Monomers and Polymers from Renewable Resources by straightforward Modification and/or catalytic Processes

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Meinen Eltern

Abstract

The use of renewable resources for the preparation of materials that are used as commodities, but also needed for special applications, is of great interest, especially in times of depleting fossil resources and steadily increasing crude oil prices. Moreover, catalytic processes allowing for the efficient transformation of renewable resources are of great importance for a sustainable production of materials from renewable resources, not only for the chemical industry.

The current thesis describes the synthesis of monomers and polymers from renewable resources by catalytic and/or efficient processes. Fatty acids are used as substrates to produce renewable polyamides, polyesters, and polycarbonates.

A more sustainable Wohl-Ziegler reaction of unsaturated fatty acid methyl esters (FAMEs here methyl oleate and methyl erucate) was developed to prepare allylic brominated FAMEs. In addition, the synthesis of AB-type polyamide monomers was accomplished by a complementary hydrobromination of FAME and subsequent modification. Herein, polyamides with aliphatic side-chains were obtained by polycondensation reaction of the amino-FAME.

Keto-FAMEs were synthesized by co-catalyst-free Wacker oxidations employing oxygen as a sole re-oxidant. The respective keto-FAMEs were transformed to the corresponding amino-FAMEs by reductive amination and then utilized to prepare polyamides with aliphatic side-chains by polycondensation. The co-polymerization of the amino-FAMEs with dimethyl adipate and hexamethylene diamine led to Nylon 6,6 co-polymers with a reduced water-uptake if compared to conventional Nylon 6,6.

Polyamides with a relatively low amide group frequency were prepared from biotechnologically derived ω-hydroxy palmitic acid by straightforward modifications. The material properties of the prepared long-chain polyamides were evaluated and compared to commercially available polyamides.

By cross-metathesis of fatty acid derived benzyl carbamates and subsequent modification, renewable PA 10, PA 11, and PA 14 were obtained. The used fatty acid carbamates were prepared by applying a catalytic Lossen rearrangement procedure.

Epoxides derived from 1,4-cyclohexadiene (CHD), the latter produced from renewable resources *via* self-metathesis of plant oil derivatives, were applied as key substrates in ring-opening co-polymerizations to produce aliphatic polycarbonates and polyesters. Herein, carbon dioxide or phthalic anhydride was used as co-monomer in the polymerization reactions catalyzed by defined metal catalysts.

Moreover, CHD was used to prepare diversely substituted caprolactone monomers, which were applied in controlled ROP to synthesize modified polycaprolactones. Here, an efficient reaction sequence of thia-Michael addition and Baeyer-Villiger oxidation was used for the monomer synthesis.

Zusammenfassung

In Zeiten von steigenden Rohölpreisen und einer absehbaren Verknappung fossiler Ressourcen ist die Verwendung nachwachsender Rohstoffe zur Herstellung von verschiedenster Materialien für den täglichen Gebrauch, aber auch für spezielle Anwendungen, von großer Bedeutung. Für die nachhaltige Herstellung von Materialien aus nachwachsenden Rohstoffen haben insbesondere katalytische Prozesse eine essentielle Bedeutung, um eine effiziente Nutzung der eingesetzten Rohstoffe zu ermöglichen. In dieser Doktorarbeit wird die Synthese von Monomeren und Polymeren aus nachwachsenden Rohstoffen durch katalytische und/oder effizienten Prozessen beschrieben. Für die Synthese verschiedenster Polyamide, Polyester und Polycarbonate wurden Fettsäuren als Ausgangsverbindungen verwendet.

Durch eine optimierte Wohl-Ziegler Bromierung von ungesättigten Fettsäure-methylestern, genauer Methyloleat und –erucat, konnten Fettsäureesterbromide erhalten werden. AB-Polyamidmonomere wurden mittels Hydrobromierung und anschließender Aminierung der erhaltenen bromierten Fettsäuremethylester synthetisiert, sodass durch Polykondensation Polyamide mit aliphatischen Seitenketten erhalten werden konnten.

Die Darstellung von Ketofettsäuren erfolgte durch eine cokatalysatorfreie Variante der Wacker Oxidation, wobei Sauerstoff als alleiniger Reoxidant eingesetzt wurde. Nach anschließender reduktiver Aminierung der Ketofettsäureester, konnten Aminofettsäureester erhalten werden, welche erfolgreich für die Synthese von Polyamiden aus nachwachsenden Rohstoffen verwendet wurden. Die darüber hinaus hergestellten Nylon 6,6 Copolymere aus Dimethyladipat, Hexamethylendiamin und dem entsprechenden Aminofettsäureester zeigten eine geringere Wasseraufnahme als konventionelles Nylon 6,6.

Polyamide mit einer vergleichsweisen niedrigen Amidgruppenfrequenz, d.h. langen aliphatischen Kettensegmenten zwischen den Amidbindungen, wurden ausgehend von der in einem biotechnologischen Prozess gewonnenen ω-Hydroxypalmitinsäure synthetisiert. Die erhaltenen langkettigen Polyamide wurden bezüglich ihrer mechanischen Materialeigenschaften näher untersucht und mit konventionellen Polyamiden verglichen. AB-Monomere zur Herstellung von PA 10, PA 11 und PA 14 wurden aus nachwachsenden Rohstoffen durch Kreuzmetathese von

fettsäurebasierenden Benzylcarbamaten erhalten. Die entsprechenden Benzylcarbamate wurden dabei durch eine katalytische Lossen-Umlagerung von Fettsäure basierenden Hydroxamsäuren hergestellt.

Die Ringöffnungs-Copolymerisation von Epoxiden aus nachwachsenden Rohstoffen wurde erfolgreich für die Synthese von Polyestern und Polycarbonaten angewandt. 1,4-Cyclohexadien, ein Produkt der Selbstmetathese von mehrfach ungesättigten Fettsäuren oder Pflanzenölen, wurde dabei als Substrat zur Synthese von verschiedenen Epoxiden verwendet und mit Kohlenstoffdioxid oder Phthalsäureanhydrid als Co-Monomer in einer metallkatalysierten Polymerisation umgesetzt.

Des Weiteren konnte 1,4-Cyclohexadien zur Synthese von unterschiedlich substituierten ε-Caprolacton Monomeren verwendet werden, wobei durch Ringöffnungspolymerisation modifizierte Poly-ε-caprolactone erhalten wurden. Dabei konnten die entsprechenden ε-Caprolacton Monomere sehr effizient und einfach mittels einer Reaktionssequenz aus Thia-Michael Addition und Baeyer-Villiger Oxidation hergestellt werden.

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1. Introduction

Now, being at the beginning of the 21st century, the world population exceeded 7 billion people.[1] It is estimated that the world population will significantly grow further in the next 30 - 40 years.[2] This massive increase in population will lead to some serious problems such as shortages of energy, resources, and food supply. Besides, we will also have to find a solution to avoid an increased environmental pollution, which will be likely due to the population growth and enhanced living standards.

A further problem is the depletion of fossil resources. Crude oil as base for energy supply and fabrication of daily life commodities will become much more expensive and will furthermore deplete soon. Still, there is an ongoing discussion about oil reserves and the maximum production capacities of crude oil extraction. However, most experts confirm that the so called "peak oil" will be reached before 2020.[3, 4] The fact that the global crude oil production reaches its maximium (“peak”) will be accompanied by significant price increases and supply bottlenecks.

Apart from this, one fact should be indisputable: fossil energy resources are not inexhaustible. Considering the cxontinous economic growth of developing countries and contemplating the unchanged mindset towards energy consumption, fossil resources will be depleted sooner or later. Extensive research will be necessary to develop new ways for a more sustainable use of the available resources, wherein we as chemist have the obligation to promote this development. The UN World Summit on Sustainable Development in 2002 already declared the sustainable use of biomass as a key factor to spare fossil resources and to counter the greenhouse effect caused by a rising CO_2 pollution.[5] It has to be outlined that the use of biomass for industrial purposes does not necessarily compete with food production for the growing global world population.[6] With regard to a possible industrial usage, it was also shown that with current available technologies, biomass could be produced in sufficient quantities.

On the other hand, science and technologies have rapidly developed in the past century, which significantly changed our daily life and made it more comfortable in many ways. Novel technologies, processes, and materials appear to be of crucial importance in solving the aforementioned future problems caused by the massive

population growth and depleting fossil resources. Herein, a significant progress in the past century was achieved through the mass production of synthetic polymer materials for nearly every imaginable application. One milestone was the invention and industrial production of Bakelit®, which was used for e.g. phones, plugs, electrical transformers, radios, light switches, covers, or cases. Other polymers such as celluloid, polystyrene, polyvinylchloride, polyethylene, or nylons became important materials for the industrial progress as well. Nowadays, synthetic polymer materials have become important materials and indispensable from our daily life, substituting natural fibers, woods, or natural rubbers in many applications. Plastics are utilized in a great variety of markets, for instance in packaging, building and construction, the automotive sector, or for electronic applications. With a worldwide production of about 288 million tons per year, the fabrication of plastics steadily increased in the past 30 years and will grow further.[7] So far, most of the utilized polymer materials originate from fossil resources; as a consequence, the increase of the polymer production will lead to an increased crude oil consumption. On the other hand, one has to take into consideration that plastic materials offer many advantages compared to conventional materials and therefore are often used to save energy or fossil resources (e.g., as lightweight materials in the automobile or aircraft industry).

Most synthetic polymers are designed to be durable, strong, and cheap - characteristic features that make them to interesting materials. In fact, for many applications the aforementioned properties might be highly desirable, but generate serious problems.[8] Plastic landfill waste or microplastic residues cause serious hazards and an enormous environmental pollution. To solve these very challenging and complex problems on depleting fossil resources and environmental pollution, one key strategy is to recycle the wasted and disposed polymeric materials. Plastic recycling has gained great importance and the utilization of novel technologies allow for an efficient material or chemical recycling. However, the problem of serious plastic pollution cannot be completely solved by recycling since it is not possible to recover all of the used plastics and emerging plastic particles. Hence, the fabrication of biodegradable polymers and the preparation of polymers from renewable resources is of great importance in order to stop the extensive plastic pollution and to enable a more sustainable use of the remaining fossil resources.

1.1. Green Chemistry

The term of Green Chemistry is often used in the discussion of chemical processes or reactions to evaluate their hazardousness, environmental impact, and sustainability.[9] Green chemistry itself is an emerging field that supports the design of reactions and processes in a sustainable and environmental friendly manner. A key criterion of Green Chemistry is sustainability that can be regarded as a responsible behavior that meets the needs of the society without compromising the ability of future generations to meet their own needs.[10, 11] The term sustainability is dating back to the 18th century; here, the term was used in forestry to keep a balance of cutting and growing trees. Nowadays, sustainability is usually categorized into economic, ecologic, and social sustainability. Economic sustainability comprises the maintenance of growth, stability and competitiveness of the current economy. Social sustainability is regarded as preservation of education, health, human rights and personal security for future generations. Green Chemistry is mainly related to ecological sustainability, wherein the use of resources needs to be in balance with their regeneration. Hence, Green Chemistry is often closely linked to the use of renewable resources. Developed by P. Anastas and J. Warner, the twelve principles of Green Chemistry are cohesive guidelines that provide the framework for sustainable reaction and process design (the listed principles of Green Chemistry are adapted from reference 9).

- Prevention:

It is better to prevent waste than to treat or clean up waste after it is formed.

- Atom Economy:

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

- Less Hazardous Chemical Syntheses:

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

- Designing Safer Chemicals:

Chemical products should be designed to meet their desired function while minimizing their toxicity.

- Safer Solvents and Auxiliaries:

The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

- Design for Energy Efficiency:

Energy requirements of chemical processes should be evaluated with regard to their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

- Use of Renewable Feedstocks:

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

- Reduce Derivatives:

Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and generate waste.

- Catalysis:

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

- Design for Degradation

Chemical products should be designed to break down into innocuous degradation products that do not persist in the environment after they have fulfilled theier function.

- Real-time analysis for Pollution Prevention

Analytical methods need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

- Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

It is noteworthy that in the context of Green Chemistry the concept of ‘’design’’ is of crucial importance. Designing of reactions is made with a clear intention and with a systematic conception in order to maximize the reaction efficiency.

The principles of Green Chemistry request the use of non-hazardous solvents, non-toxic chemicals and safe syntheses pathways. The term ‘’hazardous’’ defines the physical (e.g., explosive, flammable), toxicological (e.g., carcinogenic, mutagenic) and global impact (e.g., ozone depletion, climate change). The overall aim is to minimize a possible hazardous impact or exposure of the used chemicals to humans, animals and the environment.

Another principle of Green Chemistry is the prevention of waste. Therefore, processes, in which large portions of the initial substrate are lost or accumulate as waste are unfavorable. A very interesting and easily applicable concept was introduced by R. Sheldon in 1996, which is widely known as Environmental Impact factor (E-factor). The E-Factor is determined as quotient of the mass of the obtained product and mass of generated waste; thus, the obtained values give a relation of how much waste is produced per kilogram of the desired product. The E-factor is a very straightforward and simplified concept that allows a simple evaluation of the reaction efficiency and the environmental impact of the used reaction protocol in an early stage of development.

Table 1-1: Selected E-factors in the chemical industry.[12]

Product	**Production [tons per year]**	**E-factor [kg waste/kg product]**
Bulk chemicals	10^4-10^6	<1-5
Fine chemicals	10^2-10^4	5-50
Pharmaceutical products	10-10^3	25-100

Table 1-1 shows the order of magnitude of the waste problem for the different production sectors of the chemical industry. As expected, for most pharmaceutical

products the E-factor is significantly higher; i.e. the amount of generated waste per kg product increases dramatically with the complexity of the product. In order to design more sustainable processes, the respective reactions can be evaluated according to their E-factors.

1.2. Life cycle assessment (cradle-to-cradle model): A way for the sustainable design of reactions and processes

As briefly discussed in the introduction, polymer materials made our daily life much more comfortable, but also cause some serious problems, such as environmental pollution. To make consumers aware of the environmental impact of the used products and to create an enhanced awareness of sustainability, diverse certification labels were developed (e.g., Blauer Engel, FSC, Energy Star). However, a universal system that allows for a complete evaluation of the environmental impact of products or produced materials is not available yet. In the past years, great efforts have been made to create more detailed assessment models. Herein, the life cycle assessment is an important concept to access the environmental impact of a product at all stages of its 'life' (also often considered as cradle-to-grave concept). Figure 1-1 shows the life cycle assessment at its different stages.[13, 14]

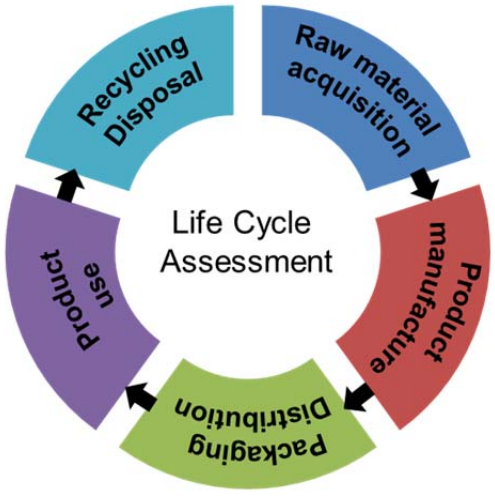

Figure 1-1: The concept of life cycle assessment with the different evaluation stages. [13, 14]

By quantifying all inputs and outputs at the different stages of the product life, the life cycle assessment provides information how to improve processes and how to design an alternative production of the desired product/material.[14]

The product life cycle starts with the raw material acquisition, i.e. the crude oil extraction or tree harvesting including the transportation of these raw materials to the point of processing. The next stage includes the manufacturing of the product, its packaging and the delivery to the consumer. Afterwards, all stages of the actual use of the product are evaluated in each way, including energy consumption or environmental impacts caused by product storage, consumption or usage. The last stage of the life cycle assessment is the waste- or recycle-management of the product, which is no longer used from the consumer and need to be disposed or recycled. This evaluation is mainly related to the quantification of the required energy for the recycling and waste disposal.

An extension of the life cycle assessment concept offers the cradle-to-cradle approach. The cradle-to-cradle concept is a biomimetic approach in order to design products and processes.[14] The cradle-to-cradle approach differentiates between the biosphere and technosphere in order to classify the products in biological nutrients (biodegradable/compostable goods) and technical nutrients (recyclable commodities). The overall aim is to design products, which can be completely regained for the biosphere and technosphere. More detailed, everything that we produce should be returned to either the nature (biosphere) by decomposition or to the technosphere by recycling and reuse of the goods. One key principle is based on the natural ecosystem; here waste = food/nutrient. For instance, in a closed biosphere animal feces or cadaver form food for other species or decompose to nutrients for the soil, which is utilized from plants to have a closed biosphere recycling.

All in all, the life cycle assessment is a very important concept for the future that allows the evaluation of the environmental impact of a processed product or material. In particular, this concept allows for the sustainable and targeted design of processes and materials. Especially, in order to promote a sustainable polymer production such an evaluation is urgently needed since it gives important insights on the production of polymers from renewable resources compared to conventionally produced polymers from fossil resources, as for example evaluated for the production of polyols for the polyurethane production using CO_2 as feedstock.[15]

1.3. Plastics and biodegradability

In the past 50 years, plastics strongly promoted the industrial and technological progress. Nowadays, plastic materials are processed for nearly every imaginable application. The global production of plastics rose to 288 million tons per year in 2012 and a significant growth is expected for the next years due to the industrial progress of developing countries.[7] Most of the produced plastics are used for packaging applications or in the building and construction sector. Non-biodegradable polyethylene (HDPE, LDPE, LLDPE) and polypropylene still form the major share of the produced plastics. So far, polymers were mainly developed and designed as durable materials that withstand environmental influences and have a long life time. Today, plastics are indispensable from our daily life, but their enormous consumption causes some serious problems such as plastic waste accumulation in nature. As exemplified for Europe, approximately 25.7 million tons of plastics waste was generated in 2012 and only 62 % of this plastic waste was used for recovery (recycling or energy recovery); hence, 38 % (= 9.6 million tons) was simply disposed (e.g., landfilled).[7] Therefore, better waste management strategies are urgently needed. In particular, non-degradable microplastics (small plastic particles < 1-5 mm) that are difficult to recycle and accumulate in the environment cause serious pollution.[16, 17]

It is known that hazardous substances such as polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) adsorb at the hydrophobic surface of microplastic particles and accumulate in drinking water.[18] Moreover, small plastic particles are classified as sources of pathogens, which are harmful to human health.[19] In order to prevent an increased environmental pollution, the investigation of biodegradable polymers that have similar material properties and performances as conventional plastic materials has become more important in recent years. Biodegradable plastics are by definition materials, in which all of its organic compounds undergo a complete biodegradation process and the material can be fully converted to water, carbon dioxide and/or methane and new cell biomass.[20] Because of the usually non-water soluble nature of polymers, the biodegradation process is usually of heterogeneous nature. The degradation process itself can be divided in biotic and non-biotic processes. Non-biotic processes include the degradation by sunlight irradiation, oxidative or thermal degradation as well as chemical hydrolysis.

For biotic degradation, the microorganisms first have to depolymerize the plastic materials with the help of excreted extracellular enzymes as polymeric materials cannot be directly metabolized in the cell (Figure 1-2). In this process, the polymer is degraded to low molecular weight and water-soluble intermediates, which can be transported into the microorganisms and further metabolized. As biotic and non-biotic processes usually take place at the same time, the overall process is often regarded as environmental degradation.

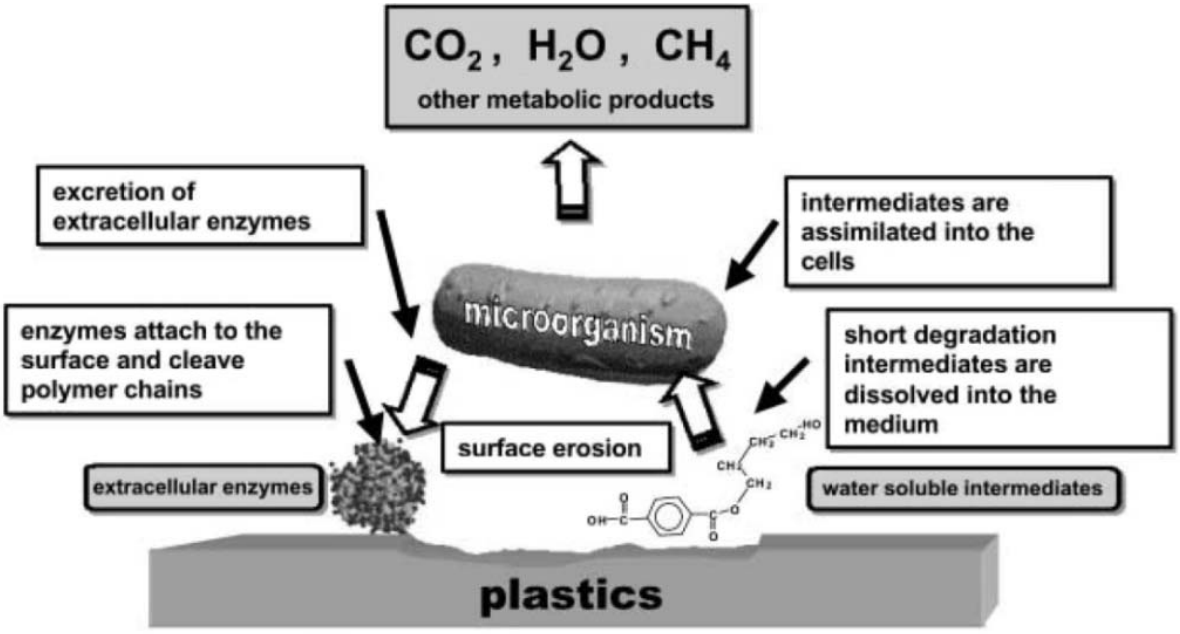

Figure 1-2: Biodegradation process of polymers (figure adapted from R.J. Müller).[20]

All in all, an in-depth understanding of biodegradation processes is important to design biodegradable and tailor-made polymers that are competitive to conventional polymeric materials, and to contribute to stop environmental pollution.

1.4. The use of renewable resources

As discussed in the introduction, the use of renewable resources will be of crucial importance for our future. Fossil resources are going to deplete and the increased CO_2 emission through expanded usage of fossil resources will have dramatic effects on nature. So far, fossil resources (coal, crude oil, gas) are exploited from nature in order to satisfy the needs of our modern society and to make profit until these natural resources are exhausted. Fossil resources are of great importance for the growing

economy, especially the chemical industry is strongly depending on platform chemicals that are based on fossil resources. The diagram shown in Figure 1-3 gives an overview of the used raw materials for the chemical industry in Germany in 2011.[21]

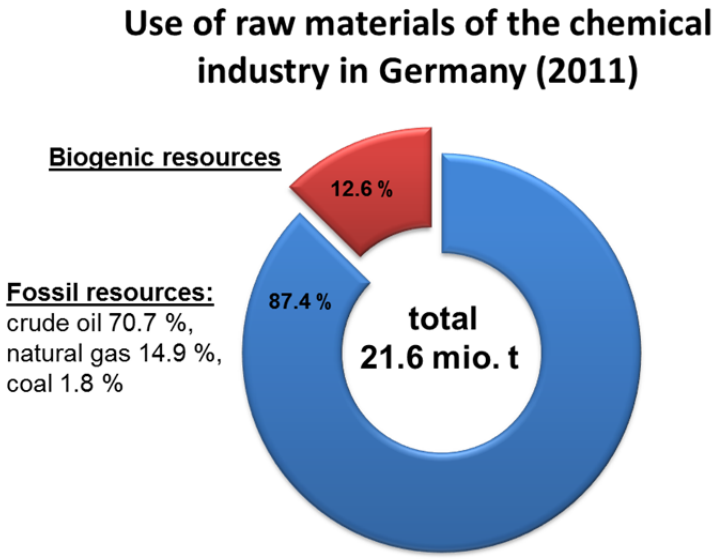

Figure 1-3: Usage of raw materials for the chemical industry in Germany in 2011.[21]

Only 12.6 % of the 21.6 million tons of used raw materials of the German chemical industry are based on renewable resources, whereas fossil resources, in particular crude oil, form the major share.[21] Biogenic resources, generally considered as renewable resources, mainly constitute of agricultural and forestry produced biomass that is not used for food or animal feed. Moreover, residues or waste (e.g., straw, beet leaf, wooden waste, manure) or residual products from bio-refining (e.g. beet pulp or rapeseed press-cake) are considered as biogenic resources as well. It has to be noted that fossil resources are still of great importance for the chemical industry and due to the well-established production lines for processing e.g. crude oil, the most extensively used raw materials will be still derived from fossil resources in the next years. However, although biogenic resources form a minor share of the used raw materials in the chemical industry, it is expected that the utilization of renewable resources will increase significantly in the next decades as the price for fossil resources will rise. From the approximately 2.7 million tons of renewable resources used as raw materials for the chemical industry in Germany, plant oils are still the most intensively utilized resource (see Figure 1-4).[21]

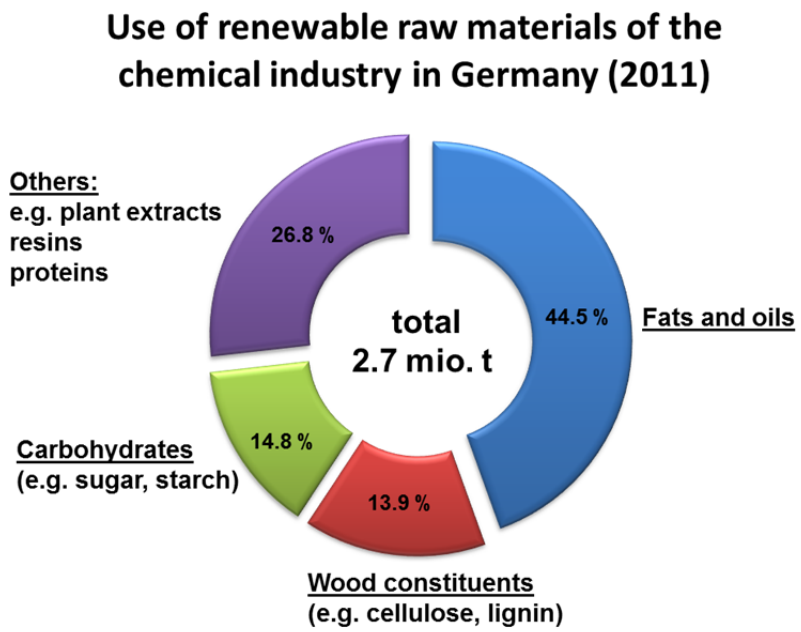

Figure 1-4: Usage of renewable raw materials for the chemical industry in Germany 2011.[21]

On the other hand, carbohydrates and wood constituents such as cellulose or lignin became more important. Herein, novel bio-refining processes allow for a more efficient extraction of the different wood components such as cellulose or lignin, which can be further converted to diverse platform chemicals. The modification of the main components of wood (lignin, hemicellulose and cellulose), which can be converted to high-performance materials, is a growing research field. In this context, ionic liquids proved to be a powerful solvent to enable further derivatization reactions. The large share of fats and oils (44.5 %, Figure 1-4) as renewable raw material for the chemical industry shows the importance of this renewable feedstock.

In general, the depletion of fossil resources and the switch to renewable raw materials is of global interest. However, in case of Germany and other European countries, the use of renewable resources will be of significant importance for the future, mainly due to economic reasons. Currently, 90 % of the fossil and only 65 % of the renewable resources are imported to Germany.[22] Therefore, part of the German economic policy is to become more independent of crude oil extracting countries and to switch to domestic renewable resources.

1.5. Plant oils

As illustrated in Figure 1-4, plant oils are important resources for the German chemical industry. The overall production of plant oils for edible and non-edible use is around 4.6 million tons per year. Table 1-2 gives an overview of the plant oil market and production data for Germany in 2013.[23]

Table 1-2: Market for edible and non-edible plant oils in Germany 2013.[23]

Oil	Production [kt]	Import [kt]	Export [kt]
Rapeseed	3780	189	1165
Soya	630	105	322
Sunflower	138	263	124
Others	69	2044	394
Total	4617	2601[a]	2005[a]

[a]Mainly for edible use

Rapeseed, soya and sunflower oil are the major share of produced plant oils in Germany, whereas most imports and exports are based on the trade of edible plant oils. Nevertheless, about 26 % of the produced plant oils in Germany are used for the chemical industry, whereas rapeseed oil is the most extensively used plant oil.

Chemically, plant oils are triglycerides of fatty acids, whereas plant oils usually contain a mixture of different fatty acids. Figure 1-5 illustrates a typical bio-refinery concept of a conventional plant oil (e.g., rapeseed or sunflower oil) in order to obtain different products (biodiesel, diverse fine chemicals, or lubricants).[22] The first step is the extraction of the rapeseeds by pressing and extraction with an appropriate solvent. The residues from this process, for instance the rapeseed press-cake, are often used as an animal feed due to a high protein content. In chemical and physical processes, the crude rapeseed oil is further purified. The refined rapeseed oil is then utilized in transesterification reactions or for hydrolysis. The latter yields different fatty acids as well as glycerol, which are separated by phase separation. The obtained glycerol can be further used as substrate to produce diverse fine-chemicals, such as triacetine or 1,3-propanediol.[24] For instance the 1,3-propanediol, a monomer for the synthesis of polyesters, is prepared by a biotechnological process involving immobilized microorganisms.[24] Lubricants are obtained by esterification of the fatty

acids with alcohols.[25, 26] Moreover, the direct transesterification of the refined rape oil with methanol is used to generate biodiesel as renewable biofuel.[26]

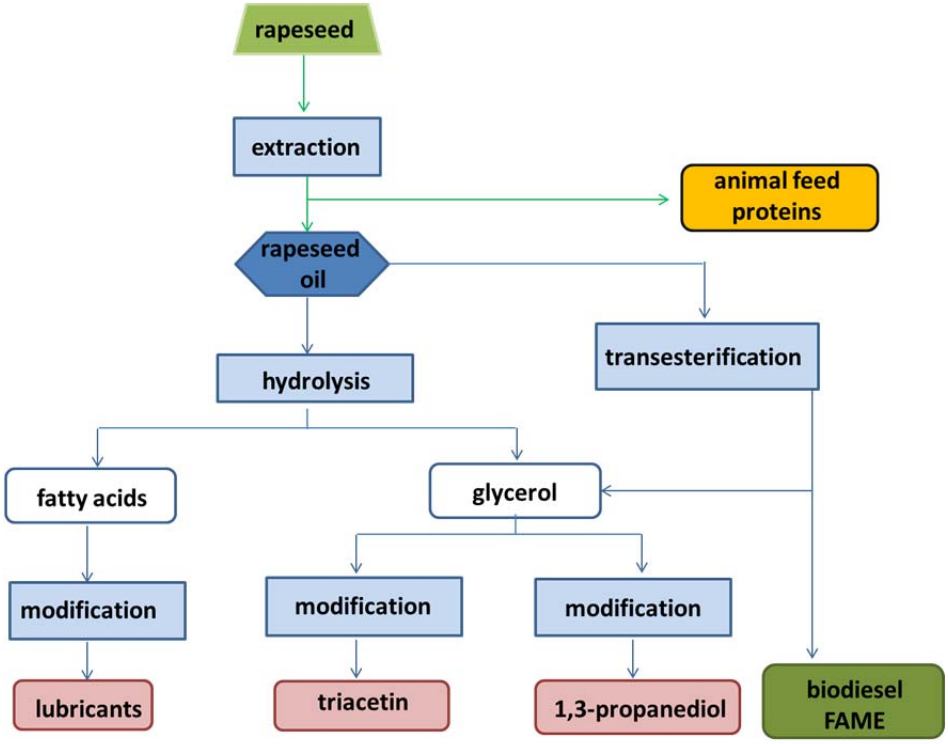

Figure 1-5: Bio-refinery concept of rapeseed oil.[22]

All in all, these bio-refinery concepts are well optimized and make use of the whole content of the extracted plant oil. Very attractive, most of the obtained fatty acids from the refinery process of oilseed crops show structural diversity expressed by different numbers of carbon atoms and different degrees of unsaturation (Table 1-3).[25]

The chain length usually varies from C8 to C20, while the carbon chain contains zero to three, usually cis configured double bonds. Table 1-3 shows different plant oils and their fatty acid composition as well as their degree of unsaturation. Depending on the application, the content of different fatty acids in the plant oils does not matter or is desired. For the synthesis of defined molecules, however, pure substrates are required otherwise extensive purification is needed. Modified rape and sunflower oil have high contents of fatty acids with a defined chain length and number of double bonds, which makes them attractive for organic and polymer chemistry. In contrast, soy oil has fatty acids with a defined chain length, but a wide spectrum of different number of double bonds. Noteworthy, through genetic modification, the content of fatty acids with a specific chain length and unsaturation can be increased for the respective plant oil (Table 1-3).

Table 1-3: Selected plant oils and their content of different fatty acids.[a]

Oil	chain length							double bonds			
	8	**10**	**12**	**14**	**16**	**18**	**20**	**0**	**1**	**2**	**3**
Coconut	8	7	48	17	9	10		2	15	1	
Palm				2	42	56		5	15	10	
Rapeseed					2	38	7	1	60	15	7
Rapeseed (modified)					4	90	2	1	60	20	9
Sunflower					6	93		4	28	61	
Sunflower (modified)					4	93		4	84	5	
Soya					8	91		4	28	53	6

[a]Content specification in %

In this way, the bio-refinery gets facilitated as the crude plant oil contains high contents of a defined fatty acid.

Generally, the physical and chemical properties of fatty acids depend on their structure. Apart from the double bonds, fatty acids can contain other functional groups such as epoxides, cyclopropanes, or hydroxyl groups. Some common fatty acids with different functional groups are shown in Figure 1-6.

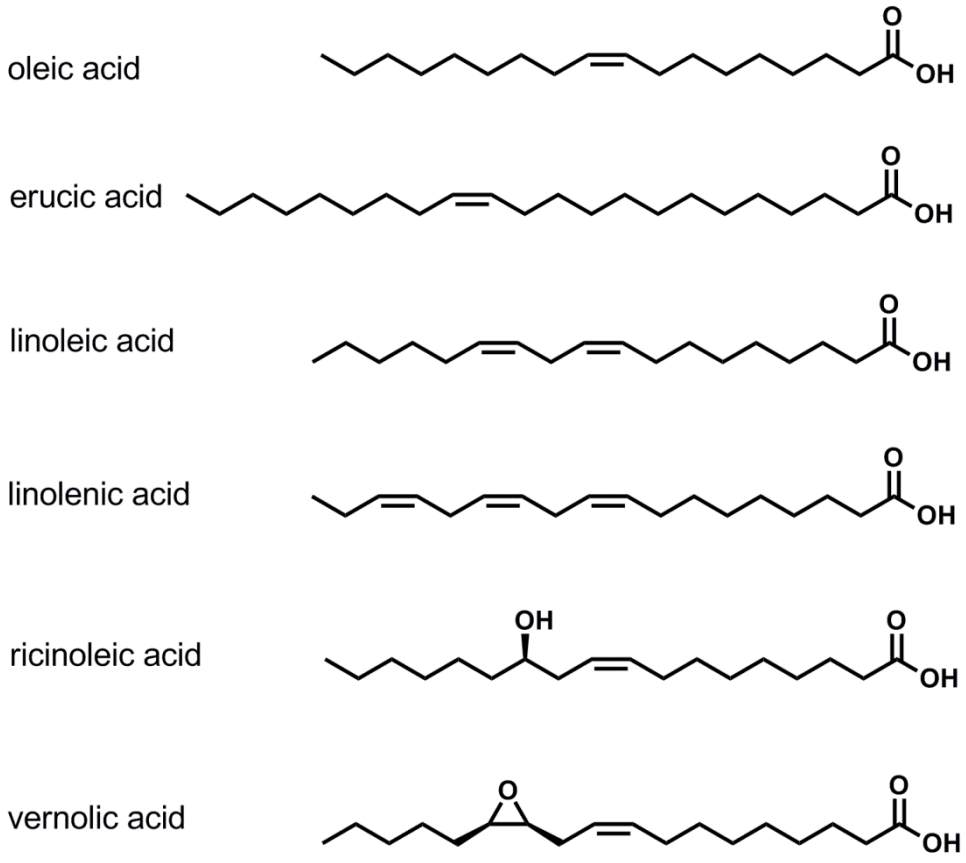

Figure 1-6: Diverse fatty acids with different functional groups.

Most important for the German chemical industry are the long-chain fatty acids linoleic, oleic or erucic acid, since these fatty acids are accessible from domestic plants and can be produced in sufficient quantities. Ricinoleic acid is an attractive fatty acid for polymer chemistry, as it can be directly used for polycondensation reactions to prepare polyesters.[27] Moreover, the ricinoleic acid derived 10-undecenoic acid, 10-undecenal or 10-undecenol are interesting building blocks in polymer chemistry as well.[28] The use of plant oils in polymer chemistry will be discussed more detailed in chapter 2.

1.6. Utilization of plant oils: A future perspective

A future vison is to prepare our fuels, chemicals and materials from feedstocks that never deplete. An interesting question is, if we will be able to address the future problems of depleting fossil resources by switching to renewable resources and how this substantial change could be realized? From diverse studies, it is assumed that nature produces about 170 billion tons per year of plant-derived biomass, whereas only 3.5 % of this biomass is used for human needs.[29] Furthermore, it is estimated that about 40 billion tons of biomass are required to switch to a completely bio-based economy. However, for a more efficient and extended usage of renewable feedstocks we will have to solve diverse technical challenges. In order to convert biomass into important chemicals or materials, low energy processes including non-toxic and catalytic processes with a low carbon footprint are needed. The development of the past years raises hope, since remarkable progress was achieved through intensive research, and efficient ways for producing platform chemicals, fuels and materials from renewable feedstocks are reported. As outlined before, besides cellulose, lignin, starch or diverse carbohydrates, plant oils are one of the most interesting renewable feedstocks. More specific, plant oil derived fatty acids seem to be an ideal raw material source to substitute currently used petrochemicals.[30] Fatty acids are promising substrates for the synthesis of renewable fine chemicals, monomers and polymers since they can be modified in a straightforward manner.[31,32] Furthermore, the processing of plant oils (bio-refinery) is well developed as shown in chapter 1.5. Already some of these renewable monomers and polymers from plant oils and fats are produced in an industrial scale and find various applications.[33-35] However, the ecological and economic benefit or impact of an extended use of plant oils as

renewable feedstock is difficult to predict. We have to keep in mind that an increased use of plant oils as substitute for fossil resources offers a great opportunity, but includes diverse risks as well. The cultivation of oilseed crops is limited as sufficient quantities for the chemical and bio-fuel industry are difficult to produce while maintaining the biodiversity and without competing to food production. Genetic modification of oilseed crops is one opportunity for a more efficient use of this renewable feedstock. On the other hand, we do not know much about the consequences of genetically modified plants yet; thus it is hard to estimate potential risks by cultivating them. The German economy, however, would benefit from an increased use of plant oils since the bio-refinery and processing of oilseed crops are already well developed. Moreover, the know-how, research and technology for processing plant oils into commodities, chemicals or materials are up-to-date and of high quality. More general, the cultivation of oilseed crops and the use of plant oils as substitute for fossil derived feedstocks are only of benefit if the renewable-based products exhibit positive life cycle assessments or a positive carbon footprint. Very promising is the research regarding the acquisition of novel renewable feedstocks to access plant oils or the thereof derived fatty acids by other means. Great progress was achieved in the cultivation of microbial lipids.[36, 37] Microbial oils are economically very interesting as microorganisms offer many advantages compared to the conventional terrestrial oilseed crop cultivation, such as less space requirement, ease of scale up and cultivation, short life cycles or season and climate independence.[38] Microorganisms, such as microalgae, bacillus and fungi (molds and yeasts) are able to produce a large fraction of their dry mass as lipids.[39] Microorganisms with a lipid content higher than 20 wt% are classified as ‘oleaginous’.[40] These oleaginous microorganisms are highly attractive candidates for the chemical industry and the biodiesel production since their fatty acid composition is similar to that of vegetable oils. Moreover, algae are one of the fastest growing plants on earth, which have much higher growth rates than terrestrial oilseed crops. Algae can be efficiently used for carbon dioxide capture and up to 60 % of their weight can be oil. Algae will be a very important renewable feedstock for the future since they can be grown almost everywhere, even on sewage or salt water and no fertile land is needed to cultivate them.

All in all, if compared to conventional terrestrial oilseed crops, microbial lipids or the cultivation of algae (microalgae) offer significant advantages and are very promising

candidates to access novel renewable feedstock for the chemical and fuel industry. In combination with conventional oilseed production, the extraction of plant oils from algae offers the opportunity for a sustainable use of our resources in the future.

1.7. Catalysis - A promising approach towards sustainability

Making reactions more efficient, meaning, to increase the product yield and reaction selectivity, and to facilitate the crude product purification, is of great interest from an economic and ecologic point of view. One way to achieve this is *via* catalysis, which offers novel reaction pathways and synthesis opportunities. Noted as one of the twelve principles of Green Chemistry, catalysis is the key to design processes that *inter alia* benefit from a lower waste production and environmental impact.[12, 41] Of course, the best catalyst is no catalyst since the ideal reaction is one that selectively affords the product in quantitative yield with a complete atom economy at mild reaction conditions (i.e., at ambient temperature, no pressure), and without the need of any further reagents such as a catalyst. In principle, an ideal 'green' reaction is mostly in-line with the concept of Click Chemistry introduced by Sharpless and coworkers.[42]

In a few words, the concept of Click Chemistry includes reactions that are highly exothermic, proceed under ambient conditions, do not need any activation reagents (e.g. catalyst), are performed in water (or environmentally benign solvent) or without any solvent, do not need any extensive purification (e.g. column chromatography), proceed on a fast timescale, provide high yields and are product-selective. These exemplary features of Click Chemistry are also key principles of Green Chemistry, thus click reactions are often "green" reactions. Interestingly, many cycloadditions, for instance some Diels-Alder reactions, are such "ideal" reactions, which fulfil most of the aforementioned criteria. However, in some cases the addition of catalysts, e.g. Lewis acids improves the product yield and selectivity.

In 1835 J. Berzelius introduced the term catalysis.[43] Herein, he described the observation that a reaction can be accelerated with the help of a so-called excipient, which does not change its initial chemical composition. A more precise definition was given by W. Ostwald, wherein a catalyst accelerates a chemical reaction without being consumed and without changing the overall thermodynamic states of the

substrates and product.[43] An important fact is that the catalyst is not consumed, thus ideally it should be reusable infinite times. However, in practice the catalyst might be deactivated during the reaction or small quantities will be lost in the work-up. Hence, especially for catalysts based on noble metals such as palladium or platinum or catalyst having expensive and complex ligands, there is a great interest to avoid loss of catalyst or to keep the catalyst loadings to a minimum mainly due to economic reasons. Catalysts are widely used in numerous larger scale industrial processes and about 90 % of all chemical industrial processes make use of a catalyst.[43] The Haber-Bosch process to generate ammonia from nitrogen and hydrogen gas, the Ostwald process to produce nitric acid, the Fischer-Tropsch process to make fuel from diverse carbon feedstocks or the Ziegler-Natta polymerization of olefins are very important catalytic processes, which are essential for our daily life. To keep these catalytic processes economically profitable, the used catalysts have to meet different requirements.[44]

- The used catalyst has to be robust at the applied reaction conditions and tolerant towards impurities resulting e.g. from the utilized substrates.
- Catalysts need to be tolerant towards different functional groups of the substrate or the product.
- To guarantee a high reaction efficiency and rate, the utilized catalyst should be highly active and yield high turnover numbers and turnover frequencies.
- The catalyst must be selective for the desired transformation and specifically promote the product formation.
- The used catalyst should be readily available and cost-efficient.
- From an economic point of view and ease of product purification, the catalyst needs to be easily separable from the reaction mixture and/or recyclable.

Very interestingly, for many catalytic transformations the exact reaction mechanism is not known and the obtained reaction efficiency and product selectivity can hardly be described. Often a pre-catalyst is used and the actual catalytic species is not even known since it is formed *in situ*. Also, the industrially used catalytic systems often consist of a complex mixture of different metals, additives and co-catalysts (promoters) in order to improve the performance (durability, activity, product selectivity, etc.).

The development of novel catalysts is of great importance since in this way novel processes by different reaction pathways are accessible. Herein, especially homogenous catalysts are promising candidates that offer new reaction possibilities as their catalytic activity can be adjusted by ligand design or adding customized promoters. In order to establish more sustainable and environmentally benign processes catalytic reactions are of crucial importance. Catalytic systems often avoid the generation of large amounts of waste and therefore contribute to environmentally benign reactions with low E-factors. Typical examples for reactions with high E-factors are for instance reductions utilizing metals (Na, Mg, Zn) or metal hydrides ($NaBH_4$ or $LiAlH_4$) instead of catalytic reagents. Also, oxidation reactions that make use of stoichiometric amounts of e.g. chromium(VI) reagents, manganese dioxide, or potassium permanganate are disfavored to catalytic reactions employing oxygen or hydrogen peroxide as oxidizing agent. Moreover, organic reactions such as conventional halogenations, nitrations, sulfonations and Friedel-Crafts acylation that make use of mineral acid (sulfuric acid or phosphonic acid) or Lewis acids ($AlCl_3$, $ZnCl_2$) produce a large amount of inorganic waste, which results in a larger environmental impact.[12] Here, efficient catalytic alternatives are needed. For conventional reductions the usage of hydrogen and an appropriate metal catalyst offers an interesting environmentally friendly alternative to reductions utilizing metal hydrides such as $LiAlH_4$.[45-48] The hydrogenation of esters and carboxylic acids, however, remains a challenging reaction (Figure 1-7). An interesting approach to reduce carboxylic esters to alcohols was described by Beller and coworkers, who made use of an iron catalyst and different silanes as reducing agent.[49]

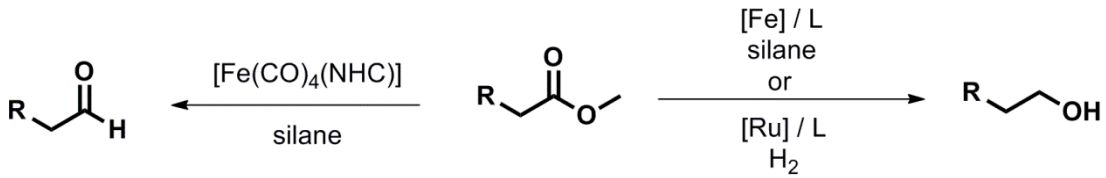

Figure 1-7: Catalytic reduction of methyl esters to alcohols or aldehydes.[48-50]

The use of iron catalysts is of special interest since the metal is cheap, abundant and non-toxic. Also, by utilizing an iron catalyst, Darcel *et. al.* demonstrated the selective catalytic reduction of different methyl esters to the respective aldehyde.[50]

Cole-Hamilton and coworkers made use of a ruthenium based catalyst to reduce diesters to diols. The reactions were performed at hydrogen pressures of up to 70 bars to afford the desired diols in good yields.[48]

One of the most fundamental processes in nature are oxidation reactions, which are key transformations in organic synthesis as well. With regard to environmentally benign oxidation procedures the catalytic oxidation of organic substrates by molecular oxygen or hydrogen peroxide is of great interest. In particular, the oxidation by a biomimetic multistep electron transfer approach offers novel possibilities in the design of efficient catalytic oxidation reactions.[51] Biomimetic oxidation procedures represent a mild, efficient and green methodology for the construction of complex molecular structures. Herein, Bäckvall and coworkers reported the biomimetic oxidation of alcohols, amines and the oxidative coupling of conjugated dienes as new environmentally friendly and general applicable synthetic oxidation routes.[51, 52]

Furthermore, Wacker-type oxidations of olefins are important transformations to prepare aldehyde or ketone functional molecules. Recent research is focused on aldehyde or ketone selective Wacker oxidation reactions.[53-55] For instance, Grubbs and coworkers described an aldehyde selective Wacker oxidation of different alkenes.[55] The introduced nitrite mediated oxidation making use of a catalytic system based on palladium chloride and copper chloride impressed through the obtained high yields and selectivity towards the desired aldehyde.

The oxidation of alkenes to epoxides is another very important oxidative transformation yielding valuable organic compounds or intermediates. *Inter alia*, fatty epoxides, which are directly used as plasticizers and plastic stabilizers, represent valuable organic compounds. An interesting epoxidation method of diverse aliphatic olefins was introduced by Rybak-Akimova *et al*.[56] With the help of aminopyridine ligands that form a redox-active iron catalyst, diverse epoxides were synthesized from unsaturated substrates. Alternatively, enzyme-catalyzed oxidation reactions are highly interesting from an economic and ecological point of view. The use of enzymes as catalysts, however, has two major disadvantages as the availability and scope of substrate is limited. On the other hand, by using enzymatic oxidation procedures, the use of peracids, peroxides or heavy-metal catalysts can be avoided. Well-investigated are the epoxidation or Baeyer-Villiger oxidation of diverse substrates using enzyme catalysts.[57-60]

Rios and coworkers reported the enzymatic Baeyer-Villiger oxidation of substituted cyclohexanones utilizing the immobilized Candida antarctica lipase B, urea–hydrogen peroxide and ethyl acetate.[61] Also, the enzymatic epoxidation of fatty acids or FAMEs using different enzyme catalysts is well-known.[58, 62, 63]

Altogether, the combination of catalysis and renewable resources offers an attractive possibility to promote the production of renewable bulk and fine chemicals as well as the production of novel bio-based products. Therefore, the development of novel robust and efficient catalytic systems will be closely related to an increased industrial usage of biomass or renewable resources.

(Note that parts of this chapter were written for the previously authored diploma thesis (M. Winkler, *Synthesis and Orthogonal Conjugation of Polymers from Renewable Resources*, 2011, Karlsruher Institut für Technologie)).

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2. Theoretical Background and State-of-the-art

The following section provides a short overview of the theoretical background and the state-of-the-art of the chemistry related to the efficient and catalytic transformation of plant oils into monomers and polymers.

2.1 Metathesis

In 2005 Grubbs, Chauvin and Schrock were awarded with the Nobel Prize for their work on olefin metathesis.[64] Since then, olefin metathesis became even more popular, in both organic and polymer science. One of the early investigations on 'metathesis' date back to 1955, herein the polymerization of norbornene was described by Anderson and Merckling, who made use of titanium tetrachloride and ethyl magnesium bromide as catalytic system.[65] A detailed study on the mechanism was published by Chauvin and Hérrisson in 1971. The metathesis reaction was described as a [2+2] cycloaddition of a C=C double bond and a metal alkylidene to yield a metallacyclobutane intermediate, which undergo a [2+2] cycloreversion (Figure 2.1-1).[66-68]

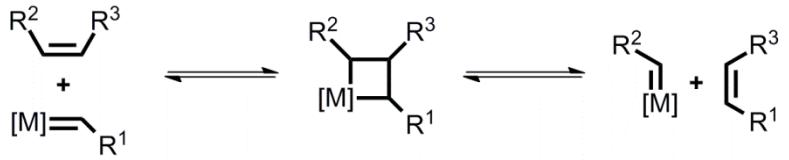


Figure 2.1-1: The mechanism of olefin metathesis as proposed by Chauvin and Hérrisson in 1971.[69]

The success of olefin metathesis is closely linked to the rapid development of novel highly active, tolerant and readily available catalysts. A great variety of catalysts, which display different advantages, are commercially available. For instance, the Schrock-type molybdenum and tungsten catalysts, which usually exhibit a high metathesis activity, are less tolerant towards functional groups (e.g., alcohols, aldehydes).[70] These catalysts are therefore often used in case of electronically deactivated and sterically hindered olefins, which are disfavored substrates for metathesis reactions. On the other hand, the ruthenium-based Grubbs-type catalysts usually show high functional group tolerance, low sensitivity towards moisture and air, and still display great metathesis activity.[71]

An improved catalytic activity of these ruthenium-based catalysts was attained through introduction of *N*-heterocyclic carbenes as ligands, which exhibit an electron donating effect on the metal center. Widely employed and commercially available ruthenium-based metathesis catalysts are the Grubbs 1st generation and the Hoveyda-Grubbs 2nd generation catalyst.

