polymerization of the thiol- and ene-components could exhibit tack-free and good film properties only if allyl triazine was incorporated into the coating formulation. Hence, it was also shown that better coating material properties could be obtained by the addition of multifunctional, hyperbranched acrylates. Instead of thiol- or ene-functionalization of epoxidized plant oils, a direct exploitation can be achieved by a polyamine cross-linker. In order to get both components renewable, a polyamine was prepared from grapeseed oil *via* thiol-ene addition of cysteamine chloride and cross-linked with epoxidized linseed oil.[207] Upon the polyamine synthesis, 3 equivalents of cysteamine chloride per double bonds present on triglyceride in the presence of 0.1 equivalents of DMPA were necessary in order to achieve 87% conversion of the internal double bonds. The DSC analysis of this fully plant oil-based material showed the polymer to have a T_g value of -38 °C and thermomechanical analysis showed classical thermoset amorphous polymer that has a storage modulus of about 10^9 Pa below -45 °C in the glassy state. Another important area of plant oil utilization is the synthesis of polyurethanes. Boutevin and co-workers synthesized a polyol *via* thiol-ene coupling of rapeseed oil with mercaptoethanol and polymerized it with different diisocyanates to yield polyurethane elastomers.[208] Before the polymerization, the authors optimized their reaction conditions with **2** and the reactions were studied by means of NMR, FT-IR, and LC-MS as well as iodine titration. Best yields were obtained after 1 hour reaction time for a thiol/ene ratio of 3, without solvent by using maximum UV irradiation intensity. The side reactions (esterification between alcohol group of mercaptoethanol and **2**; disulfide formation; inter-&intra-molecular couplings) were observed. Since all side products formed during the thiol-ene grafting anyhow bear alcohol groups, they could still incorporate into polyurethane formation. It was also shown that the higher the polyunsaturation, the lower the rate of thiol-ene reaction.

When thiol-ene addition reactions were used for the synthesis of linear polymers, two distinct approaches are realized, as already mentioned above. The first is the modification of an unsaturated monomer by a monofunctional thiol compound into a polycondensable monomer, which has been applied for more than 50 years on fatty acids, albeit the importance and exploitation of this method for renewable, tailor-made plastics were only realized in the last few years. For instance, thiol-ene reactions have often been applied for the syntheses of telechelics, prepolymers, and macromonomers from **1** and its derivative, 10-undecenol **7**, by Boutevin and coworkers (Scheme 3.4). The authors prepared an isocyanate terminated compound *via* the coupling of **1** with 2-mercaptoethanol and subsequent treatment with thionyl chloride and sodium azide to obtain the final product.[209] On the other hand, the authors were also able to synthesize a diol[210] and mercapto-alcohol[211] from **7** when a dithiol compound was used in stochiometric or excess amounts, respectively.



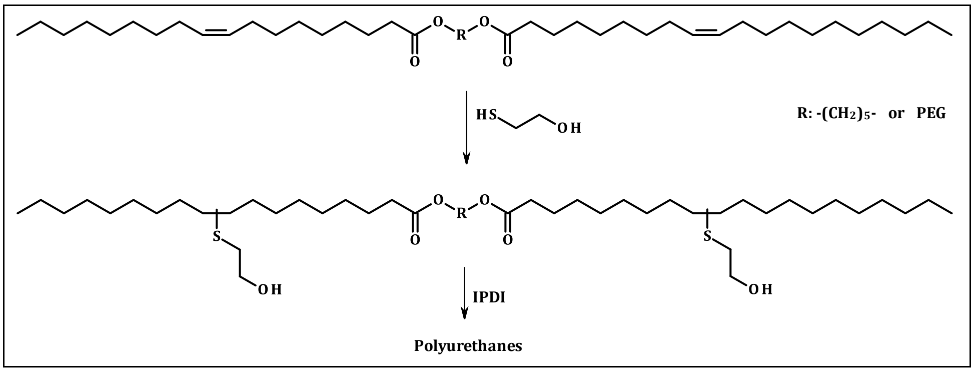
Scheme 3.4: The syntheses of telechelics from 1 and 7.[41,42,43]

Polyanhydrides are another important class of biodegradable polymers, offering, for instance, fast degradation properties for controlled drug delivery applications. 3-Mercaptopropionic acid addition to **2** and **1**, as well as to undecenoic acid triglyceride, resulted in di- and tri-functional carboxylic acid derivatives, which were first acetylated and finally melt polymerized at higher temperatures under vacuum (Scheme 3.5).[212] The thiol-ene addition reactions were carried out under UV irradiation (365 nm) in the presence of DMPA as photoinitiator and the monomers were purified with simple workup procedures to yield the carboxy monomers in good to high yields. The thermal properties of the resulting polymers were studied by means of DSC and TGA. The polyanhydride synthesized from **1**, for instance, exhibited T_g and T_m values of -38 and 72 °C (second run), and $T_{10\%}$ and T_{max} values of 279 and 413 °C, respectively. In addition, the polyanhydride synthesized from **1** and its triglyceride was subjected to hydrolytic degradation and drug release essays in phosphate buffer solution (pH 7.4) at 37 °C. The polymers exhibited fast degradation and release properties.



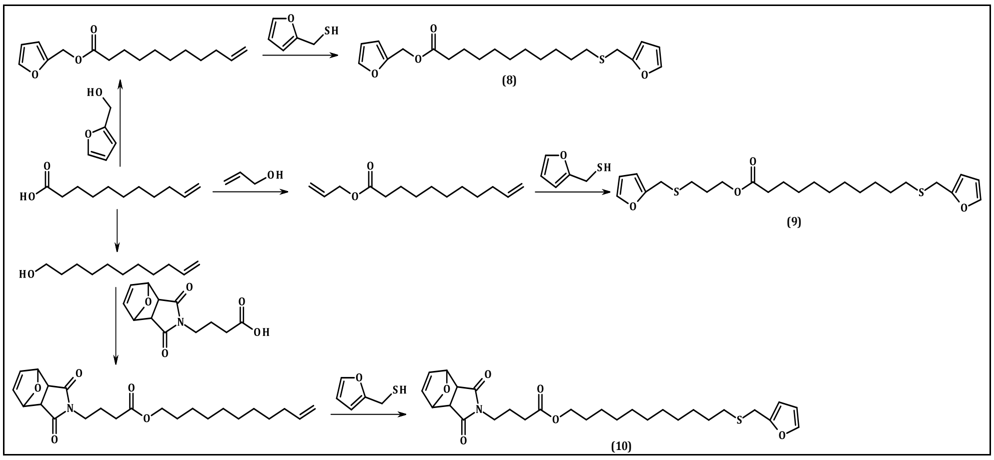
Scheme 3.5: Carboxyl monomers from sunflower and castor oils. [53]

Just like epoxy resins, polyurethanes are one of the most important materials for the plastic industry. Therefore, it would be very important to study polyurethanes synthesized from plant oils even if it is only limited to the synthesis of polyols from fatty acids and (or) triglycerides and cure with non-renewable isocyanates. For instance, the syntheses of linear and branched diol compounds from **1** and **2**, respectively, and their polymerization with 4,4'-methylenebis(phenylisocyanate) (MDI) to yield partially renewable polyurethanes were reported in 2011.[213] Linear diols were produced *via* mercaptoethanol addition to **1** and subsequent reduction or after esterification of **1** with allyl alcohol. The thiol-ene addition reactions were performed at room temperature without deoxygenation, in small amount of acetonitrile as solvent, under UV irradiation (9W, 365 nm), and DMPA was used as photoinitiator where necessary. When the same methodology was applied to **2** a branched diol compound was formed and the reaction required higher amounts of photoinitiator. These diols were then polymerized with MDI in DMF solution using tin(II)-2-ethylhexanoate as catalyst, to produce the corresponding thermoplastic polyurethanes having molecular weights in the range of about 36 – 83 kDa. The polymers were characterized and revealed good thermal and mechanical properties; for instance, the polyurethane from **1** exhibited a T_g value of 56 °C and T_m value of 141 °C (second run), and $T_{5\%}$ of 274 °C, which are comparable to the commercially available thermoplastic polyurethanes. In addition, cytotoxicity tests revealed that these materials are promising for biomedical purposes. Similarly, Cramail *et al.* reported on the syntheses of diols from castor and sunflower oil.[214] The addition of mercaptoethanol to the **2**-diesters, which were derived *via* esterification of **2** with pentane diol or PEG diols, was performed *via* both UV- and thermal initiation at different temperatures and thiol/ene ratios. The conversions were determined by ^{1}H-NMR and the best results were achieved under the following conditions: UV-initiation at 225 nm, and a thiol/ene ratio of 6 at 0 °C for 2 hours. Interestingly, the presence of benzophenone as photoinitiator did not have a remarkable effect on the final conversion, which is about 89-90% after 2 hours. Finally, the obtained diol compounds were polymerized with isophorone diisocyanate to yield linear polyurethanes (Scheme 3.6). The characterization of the obtained polyurethanes gave, for example, 35 kDa molecular weight and a T_g value of -28 °C, when it is synthesized from mercapto ethanol-modified pentamethylene dioleate.



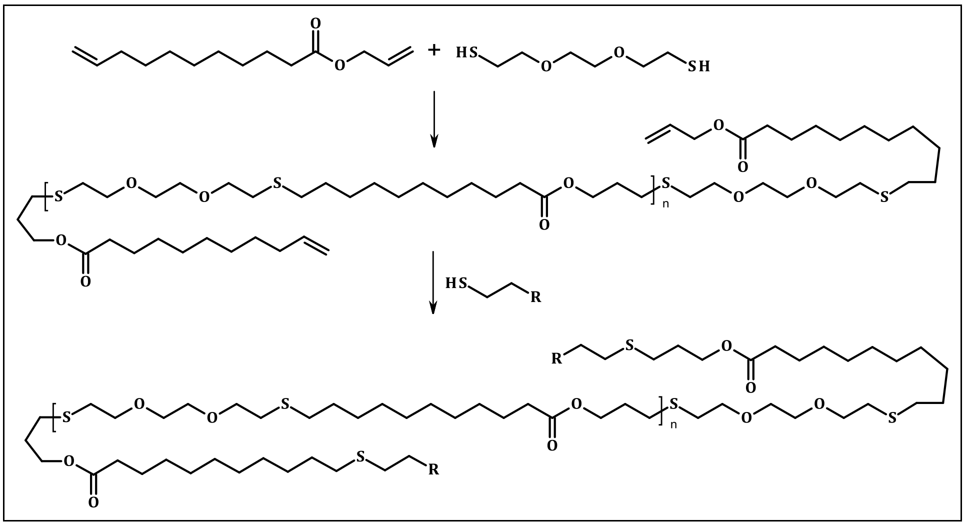
Scheme 3.6: Polyurethane synthesis from 2. [51]

Another interesting application of **1** was reported very recently by Gandini *et al.* with the synthesis of polymers with thermoreversible character.[215] The authors prepared monomers from **1** through thiol-ene addition, bearing either two furans or a combination of furan and a protected maleimide end-group that can later be polymerized *via* Diels-Alder reaction. The difunctional monomers with Diels-Alder moieties were prepared *via* 2-furylmethanethiol addition to the esterification product of either **1** with allyl alcohol, or **1** with 2-furylmethanol, or **7** with 4-maleimidobutyric acid (the monomers were represented by **8**, **9**, and **10**, respectively, at Scheme 3.7). The thiol-ene addition reactions were carried out in excess of thiol compounds under nitrogen atmosphere and 365 nm UV irradiation for 4 hours at room temperature. Later on, **8** and **9** were polymerized with 1,6-bismaleimidohexane and **10** was self-polymerized. The highest molecular weight, about 17 kDa with 1.8 PDI, was reported for **10**, having a T_g value of -2 °C, which was then depolymerised at 110 °C. Such polymers are expected to be used as amendable, recyclable, and controlled phase-changing systems.



Scheme 3.7: Syntheses of the Diels-Alder condensable polymers.[215]

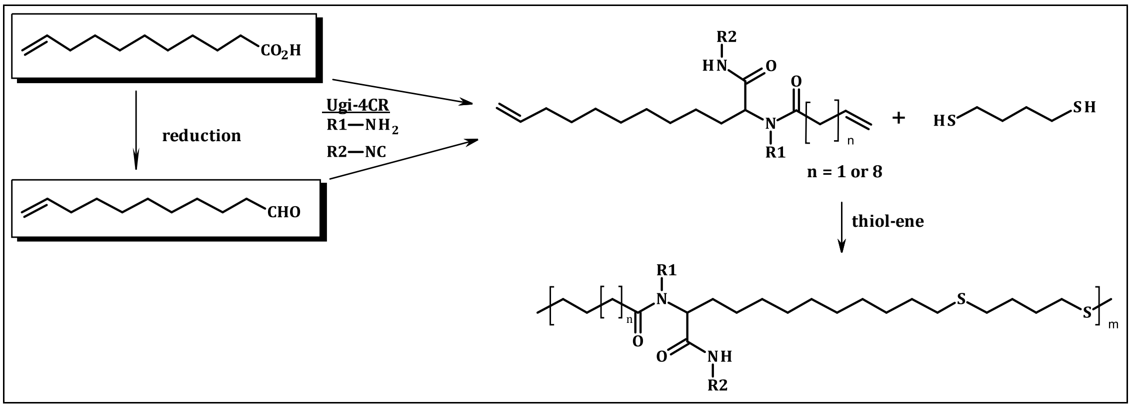
Another approach towards thermoplastics *via* step-growth polymerization is the synthesis of monomers in the form of α,ω-dienes that can be polymerized by a dithiol compound. It should be noted that such a polymerization reaction follows typical step-growth polymerization rules; therefore the diene/dithiol ratio is an important parameter for this reaction. That means, in contrast to some of the grafting reactions, the dithiol compound cannot be taken in excess amount in order to compensate the lower reaction rates with internal alkenes, and hence this polymerization reaction is limited to the use of **1** and its derivatives bearing terminal double bonds. For example, Lluch and coworkers prepared the allyl ester of **1** and polymerized it with a dithiol compound, e.g. 3,6-dioxa-1,8-octanedithiol under UV radiation (365 nm) in the presence of DMPA for 2 hours.[158] An important feature of this reaction is that telechelics could be formed in a one-pot process. The polymerization of the diene and dithiol compound was carried out with the excess of diene monomer in order to obtain polymers having double bonds at the chain terminus; the subsequent addition of mercaptoethanol resulted in alcohol-functional telechelics (Scheme 3.8). The telechelic diols were then reacted with 4,4'-methylenebis(phenylisocyanate) and 1,4-butandiol as chain extender to obtain multiblock copolymers with T_g and T_m values of -45 and -9 °C, respectively.



Scheme 3.8: Telechelics synthesis via thiol-ene addition.[57]

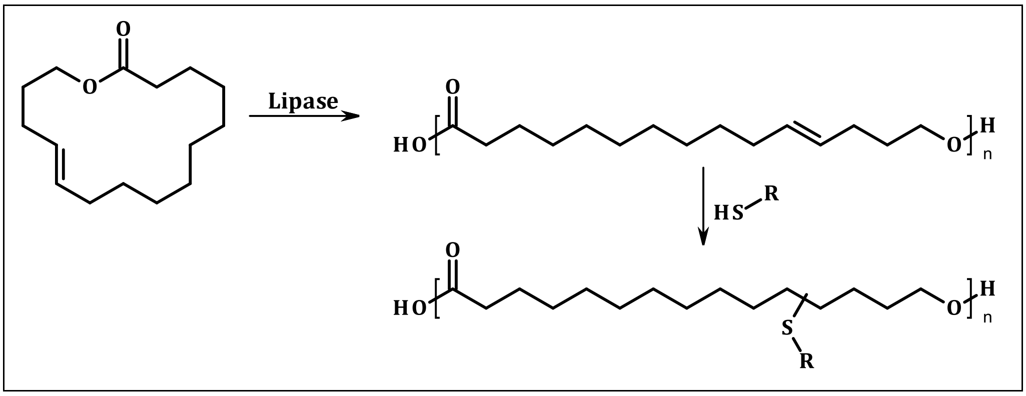
As biodegradability has been discussed as sometimes advantageous property for plastic materials, it is not always desired. Especially polyethylene or polypropylene, and their analogues, are preferred for the applications that request long-lasting use and actually are the commodity plastics produced in highest volume. Although such polymers would not be biodegradable, their production from renewable resources would still be a greener choice. Considering their long linear aliphatic chain, fatty acids seem to be a perfect renewable feed-stock for this kind of polymers.

So far, it was shown that the thiol-ene addition reaction is a very versatile tool for the polymerization of α,ω-diene monomers bearing, for example, ester, ether, and anhydride functional groups in the main chain. Nevertheless, very recently, Meier *et al.* reported the synthesis of a number of new α,ω-diene monomers bearing amide groups both in the main as well as the side chain *via* the Ugi four-component reaction; the polymerization of these monomers *via* thiol-ene addition reaction led to the formation of poly-1-(alkyl-carbamoyl)carboxamides (Scheme 3.9).[216] The Ugi four-component reactions consist of the reaction of an aldehyde (or ketone), a primary amine with a carboxylic acid and an isonitrile to form substituted α-amino acylamides, e.g. two substituted amide groups, under release of 1 equivalent of water.[217] Noteworthy, this reaction proceeds without any metallic or organic catalyst, yielding moderate to high-yields, depending on the monomers. Using **1** as carboxylic acid, 10-undecen-1-al as aldehyde, and diverse primary amines and isonitriles, the authors were able to synthesize partially renewable α,ω-diene monomers with easily tuneable peptide like side chain (Scheme 3.9). Hence, applying thiol-ene as well as ADMET polymerization reactions, linear aliphatic polyamides with aliphatic, cycloaliphatic, and aromatic side groups were obtained.



Scheme 3.9: Synthesis of monomers via the Ugi reaction and their thiol-ene polymerization.[61]

A different approach to the application of thiol-ene reaction on fatty acid-derived polymers is side-chain functionalization. The ring-opening polymerization of unsaturated lactones that are synthesized from hydroxy fatty acids resulted in unsaturated linear polyesters. The double bonds remaining on the main chain were directly utilized for the thiol-ene addition by butyl-3-mercaptopropionate, mercapto-1-hexanol, and *N*-acetylcysteamine (Scheme 3.10).[218] In the last 2 cases, more than 95% coupling yield was achieved at 80 °C in the presence of AIBN as thermal initiator and a small amount of THF was added to improve the miscibility. In contrast to the native crystalline polymer that melts at 48 °C, the modified polymers were amorphous materials.

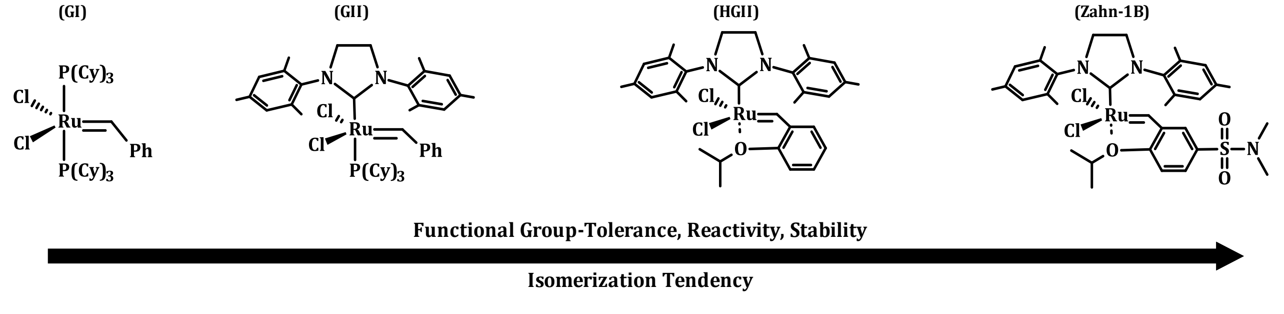


Scheme 3.10: Side-chain functionalization of the unsaturated polyesters via thiol-ene addition.[218]

3.2 Metathesis Reactions for the Synthesis of Plant Oil Derived Polymers

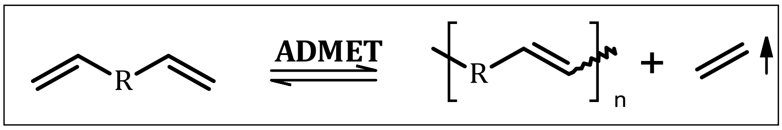
3.2.1 Development of Metathesis Catalysts

Metathesis reactions have been known for a long time and applied in organic chemistry for catalytic C-C bond formation reactions. However, their applications in polymer chemistry were first reported in the beginning of the 90s using the Mo- or W-based catalysts developed by Schrock for homo and copolymers.[219] After that, the success of Acyclic Diene Metathesis (ADMET) polymerization (Scheme 3.12) went parallel to the developments of new metathesis catalysts by means of reactivity, functional group tolerance, solvent tolerance, selectivity, and side reactions,[220] all of which will be shortly overviewed in the following paragraphs.



Scheme 3.11: The second generation metathesis catalysts.

In 1992, Grubbs reported on a novel metathesis-active ruthenium alkylidene complex (**G1**), which was found to show activity even in H_2O and MeOH (Scheme 3.11).[221] Moreover, the polymerization of 1,9-decadiene using this catalyst resulted in a polymer that has a molecular weight of 20 kDa with only 0.25 mol% catalyst load.[222] In another study, this catalyst was also shown to tolerate ether and alcohol functionalities in α,ω-diene compounds.[223] These results suggested that the success of metathesis reactions as well as ADMET polymerizations strongly dependant on the ligands. For instance, the exchange of phosphine ligands with *N*-heterocyclic carbenes (**G2**) was shown to highly improve the functional group tolerance and reactivity (Scheme 3.11).[224] The activity for a wider range of functional groups as well as the stability was advanced with Hoveyda-Grubbs 2nd generation (**HGII**) and Zannan (**Zahn-1B**) catalysts and these new generation catalysts also showed a higher reactivity. Common side reactions of such second generation catalyst are secondary metathesis reactions[225] and isomerization reactions[226] also at 50 – 60 °C temperatures.[227]



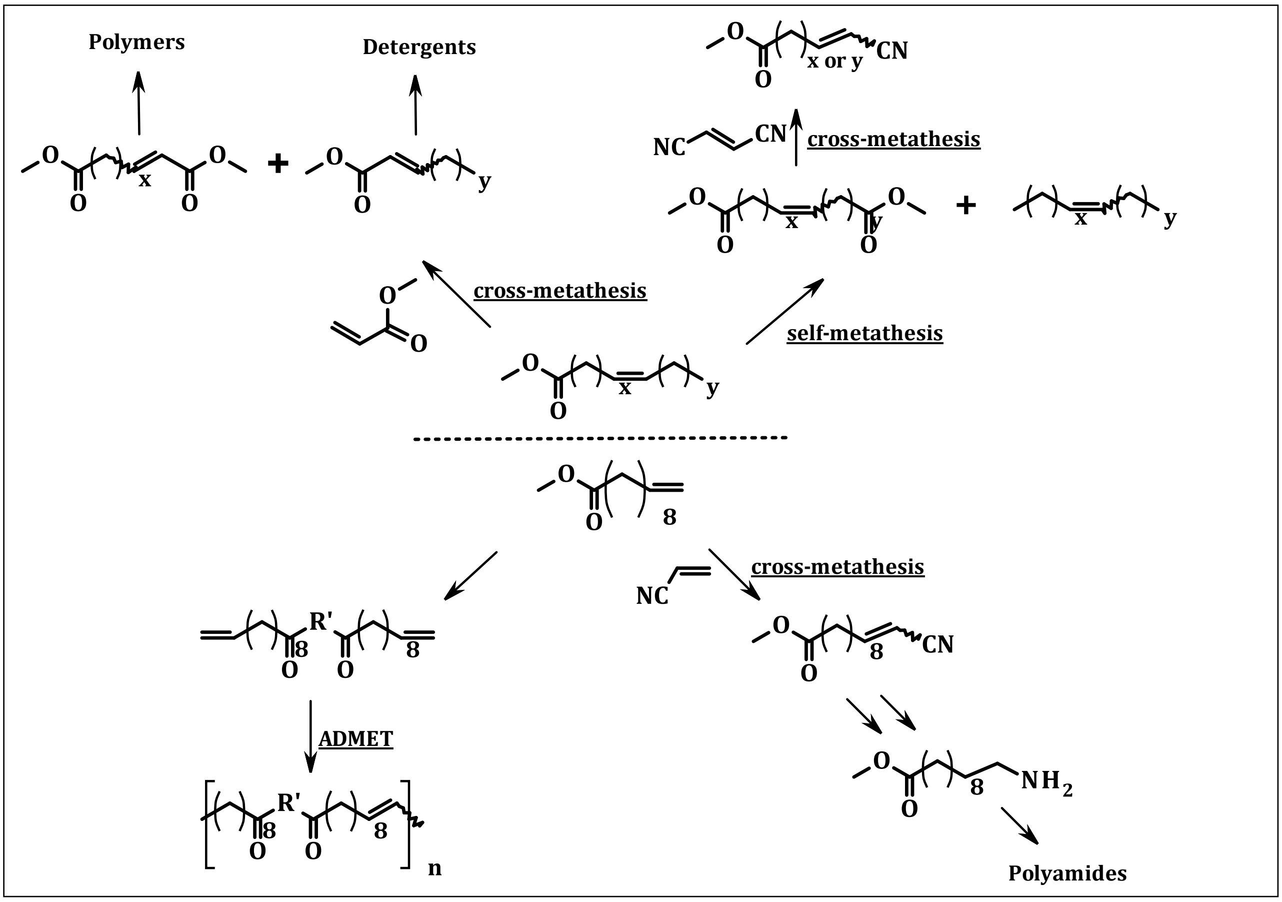
Scheme 3.12: General scheme of ADMET polymerization.

Especially olefin isomerisation is an important side reaction that occurs during metathesis reactions and can lead to undesired products. In this process, the double bond may migrate either on the polymer backbone, or in the monomer, which result in ill-defined polymers in the case of ADMET. Two possible mechanisms are the π-allyl mechanism and metal hydride addition / β-elimination mechanism, which result from an intramolecular 1,3-hydrogen shift and 1,2-hydrogen shift, respectively.[220] Noteworthy, *in situ* formed ruthenium hydride species are suspected to be responsible for these side reactions. However, benzoquinones were reported to efficiently suppress olefin isomerisation side reactions,[228] which will be discussed in the next section.

These results reveal that, in order to benefit from this fruitful C-C bond-forming reaction and obtain successful metathesis and ADMET polymerization reactions, a suitable catalyst and reaction conditions are essential.

3.2.2 Applications of Metathesis Reactions with Oleochemicals

The metathesis reaction has become one of the most useful reactions applied to polymer chemistry[229] and especially useful for oleochemicals for these reasons: i) functional group introduction *via* cross-metathesis; ii) direct use of inherently present double bonds on fatty acids; iii) breakthrough fatty acid derivatization *via* ruthenium-based catalysts.[152] Traditional metathesis reactions with oleochemicals were self-metathesis or cross-metathesis with ethylene.[230] The first cross-metathesis reaction with unsaturated fatty acids and methyl acrylate was reported by Meier *et al.* (Scheme 3.16)*.*[153] Since methyl acrylate is an electron-deficient compound, higher amounts of catalyst (>5 mol%) was used to achieve satisfactory yields. However, Meier's group was able to obtain full conversion in bulk conditions with only <0.5 mol% catalyst loading. Moreover, **HGII** catalyst was found to give best results among others. Although in the previous section it was discussed that the second generation catalysts were reported to tolerate alcohol functionality, when the cross-metathesis reaction was applied to fatty alcohols in order to obtain polyester monomers, 10 fold higher catalyst was necessary to obtain comparable results to that of protected alcohols.[154] The alcohol groups responsible for the lowering metathesis efficiency form either side products or degrade the catalyst.[152] In contrast to the Green Chemistry Principle 8 (see Chapter 1) that calls for avoiding protection/deprotection additional reaction steps, the metric calculations showed that lower E-factor numbers were obtained with protected alcohols. This result clearly reveals that the Green Chemistry Principles should be evaluated using green metrics (see Chapter 1) for each case individually in order to assess the greenness of a process. Not only methyl esters, as from methyl acrylate, but also other functional groups can be introduced to fatty acids *via* cross metathesis of fatty acids with allyl halogenides[231] and acrylonitrile.[232] The utilization of acrylonitriles has especially been studied by Bruneau and Dixneuf group and drawn much attention since, for example, fatty amines and polyamides can be prepared therefrom (Scheme 3.13).[233,234,235] The results showed that after optimization the conditions metathesis products can be obtained without isomerisation with **HGII** catalyst.



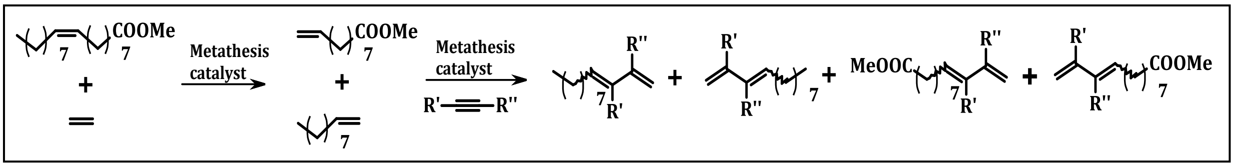
Scheme 3.13: Metathesis reactions with oleochemicals.

Foglia *et al.* applied metathesis reactions to the fatty acids obtained from soy, rapeseed, tall, and linseed oils in the absence of solvent. Long chain unsaturated α,ω-dicarboxylic acids were obtained from self-metathesis reactions.[236] It was shown that when **GII** catalyst was used at 50 °C, >80 % conversion and >70 % isolated yield were obtained for metathesis products.

Olefin isomerisation side reactions, as were aforementioned, are more pronounced for second generation metathesis catalysts, as a result of [Ru-H] species.[226,227,237] However, a quantitative study of this reaction for the first time was reported by Fokou and Meier.[163] The novel method introduced was the synthesis of a polyester *via* ADMET polymerization of a renewable ester functional α,ω-diene monomer, the acid-catalyzed transesterification of the obtained polymer with methanol followed by GC-MS analyses of the product mixture. The results revealed that **GII** showed far higher isomerisation tendency than **GI**. Moreover, the higher isomerisation tendency was found to increase at higher temperatures, and can be up to 76 % when nitrogen gas was purged, which means that only 24% of the products was not isomerized!

In contrast to the use of fatty acids, triglycerides can also be directly utilized in metathesis reactions, resulting in branched structures. Bierman *et al.* polymerized high oleic sunflower oil *via* acyclic triene metathesis (ATMET) reactions.[238] The results showed that when **GI** catalyst was used, high molecular weight non-crosslinked polymers were obtained. Moreover, the ratio between the triglyceride as monomer and methyl acrylate as chain-stopper was used to tune the molecular weight of the prepared macromolecules in the presence of **HGII** catalyst. Similarly, highly unsaturated *Plukenetia Conophora* oil (consists of 70 % linolenic and 17 % linoleic acids) originating from Nigeria was also polymerized *via* metathesis.[239] The results revealed that higher than 80 % conversion can be obtained with **HGII** catalyst at 70 °C, which yields a fully renewable hyperbranched polymer with a molecular weight number of about 30 KDa and PDI of lower than 4.

Not only double bonds, but also triple bonds can be involved in metathesis reactions; the reaction between an alkene and alkyne, e.g. enyne metathesis, is the most pronounced since diverse conjugated olefins can be prepared with this reaction. The first enyne cross-metahesis reaction with unsaturated fatty esters was reported by Bruneau *et al.* in 2009.[240] It was shown that ethenolysis products of methyl oleate can be reacted with terminal as well as internal alkynes in the same pot efficiently and selectively under mild conditions to yield 1,3-diolefins (Scheme 3.5). In addition, dimethyl carbonate (DMC) was used as eco-friendly solvent in metathesis reactions.



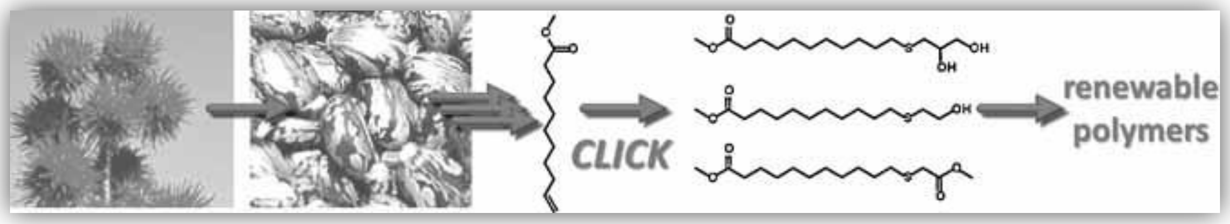
Scheme 3.5: Enyne metathesis with oleochemicals.

3.2.3 Conclusion

On the way to develop green and sustainable chemical production technologies, the urgent shift from the currently used petroleum-based feedstock to the renewable ones and the application of highly efficient and green procedures are needed. To achieve this, the use of thiol-ene addition reactions as non-catalytic carbon – heteroatom bond forming method as well as metathesis reactions as catalytic carbon – carbon bond forming method are complementary to each other with plant oils and their fatty acid derivatives, which inherently possess double bonds, is of feasible choice.

4

Fatty Acid Derived Monomers and Related Polymers *via* Thiol-Ene (Click) Additions[241]

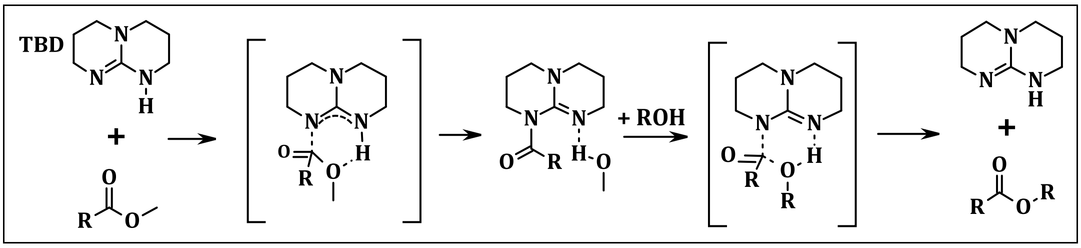


4.1 Introduction

Castor oil is a very versatile renewable feedstock for all kinds of polymeric materials, including, e.g., polyesters, polyamides, polyurethanes, and many others.[124] Being one of the commercially available castor oil derived platform chemicals, 10-undecenoic acid **1**[242] was recently used to prepare polyamides X,20,[161] a variety of acyclic diene metathesis derived polyesters, [162,163,165] as well as different cross-linked materials,[243,244,245] thus demonstrating its broad range of application possibilities. Moreover, **1** was shown to be a suitable starting material for the preparation of *α,ω*-

bisfunctional fatty acids for polycondensation polymers *via* cross-metathesis with methyl acrylate,[153] acrylonitrile,[246] and allyl chloride.[247]

Thiol-ene additions (or thiol-ene click reactions) are considered as a versatile and broadly applicable tool in polymer science.[248] The mechanism and features of this reaction were briefly discussed in Chapter 3. Today, this reaction is used in the sense of a click reaction for the synthesis of monomers as well as dendrimers,[190] the grafting of side-groups to reactive polymers,[249,250] or the synthesis of star polymers.[251]Although thiol-ene addition reactions were already used for the modification of fatty acids, no detailed studies on the preparation of monomers derived from fatty acids and/or their subsequent polymerization is described in the literature, in which a systematic optimization in order to improve the efficiency and greenness of the reaction and screening with different thiol compounds was not reported. Polycondensation reactions require specific catalysts to reach high molecular weight. Recently, non-ionic guanidine compounds were proven to exhibit a big potential as a catalyst for transesterification reactions. For instance, Schuchardt *et al.* compared the reactivity of several non-ionic bases like amidines and triamino(imino)phosphoranes as catalysts for the transesterification of rapeseed oil with methanol.[252] The results showed that 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), which has a comparable basic strength to sodium hydroxide, resulted in the highest yield of 91 % in just 1 h. The authors ascribed the high activity of TBD to the unhindered free electron pair of the sp^2 nitrogen. The proposed mechanism for **the** catalyzed transesterification, in contrast to the common ionic mechanism, consists of a concerted mechanism through the formation of a 6-membered transition compound between TBD nitrogens and ester, resulting in the weakening of ester bond, and consequently the insertion of another alcohol giving the transesterification product as depicted in Scheme 4.1.[253]



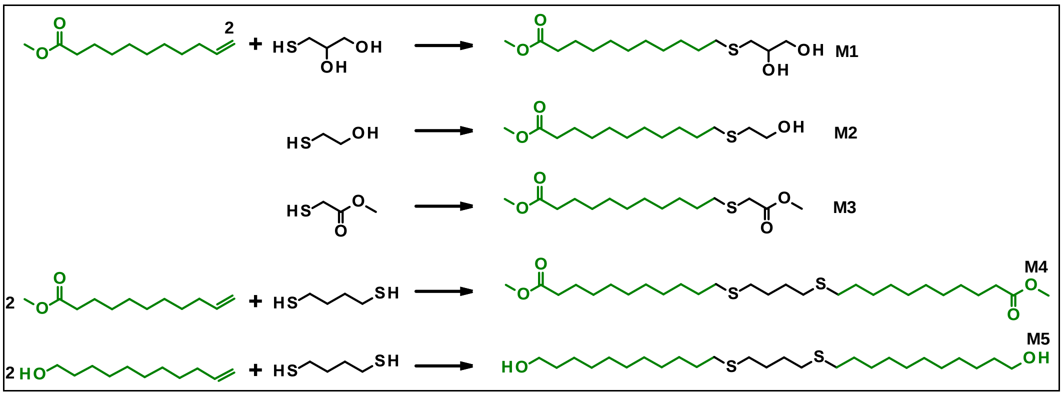
Scheme 4.1: TBD-catalyzed transesterification mechanism.

In this chapter, the use of methyl-10-undecenoate **2,** as a castor oil derived renewable platform chemical, in the context of thiol-ene click reactions is described. A variety of renewable monomers was thus obtained in high yields, their polymerization with **TBD** was subsequently studied and the material properties of the resulting polyesters were investigated. It is important to note that the presented results offer yet another efficient and sustainable entry to renewable raw materials derived from plant oils and are complementary to recently reported results on olefin cross-metathesis of fatty acid derivatives to yield renewable monomers.[152]

4.2 Results and Discussion

4.2.1 Synthesis of Novel Monomers *via* Thiol-ene (Click) Additions

In a starting set of experiments, we examined the synthesis of renewable monomers from **2** *via* thiol-ene additions with different thiols (Scheme 4.2).



Scheme 4.2: Investigated monomers and their preparation from the renewable platform chemical 2.

First, a set of model reactions was performed in order to investigate some important parameters concerning the reaction conditions, especially the reaction temperature. The reaction temperature for the synthesis of **M1** had a marginal effect on the observed conversions of **2** and essentially full conversions were obtained after 2 hours reaction time using equimolar thiol compound. Only above 40 °C conversions were somewhat lower (~80% after 2h). Therefore, 35 °C was considered as an optimum temperature for the synthesis of **M1** and also **M2**. Quite interestingly, although **2** and 1-thioglycerol are not miscible at this temperature, the reaction still proceeds and in time the mixture becomes homogeneous, probably due to the amphiphilic nature of the formed product. All these reactions were performed under vacuum since deoxygenated reaction mixtures showed better results. However, since methyl thioglycolate has a low boiling point of 42 °C, the synthesis of **M3** was performed at room temperature without the application of vacuum, also resulting in high conversions. **M4** and **M5** on the other hand had to be prepared at 60 and 70 °C, respectively, in order avoid crystallization of the product and high viscosities.

Having the basic reaction parameters established, we also performed thiol-ene addition reactions using 1.1 and 1.2 equivalents of the thiol compounds. For **M4** and **M5** we investigated an excess amount of the Ene compound (e.g. **2**:butanedithiol = 1.2:0.5) in order to avoid the formation of mono-addition-products. The results clearly showed that a 1:1 ratio of reactive groups provided similar or better results than the respective reactions with excess of one of the reactants. Therefore, we carried out all monomer syntheses with a feed ratio of ene:thiol = 1:1. However, it is worth to mention here that these reactions require highly efficient stirring techniques for higher scaled-batches. We performed the synthesis reaction of **M1** with 10 and 20 mmol of **2** using cross, and 10 mmol of **2** using three different magnetic stirrers such as cross (16.5 mm rare earth), elliptical (10 mm rare earth), and a half-moon (Teflon 40 mm rare earth) mechanical stirrer. The results revealed that the conversion of this reaction was slightly higher for 10 mmol scale (54%) than 20 mmol, (49%) with cross stirrers and mechanical stirring was found to be much more efficient (92%).

