# FATTY ACID-DERIVED BRANCHED POLYMER ARCHITECTURES

Zur Erlangung des akademischen Grades eines

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Hiermit versichere ich, die vorliegende Arbeit selbstständig angefertigt und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt zu haben. Wörtlich oder inhaltlich übernommene Stellen sind als solche kenntlich gemacht. Ich habe dabei die Satzung des Karlsruher Instituts für Technologie zur Sicherung der guten wissenschaftlichen Praxis in ihrer gültigen Fassung beachtet.

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# ABSTRACT

Since a long time, scientists in academia and industry have accepted the responsibility to develop monomers and polymers derived from renewable resources due to the depleting crude oil resources. Herein, plant oils awakened special interest due to the inherent, annual availability. Till today, almost every type of polymer based on renewable feedstocks could already be obtained with linear as well as branched structures, such as dendrimers, star-shaped or hyperbranched polymers. For the synthesis of suitable monomers, efficient and environmental benign procedures were developed to meet the criteria of Green Chemistry. Although they exhibit similar or even improved properties compared to petroleum-based polymers, the big-scale industrial production often fails due to the currently still low crude oil price. Within this context, the present thesis deals with the synthesis of monomeric and polymeric branched structures based on fatty acid derivatives.

Based on high oleic oil, two different monomers were obtained. First, polyols were synthesized *via* a modified Schenck-Ene reaction. The generated allyl hydroperoxide was reacted to the corresponding trihydroxy fatty acid derivative, catalyzed by titanium(IV) isopropoxide in a one-pot fashion without the need of purification. Here, the smoothly upscaling of the photoreaction up to 150 grams is notable. Ring-opening of the intermediate, an epoxide, under acidic conditions yielded a triglyceride with multiple hydroxy groups, whereas a fatty acid-based polyol was gained applying a basic catalyst. The hydroxyl content of polyols was determined by $^{31}$P NMR. On the other hand, a dimer fatty acid was synthesized *via* thiol-ene addition. Therefore, two molecules of methyl oleate, produced by methanolysis of the high oleic oil, were linked by the photoinitiated double bond functionalization with ethanedithiol. The generated dimer fatty acid and a commercially available dimer fatty acid were tested in the TBD-catalyzed homo- and copolymerization to Nylon-6,6. The resulting polyamides were characterized by SEC and their water uptake behavior was investigated.

In the synthesis of branched polymeric structures, star-shaped polymers with four and six arms were prepared *via* the core-first approach. Here, two multifunctional acrylates were used as core units and the monomer 10-undecenyl acrylate, based on the castor oil derivative 10-undecenol, was attached applying ADMET polymerization techniques. Thus, defined star-shaped polymers with 10 and 20 monomer units per arm were successfully synthesized and characterized *via* SEC and $^1$H NMR. The arms of the polymer contain $\alpha,\beta$-unsaturated ester groups along the chain, which are suitable for post-polymerization functionalization. Five different thiols were added to the double bonds *via* base-catalyzed thia-Michael addition. The octanol-water partition coefficients of the resulting polymers, as indicator for their hydrophilicity, were determined for the first time *via* HPLC illustrating an influence of the length of the alkyl chain or additional functional groups of the thiol. To improve the water solubility of the non-functionalized star-shaped polymers, a dendron was synthesized. Benzyl-protected diethanolamine was chosen as focal point and consecutively reacted with allyl bromide *via* *O*-allylation and thioglycerol *via* thiol-ene addition. The compounds of each step were thoroughly characterized by NMR and SEC to ensure complete functionalization and lack of defects in the structure.

# ZUSAMMENFASSUNG

Naturwissenschaftler an Hochschulen und in der Industrie übernehmen schon lange die Aufgabe, Monomere und Polymere aus nachwachsenden Rohstoffen herzustellen, um rechtzeitig auf die zur Neige gehenden Erdölvorräte vorbereitet zu sein. Unter den nachwachsenden Rohstoffen wecken besonders die Pflanzenöle das Interesse der Chemiker, da sie von Natur aus jährlich verfügbar sind. Basierend auf nachwachsenden Rohmaterialen wurde bis zum heutigen Tag nahezu jede Art von Polymer hergestellt. Dabei werden sowohl lineare als auch verzweigte Strukturen in Form von Dendrimeren, sternförmigen und hochverzweigten Polymeren realisiert. Während der Synthese wird besonders auf effiziente und umweltfreundliche Verfahren zurückgegriffen, um die Prinzipien der Grünen Chemie zu erfüllen. Obwohl die Polymere ähnliche oder sogar verbesserte Eigenschaften im Vergleich zu erdölbasierten Kunststoffen aufweisen, scheitert die großindustrielle Herstellung oft am noch vergleichsweise niedrigeren Preis des Erdöls. In diesem Zusammenhang geht die vorliegende Doktorarbeit auf die Synthese von Monomeren und Polymeren mit verzweigten Strukturen, die aus Fettsäurederivaten hergestellt werden, ein.

Ausgehend von einem Öl mit hohem Ölsäureanteil wurden zwei Monomere synthetisiert. Zuerst wurden Polyole mit Hilfe einer modifizierten Schenck-En Reaktion erzeugt und in einer Eintopfreaktion zu den entsprechenden Trihydroxyderivaten durch die Zugabe von Titanisopropoxid umgesetzt. Die problemlose Herstellung im 150 Gramm Maßstab sowie die Tatsache, dass keine Aufreinigung nötig ist, ist hierbei bemerkenswert. Die Ringöffnung des intermediären Epoxides wurde sowohl unter sauren als auch unter basischen Bedingungen durchgeführt. Hierbei entstand unter Säurekatalyse das Polyol mit Triglyceridstruktur, während die basische Katalyse die entsprechende alkoholfunktionalisierte Fettsäure ergab. Die Anzahl der Hydroxylgruppen wurde mit Hilfe von $^{31}$P-NMR bestimmt. Aus demselben Öl wurde ebenfalls eine Dimerfettsäure mittels Thiol-En Reaktion hergestellt. Dafür wurde das Öl durch Methanolyse zum entsprechenden Methyloleat umgewandelt und anschließend zwei dieser Moleküle mit Ethandithiol über die Doppelbindungen verknüpft. Die erhaltene, als auch eine käuflich erworbene Dimerfettsäure wurden anschließend mit Hilfe von TBD als Katalysator homopolymerisiert als auch zur Synthese von Nylon-6,6 Copolymeren

verwendet. Die daraus resultierenden Polyamide wurden mittels GPC charakterisiert und ihr Wasseraufnahmeverhalten geprüft.

In der Synthese verzweigter Polymerstrukturen wurden sternförmige Polymere, ausgehend vom einem Kernmolekül, mit vier und sechs Armen synthetisiert. Als Kerneinheiten wurden zwei multifunktionale Acrylate verwendet, die mit 10-Undecenylacrylat, ein Monomer basierend auf Rizinusöl, in einer ADMET Polymerisation umgesetzt wurden. Dadurch wurden definierte, sternförmige Polymere mit 10 oder 20 Monomereinheiten pro Arm erhalten, die anschließend mittels GPC und $^1$H-NMR charakterisiert wurden. $\alpha,\beta$-Ungesättigte Estergruppen entlang der Polymerarme ermöglichen eine nachträgliche Funktionalisierung. Hierzu wurden fünf unterschiedliche Thiole mittels basenkatalysierter Thia-Michael Addition an die Doppelbindung addiert. Der Octanol-Wasser Verteilungskoeffizient als Maß für die Hydrophilie wurde mit Hilfe der HPLC bestimmt, die einen Einfluss der Thiolstruktur auf die Eigenschaften des Polymers zeigte. Um die Wasserlöslichkeit des ursprünglichen Sternpolymers zu verbessern, wurde ein Dendron hergestellt. Benzyl-geschütztes Diethanolamin wurde mit Allylbromid umgesetzt und die resultierenden Doppelbindungen photochemisch mit Thioglycerol funktionalisiert. Die endständigen Hydroxylgruppen ermöglichten eine erneute *O*-Allylierung mit Allylbromid und anschließend eine erneute Addition von Thioglycerol. Die Produkte aus jedem Schritt wurden gründlich mittels GPC und NMR charakterisiert, um eine vollständige Funktionalisierung und das Fehlen von Defekten in der Dendronstrukutr zu gewährleisen.

# CONTENT

# 1. INTRODUCTION

A life without plastics is inconceivable. Several reasons argue for the application of plastics: low weight, tailored properties, easy processability and a good cost/performance ratio. Their application fields are manifold and extend to packaging for food, medical technology, electronical parts and technical uses like automobiles. Furthermore, several applications have only become possible with the development of polymers, such as airbags, Tupperware or bike helmets.[1] Packaging materials provide protection of food against air, dust and bacteria increasing the life time of the product.[2] In automobiles, the content of plastics represents 100 kilogram on average. Thus, cars today are safer, resistant to corrosion, more efficient and lightweight, which decrease the gasoline consumption.[3] In the field of medicine, components, such as prosthesis or catheter, get daily routine and polymeric capsules help to release drugs precisely timed at a defined place or to overcome missing solubility.[4, 5] Till today, the main ratio of conventional polymers is synthesized from crude oil resources. However, the rapid increase of the world population with raising living standard requires the search for alternative resources. With regard to environmental issues, *e.g.*, carbon dioxide emission and pollution of the environment, research and developments in polymer chemistry must be focused on renewable materials. In the 19th century, polymers from renewable materials were ubiquitous and modified to obtain proper characteristics. Casein, galalith and natural rubber are such well-known materials.[6-8] With increasing demand of plastics due to the growing population, crude oil presented an inherently available alternative allowing the production of polymers on large scales. In 1907, Bakelite was invented as the first fully synthetic polymer by reaction of phenol and formaldehyde and revolutionized the electric age.[9, 10] During the oil crises in the 1970s, the intensive search for alternative raw materials began. In the 1990s, the term “Green Chemistry” was coined by Anastas and Warner. It is imperative for sustainable and environmental-friendly synthesis to reduce or recycle waste, use energy and resources efficient, optimize reaction processes without the need of toxic or hazard substances and revert to renewable feedstock, if possible.[11-13] Examples for renewable raw materials include cellulose, starch, lignin and plant oils, among others. The vision of “Green Chemistry” in the context of bio-based polymers is a closed carbon cycle: During photosynthesis, carbon dioxide and water are reacted to biomass, which is then used in the production of biofuels or bioplastics. With the degradation of the material, the same amount of water and carbon dioxide will be released. Compared to crude oil as raw material, no additional carbon dioxide is formed. In fact, several aspects, such as increasing energy demand for agriculture due to a rising quantity of crops or the necessity of more fertilizer, have to be taken into account. The competition with food production is also not negligible.[14] In 2015, 0.02 % of the arable land was used for the growing of plants for bioplastics and the demand will be increased to 7 % for the complete replacement of petroleum-based polymers.[15] However, carbon dioxide neutrality is not given, the carbon footprint of bio-based materials is much lower than for petroleum-based substances. The synthesis of polymers with tailored properties can be accomplished by variation of monomer type and composition, polymerization process and the molecular structure of the polymer. Herein, the terms “Old Economy” and “New Economy” polymers were introduced. “Old Economy” polymers are well-known, such as rubber or linoleum. “New Economy” polymers are divided into chemical new polymers like poly(lactic acid) or drop-in polymers, such as bio-polyethylene. A result of the intensive research in the academic and industrial sector is the successful synthesis of both types of renewable polymers with every imaginable molecular structure and the commercialization of renewable polymers by industrial companies, such as the nylon resin Zytel® by DuPont. Here, the most promising resources are nonfood materials, such as castor oil. In this thesis, the synthesis of monomeric and polymeric branched structures based on triglycerides and fatty acids is investigated. Branching endow polymers with interesting properties compared to their linear analogs.[16] The incorporation of branched monomers in typically linear polymers affects the properties depending on the ratio of linear to branched monomer units. Star-shaped poly(lactic acid), for example, exhibit lower melting, glass transition and crystallization temperatures than linear counterparts due to the branching, which hinders stacking and thereof crystallization.[17]

# 2. THEORETICAL BACKGROUND

## 2.1 MACROMOLECULAR ARCHITECTURES – AN OVERVIEW

Polymers – deviated from the Greek words *"poly"* (many) and *"meros"* (part) – are in general large molecules build up from many repeating units, called monomers, connected to each other in many different ways. One possibility to categorize polymers is based on their molecular architecture dividing them into linear, branched and crosslinked molecules. While linear polymers consist of a single long chain, branched polymers exhibit different types and amounts of branching points, whereas crosslinking arises from three-dimensional covalent linkage of linear polymer chains (Figure 1).

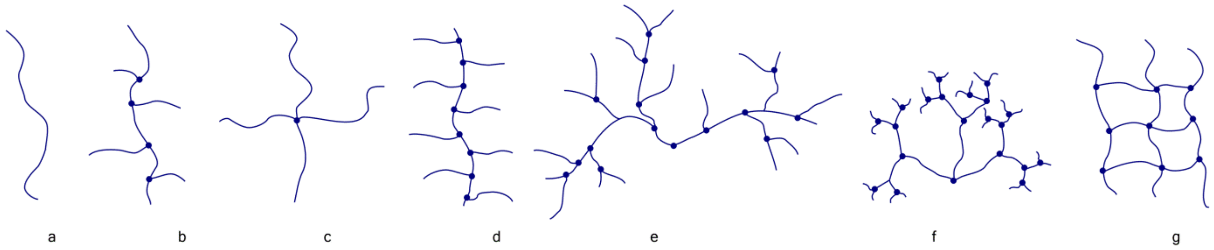


***Figure 1:*** *Exemplary polymer topologies : a) linear, b) long and short chain branches, c) star shaped, d) comb, e) hyperbranched, f) dendrimer and g) crosslinked.*

Topologies embraced under the term "branched" are comb, star-shaped, and hyperbranched polymers as well as dendrimers. Moreover, more unusual structures, like H-shaped, pom-pom shaped polymers, polyrotaxanes or polycatenanes are branched polymer architectures.[18-20]

Comb polymers are composed of a main chain with linear side chains. In particular, regular comb polymers comprise side chains of identical constitution and degree of polymerization and equal distribution along the chain.[21] In principal, three methods are adopted for the synthesis of comb polymers: "grafting from", "grafting onto" and the use of macromonomers. The presence of initiating groups on a polymer backbone, which are used for the growth of side chains by polymerization of suitable monomers, is the so called "grafting from" method. One advantage of this method is the easy purification by precipitation of the polymer. The former uncontrollable molecular weight distribution of side chains can nowadays be prevented by using controlled radical polymerization methods like atom transfer radical polymerization (ATRP), reversible addition-fragmentation polymerization (RAFT) or nitroxide-mediated polymerization (NMP).[22-29] The “grafting onto” approach describes the coupling of preformed polymeric side chains with reactive end groups to the polymer backbone, allowing a more facile control over molecular weight and distribution of both. Effective conjugation methods are required for efficient coupling, often accomplished by the application of “click” reactions.[29-34] Macromonomers are preformed polymer chains with end group that can be polymerized in a subsequent step.[35-37] For instance, comb polymers attract industrial interest as fuel additive for enhanced viscosity properties.[38, 39]

Hyperbranched polymers and dendrimers are important members of the main class of dendritic polymers. The structure of hyperbranched polymers can be described as highly, but randomly branched with terminal, dendritic and linear units in contrast to the regular, symmetrical and perfect three-dimensional structure of dendrimers. Since Flory´s theoretical report in 1952, this type of macromolecules has gained the attention of chemists although it was already known in nature in the shape of amylopectin, for example, which is a highly branched polymer consisting of glucose units.[40, 41] With the aid of theoretical calculations, Flory predicted the synthesis of hyperbranched polymers by the self-condensation of $AB_x$ monomers ($x \geq 2$) and developed a mathematical description for the prediction of molecular weights and molecular weight distributions.[42] The term “hyperbranched polymer” was then coined by Kim and Webster in the late 1980s, as a randomly branched macromolecular structure, when they synthesized highly branched polyphenylene.[43] The synthesis can be accomplished by a variety of methods including polycondensation, ring-opening polymerization, self-condensing vinyl polymerization or “click” reactions and is often conducted in a one-pot fashion.[41, 44-51] Since the synthesis of dendrimers is known to be labor- and time-intensive due to several iterative synthesis and purification steps, the easy synthesis of hyperbranched polymers paired with remarkable properties similar to dendrimers make them to promising materials for a plenty of applications like polymer additives, coatings, resins, nanotechnology or biomaterials.[44, 52] The synthesis, properties and applications of dendrimers as well as star-shaped polymers will be discussed in more detail in the following two sections.

Compared to linear polymers, branching appears as a structural variable to modify and tune the properties of polymers. Crystallinity, melting behavior, viscosity as well as physical properties can be controlled by the degree and nature of branching.[53] Polyethylene is a representative example of the influence of branching on the behavior of the material. Low-density polyethylene (LDPE) has a branched structure, which prevents crystallization, yielding a soft material mainly used for plastic bags. On the other side, essentially linear high-density polyethylene (HDPE) shows minor branching points and is therefore highly crystalline. Provided with the synthetic tools to create all kinds of polymer architectures a chemist can imagine, the array of possible structures is only limited by the creativity and imagination of researchers, who want to uncover and understand the relationship between structure and properties of the resulting polymers.[51]

Finally, network polymers are linear polymer chains connected to each other by cross-linkages either by chemical bonds or due to reversible interactions.[54] Non-covalent crosslinking based on physical interactions relies on intramolecular forces like hydrogen, ionic or coordination bonding, hydrophobic or van-der-Waals interactions.[54] Covalent crosslinking proceeds *via* covalent bond formation during the polymerization process due to the use of multifunctional linking agents or after polymerization by reaction of functional groups located at the polymer chains with cross-linkers bearing two or more functional groups, which can be promoted by irradiation, heat or catalyst. One prominent example are hydrogels, which represent one type of crosslinked polymers and are able to adsorb a large amounts of water in cavities between the linkages.[55] Another example is rubber, vulcanized by the addition of sulfur forming covalent sulfur bridges, which cannot be melted or remolded.[56]

### 2.1.1 STAR-SHAPED POLYMERS

By definition, star polymers consist of a single focal point, the core, with emanating multiple linear chains called arms.[57] Classification can be conducted due to the chemical nature of their arms: regular star polymers bear arms of identical composition and similar molecular weights, whereas miktoarm star polymers comprise arms of different composition, molecular weights or peripheral functionality.[58, 59] Furthermore, the monomer composition of the arms can be arranged as homopolymer, statistical copolymer or block copolymer. Even the core can be of polymeric structure and functional groups can be placed on arms, the core or at the end of the linear chains.[57] Star polymers, first developed in 1948 by Schaefgen and Flory, are considered as one of the major classes of branched polymer architectures due to their manifold structural variation possibilities. Due to their unique properties, they gained the interest of chemists and material researchers all over the world.[60] The synthesis of star polymers can be accomplished applying three different strategies: a) the “core first”, b) the “arm first” or c) the “grafting onto” method (Figure 2, Figure 3 and Figure 4).

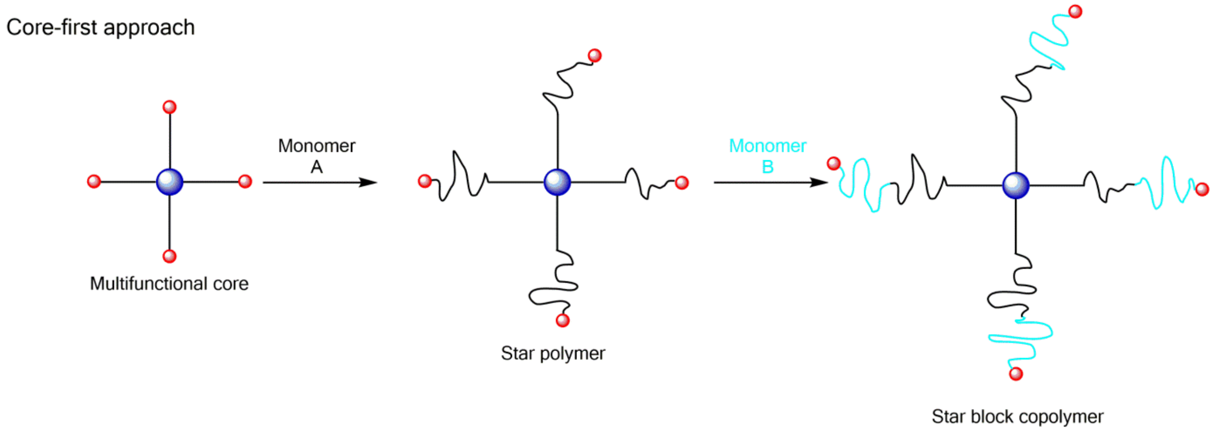


***Figure 2:** Schematic illustration of the synthesis of star polymers applying the core-first method.*[57, 60]

The core-first method is based on a core of low-molecular or macromolecular structure bearing multifunctional initiating sides as starting points for the growth of linear arms (Figure 2). The core should provide initiating groups of same reactivity, allowing efficient and simultaneous initiation of the polymerization of the monomer at each of the arms. The applied polymerization technique should be characterized by a higher initiating than propagation rate and minimal termination reactions, granted for instance by controlled radical polymerization methods.[57] However, using these controlled radical polymerization techniques, star-star coupling raises with increasing monomer conversion due to reaction of at least two "living" radical star polymers, producing star polymers with a broad molecular weight distribution.[61] A multitude of reports were published taking various core units and monomers into account, which were polymerized by ATRP, NMP or RAFT.[62-66] Benefit of this method is the easy purification of the synthesized polymers by simple precipitation to remove unreacted monomer or catalyst residues. However, the structural diversity of star polymers is limited by the quantity of initiating groups. The use of low-molecular weight initiators with less reactive sides can be expanded by substitution of macromolecular initiators. Knischka *et al.* used modified hyperbranched polyglycerol, bearing multiple hydroxyl groups as macroinitator for the anionic polymerization of ethylene oxide.[67] Calixarenes, a kind of phenol containing macrocycles, were also used to initiate the living radical polymerization of methacrylates or ATRP of styrene.[66, 68] Furthermore, the application of dendritic molecules, such as modified adamantanes, cyclodextrines or nanoparticles as multifunctional cores was described.[69-76] However, the synthesis of miktoarm star polymer stays more difficult due to the necessity of orthogonal initiating groups and implementation of different polymerization techniques.[60, 77, 78] Erdogan *et al.* accomplished the synthesis of a bifunctional initiator bearing one initiating site for ring opening polymerization and two for ATRP.[79] Additionally, the synthesis of star block copolymers can be accomplished by modification of the living chain ends of polymeric arms for subsequent polymerization of a second monomer. Star polymers synthesized *via* the core-first approach are characterized by indirect characterization methods like end group analysis or molecular weight determination of arms after cleavage.[57]

The arm-first method (Figure 3) is known since the 1960s applying anionic polymerization.[80, 81] Regarding the arm-first method, linear polymeric arms are prepolymerized and linked together in a second step. Here, three subclasses can be classified: a) macroinitiator, b) macromonomer and c) self-assembly crosslinking.[57, 82] Macroinitiators bear one terminal initiating group and are polymerized with a di- or multifunctional monomer, a vinylic compound, as the core unit. On the other side, macromonomers have a polymerizable chain end and are crosslinked by an initiator. The connection of cross-linkable blocks of block copolymers, named as self-assembly crosslinking, is the third possibility to produce star polymers *via* the arm-first approach (Figure 3). Considering the macroinitiator or macromonomer route, miktoarm star polymers can be synthesized easily by using initiating groups located at the core to polymerize a second monomer starting from the core to the outside, named the "in-out" method.

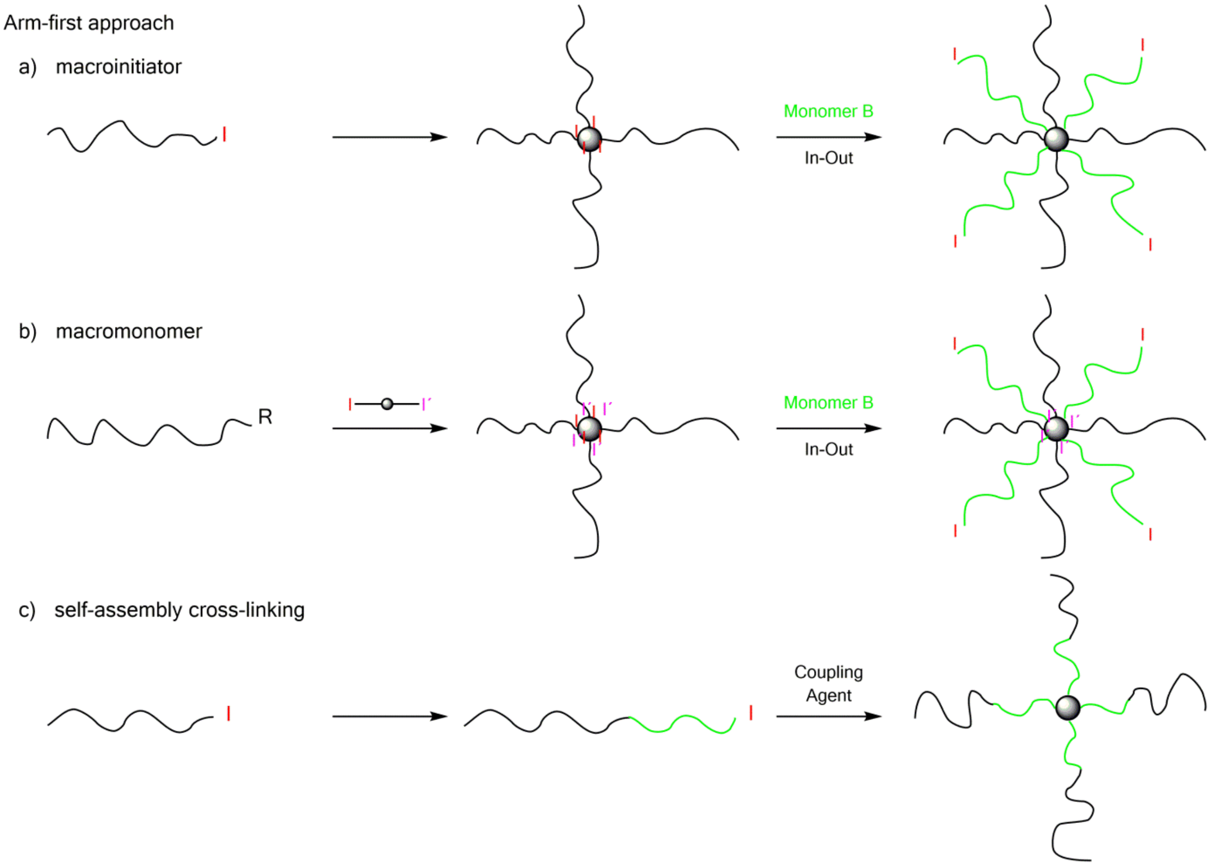


***Figure 3:*** *Schematic illustration of the three subclasses of arm-first approaches: a) macroinitiator, b) macromonomer and c) self-assembly crosslinking method.*[57, 60]

Advantage of the arm-first method is the synthesis and characterization of polymeric arms prior to star polymer formation. By the application of living radical polymerization techniques, the arms can be polymerized with precise control and narrow molecular weight distribution.[83-85] Even though the arms are preformed, well-defined star polymers can hardly be obtained because incorporation of the arms into the anchor points of the core unit depends on plenty of parameters like the used cross-linker, molecular weight and composition of the arms or cross-linker-to-arm ratio.[57] Also, steric hindrance of arms among themselves prevents complete conversion of arms. Depending on the used polymerization technique, other problems relating to the yield like bimolecular termination or disproportionation for living controlled polymerization appear. In consequence, purification is time- and labor-intensive due to the necessity of repeated precipitation or dialysis. Compared to star polymers prepared *via* the core-first approach, the arm-first method gives rise to stars with a huge number of arms or different types of arms (>100 compared to usually 3-8 for the core-first approach). The highly crosslinked core itself, giving these type of polymers the additional name "core crosslinked stars" (CCS), contains functional groups or cavities to attach or encapsulate compounds shielded by the arms around it. Liu *et al.* synthesized star polymers based on poly[(oligoethylene glycol) methyl ether methacrylate] crosslinked by addition of a bisfunctional vinylic compound and vinyl benzaldehyde, generating a core unit with aldehyde groups. The attachment of doxorubicin, used as active component against tumors, was additional shown in the work of Liu *et al*.[86]

The coupling of preformed arms with reactive end groups, either modified by post-polymerization functionalization or present due to the applied living radical polymerization methods, to a multifunctional, proper core is known as grafting-onto strategy (Figure 4). This method allows the synthesis and characterization of both, the core unit and polymeric arms, prior to star polymer formation. Nevertheless, the dimension of the formed stars is limited by the number of functionalities of the core unit and steric hindrance of arms around the core. For high yields, excess of arms, long reaction times and efficient coupling methods, usually click reactions, are necessary making thoroughly purification indispensable.[87-89] Beneficial is the easy synthesis of miktoarm star polymer similar to the arm-first approach by coupling of different arms with the same functional groups.

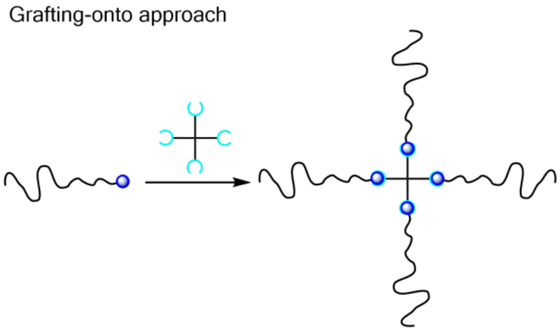


***Figure 4:*** *Schematic illustration of the grafting-onto approach.*[57, 60]

Considering star polymer synthesis, researchers must decide about the appropriate method, depending on monomer, availability of the core, composition, applications, polymerization techniques and further on.[90]

Independent of the applied synthesis strategy, star polymers are attractive for chemists and material scientists due to their unique properties differing to a great extent from linear analogs. Star polymers offer an increased quantity of functional groups per molecule. Their three-dimensional globular structure implicates a smaller hydrodynamic volume, for instance evidenced by lower molecular weights determined *via* size exclusion chromatography (SEC).[72] The compact structure increases the solubility and changes their physical properties. For instance, they show lower viscosity compared to their linear counterparts. Also, thermal properties are affected showing lower glass transition, melting temperature and crystallization temperature.[91] The structural diversity combined with distinguished properties and simple preparation procedures, if compared to dendrimers, makes star polymers interesting candidates in fields of biomedicine, nanotechnology and catalysis.[91-94] Terashima *et al.* describe the encapsulation of a ruthenium-complex simultaneous to the metal-catalyzed living polymerization of methyl methacrylate and the application of the resulting star polymer in the oxidation reaction of alcohols.[95] The one-pot removal of the encased ruthenium-catalyst and incorporation of another type of ruthenium-catalyst catalyzing living radical polymerizations was also described.[96] There are even a few commercial available star polymers known, which are used as viscosity modifier or as composite material *e.g.*[97-102]

Star polymers derived from renewable resources are also well known. Several strategies have been published regarding star polymers including cyclodextrine as core unit.[64, 71, 103-110] In addition, a few examples for the use of other renewable compounds in star polymer synthesis are described. Giguère *et al.* published the synthesis of star polymers bearing a cholic acid core.[111] Liu *et al.* described the synthesis of a star polymers based on poly(ethylene glycol) (PEG) as linear arms and mucic acid as core unit.[112] Glycerol bearing three hydroxyl groups could also been used as core unit for the ring opening polymerization of $\varepsilon$-caprolactone resulting in a biocompatible and biodegradable star polymer.[113] Sanda *et al.* described the ring-opening polymerization of $\varepsilon$-caprolactone applying trimethylpropane and pentaerithrol as core units and fumaric acid as activator. A metal-free approach to poly(caprolactone) is highly desirable due to its application in biomedicine and pharmacology.[114] The encapsulation of anticancer drugs into star-shaped poly(caprolactone)-poly(ethylene glycol) nanoparticles shows one possibility for this type of polymer in this area.[115] Wang *et al.* synthesized a amphiphilic star block copolymer with a polyamidoamine core unit initiating the ring-opening polymerization of $\varepsilon$-caprolactone and subsequent attachment of a hydrophilic poly(ethylene glycol) block. The polymer showed high loading capacity of a hydrophobic anticancer drug.[116] Hoogenboom and coworkers reported the synthesis of star-shaped poly(caprolactone) employing click and supramolecular click chemistry *via* the arm first approach. Therefore, a linear acetylene functionalized poly(caprolactone) was formed catalyzed by tin octoate and coupled in a subsequent step to a multifunctional cyclodextrine core. The supramolecular click reaction included coupling to 3,6-di(pyridine-2-yl)pyridazine and afterwards self-assembly on copper(I) ions.[117]

### 2.1.2 DENDRIMERS

The term "dendrimer" refers to the Greek words *"dendri"* (tree-branch-like) and *"meros"* (part) and was coined by Tomalia *et al.* in 1984 and published one year later.[118, 119] 50 years earlier in 1941, Flory already introduced a hypothetical concept of highly branched, three-dimensional macromolecules.[40, 120-122] Although already known theoretically, the first synthesis succeeded in 1978.[123] Buhleier *et al.* described the synthesis of a "cascade"-molecule by iterative steps starting from benzylamine and ethylenediamine.[124] Since this time, an uncountable array of reports has been published dealing with the synthesis of dendrimers based on diverse monomers and resulting in dendrimers based on polyesters, polyamidoamines, polyethers, polyurethanes and many more.[125-128] Dendrimers are three-dimensional, globular macromolecules with three structural parts: the core unit, concentric layers of branched repeating units, called "generations", and end groups on the surface building up the typical core-shell-structure (Figure 5). Their structure endows dendrimers with unique physical properties regarding their viscosity, solubility and hydrodynamic volume.[129, 130] Hawker *et al.* compared polyether dendrimers with their linear analogs of same molecular weight *via* SEC and found similar hydrodynamic volumes until generation four and a higher hydrodynamic volume for linear polymers from the 5th generation on due to the random coil structure of linear polymers compared to the globular and compact structure of dendrimers.[130]

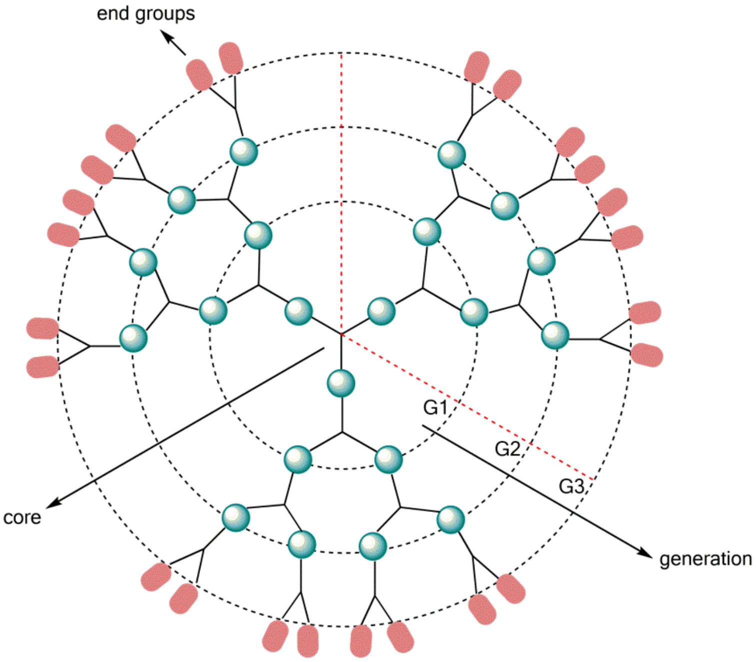


***Figure 5:*** *Schematic illustration of a dendrimer with the structural parts: Core unit, generations (G1, G2, G3) and end groups; the dendron is one „arm" of the dendrimer (marked in dotted red).*[131, 132]