Metathesis reactions are generally divided in different reaction types. In Figure 2.1-2 the most frequently examined metathesis reactions are illustrated. The most relevant for organic chemistry are the ring-closing metathesis (RCM), cross-metathesis (CM), ring-opening metathesis (ROM) and self-metathesis (SM) reaction. The ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET) are used as polymerization technique in polymer science.[72] It has to be noted that all metathesis reactions are in equilibrium, thus most reactions need a driving force to achieve good conversions and selectivity.

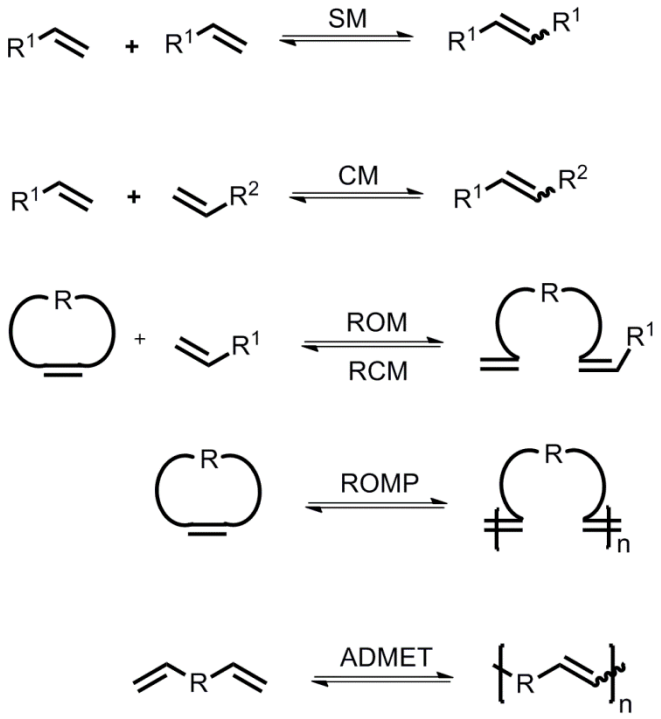


Figure 2.1-2: Frequently examined metathesis reactions for organic and polymer chemistry.[72]

A selective metathesis of two different alkenes can be achieved if two olefins of different reactivity are used. Grubbs and coworkers postulated a concept to estimate the selectivity of such a CM.[73] It is noteworthy that the classification into different olefin types is only empirical since various primary and secondary metathesis pathways are involved in cross-metathesis reactions. Also, there are different sterical and electronic effects that can be hardly assessed, making the prediction of the CM

selectivity much more complex. Grubbs *et al*. introduced a simple concept by classifying different olefins through their ability to undergo homodimerization relative to other olefins.[73]

In this way, Grubbs and coworkers made the following classification:

- Olefins of type I: rapid homodimerization and secondary metathesis of the homodimers (e.g., terminal olefins, allylic alcohols or esters).
- Olefins of type II: slow homodimerization, unreactive homodimers (e.g., acrylates, acrylamides or vinyl ketones).
- Olefins of type III: no homodimerization (e.g., allylic tertiary alcohols or allylic quaternary carbons).
- Olefins of type IV: no cross-metathesis, no catalyst deactivation (e.g., vinyl nitro olefins or disubstituted α,β-unsaturated esters).

The metathesis activity decreases from type I olefins to type IV olefins. In general, the reaction of two olefins from the same type is leading to a non-selective statistical CM. Contrary, the use of two olefins of different types having significant different rates of homodimerization enables a selective CM (Figure 2.1-3).[73] A well-examined model with high CM selectivity is demonstrated for reactions of type I terminal olefins with type II olefins (e.g., acrylates).

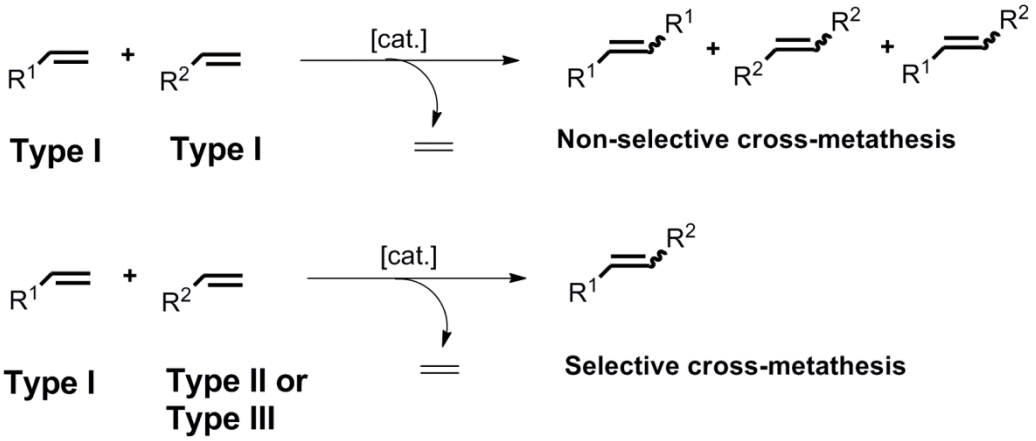


Figure 2.1-3: Selective and non-selective CM using different types of olefins.

2.1.1 Metathesis in polymer chemistry (ROMP/ADMET)

Olefin metathesis is not only an important tool for organic chemistry, but also in polymer science it became an important technique to prepare novel materials. Herein, particularly the ROMP is an attractive polymerization method, which is used to prepare defined polymer architectures. Strained ring systems such as cyclobutene or norbornene are very useful substrates, since they have a high thermodynamic driving force to undergo ring-opening metathesis (Figure 2.1.1-1). Highly reactive metal alkylidene catalysts such as the Grubbs 1st generation catalyst are used to prepare high molecular weight polymers with low dispersities. Usually, the ROMP can be performed as living polymerization i.e. the molecular weight can be adjusted by varying the monomer to initiator ratio and narrow molecular weight distributions are obtained.[74] The living character of a ROMP is due to the fact that the catalysts have high initiation rates and the active catalytic species remains on the growing polymer chain during the chain propagation. Moreover, the strained cyclic monomer preferentially reacts with the highly active catalyst situated at the end of the growing chain so that the polymer chain length can be well adjusted.

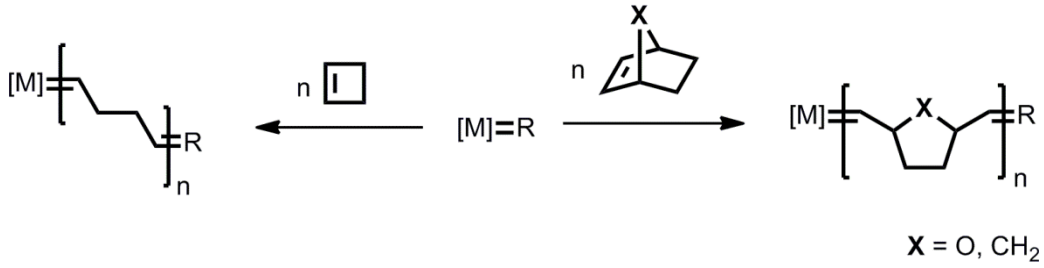


Figure 2.1.1-1: ROMP of strained cyclic monomers.[75]

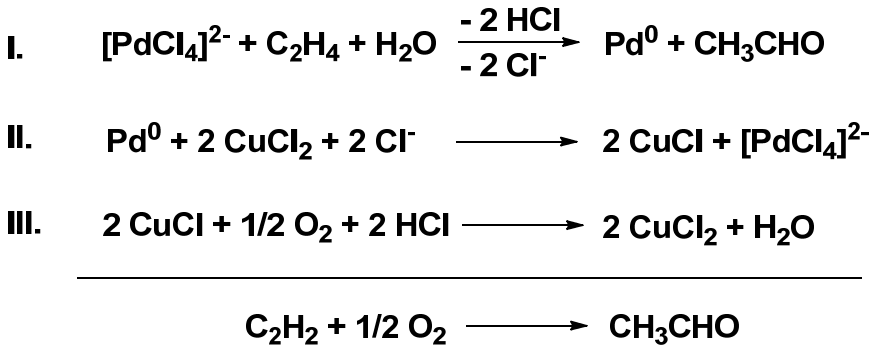
An interesting methodology to perform ROMP is the use of photo-switchable metathesis catalysts. The photo-initiated metathesis polymerization benefits from a high spatially and time-resolved initiation of the polymerization, which might be of great interest for targeted surface modification.[76-78] Another metathesis polymerization methodology is the ADMET polymerization. ADMET, a step-growth polymerization technique, is usually performed with α,ω-dienes as monomers, since in this case ethylene is released as only byproduct, which can be easily removed in order to shift the metathesis equilibrium. The ADMET polymerization enables the synthesis of defined polymer architectures (e.g., block copolymers, star-shaped polymers, comb copolymers) or polymers with defined end groups.[79-83] An interesting feature of ADMET polymerizations is the opportunity to prepare strictly linear

polyethylene-like polymers, but also polymers with a great varity of functional groups.[84, 85, 86]

Still, there are problems to overcome in order to make olefin metathesis much more attractive for industrial applications. Most catalysts are expensive and usually metal residues are found as contamination in the final product. One current topic is the development of cheap and readily available catalysts as well as the search for new efficient methods to remove and recover the catalyst residues. A promising approach is the use of ionic liquids as solvent or polymer supported catalysts to enable a straightforward recovery of the used metal catalyst.[87-89]

2.2 Wacker Oxidation

Palladium catalysts are widely employed in organic chemistry for numerous reactions such as nucleophilic substitution reactions of allylic substrates (Tsuji-Trost type reactions),[90] cross-coupling reactions[91] of aryl halides (e.g., Heck or Suzuki reaction), or the orthogonal cleavage of protecting groups (e.g. cleavage of benzyl esters or Cbz protecting groups).[92] However, the palladium-catalyzed Wacker process and related chemistry are one of the most important transformations.[93] The original Wacker process, which was introduced by the German company Wacker Chemie in 1956, is used to generate acetaldehyde from ethylene.[94, 95] The oxidation of ethylene with a palladium catalyst and a copper chloride co-oxidant can be summarized in the following reaction steps:



The initial palladium catalyst is reduced to Pd(0) (I.), whereas copper chloride is used to regenerate the active palladium species (II.); the formed copper(I) chloride is re-oxidized in the presence of air (III.). The overall Wacker process as described by the three different reaction steps (I.-III.) appeared to be a rather simplified illustration.

The actual mechanism of the oxidation is still not known in detail and part of ongoing discussions. More recent investigations describe the Wacker process mainly at three different reaction conditions with different concentrations of [Cl^-] and [$CuCl_2$]: **LL** low [Cl^-] (<1 M) and low [$CuCl_2$] (<1 M), **HH** high [Cl^-] (<3 M) and high [$CuCl_2$] (<2.5 M); and **LH** low [Cl^-] and high [$CuCl_2$].[96, 97] Depending on the concentration of [Cl^-] and [$CuCl_2$], two mechanisms are discussed, an inner-sphere or outer-sphere process, whereas the inner-sphere process seems to be unlikely based on theoretical calculations.[97]

A simplified consideration of the mechanism of the Wacker oxidation is shown in Figure 2.2-1. First, the alkene is coordinating to the palladium center to form a π-complex (Figure 2.2-1, A). In the next two reaction steps (Figure 2.2-1, B – C), the ligand of the palladium catalyst is exchanged by water and a hydroxyethyl palladium complex is formed by formal insertion of H_2O (hydroxypalladation).

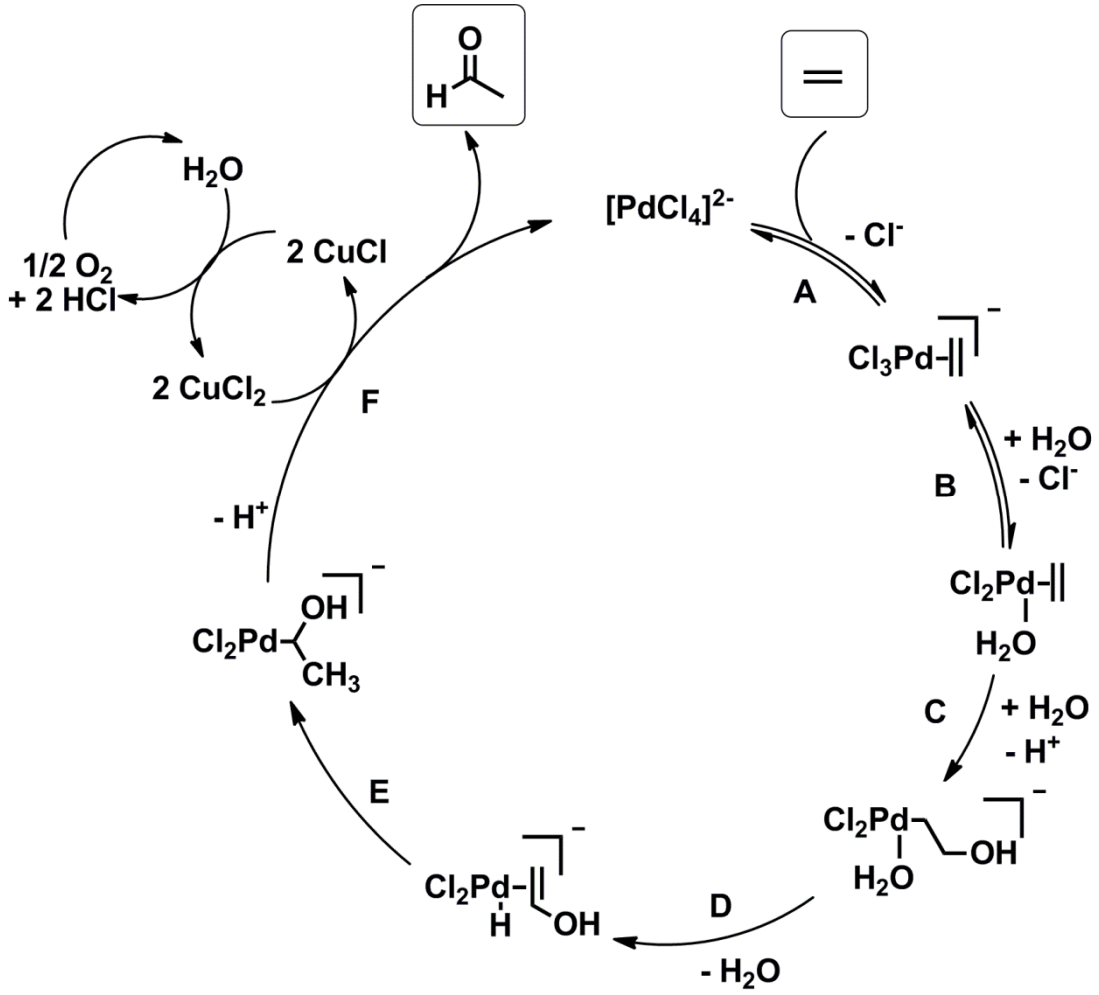


Figure 2.2-1: Simplified mechanism of the Wacker oxidation.[96]

After β-hydride elimination, the formed enol intermediate re-inserts into the Pd-H bond (D – E). Subsequent deprotonation yields the product and palladium(0), which is regenerated *in situ* by copper(II) to the initial palladium(II) species (F).

The coupled Wacker process to produce acetic acid by oxidation of the obtained acetaldehyde lost its importance as industrial-scale production since it was replaced by the Monsanto process. Nevertheless, Wacker type oxidation reactions are still of great importance in order to prepare aldehyde or ketone functional compounds.[55, 98-101] Recent research is focused on selective Wacker oxidation procedures yielding aldehyde functional products.[55, 100] Also of great interest are ''green'' Wacker oxidation procedures that are environmentally friendly and do not produce redundant waste. Qiao and coworkers described a Wacker oxidation with a water-soluble palladium catalyst to perform the reaction in water as environmentally friendly solvent. Other researcher focused on the recovery of the used palladium catalyst by using adjusted catalytic systems or ionic liquids as reaction media.[102-104] However, in most standard procedures, a co-catalyst, such as copper(II) chloride, is used, resulting in the formation of hazardous (chlorinated) byproducts. Moreover, usually residues from the employed co-catalyst are found in the final product. The Wacker oxidation reported by Kaneda and coworkers is highly interesting with regard to a green oxidation procedure.[105, 106] Oxygen was used as sole re-oxidant in combination with *N,N*-dimethylacetamide (DMAc) as solvent that allows simple workup and catalyst recycling. Similar work was reported from Sigman *et al*., who used a palladium sparteine catalyst in a direct O_2-coupled Wacker oxidation.[107]

The discussed green Wacker oxidation reactions offer an environmentally benign oxidation procedure of olefin substrates and are of special interest for the oxidation of unsaturated fatty acids. The thereof derived keto fatty acids are interesting starting materials for the preparation of fatty acid based monomers and platform chemicals.[108]

2.3 Hydrobromination / Wohl-Ziegler bromination

The hydrobromination and Wohl-Ziegler bromination are conventional procedures to achieve a (mono-)bromination of olefin substrates. Both methods enable the synthesis of bromine functional compounds, whereas the Wohl-Ziegler bromination leads to allylic bromides instead of alkyl bromides. Bromides are important compounds to be used in substitution reactions, e.g. to introduce amine groups or other nucleophiles (see chapter 2.6). The hydrobromination is a fully atom economic reaction and depending on the reaction conditions different regioselective products are obtained (Figure 2.3-1).

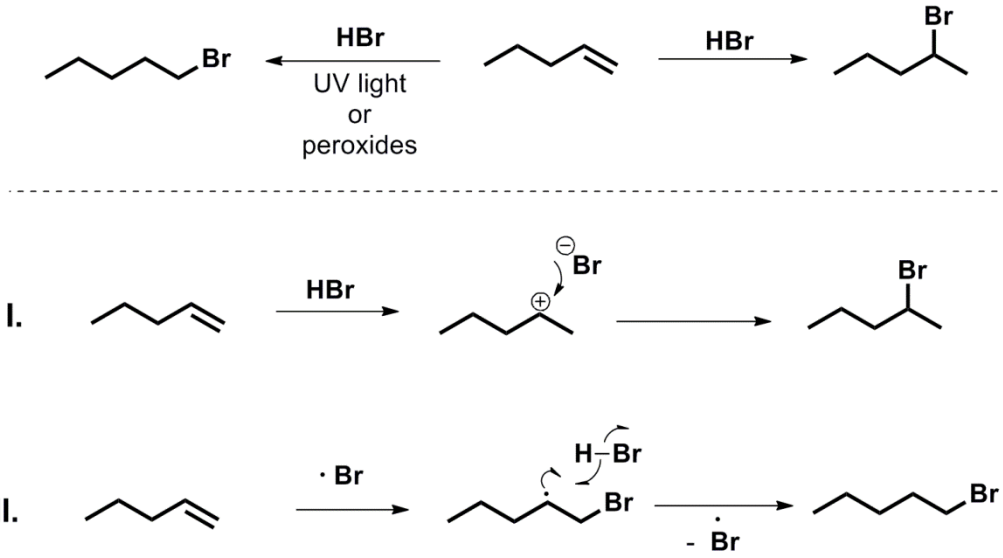
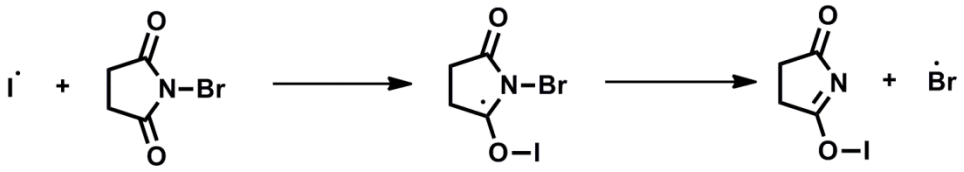


Figure 2.3-1: Hydrobromination at different reaction conditions utilizing *n*-pentene.

At conventional reaction conditions without any further reagents (Figure 2.3-1, I.), the higher substituted Markovnikov product is obtained. Herein, first a carbocation is formed by protonation of the alkene substrate and subsequent reaction with the bromide ion yields the higher substituted bromide. In presence of a radical source, for instance peroxides or UV light irradiation, first the more stable secondary radical is formed, which then will abstract a hydrogen atom to finally yield the anti-Markovnikov product. In order to prevent side reactions during bromination reactions, the concentration of [HBr] or [Br_2] has to be low. In case of the Wohl-Ziegler bromination, the concentration of bromine stays at a low level since Br_2 is generated continuously in moderate rates from *N*-bromosuccinimide (NBS) and directly reacts with the alkene substrate. Interestingly, the Wohl-Ziegler bromination yields allylic bromides. The regio-selective bromination in allylic position is explained by the stability of the

resonance-stabilized allylic radical following a radical chain mechanism (Figure 2.3-2). At first, a bromine radical is formed by reaction of a radical initiator (e.g., AIBN) with NBS, which then abstracts a hydrogen atom from the alkene substrate in allylic position to form a resonance-stabilized intermediate. Subsequent reaction of the generated hydrobromic acid with NBS results in the formation of bromine, which will immediately react with the previously formed allylic radical to yield the product.

Initiation:



Propagation:

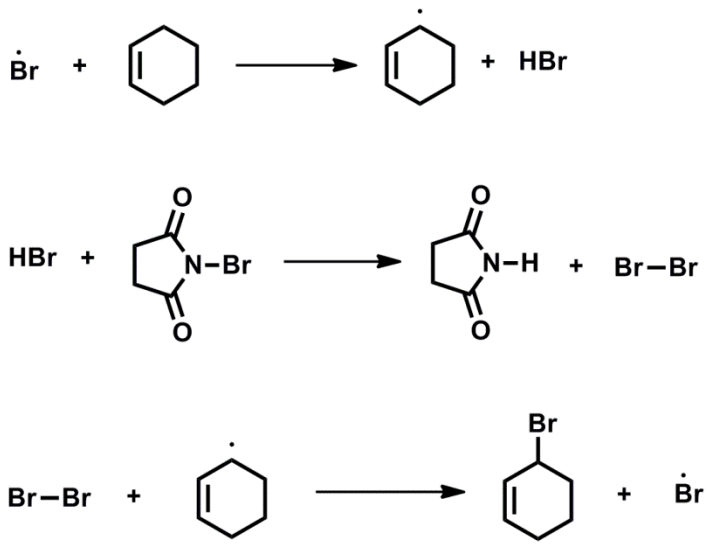


Figure 2.3-2: Mechanism of the Wohl-Ziegler bromination reaction utilizing cyclohexene.

In general, the bromination of alkenes and subsequent modification of the derived bromides are not sustainable and environmentally benign reaction procedures. The generated waste formed as byproduct in substitution reactions of the bromine functional substrates is a major problem of this modification strategy of unsaturated compounds and therefore, a direct functionalization of the alkene is favored. Moreover, in the case of the Wohl-Ziegler reaction usually carbon tetrachloride is used as solvent to improve the reaction selectivity and yields. Beside the use of toxic carbon tetrachloride, a large amount of waste is generated since NBS is used as auxiliary reagent to achieve a good regioselectivity. Researchers have mainly focused on the substitution of carbon tetrachloride as solvent to perform the allylic

bromination under more sustainable and 'green' reaction conditions. Promising results were obtained under microwave irradiation, in ionic liquids or in water as reaction media.[109-111] The use of the Wohl-Ziegler bromination in polymer chemistry is barely described. It was shown that the allylic bromination can be applied for the transformation of plant oils into isocyanates to prepare renewable polyurethanes.[112, 113] However, these approaches lack in sustainability as discussed for the transformation of alkenes by allylic bromination before.

In contrast, the industrially performed synthesis of 11-aminoundecanoic acid is quite promising regarding an environmentally friendly procedure to prepare polyamide monomers from renewable resources.[114] Herein, hydrobromic acid is used in a radical bromination of 10-undecanoic acid (a ricinoleic acid derived platform chemical) to afford the 11-bromoundecanoic that is reacted with ammonia to yield the 11-aminoundecanoic acid, the monomer for the production of polyamide 11. The process allows the continuous recycling of bromine species, which is regenerated after the ammonolysis step, making the procedure highly efficient and sustainable.

2.4 Ring-opening copolymerization of epoxides

Carbon dioxide is one of the most attractive renewable feedstock since it is cheap, abundant, a waste product and readily available. Besides methane, CO_2 is considered as one of the main contributor to the Greenhouse Effect. Indeed, carbon dioxide is thermodynamically very stable and the end-product of many energy releasing processes (e.g., combustions). Hence, in order to make use of CO_2, high activation energy barriers need to be overcome. Whereas nature annually transforms billion of tons of carbon dioxide into carbohydrates by photosynthesis, industry only barely makes use of CO_2 as feedstock. The most relevant processes are the production of salicylic acid by the Kolbe-Schmitt reaction, the preparation of methanol by the Solvay process, and the synthesis of urea or organic carbonates. It has to be noted that the use of carbon dioxide as substrate for the preparation of chemicals and materials will never compensate the level of globally emitted CO_2. Nevertheless, carbon dioxide is a very interesting feedstock, especially for the synthesis of polymer materials such as aliphatic polycarbonates, mainly since CO_2 is a potential non-toxic, low-cost and renewable resource for the future. Aliphatic polycarbonates produced from carbon dioxide are biodegradable thermoplastics with potential applications in

the electronic, automotive, healthcare or commodity sector. In Asia, there is an enormous interest and strongly growing industrial production of polycarbonates from CO_2.[115, 116] One possibility to prepare carbon dioxide-based polycarbonates is the CO_2/epoxide copolymerization. Other strained heterocyclic molecules such as aziridines, oxetanes or episulfides are able to undergo sequential copolymerization with CO_2 as well, if an appropriate catalyst is used. However, by far most widely studied is the copolymerization of carbon dioxide with epoxides catalyzed by Lewis acidic metal halides, carboxylate or alk/aryloxide complexes.[117, 118] The mechanism is proposed to proceed *via* coordination and insertion sequences as illustrated in Figure 2.4-1. First, the metal complex coordinates to the epoxide, which will be attacked by the nucleophilic group X (halide or carboxylate), a weakly bound ligand of the catalyst.

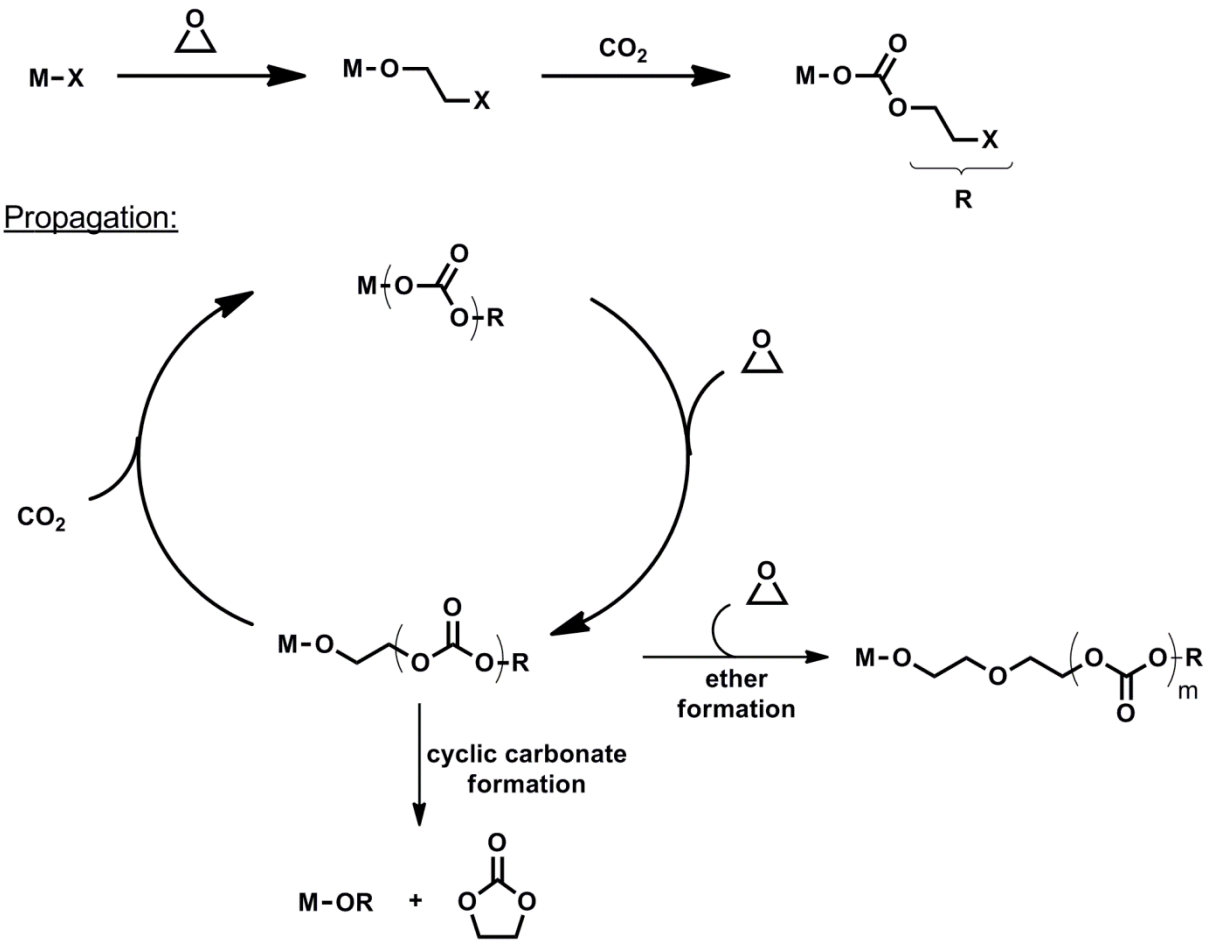


Figure 2.4-1: Proposed mechanism for the CO_2/epoxide copolymerization using ethylene oxide.

During this reaction step, the epoxide undergoes a ring-opening to form a metal- bound alkoxide. The initiation step of the copolymerization will be completed by CO_2 insertion to yield a metal bound carbonate. An ideal alternating copolymerization proceeds by repetitive ring-opening of the epoxide and insertion of CO_2. However, some catalysts favor the homopolymerization of the epoxide, which leads to ether linkages in the obtained polymer. On the other hand, if the alkoxide chain end attacks a carbonate linkage of the polymer backbone (backbiting) a more thermodynamically stable five-membered cyclic carbonate is formed that does not undergo further ring-opening.

In the late 1960s, Inoue and coworkers reported for the first time the synthesis of polycarbonates by copolymerization of CO_2 and propylene oxide making use of $ZnEt_2$ and water as catalyst.[119] In the following twenty years researchers have focused on either $ZnEt_2$ or ZnO based heterogeneous catalysts until the discovery of well-defined and homogeneous aluminium tetraphenylporphyrin (tpp), and zinc *bis*-phenoxide complexes.[120, 121] Coates and coworkers reported for the first time about zinc β-diiminate complexes as highly active catalysts for the epoxide/CO_2 copolymerization, which can be regarded as a milestone in the development of novel powerful catalysts in this research field. The zinc β-diiminate catalysts showed high activity at low CO_2 pressure and mild reaction conditions, in particular in copolymerizations with cyclohexene oxide, whereas only moderate activity was observed for copolymerizations of propylene oxide and CO_2.

Today, the most frequently applied catalysts are the chromium or cobalt salen (salen = salicylaldimine) catalysts, which show high activity in copolymerizations, both with propylene oxide and cyclohexene oxide.[118] Most of these salen-type catalysts show high stability towards moisture and air, and are commercially available or can be easily accessed by modification of commercially available precursors. The most frequently used epoxide monomers in CO_2 mediated copolymerizations are propylene oxide, cyclohexene oxide, as well as ethylene oxide since these monomers are cheap and commercially available, and also of great interest for industrial processes. However, epoxides that are derived from renewable resources, such as limonene oxide or pinene oxide, to prepare fully renewable polycarbonates have become more interesting in the past years.[117, 122]

Similar to the copolymerization of epoxides with CO_2, the ring-opening copolymerization of epoxides with anhydrides proceeds *via* a coordination-insertion

mechanism (see Figure 2.4-2). First, the metal catalyst coordinates to the epoxide and the nucleophilic group X (halide or carboxylate), a ligand from the catalyst, opens the epoxide to form a metal alkoxide. Subsequently, the anhydride inserts into the metal alkoxide to generate a metal carboxylate. Repetitive ring-opening of the epoxide and anhydride insertion yields the alternating polyester. The combination of different epoxides (e.g., propylene oxide, cyclohexene oxide, ethylene oxide) and anhydrides (e.g., succinic anhydride, phthalic anhydride or glutaric anhydride) in the ring-opening copolymerization enables the synthesis of a variety of polyesters with different material properties. Also here, the use of epoxides as well as anhydrides derived from renewable resources is of growing interest.[123, 124]

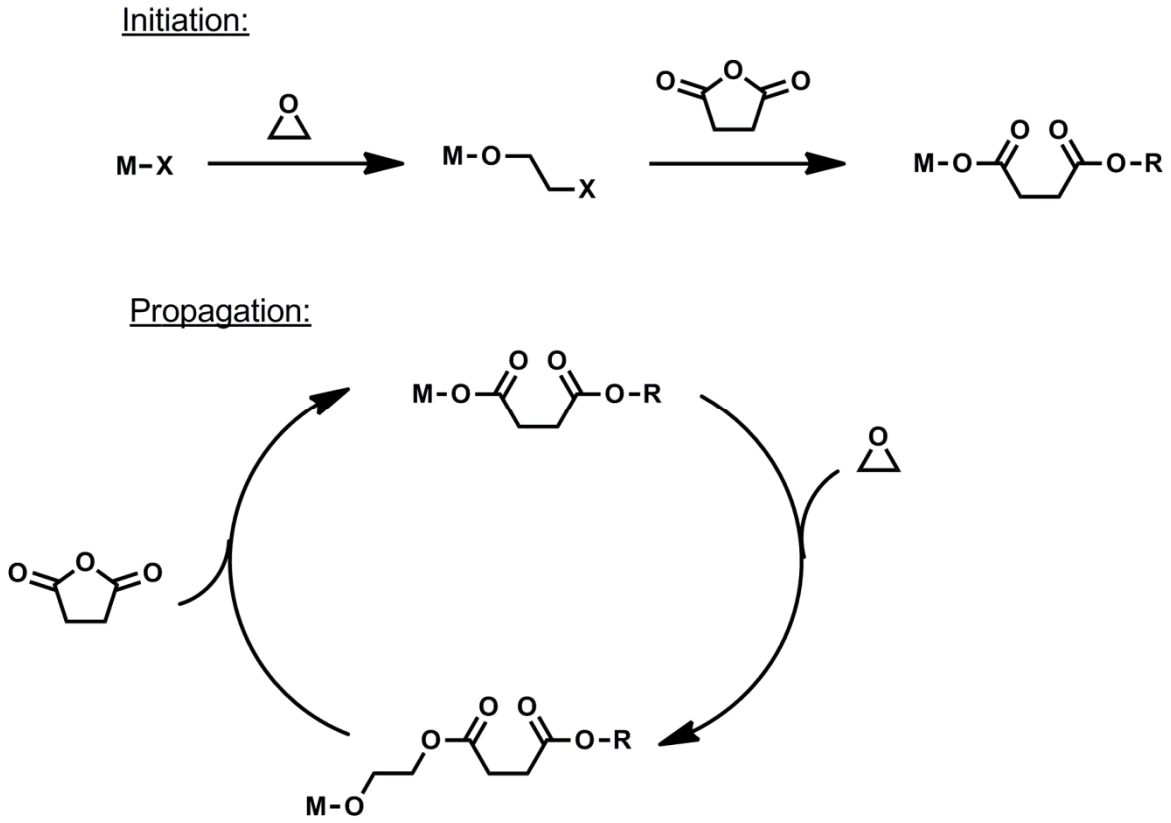


Figure 2.4-2: Proposed mechanism for the epoxide/anhydride copolymerization using ethylene oxide and succinic anhydride.

2.5 Ring-opening polymerization of lactones

Aliphatic polyesters are a class of very interesting polymers, which have good mechanical properties and show biocompatibility as well as biodegradability. They are used for biomedical applications such for tissue engineering, drug delivery or blood dialysis.[125, 126] Aliphatic polyesters can be synthesized by polycondensation of two AA-type monomers such as diols and diesters or diols and dicarboxylic acid/acid chlorides, or by an AB-type monomer having, e.g., an alcohol and ester functional group. The synthesis of polyesters by polycondensation is very straightforward, but ideally leads to polymers with broad dispersities of about 2. Depending on the used monomers, polycondensations are usually performed at high temperatures (i.e. high energy input) in order to remove the produced condensate (water, methanol or hydrochloric acid). In this way, the reaction equilibrium can be shifted to obtain high molecular weight polymers. An alternative polymerization method to access polyesters offers the ring-opening polymerization (ROP) of lactones and lactides, which enables the synthesis of defined polymers with adjustable molecular weights and narrow dispersities. Of particular interest is poly-ε-caprolactone, which is produced in an industrial scale by ROP of ε-caprolactone.

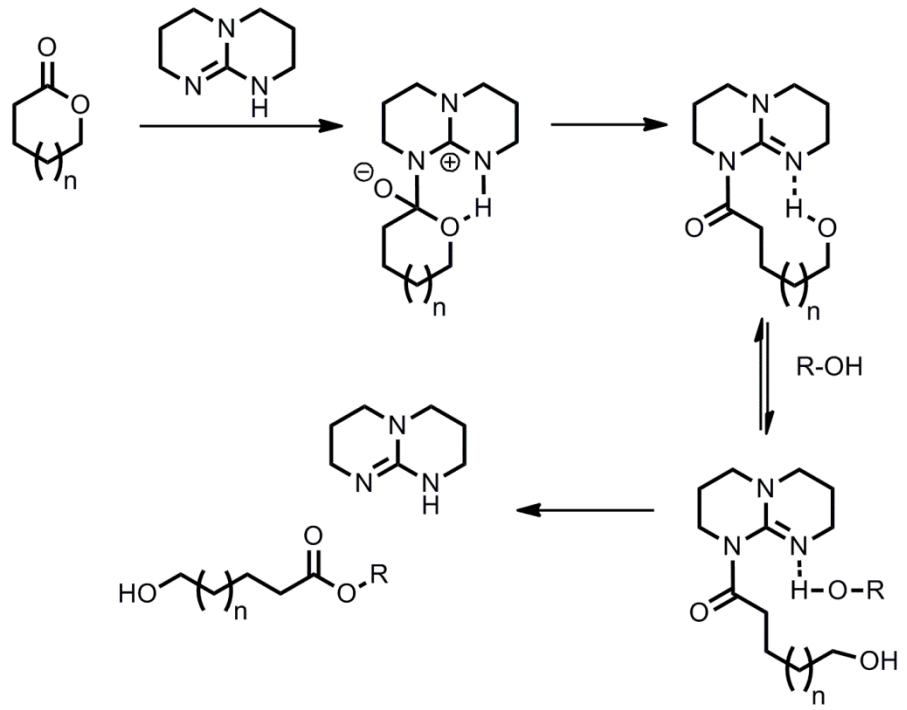


Figure 2.5-1: Mechanism of the ring-opening of lactones by TBD suggested by Hedrick and coworkers.[127]

According to the used catalytic system, the ROP of lactone or lactide monomers proceeds *via* different mechanisms, for instance through the monomer activated mechanism or the ionic (anionic or cationic) ring-opening mechanism. Due to the ease of reaction set-up and practicability, the coordination-insertion ROP is favored. Tin(II) ethylhexanoate ($Sn(Oct)_2$) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) are commonly used catalysts to prepare polycaprolactones with narrow dispersities and high molecular weights. Interestingly, TBD can be used as organo-catalyst under very mild reaction conditions and low catalyst loadings. Nucleophilic attack of the guanidine base to the carbonyl of the lactone results in the ring-opening and the formation of a TBD-amide (Figure 2.5-1). On the other hand, the incoming alcohol is activated through hydrogen-bonding facilitating the esterification reaction.

In the case of the ROP of ε-caprolactone using tin(II) octanoate as the catalyst, first the stannous alkoxide initiator is formed by double exchange of the weakly bound ethylhexanoate ligand with the alcohol initiator (e.g. *n*-octanol) as illustrated in Figure 2.5-2. Subsequent coordination and insertion of the monomer into the alkoxide bond leads to the growing species to which the second monomer can be added to continue the chain-propagation.

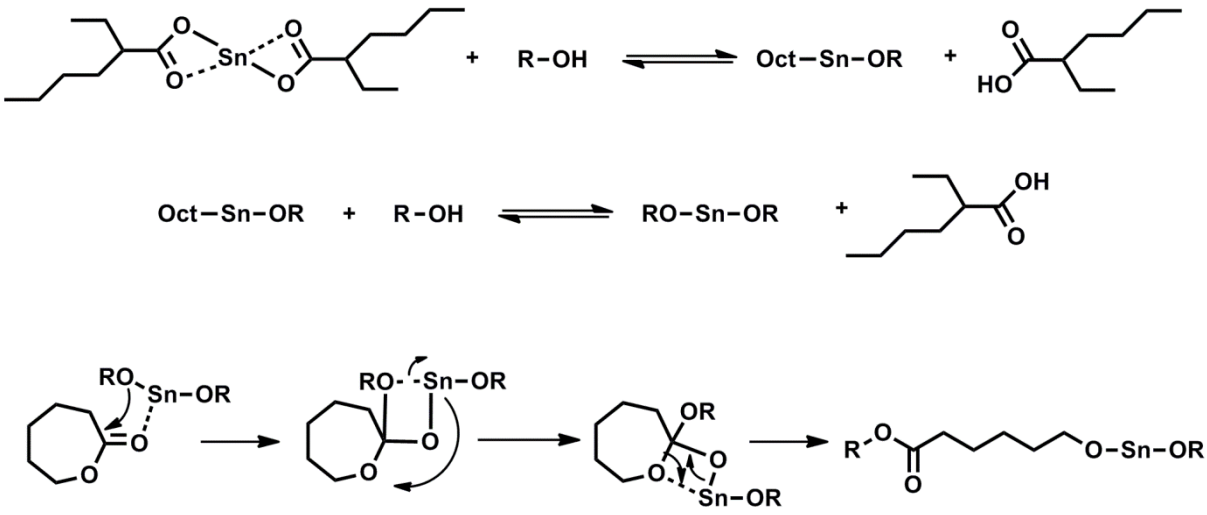


Figure 2.5-2: Initiation of the ring-opening polymerization of ε-caprolactone making use of tin(II) ethylhexanoate as catalyst.

Both TBD and $Sn(Oct)_2$ are tolerant towards diverse functional groups and stable under conventional polymerization conditions, although water impurities in the reaction mixture will lead to catalyst deactivation and/or growing chains initiated by water. However, working under neat conditions, the ROP of ε-caprolactone yields polymers with adjustable molecular weights and narrow dispersities.[127]

Modified caprolactone monomers are important to make tailor-made polyesters for specific applications. Moreover, the synthesis of caprolactone monomers from renewable feedstocks is subject of intensive research. So far, only a few reports about caprolactone monomers from renewable resources are available. For instance, Hillmyer *et al*. described the synthesis of caprolactone monomers from menthone or carvon.[128, 129] Heeres and colleagues reported about the synthesis of renewable ε-caprolactone from 5-hydroxymethylfurfural, a substrate derived from lignocellulosic biomass.

The synthesis of caprolactone monomers from fatty acids is reported in this thesis and gives access diversely substituted PCLs with interesting material properties.

2.6 Strategies for the preparation of primary amines

Polyamides are important high-performance polymers, which became indispensable for the electronic, automobile and textile industry. Polyamides can be synthesized by different polymerization techniques including the ring-opening of lactames or the radical polymerization of acrylamides. However, for most industrial processes a simple polycondensation of AA- or AB-type monomers is preferred. In particular, polyamides from renewable resources are of great interest since they benefit from a lower environmental impact. However, there remains a single example for the industrial scale production of a fully bio-based polyamide, PA11, which is prepared by polycondensation of 11-aminoundecanoic acid - a castor oil derived AB-type monomer.[114] On the other hand, fully renewable polyamides by polycondensation of AA-type monomers are hardly available since there are no efficient routes to bio-based diamines. In contrast, diacids (e.g., adipic-, sebacic- or azelaic acid) and the respective diesters are already accessible from renewable resources by efficient transformations.

To prepare bio-based polyamide monomers, the used renewable substrates have to be functionalized with a primary amine. Conventionally utilized diamine monomers such as 1,6-hexamethylenediamine or 1,4-butanediamine, are produced by hydrogenation of the corresponding dinitriles.[130] Other common strategies for the amine functionalization of diverse substrates are summarized in Table 2.6-1.

Most commonly used are halogenated substrates that are employed in substitution reactions utilizing sodium or potassium azide, cyanides, or phthalimides. After the

substitution, the functionalized compounds can be transformed into primary amines by reduction or hydrogenolysis as illustrated in Table 2.6-1. Popular name reactions for the synthesis of primary amines from halogenated substrates are the Gabriel synthesis or Delépine reaction. Another common synthesis method of primary amines is the reduction of amides using reducing agents such as lithium aluminium hydride ($LiAlH_4$). For the lab scale synthesis of primary amines these methods are particular useful since good yields and selectivity towards the primary amine is achieved. In general, for a sustainable, green and large-scale synthesis of primary amines, these methods are limited since a large amount of (halogenated) waste is produced, the atom economy is low and the used reagents are hazardous. An interesting and green alternative to accesses primary amines is the reductive amination of ketones and aldehydes. The utilization of ammonia at suitable reductive conditions (e.g., a metal catalyst and hydrogen atmosphere) makes this process very attractive, both, from an economic and ecologic point of view.

Table 2.6-1: Synthesis of primary amines from various substrates (the table was adapted from reference 131).

Reactant	Substrate	1st Reaction	Initial Product	2nd Reaction	Product
N_3^-	$R\text{-}CH_2\text{-}X$ $R_2CH\text{-}X$	S_N2	$R\text{-}CH_2\text{-}N_3$ $R_2CH\text{-}N_3$	Hydrogenolysis	$R\text{-}CH_2\text{-}NH_2$ $R_2CH\text{-}NH_2$
CN^-	$R\text{-}CH_2\text{-}X$ $R_2CH\text{-}X$	S_N2	$R\text{-}CH_2\text{-}CN$ $R_2CH\text{-}CN$	Reduction	$R\text{-}CH_2\text{-}NH_2$ $R_2CH\text{-}NH_2$
HCN	$RCH{=}CH_2$	Addition	$RCH_2\text{-}CH_2CN$	Reduction	$RCH_2\text{-}CH_2CH_2NH_2$
NH_3	RCH=O $R_2C{=}O$	Addition/ Elimination	R-CH=NH $R_2C{=}NH$	Reduction	$R\text{-}CH_2\text{-}NH_2$ $R_2CH\text{-}NH_2$
NH_3	R-(CO)X RCOOH	Addition/ Elimination	$R\text{-}(CO)NH_2$ $R\text{-}(CO)NH_2$	Reduction	$R\text{-}CH_2\text{-}NH_2$ $R\text{-}CH_2\text{-}NH_2$
NH_2CONH_2	$R_3C\text{-}OH$	S_N1	$R_3C\text{-}NHCONH_2$	Hydrolysis	$R_3C\text{-}NH_2$

X= e.g. Br, Cl, -OTs, -OMes; R=aliphatic, aromatic

Common organic reactions such as the Hofmann, Curtius or Lossen rearrangement are also widely applied methods to prepare primary amines by subsequent hydrolysis

of the obtained isocyanates or carbamates as illustrated in Figure 2.6-1. Each rearrangement procedure makes use of carboxylic acid derivatives, which are activated by different reagents. The Hofmann rearrangement involves the reaction of a primary amide with bromine to form a *N*-bromamide that rearranges to the corresponding isocyanate under basic conditions. The respective isocyanate can be hydrolyzed to the primary amine under loss of carbon dioxide. In the case of the Curtius rearrangement, the carboxylic acid is first transformed to an acyl azide that rearranges to the isocyanate under heating and release of nitrogen. Hydroxamic acids are used as substrates for Lossen rearrangements. Herein, the isocyanate is formed *via* rearrangement of a sulfonyl, O-acyl or phosphoryl intermediate.

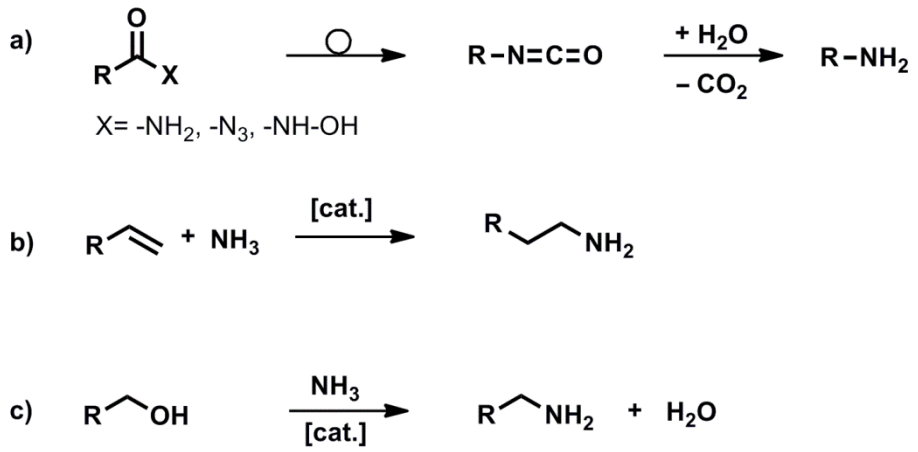


Figure 2.6-1: Synthesis of primary amines by a) rearrangement, b) hydroamination and c) direct amination of alcochols.

It is noteworthy that the use of toxic, explosive and hazardous reagents for the aforementioned rearrangement procedures do in principle not allow a sustainable and green access to primary amines or polyamide monomers, respectively.[132] Recently, Meier *et al*. reported a catalytic Lossen rearrangement procedure making use of TBD as catalyst, methanol and dimethyl carbonate as activation agents.[133] In comparison to the conventionally performed Lossen rearrangement, the presented method offers a more sustainable and green approach.

Two very interesting catalytic methods to prepare primary amines are the hydroaminomethylation of alkenes and the amination of alcohols. Both methods represent an atom-economic and environmentally benign strategy to access primary amines from readily available substrates. The hydroaminomethylation is a domino reaction including the hydroformylation of an alkene to an aldehyde and subsequent reductive amination to afford primary amines when using ammonia as reagent

(Figure 2.6-1, b).[134] However, the process is so far limited to a few substrates since the catalytic system has to be well-adjusted to achieve good conversions and selectivity. Most bio-based feedstocks or substrates possess different functional groups, often hydroxyl groups, which can be utilized in direct amination reactions (Figure 2.6-1, c). The direct amination of diverse alcohols was demonstrated by Vogt and coworkers as well as Milstein *et al*. Herein, diverse alcohols were converted to the corresponding primary amine using ruthenium catalysts and ammonia.[135, 136] The latter reaction is referred to a "hydrogen shuttling'', since the net reaction is a transfer of hydrogen from the alcohol to the amine, whereas water is the only obtained byproduct. All in all, there are promising methodologies that allow the environmentally benign synthesis of amine-functionalized compounds. However, the utilization of renewable substrates in these catalytic procedures is not well-developed and still needs optimization. Hence, the preparation of renewable polyamide monomers is mainly based on multi-step and non-environmentally friendly reactions. Although these transformations have their legitimation since in this way the properties of the potential renewable polyamides can be investigated, there is a need for more sustainable alternatives.

