Monomers from Renewable Resources:

C-H Functionalization of Saturated Fatty Acids

Zur Erlangung des akademischen Grades eines

DOKTORS DER NATURWISSENSCHAFTEN

(Dr. rer. nat.)

Fakultät für Chemie und Biowissenschaften

Karlsruher Institut für Technologie (KIT) – Universitätsbereich

genehmigte

DISSERTATION

von

Nicolai Kolb

aus

Berlin-Zehlendorf

Dekan: Prof. Dr. P. Roesky

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

Korreferent: Prof. Dr. C. Barner-Kowollik

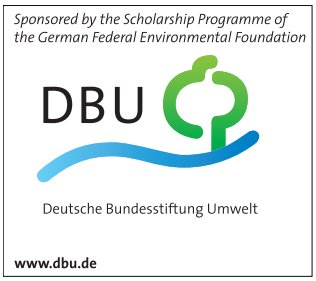
Tag der mündlichen Prüfung: 25.10.2013

Die vorliegende Arbeit wurde von Oktober 2010 bis September 2013 unter Anleitung von Prof. Dr. Michael A. R. Meier am Karlsruher Institut für Technologie (KIT - Universitätsbereich) angefertigt.

Danksagung

Es gibt einige Personen und Institutionen, welche maßgeblich an dem Gelingen dieser Arbeit beteiligt waren. Ohne sie wäre diese Arbeit nicht möglich gewesen.

Ich möchte mich herzlich bei Mike für die Aufnahme in die Arbeitsgruppe, sowie für die Möglichkeit zur eigenständigen Arbeit und das entgegengebrachte Vertrauen bedanken! Des Weiteren möchte ich mich bei allen ehemaligen und aktuellen Mitgliedern der Arbeitsgruppe für das angenehme Arbeitsklima bedanken. Dabei sind vor allem jene Mitglieder der Arbeitsgruppe angesprochen, welche mir in den Projektfindungsphasen entscheidend halfen und mich unterstützten.



Des Weiteren möchte ich der Deutschen Bundesstiftung Umwelt (DBU, www.dbu.de) danken, welche diese Arbeit durch ein großzügiges Promotionsstipendium ermöglichte. Dabei ist besonders Dr. Maximilian Hempel zu nennen, der als mein Betreuer bei der DBU stets ein offenes Ohr und viel Verständnis für neue Vorschläge hatte.

Ebenso möchte ich mich bei dem Deutschen Akademischen Austauschdienst (DAAD, www.daad.de) bedanken, welcher mir durch ein Reisekostenstipendium den Besuch der Konferenz „Sustainable Polymers“ vom 20.-23. Mai 2013 in Safety Harbor, Florida, USA, ermöglichte.

Zuletzt möchte ich meiner Verlobten, Frau Nadine Hein, danken. Ohne ihre bedingungslose und aufopferungsvolle Unterstützung hätte ich vermutlich nie die Kraft, den Ehrgeiz und das Durchhaltevermögen gehabt, diese Arbeit erfolgreich fertigzustellen. Sie hatte maßgeblichen Einfluss auf jeden Moment dieser Arbeit und ich kann nicht ausdrücken, wie unendlich dankbar ich ihr hierfür bin!

Kurzzusammenfassung

Aufgrund der kontinuierlichen Verknappung fossiler Rohstoffe ist es eine der größten Herausforderungen des 21. Jahrhunderts, nicht nur für die Chemie, alternative Rohstoffquellen auf Basis nachwachsender Rohstoffe für alltägliche Gebrauchsgüter zu entwickeln. In diesem Zusammenhang haben sich Fettsäuren als ideale Grundchemikalien für die Synthese von Monomeren und den entsprechenden Polymeren auf Basis nachwachsender Rohstoffen bewährt. Allerdings wurden bisher nahezu ausschließlich ungesättigte Fettsäuren verwendet, da die hier enthaltene C=C Doppelbindung relativ einfach für Derivatisierungen genutzt werden kann.

Das Ziel dieser Doktorarbeit ist es, Derivatisierungen von gesättigten Fettsäuren zu Monomeren und den entsprechenden Polymeren zu entwickeln, zu untersuchen und auszuwerten. Dabei liegt das Hauptaugenmerk auf der *α*-Position der Fettsäureester, da diese Stelle leicht acide ist und entsprechend selektiv angesprochen werden kann. Zusätzlich werden Möglichkeiten zur Darstellung von *ω*-ungesättigten Fettsäuren durch katalytische oder biochemische Methoden untersucht. Diese *ω*-ungesättigten Fettsäuren bieten die Möglichkeit zur Darstellung von *α*,*ω*-Diestern mit ungewöhnlich hohen Kettenlängen von über 30 Kohlenstoffatomen, wobei die daraus resultierenden Polymere hochinteressante Eigenschaften zeigen sollten.

Abstract

Due to the continuous decrease of fossil resources, it is one of today's biggest challenges, not only in chemistry, to develop renewable and sustainable routes towards daily life commodity chemicals. Within this context, fatty acids have been proven to be an ideal platform for the preparation of renewable monomers and polymers. However, so far, unsaturated fatty acids have been used almost exclusively, since their C=C double bonds can be used for derivatizations reactions in a straightforward fashion.

The aim of this doctoral thesis is to develop, investigate and evaluate possible derivatization strategies of saturated fatty acids in order to prepare monomers and the thereof derived polymers. Therefore, the main focus is the *α*-position of the fatty acid esters, since this position is slightly acidic and therefore accessible for selective derivatizations. In addition, possibilities to access *ω*-unsaturated fatty acids *via* catalytic and biochemical methods are investigated. It is important to note that such *ω*-unsaturated fatty acids are of high interest, since they offer the possibility to synthesize *α*,*ω*-diesters with unusual long carbon chains, for instance with more than 30 carbon atoms; consequently, the thus derived polymers should have highly interesting properties.

Table of content

1. Introduction

1.1. Renewable resources in general

The rapid industrial development of the recent past heavily relies on the use of fossil resources, mainly coal and crude oil. The intensive usage of crude oil or coal in power plants and elsewhere is easily explained by the relatively low price of these resources. To date, crude oil and the thereof derived products are among the most important feedstocks for the chemical industry. However, crude oil, as a fossil resource, is a depleting feedstock.

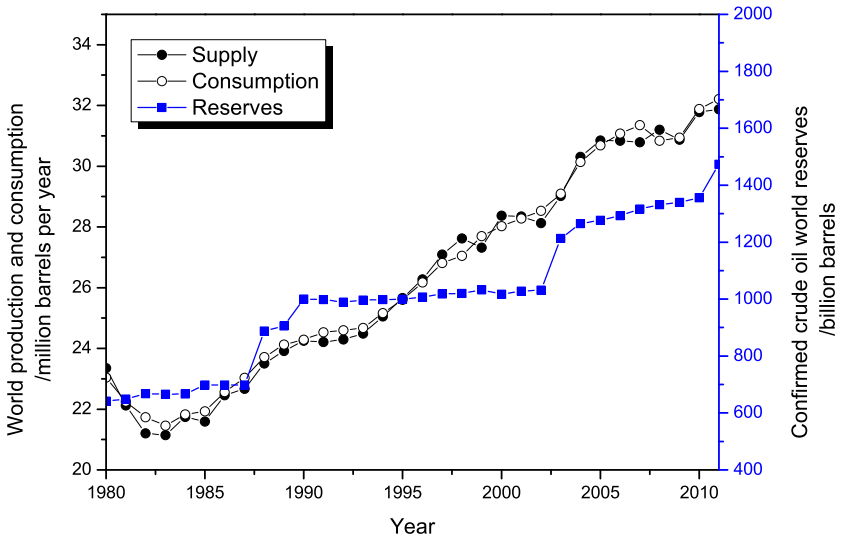
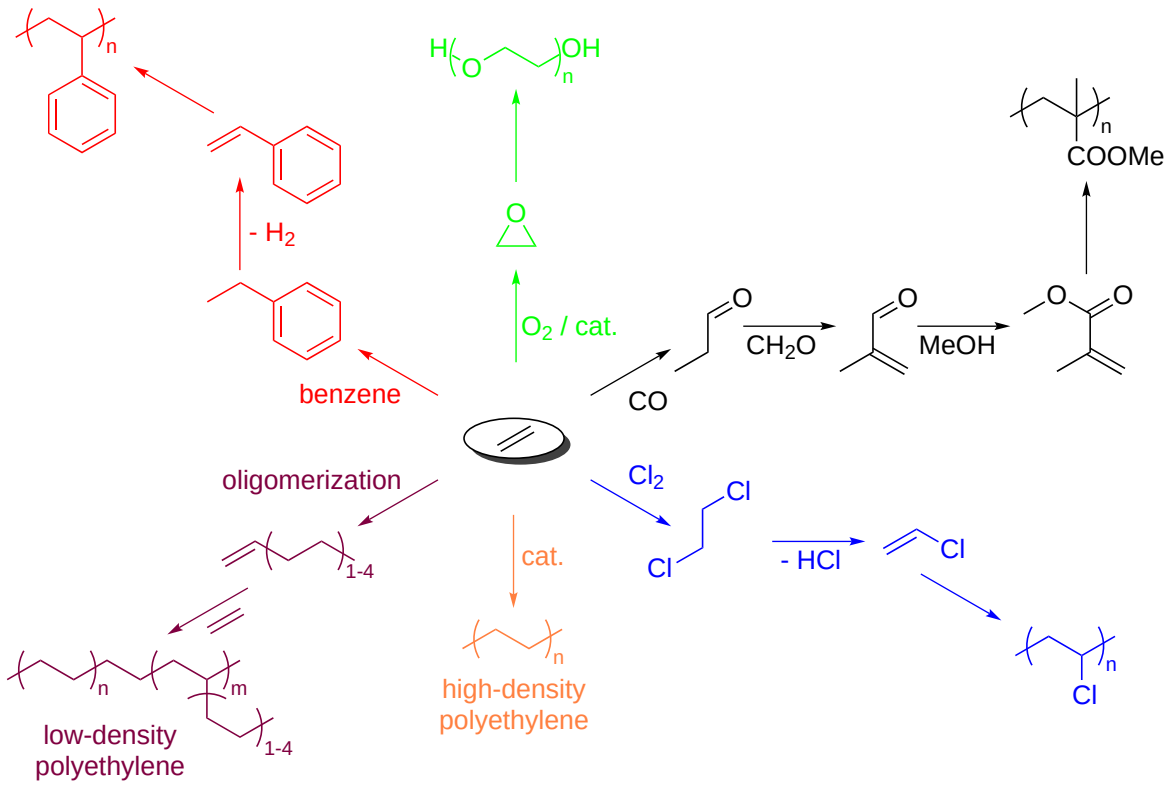