The synthesis of dendrimers can be performed following two different approaches: a) divergent or b) convergent (Figure 6).[133] The divergent approach is based on a multifunctional core and the addition of the multifunctional monomer in a step-wise manner (inside out synthesis).[118, 134-136] Herein, the monomer $AB_x$ ($x \geq 2$) bears two different functional groups. Functional group A only reacts with functional groups B and vice versa.[132] The protection of one type of functional group is necessary in order to prevent reaction of the monomers among themselves instead of selectively reacting with the end groups of the dendrimer. Another possibility is the use of a monomer with functional groups, which do not react with each other. If so, the activation of the functional group has to be carried out by conversion to a reactive functionality or coupling with a second molecule.[131] The procedures applied for the coupling of the monomer units to the dendrimer should provide complete conversion of functional end groups and avoid side reactions to prevent defects in the macromolecular structure. In a perfect synthesis, the dendrimer formed is monodisperse with a dispersity of one. Due to the increasing quantity of functional groups in the periphery, high excess of reagents are necessary to force the coupling reactions to completion.[136]

Limitation of this approach is given by the de Gennes dense packing, when perfect growth of the dendrimer becomes impossible. At this point, the surface area for terminal functional groups achieves the van-der-Waals-dimension of the group and thus the molecular space for the next generation would be insufficient.[137] In addition, rigorous purification must be conducted in every step to prevent accumulation of impurities. Nevertheless, the divergent approach is the route of choice for the large-scale synthesis of dendrimers.[138] The first divergent synthesis to polyamidoamines (PAMAM) described by Tomalia *et al.* was started from ethylenediamine as core unit, which was reacted with an acrylate ester by Michael addition followed by amidation with ethylenediamine resulting in four amine functionalities for the next reaction sequence.[118]

Following the convergent approach, the synthesis starts from small molecules, which end up at the surface of the dendrimer (outside in synthesis). Here, the arms of the dendrimers, named as “dendron”, are preformed and attached in a subsequent step to the core unit.[131] In each step, the activation of only one functional group must be conducted. Disadvantageous is the increasing steric hindrance at the focal point of the dendron, which prevents effective coupling reactions. Compared to the divergent approach, advantage of this method is the use of only small excesses of reagents facilitating the purification.[131] With the divergent approach similar macromolecules with a very low dispersity (near 1) are obtained, which results from the incorporation of defects, resulting from incomplete conversion of functional groups or cyclization, for higher generations.[129, 139, 140] Dendrimer macromolecules formed *via* the convergent approach are essentially equal to each other regarding structure and molecular weight.[131, 141] In addition, the convergent approach allows the functionalization of the focal point as well as of the end group. Besides, the synthesis of “copolymers” by attaching different dendrons to the core unit or the linking to sensible cores, which would not be stable during divergent synthesis, increase the structural diversity of dendrimers formed by the convergent approach.[141-144]

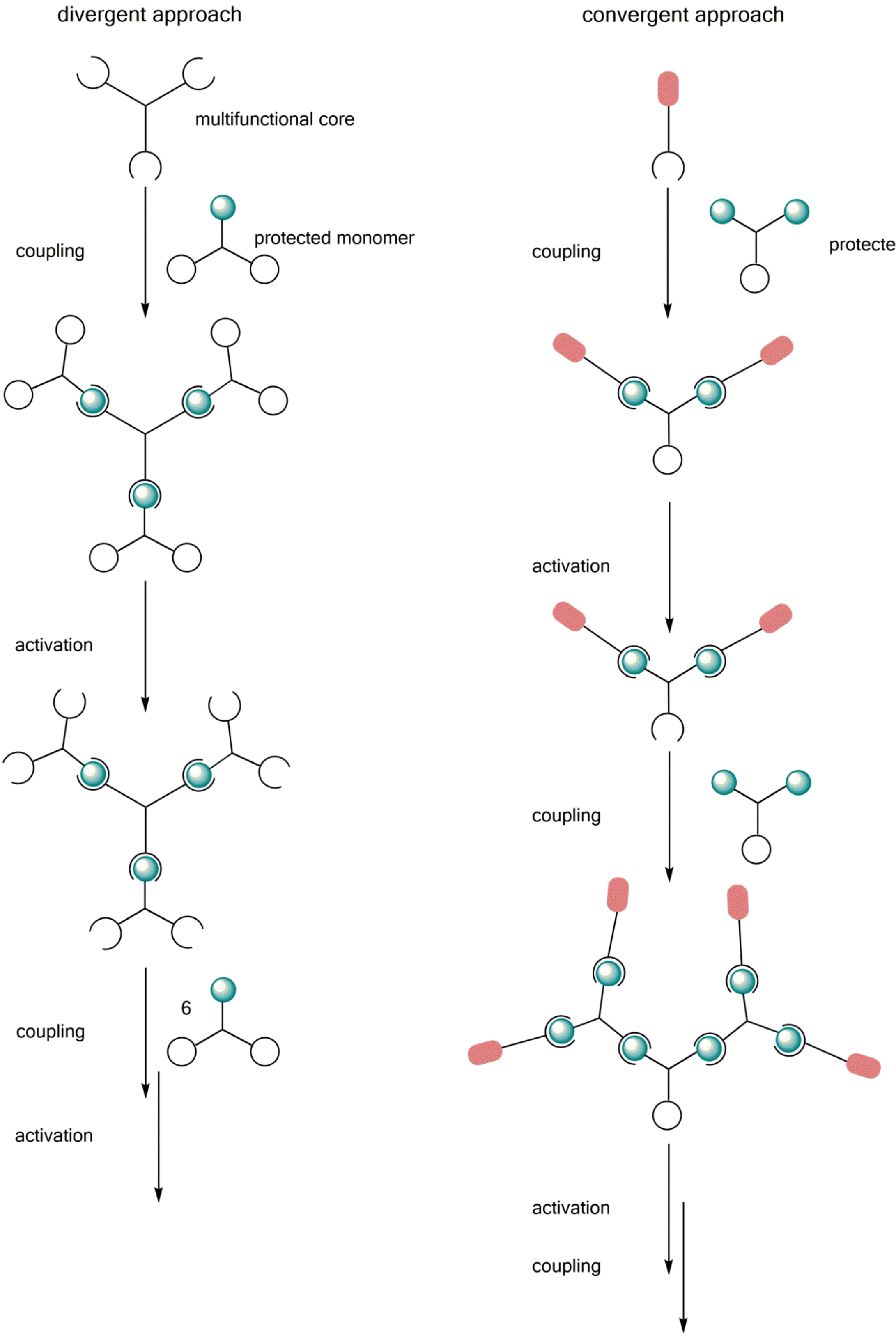


***Figure 6:*** *Schematic illustration of the divergent and convergent approach for dendrimer synthesis.*[123, 131]

Besides the two well-established synthesis routes, more efficient, time- and labor-saving procedures were developed. Ihre *et al.* reported the synthesis of dendrimers *via* the double-stage convergent growth approach. Here, dendrons are coupled divergently to a monodendron or a dendrimer, reducing the number of successive coupling and purification steps.[50, 145] The double exponential growth strategy starts from $AB_2$ monomers, one fraction with protected A functionality and one fraction with orthogonally protected B functionality, reacting with each other. The combination of deprotection and coupling enables dendrimer synthesis following the equation: $DP_n=2^{2n}-1$ (n=generation).[146] The orthogonal coupling method starting from two different monomers, which react in two orthogonal coupling reactions, saves time due to the avoidance of protection/deprotection or activation steps. Zeng *et al.* reported a combination of Mitsunobu esterifications and Sonogashira couplings for the synthesis of a dendrimer with six generations.[147] Click reactions are well-suited for dendrimer synthesis due to their special characteristics: regioselectivity, quantitative yields, easy purification and mild reaction conditions. Thus, since Sharpless published the copper-catalyzed azide alkyne coupling (CuAAC), many reports, applying the concept of click chemistry in dendrimer synthesis, have been released.[148-154] Kang *et al.* described the synthesis of a dendrimer bearing hydroxyl groups in the interior by combination of epoxy-amine and thiol-ene coupling starting from a diamine and allyl glycidyl.[155]

Dendrimers´ outstanding properties paired with the structural diversity due to the plenitude of available monomers and core units and the possibility to modify the interior and external functional groups, enables the development of tailored dendrimers. Cavities in the inner sphere of dendrimers make them ideal candidates for encapsulation of *e.g.*, drugs.[156-158] In the field of medicine, dendrimers are used as imaging agent, encapsulating metal-complexes, which detect oxygen in tumor cells, or as protein mimics.[159, 160] Other fields of interest include sensors, photochemical molecular devices, catalysis and electroluminescent devices.[50, 161-163]

## 2.2 PLANT OILS IN POLYMER CHEMISTRY

The history of plastics already began in the 19th century while the exact date is still up to discussion. In 1833, Berzelius coined the word polymer, almost 100 years before Staudinger postulated the presence of macromolecules in organic materials. In 1953, Staudinger was rewarded for his discovery in the field of macromolecular chemistry with the Nobel Prize in chemistry. Not later than this date, organic chemists accepted macromolecular chemistry as new domain of organic chemistry.[164-166] Today, a life without polymers is no longer imaginable. Packaging, constructions and automobiles are the three main application areas. Therefore, 311 million tons of polymers were produced in 2014 worldwide and every year the production volume has grown.[167] Till today, the key resource for the production of polymers is still crude oil. In Germany, only 4 - 6 % of the used crude oil was consumed by the polymer industry while 80 % are used for heating, fuel and electricity.[167] Anyway, there are several factors that argue for the search for alternatives to crude oil. The independence on oil-producing countries and on fluctuating and steadily increasing oil prices is an economically important reason. In 1970, the price was under five dollars per barrel and in 2016, the price increased to the 9-fold.[168] With regard to the environmental aspects, the emitted carbon dioxide entails detrimental effects on the climate. Crude oil incriminates the environment starting from the search for new sources and production to converting and transport. In addition, crude oil will someday deplete, although the crude oil industry reports optimistically on 239.4 billion tons reserves.[168] The challenge for chemists consists of the search for other, more sustainable resources, also in the context of “Green Chemistry” and the development of efficient procedures. Figure 7 shows the worldwide plastic production and the minor share in bio-based polymers in 2014.

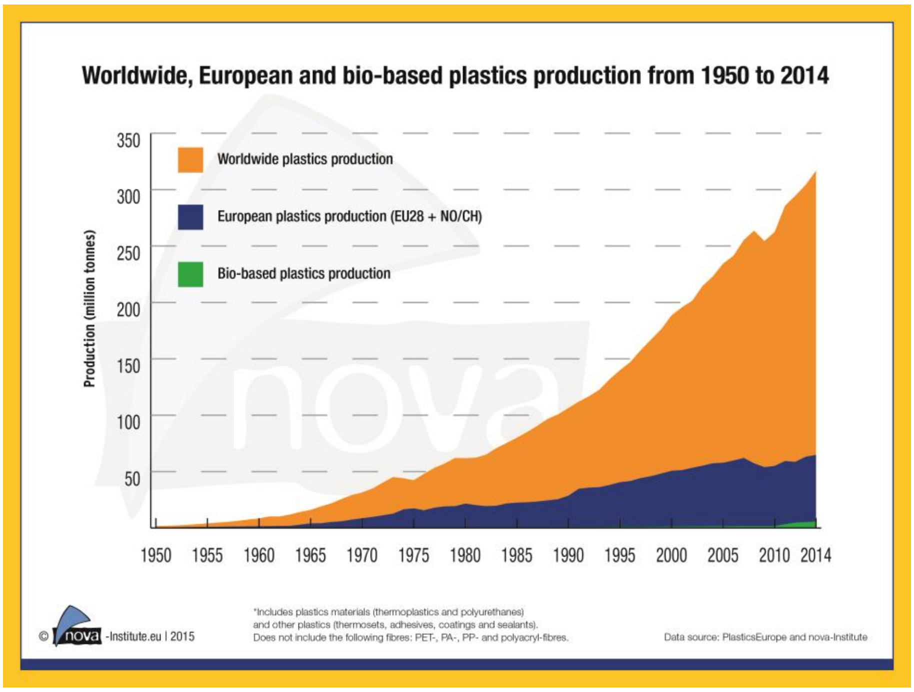


***Figure 7:*** *Illustration of worldwide, European and bio-based plastic production in 2014.*[168]

Interestingly, the first polymers reported were based on renewable resources. Celluloid is synthesized by the reaction of nitrocellulose and camphor and was discovered by Parkes in 1855 to replace ivory in the production of billiard balls.[169, 170] Hyatt created celluloid in a strip format revolutionizing the movie industry.[171-173] Today, bio-based polymers represent not exceeding one percent of the worldwide produced polymers (due to the lack of statistics about production and consumption, the found values for bio-based polymers highly vary).[168] Although, the potential of renewable resources arises not only from their molecular structure and the possible modifications, but also from the chemical products, which can be made from them and applied in further conversions (Figure 8).[174]

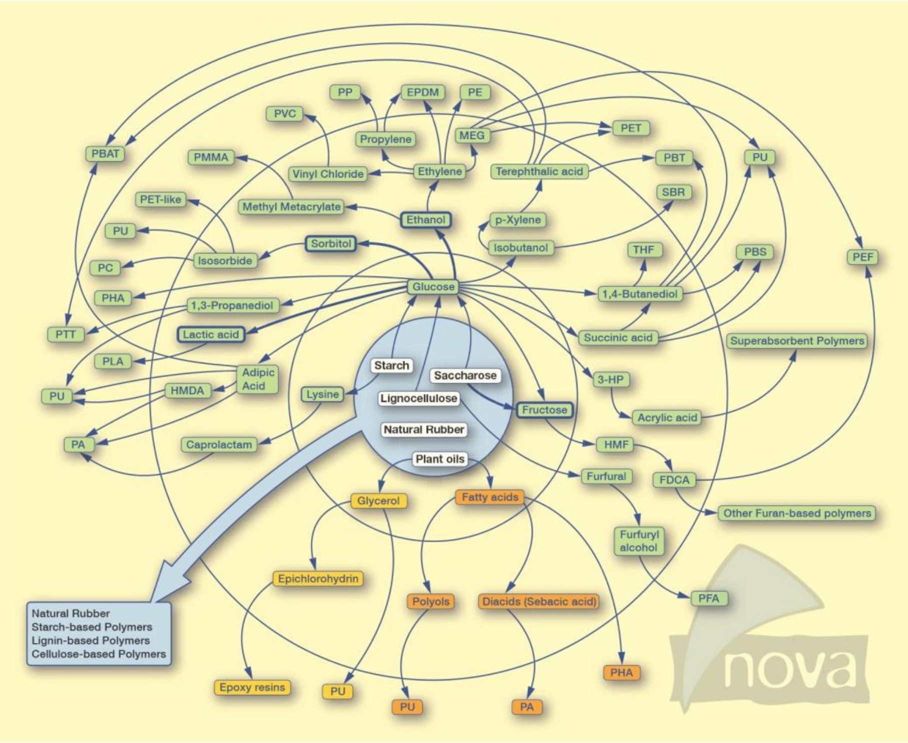


***Figure 8:*** *Illustration of renewable resources and their secondary products.*[168]

Animal resources are chitin, proteins and cellulose from mollusks.[175] Chitin is the most abundant natural polysaccharide and can be converted to chitosan *via* deacetylation already applied in cosmetics, biomedicine, hydrogels and many more.[176] Wood *e.g.* is a vegetable resource consisting of lignin, cellulose, hemicellulose and polyphenols. Lignin, as the main source of aromatic structures, has been a by-product of paper industry and a long time waste. Now, it finds industrial application *e.g.*, in epoxy resins or as substitute in phenolic powder resins.[177-180] Furthermore, the structure of lignin allows various modifications.[181-183] Suberin, natural rubber, tannins and terpenes are further components of woods.[175] In annual growing plants, starch, saccharide and vegetable oils are available.[184] Vegetable oils are thereof the most deployed renewable resource for the chemical industry. In 2013, 46 % of the used renewable raw material in Germany was allotted to fats and oils.[168] This high quantity illustrates the huge interest of chemists in providing versatile product based on fatty acids for the chemical industry and expanding the scope for both components of oils and fats alone and the modified substrates. In 1994, 63 million tons of plant oils were dissipated and today, 20 years later, 166 million tons were gained.[185]

Plant oils consist of triglycerides, the esterification product of the trivalent alcohol glycerol and three fatty acids, with C16 and C18 being the most common. The fatty acid composition depends on the source of oil, but also on crop, season and growing conditions.[186] Furthermore, breeding, genetic engineering or microalgae are possibilities to tune the composition of oils and produce *e.g.*, high oleic oil.[187-190] For example, the main component of castor oil is ricinoleic acid, whereas coconut and palm kernel oil consist mainly of short-chain C12 and C14 fatty acids.[186, 191] Linseed oil cropped in Europe contains 56-71 % $\alpha$-linolenic acid compared to 45-53 %, when grown in Argentina.[192] Figure 9 shows the general structure of triglycerides as well as the structure of some important fatty acids, which can be saturated or unsaturated bearing functionalities like hydroxyl groups or epoxides.

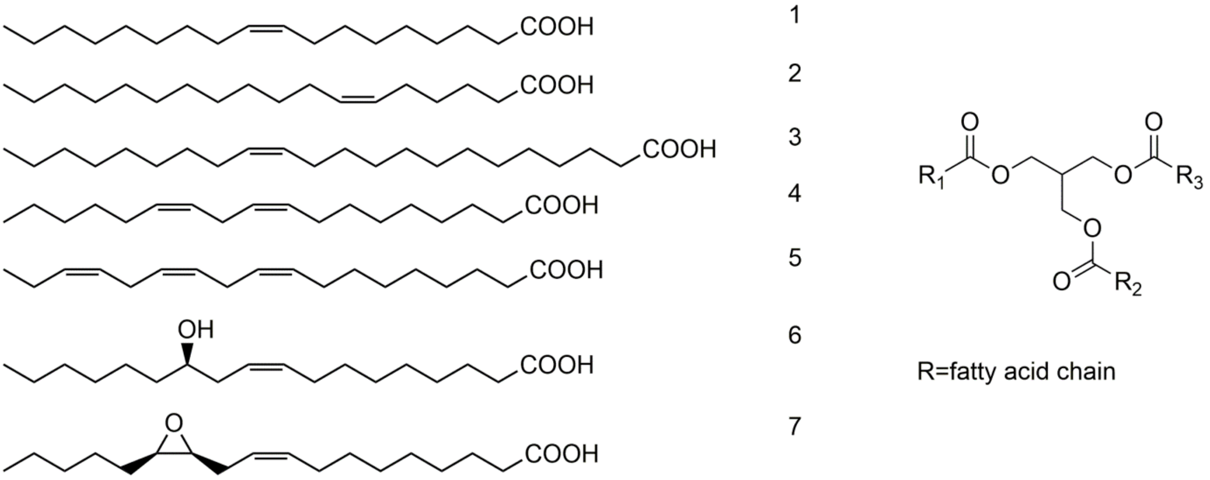


***Figure 9:*** *Structures of some fatty acids found in plant oils and the general structure of triglycerides: 1) oleic acid, 2) petroselinic acid, 3) erucic acid, 4) linoleic acid, 5) linolenic acid, 6) ricinoleic acid and 7) vernolic acid.*[188, 193, 194]

In general, there are three main strategies to utilize plant oils and fatty acids in polymer chemistry. The first method is the direct polymerization by reaction of the present double bonds or functional groups. On the other hand, the double bonds can be modified with functional groups allowing subsequent polymerization. At last, triglycerides can be converted into platform chemicals, which can be used as monomers or precursors.[195] The reactive sites of triglycerides are located at the double bond and next to it in allylic position (or bisallylic position for conjugated double bonds), at the ester bond and at the present functional groups. Here, transformations open up multiple possibilities to create new substrates.

To split triglycerides, alkaline hydrolysis and transesterification with methanol are the most important oleochemical transformations. The formed fatty acid methyl esters (FAME) can be further hydrogenated to obtain fatty acid alcohols or reacted with ammonia and afterwards hydrogenated generating fatty acid amines. These oil-based compounds can be applied directly in *e.g.*, cosmetics, soaps, as detergents or lubricants.[187] In addition, glycerol is formed as by-product in large amounts. The purified glycerol represents a valuable feedstock in several industrial applications. First, it serves as precursor in the synthesis of *e.g.*, 1,3-propanediol, acrolein and epichlorohydrin. Moreover, mainly pharmaceuticals and personal-care products benefit from the utilization of glycerol improving their solubility, humidity or viscosity.[196, 197] In the context of polymers, glycerol acts as raw material in the synthesis of dendrimers, hyperbranched polyesters or linear polyglycerols, poly(1,2-glycerol carbonate) or copolymers.[174, 198, 199]

Castor oil as inedible oil gives rise to various, versatile platform chemicals. The caustic oxidation of ricinoleic acid forms sebacic acid by cleavage of a carbon-carbon bond and 2-octanol as by-product. Main application field of sebacic acid is the polymerization to Nylon 6,10 used in *e.g.*, toothbrushes. Furthermore, several industrial uses as plasticizer, lubricant, cosmetics and in the synthesis of resins and polyesters are known.[200] The amine derivate of sebacic acid, 1,10-decanediamine, can be polymerized to linear long-chain polyamides or biodegradable and linear poly(ester amide)s fully based on renewable feedstocks as described by Wang *et al.*[201] Pyrolysis of castor oil gains access to 10-undecenoic acid and *n*-heptaldehyde. Padmaja and coworkers reported the synthesis of polyol esters based on 10-undecenoic acid reacted with multivalent alcohols, which can be used as lubricants.[202] Furthermore, it was recent used in a Passerini three-component step growth polymerization to build up linear homopolymers, copolymers and star-shaped polymers.[203] Bigot *et al.* described further possibilities for the utilization of 10-undecenoic acid constructing polyhydroxyurethanes, crosslinked polymers and photopolymers by various modifications.[204] 11-Aminoundecanoic acid can be synthesized from 10-undecenoic acid and can be used as monomer for bio-based polyamides.[205] On the other hand, reduction of 10-undecenoic acid yields 10-undecenol, which can be converted in self-metathesis to long chain diols or cross-metathesis to *e.g.,* star-shaped polyurethanes.[206-208] Seidensticker *et al.* used another route to modify 10-undecenol by *bis*-hydroaminomethylation to bifunctional monomers for polyester synthesis.[209] Figure 10 summarize possible platform chemicals derived from castor oil.

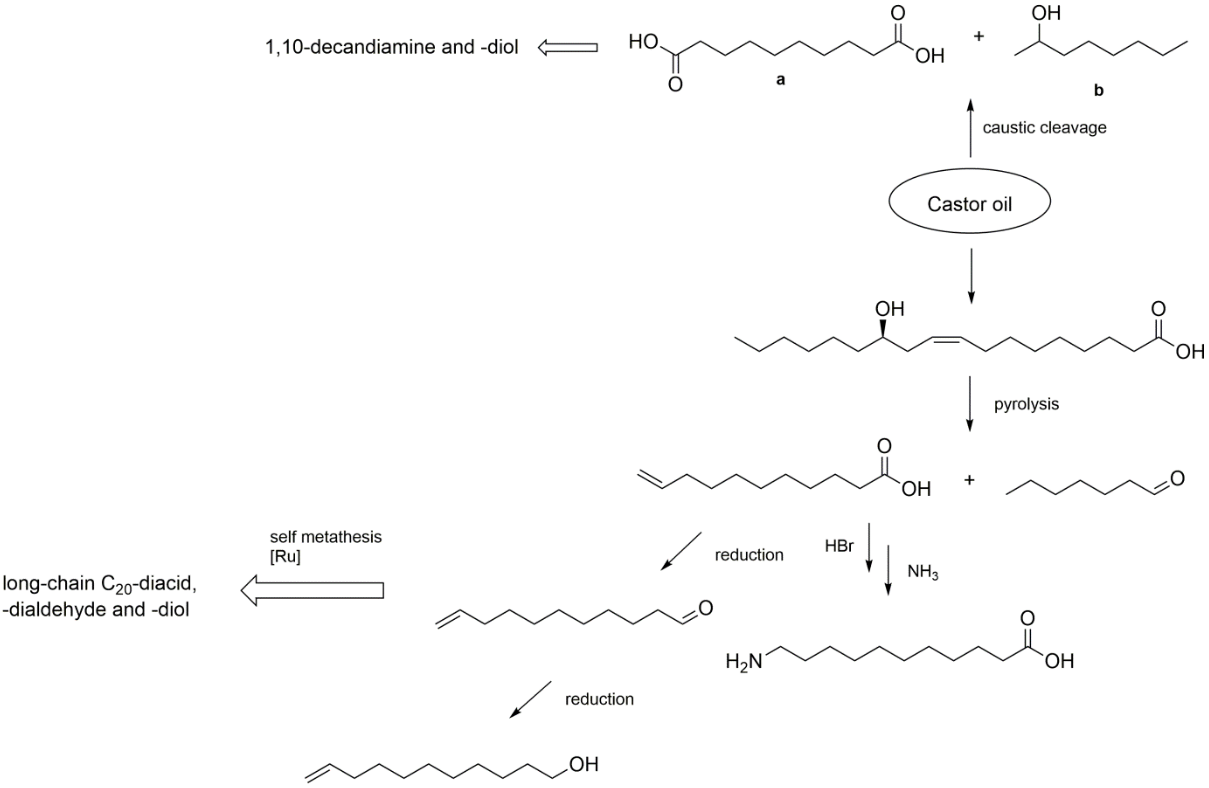


***Figure 10:*** *Castor oil-derived platform chemicals for chemical industry and research.*[191, 200]

As already mentioned, the double bonds of triglycerides are ideal starting points for various functionalization methods applying typical organic chemistry reactions like epoxidation, metathesis and addition reactions, for example. Thiol-ene addition of mercaptoalcohols, ozonolysis or hydroformylation with subsequent hydrogenation, the Schenck-Ene reaction with reductive work-up or ring-opening of epoxidized double bonds by water or alcohol are possibilities to synthesize polyols from triglycerides.[210] The Dow Chemical Company produces polyols from soybean oil *via* esterification to FAME and afterwards hydroformylation and hydrogenation. The obtained monofunctionalized fatty acid derivatives are reacted with multivalent molecules to generate polyols, which are subsequent applied as substitute for petroleum-based polyols in the production of automotive parts.[211] Recently, Alagi *et al.* published the thiol-ene addition of mercaptoethanol to soybean oil. Due to the presence of mono- and polyunsaturated fatty acids in soybean oil, the hydroxyl functionality could be controlled by varying the reaction time. The polyols were afterwards polymerized with dialcohols and a diisocyanate to yield thermoplastic polyurethanes.[212, 213] Instead of using petroleum-based isocyanates, triglyceride-derived multiisocyanates are an option. Ionescu *et al.* synthesized isocyanates by reacting mercaptanized soybean oil with allyl isocyanate under UV-irradiation at room temperature.[214] For the synthesis of non-isocyanate polyurethanes, the reaction of soybean oil with cyclocarbonate groups, obtained by catalytic reaction of carbon dioxide with the epoxidized oil, and diamines or the polycondensation of diols and dicarbamates were presented.[215, 216] Polyesters are prominent examples for biodegradable polymers and find application in various fields. Among them, poly(lactic acid) is representative in the context of polymeric biomaterials.[217-220] Plant oil-based polyesters could be *e.g.,* synthesized by the ring-opening of epoxidized broccoli seed oil with dicarboxylic acids leading to crosslinking.[221] Panda *et al.* reported about the improved properties of hybrid polymer networks combining epoxidized soybean oil acrylate and an unsaturated polyester by radical addition polymerization.[222] Renewable polyamides can be obtained following four different strategies: Polycondensation of dicarboxylic acid and diamines based on plant oils, ring-opening polymerization of lactams, the reaction of diols and diamines or polymerization of AB-monomers with one amine and one carboxylic acid functionality.[223] Recently, Takeuchi *et al.* reported the laccase-catalyzed synthesis of dicarboxylic acid by oxidative cleavage of fatty acids for polyamide synthesis.[224] In our laboratory, three fatty acid methyl esters were functionalized *via* thiol-ene addition of cysteamine hydrochloride and the formed AB-type monomers were tested in homo- and copolymerization.[225] Another approach was the formation of AB-type monomers by a sequence of Lossen-rearrangement to carbamates, cross-metathesis, carbamate deprotection and afterwards polymerization.[226] In addition, the co-catalyst-free Wacker oxidation of fatty acids was established yielding keto-fatty acids, which were converted to AB-monomers by reductive amination. The monomer was tested in homo- and copolymerization to modified Nylon 6,6.[227]

The current highlights of plant oil-derived polymers show the diversity of functionalization methods, which are almost exclusively carried out at the double bonds or ester groups of the triglyceride or the corresponding fatty acids. Plant oils and fatty acids can be applied in the synthesis of every type of polymer including polyesters, polyamides, polyurethanes, polyolefins and polyethers, beyond others. Furthermore, the formed polymers can adopt diverse polymeric architectures, namely dendrimers, star-shaped polymers or hyperbranched polymers besides simple linear analogs.[186, 193, 210, 228-232] Thus, application fields are composites and hybrid materials, paint, coatings, adhesives and biomedicine.[229] The challenge is now to change critics mind. They apprehend the trend to bio-based polymers competing against the area cultivating plants for food. Furthermore, the intensive farming will impact the environment dramatically due to the increasing amount of fertilizer and the necessity of transgenic plants or genetic bacteria. Since then, petroleum- and bio-based polymers will coexist and over the years an acceptable compromise will be found to meet the needs of modern life and simultaneously protect our planet.[211]

## 2.3 APPROACHES FOR DOUBLE BOND MODIFICATION

"The synthesis of most organic molecules can be broken down into the problems of preparing the carbon framework and that of the introduction, modification and (or) removal of various functional groups".[233]

To build up organic as well as polymeric molecules, chemists accept the responsibility to apply and improve known strategies and develop new methods creating a library of efficient reactions to overcome this challenge. To construct the backbone of molecules, carbon-carbon bond formation plays a crucial rule. Here, nucleophilic, electrophilic, radical, pericyclic as well as metal catalyzed reactions are available.[234] Transition metal catalyzed reactions, especially olefin metathesis reactions, have gained the interest of chemists due to the feasible variety of transformations and commercial availability of catalysts.[235] Olefin metathesis induces cleavage and reformation of carbon-carbon double bonds without the necessity of special functional groups.[236] Paired with the development of new catalysts, more efficient and more tolerant against several functional groups, olefin metathesis became one of the most important synthetic tools in organic chemistry.

In the context of environmental and toxicity issues, the prevention of metal catalysts became highly desirable. Roscales *et al.* discussed boronic acids and their derivatives to be a green alternative to transition metal catalyzed carbon-carbon bond formation reactions.[237] The biocatalytic formation of carbon-carbon bonds represents another possibility to avoid metal catalysts and with the development of improved enzymes as biocatalysts bond formations with high chemo-, regio- and stereoselectivity could be proceeded.[238]

Having the carbon backbone in hand, the second step is to introduce or modify functional groups. In this context, selective and highly efficient methods are necessary to facilitate the synthesis of a desired molecule or macromolecule. In 2001, Kolb, Finn and Sharpless coined the term "click chemistry", which have to fulfill following criteria:

- *Modular reactions wide in scope* with
- *very high yields* and
- formation of only *inoffensive by-products* paired with

- *stereoselectivity,*
- *simple reaction conditions* starting from
- *readily available starting materials and reagents* using
- *no, benign or easily removable solvent,*
- *simple product isolation* and *non-chromatographic purification*.[239]

The most prominent click reaction, the azide-alkyne cycloaddition, was already known since 1963 and was discovered by Huisgen.[240] Due to the necessity of high temperatures and the formation of product mixtures starting from unsymmetric alkynes, the original azide-alkyne cycloaddition do not meet the criteria of a click reaction. With the introduction of copper(I) catalysts by Kolb *et al.*, cycloadditions can now be conducted under elevated temperatures with high regioselectivity (Figure 11).[239]

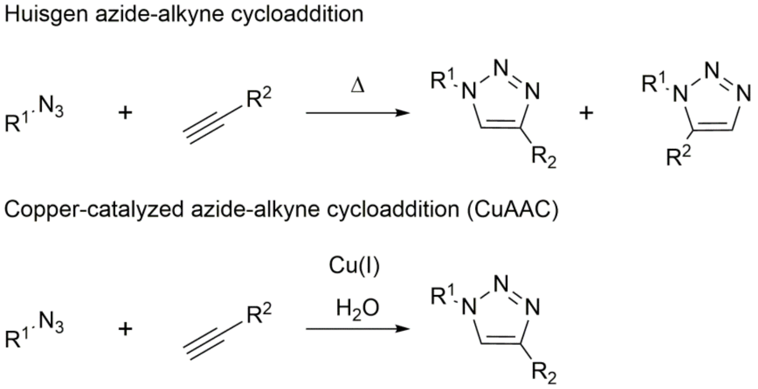


***Figure 11:*** *Illustration of the original Huisgen and the improved copper-catalyzed azide-alkyne cycloaddition.*

Till now, several types of reactions were identified that meet the criteria of click chemistry, such as certain cycloadditions, nucleophilic ring-opening (*e.g.* of epoxides), non-aldol carbonyl reactions, addition to unsaturated carbon-carbon bonds such as the Michael addition, epoxidation or thiol-ene addition.[241-245] Herein, chemists turn their attention to the development of metal-free click reactions due to the potential toxicity of metal catalysts.[246, 247] Residues of metal catalysts would preclude the applicability in the synthesis of pharmaceuticals *e.g.*[243, 248] The light-induced thiol-ene addition and the base-catalyzed

Michael addition will be discussed in detail in section 2.3.2. Since the advent of click chemistry, a multitude of reports have been published regarding the application of click reactions in fields of organic synthesis, polymers and bioscience.[249] Especially in polymer science, click chemistry overcame the problems of poor functionalization due to a growing quantity of functional groups in more complex architectures or on surfaces, of laborious purification due to incomplete functionalization and of harsh reaction conditions implicating polymer degradation.[33]

In the subsequent sections, first olefin metathesis and particular acyclic diene metathesis (ADMET) will be discussed in detail to build up the polymeric backbone (Chapter 2.3.1) and afterwards functionalization of carbon-carbon double bonds *via* thiol-ene addition (Chapter 2.3.2) and Schenck-Ene reaction (Chapter 2.3.3) will be presented as powerful tools for the construction of branched structures.