2.7 Thiol-ene, thiol-yne and thia-Michael addition

Mild, efficient, straightforward and atom-economic reactions are considered to be the key to Green Chemistry. In the past decade, the thiol-ene and thiol-yne addition became important tools for the synthesis of (renewable) monomers and polymers as well as for an efficient polymer modification.[137-139] In particular, the radical mediated thiol-ene addition of functionalized thiols to unsaturated fatty acids allows the synthesis of a great variety of different monomers and polysulfides as outlined in a recent review.[140] The thiol-ene addition is usually performed with a radical initiator, although the reaction can proceed *via* self-initiation as well. A simplified reaction mechanism is depicted in Figure 2.7-1.[141] In the first step, a thiyl radical is formed by reaction of the thiol and the radical provided from the initiator as illustrated in Figure 2.7-1 (A). The thiyl radical reacts with an alkene to yield a secondary carbon radical (B), which undergoes a chain transfer reaction to yield another thiyl radical and the addition product (C).

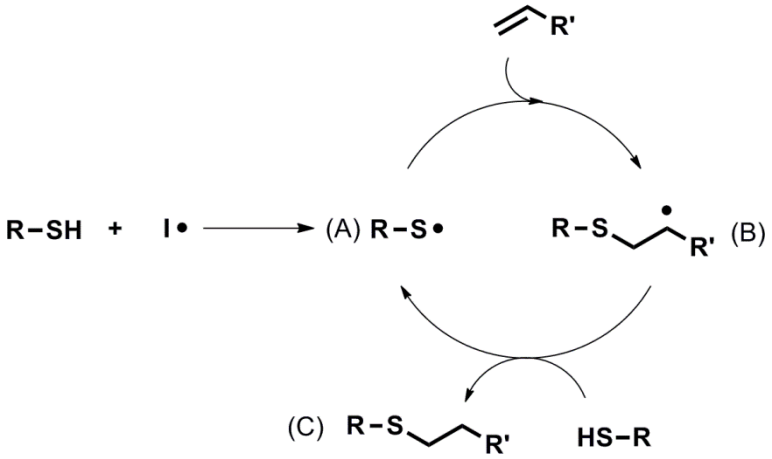


Figure 2.7-1: Mechanism of the thiol-ene addition.

In order to prepare polymers by thiol-ene addition, there is the possibility to either synthesize monomers using functionalized thiols or to directly employ the thiol-ene reaction as polymerization technique for AA- or AB-type monomers. Unsaturated fatty acids are excellent substrates to be used in thiol-ene chemistry. Applying functionalized thiols, different functional groups (e.g., –OH, -NH_2, -COOMe) can be introduced to prepare monomers for polycondensation reactions.

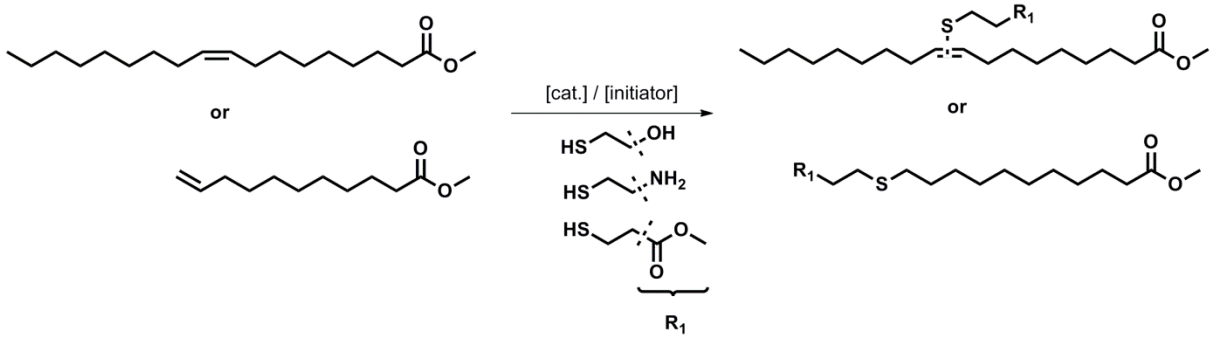


Figure 2.7-2: Thiol-ene addition of methyl oleate or methyl undecenoate with 2-mercaptoethanol, cysteamine or methyl 3-mercaptopropionate in order to synthesize plant oil derived monomers.

For instance, Meier *et al.* reported the addition of cysteamine to methyl undecenoate, methyl oleate and –erucate to prepare AB-type monomers in order to synthesize renewable polyamides (Figure 2.7-2).[142] Dienes and dithiols are suitable AA-type monomers to be directly used in thiol-ene addition polymerizations. In this context, Meier and coworkers reported the preparation of a set of anhydride, ester or ether functional biodegradable polymers from castor oil derived platform chemicals by thiol-ene addition reactions.[84, 143] For this purpose different dienes and dithiols had been used as AA-type monomers. The prepared renewable polymers were studied for their biodegradability by testing their thermal and hydrolytic stability.

In principle, an AB-type monomer having a double bond and thiol group can be directly used for thiol-ene polymerizations as well. Nonetheless, the preparation of such monomers is not simple as the compounds have to be handled and stored carefully to prevent early polymerization.[144]

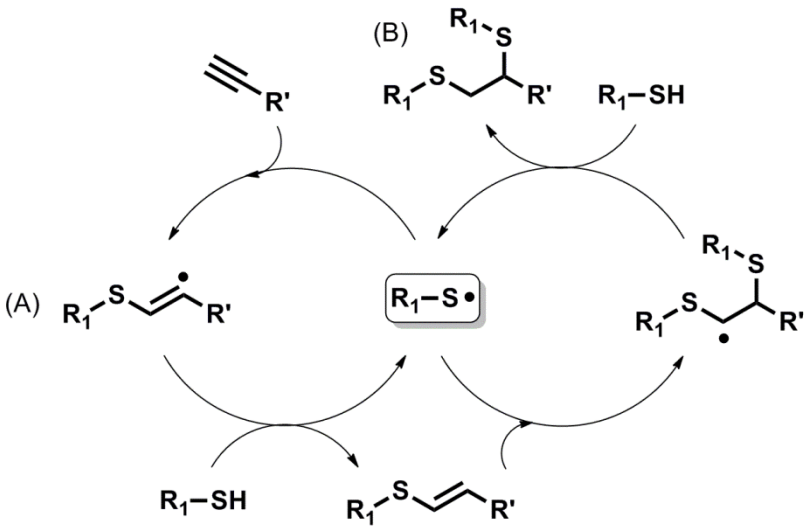


Figure 2.7-3: Mechanism of the thiol-yne addition.

The thiol-yne addition proceeds *via* a two-step reaction. As illustrated in Figure 2.7-3, the generated thiyl radical reacts with the alkyne to yield a vinyl sulfide (A). Depending on the reaction conditions the formed vinyl sulfide can undergo a further addition reaction with another thiyl radical to yield the *bis*-addition product (B). Here, in principle, two isomers can be formed depending on the substituents of the used alkyne and thiol, whereas usually, due to the stability of the vinyl sulfide radical, the 1,2-disubstituted adduct is generated (see Figure 2.7-3). *Inter alia*, Hawker and coworkers demonstrated that under specific reaction conditions, the thiol-yne reaction can be performed in a selective manner to exclusively obtain the mono-addition product.[145, 146] Interestingly, Dove and coworkers demonstrated that by using a suitable solvent/catalyst system, the thiol-yne addition to propiolic acid esters can be performed with a high regioselectivity.[147] The presented strategy enables the sequential and regioselective addition of two different thiols and, thus, the synthesis of versatile complex macromolecular architectures.

There are different possibilities to prepare polymers *via* thiol-yne chemistry. However, the most common approaches involve the utilization of a terminal alkyne in combination with a dithiol or the polymerization by mono-addition of a dithiol to a dialkyne.[148]

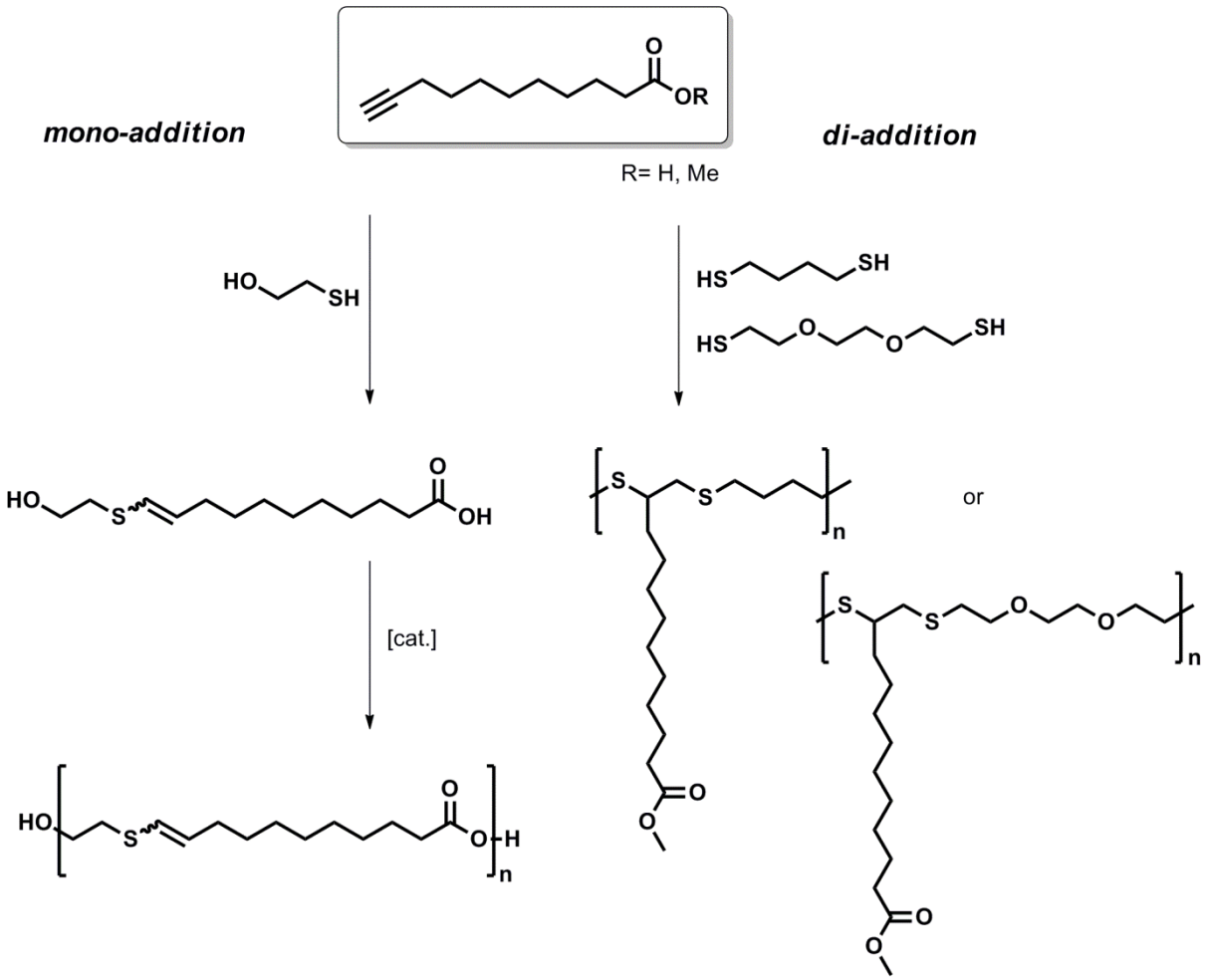


Figure 2.7-4: Thiol-yne addition of methyl undec-10-ynoate to prepare fatty acid based polymers.

Meier *et al*. demonstrated that besides diverse monoalkynes, 10-undecynoic acid, as a castor oil derived platform chemical, can be successfully used in thiol-yne polymerization reactions with different aliphatic dithiols (Figure 2.7-4). Cadiz and coworkers described the synthesis of a vinyl sulfide-containing hydroxy acid (VSHA) from 10-undecynoic acid by thiol-yne mono-addition.[149] The prepared plant oil based monomer was used to synthesize vinyl sulfide containing polymers and block copolymers, which are suitable for post-polymerization modification reactions.

However, the use of thiol-yne chemistry for the transformation of renewable substrates into monomers and polymers is limited due to the availability of the required alkynes. So far, alkynes are usually prepared by bromination/dehydrobromination from olefinic substrates. Applying this procedure, internal and terminal monoacetylenic fatty acids can be synthesized using e.g. oleic or 10-undecenoic acid.[150, 151] Nevertheless, the procedure does not meet the criteria of Green Chemistry since the transformation has a very low atom economy, toxic reagents are used and a large amount of waste is generated.

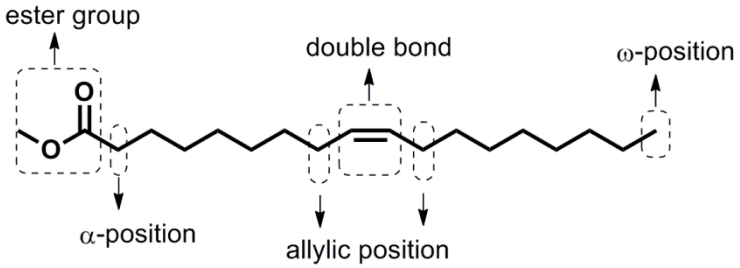
In order to make the thiol-yne chemistry more attractive for oleochemistry, novel efficient and sustainable synthesis procedures to access acetylenic fatty acids are needed. One promising strategy to access alkynes in a sustainable procedure might be the catalytic dehydrogenation of alkenes.[152]

All in all, thiol-ene and thiol-yne addition reactions proved to be a powerful tool to prepare monomers and polymers based on plant oils. Functionalized thiols are readily available or can be prepared by straightforward modification. Beside the radical-mediated thiol-ene or thiol-yne addition, thiols can be used as reagent in thia-Michael additions. These related reactions are highly efficient and proceed under mild reaction conditions as well. Typical Michael acceptors are α,β-unsaturated esters, ketones or maleimides. In contrast to the radical-mediated thiol addition to alkenes or alkynes, the thia-Michael addition proceeds by an ionic mechanism. Usually, primary and tertiary amines or phosphines are used as catalyst to provide adequate reaction rates. Thia-Michael additions are widely applied in polymer chemistry as post-polymerization modification method,[153-155] polymerization,[156-158] or ligation technique,[159, 160] or for the monomer synthesis.[160-162] In contrast, even though the thia-Michal addition fulfills many criteria of Green Chemistry, it is only rarely used to prepare bio-based monomers or polymers, since conventional renewable substrates (e.g. natural occurring plant oils) only possess double bonds along their aliphatic carbon chain and not in conjugation to the carboxylic acid.

2.8 Isomerizing transformation of plant oils

With regard to the structure of fatty acids or FAME, there are different reactive sites. Unsaturated fatty acids are considered as valuable substrates for versatile transformations, since compared to their saturated derivatives, the additional double bond(s) in the aliphatic backbone offer further reactive sites. Conventionally, the internal double bonds of fatty acids are applied for addition reactions, oxidations or allylic substitutions (Figure 2.8-1). However, the ω-position can be used in enzyme-catalyzed oxidation reactions to prepare the respective dicarboxylic acid or ω-hydroxy fatty acid, which are very interesting monomers for the synthesis of long-chain polyesters.[163, 164] The allylic position of an unsaturated fatty acid or FAME is interesting for typical substitution reactions, such as the Wohl-Ziegler bromination or the allylic photo-peroxidation.[165, 166]

The double bond offers multiple opportunities for further transformations, such as substitution and addition reactions (thiol-ene addition, epoxidation, or acylation).
The cleavage of unsaturated fatty acids is interesting for the preparation of lubricants and biofuels. Herein, olefin metathesis or ozonolysis are commonly applied and efficient organic transformations. Another modification possibility offers the α-position of fatty acids, which can be used in enolate chemistry. Meier *et al*. demonstrated the modification of saturated and unsaturated fatty acids at the α-position using dimethyl carbonate and a strong base to prepare renewable dimethyl malonates.[167]



ester group:
- transesterification
- hydrolysis
- reduction
- amidation

double bond:
- ozonolysis
- epoxidation
- metathesis
- isomerization
- acylation / alkylation
- carbonylation
- pericyclic reactions
- thiol-ene addition

α-position:
- sulfonation
- halogenation
- enolate chemistry
- dimerization

ω-position:
- substitution chemistry
- oxidation

Figure 2.8-1: Reactive sites and some possible transformation possibilities of fatty acid methyl esters.

A highly interesting alternative is the isomerization and simultaneous functionalization of the respective migrated double bond. Cole-Hamilton introduced the isomerizing alkoxycarbonylation of unsaturated fatty acid methyl esters to prepare long-chain diesters.[168] The combination of a bulky phosphine ligand and a palladium catalyst is used to achieve an isomerization of the double bond; i.e. the double bond starts to migrate along the aliphatic chain resulting in a dynamic equilibrium of different regioisomers. According to the principle of Le Chatelier, this equilibrium can be shifted by selectively trapping only one isomer. In case of the aforementioned isomerizing alkoxycarbonylation, only the isomer with a terminal double bond undergoes an alkoxycarbonylation reaction to form a thermodynamically stable

product. Mecking and coworkers used the isomerizing alkoxycarbonylation to prepare long-chain diesters and diols, both AA type monomers, which can be used to prepare long-chain polyesters by polycondensation (Figure 2.8-2).

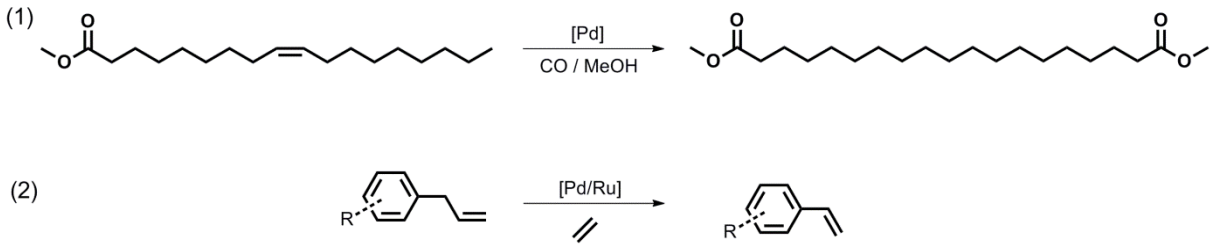


Figure 2.8-2: Isomerizing methoxycarbonylation of methyl oleate (1) and isomerizing ethenolysis of allylbenzene derivatives such as eugenol or safrol (2).

Such long-chain polyesters are considered as bio-based polyethylene mimics, since they have long linear aliphatic chain segments leading to similar material properties compared to HDPE.[169-171] These renewable long-chain polyesters are highly interesting as novel bio-based high-performance materials since they show high melting temperatures and are biodegradable due to the ester bonds in the polymer backbone. Also, Mecking *et al*. demonstrated that these long-chain polyesters obtained from renewable resources can be produced on relatively large scale and be used for injection molding, film extrusion and electrospinning to produce non-woven meshes.[172] Recently, Gooßen and colleagues reported a dimeric palladium(I) complex, a very active catalyst that in particular shows high activity and selectivity for double bond migration at mild reaction conditions.[173] The highly active palladium catalyst was used in combination with conventional ruthenium-based metathesis catalysts to perform an isomerizing olefin metathesis of unsaturated FAMEs. The presented approach offers novel synthetic opportunities to prepare diverse unsaturated oleochemicals based on a renewable feedstock, although there is not a specific application for such an approach, yet. More interesting, the bimetallic catalytic system was utilized to prepare functionalized styrenes - important monomers in polymer science and valuable synthons in organic chemistry - using renewable substrates (e.g., eugenol, safrol or estragol) as shown in Figure 2.9-1.[174]
Beller *et al*. presented a very attractive modified procedure of the isomerizing alkoxycarbonylation.[175] Carbon monoxide as toxic and difficult-to-handle gaseous reagent was replaced by methyl formate, which in combination with a palladium catalyst provided excellent yields of the methoxycarbonylated product. Interestingly, even carbon dioxide can serve as carbon monoxide substitute if a ruthenium catalyst

and an alcohol is used instead.[176] In summary, the presented strategies are highly interesting, since an isomerization transformation of unsaturated FAMEs offers the opportunity for the large scale production of bio-based polyethylene mimics and high-performance polyesters that are promising novel and biodegradable materials. Beside long-chain polyesters, diverse long-chain polyamides were produced by using these diesters and the respective diamines as monomers. Such long-chain polyamides are known to exhibit exceptional material properties such as a low water uptake and an improved tensile strength, which makes them interesting for special applications.[177]

2.9 Olefin Metathesis for the preparation of plant oil derived monomers

The preparation of platform chemicals, monomers or polymers by metathesis of substrates from renewable feedstocks is very attractive as this catalytic approach is an environmental benign synthesis approach. In particular, the metathesis of natural unsaturated fats and oils demonstrates an excellent example for Green Chemistry as it represents a clean catalytic reaction that offers the opportunity to obtain defined and value-added products under mild reaction conditions and often under solvent-free conditions.[178] The self-metathesis of fatty acids or FAMEs yields dicarboxylic acids or diesters - suitable AA-type monomers for the preparation of polyesters or polyamides (Figure 2.9-1). For instance, in the case of methyl oleate, self-metathesis yields the C18 diester and the respective C18 aliphatic alkene. Moreover, the respective diols that can be obtained by catalytic reduction of the diesters, are valuable AA-type monomers for polycondensation as well. Polyunsaturated FAMEs such as the linoleic acid methyl ester are very attractive substrates for self-metathesis, since different diester and alkenes with varying chain length are obtained.[179, 180] A significant advantage of the usage of polyunsaturated fatty acids for self-metathesis is the possibility to shift the metathesis equilibrium by simple removal of the produced volatile alkenes (e.g., hex-3-ene or 1,4-cyclohexadiene).[179] Through cross-metathesis of fatty acids or FAMEs, a wide range of functional fatty acid derivatives is accessible. Meier *et al*. reported the cross-metathesis of methyl oleate and –erucate with methyl acrylate to yield an C11 α,β-unsaturated diester and

methyl undec-2-enoate (Figure 2.9-1). The metathesis reactions were performed under solvent-free conditions and with low catalyst loadings (0.1 mol%).

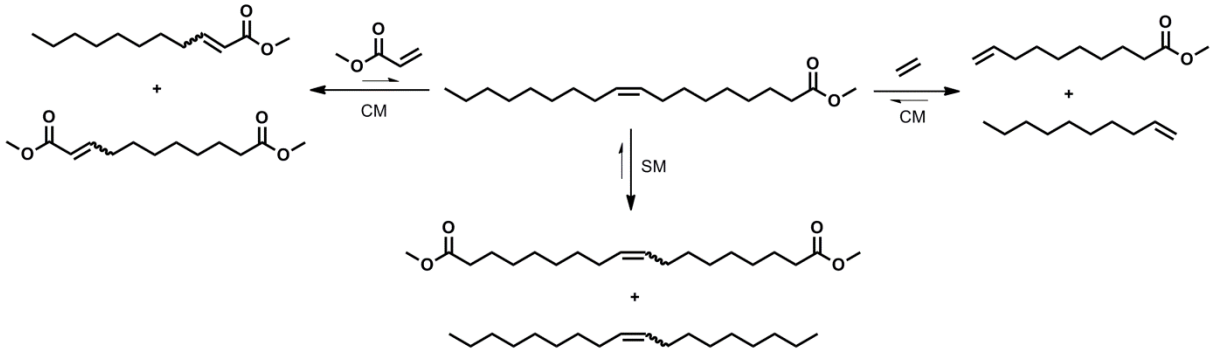


Figure 2.9-1: Synthesis of structurally diverse compounds by olefin metathesis utilizing methyl oleate.

The cross-metathesis of methyl acrylate with polar plant oil derivatives such as oleyl amine or oleyl alcohol directly yield AB-type monomers, but are more challenging due to catalyst deactivation.[181, 182] Of particular interest is the cross-metathesis of amine-functional substrates to yield amino alkenes, which are useful compounds in organic syntheses and the preparation of polyamides.

Ethenolysis or butenolysis (i.e. cross-metathesis employing ethylene or butylene) offers the possibility for the cleavage of unsaturated fatty acids to yield short terminal olefins or ω-unsaturated fatty acids. The selective cleavage of unsaturated fatty esters is a potentially useful transformation for the production of lubricants.[183] The ethenolysis, for instance of methyl oleate, yields the methyl dec-9-enoate and dec-1-ene, a patented process that is close to industrial realization.[184-186] More general, the ethenolysis of unsaturated FAMEs leads to terminal olefins, which are significantly more reactive substrates in addition reactions than internal olefins. Moreover, the preparation of plant oil-based polymers by ROMP or ADMET was intensively studied. However, the use of ROMP or ADMET is only feasible if the monomers can be prepared in a straightforward and environmentally benign procedure. In this context, the synthesis of plant oil based norbonene monomers and the thereof derived polyester by ROMP was demonstrated.[187] On the other hand, 10-undecenoic acid, a castor oil derived platform chemical, is used to prepare α,ω-dienes representing suitable monomers for ADMET polymerization.[28] The respective monomers were prepared by simple esterification/amidation utilizing diols or diamines.

(Note that parts of this chapter were written for the previously authored diploma thesis (M. Winkler, *Synthesis and Orthogonal Conjugation of Polymers from Renewable Resources*, 2011, Karlsruher Institut für Technologie)).

3. Aim of the thesis

Monomers and polymers derived from renewable resources have become competitive to fossil derived products. The depletion of fossil resources and an increased environmental pollution are the main reasons for the strong demand for materials based on renewable resources. Plant oils are well-established platform chemicals in the chemical industry and offer some promising future perspectives.

The aim of this thesis is to investigate novel catalytic or efficient processes for the synthesis of plant oil-derived monomers and polymers. Of particular interest is the use of oleic- and erucic acid, plant oil derived fatty acids, which can be obtained from domestic oilseed crops of the German agriculture. Herein, methods for the efficient use of these domestic renewable resources for the synthesis of polymeric materials are being investigated in order to promote the development of novel plant oil-based products and to show up novel opportunities for their use in the non-food sector. In particular, the synthesis of plant oil derived polyamides is subject of the current thesis. Because of their extraordinary material properties, conventional polyamides (Nylons) are considered as high performance polymers. Therefore, the synthesis of fatty acid derived polyamide monomers should be investigated in detail by using various efficient approaches. The material properties of the thereof derived renewable polyamides should be analyzed and compared to conventional polyamides. Herein, the analysis of the thermal and mechanical properties should give information about the performance of the synthesized renewable polyamides. Due to the increased environmental pollution caused by plastics, the synthesis of biodegradable polymers from renewable resources such as polyesters or polycarbonates should be investigated as well.

More general, for the synthesis of all renewable monomers and polymers, different catalytic processes should be optimized and evaluated with regard to the principles of Green Chemistry in order to achieve a straightforward, selective and efficient transformation of the used fatty acids.

4. Results and discussions

Please note that the numbering / designation of all compounds was assigned according to each chapter. For instance compounds in section 4.1 are numbered with the additional section element (**.1**) (e.g., methyl oleate **1.1**). Compounds which had been used in multiple sections might have different numbers or designations.

4.1 A more sustainable Wohl-Ziegler bromination: Versatile derivatization of unsaturated FAMEs and synthesis of renewable polyamides

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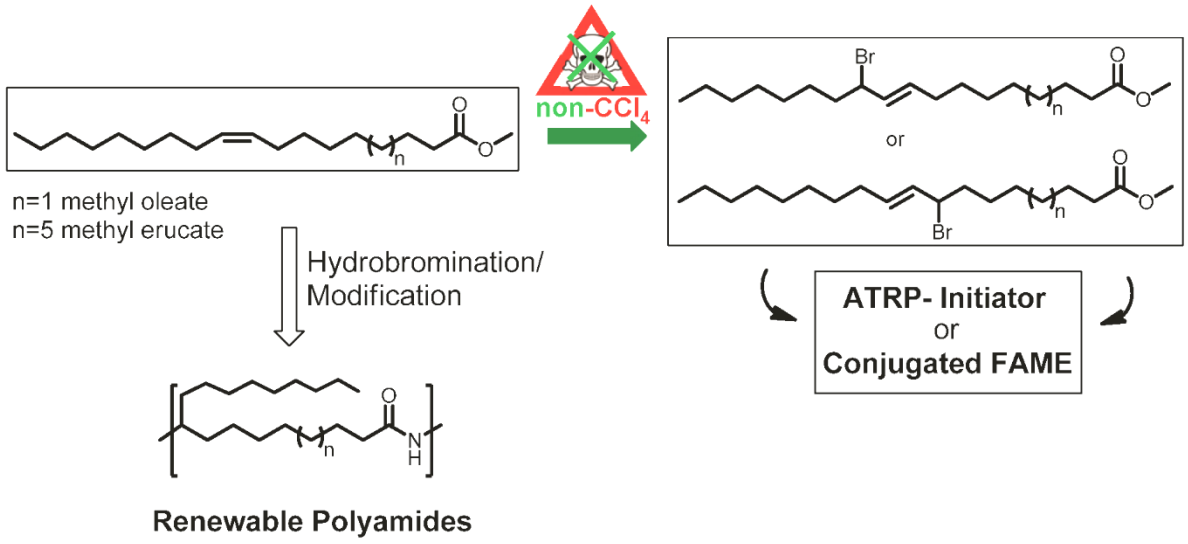

Abstract

Within this contribution, a more sustainable procedure for the Wohl-Ziegler bromination of unsaturated FAME was investigated. The resulting allylic bromide functional FAMEs were used for elimination reactions to prepare conjugated fatty acids. Moreover, the fatty acid derived allylic bromides were used as initiators for atom transfer radical polymerization (ATRP). Furthermore, the synthesis of AB-type polyamide monomers was accomplished by a complementary hydrobromination of FAMEs and subsequent modification. The obtained polyamides were characterized by SEC, NMR and DSC analysis.

Introduction

The Wohl-Ziegler bromination is a well-known and commonly used laboratory method to prepare allylic bromides from olefinic substrates. *N*-bromosuccinimide (NBS) and AIBN (2,2′-azobis(2-methylpropionitrile)) are used in this reaction to achieve a bromination at the allylic position *via* a radical chain mechanism. Recently, this allylic bromination was investigated under photochemical, microwave, sonochemical or solid state reaction conditions aiming for a more sustainable procedure for the Wohl-Ziegler bromination.[110, 188-190] In this context, also various solvents have been studied including benzene, chloroform, ionic liquids or supercritical CO_2.[109, 191, 192] Moreover, the reaction was carried out under solvent-free conditions.[193] However, carbon tetrachloride (CCl_4) is still one of the most extensively used solvents for Wohl-Ziegler brominations, since CCl_4 exhibits excellent properties with regard to the reaction temperature, solubility and simplicity of product isolation.[194, 195] Usually, simple filtration of the reaction mixture is sufficient to remove the succinimide byproduct from the reaction mixture and to obtain the allylic bromides in good purity. Nevertheless, the use of CCl_4 as an ozone-depleting substance and very hazardous and carcinogenic solvent should be avoided.

Alternatives to CCl_4 are certainly required and studies to enlarge the scope of substrates that can be functionalized in such ‘’greener’’ Wohl-Ziegler bromination procedures are necessary. In polymer chemistry, the Wohl-Ziegler bromination was already employed for the synthesis of diverse monomers, which can be used in the preparation of biobased polyurethanes, polyureas, polythiourethanes and polythioureas.[112, 113] The introduction of a bromide to unsaturated fatty acids is of high interest, since further modification can lead to amine functionalized fatty acids and other derivatives. Such amine functionalized fatty acids received an increased interest in the pharmaceutical industry and have been used as specialty surfactants, valuable intermediates for other industrial products, and more importantly as monomers for the synthesis of renewable polyamides.[196]

Within this chapter, a more sustainable Wohl-Ziegler bromination procedure for unsaturated fatty acid methyl esters and a detailed investigation of the use of the prepared allylic bromide functionalized fatty acid methyl esters is described. Moreover, the efficient synthesis of amine functional fatty acids will be demonstrated.

Results and discussions

The investigations were strated with a screening for greener and safer reaction conditions for the Wohl-Ziegler bromination, which would allow the synthesis of the allylic bromides in a selective and efficient manner (Figure 4.1-1).

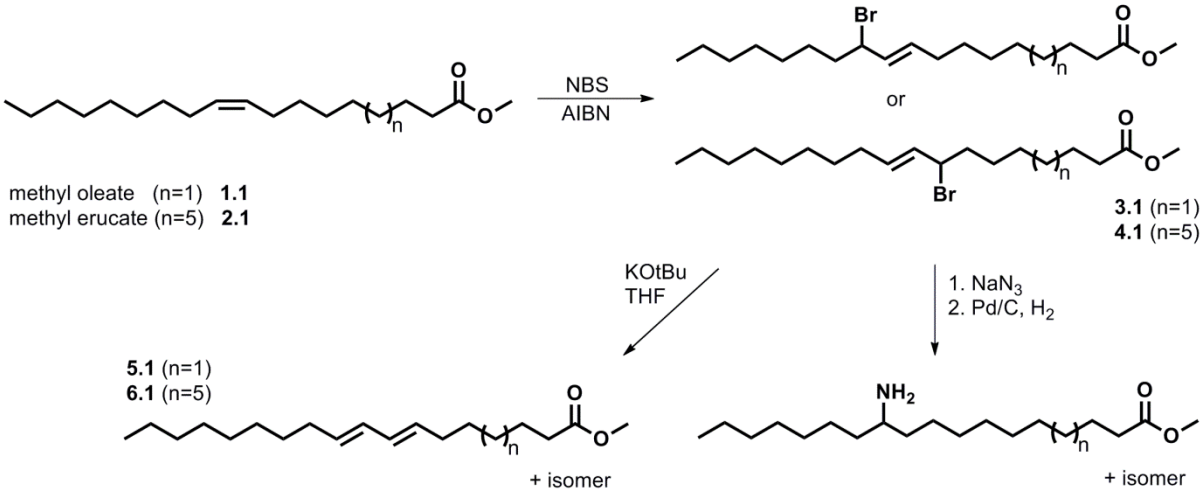

Figure 4.1-1: Synthesis strategy for the preparation of methyl oleate or –erucate derived AB-type monomers or conjugated fatty acids.

Methyl oleate **1.1** was used as the model substrate for all reactions in the allylic bromination using NBS. Besides a conventional reaction set-up (round bottom flask and heating in an oil bath), some reactions were also performed under microwave irradiation. For an adequate decomposition of 2,2'-azobis-(2-methylpropionitrile) (AIBN) and a moderate concentration of radicals and bromine, the reactions were carried out in a temperature range of 60 - 100 °C.

To compare the different reaction conditions, the Wohl-Ziegler bromination was first performed under conventional reaction conditions (Table 4.1-1, entry 1: CCl_4, 80 °C, reflux, 2h), which provided the expected results[112] and a bench-mark for our further experiments. In order to substitute the highly toxic and ozone-depleting carbon tetrachloride, several solvents were tested with the aim to perform the Wohl-Ziegler bromination in a safer and more sustainable manner (Table 4.1-1). Moreover, the allylic bromination was also carried out in bulk to avoid any solvent waste. Notably, microwave assisted allylic brominations of methyl oleate or Wohl-Ziegler brominations in water did not lead to the desired monoallylic bromide, which is in contrast to results reported for other substrates (e.g., benzylic substrates).[110, 111, 189, 197]

Table 4.1-1: Reaction screening of the Wohl-Ziegler bromination of methyl oleate **1.1**.

Entry	Solvent	Temp. (°C)	Method	Time (min)	Conversion[a] (%)	Yield[a] (%)
1	CCl_4	80	Flask	120	92	85
2	Bulk	80	Mw	20	49	-
3	Bulk	100	Mw	10	75	-
4	Bulk	80	Flask	120	89	65
5	EtOH	60	Flask	120	95	4
6	EtOH	80	Mw	20	80	-
7	$CHCl_3$	60	Flask	90	50	4-5
8	$CHCl_3$	80	Mw	10	66	-
9	MeCN	60	Flask	120	57	~2
10	DMC	60	Flask	120	23	-
11	Cy	80	Flask	120	80	74
12	Cy	80	Flask	240	95	87
13	H_2O	80	Sonication	240	60	16

[a]Determined by GC-MS analysis with internal standard, MeCN = acetonitrile, DMC = dimethylcarbonat, EtOH = ethanol, Cy = cyclohexane. Flask: reactions were run in a round bottom flask with reflux condenser installed; Mw: a microwave synthesizer was used for these reactions.

Furthermore, mainly a conventional bromination of the double bond occurred in the microwave mediated brominations was observed, most probably due to the faster decomposition of AIBN or NBS, which resulted in higher bromine concentrations. With regard to a safer and more sustainable Wohl-Ziegler bromination procedure, experiments under conventional heating performed in bulk (entry 4) or employing cyclohexane (entry 12) as solvent provided the most promising results. If compared to the CCl_4 bench mark (entry 1), cyclohexane provided similarly good results, whereas reactions in bulk showed slightly lower conversions and yields. Generally, a good selectivity towards the monoallylic brominated FAME was achieved, if the reactions were carried out at a temperature of 80°C. The reactions performed in cyclohexane were run for 4h, whereas for reactions performed in bulk the reaction time was decreased to 2h. Transferring the optimized procedure to methyl erucate **2.1** resulted in similar yields and conversions. All in all, cyclohexane is less toxic than CCl_4 and non-ozone-depleting, thus representing a valuable alternative, though it is still a hazardous solvent. However, for the allylic bromination of methyl oleate,

experiments performed in bulk probably constitute an even more valuable alternative with regard to a safer and greener handling, especially if compared to the conventional reactions employing CCl_4 as solvent. In order to be able to better compare results and evaluate the environmental impact of the Wohl-Ziegler bromination under different reaction conditions more detailed, the E-Factors of the reactions performed in CCl_4, cyclohexane and bulk were calculated considering the yields determined *via* GC-MS analysis.[198] As expected reactions performed in bulk have the lowest E-Factor of 1.19, whereas reactions performed in cyclohexane or CCl_4 have a higher E-Factor of 3.19 or 5.89, respectively.

Having the allylic bromides **3.1** and **4.1** in hands, we wanted to use them for subsequent modifications. Generally, the transformation of monounsaturated fatty acids, such as methyl oleate or –erucate, into conjugated fatty acids is highly desirable from an industrial point of view, because they can be used in alkyd resins or for further modification. Thus, as a first modification strategy, **3.1** and **4.1** were used to prepare fatty acid methyl esters having conjugated double bonds. The elimination was performed by employing a solution of potassium *tert*-butoxide in THF in an ultrasonic bath at 30°C for 3 hours. Analysis *via* NMR spectroscopy showed full conversion of the allylic bromides and the formation of conjugated double bonds, which confirmed the successful elimination. The conjugated FAMEs were obtained as a mixture of *cis*- and *trans*-configured double bonds. GC-MS analysis revealed that the product consists of about 90% conjugated and 10% monounsaturated FAME species.

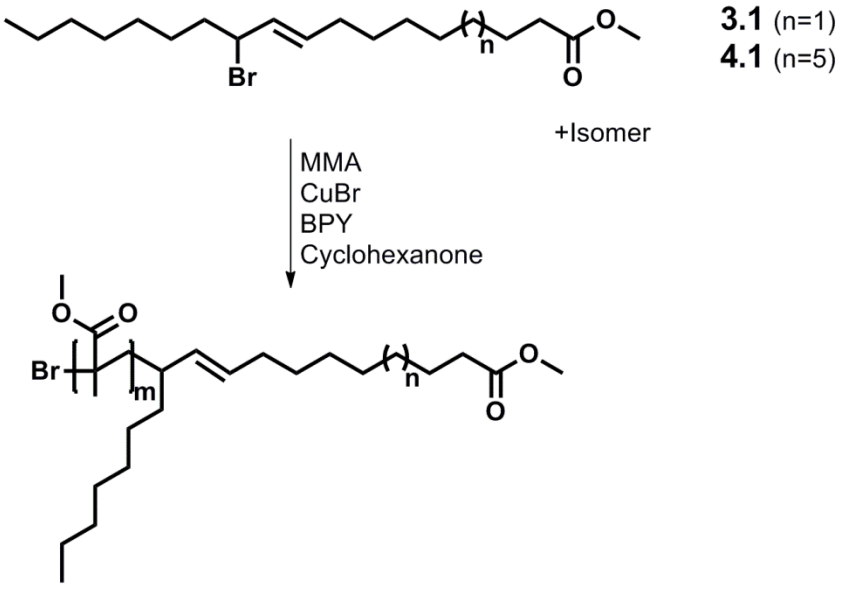

Figure 4.1-2: Application of the fatty acid derived allylic bromides as ATRP initiators.

As it is known from literature, allylic bromides can act as initiators for atom transfer radical polymerization (ATRP).[199-201] However, so far, only terminal allylic bromides, such as 3-bromoprop-1-ene, have been employed as ATRP initiators. Therefore, it would be very interesting to investigate the behavior of our plant oil based internal allylic bromides as initiators for ATRP polymerizations.

Thus, ATRP polymerizations employing methyl methacrylate (MMA) as monomer, 2,2′-bipyridyl as ligand, copper(I)bromide as catalyst and cyclohexanone as solvent for a controlled radical polymerization using **3.1** as initiator (Figure 4.1-2) were investigated. As typical for a controlled polymerization technique, it was possible to predetermine the obtained molecular weights by variation of the monomer to initiator ratio ([M]/[I] ratio), as displayed in Figure 4.1-3 and Table 4.1-2. Unfortunately, the theoretically calculated molecular weights were not in full agreement with the results from the SEC analysis (Table 4.1-2). More problematic and as also known from the literature,[112, 195] the prepared allylic bromides cannot be obtained in their pure form, because simple alkyl bromides or double allylic bromides are formed as side products. Thus, the prepared allylic bromides are not absolutely pure (about 85% mono allyl bromide, 10 % diallyl bromide, and 5 % simple alkyl bromides), and this easily explains why the obtained molecular weights are slightly deviating from the theoretically expected values. Nevertheless, this study of the polymerization of MMA utilizing different monomer to initiator ratios revealed a good control over the performed ATRP polymerizations, since the molecular weight could be well adjusted by varying the [M]/[I] ratio. Moreover, the obtained polymers exhibited narrow molecular weight distributions and no shoulders, which would be indicative for, i.e., chain-chain coupling events (Figure 4.1-3, Table 4.1-2).

Table 4.1-2: Molecular weights and dispersities of the polymers prepared by ATRP polymerization.

[M]/[I]	M_n [Da]	$Đ$
50:1	11500	1.05
100:1	18100	1.10
200:1	24800	1.38
300:1	34600	1.35

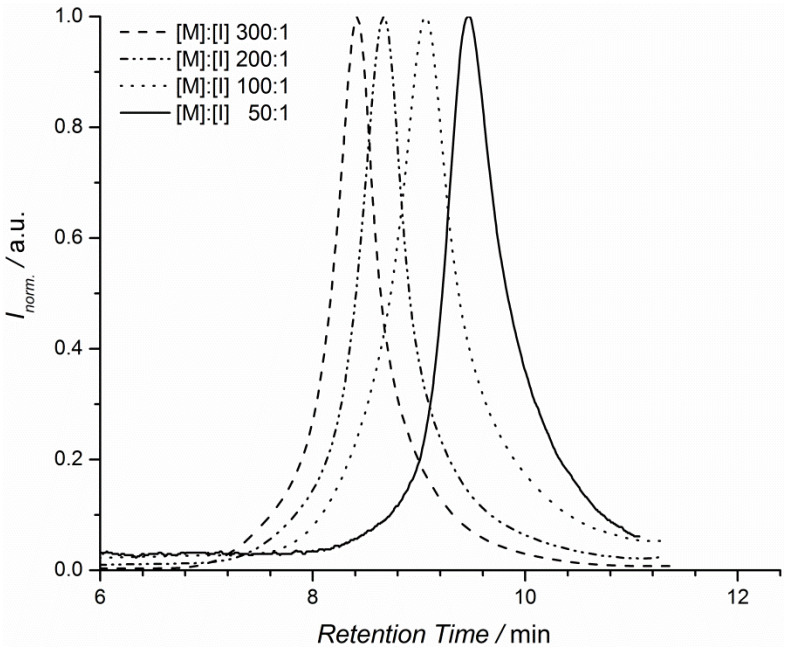

Figure 4.1-3: SEC analysis of the polymers prepared *via* ATRP polymerization of different monomer to initiator ratios [M]:[I].

These results thus show the successful utilization of plant oil based and internal allylic bromide as initiators for ATRP polymerization, offering a novel and promising application.

As a further modification strategy and with respect to the preparation of AB-type monomers suitable for a polyamide synthesis, the efficient transformation of the allylic bromide function to a primary amine was unfortunately inefficient, since the modification of **3.1** or **4.1** by conventional transformation into an azide and subsequent reduction was accompanied by several side-reactions. Another possibility for the conversion of the allylic bromides to amine functionalized fatty acid methyl esters might be realized by a Delépine or Gabriel reaction.[202, 203] However, due to their S_N2 character, these reactions are better suitable for primary halogens and therefore we did not test these alternatives in detail. However, as already mentioned before, a major problem in the synthesis of the allyic bromides from methyl oleate or –erucate *via* the introduced Wohl-Ziegler procedure is the selectivity toward mono-allylic bromination and the formation of by-products. With the long-chain fatty acids derivatives, the separation of these by-products was not possible by straightforward purification methods. Since our goal was the preparation of AB-type monomers, this exhibits a major problem due to the inaccuracy of the polycondensation stoichiometry, which will lead to decreased molecular weights. To circumvent these problems, an appropriate purification strategy is needed and the

Wohl-Ziegler bromination still has to be optimized with regard to a more selective mono-allylic bromination.

Thus, instead of employing **3.1** and **4.1** for a subsequent amine functionalization, we performed a classic hydrobromination and converted the obtained bromides into azides, which were subsequently reduced to the corresponding amines (Figure 4.1-4).

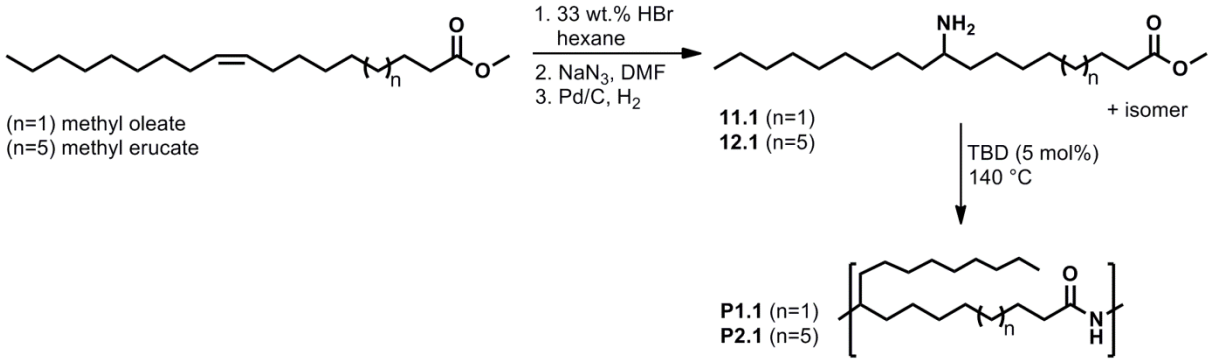

Figure 4.1-4: Preparation of polyamides through hydrobromination and subsequent modification /polymerization.

A great advantage of the hydrobromination compared to the Wohl-Ziegler bromination is the more selective and efficient transformation into the corresponding bromides, which were obtained in quantitative yields. The hydrobromination was performed in hexane with a 33 wt.% hydrobromic acid solution in acetic acid at room temperature for only 1 hour. After washing with water and phase separation, the FAME bromides were obtained in quantitative yields. Subsequent azide functionalization and reduction by palladium on charcoal catalyzed hydrogenation leads to the amine functionalized FAMEs. Interestingly, a similar (but proceeding *via* a radical mechanism) hydrobromination is used on industrial-scale for production of methyl 10-aminoundecanoate, the monomer of Nylon-11.[114] Similarly, our amine functionalized AB-type monomers **11.1** and **12.1** were employed in polycondensations to prepare polyamides bearing aliphatic side-chains and tested for their properties. In all polycondensation reactions, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was used as catalyst, since it exhibits a high amidation activity for the synthesis of polyamides.[142, 204] The obtained polymers **P1.1** and **P2.1** were studied *via* NMR, SEC and DSC analysis (Figure 4.1-5, Table 4.1-3, see also experimental part).

SEC analysis of the polyamides **P1.1** and **P2.1** revealed molecular weights of 6500 Da and 7900 Da, which are comparable to branched aliphatic polyamides already reported in literature.[142, 205] The thermal properties of the produced polyamides were studied *via* DSC analysis, which showed melting points of 40 °C for **P1.1** and 89 °C for **P2.1**. The lower melting point of the oleate derived polyamide **P1.1** compared to the polyamide **P2.1** can be explained by an easier crystallization due to less steric hindrance of the dangling aliphatic chain. This result is similar to structurally comparably renewable polyamides obtained *via* thiol-ene addition reactions.[142]

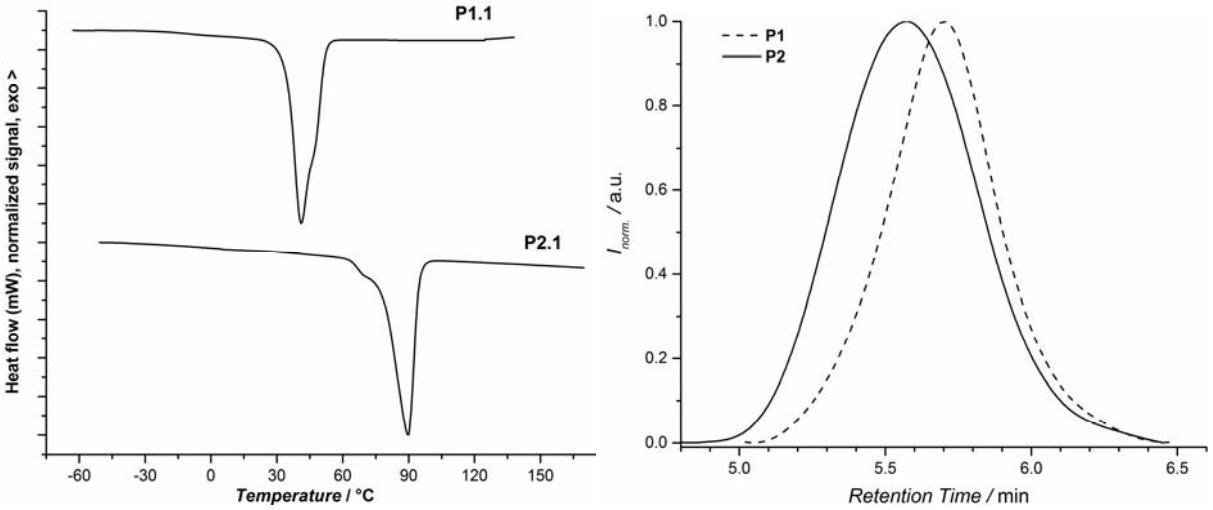

Figure 4.1-5: DSC (left) and SEC (right) analysis of the prepared polyamides **P1.1** and **P2.1**.

Table 4.1-3 Analytic data of FAME derived polyamides **P1.1** and **P2.1**.

Polymer	T_m	M_n [Da]	$Đ$
P1.1	40	6500	1.40
P2.1	89	7900	1.49

In general, the polymers obtained from the amine functionalized methyl oleate or methyl erucate are exhibiting relatively low melting points (if compared to conventional polyamides) because of their long aliphatic side-chains. Thus, these monomers might be useful as co-monomers to modify thermal and mechanical properties of conventional polyamides rather than to be used as homopolymers.

Conclusions

In summary, a more sustainable and safer procedure for the Wohl-Ziegler bromination of unsaturated FAMEs is presented. High conversions and good yields were obtained performing the allylic bromination of methyl oleate or –erucate in cyclohexane or in bulk. Moreover, the prepared allylic bromides were used in elimination reactions to obtain conjugated fatty acids. Additionally, the allylic bromides were successfully used as initiators for ATRP polymerizations of MMA demonstrating a novel and promising application of such internal allylic bromides. Finally, renewable AB-type polyamide monomers were efficiently synthesized *via* a hydrobromination (as an alternative bromination) and subsequent modification strategy.