Figure 1 - Annual world supply, consumption and confirmed reserves of crude oil from fossil resources.[1]

Despite the development of new production techniques (today's best example might be the increasing shale oil extraction) and the discovery of new oil reserves (the actual confirmed world reserves are among 1500 billion barrels, compare Figure 1), the oil reserves will be depleted and/or the exploration of crude oil will be too expensive for an economic use within a limited amount of time. Furthermore, due to

the increasing world population and the increasing demand of crude oil, which raised approximately 150 % over the last 30 years (compare Figure 1), the need to overcome the dependence on crude oil will increase continuously. In the context of this thesis, it is important to note where crude oil is applied in the chemical industry.

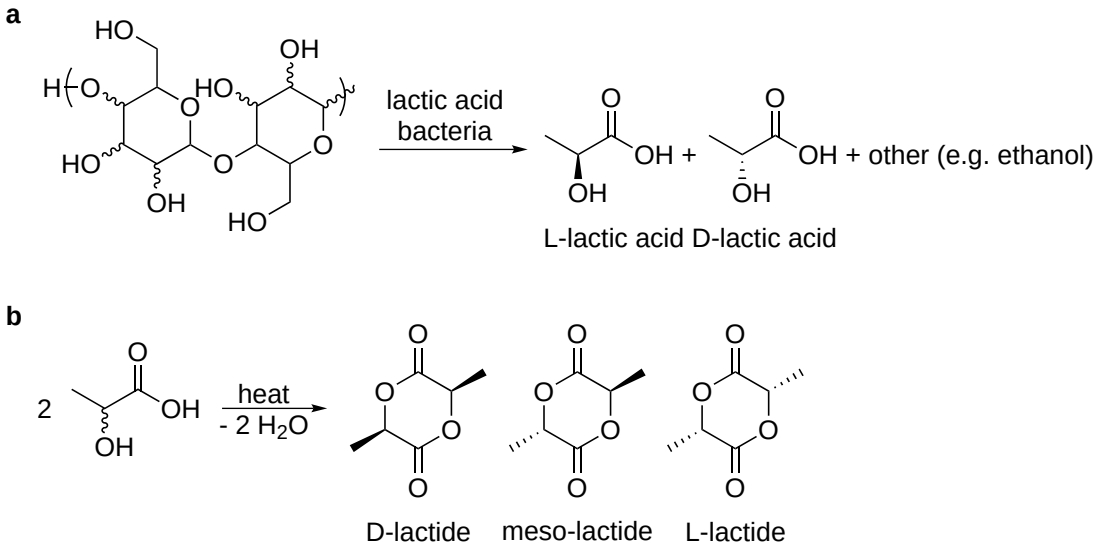
One of the major uses of crude oil is the synthesis of monomers and their respective polymers. For monomer synthesis, the hydrocarbons are usually cracked into small building blocks such as ethylene, acetylene, aromatics, propene, 1,4-butadiene, and others. Afterwards, these simple molecules can be catalytically transformed into the respective monomers in various ways as illustrated schematically for ethylene in Scheme 1.



Scheme 1 - Possibilities for the preparation of monomers and polymers derived from ethylene; schematic idea and reactions adapted from Robert T. Mathers.[2]

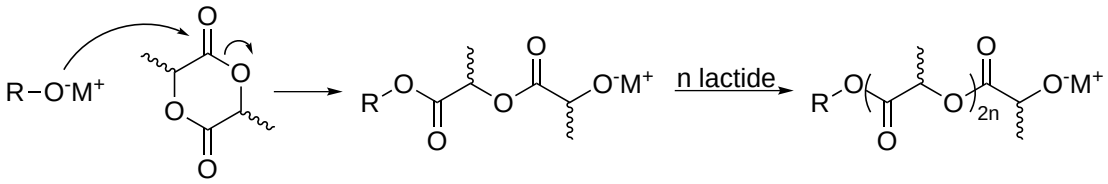
Polymers are widely used in daily life. Since the most common polymers such as poly(ethylene), poly(propylene), poly(vinyl-chloride) or poly(ethylene-terephthalate), are derived from crude oil, there is a strong focus of research on finding renewable alternatives. One possibility to overcome the strong dependence on fossil resources is the substitution of crude oil-based chemicals with renewable, bio-derived compounds. For example, ethanol can be produced by fermentation of carbohydrates, such as cellulose (2nd generation) or starch (1st generation), which is for instance derived from corn.[3-4] In this way, large quantities of bio-derived ethanol are produced with continuously increasing amounts (2000: 17.3 billion liters; 2007: over 46 billion liters).[4] Afterwards, the bio-based ethanol can be dehydrated in order to obtain ethylene[5-6] as a starting material for various transformations (Scheme 1), or it can be used directly as fuel or fuel additive.[7]

However, aside from using bio-derived products in order to substitute fossil resource based chemicals such as ethylene from bio-ethanol, it is far more interesting to directly use products “offered” by nature’s chemical portfolio. In this context, poly(lactic acid) (PLA), a polymer obtained from bio-based lactic acid, which is readily accessible by fermentation of carbohydrate rich feedstocks (e.g. corn starch), represents a valuable and by now industrially feasible model example (Scheme 2a).[8-12]



Scheme 2 - Fermentation of carbohydrates to form lactic acid (a) and its condensation to form lactides (b).

The fermentation of biomass and production of the desired products is accomplished using lactic acid bacteria (LAB). This process can be carried out using different techniques and procedures. It is important to note that, depending on the microorganism used, the L-form, the D-form or a racematic mixture of lactic acid is obtained (Scheme 2a). Afterwards, the obtained lactic acid can be directly polymerized *via* polycondensation. However, only low molecular weight polymers were obtained by this route.[13] Thus, usually first a condensation of two lactic acid molecules to the dimeric 6-membered ring lactide is performed (Scheme 2b). Subsequently, the obtained lactides can be polymerized by ring-opening polymerization (ROP, Scheme 3) using different transition metal complexes as initiators and/or catalysts.[14] Following this route, high molecular weights up to several million Daltons are accessible.



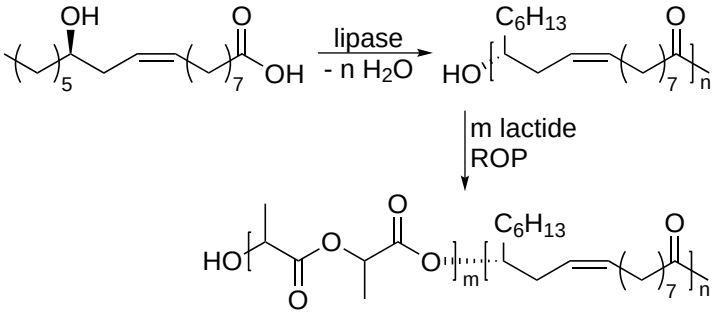
Scheme 3 - Example for the ROP of lactide: Anionic ROP using alcoholates.

In this way, PLA is produced in an industrial scale of several thousand tons per year. For example, Nature Works LLC is running a plant in Nebraska (USA) since 2002 with an annual production of 140.000 metric tons of PLA.[15] However, compared to the annual polymer production of hundreds million tons (available statistics ranges from 140 to 230 million tons per year[8, 16]) based on fossil resources, this amount of PLA is rather low. Furthermore, the relatively high price of PLA (~ 2.2 US$/kg)[8] is a major drawback compared to the cheaper polymers derived from fossil resources.

Additionally, the mechanical properties of PLA are poor, especially because of its brittleness and relatively low elongation at break of typically only 10 %.[17] In order to overcome these problems, intensive research for PLA modification has been carried out. One technique for the selective modification of PLAs mechanical properties is the (ring-opening) copolymerization. By this technique, it is possible to prepare copolymers of PLA with e.g. *ε*-caprolactone, trimethylene carbonate or glycolide, to name only a few examples.[18-19] This copolymerization strategy allows a precise design of the polymer properties, i.e. to achieve a controlled degradation behavior and desired thermal properties.

In one example, a low molecular weight co-polymer of PLA and *ε*-caprolactone was modified on its terminal hydroxyl groups using methacrylic anhydride.[20] Subsequently, thermal cross-linking leads to polymers with very good elastic

properties and an elongation at break of up to 350 %. In another approach, *α*,*ω*-dihydroxy-poly(isoprene) was employed as initiator for the ROP of lactide to prepare a PLA-poly(isoprene)-PLA triblock copolymer.[21] The derived triblock copolymers exhibited greatly improved mechanical properties in terms of elongation and elastomeric behavior. Furthermore, PLA was copolymerized with poly(ricinolenic acid) (PRA) bearing a secondary OH-group as end group where PLA can be grafted-onto *via* ROP (Scheme 4). By this method, diblock copolymers were prepared which showed improved tensile strength in the order of one magnitude compared to neat PLA.[22]



Scheme 4 - Preparation of PRA-PLA copolymer.