### 2.3.1 OLEFIN METATHESIS

Carbon-carbon bonds are the fundamental structural unit in organic chemistry and their formation is the most important synthetic tool to construct the backbone of molecules. Therefore, different synthetic reactions can be applied, including Grignard reaction, Michael addition, Aldol or Wittig reaction, cross-couplings and others.[250-253] In addition to the large number of organic and organometallic reactions available, olefin metathesis attained rising importance in organic and macromolecular chemistry.

Olefin metathesis (from Greek, *meta* = change and *thesis* = position) is a transition metal catalyzed reaction, in which alkylidene groups between two substituted alkenes are exchanged reversibly, also termed as transalkylidenation.[236] In a catalytic cycle, new products are formed *via* cleavage and reformation of carbon-carbon double bonds. The story of olefin metathesis dates back to 1955. Anderson and Merckling reported the polymerization of norbornene catalyzed by titanium(II) compounds.[254] In the same year, the first publication regarding the catalytic polymerization of ethylene was released by Ziegler *et al.*[255] In 1956, Eleuterio (DuPont) observed the “disproportionation” of propene applying molybdenum-on-aluminum-catalysts and in 1957 he reported the polymerization of norbornene in the presence of molybdenum oxide on aluminum with lithium aluminum hydride.[256, 257] Shortly later, Banks and Bailey obtained the disproportionation of propene to ethylene and butene in the presence of molybdenum catalysts.[258] The Phillips Triolefin Process, developed at Phillips Petroleum, used a heterogeneous $WO_3/SiO_2$ catalyst to convert propene to ethylene and 2-butene. The ring-opening polymerization of cyclic olefins under homogenous catalysis was reported by Natta *et al.*[259-262] In 1967, Calderon *et al.* suggested the same type of reaction for the polymerization of cyclic olefins and the disproportionation of acyclic ones and coined the term “olefin metathesis”.[263] Although several reports and patents were published in this time, the mechanism of olefin metathesis was still unknown. Calderon and Mol proved the exchange of alkylidene groups using isotopically labelled alkenes.[264-267] Several suggestions regarding the mechanism and the role of the transition metal catalyst were offered including the formation of a bisolefin metal complex, which means the coordination of both olefins to the metal, or the presence of a quasi-cyclobutane transition state proposed by Calderon or the Grubbs´ model of a metallocyclopentane.[263, 268, 269] In 1971, Chauvin and his student Hérisson proposed the today accepted mechanism of olefin metathesis to take place *via* a [2+2]-cycloaddition (Figure 12).[270-272]

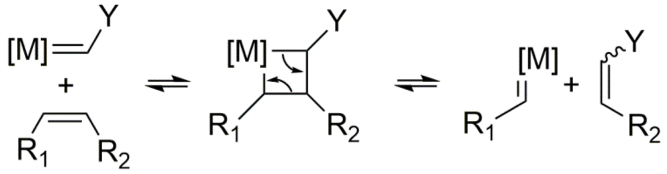


***Figure 12:*** *Olefin metathesis mechanism suggested by Chauvin and Hérisson.*[272]

The alkylidene group exchange occurs *via* an instable metallocyclobutane intermediate formed by reaction of the metal carbene and the olefin. The reversibility of the process causes the formation of mixtures of starting material and products. The driving force can be the release of ring strain in case of ring-opening metathesis (ROM) and ring-opening metathesis polymerization (ROMP), the formation of rings of favorable size for ring-closing metathesis (RCM) or the liberation of volatile by-products like ethylene in acyclic diene metathesis polymerization (ADMET). In addition to ROM, ROMP, RCM and ADMET, self-metathesis (SM) and cross-metathesis (CM) are incorporated into olefin metathesis reactions (Figure 13).

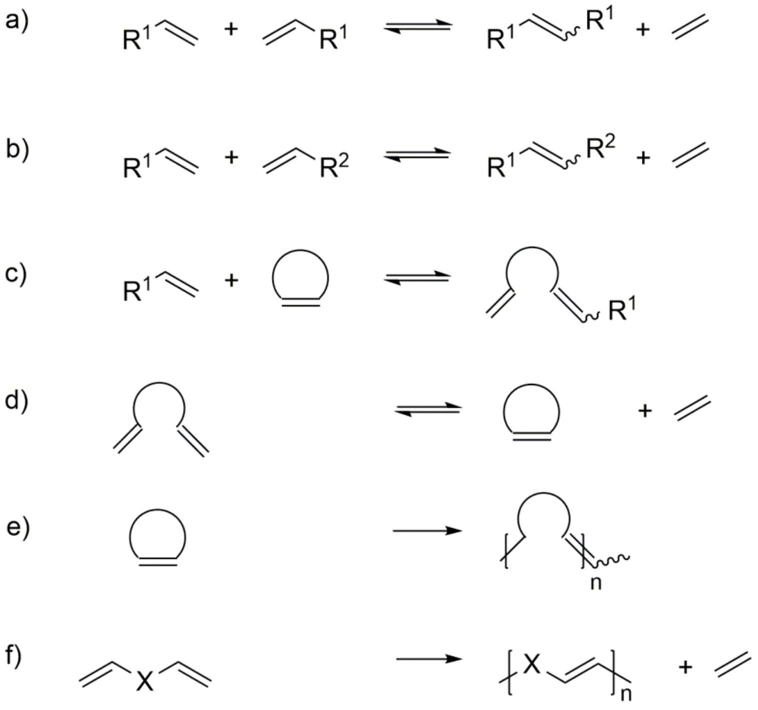


*Figure 13: Olefin metathesis reactions: a) self-metathesis, b) cross-metathesis, c) ring-opening metathesis, d) ring-closing metathesis, e) ring-opening metathesis polymerization and f) acyclic diene metathesis polymerization.*

With the increasing popularity of olefin metathesis and the vision of new molecules, which were inaccessible due to missing, successful, synthetic procedures, the requirement to develop new catalyst systems became more important. The catalysts applied in olefin metathesis can be either homogenous or heterogeneous. In the early stage of olefin metathesis, poorly defined catalysts like $WCl_6/Bu_4Sn$, $MoO_3/SiO_2$, $Re_2O_7/Al_2O_3$ combined transition metal salts with alkylating co-catalysts or solid supports. Due to their low price and their commercial availability, they are even till this day applied in several transformations. The Phillips neohexene process is an industrial process utilizing olefin metathesis, that converts ethylene with 2,2,4-trimethylpentene to neohexene (3,3-dimethyl-1-butene) and isobutene catalyzed by a $WO_3/SiO_2$+MgO. Neohexene is an important intermediate in the synthesis of synthetic musk and isobutene is recycled during the process.[273, 274] Due to their intolerance to most functional groups, new catalysts had to be developed to expand the scope of olefin metathesis reactions and to broaden the applicability in industrial and synthetic processes. In the early 1980s, homogenous single-component catalysts were discovered. Schrock *et al.* designed the first efficient molybdenum and tungsten catalysts characterized by high activity in metathesis reactions of terminal, internal as well as cyclic olefins, but these first catalysts were poorly tolerant to functional groups (especially aldehydes, alcohols and acids) and highly sensitive to air and moisture due to the oxophilicity of the metal centers.[275, 276] With the development of more efficient catalysts, the influence of the structure to the activity of the catalyst could be investigated more in detail to identify ruthenium as the metal with the highest reactivity to olefins and stability towards all common functional groups.[277] The Grubbs catalyst is a ruthenium alkylidene complex and is one of the most used catalysts in olefin metathesis, especially for ROM and ROMP. Based on $RuCl_2(PPh_3)_3$, the catalyst is synthesized by reaction with alkyl or aryl diazoalkanes und afterwards phosphine exchange.[273] Variation of the ligands *e.g.,* attachment of *N*-heterocyclic carbene (NHC) ligands or cyclohexylphosphine instead of the original triphenylphosphine, gave rise to 2nd generation catalysts of higher reactivity and improved stability.[277-279] Hoveyda *et al.* introduced chelating ligands to olefin metathesis catalysts implicating higher stability (Figure 14).[280]

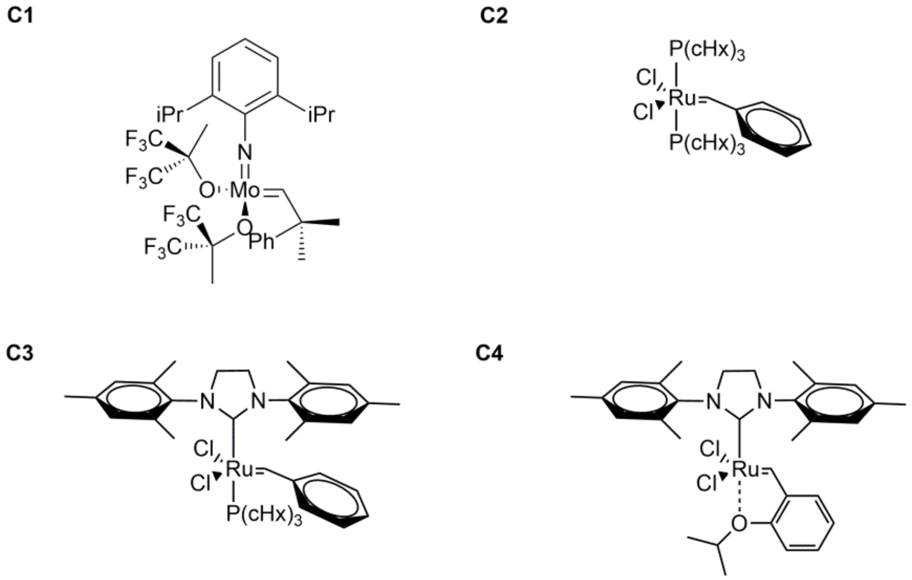


***Figure 14:*** *Common olefin metathesis catalysts:* ***C1*** *Schrock catalyst,* ***C2*** *Grubbs catalyst 1st generation,* ***C3*** *Grubbs catalyst 2nd generation and* ***C4*** *Hoveyda-Grubbs catalyst 2nd generation.*

The versatility and improvement of olefin metathesis catalysts leveraged olefin metathesis reactions to a distinguished tool in organic and polymer chemistry and facilitate the applications in manifold fields. To appreciate the efforts of Chauvin, Schrock and Grubbs, their work was awarded with the Nobel Prize in Chemistry in 2005.

Recognizing the versatility of olefin metathesis, chemists were confronted to develop catalysts for more specific tasks. Endo and Grubbs enabled the *Z*-selective cross-metathesis applying chelating NHC-ligands, a milestone for future synthesis of stereoregular polymers or complex natural products.[281, 282] The same catalyst was also shown to provide highly *Z*-selective in self-metathesis of terminal olefins.[283] Another desirable catalyst type are latent catalysts, which are inactive at room temperature and must be activated for metathesis reaction by heat, chemical reaction or photoinduction.[284] Ill-defined catalysts without an alkylidene substituent are activated *in situ* by addition of a carbene source or by coordination of the substrate to the coordinative unsaturated complex with subsequent 1,2-hydrogen shift.[284] An early example, $Ru(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) activated by ethyl diazoacetate, proved to be an efficient catalyst in the ring-opening metathesis polymerization of norbornene and derivatives.[277] Well-defined catalysts bearing an alkylidene substituent can be deactivated by inhibition, heteroatom-substituted carbene ligands or chelating ligands occupying the catalysts´ active site.[284-287] Grubbs *et al.* found out that replacement of the two chlorine ligands of the original Grubbs catalyst 1st generation catalyst by alkoxide ligands yields a novel type of highly electron-deficient catalyst, only active after addition of hydrochloric acid.[288] A recent publication regarding latent catalysts reports the activation of a polymeric form of the Grubbs catalyst by mechanical stress *via* ultrasonic scission.[289] The stereoselective or enantioselective olefin metathesis is another problem chemists have to solve, which is important in natural material synthesis.[290] Grubbs *et al.* described the enantioselective olefin metathesis catalyzed by a cyclometalated ruthenium complex functionalized with an enantiopure carboxylate ligand.[291] To facilitate the separation of the catalyst after reaction and thus purification of the product, well-defined catalysts supported on solid materials are of special interest. Polymers, ionic liquids, silica or even magnetic nanoparticles were used to immobilize the catalyst.[290, 292-295]

From the industrial point of view, olefin metathesis already found its place in the large-scale synthesis of petrochemical, oleochemical and polymeric compounds. In oleochemistry, olefin metathesis can be utilized for the synthesis of long-chain or functionalized fatty acid derivatives suitable for the formation of renewable polymers competing with petrochemical analogs.[194, 296-300] Exxonmobil, for example, have patented the cross-metathesis of triglycerides and ethylene for application as lube.[301] Besides the already introduced Phillips Triolefin process, the Shell higher olefins process (SHOP) produces linear higher olefins from ethylene, which can be converted to detergent alcohols or alkylates.[274] In the field of polymer science, ROMP plays a crucial role. Polynorbornene, the first commercial metathesis polymer, polyoctenamer, used as additive in rubber, and polydicyclopentadiene applied in vehicle cover panels due to its toughness are only three examples for polymers synthesized by ROMP.[274, 302-304] Advantageous, the ROMP route enables the synthesis of polymers with an unsaturated backbone useful for post-polymerization functionalization. Besides, ADMET is an attractive synthetic tool in polymer chemistry. Since monomers suitable for ROMP have a cyclic structure, ADMET is employed in polymerization reactions of acyclic olefins.

ADMET is a step-growth polymerization of $\alpha,\omega$-dienes to well-defined, strictly linear polymers with unsaturated polyethylene backbones.[305, 306] Driving force of the polymerization is the release of a condensate, usually ethylene, which has to be removed during the reaction to shift the equilibrium towards polymer formation. The removal can be accomplished applying vacuum or a continuous inert gas stream.[305, 306] By definition, ADMET is hence a condensation polymerization and a dispersity of two should be obtained.[307] In addition, the performance as bulk polymerization avoids the formation of cyclic by-products. However, the use of solvents is often essential to reach high conversion and thus high molecular weight polymers due to the increasing viscosity during polymerization process hindering the efficient removal of ethylene. The mechanism of ADMET is well-established. The metathesis catalyst is preactivated by reaction with the diene to form a metal alkylidene species reacting with a second one under release of the newly formed dimer. The resulting metal methylidene species is considered to be the active catalyst in the cycle, which reacts subsequent with a monomer or a polymer under elimination of ethylene.[308] In the reverse way, named ADMET depolymerization, the polymer reacts with ethylene in a cross-metathesis reaction, also termed as ethenolysis, which finds application in the recycling of polymers and the selective synthesis of oligomers.[309-312]

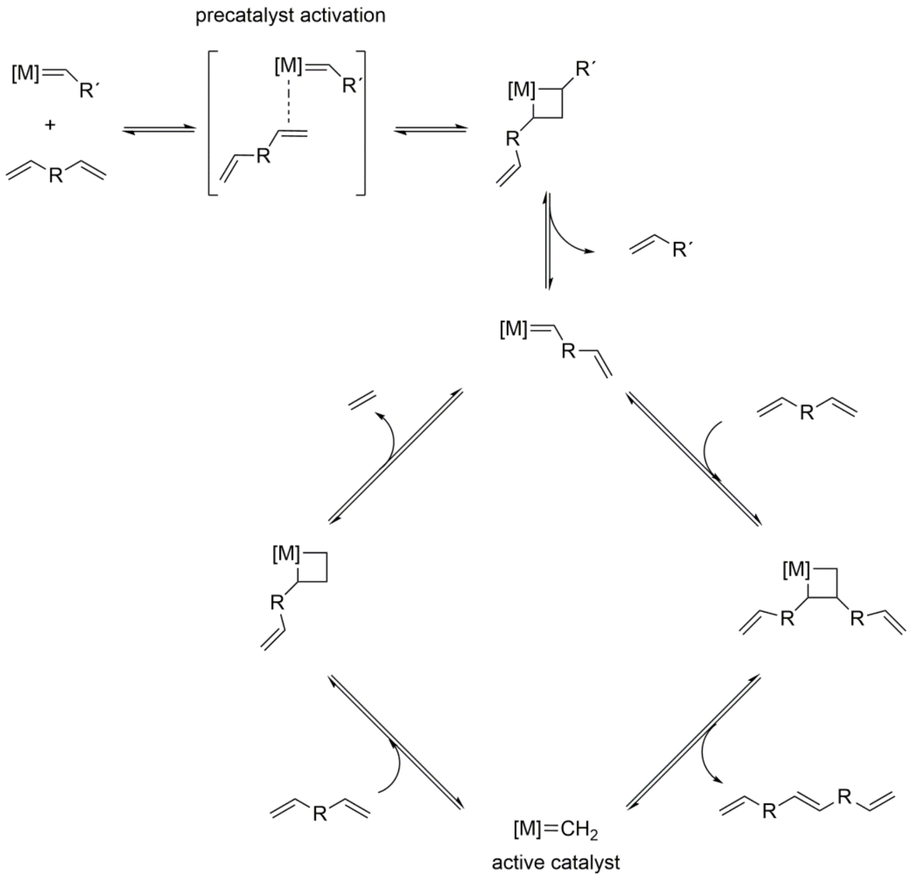


***Figure 15:*** *ADMET polymerization cycle.*[308]

To perform ADMET, the choice of the catalyst is highly important and depends on the monomer structure and the reaction conditions.[313] The first ill-defined metathesis catalysts promoted vinyl-addition, the intramolecular reaction of two double bonds catalyzed by Lewis acids, as well as desired metathesis reaction.[307, 314] With the development of new well-defined transition metal catalysts, ADMET awakened interest of chemists. The molybdenum catalyst established by Schrock is suitable for ADMET of hydrocarbon dienes due to the intolerance to most functional groups. On the other hand, Grubbs´ ruthenium catalysts tolerate most functional groups and can therefore be applied in ADMET polymerization of monomers with almost any kind of functional group.[315-320] Past research of Wagener, who introduced the term ADMET in 1987, and co-workers show the influence of the catalyst to a successful ADMET polymerization.[314] Using a tungsten hexachloride/ethylaluminum dichloride catalyst, styrene is polymerized to polystyrene due to the Lewis-acidity of the aluminum compound. Applying a Schrock-type catalyst stilbene, the self-metathesis product, was the only product formed. They suggested, that with an appropriate catalyst, ADMET polymerization could be the predominant reaction eliminating any side reactions.[321] Nowadays, the availability of suitable and versatile metathesis catalysts permits the entry of manifold unsubstituted or substituted, symmetric or asymmetric $\alpha,\omega$-dienes. Olefin isomerization, formation of cyclic compounds and vinyl addition, previously discussed, are typical side reactions, which need to be avoided. The formation of cyclic compounds, a result of polymer backbiting, is often present, if rings of favored, stable size are formed and the reaction is conducted under high dilution. Performing the ADMET polymerization in bulk or high concentration prevents cyclization.[322, 323] Double bond isomerization is the most prominent side reaction in olefin metathesis reactions applying ruthenium complexes, which means the migration of the double bond along the polymeric backbone or in the monomer. Thereby, the repeating units of the polymer differ in double bond position or chain length. Mechanistic studies revealed ruthenium hydride species as promoter of olefin isomerization, which can be minimized by addition of benzoquinone, phenylphosphoric acid and tin or iron halides.[324-327] These ruthenium hydrides can be generated by thermal decomposition, reported by Grubbs.[328, 329]

Associated with the commercial availability of efficient catalysts, the synthesis of diverse polymer architectures and functionalities *via* ADMET became possible. Grubbs *et al.* described the synthesis of a hyperbranched polymer based on an $AB_2$-monomer bearing one olefin and two acrylate groups utilizing the cross-metathesis selectivity of electron-rich and electron-poor olefins and the subsequent functionalization of terminal acrylate groups by a second cross-metathesis reaction with pyrene.[330] Furthermore, the formation of comb-shaped copolymers, block-copolymers, star polymers or telechelics was successfully reported.[331-336] Silicon-carbon hybrid materials, interesting for biomedicine, electronic devices, coatings and fibers, in form of polycarbosilanes and polycarbosiloxanes have been synthesized *via* ADMET.[320, 337-339] In the field of bioscience, polymers containing amino acids, drugs or chromophores were succeeded.[340-342] Since ADMET offers a polymerization technique, which allows the synthesis of regular branched polymer, polyethylene with different, controllable side chains could be synthesized to study the influence of branching on polymers´ properties.[343, 344]

All this examples of defined synthesis depict the versatility and utility of olefin metathesis and especially ADMET polymerization in organic and polymer chemistry and the manifold possibilities covered by metathesis reactions.

### 2.3.2 THIOL-ENE ADDITION

The concept of click chemistry specifies reactions, which are simple, efficient and selective (*i.e.*, regioselective, stereoselective and orthogonal). The performance under ambient temperatures and atmospheric conditions as well as the formation of one product, which is easy to purify, complete the demand of click reactions.[239, 345] Until now, the challenge has been the search for adequate reactions that fulfill all or most of the criteria described above, in order to expand the field of click chemistry based on the copper-catalyzed azide alkyne coupling reported by Kolb *et al.*[239] Hoyle and coworkers introduced the term thiol-click chemistry, also named thiol-X, due to the high reactivity of thiols, allowing the reaction with various substrates.[345] The toolbox of thiol-click includes the reaction with epoxides, isocyanides, halogens, alkynes, alkenes (named thiol-ene) and electron poor olefins (termed as thia-Michael addition). The last two reactions will be discussed extensively in this chapter, because they were frequently used to prepare monomers and to functionalize polymers as described in chapters 4.1, 4.2 and 4.4. Further information regarding the other examples of thiol-click reactions are described in detail in the literature.[241, 345-350] The addition of thiols to a carbon-carbon double bond can precede either radically (thiol-ene) or nucleophilic (Michael addition). The success of the reaction between an olefin and a thiol largely depends on the ability of the thiol to form the thiyl radical or the thiolate anion, respectively, as well as on the structure of the olefin. The formation of the radical species is associated with the ambition to homolytical bond cleavage, the formation of the thiolate ions with the p$K_a$ of the corresponding thiol.[351]

In general, the Michael addition, named after its inventor Arthur Michael, has been known since the 1880s and describes the 1,4-addition of nucleophiles (Michael donor) to an activated electron poor olefin (Michael acceptor).[352] This method is suitable to form mainly carbon-carbon, carbon-oxygen (oxa-Michael), carbon-nitrogen (aza-Michael) and the already discussed carbon-sulfur bond (thia-Michael).[353-355] The hydrothiolation of an electron-deficient carbon-carbon double bond is known as thia-Michael addition and leads to the formation of a new carbon-sulfur bond. Catalysts can be either acidic to activate the olefin or basic, as mostly used, to form the reactive thiolate anion. For catalysis, a magnitude of suitable catalysts are reported ranging from sodium methoxide, weak organobases like trimethylamine, nucleophiles like phosphines and boric acid to more special catalysts like inorganic salts, tetrabutylammonium halides, ionic liquids, azaphosphatrane nitrate salts or immobilized acids.[356-363] Xi *et al.* conducted thia-Michael additions under UV-irradiation applying a catalyst with a photolabile hexylamine.[364] Since Green Chemistry became a central issue in chemists´ everyday life, the call for non-toxic and environmentally beneficial reactions and reagents motivated chemists to search for catalysts. Kamal *et al.* reported the thia-Michael addition in poly(ethylene glycol) as recyclable medium without the addition of a catalyst.[365] As alternative for thiols, Zhao and coworkers described an odorless thia-Michael addition applying *S*-alkylisothiouronium salts as thiol equivalents in water.[366] Alternative to ionic liquids, deep eutectic solvents (DES) were used, which can be synthesized from biodegradable compounds with 100% atom-efficiency.[367] Even a catalyst-free approach to thioethers was published, although the range of applicable substrates was very limited.[368] The electron-deficient olefins used can be ordered according to the reactivity in of the carbon-carbon double bond: Maleimides > fumarates > maleates > acrylates/acrylamides > acrylonitriles > crotonates > cinnamates > methacrylates/methacrylamides.[369]

The mechanism of the reaction includes abstraction of a proton from the thiol by the base, thus generating the thiolate anion. This step is greatly affected by the strength and concentration of the base and the p$K_a$ of the thiol (Figure 16). The reactive thiolate ion attacks the $\beta$-carbon of the double bond to form the intermediate, resonance stabilized carbanion. The abstraction of a proton from the protonated base provides the favored thia-Michael adduct (Figure 17).[345] Since the intermediate enolate anion is a strong base, the hydrogen abstraction from every acidic compound like thiol, solvent or conjugate acid is supposable.[369] Furthermore, the polarity and pH of the solvent, steric hindrance of the thiol as well as the nature of the electron withdrawing group (EWG) plays a crucial role for the kinetic of the reaction.[345, 370]

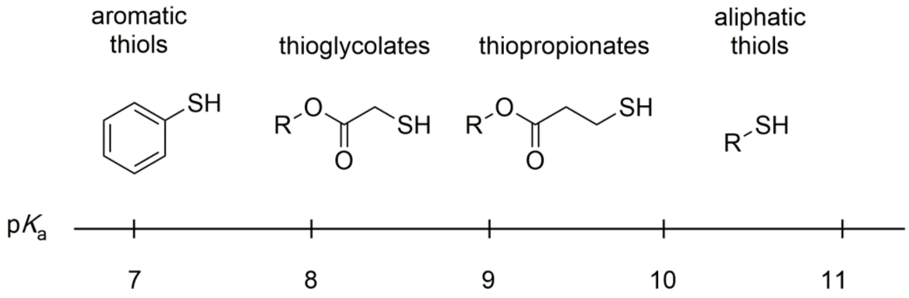


***Figure 16:*** *p$K_a$ of common thiols.*[345]

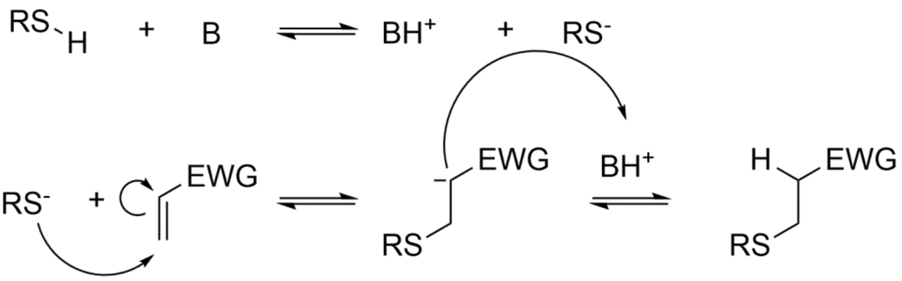


***Figure 17:*** *Mechanism of the base-catalyzed thia-Michael addition.*[345]

Chan *et al.* investigated the influence of the catalyst on the thia-Michael addition utilizing three different amine bases: trimethylamine, hexylamine and *n*-propylamine. They ascertained the influence of the p$K_a$ as well as the nucleophilicity of the catalyst on the catalytic activity. Although, hexylamine has the lowest p$K_a$, the efficiency of deprotonation is the highest. In addition, phosphines exhibit the catalytic characteristics of amine bases, although they are less basic and a deprotonation of thiol is unfeasible.[369, 371] Taking the nucleophilicity into account, another mechanism can be proposed.

The nucleophile attacks the $\beta$-carbon of the olefin forming an intermediate zwitterion, which deprotonates the thiol. The generated thiolate reacts afterwards with the activated double bond. The formed enolate deprotonates a second thiol, which is then able to attack the next olefin. The nucleophile-olefin adduct is a by-product of this reaction and impurifies the product to a minor degree (Figure 18).[369]

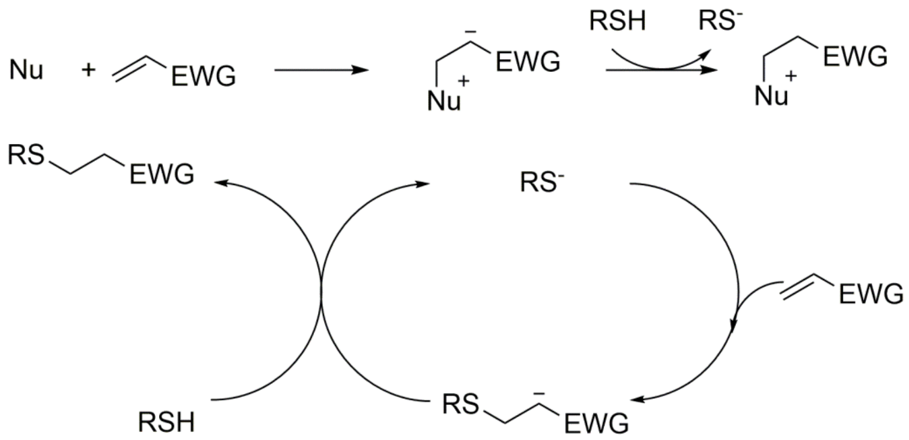


***Figure 18:*** *Mechanism of nucleophilic thia-Michael addition.*[370]

The nucleophilic pathway depends on the nucleophilicity of the catalyst. With increasing nucleophilicity, more intermediate enolate anions and thus more reactive thiolate anions are generated.[370] Li *et al.* compared amine and phosphine catalysts in the thia-Michael addition to (meth)acrylates. Phosphines turned out to be the more efficient catalysts, however side reactions, such as the addition of phosphines to the double bond, were observed.[372] Chan *et al.* reported the nucleophilic, phosphine-catalyzed thia-Michael addition in the synthesis of star polymers. The previously formed RAFT homopolymer arms were treated with hexylamine and dimethylphenylphosphine. Here, hexylamine was added to cleave the dithioester end group, while the phosphine acted as catalyst in the following thia-Michael addition to the core unit.[373]

Since the introduction of thia-Michael addition in the 1960s by Allen, several application possibilities in the field of organic chemistry, polymer formation, functionalization and bioorganic chemistry have been published.[241, 251, 374-377] In polymer chemistry, Michael additions are well-established in the step-growth synthesis, *e.g.,* of PAMAMs based on bisacrylamides and diamines.[157] The anionic polymerization of methacrylate monomers is another example for the Michael addition in macromolecular synthesis.[378] For instance, the synthesis of linear polymers *via* thia-Michael addition can be accomplished by the reaction of diacrylates and dithiols. Vandenberg *et al.* synthesized linear polymers based on 1,6-hexanediol diacrylate and 1,4-butanedithiol, which were degradable by hydrolysis of the ester linkage.[379] In the formation of more complex architectures, thia-Michael additions could be established due to the high conversions obtained and the easy purification. The dendrimer synthesis free of protection groups utilizing thia-Michael addition was described yielding a fifth-generation dendrimer with 96 functional groups synthesized in less than half a day.[380] Auty *et al.* described the synthesis of polyester dendrimers with peripheral xanthate groups, which can be deprotected to form the thiol, that can react with an acrylate in a one-pot fashion.[381] Furthermore, the formation of crosslinked polymer networks was studied intensively.[382] Chatani *et al.* illustrated the selective reaction of vinyl sulfones in a mixture with acrylates towards thia-Michael addition and the resulting control over gelation.[383] Hence, the thia-Michael addition can also be conducted in the synthesis of hydrogels for biomedical application.[384-386] Hubbell *et al.* studied networks based on PEG multiacrylate and PEG dithiol, which can be used as protein drug delivery cage. A protein based amine catalyst was applied and the network showed biodegradability due to ester bonds.[387] With regard to the post-polymerization functionalization, the orthogonal functionalization of a polycarbonate bearing unsaturated side chains, namely acrylate and allylic double bonds, was accomplished by combination of thia-Michael and radical thiol-ene addition.[388] In bioorganic chemistry, bioconjugates consisting of synthetic polymers covalently bound to biopolymers are often synthesized *via* thia-Michael addition.[251] Therefore, maleimide or vinyl sulfone functionalized PEG is attached to thiol groups on proteins. Qi *et al.* showed the formation of a triblock copolymer bearing acrylate side chains, which were able to react with thiolated hemoglobin and might act as red blood cell substitutes.[389]

Closely connected with the thia-Michael addition is the radical addition of thiols to double bonds, named as thiol-ene reaction, which is principally already known since the 19th century, when Charles Goodyear patented the vulcanization of rubber by sulfur.[390] In 2007, Schlaad and coworkers identified the thiol-ene addition as click reactions due to its simplicity, efficiency, celerity and robustness.[345, 391] Over 100 years earlier, Posner discovered the thiol-ene addition for the first time.[392] In 1938, Kharash *et al.* envisioned the mechanism of the reaction, which is shown in Figure 19.[393] The formation of thiyl radicals is achieved either thermally or photochemically. The addition to the double bond of the olefin occurs in an anti-Markovnikov fashion, leading to the more stable carbon-centered radical. The reaction of the thus formed radical with a second thiol molecule results in the desired product and a reactive thiyl radical for further addition. As common steps in typical radical reactions, the mechanism includes initiation, propagation as well as termination by radical-radical coupling.