4.2.2 Polymerization Reactions

The obtained monomers were then polymerized using **TBD** as a catalyst, which was already reported to be highly effective catalyst for the trans-esterification of plant oils among other non-ionic organic base catalysts.[254] The polymerization of **M3** and **M4** with **M5** were carried out at 120 and 140 °C, and with 5 and 10 mol% relative to the ester group of the monomers. According to GPC traces of these reactions, the best conditions were chosen to be 120 °C and 5 mol% catalyst. Therefore, all polymerization reactions were performed at these conditions and with continuous vacuum to remove the released methanol.

4.2.2.1 Synthesis of Hyperbranched and Dendritic Polymers and Their Peripheral Functionalization

Polymer **P1** is different from all other prepared polymers, since it produces a hyperbranched polymeric architecture, owing to AB_2 structure of **M1**. Amphiphilic hyperbranched polymers have recently attracted considerable attention because of their potential to be used as drug-carriers.[191,152 ,255] Therefore, a detailed attention was given to the synthesis of amphiphilic dendritic polymer from **M1** and glycerol as core material. In the very first polymerization, **M1** was directly polymerized under the aforementioned conditions. The reaction yielded a hyperbranched plymer that bears a methyl ester at "the root" and hydroxyls at the peripheriy of the polymer that has a molecular weight number of 3900 and 1.87 PDI. In addition, 5, 10, and 15 mol% of glycerol was tried for the synthesis of the dendritic polymer. GPC analyses revealed that when 5 mol% of glycerol was used, the molecular weight rapidly increased to 4350 and PDI to 2.85. However, when 10 and 15 mol% of glycerol was used, the molecular weights dropped to about 3950 and 3450, PDI values dropped to 2.70 and 2.31, respectively. These results clearly indicate that with the aid of a core material, a higher branched polymer can be obtained (Figure 4.2 and Table 4.1).

Glycerol (mol%)	Mn (g/mol)	Mw/Mn
0	**3900**	**1,87**
5	**4350**	**2,85**
10	**3950**	**2,70**
15	**3450**	**2,31**

Table 4.1: GPC calculation results of hyperbranched polymers.

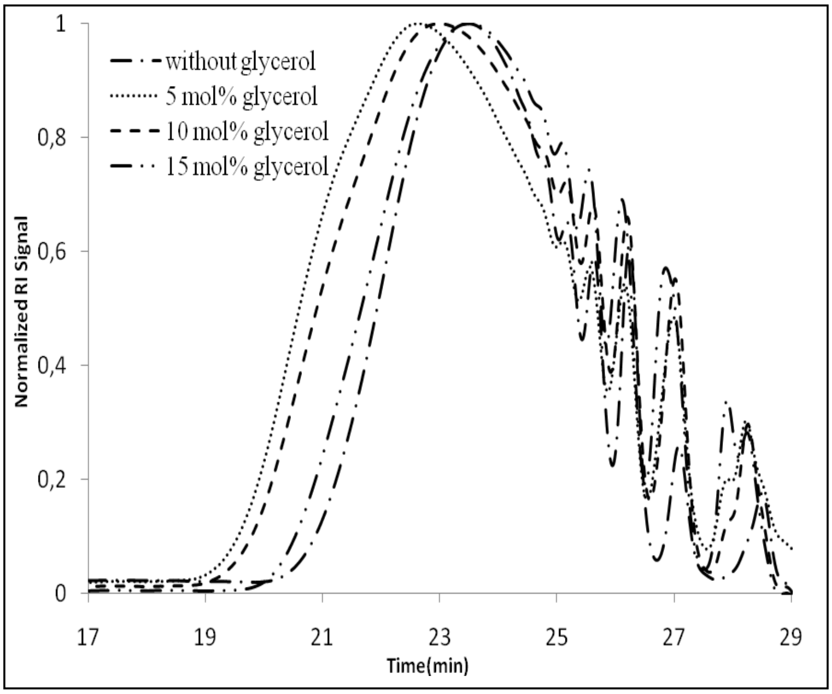


Figure 4.1: GPC traces of hyperbranched polymer with different amount of glycerol.

The structure of these polymers was further confirmed *via* ^{1}H-NMR (Figure 4.2). On the ^{1}H-NMR spectrum the singlet at 3.65 ppm from methyl ester groups indicated that a certain amount of hyperbranched polymers without core present in all polymers. Although the diastereotopic protons in glycerol in free alcohol as well as ester form make the spectrum quite complicated at first sight, their isolated chemical shifts (compare d to d' or h to h' on Figure 4.2) helps to distinguish the branching, linear, and terminal units, which are important for calculating the degree of branching (DOB).

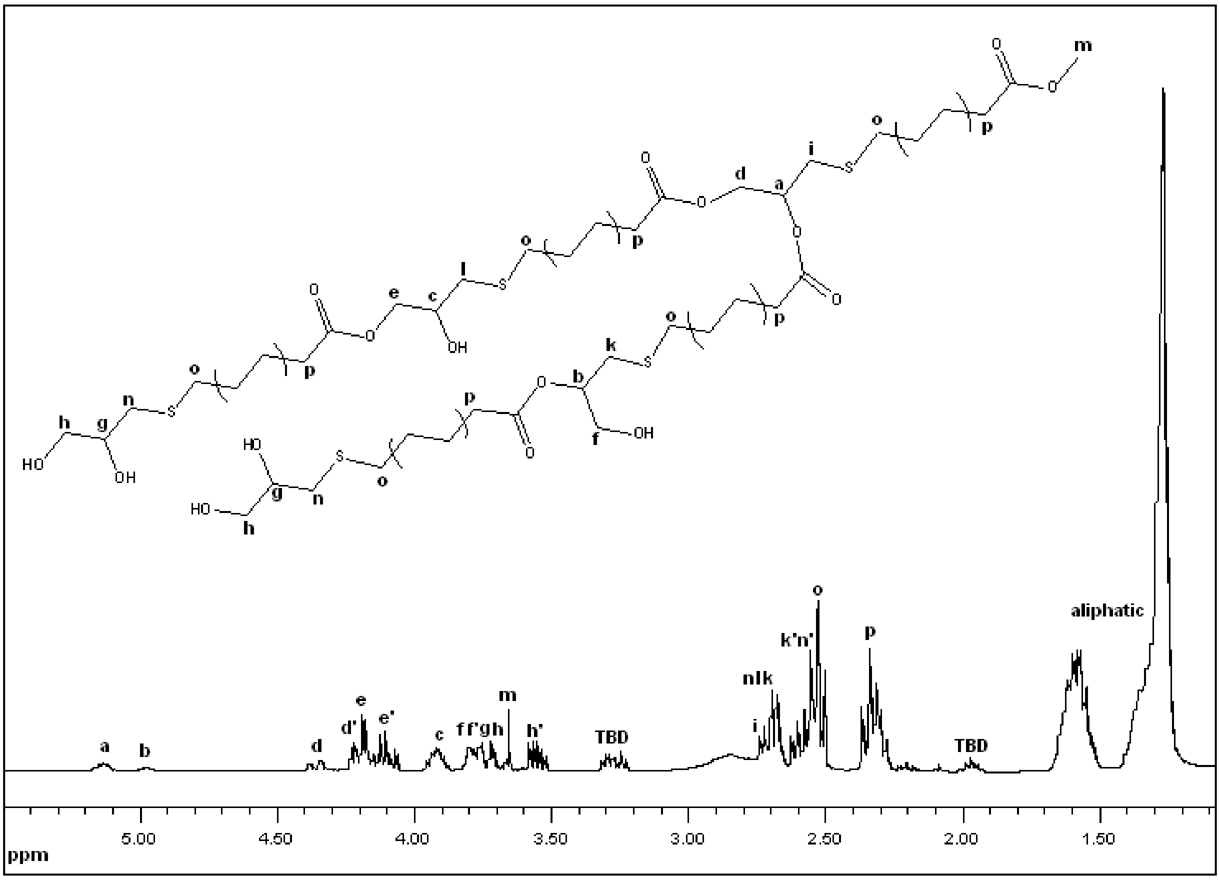
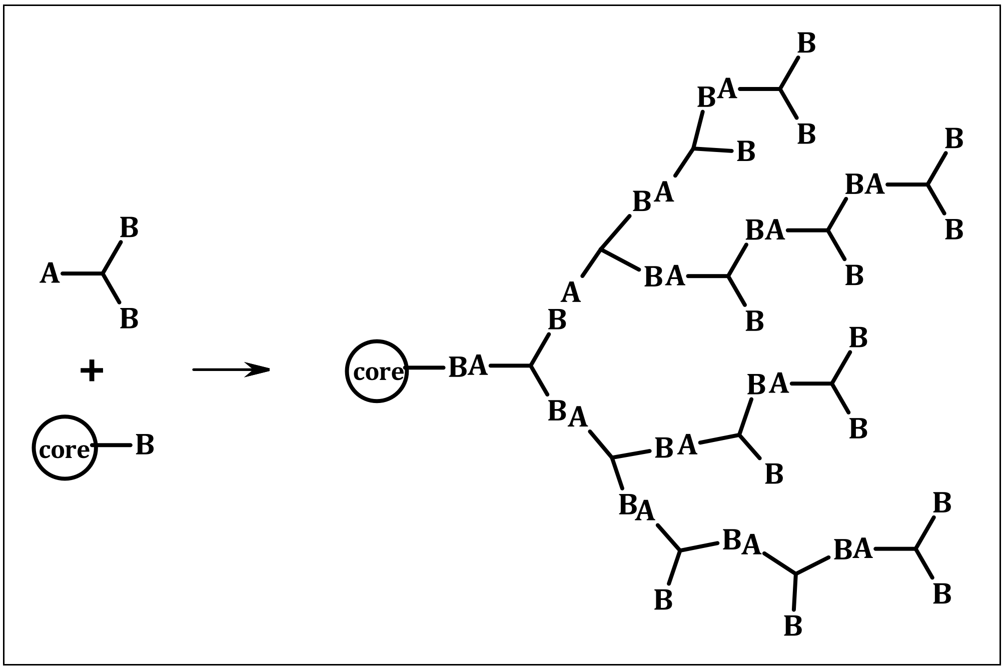


Figure 4.2: ^{1}H-NMR spectrum of the hyperbranched polymer.

The degree of branching (DOB) is obtained by comparison of the intensity of the signals for the respective units. As shown somewhere else,[256] the degree of branching is commonly calculated according to the following equation:

$$DOB = \frac{(\text{Dendritic} + \text{Terminal})}{(\text{Dendritic} + \text{Terminal} + \text{Linear})}$$

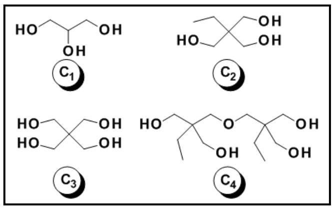
where D, T, and L are the fractions of dendritic, terminal or linearly incorporated monomers in the resulting hyperbranched polymers obtained from integration of the respective signals in NMR-spectra.



Scheme 4.3: Representative structure of the dendritic polymer.

The values commonly reported for DOB are in the range of 0.4 to 0.8. We calculated the degree of branching, *via* integration of the corresponding peaks at ^{1}H-NMR spectrum, as 0.46 which is typical for dendritic branched polymers.

It should be noted that these polymers do not exhibit perfect dendritic structures. Nevertheless, further optimization reactions were carried out using different core materials and monomer-loading methods in order to study the effects on the molecular weight of the final polymer, the polydispersity index, and the degree of branching. The studied core materials are depicted in Scheme 4.4.



Scheme 4.4: The core materials utilized.

GPC calculation results are summarized in Table 4.2. Conversion numbers are given in percentages and were calculated *via* relative area integrations from GPC chromatograms. From Table 4.2 it can be seen that the highest conversion reached was 95 %. Barathi and Moore reported that when the monomer is added to the reaction mixture slowly and continuously, higher molecular weights were obtained.[257] Similar result was also obtained in our studies, although continuous addition is not applicable to our conditions. When the polymerization was carried out in bulk, lower molecular weight and lower conversion values than the slow monomer addition method (sma) were obtained.

Entry	Monomer Addition	Core (mole%)	Catalyst (mole%)	Time [h]	M_n(GPC)	PDI	Conversion [%]	DOB
1	**bulk**	**C1 (5)**	**5**	**7**	**1400**	**1.64**	**84**	
2	**Sma***	**C1 (5)**	**5**	**7**	**3200**	**2.33**	**93**	**0,68**
3	**Sma**	**C1 (5)**	**10**	**7**	**3300**	**2.54**	**94**	
4	**Ema****	**C1 (5)**	**10**	**7**	**3600**	**2.72**	**94**	
5	**Ema**	**C2 (1)**	**10**	**7**	**3700**	**2.51**	**95**	**0,65**
6	**Ema**	**C2 (5)**	**10**	**7**	**2100**	**1.90**	**90**	
7	**Ema**	**C3 (5)**	**5**	**5**	**2800**	**2.05**	**93**	
8	**Ema**	**C3 (1)**	**10**	**7**	**3600**	**2.51**	**94**	**0,56**
9	**Ema**	**C4 (1)**	**10**	**5**	**3000**	**2.47**	**94**	**0,57**
10	**Ema*****	**C1 (1)**	**5**	**7**	**3700**	**2.47**	**93**	

**** Sma: Slow monomer addition in equal portions; ** Ema: Slow monomer addition in doubled portions; *** Up-scaled.***

Table 4.2: Summary of the polymerization entries and characterization.

It should be indicated that the necessary amount of catalyst was added to the monomer solution in THF prior to the polymerization to assure the constant catalyst / monomer ratio. Additionally, when the catalyst loading was doubled from 5 to 10 mol%, neither molecular weight nor PDI values considerably improved. On the other hand, when the monomer was introduced not in the same amounts, but in doubled amounts in order to approximately provide the necessary amount of monomers for each generation, slightly higher molecular weight and PDI values were obtained. This improvement was less than expected[258] and may be ascribed to the polymerization temperature, which hinders the homogenous addition of the new monomer portion. However, similar polymerization behaviour, but lower DOB values, e.g. 56 and 57 %, were obtained when C2, C3, and C4 was used. In addition, increasing the core material amount from 1 to 5 mol% and the catalyst amount from 5 to 10 mol% did not result in better polymerization behaviour. Therefore, a final up-scale polymerization was carried out in order to obtain an amount of polymer for peripheral functionalization studies under conditions of C1 as 1 mol% core material, 5 mol% catalyst, stepwise doubled amount monomer addition, which yielded in 3700 g/mol polymer with 2.47 PDI and 93 % conversion values (Table 4.2, Entry 10). Importantly, the similarity of those results to the best numbers obtained during optimization shows the applicability and precision of this polymerization method.

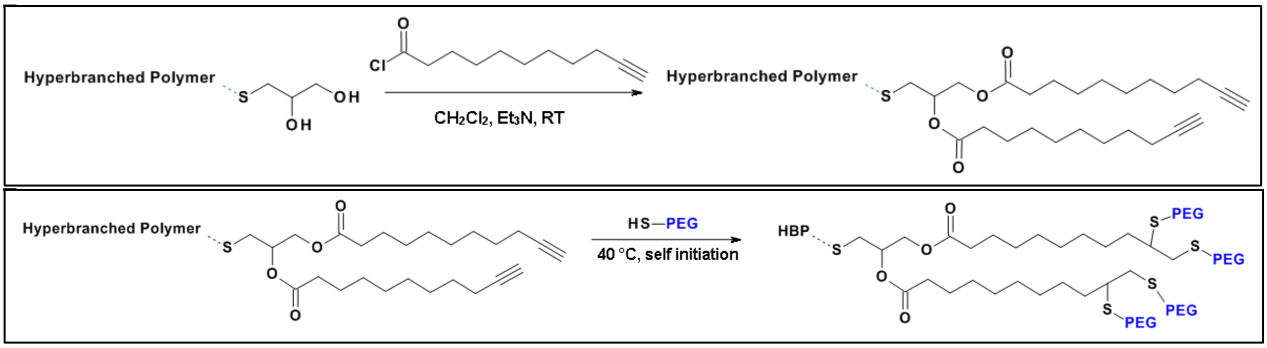


Figure 4.3: Peripheral modification of hyperbranched polymer.

Next, peripheral functionalization was carried out on the synthesized hyperbranched polymer (Figure 4.3). Although the obtained polymer bears hydroxyl groups in the periphery and hydrophobic units inside, which characterizes it as amphiphilic, this is not sufficient to make it water soluble. Hydrophylicity is important for drug delivery applications because of the fact that the majority of drugs are hydrophobic, but physiological environment is hydrophilic.[259] On the other hand, a drug carrier should naturally be biocompatible. That means any heavy metal residue remained in the polymer can result in cytotoxicity. PEGs that are non-toxic and hydrophilic are already shown to improve the biocompatibility of dendrimers.[260] Therefore, efficient and non-metallic reactions should be carried out to link PEGs to the dendrimers peripheries. To achieve this, thiol-alkyne additions exhibit a big potential, at which thiol and alkyne compounds are readily available or easily synthesized, metal-containing catalysts are not necessary, and wide range of functional groups are tolerated.[261] In order to attach a thiol-functional PEG ($M_n \cong 550$ g /mol) at the periphery of the hb polymer, the hydroxyl groups were esterified with 10-undecynoic acid (Figure 4.4 – top).

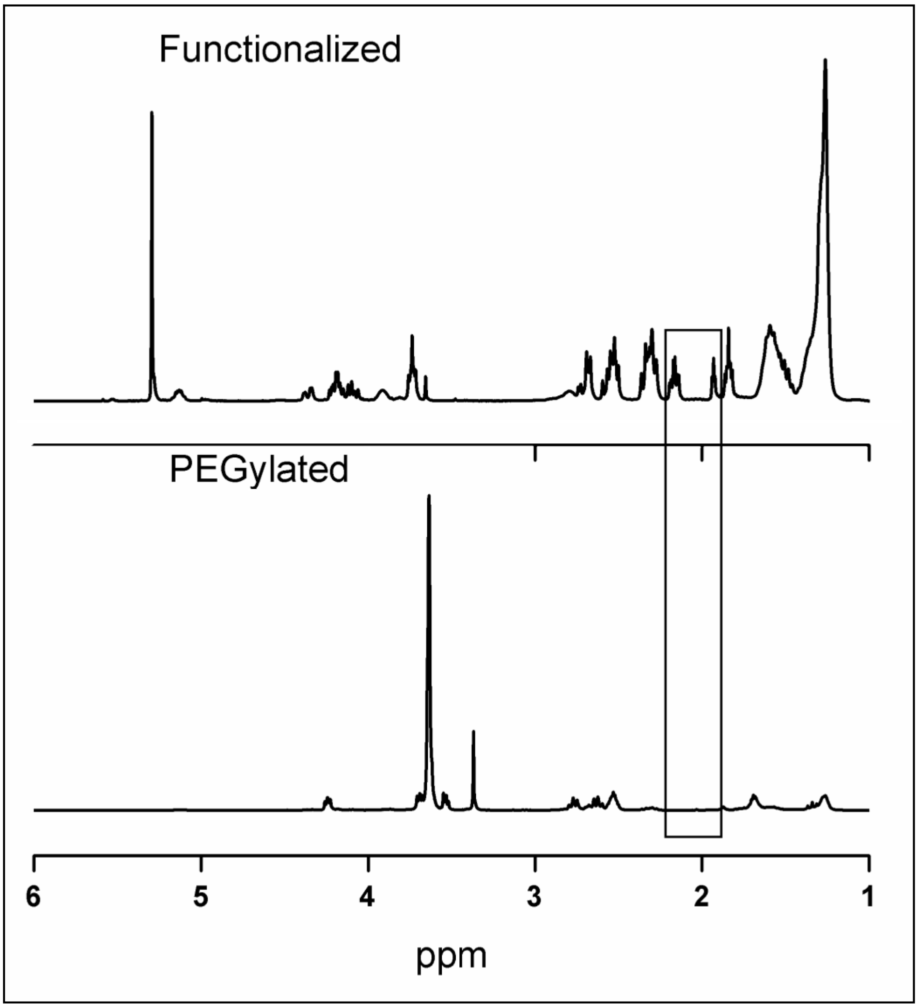


Figure 4.4: ^{1}H-NMR spectra of the hyperbranched polymers and derivatives.

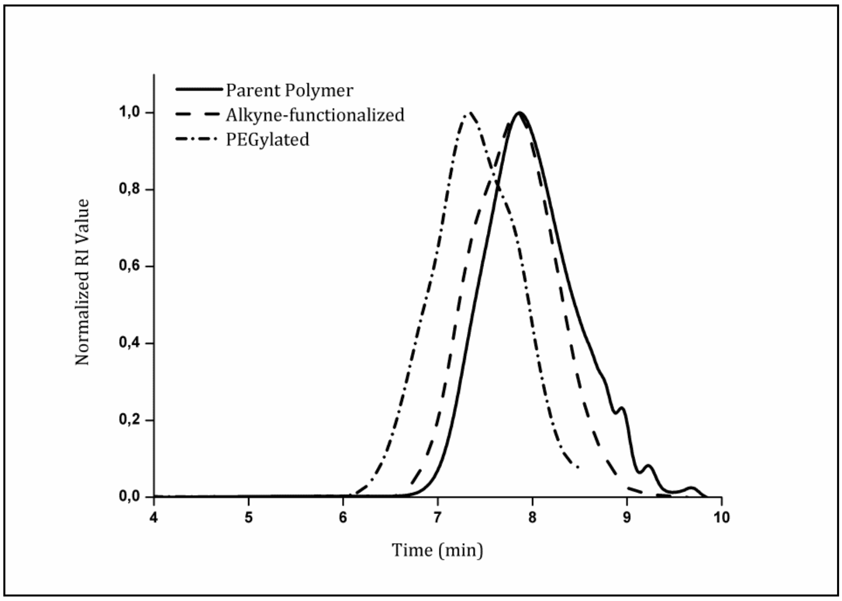


Figure 4.5: GPC traces of the hyperbranched polymer and derivatives.

Next, PEG was added to the alkyne-modified hyperbranched polymer. This reaction was carried out under UV irradiation in the presence of 2,2-dimethoxy-2-phenyl acetophenone (**DMPA)** as photoinitiator. ^{1}H-NMR spectra and GPC traces are given in Figure 4.4 and 4.5, respectively. From Figure 4.4, it can be clearly seen that the peaks at 1.90 and 2.11 ppm representing alkyne protons are completely consumed upon PEGylation, giving rise to the triplet at about 3.7 that represents ether protons of the PEG backbone. This means that the periphery was successfully modified with PEG. Moreover, GPC analysis also clearly showed the increase of the respective molecular weight after functionalization and PEGylation reactions (Figure 4.5). The molecular weight of the starting polymer was 5750 g/mol with 2.12 PDI after precipitation into methanol. When functionalized with the alkyne moieties it was 8500 g/mol (with 1.95 PDI) and after PEGylation 19400 g/mol (with 1.81 PDI) polymer was obtained. A simple solubility test showed that the final polymer is water soluble.

4.2.2.2 Synthesis of Linear Polymers

The GPC traces of the linear polymers are shown in Figure 4.6 and the GPC calculation results are summarized in Table 4.3. As in indicated in the table, the molecular weights of the linear polymers are between 5850 – 9400, and polydispersities are between 2,02 – 3,37. Since all polymers have either alcohol or metyl ester functionalities at the end and are liquid at 120°C, it is possible to further functionalize and extend the chains. It should be noted that these molecular weight numbers are not the highest for polyesters, but sufficient for a first property analysis.

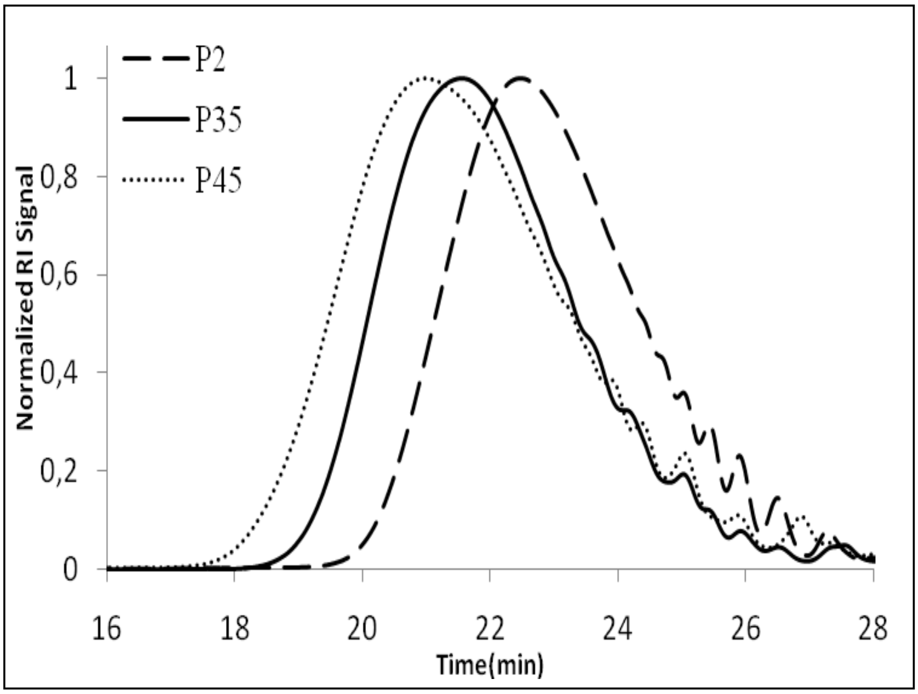


Figure 4.6: GPC traces of P2, P35, and P45.

Polymer	Mn (g.mol^{-1})	Mw / Mn
2	5850	2,02
35	8900	2,47
45	9400	3,37

Table 4.3: GPC calculation results for linear polymers.

4.2.2.3 Thermal Characterization of the Polymers

Since the aim of this study was to obtain polymers that are derived from a fatty acid to substitute materials synthesized from petroleum-originated monomers, it is also very important to perform thermal analysis of our polymers in order show their thermal behaviour and stabilities. The thermal behaviour of the polymers were analysed by means of DSC. First, the polymers were subjected to the heating rate of 10°C/min (starting from RT) and all showed very sharp melting endotherm peaks (Figure 4.7) and are thus characterized as semicrystalline polymers. It was already mentioned in the literature that thioether containing polymers, especially aliphatic ones, but also aromatic polyesters tend readily to crystallize.[262] Among those runs the polymers, except P45, exhibited multiple melting points. This phenomenon for sulphide-ether-containing homopolyesters was already mentioned[263] and ascribed to melting and recrystallization processes occurring during the calorimetric run.[264]

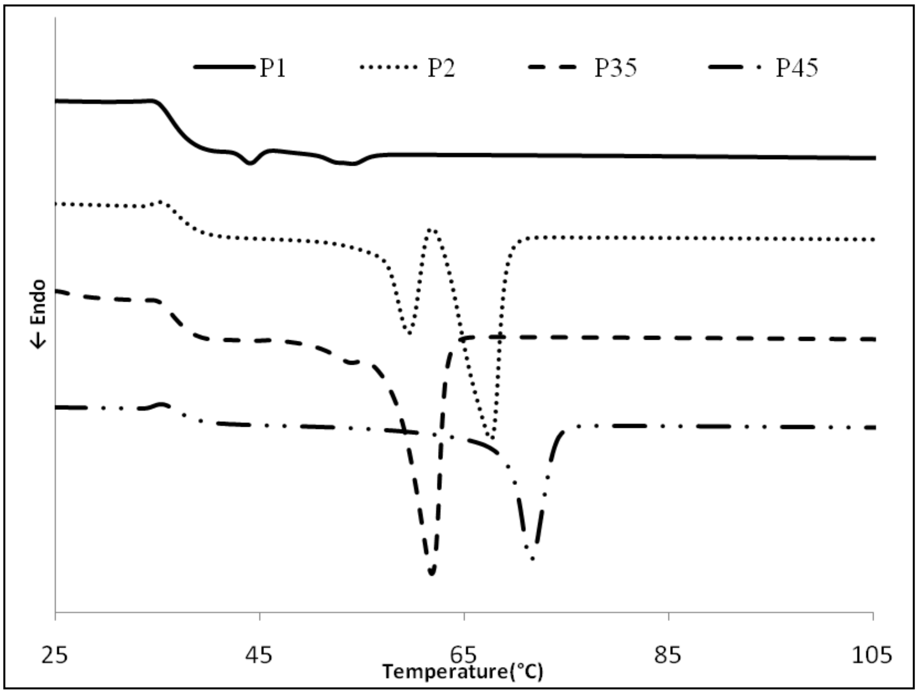


Figure 4.7: The thermogram of P1,P2, P35, and P45 with 10°C/min heating rate(2nd run).

From Figure 4.7 it is possible to assign melting points for **P35** and **P45** as 61.5 and 71.3°C, respectively. The higher T_m of **P45** is due to the longer chain length of **M4** (if compared to **M3**) and a more regular structure of **P45** (spacing of the ester groups), both allowing a better crystallization of **P45**.

On the other hand, **P1** and **P2** exhibited very sharp double melting endotherms. Further attention was paid on these polymers and we tried to obatin DSC thermograms with single melting peaks to be assigned as “real” melting points. First, we supposed that a lower heating rate would give the polymers sufficient time to rearrange themselves to a single crystalline morphology. For this reason, the polymers **P1** and **P2** were run with 5°C/min heating rate. (Figure 4.8)

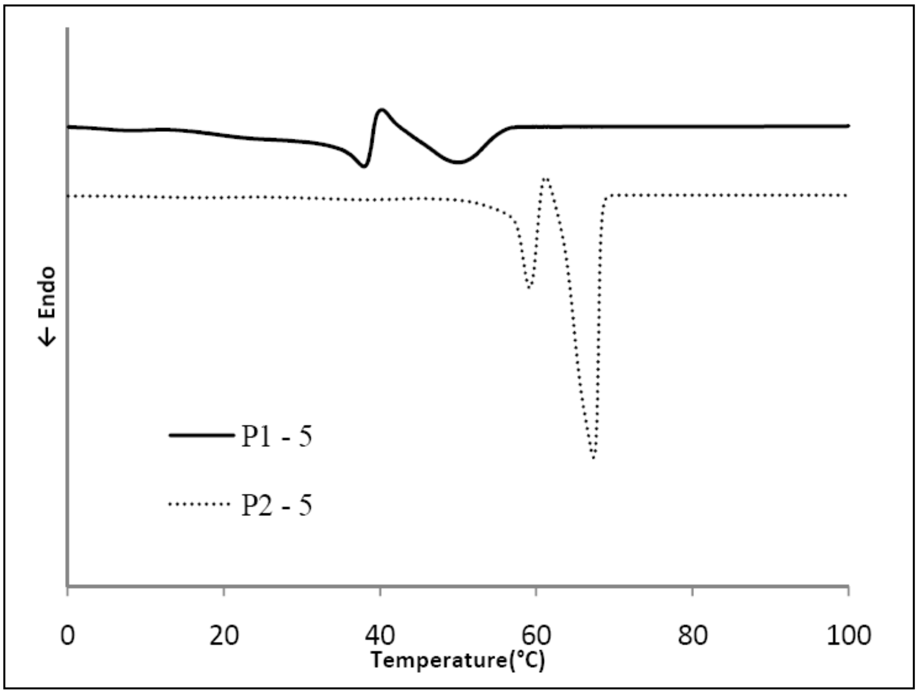


Figure 4.8: DSC thermogram of P1 and P2 with 5°C/min heating rate(2nd run).

From Figure 4.8, it is clearly seen that there is an exotherm peak (higher than base line) between two endotherm peaks and it is concluded that those polymers undergo subsequent melting and recrystallizations during the calorimetric run. Corresponding melting points are 37.88 and 50.05°C for **P1**, and 59.09 and 67.21°C for **P2**.

Annealing was then used as a pre-treatment of those polymers. The samples were heated inside the calorimeter to different temperatures for each sample, kept 2 hours at this temperature, and after cooling to -50°C, heated to 150 with 20°C/min heating rate. The isothermal temperatures chosen for **P1** are 25 and 40°C, and for **P2** are 50 and 56°C. The thermograms gathered from both polymers are collected in Figure 4.9.

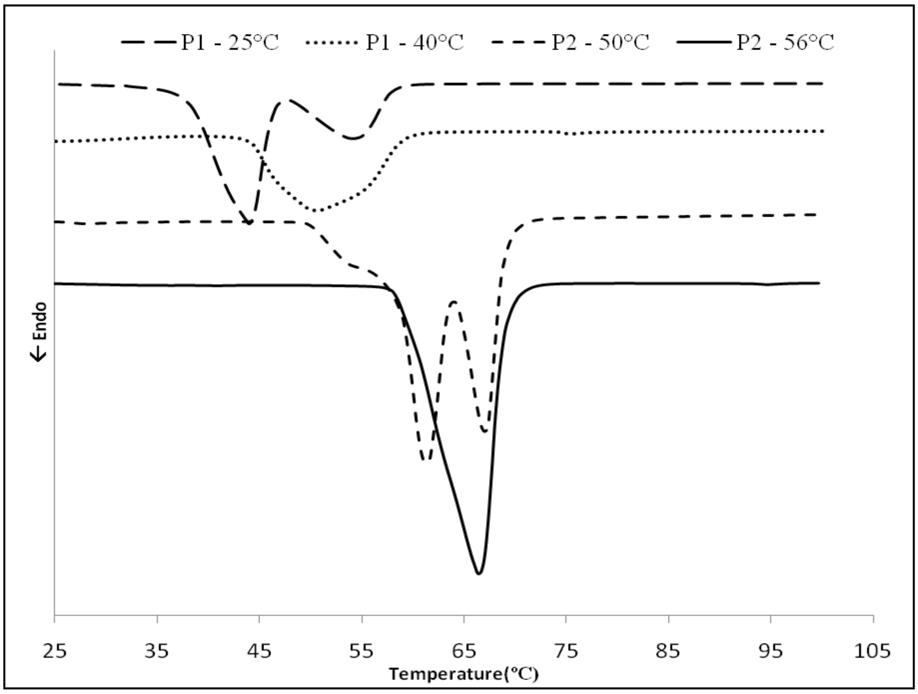


Figure 4.9: DSC thermogram of P1 and P2 with annealing-pretreatment.

It is clearly seen that annealing was an effective tool to detect real melting points of the polymers 1 and 2. Considering the relative intensities of the endotherms, annealing of **P1** at 25°C favoured the first endotherm peak, but annealing at 40°C resulted in a polymer with single type crystalline structure which has a single melting point. Similarly, annealing **P2** at 50°C favoured again the first peak, but annealing only at 6°C higher temperature resulted in a perfect sharp endotherm peak at the same temperature of the second peak. In both cases, the single peaks appeared at the temperature of the second peak before annealing applied, indicating the early endothermic peaks were a result of a kind of meta-stable states[265] and ultimately reorganize to the most stable crystal structure, and finally totally melts. The detected melting endotherms are collected in Table 4.4.

Polymer	Tm(1) (°C)	Tm(2) (°C)
P1(25°C)	45	54
P1(40°C)	-	50
P2(50°C)	61	67
P2(56°C)	-	66

Table 4.4: Melting endotherms from Figure 4.9.

Thermal stabilities of the polymers were also studied by means of TGA analysis under nitrogen atmosphere with 10 °C×min^{-1} heating rate. The calculated results are summarized in Table 4.5.

Polymer	5 wt% weight loss (°C)	Max-weight loss temperature (°C)
P1	299	372
P2	344	374
P35	353	393
P45	348	393

Table 4.5: TGA calculation results.

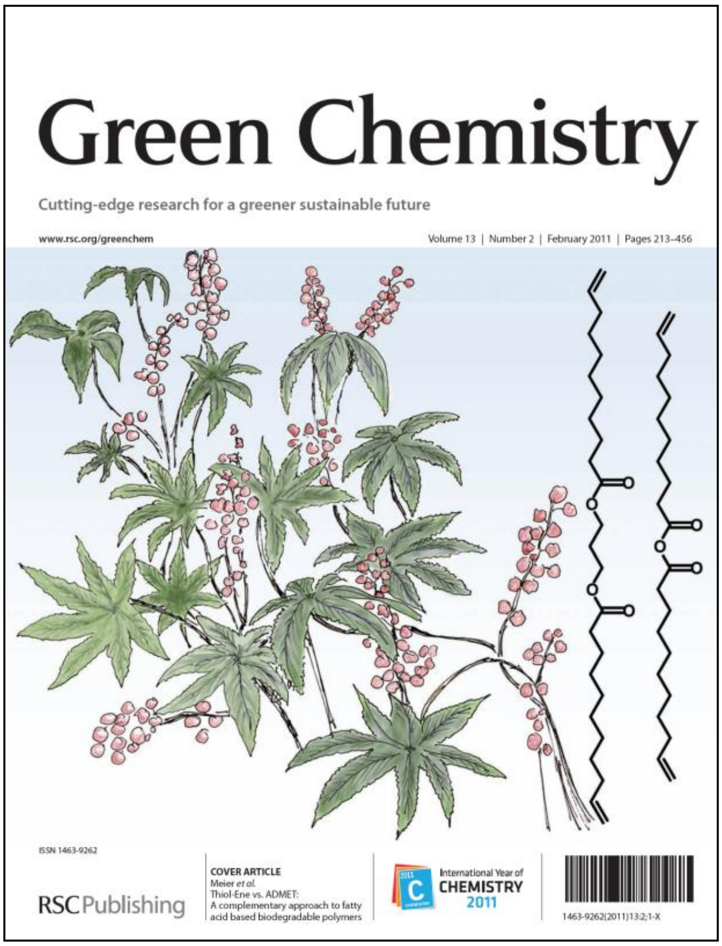
Considering initial decomposition temperatures, we observed that all linear polymers exhibited less than 5% weight loss below 340°C with similar trend, except for that of hyperbranched polymer (**P1**) which is 299°C. This phenomenon could result from relatively lower molecular weight of **P1** and its morphology. On the other hand, while the max-weight loss temperature of **P1** is 372°C, **P2** and the other linear polymers lose max-weight at 374 and 393°C, respectively, indicating that **P35**, and **P45** have almost the same thermal stability. As a result of TGA analyses, we conclude that these renewable polymers have considerable thermal stabilities and are possible candidates for some industrial applications.

4.3 Conclusion

In this study, it was aimed to synthesize a number of aliphatic polyesters, in the form of hyperbranched, dendritic, and linear, from a renewable platform chemical using thiol-ene&yne addition reactions featuring click chemistry conditions, which could be used to substitute the polymers from petroleum originated monomers. Nevertheless, thiol-ene addition reaction was studied in detail to find out the optimum conditions so that the monomers were produced in high yields. Finally the synthesized polymers were successfully characterized in order to establish the thermal behaviour and stability to guide the possible applications. To sum up, thiol-ene addition reaction is an efficient and environmentally benign tool to synthesize fatty acid derived polymers for the chemical industry.

5

Thiol-Ene Click vs. ADMET: A Complementary Approach to Fatty Acid Based Biodegradable Polymer Synthesis[266]



Green Chemistry

Cutting-edge research for a greener sustainable future

www.rsc.org/greenchem

Volume 13 | Number 2 | February 2011 | Pages 213–456

ISSN 1463-9262

RSC Publishing

COVER ARTICLE
Meier *et al.*
Thiol-Ene vs. ADMET:
A complementary approach to fatty acid based biodegradable polymers

International Year of CHEMISTRY 2011

1463-9262(2011)13:2;1-X

5.1 Introduction

Recent advances in medical applications have revealed a high demand for polymeric systems that fulfil a number of requirements, such as biodegradability and biocompatibility. Such systems are widely used in temporary implants and drug delivery systems.[267] The use of fatty acids as building blocks for such polymers introduces flexibility, low melting temperatures, hydrophobicity, and pliability.[268] Moreover, biocompatibility and the substitution of fossil resources with respect to environmental aspects are additional advantages of fatty acids in the synthesis of biopolymers. The term biopolymer is used in different aspects in material science. Cellulose, starch, and other carbohydrate-based polymers as well as proteins are examples of biopolymers by means of their origin, e.g. they are bio-derived. On the other hand, polymers such as poly(methyl methacrylate) and others that exhibit biocompatibility, but are not bio-derived, are also referred to as biopolymers, owing to their bio-applications. In any case, bio-degradability is a structure dependent property and not necessarily related to the above mentioned classifications. On the other hand, on the basis of chemical linkages, biopolymers are classified as polyesters, polyorthoesters, polyanhydrides, polyamides, and polyphosphazines.[269] The two major classes of these materials are polyesters and polyanhydrides, which undergo bulk and surface erosion degradation, respectively.[268] Polylactides and poly(lactide-co-glycolide)s, the most frequently studied members of this biopolymer family, have already been used commercially for half a century. Their degradation, likewise to other polyesters, is classified as bulk degradation with random hydrolytic scission of the polymer chain.[269] For retention of the mechanical properties during the degradation process and having more regular degradation rates,[268] which avoids acid bursting and its inflammatory consequences, the surface erosion mechanism (and therefore polyanhydrides) seems to be preferable for at least some applications. Typical fatty acid based polyanhydride syntheses, widely studied by Domb *et al*., involve condensation reactions that need high temperatures and vacuum in order to force the reaction towards polymerization, multiple steps, and/or solvents.[270,271,272,273]

While trying to find highly reliable, selective and fast synthetic methods, Sharpless *et al*.[191] mentioned that reactions that form new C-C bonds should be left to nature due to their modest thermodynamic driving force and therefore, the term "click chemistry" was introduced for the reactions that form mainly heteroatom linkages in an efficient manner. Since then, this term has been used widely for copper catalyzed Huisgen cycloadditions of an azide to an acetylene, which usually need to be attached by an additional reaction step at the desired site of reaction. On the other hand, the thiol-ene addition reaction was not considered to be one of the click reactions before 2008, when Hawker and coworkers successfully utilized thiol-ene chemistry to synthesize fourth-generation polythioether dendrimers in the absence of solvent and metal catalysts.[190] However, it should be noted that the kinetics of this reactions strongly depend on the structure of the thiol[241] and olefin compounds. These results are especially important for the applications to unsaturated fatty acids and derivatives, which naturally contain double bonds along their main chain.