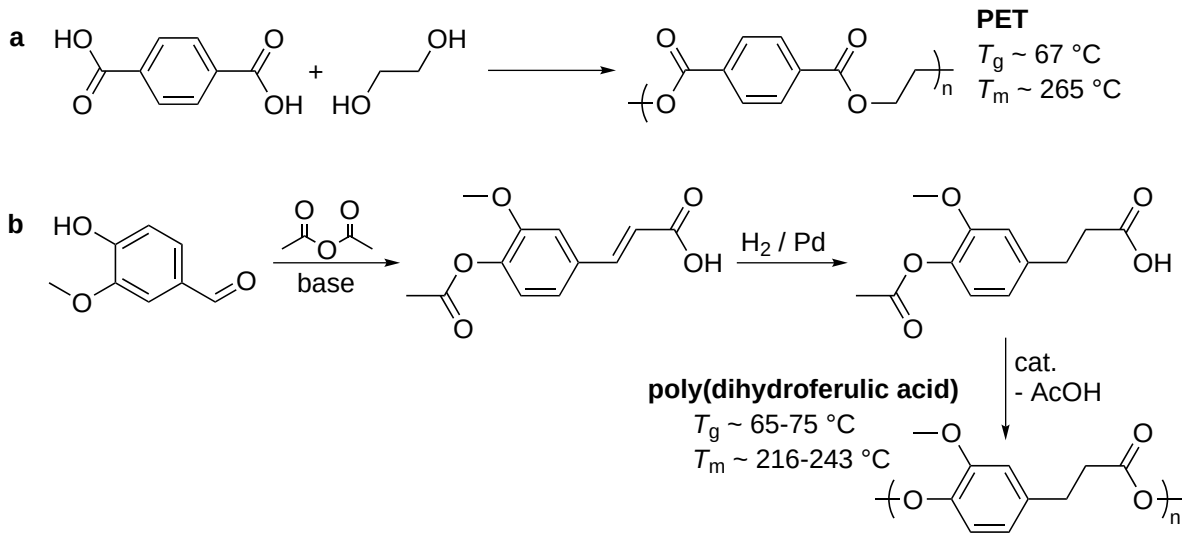
In order to modulate the hydrophilicity of PLA, lactide was copolymerized with poly(ethylene glycol) (PEG). However, PEG and PLA underwent phase separation during direct polymerization. Thus, PLA diols and PEG diacids were reacted by CDI coupling in order to prepare the respective diblock copolymers.[23]

Another technique that can be employed to enhance the properties of PLA is blending. Herein, different plasticizers were tested to modulate the properties of PLA, for instance glycerol, PEG, PEG-monolaurate or even PLA oligomers, whereas PEG (M_w ~ 400 Da) was the most promising one.[24] However, nearly all these blends suffered from aging problems such as diffusion of the plasticizers out of the polymeric

structure during the storage period was observed. Further enhancement of PLA properties can be achieved by coating. For instance, PLA was coated with PEG by entrapment at the polymeric surface.[25] As a result of this surface treatment, the polymer surface became less hydrophobic and was able to undergo cell interactions.[26] Using this technique, PLA was also coated with poly(aspartic acid) as well and the resulting polymer displayed an enhanced cell-affinity.[27]

In general, PLA is a promising example how nature-derived, renewable chemicals can be successfully used to prepare commodity polymers. Of course, several challenges have to be overcome in regards of PLA to substitute fossil-based polymers and to improve its mechanical properties. However, PLA has found its way to the market and is used for various industrial applications. The main advantage of PLA is its bio-degradability and that all degradation products are non-toxic. Therefore, it is an ideal material for packing applications, for example for food.[28] Furthermore, because of its bio-compatibility, PLA and PLA copolymers found great attention in medical applications, such as drug delivery or in orthopedic applications.[29-31]

Another interesting concept to use nature's chemical portfolio has been presented by Miller and coworkers, who aimed for a renewable substitute for poly(ethylene-terephthalate) (PET).[32]

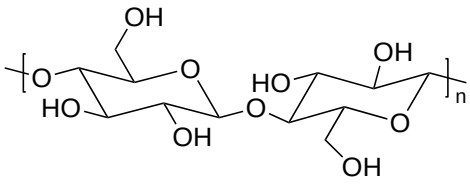


Scheme 5 - PET (a) and the preparation of poly(dihydroferulic acid) from vanilin (b).

In this approach, vanillin was used as renewable starting material, which can be obtained from lignin.[33-34] The preparation of the monomer was carried out using a straightforward transformation strategy (Scheme 5). The thus prepared monomer can be polymerized using different catalysts (i.e. zinc acetate) to obtain polymers of moderate to good molecular weight of up to M_n ~ 18 kDa. Interestingly, the thermal properties of the respective polymers are very close to these of industrially produced PET (compare Scheme 5). Again, this example illustrates how fossil resource based polymers can be substituted by polymers derived from nature's chemical portfolio.

Another interesting example, where nature's chemical portfolio is used for polymer science, is the derivatization and application of cellulose. Cellulose is a linear high molecular weight polymer consisting of β(1-4)-linked D-glucose units.[35] The annual production of cellulose by plants is about 10^{12} tons, which makes cellulose together with chitin (estimated annual production 10^{10}-10^{12} tons/year)[36] the most abundant polymer on the globe.[37] Cellulose has three hydroxyl groups per repeating unit, which results in very interesting properties of the polymer. For instance, cellulose cannot be

melted nor is it soluble in common organic solvents. The derivatization of cellulose is therefore very challenging. However, to substitute fossil-based chemicals, cellulose gains a lot of interest in recent research.

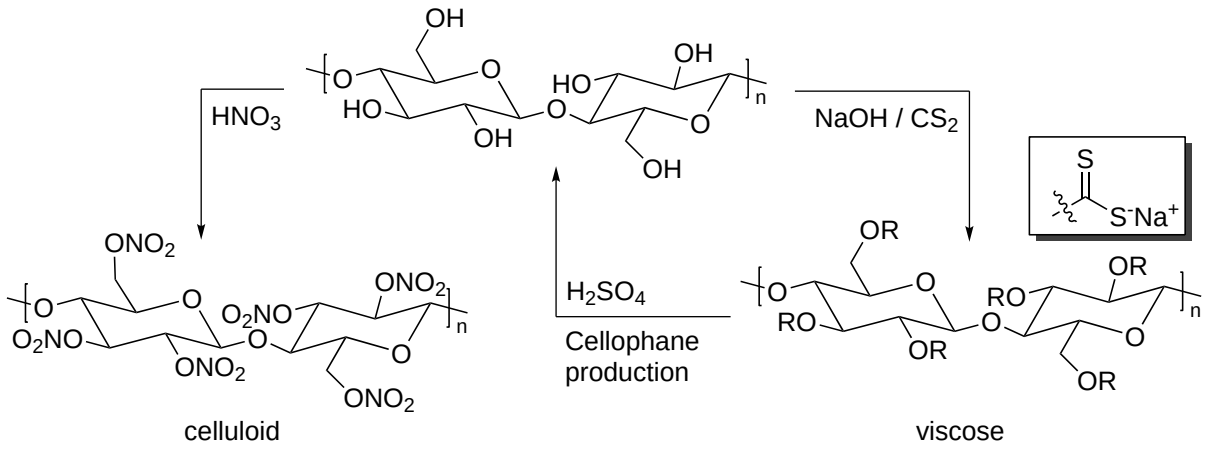


Scheme 6 – Structure of cellulose.

For example, cellulose offers manifold opportunities for the preparation of monomers, which are normally obtained from fossil resources. Most commonly, cellulose is depolymerized, for example by supercritical water, to yield D-glucose.[38] These D-glucose units can afterwards be modified to numerous different platform chemicals, which has been recently reviewed.[16]

However, more interesting is the direct utilization of the compounds obtained by nature. In this context, many derivatives of cellulose are known. Two of them are known and used since the 19th century, namely “Celluloid” and “Cellophane”. Celluloid is considered to be the first thermoplastic produced on an industrial scale and is prepared by nitration of cellulose. However, since celluloid is highly flammable, it is not used anymore. Another long-known process is the regeneration of cellulose by the “viscose” process. Herein, wood-derived cellulose is treated with sodium hydroxide and carbon disulfide to prepare the so-called viscose, which can be transferred to a precipitation bath, containing diluted sulfuric acid, to regain high-purity cellulose. The major drawback of this process however, is the use of toxic chemicals in high amounts, the high costs and the large amounts of by-products

formed. Apart from this, films and fibers made of cellophane are common packaging materials.[37]

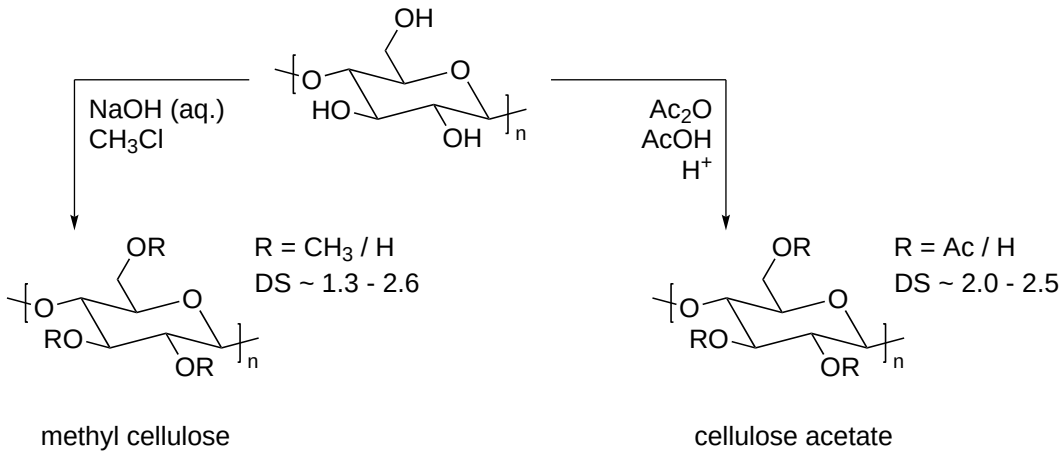


Scheme 7 - Preparation of celluloid and cellophane derived from cellulose.