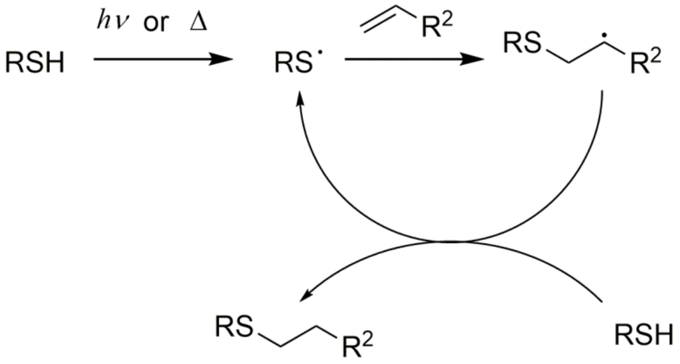


***Figure 19:*** *Mechanism of the radical thiol-ene addition.*[374]

The used olefins should be electron-rich due to the competing polymerization of electron-deficient olefins in the propagation step. Norbornene proved to be a very reactive olefin due to the release of ring strain.[394] Furthermore, the reactivity of the olefin is affected by its substitution grade showing higher reactivity for terminal double bonds compared to internal double bonds. Hoyle and coworkers found an eight times higher reactivity for 1-hexene compared to *trans*-2-hexene and an even 18 times higher reactivity compared to *trans*-3-hexene in a 1:1 mixture of alkene and thiol.[395] The reaction can be either initiated photochemically or thermally. In general, photoinitiators can be classified into two types. Type I photoinitiators undergo homolytic, unimolecular cleavage upon UV-irradiation generating free radicals, which can either react with the carbon-carbon double bond or the thiol generating the thiyl radical. 2,2-Dimethoxy-2-phenylacetophenone **1** (DMPA) and (2,4,6-trimethylbenzoyl)diphenylphosphine oxide **2** (TMDPO) are typical type I photoinitiators. Type II photoinitiators form an excited state under UV-irradiation and react subsequently with the coinitiator (typical an amine).[396] Examples therefore are benzophenone **3**, thioxanthone **4** and camphorquinone **5** (Figure 20).[397] Uygun *et al.* studied the influence of various photoinitiators on the thiol-ene click reaction applying thiol- and ene-functionalized polystyrene showing highest efficiency for type I photoinitiators.[396] In general, photochemical initiation has the advantage of controlling the reaction by variation of light intensity and irradiation time compared to thermal initiation. A typical thermal initiator is 2,2′-azobis(isobutyronitrile) (AIBN) **6** (Figure 20). The most important characteristic is their decomposition rate expressed by the half-life or the half-life temperature. The half-life is defined as time needed to reduce the initial content to 50 % at a given temperature. For AIBN the half-life is ten hours at 64 °C.[398] The possibility to switch to either thermal or photochemical initiation is practical using compounds bearing thermal sensitive or photosensitive groups.[399]

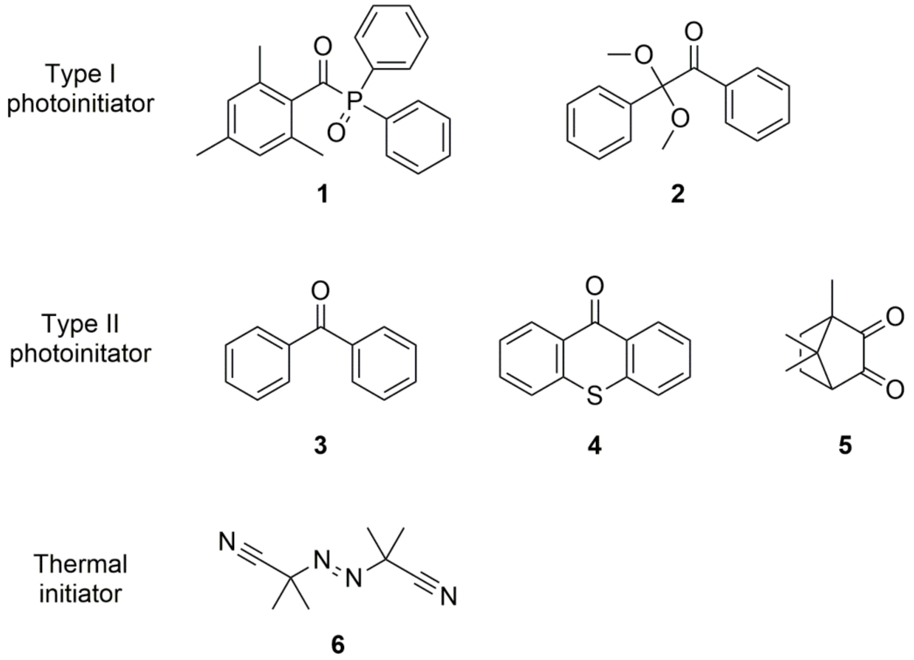


***Figure 20:*** *Typical photochemical and thermal initiators in thiol-ene addition.*[396]

Due to the weak sulfur-hydrogen bond, an initiator-free thiol-ene reaction can be considered. Cramer *et al.* described the polymerization of thiol monomers with vinyl monomers. It must be pointed out, that for effective initiation a shorter wavelength of 254 nm is beneficial instead of the usually applied 365 nm.[400] Furthermore, photoredox catalysts gained the attention of chemists. Keylor and coworkers introduced the visible light active transition metal complex $Ru(bpy)_3Cl_2$ as powerful initiator in thiol-ene coupling.[401-403] Bhat *et al.* reported the efficiency of semi-conducting titanium oxide as cheap and commercial available catalyst.[404] The third class of photoredox catalyst are represented by dyes, which absorb light and interact with additives generating initiation radicals.[405]

Thiol-ene additions were mainly applied in the synthesis of polymer networks. The most prominent example, the thiol-acrylate networks, combine initiator-less polymerization with tolerance against oxygen and uniformity of the network regarding the crosslinking density.[406] Hoyle demonstrated the applicability of thiol-ene addition in network formation in several publications.[345, 407-410] In the context of renewable resources, Yang *et al.* described the network formation based on renewable phenolic acids, which were allylated and afterwards reacted with a tetrafunctional thiol for improved mechanical strength due to the rigid aromatic ring.[411] In polymer post-functionalization, Hawker *et al.* pictured the versatility of thiol-ene, which can be utilized in functionalization of the polymer backbone bearing unsaturated side chains, chain-end modification or even the synthesis of asymmetric telechelics bearing an ene-function on one end and an azide-function on the other.[399] Krappitz *et al.* created a polymethylene, a polymer bearing side chains on every carbon atom of the backbone, with unsaturation in the side chains suitable for thiol-ene addition. Due to the addiction to self-crosslink, thin film coatings were formed enabling the surface modification by post-polymerization functionalization.[412] Comí *et al.* succeeded in the functionalization of castor oil-derived alkene- and alkyne-functionalized polyurethanes with thioglycerol yielding hydrophilic polyurethanes.[413] In the synthesis of complex macromolecular structures, thiol-ene has been extensively applied for dendrimer, star polymer and hyperbranched polymer synthesis as well as for block copolymer preparation.[109, 149, 414-418] Unsaturated carbon-carbon bonds in triglycerides and fatty acids are ideal points for thiol attack. Ionescu and coworkers reported the applicability of mercaptanized soybean oil, formed by direct addition of hydrogen sulfide, as precursors for polymer synthesis after attachment of allyl organic compounds with various functional groups as alcohol, amine, epoxy and isocyanate functionality.[214] In our laboratory, the fatty acid-based methyl 10-undecenoate was functionalized with different thiols and dithiols and established in the synthesis of linear as well as hyperbranched polyesters.[419] Furthermore, renewable $\alpha,\omega$-dienes with anhydride and ester linkages were polymerized either *via* ADMET or thiol-ene polymerization generating polyesters of higher molecular weight applying thiol-ene chemistry.[420] Besides these examples, thiol-ene addition found its place in monomer and polymer synthesis based on renewable resources.[421-431] Sequential thiol-ene reaction was applied in the synthesis of various types of well-defined polymers.[203, 432, 433] In bioorganic chemistry, the attachment of a thiol to an olefin finds application *e.g.*, in glycoconjugates, hydrogels, polymer capsules for drug delivery and photochemical surface patterning.[434-442]

In conclusion, the addition of thiols to carbon-carbon double bonds offers typical characteristics of a click reaction: mild reaction conditions, high functional group tolerance, non-sensitive against air and moisture and high yields achieved in short reaction times. However, one has to consider the reactivity of different double bonds in thiol-ene reactions and usually terminal double bonds meet the criteria of click chemistry. The discussed applications present only a minor part of possibilities, where the benefits of this type of reaction can be applied. By the choice of proper olefin, thiol and catalyst, every imaginable combination can be succeed generating interesting compounds in small molecule, polymer and bioorganic chemistry exhibiting interesting properties.

### 2.3.3 SCHENCK-ENE REACTION

The Schenck-Ene reaction was discovered in 1943 by Schenck and describes the reaction of olefins with allylic hydrogen atoms yielding allyl hydroperoxides.[443]

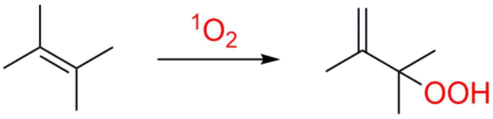


***Figure 21:*** *Schematic illustration of the Schenck-Ene reaction.*[444]

The pivotal molecule in the Schenck-Ene reaction is the singlet oxygen ($^1O_2$). Although Fritzsche already observed the formation of endoperoxides affected by the influence of oxygen and light in 1887, singlet oxygen was first observed in 1924.[445, 446] In 1931, Kautsky *et al.* observed the reaction of oxygen with an oxygen-acceptor compound in the presence of a dye, which were both separately adsorbed on silicium oxide beads. Since the diffusion of both substances could be excluded, he proposed the presence of an excited oxygen state, the singlet oxygen.[447] In fact, singlet oxygen is a highly reactive species, which causes the oxidation of biomolecules like DNA, proteins and lipids and may be involved in various chemical and biological processes.[448-452]

Regarding its electronic structure, oxygen possesses two unpaired electrons in two orbitals in the ground state. The first excited singlet state is located only 96 kJ above, holding both electrons in one orbital. The second excited singlet state accommodates both electrons with antiparallel spin in two orbitals.[453, 454] Due to the reactivity and the much shorter lifetime of the second excited state, the first excited state presents the reactive form in photoreactions. The lifetime of $^1O_2$ highly depends on the type of solvent used. The longest lifetime can be observed applying halogenated solvents, such as carbon tetrachloride and diminishing lifetime in partly halogenated solvents, acetone and short lifetime in alcohols and water (due to the varying values depending on determination method used, absolute values are not denoted).[455-457] Furthermore, deuterated solvents ensure a longer lifetime due to the absence of electronic-to-vibrational energy transfer to carbon-hydrogen or oxygen-hydrogen bonds.[458, 459] This fact can be used to prove singlet oxygen as reactive species in a reaction.

Singlet oxygen can be either generated *via* chemical or physical methods. The reaction of hydrogen peroxide and sodium hypochlorite or the thermolysis of endoperoxides generates singlet oxygen. Instead, photosensitized generation of singlet oxygen is the common method with the advantage of controlling the reaction by tunable light exposure. The photosensitizer absorbs light of a specific wavelength, while stimulated from the ground state to an excited singlet state. *Via* intersystem crossing, the triplet state of the sensitizer is formed able to interact with the ground state of oxygen by transferring energy during collision (type II mechanism). Thus, singlet oxygen is generated reforming the sensitizer in the ground state. Type I reactions include the formation of free radicals by hydrogen-abstraction or electron-transfer to a substrate, which can afterwards react with oxygen to form active oxygen species (*e.g.* superoxide radical anion).[453, 460] A plentitude of UV-Vis absorbing molecules have shown the ability to generate singlet oxygen including the following:

- dyes as rose bengal and methylene blue,[461, 462]
- aromatic hydrocarbons like anthracene,[463]
- quinones,[464]
- porphyrins,[465, 466]
- phthalocyanines,[467, 468]
- napthalocyanines,[469]
- transition metal complexes of *e.g.* ruthenium(II),[470]
- semiconductors as titanium dioxide [471] and
- immobilized photosensitizer.[472, 473]

The reaction of singlet oxygen with olefins can be divided into three classes: A) [4+2]-cycloaddition to conjugated dienes, b) [2+2]-cycloaddition to electron-rich olefins yielding dioxetane products and c) the Schenck-Ene reaction of unactivated olefins with allylic hydrogen atoms (Figure 22).[444, 474]

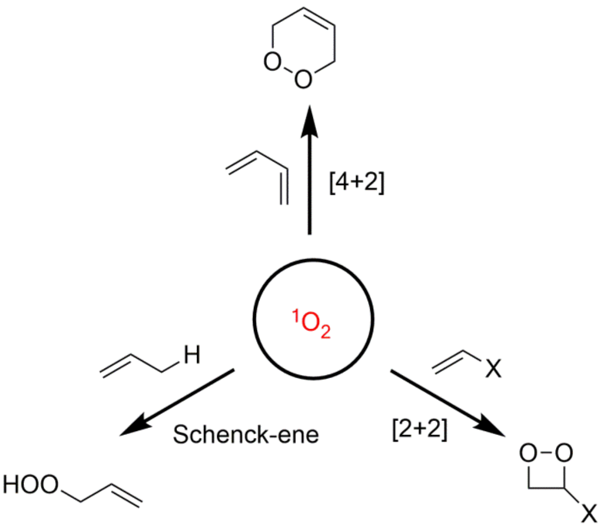


***Figure 22:*** *Illustration of the reactivity of singlet oxygen towards carbon-carbon double bonds.*[444]

The mechanism for the Schenck-Ene reaction was for a long time unknown. Several intermediates were proposed *i.e.*, transition state, diradical or zwitterionic intermediates, perepoxides or exciplexes (Figure 23).[475-479] Recent mechanistic and empirical studies reveal an intermediate perepoxide. Clennan *et al.* depicted the general accepted mechanism, including the formation of an exciplex, a complex of excited oxygen and alkene, which generates the perepoxide and afterwards the desired allyl hydroperoxide.[480] In the first step of the reaction an exciplex is formed, which geometric appearance resembles a perepoxide. Abstraction of the allylic hydrogen atom generates the hydroperoxide.[481] Singleton *et al.* reported the ene-reaction with intermediate transition state.[482]

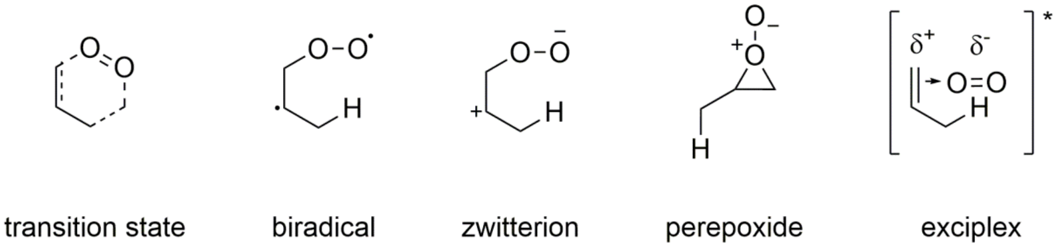
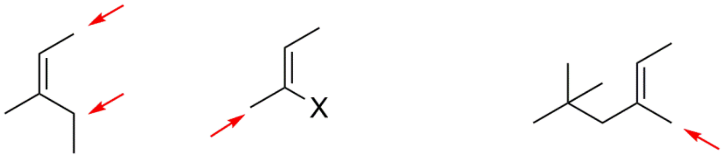


***Figure 23:*** *Supposable transition states and intermediates in the Schenck-Ene reaction.*[483]

In general, the Schenck-Ene reaction offers some desirable features as well as a few problems. If olefins are applied, providing multiple allylic hydrogen atoms, regioselectivity presents a major problem. Therefore, several rules could be established. The "*cis* effect" describes the observation of hydrogen abstraction from the more substituted side of the olefin.[444, 484] The "*gem* effect" is defined as the effect of dominant geminal hydrogen abstraction.[485] At least, the "large group nonbonding effect" is obtained for highly substituted olefins abstracting the hydrogen atom next to the large alkyl substituent (Figure 24).[486, 487] In addition, there are various effects, which are valid for special functional groups.[487]



"*cis* effect" "*gem* effect" "large group nonbonding effect"

***Figure 24:*** *Regioselectivity in the Schenck-Ene reaction – red arrows indicate preferential site of hydrogen abstraction.*[444]

Although, there are few exeptions to this empirical rules described. The "anti-cis effect" can be observed for some molecules due to steric hindrance, the lack of two allylic hydrogen atoms for interaction or non-bonding interactions.[486] Furthermore, the suprafacial attack of singlet oxygen is observed by Stephanson *et al.* Notwithstanding, he obtained diastereoselectivity for a specially designed olefin, allowing the attack of singlet oxygen only on one side of the double bond.[488] In fact, the diastereoselectivity of Schenck-Ene reactions depends on factors as non-bonding interactions (*i.e.,* repulsion), electron density, direct interactions with substituents or the presence of available hydrogen atoms.[444] To control the diastereoselctivity in Schenck-Ene reactions, the substrate must be chosen with attention to the substituents and abstractable hydrogen atoms in allylic position to force the reaction to the desirable product.[489-493]

The importance of the Schenck-Ene reaction in organic synthesis arises from the diversity of possible transformations of formed allyl hydroperoxides. Simple reduction to allylic alcohols, dehydration to enones or Ti(IV)-catalyzed transformation to epoxy alcohols are prominent and often applied examples. Adam *et al.* reported the regioselective synthesis of vinylstannanes bearing the hydroperoxide function. After reduction with sodium borohydride, their reactivity in *e.g.,* palladium-catalyzed coupling was shown.[494] In the presence of titanium isopropoxide, the hydroperoxides are converted to epoxy alcohols. Adam *et al.* demonstrated that oxygen transfer proceeded intermolecularly between two allyl hydroperoxide molecules.[495] The same author tested three catalysts for the transformation ($Ti(OiPr)_4$, $VO(acac)_2$, $MoO_2(acac)_2$) and proved the efficiency of titanium isopropoxide applying various substrates. With this method, the Schenck-Ene reaction and the rearrangement to epoxy alcohols can be performed in one pot.[496] Furthermore, the Schenck-Ene reaction can be used in drug synthesis described by the pharmaceutical company Sanofi. They propose the formation of artemisinin, a drug against malaria, which is till today extracted from a plant, based on a commercial available precursor. Here, the hydroperoxide reacts *via* Hock cleavage cyclization. A first pilot unit was already installed and the reaction was run in 50 kg-scale.[497] In fact, the Schenck-Ene reaction is mainly used in the synthesis of pharmaceuticals and natural products.[498-500] In the context of renewable resources, the Schenck-Ene reaction was successfully applied to synthesize an enone-containing triglyceride, which was crosslinked with diaminodiphenylmethane *via* aza-Michael addition.[501] In medicine, the Schenck-Ene reaction is applied in the photodynamic therapy of cancer (PDT), for blood sterilization and in photodynamic herbicides and insecticides.[453, 502-505] Even in human bodies singlet oxygen is present and $\beta$-carotene and vitamin E act as antioxidants. Quenching of singlet oxygen appears here in two different ways. $\beta$-Carotene absorbs energy from singlet oxygen generating an excited carotenoid, which is dissipated by interactions with the solvent to reform the carotenoid in the ground state. On the other hand, vitamin E acts as hydrogen donor for radicals *e.g.,* of lipids to avoid reaction with singlet oxygen.[506, 507]

# 3. AIMS

The present work deals with the synthesis of novel branched structures, either monomeric or polymeric, based on plant oils. In the context of "Green Chemistry" and the environmental and economic consequences due to the utilization of crude oil in polymer synthesis, scientists are confronted with the task to search for alternatives to replace crude oil as raw material. Starting point of this thesis were prior published results in our group dealing with the synthesis of three-arm star-shaped polymers and the subsequent functionalization *via* thia-Michael addition. The applied monomer was derived from castor oil, which was polymerized *via* ADMET polymerization. The resulting star-shaped polymer bore $\alpha,\beta$-unsaturated ester groups along the chain. The base catalyzed thia-Michael addition enabled functionalization of the terminal acrylate group, while internal double bonds remained unreacted.[508] For the preparation of four- and six-arm star-shaped polymers, the well-known, castor oil-based monomer was chosen to ensure head-to-tail selectivity during ADMET polymerization. For subsequent functionalization of the double bonds of the polymer, a mild and efficient reaction had to be applied to prevent degradation of the star-shaped polymers. Herein, the thia-Michael addition catalyzed by mild bases seemed to be superior. Furthermore, the synthesis of dendrimer-like star polymers should be studied with the purpose to synthesized water-soluble polymers able to act as nanocarrier. For the attachment of a dendron to the terminal double bond, a focal point was selected, which enable coupling *via* aza-Michael addition. The dendron itself was synthesized applying efficient organic reactions, such as photoinitiated thiol-ene addition, to provide monodispersity. In a second approach, the synthesis of branched small molecules was explored. Therefore, high oleic oil served as renewable raw material. Here, the functionalization of the naturally occurring double bonds was conducted. On the one hand, the Schenck-Ene reaction with subsequent conversion to the corresponding epoxy alcohol was performed in a one-pot fashion. Herein, another aim is the optimization of the process conditions regarding solvent, catalyst and concentration with regard to the issues of sustainable chemistry. The ring-opening of the epoxide gives access to renewable polyols, which can be applied as additives in food and cosmetics or polymerized to *e.g.,* polyurethanes. On the other hand, a dimer fatty acid was obtained by coupling two fatty acid methyl esters *via* photoinitiated thiol-ene addition. The generated branched monomer was tested in polycondensation reactions to polyamides and the influence of different amounts of the dimer fatty acid on the properties of the polyamide was investigated.

# 4. MAIN PART

## 4.1 SYNTHESIS AND FUNCTIONALIZATION OF STAR POLYMERS *VIA* ACYCLIC DIENE METATHESIS

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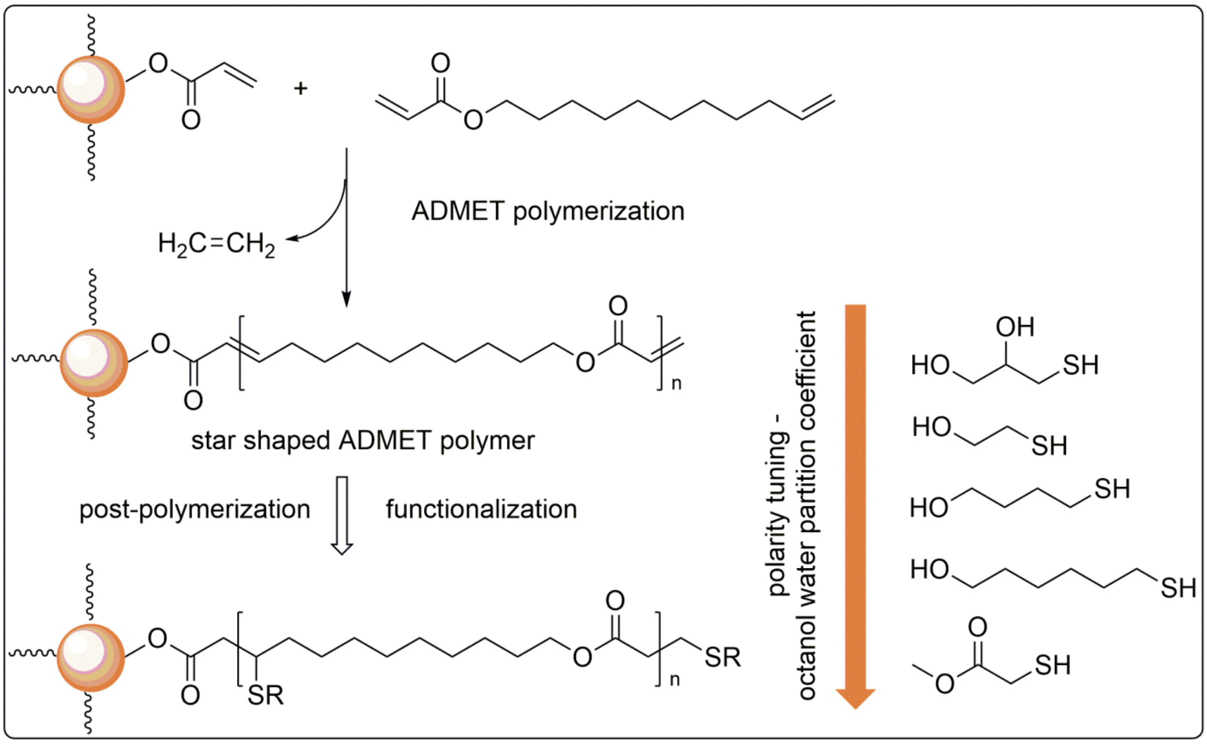


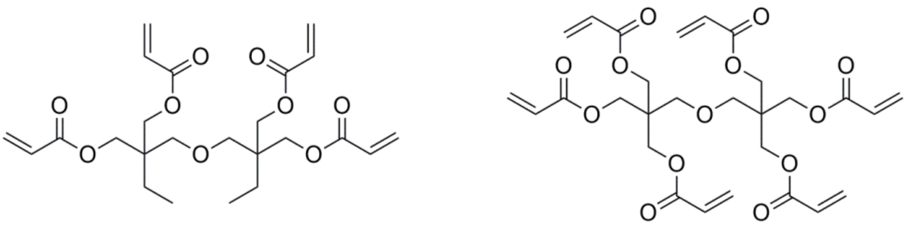
### ABSTRACT

The synthesis of defined star-shaped polymers *via* head-to-tail acyclic diene metathesis (ADMET) polymerization is described in this chapter, whereby di(trimethylolpropane) tetraacrylate (4-arm) and dipentaerythritol hexaacrylate (6-arm) served as core units and fatty acid-derived 10-undecenyl acrylate as unsymmetric *α,ω*-diene monomer. The core-first approach was applied to synthesize star-shaped polymers having arms of ten or twenty monomer units exhibiting an *α,β*–unsaturated ester backbone. Subsequent post-

polymerization modification of the $\alpha,\beta$-unsaturated esters *via* base-catalyzed thia-Michael addition is demonstrated. Therefore, five different thiols were employed in a simple and efficient procedure, without observing degradation of the polymer backbone. The polarity of these modified star-shaped polymers could thus be tuned by the choice of the thiol as it was shown by determining the octanol-water partition coefficients of these functionalized polymers by high pressure liquid chromatography (HPLC).

The hydrothiolation of alkenes can proceed *via* radically-initiated thiol-ene addition or *via* an anionic mechanism named thia-Michael addition.[369, 509] The latter, discovered in 1887 by the American chemist Arthur Michael, generally involves the nucleophilic addition of stabilized anions, called "Michael donors", to electron-deficient alkenes such as $\alpha,\beta$-unsaturated carbonyl compounds, the "Michael acceptors".[510] The reaction can be promoted by numerous catalysts including strong bases, metals, organometallics or Lewis acids.[251, 363] Especially the thia-Michael addition shows general applicability to numerous thiols and Michael acceptors, which turns it, combined with the benefits of click chemistry, to a versatile, favored and indispensable tool in small molecule synthesis, polymer modification or the synthesis of linear or star-shaped polymers.[373, 511-514]

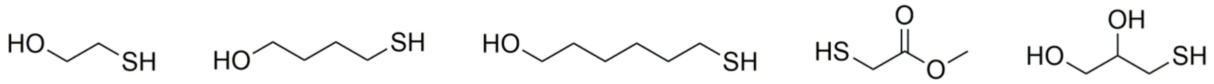
Star-shaped polymers bearing an $\alpha,\beta$-unsaturated ester backbone are ideal candidates for post-polymerization functionalization *via* thia-Michael addition. They can be synthesized *via* ADMET polymerization using a multifunctional acrylate as core (**3**, **4**) and 10-undecenyl acrylate **2** as monomer, which can be prepared by acrylation of 10-undecenol **1**, a castor oil-derived chemical (Figure 25).[191]



**3** **4**

***Figure 25:*** *Multifunctional core units applied in star polymer synthesis.*

Essentially, ADMET polymerization is a step-growth polycondensation reaction of two terminal olefins forming an internal carbon–carbon double bond.[515] Similar to other olefin metathesis reactions, ADMET proceeds *via* transalkylidenation, the exchange of substituents of two olefins in an equilibrium reaction.[516] If symmetric, terminal dienes are used as monomers, strictly linear polymers with an unsaturated backbone can be obtained by release of the volatile by-product ethylene, which is usually removed by vacuum or a stream of inert gas, thus forcing the equilibrium of ADMET polymerization towards the high molecular weight polymers.[517, 518] The process applied here allows a very high head-to-tail selectivity of the used unsymmetric monomers and the absence of secondary metathesis reactions on the polymer backbone, which turn this step-growth polymerization into a tool for block- and star-polymer synthesis. Protocols for the synthesis have been previously established in our laboratory for three- and four-arm star-shaped polyesters and subsequent functionalization of the terminal acrylate groups was shown.[508, 519] Using mild reaction conditions for the thia-Michael addition, complete functionalization without degradation of the star-shaped polymers could be achieved. HPLC measurements revealed the influence of various thiols **5** - **9** on the polarity of the functionalized star-shaped polymers (Figure 26).



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

***Figure 26:*** *Thiols used in the thia-Michael additions as post-polymerization modification of the star-shaped polymers: Mercaptoethanol* ***5,*** *mercaptobutanol* ***6,*** *mercaptohexanol* ***7,*** *methyl thioglycolate* ***8*** *and thioglycerol* ***9****.*

## RESULTS AND DISCUSSION

The high cross metathesis selectivity between terminal double bonds and acrylates, and thus the synthesis of unsaturated polyesters by selective head-to-tail ADMET polymerization, has already been described by our group.[520] In this case, the monomers were prepared by multicomponent reactions and the block copolymers formed micelles in aqueous solution. Furthermore, we described the synthesis of star polymers using a multifunctional acrylate core unit and an unsymmetric *α,β*-diene, containing both a terminal double bond and an acrylate, like 10-undecenyl acrylate **2**.[508] In general, steric and electronic factors affect the selectivity in cross-metathesis.[521] Olefins can be classified according to their ability to homodimerize relative to other olefins. Sterically unhindered, electron-rich type I olefins homodimerize quickly and homodimers as well as terminal olefins can participate in CM. Type II olefins homodimerize slowly and react also slowly in CM. Type III are unable to homodimerize, but can react with type I and II in CM. At least, type IV does not attend in CM and does not deactivate the catalyst. All other olefins deactivate the metathesis catalyst. The activity of olefins in cross-metathesis decrease from type I to more sterically hindered and electron-deficient olefins to type IV.[522] For selective CM, olefins of two different types should be combined to favor cross-metathesis instead of dimerization.

10-Undecenyl acrylate **2** bears a terminal olefin group classified as type I and an acrylate group, a type II olefin allowing the selective reaction of both groups, but no reaction was obtained for reaction of the same type of olefin.[521, 523, 524] In order to synthesize four- and six-arm star-shaped polyesters, di(trimethylolpropane) tetraacrylate **3** and dipentaerythritol hexaacrylate **4** were used as core units. The use of 1.5 mol% Hoveyda Grubbs 2nd generation catalyst (in relation to acrylate groups) allowed the synthesis of defined star-shaped polymers by the core-first approach with ten or twenty monomer units respectively per arm in a reaction time of 3 hours. Table 1 shows the $^1$H NMR analysis of the resulting polymers **P1** – **P4** with good correlation of end group and core signals. The observed molecular weights were higher than expected, probably due to the aggregation of star polymers. However, if the expected molecular weights are compared to the $M_n$ values obtained by NMR integration, a very good agreement was found (Table 1). Full monomer conversion and symmetric molecular weight distributions were observed by SEC analysis (Figure 27). Therefore, it can be concluded, that ADMET polymerization allows the easy synthesis of defined star-shaped polyester bearing $\alpha,\beta$-unsaturated ester moieties and terminal acrylate groups, which can be used for further functionalization.

***Table 1:** Analytic data of the obtained star-polymers.*

| entry | core | monomer units/arm | $M_n$ (theo.) | $M_n$ (NMR) | $M_n$ (SEC) | Đ (SEC) |
|---|---|---|---|---|---|---|
| **P1** | **3** | 10 | 8300 | 8600 | 10700 | 1.44 |
| **P2** | **3** | 20 | 16200 | 16700 | 13800 | 1.72 |
| **P3** | **4** | 10 | 12400 | 13100 | 11700 | 1.73 |
| **P4** | **4** | 20 | 24100 | 22500 | 14900 | 1.91 |

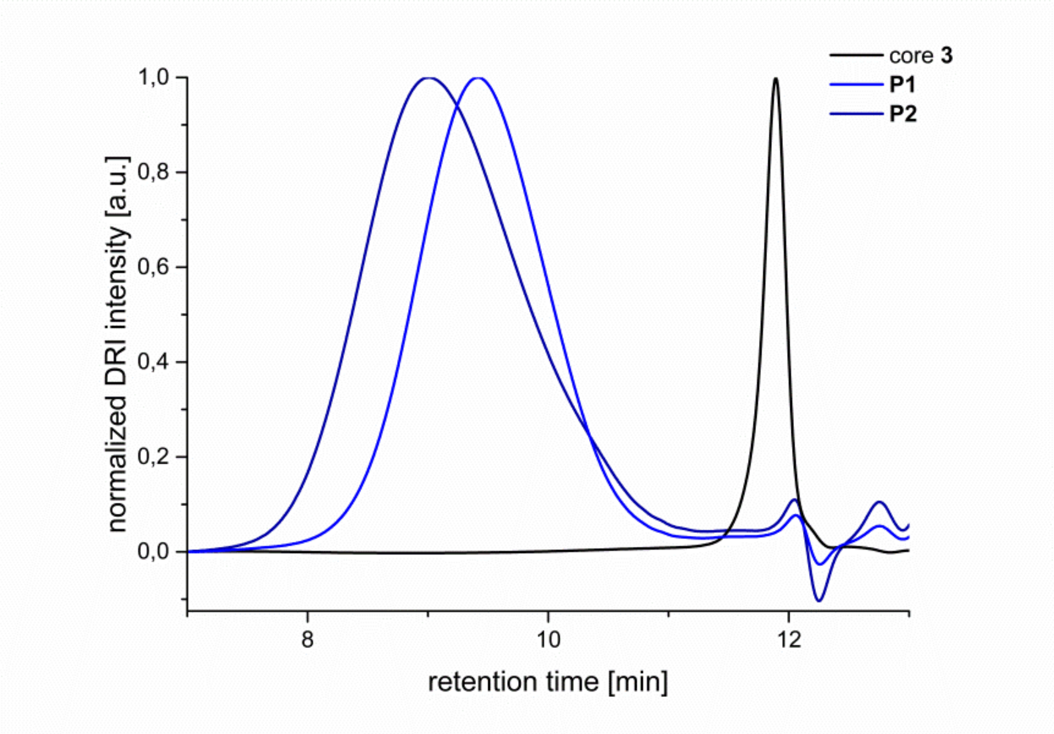


***Figure 27:** SEC data of the original core unit **3** (black) and resulting star polymers with 10 monomer units/arm **P1** (light blue) and 20 monomer units/arm **P2** (dark blue).*

To functionalize both internal and terminal double bonds of these star-shaped polyesters, a mild base-catalyzed thia-Michael addition as promising method was selected. Hexylamine (10 mol% regarding to the thiol) was chosen as base to catalyze this hydrothiolation reaction. In general, the reaction was carried out in a mixture of 1.0 equivalents of star-shaped polymer, 10 equivalents of the desired thiol (according to double bonds present in the respective polymer) and catalytic amounts of hexylamine at 50 °C. Optimization experiments showed that an excess of the thiol compound is necessary in order to provide full double bond conversion in moderate time (one day in case of mercaptoethanol and thioglycerol and up to four days for methyl thioglycolate). $^1$H NMR analysis further revealed a quick disappearance of terminal acrylate end groups, whereas the functionalization of internal double bonds, which behave like crotonates, required longer reaction times. The $^1$H NMR spectrum is consistent with a successful complete functionalization of all double bonds showing the disappearance of double bond signals (Figure 29a, signals 1-4) and the appearance of the expected signals of the thiols (Figure 29b, signals 1-7), while the integrals of the polymer backbone remained unchanged, indicating the absence of degradation.[369] SEC measurements of functionalized polymers **P5** - **P24** had to be performed using two different systems, one operating with dimethylacetamide (DMAc) and another operating with tetrahydrofuran (THF), due to the different solubility of the modified polymers. These measurements showed a shift towards higher molecular weight after functionalization, while maintaining a symmetric molecular weight distribution (Figure 28). The resulting polymers were purified by simple vacuum distillation, thereby removing the excess of thiol and base. Hence, it was demonstrated, that star-shaped polymers containing $\alpha,\beta$-unsaturated ester groups can be easily functionalized by base-catalyzed thia-Michael addition using with a variety of thiols.