On the contrary to leaving C-C bond-forming reactions to nature, recent developments in olefin metathesis, especially in acyclic diene metathesis (ADMET), have revealed the great potential of olefin metathesis as a polymerization method for fatty acid-derived α,ω-diene monomers.[274] Since the quantitative polymerization of 1,5-hexadiene and 1,9-decadiene with Lewis acid-free catalysts,[275,276] ADMET polymerization has advanced in correlation with the development of a set of metathesis catalysts with highly improved activity and functional group tolerance, very recently reviewed by Meier *et al.*[220] Although this highly efficient catalytic polymerization method can suffer olefin isomerization side reactions, preventing the synthesis of defined polymeric structures, the use of quinone-type compounds was shown to suppress this isomerization to a large extent.[277,164] Nevertheless, even very small amounts of heavy metal catalyst residue within the polymer might be accompanied by biocompatibility issues, especially for medical applications. In addition, since the ADMET reaction itself releases an ethylene molecule for each new C-C double bond formation, the atom efficiency of the overall polymerization is another minor drawback of this method, although it should be possible to recover the ethylene on industrial scale.

In this part of the study, a new complementary synthetic approach to fatty acid derived biodegradable polymers is reported and the efficiency of this method considering environmental as well as application issues is discussed. Thus, fatty acid derived *α,ω*-dienes with ester and anyhdride linkages were polymerized *via* ADMET and thiol-ene click reactions. Furthermore, the thermal properties and solution stabilities of the synthesized polymers were studied and compared in order to gain an insight into their application possibilities.

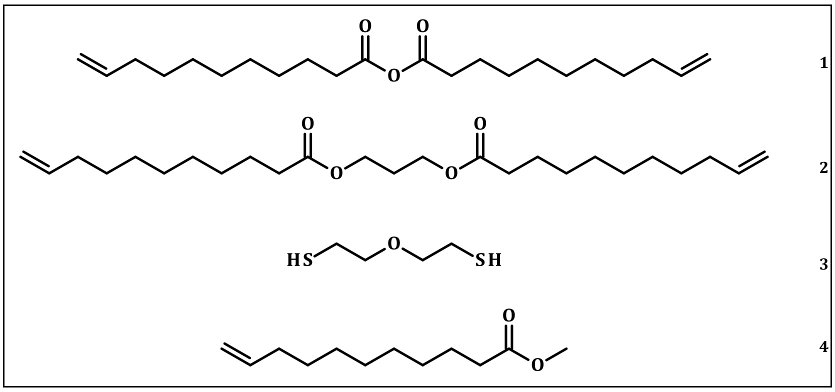
5.2 Results and Discussion

5.2.1 Synthesis of Monomers

First, the anhydride-functional monomer **1** from 10-undecenoic acid and the corresponding acid chloride was synthesized. A number of methods are reported in the literature dealing with the synthesis of anhydrides. Typically, anhydride synthesis is carried out using carboxylic acids and a dehydrating agent, such as dicyclohexylcarbodiimide,[278] carbodimidazole, phosgene, diphosgene, or methoxyacetylene.[279] However, these methods produce a mixture of symmetric and mixed anhydrides, which require challenging purification methods in order to gather pure symmetric anhydrides. Condensation of carboxylic acids with acetic anhydride in the presence of heterogeneous coordination catalysts[280] also requires high reaction temperatures, vacuum, and long reaction times. On the other hand, condensation of a carboxylic acid and an acid chloride in the presence of an acid scavenger (e.g. triethylamine or pyridine) results in an almost complete conversion into symmetric anhydrides by much milder conditions, although a negligible amount of free acid is always present in the reaction mixture.[281,282] Therefore, the synthesis of anhydride functional α,ω-diene monomer **1** was performed *via* the reaction of 10-undecenoic acid and undec-10-enoyl chloride in the presence of triethylamine as acid scavenger. It should be noted that water free conditions are essential, especially concerning solvents, in order to prevent product hydrolysis. The ^{1}H-NMR of **1** proved the structure of the product with the shift of the triplet stemming from the α-H at 2.35 ppm to 2.45 ppm which indicates the anhydride functionality. Nonetheless, a very small amount of free acid was always observed in the NMR spectra, resulting from the high-reactivity of anhydride groups towards water (vapour).

5.2.2 Polymerization Reactions

The aim of this part of the studies was the synthesis of some biodegradable polymers with ester and anhydride functionalities from fatty acid derived monomers (Scheme 5.1). Two synthetic approaches, thiol-ene and ADMET polymerizations, were applied and compared. The diester functional monomer **2** was already ADMET polymerized in our group. Reaction conditions, catalyst screening, and isomerization tendencies were discussed.[163] In this contribution, this monomer as well as the new anhydride functional monomer **1** were used in order to establish and compare the efficiency of ADMET and thiol-ene polymerization reactions for biodegradable polymer syntheses. According to our previous study, the best conditions to polymerize **2**, e.g. lowest isomerization together with highest molecular weight, was obtained with the use of 1 mol% **Zahn-1B** catalyst together with 2 mol% benzoquinone at 80 °C.



Scheme 5.1: Investigated ene and thiol monomers as well as chain-stopper 4.

Herein, these optimized conditions were used, but instead of a continuous nitrogen purge, continuous vacuum (~100 mbar) was applied in order to remove the ethylene more efficiently and obtain higher molecular weight polymers. Additionally, methyl 10-undecenoate **4** was used as a chain-stopper to see if it would be possible to synthesize telomers with ester end-groups. Moreover, these telechelic polymers would be very useful for the determination of absolute molecular weights by NMR. A set of experiments was performed with **2** in order to find the optimum amount of methyl 10-undecenoate for the aforementioned purpose and to check the effect on the resulting molecular weight. It was observed that the addition of **BQ** to the reaction resulted in higher molecular weights, slightly lower PDI values of the polymer and much lower isomerization side reactions (compare Table 5.1). Moreover, a decrease in molecular weight with increasing amount of **4** was observed, as it was expected. Inclusion of higher amounts of **4** (*entries 6 and 7, Table 5.1*) lowered the molecular weights to around 8000 and 5450 Da with PDIs of 1.92 and 2.02, respectively.

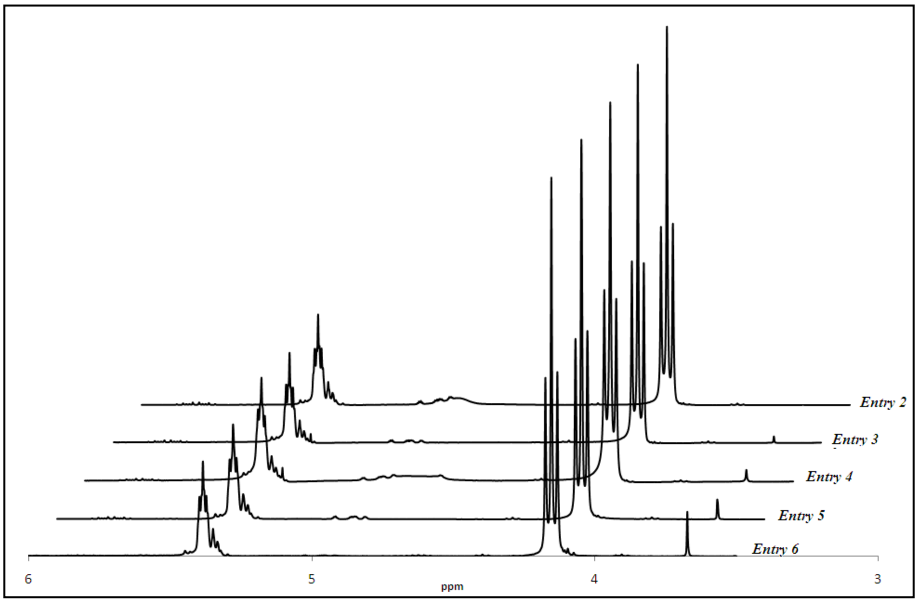


Figure 5.1: ***^{1}H-NMR spectra of polyesters derived from 2 and prepared via ADMET using different amounts of 4 as a chainstopper (Table 5.1).***

As it was already mentioned, the aim was to produce polymers with complete end-group functionalization. Thus, these polymers were investigated with ^{1}H-NMR in order to establish end-capping efficiency.

As can be clearly seen from the Figure 5.1, an increase in the amount of **4** is accompanied by an increase in the intensity of the peak at 3.6 ppm corresponding to the methyl ester functionality. With the use of 7 mmol of **4** (Table 5.1, *entry 6*), no terminal double bond peaks, which appear at 5.0 and 5.7 ppm, were observed, indicating complete capping of all end groups by **4**. Typical side-reactions of ADMET polymerizations are olefin isomerizations resulting from ruthenium hydride species that are formed *in situ* during the reaction.**Error! Bookmark not defined.** First, the study of the isomerization-uppression effect of **BQ** was conducted by setting up ADMET polymerizations of **2** with and without **BQ** under vacuum. The ADMET polymerization in the absence of **BQ** resulted in quite high isomerization (*64 %, Table 5.1, entry 1*), while the use of only 2 mmol of **BQ** (*Table 5.1, entry 5*) resulted in almost 5 times less isomerization. After having the reaction conditions in hand, the ADMET polymerization of the anhydride-functional monomer **1** was studied. Since the anhydride functionality is extremely susceptible to hydrolysis, the monomer should be freshly prepared and the solvent used to terminate the reaction and precipitate the polymer must be freshly distilled over CaH_2. For instance, it was possible to store **1** in the refrigerator under inert atmosphere without anhydride hydrolysis for only several weeks. Moreover, a faster decrease of molecular weight was observed when technical grade THF was introduced into the reaction mixture in order to terminate the polymerization reaction. GPC calculations showed that the ADMET derived polyanhydride polymer **P1** has a M_n of 9000 g/mol and PDI of 1.97 (*see* Table 5.2). Moreover, ^1H NMR analysis revealed that the optimized conditions also led to completely end-capped telechelic polymers, as shown in Figure 2. Thus we had two structurally very similar polymers in hand (**P1** and **P2**), that only differed by their connectivity (e.g. ester vs. anhydride) that would be very useful for comparative stability studies what will be discussed later.

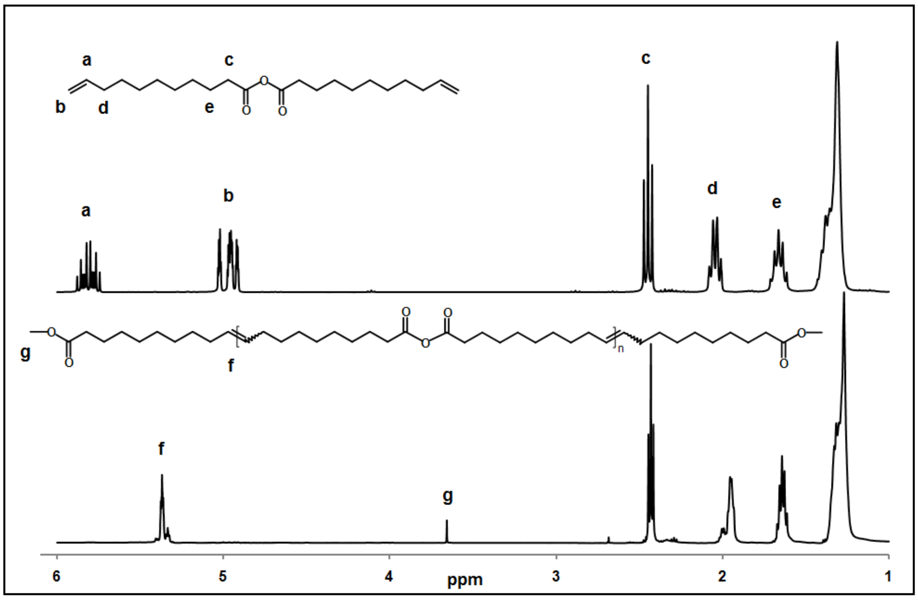


Figure 5.2: ^{1}H-NMR spectra of 1 (top) and the thereof derived polymer via ADMET P1 (bottom).

On the other hand, thiol-ene click reactions are presently used very broadly in polymer science.[190] Since monomers **1** and **2** are also perfectly suited to be polymerized *via* thiol-ene click chemistry with a dithiol, this route was investigated as an alternative and compared with the ADMET polymerization.

Although low temperatures are favourable for thiol-ene additions, when it comes to polymerizations, the reaction temperature should be elevated to avoid crystallization of the polymer during polymerization. Therefore, the reaction temperature was increased to 80 °C and carried out the polymerization reaction of **1** without initiator. GPC analysis showed that even after 6 hours only some oligomers were formed. However, an extraordinary improvement was observed with the use of a radical initiator.

Entry	**Monomer (mmol)**	**4 (mmol)**	**Zhan-1B (mmol)**	**p-BQ (mmol)**	**M_n(1h) (g/mol)***	**M_n(1h) (g/mol)****	**PDI**	**DI*****
1	**1,07**	**0,00**	**0,01**	**0,00**	**15950**	**-**	**1,67**	**64**
2	**1,05**	**0,00**	**0,01**	**0,02**	**18500**	**32750**	**1,61**	**12**
3	**1,05**	**0,01**	**0,01**	**0,02**	**17900**	**na**	**1,58**	**7**
4	**1,06**	**0,02**	**0,01**	**0,02**	**17300**	**na**	**1,57**	**12**
5	**1,06**	**0,04**	**0,01**	**0,02**	**15100**	**na**	**1,65**	**4**
6	**1,07**	**0,07**	**0,01**	**0,02**	**8050**	**19050**	**1,92**	**7**
7	**1,08**	**0,16**	**0,01**	**0,02**	**5450**	**6389**	**2,02**	**-**

*** GPC calculation results after 1 hour of reaction time. ** ^{1}H-NMR calculation results. *** GCMS calculation results of hydrolyzed polymers.(see experimental part)**

Table 5.1: Performed ADMET polymerizations of monomer 2.

Only 2.5 mol % AIBN was sufficient to obtain almost full conversion of the monomer after 1 hour; the polymerization was completed within 2 hours at these conditions. Therefore, these conditions were used for all further experiments. GPC analyses thus showed that fatty acid-based polyesters with high molecular weights could also be synthesized *via* thiol-ene polymerization (compare Figure 5.3). However, thiol-ene click polymerization was less suitable for the polymerization of **1**. The high reactivity of the anhydride functionalities towards nucleophiles, in this case thiol groups, caused the scission of either the monomer or polymer backbone *via* thioester formation, resulting in a molecular weight decrease. ^{1}H-NMR analysis (Figure 5.4) confirmed the expected structure of these polymers.

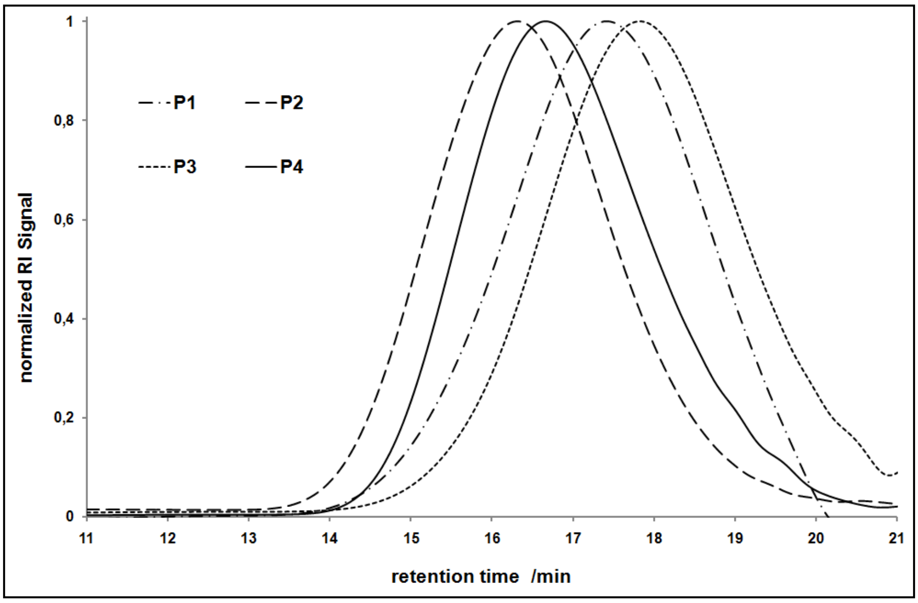


Figure 5.3: GPC of the polyesters and polyanhydrides prepared via ADMET and thiol-ene chemistry.

In addition to the expected signals of the polymer backbone, the ^{1}H NMR of **P3** also showed two triplets at 3.1 and 2.4 ppm, which were assigned to thioesters and free carboxylic acids, respectively.

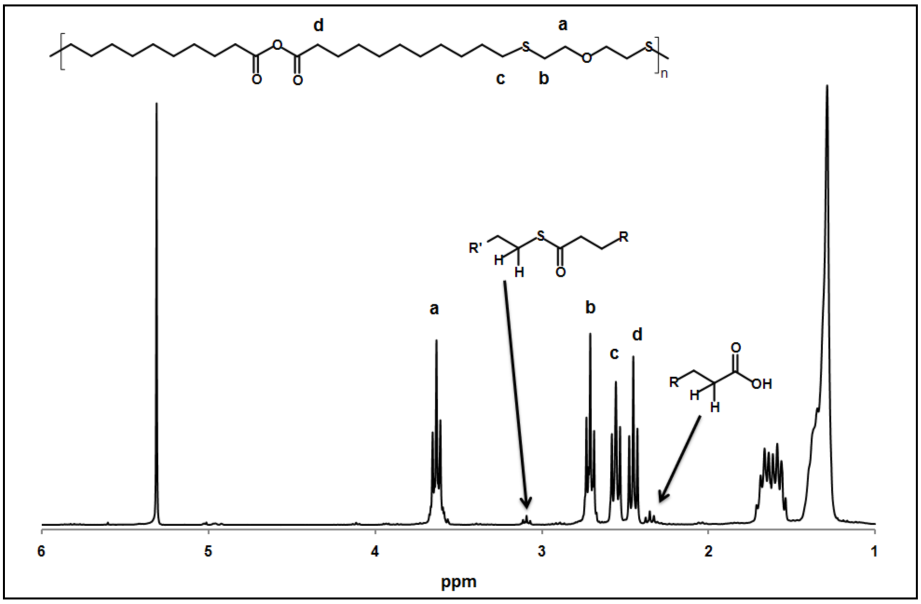


Figure 5.4: ^{1}H-NMR spectrum of P3 (the peak at 5.3 ppm stems from CH_2Cl_2 solvent).

These signals confirm the nucleophilic attack of a thiol group to an anhydride carbonyl, which prevents further polymer chain growth and limits the obtainable molecular weights. In addition, we also prepared random copolymers of **1** and **2**. Since we already had the optimized conditions in hand, we used both ADMET and thiol-ene polymerization methods. The results are summarized in Table 5.2.

5.2.3 Thermal Characterization

The thermal properties of the polymers with similar molecular weights were also analyzed by DSC. All DSC analyses were carried out under nitrogen atmosphere with a 10 °C / min heating rate (Figure 5.5).

All polymers showed single melting points, while **P2** exhibited two endotherms. In our previous report, a similar behaviour was observed for aliphatic polyesters bearing thio-ethers[241] and annealing was shown to be an efficient technique to obtain a single endotherm. If the polymer was heated within the calorimeter to a prefixed temperature and left for a sufficiently long time for the polymeric chains to rearrange, a single melting point was detected. In the present case, we applied annealing for 2 hours at 37 °C for **P2** resulting in a single melting point, which was then detected at 44 °C.

Polymer	Monomers	Polymerization Method	M_n (g/mol)*	PDI	T_m(°C)
P1	1 (4**)	ADMET	9000	1.97	57.7
P2	2 (4**)	ADMET	8300	1.90	45.2***
P3	1&3 (1:1eq)	Thiol-ene	5400	2.29	-
P4	2&3 (1:1eq)	Thiol-ene	11850	2.00	43.8
P5	1&2 (1:1eq)	ADMET	7400	1.84	44.8
P6	1&2&3 (1:1:2eq)	Thiol-ene	6650	2.01	-

*GPC calculation results. **4 was used as chain stopper in amount of 6.5 mol% per diene monomer.***Annealed at 37 °C.

Table 5.2: Summary of the properties of the investigated polymers

Both ADMET and thiol-ene products of monomer **2** exhibited similar melting temperatures, e.g. 44.7 and 43.8 °C, respectively, indicating that not the choice of polymerization method, but the structure of the monomer does have the most pronounced effect on the thermal properties of the polymer derived from this diene monomer. Only **P1** showed a somewhat higher T_m, which might be attributed to a better packing ability of the anhydride functionality present on the main chain.

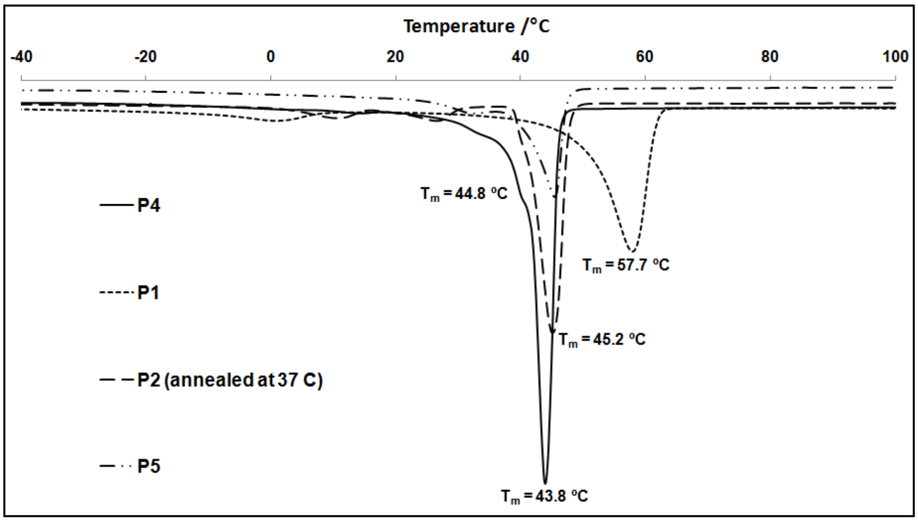


Figure 5.5: DSC thermogram of the investigated polymers.

5.2.4 Polymer Stability Essay

The stabilities of the polyanhydride and polydiester polymers that were synthesized were compared in order to gain first information on possible medical applications. Since thiol-ene polymerization does not seem to tolerate the anhydride functionality as efficiently as the ester functionality for the reasons discussed above, only the polymers that were prepared *via* ADMET polymerization were used in order to establish their stabilities. Moreover, **P1** and **P2** showed similar molecular weights and were both fully end-capped with **4**. These features are important for the comparative study in order to avoid the influence of any other parameters on the degradation, except the ester and anhydride functional groups. Three different conditions, namely only solvent (e.g. THF) as reference, acidic solution (H_2SO_4 in THF) and heterogeneous enzymatic conditions (Novozyme 435 in THF) were set at 37 °C. At each time interval a sample was taken from the reaction mixture and immediately analyzed by GPC (after dilution). The percentage of the monomer was calculated from the percent area of the thus obtained chromatograms.

The stability of a polymer towards degradation strongly depends on the chemical structure, namely the functional groups present along the backbone and their reactivity. In the present study, since the monomers and the molecular weights of the polymers used are very similar, the observed reactivity of the polymers can be directly correlated to the functional groups that they bear. In the present study, polyesters and polyanhydrides, two typical classes of polymers that are known to degrade *via* bulk and surface erosion, respectively, were compared.

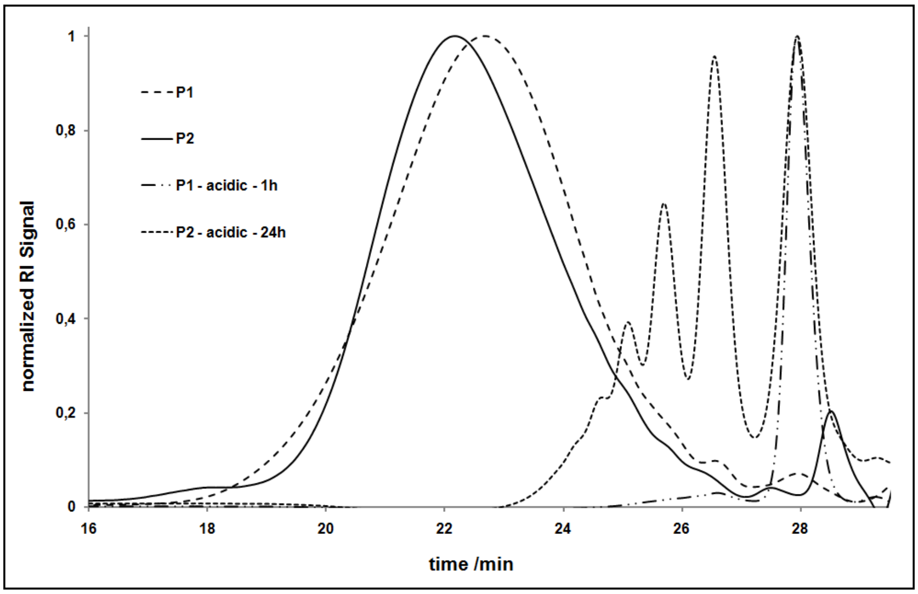


Figure 5.6: Degradation of anhydride and ester functional polymers in time under acidic conditions monitored by GPC.

For drug delivery applications, the surface erosion degradation mechanism is often preferred since it ensures a regular delivery of the loaded drug. In this case, it was clearly observed that the anhydride functional polymer was much less stable than the ester functional one (as it was expected and as it is known from other examples),[283,284,285,286] promising fast degradation in both acidic and enzymatic conditions (compare Figures 5.6 and 5.7).

It is important to note that both polymers were stable in the control experiment (pure THF solution, see Figure 5.8) allowing it to correlate the observed degradation under enzymatic and acidic conditions to the connectivity of these polymers. The fastest degradation was observed in acidic conditions, as expected. While the anhydride functional polymer degraded almost completely into the monomer within 1 hour, the ester functional polymer degraded much slower, and even after 24 hours contained only around 35% monomer (Figures 5.6

and 5.8). On the other hand, under enzymatic conditions both polymers exhibited slower degradation rates (Fig. 5.7 and 5.8), but the polyanhydride still degraded faster than the polyester. The anhydride polymer degraded to around 65 % monomer, whilst ester functional polymer to only around 10 %. All these results are summarized in Figure 5.8 and agree well with the expectations.

For applications requiring a combination of polyanhydride and polyester-type hydrolysis, e.g. faster than polyester but slower than polyanhydride, random copolymers of **1** and **2** might be a solution. Therefore, the solution stability of the copolymer **P5** was studied and directly compared to **P1** and **P2**. Figure 5.9 shows the comparison of the monomer percentages of the copolymer and the homopolymers under enzymatic conditions.

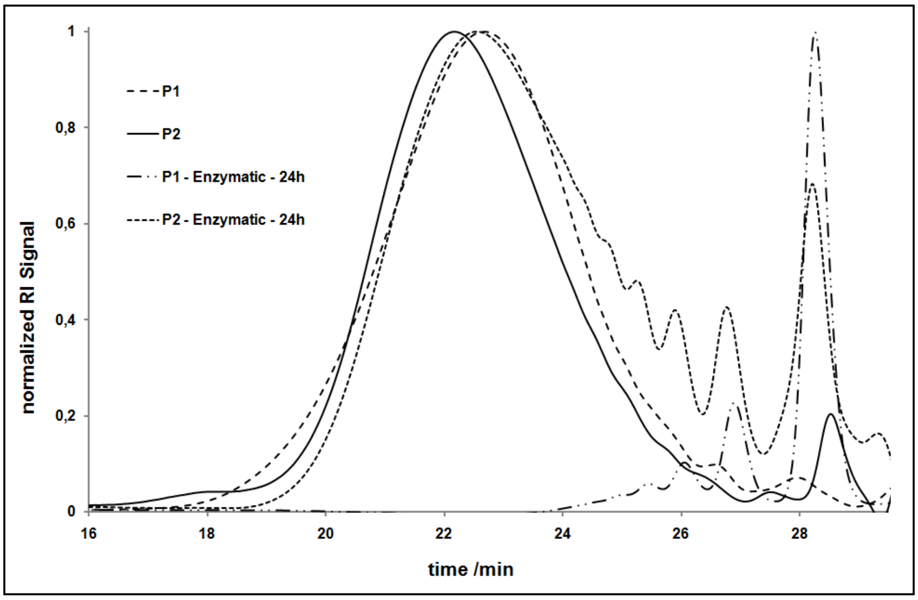


Figure 5.7: Degradation rate of anhydride and ester functional polymers in enzymatic conditions.

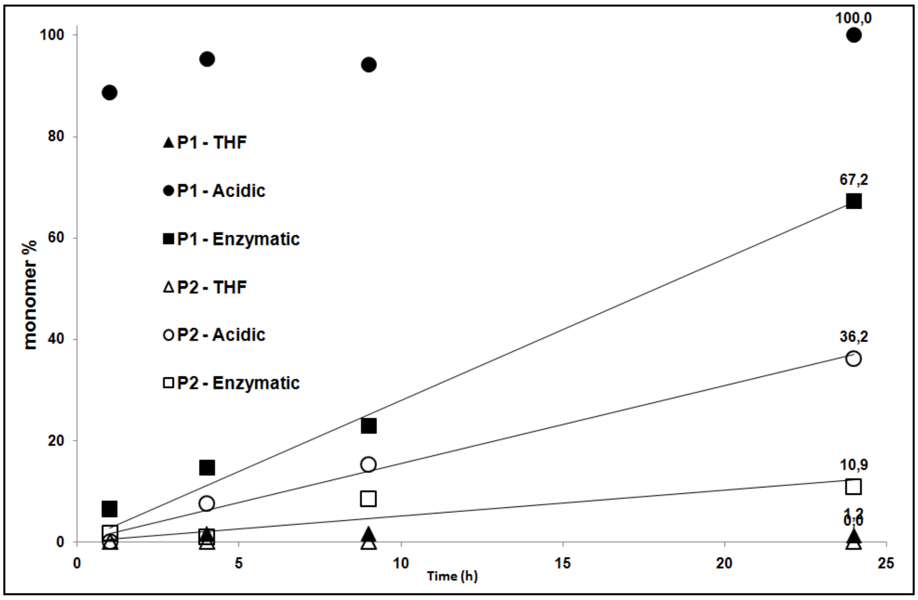


Figure 5.8: Monomer percentages in homopolymer stability essay.

It is obvious that **P1** converts into the monomer faster than **P2** and after 24 hours **P1** degraded almost completely while **P2** degraded to only 50% monomer. This result agrees well with the theory and previous results. Most importantly, the monomer percentage (and therefore the degradation) of the copolymer **P5** stays between **P1** and **P2**, revealing that it is possible to finely tune the degradation of these biopolymers by copolymerization.

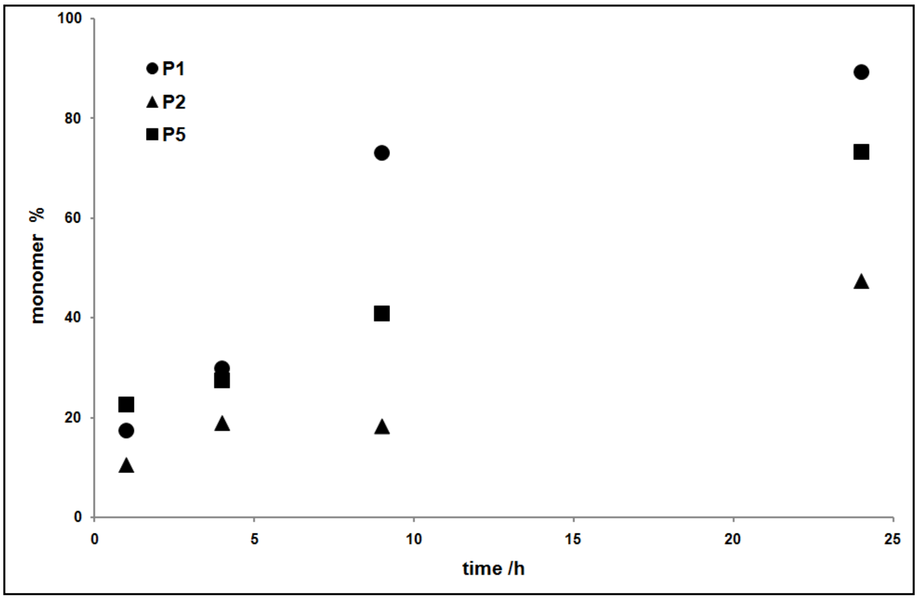


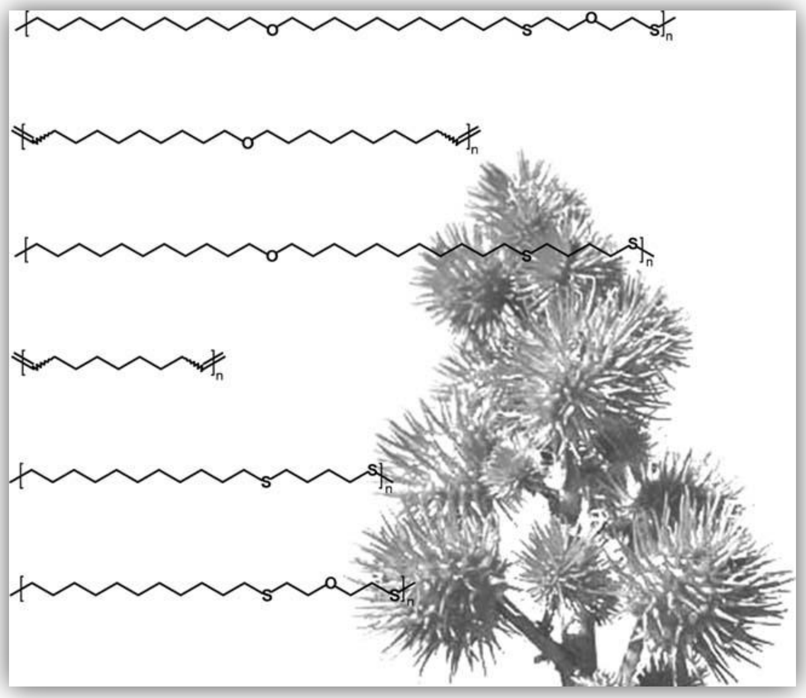
Figure 5.9: Stability comparison of the copolymer P5 with the homopolymers P1 and P2.

5.3 Conclusion

In this part of the thesis, the aim was to establish two complementary synthetic approaches to biodegradable polymers from a renewable platform chemical using thiol-ene addition reactions and ADMET polymerizations. The synthesized polymers could be used to substitute some biomedically useful polymers usually produced from petroleum originated monomers. Additionally, thiol-ene and ADMET polymerizations were studied and compared to each other. Finally, the synthesized polymers were successfully characterized in order to establish their thermal behaviour and stability to guide the possible applications. Within this contribution, it could be concluded that ADMET polymerization can tolerate both ester and anhydride functionality, but thiol-ene addition reactions, although being an efficient and environmentally benign tool, cannot tolerate the anhydride functionality too well, while the synthesis of polyesters *via* thiol-ene polymerization was more effective giving rise to high molecular weight polymers.

6

Renewable Polyethylene Mimics Derived from Castor Oil[287]



6.1 Introduction

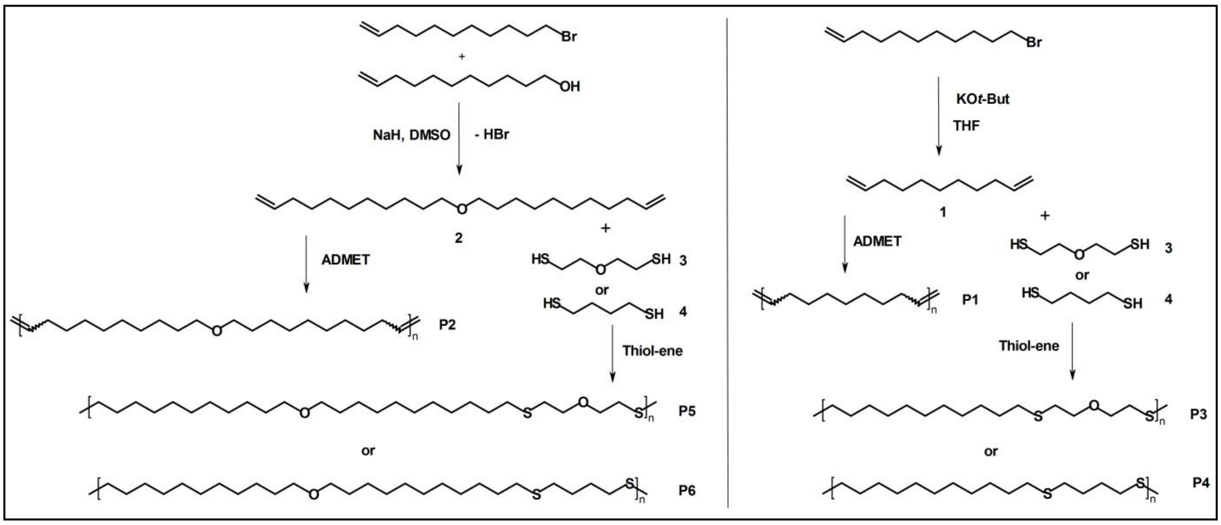
Polyethylene is the largest volume synthetic polymer produced worldwide.[288] It is produced in various forms and has acquired a large commercial market in films, sheets, pipes, fibers, containers, bottles, and many other applications. Its production relies on petroleum based ethylene gas. Depending on the polymerization process, low or high density polyethylene can be produced under high or low pressure, respectively. Moreover, the catalyst used for the production process has an effect on the macromolecular architecture of the formed polyethylene. A still important procedure for the production of polyethylene was introduced by Philips using a chromium based catalyst (Cr/SiO_2).[289] Although this system has poor control on the molecular weight distribution and in turn on the final mechanical properties, it still covers the major volume of the global polyethylene production. In the mid 50's, with the discovery of Ziegler-Natta catalysts and later on the metallocene catalysts, it was possible to achieve higher control on polydispersity indices, which are about 4 and 2, respectively.[1,290,291] In 2003, the volume of the total polyethylenes prepared *via* the Ziegler slurry process reached about 8 Mt per annum and is operated worldwide alongside the high pressure processes.[292] For all mentioned processes fully petroleum derived ethylene is being used in order to synthesize large amounts of this highly important polymer. Using these state-of-the-art production technologies, the catalyst residue remains in the final product, which is a major problem if these polymers are intended for use in food packaging or other applications. However, in some cases it is possible to partially remove the catalyst residue using a special washing procedure with butanol.[1] Therefore, alternative (also metal free) pathways to a number of renewable polymers, which could substitute this important class of polymers, are needed. Remarkably, in 2007 a Brazilian chemical company, Braskem, has launched renewable LLDPE and HDPE (200 kt production p.a. each) to be made from sugarcane ethanol.[293] On the other hand, due to their similar chemical structure to linear polyethylene chains, obviously plant oils have the highest potential among the available renewable resources (e.g. starch, cellulose, lignin, and others) to substitute this class of polymers. Linking long chain fatty acids to form monomers or polymers efficiently and selectively has already been achieved. For instance, Quinzler and Mecking reported a cobalt-catalyzed conversion of 10-undecen-1-ol into long chain polyesters in the presence of carbon monoxide.[294] Very recently, they also reported a palladium(II)-catalyzed conversion of methyl oleate and methyl erucate into long-chain diesters in the presence of carbon monoxide and methanol; polycondensation of these diesters with their corresponding diols resulted in a linear semi-crystalline polyesters with properties comparable to thermoplastic low-density polyethylene.[295] Moreover, Duchateau *et al.* have recently reported on the synthesis of renewable polyethylene like materials *via* ring opening polymerization of a renewable macrolactone.[296] On the other hand, it was shown that 10-undecenoic acid can be used to synthesize a large variety of renewable monomers and polymers.[160,161,231] Especially olefin metathesis and thiol-ene addition reactions were used as versatile tools to functionalize and polymerize derivatives of this renewable platform chemical.[7,8,266] Due to the presence of ester and/or anhydride functionalities within the monomers reported therein, the prepared polymers can be considered as biodegradable, thus differing considerably from polyethylene. Although biodegradability is sometimes a desired property due to accumulating plastic waste and some special applications require degradability (e.g. agriculture or medicine), it is not always desirable.[297] Attempts to synthesize a number of linear low density polymers with controllable morphology *via* ADMET polymerization was also reported by Wagener,[298,299] but the monomers used were not renewable.