Other long-known and chemically simple cellulose derivatives are cellulose acetate and methyl cellulose (Scheme 8). Cellulose acetate for example is produced by reacting cellulose with acetic anhydride in concentrated acetic acid in order to form the ester. As a result of the esterification, the polymer becomes soluble in common organic solvents. Furthermore, because of the lower amount of free hydroxyl groups, cellulose acetate can be melted and therefore processed by injection molding. Nowadays, cellulose acetate is a widely used thermoplastic material which can be found in many daily-life products, for example in clothing as fibers or as films for photography where it substituted celluloid, because it is hardly flammable.

The last example of cellulose derivatives within this thesis is methyl cellulose. Methyl cellulose can be prepared from cellulose in a basic solution by the reaction with methyl chloride. Normally, the degree of substitution (DS) varies from 1.3 to 2.6 where methyl cellulose with a low DS is well-soluble in cold water. With an increase of the DS, the water solubility is decreased but enhanced for several organic

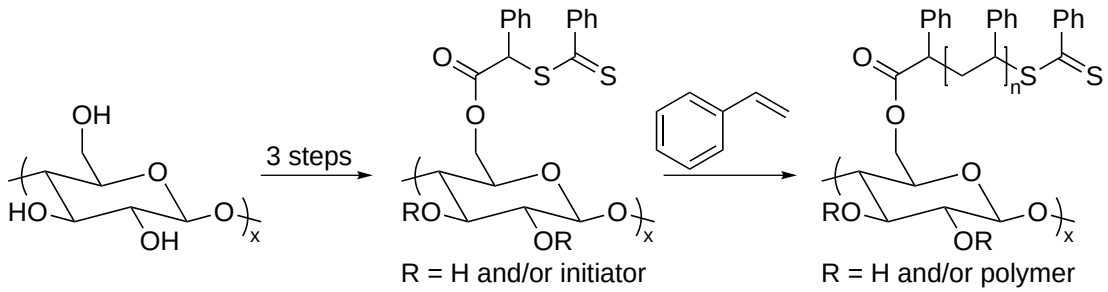
solvents. Because of the hydrophilic OH-groups and the non-polar methyl-ethers, methyl cellulose has amphiphilic properties and therefore, it is widely used as thickener or suspender, for instance in glues and paints. Furthermore, methyl cellulose is used to enhance the viscosity of daily-care products or medicines.



Scheme 8 - Methyl cellulose and cellulose acetate prepared from cellulose.

Moreover, the modification of cellulose by grafting-onto and grafting-from approaches is of great interest. For this purpose, initiators can be introduced onto the cellulose. Usually, this is achieved by selective esterification or etherification of a hydroxyl group of the glucose repeating units. A recent review summarizes the synthetic possibilities for selective modifications of the different hydroxyl groups.[39] After the selective introduction of the initiator, a controlled polymerization reaction, such as the ROP or atom transfer radical polymerization (ATRP) can be carried out. Recently, these reactions to selectively modify cellulose have been reviewed as well.[40] Scheme 9 illustrates a grafting-from polymerization of styrene employing the introduced dithioester as an chain transfer agent for a reversible addition fragmentation chain transfer (RAFT) polymerization.[41] The underlying principle of this approach is representative for all other grafting-from reactions. Only grafting-from approaches by ROP, for example of ε-caprolactone or lactide, can be achieved without a previously

introduced initiator. In this case, the hydroxyl groups of the glucose repeating units can directly initiate the ROP, which has been shown for several examples, where sometimes also free initiators were used to support the ROP.[42-43]



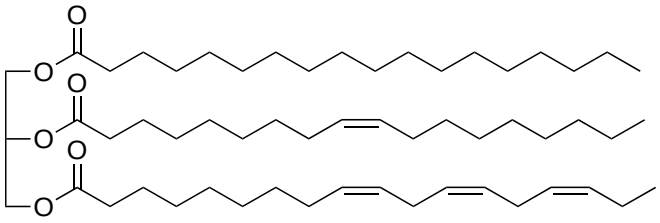
Scheme 9 - Grafting of poly(styrene) onto cellulose by RAFT.

In principle, countless modifications of cellulose are conceivable using such grafting-onto approaches. Thereby, the range of possible applications varies from already-used packaging materials to more complex “smart” materials such as drug carriers[44-46] or physical sensors[47-48] which are thinkable but not yet industrially applied.

In conclusion, the presented examples clearly illustrate the great potential of the different feedstocks derived from nature’s chemical portfolio. Another highly interesting class of renewable and bio-based compounds are fatty acids, which will be discussed in the next chapter.

1.2. Industrial use of fatty acids

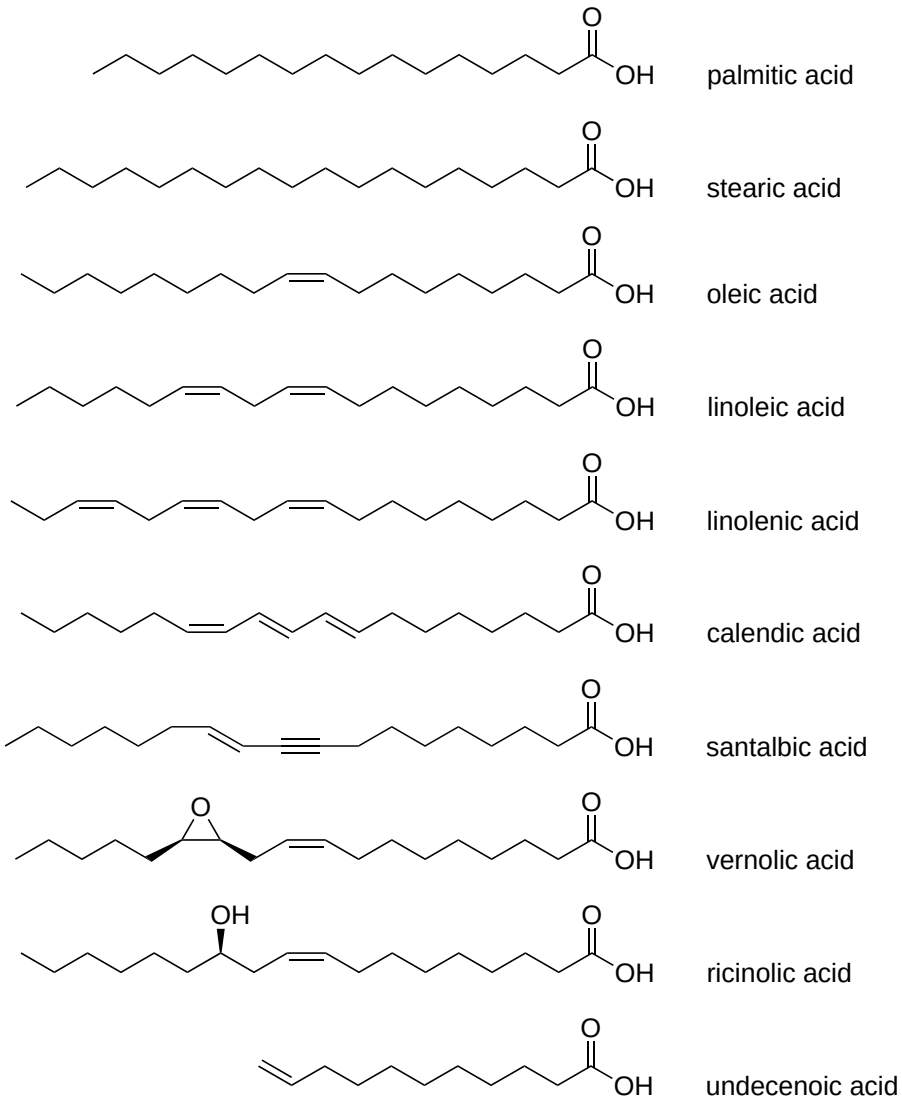
Fatty acids are among the most frequently used renewable resources with an annual world production of more than 160 Mt,[49] where the main share of this production is for food and only a limited amount is used for industrial processes. Fatty acids occur in nature as plant oils and animal fats, where they are bound on glycerol as triglycerides. Such triglycerides usually contain a mixture of different fatty acids (Scheme 10).



Scheme 10 - Example for a naturally occurring plant oil with three different fatty acid units; stearic acid (top), oleic acid (middle) and linolenic acid (bottom).