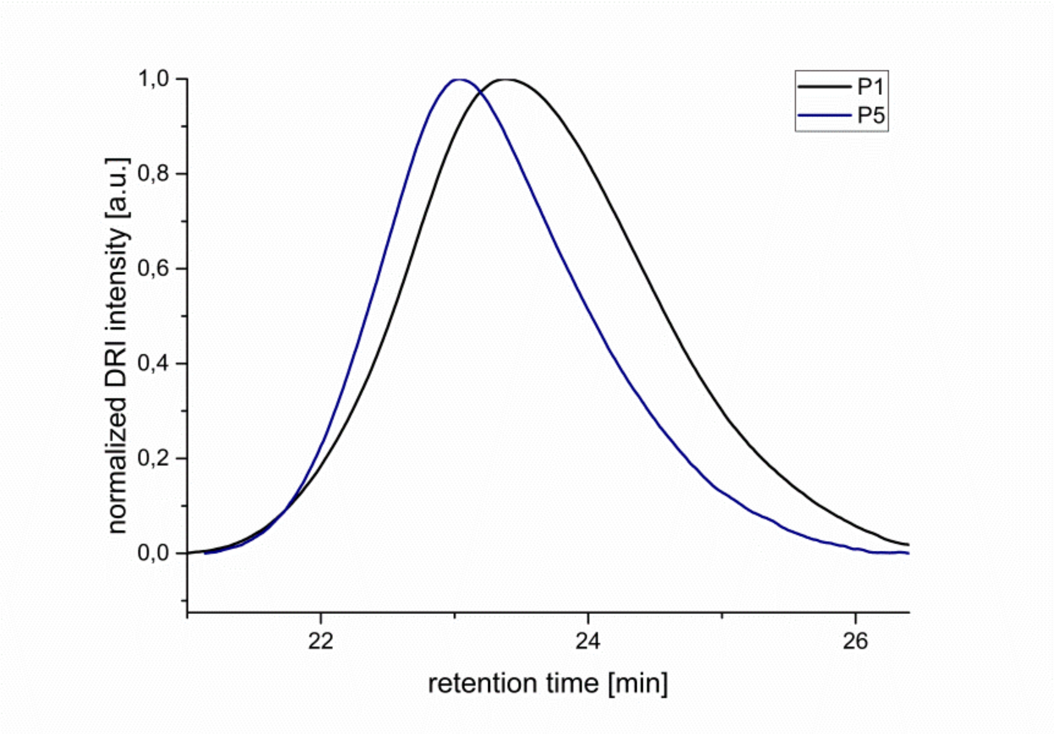


***Figure 28:*** *Exemplary SEC traces of polyester* ***P1*** *(black) and* ***P5*** *(blue) after functionalization with mercaptoethanol* ***5****.*

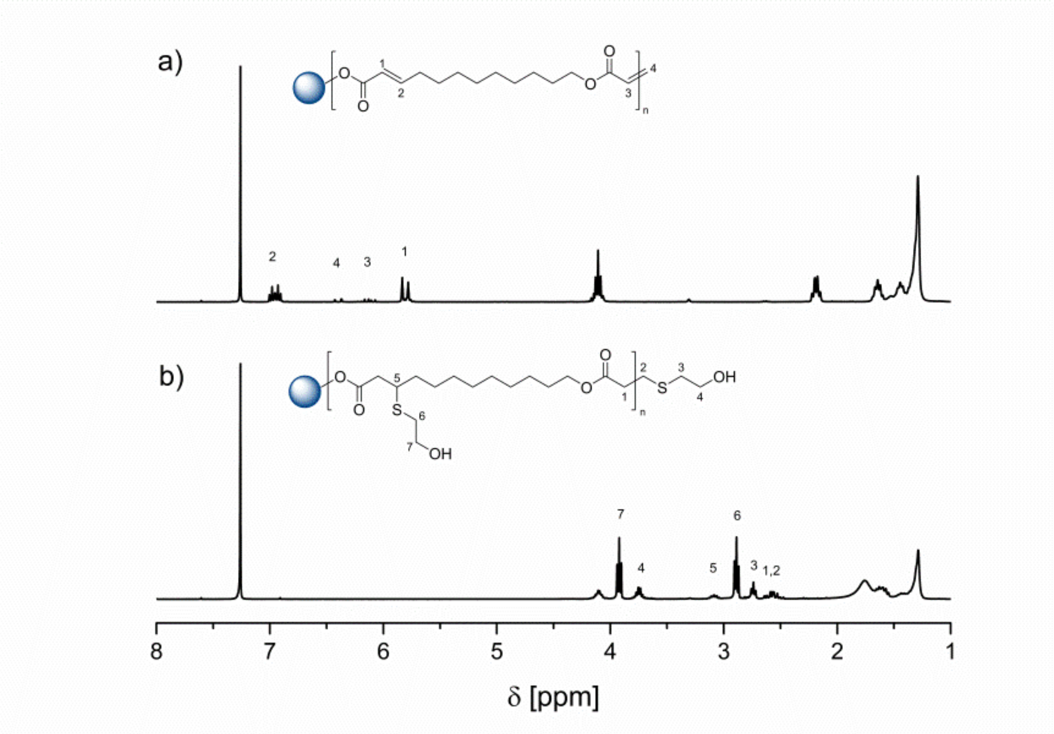


***Figure 29:*** *Exemplary $^1$H NMR spectra of star polymer* ***P1*** *(a) and star polymer* ***P5*** *functionalized with thiol* ***5*** *(b).*

***Table 2:*** *SEC data of functionalized polyesters.* $^{a)}$ *SEC measurement with system a;* $^{b)}$ *SEC measurement with system b; see experimental section (Chapter 6.1).*

| entry | core | monomer units/arm | thiol | $M_n$ [g/mol] | $M_w$ [g/mol] | Đ (SEC) |
|---|---|---|---|---|---|---|
| **P5**[a] | **3** | 10 | **5** | 13600 | 17800 | 1.31 |
| **P6**[a] | **3** | 20 | **5** | 13200 | 25600 | 1.52 |
| **P7**[a] | **4** | 10 | **5** | 14200 | 17600 | 1.24 |
| **P8**[a] | **4** | 20 | **5** | 16100 | 26000 | 1.62 |
| **P9**[b] | **3** | 10 | **8** | 9200 | 12600 | 1.37 |
| **P10**[b] | **3** | 20 | **8** | 11600 | 17600 | 1.52 |
| **P11**[b] | **4** | 10 | **8** | 15600 | 22100 | 1.42 |
| **P12**[b] | **4** | 20 | **8** | 15700 | 24300 | 1.55 |
| **P13**[a] | **3** | 10 | **9** | 17600 | 20100 | 1.14 |
| **P14**[a] | **3** | 20 | **9** | 16700 | 22300 | 1.34 |
| **P15**[a] | **4** | 10 | **9** | 21400 | 24300 | 1.14 |
| **P16**[a] | **4** | 20 | **9** | 15500 | 20400 | 1.31 |

To further characterize the hydrophilicity of the resulting star polymers after the functionalization with polar groups, namely hydroxy groups, should be determined. The octanol-water partition coefficient (P) directly correlates with the lipophilicity or hydrophobicity of chemical substances and is consequently associated with the polarity of the substrate.[525-527] Defined as the ratio of activities of a substance in two phases at equilibrium, the partition coefficient can be calculated from the concentration ratio, which can replace activities in systems of high dilution.[528] Governing the partition between aqueous and non-aqueous phase, hydrophobicity is an essential parameter in nature, engineering and pharmacology.[529, 530] Thus, it interferes with the biological activity of a chemical and characterizes the interaction between the chemical and the biological system and is indirectly related to the bioaccumulation coefficient in aqueous organisms, the soil sorption constant, and water solubility.[531, 532] Hence, it is a useful dimension in the design and research of pharmaceuticals and pesticides, the prediction of toxicology of chemicals and part of the environmental fate measurements.[533-537] The octanol-water partition coefficient can be determined by experimental methods, such as the stir- or shake-flask method or it can be calculated indirectly.[538, 539] The disadvantage of these methods lies in the long time, required to reach the equilibrium state. Easier and less time consuming is the indirect determination of partition coefficients from chromatographic retention data. Regarding the reverse phase HPLC (RP-HPLC) method, octanol is displaced by an apolar stationary phase and a mixture of methanol and water (70:30 vol%) as eluent is used to measure the hydrophobicity of the solute.[540] While widely used for simple organic structures, there is no report of this important property of polymers and its correlation to the functionalization of polymer backbones described. Therefore, a HPLC system was calibrated with six different substances of known octanol-water partition coefficient P. We chose substances, which cover a large scope of partition coefficients.[541] Thiourea was chosen to determine the dead time of the column, meaning the time needed for a compound not partitioning into the stationary phase to pass the column ($t_0$). The retention of one compound is described by the capacity factor k, where t is the retention time of the polymer analyte. A linear relation between k and the octanol-water partition coefficient P is the used to determine P.

$$k = \frac{t - t_0}{t_0}$$

To easily compare the P value of the functionalized polymers with well-known chemicals, acetone, THF and chloroform were also measured to better clarify the polarity behavior of the modified polymers. Figure 30 displays the obtained results for **P5**, **P9**, **P13**, **P17**, and **P21** (the series of functionalized polymers with four arms and 10 repeating units per arm). Thioglycerol **9**, bearing two hydroxyl groups, increases the hydrophilicity of the parent polymer, as indicated by a negative value of log k of **P13**. In the series of thiols with one hydroxyl group, the hydrophilicity decreases with longer alkyl chain, as expected. Interestingly, **P5** has a comparable polarity to acetone. The star-shaped polymer **P9**, functionalized with methyl thioglycolate **8**, is the most lipophilic substrate in this series, because esters are significantly less polar than alcohols. In summary, this is clear evidence that the polarity of these star-shaped polymers can be tuned by functionalization with different thiols.

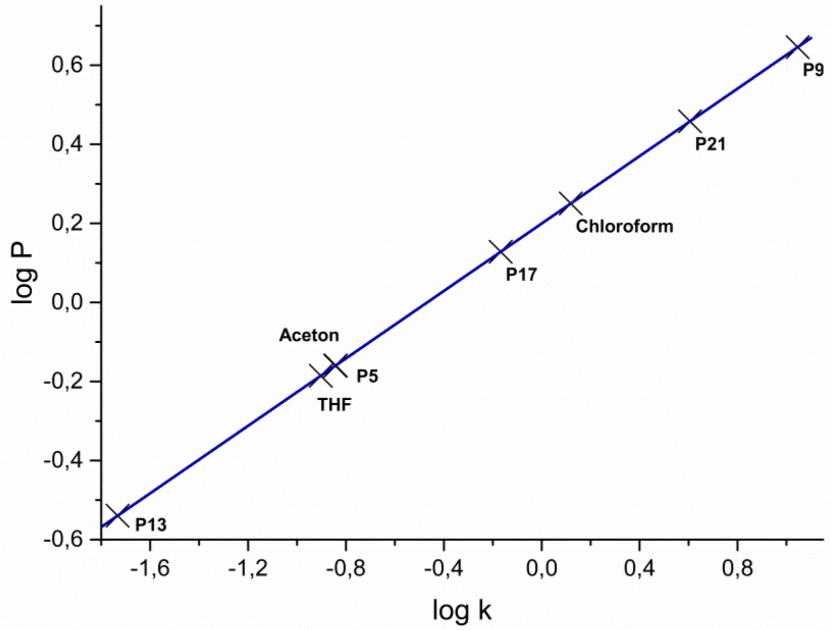
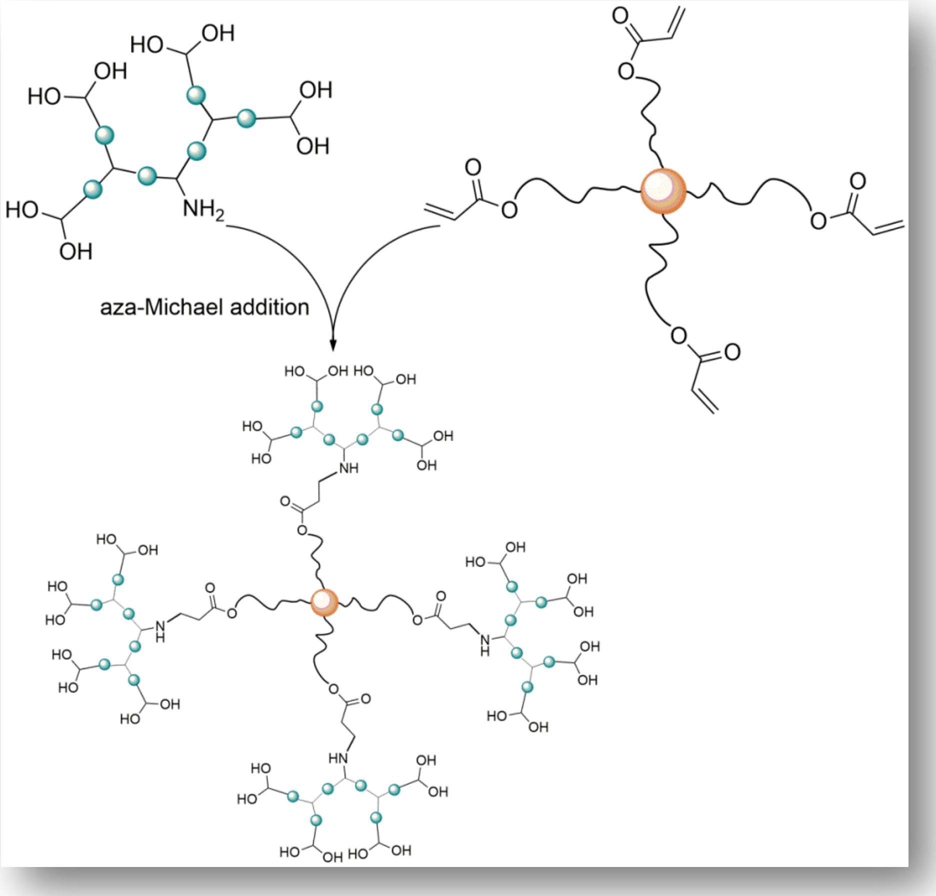


***Figure 30:*** *RP-HPLC determination of octanol-water partition coefficients of star-shaped polymers functionalized with thioglycerol **(P13),** mercaptoethanol **(P5),** mercaptobutanol **(P17),** mercaptohexanol **(P21)** and methyl thioglycolate **(P9)**.*

## CONCLUSION

Thia-Michael addition reactions proved to be suitable to functionalize star-shaped polyesters. Thus, star-shaped polyesters with both internal $\alpha,\beta$–unsaturated ester moieties and terminal acrylate units were synthesized using castor oil-derived 10-undecenyl acrylate **2** as monomer unit and multi-functional acrylates as core units applying a core-first method *via* ADMET as step-growth polycondensation. These polymers were functionalized by base-catalyzed thia-Michael additions, which were characterized by mild reaction conditions and simple purification, allowing the complete functionalization of both double bond types without degradation of the polymer. By choosing variable thiols, the polarity of the synthesized star-shaped polymers could be easily tuned, as confirmed *via* HPLC determination of the octanol water partition coefficient P.

## 4.2 DENDRON FUNCTIONALIZED STAR POLYMERS



### ABSTRACT

Dendrimer-like star polymers present a promising subclass of branched polymers, often studied for their encapsulation and transport properties. Herein, the synthesis of a dendron is described using diethanolamine as focal point. By successive *O*-allylation with allyl bromide and thiol-ene addition of thioglycerol, a defined dendron was generated. To prove full conversion of terminal, functional groups and avoid defects in the structure of the dendron, NMR and SEC analysis were conducted. In a second step, the formed dendron can

be attached to star-shaped polymers bearing terminal acrylate end groups *via* a mild aza-Michael addition.

In general, polymer architectures include three main classes, namely linear, branched and crosslinked structures. Depending on the structure and type of monomer and the polymerization technique applied, interesting structures can be generated. Among branched polymers, dendrimers are of special interest since their discovery by Tomalia, Newkome, Vögtle, Hawker and Fréchet.[48, 118, 134, 135, 542] The synthesis can either be conducted in a divergent fashion (from the inside out) or in a convergent way (from the outside in).[543] The formation of the dendrimer succeeds *via* multiple step-by-step reactions utilizing the versatile toolbox of organic chemistry reactions. Dendrimers exhibit a globular structure of high regularity with controlled molecular weight. Many applications of this polymer class arise from cavities inside these macromolecules, suitable for encapsulation, or the high quantity of functional groups on the surface, which facilitate the use as sensors, for example.[50] Due to their unique properties, an exceptional quantity of dendrimer types has been published, such as polyamidoamines, polyethers, polyesters as well as others.[544] The uniform structure of dendrimers requires time-consuming, successive synthesis protocols and purification procedures. In contrast, star-shaped polymers present much simpler branched polymeric materials. Here, several linear polymer chains are attached to a core unit, the only branching point. The synthesis can proceed *via* the arm-first approach or the core-first approach utilizing various polymerization techniques.[57, 59] Star-shaped polymers feature the easy synthesis of miktoarm star polymers, containing chemically different arms, or block copolymer stars.[77, 545, 546] Application fields include gene and drug delivery or imaging.[547-549]

In 1998, Trollsås and Hedrick introduced a new macromolecular class, combining dendrimers and star-shaped polymers, coined as dendrimer-like star polymers. The synthesis proceeded *via* repetitive ring-opening polymerization of $\varepsilon$-caprolactone and functionalization of terminal hydroxyl groups with a $AB_2$ branching unit.[550] Here, the generations are presented by high molecular weight polymers.[551] Furthermore, they synthesized dendrimer-like star block copolymers of poly($\varepsilon$-caprolactone) and poly(methyl methacrylate) to build up structures able to form unimolecular micelles, which find application as nanocarriers or nanoreactors.[551] As a promising candidate for the delivery of hydrophobic drugs, amphiphilic, dendrimer-like star polymers with a hydrophobic, star-shaped poly(L-lactide) as core and a hydrophilic polyamidoamine dendron shell was described. Drug delivery tests applying doxorubicin showed an enhanced water solubility of the drug.[552] In addition, they reported the ability for drug delivery for amphiphilic dendrimer-like star polymers, which consisted of a poly(L-lactide) core and attachment of multiple poly(ethylene glycol) arms.[553] In general, amphiphilic dendrimer-like star polymers offer a small particle size and a well-defined structure with multiple functional groups in the periphery. The particle size itself can be tailored by the size of the inner star-shaped polymer. Moreover, the water solubility can be controlled by varying the ratio of hydrophilic to hydrophobic part. The high quantity of functional surface groups, similar to dendrimers, combined with the large cavities due to the flexible structure of the interior in contrast to the rigid inner structure of dendrimers, offer novel possibilities for this type of branched polymers.[553] Following the arm-first approach, the preparation of a dendritic macroinitiator with a single initiating site for the polymerization of each linear arm was described. The resulting macromolecules were cured to obtain core crosslinked star polymers with multiple functional groups due to the dendron.[554]

This chapter describes the synthesis of a dendron, which can be attached in a second step to the terminal acrylate end groups of castor oil-derived star-shaped polymers synthesized *via* ADMET polymerization (see Chapter 4.1). The selective functionalization of terminal double bonds should provide access to dendrimer-like star polymers with multiple hydroxyl groups on the surface, which induce water solubility to the resulting polymers. The aza-Michael addition was chosen as mild and selective reaction for the coupling of star-shaped polymers and dendron.

## RESULTS AND DISCUSSION

The synthesis of star-shaped polymers with $\alpha,\beta$-unsaturated ester functionalities along the arms was successfully described by the ADMET polymerization of castor oil-derived 10-undecenyl acrylate **2** in the presence of a multifunctional core unit.[508, 555] The polymers obtained *via* this method contain internal $\alpha,\beta$-unsaturated ester moieties as well as acrylate end groups, which allow direct post-polymerization functionalization. Earlier experiments showed the susceptibility to acidic and basic conditions during functionalization, resulting in degradation of the polymer. Therefore, mild functionalization processes have to be applied to preserve the defined macromolecular structure. Here, the Michael-type addition reactions of thiols or amines to double bonds present a versatile method under mild conditions.[251] Recently, Farmer *et al.* reported the functionalization of bio-based unsaturated polyester *via* Michael addition of dimethyl malonate and acetylacetone.[556] Chanda *et al.* functionalized the *exo*-chain double bonds of poly(alkylene itaconate) with various amines and thiols.[557] The thia-Michael addition was already applied in the functionalization of star-shaped polymers with $\alpha,\beta$-unsaturated ester groups. Herein, the amine base ascertains whether all type of double bonds using hexylamine or only acrylate end groups in the case of trimethylamine were functionalized.[508, 555] Therefore, the related aza-Michael addition was chosen for functionalization.[558-560] Here, elongated reaction times were necessary to reach complete conversion due to the lower nucleophilicity of amines compared to thiols.[561] With a view to synthesize water-soluble star-shaped polymers, dendrimer-like star polymers represent an attractive structure variation of star polymers.[550] Two different approaches can be applied to synthesize the dendrimer-like star polymer: The attachment of a preformed dendron or the buildup of the dendron directly from the end groups of the polymer arms. To protect the defined macromolecular structure of the star polymers from degradation and broaden the toolbox of applicable organic reactions, the dendron was preformed separately (Figure 31). Diethanolamine **10** was chosen as focal point, which offers the subsequent coupling to the star-shaped polymer *via* aza-Michael addition. To avoid undesired reactions of the amine functionality during the synthesis of the dendron, the amine group was first protected by the benzyl protection group, which can be easily removed by hydrogenation.[562] Therefore, diethanolamine **10** was reacted with benzyl bromide. The benzyl-protected diethanolamine **11** was obtained as light-yellowish, oily liquid in a yield of 72 %. For *O*-allylation, **11** was etherified with allyl bromide under inert gas atmosphere in the presence of sodium hydride in dry THF. The use of 2 equivalents of allyl bromide and sodium hydride resulted in incomplete functionalization of the two hydroxyl groups, verified by $^1$H NMR spectroscopy. Thus, the amounts were increased to 5 equivalents of allyl bromide and 3 equivalents of sodium hydride and both hydroxyl groups of **11** were successfully etherified. After purification by column chromatography, **12** was obtained as light-brown, oily liquid in a yield of 43 %. The terminal, allylic double bonds were subsequently functionalized with thioglycerol **9** *via* photochemical thiol-ene addition. **12** was mixed with 2 equivalents of thioglycerol **9** and irradiated with UV-light overnight in the presence of 5 mol% DMPA. Due to the oily, viscous nature of the mixture, the addition of minimal amounts of THF was necessary to enable efficient agitation. The product was converted in the following step without further purification. Figure 32 shows the $^1$H NMR spectra of **11**, **12** and **13** with designation of all signals. The integration of the allylic double bond signals (signals 6 and 7, spectrum b) proved complete conversion of the hydroxyl groups. After functionalization the absence of the double bond signals and appearance of new signals for the thiol (signals 8, 9, 10, spectrum c) revealed the successful thiol-ene addition. SEC measurements showed narrow molecular weight distributions with a shift to higher molecular weights as well as dispersity indices of approximately 1.00 for **11** and 1.01 for **12** (Figure 33). The SEC trace of **13** shows residues of DMPA as low molecular weight impurity and a small shoulder in the higher molecular weight region (Đ = 1.05). Here, a lower amount of DMPA in the thiol-ene addition should be tested in future works as well as purification prior to the following *O*-allylation reaction.

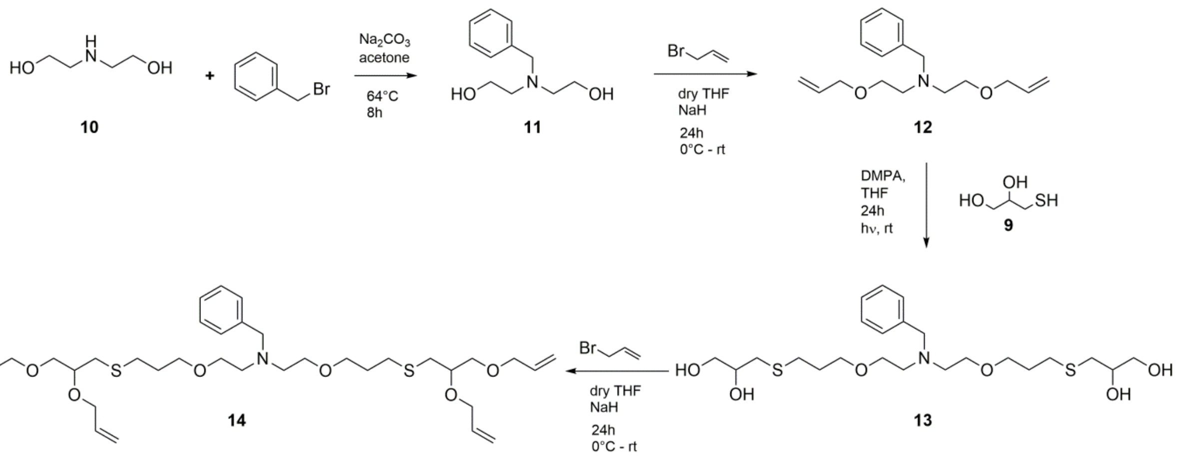


***Figure 31:*** *Pathway for the synthesis of the dendron starting from diethanolamine* ***10****.*

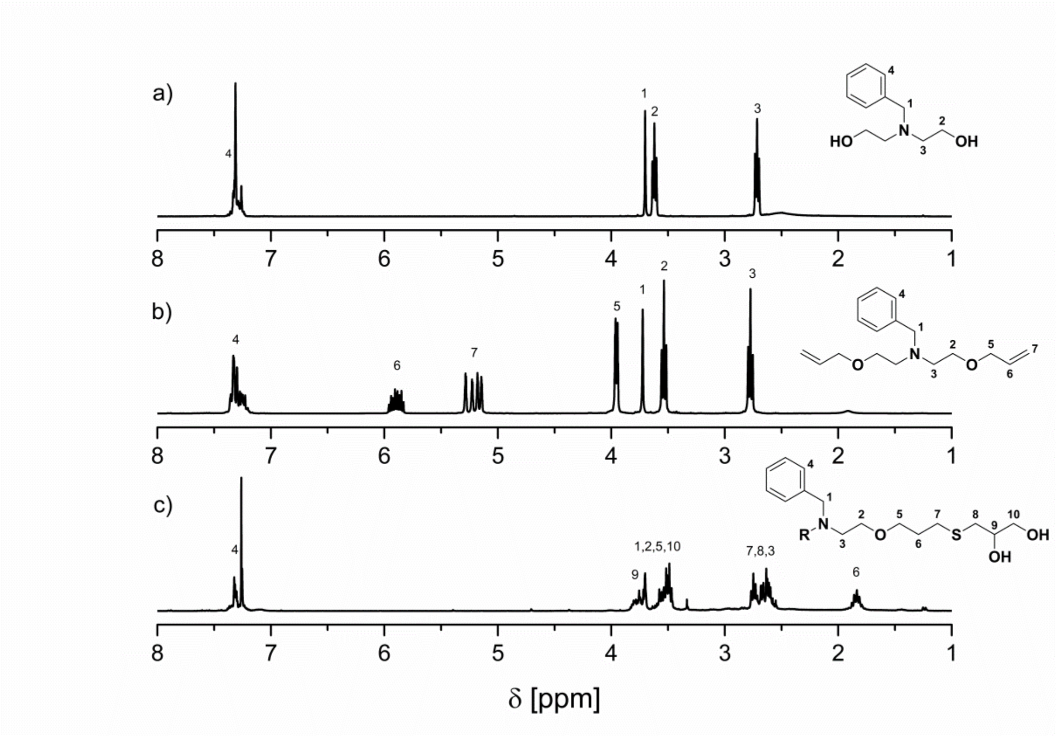


***Figure 32:*** *$^1$H NMR spectra of **11**, **12** and **13** with designation of all signals.*

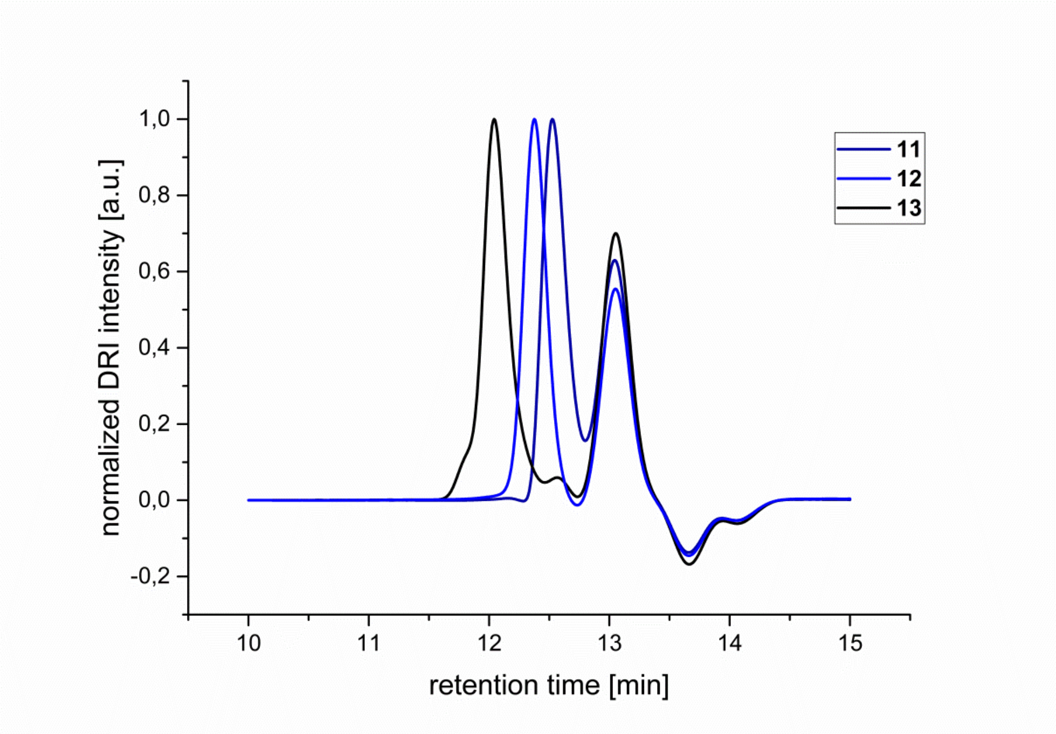


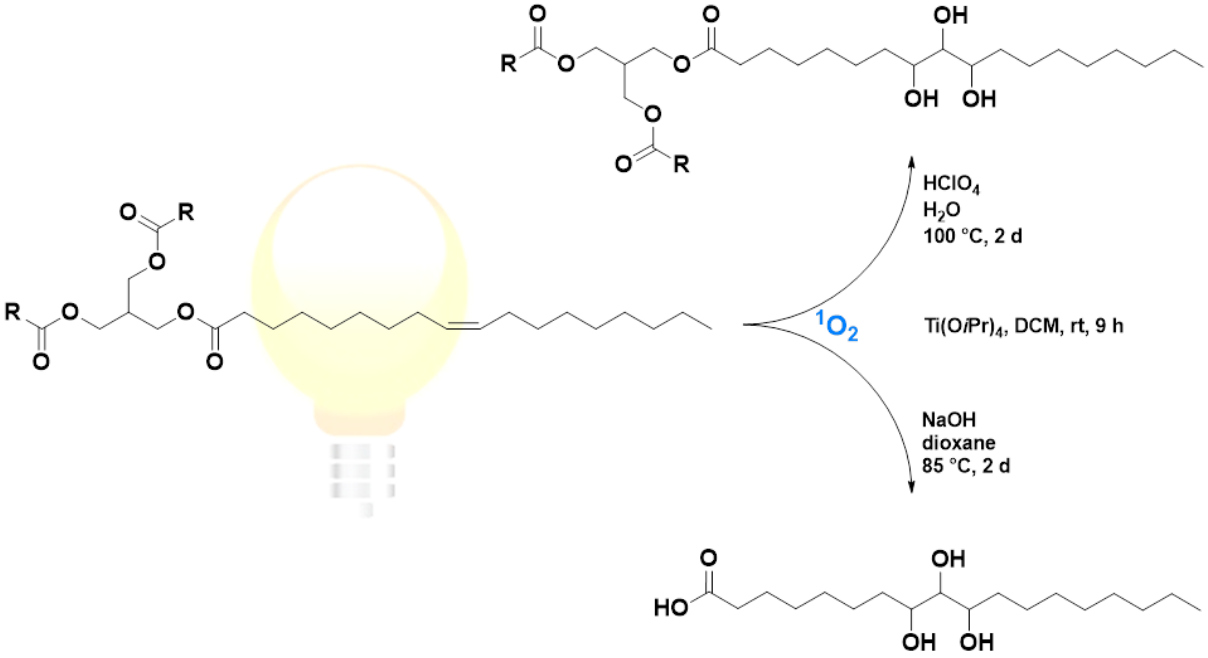
***Figure 33:*** *SEC traces of **11**, **12** and **13** (the overlapping signals at 13.2 min result from THF used for sample preparation).*

The product **13** was used in the following *O*-allylation reaction without purification. In a test reaction, **13** was converted with 10 equivalents of allyl bromide and 6 equivalents of sodium hydride in dry THF under inert gas atmosphere. **14** was obtained in a yield of 33 %. Due to the low yield, the reaction needs to be optimized. In future experiments, the amounts of allyl bromide and sodium hydride should be decreased, while maintaining full conversion of double bonds.

## CONCLUSION

The synthesis of a dendron was described starting from benzyl-protected diethanolamine **11**. The amine functionality was chosen to allow coupling to star-shaped polymers with terminal acrylate end groups *via* mild aza-Michael addition. The first *O*-allylation as well as thiol-ene addition were successfully performed. The resulting product **12** was characterized *via* $^1$H NMR and SEC indicating a narrow molecular weight distribution with a dispersity index of 1.01. However, **13** showed small impurities, which require optimization of the reaction conditions or purification prior to the next step. In future studies, the successive repetition of the described *O*-allylation and thiol-ene functionalization, should lead to the generation of a dendron with multiple hydroxyl groups.

## 4.3 SYNTHESIS OF FATTY ACID-BASED POLYOLS *VIA* PHOTOPEROXIDATION AND FOLLOW-UP CHEMISTRY



### ABSTRACT

Herein, the synthesis of polyols derived from high oleic oil is described. Therefore, the photochemical Schenck-Ene reaction was applied to obtain the allyl hydroperoxides of triglycerides and reacted directly in a one-pot, tandem reaction to the corresponding epoxy alcohols catalyzed by titanium(IV) isopropoxide. The subsequently, performed acidic epoxide ring-opening with perchloric acid yielded a triglyceride-based polyol with 6.2 hydroxyl groups per molecule. On the other hand, under basic catalysis with aqueous sodium hydroxide solution, cleavage of the ester bonds occurred and generated a fatty acid-derived polyol. This approach enables more hydroxyl functionalities per double bond, namely three, compared to other published procedures, where usually a maximum of two hydroxyl groups per double bond can be obtained.