Therefore, this chapter reports on the synthesis of new monomers from commercially available 10-undecenoic acid derivative, 11-bromo-1-undecene, and the synthesis of a number of non-biodegradable polymers derived thereof, which can be considered as renewable plant oil derived substitutes for polyethylene.

6.2 Results and Discussion

6.2.1 Synthesis of Monomers

In a starting set of experiments, diene monomers **1** and **2** were synthesized from 11-bromo-1-undecene (Scheme 6.1). 11-Bromo-1-undecene is a very useful derivative of 10-undecenoic acid, which is the pyrolysis product of castor oil and is commercially available. In order to synthesize monomer **1**, a very well-known dehydrohalogenation reaction was performed with the aid of potassium *tert*-butoxide, as a sterically hindered strong base, to favour the reaction towards elimination against substitution. After distillation at 70 °C, about 63% pure product was collected. Starting from the same compound, 11-bromo-1-undecene, monomer **2** was synthesized *via* Williamson ether synthesis.



Scheme 6.1: Investigated monomers and their preparation from castor oil derived platform chemicals (11-bromo-1-undecene and 10-undecenol).

Monomer **2** structurally differs from monomer **1** by having an ether linkage, but ethers are known as one of the most stable functional groups in organic chemistry. Therefore, the chemical inertness of polyethers can be considered similar to polyethylenes within acceptable conditions, e.g. excluding extremely acidic, basic, or oxidizing conditions.

6.1.2 Polymerization Reactions

After having both monomers in hand, their polymerization behaviour was investigated. The use of both ADMET and thiol-ene polymerization reactions with fatty acid-derived monomers to yield biodegradable polymers were well established (see chapter 5).[266] Within this study, the same polymerization chemistry was applied to the new monomers, this time, to synthesize non-biodegradable polyethylene-like polymers (Scheme 6.1).

Polymer	Monomers	Polymerization	M_n[a] (KDa)	PDI	T_c (onset, °C)	ΔT	ΔH_m (J/g)	T_m (peak temp., °C)	X_C
P1-G1	1	ADMET[c]	11.4	2.25	45.1	12.0	101.2	57.1	36
P1-G2	1	ADMET[c]	8.3	2.04	28.7	11.7	97.0	40.4	35
P2-G1	2	ADMET[c]	9.3	2.37	49.0	11.0	133.3	60.0	48
P2-G2	2	ADMET[c]	16.2	2.64	49.6	9.3	130.1	58.9	47
P3	1&3	Thiol-ene[d]	24.3	1.88	37.5	16.0	87.4	53.5	31
P4	1&4	Thiol-ene[d]	-[b]	-	64.4	15.7	116.4	80.1	42
P5	2&3	Thiol-ene[d]	17.7	2.63	47.0	13.8	113.5	60.8	41
P6	2&4	Thiol-ene[d]	-[b]	-	63.5	13.0	144.2	76.5	52
P7	1&5	Thiol-ene[e]	19.4	2.97	78.3	13.2	128.4	91.5	46

(a)GPC data; b) insoluble in THF; c) reaction conditions: 0.01 eq catalyst, 0.02 eq. benzoquinone, 100 mbar, 80 °C; d) reaction conditions: 0.05 eq AIBN, 80 °C, degassed; e) 0.05 eq DMPA, 100 °C)

Table 6.1: Summarized analytic data of the prepared polymers.

The ADMET polymerization of monomer **1** with Grubbs first (**G1**) and Grubbs second (**G2**) generation catalysts resulted in a completely fatty acid-derived unsaturated polyethylene structure. The ADMET of monomer **2** gives a backbone very similar to polyethylene, which differs only due to the presence of an ether linkage on every 20th carbon atom and unsaturated sites (Scheme 6.1). GPC analysis of these ADMET polymers was carried out in THF and the samples had to be well diluted and filtered in order to assure good solubility. The thus obtained results indicated rather similar performance of **G1** and **G2** for monomer **1**, whereas **G2** provided considerably better results for monomer **2**. Additional molecular weight data for the ADMET polymers was obtained from the ^{1}H NMR signal integration of the peaks corresponding to terminal and internal functional groups, confirming that **G2** provided better results. A molecular weight calculation was not possible in the case of **P2-G2**, since terminal double bond peaks were not detectable, thereby confirming the highest molecular weight of this polymer within the series of ADMET polymers (**P1**-**P2**, see Table 6.1). The resulting unsaturated polymers can be functionalized according to the desired application by, e.g., cross-linking, grafting onto, or chain-end functionalization. For instance, thiol-ene addition can be used in order to graft onto the double bonds[218] and this feature is especially important since grafting on polyethylene is limited by cross-linking side reactions.[300]

In order to synthesize polyethylene-like polymers, the hydrogenation of **P2-G2**, the highest molecular weight polymer of the series, was performed to obtain a saturated polymer backbone that basically resembles polyethylene. Hydrogenation was carried out in a high-pressure reactor at 65 °C under 10 bar hydrogen atmosphere and catalyzed by palladium on charcoal in toluene. ^{1}H-NMR analyses of the hydrogenated polymer (**P2-H**) showed complete double bond conversion, while the aliphatic and -O-CH_2- proton signals remained unchanged (Figure 6.1).

The monomers were also polymerized *via* thiol-ene addition polymerization, giving both polythioethers and mixed polythio/oxo-ethers (Scheme 6.1). GPC analyses showed considerably higher molecular weights for thiol-ene polymers as for ADMET polymers (see Table 6.1 and Figure 6.2), indicating a higher efficiency of thiol-ene polymerizations if compared to ADMET for these monomers.

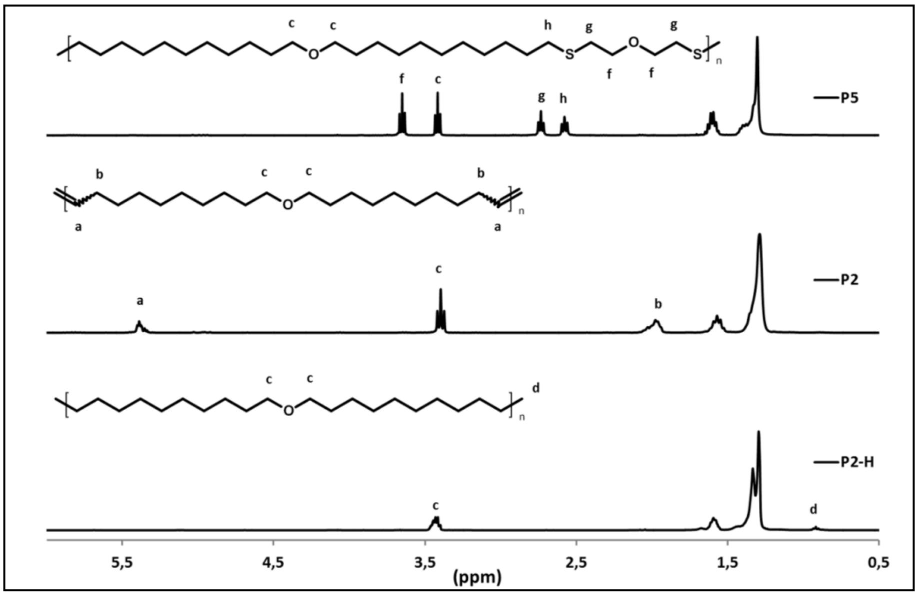


Figure 6.1: ^{1}H-NMR spectra of P5, of P2-G2 and of its hydrogenated analogue P2-H.

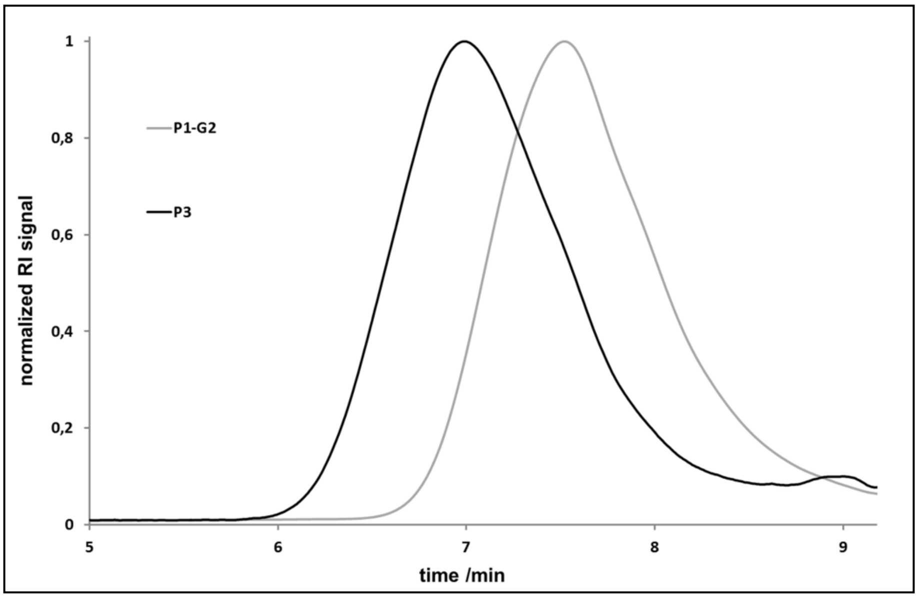
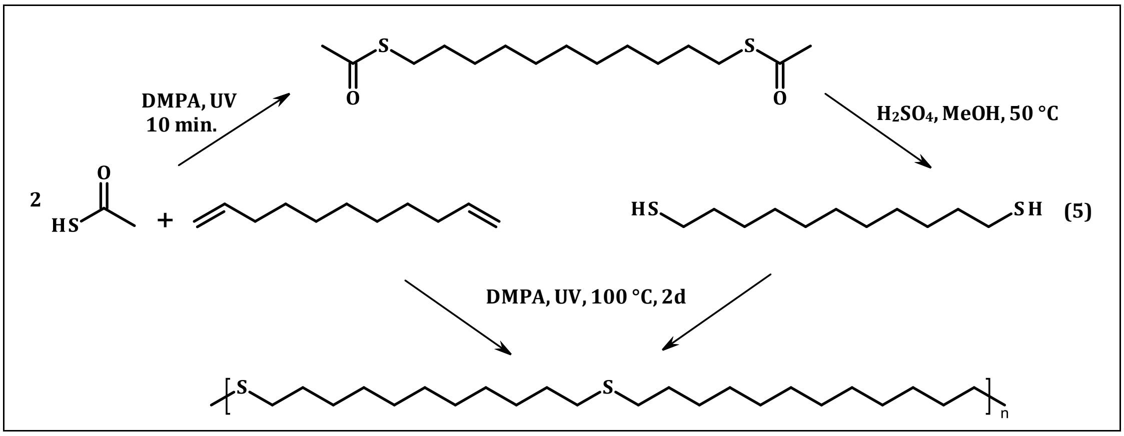


Figure 6.2: Comparison of the GPC traces of the ADMET (P1-G2) and thiol-ene (P3) polymers derived from monomer 1.

It is important to mention that copolymerization of dithiol **4,** which leads to a polymer backbone most comparable to polyethylene, resulted in THF insoluble polymers, and thus GPC analysis of **P4** and **P6** was not possible. Therefore, using dithiol **3** as a monomer and model compound for these reactions was considered, since these polymerizations resulted in soluble polymers (**P3** and **P5**), most likely due to the presence of more hetero-atoms. Assuming that **4** behaves similar to **3** in these copolymerizations and also considering that **P4** and **P6** were completely insoluble in THF and very badly soluble in $CHCl_3$, it can thus be assumed that we obtained similarly high (or even higher) molecular weight with **4**, if compared with **3**. Since these polymers (**P3**-**P6**) do not contain any unsaturation, it is not necessary to carry out an additional hydrogenation step and even more importantly, the polymer is produced under completely metal free conditions. ^{1}H-NMR analysis of the polymer **P5** clearly shows almost complete conversion of double bonds and reveals the corresponding thio/oxo ether functionalities (Figure 6.1).

6.1.3 Synthesis of Fully Renewable Thiol-ene Polymer

In the thiol-ene addition polymerizations, so far, **3** and **4** were used as the dithiol compounds that are commercially available and petroleum-based. In the previous section, it was shown that the thiol-ene addition reaction exhibits superior properties comparing to ADMET polymerization by means of molecular weight and solubility. However, the use of non-renewable dithiol compounds makes these polymers only partially renewable. In order to obtain a fully renewable polymer, which has not yet been reported for thiol-ene polymers, a fully bio-based dithiol compound was prepared from **1**. Thiol groups were introduced *via* the addition of 2 equivalents of thioacetic acid to **1** and subsequent methanolysis, which yielded 1,11-undecanedithiol (**5**, Scheme 6.2). This compound was later polymerized with **1** either with AIBN or with DMPA under UV irradiation at 100 °C (**P7**, Table 6.1). GPC analysis showed that UV-initiated polymerization yielded a polymer with a molecular weight number of c.a. 20 KDa, which is higher than that of the AIBN-initiated reaction. Moreover, **P7** exhibited very poor solubility in boiling chloroform and THF. GPC runs with THF were carried out *via* slightly heating the sample with very low concentration untill a clear solution was obtained and immediately submitting it for GPC analyses before the reprecipitation started.



Scheme 6.2: Synthesis of a fully renewable dithiol compound and polymer thereof.

6.1.4 Thermal Characterization

The thermal properties of the polymers were evaluated by means of DSC (Table 6.1). Considering the molecular weights and structures, we prefered to compare ADMET (Figure 6.3) and thiol-ene polymers (Figure 6.4) separately. In the case of ADMET polymers, melting exotherms of 38 °C for **P1-G2** (the lowest molecular weight polymer) and around 57 - 61 °C for the other polymers were observed.

After hydrogenation of polymer **P2** the T_m shifted from 61 to 73 °C. In the case of thiol-ene polymers, higher melting points were observed, ranging from 53 to 80 °C. The additional ether function in monomer **2** did not exhibit any pronounced effect. On the other hand, if dithiol **3** was used instead of dithiol **4**, somewhat lower melting points were observed.

Regarding practical aspects, the rate of crystallization is an important parameter in polymer fabrication operations such as spinning, extrusion, compression, injection molding, and processing of clear films.[301] The degree of supercooling ($\Delta T = T_m - T_{c,onset}$) is a thermal parameter used to compare the crystallization rate of polymers with similar structures. In general, a decrease in ΔT indicates a higher crystallization rate.[300]

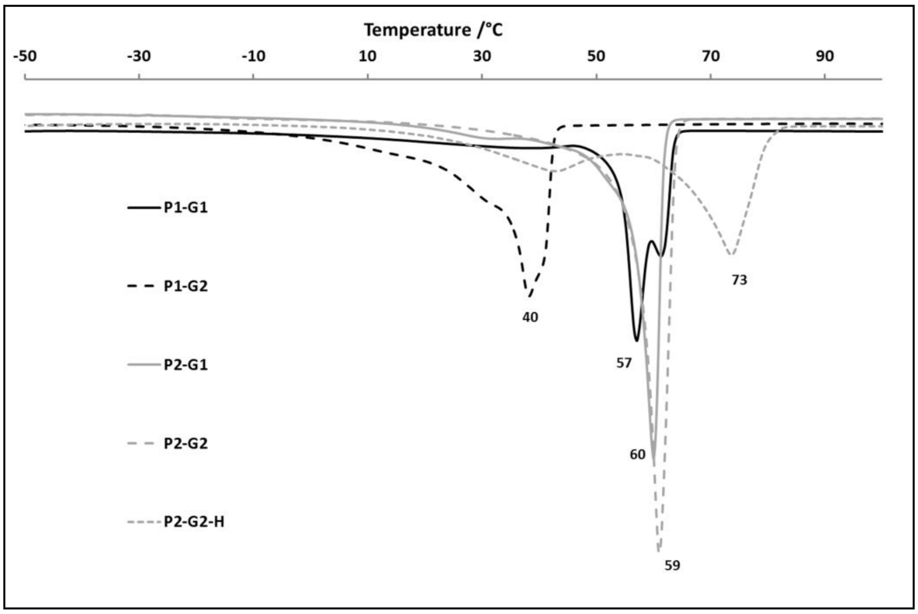


Figure 6.3: DSC analysis of ADMET polymers.

The ΔT values of ADMET polymers (**P1** and **P2**), which are between 8 and 12, are found to be lower than the ones of thiol-ene polymers (**P3**-**P6**), which are between 13 and 16. These results can probably be attributed to the higher molecular weight and saturated nature of polymers **P3**-**P6**. The melting enthalpies (**ΔH_m**) and degrees of crystallization (X_c, see Table 6.1) of these polymers were also calculated.

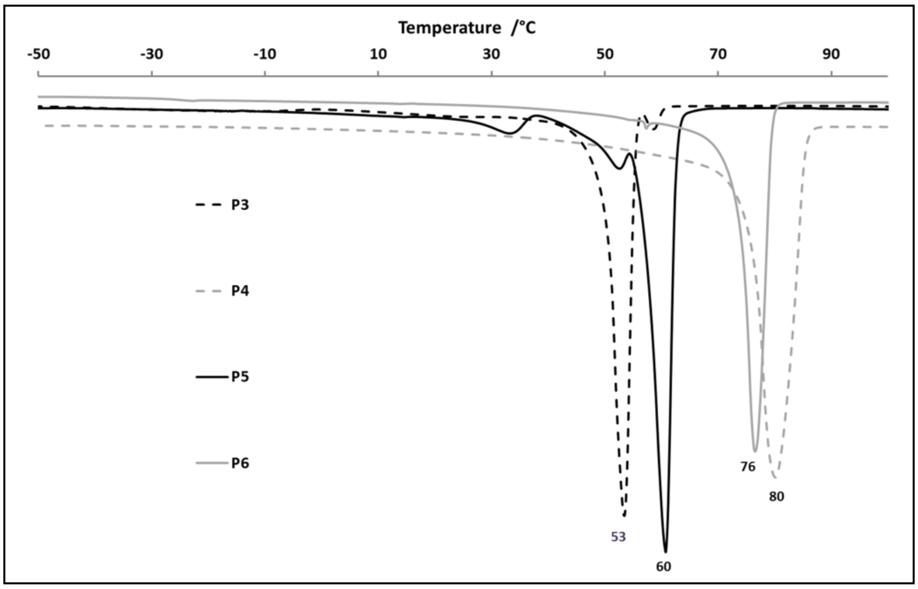


Figure 6.4: DSC analysis of the thiol-ene polymers.

Excluding **P3**, all other polymers showed **ΔH_m** between 101 and 144 J/g and X_c values between 36 and 52, which are higher than reported for LLDPE in the literature.[300] Interestingly, after the hydrogenation reaction of **P2**, one would expect that the resulting saturated structure should show higher crystallinity and melting exotherm. However, in this case, it was observed an increase of the melting point of about 20 °C as expected, but a decrease of about 30 J/g of the enthalpy of melting. Finally, the DSC analyses of **P7** revealed a higher melting temperature than for the other thiol-ene-derived polymers. This result can very likely be ascribed to the more regular structure, e.g. equally distributed 11C-chain between sulphide ether units, which was not the case for **P3-6**.

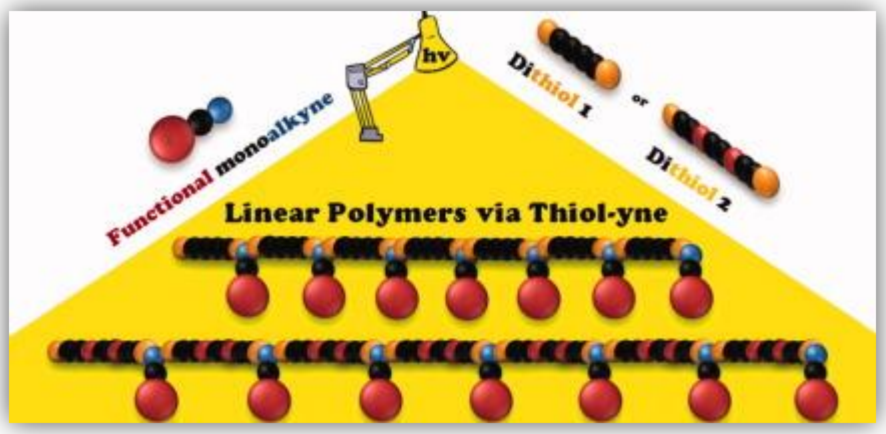
When the thermal properties of the all polymers prepared are overlooked, it can be seen that the melting temperature range remains still beyond those of commercial PEs. However, this new class of renewable polymers can still be used to substitute some other petroleum-derived materials, such as polyethylene paraffins.

6.3 Conclusion

Within this part of the thesis, a number of polymers that are polyethylene-like considering their chemical structure from renewable platform chemicals using thiol-ene addition as well as ADMET polymerization reactions were synthesized, which might be used to substitute polymers from petroleum originated monomers. The synthesized polymers were successfully characterized and their thermal behaviour was established in order to guide towards the possible applications. Importantly, a renewable dithiol compound was prepared for the first time from a derivative of 10-undecenoic acid *via* thiol-ene addition and it was used for the thiol-ene polyaddition, yielding a fully renewable thiol-ene polymer with good thermal properties. These results revealed that the thiol-ene addition reaction is a very useful method for the synthesis of renewable and metal-free polyethylene mimics under mild conditions.

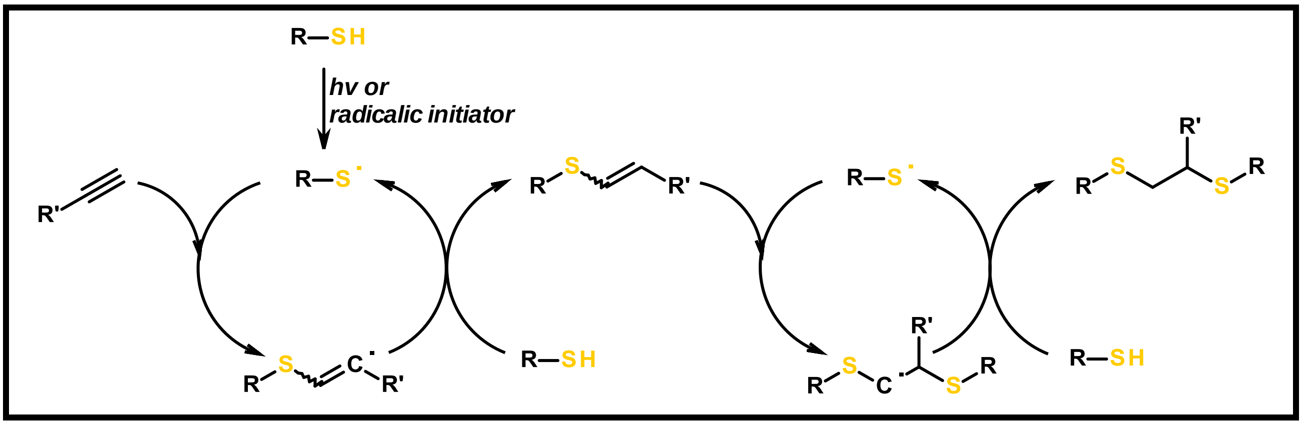
7

A Novel Polymerization Approach *via* Thiol-yne Addition[302]



7.1 Introduction

Thiol-ene addition reactions are known for more than a century.[168] Moreover, a patent concerning the polymerization of dithiols and dialkenes *via* radical additions dates back to 1941.[303] The reaction is well known to proceed *via* a radical mechanism.[169,304] Generally, radical reactions are known to be quite fast reactions and thiol-ene additions offer some additional features such as robustness, efficiency, and orthogonality, which have made this reaction to be considered as one of the click reactions and very popular during the last years.[190,305,306,307] Although, the efficiency of this reaction requires the unsaturation to be in terminal position and strongly depends on the thiol compound used,[308] it has been successfully applied for a large number of end- & side-group functionalizations,[309,310] dendrimer synthesis,[190,311] coupling reactions[312] as well as for the polymerization of *α,ω*-diene compounds with dithiols.[266] The propagation step of this reaction is the addition of a thiyl radical to a C=C double bond and the subsequent abstraction of a hydrogen atom by the formed carbon radical from another thiol compound, forming a new thiyl radical. The formation of the carbon radical is reversible and the rate-determining step, which is the explanation of the low reactivity of internal alkenes.[181] Noteworthy, this reaction is not limited to alkenes, but alkyne compounds can also be used. Hence, thiol-yne addition, with the ability of an acetylene group to add two thiols rapidly without any metallic catalyst, is addressed to be a powerful tool for creating highly functional polymers (Scheme 7.1).[313]



Scheme 7.1: The reaction mechanism of a thiol-yne addition reaction.[320]

Thiol-yne addition reactions have also become a very popular and useful synthetic method in polymer science for the synthesis of dendrimers,[314] hyperbranched polymers,[315] gels,[316] as well as for post functionalization of readily synthesized polymers with desired functional groups.[317] Moreover, this efficient functionalization reaction was also applied for microprinting,[318] the synthesis of lipid mimetics,[319] and reactions on solid surfaces.[320] The thiol addition to unsaturations can proceed not only *via* radical, but also nucleophilic mechanisms and both reaction routes are currently exploited,[321,322] although the number of radical reactions applied dominates.

The mechanism of a thiol-ene addition reaction also counts for thiol-yne additions, but an additional propagation cycle is operative. From the first cycle a vinyl sulfide adduct is formed, which then undergoes a second thiol addition to give the final product. Therefore, a full addition reaction consists of the consecutive addition of 2 equivalents thiol to an alkyne (Scheme 7.1). Kinetic investigations of the UV initiated radical addition of thiols to various alkynes revealed that the second addition proceeds approximately three times faster than the first addition.[323] Hence, the rate of the overall addition reaction strongly depends on the alkyne structure. In contrast to thiol-ene additions, the structure of the thiol compound does not have a pronounced effect on thiol-yne additions. Studies described in the literature reveal a reactivity order of alkynes as follows: 1-octyne > propargyl acetate > methyl propargyl ether > 2-octyne >> ethyl propiolate, methyl propargyl amine.[324]

Recently, Liu *et al*. reported a new type of click polymerization technique using thiol-yne additions. Rh catalyzed alkyne polyhydrothiolations of diynes and dithiols resulted in polymerization of aromatic diacetylene and dithiol compounds to form poly(vinylene sulfide)s that are a new member of the family of conjugated polymers. The results revealed that with engineering control on the sequential addition of monomers during the polymerization process and postmanipulation by light irradiation, the authors were able to control the structure of the final polymers.[318] Konkolewicz *et al*. polymerized a compound bearing an alkyne and a thiol *via* UV initiation to give a hyperbranched polymer. The reactions were carried out at room temperature and over 95% yield was reached in less than 2 hours.[325] Very recently, Han *et al*. combined thiol-ene and -yne addition reactions for the synthesis of hyperbranched polymers *via* an A_2 + CB_2 approach, where A_2 represented a dithiol and CB_2 represented propargyl acrylate compounds. Michael addition of a dithiol to propargyl acrylate was carried out to synthesize an AB_2 type intermediate. Subsequently, thermally-initiated thiol-yne polymerization of this intermediate led to a hyperbranched polymers with peripheral alkyne groups.[326] Moreover, a series of network polymers was synthesized by rapid step-growth radical mediated thiol-yne photopolymerization process from multifunctional alkynes and thiols.[327]

In all above mentioned literature examples, the thiol-yne addition reaction is used either for the synthesis of cross-linked structures, the synthesis of hyperbranched polymers, or a number of post-functionalization protocols. To our knowledge, the use of this reaction for the synthesis of linear polymers bearing different side-chain functionalities that are precisely located on the main chain was not yet reported. Therefore, within this chapter, a novel and simple step-growth polymerization approach to yield well defined linear polymers *via* the addition reaction of terminal monoalkynes with dithiols is reported.

7.2 Results and Discussion

7.2.1 Model Reaction

The investigations were started by studying the addition of 1-octanethiol to 1-octyne (**1**) under different conditions that are applicable for polymer synthesis in order to optimize the conditions and develop an understanding of the reaction. Thus, we performed the mentioned reaction without any initiator, with AIBN (thermally-activated radical initiator), and with DMPA (UV-activated radical initiator). The alkyne:thiol ratio was kept 1:2. These reactions were followed by GC and the results of these first investigations are summarized in Figure 7.1. These GC results revealed that thiol-yne addition reaction proceeded very well with all types of initiations. Self-initiated reactions yielded about 67 and 71% final product after 1 and 2 hours reaction time, respectively. However, in the case of AIBN initiated reactions, about 90% final product was obtained after 2 hours, which is clearly higher than in the case of self-initiation. Finally, the UV initiated reaction gave the highest conversion and completed in less than 2 hours. These results exhibit the same trend as known for thiol-ene addition reactions that are also known to proceed best *via* UV initiation.[328] It is worth to mention that the theoretically possible formation of disulfides was, if at all, only detected in trace amounts (< 0.5%). This result strongly confirms that thiyl radicals preferentially add to an unsaturation and coupling to another thiyl radical is far less likely.[255]

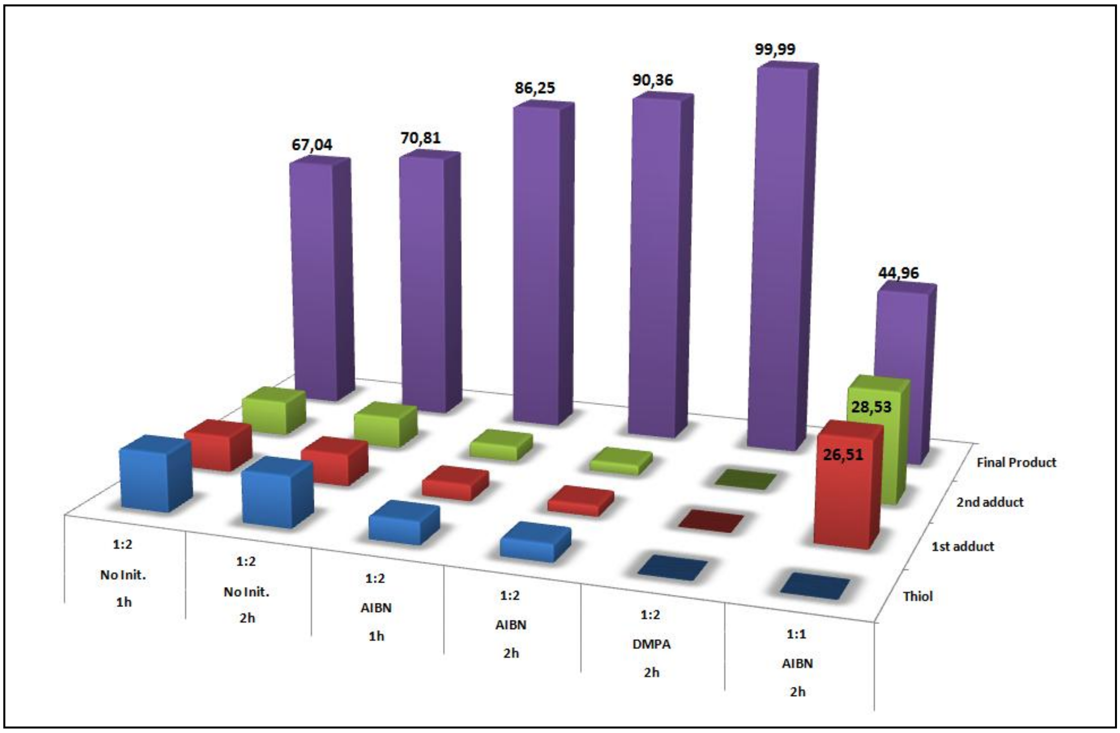
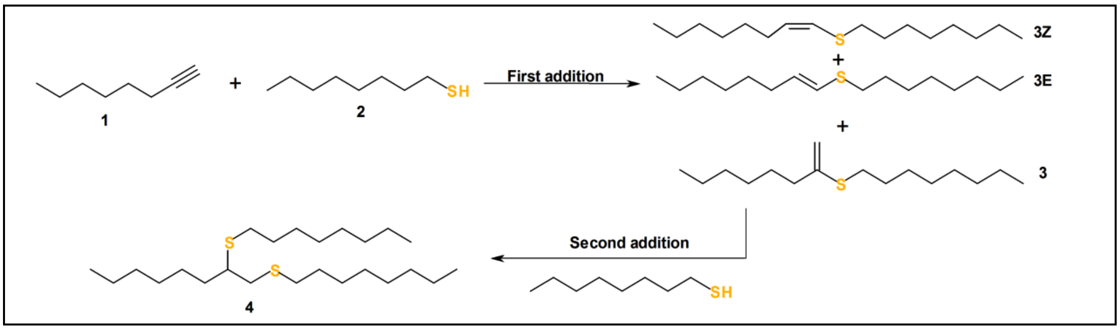


Figure 7.1: GC calculation results of the model reactions.

Apart from the final product, two other compounds were detected on GC and GC-MS chromatograms. In a typical thiol-yne addition, with addition of the first thiol compound to an alkyne, theoretically three different vinyl sulfide species can form. The structures of these intermediate vinyl sulfide species are illustrated in Scheme 7.2. Subsequently, a second thiol compound is added to one of the *in situ* formed vinyl sulfide species, resulting in a single final product.



Scheme 7.2: Reaction scheme of the model reaction.

Our monitoring by GC revealed that only two of the three possible adducts were detected. From a thermodynamic point of view, one could expect that **3E** and **3Z** form preferably, if compared to **3** and that the trans isomer **3Z** is formed in higher amounts than **3E**. In order to prove this, another control reaction was carried out with an alkyne:thiol ratio of 1:1 in order to obtain these intermediate isomers in higher amounts for further analysis. The structures of the intermediate products formed during this model reaction were thus studied by ^{1}H-, ^{13}C-, and HMQC NMR. In the ^{13}C-NMR spectrum, (Figure 7.2) the four peaks observed between 120 and 140 ppm were attributed to the vinylic carbons of **3E** and **3Z**.

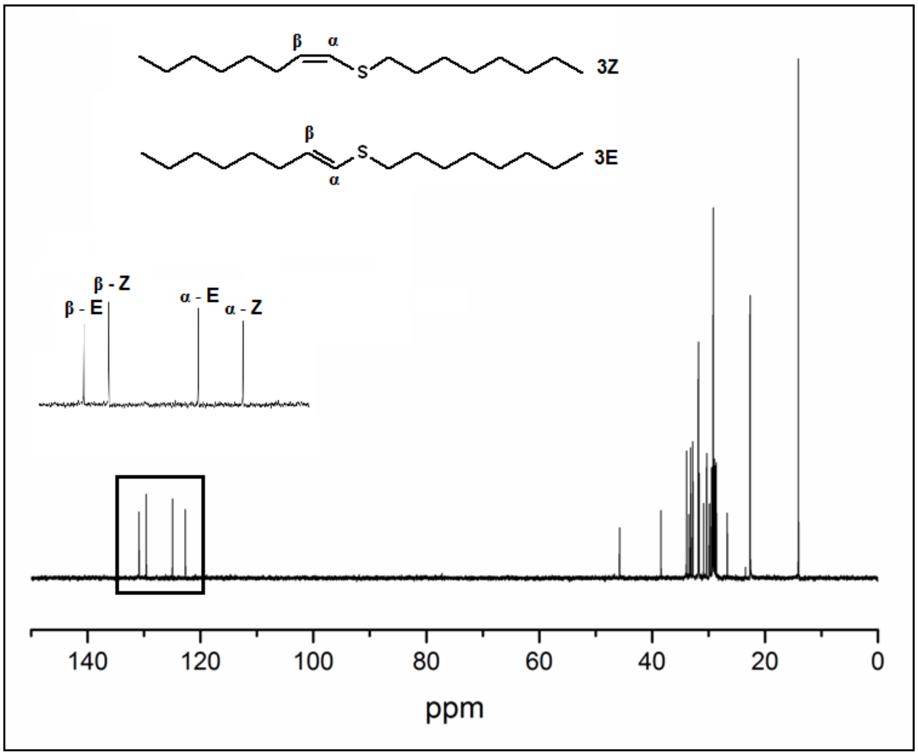


Figure 7.2: 13C-NMR spectrum of the model reaction.

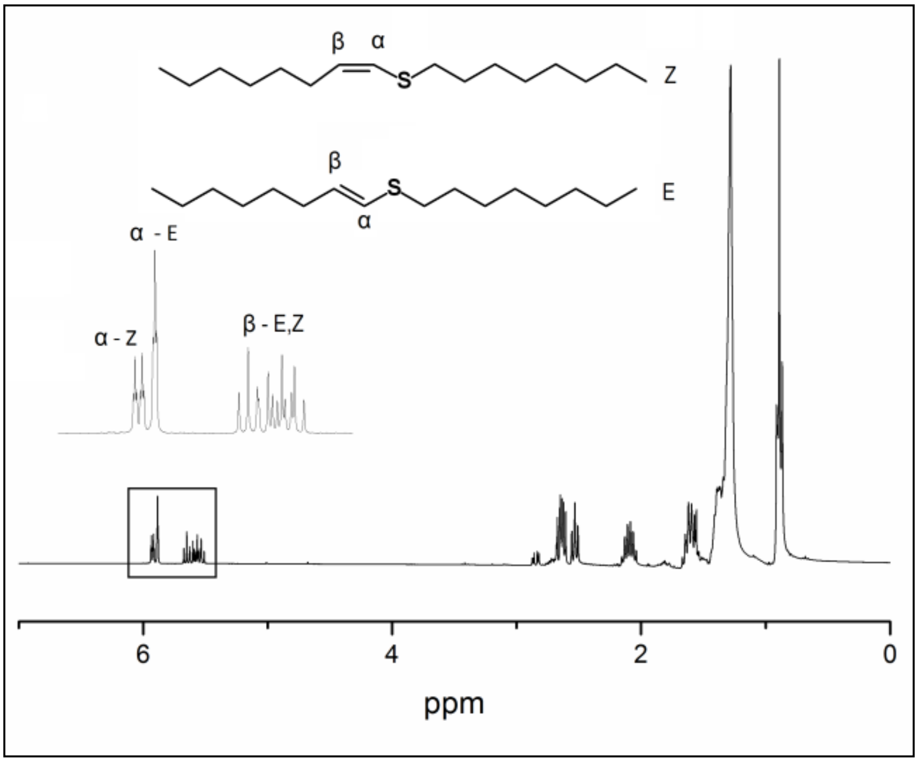


Figure 7.3: 1H-NMR spectrum of the model reaction.