4.2 Long-chain polyamides from ω- hydroxypalmitic acid

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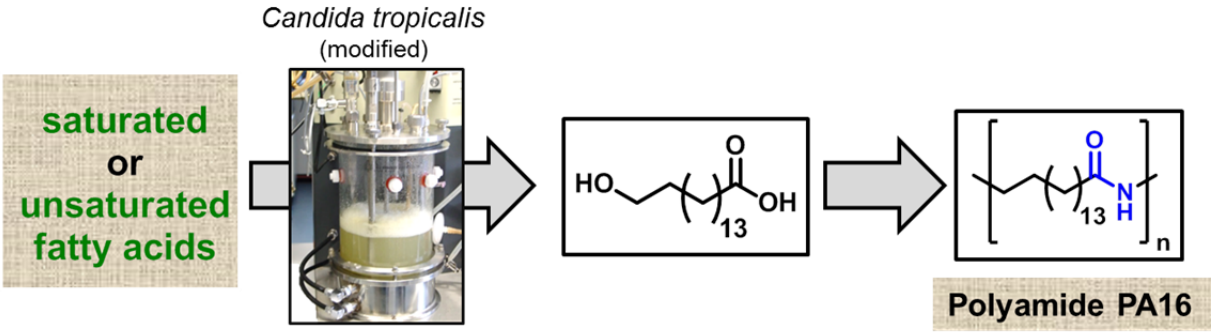

Abstract

Within this chapter the use of the biochemically derived 16-hydroxypalmitic acid as starting material for renewable polyamides is described. The required long-chain monomer was obtained by chemical derivatization of the biochemically derived ω-hydroxy fatty acid. The respective long-chain 16-aminohexadecanoic acid methyl ester was synthesized and subsequently used to prepare polyamide PA 16. The long-chain polyamide, having a low amide-group frequency, was prepared by amidation using TBD as catalyst, resulting in an average molecular weight of M_n = 20.3 kDa and a melting point of 166 °C. The polyamide was further studied by stress-strain measurements to evaluate its mechanical properties.

Introduction

Fatty acids are ideal substrates for the synthesis of valuable monomers, for instance using thiol-ene addition reactions[142, 206-215] or ruthenium-catalyzed olefin (cross)-metathesis.[216-224] However, for these derivatizations the double bond of unsaturated fatty acids at a specific position within the aliphatic chain is usually used as reactive site, which limits the scope of the obtained monomers.

Long-chain linear polyamides are of high interest since, due to a reduced hydrogen bonding in relation to the carbon chain length, such long-chain polyamides profit from reduced water vapor uptake and molded parts show no or only little dimensional changes with variation of the atmospheric humidity.[177] Additionally, the lower melting point caused by a reduced hydrogen bond frequency can lead to an easier processing of such polyamides. A commercially available long-chain linear polyamide is PA 12, which has a melting point of 180 °C. PA 12 is prepared on industrial scale *via* ring-opening polymerization of lauryl lactam, which can be prepared in a multiple step synthesis starting from butadiene.[225] In principle, PA 12 could also be prepared from the ω-aminododecanoic acid. Interestingly, a pilot plant in Slovakia is already making use of palm kernel oil derived ω-aminoundecanoic acid to synthesize renewable PA 12.[226] Additionally, with regard to the preparation of renewable polyamides, ω-aminoundecanoic acid, which is synthesized from the castor oil derived 10-undecenoic acid, is already used for a large scale production of PA 11.[227]

On the other hand, long-chain linear polyamides are usually prepared from dicarboxylic acids or their corresponding diesters and an appropriate diamine. Long-chain diacids can be prepared, for instance, by self-metathesis reactions of unsaturated fatty acids to yield e.g. diacids/ diester having 20 (from undecenoic acid)[223, 228] or 26 (from erucic acid) [229] carbon units.

With regard to the preparation of long-chain polyamides from AA-type monomers, Mecking and coworkers recently reported the preparation of renewable PA 23,23, PA 23,19, PA 12,23, and PA 11,23 from methyl oleate or ethyl erucate *via* isomerization transformation and subsequent modification.[171] Herein, the double bond of the unsaturated FAME was isomerized along the carbon chain using a palladium catalyst; the subsequent methoxycarbonylation reaction then only occurs at the terminal position of the fatty acid chain resulting in the formation of the

α,ω-diester as outlined in chapter 2.8.[230, 231] The prepared renewable polyamides exhibited melting points in the range of 152-168 °C.

Based on a dimer fatty acid derived from rapeseed oil, Avérous and coworkers synthesized bio-polyamides utilizing diamines with different chain length to study their thermal, physical, and mechanical properties.[232] Fradet and coworkers reported the synthesis of unsaturated biobased polyamides based on *Z*-octadec-9-enedioic acid. By utilizing different kinds of diamines, the properties of these biobased polyamides could be modified.[233] However, a disadvantage in the utilization of AA-type monomers is the necessity of an exact stoichiometry to reach high degrees of polymerization. Very interestingly, different high performance bio-polyamides, which are partly or entirely derived from castor oil, are also produced on an industrial scale.[234] Also, in order to synthesize renewable polyamides, Meier *et al*. already introduced different strategies to synthesize diverse monomers derived from fatty acids. However, all these modifications were performed at the naturally occurring positions of the unsaturations so far.[142, 165, 167, 223]

To broaden the scope of available renewable starting materials for polyamide synthesis, the derivatization of fatty acids using biotechnology is of high interest. Gross and Coworkers have shown that a modified strain of the yeast *Candida tropicalis* can be used to prepare ω-hydroxy fatty acids from different fatty acids in good yields and excellent selectivity.[235] Moreover, it is known for a long time that the yeast *Candida brobicila* is capable to ferment fatty acids with glucose toward sophorose lipids that contain a ω-1 hydroxy fatty acid.[236] Such sophorose lipids can be used as monomers for ruthenium-catalyzed ring-opening metathesis polymerization reactions.[237, 238]

These biochemically modified fatty acids are ideal starting materials for the synthesis of long-chain monomers and the thereof derived polyamides. Therefore, the 16-hydroxyhexadecanoic acid was used as starting material to prepare the 16-aminohexadecanoic acid methyl ester and the respective long-chain polyamide PA 16. The thermal and mechanical properties of this long-chain polyamide were investigated and compared to conventional and commercially available polyamides.

Results and discussions

The synthesis of monomer **3.2**, necessary for the preparation of long-chain polyamides, was achieved by transformation of the mesylated FAME **1.2** to the azide **2.2** and subsequent reduction to the ω-amino-FAME (**3.2**). The azide functionalization was accomplished employing 3 eq. of sodium azide in DMF at 80 °C with stirring for 7 hours. Afterwards, reduction under hydrogen atmosphere by palladium on charcoal in ethyl acetate as solvent leds to the amine functionalized fatty acid methyl ester (Figure 4.2-1). One crucial parameter of the reduction of the azide functionalized FAME (**2.2**) was the dilution and applied hydrogen pressure, since only at low concentrations and high hydrogen pressure (1.6 mmol **2.2** / 40 mL solvent and 40 bar H_2) side reactions like nucleophilic substitution of the azide with an amino FAME could be avoided. If less solvent (e.g., 5-20 mL per 1.6 mmol **2.2**) was used diverse side products were formed. The prepared ω-amino-FAME **3.2** was then directly used for the preparation of **P1.2**.

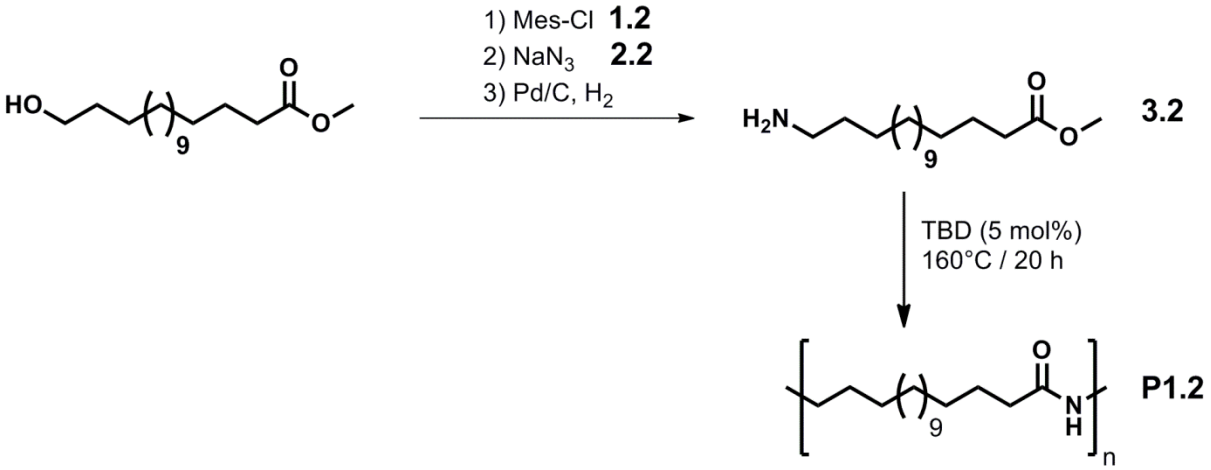

Figure 4.2-1: Preparation of PA 16 (**P1.2**) from methyl 16-hydroxypalmitate.

The polycondensation of **3.2** was performed at 160 °C, using TBD (5 mol%) as organo-catalyst and high vacuum to remove methanol. The polymerization was stopped after 20 hours and **P1.2** was precipitated from hexafluoroisopropanol (HFIP) into cold methanol. The polymer was obtained as a white solid showing a molecular weight of about 20 kDa, *Đ* of 1.65, and a melting point of 166 °C. The melting point is about 14 °C lower than the one of PA 12 and about 40-50 °C higher than the one of linear polyethylene. The longer carbon spacing between the ester and amine function, if compared to PA 12, results in a lower melting point because of less chain-chain interaction due to reduced hydrogen bonding.

If compared to the long-chain polyamides prepared by Mecking and coworkers, having a melting point of 152-168 °C, the synthesized PA 16 shows a similar thermal behavior.[171] The obtained molecular weights of about 20 kDa are in the expected range of linear, non-branched polyamides. To evaluate the mechanical properties of the long chain PA 16, the Young's modulus was determined in tensile-stress experiments. The measurements revealed a Young's modulus for **P1.2** of 1550 MPa, which is similar to the modulus of commercial PA 11 (1740 MPa) and in the range of PA 12 (2320 MPa) (for details of the tensile-stress experiments see also chapter 4.4). Interestingly, the prepared PA 16 showed an upper critical solution temperature (UCST) behavior in HFIP. For measurement of the UCST, a solution of 3.0 wt% of **P1.2** in HFIP was prepared. The standard polyamide-solvent permits the formation of hydrogen bonds, which is the prerequisite for a UCST behavior. For the UCST experiment, the solubility of **P1.2** was examined by cooling the solution to 4 °C and slow heating towards room temperature. To observe a possible UCST behavior, the temperature at which the solution was completely clear or turbid was visually determined. The UCST for **P1.2** was in the range of 10-13°C. In summary, it was thus shown that the commercially available ω-hydroxy palmitic acid was successfully used for the straightforward synthesis of AB-type monomers in order to prepare fully renewable polyamides having interesting thermal properties.

Conclusions

In conclusion, the synthesis of the long-chain polyamide PA 16 from biotechnologically derived 16-hydroxyhexadecanoic acid is described. Because of their unusually long aliphatic chain, the resulting polymers have interesting thermal properties. With the preparation of the PA 16, the use of renewable long-chain polyamides in a straightforward manner employing the enzymatically prepared and commercially available ω-hydroxy palmitic acid was demonstrated. Interestingly, the prepared PA 16 showed only a slightly lower melting point than PA 12 and comparable mechanical properties to the commercially available PA 11 and PA 12. Additionally, the long-chain PA 16 exhibited an UCST in HFIP of 10 – 13 °C. These results add to the manifold possibilities in the derivatization of fatty acids for the synthesis of high-performance polymers derived from renewable resources.

4.3 Highly efficient oxyfunctionalization of unsaturated fatty acid esters: An attractive route for the synthesis of polyamides from renewable resources

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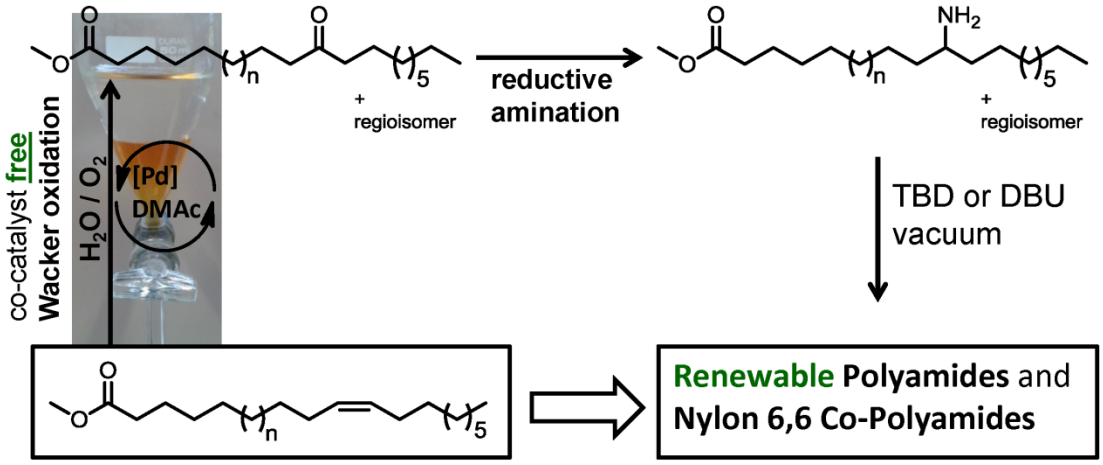

Abstract

An efficient and environmentally benign strategy for the oxyfunctionalization of fatty acid methyl esters (FAMEs) employing molecular oxygen as oxidizing agent is described. Keto-fatty acid esters were directly synthesized by co-catalyst-free Wacker oxidations employing oxygen as sole re-oxidant. Amine functionalization of the thus obtained keto-fatty acid esters was achieved by reductive amination. The prepared renewable AB-type monomers were studied in homopolymerizations as well as in copolymerization reactions with hexamethylendimethylamine and dimethyl adipate to modify the properties of conventional Nylon 6,6. The obtained (co)-polymers were characterized by SEC, NMR and DSC analysis, water uptake tests as well as tensile-stress measurements.

Introduction

Ketone-functionalized fatty acid derivatives, yet rather unexplored renewable platform chemicals, can be applied in detergent formulations, as surfactants, plasticizers, or ingredients of multipurpose greases.[239-242] Thus, the development of efficient procedures for a selective oxidation of unsaturated fatty acids employing molecular oxygen is highly desirable from an economic and ecologic point of view. Cádiz and colleagues reported the synthesis of an α,β-unsaturated ketone containing triglyceride *via* photoperoxidation of high oleic sunflower oil by a two-step, one-pot procedure.[166] The key step of this oxyfunctionalization method is the Schenck-Ene reaction that uses *in situ* generated singlet oxygen, which was employed to oxidize the unsaturated triglyceride at the allylic position. The obtained enone containing triglycerides were subsequently used in aza-Michael additions to prepare polymeric networks.[243]

Very recently, Bruneau *et al*. published a dehydrogenation protocol for the regioselective preparation of methyl-12-oxooctadecanoate using renewable methyl ricinoleate and $RuCl_2$(*p*-cymene)(IMes) as catalyst.[244] Indeed, this regioselective and efficient introduction of a ketone functional group to the fatty acid carbon chain is very interesting. Unfortunately, long reaction times (48 h) at 125 °C under reflux in toluene were required and the method is restricted to methyl ricinoleate.

Another interesting possibility for the oxyfunctionalization and synthesis of ketone-functionalized fatty acids is a direct ketonization utilizing nitrous oxide. *Inter alia*, Sels and colleagues described an efficient procedure for the ketonization of methyl oleate under solvent-free conditions and without the need of any metal catalyst, while obtaining high volume-time yields.[108] However, relatively harsh reaction conditions, 220 °C and a partial pressure of 4.0 MPa nitrous oxide are required. Furthermore, if compared to other oxyfunctionalization methods employing molecular oxygen as oxidizing agent, the use of nitrous oxide is disadvantageous from an ecological point of view. As an alternative oxyfunctionalization strategy, the palladium catalyzed acetoxylation or Wacker oxidation proved to be a very useful method for a direct oxyfunctionalization of terminal olefins, although these procedures usually require reducing agents or co-catalyst (e.g., copper, benzoquinone, etc.) to facilitate the regeneration of the palladium(II) species by oxygen and to avoid precipitation of the metal catalyst.[245-248]

Very recently, Grubbs *et. al*. reported an efficient preparation of ketones from internal olefins.[249] Remarkably, the oxidation of internal olefins employing $Pd(OAc)_2$, benzoquinone and/or an iron co-catalyst were performed at room temperature and an atmospheric pressure of oxygen. Also the Wacker oxidation of FAME was already reported.[249] For example, Lam and colleagues described the Wacker oxidation of methyl undecenoate and methyl oleate.[250] However, an excess of the co-catalyst benzoquinone and a catalyst loading of 5.6 mol% were used to obtain moderate yields of 41–65%.

A few examples report on the oxyfunctionalization of diverse olefins using oxygen as the sole re-oxidant, even though these procedures often lack from low activities and have a limited substrate scope.[251, 252] Recently, Kaneda and coworkers reported a very interesting co-catalyst-free Wacker oxidation procedure employing oxygen as sole re-oxidant.[105] High yields and selective oxyfunctionalizations were achieved in dimethylacetamide as active solvent, which allowed for an efficient and straightforward recycling of the solvent-catalyst system and facilitating the product isolation by simple extraction. *Inter alia*, methyl undecenoate was oxidized to the corresponding methyl ketone, but also olefins having an internal double bond could be employed in this oxidization procedure. Indeed, employing this methodology to fatty acids having an internal double bond would be highly interesting, since it would offer an efficient way for a direct one step oxyfunctionalization, which can be carried out in an environmentally friendly fashion.

Within this chapter, the extraordinary potential of molecular oxygen for selective, highly efficient and environmentally friendly oxyfunctionalizations of FAMEs is demonstrated. A co-catalyst-free Wacker oxidation performed in a dimethylacetamide/ palladium(II)chloride solvent-catalyst system was utilized for the efficient synthesis of ketone FAMEs, which were subsequently transformed to amino-FAMEs. Herein, also the ability to employ low catalyst loadings, straightforward product isolation as well as the recycling of the solvent-catalyst mixtures was demonstrated. Furthermore, a first application of the obtained ketone derivatives is demonstrated by the synthesis of AB-type polyamide monomers *via* selective reductive amination and their subsequent polymerization to renewable polyamides.

Results and discussions

As an alternative to other oxyfunctionalization strategies mentioned above, an efficient method for the oxyfunctionalized FAMEs in only one step and in an environmentally friendly manner would be highly desirable. In this context, Kaneda and coworkers recently reported the very efficient conversion of methyl-10-undecenoate (a castor oil derivative) to the corresponding methyl ketone by a co-catalyst free Wacker oxidation procedure.[105] In this report dimethylacetamide as solvent exhibited excellent properties by means of product isolation, activity and the recycling of the catalyst-solvent mixture. In order to transfer the co-catalyst free Wacker oxidation procedure to unsaturated FAMEs having an internal double bond, such as methyl oleate or methyl erucate, a detailed reaction screening (Figure 4.3-1, Table 4.3-1) was first performed. The catalyst loading, oxygen pressure as well as the reaction temperature were optimized with respect to a maximum conversion of the internal double bond, which was monitored *via* ^{1}H-NMR spectroscopy.

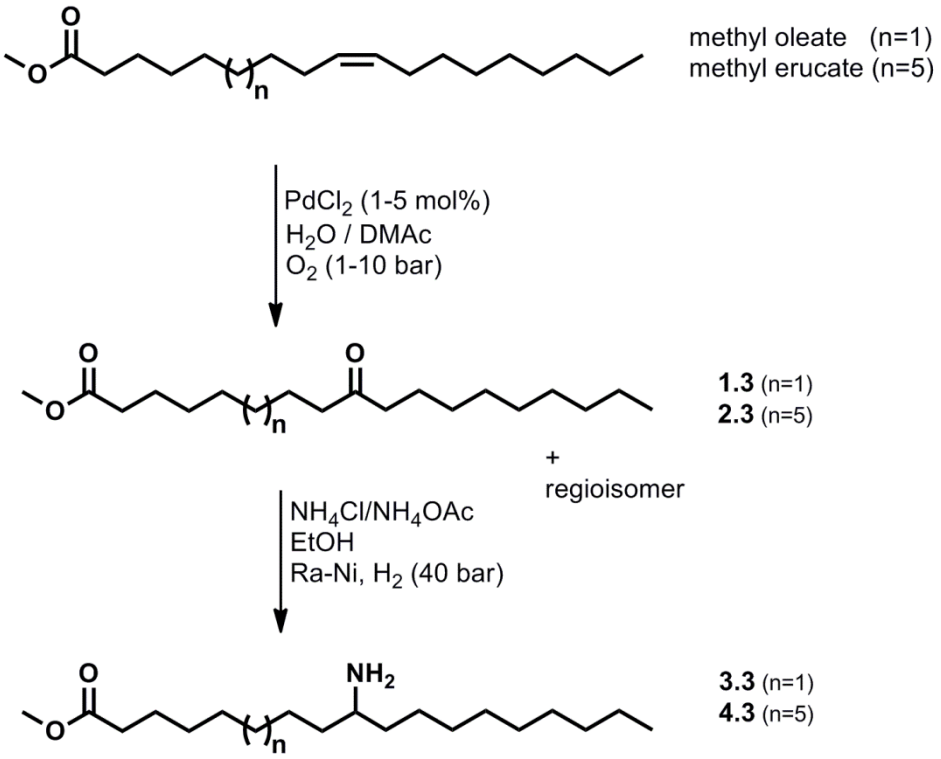

Figure 4.3-1: Co-catalyst free Wacker oxidation of unsaturated FAMEs and subsequent reductive amination to prepare amino FAMEs **3.3** and **4.3**.

Table 4.3-1: Reaction screening of the Wacker oxidation of methyl oleate.

Entry	Temp. [°C]	Time [h]	$PdCl_2$ [mol%]	P (O_2) [bar]	Conversion[a] [%]	Conditions
1	80	17	10	2	80	Classic: CuCl/DMF/H_2O
2	80	17	10	2	85	Classic: CuCl/DMAC/H_2O
3	30	24	1	8	4-5	
4	50	24	1	8	8-10	
5	80	24	1	8	72-75	
6	70	48	1	10	100	
7	70	24	2.5	10	100	
8	75	17	5	10	100	synthetic air
9	140	4	5	atm.	-.	
10	150	24	1	10	5-10	

[a]Determined by NMR analysis. All reactions were performed in DMAc if not indicated.

First, the Wacker oxidation of methyl oleate was performed under conventional conditions employing a DMF/H_2O solvent mixture and CuCl as co-catalyst, which provided the expected results (Table 4.3-1, entry 1) and a bench-mark for further optimization studies.[242] The same reaction was also carried out using dimethylacetamide instead of dimethylformamide as solvent (Table 4.3-1, entry 2), which slightly increased the conversion. Obviously, in this case, dimethylacetamide exhibits an improved activity for the Wacker oxidation, which is consistent with the previously published results.[105] Generally, the Wacker-oxidation of internal olefins performed under the classic Wacker-Tsuji conditions or with DMAc as solvent suffers from the addition of copper as a co-catalyst.[106] However, performing the oxyfunctionalization of methyl oleate without co-catalyst and with oxygen as sole re-oxidizing agent provided good results, showing full conversions at an oxygen pressure of 10 bar (Table 4.3-1, entries 3-7).

In general, it is noticeable that with an increasing oxygen pressure the co-catalyst free reaction is accelerated and the conversions are higher. Our reaction set-up allowed us to carry out the Wacker oxidations under a maximum oxygen pressure of 10 bar. However, as it is known for the co-catalyst free Wacker oxidation of terminal double bonds, an increased oxygen pressure has a crucial influence on the reaction

rate.[105] In this regard, additional increase of the oxygen pressure can further accelerate the Wacker oxidation to shorten the reaction times. In our case, the best results were obtained with a catalyst loading of only 1 - 2.5 mol% at 70 °C-75 °C and an oxygen pressure of 10 bar.

Highly interesting with regard to safety issues and handling of the Wacker oxidation reaction for an industrial scale application, the oxyfunctionalization of the FAMEs can also efficiently be performed employing air (Table 4.3-1, entry 8, synthetic air was used in this case for simplicity). Moreover, the product can be isolated by simply extracting the reaction mixture with heptane or diethylether. In this way, the dimethylacetamide, which retains the catalyst, could be separated from the product. In further experiments, we thus tested the recyclability of the solvent-catalyst mixture (for more experimental details see experimental part, chapter 6.3.3). After performing the Wacker oxidation under the optimized reaction conditions, the solvent-catalyst mixture was separated while extracting the ketone functionalized FAME with heptane. The isolated dimethylacetamide phase containing the palladium catalyst was then reused for further oxidation reactions (Figure 4.3-2).

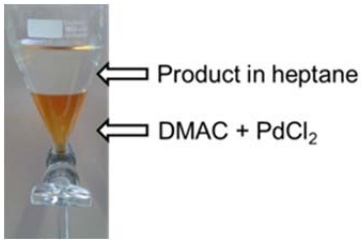

Figure 4.3-2: Extraction of the reaction mixture with heptane and separation of the catalyst/solvent-mixture.

Remarkably, in this way the solvent-catalyst mixture could be used up to three times without a significant loss of its activity. After these optimization studies, the procedure was also applied to methyl erucate, showing similar results.

Subsequently, the prepared ketone functionalized FAMEs **1.3** and **2.3** were converted to the amine functional FAMEs *via* selective reductive amination (Figure 4.3-1). The reductive amination was carried out with an excess of ammonium chloride/ ammonium acetate and with 10 mol% of the freshly prepared Raney®-Nickel catalyst. These reaction conditions provided the amine functional FAMEs in good yields and excellent selectivity towards the primary amine. In this way, AB-type monomers were prepared in order to synthesize fully renewable polyamides. Meier *et al*. already introduced a strategy to obtain similar amino FAME in order to prepare

polyamides with aliphatic side-chains.[142] Herein, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) proved to be a powerful catalyst to prepare the respective polyamides.

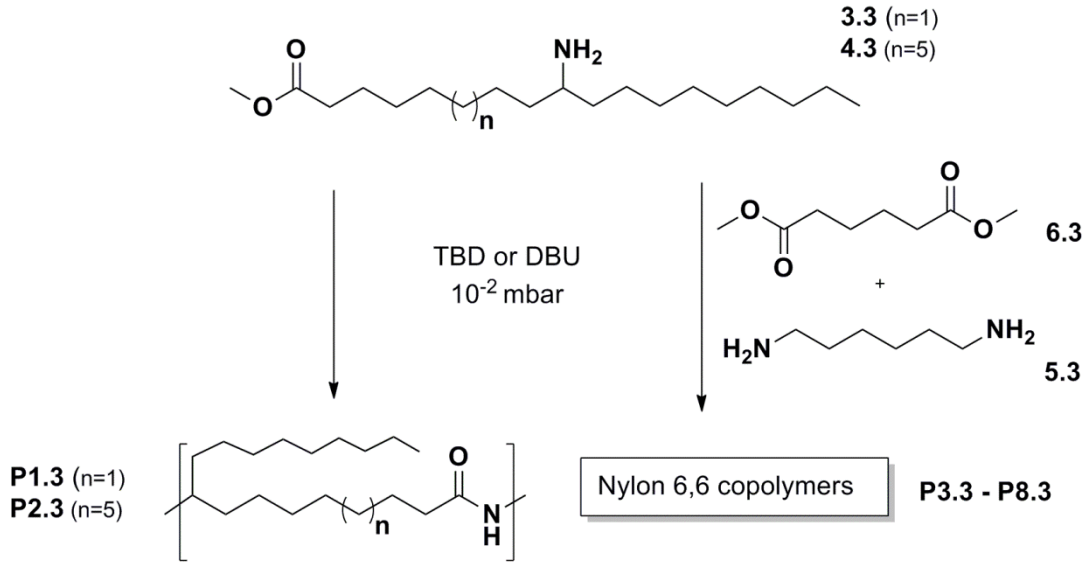

Figure 4.3-3: Synthesis of polyamides with aliphatic side-chains and co-polyamides utilizing the methyl oleate and –erucate derived monomers **3.3** and **4.3**.

The homopolymers **P1.3** and **P2.3** were prepared by TBD catalyzed polycondensation leading to polyamides with aliphatic side-chains (Figure 4.3-3) with an average molecular weight of about M_n = 7.2 kDa and 7.5 kDa having a melting point of 45 °C or 90 °C, respectively. On the other hand, if compared to conventional Nylon 6,6, the renewable polyamides prepared by polycondensation of monomer **3.3** or **4.3** are highly hydrophobic due to their unpolar alkyl side chains. In contrast, Nylon 6,6 exhibits good impermeability of gases, odors and flavors, but is highly hydrophilic and suffers from water vapor uptake, which can detrimentally effect the mechanical properties. Thus, Nylon 6,6 copolyamides were prepared by copolymerization of hexamethylendiamine, dimethyl adipate and the renewable monomers **3.3** or **4.3** (Figure 4.3-3) in order to modify the thermal properties and water uptake behavior of conventional Nylon 6,6. Nevertheless, applying the same polymerization conditions for the copolymerization with hexamethylenediamine **5.3** and dimethyl adipiate **6.3** only led to low molecular weight polyamides, most likely since at the evaluated polymerization temperature of 160 °C the copolymers solidified. Performing the polymerization reactions at higher temperatures resulted in insoluble products, most likely since the decomposition of the catalyst TBD led to side reactions at such elevated temperatures. In order to obtain higher molecular weights, we thus performed polycondensations at higher temperatures (up to 270 °C) without any

catalyst or employing DBU as a more temperature stable organocatalyst (stable to about 190 °C).

Indeed, when performing the polycondensation at higher temperatures, the molecular weights significantly increased. DBU as catalyst enabled us to shorten the reaction time, whereas for polymerizations performed without any catalyst longer reaction times were needed. It has to be noted that polymerizations with DBU as catalyst were performed in a two-step procedure including the isolation of a pre-polymer (for more details see experimental part in chapter 6.3.3). The average molecular weights of the prepared copolyamides ranged from M_n = 11.2 kDa – 21.4 kDa having a dispersity of 1.45 to 2.28 (Table 4.3-2). These results show that with an increase of the amount of the renewable monomer **3.3** or **4.3**, the molecular weight decreases. This can be explained with the increased steric hindrance of monomer **3.3** and **4.3** and is in accordance with previous reports.[142, 253] The main reason for the loss of the catalytic activity of the guanidine based catalyst for sterically demanding monomers is a consequence of the proposed dual-activation mechanism.[254, 255]

Table 4.3-2: Results of the prepared homopolymers and copolymers utilizing the methyl oleate or –erucate derived monomers **3.3** and **4.3**, hexamethylenediamine **5.3** and dimethyl adipiate **6.3**.

Polymer	**M1** (eq.)	**M2** (eq.)	**M3** (eq.)	M_n (kDa)	$Đ$	T_m (°C)	**Type**
P0.3	**5.3** (1)	**6.3** (1)	-	34.1	2.17	258	Nylon 6,6
P1.3	**3.3**	-	-	7.50	1.65	45	fatty acid polyamides
P2.3	**4.3**	-	-	7.28	1.85	90	
P3.3	**3.3** (0.2)	**5.3** (1)	**6.3** (1)	21.2	2.10	242	fatty acid-copolyamides
P4.3	**3.3** (0.5)	**5.3** (1)	**6.3** (1)	19.8	2.18	231	
P5.3	**3.3** (0.8)	**5.3** (1)	**6.3** (1)	11.7	1.71	224	
P6.3	**4.3** (0.2)	**5.3** (1)	**6.3** (1)	21.4	2.28	250	
P7.3	**4.3** (0.5)	**5.3** (1)	**6.3** (1)	20.9	1.45	235	
P8.3	**4.3** (0.8)	**5.3** (1)	**6.3** (1)	11.2	1.50	233	

The thermal properties of the copolyamides were studied by differential scanning calorimetry (DSC) analysis, which showed melting points of 224 °C to 250 °C and indicated a thermal stability up to 350 °C (Table 4.3-2).

Thus, it is obvious that with an increase of the amount of the renewable monomers **3.3** and **4.3**, the melting points of the copolyamides decrease due to the steric hindrance of the long aliphatic side chains.

For further investigations of the properties of the synthesized plant oil based co-polyamides, we performed additional tests to learn about their water-uptake behavior compared to conventional Nylon 6,6. Therefore, the co-polymers were compression molded and immersed into a certain amount of water for a specific time, similar to already known standard procedures.[239, 240] Afterwards, the polymer samples were carefully blotted on a tissue to remove the water on the surface and weighed. After 1 hour on the lab bench for further drying, the polymer sticks were again blotted and weighed. To obtain accurate results and to avoid weighing errors the measurements were repeated 3 times using different polymer specimen. The average increase in weight of the different co-polymers and Nylon 6,6 are listed in Table 4.3-3.[256, 257]

Table 4.3-3: Results of the water uptake test of the different copolyamides.

Polymer	Water-uptake [wt.%][a]
Nylon 6,6	2.10
P3.3	1.40
P4.3	1.21
P5.3	0.94
P7.3	1.10
P8.3	0.75

[a]Calculated according to reference 256, 257

These results clearly demonstrate that with an increasing content of the plant oil based monomers **3.3** or **4.3**, the Nylon 6,6 co-polymers exhibit a lower water-uptake. Compared to Nylon 6,6, the plant oil based copolyamides having only a small content of the renewable monomers, e.g. **P3.3** or **P7.3**, showed a distinctively reduced water uptake demonstrating that the hydrophilicity of conventional Nylon 6,6 can be well modified. Next, the mechanical properties of the plant oil based copolyamides were studied in tensile-stress measurements. The results of the performed tensile-stress measurements are shown in Table 4.3-4. The plant oil based copolyamides **P9.3** and **P10.3** having a small content of the renewable monomer **3.3** show a high Young's modulus, if compared to Nylon 6,6 (**P0.3**).

Table 4.3-4: Results of the tensile-stress measurements of **P9.3** – **P12.3**.

Polymer	**M1** (eq.)	**M2** (eq.)	**M3** (eq.)	M_n (kDa)	*Đ*	*E* [MPa][a]
P0.3	**5.3** (1)	**6.3** (1)	-	34.1	2.17	1150
P9.3	**3.3** (0.1)	**5.3** (1)	**6.3** (1)	14.5	2.29	900
P10.3	**3.3** (0.3)	**5.3** (1)	**6.3** (1)	11.8	2.15	760
P11.3	**4.3** (0.1)	**5.3** (1)	**6.3** (1)	16.4	1.55	510
P12.3	**4.3** (0.3)	**5.3** (1)	**6.3** (1)	15.5	1.62	480

[a]Please note that the measurements were not performed exactly to the offical DIN norm

On the other hand, copolyamides synthesized by polycondensation of the methyl erucate derived monomer **4.3**, hexamethylenediamine and dimethyl adipate show a significantly reduced Young's modulus. The lower Young's modules for the methyl erucate derived copolyamides can be explained with the reduced amide group frequency in comparison to copolyamides derived from **3.3**. Generally, the fatty acid derived copolyamides show lower Young's modules than Nylon 6,6 as the the amide group frequency is reduced and the long aliphatic side chains hamper chain-chain interactions. However, copolyamides with a low content of **3.3** show promising mechanical properties and a significantly reduced water uptake as well, if compared to conventional Nylon 6,6.

Conclusions

The synthesis of renewable AB-type monomers for the preparation of polyamides was achieved by an efficient Wacker oxidation procedure employing oxygen as sole re-oxidant. The co-catalyst free Wacker oxidation procedure utilizing a dimethylacetamide/palladium(II)chloride solvent-catalyst mixture showed extraordinary activity in the oxyfunctionalization of FAMEs having an internal double bond. Importantly, dimethylacetamide as a solvent for the Wacker oxidation can retain the noble metal catalyst ($PdCl_2$) allowing for a very straightforward recycling of the catalyst-solvent mixture for several times and significantly facilitating the isolation of the product. Furthermore, with regard to safety issues and handling of the Wacker oxidation reaction, not only at an industrial scale, the oxyfunctionalization of the FAMEs can also efficiently be performed employing air. Altogether, the ability to

employ low catalyst loadings, to have a straightforward product isolation, as well as the opportunity to recycle the solvent-catalyst mixtures appeared to be highly attractive, both from an economic and ecologic point of view. Transformation of the ketone containing FAME to the amino-FAME was achieved by selective reductive amination. Finally, the prepared (co)-polyamides were characterized in detail by NMR, SEC, DSC, water uptake tests as well as tensile-stress measurements. Herein, the obtained results of the prepared copolyamides revealed that conventional Nylon 6,6 can be well modified by co-polymerization with the renewable methyl oleate or –erucate derived monomers.

4.4 Olefin cross-metathesis as a valuable tool for the preparation of renewable polyesters and polyamides from unsaturated fatty acid esters and carbamates

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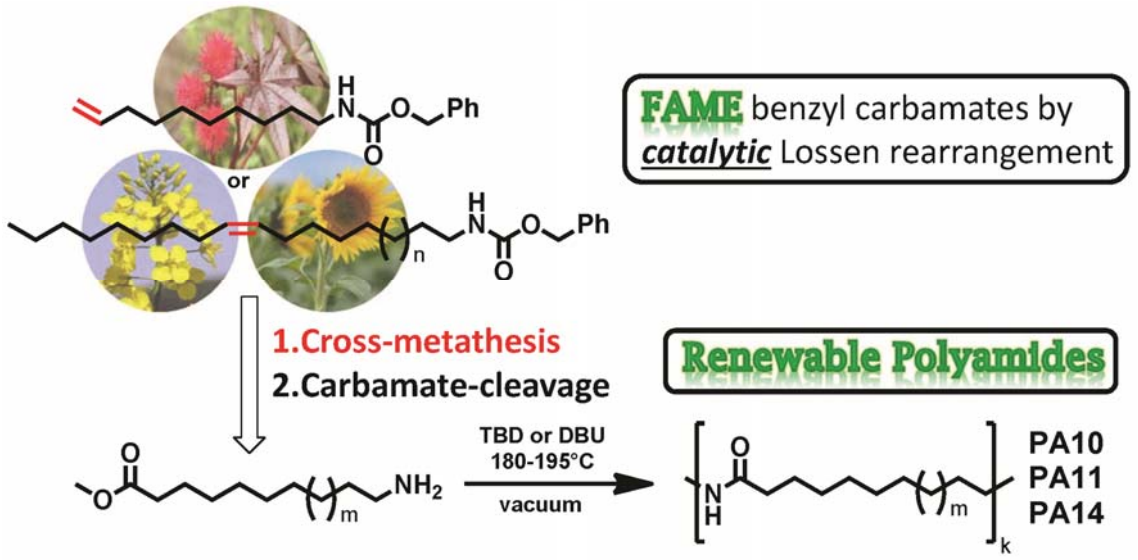

Abstract

Olefin cross-metathesis of unsaturated fatty acid methyl ester (FAMEs) derived benzyl carbamates with methyl acrylate is described. The obtained by-product, an α,β-unsaturated ester, was further modified *via* thia-Michael addition reactions in order to synthesize branched AA-type or AB-type monomers for the preparation of polyesters, which are tuneable by oxidation. Cross-metathesis of fatty acid derived carbamates was used as a novel approach to prepare linear AB-type monomers, which can be used for the preparation of renewable polyamides PA 10, PA 11 and PA 14. The necessary fatty acid carbamates were prepared by applying a catalytic Lossen rearrangement procedure. The presented synthesis strategy has potential for the bio-sourced preparation of monomers for the production of polyamides. All prepared polymers were fully characterized by NMR, SEC, and DSC analyses. Additionally, the Young's modulus of the prepared long-chain polyamide PA 14 was determined.

Introduction

Price, availability, and environmental impact are the main reasons for the chemical industry to move away from fossil resources. However, the polymer industry is still strongly depending on the use of petroleum derived monomers. In order to substitute these monomers, efficient synthetic routes utilizing renewable resources are needed and of high interest. Moreover, processes making use of the synthetic potential of nature and produce little to no waste are highly desirable. Recognized as one of the most important and the most frequently used renewable raw materials, plant oils are valuable alternatives not only for the synthesis of diverse fine chemicals, but also for polymer chemistry.[10, 28] So far, many efficient catalytic modification reactions of fatty acids or FAMEs to prepare monomers or monomer precursors have been developed. Herein, the methoxycarbonylation,[168, 171] ketonization,[108, 249, 258] acetoxylation,[248, 259] or enzymatic transformations[164, 260, 261] offer interesting modification possibilities.

Olefin metathesis proved to be an especially powerful tool in this context and was used to prepare different monomers from diverse plant oils in an efficient catalytic manner.[28, 262-264] In 2007, our group reported on the cross-metathesis of FAMEs and methyl acrylate.[222] All metathesis reactions were performed in bulk using an excess of methyl acrylate and the Hoveyda-Grubbs 2nd generation catalyst. Full conversion of the FAMEs and a very good cross-metathesis selectivity were obtained using catalyst loadings below than 0.5 mol%. Moreover, self-metathesis (SM) of fatty acids to prepare diesters is described as catalytic procedure to obtain renewable monomer precursors. In the case of undecenoic acid (a castor oil derivative),[265] self-metathesis was used to generate the C20 diacid, an AA-type monomer to prepare polyesters by polycondensation.[266] Employing oleic acid or erucic acid for SM reactions revealed to be slightly more challenging since the metathesis equilibrium cannot be shifted by simply removing ethylene as byproduct. However, also several procedures to prepare the oleic or erucic acid derived diacids *via* metathesis reactions are known.[267-269] Furthermore, the metathesis reaction of FAME with diverse functional compounds allows the synthesis of functionalized FAMEs.

Herein, the CM of FAMEs with allyl alcohol, allyl chloride, diethyl maleate or *cis*-butene-1,4-diyl diacetate is well investigated.[270-273] The above mentioned approaches demonstrate the versatility of the (cross-) metathesis reaction in order to synthesize valuable functionalized fatty acid derivatives or fatty acid based monomers.

However, the synthesis of polyamide monomers using metathesis reactions is barely described. Such an efficient catalytic synthesis procedure, however, is highly interesting since polyamides represent a class of highly valuable engineering plastics. The (cross)-metathesis of amine or amide functionalized substrates still remains a great challenge. Usually, either the amine function is protected prior to the metathesis reaction or the metathesis reaction is performed in acetic media in order to *in situ* protonate the amine and prevent catalyst deactivation.[182, 274] Robinson and coworkers reported the SM of 10-undecenylamine to prepare the corresponding diamine, a valuable and renewable AA-type monomer for the preparation of polyamides. Bruneau *et al.* reported the cross-metathesis of 10-undecenenitrile or acrylonitrile with methyl 10-undecenoate or methyl acrylate, respectively.[275] The presented tandem procedure provides a sustainable and very interesting route to linear amino esters as useful polyamide precursors.

These findings prompted us to search for novel catalytic procedures allowing the preparation of fatty acid based amino esters, which can be used to prepare renewable polyamides.

Thus, the olefin cross-metathesis of unsaturated FAMEs derived carbamates with methyl acrylate was investigated for the first time in order to synthesize renewable polyamides and polyesters. Moreover, utilizing all products of the respective metathesis reactions, the cross-metathesis byproducts were also converted to valuable monomers and subsequently polymerized.

Results and discussions

In an earlier publication, our group reported on the efficient olefin cross-metathesis of methyl acrylate and unsaturated FAMEs.[222] The cross-metathesis reactions were performed under solvent-free conditions using low catalyst loadings and selectively provided the corresponding diesters and an

α,β unsaturated ester. The presented catalytic synthesis procedure offers a sustainable access to polyester precursors.

These findings prompted us to search for a possibility to perform efficient cross-metathesis reactions of fatty acid based substrates in order to obtain renewable polyamide precursors. In principle, instead of employing FAMEs in the cross-metathesis with methyl acrylate, the use of the corresponding amine would directly provide the desired amino FAME. However, cross-metathesis reactions of compounds having an amine moiety are still quite challenging and usually the amine function is protected.[182] In this context, Bruneau and colleagues reported the cross-metathesis of 10-undecenenitrile with methyl acrylate.[275] Subsequent hydrogenation of the cross-metathesis product yielded the desired AB-type monomer as polyamide precursor. Recently, we reported the synthesis of fatty acid derived carbamates, which can be obtained in an environmentally friendly fashion *via* a catalytic Lossen rearrangement.[133]

The prepared methyl carbamates can be used to synthesize the corresponding amines by simple carbamate cleavage under basic conditions. Thus, a cross-metathesis of such carbamates and subsequent carbamate cleavage would enable the synthesis of the desired AB-type monomers as illustrated in Figure 4.4-1. In order to enable a mild deprotection of the carbamate and hydrogenation of the double bond in one step, we used fatty acid derived benzyl carbamates as starting materials for the cross-metathesis reaction with methyl acrylate (Figure 4.4-1).

The catalytic Lossen rearrangements were performed according to our previously reported procedure utilizing TBD as catalyst, methanol, and dibenzyl carbonate.[133] It is noteworthy that dibenzyl carbonate was synthesized by simple trans-esterification of dimethyl carbonate (a renewable and non-toxic reagent), according to the procedure reported by our group earlier.[276] An advantage of the Lossen rearrangement performed with dibenzyl carbonate and benzyl alcohol is the reaction efficiency.

Thus, higher yields were obtained as in the synthesis of the corresponding methyl carbamates.[133] Moreover, the excess of the required alcohol and carbonate was significantly reduced. On the other hand, the regeneration of the used benzyl alcohol and dibenzyl carbamate in order to perform the Lossen rearrangement in a sustainable manner is not as straightforward.

However, the use of a Kugelrohr distillation apparatus allowed for a simple and efficient recycling of the benzyl alcohol and dibenzyl carbamate by distillation. It has to be noted that all Lossen rearrangements were performed with 20 mol% of the TBD catalyst. Interestingly, the reaction can be also carried out with lower catalyst loadings (5 - 10 mol%), though longer reaction times are needed. The cross-metathesis reactions were performed similar to a known procedure.[222] Thus, all metathesis reactions were performed in bulk using the Hovedyda-Grubbs 2nd generation catalyst (0.5 mol%) and an excess of the methyl acrylate. The desired products **4.4** – **6.4** were obtained in good yields (up to 91 %) and were subsequently used for the preparation of the ω-amino FAMEs.

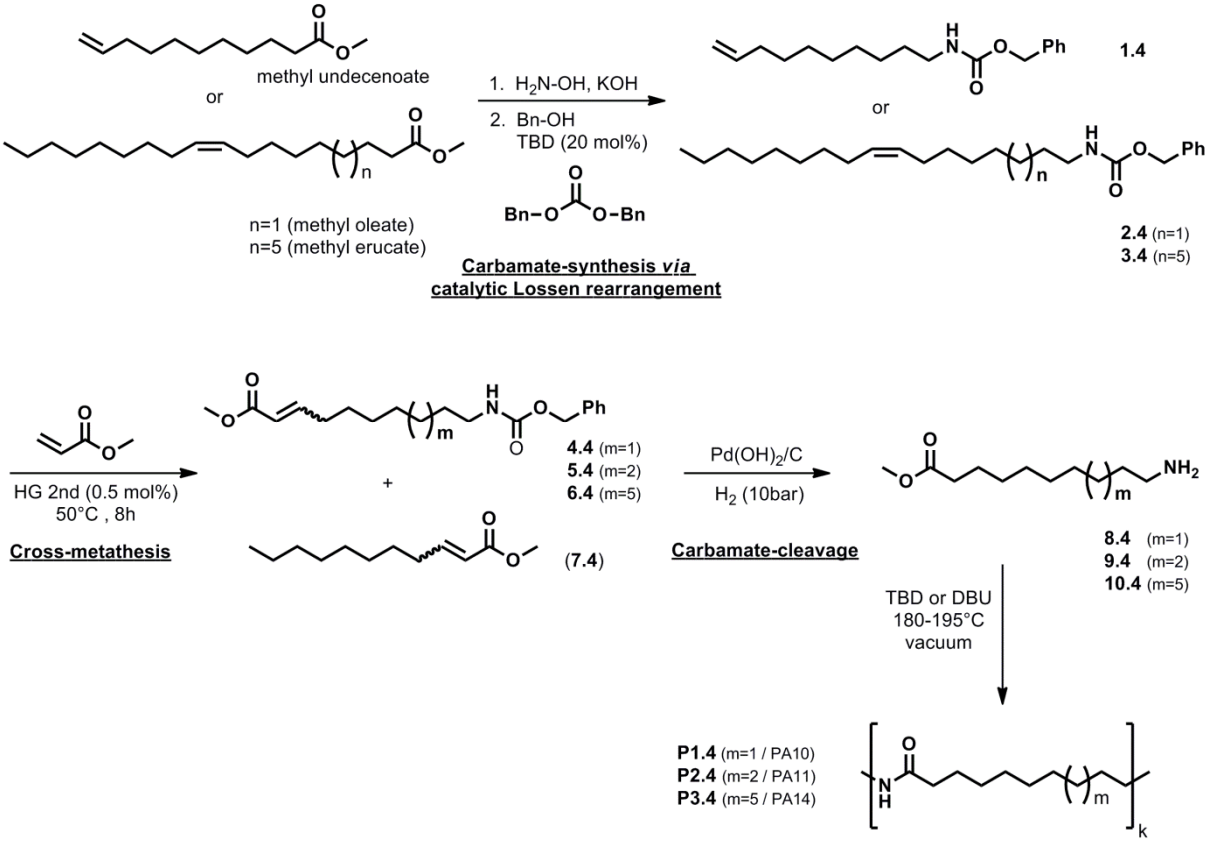

Figure 4.4-1: Synthesis of renewable AB-type monomers *via* Lossen rearrangement, cross-metathesis, and subsequent deprotection.

In the case of the cross-metathesis of the benzyl carbamate **3.4**, a white precipitate was formed after a short reaction time, caused by self-metathesis, and only rather low yields (47-50 %) were obtained. Improved yields of up to 80 % were obtained if the reaction was performed at higher temperatures (60 - 65 °C, similar to the procedure reported by Slugovc *et al.* using ethyl acrylate at a reaction temperature of 75 - 80 °C[182]).

Yields of up to 80 % were also obtained if the reaction was performed on a smaller scale (1.5 g / 3.4 mmol) under vigorous stirring. As a by-product, methyl undec-2-enoate **7.4** is formed, which can be further derivatized as described below (Figure 4.4-3). The hydrogenation of the double bond and the cleavage of the benzyl carbamate were performed in one step. First, Pd/C was used as convenient catalyst for heterogeneous hydrogenations and cleavage of benzyl carbamates. Although, a pressure of 20 bar of hydrogen at a temperature of 35 °C was employed, the benzyl carbamate was not cleaved after two days. If the Pearlman's catalyst ($Pd(OH)_2/C$) was used instead, the hydrogenation as well as the cleavage of the carbamate was completed after 16 hours providing the ω-amino FAMEs in very good yields and in high purity without further purification.