The main components of vegetable oils are triglycerides. Their structure allows various functionalization methods, which turn triglycerides into a suitable feedstock for the preparation of novel, renewable monomers for macromolecular chemistry (Chapter 2.2, Figure 9). Due to their versatile reactivity, double bonds of unsaturated fatty acids present a favored point for modification including metathesis, addition reactions, epoxidation or ozonolysis.[186, 194, 207, 563-565] The functionalization of triglycerides with polymerizable groups enables their conversion by diverse polymerization techniques. Epoxidized triglycerides can be ring-opened by acrylic acid incorporating acrylates onto the triglyceride, which can be used in a free radical polymerization to vinyl ester resins.[566, 567] Epoxide ring-opening with alcohols or other nucleophiles yield a triglyceride-based polyol with secondary hydroxyl groups suitable for polycondensation.[568-571] In general, polyols are valuable monomers in the formation of polyurethanes, polyester and alkyd resins.[231, 572-576] In addition, polyols, such as sorbitol, have been used as additives in foods, cosmetics or as intermediate in the synthesis of pharmaceuticals.[577] Other methodologies to produce polyols from fatty acids include the hydroformylation of the double bond with subsequent hydrogenation. By this reaction sequence, one primary hydroxyl group per double bond can be obtained, which was successfully applied in the formation of polyurethane precursors.[574, 578] Ozonolysis causes cleavage of the carbon-carbon double bond of triglycerides generating carboxylic acids, aldehydes or alcohols depending on reaction conditions. Combination of ozonolysis and reduction offers polyols with a maximum of three, primary and terminal, hydroxy groups per triglyceride. The resulting polyols entail the advantage of the absence of chain dangling in polyurethane synthesis.[573] Thiol-ene addition of mercaptoalcohols also presents a possibility to gain hydroxyl groups.[579, 580] Other approaches in the synthesis of polyols located at the ester functionality of triglycerides involve the transesterification with multifunctional alcohols, such as glycerolysis, or amidation with amines bearing several hydroxy groups.[581, 582] An overview of synthetic protocols for the polyol synthesis based on triglycerides is given in Figure 34.

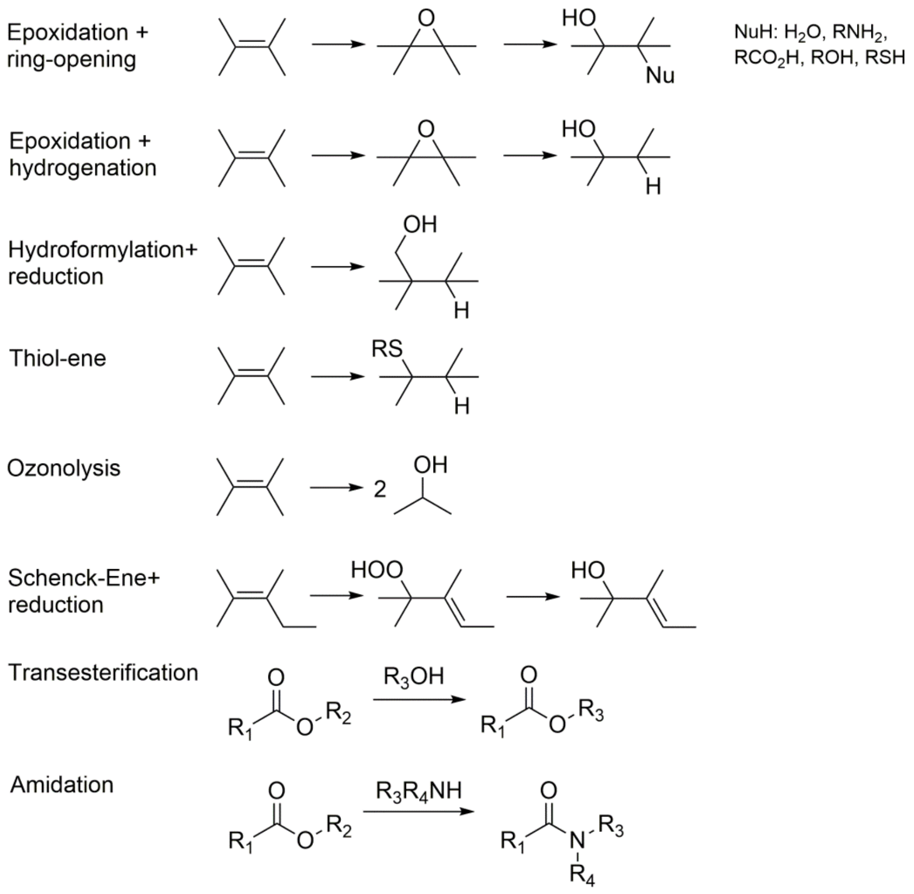
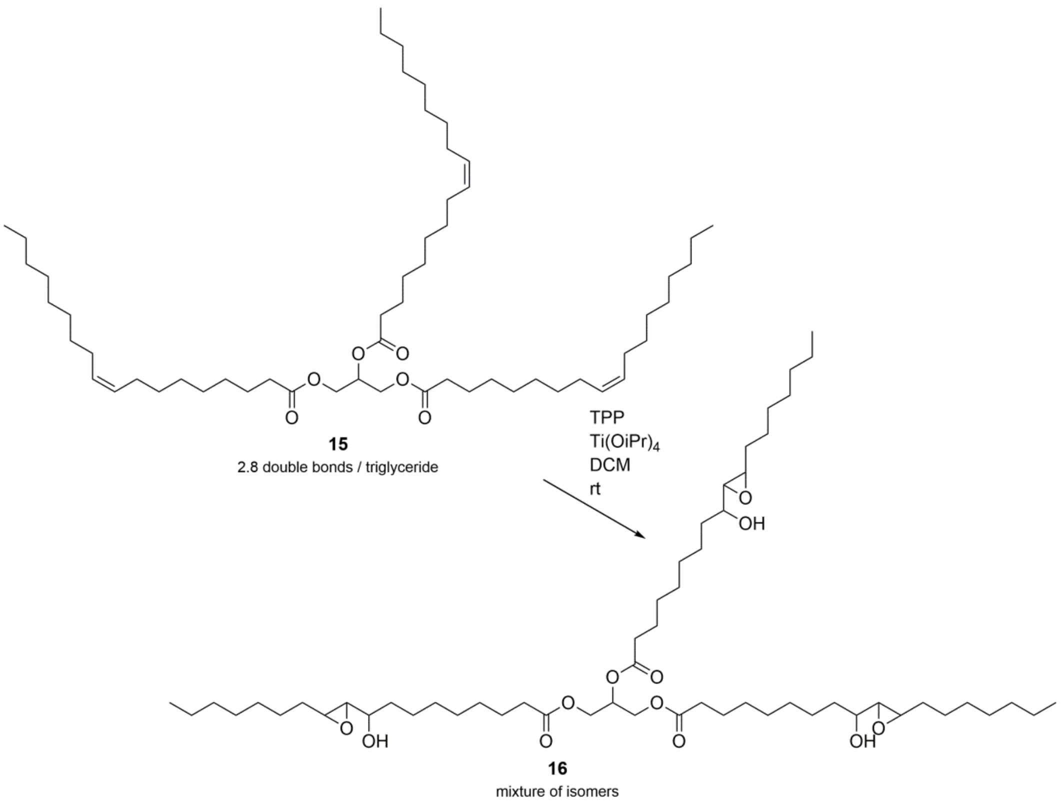


***Figure 34:*** *Schematic illustration of polyol synthesis methods based on triglycerides.*[575]

The Schenck-Ene reaction grants access to polyols *via* oxidation of the allylic position of double bonds by singlet oxygen ($^1O_2$). In a photochemical process, oxygen is excited to the singlet state by photosensitizers (Chapter 2.3.3). Other methodologies to synthesize allyl hydroperoxides include the reaction of allyl halides or allyl sulfonates with hydrogen peroxide and the reaction of endoperoxides with acids or hydroxyl-containing compounds.[583] Nonetheless, the photochemical Schenck-Ene reaction has been the most employed method due to the particular convenience and also advantages in terms of sustainability. The allyl hydroperoxides have proven to be synthetically useful intermediates in organic synthesis. Simple reduction of the allyl hydroperoxides forms allyl alcohols, whereas the reaction with titanium(IV) has been applied to synthesize epoxy alcohols suitable for subsequent epoxide ring-opening. With regard to triglyceride-based polyols, the Schenck-Ene reaction has definitely been underestimated. Zobel and Schäfer described the synthesis of allyl hydroperoxides by oxidation applying selenium dioxide and *tert*-butyl hydroperoxide compared to the oxidation with singlet oxygen and tetraphenylporphyrin as photosensitizer. The Schenck-Ene reaction was favored due to high yields, absence of toxic selenium dioxide and the application of inexpensive reagents. Furthermore, they showed the activation by converting the formed allyl hydroperoxides to methyl carbonates suitable for the subsequent attachment of carbohydrates and phenol derivatives.[584] Moreno *et al.* synthesized enone-containing triglycerides by the Schenck-Ene reaction and following dehydration. These derivatives were partly functionalized *via* phospha-Michael addition and afterwards crosslinked with diaminodiphenylethane to obtain thermosets.[585] The reduction of allyl hydroperoxides and the partial functionalization of hydroxyl groups with chlorodiphenylphosphine to prepare phosphorus-containing triglycerides was also described. After acrylation, the phosphorus-containing triglycerides were crosslinked with a multifunctional acrylate.[586]

In this chapter, the Schenck-Ene reaction of high oleic oil is described. In a one-pot fashion, the intermediate allyl hydroperoxide was reacted with titanium(IV) isopropoxide to yield the corresponding epoxy alcohol.[495] Titanium(IV) isopropoxide is a well-known catalyst in the asymmetric epoxidation of allyl alcohols first described by Sharpless *et al*.[587-590] Furthermore, silica-supported titanium(IV) isopropoxide were reported to convert alkenes to the corresponding diols in the presence of hydrogen peroxide. An intermediate allyl hydroperoxide was transformed to the corresponding diol by intramolecular oxygen transfer similar to the here described Schenck-Ene reaction.[591] In addition to $Ti(O\textit{i}Pr)_4$, other efficient titanium catalysts have been described, such as titanium-substituted zeolites, titanium-containing molecular sieves, titanium cyclopentadienyl–silsesquioxane complexes and titanium-salan-complexes, beside others.[592-595] Here, variation of the solvent, catalyst and concentration was performed to facilitate complete conversion. Subsequent epoxide ring-opening was conducted either under acidic catalysis generating a triglyceride-based polyol or under basic catalysis cleaving the ester linkages to form a fatty acid polyols. Thus, a maximum of three hydroxyl functionalities per double bond could be introduced, which has been till today only available from fatty acids with natural occurring hydroxyl groups beside the double bond.

In 1948, Schenck demonstrated the versatile reaction of unsaturated substrates with photochemically generated singlet oxygen ($^1O_2$) to allyl hydroperoxides.[443] Since then, the reaction has been the subject of intensive research and is today a well-known process for the functionalization of the allylic carbon-hydrogen bond. The photooxidation proceeds *via “in situ”* generated singlet oxygen, which reacts with the olefin. Irradiation with a high pressure sodium lamp ($\lambda$=589 nm) excites tetraphenylporphyrin (TPP), which transfers the energy to the oxygen originating $^1O_2$, a highly reactive species. As described before, TPP was proven to be an effective photosensitizer in the Schenck-Ene reaction of triglycerides and other compounds.[501, 585] A mixture of isomeric allyl hydroperoxides is produced and can be converted in interesting reactions afterwards.[479] A well-known, but rarely used transformation is the conversion of the allyl hydroperoxides to the corresponding epoxy alcohols in the presence of titanium(IV) isopropoxide (Scheme 1).[495, 496] The mechanism was proposed by Adam *et al.* in 1986. They assumed the intermolecular transfer of oxygen due to the stability of allyl hydroperoxides in the presence of Ti(O*i*Pr)$_4$ (Figure 35).[495]



***Scheme 1:*** *Synthesis of triglyceride-based epoxy alcohol* ***16*** *via intermediate allyl hydroperoxide.*

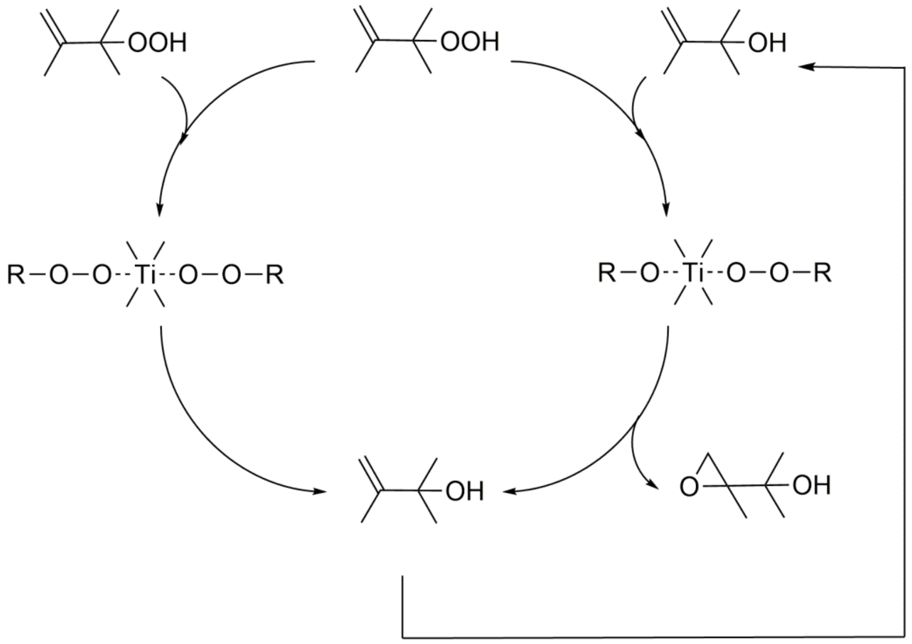


***Figure 35:*** *Mechanism of the conversion of allyl hydroperoxides to epoxy alcohols in the presence of titanium(IV) isopropoxide proposed by Adam et al.*[495]

Up to date, the synthesis of an epoxy alcohol by combining this easy one-pot reaction with the subsequent ring-opening generating polyols has not been investigated. Advantage of the reaction is the lack of purification except evaporation of the solvent for the following step. In this way, an epoxy alcohol with 2.4 epoxy rings per triglyceride was formed. However, the $^1$H NMR confirmed the disappearance of the double bond; the conversion of double bonds to epoxides was 82 %. In Figure 36, the $^1$H NMR spectrum of the resulting epoxy alcohol **16** (spectrum b) is shown compared to the original high oleic oil **15** (spectrum a) showing the complete conversion of the double bonds (signals 4 and 5)and new signals in the region 2.5 – 3.0 ppm (signals 5 and 6) for the epoxide. In the expanded version of the $^1$H NMR, four signals could be assigned to the epoxide and adequate signals for the methine next to the alcohol functionality (3.0 – 4.0 ppm). Due to the similar chemical neighborhood, separate signals for the two regioisomers cannot be expected. The signals fit to shifts of *syn*- and *anti*-epoxy alcohols, reported earlier, indicating a downfield shift for *syn*-epoxy alcohols.[596, 597] Integration of the proper signals revealed 55 % *anti*- and 45 % *syn*-epoxy alcohol.

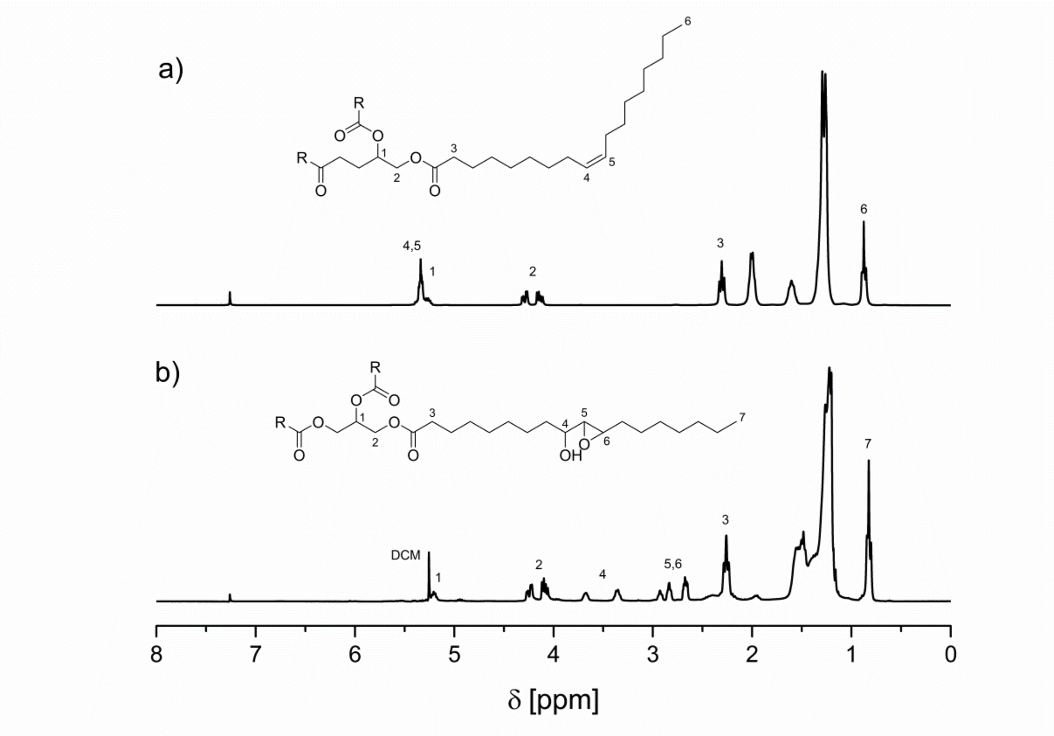


***Figure 36:*** *$^1$H NMR spectrum of a) the original high oleic oil **15** and of b) the epoxy alcohol **16**.*

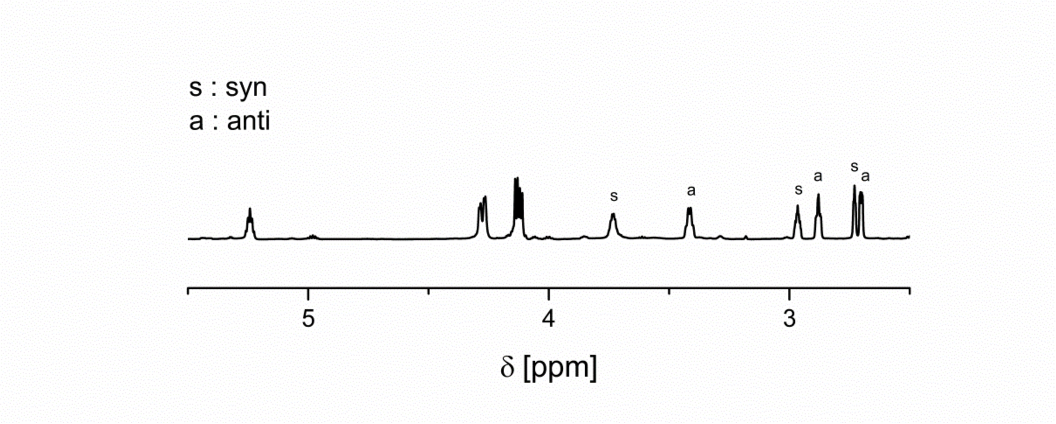


***Figure 37:*** *Expanded $^{1}$H NMR of the syn- (s) and anti-epoxy alcohol (a) with identified signals.*[596, 597]

In the context of sustainable chemistry, the prevention of waste, high atom efficiency, application and production of nontoxic substrates, solvents and products as well as the use of renewable feedstocks is highly desirable. To replace harmful and easily evaporating dichloromethane (DCM), the usually used solvent in Schenck-Ene reactions, ethyl acetate (EE), tetrahydrofuran (THF), dimethyl carbonate (DMC) and *tert*-butanol (*t*BuOH) were tested as alternatives. Table 3 depicts the conversion of the double bonds after a certain time depending on the solvent used with otherwise unchanged reaction conditions.

***Table 3:*** *Double bond conversion according to the solvent used in the Schenck-Ene reaction.*

| **entry** | **solvent** | **time [h]** | **double bond conversion [%]** |
|---|---|---|---|
| **1** | **DCM** | 3 | 31 |
| **2** | **EE*** | 3 | 20 |
| **3** | **THF** | 3 | 10 |
| **4** | ***t*BuOH** | 3 | 9 |
| **5** | **DMC** | 11 | 22 |

* addition of DCM necessary to dissolve TPP. All reactions were carried out with 3 mol% Ti(OiPr)$_4$ and 0.01 mol% TPP.

As mentioned in chapter 2.3.3, the lifetime of singlet oxygen is highest in halogenated solvents, such as carbon tetrachloride, chloroform or dichloromethane.[456] The lifetime of $^1O_2$ in THF is, for example, one-third of the lifetime reported for dichloromethane.[598] Furthermore, the solubility of TPP was obviously lower in other solvents than dichloromethane. If the reaction is performed in a flask or in a modified photoreactor with a reflux condenser, evaporation of dichloromethane could be avoided. Evaporation of the solvent for the following step presents a possibility to recycle the solvent for further reactions. DMC might be a sustainable alternative to investigate in more detail in the future. However, since no true alternative for DCM, in terms of conversion, could be found, a reduction of the amount of required DCM was accomplished by variation of the concentration. A concentrated solution reduced the reaction time (Table 4, entry 1 and 2), but a concentration of double bonds higher than 1.2 mol/L increased the reaction time due to the higher viscosity of the oily solution (Table 4, entry 3 and 4). Moreover, the optimization showed the highest quantity of epoxides formed with a concentration of 1.2 mol/L (Table 4, entry 2).

***Table 4:** Variation of the concentration of high oleic oil in the Schenck-Ene reaction.*

| entry | c [mol/L]* | t [h] | epoxides / molecule |
|---|---|---|---|
| **1** | 0.6 | 9.5 | 2.0 |
| **2** | 1.2 | 9 | 2.4 |
| **3** | 1.5 | 12.5 | 2.4 |
| **4** | 2 | 12.5 | 2.3 |

* concentration of the double bonds.

To study the influence of the amount of catalyst, the Schenck-Ene reaction was performed with different amounts of TPP and Ti(O*i*Pr)$_4$. Table 5 shows the double bond conversion depending on the amount of Ti(O*i*Pr)$_4$ after three hours. Although, double bond conversions were in the same range, with the use of 1 mol% catalyst, unexpected signals in the double bond region (5.3 – 6.0 ppm) could be observed. The signals resulted from the formation of allyl hydroperoxides, which did not react to the corresponding epoxy alcohol due to the smaller amounts of Ti(O*i*Pr)$_4$, which is necessary for the epoxidation. With an increasing amount of catalyst from 3 to 5 mol%, no further improvement could be achieved.

***Table 5:** Variation of the amount of Ti(OiPr)$_4$ in the Schenck-Ene reaction.*

| entry | mol% Ti(O*i*Pr)$_4$* | double bond conversion [%] |
|---|---|---|
| **1** | 1 | 26 |
| **2** | 3 | 31 |
| **3** | 5 | 29 |

* relative to double bonds.

Since the photosensitizer generates the singlet oxygen, a dependence of the reaction time and hence the conversion on the amount of photosensitizer can be expected. Variation of the amount of TPP (0.01, 0.03 and 0.05 mol%) revealed 0.01 mol% as sufficient portion to achieve complete conversion, which meets the criteria of sustainable chemistry. In conclusion, optimization studies showed an appropriate reaction time (9 hours) applying

0.01 % TPP and 3 mol% Ti(O*i*Pr)$_4$ and performing the reaction with 1.2 mol/L concentration of the double bonds in dichloromethane.

Epoxides are versatile substrates, which are ring-opened easily due to the considerable ring strain. In a nucleophilic substitution, the epoxide can be either opened under acidic or basic catalysis. With an acidic catalyst, the oxygen of the epoxide is protonated and the nucleophile attacks the more substituted carbon atom from the backside ($S_N1$-$S_N2$ hybrid). Although, an intermediate carbocation is not formed, the carbocationic character is important. Under basic catalysis, the nucleophile attacks the least hindered end of the epoxide from the backside ($S_N2$).[599] The product is finally formed by acidic work-up (Figure 38). Nucleophiles include alkyl halides, thiols, amines, carboxylic acids, water and Grignard-reagents, among others, which allow derivatization of epoxides in various ways.

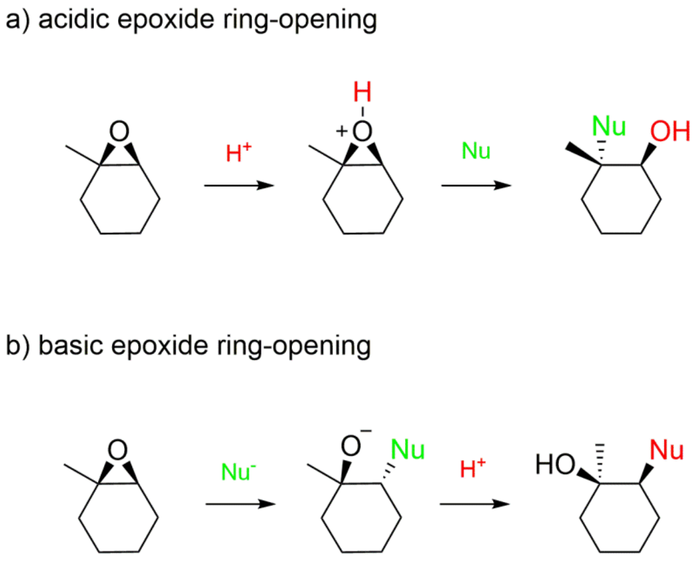


***Figure 38:*** *Mechanism of a) acidic or b) basic epoxide ring-opening.*

Furthermore, the enzymatic ring-opening of epoxides is a well-established method in the enantioselective synthesis of alcohol derivatives.[600-602] For the performance of ring-opening reactions applying epoxidized triglycerides, the hydrolysis stability must be considered. Acids tend to destroy the triglyceride structure by breaking the ester linkages. Dahlke *et al.* reported the ring-opening of epoxidized rapeseed and soybean oil with different nucleophiles, such as water, methanol and diethanolamine, catalyzed by sulfuric acid-activated bleaching earth.[603] The consecutive epoxidation and ring-opening of milkweed oil using formic acid, hydrogen peroxide and hydrochloric acid in one pot was also described.[569, 604] Perchloric acid has been often applied in ring-opening reactions.[605-608] Because of the diverse amounts of perchloric acid reported, optimization studies presented in this work focused on the proportion of added acid. The first epoxide ring-opening was performed with 14 wt% perchlorid acid, which was added dropwise to a refluxing solution of **16** in water. $^1$H NMR revealed full conversion of epoxides due to the absence of epoxide signals (2.5 – 3.0 ppm), but the broadening of signals combined with the SEC measurement indicated oligomerization during the reaction. Oligomerization occurs due to the ring-opening of an epoxide by an alcohol group of another molecule or by ring-opening polymerization of epoxides. The degree of oligomerization increases with higher concentration of the catalyst and lower concentration of the nucleophile.[609] To investigate the influence of a higher amount of acid on oligomerization, the reaction was performed with a constant amount of **16**, but increasing concentrations of perchloric acid (Table 6).

***Table 6:*** *Variation of the amount of perchloric acid in epoxide ring-opening reactions.*

| **entry** | **wt% [$HClO_4$]** | **$M_n$ [g/mol]** | **Đ (SEC)** |
|---|---|---|---|
| **1** | 10 | 3300 | 5.1 |
| **2** | 30 | 2700 | 3.5 |
| **3** | 50 | 2300 | 2.8 |
| **4** | 70 | 1500 | 1.4 |
| **5** | 90 | 1500 | 1.3 |
| **6** | 115 | 1500 | 1.4 |
| **7** | 150 | 1900 | 1.9 |

Optimization showed that with 10 wt% perchloric acid, oligomerization took place to a considerable amount (Figure 39, Table 6, entry 1). For high concentrations of acidic catalyst, the ester groups of the triglycerides are hydrolyzed confirmed *via* $^1$H NMR measurements due to the absence of the triacylglycerol signals (Figure 40, Table 6, entry 4-7).

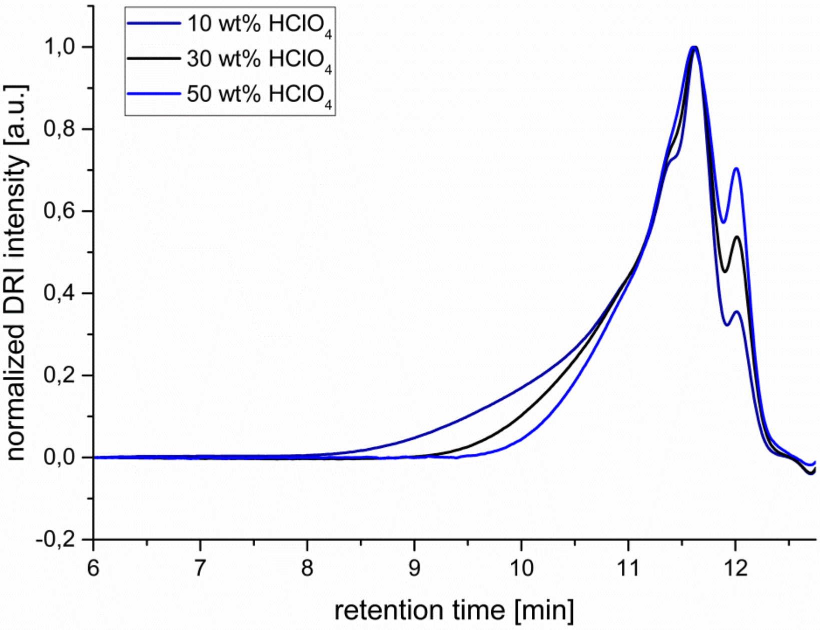


***Figure 39:*** *Exemplary SEC traces for epoxide ring-opening with varying amounts of perchloric acid.*

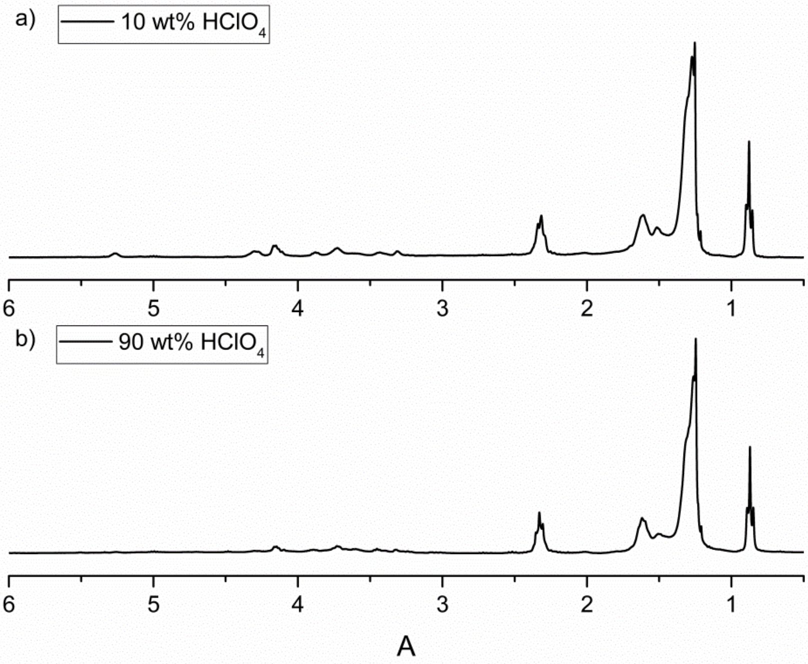


***Figure 40:*** *Exemplary $^1$H NMR spectra of the epoxide ring-opening applying 10 and 30 wt% perchloric acid.*

With these results in hand, the concentration of **16** was varied applying 30 wt% perchloric acid. Although an increasing amount of the nucleophile water should prevent oligomerization, it resulted in incomplete conversion of epoxides after two days, while oligomerization remained constant. Interestingly, $^{1}$H NMR showed a faster reaction of the *anti*-epoxy alcohol illustrated by the disappearance of the corresponding signals. The influence of steric hindrance of the hydroxyl group during ring-opening and the effect of hydrogen bonds between oxirane and neighboring hydroxyl groups on the reactivity of the epoxide have to be investigated. To determine the content of hydroxyl groups, $^{31}$P NMR was measured (preparation of samples is described in Chapter 6.1). *N*-Hydroxy-5-norbornene-2,3-dicarboximide was selected as internal standard due to the signal of its phosphitylated derivative at 151.0 ppm well separated from the triglyceride derivatives ($\delta$ = 145.5 - 147.5 ppm).[610-613] To verify the reliability of measurements, a commercially available, structural related compound, 12-hydroxyoctadecanoic acid, was characterized by $^{31}$P NMR revealing an excellent precision of determined hydroxyl groups. The determination of the hydroxyl group content of the triglyceride-based polyol **17** offered 6.2 hydroxy groups per triglyceride polyol.

Performing the reaction under basic catalysis resulted in degradation of the triglyceride structure and formation of the oleic acid based polyol **18**. Therefore, in a first reaction, the triglyceride-based epoxy alcohol **16** was heated to 85 °C with 1 M sodium hydroxide solution and dioxane (1:1 vol%) overnight. Due to the incomplete conversion of epoxides indicated by $^{1}$H NMR analysis, the reaction was improved by variation of the amount and molarity of the sodium hydroxide solution (Table 7) and extension of the reaction time. Table 7 and Table 8 summarize the results of optimization reactions.

***Table 7:** Variation of the amounts of sodium hydroxide solution and dioxane in the basic epoxide ring-opening.*

| entry | V (1 M NaOH) [ml] | V dioxane [mL] | reaction time [h] | epoxide conversion [%] |
|---|---|---|---|---|
| **1** | 4.5 | 4.5 | 24 | 81 |
| **2** | 6 | 6 | 24 | 81 |
| **3** | 9 | 9 | 24 | 79 |
| **4** | 9 | 5 | 24 | 92 |
| **5** | 12 | 5 | 24 | 92 |
| **6** | 15 | 5 | 24 | 92 |
| **7** | 15 | 4.5 | 48 | 97 |
| **8** | 15 | 4.5 | 72 | 97 |

*all reactions were performed with 0.5 g epoxidized triglyceride

***Table 8:** Variation of the molarity of sodium hydroxide solution and amount of dioxane in the basic epoxide ring-opening.*

| entry | V (2.5 M NaOH) [mL] | V dioxane [mL] | reaction time [h] | epoxide conversion [%] |
|---|---|---|---|---|
| **1** | 15 | 4.5 | 24 | 87 |
| **2** | 15 | 2 | 24 | 89 |
| **3** | 15 | 0 | 24 | 88 |

*all reactions were performed with 0.5 g epoxidized triglyceride

Application of the same volume percentage of sodium hydroxide solution and dioxane offered similar conversions of the epoxide (Table 7, entry 1 – 3). Increased conversion could be obtained with a higher amount of sodium hydroxide solution compared to the amount of dioxane (Table 7, entry 4 – 6). A higher molarity of the sodium hydroxide solution did not improve the conversion (Table 8). Best results could be obtained with an elongated reaction time of two days, however full conversion could not be obtained even after three days (Table 7, entry 7, 8). Similar to acidic epoxide ring-opening, oligomerization occurred in all reactions. SEC measurements for the entries with two and three days reaction time, for example, showed a molecular weight of 1100 g/mol and a dispersity index of 1.1 (Table 7, entry 7, 8).