Any other terminal vinylic carbon peak was not observed by ^{13}C-NMR. Additionally, the ^{1}H-NMR spectrum of the same reaction (Figure 7.3) revealed a doublet of a triplet at 5.93 ppm and a multiplet between 5.90 – 5.87 ppm, which were attributed to **3Z** and **3E**, respectively. From the same spectra, the **Z/E** ratio was calculated as 0.44:0.56, which also agrees with GC results (Figure 7.1, 1:1 eq. with AIBN). In order to support our NMR interpretation, we also studied the HMQC spectrum of the same mixture (Figure 7.4). The cross-peaks of this spectrum clearly reveal the correlation between the β-carbon and -hydrogen atoms and α-carbon and -hydrogen atoms. These results agree well with the thermodynamic expectations and the literature.[320]

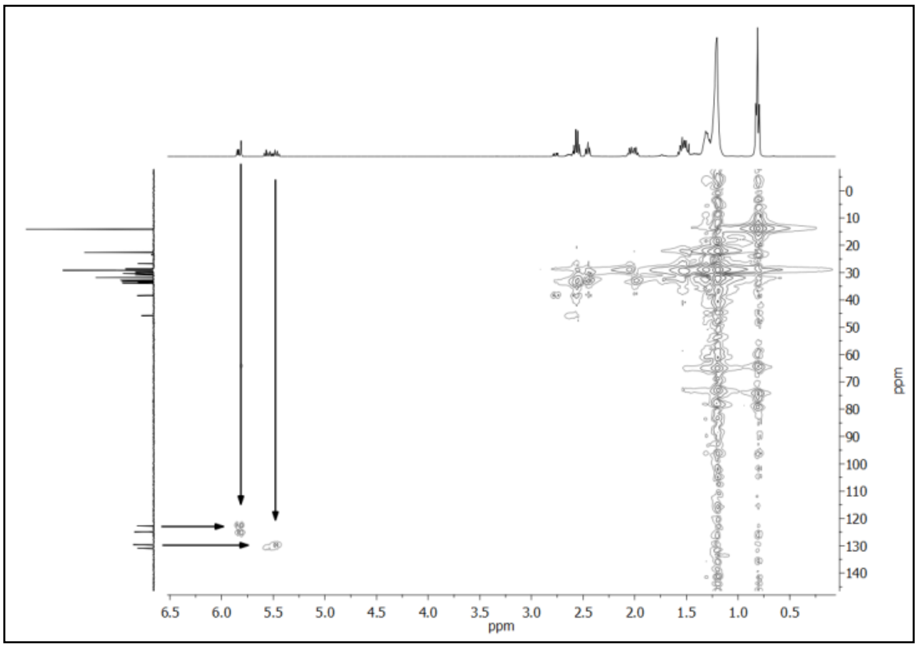
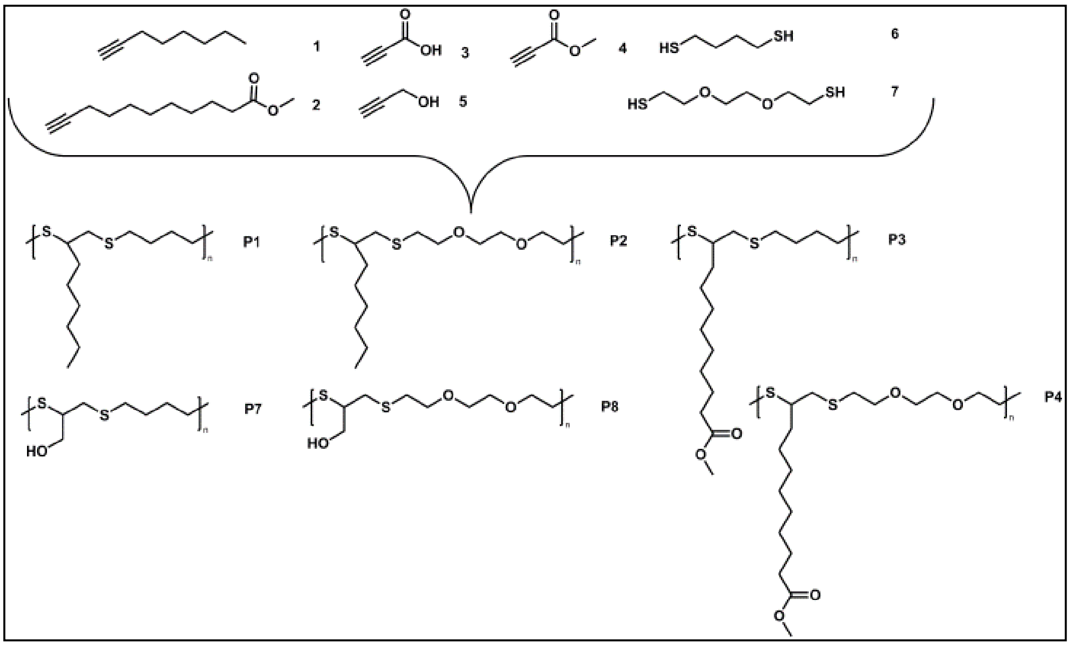


Figure 7.4: HMQC spectrum of the model reaction.

7.2.2 Polymerization Reactions

Having established the optimized reaction conditions, the same polymerization route was applied to a number of alkyne monomers with different functional groups: alcohol, carboxylic acid (or methyl ester), aliphatic chain (with and without methyl ester end group), whose frequency can very precisely be tuned with the choice of the corresponding dithiol compound (Figure 7.3). Since a difunctional thiol compound is used for these reactions, polymerization should occur in a step-growth fashion and polymers as depicted in Figure 7.3 should be obtained. In the aforementioned model reaction, 1-octyne (**1**) and 1-octanethiol were used and it was possible to show that the highest conversion to the final product was achieved *via* UV initiation, whereas thermally- and self- initiated reactions exhibited also good results. Therefore, the same conditions were applied to the polymerization between **1** and 1,4-butanedithiol (**6**) in order to see if the same trend in the case of polymerization would be observed. The second screening was found to be of importance, since optimal conditions resulting in high functional group conversions are known to be essential for molecular weight build up in step-growth polymerizations.



Scheme 7.3: General scheme of the polymerization reactions and the functional groups employed.

Although the polymerization between **1** and **6** proceeded without initiator (Figure 7.5), the completion of the reaction took rather long. The addition of AIBN to the reaction improved the polymerization rate and resulted in higher molecular weight after 8 hours reaction time

(Figure 7.6). However, with the aid of UV-initiation, the polymerization completed in only 2 hours and higher molecular weight was achieved (Figure 7.7). The same trend was observed with the use of 3,6-dioxa-1,8-octane-dithiol (**7**) (Figure 7.7). Therefore, it was concluded that UV-initiated thiol-yne polymerization is the most efficient polymerization procedure of our investigated reactions and the same conditions were thus further applied to the polymerization of other alkyne monomers.

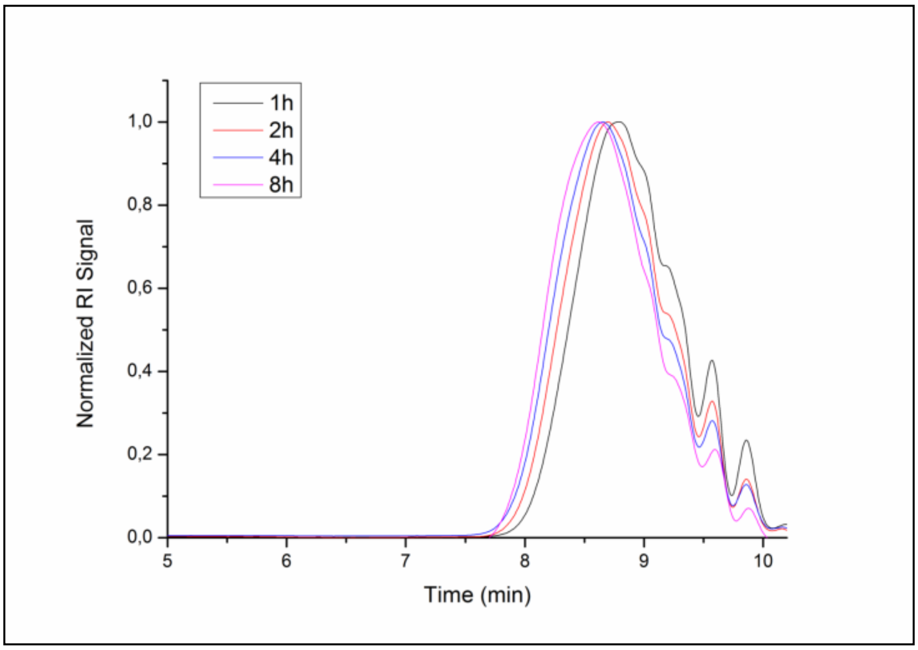


Figure 7.5: GPC traces of P1 obtained without initiator.

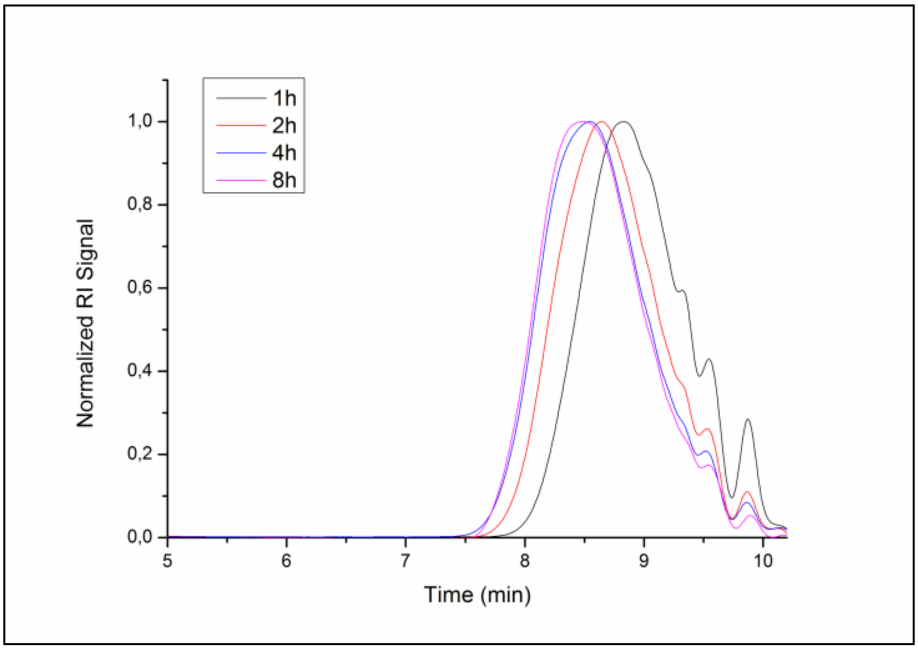


Figure 7.6: GPC traces of P1 obtained with AIBN initiation.

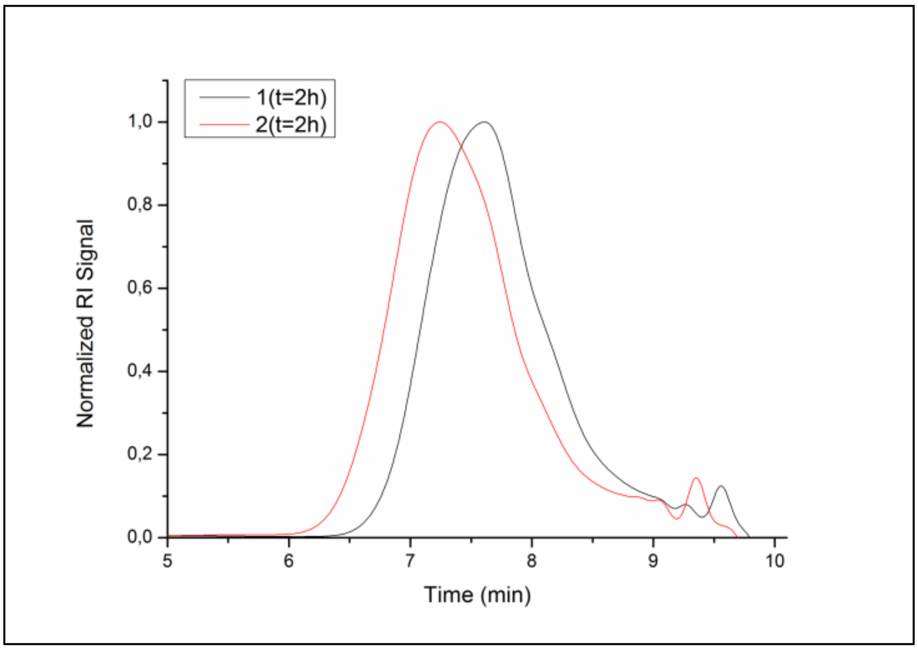


Figure 7.7 GPC traces of P1 and P2 obtained via UV initated polymerization after 2 hours reaction time.

The second alkyne monomer employed was methyl 10-undecynoate (**2**); the same polymerization method was applied using **6** and **7** as dithiols. As it can be seen from the GPC chromatogram (Figure 7.8), the UV-initiated polymerization proceeded very well and GPC chromatograms of the reaction samples after 2 and 5 hours were identical, revealing completion of the polymerization within 2 hours reaction time.

Polymer	Alkyne	Dithiol	M_n (kDa)	PDI
P1	1	6	10,5	1,68
P2	1	7	27,8	1,76
P3	2	6	11,2	2,04
P4	2	7	18,1	2,16
P5	3	7	n.a.	n.a.
P6	4	6	n.a.	n.a.
P7	5	6	5,3	1,96
P8	5	7	7,8	2,22

Table 7.1: Polymer compositions and molecular weight data.

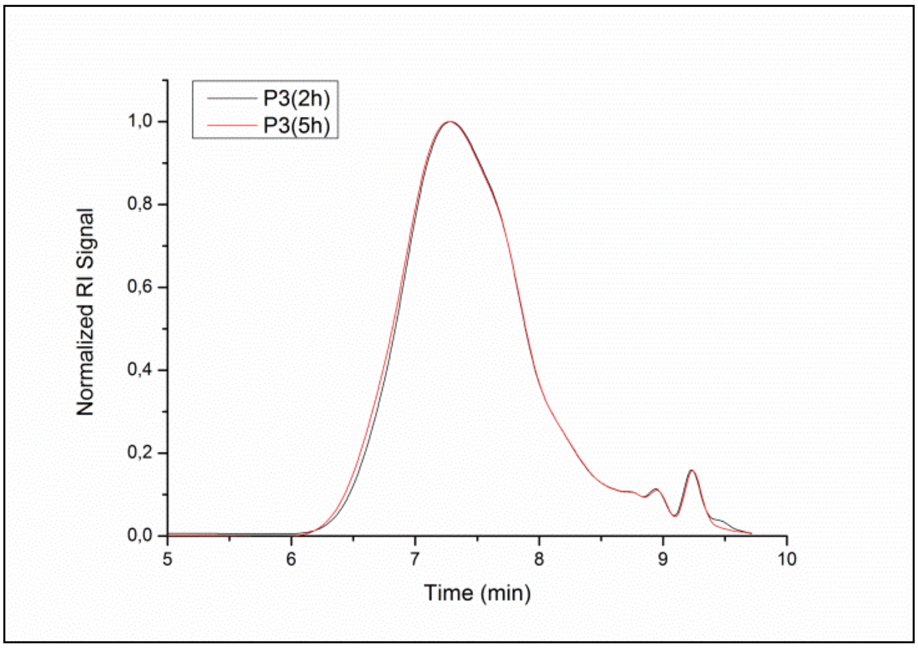


Figure 7.8: GPC traces of P3 after 2 and 5 hours reaction times.

The polymers synthesized till this point had long aliphatic side-chains with and without an ester functionality at the chain-end. Next, it was desired to polymerize propargylic acid (**3**) and its methyl ester (**4**). The polymerization of **3** with **7** was not successful *via* thermal-initiation or *via* UV-initiation. Even after 5 hours of irradiation, only some oligomers were formed (Figure 7.9). In order to see if the free carboxylic acid would have any effect on the thiol-yne polymerization, the polymerization of **4** with **6** (**P6**) was also tested. Unfortunately, this polymerization was not successful either. However, these results are not too surprising since Fairbanks *et al*. already reported the lower reactivity of ethyl propargylate against thiol addition.[316] The kinetic studies revealed that a propargyl group could only accept one thiol compound and the consecutive second thiol addition did not take place. However, the present polymerization reactions, it was observed that some oligomers had formed (Figure 7.9). This means the second addition has to proceed to a certain extent, since otherwise oligomerization should not have been observed. Especially **P5** seemed to be more promising comparing to **P6**. Fairbanks *et al*. tried to find an explanation for this lower reactivity of propargylates and tried to perform this reaction using methyl propargyl amine, which was supposed to increase the density of π electrons and increase the reactivity. However, also this reaction did not work, invalidating the hypothesis and this phenomenon remained unclear.

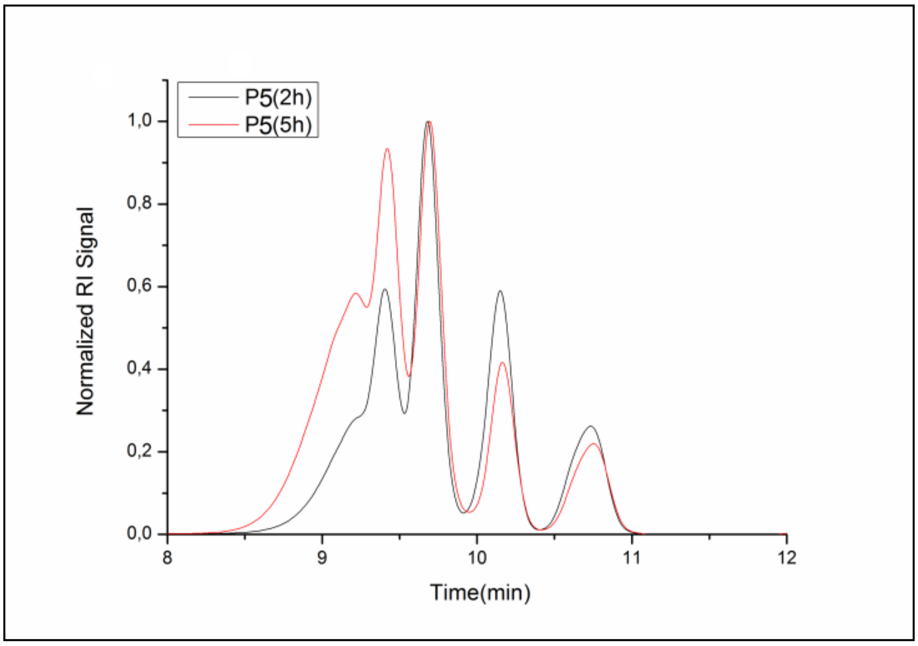


Figure 7.9: GPC traces of P5 after 2 and 5 hours reaction times.

Applying the same chemistry to propargyl alcohol (**5**), a polyalcohol was synthesized with both **6** and **7** *via* UV-initiation (Figure 7.10). These polymerizations also proceeded successfully and completed in 2 hours. It should be noted that this reaction is a very simple and versatile synthetic route to polyvinyl alcohol analogues, in which the frequency of the alcohol functionalities can be easily tuned with the dithiol selection. It is also important to mention that, due to the high hydroxyl group density in the polymer, this polymer is highly viscous and very hard to dissolve in common organic solvents. Therefore, a very small amount of monomer (<5%) remained in the polymer. The relatively lower molecular weight of **P7** and **P8**, which are 5,3 and 5,8 kDa, respectively, could be attributed to this fact (Table 7.1).

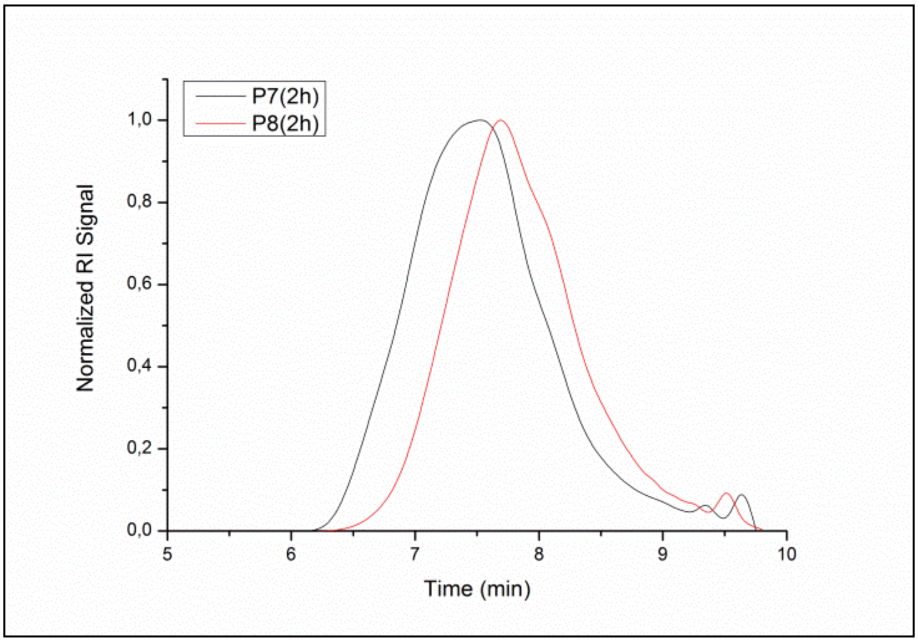


Figure 7.10: GPC traces of P7 and P8 after 2h reaction time.

Apart from the already discussed GPC results, NMR analysis of all prepared polymers was in full agreement with the expected polymer structures.

7.3 Conclusion

This chapter clearly shows the success of UV-initiation for the polymerization of a monoalkyne and a dithiol compound, though this reaction can also proceed *via* self-initiation or be thermally initiated. Thus, a new polymerization method for the convenient and versatile synthesis of linear polymers with various side groups *via* a step-growth procedure was introduced. In all polymerizations, a clear reactivity trend between **6** and **7** was not observed. However, the structure of the alkyne compound did show a pronounced effect on this new polycondensation reaction, as expected from the literature data. 1-Octyne, metyl 10-undecynoate, and propargyl alcohol were successfully polymerized and all NMR and GPC analyses showed the expected structures. In contrast, propargylic acid and its methyl ester formed only some oligomers. Another important feature of this type of polymerization comes from the selection of the dithiol compound, making it possible to design the characteristics of the back-bone as well as the density of the grafted functional groups stemming from the alkyne compound. Noteworthy, the successfully synthesized polymers should be suitable for the synthesis of diverse comb polymers.

8

New Renewable Polyamides from Fatty Acids[329]

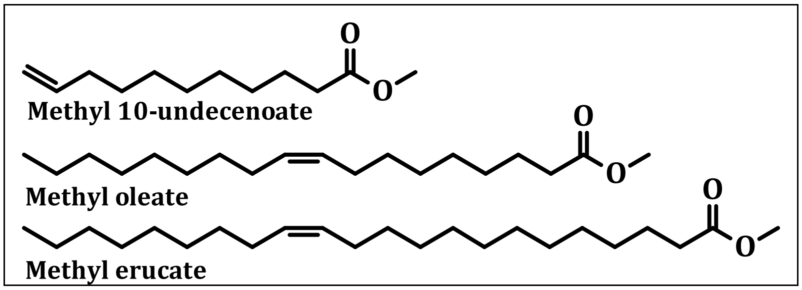
8.1 Introduction

The importance of plastic materials in our daily life and their synthesis from renewable resources has already been briefly discussed in the earlier chapters. 10-Undecenoic acid (a derivative of ricinoleic acid of castor oil), oleic acid from "new sunflower," and erucic acid from rape seeds are three of the most important ones for chemical transformations for either polymer additives, or building blocks; some of them have already been successfully commercialized as dicarboxylic acids for polyesters or polyamides.[21]

Polyamides (Nylons) are a class of engineering plastics since they are strong, tough, and heat resistance; they can be extruded and molded to form tubings, furniture casters, automotive air intake ducts,[330] and many others; their demand increased by 20% from

2009 to 2010 in Europe.[1] Among the types of polyamides, approximately 85-90 percent of nylons in the global market are nylon 6, the polymer of caprolactam, and nylon 6,6, the polymer of adipic acid and 1,6-hexamethylene diamine. Their use is mainly in the form of fibres. Polyamides can be synthesized *via* the polycondensation of ω-amino carboxylic acid compounds or dicarboxylic acids with diamines, or the ring opening polymerization of lactams.[330] Although Nylon 6 and 6,6 are highly crystalline polymers and are good gas, odour, and flavour barriers; their highly hydrophilic character results in poor barrier property to water vapour uptake. To overcome this phenomenon, an ethyl-branched aliphatic polyamide was studied, but this polymer was found to have a higher gas permeability than Nylon 6 and 6,6, probably because of the amorphous, glassy state.[331] On the other hand, the production of Nylons solely from oleochemicals has been limited to Polyamide 11, which is synthesized by self condensation of 11-amino-10-undecylenic acid that is synthesized from 10-undecenoic acid.[109] Moreover, Nylon 6,9 and Nylon 6,6,9 are synthesized from azelaic acid, which is the ozonolysis product of oleic acid, and non-Nylon polyamides used as hotmelt adhesives are synthesized from dimer fatty acids, which are high temperature catalytic dimerized product mixtures of multiply unsaturated fatty acids.[332] Very recently, Mecking *et al.* reported on the isomerising alkoxycarbonylation of oleic and erucic acids to yield linear C19 and C23-long α,ω-diacid compounds in >99% purity.[333] The reduction and amination of these compounds yielded the first examples of fully renewable C19 and C23 diamine compounds. The polycondensation of the diester compounds with their diamine derivatives resulted in polyamides with about 10 kDa molecular weights. Polyamides 23,19 and 23,23, based on 1,23-tricosanediamine, exhibited a T_m value of 156 and 152 °C, respectively. Another recent example of fully renewable polyamide was synthesized from sebacic acid and diaminoisoidide as well as 1,4-diaminobutane, known as putrescine in Nature.[334] The polyamide 10,4 was obtained with a molecular weight of about 20 kDa and PDI of 3, and upon the thermal analysis, this polymer exhibited $T_{5\%}$ value of 424 and T_m of 246 °C.

In all aforementioned procedures to synthesize amine functional polycondensable compounds, either catalytic and non-catalytic amination or azidation/hydrogenation reactions were used, which request harsh conditions or multiple step organic reactions. Considering the fatty acid structure, a simple and efficient methodology is necessary to introduce the desired functional groups. In this survey, radical thiol-ene addition reactions have already been shown to be a unique reaction for the diverse transformations of the natural double bonds to a number of groups.[335] Boutevin *et al.* prepared mercaptoalcohols *via* the addition of mercaptoethyl ether to 10-undecen-1-ol for telechelics syntheses;[336] Galià *et al.* added mercaptopropionic acid to **1** and **2** to synthesize polyanhydride precursors;[337] Cádiz and Cramail e*t al.* prepared polyols *via* the addition of mercaptoethanol to **1** and **2** for polyurethane synthesis;[338,339] Bantchev *et al.* modified corn and canola oils with 1-butanethiol for lubricants;[204] and Heise *et al.* coupled different thiol compounds to an unsaturated polyester.[218] Nevertheless, four different thiol compounds were added to 10-undecenoic acid under mild conditions, e.g. moderate temperatures, solvent- and intiator-free, and the resulting compounds were polycondensed to yield linear as well as hyperbranched polyesters.[241] However, the introduction of an amine functionality to plant oils *via* thiol-ene addition reactions in order to obtain polyamides was not yet reported. The only procedure reported was the synthesis of a polyamine compound from cysteamine addition to grapeseed oil and it was used to cure an epoxidized linseed oil.[207]



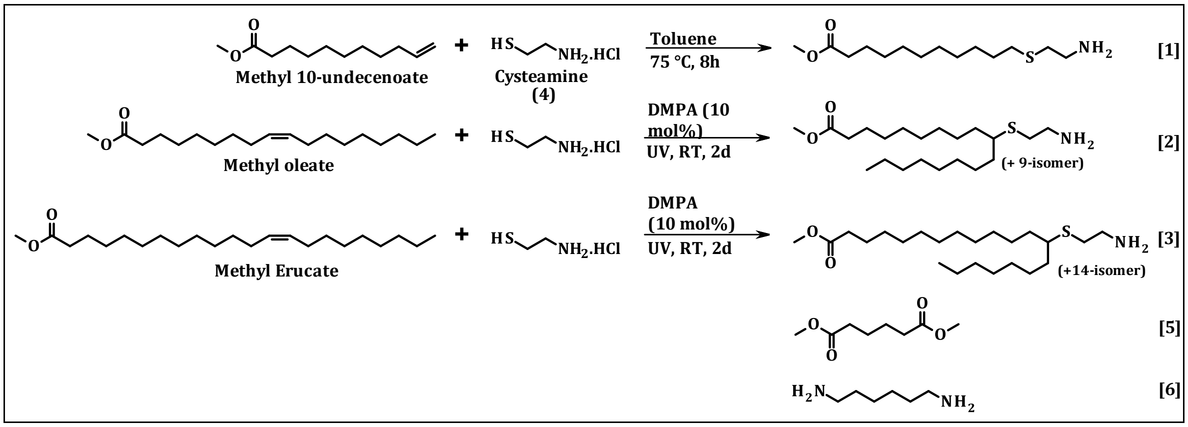
Scheme 8.1: The structures of the renewable monomer precursors investigated.

Therefore within this chapter, we report on the syntheses of new fully renewable amino compounds from fatty acids *via* thiol-ene addition reactions. The synthesized monomers were polymerized to obtain a number of linear aliphatic polyamides as well as in copolyamides. Moreover, copolymers with Nylon 6,6 were prepared and the thermal properties were studied by means of DSC in order to show the possible use of these new monomers as comonomers for common Nylons.

8.2 Results and Discussion

8.2.1 Synthesis of the Monomers

Herein, for the first time, amine functionalization of free fatty acids *via* thiol-ene addition reaction is reported. At the beginning of this study, cysteamine was used both in the form of hydrochloride salt and as such and the results of the addition reactions to methyl 10-undecenoate were compared by means of the ease of the reaction, the costs, and the final conversion. The hydrochloride salt form is cheaper, exhibits lower melting point (~70 °C), has better solubility, and most interestingly gave higher conversions comparing to pure form. Therefore, for the rest of the study, cysteamine was used in hydrochloride salt form. Nevertheless, as it is well known for thiol-ene addition reactions, the structure of alkene has an extraordinary effect on the overall reaction yield.[172] (see Chapter 3)



Scheme 8.2: The synthetic pathway to the new fatty and terpene amines, and the structures of the other monomers utilized.

Hence in this study, the synthesis of the monomer **1** was successfully performed using equivalent amounts of the thiol to the alkene at 75 °C, and the high yield of 85% was obtained after recrystallization. The complete conversion was evidenced by the ^{1}H-NMR spectrum, at which the peaks at 5.74 and 4.91 ppm corresponding to the terminal double bond disappeared and the new triplets at 2.78 and 2.62 ppm corresponding to the protons at the α- and β-positions to thioether formed. On the other hand, because of the reversibility of the addition of thiyl radical to the internal unsaturation, the efficiency of thiol-ene addition reaction is higher for *trans*-alkenes than *cis*-alkenes.[181] In the literature, it was reported that when 3-mercaptopropionic acid and mercaptoethanol were added to **2**, 2 and 3 equivalents, respectively, of the thiol compounds relative to the double bond *via* UV-initiation was necessary to obtain complete conversion.[339,337] In our study, we found it necessary to first optimize our conditions for the syntheses of the monomers **2** and **3** to find conditions that use the least amount of thiol compound possible. When **4** was used in equivalent amount to methyl oleate, even after 5 days of irradiation in the presence of DMPA as photo-initiator the conversion was still low (about 50 % by ^{1}H-NMR). Only after the increase of **4** to 3 equivalents and 0.1 equivalents of DMPA relative to double bond, as it was reported for the synthesis of polyamines elsewhere,[207] full conversion was obtained after 2 days of reaction time. As expected, the excess amount of thiol compound gave rise to the formation of the disulfide product, but this reaction was out of the scope of this report and was not investigated in detail. The NMR spectra of the products clearly showed the formation of the expected products. For instance, the triplet at 5.36 ppm corresponding to the vinyl protons shifted to 2.55 ppm representing the proton at the α-position to the sulfide ether on the fatty acid chain. After column chromatography of the reaction mixture obtained from the aforementioned conditions, **2** and **3** were obtained in 75 and 66% isolated yields, respectively. On the other hand, reaction engineering was applied in order to improve the efficiency of this reaction. A new reactor setup was prepared with enhanced UV light and chemical engineering, which allowed us to considerably reduce the reaction time and amount of thiol compound that was used in excess. (Figure) These results showed that it is possible to easily and efficiently synthesize mono-functional amines from fatty acids *via* **4** addition.

8.2.2 Polymerization Reactions

The synthesized monomers were then polymerized in order to obtain renewable polyamides. The monomers **1-3** are heterodifunctional and they can be directly polymerized. Moreover, the monomers prepared within this report were also copolymerized with dimethyl adipate (**5**) and 1,6-hexamethylene diamine (**6**) since it would be interesting to study how the thermal properties of Nylon 6,6 could be altered when copolymerized with the renewable monomers bearing linear and branched moieties. All polymerization reactions were performed under continuous vacuum in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as basic organocatalyst. TBD was already shown to successfully catalyze the formation of amides from methyl esters and primary amines.[340] Moreover, it was also reported to catalyze polyamidation reactions of diesters and diamines.[161] In our study, the primary optimization reactions were carried out and the best results were obtained at 140 °C and with 0.05 equivalents of TBD per ester group - the conditions that were used for the next polymerization reactions. We first started to study fatty acid-based polyamides. The polymerization of **1** resulted in a linear polyamide chain, whereas **2** and **3** in branched ones. Noteworthy, **P3** is highly viscous at room temperature, whereas all others are solid, exhibiting polyamides with a broad range of melting points.

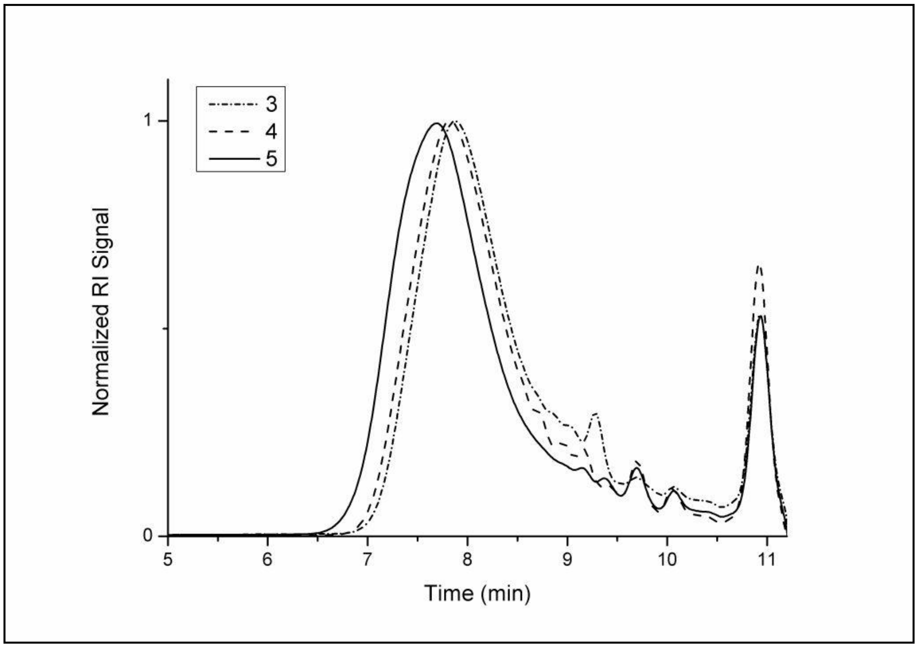


Figure 8.1: GPC traces of the precipitated fatty acid-based polyamides.

Since thiol-ene addition reactions do not exhibit any selectivity for internal double bonds, **4** may bind to the 9th or 10th carbon of **2** and 13th or 14th carbon of **3**, yielding two regioisomers with identical population in each case. This reveals that **2** contains two isomers with 8 or 9 carbon atoms at the main chain and 9 or 8 at the side chain, respectively; **3** contains two isomers with that of 12 or 13 at the main chain and 9 or 8 at the side chain, respectively. This phenomenon resulted in two interesting issues, the solubility and thermal properties of the polymers that will be discussed in the following sections. Quite interestingly **P1**, as expected from the linear structure, was only soluble in HFIP; whereas **P2** and **P3**, the branched polymers, were only soluble in THF. This result forced us to use two different GPC systems, which are running with THF and HFIP solvents, throughout the study. Interestingly, when **1** and **3** were copolymerized in a 1:1 ratio, the obtained polymer with M_n of 8350 was soluble in both solvents.

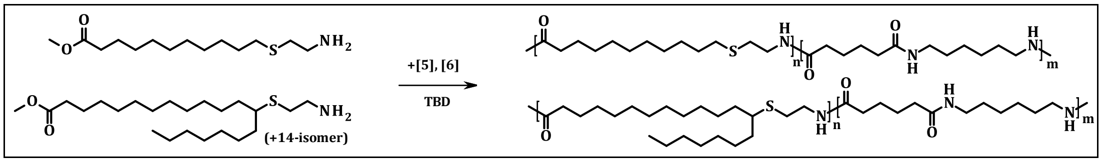
Polymer	M1(Eq)	M2(Eq)	M3(Eq)	Mn* (g.mol^{-1})	PDI	T$_m$ (C)	ΔH$_m$ (J.g^{-1})	Polymer Type
P1	1			15850[b)]	3.33	138	36	Fatty acid polyamides
P2	2			7250[a)]	1.78	n.a	n.a.	
P3	3			6200[a)]	1.80	43	28	
P4	1(1)	3(1)		8350[a)]	1.94	86	17	
P5	1(2)	5(1)	6(1)	10200[b),c)]	3.07	n.a.	n.a.	1 / Nylon 6,6 copolyamides
				6100[b)]	2.14			
P6	1(6)	5(1)	6(1)	14500[b)]	1.55	121	n.a.	
P7	1(2)	5(3)	6(3)	6590[b),c)]	2.13	182	n.a.	
				3700[b)]	2.25			
P8	5(1)	6(1)		19200[b)]	2.8	255	-	Nylon 6,6

[a)]Analyzed with THF system, [b)]Analyzed with HFIP system, [c)]Polymerized in xylene

Table 8.1: Polymerization entries and the properties.

The molecular weights obtained (see Table 8.1) clearly show that cysteamine-functionalized monomers can be used for TBD-catalyzed polyamide synthesis.

Nylon 6,6 copolymers. Nylon 6,6 is the commercial polyamide that has the highest crystallinity and therefore the highest melting point after Nylon 4,6. However, because of the high frequency of the highly hydrophobic peptide bonds on the main chain, Nylon 6,6 exhibits hygroscopic behavior that results in the some sensitivity to humidity upon the high temperature production as well as final material use.[331]



Scheme 8.3: Fatty acid / Nylon 6,6 copolyamides.

Therefore, we also copolymerized the monomer **1** with **5** and **6** to see if the properties of Nylon 6,6 can be modified with fatty acids (Scheme 8.3). **1** was incorporated into Nylon 6,6 in the following ratios: 1:1 (**P5**), 3:1 (**P6**), and 1:3 (**P7**, 1:Nylon6,6) in order to see if one can tune the properties with the amount of **1**. The GPC measurements of these polymers showed large difference in molecular weight. For instance, **P7** has a molecular weight of about 3700 Da, whereas **P6** has that of 14500 Da. When we correlate the molecular weights to the 1:Nylon 6,6 ratio, it can be seen that increasing the ratio results in an increase of molecular weight. Since thermal properties cannot be compared with that different molecular weight values, p-xylene was used as a solvent for the polymerization of **P5** and **P7** with the hope to obtain higher molecular weights. Although the solvent used in the reaction was completely evaporated after 4 hours, this procedure indeed almost doubled the obtained molecular weight values. This result reveals that if the percentage of Nylon 6,6 is increased in the polymer, macromolecular diffusion is restricted by the high intermolecular interactions, which in turn results in lower molecular weight; hence, a high-boiling solvent, which acts as a kind of plasticizer, is necessary to reach higher molecular weight.

8.2.3 Thermal Characterization

One of the most important properties of polyamides is their high melting temperatures and thermal stability. Thus, it is important to thermally characterize the polymers obtained. **P2** exhibited a T_m of 138 °C. If we compare this value to that of Nylon 11, which is about 180 °C, the difference of about 40 degrees might result from the existence of 2 more carbon atoms, which lowers the peptide bond frequency, and a sulfur atom on the main chain, which might interrupt the intermolecular organization (S is considerably larger than C). More interestingly, **P2** remained in a highly viscous state at room temperature; no thermal transition was observed by DSC analysis when cooled down to -50 °C. On the other hand, **P3** exhibited T_m of 43 °C. This difference between **P2** and **P3** obviously results from the number of carbon atoms presents between the peptide bonds on the main chain since they bear comparable number of carbon atoms on their side chains, e.g. 8 or 9 in the same ratio for both polymers. In order to contribute to this wide melting point range that could be obtained from fatty acid-derived polymers, we also copolymerized **1** and **3** in 1:1 ratio (**P4**) and the polymer obtained exhibited a broad T_m of 86 °C, which ranked fairly between that of **P1** and **P3**.

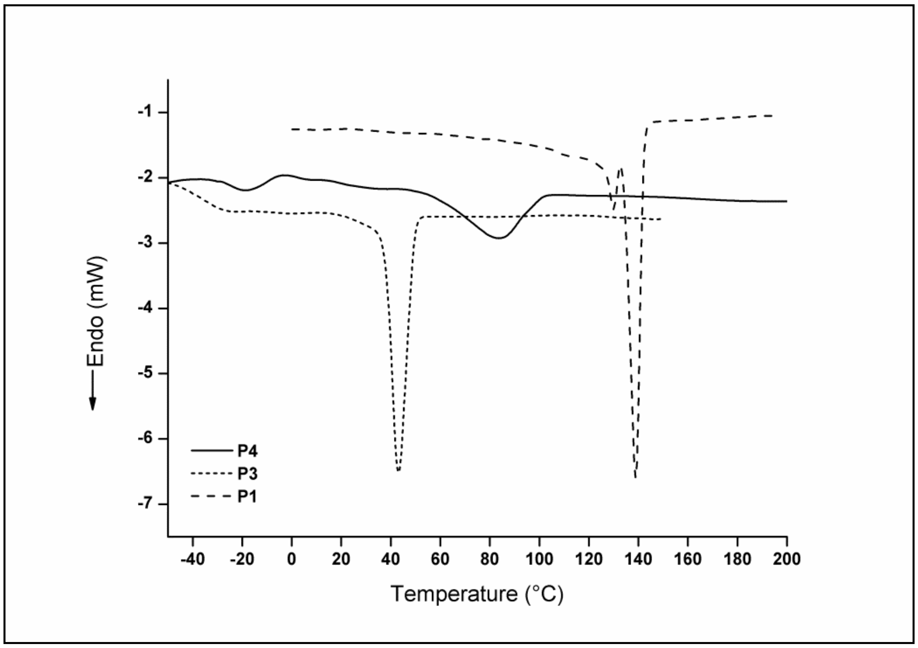


Figure 8.2: DSC thermograms of fatty acid-based polyamides.