In general, fatty acids can be divided in two main categories: saturated and unsaturated fatty acids. For saturated fatty acids, the molecule consists of the polar carboxylic acid functional group and a non-polar, most often linear carbon chain of varying length, bearing no other functional group. The most common examples of saturated fatty acids are palmitinic (C_{16}) or stearic (C_{18}) acid, which can be found for example in cacao butter. For unsaturated fatty acids on the other hand, the molecule contains at least one C=C double bond within the carbon chain. Oleic acid might be the best known unsaturated fatty acid having a *cis*-configured double bond at the $C_{9=10}$ position (Scheme 11). However, there are numerous unsaturated fatty acids having multiple double bonds (linoleic / linolenic acid), conjugated double bonds (for example calendic acid) or triple bonds (santalbic acid). Furthermore, fatty acids can be functionalized with an epoxide (vernolic acid) or a free hydroxyl group (ricinolic

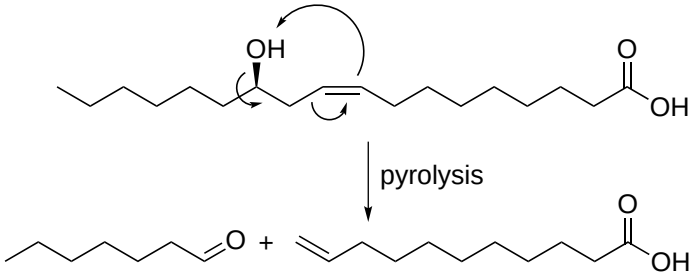
acid). It is noteworthy that this OH-group naturally occurs enantiopure and that these fatty acids can be considered as a valuable chiral feedstock available on a multi-ton scale for a considerably low price. An overview of different saturated and unsaturated fatty acids is given in Scheme 11.



Scheme 11 - Overview of different saturated and unsaturated fatty acids.

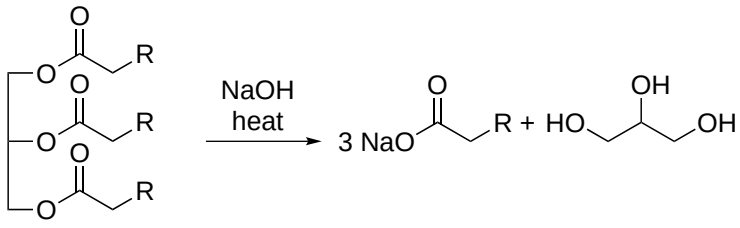
A fatty acid of high interest for polymer science is 10-undecenoic acid, which can be derived from ricinolic acid, the main fatty acid of castor oil.[50] 10-Undecenoic acid can be obtained by pyrolysis of ricinolic acid at high temperatures, leading to the desired product and a stochiometric amount of heptanal as by-product (Scheme 12). The

unique feature of 10-undecenoic acid is the terminal double bond within the carbon-chain, which offers manifold derivatization possibilities. For example, the French company Arkema (www.arkema.com) uses castor-oil derived 10-undecenoic acid for the production of 11-aminoundecanoic acid, an AB-monomer for the preparation of fully renewable polyamide 11 (PA 11).[51]



Scheme 12 - Preparation of 10-undecenoic acid by pyrolysis of ricinolic acid.

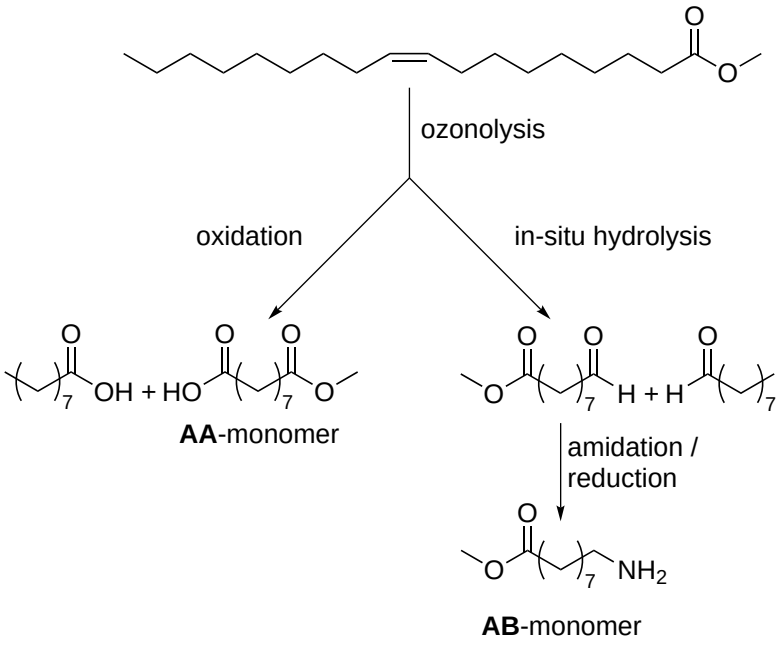
Besides the production of PA 11 from 10-undecenoic acid, fatty acids find manifold applications in the chemical industry. Most often, fatty acids are used for the production of waxes, detergents, lubricants and cosmetics because of their amphiphilic properties. The probably best known and easiest modification is the preparation of soaps from natural oils by basic saponification, yielding the fatty acid salts and glycerol as by-product (Scheme 13).



Scheme 13 - Saponification of plant oils with sodium hydroxide.

Other transformations carried out on an industrial scale are the conversion of fatty acids to the respective fatty alcohols or fatty amines by catalytic hydrogenation reactions. These compounds find applications as detergents, lubricants or also as coatings.

Another industrially applied derivatization process of unsaturated fatty acids, for example methyl oleate, is the cleavage of the double bond by ozonolysis, which yields either *α*,*ω*-diesters or *α*-ester-*ω*-aldehydes, that can be further modified. One possible product is an *ω*-amine for the preparation of polyamides (Scheme 14).[52]



Scheme 14 - Monomers derived from ozonolysis of methyl oleate.

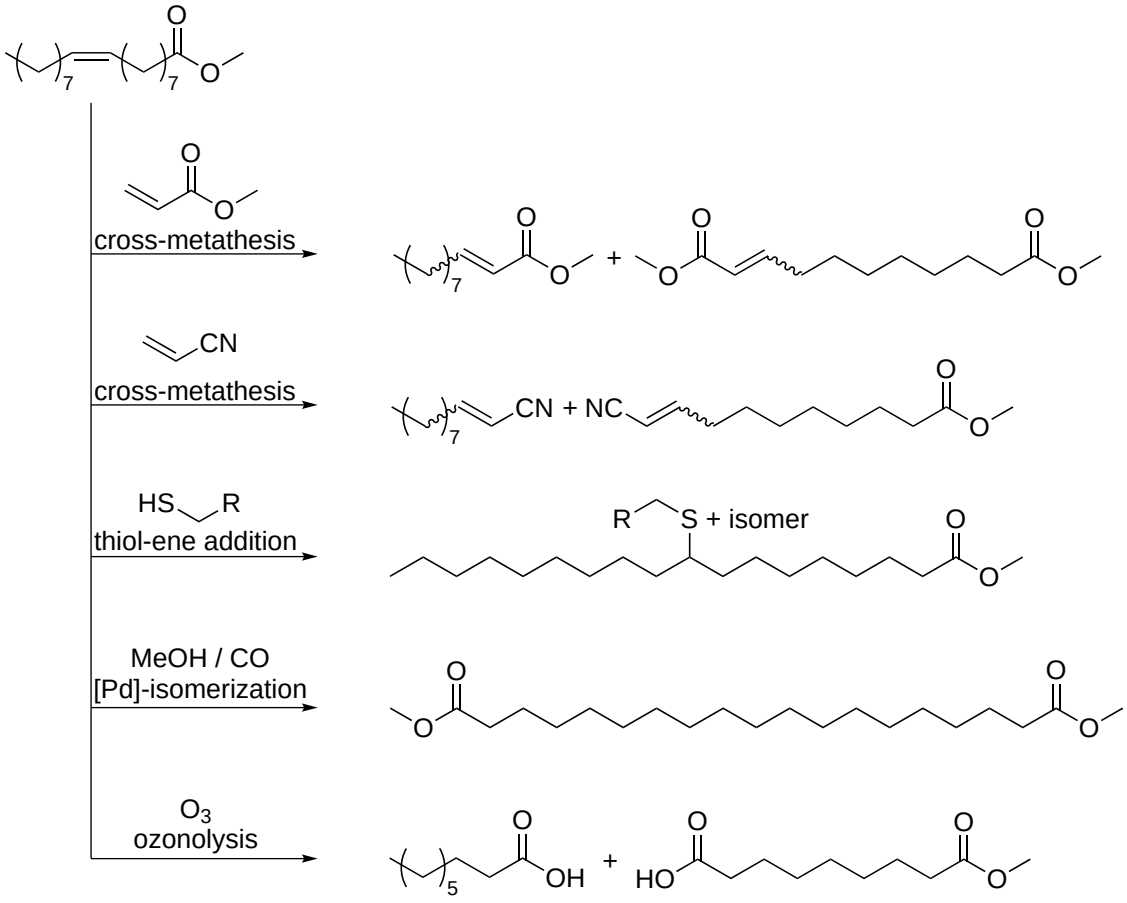
In general, beside these given industrially applied transformations, many other derivatizations of fatty acids towards renewable monomers are possible, which have not found use in the chemical industry, yet. A short overview of the latest developments in the functionalization of unsaturated fatty acids towards renewable monomers is given in the next section, chapter 1.3.