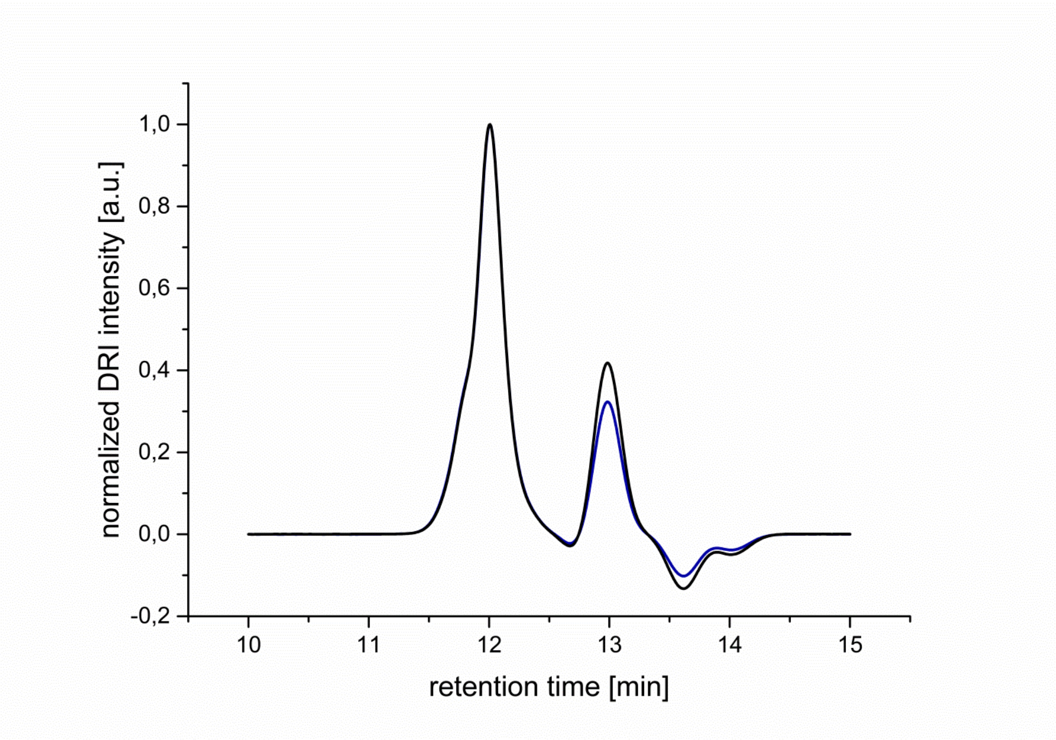


***Figure 41:*** *SEC traces of basic epoxide ring-opening after two and three days according to Table 7, entry 7 and 8.*

To determine the content of hydroxy groups, $^{31}$P NMR has to be measured as described before.

## CONCLUSION

The photochemical Schenck-Ene reaction was successfully applied in the synthesis of allyl hydroperoxides based on high oleic oil and *in situ* reacted to the corresponding epoxy alcohols catalyzed by titanium(IV) isopropoxide. The reaction could be scaled up to 150 grams, while providing full conversion within nine hours. Optimization showed the necessity of dichloromethane as solvent due to the dramatically decreased lifetime of singlet oxygen in other solvents. Catalyst screening revealed 0.01 mol% TPP and 3 mol% $Ti(O\textit{i}Pr)_4$ as sufficient to complete the transformation to epoxy alcohols. Acidic epoxide ring-opening was performed with perchloric acid and improved to avoid degradation of the triglyceride structure. Finally, a triglyceride-based polyol **17** with 6.2 hydroxyl groups per molecule were obtained determined by $^{31}P$ NMR. The basic epoxide ring-opening was optimized to 97 % conversion.

## 4.4 Selective Formation of $C_{36}$-Dimer Fatty Acids *via* Thiol-Ene Addition for Copolyamide Synthesis

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### Abstract

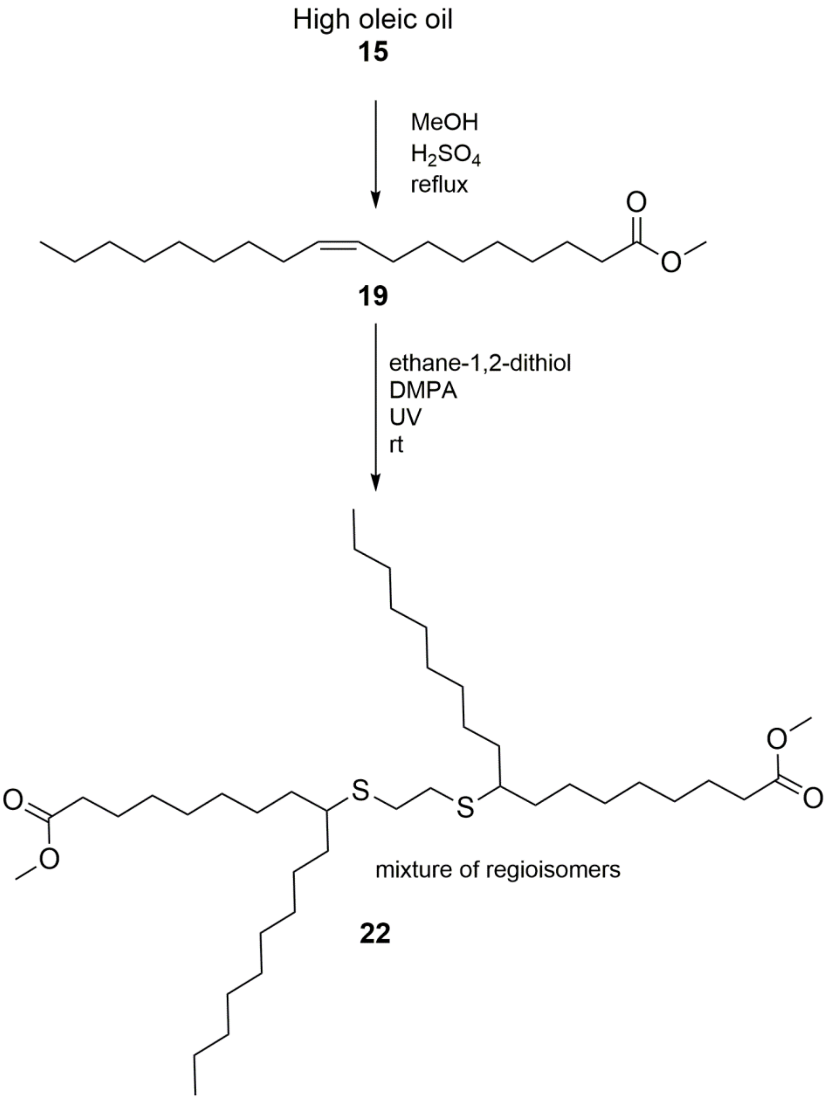
Dimer fatty acids demonstrate interesting raw materials for the synthesis of polyamides and polyurethanes. The industrially well-established procedure of dimerizing polyunsaturated fatty acids yields a mixture of monomer, dimer and trimer structures, requiring the isolation of the pure dimer fatty acid. Within this study, the selective synthesis of $C_{36}$ – dimer fatty acids derived from oleic acid is shown by simple thiol-ene addition of ethane-1,2-dithiol. Subsequently, the dimer fatty acid is used as comonomer for copolyamide synthesis in

different ratios with hexamethylenediamine and dimethyl adipate. Experiments of water uptake and release are presented for these copolyamides showing improved properties compared to conventional polyamides.

# INTRODUCTION

Dimer fatty acids (DFA), in general, are dicarboxylic acids prepared by intermolecular reaction of unsaturated fatty acids or their esters.[614] In industry, tall oil - a mixture of $C_{18}$ fatty acids such as oleic acid and linoleic acid - is mainly used as raw material, resulting in a mixture of dimer fatty acids consisting of 36 carbon atoms. Emery Industries established the first large-scale procedure for the synthesis of dimer acids proceeding by heating tall oil to 275-325 °C. The dark color of the product, the low yield, as well as decarboxylation side reactions due to the high temperature resulted in the quest for more selective methods.[615] Commercially available from several manufacturers, dimer fatty acids have been synthesized by clay-catalyzed dimerization at 230-250 °C since the 1950s. However, due to the complex reaction mechanism, mainly proceeding *via* isomerization followed by a Diels-Alder reaction, the obtained product is a mixture of monomer, dimer, trimer as well as linear, cyclic, and aromatic structures. In mechanistic studies, the rearrangement of dimer structures to aromatic and polycyclic structures as a function of reaction time was established. Nevertheless, the exact mechanism could not be described, but a combination of isomerization, conjugation, Diels-Alder cycloaddition and hydration/dehydration reactions is widely accepted.[615] After dimerization, the content of the desired dimer fatty acid can be increased to over 95% by thorough distillation. The obtained products exhibit high boiling points and are mostly clear to dark brown and viscous liquids. Solids are rarely observed due to the diversity of possible structures preventing crystallization.[616] In fact, the long carbon chain provide the dimer acids with high flexibility, distinctive hydrophobicity and hydrolysis stability; in case of hydrogenated dimer fatty acids also oxidative stability.[617] The largest key market for dimer fatty acids is the production of polyamides divided in reactive and non-reactive polyamides.[614] The reaction with diamines results in the formation of non-reactive polyamides used for hot melt adhesives and printing inks.[618-620] On the other hand, reactive polyamides are formed by the reaction of dimer fatty acids and polyamines. Secondary amine groups within the backbone can link with other functional groups and are useful as curing agent in epoxy resins as well as surface coatings.[621] The incorporation of dimer fatty acid structures into polymers results in a lower grade of crystallinity and thereby lower melting transition and lower molecular weight for obtained polyamides. Furthermore, the reduction to dimerized fatty alcohols presents another interesting application for the use as building block in polymer synthesis. As long-chain dialcohols, they can be condensed to polyether or polyester polyols used as soft segments in polyurethane formulations. These polyurethanes are characterized by hydrolytic and oxidative stability and resistance against polar or basic solutions.[617, 622] Lubricating oils and corrosion inhibition are two more possible application fields for dimer fatty acids.[623, 624]

Only a few attempts on the defined synthesis of dimer fatty acid have been published so far. Behr *et al*. investigated the influence of metal salts, such as tin dichloride, on the formation of dimer fatty acids, but in this case only more trimer product was formed.[625] In 1995, Nützel and Haslinger published a pathway consisting of four consecutive reactions including a McMurry coupling as key step. Here, column chromatography was necessary for every step.[626] To the best of our knowledge, a two-step procedure is the easiest way to obtain defined dimer acids by now. The combination of hydrobromination of oleic acid followed by nucleophilic substitution with ethane-1,2-dithiol and butan-1,4-dithiol, catalyzed by 1,8-diazabicyclo[5.4.0]undece-7-ene (DBU), was performed to obtain a new bolaform surfactant.[627] The objective of this work thus was to introduce a simple one-pot procedure to obtain a defined dimer fatty acid structure *via* photoinduced thiol-ene linkage of two methyl oleate molecules and ethane-1,2-dithiol. The synthesized dimer fatty acid was subsequently tested in copolymerization with hexamethylenediamine and dimethyl adipate (Scheme 2). The influence of different ratios of dimer fatty acid incorporated into the copolyamide was studied regarding the ability for water uptake and release.



***Scheme 2:*** *Synthesis of the dimer fatty acid starting from methyl oleate.*

## RESULTS AND DISCUSSION

In order to dimerize oleic acid, a UV-initiated (with 2,2-dimethoxy-2-phenylacetophenone, DMPA) thiol-ene addition was chosen. In the first dimerization experiments, we observed that the reaction rate of thiol-ene addition of ethane-1,2-dithiol to oleic acid was much lower, if compared to the one of methyl oleate **19**. Moreover, thermally induced thiol-ene additions using AIBN as radical initiator led to increased reaction time performing the reaction with methyl oleate **19** or oleic acid and furthermore, the complete formation of the dimer could not be obtained. Therefore, all further experiments were carried out with methyl oleate **19** using the UV-initiated protocol. For thiol-ene addition of **19** and ethane-1,2-dithiol, the two starting materials were mixed in different ratios and irradiated with UV-light overnight. First, a stoichiometric ratio of 2:1 was employed that led to an inseparable mixture of mono-reacted and dimerized compounds. Optimization studies comparing different ratios of reactants in the range from 1.85:1 to 2.2:1 revealed that the ratio of 1.9:1 of **19** to ethane-1,2-dithiol yielded the best results. Here, a dimer content of approximately 98% was achieved without further purification (determined *via* SEC measurements in THF; please note that residual DMPA and/or its degradation products remained in the product).

As mentioned above, dimer acids are often used for polymer synthesis. Thus, we prepared polyamides using hexamethylenediamine **20**, dimethyl adipate **21** and dimer fatty acid **22** without further purification in copolymerizations. In order to investigate the influence of dimer fatty acid on the polymer properties, **22** was added in different amounts while keeping a 1:1 ratio of amine to ester functional groups to ensure successful polycondensation. Polymerizations were performed using different well-established catalysts (titanium isopropoxide, tin (II) octoate, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)). Optimization studies showed good results for TBD-catalyzed copolymerization (stepwise addition of TBD simultaneous to temperature increase) in *o*-xylene as solvent to prevent early solidification of the polymers. Table 9 shows molecular weights and thermal data for obtained copolyamides. All polymers exhibit $M_n$ values in the range of 3.9 to 5.2 kDa (relative to poly(methyl methacrylate) (PMMA) standards) and when using a high content of **21**, high melting temperatures of >240 °C were observed. In contrast, a high content of **22** led to amorphous polymers as expected.

***Table 9:** Copolymerization with variable equivalents of dimer fatty acid **22**.*

| polymer | eq. [20] | eq. [21] | eq. [22] | $M_n/M_w/Đ$ | $T_m$ [°C] |
|---|---|---|---|---|---|
| **P25** | 1.00 | 0.90 | 0.10 | 3900/8400/2.1 | 244 |
| **P26** | 1.00 | 0.75 | 0.25 | 4800/10300/2.1 | 240 |
| **P27** | 1.00 | 0.50 | 0.50 | 5200/12400/2.4 | / |
| **P28** | 1.00 | 0.25 | 0.75 | 5200/12300/2.4 | / |
| **P29** | 1.00 | / | 1.00 | 4100/7230/1.8 | 256 |

In order to test if the new dimer acid **22** indeed hydrophobizes the polyamides, water uptake tests were performed using copolyamides with a ratio of dimer fatty acid to dimethyl adipate of 0.90 : 0.10 and 0.75 : 0.25 (see Table 10, entry 1 and 2 ). For comparison, a commercial dimer fatty acid from Sigma-Aldrich was copolymerized in the same way. Table 10 shows the results of water uptake tests of polyamide samples after one night storage in water at two different temperatures.

***Table 10:** Water uptake test of different copolyamides.*

| polymer | remark | water uptake at 25 °C[%] | water uptake at 80 °C [%] |
|---|---|---|---|
| **P25** | 10mol% DFA | 1.8 | 4.1 |
| **P26** | 25mol% DFA | 1.2 | 4.9 |
| **P30** | 10mol% DFA commercial | 4.4 | 5.7 |
| **P31** | Nylon 6,6 commercial | 1.5 | 5.5 |
| **P32** | Nylon 6,6 | 1.7 | 5.1 |

At 25 °C (room temperature), the low water uptake of copolyamides with novel dimer fatty acid **22** was remarkable (Table 10, entries 1 and 2). Here, a higher amount of dimer fatty acid resulted in a lower water uptake due to higher content of hydrophobic monomer units. Compared to these copolyamides, the copolyamide with commercially available dimer fatty acid (Table 10, entry 5) had a significantly higher water uptake for both temperatures. At 80 °C, commercial and synthesized Nylon 6,6 had a higher water uptake than copolyamides with dimer fatty acid **22**. However, this time, the copolyamide with 25 mol% dimer fatty acid had a higher water uptake than the one with 10 mol%. The larger space between polymer chains due to long side chains of dimer fatty acid disrupts the crystalline structure of copolyamides and the higher temperature enables water molecules to enter. After the water uptake experiments, the compression molded polyamide samples were weighed after specific times to analyze the water release. The rapid release of absorbed water by copolyamides with dimer fatty acid must be highlighted (Figure 42). Already after a few hours, copolyamides containing dimer fatty acid **22** released half of the water, whereas Nylon 6,6 only lost approximately 1 % of its water content within 24 hours.

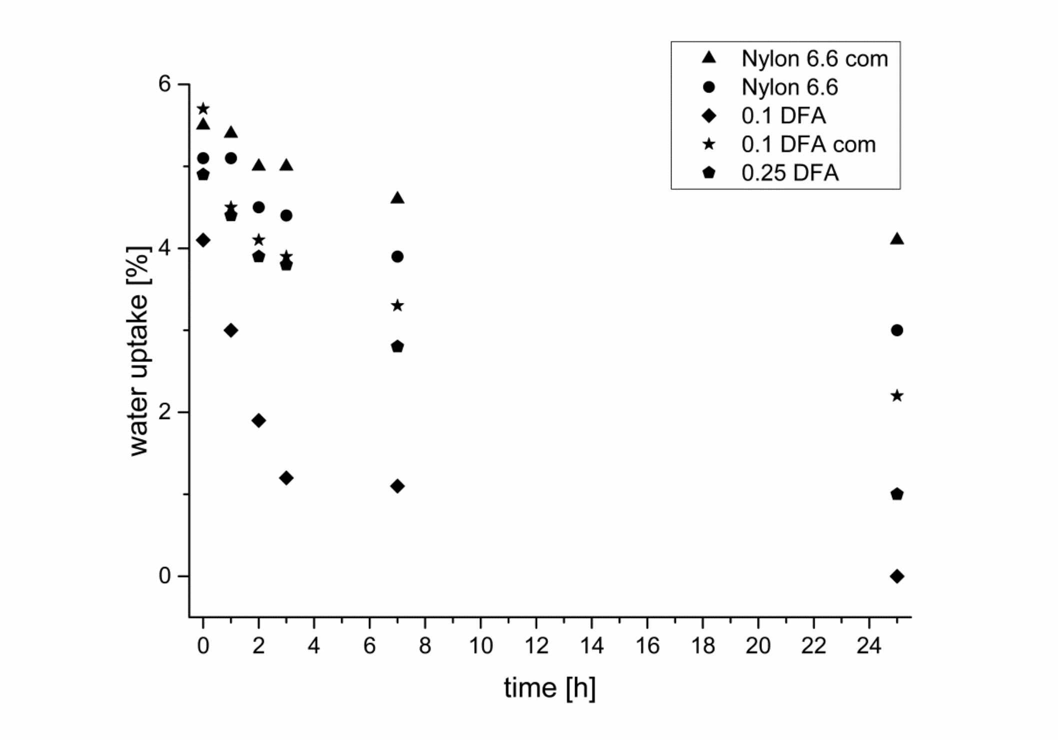


***Figure 42:** Water release of polyamides and copolyamides (soaked at 80 °C) as a function of time.*

## CONCLUSION

In summary, a novel dimer fatty acid was successfully synthesized in a simple UV-induced one-pot procedure based on thiol-ene chemistry. Starting from renewable methyl oleate, $C_{36}$-dimer fatty acid was prepared without the need of time-consuming and thorough work-up procedures versus known laboratory procedures or even methods commonly used in industry. With a content of 98%, dimer fatty acid **22** can directly be used for copolymerization reactions; copolyamides with hexamethylendiamine **20** and dimethyl adipate **21** could thus be established. Compared to water uptake data of Nylon 6,6, the dimer fatty acid showed a lower water uptake due to the long alkyl chain featuring hydrophobicity. Furthermore, a significantly faster release of water can be emphasized not only compared to Nylon 6, 6 but also to commercial dimer fatty acid.

# 5. CONCLUSION AND OUTLOOK

In summary, monomeric as well as polymeric branched structures were successfully synthesized starting from plant oils as renewable feedstock. The conversion of high oleic oil to epoxy alcohols was described applying the photochemical Schenck-Ene reaction. The intermediately formed allyl hydroperoxides were reacted to the corresponding epoxy alcohols catalyzed by titanium(IV) isopropoxide in a one-pot fashion. Till today, this well-known transformation has not been applied for plant oil-based compounds. The following ring-opening of epoxides could be conducted either under acidic catalysis yielding a triglyceride-based polyol with 6.2 hydroxyl groups or base-catalyzed resulting in a fatty acid polyol. Although, oligomerization could not be avoided, the polyols are suitable precursors for the synthesis of polymers, such as polyurethanes (Chapter 4.3). Another approach included thiol-ene coupling of methyl oleate derived from high oleic oil. By simple reaction of methyl oleate and a dithiol under UV-irradiation, the dimer fatty acid was obtained, which was tested in homopolymerization and copolymerized to Nylon 6,6. In copolymers, the dimer fatty acid prevents crystallization yielding in amorphous copolyamides. Due to the long aliphatic and hydrophobic alkyl chain, copolyamides with the dimer fatty acid showed significant lower water uptake and rapid release of the incorporated water compared to Nylon 6,6 and a commercially available dimer fatty acid (Chapter 4.4).

Regarding polymeric branched structures, defined star-shaped polymers with $\alpha,\beta$-unsaturated ester moieties were synthesized *via* ADMET polymerization. Here, castor oil-based 10-undecenyl acrylate was applied as monomer to take advantage of the high head-to-tail-selectivity during ADMET polymerization resulting from the different reactivity of acrylates and olefins in cross-metathesis reactions. The base-catalyzed thia-Michael addition proved to be ideal to functionalize both internal double bonds and terminal acrylate groups without degradation of the polymer. By variation of the thiol, the hydrophilicity of the resulting polymers was influenced by the structure of the thiol. Thereby, a longer alkyl chain of mercaptoalcohols increased the hydrophobicity, whereby two hydroxyl groups in the case of thioglycerol increased the hydrophilicity of the functionalized polymers. For the first time, HPLC was applied to determine the hydrophilicity of polymers expressed by the octanol-water partition coefficient. To further improve the water solubility of star-shaped polymers, a dendron was generated with an amine as focal point able couple to the acrylate groups of the star polymer *via* mild aza-Michael addition. Therefore, diethanolamine was etherified with allyl bromide. The resulting allylic double bonds were further functionalized by photochemical thiol-ene addition. The obtained products were characterized by $^{1}$H NMR and SEC, which indicate narrow molecular weight distribution and polydispersity indices.

In the future, the synthesis of the dendron should be continued. Special attention should be paid to thoroughly characterization of the products to prevent defects in the structure and achieve a high quantity of hydroxyl groups at the surface. The different generations of the dendron should be coupled to the acrylate end groups of the star-shaped polymers to investigate their water solubility. In the case of water soluble star-shaped polymers, dynamic light scattering must be measured to examine the size of micelles. Furthermore, the ability for transport of dyes or drugs should be studied.

On the other hand, the structure of the fatty acid polyol derivative must be analyzed. $^{31}$P NMR will reveal the quantity of hydroxyl groups. Depending on the results further research on epoxide ring-opening could follow. The applicability of the resulting polyols as precursor in polymer synthesis, such as polyurethanes, could be investigated.

# 6. EXPERIMENTAL PART

## 6.1 CHARACTERIZATION METHODS

### NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

NMR spectra were obtained in $CDCl_3$ and recorded with a Bruker AC 300. All $^1H$ NMR spectra are reported in ppm relative to the solvent signal for $CDCl_3$ at 7.26 ppm. All $^{13}C$ NMR are reported in ppm relative to the central line of the triplet for $CDCl_3$ at 77.00 ppm. For the analysis of polymers, the relaxation time (d1) was set to 5 seconds.

For $^{31}P$ NMR a 25 mL stock solution was prepared containing *N*-hydroxy-5-norbornene-2,3-carboxylic acid imide (4 mg $mL^{-1}$) as standard reagent and chromium(III) acetylacetonate (3.6 mg/mL) as relaxation agent dissolved in a mixture of pyridine and $CDCl_3$ (1.6:1 vol%). 28 – 34 mg of the compound to be analyzed was dissolved in 0.5 mL $CDCl_3$ and 150 $\mu$L pyridine followed by addition of 100 $\mu$L 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxophospholane as phosphorylation agent and stirred for 5 minutes. 150 $\mu$L Standard solution was added and stirred again for 5 minutes and transferred to an NMR tube. The measurement was conducted in a Bruker Avance 400. The chemical shifts are reported relative to the reaction product of 2-chloro-4,4,5,5-tetramethyl-1,2-3-dioxophospholane with water at 132.2 ppm. An excess of phosphorylation agent and thus complete conversion of hydroxyl groups was verified by its peak at 174.9 ppm.

### FAST ATOM BOMBARDMENT MASS SPECTROMETRY (FAB)

FAB mass spectra and high resolution mass spectra HRMS were measured with MAT95 of the company Finnigan. The protonated ion was abbreviated with $[M+H]^+$.

### INFRARED SPECTROSCOPY (IR)

Infrared spectra were recorded on a Bruker alpha-p instrument applying KBr- and ATR-technology.

## SIZE EXCLUSION CHROMATOGRAPHY (SEC)

For size exclusion chromatography three different systems were used:

1) Shimadzu LC-20A system equipped with a SIL-20A autosampler, RID-10A refractive index detector in THF (flow rate 1 mL/min) at 50 °C. The analysis was performed on the following column system: main column PSS SDV analytical (5 µm, 300 mm × 8.0 mm, 10000 Å) with a PSS SDV analytical precolumn (5 µm, 50 mm × 8.0 mm). For the calibration narrow linear poly(methyl methacrylate) standards (Polymer Standards Service PPS, Germany) ranging from 1100 to 981000 Da were used;

2) Tosoh EcoSEC HLC-8320 GPC system with hexafluoroisopropanol (HFIP) containing 0.1 wt% potassium trifluoroacetate as solvent. The solvent flow was 0.40 mL/min at 30 °C. The analysis was performed on a 3-column system: PSS PFG Micro precolumn (3.0 × 0.46 cm, 10000 Å), PSS PFG Micro (25.0 × 0.46 cm, 1000 Å) and PSS PFG Micro (25.0 × 0.46 cm, 100 Å). The system was calibrated with linear poly(methyl methacrylate) standards (Polymer Standard Service, $M_\mathrm{p}$ 102–981 000 Da);

3) a PL-GPC 50 Plus integrated system equipped with autosampler, one PLgel 5 µm bead-size column (50 × 7.5 mm), three PLgel 5 µm MixedC columns (300 × 7.5 mm) and a refractive index detector. Dimethylacetamide (DMAc) was used as eluent at a flow rate of 1.0 mL/min at 50°C. The determination of molecular weights was performed relative to PMMA standards (Polymer Standard Services, $M_\mathrm{p}$ 700 – $10^6$ g/mol).

## WATER UPTAKE TEST

For water uptake testing, copolymers were compression molded. Three samples of each polymer were dried overnight in a desiccator and immersed into 10 mL of distilled water for a specific time. Afterwards, the samples were blotted with a tissue to remove surface water and weighed. The water uptake was determined using the following equation:

$$water\ uptake\ [\%] = \frac{Ww - Wi}{Wi} * 100$$

With $W_w$= weight of sample after water uptake

$W_i$ = initial weight

## HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

HPLC measurements were performed using an Agilent HPLC 1200 system equipped with a MZ Refill PerfectSil Target ODS-3 5 µm column (4.0 × 250 mm) and a DAD detector. A mixture of methanol and water (70:30) was used as eluent with a flow rate of maximum 5.0 mL/min and an injection volume of maximum 100 µL.

## DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Melting points were determined by differential scanning calorimetry (DSC). The experiments were carried out under nitrogen atmosphere at a heating rate of 10 and 20 $°C \times min^{-1}$ with a DSC star$^{e}$ (Mettler Toledo) calorimeter starting from -20 °C up to a temperature of 300 °C using 40 µl aluminum crucibles and a sample mass of 4-8 mg. The melting temperature was reported as the minimum of the endothermic peak of the second heating scan unless annealing was used as a pretreatment.

## THIN LAYER CHROMATOGRAPHY (TLC)

All thin layer chromatography experiments were performed on silica gel coated aluminum foil (silica gel 60 F254, Aldrich). Compounds were visualized by staining with Seebach-solution (mixture of phosphomolybdic acid hydrate, cerium(IV)-sulfate, sulfuric acid and water).

## 6.2 MATERIALS

The following chemicals were used as received: 10-undecen-1-ol **1** (99 %, ABCR), acryloyl chloride (≥97 %, Aldrich), triethylamine (99 %, Acros), ethyl vinyl ether (Aldrich), hexylamine (99 %, Acros), [1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxyphenyl-methylene)ruthenium (Hoveyda-Grubbs catalyst 2nd generation) (97 %, Aldrich), 2-mercaptoethanol **5** (>99 %, Sigma Aldrich), 4-mercaptobutanol **6** (99+ %, Acros), methyl thioglycolate **8** (97 %, Fluka), 6-mercaptohexanol **7** (95 %, Acros), thioglycerol **9** (>99 %, Sigma Aldrich), calcium hydride (93 %, Acros), deuterated chloroform ($CDCl_3$, 99.8 %, eurisotop), THF (≥99.9 %, Sigma Aldrich), diethanolamine (≥98 %, Sigma Aldrich), benzyl bromide (98 %, Aldrich), dry THF (99.9 %, Sigma Aldrich), allyl bromide (99 %, Acros), sodium hydride (60 % dispersion in oil, Aldrich), titanium(IV) isopropoxide ($Ti(OiPr)_4$, 97 %, Acros), tetraphenylporphyrin (TPP, 97 %, Acros), *tert*-butanol (99.5 %, Acros), *N*-hydroxy-5-norbornene-2,3-dicarboximide (97 %, Alfa Aeser), pyridine anhydrous (99.8 %, Sigma Aldrich), 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxophospholane (95 %, Sigma Aldrich), perchlorid acid (70 %, ), sodium chloride (Fisher), 12-hydroxyactadecanoic acid (99 %, Aldrich), dimethyl carbonate (99 %, Sigma Aldrich), dimethyl sulfoxide (≥99.9 %, Sigma Aldrich), activated charcoal (8-20 mesh, Sigma Aldrich), chromium acetylacetonate (99.9 %, Aldrich), sodium hydroxide (≥99.9 %, Roth), sodium hydrogencarbonate (Fisher), ethane-1,2-dithiol (>98 %, Fluka), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 97 %, Aldrich), sodium carbonate (>99 %, Sigma Aldrich), sodium sulfate (> 99%, Kraft), 2,2′-azobis(2-methylpropionitrile) (AIBN, 98 %, Fluka), hexamethylenediamine (98 %, Sigma Aldrich), dimethyl adipate (98 %, Sigma Aldrich), *o*-xylene (97 %, Sigma Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98 %, Sigma Aldrich), dimer fatty acid ($M_n$≈570, Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98 %, Aldrich), tin(II) octoate (95 %, Aldrich), sulfuric acid. Hexafluoroisopropanol (HFIP, >99.9%) was purchased from ChemPur. High oleic acid oil was supplied by Solazyme (USA). Di(trimethylolpropane) tetraacrylate **3** and dipentaerythritol hexaacrylate **4** were purified *via* column chromatography. Dichloromethane was distilled from calcium hydride. All other solvents used were of technical grade.

## 6.3 SYNTHETIC PROCEDURES

### 6.3.1 SYNTHETIC PROCEDURES CHAPTER 4.1

#### GENERAL PROCEDURE FOR THE SYNTHESIS OF STAR POLYMERS (**P1** - **4**)

To a 3 mL conical vial (Supelco) equipped with magnetic stir bar, screw cap, and septa, monomer **2** (0.05 g, 0.22 mmol) and the desired core unit, di(trimethylolpropane) tetraacrylate **3** (2.6 mg, $5.5 \times 10^{-3}$ mmol for 10 units per arm; 1.3 mg, $2.8 \times 10^{-3}$ mmol for 20 units per arm) or dipentaerythritol hexaacrylate **4** (2.1 mg, $3.7 \times 10^{-3}$ mmol for 10 units per arm; 1.1 mg, $1.9 \times 10^{-3}$ mmol for 20 units per arm) were added. The mixture was heated to 40 °C while stirring, and then a solution of Hoveyda-Grubbs 2nd generation catalyst (1.5 mol% corresponding to acrylate groups) in 0.1 mL dichloromethane was added in one shot. A needle was placed to allow ethylene to be removed and the mixture was stirred for 3 h at 40 °C. The catalyst was quenched by addition of THF and ethyl vinyl ether. The polymers were purified by precipitation into hexane.

#### DOUBLE BOND FUNCTIONALIZATION BY THIA-MICHAEL ADDITION (**P5** - **24**)

Star polymer (15–20 mg), thiol (10 eq. relative to number of double bonds) and hexylamine (10 mol% relative to thiol) were dissolved in chloroform (0.1–0.2 mL) in a 3 mL conical vial equipped with magnetic stir bar, screw cap and septa and heated to 50 °C. Conversion of the double bonds was followed by $^1$H NMR. The excess of thiol and amine base were removed by vacuum distillation.

## 6.3.2 SYNTHETIC PROCEDURES CHAPTER 4.2

### *N*-BENZYLDIETHANOLAMINE **11**[562]

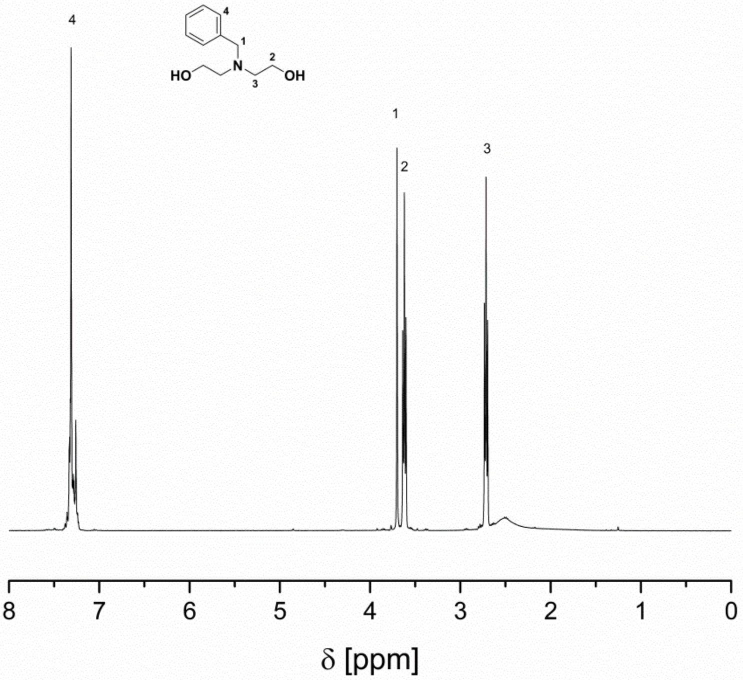
Benzyl bromide (7.14 g, 41.7 mmol, 1.00 eq.) were added to a solution of diethanolamine (4.82 g, 45.9 mmol, 1.10 eq.) and sodium carbonate (4.42 g, 41.7 mmol, 1.00 eq.) in acetone (30 mL). The mixture was stirred for 8 h at 64 °C. The reaction was cooled down to room temperature and water (20 mL) was added after removing acetone. The mixture was extracted with dichloromethane (3 × 20 mL) and the combined organic phase washed with water (3 × 10 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The product was obtained as light-yellowish liquid in a yield of 72 %.