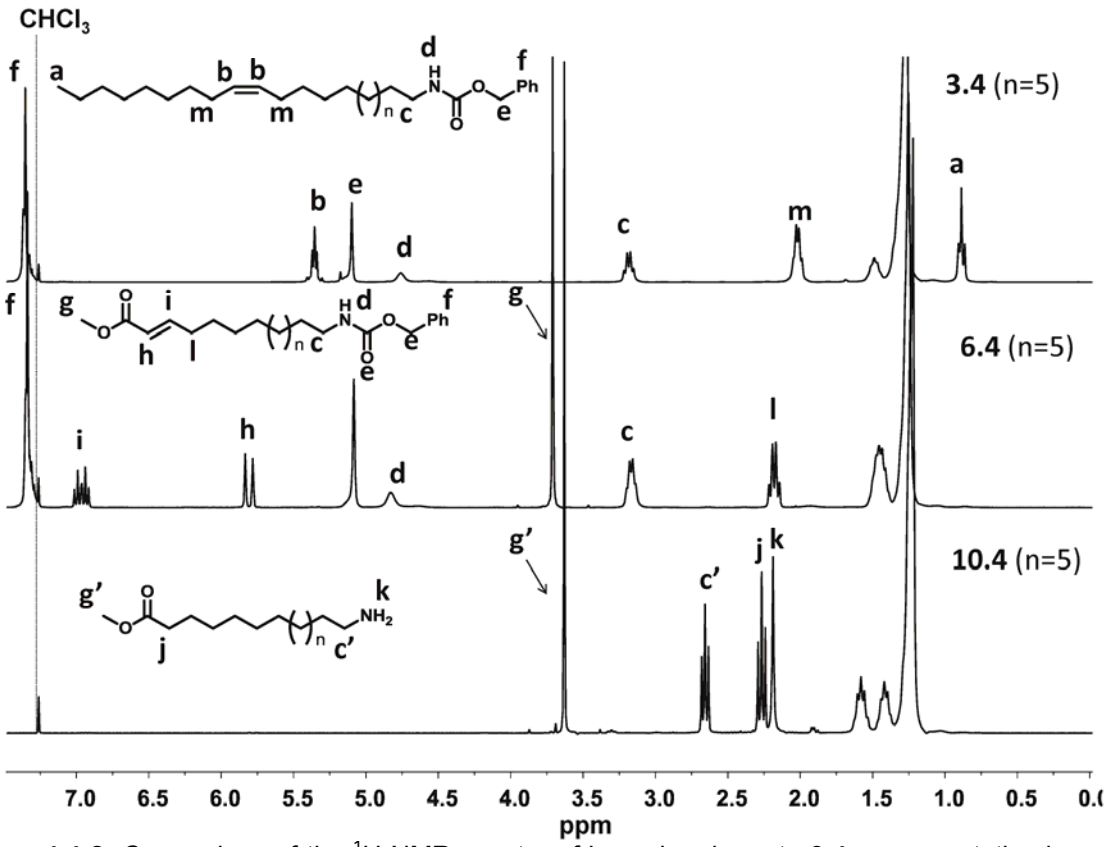

Figure 4.4-2: Comparison of the ^{1}H-NMR spectra of benzyl carbamate **3.4**, cross-metathesis product **6.4**, and the amino FAME **10.4**.

The solvent used for the carbamate-cleavage/hydrogenation reaction appeared to be of crucial importance. The desired product was only obtained in a high purity if alcohols, such as methanol or ethanol, were used. As an example, the ^{1}H-NMR spectra of benzyl carbamate **3.4**, cross-metathesis product **6.4**, and the final amino FAME **10.4** is shown in Figure 4.4-2, demonstrating the overall successful

transformation of methyl erucate to the desired AB-type monomer. Subsequently, the prepared amino FAMEs were used in polycondensation reactions to prepare polyamides (PAs) with a varying carbon chain length using TBD or DBU as the catalyst. SEC analysis of **P1.4**, **P2.4** and **P3.4** revealed molecular weights of 14.9 kDa to 22.6 kDa and a dispersity of 1.73 to 2.20 (molecular weights were determined relative to narrow poly(methylmethacrylate) standards). The melting points were determined by differential scanning calorimetry (DSC) ranging from 169 °C to 186 °C (Table 4.4-1).

Table 4.4-1: Analytic data of the prepared renewable polyamides.

Polymer	M_n [kDa]	$Đ$	T_m [°C]	Young's modulus [MPa]
P1.4 (PA 10)	14.9	2.20	186	-
P2.4 (PA 11)	22.6	2.13	182	1740[a]
P3.4 (PA 14)	15.2	1.73	169	1480
P1.2 (PA16)[b]	20.3	1.65	166	1550

[a]Values are given for commercial nylon 11 (M_n = 31.6 kDa, $Đ$ = 1.53). [b]See chapter 4.2.[277]

Compared to commercially available polyamides, the melting points are in the expected range. For commercially available PA 11, a melting point of 183 °C is reported, which is similar to the measured melting points of FAME based polyamides **P1.4** and **P2.4** (Table 4.4-1).[234] Compared to PA 10 and PA 11, the amide frequency of PA 14 is lower, and thus the melting point of the fatty acid derived polyamide **P3.4** (T_m = 169 °C) is lower. If compared to PA 16 (see chapter 4.2) with a melting point of 166 °C, the melting point of **P3.4** is slightly higher due to an increased amide frequency.[277] Both polymers **P3.4** and **P1.2** (PA 16) are polyamides having an extended aliphatic segment and represent a class of interesting materials.[177]

Beside DSC, NMR and SEC analysis, we performed tensile-stress measurements of the long-chain polyamide **P3.4** to determine the Young's modulus and compared the results to commercial PA 11 (1740 MPa) and PA 12 (2320 MPa) (for exact experimental details of the tensile-stress measurements see experimental part chapter 6.3.5). The measurements revealed a Young's modulus for **P3.4** of 1480 MPa, which is lower than the modulus for the commercial PA 11 and PA 12. Apparently, the longer chain polyamides PA 14 and PA 16 having a lower amide group frequency have lower Young's modulus due to reduced hydrogen bonding.

On the other hand, PA 11 has a higher amide group frequency, thus having a stronger hydrogen bond interaction, but its Young's modulus is lower than that of PA 12 having a similar molecular weight. Herein, the slightly longer aliphatic chain segments have a significant impact on the Young's modulus. This effect can be explained by the different crystallinity of odd- and even-nylons.[278]

As a byproduct of the cross-metathesis of the fatty acid derived benzyl carbamates, an α,β unsaturated ester, methyl undec-2-enoate **7.4**, is obtained, which appeared to be an interesting starting material for further modifications. As is known, α,β-unsaturated carbonyl compounds undergo Michael type addition reactions; thus, the use of **7.4** as a Michael acceptor appears to be an appropriate synthetic strategy to transform the methyl undec-2-enoate to value-added compounds. In order to obtain monomers, we used 2-mercaptoethanol and methyl thioglycolate as Michael-donors to obtain monomers **11.4** and **12.4**, respectively (Figure 4.4-3).

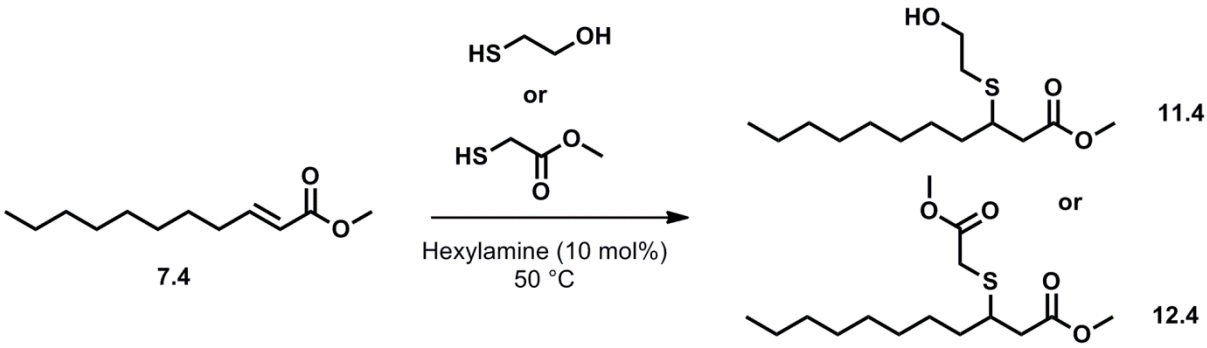

Figure 4.4-3: Thia-Michael addition of 2-mercapto-ethanol or methyl thioglycolate to **7.4**.

Thia-Michael additions performed in bulk and with a small excess of the thiol (1.2 equivalents) provided the best results. Full conversion of **7.4** was achieved after stirring for 5 h at 50 °C using hexylamine (10 mol%) as catalyst. The obtained monomer **11.4** was directly used in polycondensation reactions. The monomer **12.4** can be used in polycondensation reactions as well, if an appropriate diol or diamine is used. Thus, we transformed the obtained diesters from the metathesis of methyl oleate or –erucate to the corresponding diols **17.4** and **18.4** by standard reduction procedures (the experimental procedure for the synthesis of **17.4** and **18.4** is described in chapter 6.3.5) and used them as co-monomers (Figure 4.4-4). In this way, we were able to use all products of the respective cross-metathesis reaction for the synthesis of renewable monomers.

In previous studies, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) showed very good performance as organocatalyst for the synthesis of diverse polyesters and polyamides.[127, 165, 279]

In the case of monomers **11.4** and **12.4**, this catalyst did not work since elimination of the thiol moiety occurred. However, using tin(II) ethylhexanoate or titanium isopropoxide as catalyst yielded the desired polyesters without the occurrence of elimination side reactions (Figure 4.4-4).

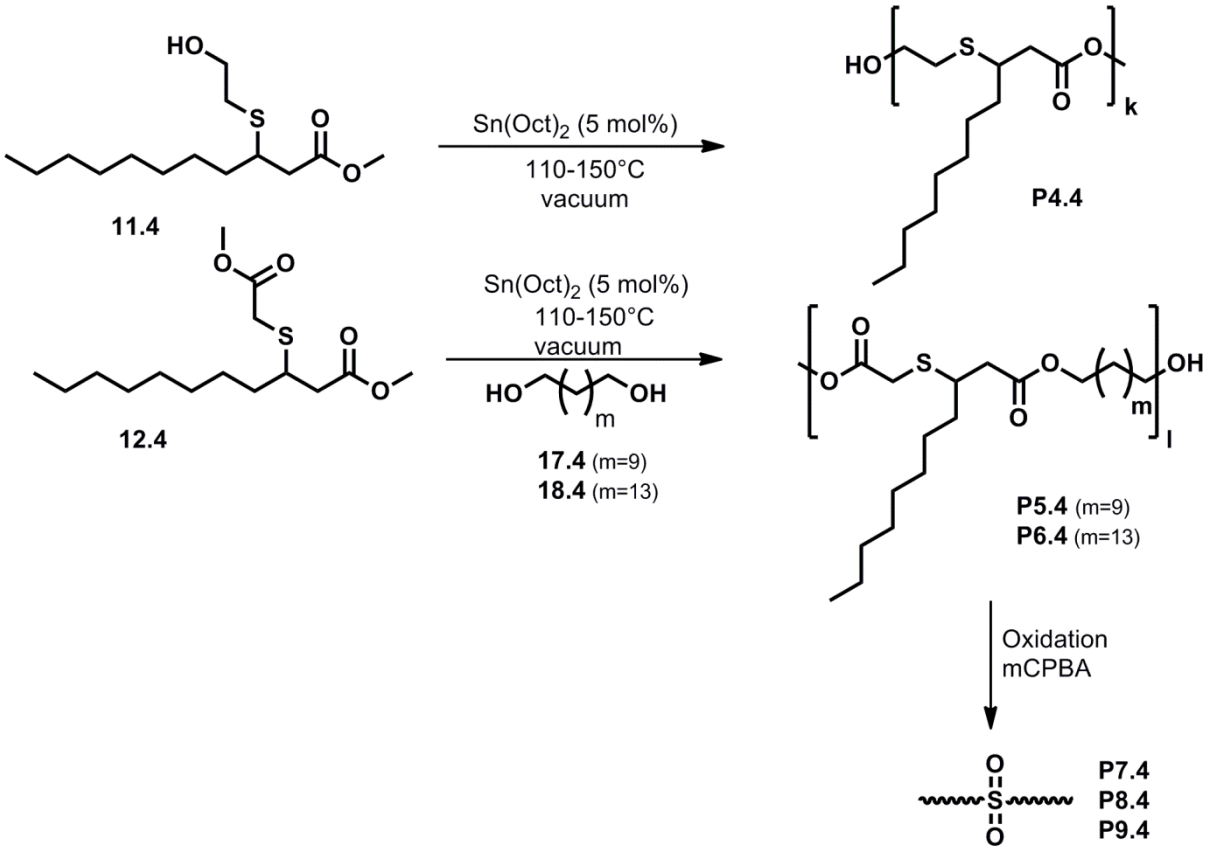

Figure 4.4-4: Polymerization of the monomers derived from **7.4**.

Size exclusion chromatography (SEC) revealed polymers with a molecular weight of 17.0 – 19.0 kDa and a dispersity of 1.52 - 1.90. The thermal properties of the prepared polyesters were studied using DSC, revealing melting points of -18.6 °C – 15.5 °C. As expected, the branched polyesters show low melting points due to their dangling side-chains. The polymer **P6.4** displayed the highest melting point of 15.5 °C, since the employed long-chain C15 diol, derived from methyl erucate, provided increased crystallinity. The polymer **P4.4** showed a *T*g of 8 °C (Table 4.4-2). To modify the thiol containing polyesters (**P4.4** - **P6.4**), we performed some oxidation reactions with *meta*-chloroperoxybenzoic acid (mCPBA) in order to convert the sulfur atoms in the backbone of these polyesters to sulfones (**P7.4** – **P9.4**, Figure 4.4-5,

Table 4.4-2). SEC analysis of the oxidized polymers was not possible, since after the oxidation the polymers were not soluble in common SEC solvents (e.g., $CHCl_3$, THF, DMAC, DMF, HFIP, or toluene) anymore.

Table 4.4-2: Analytic data of the polyesters and oxidized polyesters based on monomers **11.4** and **12.4**.

Polymer	M_n [kDa]	Đ	T_m [°C]
P4.4	17.1	1.52	*T*g = 8
P5.4	18.9	1.74	-18.6
P6.4	18.0	1.90	15.5
P7.4	-	-	21
P8.4	-	-	-5
P9.4	-	-	25

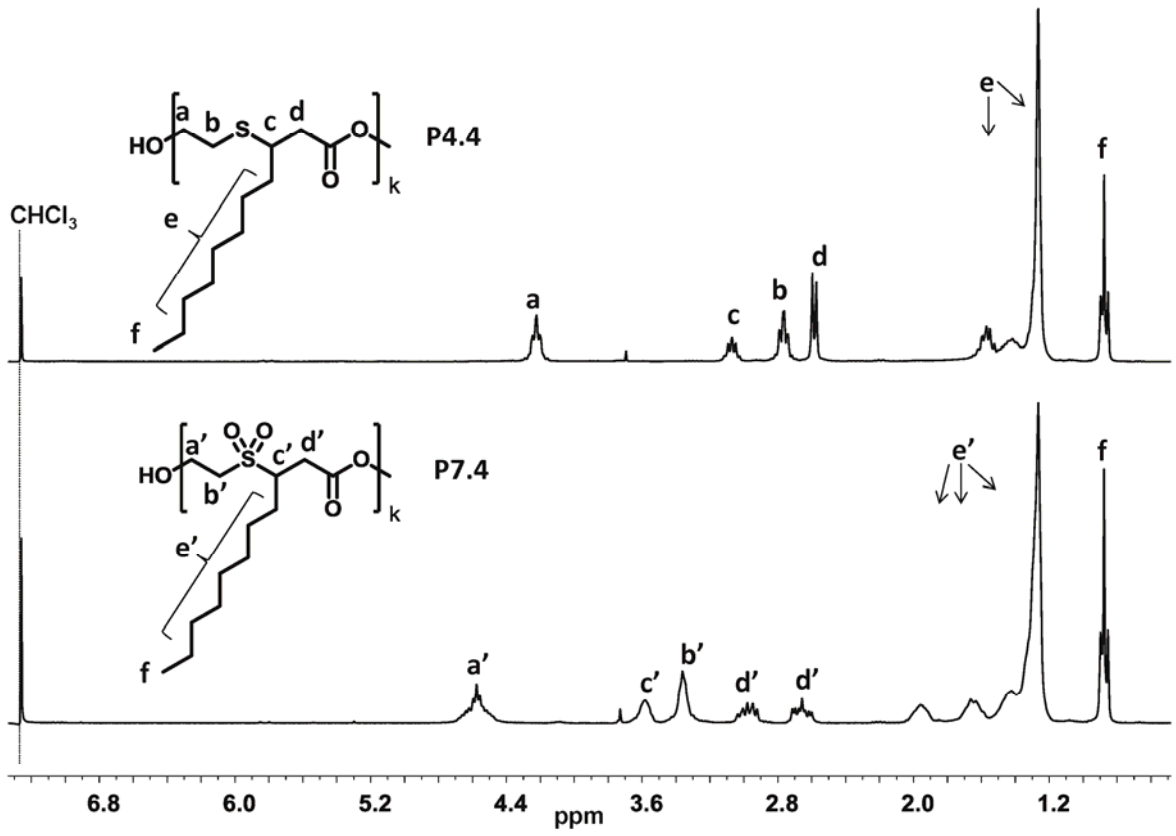

Figure 4.4-5: Comparison of the ^{1}H-NMR spectra before (top) and after (bottom) the oxidation of the sulfur containing polyester **P4.4**.

Nevertheless, the slight solubility of the prepared polymers in chloroform allowed for ^{1}H-NMR analysis of the oxidized products, which revealed the full oxidation of the sulfur, while no degradation of the polymer was observed (Figure 4.4-5). DSC analysis of the polymers showed that the melting point of the polyesters increased due to this oxidation (Table 4.4-2).

Conclusions

The synthesis of plant oil derived renewable polyesters and polyamides is described. Based on the products obtained by cross-metathesis of the FAME derived carbamates with methyl acrylate, diverse monomers were prepared. Methyl undec-2-enoate (as byproduct) was utilized in thia-Michael additions to synthesize an AB- or AA-type monomer. On the one hand, the obtained diesters from the cross-metathesis were reduced to the corresponding diols and used for polymerizations with the prepared AA-type monomer. The synthesized sulfur containing polyesters were oxidized to the corresponding sulfone-polyesters by a simple oxidation procedure, which led to increased melting points and significantly different solubility of the polymers.

On the other hand, in order to synthesize FAME based renewable polyamides, a novel efficient and catalytic strategy including the cross-metathesis of FAME derived benzyl carbamates is introduced. These carbamates were prepared *via* a catalytic Lossen rearrangement utilizing dibenzyl carbonate and benzyl alcohol.

High yields were achieved in the cross-metathesis of these benzyl carbamates with methyl acrylate leading to AB-type monomer precursors, while using low catalyst loadings (0.5 mol%) and performing the reaction under bulk conditions. Under very mild reaction conditions (ambient temperature and atmospheric hydrogen pressure), the carbamate was cleaved and the remaining double bond was hydrogenated in one step, leading to the amino FAMEs in quantitative yields. The corresponding polyamides were prepared in organocatalyzed polycondensation reactions yielding PA 10, PA 11 or PA 14. The tensile measurement of the long-chain PA 14 revealed a high Young's modulus, further demonstrating the potential use of this synthesis strategy for the preparation of new bio-sourced polyamides with good material properties.

4.5 Modified poly(ε-caprolactone)s: An efficient and renewable access *via* thia-Michael addition and Baeyer-Villiger oxidation

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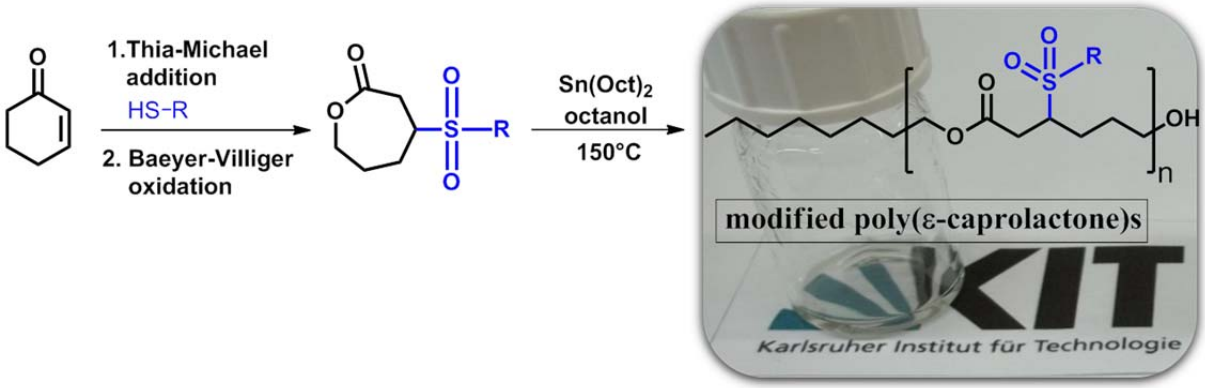

Abstract

The preparation of a novel class of ε-caprolactone (CL) monomers, modified at the β-position of the ester function, is described. The efficient thia-Michael addition to cyclohex-2-en-1-one and subsequent Baeyer-Villiger oxidation provided the regio-selectively modified CL monomers. To enable a sustainable Baeyer-Villiger oxidation, several reaction procedures were investigated. In order to test a controlled ring-opening polymerization of the prepared monomers, the kinetics were studied and the monomer to initiator ratios were varied in order to prepare poly(ε-caprolactone)s with different molecular weights and different side groups.

Introduction

Aliphatic polyesters are a class of interesting polymeric materials. In particular, biodegradable and biocompatible aliphatic polyesters are highly attractive and valuable biomaterials, which can be used in a wide range of different applications.[126, 280-285] Lactones and lactides are especially important monomers used to prepare versatile aliphatic polyesters with predictable molecular weights, narrow dispersities, and well-defined end-groups. Among different polymerization techniques, the controlled ring-opening polymerization utilizing diverse catalysts is most widely applied.[286] In order to promote a controlled ring-opening polymerization of lactones or lactides, a wide range of catalyst/initiators can be used, while tin and aluminium alkoxides are most frequently applied.[286] Considered as environmentally friendly and valuable thermoplastics, polycaprolactones (PCLs) have gained much interest since they can be functionalized and tailored for special applications in a straightforward manner.[287-290] Due to its biodegradability and biocompatibility, PCL is of great interests for tissue engineering and drug delivery applications.[126] Especially, PCL is an excellent material for tissue engineering since it is of non-toxic nature and revealed to be cyto-compatible with diverse body tissues.[126, 291] Moreover, PCL can be used as drug carrier enabling a homogenous drug distribution and long term drug release.[292, 293]

Industrially, the CL monomer is prepared by Baeyer-Villiger oxidation of cyclohexanone using peracetic acid, whereas for lab scale synthesis of CL monomers preferentially *meta*-chloroperbenzoic acid (*m*CPBA) is used as oxidant.[294, 295] Organic peracids are usually not environmentally benign, shock sensitive, and the reactions are preferably carried out in chlorinated solvents. Thus, green alternatives and environmentally benign oxidation procedures making use of e.g. diverse metal or enzyme catalysts and hydrogen peroxide as clean oxidant or potassium peroxymonosulfate ($KHSO_5$) as green oxidant are of great interest for the synthesis of the desired CL monomers.

Besides the development of greener and more efficient Baeyer-Villiger oxidation procedures there is a great interest in CL monomers from renewable resources. In a very interesting contribution by Heeres *et al.*, the synthesis of CL was achieved by catalytic transformation of 5-hydroxymethylfurfural, which can be obtained from, e.g., D-fructose, starch or cellulose.[296]

Hillmyer and colleagues described the synthesis of diverse CL monomers from carvone or menthol.[128, 129] Interestingly, the use of these renewable monomers enabled the synthesis of functional PCLs with different material properties.

Generally, the attachment of functional groups along the aliphatic chain of PCL (and other polymers) is highly attractive in order to tailor important material properties such as crystallinity, hydrophilicity, biodegradability, bioadhesion, and mechanical properties. Furthermore, pendent functional groups allow for a covalent attachment of molecules or probes of biological interest.[287] One common and important approach is to directly attach pendent functional groups (e.g., initiators, acrylates, alkynes, or halogens) to the lactone ring.[297, 298] However, usually multi-step synthesis procedures and extensive purification steps are required to obtain the desired pure monomers.

Considering the importance of functionalized PCLs and the demand of CL monomers from renewable resources, we searched for a very efficient and straightforward approach to synthesize functionalized CL monomers, which can be derived from renewable resources. Therefore, the efficient thia-Michael addition to cyclohex-2-en-1-one is presented as universal approach to synthesize modified CL precursors. A subsequent Baeyer-Villiger oxidation of the cyclohexanone derivatives is used to prepare the corresponding modified CL monomers in a highly regio-selectivity manner.

Results and discussions

One aspect of this work was to synthesize the desired CL monomers from renewable resources. In the range of renewable resources given by nature, plant oils appeared to be very useful substrates to produce a variety of valuable chemicals.[299] The use of olefin metathesis appeared to be a very interesting oleochemical process to transform plant oils into valuable chemicals.[299] If polyunsaturated fatty acid derivatives are used for self-metathesis reactions, an intramolecular ring closing metathesis (RCM) to form 1,4-cyclohexadiene (CHD) as a byproduct occurs.[300] Our group also reported the self-metathesis of polyunsaturated fatty acid methyl esters to prepare long-chain diesters, wherein CHD is obtained as a by-product (Figure 4.5-1).[179] Moreover, the group of Cole-Hamilton reported the metathesis of cardanol with ethylene, also yielding CHD as a by-product.[301]

The described synthetic procedures offer a green alternative to the conventionally produced CHD from fossil resources. In particular, the valorization of CHD as byproduct is beneficial in a biorefinary concept, where all products of a feedstock should be utilized.

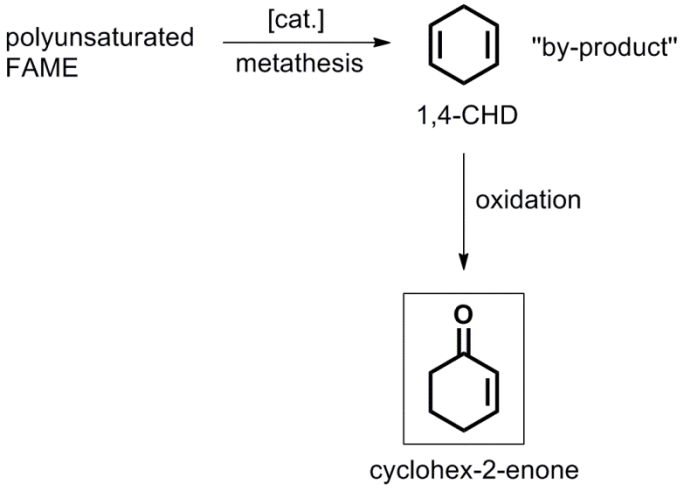

Figure 4.5-1: Generation of 1,4-cyclohexadiene (CHD) as byproduct of the olefin metathesis of polyunsaturated fatty acid methyl esters (FAMEs) and preparation of cyclohex-2-en-1-one from 1,4-CHD.

CHD cannot be directly converted to the desired modified CL monomers. A possibility to synthesize CL monomers is the Baeyer-Villiger oxidation of cyclohexanones. In order to prepare chemically modified CL, we thus used cyclohex-2-en-1-one as key substrate for Michael additions (Figure 4.5-2). Interestingly, cyclohex-2-en-1-one can be obtained from CHD in a sustainable way by selective two-phase hydrogenation and subsequent oxidation or direct liquid-phase oxidation of CHD.[302-305] As these reaction steps are described in literature in detail, we did not further investigate this transformation and directly used commercially available cyclohex-2-en-1-one as starting material. Cyclohex-2-en-1-one is an ideal substrate for efficient Michael addition reactions. The reaction of such enones with thiols is also classified as click-reaction, allowing for an equimolar use of the reagents, enabling a very simple purification of the products by evaporation of the amine catalyst or washing with water, while performing the reaction under mild and solvent-free conditions.[306]
Hence, we first used different thiols to prepare the cyclohexanones **1.5** – **4.5** by thia-Michael addition (Figure 4.5-2). To prepare the modified CL monomers **5.5** – **8.5**, the cyclohexanones **1.5** – **4.5** were subsequently transformed by Baeyer-Villiger oxidations.

Thia-Michael additions were performed under solvent-free conditions using triethylamine as catalyst. Full conversion of the substrates was observed by GC-MS after 16 h at 30 °C. The obtained products were purified by simple washing with 1 M aqueous NaOH solution in order to remove the amine catalyst and the slight excess of the used thiol.

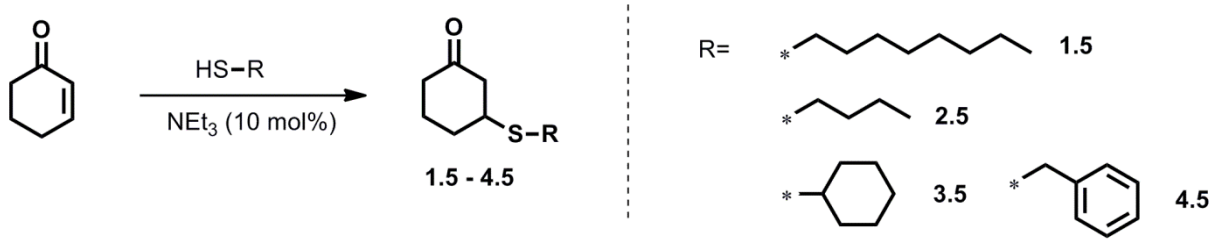

Figure 4.5-2: Thia-Michael addition of cyloehex-2-enone using different thiols.

Without further purification steps, the cyclohexanone derivatives were directly used in Baeyer-Villiger oxidations to prepare the desired monomers (Figure 4.5-3). For the Baeyer-Villiger oxidations, we first used conventional reaction conditions, utilizing *mCPBA* as oxidant and dichloromethane as solvent in order to have the modified CL monomers in hands and to study their polymerization and material properties. Further studies of more sustainable Baeyer-Villiger procedures will be discussed below. It has to be noted that during the Baeyer-Villiger oxidation, the sulfide moiety was oxidized to the sulfone. Reaction studies utilizing *m*CPBA as oxidant revealed that the oxidation of the ketone and the sulfide proceed simultaneously. Therefore, to ensure full oxidation of the sulfide to the sulfone and the oxidation of the ketone to the ester an excess of *m*CPBA was used (see also experimental part, chapter 6.3.4). Using ice bath cooling, *m*CPBA was added and full conversion was observed after stirring the reaction mixture for 24 hours at room temperature. The desired monomers could be isolated in yields up to 85 %. Very interestingly, detailed NMR analysis revealed the formation of only one regio-isomer, namely 3-(substituted-sulfonyl)-ε-caprolactone, during the Baeyer-Villiger oxidation allowing the preparation of well-defined and modified PCLs (see supporting information). Generally, the synthetic strategy using cyclohex-2-en-1-one as an efficient Michael acceptor to prepare modified cyclohexanones as CL precursors and subsequent monomer synthesis by Baeyer-Villiger oxidations is of outstanding simplicity (Figure 4.5-3). Interestingly, the functionalization at the β-position of CL is rarely described, which will lead to a novel class of modified CL monomers having sulfonyl moieties for the preparation of poly(3-sulfonyl-ε-caprolactone)s.

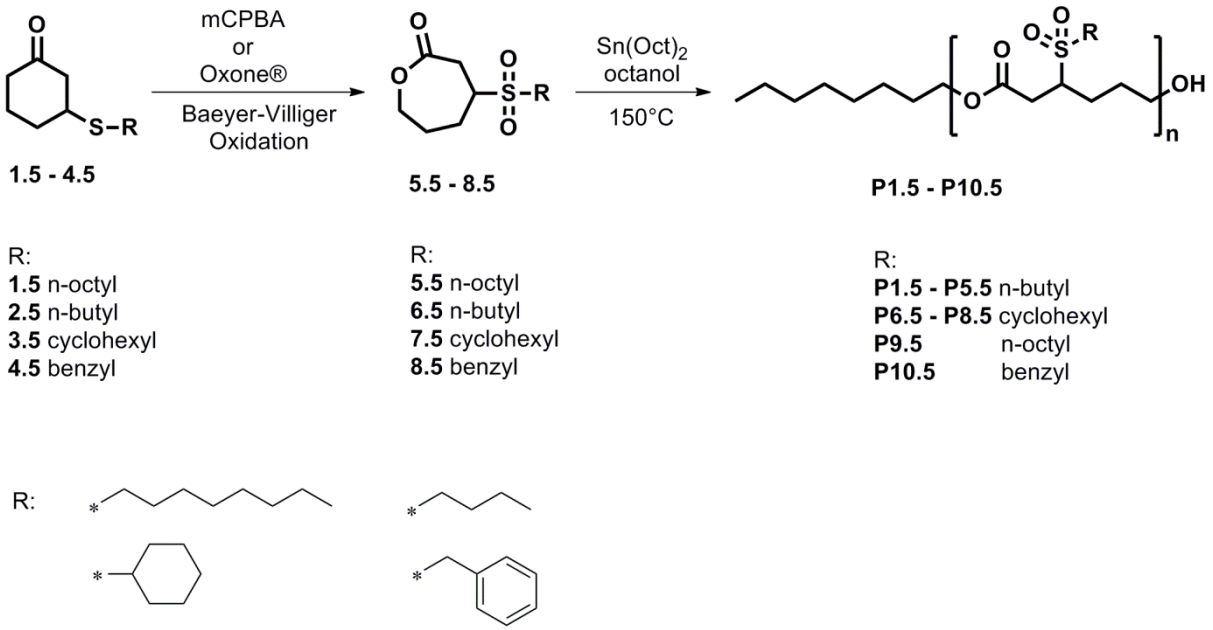

Figure 4.5-3: Baeyer-Villiger oxidation of the cyclohexanone substrates **1.5** – **4.5** and the ring-opening polymerization of the ε-caprolactone monomers **5.5** – **8.5**.

To enable a more sustainable Baeyer-Villiger oxidation of the cyclohexanone derivatives, we studied several alternative oxidation procedures (Table 4.5-1). It has to be noted that the Baeyer-Villiger oxidation should be performed under mild reaction conditions to avoid an elimination of the sulfide (more precisely the intermediately formed sulfoxide). At first, with regard to a reaction optimization, the produced *meta*-chlorobenzoic acid was isolated from the crude reaction mixture in order to enable a recycling of the used *m*CPBA as already described by, e.g., Jain and coworkers.[307] In Baeyer-Villiger oxidations using octanoic acid (Table 4.5-1, entry A) or ethyl acetate (entry B) as peracid source and Novozyme 435® as the catalyst, only low conversions were obtained after a reaction time of 7 days. Thus, contrary to the conversion of, e.g., cyclohexanone to CL *via* Novozyme 435® catalyzed Baeyer-Villiger oxidation,[57, 61] the thiol functionalized substrates are not compatible with the enzyme catalyst and/or the applied reaction conditions. Baeyer-Villiger oxidations preformed with urea hydrogen peroxide as oxidant as reported by Mecking and coworkers[308] yielded full conversions of the substrates, but low yields and regio-selectivity were obtained (entry C). Most promising, the utilization of Oxone® as green oxidant for Baeyer-Villiger oxidations, as, e.g., described by Hillmyer *et al.,*[128] yielded full conversion of the substrates performing the reaction at room temperature (entry D). Thereby, the utilized solvent is of crucial importance. In oxidation reactions performed in dichloromethane or methanol/water, low yields were

obtained. However, if the reaction was performed in *N,N*-dimethylformamide full conversion, a high region-selectivity and yields up to 70 % were achieved.

Table 4.5-1: Results obtained from the different Baeyer-Villiger oxidation procedures employing monomer **6.5**.

Procedure	Conversion[%][a]	Yield [%][b]
A (Novozyme 435®/ethyl acetate)	≤10	n.d.
B (Novozyme 435®/octanoic acid)	~5	n.d.
C (urea hydrogen peroxide/TFAA)	100	n.d.
D (Oxone®)	100	55 - 70
E (*m*CPBA)	100	77 - 85

[a]Determined *via* GC-MS, [b]isolated yield, n.d.=not determined

Although the conventionally performed Baeyer-Villiger oxidation afforded higher yields, the applied procedure making use of Oxone® appeared to be a promising green alternative.

Subsequently, the prepared CL monomers were studied in ring-opening polymerizations. Because of the poor solubility of the monomers, the best results were obtained if the polymerizations were performed at 150 °C under solvent-free conditions using tin(II) octanoate as catalyst and 1-octanol as initiator. The kinetics of the polymerization were studied by SEC analysis by monitoring the monomer conversion (Figure 4.5-4). Compared to CL, the polymerizations of the modified CLs proceeded slower, except for monomer **5.5** having the *n*-octylsulfonyl moiety. Although **5.5** seemed to be sterically more hindered than monomer **6.5**, the polymerization was significantly faster (Figure 4.5-4). This might be due to a difference of the viscosity of the reaction mixture containing the monomer and growing polymer, resulting in different diffusion coefficients. This assumption is supported by the result of the kinetic measurement of monomer **7.5** having a cyclohexylsulfonyl moiety. Monomer **7.5** displayed the highest melting point (136 °C) and the polymerization mixture was hardly stirrable after 45 min of reaction time, resulting in a slower polymerization rate.

However, the kinetic measurements revealed a living character of all performed ring-opening polymerizations (linear correlation of $-\ln([M_t]/[M_0])$ vs. reaction time and M_n vs. conversion; Figure 4.5-4 and Figure 6.3.5-2 in the experimental part 6.3.4).

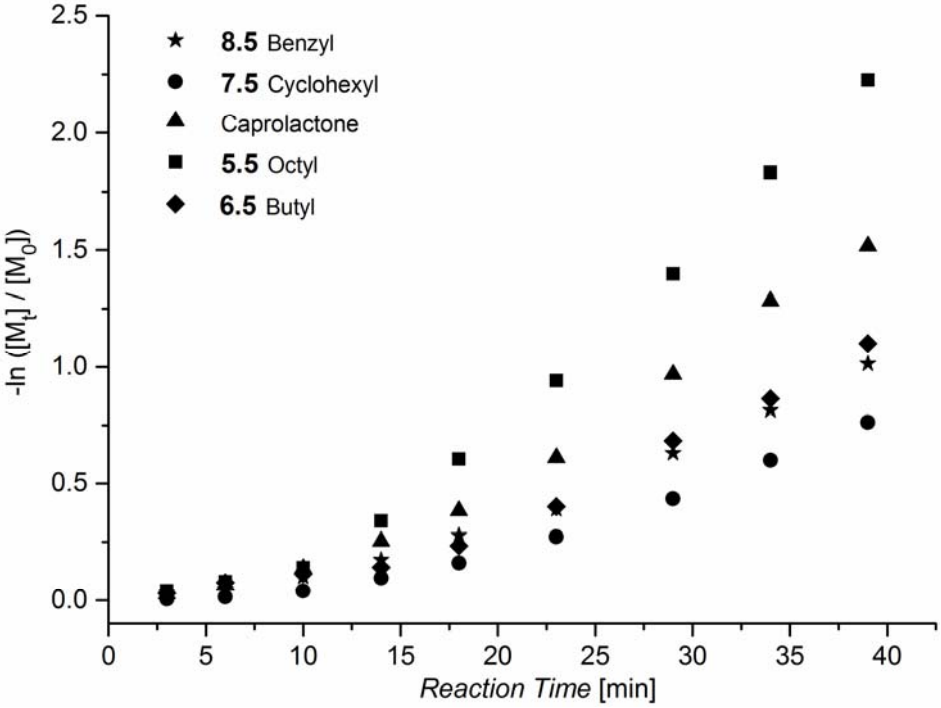

Figure 4.5-4: Kinetic studies of the ring-opening polymerization of the modified caprolactone monomers **5.5** – **8.5** and CL.

It has to be noted that the beginning the polymerization displayed a short induction time, but in this time range, the determination of the monomer conversion was difficult by SEC due to overlapping peaks. It should also be noted here that a determination of conversions by NMR and/or GC was not possible due to indistinguishable peaks in NMR and impossible detection of the monomers in GC.
Moreover, it should be noted that the molecular weights determined by SEC analysis differ from the theoretically expected values due to an inaccuracy of SEC analysis since the prepared polyesters with the sulfonyl moieties are very different to the PMMA standards used for the calibration. However, the SEC analysis of all polyesters revealed polymers with narrow dispersities of 1.10 – 1.28 and homogenous molecular weight distributions (Figure 4.5-5, Table 4.5-2). **P4.4** and **P5.4** showed small shoulders at higher molecular weights, which can be explained by a slow intermolecular transesterification process occurring after complete conversion.[129, 309, 310] For further studies, (*n*-butylsulfonyl)cyclohexane was used to

investigate the stability of the sulfone moiety (details for the exact experimental procedure can be found in the experimental part 6.3.4).

The results demonstrated that the sulfone is stable under the applied polymerization conditions and no side reactions occurred. By varying the monomer to initiator ratio, the molecular weight of the polymers could be well adjusted, also clearly demonstrating a good control of the ring opening polymerization (Figure 4.5-5, Table 4.5-2).

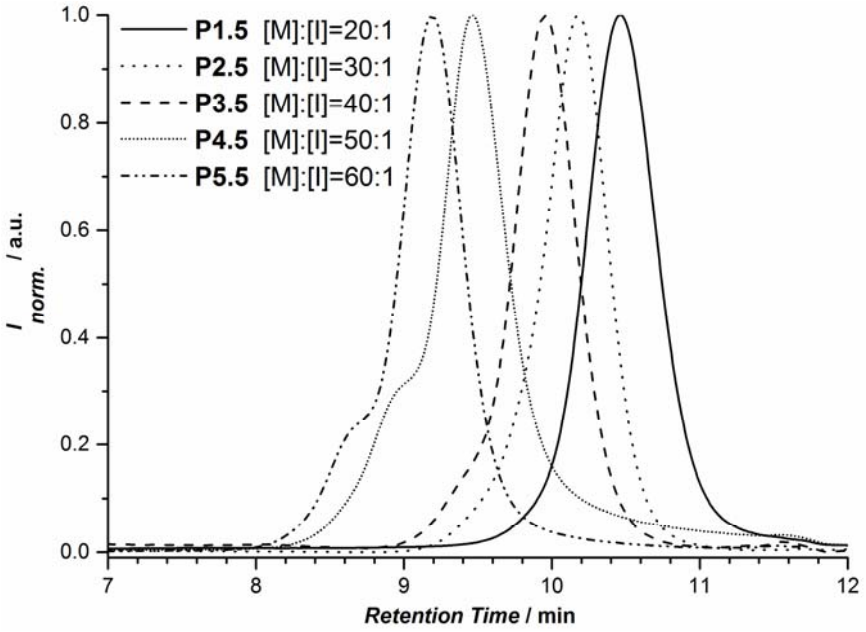

Figure 4.5-5: SEC analysis of the polyesters **P1.5** – **P5.5** prepared from monomer **6.5** using different monomer to initiator ratios.

Table 4.5-2: Results of the SEC analysis of the prepared polyesters **P1.5** – **P5.5** using monomer **6.5** and different monomer to initiator ([M]/[I]) ratios.

Polymer	[M]/[I]	$M_{n,\,theo.}$ [Da]	$M_{n,\,SEC}$ [Da]	$Đ$
P1.5	20 : 1	4812	2740	1.28
P2.5	30 : 1	7153	6320	1.13
P3.5	40 : 1	9494	7400	1.10
P4.5	50 : 1	11835	12540	1.16
P5.5	60 : 1	14176	18420	1.17

The resulting polyesters were obtained as transparent materials in nearly quantitative yields after a reprecipitation and their thermal properties were studied by DSC analysis. All polyesters containing the sulfonyl-moieties displayed no melt transitions

and no thermal degradation up to 180°C. In contrast to conventional CL, the sterically demanding sulfonyl moieties prevent interactions of the polymer chains and formation of crystalline segments. The DSC measurements showed glass transition temperatures of the polyesters between 0 – 52 °C (Table 4.5-3). Polymer **P10.5** showed the highest T_g with 52 °C, whereas polymer **P9.5** having a long dangling side chain showed the lowest T_g of 0 °C. Generally, the T_g decreases with a longer dangling sulfonyl moiety, which prevents chain-chain interactions. In case of **P10.5**, the polymer shows a higher T_g than the other polymers due to increased chain interaction by *π-π* interaction of the aromatic moiety. ^{1}H-NMR analysis of the crude and precipitated polymers revealed defined polyesters without the occurrence of side reactions, such as elimination, also demonstrating the compatibility of the monomers with the applied polymerization conditions. The obtained results prove the successful use of the modified CL monomers for the preparation of defined polyesters with narrow dispersities and varying pendent side groups.

Table 4.5-3: Results of the SEC and DSC analysis of the polyesters **P3.5**, **P8.5** – **P10.5** using a monomer to initiator ratio of [M]/[I] = 40 : 1.

Polymer	$M_{n,\,SEC}$ [Da]	Đ	T_g [°C]
P3.5 (*n*-butyl)	7400	1.10	7.0
P8.5 (cyclohexyl)	7680	1.17	40
P9.5 (*n*-octyl)	8840	1.12	0.0
P10.5 (benzyl)	6100	1.15	52

Depending on the thiol used in the thia-Michael reaction to modify cyclohex-2-en-1-one, the thermal properties of the corresponding polyester are significantly different. Moreover, the presented synthesis strategy offers an efficient and very straightforward possibility for the design of diverse modified CL monomers. Additionally, the method can be extended to other Michael donors making this strategy a universal approach to prepare versatile CL monomers and polyesters with novel material properties.

Conclusions

The preparation of a novel class of CL monomers modified with different sulfonyl moieties at the β-position of the carbonyl function is described. To achieve this, the thia-Michael addition to cyclohex-2-en-1-one revealed to be an excellent strategy to prepare modified CL precursor since complete atom-efficiency, simple purification, and performance at very mild and solvent-free conditions makes this approach highly attractive. The modified CL monomers were prepared by Baeyer-Villiger oxidation of the cyclohexanone derivatives. As an alternative and more sustainable Baeyer-Villiger reaction procedure, the use of Oxone® as green oxidant revealed to be very promising. Interestingly, the performed Baeyer-Villiger oxidations are highly regio-selective, allowing the synthesis of well-defined polyesters. The kinetics of the ring-opening polymerizations of the modified CL monomers were studied and compared to CL, revealing a controlled ring-opening polymerization of these novel monomers. Furthermore, by changing the monomer to initiator ratio, the molecular weights of the PCL bearing sulfonyl groups could be well adjusted. The resulting polymers were transparent and showed variable glass transitions depending on the sulfonyl moiety attached to the polyester. All in all, the presented synthetic strategy is of high simplicity and the desired modified CL monomers, which were used to prepare PCLs having different sulfonyl groups, are obtained in only two very straightforward and efficient synthesis steps.

4.6 Renewable polycarbonates and polyesters from 1,4-cyclohexadiene

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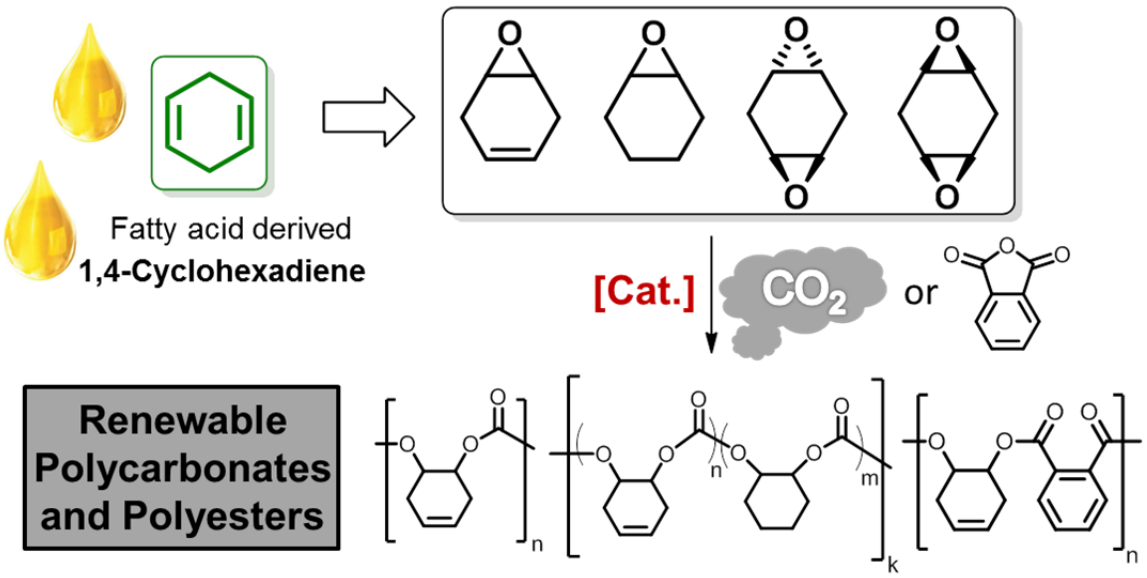


Abstract

Epoxides derived from 1,4-cyclohexadiene (CHD), the latter produced from renewable resources *via* self-metathesis of plant oil derivatives, are applied as key substrates in ring-opening copolymerizations to produce polyesters and aliphatic polycarbonates. Renewable, unsaturated polycarbonates were prepared by the ring-opening copolymerization of epoxide/CO_2; these are catalysed by di-zinc/magnesium complexes previously reported by Williams *et al.* or by using chromium(III) or cobalt(III) salen complexes. Renewable, unsaturated polyesters, with glass transition temperatures up to 128 °C, were obtained by the ring-opening copolymerization of epoxide/phthalic anhydride. The relative rates of these copolymerizations were monitored using *in situ* attenuated total reflectance infra-red (ATR-IR) spectroscopy. The polymers were fully characterized using spectroscopy (nuclear magnetic resonance, infra-red), mass spectrometry (matrix assisted laser desorption ionization), and by thermal methods (differential scanning calorimetry and thermogravimetric analysis).

Introduction

Polycarbonates (PC) are important commodity materials, widely applied in electronics, construction, and as rigid plastics. The most common PC is produced from bisphenol A, which benefits from a high glass transition temperature (149 °C) and good mechanical properties.[311] There are, however, concerns associated with the toxicity of reagents, including the possible endocrine disruptor pathways attributed to bisphenol A. Moreover, such classic PCs are produced *via* polycondensation using phosgene as co-monomer. This has motivated the quest for alternative materials.