1.3. Monomers derived from fatty acids: State of the art

Numerous reports are available on the selective derivatization of fatty acid methyl esters (FAMEs) to obtain sustainable monomers and the thereof derived polymers. However, since the double bond is usually used for these derivatizations, mainly unsaturated fatty acids were investigated. Herein, most of the recent derivatizations of unsaturated FAMEs are performed, employing thiol-ene additions and olefin (cross-) metathesis reactions. Furthermore, isomerization reactions with subsequent transformations were frequently reported for unsaturated fatty acids. Since many recent reviews give an excellent overview of the numerous modification opportunities of unsaturated FAMEs towards sustainable monomers, only some basic and important reaction types for these transformations of unsaturated fatty acids are described in this chapter. On the other hand, only very few modifications for saturated fatty acids towards monomers and polymers are known, because the derivatization possibilities of saturated fatty acids are considerably limited. Since this thesis focuses on the derivatizations of saturated fatty acids, a more detailed overview of the known reaction possibilities of saturated fatty acids will be given in the further sections, chapters 1.3.2-1.3.4.

1.3.1. Monomers for polycondensations derived from unsaturated fatty acids

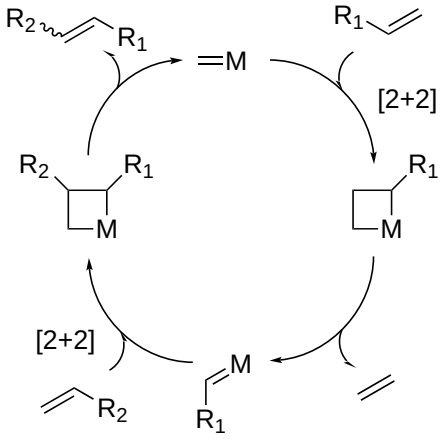
As already mentioned, various possibilities are known for the derivatization of unsaturated FAMEs. A short overview of a few reaction possibilities for methyl oleate is given in Scheme 15. Obviously, the double bond is crucial for the shown derivatization reactions towards sustainable monomers.



Scheme 15 - Overview of reaction possibilities for methyl oleate.

One of the most frequently used reaction for the derivatization of unsaturated FAMEs is the olefin (cross-) metathesis reaction. The use of olefin metathesis for efficient modifications of unsaturated fatty acids has been more deeply investigated after the development of the metathesis catalysts by Schrock and coworkers as well as Grubbs and coworkers, which display a great tolerance towards many functional

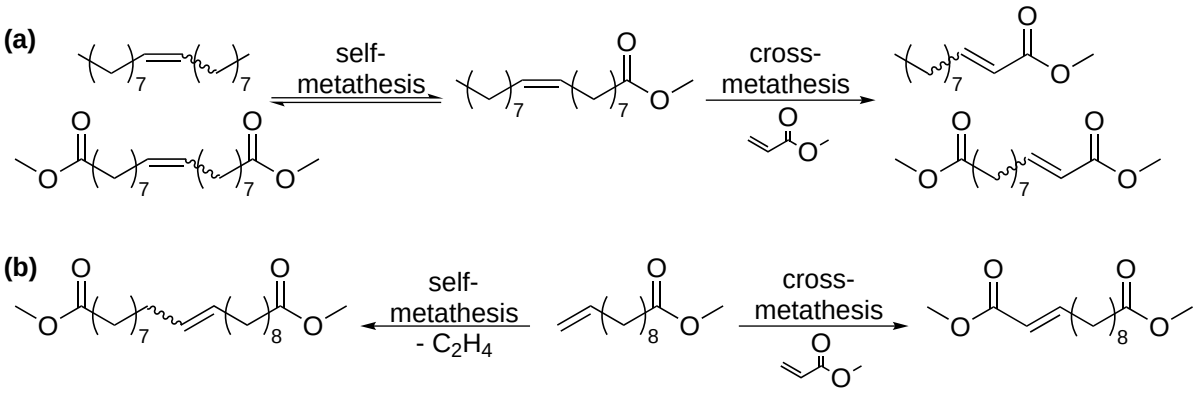
groups.[53-54] Such catalysts feature a M=C double bond (metal alkylidene) which, upon exposure towards olefins, forms a 4-membered ring by a [2+2]-cycloaddition.[55-56] This intermediate can subsequently undergo a cycloreversion to form either the starting material or a new metal alkylidene which can react again with an olefin in a [2+2]-cycloaddition. Another cycloreversion leads to the release of the metathesis product and the initial active species is recovered. However, it is noteworthy that all of these steps are in equilibrium. Because of this, it is important to selectively remove side-products (such as ethene) from the metathesis reaction.



Scheme 16 - Schematic mechanism of the olefin-metathesis reaction by Chauvin.[55]

In this context, two different types of metathesis reactions are important: the cross-metathesis reaction and the self-metathesis reaction. For the cross-metathesis reaction, at least two different olefins are used. Employing two different types of olefins (for example electron-rich and electron-deficient), it is possible to shift the equilibrium of the reaction and selectively form one defined product.[57] In this way, it is possible to selectively synthesize *α*,*ω*-diesters from two renewable platform chemicals, namely methyl oleate and methyl undec-10-enoate, in high yields and a very good selectivity (Scheme 17).[58] For the self-metathesis reaction on the other hand, such selectivity is not obtained if, for example, methyl oleate is employed. This

is because the metathesis-reaction relies on an equilibrium and in the self-metathesis reaction of methyl oleate, none of the self-metathesis products can selectively be removed to shift this equilibrium.[59] Thus, a statistic mixture of products is obtained. This problem was overcome by using oleic acid where, after self-metathesis, the produced diacid precipitates in *n*-hexane and is removed from the equilibrium.[60] However, if methyl undec-10-enoate is employed for the self-metathesis, ethylene is formed as by-product and can be removed easily during the reaction, which leads to the C_{20} diester as desired product in good yields and high purity.[59, 61]

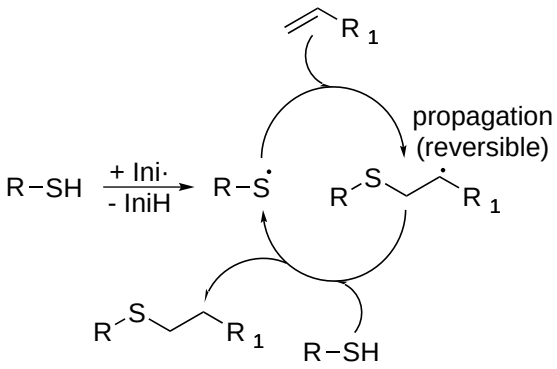


Scheme 17 - Metathesis reactions of methyl oleate and methyl undec-10-enoate.

Very interesting (cross-) metathesis reactions with e.g. allyl chloride[62] or acrylonitril[63] allow an efficient synthesis of AB-type monomer precursors, which can be used for the preparation of bio-based polyamides. Furthermore, it is possible to perform the cross-metathesis reaction in an ethylene atmosphere in order to prepare *ω*-unsaturated fatty acids and *α*-alkenes.[64] Such *ω*-unsaturated fatty acids are highly interesting substrates for the preparation of monomers similar to 10-undecenoic acid, which has been discussed before. The ethenolysis can also be combined with an isomerization of the double bond within the chain employing a palladium catalyst and an appropriate ligand to obtain a statistical distribution of *ω*-unsaturated FAMEs.[65] The olefin metathesis reaction can furthermore be applied as a polymerization

technique for *α*,*ω*-unsaturated compounds, which are readily accessible from 10-undecenoic acid or even from triglycerides of 10-undecenoic acid.[66-68] For a detailed overview of the possibilities to derivatize FAMEs *via* olefin metathesis, several reviews have been published very recently.[59, 69-70]

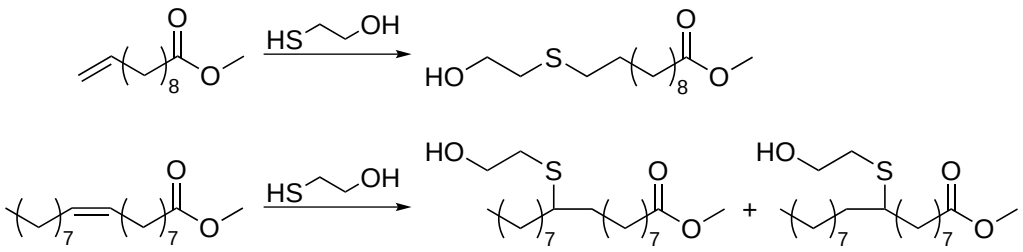
Another technique for the selective and highly efficient derivatization of fatty acids is the thiol-ene addition reaction. It is long known that thiols can add to double bonds *via* a radical mechanism leading to anti-Markovnikov products.[71] The thiol-ene addition follows a two-step radical mechanism (Scheme 18).[72-73] First, it is important to form the thiyl-radical from the thio-compound. This can be achieved by various initiators such as azo-compounds or UV-initiators. However, it has been shown that the radicals can form even without initiator.[74] After the radical formation, the thiyl radical can add to the C=C double bond, yielding a carbon radical. It is important to note that this step is reversible and leads to *cis/trans*-isomerization of internal double bonds. The second step of the thiol-ene addition is the reaction of the carbon radical with a second thiol compound which irreversible leads to the desired product and the formation of another thiyl radical which can propagate the radical reaction.



Scheme 18 - Mechanism of the radical thiol-ene addition reaction.