In case of **1**:Nylon6,6 copolymers, however, somewhat more complicated thermograms were obtained. A sharp T_m peak could be obtained from **P6**, e.g. **1**:Nylon6,6 ratio of 1:3, at about 120 °C. Noteworthy, this is lower than T_m of the homopolymer of **1**, **P1**. In contrast, when **1** was copolymerized with a **1**:Nylon 6,6 ratio of 3:1, a broad T_m of 182 °C was obtained. These results clearly indicate that the thermal properties of Nylon 6,6 can be tuned in a wide range of melting temperatures when copolymerized with the fatty acid-derived monomers prepared herein. The thermogram of **P5** showed multiple endothermic peaks with lack of a clear baseline. Annealing as a pretreatment method was applied at different temperatures, but no clear results could be obtained.

8.3 Conclusion

This study clearly showed that a wide range of aliphatic polyamides can be synthesized from monomers which are derived from plant oils. The thiol-ene addition reaction was successfully applied to fatty acids in order to introduce primary amine functionalities; the resulting products were then used the prepare polyamides. The DSC analyses of the resulting polymers revealed that renewable polyamides from amorphous state at room temperature to high-melting semi-crystalline polymers can be obtained *via* the selective combination of the aforementioned monomers as well as Nylon 6,6 copolymers.

9

Experimental Part

9.1 General Methods

Thin layer chromatography (TLC) was performed on silica gel TLC-cards (layer thickness 0.20 mm, Fluka). Seebach and 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.

9.2 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 untill 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$_{\text{MICRO}}$ instrument.

Gas Chromatography (GC). Analytical GC characterization was carried out with a Bruker 430 GC instrument equipped with a capillary column FactorFourTM VF-5 ms (30 m x 0.25 mm x 0.25 µm), using flame ionization detection. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C x min^{-1} to 220 °C, hold for 4 min, ramp at 15 °C x 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) Varian 431 GC instrument with a capillary column FactorFourTM VF-5 ms (30 m x 0.25 mm x 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 x s^{-1}. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C x min^{-1} to 200 °C, hold for 2 min, ramp at 15 °C x 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 x min^{-1}).

2) Varian 3900 GC instrument with a capillary column FactorFour™ 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: SEC System LC-20 A from Shimadzu equipped with a SIL-20A auto sampler, PL gel 5 mm MIXED-D column (Polymer Laboratories, 300 mm x 7.5 mm, 100 Å, 1000 Å, 10000 Å) and a RID-10A refractive index detector in THF (flow rate 1 mL x 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 0.1wt% potassium trifluoroacetate (Sigma Aldrich, 98%) as the solvent. The solvent flow was 0.40ml/min at 30.0°C. The analysis was performed on a 3-column system: PSS PFG Micro precolumn (3.0x0.46cm, 10.000 Å), PSS PFG Micro (25.0x0.46cm, 1000 Å) and PSS PFG Mirco (25.0x0.46cm, 100 Å). The system was calibrated with linear poly(methyl methacrylate) standards (Polymer Standard Service, M_P 102 – 981 000 Da).

3) PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 μm bead-size guard column (50 × 7.5 mm) followed by three PLgel 5 μm Mixed-C and one PLgel 3 μm Mixed-E columns (300 × 7.5 mm) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 mL × min^{-1}. The SEC system was calibrated using linear poly(methyl methacrylate) (PMMA) standards ranging from 700 to 6.106 g × mol^{-1}.

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 5-10 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. The crystallization temperature, T_c, was recorded as the peak of the exotherm on the cooling scan, and the enthalpy of melting, ΔH_m, was calculated *via* the integration of the area below the melting endotherm on the second scan divided by the weight of the sample. In chapter 6, the degree of crystallinity was calculated as the percentage relative to the melting enthalpy value of 100% crystalline sample given for LLDPE as 279 J/g in the literature.[341]

Thermogravimetric Analysis (TGA). Thermal stability of the polymers was studied on a TGA/SDTA851e instrument (Mettler Toledo) at a heating rate of 10 $°C \times min^{-1}$ under nitrogen. The weights of the samples were about of 8 mg.

9.3 Other Methods

All parallel reactions were carried out in Radley Carousel 12 plus parallel reactor system using tetradecane (10 vol%) as internal standard for chromatographic analyses.

Determination of the degree of isomerizations for ADMET derived polymers.

The respective polymer (30 mg), excess methanol (4 mL), and concentrated sulfuric acid (5 drops) were refluxed at 85 °C over night. At the end of the reaction, the excess of methanol was removed *in vacuo*. Then, the residue was dissolved in dichloromethane and filtered over a small plug of basic aluminum oxide. Subsequently, the samples were analyzed by GC-MS and the degree of isomerization (DI) was calculated using the following equation:

$$\mathrm{DI} = 100 - \frac{(Integration\ of\ the\ non - isomerized\ product)}{(Integration\ of\ the\ total\ products)} \mathrm{x}\ 100$$

9.4 Fatty Acid Derived Monomers and Related Polymers *via* Thiol-Ene (Click) Additions

9.4.1 Materials

10-undecenoic acid (Aldrich, 98%), 10-undecen-1-ol (Aldrich 98%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; Aldrich, 98%), 1-thioglycerol (Aldrich, >99%), 1,4-butanedithiol (Aldrich, >97%), 2-mercaptoethanol (Aldrich >99%), methyl thioglycolate (Aldrich, >97%), tetradecane (Aldrich, ≥99,5%), ethylene glycol (Aldrich, >99%), 1,3-propanediol (Aldrich, >99%), glycerol (Aldrich, >99%), and 2,2-dimehoxy-2-phenylacetophenone (DMPA, Aldrich, 99%) were used as received. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%) was used after recrystallization from methanol.

Methyl 10-undecenoate (**2**) was prepared by esterification with methanol from corresponding 10-undecenoic acid according to a standard laboratory procedure.

9.4.2 Monomer Synthesis

Methyl 11-((2,3-dihydroxypropyl)thio)undecanoate (**M1**): **2** (9.915 g, 50 mmol) and 1-thiogycerol (5.408 g, 50 mmol) were weighed into a flask and vacuum was subsequently applied for 5 minutes for degassing. The closed flask was then stirred at 35 °C and 1500 rpm for 6 days. The reaction mixture was collected with THF and precipitated into hexane. A weight solid product was isolated (8.87g, 58%). ^{1}H NMR (500MHz, CDCl$_3$, δ): 3.72 (m, 1H, HO-C*H*<), 3.69 (dd, *J* = 3.05 and 11.60 Hz, 1H, HO-CH_a(H$_b$)-), 3.59 (s, 3H, CH_3-OOC-), 3.49 (dd, *J* = 5.76 and 11.14 Hz, 1H, HO-CH$_a$(H_b)-), 2.63 (dd, *J* = 4.32 and 13.69 Hz, 1H, -CH_c(H$_d$)-S-), 2.52 (dd, *J* = 8.38 and 13.63 Hz, 1H, -CH$_c$(H_d)-S-), 2.46 (t, *J* = 7.42 Hz, 2H, -S-CH_2-), 2.23 (t, *J*

= 7.54 Hz, 2H, -CH_2-COO-), 1.55-1.45 (m, 4H, -SCH_2-CH_2- and –CH_2-CH_2COO-), 1.35-1.15 (m, aliphatic, -[CH_2]-) ppm. MS (ESI-positive, MeOH): m/z = 329.1 ([M+Na]$^+$, calc. 329.2)

Methyl 11-((2-hydroxyethyl)thio)undecanoate (**M2**): **2** (3.968 g, 20 mmol) and mercaptoethanol (1.586 g, 20 mmol) were weighed into a flask and vacuum was subsequently applied for 5 minutes for degassing. Capped vessels were left to stir at 35°C and 1500 rpm for 68 hours. A white solid product was isolated by column chromatography (silicagel 60, hexane:ethyl acetate = 1:1) (5.21 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$, 3.71 (t, J = 5.97 Hz, 2H, HO-CH_2-), 3.66 (s, 3H, CH_3-OOC-), 2.73 (t, J = 5.99 Hz, 2H, HOCH_2-CH_2-S-), 2.51 (t, J = 7.32 Hz, 2H, -S-CH_2-CH_2), 2.26 (t, J = 7.56 Hz, 2H, -CH_2-COO-), 1.56 (m, 4H, -SCH_2-CH_2- and –CH_2-CH_2COO-), 1.35-1.15 (m, aliphatic, -[CH_2]-) ppm. MS (ESI-positive, MeOH): m/z = 299.1 ([M+Na]$^+$, calc. 299.2)

Methyl 11-((2-methoxy-2-oxoethyl)thio)undecanoate (**M3**): **2** (3.97g, 20 mmol) and methyl thioglycolate(2.12g, 20 mmol) were weighed into a flask and stirred without degassing at room temperature at 1500 rpm for 48 hours. The yield of reaction was so high that we did not need further purification. The reaction mixture is a weight solid at RT and used directly for further purposes. ^{1}H NMR (500 MHz, $CDCl_3$, 3.71 (s, 3H, CH_3-OCO$CH_2$$CH_2$-), 3.64 (s, 3H, CH_3-OCOCH_2S-), 3.20 (s, 2H, -OCO-CH_2-S-), 2.59 (t, J = 7.40 Hz, 2H, -CH_2S-CH_2-), 2.27 (t, J = 7.55 Hz, 2H, -OCO-CH_2-), 1.61 - 1.53 (m, 4H, -SCH_2-CH_2- and –CH_2-CH_2COO-), 1.36-1.22 (m, aliphatic, -[CH_2]-) ppm. MS (ESI-positive, MeOH): m/z = 327.1 ([M+Na]$^+$, calc. 327.2)

Dimethyl 11,11'-(butane-1,4-diylbis(sulfanediyl))diundecanoate (**M4**): 3.97g **2** (20 mmol) and 1.23 g 1,4-butanedithiol (10 mmol) were weighed into flask, degassed, and stirred at 60 °C and 1500 rpm. After 5 hours, the reaction mixture solidified. The mixture was collected in dichloromethane and precipitated into hexane (3.82 g, 73.5%). ^{1}H NMR (500 MHz, CDCl$_3$, 3.66 (s, 3H, H_3C- OOC-), 2.51 (t, *J* = 7.41 Hz, 8H, 2x-CH_2-S-CH_2-), 2.30 (t, *J* = 7.56 Hz, 4H, -CH_2-COO-), 1.71-1.65 (m, 4H, -SCH$_2$-[CH_2]$_2$-CH$_2$S-), 1.62-1.51 (m, 8H, 2x-SCH$_2$-CH_2- and 2x–OCCH$_2$-CH_2-), 1.25-1.12 (m, aliphatic, 2x-[CH_2]-) ppm. MS (ESI-positive, MeOH): *m/z* = 541.2 ([M+Na]$^+$, calc. 541.3)

11,11'-(butane-1,4-diylbis(sulfanediyl))bis(undecan-1-ol) (**M5**): 10-Undecen-1-ol (3.406 g, 20 mmol) and 1,4-butanedithiol (1.222 g, 10 mmol) were weighed into flask, degassed, and stirred at 70 °C and 1500 rpm. After 3 days, the reaction mixture was totally solid. The product was purified by recrystallization from MeOH (3.80 g, 82.1%). ^{1}H NMR (300 MHz, CDCl$_3$) 3.56 (t, *J* = 6.60 Hz, 4H, HO-CH_2-), 2.51 (t, *J* = 7.43 Hz, 8H, 2x-CH_2-S-CH_2-), 1.78-1.66 (m, 4H, -SCH$_2$-[CH_2]$_2$-CH$_2$S-), 1.64-1.20 (m, aliphatic, 2x-[CH$_2$]-) ppm. MS (ESI-positive, MeOH): *m/z* = 485.3 ([M+Na]$^+$, calc. 485.4)

9.4.3 Polymerization Reactions

All polycondensation reactions were carried out at 120 °C applying a continuous vacuum (200±35 mbar) in order to remove the methanol. 5 mol% of TBD was used as catalyst per mol of ester groups present in the respective monomers, unless otherwise indicated.

P1: 0.5181 g (1.69 mmol) of **M1** and 6.17 µL (0.08 mmol) of glycerol were polymerized with 0.0118 g (0.08 mmol) of TBD for 8h. The polymer was purified via precipitation from THF into hexane (0.3061 g, 66%). ^{1}H NMR (300 MHz, CDCl$_3$, 5.19-5.08 (-COOCH$_2$(CH-OOC)CH$_2$-S), 5.02-4.92 (HOCH$_2$(CH-OOC)CH$_2$-S-), 4.36 (-COOCH_aH$_b$(CH-OOC)CH$_2$-S-), 4.25-

4.05 (-COOCH$_a H_b$(CH-OOC)CH$_2$-S- and -SCH$_2$CH(OH)-CH_a(H$_b$)-OOC-), 4.00-3.88 (-SCH$_2$-CH(OH)-CH$_2$OOC-), 3.58 (-SCH$_2$CH(OH)-CH$_a$(H_b)-OOC-), 3.36-3.23 (TBD), 2.78-2.57 (>CH-CH$_2$-S-), 2.55 (-[CH$_2$]$_8$-CH_2-S-), 2.36 (-OOC-CH_2-), 2.00 (TBD), 1.72-1.14 (m, aliphatic) ppm.

P2: 0.5012 g (1.81 mmol) of **M2** was polymerized with 0.0117 g (0.08 mmol) of TBD for 8h. The polymer was purified via precipitation from THF into hexane (0.3756 g, 85%). ^{1}H NMR (300 MHz, CDCl$_3$, 4.22 (-COO-CH_2-), 2.74 (-OCH2-CH_2-S-), 2.56 (-CH_2-S-CH$_2$-), 2.32 (-CH_2-COO-), 1.68-1.53 (-OOCCH$_2$-CH_2- and –CH_2-CH$_2$-S-), 1.42-1.22 (m, aliphatic) ppm.

P35: 0.3813 g (1.25 mmol) of **M3** and 0.5799 g (1.25 mmol) of **M5** were polymerized with 0.0174 g (0.12 mmol) of TBD for 8h. The polymer was purified via precipitation from THF into methanol (0.7598 g, 86%). ^{1}H NMR (300 MHz, CDCl$_3$) 4.12 (-SCH$_2$COO-CH_2-), 4.05 (-CH$_2$CH$_2$COO-CH_2-), 3.21 (-SCH_2COO-), 2.63 (-CH$_2$-CH_2-SCH$_2$COO-), 2.50 (-CH_2-S-CH_2-), 2.29 (-OOC-CH_2-), 1.73-1.18 (m, aliphatic) ppm.

P45: 0.3328 g (0.64 mmol) of **M4** and 0.2968 g (0.64 mmol) of **M5** were polymerized using 0.0091 g (0.06 mmol) of TBD for 8h. The polymer was purified via precipitation from THF into methanol (0.4081 g, 69%). ^{1}H NMR (300 MHz, CDCl$_3$) 4.05 (-COO-CH_2-), 2.54 (-CH_2-S-CH_2-), 2.28 (-OOC-CH_2-), 1.76-1.71 (-SCH$_2$-[CH_2]$_2$-CH$_2$S-), 1.68-1.57 (m, aliphatic) ppm.

9.5 Thiol-Ene click vs. ADMET: A complementary approach to fatty acid based biodegradable polymer synthesis

9.5.1 Monomer Syntheses

Undec-10-enoic anhydride (1): A solution of 10-undecenoic acid (5.87 g, 31.85 mmol) and triethylamine (3,79 g, 37.43 mmol) was placed into a flash-dried reflux setup equipped with dropping funnel and undec-10-enoyl chloride (6.52 g, 32.16 mmol) in 50 mL of CH_2Cl_2 was added to the reaction mixture drop-wise while stirring and refluxing for 2 hours. Then, the reaction mixture was cooled down, the solvent was removed *in vacuo*, and the residue was collected with hexane and quickly filtered from a small plug of Na_2SO_4 to remove the by-product, triethylammonium chloride salt. The filtrate was concentrated *in vacuo* and the unreacted acid chloride, if any, was removed *via* reduced pressure at 120 °C. The remaining product was a light-brown liquid with quantitative yield. δ_H (300 MHz; $CDCl_3$; Me_4Si): 5.82 (tdd, J = 16.91, 10.16, 6.66 Hz, 2H, vinylic), 5.06-4.89 (m, 4H, vinylic), 2.45 (t, J 7.43 Hz, 4H, -CH_2(C=O)O-), 2.05 (q, J = 6.86 Hz, 4H, allylic), 1.73-1.60 (m, 4H, aliphatic), 1.36 (m, 20H, aliphatic) ppm. δ_C (300 MHz; $CDCl_3$; Me_4Si) 170.0 (C=O), 139.5 (H_2C=CH-), 114.5 (H_2C=CH-), 35.7 (C=O-CH2-), 34.1 (H_2C=HC-CH_2-), 29.4 (-CH_2- aliphatic), 24.6 (-CH_2- aliphatic) ppm. MS (ESI-positive, CH_2Cl_2): m/z = 373.29 ($[M+Na]^+$, calc. 373.27).

9.5.2 Polymerization Reactions

***General procedure for ADMET polymerizations*.** Into a flash-dried three necked flask the diene monomer(s) (in case of copolymers 1:1 eq), methyl 10-undecenoate (when used, see Table 1), p-benzoquinone (when used, **BQ**, 0.02 eq), and Zahn-1B (0.01 eq) were introduced and let to stir mechanically (500 rpm) at 80 °C for one hour under 100 (±20) mbar continuous vacuum. The reaction was quenched with ethyl vinyl ether (**EVE**, 50 eq considering the catalyst amount) in THF and precipitated into the corresponding solvent.

Polyanhydride *via* ADMET (P1). The polymer was precipitated into hexane (74.8%). δ_H (500 MHz; $CDCl_3$;Me_4Si) 5.54 – 5.29 (m, vinylic), 3.68 (s, ester), 2.46 (t, J = 7.5 Hz, $(C=O)OC=O-CH_2-$), 2.10 – 1.89 (m, allylic), 1.68 (m, aliphatic), 1.48 – 1.15 (m, aliphatic).

Polyester *via* ADMET (P2). The polymer was precipitated into methanol (82.4%). δ_H (500 MHz; $CDCl_3$; Me4Si) 5.51 – 5.25 (m, vinylic), 4.16 (t, J = 6.3 Hz, ester), 3.68 (s, methyl ester), 2.30 (t, J = 7.6 Hz, $OC=O-CH_2-$), 1.97 (m, allylic), 1.61 (m, aliphatic), 1.44 – 1.06 (m, aliphatic).

Poly(anhydride-co-ester) *via* ADMET (P5). The polymer was precipitated into methanol (73.6%). δ_H (300 MHz; $CDCl_3$; Me_4Si) 5.58 – 5.23 (m, vinylic), 4.15 (t, J = 6.3 Hz, ester), 2.46 (t, J = 7.4 Hz, $-CH_2-(C=O)OC=O-$), 2.31 (t, J = 7.5 Hz, $OC=O-CH_2-$), 2.12 – 1.89 (m, allylic), 1.77 – 1.47 (m, aliphatic), 1.48 – 1.13 (m, aliphatic).

General procedure for thiol-ene polymerizations. Into a dry reaction vessel the diene monomer(s) (0.5 eq, in case of copolymer 0.25:0.25 eq), di(2-mercaptoethyl) ether (**3**, 0.5 eq), and AIBN (0.025 eq) were introduced and let to stir magnetically (500 rpm) for 5 minutes at RT and then at 80 °C for 2 hours with continuous nitrogen purging. The reaction mixture was dissolved in THF and precipitated into the corresponding solvent.

Polyanhydride *via* thiol-ene (P3). The polymer was precipitated into hexane (70.4%). δ_H (300 MHz; $CDCl_3$; Me_4Si) 3.64 (m, $-CH_2-O-CH_2-$), 3.10 (t, J = 6.5 Hz, $-CH_2-SC=O-$), 2.72 (t, J = 7

Hz, -*S*-CH_2-), 2.56 (t, -CH_2-S-), 2.46 (t, J = 7.4 Hz, -CH_2-C=O-OC=O-CH_2-), 2.36 (t, 3H, -CH_2-COOH), 2.11 – 1.99 (m, 1H), 1.75 – 1.47 (m, aliphatic), 1.46 – 1.21 (m, aliphatic).

Polyester *via* thiol-ene (P4). The polymer was precipitated into methanol (85.0%). δ_H (300 MHz; $CDCl_3$; Me_4Si) 4.12 (t, J = 6.7 Hz, ester), 3.63 (t, J = 7 Hz, -CH_2-O-CH_2-), 2.74 (t, J = 7 Hz, -S-CH_2-), 2.54 (t, -CH_2-S-), 1.78 – 1.52 (m, aliphatic), 1.45 – 1.17 (m, aliphatic).

Poly(anhydride-co-ester) *via* thiol-ene (P6). The polymer was precipitated into methanol (70.4%). δ_H (300 MHz; $CDCl_3$; Me_4Si) 4.16 (t, J = 6.3 Hz, ester), 3.64 (t, J = 7Hz, -CH_2-O-CH_2-), 2.71 (t, J = 7 Hz, -S-CH_2-), 2.56 (t, -CH_2-S-), 2.46 (t, J = 7.4 Hz, -(C=O)OC=O-), 2.31 (t, J = 7.5 Hz, OC=O-CH_2-), 2.08 – 1.91 (m, allylic), 1.78 – 1.50 (m, aliphatic), 1.33 (m, aliphatic).

9.6 Renewable polyethylene mimics derived from castor oil

9.6.1 Materials

11-bromo-1-undecene (Aldrich, 95%), 10-undecen-1-ol (Aldrich 98%), potassium *tert*-butoxide (Aldrich, 95%), 2,2′-Azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%), 1,4-butanedithiol (Aldrich, ≥97%), 2-mercaptoethyl ether (Aldrich, 95 %), sodium hydride (Aldrich, 60 % dispersion in mineral oil), palladium (Aldrich, 10 % on activated charcoal), benzylidene-*bis*(tricyclohexylphosphine) dichlororuthenium (G1, Grubbs Catalyst 1st Generation, Aldrich), benzylidene [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine) ruthenium (G2, Grubbs Catalyst 2nd Generation, Aldrich), 1,4-benzoquinone (Aldrich, >99 %), ethyl vinyl ether (Aldrich, 99%), chloroform-d (Armar Chemicals, 99.8 atom-% D), and all solvents were used as received.

9.6.2 Monomer Synthesis

Undeca-1,10-diene (1): Into a solution of 11-bromo-1-undecene (5.0 g, 21,4 mmol) in 15 mL THF, potassium tert-butoxide (3.6 g, 32,1 mmol) was added in 1 gram portions at room temperature and let to stir for an additional hour. The reaction was terminated with 1M HCl solution and the organic layer was concentrated *in vacuo*. The product was distilled under reduced pressure at 70 °C. (2.1 g, 62.7 %) ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.89 – 5.57 (m, 2H, $H_2C{=}C\mathit{H}$-), 5.03 – 4.77 (m, 4H, $\mathit{H}_2C{=}CH$-), 1.97 (dd, J = 14.0, 6.8 Hz, 4H, =CH-CH_2-), 1.43 – 1.14 (m, 10H, aliphatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 139.15 ($H_2C{=}\mathit{C}H$-), 114.50 ($H_2\mathit{C}{=}CH$-), 33,60 (=CH-$\mathit{C}H_2$-), 29.30 – 28.90 (aliphatic). EIMS m/z: $[M + H]^+$ calcd for $C_{11}H_{20}$, 153.2; found, 153.0.

11-undec-10-enoxyundec-1-ene (2): This monomer was synthesized *via* modification of a method described elsewhere.[342] Into a solution of 10-undecen-1-ol (3.0 g, 17.6 mmol) in 3 mL DMSO and 10 mL THF, NaH (1.0 g, 25.0 mmol) (after having washed with hexane) was added stepwise and let to stir at 70 °C for 1 hour. After cooling down to room temperature, 11-bromo-1-undecene (4.11 g, 17.6 mmol) was added dropwise under inert atmosphere. Afterwards, the solution was refluxed overnight. The reaction mixture was taken into a separatory funnel and the layers were separated. The water phase was extracted three times with diethyl ether, the collected organic layers were extracted once more with water and then concentrated *in vacuo*, where unreacted species were removed under reduced pressure. The residue was filtered through a very short pad of silica gel with hexane, yielding a slightly yellow clear liquid. (3.92 g, 69.0 %) ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.74 (m, 2H, $H_2C{=}CH$-), 5.02 – 4.77 (m, 4H, $H_2C{=}CH$-), 3.32 (t, J = 6.7 Hz, 4H, -CH_2-O-CH_2-), 1.97 (dd, J = 14.2, 6.8 Hz, 4H, =CH-CH_2-), 1.62 – 1.11 (m, 28H, aliphatic). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 139.20 ($H_2C{=}CH$-), 114.10 ($H_2C{=}CH$-), 70.90 (-CH_2-O-CH_2-), 33.80 (=CH-CH_2-), 30.80 – 28.90 (aliphatic). EIMS *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{42}O$, 323.3; found, 323.3.

9.6.3 Polymerization Reactions

General procedure for ADMET polymerizations. Into a dry flask 1 mmol of the diene monomer (**1** or **2**, 1.00 eq), p-benzoquinone (**BQ**, 0.02 eq), G1 or G2 (see ***Table 1***, 0.01 eq) were introduced and let to stir magnetically (500 rpm) at 80 °C for one hour under 100 (±20) mbar continuous vacuum. The reaction was quenched with ethyl vinyl ether (**EVE**, 50.00 eq of the catalyst amount) in THF and precipitated into 1M HCl in methanol solution.

P1-G1. *(52 %)* ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ (ppm) = 5.84 (m, $H_2\mathrm{C{=}CH}$-), 5.53 – 5.29 (m, -$\mathrm{C}H{=}\mathrm{C}H$-), 5.10 – 4.89 (m, $\mathrm{H_2C{=}C}H$-), 2.01 (dd, J = 19.5, 5.0 Hz, =CH-$\mathrm{C}H_2$-), 1.72 – 1.04 (m, aliphatic).

P1-G2. *(68 %)* ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ (ppm) = 5.84 (m, $H_2\mathrm{C{=}CH}$-), 5.52 – 5.27 (m, -$\mathrm{C}H{=}\mathrm{C}H$-), 5.10 – 4.89 (m, $\mathrm{H_2C{=}C}H$-), 2.13 – 1.85 (m, =CH-$\mathrm{C}H_2$-), 1.72 – 1.14 (m, aliphatic).

P2-G1. *(61 %)* ^{1}H NMR (**300** MHz, $\mathrm{CDCl_3}$): δ (ppm) = 5.93 – 5.73 (m, $H_2\mathrm{C{=}CH}$-), 5.52 – 5.29 (m, -$\mathrm{C}H{=}\mathrm{C}H$-), 5.10 - 4.89 (m, $\mathrm{H_2C{=}C}H$-), 3.41 (t, *J* = 6.7 Hz, -$\mathrm{C}H_2$-O-$\mathrm{C}H_2$-), 2.03 (dd, *J* = 19.0, 13.4 Hz, =CH-$\mathrm{C}H_2$-), 1.74 – 1.11 (m, aliphatic).

P2-G2. *(61 %)* ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ (ppm) = 5.39 – 5.20 (m, -$\mathrm{C}H{=}\mathrm{C}H$-), 3.31 (t, *J* = 6.7 Hz, -$\mathrm{C}H_2$-O-$\mathrm{C}H_2$-), 2.00 – 1.80 (m, =CH-$\mathrm{C}H_2$-), 1.56 – 1.13 (m, aliphatic).

General procedure for thiol-ene polymerizations. Into a reaction vessel 1 mmol of the diene monomer (**1** or **2,** 1.00 eq), the corresponding dithiol compound (see **Table 1**, 1.00 eq), and AIBN (0.05 eq) were introduced and degassed via 3 times 200 mb vacuum and subsequent Ar purge. Afterwards, the reaction was let to stir magnetically (500 rpm) at 80 °C for 1 hour. The reaction mixture was dissolved in THF and precipitated into 1M HCl in methanol solution.

P3. *(81 %)* ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ (ppm) = 3.55 (t, *J* = 7.0 Hz, -$\mathrm{C}H_2$-O-$\mathrm{C}H_2$-), 2.63 (t, *J* = 7.0 Hz, -S-$\mathrm{C}H_2$-$\mathrm{CH_2O}$-), 2.48 (t, *J* = 7.0 Hz, -$\mathrm{C}H_2$-$\mathrm{SCH_2CH_2O}$-), 1.51 – 1.15 (m, aliphatic).

P4. *(89 %)* ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ (ppm) = 2.50 – 2.39 (m, HS-$\mathrm{CH_2}$- and -$\mathrm{C}H_2$-$\mathrm{SC}H_2$-$[\mathrm{CH_2}]_2$-$\mathrm{C}H_2\mathrm{SC}H_2$-), 1.65 – 1.59 (m, -$\mathrm{SCH_2}$-$[\mathrm{C}H_2]_2$-$\mathrm{CH_2S}$-), 1.55 – 1.15 (m, aliphatic).

***P5**. (84 %)* ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.55 (t, *J* = 7.0 Hz, $\text{-C}\mathit{H}_2\text{-O-C}\mathit{H}_2\text{-}$), 3.32 (t, *J* = 6.8 Hz, $\text{-SCH}_2\text{-C}\mathit{H}_2\text{-O}$), 2.63 (t, *J* = 6.9 Hz, $\text{-S-C}\mathit{H}_2\text{-CH}_2\text{O-}$), 2.48 (t, *J* = 7.4 Hz, $\text{-C}\mathit{H}_2\text{-SCH}_2\text{CH}_2\text{O-}$), 1.56 – 1.14 (m, aliphatic).

***P6**. (92 %)* ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.32 (t, *J* = 6.8 Hz, $\text{-C}\mathit{H}_2\text{-O-C}\mathit{H}_2\text{-}$), 2.49 – 2.38 (m, HS-CH2- and $\text{-C}\mathit{H}_2\text{-SC}\mathit{H}_2\text{-[CH}_2]_2\text{-C}\mathit{H}_2\text{SC}\mathit{H}_2\text{-}$), 1.68 – 1.56 (m, $\text{-SC}\mathit{H}_2\text{-[C}\mathit{H}_2]_2\text{-C}\mathit{H}_2\text{S-}$), 1.56 – 1.10 (m, aliphatic).

9.7 A Novel Polymerization Approach *via* Thiol-yne Addition

9.7.1 Materials

1-Octyne (Aldrich, 97%), 1-octanethiol (Aldrich, 98.5%), 2,2′-Azobis(2-methylpropionitrile) (AIBN, Aldrich, 98%), propargyl alcohol (Aldrich, 99%), 10-undecynoic acid (Aldrich 95%), propargylic acid (Aldrich 95%), 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), 1,4-butanedithiol (Aldrich, ≥97%), 3,6-Dioxa-1,8-octane-dithiol (Aldrich, 95%), chloroform-d (Armar Chemicals, 99.8 atom-% D), and all solvents were used as received. Esterification of 10-undecynoic acid with methanol was carried out via typical laboratory procedures and all analytic data well agreed with the structure.

9.7.2 Polymerization reactions

All GPC samples were taken from crude reaction mixtures to avoid any possible effect of the precipitation procedure on the polymer composition.

Typical thermally-initiated polymerization setup. The corresponding alkyne and dithiol compounds were introduced in 1:2 ratio into a round bottom flask with magnetic stirrer. After the addition of AIBN, (when necessary 0.05 eq) the flask was degassed (3 times 200 mb vacuum and subsequent Ar purge) and let to stir at 80 °C.

Typical UV-initiated polymerization setup. The corresponding alkyne and dithiol compounds were introduced in 1:1 eq. ratio into a round bottom flask with magnetic stirrer. After the addition of DMPA, (when necessary 0.05 eq., see Table) the flask was placed onto a magnetic stirrer equipped with handheld UV lamps (2 times 4W) and left to stir without any degassing at room temperature. The raise of the reaction flask temperature by UV lamps was controlled and found to maintain lower than 35 °C.

9.7.3 NMR data

Model Reaction. ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.93 (dt, *J* = 5.4, 1.3 Hz, 1H, α-Z), 5.88 (t, *J* = 1.3 Hz, 1H, α-E), 5.59 (ddt, *J* = 20.1, 9.4, 7.0 Hz, 1H, β-Z,E), 2.85 (dd, *J* = 11.8, 3.9 Hz, 1H), 2.53 (dd, *J* = 10.7, 4.0 Hz, 1H), 2.17 – 2.03 (m, 2H), 1.69 – 1.52 (m, 3H), 1.46 – 1.15 (m, 28H), 0.89 (t, *J* = 6.7 Hz, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 130.87(β-E), 129.59(β-Z), 124.95(α-E), 122.67(α-Z), 45.79, 38.45, 33.92, 33.53, 33.22, 33.12, 32.79, 31.82, 31.76, 31.72, 31.69, 30.90, 30.35, 29.90, 29.82, 29.51, 29.34, 29.23, 29.19, 29.02, 28.98, 28.94, 28.92, 28.81, 28.75, 28.63, 26.70, 22.66, 22.64, 22.62, 14.09.

P1. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.76 (dd, *J* = 11.0, 3.6 Hz, 1H, >CH-C(H_a)H$_b$-S-), 2.71 – 2.38 (m, 6H, -CH_2-S-CH(CH$_2$-)-C(H$_a$)H_b-S-CH_2-), 1.81 – 1.53 (m, 6H, -SCH$_2$-[CH_2]$_2$-CH$_2$S-), 1.53 – 1.11 (m, 9H, aliphatic CH$_2$), 0.82 (t, *J* = 6.6 Hz, 3H, -CH$_3$).

P2. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 3.76 – 3.51 (m, 8H, -SCH_2-[CH_2-O-CH_2]$_2$-CH$_2$S-), 2.88 (dd, *J* = 11.4, 4.0 Hz, 1H, >CH-C(H_a)H$_b$-S-), 2.83 – 2.61 (m, 6H, -CH_2-S-CH(CH$_2$-)-C(H$_a$)H_b-S-CH_2-), 1.90 – 1.65 (m, 2H, >CH-CH_2-), 1.60 – 1.17 (m, 8H, aliphatic CH$_2$), 0.88 (t, *J* = 6.6 Hz, 3H, -CH$_3$).

P3. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 3.64 (s, 3H, -COO-CH$_3$), 2.80 (dd, *J* = 10.9, 3.3 Hz, 1H, >CH-C(H_a)H$_b$-S-), 2.75 – 2.43 (m, 6H, -CH_2-S-CH(CH$_2$-)-C(H$_a$)H_b-S-CH_2-), 2.28 (t, *J* = 7.5 Hz, 2H, -CH_2-COOCH$_3$), 1.85 – 1.53 (m, 2H, >CH-CH_2-), 1.52 – 1.14 (m, 12H, aliphatic CH$_2$).

P4. ^{1}H-NMR (300 MHz, CDCl$_3$) δ 3.77 – 3.51 (m, 11H, -COO-CH_3 and -SCH_2-[CH_2-O-CH_2]$_2$-

$\mathrm{CH_2S}$-), 2.91 – 2.84 (m, 1H, >CH-C(H_a)$\mathrm{H_b}$-S-), 2.83 – 2.62 (m, 6H, -CH_2-S-C*H*($\mathrm{CH_2}$-)-C($\mathrm{H_a}$)H_b-S-CH_2-), 2.30 (t, *J* = 7.5 Hz, 2H, -CH_2-$\mathrm{COOCH_3}$), 1.85 – 1.69 (m, 2H, >CH-CH_2-), 1.64 – 1.16 (m, 12H, aliphatic $\mathrm{CH_2}$).

P7. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 3.75 (dd, *J* = 11.5, 4.9 Hz, 1H, >CH-C(H_a)$\mathrm{H_b}$-S-), 3.64 (dd, *J* = 10.8, 5.5 Hz, 1H, >CH-C($\mathrm{H_a}$)H_b-S-), 2.93 – 2.62 (m, 3H, >C*H*-CH_2-OH), 2.51 (m, 4H, -S-CH_2-[$\mathrm{CH_2}$]$_2$-CH_2-S-), 2.39 – 2.11 (br., 1H, -O*H*) 1.66 (m, 4H, -S-$\mathrm{CH_2}$-[CH_2]$_2$-$\mathrm{CH_2}$-S-).

P8. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 3.82 (dd, *J* = 11.6, 5.0 Hz, 1H, >CH-C(H_a)$\mathrm{H_b}$-S-), 3.77 – 3.55 (m, 11H, >CH-CH_2OH and >CH-C($\mathrm{H_a}$)H_b-S-$\mathrm{CH_2}$-[CH_2-O-CH_2]$_2$-$\mathrm{CH_2S}$-), 3.01 (m, 1H, >C*H*-$\mathrm{CH_2OH}$), 2.94 – 2.62 (m, 4H, -S-CH_2-[$\mathrm{CH_2OCH_2}$]$_2$-CH_2-S-).

9.8 New Renewable Polyamides from Fatty Acids

9.8.1 Materials

Methyl oleate and erucate were kindly supplied by Croda (90% by GC), 10-undecenoic acid (Aldrich, 95%), Cysteamine hydrochloride (Fluka, >97%), Na_2CO_3 (Fisher Scientific), Na_2SO_4 (Fluka, >99%), silica gel 60 (0.035 – 0.070mm, Aldrich), chloroform-d (99.8 atom-% D, Armar Chemicals), 1,5,7-triazabicyclo[4.4.0]dec-5-ene, (TBD, Aldrich, 98%), 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Aldrich, 99%), trifluoroacetic anhydride (Aldrich) were used as received. All solvents (technical grade) were used without purification. Methyl 10-undecenoate was prepared from 10-undecenoic acid *via* classical laboratory procedures.

9.8.2 Synthesis of the Monomers

Methyl 11-(2-aminoethylsulfanyl)undecenoate (1). 1 eq of Cystemaine hydrochloride for 5g of methyl 10-undecenoate and 10 vol% of toluene were placed into a round bottom flask and set with a mechanical stirrer after degassing (3 times 200 mb vacuum for 1 min and nitrogen purge). The reaction mixture was stirred at 75 °C for 1 day. The mixture was collected with CH_2Cl_2, extracted with saturated K_2CO_3 solution, brine solution, and water. The collected organic phase was concentrated in *rotavap*. The product in the form of white precipitate was purified *via* recrystallization from cyclohexane. Yield: 85%

General Procedure for methyl 10-(2-aminoethylsulfanyl)octadecanoate (2) and methyl 14-(2-aminoethylsulfanyl)docosanoate (3). 3 eq of 12 and 0.1 eq of DMPA for 5g of methyl oleate or erucate in 3 mL of EtOH was placed into a round bottom flask and set with a mechanical stirrer and 2x4W hand-type UV lamps aside for 2 days. The mixture was neutralized with saturated sodium carbonate solution; the product was extracted with diethyl ether, dried over anhydrous sodium sulphate, and concentrated in rotavap. The crude mixture was purified via silicagel column using first Hexane:ethyl acetate=1:1 solvent mixture to remove all unreacted residue (saturated fatty acids) and finally the product was collected using MeOH:Ethyl acetate=1:10. The product was concentrated in rotavap, dissolved once more in hexane and filtered through cotton to remove silicagel completely, and finally concentrated in rotavap and obtained as yellowish viscous liquid. It should be noted that excessive heat should not be applied and the purified product should be stored in the fridge in order to avoid dimerizations. The isolated yields were 75 and 66 % for **2** and **3**, respectively.

Analytical Data. **(1):** ^{1}H NMR: (300 MHz, CDCl$_3$) δ 3.66 (s, 3H, H_3COOC-), 2.86 (t, *J* = 6.3 Hz, 2H, H$_2$N-CH_2-), 2.60 (t, *J* = 6.3 Hz, 2H, H$_2$NCH$_2$-CH_2-S), 2.52 – 2.45 (t, 2H, -CH$_2$S-CH_2-), 2.29 (t, *J* = 7.5 Hz, 2H, -CH_2-COO), 1.70 – 1.47 (m, 2H, aliphatic), 1.44 – 1.15 (m, 14H, aliphatic).

^{13}C NMR: (75 MHz, CDCl$_3$) δ 174.45 (-*C*OO-), 51.57 (H$_2$N-*C*H$_2$-), 41.36 (H$_2$NCH$_2$-*C*H$_2$-S), 36.55 (-CH$_2$S-*C*H$_2$-), 34.24 (-*C*H$_2$-COO), 32.00 – 25.07 (aliphatic).