Aliphatic polycarbonates, produced by the metal catalysed alternating ring-opening copolymerization (ROCOP) of CO_2/epoxides (Figure 4.6-1), are attracting considerable attention as semi-renewable polymers. The use of carbon dioxide as a monomer (or generally reagent) is attractive, because it is inexpensive, non-toxic, abundant, renewable and a common waste product of many industrial processes. Although the properties of these materials do not yet match those of PC from bisphenol A, recent research highlights their potential with polymers being produced by this method which show T_g up to 140°C.[312] Another promising application for such polycarbonates is as low molecular weight polyols (hydroxyl terminated polymers), mainly to be used for the production of polyurethanes. Indeed, poly(ethercarbonate) polyols, produced by ROCOP, have been successfully applied to prepare polyurethane foams;[313] an in depth life cycle analysis, published last year, found that these materials benefited from reductions in energy use and greenhouse gas emissions of 10-20 % compared to conventional polyols.[15]

Considering the sources for the ROCOP monomers, several authors have commented on the ability to use purified carbon dioxide, which might be obtained by carbon capture and sequestration, to prepare the polyols. Others have reported catalysts that tolerate high levels of water, a common contaminant in captured carbon dioxide. In terms of epoxides, the majority of studies apply cyclohexene oxide (CHO) or propylene oxide (PO),[117, 118, 314] both of which are usually derived by oxidation of petrochemicals. There remains just a single report of the application of a renewable epoxide, limonene oxide, to produce a fully renewable polycarbonate.[122] It is also worth mentioning that since 1970, many groups have investigated protected glycidyl ethers, which could, in principle, be derived from glycerol.[315-317]

Epoxides are also applied in ROCOP with anhydrides, utilizing similar catalysts as for epoxide/CO_2 ROCOP. This allows the production of polyesters and, in particular, is an attractive controlled polymerization route to semi-aromatic polyesters with improved thermal properties (i.e. higher glass transition temperatures).[318] Various authors have reported the ROCOP using anhydrides from renewable resources, including maleic or succinic anhydride.[123, 319, 320] Furthermore, phthalic anhydride, which is particularly attractive as it yields thermally resistant aromatic moieties in the polymer backbone, can be produced from carbohydrate derived biomass.[321] In terms of epoxides, so far the only renewable options reported for this anhydride mediated ROCOP are limonene and pinene oxide.[123, 124]

Thus, there is an impetus to consider routes to prepare epoxides from renewable resources as this will allow the production of 100% renewable polyesters/carbonates and is furthermore expected to expand the property profiles for this class of material. In this context, plant oils are an interesting feedstock, as they are produced on sufficient scale and at relatively low cost. Already today, they are used as biofuels and as a source of renewable monomers.[10, 322, 323] A range of transformations of such triglycerides and fatty acids, including polymerizations, have already been reported.[299] Of these methods, olefin metathesis is particularly interesting, as it can be used to produce long-chain carboxylic acids/esters. These are interesting monomers to produce materials with properties approaching some of those of polyetheylene.[266, 277, 324, 325] *Inter alia*, during oleochemical olefin metathesis reactions, a common byproduct is 1,4-cyclohexadiene (CHD), if polyunsaturated fatty acids (i.e. linoleic and/or linolenic acid) are present in the fatty acid mixture.[300] For instance, the self-metathesis of polyunsaturated fatty acid methyl esters was used to prepare long-chain diesters, which are important AA-type monomers.[169, 266] In these metathesis processes, CHD is obtained as a waste byproduct, as recently reported by Meier *et al*.[179] Cole-Hamilton and coworkers reported the metathesis of cardanol and ethylene, also yielding CHD as a byproduct,[301] offering an alternative route to renewable CHD. In this context, the valorisation of CHD would be particularly beneficial to the biorefinery concept, where all products of a feedstock should be utilized. Recently, Meier *et al.* described the synthesis of substituted caprolactones and their polymers, prepared *via* the modification of cyclohex-2-en-1-one, which was obtained from CHD.[326] Moreover, 1,3-cyclohexadiene, obtained *via* isomerization of CHD, can directly be used in polymerization reactions involving anionic, cationic, and

free-radical mechanisms.[327, 328] The poly(cyclohexadiene)s are of interest, since these polymers display good properties and can be transformed into conducting polymers and proton conductors.[311, 329-331] Mathers and coworkers presented a very attractive strategy using 1,4-CHD, obtained from un-purified plant oils, to prepare poly(cyclohexadiene)s *via* a one- or two-step isomerization polymerization cascade.[332] Here, the strategy to valorise CHD is to investigate its transformation into epoxides and the subsequent ROCOP reactions using these bio-derived epoxides.

Results and discussions

Epoxides from 1,4-Cyclohexadiene

Epoxides are interesting and important monomers to prepare polycarbonates or polyesters by ROCOP methods. Given the widespread application of cyclohexene oxide (CHO) in ROCOP polymerizations, CHD should be a promising substrate to produce both new and known materials that are fully renewable.

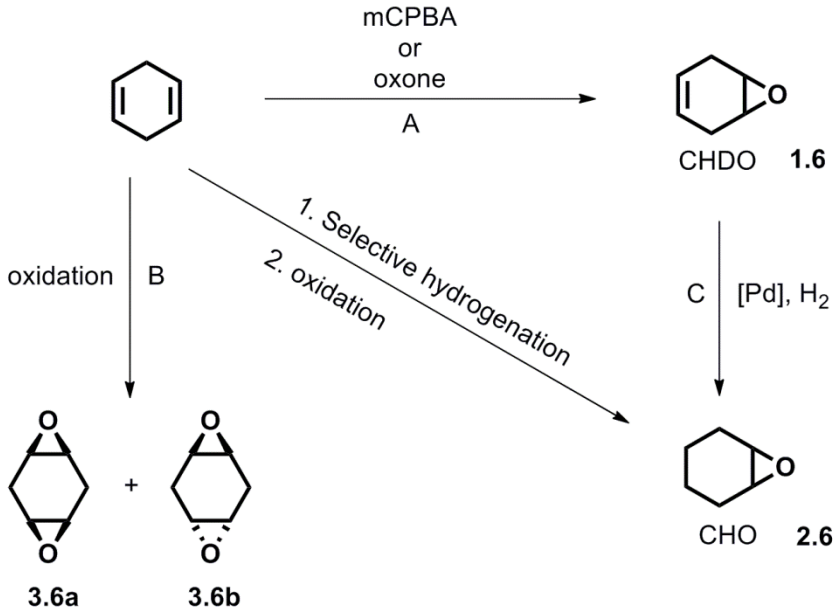


Figure 4.6-1: Synthesis of 1,4-cyclohexadiene oxide (CHDO), cyclohexene oxide (CHO), and two *bis*-epoxides (*syn*-1,4-cyclohexadiene diepoxide (**3.6a**), *anti*-1,4-cyclohexadiene diepoxide (**3.6b**)) from 1,4-cyclohexadiene (CHD). A: Oxone®, DCM/acetone/H_2O/$NaHCO_3$, rt, 6h or *m*CPBA/DCM/H_2O/$NaHCO_3$, rt, 6h, B: same as for A except the slight excess of *m*CPBA or Oxone® used per double bond, C: Pd/C(en), 1 wt.%, H_2, r.t, 24h.

We observed that CHD can be converted into various epoxides, including 4,5-epoxycyclohex-1-ene (cyclohexadiene oxide **1.6** = CHDO), cyclohexene oxide (CHO, **2.6**) and two diasteromeric *bis*-epoxides (**3.6a**, **3.6b**) using the reagents and

conditions shown in Figure 4.6-1.The oxidation of CHD was accomplished using *meta*-chloroperbenzoic acid (mCPBA)[333, 334] in dichloromethane at 298 K to yield monomer **1.6** in 82 % yield. Alternatively, a more sustainable oxidation of CHD was successfully performed using Oxone® leading to the production of **1.6** in 65 % yield. Interestingly, cyclohexene oxide (CHO) **2.6** was also prepared from CHD by a selective bi-phasic hydrogenation leading to cyclohexene, and its subsequent oxidation.[302-305] For the hydrogenation reaction using **1.6**, the use of Pd/C under 1 atm of H_2 was unsuccessful, but the use of Pd/C(en)[335] in THF under 1 atm of H_2 for 24 h enabled formation of CHO, together with the formation of side-products such as, among others, the corresponding vicinal diols (as determined by ^{1}H NMR). Thus, this route allows access to CHO from renewable resources as an alternative to the more usual routes to petrochemicals (benzene).

Finally, in order to explore the range of epoxides accessible from CHD, a complete oxidation of **1.6** to the *bis*-epoxides **3.6a** and **3.6b** was investigated. Thus, the oxidation of **1.6** was performed using a slight excess of *m*CPBA (1.05 equivalents per double bond) at 298 K in dichloromethane to yield the corresponding *bis*-epoxides (**3.6a** (20%), **3.6b** (65%)). Alternatively, Oxone® can also be used as the oxidant leading to variable proportions of the *bis*-epoxides (depending on the quantity of Oxone® applied, for more experimental details see chapter 6.3.6).

ROCOP using bio-derived epoxides

The bio-derived epoxides were applied in ROCOP reactions, using either CO_2 or phthalic anhydride as a co-monomer. These polymerizations all require catalysts; four different homogeneous catalysts with a well established activity in these fields were compared (the structures of which are illustrated in Figure 4.6-2).[336-339] ROCOP using monomer **1.6**, catalysed by the di-zinc complex **C1.6**, did not result in polymer formation, even under the conditions previously successfully used for the ROCOP of CHO (80°C, atmospheric CO_2 pressure). Increasing the temperature to 100°C led to some formation of the cyclic carbonate, but no polymer.

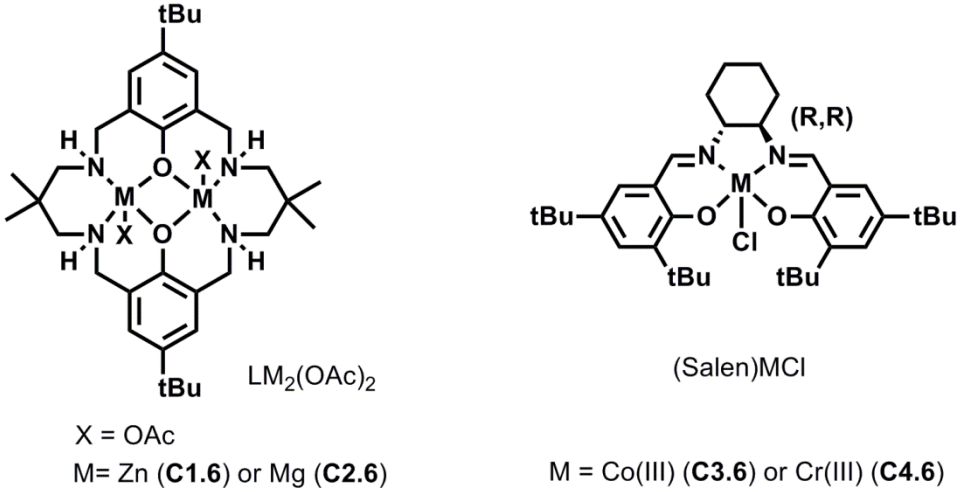


Figure 4.6-2: Structures of the four homogeneous catalysts investigated for ROCOP (for catalyst synthesis methods, see chapter 6.1).

These results prompted us to investigate the magnesium analogue **C2.6**, which had previously been found to be both more active and more selective than **C1.6**.[336] Thus, ROCOP using **1.6**, catalysed by **C2.6** (0.2 mol%) under atmospheric CO_2 pressure, afforded well-defined, perfectly alternating polycarbonates (i.e. no formation of ether linkages or cyclic carbonate was observed (Figure 4.6-3)), albeit with considerably lower activity than the analogous copolymerizations using **2.6**.

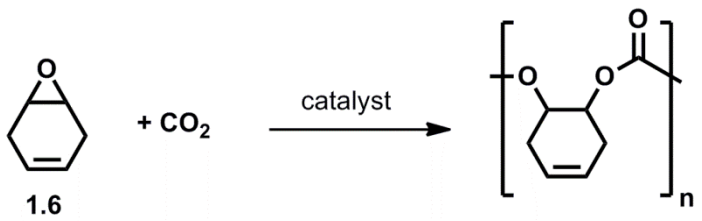


Figure 4.6-3: ROCOP of monomer **1.6** utilizing catalysts **C1.6** – **C3.6**. Catalyst **C3.6** was applied in combination with a co-catalyst (PPN-Cl).

The ^{1}H NMR spectrum of the crude product (Figure 6.3.6-2) was used to determine the monomer conversion; specifically this was achieved by comparison of the relative, normalized integrals for the cyclohexyl resonances (3.24 ppm **1.6**, 4.96 ppm polymer) and for the olefin signals (5.43 ppm **1.6**, 5.57 ppm polymer). In both cases, the same conversions were obtained, suggesting that the double bond was unreactive and that there was no formation of cross-linked polymers. In addition, monitoring the reaction by *in situ* ATR-IR spectroscopy using **1.6** showed linear formation of the polymer and conversion of the monomer with time, in accordance

with results previously obtained with **C1.6** for CHO/CO_2 copolymerization (see Figure 6.3.6-3).[340]

Size-exclusion chromatography (SEC) analysis of the polymers exhibited molecular weight distributions with a small shoulder to higher molecular weights, similar to previous obtained ROCOP results using these types of catalysts.[340] The structure of the polymers was confirmed by MALDI-ToF mass spectrometry. The MALDI-ToF spectrum exhibited two series of chains, corresponding to chains end-capped with α-acetate-ω-hydroxyl and α,ω-dihydroxyl moieties (Figure 4.6-4).

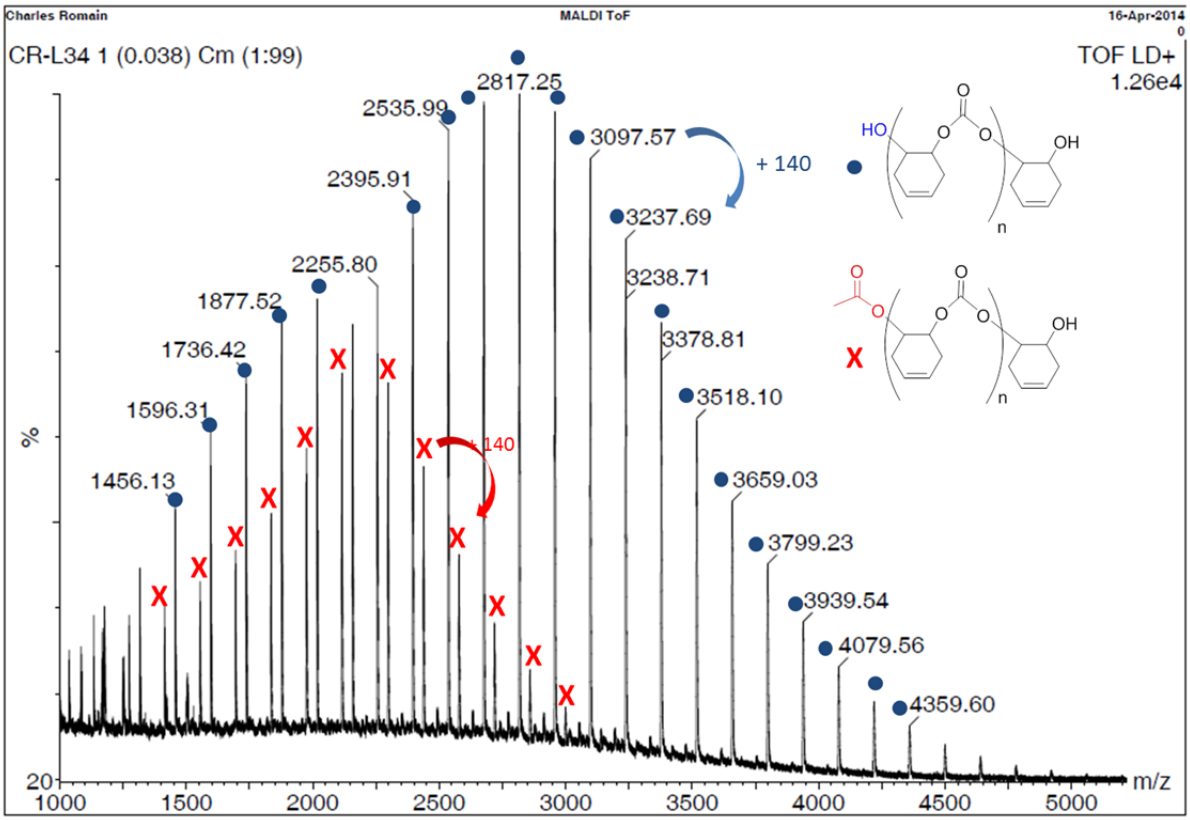


Figure 4.6-4: MALDI-ToF-MS of polymer **P3.6** prepared by co-polymerization of CO_2 and monomer **1.6** (conditions as described in Table 4.6-1).

In order to further investigate the reactivity of **1.6** in ROCOP, a well-known CHO/CO_2 catalyst, (*1R,2R*)SalcyCo(III)-Cl complex **C3.6**, was applied. Thus, the ROCOP using **1.6**, catalysed by **C3.6** (0.2 mol%) and with PPN-Cl (0.2 mol%) as co-catalyst, under 20 bar CO_2 pressure, also afforded polycarbonate without formation of any cyclic carbonate or ether linkages. In addition, the ^{1}H NMR spectra of both the crude and purified polymer showed that the double bond remained unreacted after polymerization, allowing access to unsaturated CO_2-derived polycarbonates.

Table 4.6-1: Shows the results of ROCOP using monomer **1.6** (and **2.6**).

Polymer	Catalyst	CO_2 [bar]	[M]:[Cat.]	T [°C]	Conv. [%][d]	TOF [h^{-1}]	M_n [kDa]	$Đ$
P1.6[a]	**C1.6**	1	500:1	80	0	-	-	-
P2.6[a.]	**C1.6**	1	500:1	100	12	4	-	-
P3.6	**C2.6**	1.	500:1	80	25	5	2.9	1.17
P4.6	**C2.6**	1	250:1	80	20	3	2.5	1.08
P5.6	**C2.6**	1	500:1	100	21	6	2.8	1.15
P6.6	**C3.6**	20	200:1	20	15	1	5.3	1.43
P7.6	**C3.6**[e]	20	500:1	28	78	65	12.9	1.18
P8.6[b]	**C2.6**	1	500:1	80	(11/56)[b]	21	4.0	1.15
P9.6[c]	**C3.6**[e]	20	500:1	28	(22/72)[c]	118	11.5	1.12

[a] The only product of this reaction was cyclic carbonate, [b] Mixtures of monomers **1.6** and **2.6** were applied such that the ratio of **1.6** : **2.6** was 4 : 1 and the conversion is given for the respective monomer, [c] Mixtures of monomers **1.6** and **2.6** were applied such that the ratio of **1.6** : **2.6** was 1 : 1 and the conversion is given for the respective monomer, [d] Conversion was determined by ^{1}H-NMR, [e] PPN-Cl was used as co-catalyst.

The polymers prepared using the cobalt catalyst showed slightly higher molecular weights (12.9 kg/mol), bimodal molecular weight distributions and narrow dispersities (1.18) (Table 4.6-1). Furthermore, ROCOP occurred in a controlled manner, as evidenced by a linear correlation between the monomer conversion and the polymer molecular weight (see also experimental part, Figure 6.3.6-4). Thus, applying a range of different copolymerization catalysts (**C2**, **C3**) enabled the successful copolymerization of **1.6**/CO_2, although the rates were lower than the analogous polymerizations run using cyclohexene oxide (**2.6**)/CO_2. This likely relates to different metal binding energies of the two epoxides.

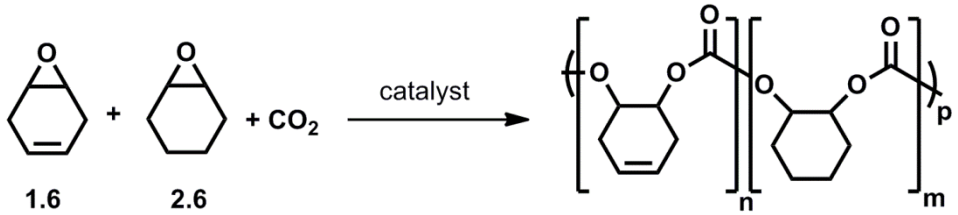


Figure 4.6-5: The terpolymerizations of **1.6**, CHO and CO_2 so as to produce partially unsaturated polycarbonates.

Terpolymerizations of **1.6**/CHO/CO_2 were also investigated (Figure 4.6-5); the incorporation of **1.6** was attractive as a means to introduce unsaturation into the polymer backbone, allowing for further post-polymerization modifications.[341] Different catalysts and ratios of monomers **1.6**:**2.6** were investigated (Table 4.6-1). The relative monomer conversions were determined by ^{1}H NMR spectroscopy by integrating the signals of the cyclohexyl moiety in the polymer (4.96 ppm for incorporated **1.6**, 4.66 ppm for incorporated **2.6**) and monomer (3.24 ppm **1.6**, 3.11 ppm **2.6**), respectively. Once again, the terpolymerizations using di-magnesium **C2.6** are significantly slower than those with the cobalt salen complex **C3.6**. SEC analysis revealed polycarbonates with moderate molecular weights of (4 - 11.5 kDa) and narrow dispersities (<1.15).

Finally, the bis-epoxides **3.6a** and **3.6b** were selected to prepare branched or cross-linked polycarbonates, however, in all cases completely insoluble material was produced, which limited further analysis but was indicative of the formation of cross-linked products.

Unsaturated Polyesters by ROCOP

Monomer **1.6** was also used for the synthesis of unsaturated polyesters *via* ROCOP with phthalic anhydride (Figure 4.6-6). An attractive feature of the products would be the facility to introduce unsaturation into the polymer backbone. It is notable, that many researchers have reported problems in copolymerizing maleic anhydride (a similarly unsaturated co-monomer) and thus novel routes to unsaturated polyesters are of interest.[337, 338]

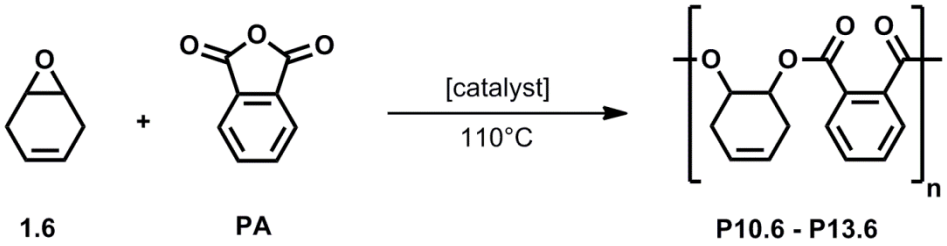


Figure 4.6-6: ROCOP using epoxide **1.6** and phthalic anhydride (**PA**).

Catalyst **C1.6** did not afford any polymerization, whereas **C2.6** enabled the slow formation of perfectly alternating polyesters. Similarly, catalysts **C3.6** and **C4.6** were effective and yielded unsaturated polyester. In each case, the monomer conversion was estimated using ^{1}H NMR spectroscopy.

In particular, the relative integrals were compared for the aromatic signals (for PA at 7.81 - 7.67 ppm and for polymer at 7.66 - 7.36 ppm, see Figure 6.3.6-5, Table 4.6-2).

Table 4.6-2: Results of the co-polymerization of monomer **1.6** and phthalic anhydride (**PA**).

Polymer	Catalyst	[**1.6**]:[**PA**]:[Cat.]	T [°C]	Conv.[%][c]	TOF	M_n [kDa][d]	$Đ$
P10.6[a]	**C2.6**	250:250:1	120	10	6.25	1.6	1.18
P11.6	**C3.6**	250:250:1	110	48	60	4.3	1.23
P12.6	**C4.6**	250:250:1	110	74	246	4.5	1.34
P13.6[b]	**C4.6**	250:250:1	110	91	75.8	7.5	1.17

[a]Reaction was performed without co-catalyst. [b]Reaction was conducted in toluene (2.5 M). [c]Conversion was determined from the ^{1}H-NMR spectrum of the crude product by comparison of the relative, normalized integrals for the cyclohexyl resonances (4.96 ppm polymer, 4.64 ppm polymer, 3.24 ppm **1.6**, 3.11 ppm **2.6**). [d] Molecular weights and polymer dispersities were determined by GPC calibrated with polystyrene standards.

Utilizing the salen based catalysts yielded polyesters of moderate molecular weights (7.5 kDa) and narrow dispersities (1.20) with TOF values up to 246 h^{-1}. The chromium salen catalyst (**C4.6**) showed the best performance at a reaction temperature of 110 °C in presence of PPN-Cl as co-catalyst. Polymerizations in bulk were hampered by viscosity increases; however, using monomer solutions (2.5 M in toluene) led to conversions of 91 % within 3 hours. ROCOP occurred in a controlled manner, as evidenced by a linear correlation between the monomer conversion and the polymer molecular weight (see Figure 6.3.6-6). Interestingly, for both **C3.6** and **C4.6**, the use of PPN-Cl as the co-catalyst was required to increase the activity. It is notable that compared to maleic anhydride/epoxide copolymerization, where the co-catalyst was purported to react with the olefin moiety,[337] in this case the double bonds remained unreacted in the polymer.

Thermal properties of polyesters and polycarbonates

The thermal properties of the unsaturated polycarbonates were studied by TGA and DSC analysis (Table 4.6-3). The polycarbonates prepared from **1.6** showed glass-transition temperatures of approximately 115 °C (depending on the molecular weight), a value close to that reported for PCHC.[311, 342]

The thermal degradation temperature (10% weight loss) of **P7.6** was 255 °C, whereas that of **P9.6** was higher at 285 °C. Both values are somewhat lower than that reported for PCHC (T_d ~ 300 °C [343, 344]), suggesting that the olefin group slightly lowers the thermal stability. Terpolymers, especially **P8.6** (T_g = 106 °C), showed slightly lower glass transition temperatures than PCHC or **P3.6** – **P7.6** (T_g = 115 °C), which is most likely due to the low molecular weight of **P8.6**. The thermal properties of the polyesters derived from **2.6**/phthalic anhydride showed better thermal properties, with glass transition temperature of 128 °C and a thermal decomposition temperature (10% weight loss) of 325 °C. It is noteworthy that polyesters derived from CHO/phtalic anhydride typically show a T_g below 100 °C.[339, 345]

Table 4.6-3: Shows the results of the thermal analysis of the polycarbonates.

Polymer		M_n *[kDa] / (Đ)*	T_d[°C][a]	T_g [°C][a]
P7.6	**1.6**/CO_2	12.9 (1.18)	255	115
P9.6	CHO/**1.6**/CO_2	11.5 (1.12)	285	112
P13.6	**1.6**/PA	7.5 (1.17)	325	128

[a]Representative DSC and TGA figures are included in the ESI

Conclusions

The preparation of a series of epoxides from 1,4-cyclohexadiene, which is itself a byproduct of the self-metathesis of triglycerides and other fatty acid derivatives, are presented. The diene was epoxidized, using various oxidants, to yield cyclohexadiene oxide or a *bis*-epoxide product. The diene could also be partially hydrogenated to cyclohexene and then oxidized to yield the well-known monomer cyclohexene oxide. The development of a bio-derived route to cyclohexene oxide is of interest, as the monomer is widely applied in various ring-opening copolymerization reactions, including epoxide/CO_2 to produce polycarbonates or epoxide/anhydride to produce polyesters. Thus, the method presented here provides an alternative route to prepare cyclohexene oxide.

Furthermore, the preparation of the bio-derived, unsaturated epoxide is also of high interest as it enables the preparation of partially unsaturated polycarbonates and polyesters. For the co-polymerization with CO_2 and cyclohexadiene oxide, the readily available cobalt salen complex provided the best results and yielded a polycarbonate

with closely related thermal properties to the well-known poly(cyclohexene carbonate). Terpolymerizations of CO_2, cyclohexene oxide, and cyclohexadiene oxide were also successful yielding polycarbonates with controllable quantities of unsaturation. Copolymerization of cyclohexadiene oxide and phthalic anhydride leads to renewable, unsaturated polyesters having high glass-transition and decomposition temperatures. These unsaturated polycarbonates and polyesters offer the possibility for further modification of the double bond, which would be expected to alter the polymer properties. Future research will focus on further development of the synthesis of epoxides from biomass as well as the post-polymerization functionalization and application of such unsaturated polyesters and polycarbonates.

5. Conclusion and Outlook

Plant oils and the thereof derived fatty acids are interesting substrates to be used for the synthesis of renewable monomers and polymers. The use of fatty acids for the synthesis of novel renewable materials is of great interest not only for the chemical industry. Of particular interest for the German chemical industry is the use of oleic- and erucic acid, plant oil derived fatty acids, which can be obtained from domestic oilseed crops. Within this thesis, the synthesis of novel polymeric materials from oleic and erucic acid is demonstrated. Additionally, the plant oil derived 16-hydroxypalmitic acid and 1,4-cyclohexadiene were used as renewable substrates to prepare polymers with interesting material properties.

In chapter 4.1, a more sustainable Wohl-Ziegler bromination procedure was introduced, while performing the reactions in bulk or using cyclohexane as solvent. In this way, it was shown that the use of highly toxic CCl_4 can be avoided, while similar yields are obtained. Oleic and erucic acid derived allylic bromides were synthesized, which are interesting compounds also for special applications such as the use as initiator for ATRP polymerizations. The use of NBS as bromination reagent makes this process unsustainable, as large amounts of waste are generated. Therefore, very interesting would be a catalytic alternative such as an *in situ* regeneration of NBS. In contrast, the hydrobromination of the FAMEs and subsequent modification appeared to be by far more promising in terms of a green and sustainable synthesis procedure of polyamides based on oleic or erucic acid. The analytical data for the polyamides with aliphatic side-chains show the potential of these renewable polyamides and the reported synthesis procedures are an important contribution to the production of novel plant oil based polyamides. Herein, the synthesis of fatty acid based polyamide monomers through a similar, but radical mediated bromination process and subsequent substitution reaction of the fatty acid bromides using a high ammonia pressure would be a potential implementation for an analogous industrial process.

The synthesis of novel polyamides from the biochemically derived 16-hydroxypalmitic acid was demonstrated in chapter 4.2. The long-chain PA16 showed a similar Young's modulus as conventional PA11 or PA12, and benefit from the long aliphatic chain segments, by means of a reduced hydrophilicity.

The monomer synthesis through azide functionalization and subsequent reduction was adapted from Lecamp *et al.*, who prepared polyamides with long dangling side chains using methyl ricinoleate as substrate.[346] The performed modification of 16-hydroxy palmitic acid through mesylation, azide functionalization and subsequent reduction is not very sustainable, since the used reagents are hazardous and large amounts of waste are generated. Nevertheless, the reported material properties of PA16 are very interesting; hence, the amine functionalization for instance *via* direct catalytic amination of the hydroxy fatty acids would be a very attractive process for the production of a renewable PA16.

A very efficient and catalytic process for the synthesis of polyamide monomers was demonstrated with the optimized co-catalyst-free Wacker oxidation procedure and subsequent reductive amination of the keto-FAMEs (chapter 4.3). Meanwhile, the oxidation was scaled up to a 40 to 60 g reaction using synthetic air as oxygen source. The use of lower catalyst loadings and higher pressures of synthetic air to further optimize the established process is under current investigation. Still, the accurate isolation of the product and separation of the solvent-catalyst mixture can be improved, since the product is usually contaminated with catalyst residues and small amounts of dimethylacetamide. Herein, the usage of other solvents or heterogeneous catalysts, such as Pd/C offers the possibility for further optimization. In addition, the introduced reductive amination procedure using a mixture of ammonium chloride, ammonium acetate and Raney-Nickel® as the catalyst proved to be powerful with regard to the obtained reaction efficiency and selectivity. In particular, the introduced procedure is very attractive for reductive aminations of dialkyl ketones performed on a lab-scale to yield primary amines, since there is no need for special high-pressure equipment. The obtained results from tensile-stress measurements and water-uptake tests of the prepared copolyamides revealed that conventional Nylon 6,6 can be well modified by co-polymerization with the renewable methyl oleate or –erucate derived monomers.

By cross-metathesis of fatty acid derived benzyl carbamates with methyl acrylate, renewable polyamides were synthesized from oleic, erucic, and undecenoic acid (chapter 4.4). The respective benzyl carbamates were synthesized by a catalytic Lossen rearrangement of hydroxamic fatty acids using TBD as the catalyst. Compared to other rearrangement procedures (e.g., Curtius or Hofmann rearrangement) the presented catalytic Lossen rearrangement is more sustainable,

but needs optimization to become an even more environmentally benign. One key problem is the purification of the crude product by column chromatography since this purification method generates large amounts of waste and is not feasible for large scale productions. Hence, purification by distillation at high vacuum or a one-pot synthesis of the monomers without isolation of the intermediates would be highly desirable. The cross-metathesis of the benzyl carbamates with methyl acrylate and subsequent carbamate cleavage appeared to be a very efficient process. High yields and a very good selectivity were obtained, whereas unreacted methyl acrylate can simply be removed and regenerated under reduced pressure. One problem might be the abruptly generated heat during the initiation of the metathesis reaction, which might be difficult for a large scale production of the polyamide monomers. Here, cross-metathesis reactions performed in a flow-reactor set-up would benefit from a better heat dissipation and mixing of the reagents, especially if the introduced strategy is transferred to a large scale industrial process. In summary, the demonstrated synthesis approach has great potential for the preparation of bio-sourced polyamides exhibiting good material properties.

Within chapter 4.5 the synthesis of modified CL monomers from renewable 1,4-cylohexadiene was demonstrated. The presented synthesis strategy is of great simplicity and can in principle be extended to other Michael donors. The performed Baeyer-Villiger oxidation of the modified cyclohexanes was performed with *m*CPBA as oxidizing agent, whereas enzyme catalyzed reactions were not successful. In order to turn the introduced synthesis strategy into a more sustainable process, *m*CPBA need to be substituted and further studies, involving the use of alternative oxidation procedures, are required. Very interestingly, the synthesis strategy making use of the 1,4-cyclohexadiene derived 1,2-cyclohexenone as highly reactive Michael acceptor for thia-Michael additions was now adapted for the synthesis of renewable caprolactames within our group within a Master Thesis.[347]

Instead of a Baeyer-Villiger oxidation of the sulfone functionalized cyclohexanes, a Beckmann rearrangement of the respective hydroxyl amine functionalized substrates was used to prepare the modified ε-caprolactam monomers. Alternatively, the prepared caprolactone monomers can directly be converted to the respective caprolactams using ammonia, similar to already known industrial processes.[296] All in all, the presented synthesis strategy is an important contribution to the

straightforward synthesis of modified PCLs, which are very versatile polymers that are useful for various applications, such as tissue engineering or drug delivery.

In chapter 4.6, the use of 1,4-cyclohexadiene derived renewable epoxides in CO_2 mediated copolymerizations is described. Interestingly, the presented synthesis strategy has already been adapted by Darensbourg and coworkers, and Sugimoto *et al.* to prepare cyclohexadiene oxide based polycarbonates, which had been used in post-polymerization modifications.[348, 349] The introduced strategy, using an epoxide derived from renewables is an important contribution to the synthesis of fully renewable polycarbonates by CO_2 mediated ring-opening copolymerization. Moreover, the use of CO_2 as an abundant, non-toxic, cheap and renewable feedstock is of particular interest. Also, the synthesis of renewable polyesters with excellent thermal material properties by the ring-opening copolymerization of epoxides with phthalic anhydride demonstrated to be a powerful approach allowing an access to novel renewable high-performance materials. In further studies a detailed material characterization of the prepared unsaturated polycarbonates and polyesters, and the use of the *bis*-epoxides as cross-linking agent would be interesting.

All in all, different strategies for the efficient valorization of fatty acids and their derivatives are demonstrated. Novel polymeric materials with remarkable and tunable material properties are synthesized and optimized catalytic processes for the efficient transformation of fatty acids into renewable monomers are reported. Moreover, oleic and erucic acid, as well as other plant oil derived platform chemicals proved to be valuable substrates for diverse transformations. Herein, methods for the efficient use of these domestic renewable resources for the synthesis of polymeric materials were investigated in order to promote the development of novel products based on renewable resources and to show up novel opportunities for their use in the non-food sector.

The use of plant oils and the thereof derived fatty acids as substrates for the production of polymeric materials, used as daily commodities or in special applications, will be of great interest for the future chemical industry in order to produce products based on renewable resources. In particular, the production of plant oils from alternative sources, such as algae, offers some very promising perspectives for an expanded use of fatty acids as substitutes for petrochemical based products.

6. Experimental part

Please note that the numbering / designation of all compounds was assigned according to each chapter. For instance compounds in section 4.1 are numbered with the additional section element (**.1**) (e.g., methyl oleate **1.1**). Compounds which had been used in multiple sections, might have different numbers or designations.

6.1 Materials

1-butanethiol (99 %, Sigma Aldrich), 1-octanethiol (≥98.5 %, Sigma Aldrich), 1,4-cyclohexadiene (97 %, Sigma Aldrich), 1,4-diazabicyclo[2.2.2]octane (DABCO, > 99 %, Sigma Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 99 %, Sigma Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-en (DBU, 98 %, Sigma Aldrich), 2-mercaptoethanol (>99 %, Sigma Aldrich), 2,2′-azobis(2-methylpropionitrile) (98 %, Sigma Aldrich), 2,2′-bipyridyl (≥99 %, Sigma Aldrich), 16-hydroxyhexadecanoic acid (98 %, Sigma Aldrich), 33 wt. % hydrobromic acid solution in acetic acid (Sigma Aldrich), ammonium acetate (>98 %, Sigma Aldrich), ammonium chloride (99.5 %, Sigma Aldrich), benzyl alcohol (>99 %, Sigma Aldrich), benzyl mercaptan (99 %, Sigma Aldrich), *bis*(triphenylphosphoranylidene)ammonium chloride (PPN-Cl, 97 %, Sigma Aldrich) was re-crystallized from dry chloroform. Cu(I)Cl (97 %, Sigma Aldrich), Cu(I)Br (Sigma Aldrich), cyclohex-2-enone (≥98 %, Sigma Aldrich), cyclohexanethiol (97 %, Sigma Aldrich). Cyclohexene oxide (98 %, Sigma Aldrich) (CHO) was dried over $MgSO_4$ and fractionally distilled under nitrogen atmosphere. Dibenzyl carbonate was prepared by simple transesterification of dimethyl carbonate with benzyl alcohol.[276] Dimethylacetamide (99 %, Acros), dimethylcarbonate (99 %, Acros), hexylamine (99 %, Acros). Hoveyda-Grubbs 2nd generation catalyst (97 %, Sigma Aldrich), hydrogen gas (N50, ≥ 99,999 % Air Liquide), methanesulfonyl chloride (98 %, Sigma Aldrich), *meta*-chloroperoxybenzoic acid (≤77 %, Sigma Aldrich), methyl acrylate (99 %, containing ≤100 ppm monomethyl ether hydroquinone as inhibitor, Sigma Aldrich), methyl methacrylate (≥99.5 %, Sigma Aldrich), methyl oleate and methyl erucate (~92 %) were kindly provided by Croda.

Methyl thioglycolate (95 %, Sigma Aldrich), *N*-bromosuccinimide (99 %, Sigma Aldrich), Novozyme 435 (Lipase acrylic resin from Candida Antarctica, Sigma Aldrich), Nylon 11 (Sigma Aldrich), Nylon 12 (Sigma Aldrich), palladium(II)chloride (99,9 %, Strem Chemicals), oxygen (99,5 %, Air Liquide). Pd(en)/C was synthesized according to a known literature procedure.[335] Palladium on activated charcoal (Pd/C, 10 % Pd basis, Sigma Aldrich), phthalic anhydride (≥99 %, Sigma-Aldrich) was washed with benzene, re-crystallized from chloroform and sublimated at 100°C under reduced pressure (approx. 10^{-2} mbar). Potassium tert-butoxide (KO^tBu, > 98 %, Sigma Aldrich), *p*-benzoquinone (> 98 %, Sigma Aldrich), Oxone® (potassium peroxymonosulfate, Sigma Aldrich), sodium azide (≥ 99 %, Sigma Aldrich), synthetic air (20.5 % O_2 in N_2, Air Liquide), triethylamine (99 %, Acros), trifluoroacetic anhydride (≥99 %, Sigma Aldrich) were used as received. The Ra-Ni catalyst was prepared as a slurry solution in ethanol.[350] Urea hydrogen peroxide was synthesized according to a known literature procedure.[351] The hydroxamic acids necessary for Lossen rearrangements were prepared according to an already reported procedure of our group.[133] Research grade CO_2 for polymerization reactions was purchased from BOC (Linde Gas). (*R*,*R*)-(-)-*N*,*N*'-*Bis*(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino cobalt(II) ([(*R*,*R*)SalcyCo(II)], (Strem chemicals), (1*R*,2*R*)-(-)-*N*,*N*'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride (**C4.6**). The catalyst **C1.6** - **C3.6** were synthesized according to literature procedures.[336, 352] The epoxides **1.6**, **3.6a** and **3.6b** were prepared by standard oxidation using *m*CPBA as already described in literature.[333, 353]

All solvents (technical grade) were used without purification and unless otherwise noted, all reactions were performed under atmospheric conditions.

6.2 Characterization methods

^{1}H-NMR measurements were performed on a Bruker Avance spectrometer operating at 300 MHz or 400 MHz for ^{1}H and 75 MHz or 100 MHz for ^{13}C. All samples were dissolved in common deuterated solvents, such as $CDCl_3$, DMSO-D6 or MeOD, and the chemical shifts δ are reported in ppm relative to the characteristic solvent signal for e.g. $CHCl_3$ (7.260 ppm).

For the characterization of the prepared polyamides, trifluoroacetic anhydride was added dropwise to the polymer in $CDCl_3$ with continuous shaking until a homogenous solution was obtained.

Molecular weight determinations were performed on different SEC instruments.

For polyamides a Tosoh EcoSEC HLC-8320 GPC system using HFIP (0.1 wt.% potassium trifluoroacetate as additive) as the solvent with a flow rate of 0.40 mL/min at 30 °C was used. The analysis was performed on a three column system: PSS PFG Micro pre-column (3.0 x 0.46 cm, 10.000 Å), PSS PFG Micro (25.0 x 0.46 cm, 1000 Å) and PSS PFG Micro (25.0 x 0.46 cm, 100 Å). The system was calibrated with linear poly(methylmethacrylate) standards (Polymer Standard Service, Mp 102 – 981 000 Da).

Molecular weights of the prepared polyesters (except chapter 4.6) were determined on a Shimadzu SEC System LC-20 A equipped with a SIL-20A auto sampler, GPC pre-column PSS SDV analytical (5 µm, 8 x 50 mm), main-column PSS SDV analytical 10000 Å (5 µm, 8 x 300 mm) and a RID-10A refractive index detector in THF (flow rate 1 mL/min) at 50 °C. The molecular weight distributions were determined relative to PMMA standards (Polymer Standards Service, M_p 1100 – 981000 Da).

Molecular weights of the polymers in chapter 4.6 were determined by size exclusion chromatography (SEC) using a Polymer Laboratories PL GPC 50 instrument (2xPolymer Laboratories Mixed D columns) operating with THF as the eluent, at a flow rate of 1 mL/min at 40°C. The SEC instrument was calibrated with polystyrene standards.

FAB (Fast-Atom-Bombardement) or EI (Electron-ionization) mass spectra and high resolution mass spectra (HRMS) were measured on a Finnigan MAT 95.

Differential scanning calorimetry (DSC) experiments were carried out on a DSC821e (Mettler Toledo) calorimeter under nitrogen atmosphere (except chapter 4.6).
Data for the melting points or glass-transition temperatures are reported from the second heating scan at 10 °C/min using a sample mass of approximately 5 mg. The melting temperature, T_m, is recorded as the minimum (endothermic transitions are represented downwards) of the endothermic melting peak.
Differential scanning calorimetry (DSC) experiments in chapter 4.6 were carried out on a DSC4000 (Perkin Elmer) calorimeter under nitrogen atmosphere at a heating rate of 10 °C per min^{-1} up to a temperature of 130 °C/200°C, using a sample mass of approximately 5 mg. Data from second heating scans are reported. TGA measurements were performed on a TGA4000 (Perkin Elmer) instrument. A heating rate of 1°C/min was used.
GC-MS (EI) chromatograms were recorded using: Varian 431 GC instrument with a capillary column FactorFourTM VF-5 ms (30 m × 0.25 mm × 0.25 µm) and a Varian 210 ion trap mass detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scan/s. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C/min to 200 °C, hold for 2 min, ramp at 15 °C/min to 325 °C, hold for 5 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in split–split mode (split ratio 50 : 1) using helium as the carrier gas (flow rate 1.0 mL/min).[142]
Elimination reactions in chapter 4.1 were performed with an ultrasound bath Elmasonic P of the company Elma at 37 kHz in a pulse mode.
Infrared spectra (IR) spectra were recorded on a Bruker alpha-p instrument applying KBr- and ATR-technology. *In situ* ATR-FTIR measurements were performed on a Mettler-Toledo ReactIR 4000 spectrometer equipped with a MCT detector and a silver halide DiComp probe.
Reductive aminations, Wacker oxidations and reactions under a high hydrogen pressure were performed with a High-Pressure Laboratory Reactor (highpreactorTM) BR-100 of the company Berghof equipped with grease-free valves and connections.
Mass spectrometry measurements were performed using a MALDI micro MX micromass instrument. The matrix used was dithranol with KTFA as the ionising agent and THF as the solvent.
The compression molten polymer samples (2 cm x 1 cm x 1 mm / 4 cm x 1 cm x 1 mm) were prepared with a Weber press PW10, heating the polymer samples to

10°C above the corresponding melting point and pressing the samples with a pressure of 10 kN for 10 min, then slowly cooling down to room temperature.

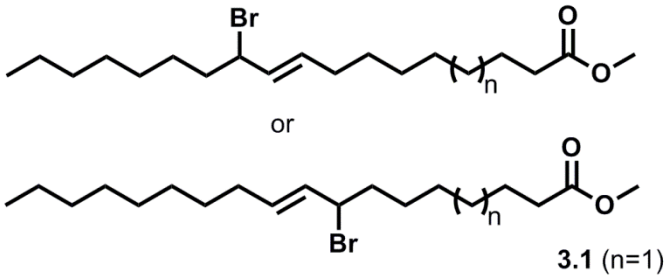
Tensile-stress measurements were performed on a Gabo Eplexor 150N instrument using the prepared compression molten polymer samples (4 cm x 1 cm x 1 mm) and a 25 N force probe head. The polymer samples were preconditioned at ambient temperature and room humidty. The measurements were performed with following parameters: Target Load (force) = 23.00 N, strain rate = 1 %/min, max. elongation = 5 mm, initial load = 0.50 N. The E-modulus was determined by a linear fit of the analytical data.

Please note that the determined Young's moduli for the compression molden samples are not absolute values according to the official DIN norm.

6.3 Experimental procedures

6.3.1 Chapter 4.1 – Experimental procedures

General procedure for Wohl-Ziegler brominations



3.1 (n=1)
4.1 (n=5)

A round bottom flask was charged with 1.00 g methyl oleate (3.37 mmol) or 1.19 g methyl erucate (3.37 mmol) and 3.5 mL of the solvent was added, if the reaction was not carried out in bulk. Then, NBS (1.03 eq., 3.47 mmol) and AIBN (0.04 mmol, 1.1 mol%) were added and the reaction mixture was stirred under an argon atmosphere for the indicated time and temperature (see Table 4.1-1). Afterwards, the reaction mixture was filtered and the solvent was evaporated at 30 °C. If possible, the product was purified by column-chromatography (n-pentane : $CHCl_3$ = 8.5 : 1.5).
NMR data are consistent to those already reported for Wohl-Ziegler bromination in CCl_4.[112]
NMR analysis exemplary for methyl 8(11)-bromooctadec-9-enoate **3.1** (mixture of isomers) the product was obtained as a mixture of about 85 % mono allyl bromide, 10 % diallyl bromide and 5 % saturated alkyl bromides:

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 5.79 – 5.83 (m, -CHBr-C*H*=C*H*-CHBr-), 5.66 – 5.57 (m, -C*H*=CH-CHBr-), 5.38-5.34 (m, -CH=C*H*-CHBr-), 4.87 – 4.78 (m, -C*H*Br-CH=CH-C*H*Br-), 4.56 – 4.40 (m, -C*H*Br-CH=CH-CH_2-), 4.22 – 4.10 (m, -CH_2-CHBr-CH_2-) 3.66 (s, 3H, -OMe), 2.30 (t, *J* = 7.5 Hz, 2H, -CH_2-COOMe), 2.16 – 1.53 (m, -CH_2-CHBr), 1.50 – 1.13 (m, -CH_2-), 0.88 (t, *J* = 6.3 Hz, 3H, -CH_3).

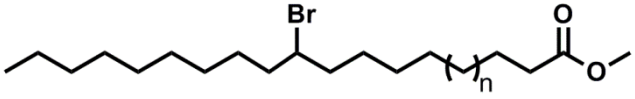
^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 174.4, 133.6, 132.0, 130.5, 57.2, 51.6, 39.6, 34.2, 32.7, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.0, 28.0, 27.3, 25.1, 22.8, 14.2.

HRMS (FAB):

3.1: $C_{19}H_{35}BrO_2$ $[M+H]^+$ calc. 375.1893 found 375.1901.

4.1: $C_{23}H_{43}BrO_2$ $[M+H]^+$ calc. 431.2519 found 431.2527.

Methyl 9(10)-bromostearate 7.1 (mixture of isomers) and Methyl 13(14)-bromodocosanoate 8.1 (mixture of isomers)



7.1 (n=1)
8.1 (n=5)

15.0 g methyl oleate (50.6 mmol) or 17.8 g methyl erucate (50.6 mmol) in 60 mL hexane was placed in a round bottom flask and 60 mL of a 33 wt.% hydrobromic acid solution in acetic acid was added. The reaction mixture was stirred for 90 minutes at room temperature. Afterwards, 100 mL ethyl acetate and 50 mL water were added to the reaction mixture. The organic phase was separated and washed with H_2O (3 x 50 mL) and the combined organic layers were dried over Na_2SO_4. The solvent was evaporated and the product was obtained as an orange oil in quantitative yield.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.09 – 3.93 (m, 1H, -C*H*-Br), 3.66 (s, 3H, -OMe), 2.30 (t, *J* = 7.5 Hz, 2H, -COOMe-C*H*$_2$-), 1.91 – 1.69 (m, 4H, -C*H*$_2$-CH(Br)-C*H*$_2$-), 1.68 – 1.12 (m, 24H, 12x -C*H*$_2$- for oleate or 32H, 16x-C*H*$_2$- erucate), 0.88 (t, *J* = 6.3 Hz, 3H, -C*H*$_3$).

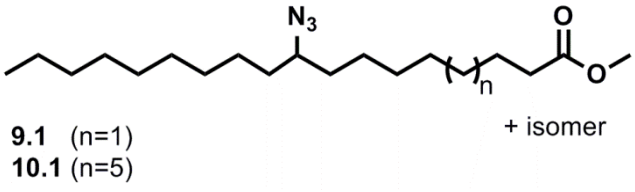
^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 174.4, 51.5, 51.3, 38.3, 34.2, 32.0, 29.9, 29.7, 29.5, 29.4, 29.4, 29.4, 29.2, 26.3, 25.1, 22.8, 14.2.

HRMS (FAB):

7.1: $C_{19}H_{37}BrO_2$ $[M+H]^+$ calc. 377.2049 found 377.2057.

8.1: $C_{23}H_{45}BrO_2$ $[M+H]^+$ calc. 433.2675 found 433.2682.

Methyl 9(10)-azidostearate 9.1 (mixture of isomers) and Methyl 13(14)-azidodocosanoate 10.1 (mixture of isomers)



9.1 (n=1)
10.1 (n=5)

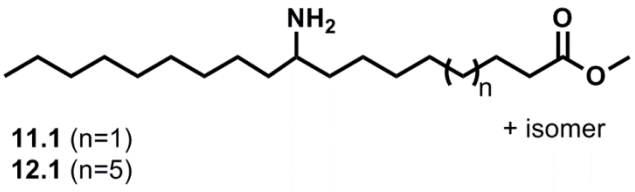
To 15.0 g of **7.1** or 17.2 g of **8.1** (39.9 mmol), 7.78 g sodium azide (0.112 mol) and 35 mL dimethylformamide were added. The reaction mixture was stirred for 5 hours at 80 °C. Afterwards, the reaction was quenched by addition of 50 mL of a 1 M ammonium chloride solution. Then, 100 mL ethyl acetate was added and the organic layer was separated and washed with H_2O (50 mL). The azide functionalized fatty acid methyl esters (**9.1** and **10.1**) were obtained as orange oils in quantitative yields.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.66 (s, 3H, -O*Me*), 3.32 – 3.12 (m, 1H, -C*H*-N_3), 2.30 (t, J = 7.5 Hz, 2H, -COOMe-C*H*$_2$-), 1.75 – 1.13 (m, 28H, 14x-C*H*$_2$- for oleate or 36H, 18x-C*H*$_2$- erucate), 0.88 (t, J= 6.2 Hz 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 174.5, 59.8, 51.6, 51.4, 38.3, 38.3, 38.3, 34.3, 32.1, 30.0, 30.0, 29.9, 29.8, 29.6, 29.5, 29.5, 29.5, 29.4, 29.3, 29.3, 29.0, 26.4, 26.4, 26.3, 25.1, 22.9, 14.3.

HRMS (FAB):
9.1: $C_{19}H_{37}N_3O_2$ $[M+H]^+$ calc. 340.2958 found 340.2967.
10.1: $C_{23}H_{45}N_3O_2$ $[M+H]^+$ calc. 396.3584 found 396.3591.

Methyl 9(10)-aminostearate 11.1 (mixture of isomers) and Methyl 13(14)-aminodocosanoate 12.1 (mixture of isomers)



11.1 (n=1)
12.1 (n=5)

To 10.0 g **9.1** or 11.7 g **10.1** (29.5 mmol) in 100 mL ethyl acetate, 1.00 g Pd/C (10 wt %) was added and a gently stream of hydrogen was bubbled through the reaction mixture for about 20 minutes. Subsequently, the reaction mixture was stirred for 24 hours under a hydrogen atmosphere at room temperature.