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 7.28 – 7.36 (m, 5 H, $CH^{4}$), 3.70 (s, 2 H, $CH_2{}^{1}$), 3.62 (t, J = 3.62 Hz, 4 H, $CH_2{}^{2}$), 2.72 (t, J = 2.72 Hz, 4 H, $CH_2{}^{3}$).

$^{13}$C NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 138.59, 128.92, 128.29, 127.01 (benzyl), 59.44 ($CH_2{}^{3}$), 58.99 ($CH_2{}^{1}$), 55.65 ($CH_2{}^{2}$).

IR (ATR) $\nu$ = 3346.7, 3025.6, 2943.5, 2875.1, 2815.3, 1600.6, 1493.3, 1450.5, 1405.4, 1364.5, 1140.3, 1025.2, 873.7, 776.3, 731.5, 698.2, 620.7, 475.5 cm$^{-1}$.

FAB of $C_{11}H_{17}NO_2$ ($M+H^+$ = 196.2)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## 1ST *O*-ALLYLATION **12**

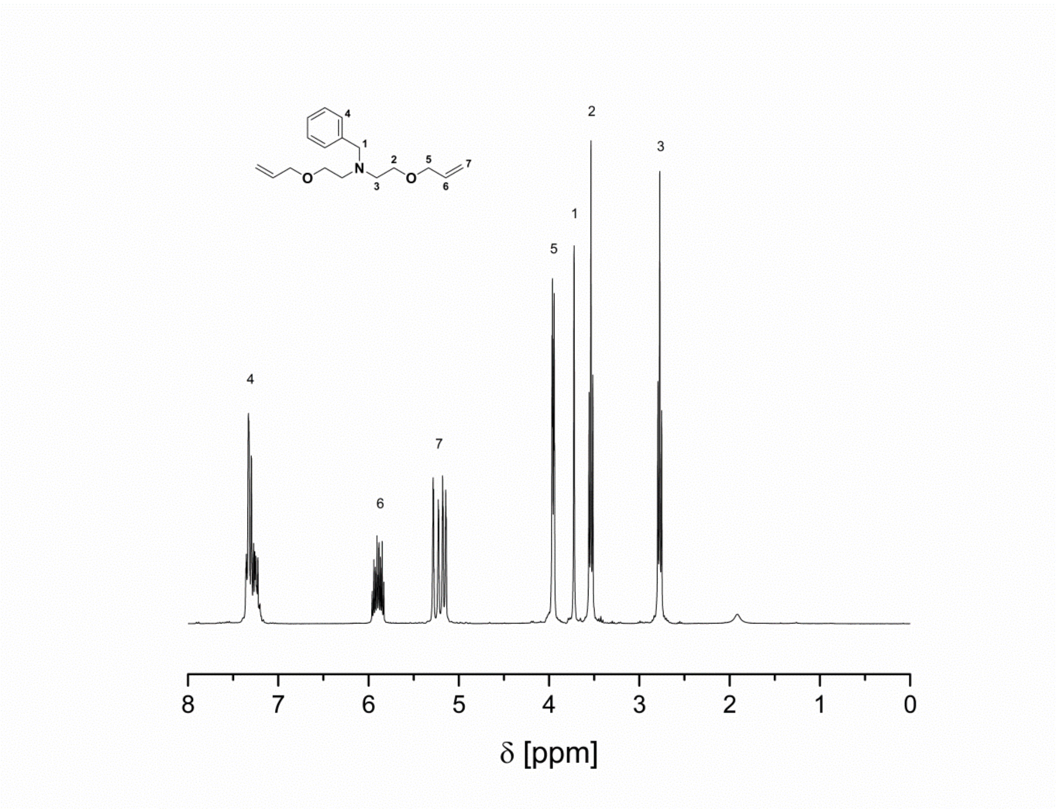
**11** (5.15 g, 26.4 mmol, 1.00 eq.) were cooled under Argon atmosphere in dry THF (23 mL). Sodium hydride (3.40 g, 0.142 mol, 3.00 eq.) were added and stirred for 15 min under cooling. After the addition of allyl bromide (15.96 g, 0.132 mol, 5.00 eq.), dissolved in dry THF (16.5 mL), the reaction was stirred for 8 h. Water was carefully added under cooling to destroy the excess of sodium hydride. The solution was extracted twice with diethyl ether (2 × 40 mL), the organic phase dried over anhydrous sodium sulfate and concentrated under reduced pressure. The product was purified *via* column chromatography (eluent: hexane → ethyl acetate) and obtained as light-brown liquid in a yield of 43 %.

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 7.22 – 7.36 (m, 5 H, $CH^4$), 5.83 – 5.96 (m, 4 H, $CH^6$), 5.28 – 5.14 (dq, *J* = 1.61, 3.28, 17.25 Hz, 8 H, $CH_2{}^7$), 3.95 (dt, *J* = 1.35, 5.55 Hz, 4 H, $CH_2{}^5$), 3.72 (s, 2 H, $CH_2{}^1$), 3.53 (t, J = 6.20 Hz, 4 H, $CH_2{}^2$), 2.72 (t, J = 6.20 Hz, 4 H, $CH_2{}^3$).

$^{13}$C NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 139.64, 134.85, 128.77, 128.08, 126.76, 116.68, 71.92, 68.79, 59.70, 53.80.

IR (ATR) $\nu$ = 3079.7, 3024.0, 2847.7, 1645.1, 1493.3, 1451.1, 1420.0, 1345.2, 1098.9, 1026.7, 989.7, 918.9, 732.5, 697.6, 556.9, 474.8, 422.8, 398.8 cm$^{-1}$.

HRMS-FAB of $C_{17}H_{25}NO_2$: calc. 276.1885, found 276.1956.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## 1<sup>ST</sup> THIOL-ENE **13**

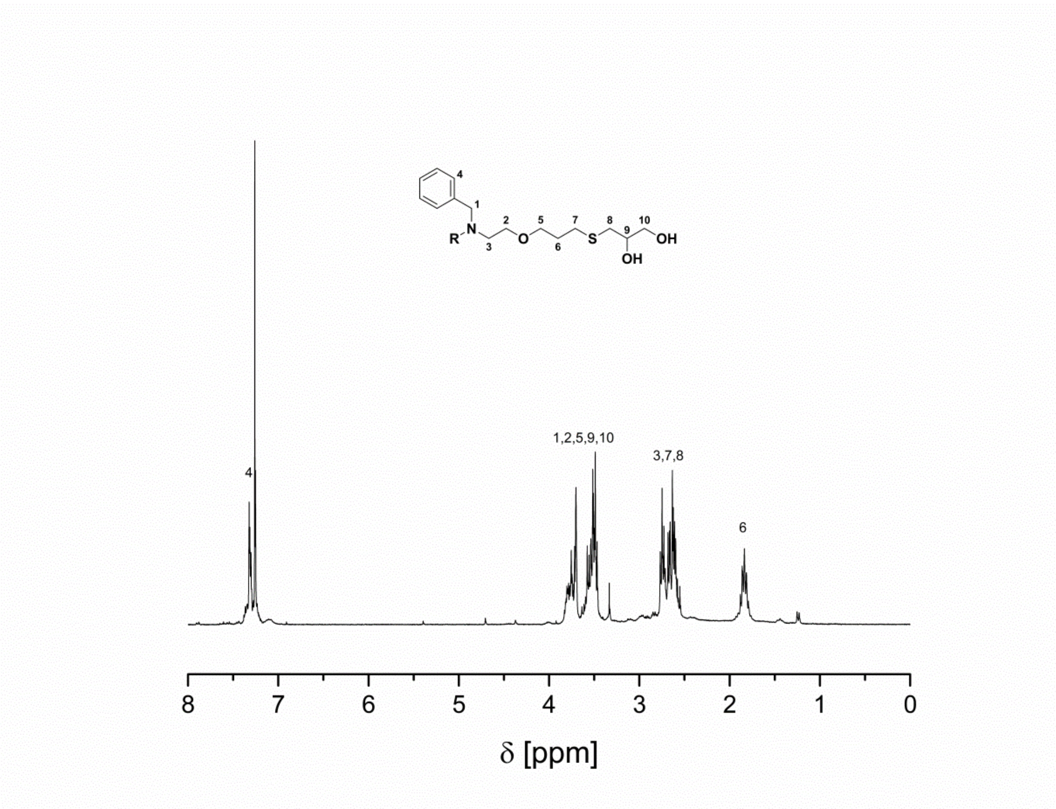
**12** (0.774 g, 2.81 mmol, 1.00 eq.) were mixed with 60 mg 2,2-dimethoxy-2-phenylacetophenone (DMPA) (60 mg, 0.234 mmol, 8 mol%) and thioglycerol **9** (0.49 mL, 5.66 mmol, 2.00 eq.) and 0.5 mL THF. The reaction mixture was stirred under UV-irradiation at room temperature overnight. The solvent was removed under reduced pressure and the mixture was directly converted in the next step.

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 7.20 – 7.36 (m, 5 H, $CH^{4}$), 3.45 – 3.81 (m, 16 H, $CH_2^{1, 2, 5, 9, 10}$), 2.53 – 2.75 (m, 12 H, $CH_2^{7, 8, 3}$), 1.82 (t, J = 6.20 Hz, 4 H, $CH_2^{6}$).

$^{13}$C NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 139.34, 128.84, 128.25, 126.93, 70.35, 69.46, 69.23, 65.30, 59.51, 53.88, 35.58, 29.80, 29.10.

IR (ATR) $\nu$ = 3355.8, 2915.8, 2862.2, 1638.4, 1450.9, 1290.5, 1096.5, 1066.0, 1026.0, 923.6, 88.8, 735.2, 699.3, 623.4 cm$^{-1}$.

HRMS-FAB of $C_{23}H_{41}NO_6S_2$: calc. 491.2375, found 490.2291.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δ [ppm]

## $2^{\mathrm{ND}}$ *O*-ALLYLATION **14**

**13** (0.584 g, 1.18 mmol, 1.00 eq.) were cooled under Argon atmosphere in dry THF (2 mL). Sodium hydride (0.103 g, 4.29 mmol, 6.00 eq.) were added and stirred for 15 min under cooling. After the addition of allyl bromide (1.43 g, 11.8 mol, 10.00 eq.), dissolved in dry THF (1 mL), the reaction was stirred for 8 h. Water was carefully added under cooling to destroy the excess of sodium hydride. The solution was extracted twice with diethyl ether (2 × 5 mL), the organic phase dried over anhydrous sodium sulfate and concentrated under reduced pressure.

$^{13}$C NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 134.43, 132.43, 128.82, 128.12, 126.84, 117.18, 78.83, 72.78, 72.31, 70.83, 69.57 - 69.05, 65.35, 59.70, 53.80.

IR (ATR) $\nu$ = 3405.4, 2915.8, 2856.0, 1640.4, 1493.2, 1451.1, 1421.2, 1349.4, 1267.2, 1104.3, 991.6, 920.2, 734.7, 699.2, 558.9, 410.1 cm$^{-1}$.

HRMS-FAB of $C_{35}H_{57}NO_6S_2$: calc. 651.3627, found 652.3700.

## 6.3.3 SYNTHETIC PROCEDURES CHAPTER 4.3

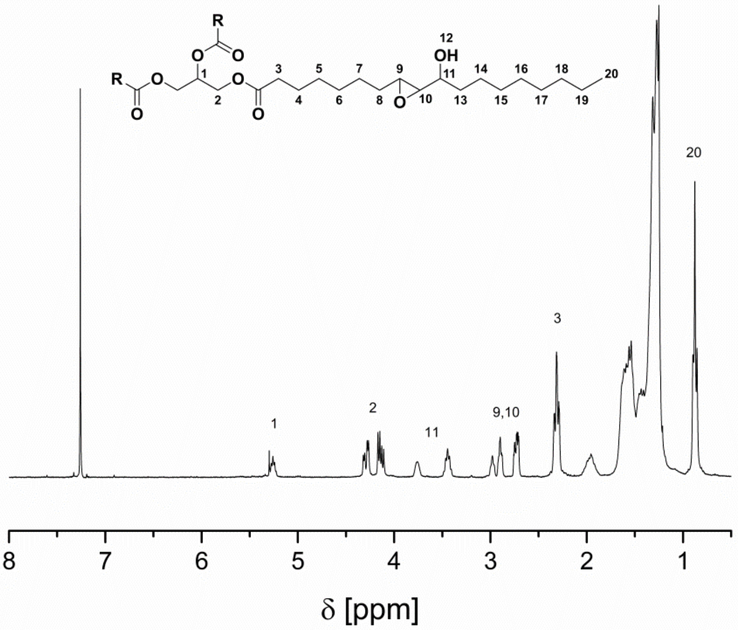
### EPOXY ALCOHOL **16**

In a 450 ml standard immersion-well photochemical reactor with a 400W high pressure sodium vapor lamp, high oleic oil, 0.01 mol%$^*$ tetraphenylporphyrine, 3 mol%$^*$ titanium isopropoxide (Ti(O*i*Pr)$_4$) and dichloromethane (c=1.1 mol/L$^*$) were introduced. Cold water was circulated through the lamp jacket, while a gentle stream of oxygen was bubbled through the stirred mixture. The lamp was turned on and the reaction stirred for 9 hours. An alternativ set-up consisting of round bottom flask next to the lamp and reflux condenser can be used for photoperoxidation. ($^*$relative to double bonds)

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ [ppm] = 5.26 (m, 1 H, CH$^1$), 4.11 – 4.32 (m, 4 H, CH$_2^{2}$), 3.76 (m, 3 H, CH$^{11}$), 3.45 (m, 3 H, CH$^{11}$), 2.72 – 2.98 (m, 6 H, CH$^{9,10}$), 2.31 (td, *J* = 1.52, 7.61, 7.74 Hz, 6 H, CH$_2^{3}$), 1.25 – 1.97 (m, 72 H, CH$_2^{4\text{-}8,\ 13\text{-}19}$), 0.88 (t, *J* = 6.37 Hz, 3 H, CH$_3^{20}$).

$^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ [ppm] = 173.19, 71.25, 68.86, 68.67, 62.05, 61.75, 61.02, 565.91, 56.66, 55.03, 34.34 – 33.43, 31.87 – 31.51, 29.64 – 28.86, 25.97 – 25.75, 25.25, 24.80 – 24.64, 22.60, 21.79, 14.04.

IR (ATR) $\nu$ = 3401.1, 2920.4, 2850.4, 1736.5, 1645.1, 1465.0, 1377.0, 1320.1, 1157.3, 1101.3, 1026.1, 944.2, 886.8, 722.5, 702.0, 576.9, 417.2 cm$^{-1}$.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δ [ppm]

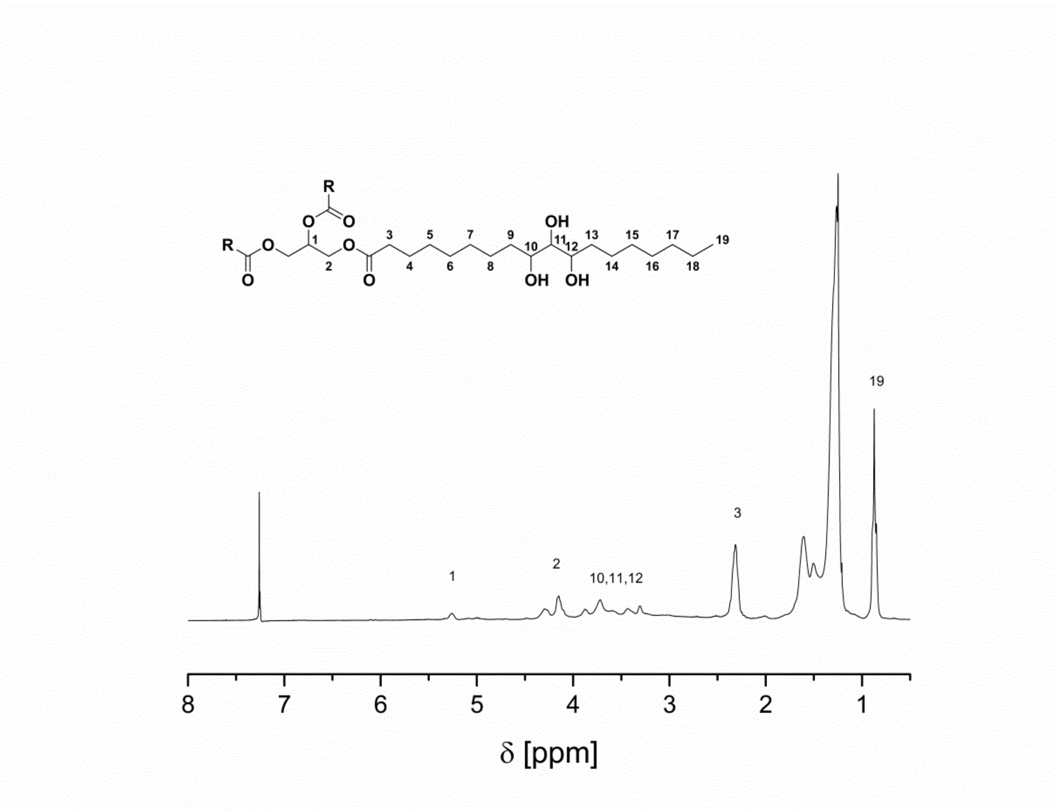
### TRIGLYCERIDE-BASED POLYOL **17**

16 (0.98 g, 1.00 mmol) were heated with water (15 mL) to 100 °C and perchloric acid (0.30 g) were added. The mixture was stirred for two days at 100 °C. The mixture was extracted with chloroform and the organic layer washed twice with water (2 × 15 mL), dried over ahydrous sodium sulfate and concentrated under reduced pressure. The product was obtained as light-yellowish, waxy solid.

$^1$H NMR (300 MHz, $CDCl_3$) $\delta$ [ppm] = 5.27 (1 H, $CH^1$), 4.15 – 4.30 (4 H, $CH_2^{2}$), 3.88 (3 H, $CH^{11}$), 3.72 (3 H, $CH^{11}$), 3.44 – 3.11 (6 H, $CH^{9,10}$), 2.31 (6 H, $CH_2^{3}$), 1.26 – 1.60 (72 H, $CH_2^{4\text{-}8,\ 13\text{-}19}$), 0.87 (3 H, $CH_3^{20}$).

$^{13}$C NMR (300 MHz, $CDCl_3$) $\delta$ [ppm] = 173.35, 74.59, 73.74, 71.01, 68.93, 62.07, 34.14 – 33.59, 31.83, 29.66 – 28.89, 25.99, 25.70 – 25.48, 24.79, 22.60, 14.04.

IR (ATR) $\nu$ = 3342.0, 2919.2, 2850.4, 1738.0, 1464.0, 1377.0, 1168.0, 1065.6, 722.4, 590.7 cm$^{-1}$.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δ [ppm]

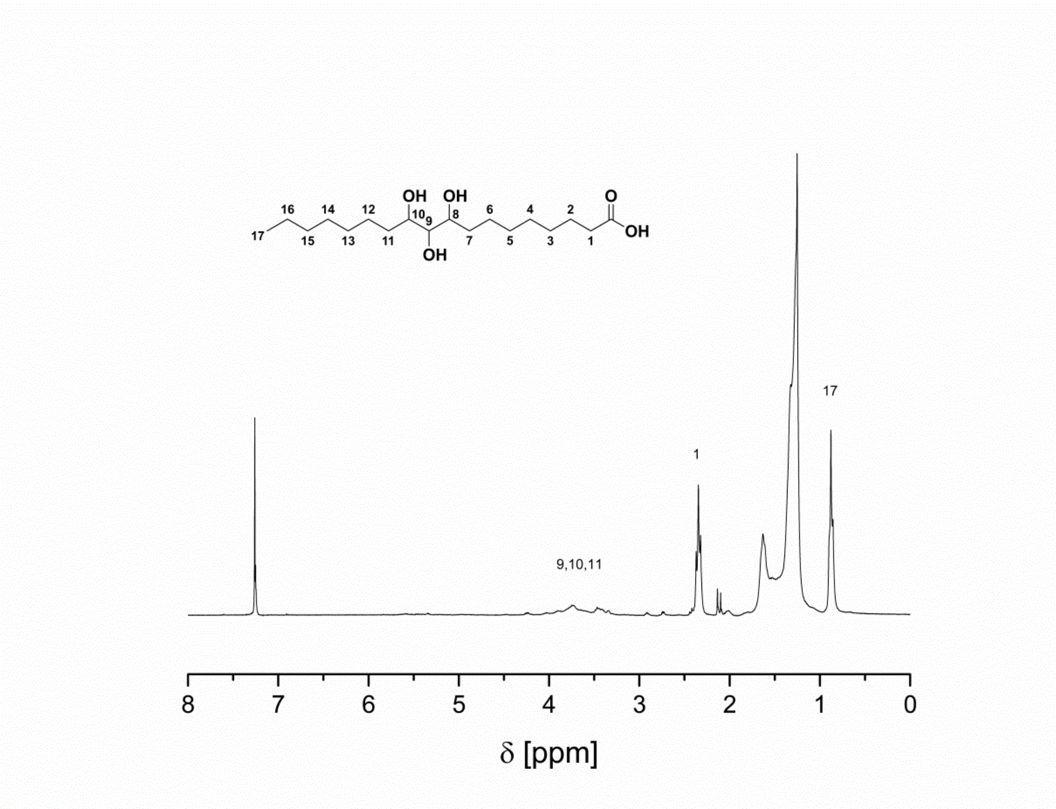
### FATTY ACID TRIOL **18**

Epoxy alcohol (0.521 g, 0.53 mmol), 1M sodium hydroxide solution (15 ml) and dioxane (4.5 ml) were mixed and heated to 85 °C for 48 hours. Dioxane was removed under reduced pressure, the residue was acidified with 1M HCl, extracted with ethyl acetate for two times and washed two times with water to remove glycerol. Afterwards, the organic phase is stirred with sodium sulfate (to remove water) and activated charcoal to remove the coloured catalyst. The product was obtained as off-white waxy solid in a yield of 67 %.

$^1$H NMR (300 MHz, $CDCl_3$) $\delta$ [ppm] = 4.22 – 3.33 (3 H, $CH^{8, 9, 10}$), 2.35 (t, J = 7.36 Hz, 3 H, $CH_2^{1}$), 1.61 – 1.25 (m, $CH_2^{2-7, 11-16}$), 0.87 (t, $CH_2^{17}$).

$^{13}$C NMR (300 MHz, $CDCl_3$) $\delta$ [ppm] = 179.20, 71.43, 68.61, 67.00, 61.12, 33,89, 31.89 – 31.57, 29.65 – 28.83, 25.97, 24.52, 14.06.

IR (ATR) $\nu$ = 2920.9, 2851.7, 1707.1, 1590.0, 1503.6, 1462.2, 1416.8, 1326.8, 1221.3, 1120.4, 1068.8, 722.0, 529.1 cm$^{-1}$.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## 6.3.4 SYNTHETIC PROCEDURES CHAPTER 4.4

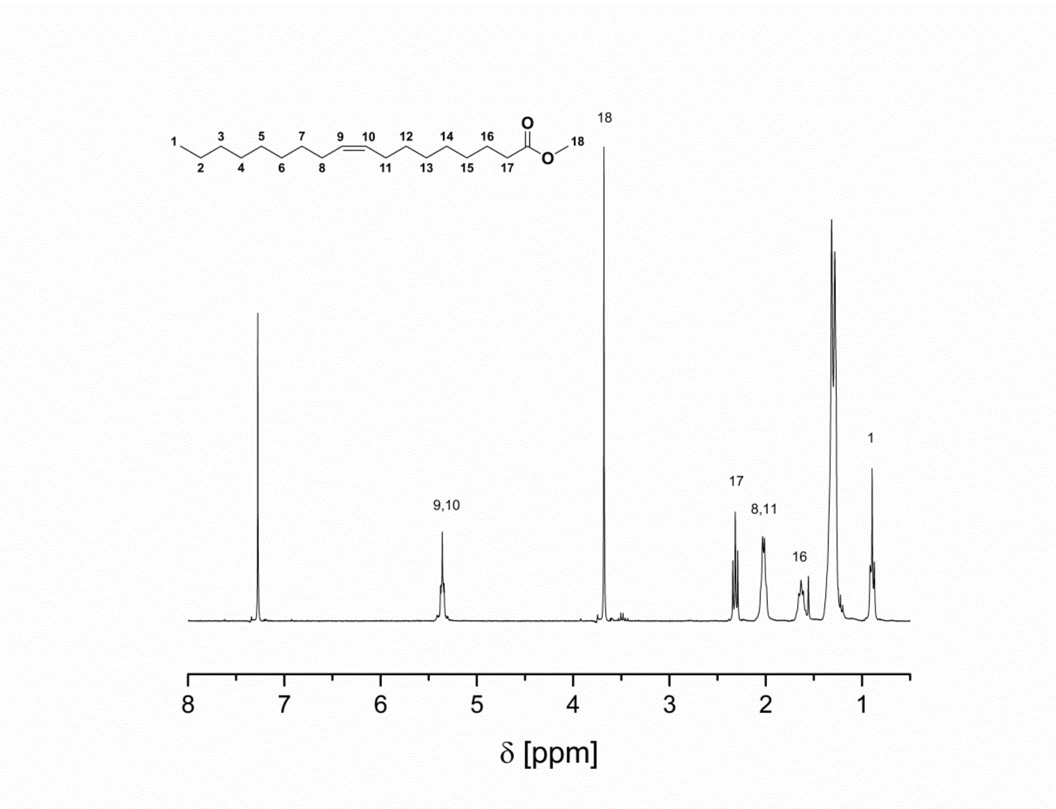
### METHYL OLEATE **19**

Triglyceride of oleic acid **15**, an excess of methanol and catalytic amounts of sulfuric acid (some drops) were mixed and refluxed overnight. The reaction mixture was diluted with diethyl ether and washed with water, sodium carbonate solution and water. The organic fraction was dried over anhydrous sodium sulfate, filtered and the solvent was removed under reduced pressure. Methyl oleate **19** was obtained as yellowish liquid in quantitative yield.

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 5.36–5.32 (m, 2 H, $CH^{9,10}$), 3.66 (s, 3 H, $CH_3{}^{18}$), 2.30 (t, *J* = 7.54 Hz, 2 H, $CH_2{}^{17}$), 2.04–1.97 (m, 4 H, $CH_2{}^{8,11}$), 1.66–1.57 (m, 2 H, $CH_2{}^{16}$), 1.37–1.24 (m, 20 H, $CH_2{}^{2\text{-}7,12\text{-}15}$), 0.87 (t, *J* = 6.64 Hz, 3 H, $CH_3{}^{1}$).

$^{13}$C NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 173.91, 129.81, 129.56 ($CH_2{}^{9,10}$), 51.31 ($CH_3{}^{18}$), 34.09 ($CH_2{}^{17}$), 31.90 ($CH_2{}^{3}$), 29.76 – 29.09 ($CH_2{}^{4\text{-}7,12\text{-}15}$), 24.96 ($CH_2{}^{16}$), 22.70 ($CH_2{}^{2}$).

FAB of $C_{19}H_{36}O_2$ ($M+H^+ = 297.3$).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### DIMETHYL 9,9'-(ETHANE-1,2-DIYLBIS(SULFANEDIYL))DISTEARATE **22**

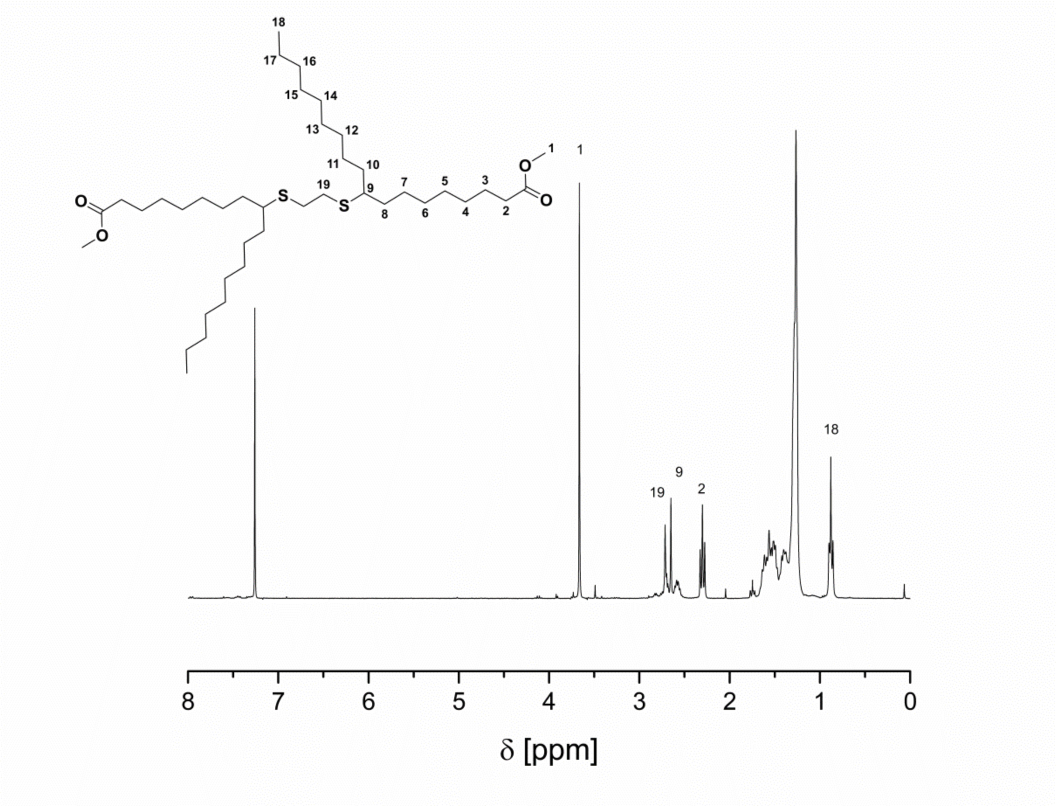
Methyl oleate **19** and ethane-1,2-dithiol were mixed in a 1.9:1 ratio. 2.00 wt% DMPA was added and the mixture in a round-bottom flask irradiated with two UV-lamps (λ = 345 nm, 2 × 4 W) overnight. The yellow mixture was used without further purification.

$^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 3.66 (s, 6 H, $CH_3^{1}$), 2.65 (s, $CH_2^{19}$), 2.58 (m, $CH^{9}$), 2.30 (t, $J$ = 7.52 Hz, $CH_2^{2}$), 1.61–1.26 (m, $CH_2^{3\text{-}8,\ 10\text{-}17}$), 0.88 (t, $J$ = 6.55 Hz, $CH_3^{18}$).

$^{13}$C NMR ($CDCl_3$, 300 MHz) $\delta$ [ppm] = 174.19, 51.36 ($CH_3^{1}$), 46.09 ($CH^{9}$), 34.88, 34.59, 34.02 ($CH_2^{2}$, $CH_2^{8,10}$), 31.83 ($CH_2^{16}$), 29.60 - 29.03 ($CH_2^{4\text{-}7,11\text{-}15}$), 24.87 ($CH_2^{3}$), 22.62 (2 $CH_2^{17}$), 14.05 ($CH_3^{18}$).

FAB of $C_{40}H_{78}O_4S_2$ ($M+H^+$ = 687.6).

$T_m$ (DSC) = 0 °C.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### GENERAL PROCEDURE FOR POLYMERIZATION

For polymerizations, hexamethylenediamine **20**, dimethyl adipate **21** and dimer fatty acid **22** were weighed into a carousel tube. *o*-Xylene was added and the mixture heated to 100 °C. One third of the amount of needed TBD (total amount of 10 mol% relative to ester groups) was added and the mixture stirred for two hours. The mixture was heated to 120 °C and another third of the catalyst was added. After two hours, the mixture was heated to 145 °C and the last third of the catalyst was added. The reaction was stirred overnight. Meanwhile, the mixture solidified and high vacuum was applied to remove residues of solvent and released methanol. The polymer was dissolved in hexafluoroisopropanol and precipitated into cold methanol. Typical polymerizations were performed in a 1.5 g scale with 2 mL of *o*-xylene. The copolyamides **P25** - **29** were obtained as solids with sandy color.

# 7. ABBREVIATIONS

| | |
|---|---|
| ADMET | acyclic diene metathesis polymerizaion |
| AIBN | 2,2’–azobis(2–methylpropionitrile) |
| ATR | attenuated total reflectance |
| ATRP | atom transfer radical polymerization |
| CCS | core crosslinked stars |
| CM | cross-metathesis |
| CuAAC | Cu(I)-catalyzed azide-alkyne cycloaddition |
| Đ | dispersity index |
| DBU | 1,8-diazabicyclo[5.4.0]undec-7-ene |
| DCM | dichloromethane |
| DES | deep eutectic solvent |
| DFA | dimer fatty acid |
| DMAc | dimethylacetamide |
| DMC | dimethyl carbonate |
| DMPA | 2,2-dimethoxyphenyl-2-acetophenone |
| DSC | differential scanning calorimetry |
| EE | ethyl acetate |
| EWG | electron withdrawing group |
| FAB | fast atom bombardement |
| FAME | fatty acid methyl ester |
| G | generation |
| GPC | gel permeation chromatography |
| h | hour |
| HDPE | high-density polyethylene |
| HFIP | hexafluoroisopropanol |
| HPLC | high pressure liquid chromatography |
| HRMS | high resolution mass spectrometry |
| Hz | Hertz |

| | |
|---|---|
| IR | infrared |
| k | capacity factor |
| LDPE | low-density polyethylene |
| min | minute |
| mL | milliliter |
| $M_\mathrm{n}$ | number average molecular weight |
| mol% | mole percent |
| MS | mass spectrometry |
| NHC | *N*-heterocyclic carbene |
| NMP | nitroxide mediated polymerization |
| NMR | nuclear magnetic resonance |
| P | octanol-water partition coefficient |
| PAMAM | polyamidoamine |
| PEG | poly(ethylene glycol) |
| p$K_\mathrm{a}$ | acid constant |
| PMMA | poly(methyl methacrylate) |
| RAFT | reversible addition–fragmentation chain transfer |
| RCM | ring-closing metathesis |
| ROM | ring-opening metathesis |
| ROMP | ring-opening metathesis polymerization |
| RP-HPLC | reverse phase high pressure liquid chromatography |
| SEC | size exclusion chromatography |
| SHOP | shell higher olefin process |
| SM | self-metathesis |
| $t_0$ | deadtime |
| *t*BuOH | *tert*-butanol |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |
| $T_\mathrm{m}$ | melting point |
| TMDPO | (2,4,6-trimethylbenzoyl)diphenylphosphine |

| | |
|---|---|
| | oxide |
| TPP | tetraphenylporphyrin |
| UV | ultra violet |
| UV-Vis | ultra violet and visible |
| vol% | volume percent |
| wt% | weight percent |
| μL | microliter |

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