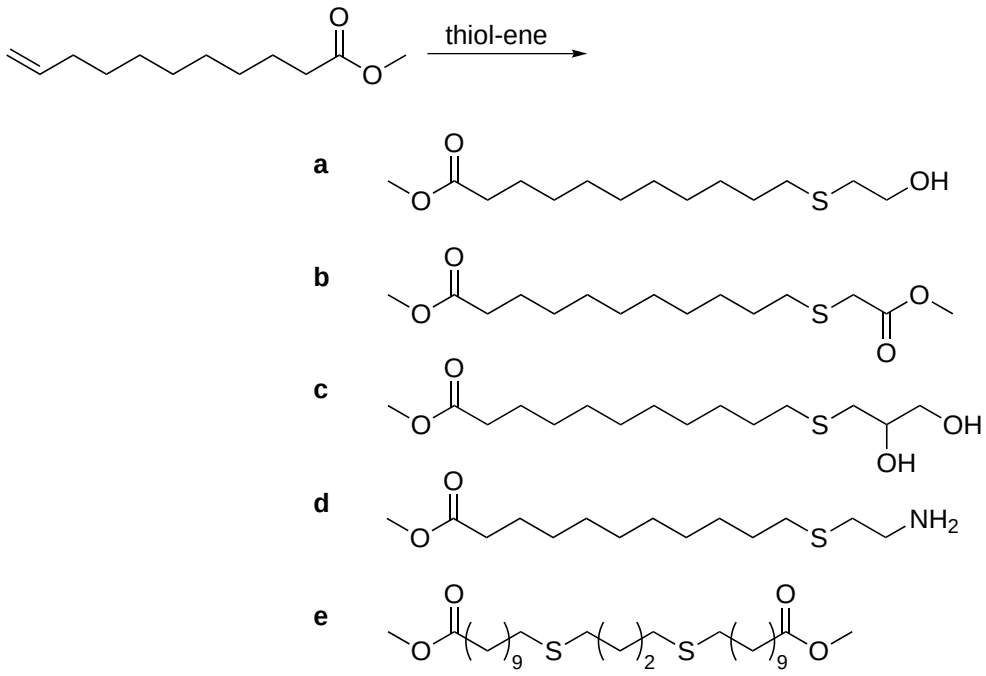
The thiol-ene reaction itself is a highly efficient reaction exhibiting great tolerance towards functional groups. The reaction usually can be carried out under atmospheric conditions without taking any intensive precautions such as inert gas atmosphere. Furthermore, the possibility to perform the thiol-ene reaction under very mild and solvent-free conditions makes it a highly interesting synthetic tool for very efficient transformations of fatty acids. The thiol-ene addition to terminal double bonds is often considered as a “click” reaction,[75] although this opinion is not consistently accepted. However, because of its atom-efficiency, the thiol-ene reaction has found broad application in the preparation of fatty acid derived monomers,[66, 73, 76-79] the selective functionalization of polymers[80-84] as well as for the synthesis of dendritic structures.[85-87]

In the context of monomer preparation *via* thiol-ene additions, the main focus was drawn on methyl undec-10-enoate having a terminal double bond. This is because terminal double bonds are more reactive in thiol-ene addition reactions than internal ones. Also, by applying the thiol-ene addition reaction to methyl undec-10-enoate, a *ω*-functionalized ester can be prepared, which can be used for the synthesis of linear polymers (Scheme 19). In contrast, if the thiol-ene addition reaction is applied to methyl oleate which has an internal double bond, a branched monomer is obtained and the resulting polymers would contain aliphatic side-chains. Such aliphatic side-chains can act as softeners in the resulting polymer, which limits their thermal properties. Furthermore, the thiol-ene addition reaction to internal double bonds results in a 1:1 mixture of two regioisomers and requires an excess of the reacting thiol (Scheme 19).[73]



Scheme 19 – Thiol-ene addition of mercaptoethanol to methyl undec-10-enoate and methyl oleate.

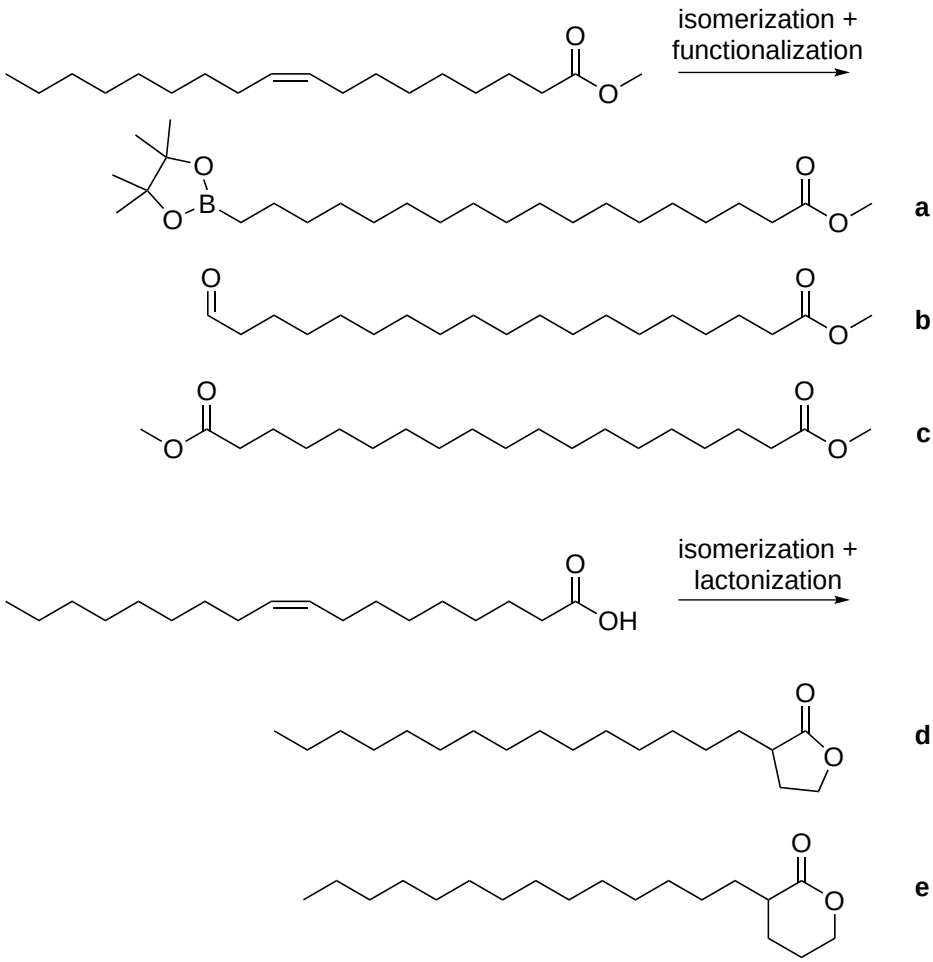
The scope of possible monomers derived from fatty acids and thiols is enormous. This chapter features only a short overview of the thiol-ene addition reaction of methyl undec-10-enoate to prepare renewable monomers (Scheme 20). However, polymerizations *via* thiol-ene addition reactions or post polymerization modifications are also possible. For a more detailed overview, several reviews have been published recently covering the modification of fatty acids by thiol-ene addition reactions in all aspects.[73, 88]



Scheme 20 - Thiol-ene modifications of methyl undec-10-enoate.

For the preparation of monomers from methyl undec-10-enoate *via* thiol-ene addition, it has been shown that mercaptoethanol can be utilized in order to synthesize an AB-type monomer (Scheme 20**a**), which can be directly polymerized with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as organocatalyst.[79] In the same report, it has been shown that by thiol-ene addition with mercapto-thioglycolate, an *α*,*ω*-diester can be prepared as an AA-type monomer (Scheme 20**b**) as well as an AB_2-type monomer by employing thioglycerol (Scheme 20**c**). Furthermore, the thiol-ene addition of cysteamine hydrochloride leads to an AB-type monomer (Scheme 20**d**), which was utilized for the preparation of renewable polyamides.[76] Moreover, it has been shown that methyl undec-10-enoate can be reacted with 1,4-butanedithiol to prepare a long-chain diester (Scheme 20**e**)[76] and the respective polymers, to name only a few examples.

Another interesting concept for the preparation of monomers derived from unsaturated fatty acids is the isomerization of the internal double bond and a selective subsequent reaction at the *ω*-position (Scheme 21). The double-bond isomerization relies on an equilibrium, which is shifted by a selective reaction only at the *ω*-position.



Scheme 21 - Products derived from isomerization reactions and subsequent modifications of methyl oleate.

In this context, it has been shown that methyl oleate can be selectively borylated at the *ω*-position by isomerization with an iridium catalyst and subsequent hydroboration using pinacolborane (Scheme 21**a**) in approximately 50 % yield.[89] The respective product offers many derivatization possibilities. Another isomerization transformation was achieved with a simple rhodium catalyst under a CO/hydrogen atmosphere to yield the *ω*-aldehyde of methyl oleate (Scheme 21**b**) in good selectivity.[90] However, for this approach, only a limited yield of 26 % was achieved for methyl oleate. Although the respective product is highly interesting since it can easily be modified to the amine or alcohol functionalized FAME, the low yield limits the possible applications of this reaction. A far more efficient reaction in terms of yield

and selectivity is the preparation of diesters *via* isomerization transformations of unsaturated fatty acids such as methyl oleate (Scheme 21**c**). The diesters were obtained by a methoxycarbonylation employing a palladium catalyst and the bulky phosphor ligand (1,2-*bis*[(di-*t*-butylphosphino)methyl]benzene).[91-94] Long-chain non-branched *α*,*ω*-diesters with C_{19} (from methyl oleate) or C_{23} (from methyl erucate) chains were obtained in yields of more than 70 % and a high purity after straightforward recrystallization from methanol.[92] For this reaction, it has been shown that the bulky palladium catalyst has a high selectivity for the methoxycarbonylation of *α*-olefins since only a small amount of branched products was obtained. Generally, the branched products can range from *ω*-1 esters to the malonate derivatives.[95] In addition, if fatty acids with two or more double bonds were used, the residual double bonds were hydrogenated after the methoxycarbonylation reaction yielding only one single product. The respective diols were obtained by reduction with lithium aluminium hydride to have the monomers in hands to prepare the corresponding 19:19 and 23:23 polyesters. Additionally, the diamines, which were prepared from the diols, were used to prepare the respective polyamides by polycondensation reactions.[92] These long-chain polymers display very interesting thermal properties. The long-chain polyamides have a melting transition of approximately 155 °C, which is relatively low for a polyamide but can be explained with the high content of non-polar carbon-chains compared to the polar amide-groups, which mainly influence the thermal properties by hydrogen bonding. On the other hand, the long-chain polyesters have relatively high melting transitions of more than 100 °C, which is comparable to the melting transitions of common thermoplastics. It has been shown that the melting point of the polyesters can be increased with longer aliphatic chains, since a higher *ratio* of methylene groups per ester group is increasing the melting

transition. However, since this increase is not linear, it was stated that a diester/diol with the length of approximately four fatty acids was needed in order to obtain thermal properties similar to high-density polyethylene.[96]