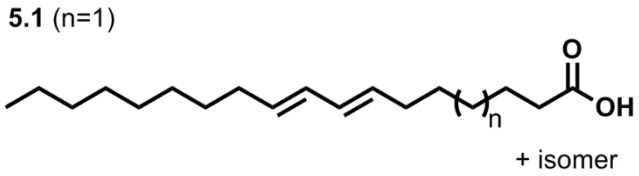
Then, the palladium catalyst was removed by filtration through a filter funnel (pore size 4) and the solvent was removed under reduced pressure. The crude product was isolated through a short silica column. First, the non-amine functional residues were separated by flushing the column with hexane : ethyl acetate = 4 : 1. Afterwards, the amine functional fatty acid methyl ester was collected with ethyl acetate : MeOH : Et_3N = 10 : 1 : 1. The product was obtained as yellowish oil (85 %) or as brownish solid (87 %) in case of the amine functional erucic acid methyl ester.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.66 (s, 3H, -OCH_3), 2.70 – 2.58 (m, 1H, C*H*-NH_2), 2.29 (t, *J* = 7.5 Hz, 2H, CH_2-COOMe), 1.70 – 1.10 (m, 30H, 15x -C*H*$_2$- for oleate or 38H, 19x-C*H*$_2$- erucate), 0.87 (t, *J* = 6.5 Hz, 3H).

^{13}C-NMR (CDCl3, 75 MHz) δ (ppm): 174.4, 63.2, 51.6, 34.5, 34.5, 34.2, 34.2, 32.0, 32.0, 29.6, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 26.3, 26.2, 26.2, 25.0, 25.0, 22.8, 22.8, 14.2.

HRMS (FAB):
11.1: $C_{19}H_{39}NO_2$ $[M+H]^+$ calc. 314.3054 found 314.3059.
12.1: $C_{23}H_{47}NO_2$ $[M+H]^+$ calc. 370.3679 found 370.3685.

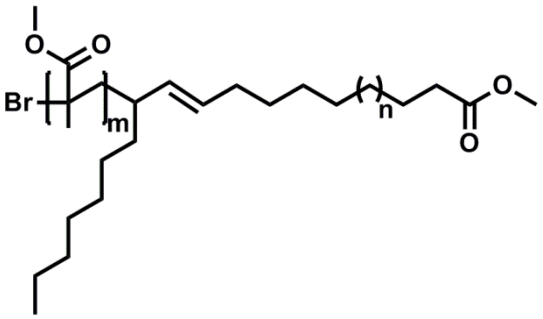
Conjugated linoleic acid 5.1 (mixture of isomers)



A solution of the **3.1** (0.30 g 0.80 mmol) in 2.0 mL THF and KO^{t}Bu (1.2 mmol) was sonicated at 30°C for 3 hours. Then, ethyl acetate was added and the pH was adjusted to <4. The organic phase was washed with 1 M HCl (2 x 50 mL) and dried over Na_2SO_4. After evaporation of the solvent, the product was obtained as highly viscous orange oil in 80 % yield. (GC-MS analysis revealed a content of 90 % conjugated and 10 % monounsaturated FAME).

^{1}H-NMR (MeOD, 300 MHz) δ (ppm): 6.35-5.15 (m, conjugated db + non-conjugated db), 3.66 (s, 3H, -OCH3), 2.30 (t, *J* = 7.5 Hz, 2H, -COOH-C*H*$_2$-), 2.20-1.90 (m, -C*H*$_2$-CH=CH-) 1.68 – 1.12 (m, 24H, 12x -C*H*$_2$- for oleate or 32H, 16x-C*H*$_2$- erucate), 0.88 (t, *J* = 6.3 Hz, 3H, -C*H*$_3$).

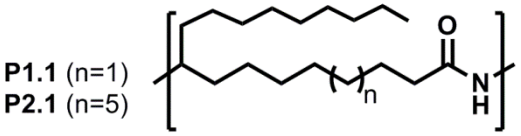
Procedure for ATRP polymerizations



To a dried round bottom flask copper (I) bromide, 2,2′-bipyridyl (bpy), methyl methacrylate (MMA), the initiator **3.1** or **4.1** and cyclohexanone (m_{MMA} : $m_{cyclohexanone}$ = 1 : 2) were added. The initial ratio of [MMA] : [I] : [Cu(I)Br] : [bpy] was [50/100/200/300] : [1] : [2] : [3]. Afterwards, the flask was equipped with a rubber septum and argon was bubbled through the reaction mixture for 15 minutes. The reaction mixture was stirred under an argon atmosphere at 80°C. The polymerization was stopped by cooling the mixture in an ice-bath and exposure to oxygen. Then, the reaction mixture was diluted with THF and passed through a short column of neutral alumina to remove the copper catalyst. The poly(methyl methacrylate) (PMMA) polymer was isolated by precipitation into cold methanol. The obtained polymers were characterized by SEC analysis (see also Figure 4.1-3 and Table 4.1-2), which revealed molecular weights of 11.5 – 34.6 kDa and dispersities of 1.05 - 1.35.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm)*:* 5.36 – 5.30 (m, 2H, -C*H*=C*H*-), 3.65 (s, 3H, -OMe), 5.59 (s, PMMA-OMe), 2.10-0.70 (m, PMMA-backbone).

General procedure for TBD catalyzed polycondensations



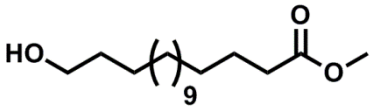
All polymerizations were performed in a RR98072 carousel reactor (from Radleys^{TM} Discovery Technologies, UK). The monomer **11.1** or **12.1** and TBD (10 mol%, relative to ester groups) were weighted into the reaction tube and placed in the reactor system. The reaction mixture was stirred for 24 h under continuous vacuum (10^{-2} mbar) at 140 °C. The pure polymers were obtained by precipitation from hexafluoroisopropanol into cold methanol.

SEC analysis revealed a molecular weight of 6.5 kDa for **P1.1** and 7.9 kDa for **P2.1** and a dispersity of 1.40 and 1.49, respectively.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 5.35 (b, -N*H*-), 3.80 (s, 1H), 3.26-3.14 (m, 1H), 2.08 (t, *J* = 7.5 Hz, 2H), 1.65 – 1.05 (m, 30H for P1/ 38 H for P2), 0.80 (t, *J* = 6.5 Hz, 3H).

6.3.2 Chapter 4.2 – Experimental procedures

Synthesis of methyl 16-hydroxypalmitate



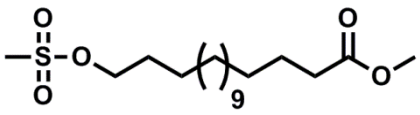
To 2.5 g 16-hydroxyhexadecanoic acid (9.2 mmol), 150 mL MeOH, 0.50 mL H_2SO_4 and 0.80 mL trimethylorthoformiate were added. The reaction mixture was stirred under reflux for 12 hours. Then, 250 mL diethyl ether and 100 mL H_2O were added and the organic phase was separated and washed with 1 M HCl, saturated $NaHCO_3$ and NaCl solution. The product was obtained as a white solid (2.84 g, 85 % yield).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 3.65 (s, 3H, -OMe), 3.53 (t, *J* = 6.7 Hz, 2H, -C*H*$_2$-OH), 2.50 (bs, 1H, -O*H*) 2.22 (t, *J* = 7.5 Hz, 2H, -C*H*$_2$-COOMe), 1.60-1.40 (m, 4H, 2x-C*H*$_2$-), 1.34-1.00 (m, 22H, chain).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm): 174.4 (*C*$OOCH_3$), 63.1 (HO-*C*H_2-), 51.5 (COO*C*H_3), 37.4 - 25.0 (chain).

HRMS (FAB): $C_{17}H_{34}O_3$ $[M+H]^+$ calc. 287.2580 found 287.2587.

Synthesis of methyl 16-((methylsulfonyl)oxy)hexadecanoate (1.2)



2.29 g methyl 16-hydroxypalmitate (8.00 mmol) was dissolved in 20 mL DCM. Afterwards a mixture of 5.54 mL triethylamine (40.0 mmol, 5.0 eq.) and 1.86 g mesyl chloride (24.0 mmol, 3.0 eq.) in 10 mL DCM were added slowly while the mixture was

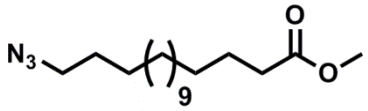
cooled on ice. Subsequently, the reaction was stirred at room temperature for 4 hours. Afterwards, the solvent was removed under reduced pressure and the product was washed with 3 x 50 mL diluted hydrochloric acid. For purification the product was recrystallized from hot methanol to yield 2.48 g (6.80 mmol, 85 %).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 4.20 (t, *J* = 6.6 Hz, 2H, -C*H*$_2$-OSO_2Me), 3.64 (s, 3H, -OMe), 2.98 (s, 3H, -SO_2Me), 2.28 (t, *J* = 7.5 Hz, 2H, -C*H*$_2$-COOMe), 1.80-1.67 (m, 2H,-C*H*$_2$-CH_2-OSO_2Me), 1.61-1.50 (m, 2H,-C*H*$_2$-CH_2-COOMe), 1.40-1.15 (m, 22H, 11xC*H*$_2$).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm): 174.1 (*C*$OOCH_3$), 70.1 (CH_3-SO_2-*C*H_2-), 52.0 (COO*C*H_3), 37.0 - 25.0 (-*C*H_2).

HRMS (FAB): $C_{18}H_{36}O_5S$ $[M+H]^+$ calc. 365.2362 found 365.2366.

Synthesis of methyl 16-azidohexadecanoate (2.2)



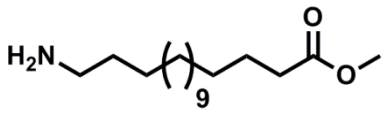
1.00 g methyl 16-((methylsulfonyl)oxy)hexadecanoate (2.75 mmol) was dissolved in 5.0 mL DMF and 0.540 g NaN_3 (8.25 mmol, 3 eq.) was added. The reaction mixture was stirred for 7 hours at 80 °C. Then, water (10 mL) and ethyl acetate (80 mL) were added. The organic layer was separated and washed with water (4 x 40 mL), saturated sodium chloride solution (2 x 40 mL) and dried over Na_2SO_4. After evaporation of the solvent, the product was obtained as a slightly yellowish solid (yield 0.820 g, 95 %,).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 3.65 (s, 3H, COOC*H*$_3$), 3.24 (t, *J* = 6.9 Hz, 2H, -C*H*$_2$-N_3), 2.29 (t, *J* = 7.5 Hz, 2H, α-*H*), 1.68-1.52 (m, 4H, 2x -C*H*$_2$-), 1.40-1.15 (m, 22H, chain).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm): 174.4 (*C*$OOCH_3$) , 51.6 - 25.1 (chain).

HRMS (FAB): $C_{17}H_{33}N_3O_2$ $[M+H]^+$ calc. 312.2651 found 312.2654.

Synthesis of methyl 16-aminohexadecanoate (3.2)



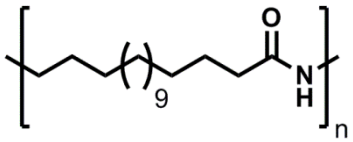
To 0.50 g methyl 16-azidohexadecanoate (1.6 mmol) 0.10 g Pd/C (10 wt.% palladium) and 40 mL ethyl acetate was added. The reaction mixture was stirred for 24 hours under a hydrogen pressure of 40 bar. To remove the palladium catalyst, the reaction mixture was afterwards filtered through a pore filter and it was rinsed with $CHCl_3$. If necessary, the product can be purified on a silica gel column using chloroform : methanol : aqueous ammonia in a 90 : 10 : 1 mixture as solvent. The product was obtained as a white solid (yield 0.37 g, 80%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 3.65 (s, 3H, COOC*H*$_3$), 2.67 (t, *J* = 6.9 Hz, 2H, -C*H*$_2$-NH_2), 2.29 (t, *J* = 7.5 Hz, 2H, α-*H*), 1.65-1.55 (m, 2H,β-*H*), 1.50-1.38 (m, 2H,-C*H*$_2$-CH_2-NH_2), 1.34-1.21 (m, 22H, chain), 1.16 (bs, 2H, -N*H*$_2$).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm): 174.4 (*C*OOCH$_3$), 51.5 (COO*C*H$_3$), 42.4 (NH_2-*C*H_2-), 34.2 - 25.0 (chain).

HRMS (FAB): $C_{17}H_{35}NO_2$ $[M+H]^+$ calc. 286.2741 found 286.2745.

Preparation of PA 16 (P1.2) from methyl 16-aminohexadecanoate

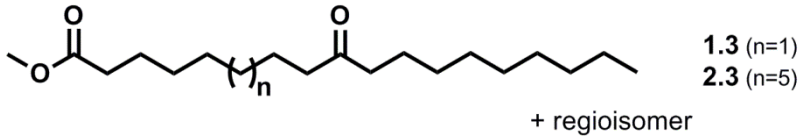


Preparations of **P1.2** were performed on a 0.2 g scale in a RR98072 carousel reactor (from Radleys^{TM} Discovery Technologies, UK). The monomer methyl 16-aminohexadecanoate (**3.2**) was weighed into the reaction tube and placed in the reactor system at 80 °C. Subsequently, TBD (5.0 mol%) was added. The polymerization was performed for 20 hours under continuous vacuum (10^{-2} mbar) at 166 °C. The pure polymers were obtained by precipitation from hexafluoroisopropanol into cold methanol. GPC analysis revealed a molecular weight of 20.3 kDa and a *Đ* of 1.65.

^{1}H-NMR (300 MHz, $CDCl_3$/TFA) δ (ppm): 3.68 (t, *J* = 7.3 Hz, -CONH-C*H*$_2$-), 2.78 (t, *J* = 7.3 Hz, -C*H*$_2$-CONH-), 1.70-1.49 (m, 2H,-C*H*$_2$-CH_2-CONH-, -CONH-CH_2-C*H*$_2$-, -CON*H*-), 1.40-1.00 (m,-C*H*$_2$-).

6.3.3 Chapter 4.3 – Experimental procedures

Preparation of methyl 9(10)-oxostearate 1.3 (mixture of isomers) and methyl 13(14)-oxodocosanoate 2.3 (mixture of isomers)



1.3 (n=1)
2.3 (n=5)
+ regioisomer

0.30 g methyl oleate (1.0 mmol) or 0.35 g methyl erucate (1.0 mmol) in 3 mL dimethylacetamide and 0.5 mL H_2O was placed in a Teflon reactor tube inset and palladium(II)chloride (2-5 mol%) was added. The reaction mixture was pressurized with oxygen (10 bar) and stirred for 48 hours at 70 °C ± 5 °C. Afterwards, the reaction mixture was extracted with diethylether (2 x 5 mL) and washed with H_2O (2 x 5 mL). The product was recrystallized from hexane and dried under vacuum. The ketone functionalized fatty acid methyl ester was obtained as white solid (yield 85 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.65 (s, 3H, -OC*H*$_3$), 2.37 (t, *J* = 7.4 Hz, 4H, -C*H*$_2$-C(O)-C*H*$_2$), 2.29 (t, *J* = 7.5 Hz, 2H, C*H*$_2$-COOMe), 1.71 – 1.42 (m, 6H, 3x -C*H*$_2$-) 1.36 – 1.15 (m, 18H, 9x -C*H*$_2$- for oleate or 26H, 13x -C*H*$_2$- for erucate), 0.87 (t, *J* = 6.6 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 211.9, 174.5, 51.5, 42.9, 34.2, 29.7, 29.5, 29.4, 29.2, 25.1, 24.0, 22.8, 14.2.

HRMS (FAB):
1.3: $C_{19}H_{36}O_3$ $[M+H]^+$ calc. 313.2737 found 313.2743.
2.3: $C_{23}H_{44}O_3$ $[M+H]^+$ calc. 369.3363 found 369.3368.

Please note: All Wacker oxidations were carried out in an appropriate high pressure reactor equipped with grease-free valves and connections to prevent any explosions!

General procedure for recycling experiments of the Wacker oxidation

0.30 g methyl oleate (1.00 mmol) or 0.35 g methyl erucate (1.00 mmol) in 3 mL dimethylacetamide and 0.5 mL H_2O was placed in a Teflon reactor tube inset and palladium(II)chloride (2.5 mol%) was added. The reaction mixture was pressurized with oxygen (10 bar) and stirred for 48 hours at 70 °C ± 5 °C.

Afterwards, the reaction mixture was extracted with heptane (2 x 5 mL) and washed with H_2O (2 x 5 mL). To the DMAC phase, containing the palladium catalyst, another portion of the unsaturated fatty acid methyl ester was added and the Wacker oxidation was repeated under the same conditions as already described.

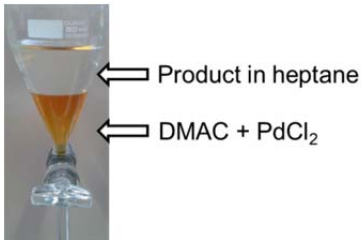


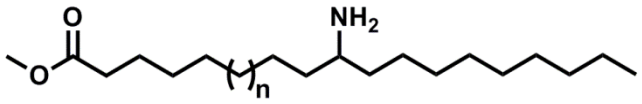
Figure 6.3.3-1: Extraction of the reaction mixture with heptane and separation of the catalyst/solvent-mixture.

Table 6.3.3-1: Results of the recycling experiments of the co-catalyst free-Wacker oxidation.

Reaction cycle	Conversion [%][a]
1	100
2	96
3	95

[a]Conversion was determined via NMR spectroscopy based on the protons of the double bond of the FAME.

Preparation of methyl 9(10)-aminostearate 3.3 (mixture of isomers) and methyl 13(14)-aminodocosanoate 4.3 (mixture of isomers)



3.3 (n=1)
4.3 (n=5)

To the keto functional fatty acid methylester **1.3** or **2.3** (22.3 mmol), 7.22 g ammonium acetate (134 mmol), 1.72 g ammonium chloride (22.3 mmol) and the freshly prepared Raney-Nickel catalyst (20 wt%) in 80 mL Ethanol was added. The reaction mixture was pressurized with hydrogen (40 bar) and stirred at 35 °C for 48 hours to ensure full conversion. If necessary, for some reactions the crude product was further purified by a short silica column. First, the non-amine functional residues were separated by flushing the column with hexane : ethyl acetate = 4 : 1.

Afterwards, the amine functionalized fatty acid methyl ester was collected with ethyl acetate : MeOH : Et_3N = 10 : 1 : 1. The product was obtained as light yellow oil (**3.3**) or light brown solid (**4.3**) in isolated yields >90%.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.67 (s, 3H, -OCH_3), 2.73 – 2.57 (m, 1H, C*H*-NH_2), 2.30 (t, *J* = 7.5 Hz, 2H, CH_2-COOMe), 1.70 – 1.10 (m, 30H, 15x -C*H*$_2$- for **3.3** or 38H, 19x-C*H*$_2$- **4.3**), 0.87 (t, *J* = 6.5 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 174.4, 77.6, 77.2, 76.7, 51.5, 42.4, 34.2, 34.0, 29.7, 29.7, 29.6, 29.5, 29.3, 29.2, 27.0, 25.0.

HRMS (FAB):
3.3: $C_{19}H_{39}NO_2$ $[M+H]^+$ calc. 314.3054 found 314.3061.
4.3: $C_{23}H_{47}NO_2$ $[M+H]^+$ calc. 370.3679 found 370.3689.

General procedure for TBD catalyzed polycondensations

All polymerizations were performed in a RR98072 carousel reactor (from RadleysTM Discovery Technologies, UK). The respective monomers were weighed into a reaction tube and the catalyst was added. The reaction mixture was stirred at evaluated temperatures for a specific time

For the preparation of polymer **P1.3** and **P2.3**, TBD (5 mol%, relative to ester groups) was used. First the reaction mixture was stirred for 6 hours under a gentle stream of argon at 120 °C. For additional 18 hours the reaction mixture was stirred at 130 °C under vacuum (10^{-2} mbar). The polymers were dissolved in hexafluoroisopropanol and precipitated in cold methanol.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 3.88 (bs, 1H, -N*H*-CO-), 3.33-3.17 (m, 1H, -C*H*-NHCO-), 2.14 (t, *J* = 7.5 Hz, 2H, -C*H*$_2$-CONH-), 1.65 – 1.15 (m, 30H for **P1.3**/ 38 H for **P2.3**), 0.87 (t, *J* = 6.5 Hz, 3H, -C*H*$_3$).

For the preparation of all other polyamides, two different procedures were used leading to comparable results.

Method A:

DBU (10 mol%, relative to ester groups) was used. First, the reaction mixture was stirred for 6 hours under a gentle stream of argon at 120 °C. Afterwards the reaction mixture was heated to 180 °C and stirred for 1 hour maintaining the gentle argon stream.

For additional 3 hours the reaction mixture was stirred at 190 °C under high vacuum (10^{-2} mbar) and the pre-polymer was dissolved in hexafluoroisopropanol and precipitated in cold methanol.

Then, the pre-polymer was heated to 275 °C and stirred for about additional 4-6 hours at high vacuum. The final polymers were dissolved in hexafluoroisopropanol and precipitated in cold methanol.

Method B:

The reaction mixture without a catalyst was stirred for 6 hours under a gentle stream of argon at 120 °C. Afterwards the reaction mixture was heated to 275 °C and stirred for 24 additional hours under high vacuum (10^{-2} mbar). The final polymers were dissolved in hexafluoroisopropanol and precipitated in cold methanol.

^{1}H-NMR (300 MHz, $CDCl_3$/TFAA) δ (ppm): 3.73-3.61 (m,-C*H*-NH-, -N*H*), 3.35-3.20 (m, -CH_2-NH-), 2.88-2.72 (m, -CH_2-COONH-), 2.68-2.55 (m, -CH_2-COONH-), 2.50-2.30 (m, -CH_2-), 1.80 – 1.05 (m, -C$H_{2\ aliphatic}$-), 0.87 (t, *J* = 6.5 Hz, -CH_3).

Water-uptake tests:

The polymers were compression molded into a unified rectangle-shape (l × w × h=2 cm × 1 cm × 1 mm), kept in the desiccator overnight and immersed into 10 mL water for 16 hours at 25 °C, similar to already known described procedures.[20-21] Afterwards, the polymer samples were carefully blotted on a tissue to remove the water on the surface and weighed. After 1 hour on the lab bench for further drying, the polymer sticks were again blotted and weighed. To obtain accurate results and to avoid weighing errors, the measurements were repeated 3 times using different polymer specimen. The average increase in weight was calculated according to the conventional equation.[256, 257]

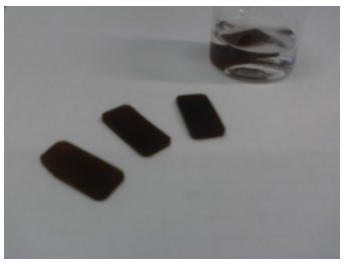


Figure S6.3.3-2: Water-uptake test with the compression molded polymer samples.

6.3.4 Chapter 4.4 – Experimental procedures

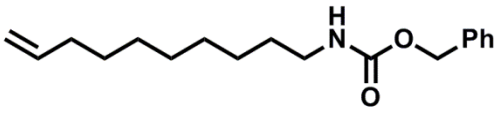
General procedure for the Lossen rearrangement

To a mixture of the corresponding hydroxamic acid (10.0 mmol), dibenzyl carbonate (100 mmol) and benzyl alcohol (10.0 mmol) was added. After the reaction mixture was heated to 120 °C, TBD (2.00 mmol) was added and stirring was kept overnight. The crude reaction mixture was filtrated over a short silica pad while using ethyl acetate as eluent. After removal of ethyl acetate, the benzyl alcohol and dibenzyl carbonate were redistilled under reduced pressure (10^{-3} - 10^{-4} mbar) at a temperature of about 155 °C.

The mixture of dibenzyl carbonate and benzyl alcohol can be reused after analysis of the distillate by NMR and GC-MS.

Caution has to be taken for the Kugelrohr distillation of benzyl alcohol and dibenzyl carbonate in case of the benzyl dec-9-en-1-ylcarbamate **1.4**, here the vacuum and temperature has to be well adjusted to obtain a good separation of **1.4** and the other reagents.

Benzyl dec-9-en-1-ylcarbamate (**1.4**)



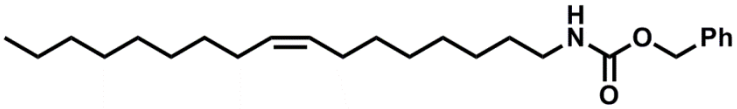
Purification *via* column chromatography (hexane : ethyl acetate = 11 : 1 → 7 : 1) led to a low melting colorless solid (yield 78 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.40 – 7.29 (m, 5H, Ph), 5.89 - 5.73 (m, 1H, -C*H*=CH_2), 5.09 (s, 2H, -CH_2-Ph), 5.04 – 4.85 (m, 2H, -CH=CH_2), 4.74 (bs, 1H, N*H*), 3.27 – 3.09 (m, 2H, -CH_2-NH-), 2.10 – 1.94 (m, 2H, -CH_2-), 1.55 – 1.20 (m, 12H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 156.5, 139.3, 136.8, 128.6, 128.2, 128.2, 114.3, 66.7, 41.2, 33.9, 30.1, 29.5, 29.3, 29.1, 29.0, 26.8.

HRMS (FAB): $C_{18}H_{27}NO_2$ $[M+H]^+$ calc. 290.2115 found 290.2112.

Benzyl heptadec-8-en-1-ylcarbamate (**2.4**)



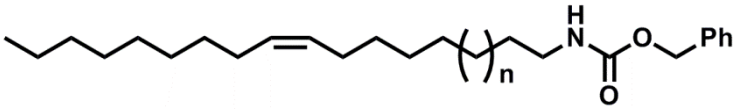
Purification *via* column chromatography (hexane : diethyl ether = 12 : 1 → 7 : 1) led to a colorless solid (yield 75 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.41 – 7.28 (m, 5H, Ph), 5.43 – 5.28 (m, 2H, -C*H*=C*H*-), 5.10 (s, 2H, -CH_2-Ph), 4.76 (bs, 1H, N*H*), 3.26 – 3.07 (m, 2H, -CH_2-NH), 2.10 – 1.90 (m, 4H, -CH_2-CH=CH-CH_2-), 1.60 – 1.12 (m, 22H, -CH_2-), 0.88 (t, *J* = 6.6 Hz, 3H, -CH_3).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 156.9, 156.5, 136.8, 130.1, 129.8, 128.6, 128.2, 66.7, 41.2, 32.0, 30.1, 29.9, 29.8, 29.7, 29.4, 29.3, 27.3, 26.8, 22.8, 14.2.

HRMS (FAB): $C_{25}H_{41}NO_2$ $[M+H]^+$ calc. 388.3210 found 388.3212.

Benzyl henicos-12-en-1-ylcarbamate (**3.4**)



(n=5)

Purification *via* column chromatography (hexane : diethyl ether = 12 : 1 → 7 : 1) led to a colorless solid (yield 80 %).

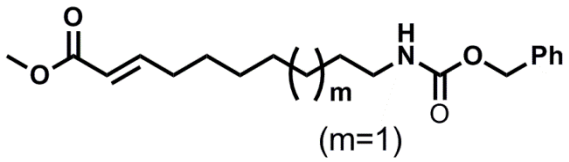
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.45 – 7.29 (m, 5H, Ph), 5.43 – 5.29 (m, 2H, -C*H*=C*H*-), 5.10 (s, 2H, -CH_2-Ph), 4.76 (bs, 1H, N*H*), 3.24 – 3.07 (m, 2H, -CH_2-NH), 2.14 – 1.91 (m, 4H, -CH_2-CH=CH-CH_2-), 1.62 – 1.15 (m, 30H, -CH_2-), 0.89 (t, *J* = 6.6 Hz, 3H, -CH_3).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 156.9, 156.5, 136.8, 130.1, 129.8, 128.6, 128.2, 41.2, 32.0, 30.1, 29.9, 29.8, 29.7, 29.4, 29.3, 27.3, 26.8, 22.8, 14.2.

HRMS (FAB): $C_{29}H_{49}NO_2$ $[M+H]^+$ calc. 444.3836 found 444.3835.

Cross-metathesis of benzyl carbamates

Methyl 10-(((benzyloxy)carbonyl)amino)dec-2-enoate (**4.4**)



(m=1)

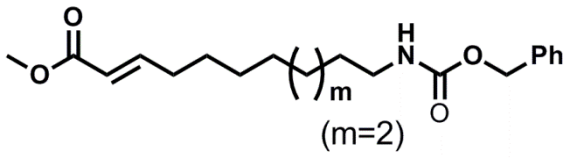
To a vigorously stirred mixture of 2.20 g carbamate **2.4** (5.68 mmol) and 4.89 g methyl acrylate (56.7 mmol) at 50 °C, 17.8 mg of the Hoveyda-Grubbs 2nd generation catalyst (0.5 mol%) was added. The reaction mixture was stirred under argon atmosphere for 16 hours. Then, ethyl vinyl ether was added to quench the reaction. Methyl acrylate was evaporated and the crude reaction mixture was purified *via* column chromatography (hexane : ethyl acetate: 7 : 1 → 4 : 1). Pure **4.4** was obtained as colorless solid (yield 91 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.40 – 7.27 (m, 5H, Ph), 7.03 – 6.87 (m, 1H, -CH=C*H*-), 5.80 (d, *J* = 15.7 Hz, 1H, -(CO)-C*H*-), 5.08 (s, 2H, -CH_2-Ph), 4.84 (bs, 1H, N*H*), 3.71 (s, 3H, -OMe), 3.27 – 3.06 (m, 2H, -CH_2-NH), 2.28 – 2.08 (m, 2H, -CH_2-), 1.58 – 1.16 (m, 10H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.2, 156.5, 149.7, 136.8, 128.6, 128.1, 121.0, 66.6, 51.4, 41.1, 32.2, 30.0, 29.1, 28.0, 26.6.

HRMS (FAB): $C_{19}H_{27}NO_4$ $[M+H]^+$ calc. 334.2013 found 334.2015.

Methyl 11-(((benzyloxy)carbonyl)amino)undec-2-enoate (**5.4**)



(m=2)

To a vigorously stirred mixture of 2.00 g carbamate **1.4** (6.91 mmol) and 5.95 g methyl acrylate (69.1 mmol) at 25 °C, 21.7 mg of the Hoveyda-Grubbs 2nd generation catalyst (0.5 mol%) was added. Subsequently, the reaction temperature was raised to 50 °C within 20 min and stirred under argon atmosphere for 16 hours at 50 °C. Then, ethyl vinyl ether was added to quench the reaction.

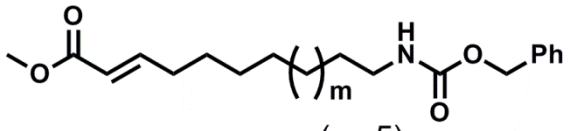
Methyl acrylate was evaporated and the crude reaction mixture was purified *via* column chromatography (hexane : ethyl acetate: 7 : 1→ 4 : 1). Pure **5.4** was obtained as colorless solid (yield 90 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.42 – 7.27 (m, 5H, Ph), 7.02 – 6.87 (m, 1H,-CH=C*H*-), 5.80 (d, *J* = 15.7 Hz, 1H,-(CO)-C*H*-), 5.08 (s, 2H, -CH_2-Ph), 4.84 (bs, 1H, N*H*), 3.71 (s, 3H, -OMe), 3.29 – 3.02 (m, 2H, -CH_2-NH), 2.28 – 2.05 (m, 2H, -CH_2-), 1.59 – 1.12 (m, 12H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.2, 156.5, 149.8, 136.8, 128.6, 128.1, 120.9, 66.6, 51.4, 41.2, 32.2, 30.0, 29.3, 29.2, 29.1, 28.0, 26.7.

HRMS (FAB): $C_{20}H_{29}NO_4$ $[M+H]^+$ calc. 348.2169 found 348.2167.

Methyl 14-(((benzyloxy)carbonyl)amino)tetradec-2-enoate (**6.4**)



(m=5)

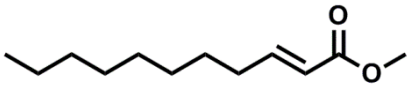
To a vigorously stirred mixture of 1.50 g carbamate **3.4** (3.38 mmol) and 2.91 g methyl acrylate (33.4 mmol) at 50 °C, 10.6 mg of the Hoveyda-Grubbs 2nd generation catalyst (0.5 mol%) was added. The reaction mixture was stirred under argon atmosphere for 16 hours. Then, ethyl vinyl ether was added to quench the reaction. Methyl acrylate was evaporated and the crude reaction mixture was purified *via* column chromatography (hexane : ethyl acetate: 7 : 1 → 4 : 1). Pure **6.4** was obtained as colorless solid (yield 80 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.40 – 7.27 (m, 5H, Ph), 7.03 – 6.90 (m, 1H,-CH=C*H*-), 5.81 (d, *J* = 15.7 Hz, 1H,-(CO)-C*H*-), 5.08 (s, 2H, -CH_2-Ph), 4.83 (bs, 1H, N*H*), 3.71 (s, 3H, -OMe), 3.26 – 3.06 (m, 2H, -CH_2-NH), 2.26 – 2.10 (m, 2H, -CH_2-), 1.58 – 1.12 (m, 18H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.3, 156.5, 149.9, 136.8, 128.6, 128.1, 120.9, 66.6, 51.4, 41.2, 32.3, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 28.1, 26.8.

HRMS (FAB): $C_{23}H_{35}NO_4$ $[M+H]^+$ calc. 390.2639 found 390.2630.

Methyl undec-2-enoate (**7.4**)



7.4 is obtained in cross-metathesis reactions of **2.4** and **3.4**.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.08 – 6.86 (m, 1H, -CH=C*H*-), 5.81 (d, *J* = 15.6 Hz, 1H, C(O)-C*H*=CH-), 3.72 (s, 3H, -OMe), 2.28 – 2.08 (m, 2H, -CH_2-), 1.73 – 1.12 (m, 12H, -CH_2-), 0.87 (t, *J* = 6.1 Hz, 3H, -CH_3).

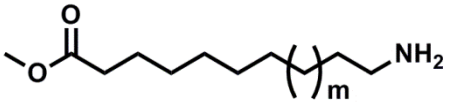
^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.3, 149.9, 120.9, 51.5, 32.7, 32.5, 31.9, 29.6, 29.5, 29.2, 28.2, 22.8, 14.2.

HRMS (FAB): $C_{12}H_{22}O_2$ $[M+H]^+$ calc. 199.1693 found 199.1698.

General procedure for the carbamate cleavage

The benzyl carbamate (3.30 mmol) and $Pd(OH)_2$ (10 wt%) were weighed into a round bottom flask capped with a septum. 25 mL methanol for carbamate **4.4** or 25 mL ethanol for carbamate **5.4** – **6.4** was added and hydrogen was gently bubbled through the reaction mixture for 15 minutes using a balloon. Subsequently, the reaction mixture was stirred at an atmospheric pressure of hydrogen at room temperature for 16 hours. The reaction mixture was filtrated over a pore size 4 filter and the solvent was removed under reduced pressure. The amino fatty acid methyl esters were obtained as colorless solids (yield 95 - 99 %).

Methyl 10-aminodecanoate (**8.4**)



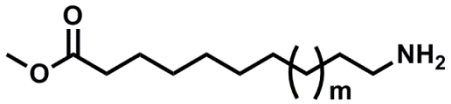
(m=1)

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.66 (s, 3H, -OMe), 2.69 (t, *J* = 7.1 Hz, 2H, -CH_2-NH_2), 2.59 (s, 2H, -NH_2), 2.29 (t, *J* = 7.5 Hz, 2H, -CH_2-COOMe), 1.68 – 1.53 (m, 2H, -CH_2-), 1.53 – 1.37 (m, 2H, -CH_2-), 1.38 – 1.21 (m, 10H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 174.4, 51.5, 41.5, 34.2, 32.3, 29.4, 29.4, 29.3, 29.2, 26.9, 25.0.

HRMS (EI): $C_{11}H_{23}NO_2$ calc. 201.1723 found 201.1725.

Methyl 11-aminoundecanoate (**9.4**)



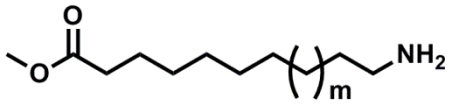
(m=2)

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.64 (s, 3H, OMe), 2.66 (t, *J* = 7.0 Hz, 2H, -C*H*$_2$-NH$_2$), 2.28 (t, *J* = 7.5 Hz, 2H, -C*H*$_2$-COOMe), 1.99 (bs, 2H, -N*H*$_2$), 1.68 – 1.52 (m, 2H, -C*H*$_2$-), 1.48 – 1.14 (m, 14H, -C*H*$_2$-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 174.4, 51.5, 42.1, 34.2, 33.4, 29.6, 29.5, 29.4, 29.3, 29.2, 26.9, 25.0.

HRMS (EI): $C_{12}H_{25}NO_2$ calc. 215.1880 found 215.1881.

Methyl 14-aminotetradecanoate (**10.4**)



(m=5)

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.63 (s, 3H, OMe), 2.66 (t, *J* = 7.0 Hz, 2H, -C*H*$_2$-NH$_2$), 2.27 (t, *J* = 7.5 Hz, 2H, -C*H*$_2$-COOMe), 2.19 (bs, 2H, -N*H*$_2$), 1.65 – 1.50 (m, 2H, -C*H*$_2$-), 1.49 – 1.35 (m, 2H, -C*H*$_2$-), 1.34 – 1.13 (m, 18H, -C*H*$_2$-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 174.4, 51.5, 42.1, 34.2, 33.4, 29.7, 29.6, 29.5, 29.3, 29.2, 27.0, 25.0.

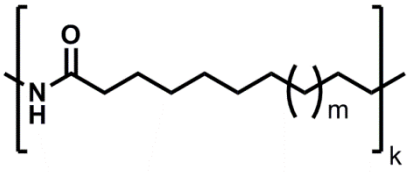
HRMS (FAB): $C_{15}H_{31}NO_2$ $[M+H]^+$ calc. 258.2428 found 258.2425.

General procedure for the synthesis of polyamides

All polymerizations were performed in a RR98072 carousel reactor (from Radleys^{TM} Discovery Technologies, UK). The respective monomers were weighed into a reaction tube and the catalyst was added. The reaction mixture was stirred at evaluated temperatures for a specific time, first at 120 °C for 2 hours under a gentle argon flow. Subsequently, the reaction mixture was set under vacuum (10^{-2} mbar) and stirred for further 3 hours at 135 °C. Finally, the temperature was raised to 180 - 195 C depending on the employed monomer.

Polymerizations of monomer **10.4** were performed at a final temperature of 180 C using TBD as catalyst. Polymerization of monomer **9.4** and **8.4** was performed at a temperature of 195 °C. Herein, DBU was used as catalyst.

P1.4 was obtained by polymerization of monomer **8.4**.

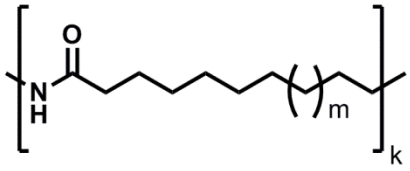


(m=1 / PA10)

^{1}H-NMR ($CDCl_3$ / TFAA, 300 MHz) δ (ppm): 3.78 – 3.59 (m, 2H, -C*H*$_2$-N(CO)CF_3), 2.78 (t, *J* = 7.3 Hz, 2H, -C*H*$_2$-(CO)N(CO)CF_3), 1.77 – 1.46 (m, 4H, -C*H*$_2$-), 1.42 – 1.10 (m, 11H, -C*H*$_2$-, -N*H*).

SEC: M_n= 1.49 kDa, *Đ* = 2.20, DSC: T_m = 186 °C.

P2.4 was obtained by polymerization of monomer **9.4**.

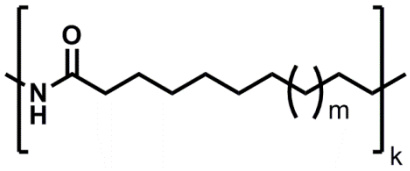


(m=2 / PA11)

^{1}H-NMR ($CDCl_3$ / TFAA, 300 MHz) δ (ppm): 3.79 – 3.57 (m, 2H, -C*H*$_2$-N(CO)CF_3), 2.78 (t, *J* = 7.4 Hz, 2H, -C*H*$_2$-(CO)N(CO)CF_3), 1.77 – 1.44 (m, 4H, -C*H*$_2$-), 1.44 – 1.07 (m, 13H, -C*H*$_2$-, -N*H*).

SEC: M_n = 1.52 kDa, *Đ* = 1.73, DSC: T_m = 182 °C.

P3.4 was obtained by polymerization of monomer **10.4**.



(m=5 / PA14)

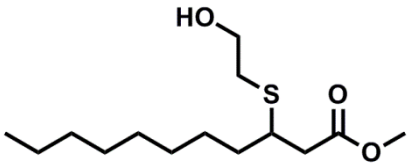
^{1}H-NMR ($CDCl_3$ / TFAA, 300 MHz) δ (ppm): 3.81 – 3.56 (m, 2H, -C*H*$_2$-N(CO)CF_3), 2.78 (t, *J* = 7.4 Hz, 2H, -C*H*$_2$-(CO)N(CO)CF_3), 1.78 – 1.46 (m, 4H, -C*H*$_2$-), 1.43 – 0.99 (m, 19H, -C*H*$_2$-, -N*H*).

SEC: M_n = 2.26 kDa, *Đ* = 2.13, DSC: T_m = 169 °C.

General procedure for Thia-Michael additions

Thia-Michael additions were performed in bulk and with a small excess of the thiol (1.20 equivalents). Thus, methyl undec-2-enoate (5.05 mmol) and the respective thiol (6.06 mmol) were weighed into a round bottom flask. Hexylamine (10 mol%) was added and the reaction mixture was stirred at 50 °C for 8 hours. The crude reaction mixture was purified by column chromatography (hexane : ethyl acetate = 4 : 1).

Methyl 3-((2-hydroxyethyl)thio)undecanoate (**11.4**)



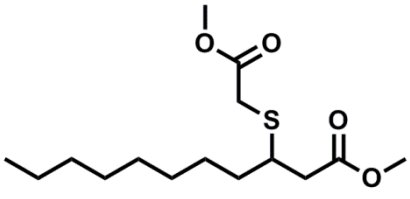
Pure **11.4** was obtained as light yellow oil (yield 86 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.83 – 3.64 (m, 5H, -OMe, -C*H*$_2$-OH), 3.15 – 3.00 (m, 1H, -S-C*H*-), 2.73 (t, *J* = 5.8 Hz, 2H, -C*H*$_2$-S-), 2.67 – 2.46 (m, 2H, -C*H*$_2$-COOMe), 2.36 (bs, 1H, -O*H*), 1.66 – 1.51 (m, 2H, -C*H*$_2$-), 1.50 – 1.17 (m, 12H, -C*H*$_2$-), 0.87 (t, *J* = 6.6 Hz, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 172.6, 61.2, 51.9, 41.7, 40.8, 35.8, 34.4, 31.9, 29.5, 29.5, 29.3, 28.8, 26.9, 22.7, 14.2.

HRMS (FAB): $C_{14}H_{28}O_3S$ $[M+H]^+$ calc. 277.1832 found 277.1830.

Methyl 3-((2-methoxy-2-oxoethyl)thio)undecanoate (**12.4**)



Pure **12.4** was obtained as light yellow oil (yield 81 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.74 (s, 3H, -OMe), 3.70 (s, 3H, -OMe), 3.38 – 3.12 (m, 3H, -C*H*-S-CH_2-COOMe), 2.71 – 2.53 (m, 2H, -CH_2-COOMe), 1.69 – 1.18 (m, 14H, -CH_2-), 0.88 (t, *J* = 6.7 Hz, 3H, -CH_3).

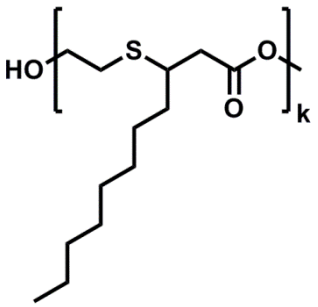
^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 172.0, 171.1, 52.5, 51.8, 42.74, 40.5, 34.8, 32.8, 32.0, 29.6, 29.5, 29.3, 26.8, 22.8, 14.2.

HRMS (FAB): $C_{15}H_{28}O_4S$ $[M+H]^+$ calc. 305.1781 found 305.1781.

General procedure for the synthesis of polyesters

All polymerizations were performed in a RR98072 carousel reactor (from Radleys^{TM} Discovery Technologies, UK). The respective monomers were weighed into a reaction tube and tin(II) octanoate (5 mol%) was added. The reaction mixture was stirred at evaluated temperatures for a specific time. 120 °C for 2 hours under a gentle argon flow. Subsequently, the reaction mixture was set under vacuum (10^{-2} mbar) and stirred for further 12 hours at 135 °C. It should be noted that the use of Ti(O^{i}Pr)$_4$ as catalyst led to similar results.

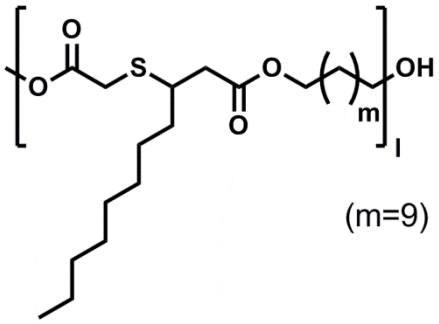
P4.4 was obtained by polymerization of monomer **11.4**.



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.34 – 4.11 (m, 2H, -CH_2-O-), 3.17 – 2.98 (m, 1H, -S-C*H*-), 2.85 – 2.67 (m, 2H, -S-CH_2-), 2.65 – 2.46 (m, 2H, -CH_2-COO-), 1.75 – 1.14 (m, 14H, -CH_2-), 0.88 (t, *J* = 6.6 Hz, 3H, -CH_3).

SEC: M_n = 17100 Da, *Đ* = 1.52, DSC: T_g = 8 °C.

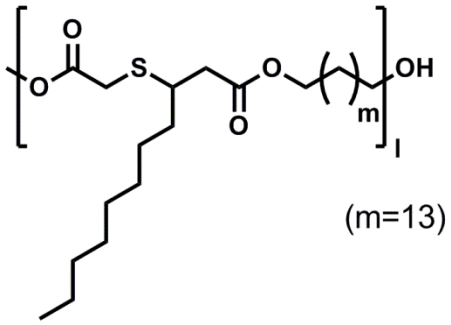
P5.4 was obtained by polymerization of monomer **12.4** and **17.4**.



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.19 – 4.00 (m, 4H, -C*H*$_2$-O-), 3.35 – 3.10 (m, 3H, -S-C*H*$_2$-, -S-C*H*-), 2.70 – 2.49 (m, 2H, -C*H*$_2$-COO-), 1.75 – 1.16 (m, 32H, -C*H*$_2$-), 0.87 (t, *J* = 6.7 Hz, 3H, -C*H*$_3$).

SEC: M_n = 18930 Da, *Đ* = 1.74, DSC: T_m = -18.6 °C.

P6.4 was obtained by polymerization of monomer **12.4** and **18.4**.



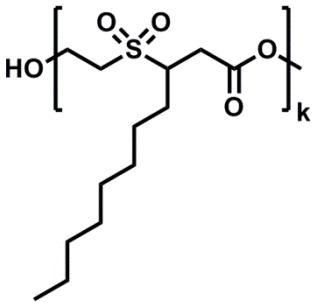
^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.20 – 3.97 (m, 4H, -C*H*$_2$-O-), 3.36 – 3.11 (m, 3H, -S-C*H*$_2$-, -S-C*H*-), 2.71 – 2.49 (m, 2H, -C*H*$_2$-COO-), 1.79 – 1.10 (m, 40H, -C*H*$_2$-), 0.87 (t, *J* = 6.7 Hz, 3H, -C*H*$_3$).

SEC: M_n = 18030 Da, *Đ* = 1.90, DSC: T_m = 15.5 °C.

General procedure for the oxidation of the sulfur containing polyesters

To the polyester (**P4.4** - **P6.4**) (0.15 g) dissolved in 15 mL $CHCl_3$, *m*CPBA (3.0 equivalents per sulfur) was added. The reaction mixture was stirred at room temperature for 24 hours. To the reaction mixture a saturated aqueous solution of $Na_2S_2O_3$ was added to quench the oxidizing agent and the phases were separated. The turbid polymer solution was evaporated to dryness under high vacuum.

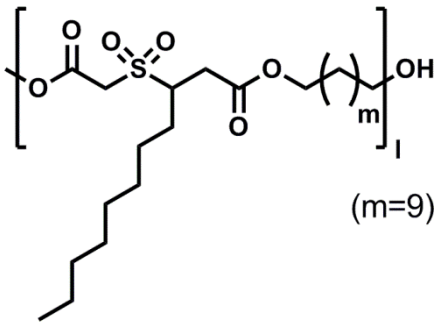
P7.4



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.75 – 4.40 (m, 2H, -C*H*$_2$-O-), 3.69 – 3.48 (m, 1H, -C*H*-SO_2-), 3.46 – 3.23 (m, 2H, -C*H*$_2$-SO_2-), 3.10 – 2.83 (m, 1H, -C*H*$_2$-CO-), 2.66 (m, 1H, -C*H*$_2$-CO-), 2.09 – 1.85 (m, 1H, -C*H*$_2$-), 1.78 – 1.14 (m, 13H, -C*H*$_2$-), 0.88 (t, *J* = 6.6 Hz, 3H, -C*H*$_3$).

DSC: T_m = 21 °C.

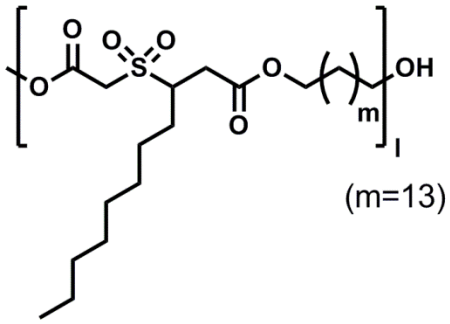
P8.4



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.19 (t, *J* = 6.7 Hz, 2H, -C*H*$_2$-O(CO)-), 4.14 – 4.03 (m, 3H, -C*H*$_2$-O(CO)-, -SO_2-C*H*-), 4.03 – 3.83 (m, 2H, -SO_2-C*H*$_2$-COO-), 3.01 (dd, *J* = 17.1, 6.2 Hz, 1H, -C*H*$_2$-COO-), 2.61 (dd, *J* = 17.1, 6.2 Hz, 1H, -C*H*$_2$-COO-), 2.09 – 1.90 (m, 1H, -C*H*$_2$-), 1.79 – 1.11 (m, 31H, -C*H*$_2$-), 0.86 (t, *J* = 6.6 Hz, 3H, -C*H*$_3$).

DSC: T_m = -5 °C.

P9.4



^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.20 (t, *J* = 6.8 Hz, 2H, -C*H*$_2$-O(CO)-), 4.15 – 4.03 (m, 3H, -C*H*$_2$-O(CO)-, -SO$_2$-C*H*-), 4.03 – 3.85 (m, 2H, -SO$_2$-C*H*$_2$-COO-), 3.02 (dd, *J* = 17.1, 6.2 Hz, 1H, -C*H*$_2$-COO-), 2.62 (dd, *J* = 17.1, 6.2 Hz, 1H, -C*H*$_2$-COO-), 2.09 – 1.92 (m, 1H, -C*H*$_2$-), 1.78 – 1.15 (m, 39H, -C*H*$_2$-), 0.87 (t, *J* = 6.6 Hz, 3H, -C*H*$_3$).

DSC: T_m = 25 °C.