GC-MS: 199.1, 231.2 *m/z* (calc. $[M\text{-}[CH_2]_2NH_2]^{+\bullet}$ = 231.1; $[M\text{-}S[CH_2]_2NH_2]^{+\bullet}$ = 199.1)

(2): ^{1}H NMR: (300 MHz, CDCl$_3$) δ 3.52 (s, 3H, H_3COOC-), 2.71 (t, *J* = 6.4 Hz, 2H, H$_2$N-CH_2-), 2.53 – 2.31 (m, 3H, NCH$_2$-CH_2-S-C*H*<), 2.15 (t, *J* = 7.5 Hz, 2H, -*C*H$_2$-COO), 1.61 – 0.98 (m, 41H, aliphatic), 0.73 (t, *J* = 6.6 Hz, 3H, -CH_3).

^{13}C NMR (75 MHz, CDCl$_3$) δ 174.28 (-*C*OO-), 51.42 (H$_2$N-*C*H$_2$-), 45.89 (H$_2$NCH$_2$-*C*H$_2$-S), 41.65 (S-*C*H<), 36.75 (-*C*H$_2$-COO), 35.09 – 24.91 (aliphatic), 14.09 (-*C*H$_3$).

FAB-MS: 374.3 *m/z* (calc. [M+H]$^+$=374.6)

(3): ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.64 (s, 3H, *H$_3$*COOC-), 2.83 (t, *J* = 6.4 Hz, 2H, H$_2$N-C*H$_2$*-), 2.65 – 2.44 (m, 3H, NCH$_2$-C*H$_2$*-S-C*H*<), 2.28 (t, *J* = 7.5 Hz, 2H, -C*H$_2$*-COO), 1.74 – 1.03 (m, 47H, aliphatic), 0.86 (t, *J* = 6.5 Hz, 3H, -C*H*$_3$).

^{13}C NMR (75 MHz, CDCl$_3$) δ 174.29 (-*C*OO-), 51.40 (H$_2$N-*C*H$_2$-), 45.85 (H$_2$NCH$_2$-*C*H$_2$-S), 41.67 (S-*C*H<), 36.79 (-*C*H$_2$-COO), 35.01 - 22.65 (aliphatic), 14.09 (-*C*H$_3$).

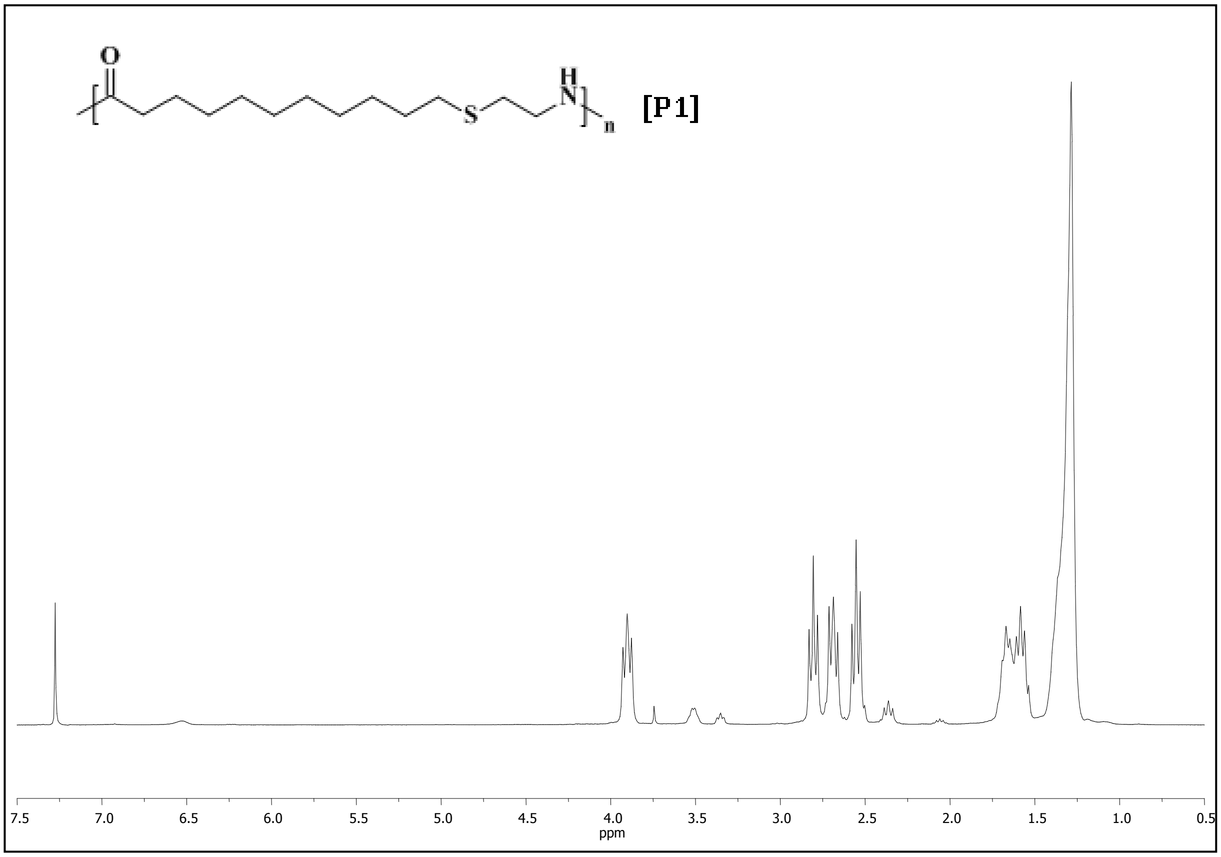
FAB-MS: 430,4 *m/z* (calc. [M+H]$^+$=430,7)

9.8.3 Polymerization Reactions

General Procedure for Polymerizations: All polymerization reactions were carried out at a carousel reactor system (RR98072 from Radleys™ Discovery Technologies, UK) in order to assure the comparable reaction conditions. The corresponding monomers (see the entries Table) and 0.05 eq of TBD (relative to ester groups) were weighted into the reaction vessel and placed to the reactor system. The polymerization was carried out under continuous vacuum (10±5 mbar). When low boiling point monomers were used, the polymerization started at lower temperatures and gradually increased to 140 °C.

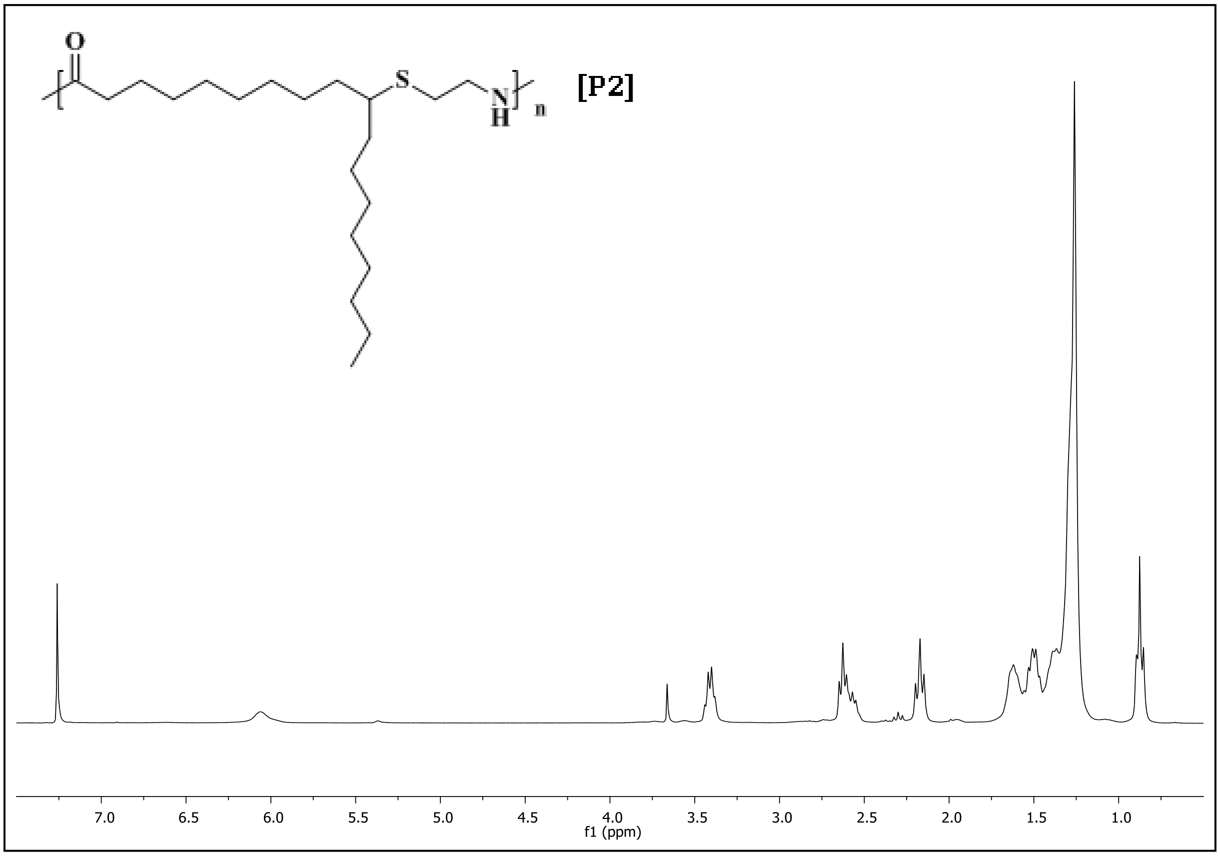
(P1): Polymerized at 140 ˚C for 20 h. The reaction mixture was dissolved in HFIP and precipitated into methanol. Trifluoroacetic anhydride treatment was applied prior to the NMR analysis.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.95 – 3.86 (m, -CH_2.NH-), 3.74 (s, H_3C-OOC-), 2.81 (t, J = 7.4 Hz, -S-CH_2-CH_2NH-), 2.72 – 2.64 (m, -CH_2-S-), 2.55 (t, J = 7.4 Hz, -OOC-CH_2-), 2.41 – 2.31 (m, -SCH_2-CH_2-NH_2), 1.81 – 1.50 (m, aliphatic), 1.28 (m, aliphatic).



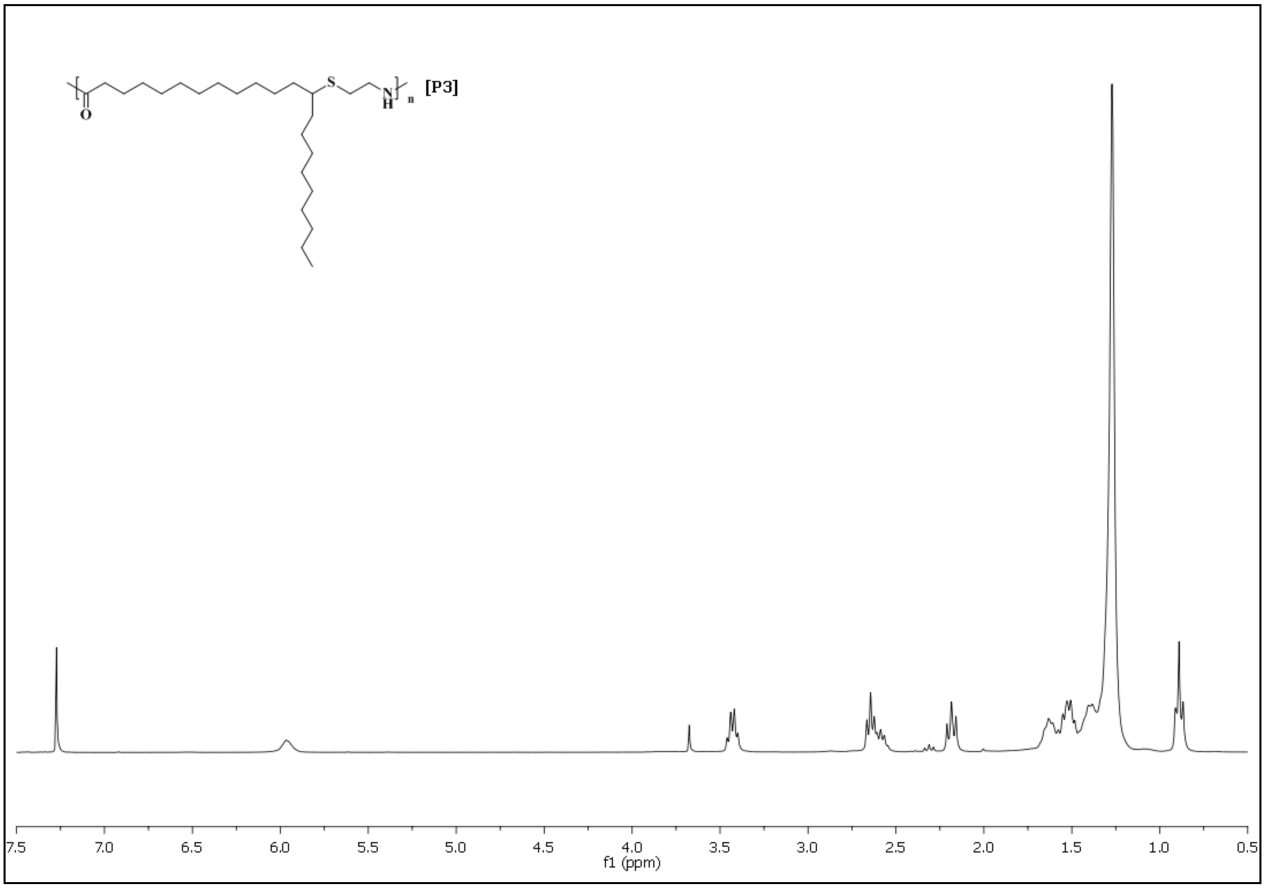
(P2): Polymerized at 140 °C for 20 h. The reaction mixture was collected with THF and precipitated into ice-cold methanol.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (b, -N*H*-), 3.66 (s, 1H), 3.42 (dd, J = 12.1, 6.0 Hz, 2H), 2.70 – 2.48 (m, 3H), 2.30 (t, J = 7.5 Hz, 1H), 2.17 (t, J = 7.6 Hz, 2H), 1.80 – 1.08 (m, 45H), 0.88 (t, J = 6.4 Hz, 4H).



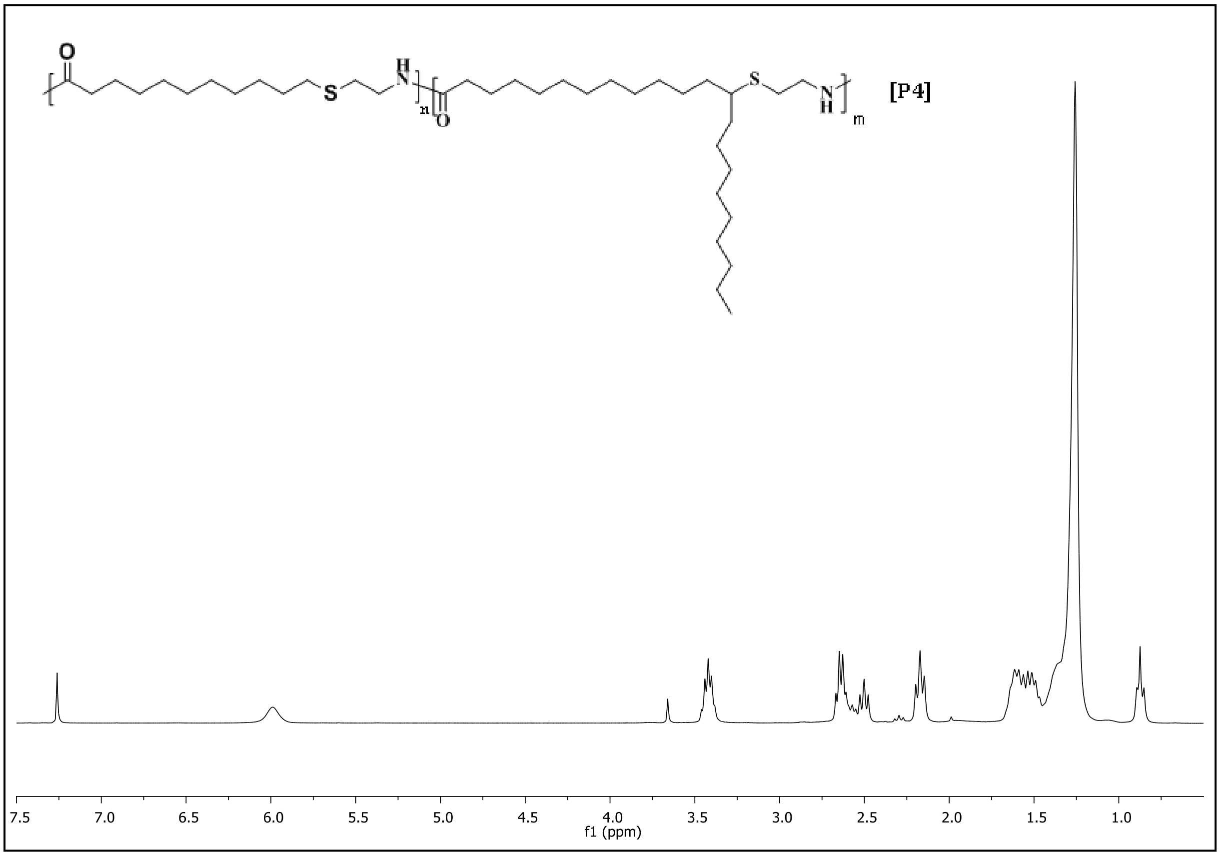
(P3): Polymerized at 140 °C for 20 h. The reaction mixture was collected with THF and precipitated into ice-cold methanol.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (b, -N*H*-), 3.66 (s, 1H), 3.42 (dd, J = 12.1, 6.0 Hz, 2H), 2.70 – 2.48 (m, 3H), 2.30 (t, J = 7.5 Hz, 1H), 2.17 (t, J = 7.6 Hz, 2H), 1.80 – 1.08 (m, 45H), 0.88 (t, J = 6.4 Hz, 4H).



(P4): Polymerized at 140 °C for 20 h. The reaction mixture was collected with THF and precipitated into ice-cold methanol.

^{1}H NMR (300 MHz, CDCl$_3$) δ 5.99 (b, -N*H*-), 3.66 (s, $_3$*H*C-OOC-), 3.42 (m, -C*H*$_2$-NHCO-), 2.74 – 2.44 (m, -C*H*$_2$-S-C*H*$_2$- and >C*H*-S-C*H*$_2$-), 2.30 (t, *J* = 7.5 Hz, -C*H*$_2$-COO-), 2.17 (t, *J* = 7.5 Hz, -C*H*$_2$-CONH-), 1.75 – 1.11 (m, aliphatic), 0.87 (t, *J* = 6.3 Hz, -C*H*$_3$).



10

Concluding Remarks and Outlook

The goal of this dissertation was to access valuable monomers and polymers from renewable resources through efficient pathways. Plant oils were chosen as the renewable resource since a wide range of fatty acids, with long aliphatic chain and unsaturations, and in high purity, can readily be obtained from Nature. All a polymer chemist has to do is to link these valuable monomers, either directly or after modification / functionalization, into polymers *via* simple, but highly efficient and green chemical pathways.

New synthetic routes to a number of aliphatic polyester monomers were introduced in chapters 4 and 5 resulting in hyperbranched and linear polyesters from renewable resources, which could be used to substitute the polyesters from petroleum originated monomers. Thiol-ene&yne addition reactions featuring click chemistry conditions were introduced and utilized for the modification / functionalization as well as polymerization of fatty acid derivatives as a complementary method to the ongoing metathesis studies in our group. Not only in this respect, was it important to study and achieve optimal reaction conditions to produce monomers in high yields.

The concept of "programmed-life plastics" has already been discussed in literature[297] and seems to be a promising concept to fill in the gap between non-degradable plastics that accumulate on land and highly degradable soft polymers. In chapter 5, two complementary synthetic pathways to a new range of biodegradable polymers from a renewable platform chemical using thiol-ene addition reactions and ADMET polymerizations were introduced and discussed. The synthesized polymers, which may substitute plastics from biomedically useful polymers to packaging materials, were structurally almost identical, and differed only in connectivity. This feature was very important to achieve since it is hardly possible by any other reaction pathway. Additionally, thiol-ene and ADMET polymerizations were studied and compared to each other for the polymerization of the same monomers for the first time. Thiol-ene addition polymerizations, despite the nucleophilic nature of thiol compounds that makes ADMET reactions preferable for high molecular weight polyanhydride preparation, exhibit unique properties for being efficient and environmentally benign.

In contrast to polyesters and polyanhydrides, polyethylenes (and other polyolefins) are non-degradable and the highest volume plastics among others. Recently commercialized processes for the preparation of polyethylenes from renewable resources, such as ethylene from bio-ethanol by Braskem, Brazil, clearly indicates the great interest on sustaining the polyethylene production. Thus, in chapter 6 a number of polymers that are polyethylene-like considering their chemical structure were synthesized from plant oil-derived renewable platform chemicals using thiol-ene addition as well as ADMET polymerization reactions. The thermal properties of the synthesized polymers resulted in lower melting temperatures relative to those of commercial polyethylenes, which indicate that these polymers might substitute polyethylene paraffins. Importantly, a renewable dithiol compound was prepared and was used for the thiol-ene polyaddition, yielding a fully renewable thiol-ene polymer for the first time with good thermal properties. This contribution should be considered as an example to overcome the non-renewable character of the so far used dithiol compounds and should be extended and optimized for other dithiol compounds in the future. These results revealed that the thiol-ene addition reaction is a very useful method for the synthesis of renewable and metal-free polyethylene mimics under mild conditions.

As the demand of plastics with improved properties increases, new synthetic strategies to access complex structures are being intensively researched. The highest production volume polyethylenes are very difficult to precisely modify because of the lack of functional groups. Chapter 7 introduced a novel polymerization approach utilizing thiol-yne addition reaction to produce precisely functionalized linear polymers. Alcohol, aliphatic, and ester (&acid) functional linear polythioethers are obtained from dithiols and functional monoalkynes under mild thiol-yne reaction conditions. The resulting polymers exhibit structurally high similarity to the some commercially available polymers, like polyvinyl alcohols, polyacrylates, and LDPEs that require more complicated production conditions. The independency of reactivity on the dithiols employed and adjustability of functional group frequency are of the uniqueness of this new polymerization method.

Noteworthy, the successfully synthesized polymers should be suitable for the synthesis of diverse comb and dendritic polymers.

Last but not least, aliphatic polyamides can be synthesized from monomers that are derived from plant oils. The introduction of primary amine groups was achieved *via* thiol-ene addition reactions to methyl- 10-undecenoate, -oleate, and -erucate, which were then used the prepare polyamides. A wide range of renewable polyamides from amorphous state at room temperature to high-melting semi-crystalline polymers were obtained *via* the combination of these monomers. In addition, these flexible and hydrophobic character of these new fatty monomers allowed the modification of Nylon 6,6 *via* simply copolymerization in selected ratios.

To sum up, a considerable amount of novel monomers and polymers from plant oils as well as highly efficient synthetic procedures were introduced within this dissertation. 10-Undecenoic acid was mainly used as a monomer directly or after modification in order to achieve efficient thiol-ene&yne and metathesis reactions. Not only synthesis, but also intensive thermal analysis of the prepared polymers was reported. As a result, a library of fatty acid-derived monomers and polymers is formed. Due to the fact that the world is running out of mineral oil, mankind has to shift from the use of petroleum-dependant resources to bio-based renewable resources through environmentally friendly and sustainable procedures. Therefore, the polymer library resulting from this dissertation clearly shows the usefulness of plant oils for polymer synthesis and is a valuable contribution to a sustainable development and hopefully some of these investigations will also find their way into industrial applications.

List of Abbreviations

ADMET : Acyclic diene metathesis polymerization

AIBN : 2,2’-azobisisobutyronitrile

BQ : p-Benzoquinone

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

DVB : Divinyl benzene

EI : Electron Impact

ESBO : Epoxidized Soybean Oil

ESI : Electro-spray Ionization

FAB : Fast Atom Bombardment

FAME : Fatty acid methyl ester

G : Glycerol

GC : Gas Chromatography

GC-MS : Gas Chromatography – Mass Spectroscopy

HAP : Hazardous air pollutant

HMQC : Heteronuclear Multiple-Quantum Correlation

IPN : Interpenetrating network

LDPE : Low Density Polythylene

LLDPE : Linear Low Density Polythylene

LOI : Limiting oxygen index

METU : Methyl undec-10-enoat

MS	: Mass Spectroscopy
NMMO	: N-methylmorpholine-N-oxide
NMR	: Nuclear Magnetic Resonance Spectroscopy
PGA	: Poly(glycolic acid)
PHA	: Polyhydroxyalkanoate
PHB	: Poly(3-hydroxybutyrate)
PHBV	: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	: Poly(lactic acid)
PLLA	: Poly(l-lactic acid)
PU	: Polyurethane
PVA	: Poly(vinyl alcohol)
UA	: Undec-10-enoic acid
UV	: Ultraviolet
VOC	: Volatile organic compounds

Curriculum Vitae

Personal Information:

Date of Birth	: 27/05/1981
Place of Birth	: Samandağ, Turkey
Nationality	: Turkish

Education:

03.2009 – 07.2012: Ph.D. student under supervision of Prof. Dr. Michael A. R. Meier (moved with the group from Emden University of Applied Sciences to University of Potsdam and to the current destination at the Karlsruhe Institute of Technology)

07.2005 – 07.2007: Master of Science in Organic Polymer Chemistry at Marmara University, Istanbul, Turkey, under supervision of Prof. Dr. Nilhan Kayaman-Apohan.

09.2001 – 06.2005: Study of chemistry at Marmara University, Istanbul, Turkey.

09.2000 – 06.2001: Prep school for English at Marmara University, Istanbul, Turkey.

Work Experience:

09.2011 - Present : Research assistant at the Laboratory of Applied Chemistry at KIT, Karlsruhe, Germany.

03.2009 – 08.2011: Research assistant within the group “renewable raw materials” at the University of Applied Sciences Emden/Leer, Faculty of Technology, Emden, Germany.

09.2008 – 02.2009: R&D specialist for product and process development at Biota Laboratories for Cosmetics, Istanbul, Turkey.

01.2007 – 07.2007: R&D researcher for product and process development at Izomas Corrosion Control Eng. A.C., Istanbul, Turkey.

08.2003 : Summer internship at Marsa – Kraft General Foods (currently Marsa Yağ Sanayi ve Tic. A.Ş.), Adana, Turkey.

08.2004 : Summer internship at Türk – Henkel, Istanbul, Turkey.

Awards, grants, scholarships:

2012: The publication Nr. 4 was chosen to be included in **"Best of Macromolecular Journals 2011"**

2011: Journal front cover at Green Chemistry (See Publication Nr. 6)

2011: One of the top posters and Karl-Ziegler travel grant at German Chemists Society (GDCh) Scientists Forum 2011, Bremen, Germany

2011: Abiosus e.V. and German Chemists Society (GDCh) travel grant for the ACS 15th Annual Green Chemistry & Engineering Conference, Washington, DC.

2000: Scholarship for 5 years of high-education by Turkish Republic Prime Ministry.

Professional Societies:

- German Chemists Society (GDCh)
- American Chemical Society (ACS)

List of Publications and Conference Contributions

Refereed Journal Publications:

12. *O. Türünç*, M. Firdaus, G.Klein, M. A. R. Meier, Fatty acid derived renewable polyamides via thiol-ene additions, *Green Chem.*, **2012**, doi: 10.1039/C2GC35982K.

11. *O. Türünç* and M. A. R. Meier, The Thiol-Ene (Click) Reaction for the Synthesis of Plant Oil derived Polymers, *Eur. J. Lipid Sci. Technol.* **2012**, doi: 10.1002/ejlt.201200148.

10. U. Biermann, W. Butte, R. Koch, P. Fokou, *O. Türünç*, M.A.R. Meier, J. O. Metzger, Initiation of radical chain reactions of thiols and alkenes without any added initiator: Thiol-catalyzed *cis-trans* isomerization of methyl oleate, *Chem. Eur. J.* **2012**, *18*, 8201–8207.

9. O. Kreye, *O. Türünç*, A. Sehlinger, J. Rackwitz, M. A. R. Meier, Structurally diverse polyamides obtained from Ugi multicomponent reaction derived monomers, *Chem. Eur. J.* **2012**, *18*, 5767–5776.

8. *O. Türünç*, M. A. R. Meier, A Novel Polymerization Approach via Thiol-yne Addition, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 1689–1695.

7. *O. Türünç*, L. Montero de Espinosa, M. A. R. Meier, Renewable Polyethylene Mimics Derived from Castor Oil, *Macromol. Rapid Commun.* **2011**, 1357-1361.

6. *O. Türünç*, M. A. R. Meier, Thiol-Ene vs. ADMET: A complementary approach to fatty acid based biodegradable polymers, *Green Chem.* **2011**, *13*, 314–320.

5. H. Mutlu, L. Montero de Espinosa, *O. Türünç*, M. A. R. Meier, About the activity and selectivity of less well-known metathesis catalysts during ADMET polymerizations, *Beilstein J. Org. Chem.* **2010**, *6*, 1149-1158.

4. *O. Türünç*, M. A. R. Meier, Fatty acid derived monomers and related polymers via thiol-ene (click) additions, *Macromol. Rapid Commun.* **2010**, *31*, 1822–1826.

3. S. Karataş, N. Kayaman-Apohan, *O. Türünç*, A. Güngör, Synthesis and characterization of UV-curable phosphorus containing hybrid materialsp repared by sol–gel technique, *Polym. Advan. Technol.* **2010**, DOI Number:10.1002/pat.1546.

2. *O. Türünç*, M.V. Kahraman, Z.S. Akdemir, N. Kayaman-Apohan, A. Güngör, Immobilization of a-Amylase onto Cyclic Carbonate Bearing Hybrid Material, *Food Chemistry* **2009**, 112(4), 992-997.

1. *O. Türünç*, N. Kayaman-Apohan, M. V. Kahraman, Y. Menceloglu, A. Gungor, Nonisocyanate based polyurethane / silica nanocomposites and their coating performance *J. Sol-Gel Sci.Tech.* **2008**, 47(3), 290-299.

Book Chapter:

1. *O. Türünç* and M.A.R. Meier, Food and Industrial Bioproducts and Bioprocessing (Ch. 11 Biopolymers): N. Dunford, Ed. Wiley-Blackwell Food Science Books, **2012**.

Poster Presentations and talks:

11. Talk: Synthesis of fatty acid derived monomers and polymers thereof via efficient catalytic and non-catalytic approaches, O. Türünç, Michael A. R. Meier, 5th Workshop on

Fats and Oils as Renewable Feedstock for the Chemical Industry, March 18 – 20, **2012**, Karlsruhe, Germany.

10. Poster: Amphiphilic Hyperbranched Polymers from a Castor Oil Derived Monomer, O. *Türünç*, K. Pahnke, M.A.R. Meier, 5th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry, March 18 – 20, **2012**, Karlsruhe, Germany.

9. Poster + 5 min Talk: A novel Polymerization Approach to Fatty Acid Based Polymers via Thiol-yne addition, *O. Türünç*, M.A.R. Meier. GDCh-Wissenschaftsforum Chemie, September 4-7, **2011**, Bremen, Germany.

8. Talk: New and efficient approaches to fatty acid derived monomers and polymers, *O. Türünç*, M.A.R. Meier. ACS 15th Green Chemistry and Engineering Conference, June 21-23, **2011**, Washington, DC.

7. Talk: Renewable Polyethylene-like Materials with Tunable Properties, *O.Türünç*, M.A.R. Meier. Karlsruhe Institute of Technology, Institute of Organic Chemistry Ph.D. students seminar, **2011**, Karlsruhe, Germany.

6. Poster: Renewable polyethylene mimics derived from castor oil, *O. Türünç*, M.A.R. Meier. 4th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry, March 14-16, **2011** Karlsruhe, Germany.

5. Poster: Thiol-ene vs. ADMET: a complementary approach to fatty acid-based biodegradable polymers, *O. Türünç*, M.A.R. Meier. 4th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry, March 14-16, **2011** Karlsruhe, Germany.

4. Poster: Biodegradable polymers from renewable resources via thiol-ene addition. *O. Türünç*, Michael A.R. Meier. 43rd IUPAC World Polymer Congress, July 11-16, **2010** Glasgow, UK.

3. Poster: Clicking renewable resources: Fatty acid derived monomers and related polymers via thiol-ene additions. *O. Türünç*, Michael A.R. Meier. 43rd IUPAC World Polymer Congress. July 11-16, **2010** Glasgow, UK.

2. Poster: Immobilization of a-amylase onto cyclic carbonate bearing hybrid material. Z.S. Akdemir, *O. Türünç*, M. V. Kahraman, N. Kayaman-Apohan, A. Güngör. XXII. National Chemistry Congress, October 6-10, **2008** Magusa, Cyprus.

1. Poster: Nonisocyanate based polyurethane / silica nanocomposites and their coating performance. Z. Hoşgör, *O. Türünç*, S. Karataş, N. Kayaman-Apohan, M. V. Kahraman, Y. Menceloğlu, A. Güngör, NanoTRIV, 4. Nanoscience and Nanotechnology Conference, July 9-13, **2008** Istanbul, Turkey.

Acknowledgements

First of all and at most, I am thankful to Mike for letting me work in a self decisive manner and for his infinite patience. Without your prompt responses to each question and encouragement for all small ideas, this dissertation would be much tinier. It has been great honour for me to work with you and most importantly, you will always be one of the most important people for me, who contributed to my personality. Gratefully thank you!

My studies were funded by the German Federal Ministry of Food, Agriculture and Consumer Protection. Their financial support is kindly acknowledged.

My story in Germany started in Emden. First, thanks to Hatice for encouraging me to apply to this position. Tina, thank you for your generous and warm help and for being there for every single thing I needed. Many thanks to Patrice, for my first get to know to GC-MS and column chromatography. Guy, it was very nice to meet you and have your accompany in tiny Emden. Dr. Klaassen is also acknowledged for TGA and DSC analyses. I cannot leave Emden without mentioning Bilge, Emre, and Ibrahim. Thank you, guys, for your warm friendship in ‘four-season-in-one-day’ Emden.

And the story moves to Potsdam, one of the ever lovely cities I lived. Jenny Rackwitz partially contributed to Chapter 4, thank you for your work. Elke, you cannot imagine how grateful I am to get to know you and have your friendship. Lucia, I cannot compensate your generous help upon setting our new lab up and thank you for each “Guten Morgen” at the door with a big smile. I had probably the greatest moments with our in-Potsdam-everyday-out-group “Turkilla”. Thank you all, guys!

Finally, the group came to Karlsruhe. Thank you, Lucas, for the accompany and the stay at your apartment in these difficult times, and for the help with DSC interpretation; Kai Pahnke, for your contribution to Chapter 4; Olli, for the great times discussing politics with you and saving the world with bier; and all other group members that I could not mention here individually. Tommy, I will always remember you as purely nice person. Özcan, I appreciate your friendship and support at the late and hard times of my studies. I cannot finish this story without mentioning one person; Eleni, good that I got to know you and good that we became friends. Thank you very much for your sincere support in difficult times and all the good moments I had with you, and for making it possible to visit Athens.

Without the support of my family, this story would have never existed. I gratefully thank my parents for devoting their lives for the education of their children, and endless effort. How fabulous you are..!

Thank you all for making my life more meaningful…

Oğuz Türünç
Karlsruhe, 31.05.2012

References

---

1 Plastics – The Facts 2011, PlasticsEurope Association of Plastics Manufacturers under www.plasticseurope.org.

2 Anastas, Paul T. ; Williamson, Tracy C. Green Chem. 1996, 5, 1-17.

3 Anastas, P. and Eghbali, N. Chem. Soc. Rev. 2010, 39, 301–312; Poliakoff, M., Fitzpatrick, J.M., Farren, T.R., Anastas, P.T. Science 2002, 297, 807-810.

4 Anastas, P. T., Zimmerman, J. B., Environ. Sci. Technol. 2003, 37, 94A-101A; McDonough, W., Braungart, M., Anastas, P.T., Zimmerman, J.B. Environ. Sci. Technol. 2003, 37, 434A-441A.

5 Metzger, J.O. Eur. J. Lipid Sci. Technol. 2009, 111, 865–876.

6 Metzger, J.O. Chemosphere 2001, 43, 83-87.

7 Leither, W. Green Chem. 2007, 9, 923-923.

8 Capello, C., Fischer, U. and Hungerbühler, K. Green Chem., 2007, 9, 927–934.

9 Jessop, P.G. Green Chem., 2011, 13, 1391-1398.

10 Pace, V. Aust. J. Chem. 2012, 65, 301–302.

11 Licence, P., Ke, J., Sokolova, M., Ross, S. K., Poliakoff, M. Green Chem. 2003, 5, 99–104.

12 Hyde, J.R., Licence, P., Carter, D., Poliakoff, M. Appl. Catal. A: General 2001, 222, 119–131.

13 Hitzler, M.G. and Poliakoff, M. Chem. Commun. 1997, 17, 1667-1668.

14 Anastas, P. T., Bartlett, L. B., Kirchhoff, M. M. and Williamson, T. C. Catal. Today 2000, 55, 11–22.

15 Anastas, P.T., Kirchhoff, M.M., Williamson, T.C. Appl. Catal. A: General 2001, 21, 3–13.

16 "The Nobel Prize in Chemistry 2005". Nobelprize.org. 15 May 2012 http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/

17 Neghishi, E. Keynote abstract at the 5th International Green Chemistry and Engineering Conference 2011, Washington DC, USA; Negishi, E. Pure & Appl. Chem. 53, 2333—2356.

18 Negishi, E. Bull. Chem. Soc. Jpn. 2007, 80, 233–257.

19 Curzons, A. D., Constable, D. J. C., Mortimer, D. N., and Cunningham, V. L. Green Chem. 2001, 3, 1–6.

20 Hoyle, C. E., Lee, T. Y. & Roper, T. J. Polym. Sci. Part A: Polym. Chem. 2004, 42, 5301–5338.

21 Türünç, O. and Meier, M. A. R. Biopolymers. Food and Industrial Bioproducts and Bioprocessing . [Ed. Nurhan T. Dunford] 2012, 267–292. Wiley-Blackwell.

22 Voet D, Voet JG, Pratt CW. 2006. Fundamentals of Biochemistry: Life at the Molecular Level. 2nd Ed. John Wiley & Sons, Inc. 1264p.

23 Avella M, De Vlieger JJ, Errico ME, Fischer S, Vacca P, Volpe MG. 2005. Food Chem 93(3):467-474.

24 Mecking S. 2004. Angew Chem Int Ed 43(9):1078-1085.

25 Li G, Sarazin P, Favis BD. 2008 Macromol Chem Phys 209(10):991-1002.

26 Chuayuljit S, Hosililak S, Athisart A. 2009. J Mater Min 19(1):59-65.

27 Arvanitoyannis I, Psomiadou E, Biliaderis CG, Ogawa H, Kawasaki N, Nakayama A. 1997. Starch/Stärke 49(7/8):306-322.

28 Arvanitoyannis I, Biliaderis CG, Ogawab H, Kawasakib N. 1998. Carbohyd Polym 1998 36:89-104.

29 Gandini A. 2008. Macromolecules 41(24):9491-9504.

30 Lee WJ, Youn YN, Yun YH, Yoon SD. 2007. J Polym Envir 15(1):35-42.

31 Mooney BP. 2009. Biochem J 418(2):219-232.

32 Nabar YU, Draybuck D, Narayan R. 2006. J Appl Polym Sci 102(1):58-68.

33 Mihai M, Huneault MA, Favis BD. 2007. J Cell Plast 43(3):215-236.

34 Biswas A, Willet JL, Gordon SH, Finkenstadt VL, Cheng HN. 2006. Carbohyd Polym 65(4):397-403.

35 Lee WJ, Youn YN, Yun YH, Yoon SD. 2007. J Polym Envir 15(1):35-42.

36 Flieger M, Kantorová M, Prell A, Řezanka T, Votruba J. 2003. Folia Microbiol 48(1):27-44.

37 Lim S and Jane J. 1992. Biotechnol Progr 8(1):51-57.

38 Bagheri R and Naimian F. 2002. Polym Int 51:907-911

39 Jansson A, Järnström L, Rättö P, Thuvander F. 2006. Starch/Stärke 58(12):632-641.

40 Persico P, Ambrogi V, Acierno D, Carfagna C. 2009. J Vinyl Addit Techn 15(3):139-146.

41 Sagar AD and Merrill EW. 1995. J Appl Polym Sci 58(9):1647-1656.

42 Fringant C, Rinaudo M, Gontard N, Guilbert S, Derradji H. 1998. Starch/Stärke 50(7):292-296.

43 Donnelly MJ, Stanford JL, Still RH. 1991. Carbohyd Polym 14(3):221-240.

44 Otey FH and Miehltretter. 1962. US Pat. 3,165,508.

45 Ge J, Zhong W, Guo Z, Li W, Sakai K. 2000. J Appl Polym Sci 77(12):2575-2580.

46 Kim DH, Kwon OJ, Yang SR, Park JS. 2007. Fibers Polym 8(3):249-256.

47 Cunha FOV, Melo DHR, Veronese VB, Forte MMC. 2004. Mater Res 7:539-543.

48 Gomes ME, Ribeiro AS, Malafaya PB, Reis RL, Cunha AM. 2001. Biomaterials 22(9):883-889.

49 Salgado AJ, Coutinho OP, Reis RL. 2004. Macromol Biosci 4(8):743-765.

50 Finkenstadt VL. 2005. Appl Microbio Biot 67(6):735-745.

51 Khiar ASA, Arof AK. 2010. Ionic 16(2):123-129.

52 Véchambre C, Chaunier L, Lourdin D. 2010. Macromol Mater Eng 295(29):115-122.

53 Guerra NP, Macías CL, Agrasar AT, Castro LP. 2005. Lett Appl Microbiol 40(2):106-110.

54 Klemm D, Heublein B, Fink HP, Bohn A. 2005. Angew Chem Int Ed 44:3358-3393.

55 Schaub M, Wenz G, Wegner G, Stein A, Klemm D. 1993. Adv Mater 5(12):919-922.

56 Kontturi E, Tammelin T, Österberg M. 2006. Chem Soc Rev 35:1287-1304.

57 Gindl W and Jeronimidis G. 2004. J Mater Sci 39(9):3245-3247.

58 Mohanty AK, Misra M, Hinrichsen G. 2000. Macromol Mater Eng 276-277(1):1-24.

59 Felix JM and Gatenholm P. 1993. Polym Composite 14(6):449-457.

60 Nair KCB and Thomas S. 2003. Polym Composite 24(3):332-343.

61 Bogoeva-Gaceva G, Avella M, Malinconico M, Buzarovska A, Grozdanov A, Gentile G, Errico ME. 2007. Polym Composite 28(1):98-107.

62 Netravali AN and Chabba S. 2003. Mater Today 6(4):22-29.

63 Liebert T, Häsch C, Heinze T. 2006. Macromol Rapid Commun 27:208-213.

64 Zhao GL, Deiana L, Córdova A. 2010. Macromol Rapid Commun 31:740-744.

65 Buchanan CM, Gardner RM, Komarek R. 1993. J Appl Polym Sci 47(10):1709-1719.

66 Yan Y, Pang H, Yang X, Zhang R, Liao B. 2008. J Appl Polym Sci 110(2):1099-1111.

67 Kamel S, Ali N, Jahangir K, Shah SM, El-Gendy AA. 2008. eXPRESS Polym Lett 2(11):758-778.

---

68 Lichtenthaler FW. 2006. Biorefineries - Industrial Processes and Products. Status Quo and Future Directions. Vol. 2. Ames: Wiley - VCH Verlag GmbH & Co. KGaA, Weinheim/Germany.

69 Rasal RM, Janorkar AV, Hirt DE. 2010. Prog Polym Sci 35(3):338-356.

70 Dechy-Cabaret O, Martin-Vaca B, Bourissou D. 2004. Chem Rev 104:6147-6176.

71 Yang TH, Kim TW, Kang HO, Lee SH, Lee EJ, Lim SC, Oh SO, Song AJ, Park SJ, Lee SV. 2010. Biotechnol Bioeng 105(1):150-160.

72 Williams CK and Hillmyer MA. 2008. Polym Rev 48(1):1-10.

73 Zhong Z, Dijkstra PJ, Feijen J. 2003. J Am Chem Soc 125:11291-11298.

74 Kricheldorf HR, Lomadze N, Schwarz G. 2008. Macromolecules 41:7812-7816.

75 Tang Z, Gibson VC. 2007. Europ Polym J 43:150-155.

76 Amgoune A, Thomas CM, Roisnel T, Carpentier JF. 2006. Chem Eur J 12:169-179.

77 Csihony S, Culkin DA, Sentman AC, Dove AP, Waymouth RM, Hedrick JL. 2005. J Am Chem Soc 127:9079-9084.

78 Dove AP, Gibson VC, Marshall EL, Rzepa HS, White AJP, Williams DJ. 2006. J Am Chem Soc 128:9834-9843.

79 Lohmeijer BGG, Pratt RC, Leibfarth F, Logan JW, Long DA, Dove AP, Nederberg F, Choi J, Wade C, Waymouth RM, and Hedrick JL. 2006. Macromolecules. 39(25): 8574-8583.

80 Anderson KS, Schreck KM, Hillmyer MA. 2008. Toughening Polylactide. Polym Rev 48(1):85-108.

81 Robertson ML, Chang K, Gramlich WM, Hillmyer MA. 2010. Macromolecules 43:1807-1814.

82 Pounder RJ, Stanford MJ, Brooks P, Richards SP, Dove AP. 2008. Chem Commun 7(41):5158-5160.

83 Jiang X, Smith MR, Baker GL. 2008. Macromolecules 41:318-324.

84 Suggs LJ, Moore SA, Mikos AG. 2007. Physical Properties of Polymers Handbook. New York: Springer. p 939-950.

85 Reed AM and Gilding DK. 1981. Polymer 22(4):494-498.

86 Kayaman-Apohan N, Karal-Yılmaz O, Baysal K, Baysal BM. 2001. Polymer 42:4109-4116.

87 Steinbüchel A and Flüchtenbusch B. 1998. Trends Biotechnol 16:419-427.

88 Shimao M. 2001. Curr Opin Biotechnol 12:242-247.

89 Ramakrishna S, Mayer J, Wintermantel E, Leong KW. 2001. Compos Sci Technol 61:1189-1224.

90 Eschenlauer AC, Stoup SK, Srienc F, and Somers DA. 1996. Int J Biol Macmol 19:121-130.

91 Mittendorf V, Bongcam V, Allenbach L, Coullerez G, Martini N, Poirier Y. 1999. Plant J 20(1):45-55.

92 Snell KD and Peoples OP. 2002. Metab Eng 4:29-40.

93 Yunus AMM, Parveez GKA, and Ho C-L. 2008. AsPac J Mol Biol Biotechnol 16(1):1-10.

94 Tan IKP, Kumar KS, Theanmalar M, Gan SN, Gordon B III. 1997. Appl Microbiol Biotechnol 47: 207-211.

95 Chakraborty P, Gibbons W and Muthukumarappan K. 2009. J Appl Microbiol 106(6):1996-2005.

96 Ibrahim MHA and Steinbüchel A. 2009. J Appl Microbiol 108:214–225.

97 Marsudi S, Unno H, Hori K. 1998. Appl Microbiol Biotechnol 78:955–961.

98 Lemos PC, Serafim LS, Reis MAM. 2006. J Biotechnol 122:226-238.

99 Füchtenbusch B and Steinbüchel A. 1999. Appl Microbiol Biotechnol 52: 91-95.

100 Baldwin AD, Kiick KL. 2009. Peptide Sci 94(1):128-140.

101 Wani MY, Hasan N, Malik MA. 2010. J Disper Sci Technol 31(6):799-811.

102 Aam BB, Heggset EB, Norberg AL, Sørlie M, Vårum KM, Eijsink VGH. 2010. Mar Drugs 8:1482-1517.

103 Felse PA, Panda T. 2000. Bioprocess Eng 23:127-134.

104 Sahoo D, Sahoo S, Mohanty P, Sasmal S, Nayak PL. 2009. Des Monomers Polym 12:377-404.

105 Da Sacco L and Masotti A. 2010. Mar Drugs 8:1518-1525.

106 Derksen JTP, Cuperus FP, Kolster P. 1995. Ind Crop Prod 3:225-236.

107 Güner FS, Yağcı Y, Erciyes AT. 2006. Prog Polym Sci 31(7):633-670.

108 Valverde M, Andjelkovic D, Kundu PP, Larock RC. 2008. J Appl Polym Sci 107:423-430.

109 Meier MAR, Metzger JO, and Schubert US. 2007. Chem Soc Rev 36:1788–1802.

110 Henna PH, Andjelkovic DD, Kundu PP, Larock RC. 2007. J Appl Polym Sci 104:979-985.

111 John J, Bhattacharya M, Turner RB. 2002. J Appl Polym Sci 86:3097-3107.

112 Guo A, Demydov D, Zhang W, Petrović ZS. 2002. J Polym Environ 10(1-2):49-52.
113 Petrović ZS, Guo A, Javni I, Cvetković I, Hong DP. 2008. Polym Int 57:275-281.
114 Guo A, Zhang W, Petrović ZS. 2006. J Mater Sci 41(15):4914-4920.
115 Lu Y and Larock RC. 2008. Biomacromolecules 9(11):3332-3340.
116 Dwan'Isa JPL, Mohanty AK, Misra M, Drzal T, Kazemizadeh M. 2003. J Polym Environ 11(4):161-168.
117 Petrović ZS, Zhang W, Javni I. 2005. Biomacromolecules 6(2):713-719.
118 Türünç O, Kayaman-Apohan N, Kahraman MV, Menceloğlu Y, Güngör A. 2008. J Sol-Gel Sci Technol 47(3):290-299.
119 Tamami B, Sohn S, Wilkes GL. 2003. J Appl Polym Sci 92(2):883-891.
120 Javni I, Hong DP, Petrović ZS. 2008. J Appl Polym Sci 108(6):3867-3875.
121 Eren T, Küsefoğlu S, Wool R. 2003. J Appl Polym Sci 90:97-202.
122 Biswas A, Willet JL, Gordon SH, Finkenstadt VL, Cheng HN. 2006. Carbohyd Polym 65(4):397-403.
123 Ogunniyi DS. 2006. Bioresource Technol 97(9):1086-1091.
124 Mutlu H and Meier MAR. 2010. Eur J Lipid Sci Technol 112(1):10-30.
125 Moeini HR. 2007. J Appl Polym Sci 106:1853-1859.
126 Petrović ZS, Ionescu M, Javni I. 2009. US Patent Application 20090082483.
127 Valero MF, Pulido JE, Ramírez Á, Cheng Z. 2008. Quím Nova 31:2076-2082.
128 Karak N, Rana S, Cho JW. 2009. J Appl Polym Sci 112:736-743.
129 Mendes RK, Claro-Neto S, Cavalheiro ETG. 2002. Talanta 57:909-917.
130 Amado FDR, Rodrigues LF, Forte MMC, Ferreira CA. 2006. Polym Eng Sci 46:1485-1489.
131 Athawale VD, Kolekar SL, and Raut SS. 2003. J Macromol Sci Part C-Polym Rev 43(1):1-26.
132 Yenwo GM, Manson JA, Pulido J, Sperling LH, Conde A, Devia N. 1977. J Appl Polym Sci 21:1531-1541.
133 Cunha FOV, Melo DHR, Veronese VB, Forte MMC. 2004. Mater Res 7:539-543.
134 Sanmathi CS, Prasannakumar S, Sherigara BS. 2004. J Appl Polym Sci 94:1029-1034.
135 Suthar B, Dave M, Jadav K. 2003. J Appl Polym Sci 50:2143-2147.
136 Mohapatra DK, Das D, Nayak PL, Lenka S. 1996. J Appl Polym Sci 70:837-842.

137 Wang HJ, Rong MZ, Zhang MQ, Hu J, Chen HW, Czigány T. 2008. Biomacromolecules 9:615-623.

138 Kundu PP and Larock RC. 2005. Biomacromolecules 6:797-806.

139 Henna PH, Andjelkovic DD, Kundu PP, Larock RC. 2007. J Appl Polym Sci 104:979-985.

140 Carter DT, Stansfield N, Mantle RJ, France CM, Smith PA. 2008. Ind Crop Prod 2 8:309-319.

141 Henna PH, Kessler MR, Larock RC. 2008. Macromol Mater Eng 293:979-990.

142 Casado U, Marcovich NE, Aranguren MI, Mosiewicki MA. 2009. Polym Eng Sci DOI 10.1002/pen.21315.

143 Petrović ZS, Zhang W, Javni I. 2005. Biomacromolecules 6(2):713-719.

144 Metzger JO, Bornscheuer UT. 2006. Appl Microbiol Biotechnol 71:13-22.

145 Biermann U, Fürmeier S and Metzger JO. 2001. New Chemistry of Oils and Fats, in Oleochemical Manufacture and Applications (Frank D. Gunstone, Richard J. Hamilton, Eds.), Sheffield Academic Press and CRC Press, 2001, ISBN 1-84127-219-1, pp. 266-299.

146 Biermann U, Metzger JO. 2004. Topics in Catalysis 38:3675-3677.

147 Biermann U, Butte W, Eren T, Haase D, Metzger JO. 2007. Eur J Org Chem 2007(23): 3859-3862.

148 Domb AJ and Nudelman R. 1995. J Polym Sci: Part A: Polym Chem 33: 717-725.

149 Slivniak R, Domb AJ. 2005. Biomacromolecules 6:1679-1688.

150 Sokolsky-Papkov M, Shikanov A, Kumar N, Vaisman B, Domb AJ. 2008. Bull Israel Chem Soc 23:12-17.

151 Warwel S, Brüse F, Demes C, Kunz M, Rüsch gen. Klaas M. 2001. Chemosphere 43:39-48.

152 Meier MAR. 2009. Macromol Chem Phys 210:1073-1079.

153 Rybak A, Meier MAR. 2007. Green Chem 9:1356-1361.

154 Rybak A and Meier MAR. 2008. Green Chem 10:1099-1104.

155 Wang W, Zhang Z, Xu M and Zhang Y. 2009. J Wuhan Univ Technol 24(3):367-370.

156 Campanella A, La Scala JJ, Wool RP. 2009. Polym Eng Sci 49(12):2384 - 2392.

157 Baughman TW, Wagener KB. 2005. Recent Advances in ADMET Polymerization Advances in Polymer Science. Ed. Michael Buchmeiser, Publishers, Springer-Verlag GmbH, Chapter 1, Volume 176, Page 1-42 (2005).

158 Lluch, Ronda JC, Galiá M, Lligadas G, Cádiz V. 2010. Biomacromolecules 11(6):1646–1653.

159 Rybak A, Fokou PA, Meier MAR. 2008. Eur J Lipid Sci Technol 110:797-804.

160 Djigoué GB, Meier MAR. 2009. Appl Catal A 368:158-162.

161 Mutlu H, Meier MAR. 2009. Macromol Chem Phys 210:1019-1025.

162 Rybak A and Meier MAR. 2008b. ChemSusChem 1:542-547.

163 Fokou PA and Meier MAR. 2009. J Am Chem Soc 131:1664–1665.

164 Fokou PA and Meier MAR. 2010. Macromol Rap Com 31:368-373.

165 Montero de Espinosa L, Ronda JC, Galià M, Meier MAR. 2009. J Polym Sci Part A: Polym Chem 47:5760-5771.

166 Montero de Espinosa L, Meier MAR, Ronda JC, Galià M, Cádiz V. 2010. J Polym Sci Part A: Polym Chem 48:1649-1660.

167 Türünc, O., Meier, M.A.R. Eur. J. Lipid Sci. Technol. 2012, *submitted.*

167 Posner, T. Ber. Dtsch. Chem. Ges. 1905, 38, 646–657.

168 Marvel C.S. and Chambers R.R. J. Am. Chem. Soc. 1948, 70, 993–998.

169 Walling, C. and Helmreich, W. J. Am. Chem. Soc. 1959, 81, 1144–1148.

170 Testa, A.C., J. Org. Chem. 1964, 29, 2461–2962.

171 Griesbaum, K. Angew. Chem. Int. Edit. 1970, 9, 273–287.

172 Pryor, W.A., Coco, J.H., Daly, W.H., Houk, K.N. J. Am. Chem. Soc. 1974, 96 , 5591–5593.

173 Nuyken, O. and Volkel, T. Makromol. Chem. – Rapid Commun. 1990, 11, 365-373.

174 Nuyken, O., Volkel, T., and Pohlmann, T. Macromol. Chem. Phys. 1991, 192, 1959–1968.

175 Klemm, E., Sensfuß, S., Holfter, U., and Schütz, H. Makromol. Chem. 1990, 191, 2403–2411.

176 Klemm, E., Sensfuß, S. Makromol. Chem. 1991, 192, 159–164.

177 Biermann, U., Butte, W., Koch, R., Fokou, P., Türünç O., Meier, M.A.R., Metzger, J.O. Chem. Eur. J. 2012, 18, accepted.

178 Boutevin, B., Hervaud, Y., and Moulédous, G. Polym. Bull. 1998, 41, 145–151.

179 Kozhushkov, S.I., Brandl, M., and de Meijere, A. Eur. j. Org. Chem. 1998, 1998, 1535–1542.

180 Samuelsson, J., Jonsson, M., Brinck, T. and Johansson, M. J. Polym. Sci. A Polym. Chem. 2004, 42, 6346–6352.

181 Lou, F.-W., Xu, J.-M., Liu, B.-K., Wu, Q., Pan Q., Lin, X.-F, Tetrahed. Lett. 2007, 48, 8815–8818.

182 Uygun, M., Tasdelen, M. A., and Yagci, Y. Macromol. Chem. Phys. 2010, 211, 103–110.

183 ten Brummelhuis, N., Diehl, C., and Schlaad, H. Macromolecules 2008, 41, 9946–9947.

184 Gress, A., Völkel, A., Schlaad, H., . Macromolecules 2007, 40, 7928–7933.

185 Sun, J. and Schlaad, H. Macromolecules 2010, 43, 4445–4448.

186 Bertin, A. and Schlaad, H. Chem. Mater. 2009, 21, 5698–5700.

187 Madaan, N., Terry, A., Harb, J., Davis, R.C., Schlaad, H., and Linford M.R., NA. J. Phys. Chem. C. 2011, 115, 22931–22938.

188 Rissing, C. and Son, D. Y. Organometallics 2008, 27, 5394–5397.

189 Killops, K. L., Campos, L. M., and Hawker, C. J. J. Am. Chem. Soc. 2008, 130, 5062–5064.

190 Kolb, H. C., Finn, M. G. & Sharpless, K. B. Angew. Chem. Int. Ed. 2001, 40, 2004–2021.

191 Kade, M.J., Burke D.J., and Hawker, C.J. J. Polym. Sci. A Polym. Chem. 2010, 48, 743–750; Hoyle, C.E. and Bowman, C.N. Angew. Chem. Int. Ed. 2010, 49, 1540–1573.

192 Barner-Kowollik, C. and Inglis, A.J. Macromol. Chem. Phys. 2009, 210, 987–992; Lodge, T.P. Macromolecules 2009, 42, 3827–3829.

193 Iha, R.K., Wooley, K.L., Nystroem A.M., Burke, D.J., Kade, M.J., Hawker C.J. Chem Rev. 2009, 109, 5620-5686.

194 Koo, S. P. S., Stamenović, M.M., Prasath, R.A., Inglis, A.J., Du Prez, F.E., Barner-Kowollik, C., Camp, W.V., Junkers T. J. Polym. Sci. A Polym. Chem. 2010, 48, 1699-1713.

195 Koenig, N. and Swern, D. J. Am. Chem. Soc. 1957, 79, 362–365.

196 Koenig, N. and Swern, D. J. Am. Chem. Soc. 1957, 79, 4235–4237.

197 Koenig, N., Sasin, G. and Swern, D. J. Org. Chem. 1958, 23, 1525–1530.

198 Schwab, A. and Gast, L. J. Am. Oil Chem. Soc. 1968, 45, 461-464.

199 Schwab, A., Gast, L., and Cowan, J. J. Am. Oil Chem. Soc. 1970, 47, 371– .

200 Bexell, U., Olsson, M., Johansson, M., Samuelsson, J., and Sundell, P.-E. Surf. Coat. Tech. 2003, 166, 141–152.

201 Bexell, U., Olsson, M., Sundell, P.E., Johansson, M., Carlsson, P., Hellsing, M. Appl. Surf. Sci. 2004, 231–232, 362–365.

202 Bexell, U., Berger, R., Olsson, M., Grehk, T.M., Sundell, P.E., Johansson, M. Thin Solid Films 2006, 515, 838–841.

203 Bantchev, G. B., Kenar, J. A., Biresaw, G., and Han, M. G. J. Agric. Food Chem. 2009, 57, 1282–1290.

204 Black, M. and Rawlins, J. W. Eur. Polym. J. 2009, 45, 1433–1441.

205 Chen, Z., Chisholm, B.J., Patani, R., Wu, J.F., Fernando, S., Jogodzinski, K., Webster, D.C. J. Coat. Technol. Res. 2010, 7, 603–613.

206 Stemmelen, M., Pessel F., Lapinte V., Caillol S., Habas J.-P., Robin J.-J. J. Polym. Sci. Part A: Polym. Chem. 2011, 49, 2434–2444.

207 Desroches, M., Caillol, S., Lapinte, V., Auvergne, R., Boutevin, B. Macromolecules 2011, 44, 2489–2500.

208 Boutevin, B., Chaib, M., and Robin, J.-J. Polym. Bull. 1991, 26, 177–179.

209 Ameduri, B., Berrada, K., Boutevin, B. and Bowden, R. D. Polym. Bull. 1992, 28, 497–503.

210 Ameduri, B., Berrada, K., Boutevin, B. and Bowden, R. D. Polym. Bull. 1993, 31, 1–7.

211 Lluch, C., Lligadas, G., Ronda, J.C., Galià, M. and Cadiz, V. Macromol. Rapid Commun. 2011, 32, 1343–1351.

212 González-Paz, R. J., Lluch, C., Lligadas, G., Ronda, J.C., Galià, M. and Cadiz, V. J. Polym. Sci. A Polym. Chem. 2011, 49, 2407–2416.

213 Palaskar, D. V., Boyer, A., Cloutet, E., Le Meins, J.-F., Gadenne, B., Alfos, C., Farcet, C. and Cramail, H. J. Polym. Sci. A Polym. Chem., doi: 10.1002/pola.25944, 2012.

214 Vilela, C., Cruciani, L., Silvestre, A. J. D. , and Gandini, A. RSC Adv. 2012, 2, 2966–2974.

215 Kreye, O., Türünç, O., Sehlinger, A., Rackwitz, J. and Meier, M. A. R. Chem. Eur. J. 2012, 18, doi:10.1002/chem.201103341.

216 Pirrung, M.C., Sarma, K.D. J. Am. Chem. Soc. 2003, 126, 444–445.

217 Ates, Z., Thornton, P. D., Heise, A. Polym. Chem. 2011, 2, 309–312.

219 K. B. Wagener, J. M. Boncella, J. G. Nel, R. P. Duttweiler and M. A. Hillmyer, Makromol. Chem., 1990, 191, 365; K. B. Wagener, J. G. Nel, J. Konzelman and J. M. Boncella, Macromolecules, 1990, 23, 5155.

220 Mutlu, H. Montero de Espinosa, L., Meier, M.A.R. Chem. Soc. Rev. 2011, 40, 1404–1445.

221 S. T. Nguyen, L. K. Johnson, R. H. Grubbs and J. W. Ziller, J. Am. Chem. Soc., 1992, 114, 3974.

222 K. Brzezinska, P. S. Wolfe, M. D. Watson and K. B. Wagener, Macromol. Chem. Phys., 1996, 197, 2065.

223 D. J. Valenti and K. B. Wagener, Macromolecules, 1998, 31, 2764.

224 M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, Org. Lett., 1999, 1, 953.

225 E. T. Csanyi and J. U. Zilles, J. Mol. Catal. A: Chem., 2002, 190, 85.

226 F. C. Courchay, J. C. Sworen and K. B. Wagener, Macromolecules, 2003, 36, 8231; V. I. Petkovska, T. E. Hopkins, D. H. Powell and K. B. Wagener, Macromolecules, 2005, 38, 5878.

227 B. Schmidt, Eur. J. Org. Chem., 2004, 1865; B. Schmidt, Chem. Commun., 2004, 742.

228 S. H. Hong, D. P. Sanders, C. W. Lee and R. H. Grubbs, J. Am. Chem. Soc., 2005, 127, 17160.

229 T. M. Trnka, R. H. Grubbs, Acc. Chem. Res. 2001, 34, 18; K. C. Nicolaou, P. G. Bulger, D. Sarlah, Angew. Chem. Int. Ed 2005, 44, 4490; A. Fürstner, Angew. Chem. Int. Ed. 2000, 39, 3012; S. J. Connon, S. Blechert, Angew. Chem. Int. Ed. 2003, 42, 1900; C. Slugovc, Macromol. Rapid Commun. 2004, 25, 1283; T. W. Baughman, K. B. Wagener, Adv. Polym. Sci. 2005, 176, 1; C. W. Bielawski, R. H. Grubbs, Prog. Polym. Sci. 2007, 32, 1.

230 Mol, J.C. and Buffon, R. J. Braz. Chem. Soc. 1998, 9, 1-11.

231 Jacobs, T., Rybak, A., Meier, M.A.R. Appl. Catal., A 2009, 353, 32-35.

232 Xiaowei Miao, Pierre H. Dixneuf, C´edric Fischmeister and Christian Bruneau, C. Green Chem., 2011, 13, 2258.

233 Christian Bruneau, Cédric Fischmeister, Xiaowei Miao, Raluca Malacea and Pierre H. Dixneuf. Eur. J. Lipid Sci. Technol. 2010, 112, 3–9.

234 Raluca Malacea, C´edric Fischmeister, Christian Bruneau, Jean-Luc Dubois, Jean-Luc Couturier and Pierre H. Dixneuf. Green Chem., 2009, 11, 152–155.

235 X. Miao, R. Malacea, C. Fischmeister, C. Bruneau and P. H. Dixneuf. Green Chem. 2011, 13, 2911.

236 Ngo, H.L., Foglia, T.A., J. Am. Oil Chem. Soc. 2007, 84, 777–784.

237 Lehman, S.E., Schwendeman, J.E., O'Donnell, P.M., Wagener, K.B. Inorg. Chim. Acta 2003, 345, 190.

238 Biermann, U., Metzger, J.O., Meier, M.A.R. Macromol. Chem. Phys. 2010, 211, 854–862.

239 Akintayo, C.O., Mutlu, H., Kempf, M., Wilhelm, M., Meier, M.A.R. Macromol. Chem. Phys. 2012, 213, 87–96.

240 Le Ravalec, V., Fischmeister, C., Bruneau, C. Adv. Synth. Catal. 2009, 351, 1115 – 1122.

241 Türünç, O., Meier, M.A.R. Macromol. Rapid Commun. 2010, 31, 1822–1826.

242 Van der Steen, M., Stevens, C.V. ChemSusChem 2009, 2, 692-713.

243 Lligadas, G., Ronda, J.C., Galià, M., Cádiz, V. Biomacromolecules 2006, 7, 2420-2426.

244 Lligadas, G., Ronda, J.C., Galià, M., Cádiz, V. J. Polym. Sci. Part A: Polym. Chem. 2006, 44, 5630-5644.

245 Lee, J.-H., Danino, D., Raghavan, S.R. Langmuir 2009, 25, 1566-1571.

246 Malacea, R. Fischmeister, C., Bruneau, C., Dubois, J.-L., Couturier, J.-L., Dixneuf, P.X. Green Chem. 2009, 11, 152-155.

247 Jacobs, T. Rybak, A., Meier, M.A.R. Appl. Catal., A 2009, 353, 32-35.

248 Dondoni, A. Angew. Chem. Int. Ed. 2008, 47, 8995-8997.

249 David, R.L.A., Kornfield, J.A. Macromolecules 2008, 41, 1151-1161.

250 Gress, A., Völkel, A., Schlaad, H. Macromolecules 2007, 40, 7928-7933.

251 Chan, J.W., Yu, B. Hoyle, C.E., Lowe, A.B. Chem. Commun. 2008, 4959-4961.

252 Schuchardt, U., Sercheli, R., Vargas, R. M., J. Braz. Chem. Soc. 1998, 9, 199-210.

253 Simón, L., Goodman, J. M., J. Org. Chem. 2007, 72, 9656-9662.

254 Schuchardta, U., Serchelia, R. and Vargas, R.M. J. Braz. Chem. Soc. 1998, 9(1), 199-210.

255 Koo, S. P. S., Stamenović, M. M.; Prasath, R. A.; Inglis, A. J., Du Prez, F. E., Barner-Kowollik, C., Van Camp, W., Junkers, T., J. Polym. Sci. Part A Polym. Chem. 2010, 48 (8), 1699-1713.

256 Hawker, C.J., Lee, R., Fréchet, J.M.J. J. Am. Chem. Soc. 1991, 113, 4583-4595.

257 Bharathi, P. and Moore, J.S., Macromolecules 2000, 33, 3212-3218.

258 ZhiPing, Z., ZhengWei, J., DeYue, Y. Sci. China Chem. 2010, 53, 891–897.

259 Kolhe, P., Misra, E., Kannan, R.M., Kannan, S., Lieh-Lai, M. Int. J. Pharm. 2003, 259, 143–160.

260 Kojima, C., Kono, K., Maryama, K., Takagishi, T., Bioconjug. Chem. 2000, 11, 910–917.

261 Chen, G., Kumar, J., Gregory, A. and Stenzel, M.H. Chem. Commun., 2009, 6291-629.

262 Lotti, N., Siracusa , V., Finelli, L., Marchese, P., Munari, A. Eur. Polym. J. 2006, 42, 3374–3382.

284 Lotti, N., Finelli, L., Messori, M., Munari, P. e-Polymers 2006, no. 017.

264 Finelli, L., Lotti, N., Munari, A., Gazzano, M., Malta, V. J. Polym. Sci., Part B: Polym. Phys. 2004, 42, 553–566.

265 Threlfall, T. Org. Process Res. Dev. 2003, 7, 1017-1027.

266 Türünç, O., Meier, M.A.R. Green Chem. 2011, 13, 314–320.

267 Hofmann, D., Entrialgo-Castaño, M., Kratz, K., Lendlein, A. Adv. Mater. 2009, 21, 3237-3245.

268 Sokolsky-Papkov, M., Shikanov, A., Kumar, N., Vaisman, B. and Domb, A.J. Bull. Isr. Chem.Soc. 2008, 23, 12-17.

269 Uhrich, K.E., Cannizaro, S.M., Langer, R.S., Shakesheff, K.M. Chem. Rev. 1999, 99, 3181-3198.

270 Jain, J.P., Modi, S., Kumar, N. J. Biomed. Mat. Res. Part A 2008, 84A (3), 740-752.

271 Krasko, M.Y., Shikanov, A., Kumar, N., Domb, A.J. Polym. Adv. Technol. 2002, 13, 960-968.

272 Domb, A.J., Ron, E., Langer, R. Macromolecules 1988, 21, 1925-1929.

273 Kumar, N., Langer, R.S., Domb, A.J.Adv. Drug Deliv. Rev. 2002, 54, 889-910.

274 Meier, M.A.R. Macromol. Chem. Phys. 2009, 210, 1073-1079.

275 Wagener, K.B., Boncella, J.M., Nel, J.G., Duttweiler, R.P. and Hillmyer, M.A. Makromol. Chem. 1990, 191(2), 365-374.

276 Wagener, K.B., Nel, J.G., Konzelman, J. and Boncella, J.M. Macromolecules 1990, 23(24), 5155-5157.

277 Hong, S.H., Sanders, D.P., Lee, C.W., Grubbs, R.H. J. Am. Chem. Soc. 2005, 127 (49), 17160–17161.

278 Selinger, Z. and Lapidot, Y. J. Lip. Res. 1966, 7, 174-175.

279 Kumar, N., Krishnan, M., Azzam, T., Magora, A., Ravikumar, M.N.V., Flanagan, D.R., Domb, A.J. Anal. Chim. Acta 2002, 465, 257–272.

280 Domb, A.J. and Langer, R. J. Polym. Sci., Part A: Polym. Chem. 1987, 25, 3373-3386.

281 Youngs, C.G. J. Am. Oil Chem. Soc. 1958, 35, 416-417.

282 Sonntag, N.O.V., Trowbridge, J.R., Krems, I.J. J. Am. Oil Chem. Soc. 1954, 31, 151-157.

283 Park, E.-S., Maniar, M., Shah J. J. Control. Release 1996, 40, 55–65.

284 Leong, K.W., Brott, B.C., Langer, R. J. Biomed. Mater. Res. 1985, 19, 941–955.

285 Heller, J. Adv. Drug Deliv. Rev. 1993, 10, 163–204.

286 Ron, E., Turek, T., Mathiowitz, E., Chasin, M., Hageman, M., Langer, R. Proc. Natl. Acad. Sci. USA 1993, 90, 4176–4180.

287 Türünç, O., Montero de Espinosa, L., Meier, M.A.R. Macromol. Rapid Commun. 2011, 32, 1357-1361.

288 Peacock, A.J. Handbook of polyethylene structures, properties, and applications, Marcel Dekker Inc., 2000 New York.

289 Groppo, E., Lamberti, C., Bordiga, S., Spoto, G., Zecchina, A. Chem. Rev. 2005, 105, 115-183.

290 Huang J. and Rempel, G.L. Prog. Polym. Sci. 1995, 20, 459-526.

291 Soga, K. Shiono, T. Prog. Polym. Sci. 1997, 22, 1503-1546.

292 Böhm, L.L. Angew. Chem. Int. Ed. 2003, 42, 5010 – 5030.

293 http://www.braskem.com/plasticoverde/EN_HOME.html

294 Quinzler, D. and Mecking, S. Chem. Commun., 2009, 5400 – 5402.

295 Quinzler, D. and Mecking, S. Angew. Chem. Int. Ed. 2010, 49, 4306 - 4308.

296 van der Meulen, I., Gubbels, E., Huijser, S., Sablong, R., Koning, C.A. Heise, A. Duchateau, R. Macromolecules 2011, 44 (11), 4301–4305.

297 Scott, G. and Wiles, D.M. Biomacromol. 2001, 2, 615 – 622.

298 Sworen, J.C. and Wagener, K.B. Macromolecules 2007, 40, 4414-4423.

299 Rojas, G. and Wagener, K.B. Macromolecules 2009, 42, 1934-1947.

300 Huang, L.-P., Zhou, X.-P., Cui, W., Xie, X.-L., Tong, S.-Y. J. Mater. Sci. 2008, 43, 4290–4296.

301 Khanna, Y.P. Polym. Eng. Sci. 1990, 30(24), 1615–1619.

302 Türünç, O., Meier, M.A.R. J. Polym. Sci. Part A: Polym. Chem. 2012, 50, 1689–1695.

303 Coffman, D. US Patent 2347182, 1944.

304 Nuyken, O., Völkel T. Makromol. Chem., Rapid. Commun. 1990, 11, 365-373.

305 Kade, M.J., Burke D.J., Hawker, C.J. J. Polym. Sci. Part A Polym. Chem. 2010, 48, 743-750.

306 Hoyle C.E. and Bowman, C.N. Angew. Chem. Int. Ed. 2010, 49, 1540-1573.

307 Altintas, O., Vogt, A.P., Barner-Kowollik C. and Tunca, U. Polym. Chem. 2011, 3, 34-45.

308 Firdaus, M., Montero de Espinosa, L. and Meier, M.A.R. Macromolecules 2011, 44, 7253-7262.

309 Lorenz, K., Frey, H., Sthn, B. and Mlhaupt, R. Macromolecules 1997, 30, 6860-6868.

310 Gress, A., Vlkel, A. and Schlaad, H., Macromolecules 2007, 40, 7928-7933.

311 Rissing, C. and Son, D.Y. Organometallics 2008, 27, 5394-5397.

312 Benyahya, S., Desroches, M.; Auvergne, R., Carlotti, S., Caillol, S. and Boutevin, B. Polym. Chem. 2011, 2, 2661-2667.

313 Hoogenboom, R. Angew. Chem. Int. Ed. 2010, 49, 3415-3417.

314 Chen, G., Kumar, J. Gregory A. and Stenzel, M.H. Chem. Commun. 2009, 41, 6291-6293.

315 Konkolewicz, D., Poon, C.K., Gray-Wealeb, A. and Perrier, S. Chem. Commun. 2011, 47, 239-241.

316 Fairbanks, B.D., Sims, E.A.; Anseth, K.S. and Bowman, C.N. Macromolecules 2010, 43, 4113-4119.

317 Chan, J.W., Shin, J., Hoyle, C.E., Bowman, C.N. and Lowe, A.B. Macromolecules 2010, 43, 4937-4942.

318 Liu, J., Lam, J.W.Y., Jim, C.K.W., Ng, J.C.Y., Shi, J., Su, H., Yeung, K.F., Hong, Y., Faisal, M., Yu, Y., Wong, K.S. and Tang, B.Z. Macromolecules 2011, 44, 68-79.

319 Lowe, A.B., C. E. Hoyle, C.E. and Bow, C.N. J. Mater. Chem. 2010, 20, 4745-4750.

320 Minozzi, M., Monesi, A., Nanni, D., Spagnolo, P., Marchetti, N. and Massi, A. J. Org. Chem. 2011, 76, 450-459.

321 Hensarling, R.M., Doughty, V.A., Chan, J.W. and Patton, D.L. J. Am. Chem. Soc. 2009, 131, 14673-14675.

322 Wendeln, C., Rinnen, S., Schulz, C., Arlinghaus, H.F. and Ravoo, B.J. Langmuir 2010, 26, 15966-15971.

323 Fairbanks, B.D., Scott, T.F. Kloxin, C.J., Anseth, K.S. and Bowman, C.N. Macromolecules 2009, 42, 211-217.

324 Gokmen, M.T., Brassinne, J., Prasath R.A. and Du Prez, F.E. Chem. Commun. 2011, 47, 4652-4654.

325 Konkolewicz, D.; Gray-Weale, A. and Perrier, S. J. Am. Chem. Soc. 2009, 131, 18075-18077.

326 Han, J., Zhao, B.; Gao, Y., Tang A. and Gao, C. Polym. Chem. 2011, 2, 2175-2178.

327 Chan, J.W., Shin, J., Hoyle, C.E. Bowman, C.N. and Lowe, A.B. Macromolecules 2010, 43, 4937-4942.

328 Uygun, M., Tasdelen, M.A., Yagci, Y. Macromol. Chem. Phys. 2010, 211, 103-110.

329 O. Türünç, M. Firdaus, G.Klein, M. A. R. Meier, Fatty acid derived renewable polyamides via thiol-ene additions, Green Chem., 2012, DOI: 10.1039/C2GC35982K.

330 Peacock, A. and Calhoun, A. Polymer Chemistry: Properties and Applications, Carl Hanser Verlag, Munich 2006.

331 Kanekura, K., Tsujita, Y., Yoshimizu, H., Okamoto, S., Kunisada, H. and Goto, M. J. Appl. Polym. Sci. 2005, 98, 1955–1960.

332 Hill, K. Pure Appl. Chem. 2000, 72, 1255–1264; Huf, S., Krügener, S., Hirth, T., Rupp, S. and Zibek, S. Eur. J. Lipid Sci. Technol. 2011, 113, 548–561; Hablot, E., Matadi, R., Ahzi, S. and Avérous, L. Compos. Sci. Technol. 2010, 70, 504–509; Hablot, E., Matadi, R., Ahzi, S., Vaudemond, R., Avérous, L. Compos. Sci. Technol. 2010, 70, 525–529.

333 Stempfle, F., Quinzler, D., Heckler, I., and Mecking, S. Macromolecules 2011, 44, 4159–4166.

334 Jasinska, L., Villani, M., Wu, J., van Es, D., Klop, E., Rastogi, S., and Koning, C.E. Macromolecules 2011, 44, 3458–3466.

335 Kade, M.J., Burke D.J., and Hawker, C.J. J. Polym. Sci. A Polym. Chem. 2010, 48, 743–750; Hoyle, C.E. and Bowman, C.N., Thiol–Ene Click Chemistry. Angew. Chem. Int. Ed. 2010, 49, 1540–1573.

336 Ameduri, B., Berrada, K., Boutevin, B. and Bowden, R. D. Polym. Bull. 1993, 31, 1–7.

337 Lluch, C., Lligadas, G., Ronda, J. C., Galià, M. and Cadiz, V. Macromol. Rapid Commun. 2011, 32, 1343–1351.

338 González-Paz, R. J., Lluch, C., Lligadas, G., Ronda, J. C., Galià, M. and Cádiz, V. J. Polym. Sci. A Polym. Chem. 2011, 49, 2407–2416.

339 Palaskar, D. V., Boyer, A., Cloutet, E., Le Meins, J.-F., Gadenne, B., Alfos, C., Farcet, C. and Cramail, H. J. Polym. Sci. A Polym. Chem. 2012, 50, 1766–1782.

340 Kiesewetter, M.K., Scholten, M.D., Kirn, N., Weber, R.L., Hedrick, J.L., and Waymouth, R.M., J. Org. Chem. 2009, 74, 9490–9496.

341 Run, M., Gao, J., Li, Z., Thermochim Acta 2005, 429, 171–178.

342 Smitha, R.G., Vanterpool, A., Kulak, H.J. Canad. J. Chem. 1969, 47, 2015 – 2019.