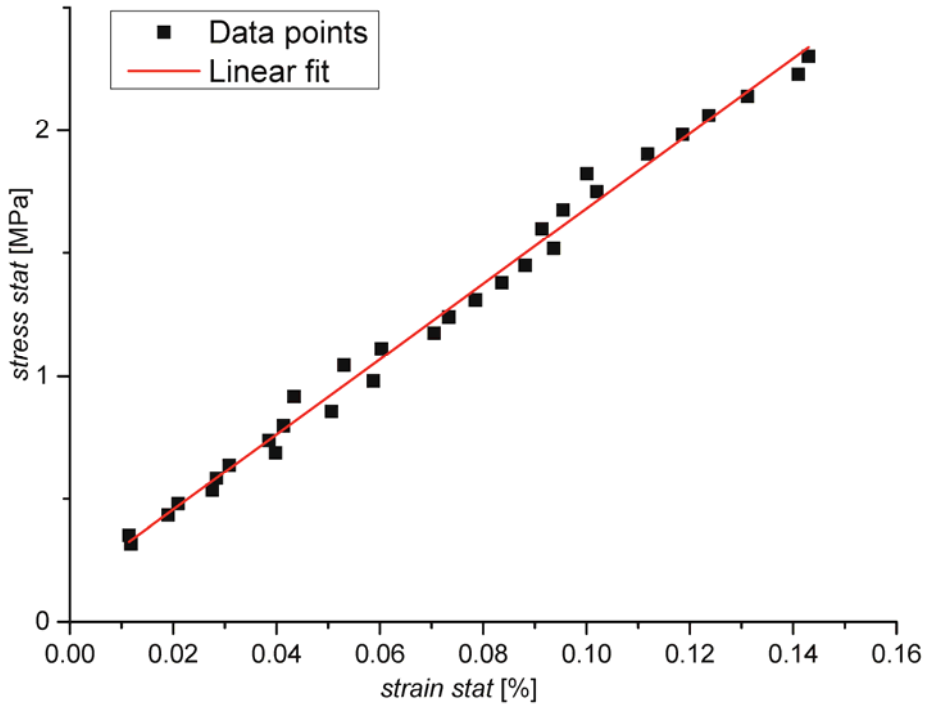


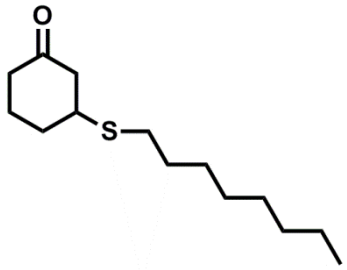
Figure 6.3.4-1: Determination of the Young's modulus by linear fit of the obtained data.

6.3.5 Chapter 4.5 – Experimental procedures

General procedure for Thia-Michael Additions

2.5 g cyclohex-2-enone (26.0 mmol), the respective thiol (31.2 mmol) and triethylamine (10 mol%) were weighted into a round bottom flask and vigorously stirred for 16 hours at 40 °C. Washing with 1 M aqueous NaOH (2 x) afforded the pure products.

3-(*n*-octylthio)cyclohexanone (1.5)



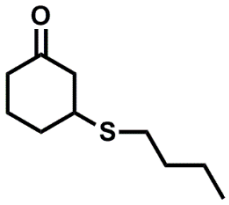
1.5 was obtained as light yellow oil (yield 97 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.10 – 2.97 (m, 1H, -S-C*H*-), 2.69 (dd, *J* = 14.2, 4.4 Hz, 1H, -CH-CH_2-C(O)-), 2.51 (t, *J* = 7.5 Hz, 2H, -S-CH_2-), 2.42 – 2.24 (m, 3H, -CH_2-(CO)-CH_2-), 2.21 – 2.04 (m, 2H, -CH-CH_2-CH_2-), 1.80 – 1.62 (m, 2H, -CH_2-CH_2-CO-), 1.61 – 1.47 (m, 2H, -S-CH_2-CH_2-), 1.44 – 1.15 (m, 10H, -CH_2-), 0.86 (t, *J* = 6.7 Hz, 3H, -CH_3).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 209.0, 48.4, 42.9, 41.1, 31.9, 31.8, 30.6, 29.8, 29.2, 29.0, 24.4, 22.7, 14.2.

HRMS (EI): $C_{14}H_{26}OS$ [M] calc. 242.1699 found 2421698.

3-(*n*-butylthio)cyclohexanone (2.5)



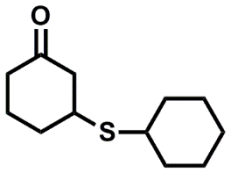
2.5 was obtained as light yellow oil (yield 96 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.09 – 2.95 (m, 1H, -S-C*H*-), 2.68 (dd, *J* = 14.2, 3.0 Hz, 1H, -CH-C*H*$_2$-C(O)-), 2.52 (td, *J* = 7.5, 1.5 Hz, 2H, -S-C*H*$_2$-), 2.41 – 2.22 (m, 3H, -C*H*$_2$-(CO)-C*H*$_2$-), 2.19 – 2.03 (m, 2H, -CH-C*H*$_2$-CH$_2$-), 1.77 – 1.60 (m, 2H, -CH$_2$-C*H*$_2$-CO-), 1.59 – 1.45 (m, 2H, -S-CH$_2$-C*H*$_2$-), 1.44 – 1.29 (m, 2H, -C*H*$_2$-), 0.88 (td, *J* = 7.3, 1.4 Hz, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 209.0, 48.3, 42.8, 41.0, 31.8, 31.7, 30.3, 24.3, 22.1, 13.7.

HRMS (EI): $C_{10}H_{18}OS$ [M] calc. 186.1073 found 186.1075.

3-(cyclohexylthio)cyclohexanone (3.5)



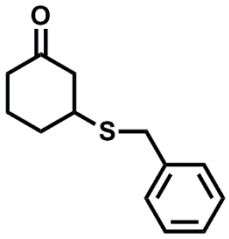
3.5 was obtained as light yellow oil (yield 91 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.19 – 3.03 (m, 1H, -S-C*H*-), 2.78 – 2.59 (m, 2H, -CH-C*H*$_2$-C(O)-, -S-C*H*-), 2.42 – 2.20 (m, 3H, -C*H*$_2$-(CO)-C*H*$_2$-), 2.19 – 2.02 (m, 2H, -CH-C*H*$_2$-CH$_2$-), 1.98 – 1.81 (m, 2H, -C*H*$_2$-), 1.80 – 1.50 (m, 5H, -C*H*$_2$-), 1.38 – 1.11 (m, 5H, -C*H*$_2$-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 209.2, 48.9, 42.4, 41.2, 41.0, 34.1, 34.0, 32.2, 26.1, 26.1, 25.8, 24.5.

HRMS (EI): $C_{12}H_{20}OS$ [M] calc. 212.1229 found 212.1230.

3-(benzylthio)cyclohexanone (4.5)



4.5 was obtained as light yellow oil (yield 95 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.36 – 7.19 (m, 5H, Ph), 3.75 (s, 2H, -C*H*$_2$-Ph), 3.01 – 2.86 (m, 1H, -S-C*H*-), 2.66 (dd, *J* = 14.2, 4.5 Hz, 1H, -CH-C*H*$_2$-C(O)-), 2.45 – 2.23 (m, 3H, -C*H*$_2$-(CO)-C*H*$_2$-), 2.18 – 2.00 (m, 2H, -CH-C*H*$_2$-CH$_2$-), 1.81 – 1.56 (m, 2H, -CH$_2$-C*H*$_2$-CO-).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 208.7, 138.0, 128.8, 128.7, 127.2, 47.8, 42.0, 41.0, 35.0, 31.3, 24.1.

HRMS (EI): $C_{13}H_{16}OS$ [M] calc. 220.0916 found 220.0917.

General procedure for conventional Baeyer-Villiger oxidations:

The cyclohexanone substrate **1.5** – **4.5** (16.1 mmol) was dissolved in 75 mL dichloromethane and cooled with an ice bath. Subsequently, *m*CPBA (3.5 eq.) was added in small portions and the reaction mixture was stirred overnight. To the crude product, dichloromethane (75 mL) was added and the reaction mixture was filtered. The solvent was evaporated and the crude product was dissolved in acetone and purified via column chromatography using hexane : acetone = 2 : 1 as eluent. If the product was still contaminated with *m*CPBA residues a second short column was performed using hexane : acetone = 1 : 1 as eluent.

Baeyer-Villiger oxidations using Oxone®:

The cyclohexanone substrate **1.5** – **4.5** (4.54 mmol) was dissolved in 20 mL DMF, set under an argon atmosphere and cooled with an ice bath. Subsequently, 7.68 g Oxone® (25.0 mmol) was added in small portions and the reaction mixture was stirred for 24 hours slowly warming to room temperature. Another portion of Oxone® (4.5 mmol) was added and the reaction mixture was stirred for further 24 hours. Afterwards, reaction mixture was filtered, 100 mL dichloromethane was added and the reaction mixture was washed with saturated NaCl solution (1 x 80 mL). The aqueous phase was again extracted with dichloromethane and the combined organic layers were dried over Na_2SO_4. The crude product was further purified by column chromatography using hexane : acetone = 2 : 1 as eluent.

Baeyer-Villiger oxidations using urea hydrogen peroxide / TFAA:

5.00 g Urea hydrogen peroxide (52.8 mmol), 4.50 g Na_2HPO_4 (31.8 mmol) were weighted in a round bottom flask and set under an argon atmosphere. The cyclohexanone substrate **1.5** – **4.5** (4.54 mmol) dissolved in 70 mL dry dichloromethane was added. The mixture was cooled with an ice bath and 6.68 g trifluoroacetic anhydride (31.8mmol) was slowly added. The reaction mixture was stirred for 48 hours slowly warming to room temperature. The crude reaction mixture was washed with $NaHCO_3$ (1 x 25 ml), saturated NaCl solution (1 x 25 mL) and dried over Na_2SO_4. After evaporation of the solvent the crude product was analyzed via GC-MS and NMR analysis.

Baeyer-Villiger oxidations using hydrogen peroxide and Novozyme 435:

Method A:

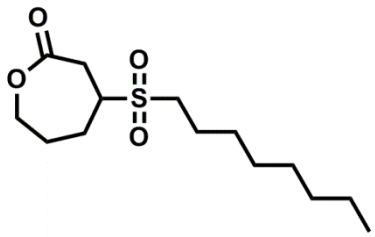
The cyclohexanone substrate **1.5** – **4.5** (1.60 mmol) was dissolved in 2 mL toluene, 0.690 g octanoic acid (4.81 mmol) and 50.0 mg Novozyme 435 were added. To the reaction mixture 2 x 1 mL H_2O_2 (30%) was added at 0 hours and 72 hours. The reaction mixture was stirred at 50 °C for 7 days. The crude reaction mixture was diluted with 25 mL dichloromethane and washed with $NaHCO_3$ (1 x 10 mL), saturated NaCl solution (1 x 10 mL) and dried over Na_2SO_4. After evaporation of the solvent the crude product was analyzed via GC-MS and NMR analysis.

Method B:

The cyclohexanone substrate **1.5** – **4.5** (1.50 mmol) was dissolved in 5 mL ethyl acetate, 50.0 mg Novozyme 435 and urea-hydrogen peroxide (8.00 mmol) were added. The reaction mixture was stirred for 7 days. Subsequently, the crude reaction mixture was diluted with 25 mL ethyl acetate and washed with $NaHCO_3$ (1 x 10 mL), saturated NaCl solution (1 x 10 mL) and dried over Na_2SO_4. After evaporation of the solvent the crude product was analyzed via GC-MS and NMR analysis.

Note: The yields given for the compounds **5.5** – **8.5** are related to the oxidation procedure making use of *m*CPBA.

6-(*n*-octylsulfonyl)oxepan-2-one (5.5)



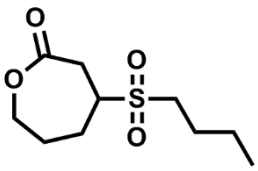
5.5 was obtained as colorless solid (yield 82 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.42 – 4.34 (m, 1H, -C*H*$_2$-O-(CO)-), 4.29 – 4.20 (m, 1H, -C*H*$_2$-O-(CO)-), 3.21 – 2.87 (m, 5H, -C*H*$_2$-SO_2-, -(CO)-C*H*$_2$-, -SO_2-C*H*-), 2.51 – 2.39 (m, 1H, -C*H*$_2$-), 2.30 – 2.17 (m, 1H, -C*H*$_2$-), 2.08 – 1.74 (m, 4H, -C*H*$_2$-), 1.50 – 1.38 (m, 2H, -C*H*$_2$-), 1.37 – 1.21 (m, 8H, -C*H*$_2$-), 0.88 (t, *J* = 6.7 Hz, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 171.2, 68.7, 55.9, 50.6, 34.1, 31.8, 29.1, 29.0, 28.7, 27.3, 26.8, 22.7, 21.7, 14.2.

HRMS (FAB):$C_{14}H_{26}O_4S$ $[M+H]^+$ calc. 291.1625 found 291.1626.

6-(*n*-butylsulfonyl)oxepan-2-one (6.5)



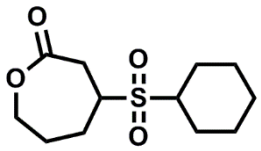
6.5 was obtained as light yellow and highly viscous oil (yield 77 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.45 – 4.33 (m, 1H, -C*H*$_2$-O-(CO)-), 4.31 – 4.18 (m, 1H, -C*H*$_2$-O-(CO)-), 3.18 – 2.89 (m, 5H, -C*H*$_2$-SO_2-, -(CO)-C*H*$_2$-, -SO_2-C*H*-), 2.53 – 2.38 (m, 1H, -C*H*$_2$-), 2.33 – 2.19 (m, 1H, -C*H*$_2$-), 2.08 – 1.76 (m, 4H, -C*H*$_2$-), 1.57 – 1.39 (m, 2H, -C*H*$_2$-), 0.98 (t, *J* = 7.3 Hz, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 171.5, 68.6, 55.9, 50.1, 33.7, 30.9, 29.2, 27.1, 26.9, 23.5, 23.3, 21.8, 13.6.

HRMS (FAB): $C_{10}H_{18}O_4S$ $[M+H]^+$ calc. 235.0999 found 235.0996.

6-(cyclohexylsulfonyl)oxepan-2-one (7.5)



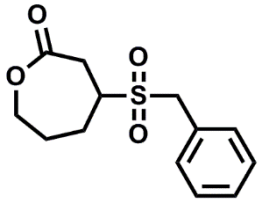
7.5 was obtained as colorless solid (yield 79 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.46 – 4.18 (m, 2H, -C*H*$_2$-O(CO)-), 3.30 – 2.87 (m, 4H, -C*H*-SO$_2$-C*H*-, -(CO)-C*H*$_2$), 2.48 – 2.35 (m, 1H, -CH$_2$-C*H*-), 2.31 – 2.18 (m, 1H, -C*H*$_2$-CH-), 2.16 – 1.82 (m, 5H, -C*H*$_2$), 1.79 – 1.45 (m, 4H, -C*H*$_2$), 1.43 – 1.16 (m, 3H, -C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 171.5, 68.7, 58.5, 52.5, 33.9, 27.3, 26.7, 25.3, 25.1, 25.1, 24.4.

HRMS (FAB): $C_{12}H_{20}O_4S$ $[M+H]^+$ calc. 261.1155 found 261.1152.

6-(benzylsulfonyl)oxepan-2-one (8.5)



Pure **8.5** was obtained as colorless solid (yield 85 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.53 – 7.35 (m, 5H, -Ph), 4.49 – 4.12 (m, 4H, -C*H*$_2$-O-(CO)-, -C*H*$_2$-Ph), 3.19 – 3.05 (m, 1H, -C*H*), 3.04 – 2.89 (m, 2H, -C*H*$_2$), 2.44 – 2.30 (m, 1H, -C*H*$_2$), 2.26 – 2.12 (m, 1H, -C*H*$_2$), 2.06 – 1.87 (m, 1H, -C*H*$_2$), 1.86 – 1.69 (m, 1H, -C*H*$_2$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 170.9, 130.8, 129.45, 129.4, 127.2, 68.6, 57.1, 53.5, 34.4, 27.1, 26.4.

HRMS (FAB): $C_{13}H_{16}O_4S$ $[M+H]^+$ calc. 269.0842 found 269.0844.

General procedure for the synthesis of polyesters:

Monomer **5.5** – **8.5** (0.40 g) was weighted in a 5 mL round bottom flask, heated up to 150 °C and degased with argon for 15 minutes. Subsequently, the corresponding amount of 1-octanol (1/20, 1/30, 1/40 or 1/50 mol to monomer) and tin(II) octanoate (1/20 mol to 1-octanol) was added. Depending on the monomer to initiator ratio the polymerization was quenched after 2 – 4 hours by cooling the reaction mixture in an ice bath. The polymer was dissolved in THF and precipitated in a mixture of cold hexane : acetone = 10 : 1.

Note: Octanol and tin(II) octanoate were added as solution in dry toluene 0.627 mol/L and $3.1 \cdot 10^{-3}$ mol/L, respectively.

Polyester P9.5 octyl

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.32 – 4.02 (m, 2H, -C*H*$_2$-O-), 3.82 – 3.68 (m, 1H, -(CO)-C*H*$_2$-), 3.59 – 3.41 (m, 1H, -C*H*-), 3.08 – 2.88 (m, 3H, -SO_2-C*H*$_2$, -CH-C*H*$_2$-), 2.68 – 2.51 (m, 1H, (CO)-C*H*$_2$-), 2.16 – 1.97 (m, 1H, -C*H*$_2$-), 1.96 – 1.65 (m, 5H, -C*H*$_2$-), 1.52 – 1.15 (m, 9H, -C*H*$_2$-), 0.88 (t, *J* = 6.6 Hz, 3H, -C*H*$_3$).

Polyester P3.5 butyl

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.31 – 4.03 (m, 2H, -C*H*$_2$-O-), 3.80 – 3.68 (m, 1H, -(CO)-C*H*$_2$-), 3.59 – 3.44 (m, 1H, -C*H*-), 3.07 – 2.87 (m, 3H, -SO_2-C*H*$_2$, -CH-C*H*$_2$-), 2.68 – 2.52 (m, 1H, (CO)-C*H*$_2$-), 2.17 – 1.97 (m, 1H, -C*H*$_2$-), 1.94 – 1.68 (m, 3H, -C*H*$_2$-), 1.57 – 1.39 (m, 2H, -C*H*$_2$-), 1.36 – 1.21 (m, 1H, -C*H*$_2$-), 0.97 (t, *J* = 7.3 Hz, 3H, -C*H*$_3$).

Polyester P8.5 cyclohexyl

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.31 – 4.04 (m, 2H, -C*H*$_2$-O-), 3.82 – 3.71 (m, 1H, -(CO)-C*H*$_2$-), 3.72 – 3.56 (m, 1H, -C*H*-), 3.09 – 2.88 (m, 2H, -C*H*-, -C*H*$_2$-), 2.68 – 2.51 (m, 1H, -(CO)-C*H*$_2$-), 2.24 – 1.67 (m, 7H, -C*H*$_2$-), 1.67 – 1.47 (m, 2H, -C*H*$_2$-), 1.44 – 1.15 (m, 4H, -C*H*$_2$-).

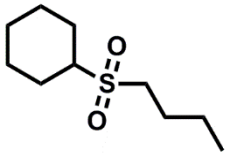
Polyester P10.5 benzyl

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.45 – 7.31 (m, 5H, -Ph), 4.37 – 3.89 (m, 4H, -C*H*$_2$-O-, -C*H*$_2$-Ph), 3.62 – 3.41 (m, 1H, -C*H*-), 2.99 – 2.79 (m, 1H, -(CO)-C*H*$_2$-), 2.62 – 2.44 (m, 1H, -(CO)-C*H*$_2$-), 2.06 – 1.81 (m, 1H, -C*H*$_2$-), 1.79 – 1.46 (m, 3H, -C*H*$_2$-).

Table 6.3.5-1: Results of the SEC and DSC analysis of the prepared polyesters **P5.5** – **P7.5** using monomer **7.5** and different monomer to initiator ([M] : [I]) ratios.

Polymer	[M] : [I]	$M_{n,\ theo.}$ [Da]	$M_{n,\ SEC}$ [Da]	$Đ$
P6.5	20 : 1	5333	3760	1.16
P7.5	30 : 1	7935	6340	1.11
P8.5	40 : 1	10536	7680	1.17

Synthesis and stability test of (*n*-butylsulfonyl)cyclohexane



1.00 g cyclohexene (12.2 mmol) and 5.50 g *n*-butanethiol (61.0 mmol) were added in a quartz glass vial. 2,2-dimethoxy-2-phenylacetophenone (DMPA) (2 mol%) was added and the reaction was stirred for 16 hours under UV light (251 nm) irradiation. Afterwards, ethyl acetate (20 mL) was added and the crude reaction mixture was washed with 1 M HCl (2 x 20 mL), 1 M NaOH (2 x 20 mL), H_2O (1 x 20 mL) and brine (1 x 20 mL), dried over Na_2SO_4 and evaporated to dryness. 0.5 g of the obtained yellow oil was diluted with dichloromethane (20 mL) and *m*CPBA (3.5 equivalents) was carefully added under ice cooling. The reaction mixture was stirred for 16 hours at room temperature. Subsequently, 20 mL dichloromethane was added and the crude product was washed with a saturated solution of $Na_2S_2O_3$ (20 mL), Na_2SO_3 (20 mL) and NaCl (20 mL), dried over Na_2SO_4 and evaporated to dryness. Pure (n-butylsulfonyl)cyclohexane was obtained by column chromatography (hexane : ethyl acetate = 5 : 1 → 3 : 1).

To 0.1 g (*n*-butylsulfonyl)cyclohexane (0.49 mmol) , tin(II)octanoate (1/20 mol to *n*-octanol) and *n*-octanol (0.025 mmol) was added. The reaction mixture was stirred for 4 hours at 150 °C and then analyzed by ^{1}H-NMR analysis.

Note: Octanol and tin(II) octanoate were added as solution in dry toluene.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.97 – 2.74 (m, 3H, -C*H*$_2$-SO$_2$-C*H*-), 2.21 – 2.06 (m, 2H, -C*H*$_2$-), 2.00 – 1.86 (m, 2H, -C*H*$_2$-), 1.86 – 1.64 (m, 3H, -C*H*$_2$-), 1.62 – 1.38 (m, 4H, -C*H*$_2$-), 1.37 – 1.11 (m, 3H, -C*H*$_2$-), 0.95 (t, *J* = 7.3 Hz, 3H, --C*H*$_3$).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 60.9, 49.2, 25.2, 25.1, 23.4, 22.0, 13.7.

HRMS (FAB): $C_{10}H_{20}O_2S$ $[M+H]^+$ calc. 205.1257 found 205.1262.

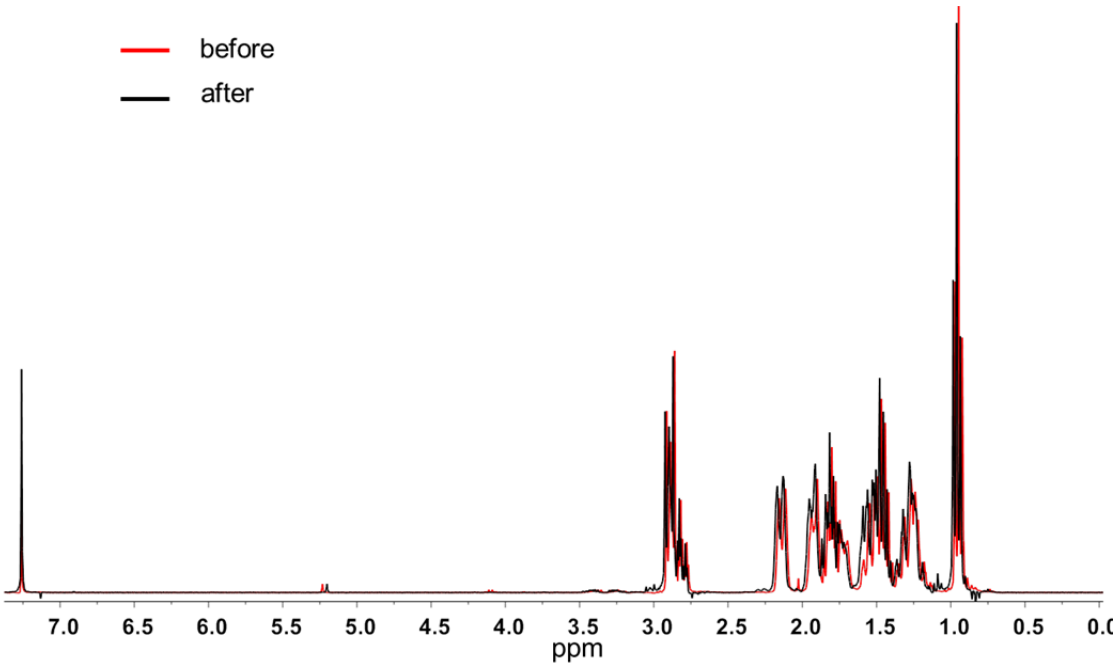


Figure 6.3.5-1: ^{1}H-NMR (300 MHz/$CDCl_3$) of (*n*-butylsulfonyl)cyclohexane before and after the stability test.

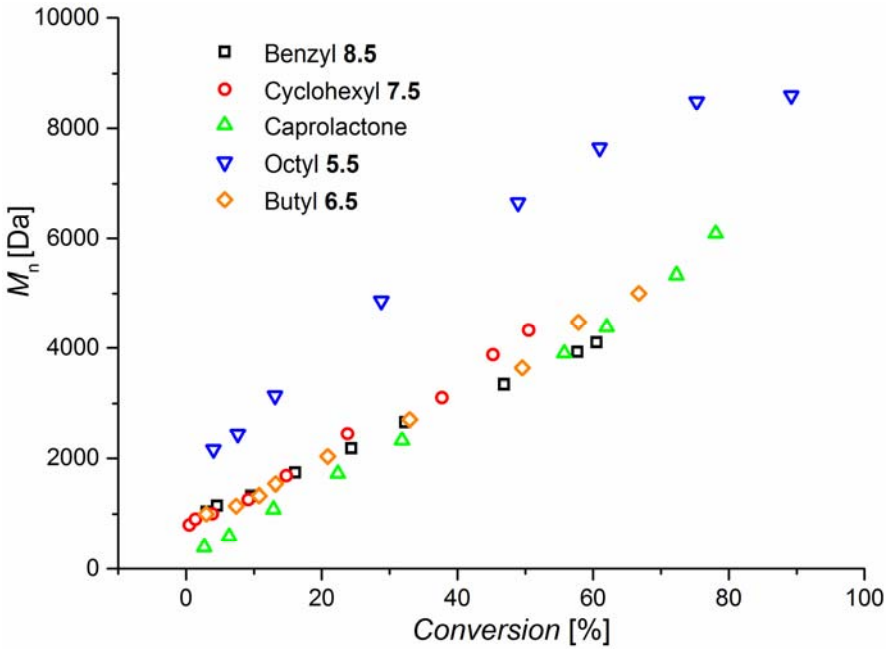


Figure 6.3.5-2: Kinetic plot of the polymerization of the different modified CL monomers with a monomer to initiator ratio [40] : [1].

6.3.6 Chapter 4.6 – Experimental procedures

General procedure for the epoxidation of 1,4-cyclohexadiene using Oxone® adapted from the literature[354]

To 1.00 g of 1,4 cylohexadiene (12.5 mmol) in 50 mL dichloromethane, 5 mL acetone and 100 mL of a saturated solution of $NaHCO_3$, a solution of 3.84 g Oxone® (12.5 mmol) in 60 mL water was added drop-wise to the ice cooled solution. The reaction mixture was vigorously stirred at 0 °C for 30 minutes and at room temperature for 6 hours. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over Na_2SO_4 and CH_2Cl_2 was carefully removed under reduced pressure (40 °C, >80 – 100 mbar). Fractionated distillation under reduced pressure (55 °C, 20 mbar) afforded epoxide **1.6** (0.73 g, yield 65 %).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.43 (s, 2H, -C*H*=C*H*-), 3.24 (s, 2H, -C*H*-O-C*H*-) 2.64 – 2.36 (m, 4H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 121.5, 49.8, 24.8.

General procedure for the one-pot epoxidation of 1,4-cyclohexadiene using Oxone®

To 1.00 g of 1,4 cylohexadiene (12.5 mmol) in 50 mL dichloromethane, 5 mL acetone and 100 mL of a saturated solution of $NaHCO_3$, a solution of Oxone® (1.0, 2.0 or 4.0 equivalents) in 60 mL water was added drop wise to the ice cooled solution. The reaction mixture was vigorously stirred at 0°C for 30 minutes and at room temperature for 6 hours. After TLC and ^{1}H-NMR analysis of the crude reaction mixture showed full conversion of the 1,4-cyclohexadiene, the organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over Na_2SO_4 and CH_2Cl_2 was carefully removed under reduced pressure (40 °C, >80 - 100 mbar). The content of the respective epoxide was estimated by ^{1}H-NMR spectroscopy.

Table 6.3.6-1: Results of the one-pot epoxidation using varying amounts of Oxone®.

Entry	Oxone® [equivalents][a]	1.6 [%][b]	3.6a + 3.6b [%][b]
1	1	79.5	20.5
2	2	67.0	33.0
3	4	49.5	50.5

[a]Equivalents respective to 1,4-cyclohexadiene, [b] determined by ^{1}H-NMR

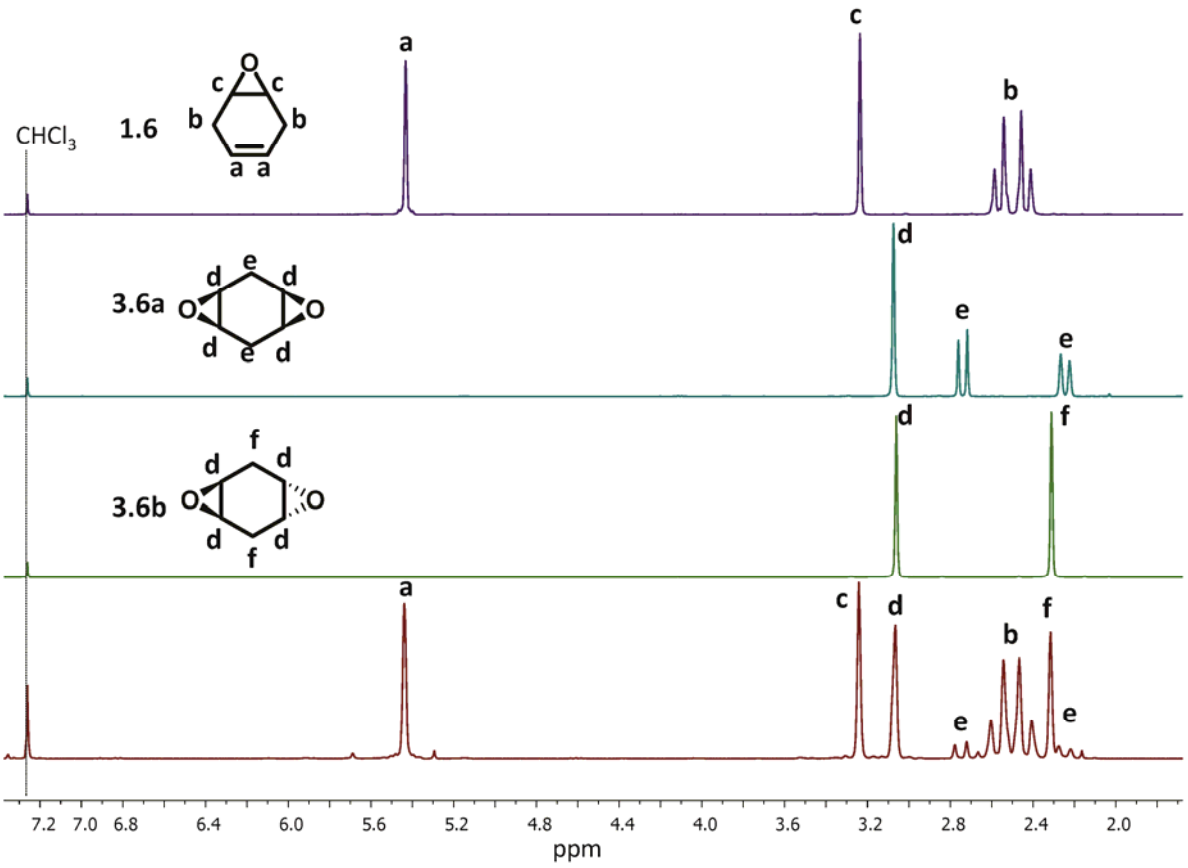
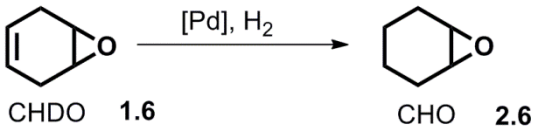


Figure 6.3.6-1: Overlay of the ^{1}H-NMR (400 MHz, $CDCl_3$) of the crude reaction mixture (bottom), epoxide **1.6**, **3.6a** and **3.6b.**

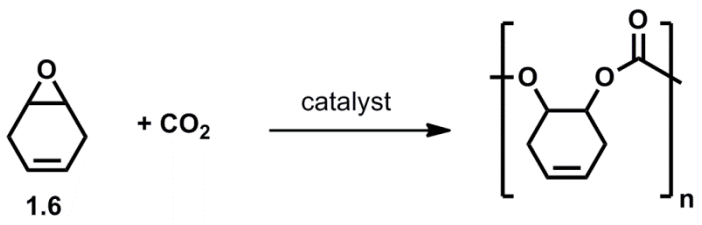
General procedure for the reduction of CHDO 1.6 by Pd/C or Pd(en)/C



To 1.00 g of 1,4-cyclohexadiene oxide (10.4 mmol) in 10 mL ethyl acetate or THF, 0.10 g of the palladium catalyst (Pd/C or Pd(en)/C[335, 355], 10 wt%) was added. The reaction mixture was stirred for 24 hours under a hydrogen atmosphere (balloon).

The crude reaction mixture was then filtered through a pore filter to remove the palladium catalyst. After evaporation of the solvent the crude product mixture was analysed by ^{1}H NMR spectroscopy and GC analysis showing presence of CHO.

CO_2 co-polymerization of monomer 1.6



1.6

Monomer **1.6** and the catalyst (and co-catalyst) were weighted in a Schlenk flask. For reactions at atmospheric pressure of CO_2, the Schlenk flask was shortly evacuated and back-filled with CO_2 two times to generate a carbon dioxide atmosphere. Then, the reaction mixture was heated to the desired temperature and stirred for the given time. The polymer was precipitated in cold methanol from THF. For the analysis of the polymer by GPC and NMR, a sample was taken of the crude reaction mixture.

Reactions under CO_2 pressure were performed in a Parr 5513 100 mL bench reactor. Therefore, the pre-dried reactor was set under a CO_2 atmosphere and the reaction mixture was injected. Then, the reaction mixture was stirred at an evaluated pressure and temperature for the given time.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.57 (s, 2H, -C*H*=C*H*-), 4.96 (s, 2H, -C*H*-O-), 2.77 – 2.15 (m, 4H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 154.0, 123.4, 73.7, 29.9.

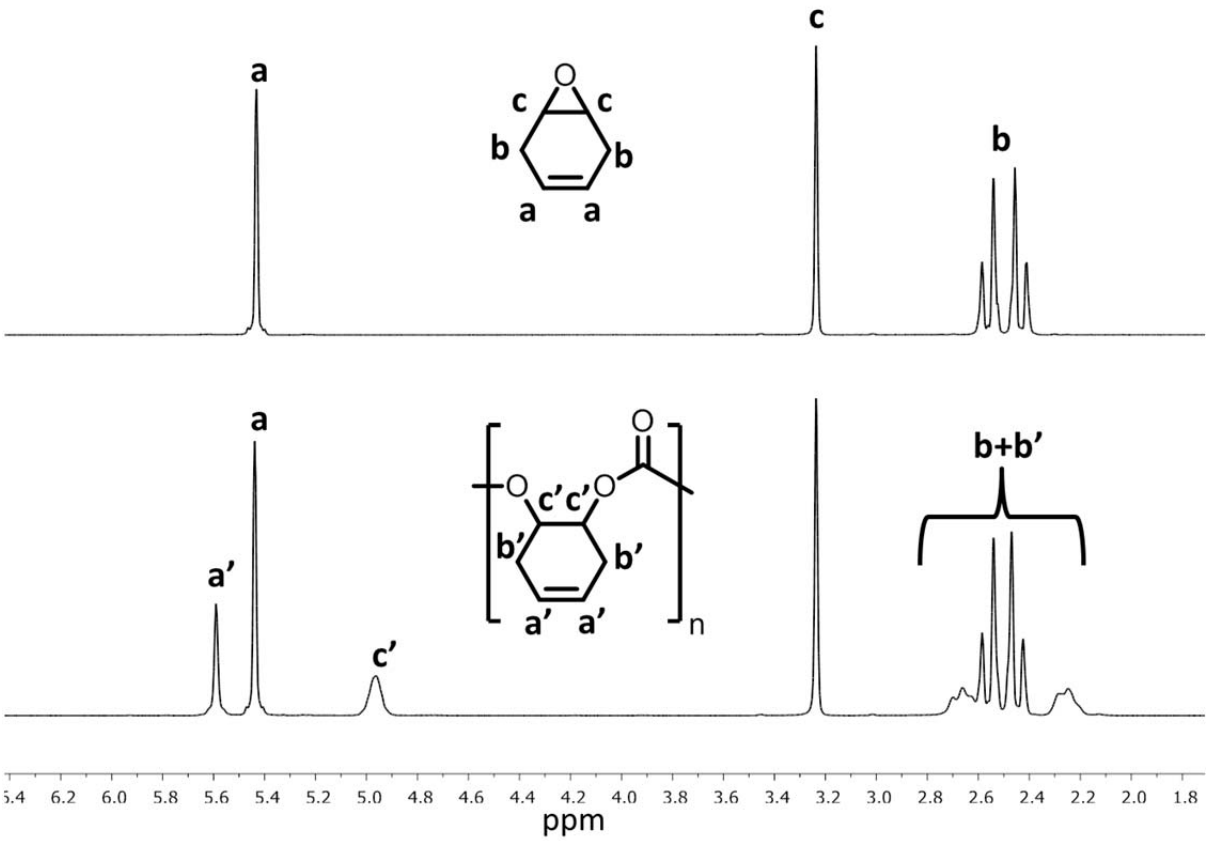


Figure 6.3.6-2: ^{1}H-NMR spectra (400 MHz, $CDCl_3$) of the crude reaction mixture (bottom) and monomer **1.6**

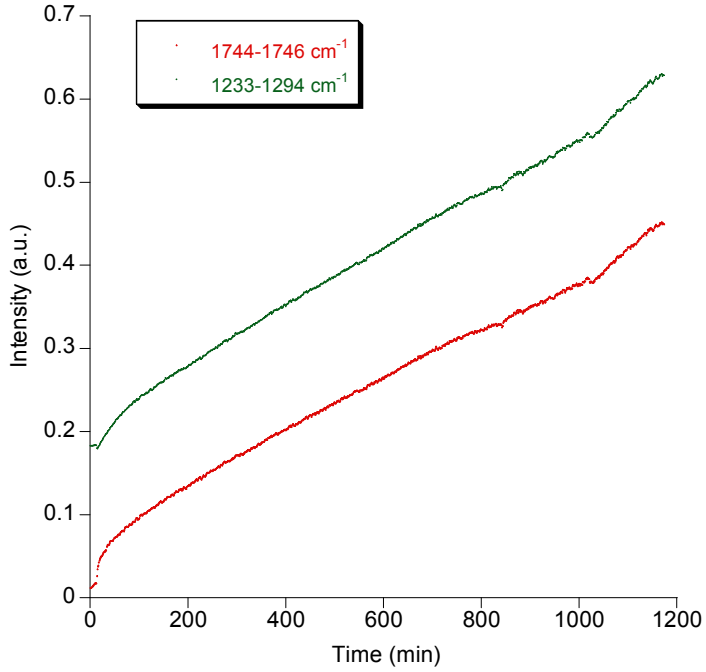


Figure 6.3.6-3: Changes in intensity of IR resonances for **1.6**/CO_2 copolymerization in the presence of **C1.6**.

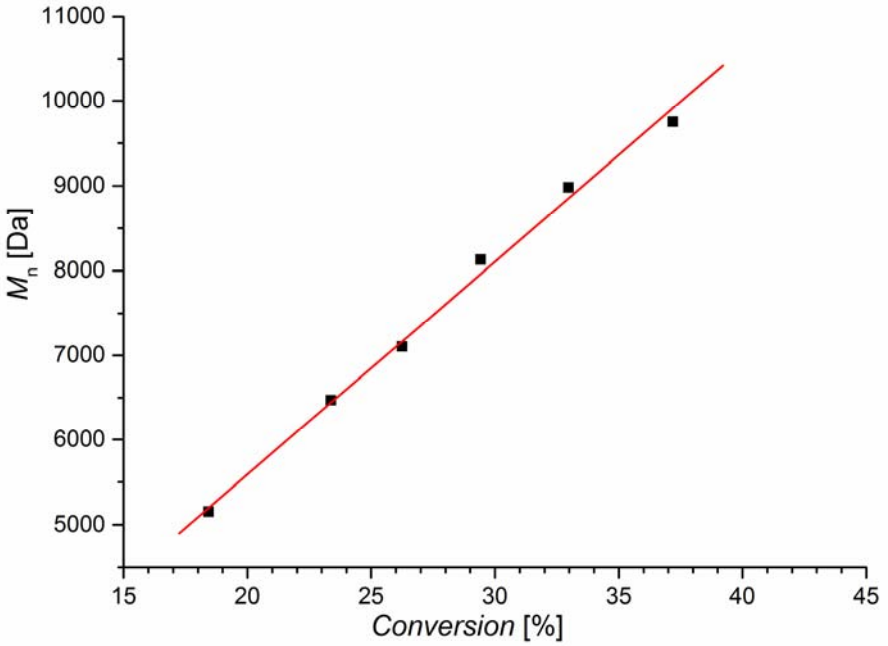
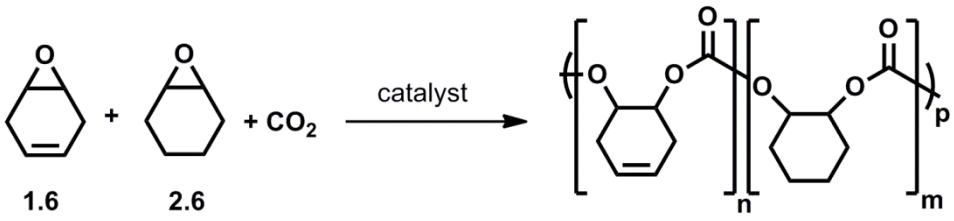


Figure 6.3.6-4: Kinetic investigation of the co-polymerization of monomer **1.6** and CO_2 performed at 28 °C under a CO_2 pressure of 20 bar.

Terpolymerization of CO_2, monomer 1.6 and cyclohexene oxide 2.6

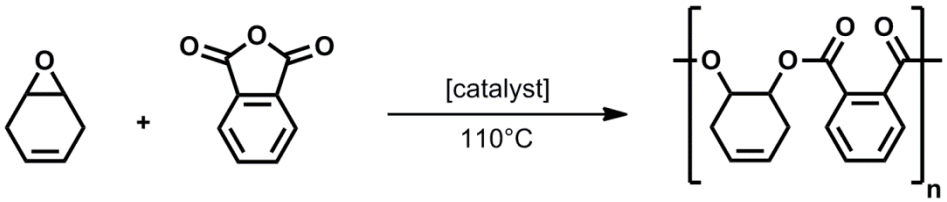


CO_2 –mediated terpolymerizations of monomer **1.6** and cyclohexene oxide **2.6** were performed according to the procedure given for the CO_2 copolymerization of monomer **1.6**.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.57 (s, 2H, -C*H*=C*H*-), 4.96 (s, 2H, -C*H*-O-C*H*-), 4.66 (s, 2H, -C*H*-O-C*H*-), 2.85 – 2.17 (m, 4H, -CH_2-), 2.16 – 1.62 (m, 4H, -CH_2-), 1.61 – 1.18 (m, 4H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 154.0, 153.6, 123.2, 123.3, 73.7, 29.9, 29.6.

Co-polymerization of epoxide 1.6 and phthalic anhydride



1.6 **PA** **P10.6 - P13.6**

Under nitrogen atmosohere, phthalic anhydride, monomer **1.6**, and the catalyst (and co-catalyst) were weighed into a 2 mL vial. Dry toluene was added if reactions were performed in a 2.5 M solution. The reaction mixture was heated to 110 °C and stirred for the given time. The polymer was precipitated in methanol from THF. For the analysis of the polymer by GPC and NMR, a sample was taken of the crude reaction mixture.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.66 – 7.36 (m, 4H, -CH_{arom}-), 5.62 (s, 2H, -C*H*=C*H*), 5.42 (s, 2H, -C*H*-O-), 2.87 – 2.22 (m, 4H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 166.7, 132.1, 132.0, 131.3, 129.1-128.8, 123.9-123.6, 71.2-70.8, 29.8, 29.7.

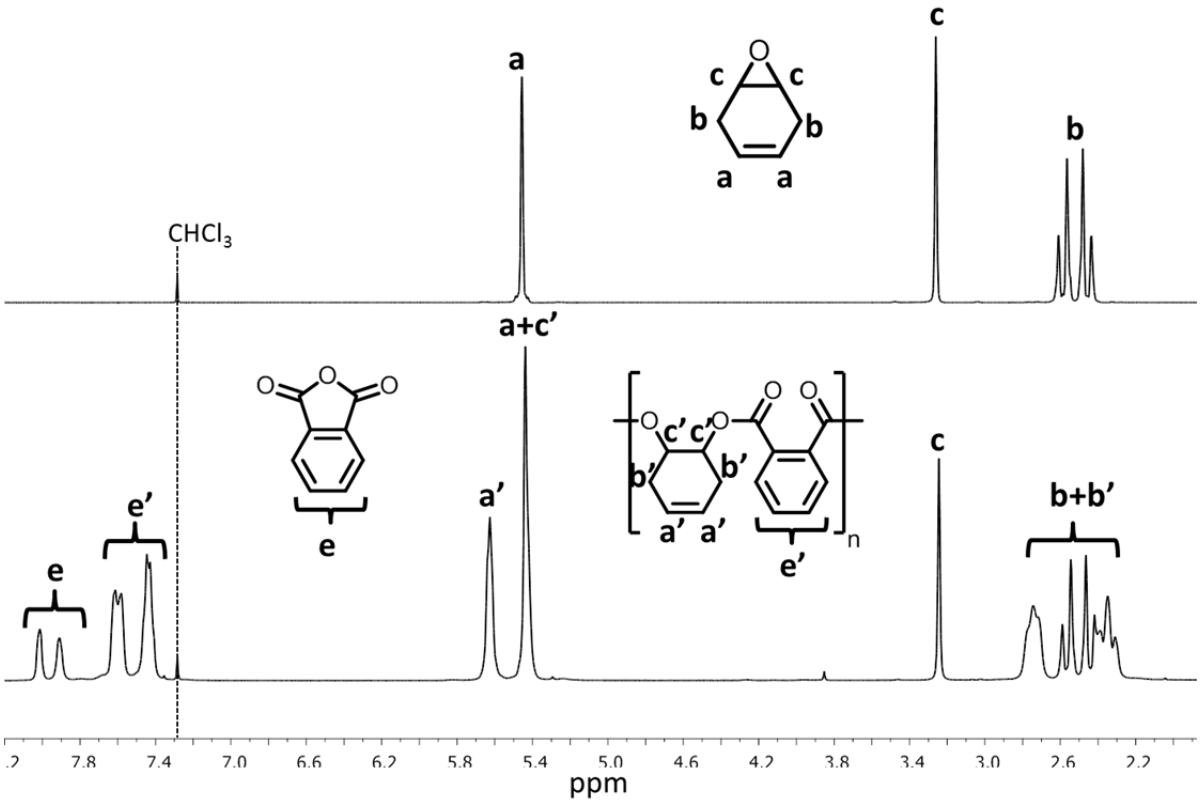


Figure 6.3.6-5: ^{1}H-NMR spectra (400 MHz, $CDCl_3$) of monomer **1.6** (top) and the crude reaction mixture (bottom).

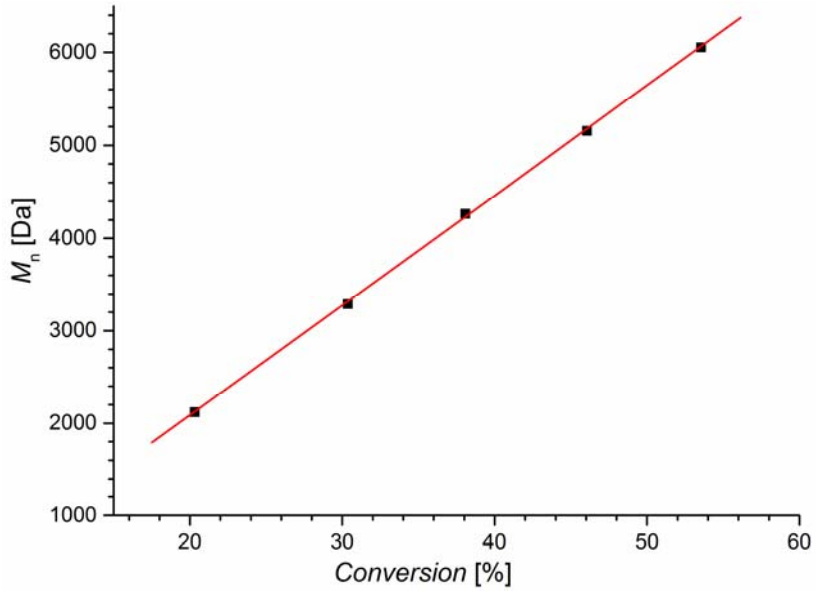


Figure 6.3.6-6: Kinetic investigation of the co-polymerization of monomer **1.6** and PA performed at 110 °C.

7. Abbreviations

ADMET	Acyclic-diene-metathesis
AIBN	2,2'–Azobis(2–methylpropionitrile)
ATR-	Attenuated Total Reflectance
ATRP	Atom Transfer Radical Polymerization
CHD	1,4-Cyclohexadiene
CHDO	Cyclohexadieneoxide
CL	ε-Caprolactone
CM	Cross-metathesis
CHO	Cyclohexeneoxide
Cy	Cyclohexane
DABCO	1,4-Diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	Dichloromethane
DMAC	*N,N*–Dimethylacetamide
DMC	Dimethylcarbonate
DMF	*N,N*–Dimethylformamide
DSC	Differential Scanning Calorimetry
DMSO	Dimethylsulfoxide
EI	Electron-Ionization
EtOH	Ethanol
FAB	Fast-Atom-Bombardment
FAME	Fatty acid methyl ester
GC-MS	Gas chromatography – mass spectrometry
HFIP	Hexafluoroisopropanol
HRMS	High-resolution-mass spectrometry
IR	Infrared
MALDI	Matrix assisted laser desorption ionization
*m*CPBA	*meta*-Chloroperoxybenzoic acid
MeCN	Acetonitrile
MeOH	Methanol
MMA	Methyl methacrylate

Mes-Cl	Methanesulfonyl chloride
wt.%	Weight percentage
Mw	Microwave
NBS	*N*-Bromosuccinimide
NMR	Nuclear Magnetic Resonance
PA	Polyamide
PC	Polycarbonate
PCHC	Polycyclohexanecarbonate
PCL	Poly(ε-caprolactone)
Pd/C	Palladium on carbon
PO	Propyleneoxide
PPN-Cl	*Bis*(triphenylphosphoranylidene)ammonium chloride
Ra-Ni	Raney-Nickel®
ROCOP	Ring-opening copolymerization
ROMP	Ring-opening-metathesis polymerization
ROP	Ring-opening polymerization
SEC	Size exclusion chromatography
SM	Self-metathesis
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TGA	Thermogravimetric analysis
THF	Tetrahydrofurane
TOF	Turnover frequency
ToF	Time-of-flight
UCST	Upper critical solution temperature

8. Bibliography

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