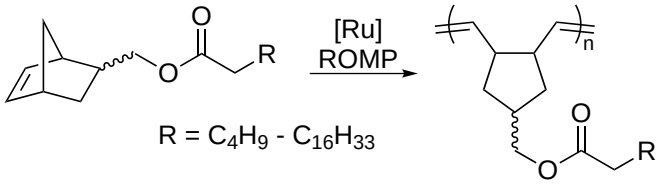
Aside from the *ω*-position, it was shown that by double bond isomerization, lactones can be selectively prepared from free fatty acids. For instance, employing silver triflate as catalyst for both the double bond isomerization and the lactone preparation, *γ*-lactones can be obtained selectively (Scheme 21**d**).[97] On the other hand, by using sulfuric acid as catalyst for the isomerization and lactonization, *δ*-stearolactone was obtained with a high selectivity and good yields (Scheme 21**e**).[98]

All in all, these results demonstrate that unsaturated fatty acids offer manifold derivatization opportunities for the preparation of renewable monomers and respective polymers. Different kinds of monomers for the preparation of polyesters and polyamides have been described which shows the great potential for unsaturated fatty acids to serve as a renewable feedstock for polymer science.

1.3.2. Fatty acid derived monomers suitable for living polymerizations

Another route to derivatize fatty acids without using a double bond functionalization strategy is the preparation of esters or amides, which can be directly polymerized. In this context, several different compounds have been prepared such as norbornenes,[99] vinyl-ether esters,[100] or 2-oxazolines.[101] Furthermore, acrylates and methacrylates have been prepared from the corresponding fatty alcohols.[102-104]

For instance, 5-norbornene-2-methanol was esterified with saturated fatty acids ranging from C_6 to C_{18}. Afterwards, the respective monomers were tested for their ring opening metathesis polymerization (ROMP) behavior using different metathesis catalysts (Scheme 22).[99]

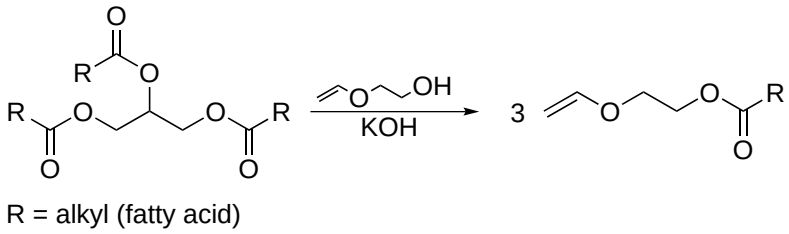


Scheme 22 - ROMP of fatty acid derived norbornenes.

For the ROMP of the respective monomers, the Grubbs olefin metathesis catalyst 3rd generation, which bears a pyridine-derived ligand, showed the best results. In general, this catalyst is known to be very well suited especially for the initiation of ROMPs of norbornenes.[105] For the ROMP of the norbornenes fatty acid esters, it was shown that the polymerization occurs in a living manner, which was verified by kinetic and molecular weight measurements. It has been shown that the polydispersities (PDIs) of the respective polymers were very narrow (~ 1.1 – 1.2), an important criteria for living polymerizations. Furthermore, the differential scanning calorimetry (DSC) measurements of the prepared polymers revealed a significant influence of the

fatty acid chain length on the thermal properties of the polymer. It has been stated that the aliphatic side chains seem to act as internal plasticizers for the respective polymers. Thus, it was shown that the glass transition temperature (T_g) decreases with an increasing chain length, ranging from T_g = 102 °C for hexanoic acid (C_6) to T_g = -32 °C for stearic acid (C_{18}). Furthermore, only the polymers having a relative long side chain length of minimum C_{14} exhibited a melting transition, which decreases with an increasing chain length (T_m = 30 °C (C_{14}), 15 °C (C_{16}) and 6 °C (C_{18})). On the other hand, polymers with shorter aliphatic side chains did not exhibit any melting transition.[99]

An interesting possibility for the preparation of monomers from saturated fatty acids is the derivatization to vinyl-ether esters. This reaction was carried out directly utilizing soybean oil and potassium hydroxide as base employing 2-(vinyloxy)-ethanol to yield the respective monomers (Scheme 23).[100]

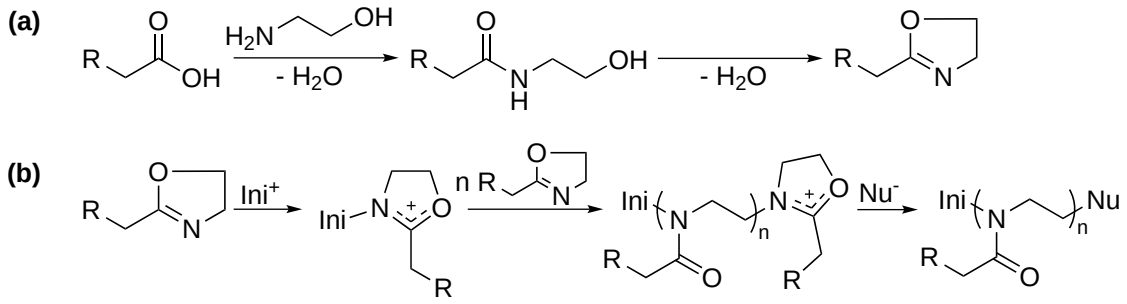


Scheme 23 - Preparation of vinyl-ether esters directly from soybean oil.

For these monomers, it has been demonstrated that the Lewis base promoted polymerization also occurs in a living manner. Although soybean oil was used for this study, which bears a high content of unsaturated fatty acids, the derivatization strategy is also easily applicable for saturated fatty acids. For instance, it is known for a long time that vinyl- and allyl-stearate can be polymerized in a free radical polymerization very efficiently with a high monomer consversion.[106] Interestingly, for

this radical polymerization it is stated that saturated fatty acids performed much better than unsaturated ones, since the double bonds in the aliphatic chain could act as radical scavengers to terminate the polymerization reaction.

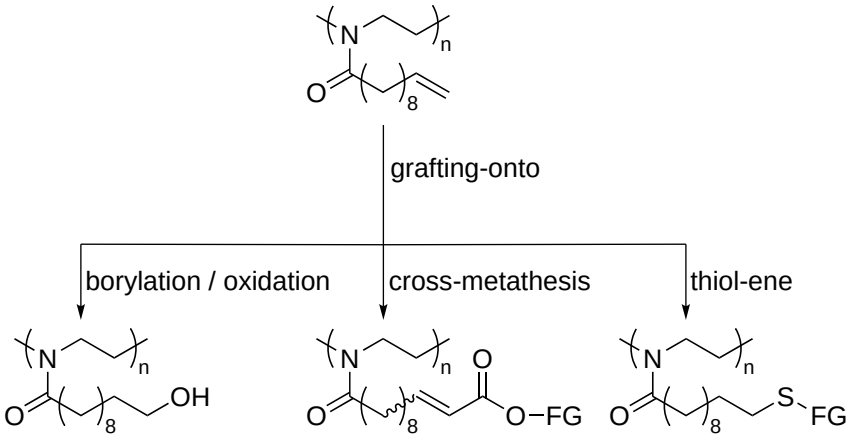
Beside the preparation of esters, which are capable to undergo a living polymerization, the synthesis of 2-oxazolines offers a straightforward access to diverse monomers. In order to obtain 2-oxazolines, the free fatty acid first reacts with ethanolamine to yield the corresponding amide, which can afterwards be condensed to obtain the fatty acid derived 2-oxazoline. These monomers can be polymerized by cationic ring-opening polymerization reactions (Scheme 24**b**).



Scheme 24 - Preparation of fatty-acid derived 2-oxazolines (a) and their polymerization (b).

Such cationic polymerizations have been carried out with 2-oxazolines derived from saturated fatty acids of different chain length.[107] It was apparent that the aliphatic side chain has a significant effect on the thermal properties of the polymers, although the effect is not as distinctive as for the ROMP of norbornenes. For the shortest fatty acid derived polymer from hexanoic acid, the melting transition was T_m = 161 °C, whereas the polymer with the longest aliphatic side chain derived from stearic acid showed a melting transition of T_m = 133 °C. Moreover, it should be noted that the obtained average molecular weights were up to 100 kDa with usually narrow PDI values.[107] In general, it has been shown that the 2-oxazolines derived from fatty acids

are a very interesting class of monomers with manifold opportunities for the preparation of polymers, such as for example the synthesis of statistical copolymers or block copolymers, which have been recently reviewed.[101] Very interesting polymers were obtained when utilizing the 2-oxazolines derived from 10-undecenic acid since the obtained polymers exhibit aliphatic side chains bearing a terminal double bond. These terminal double bonds allow several post-polymerization modification reactions (Scheme 25).



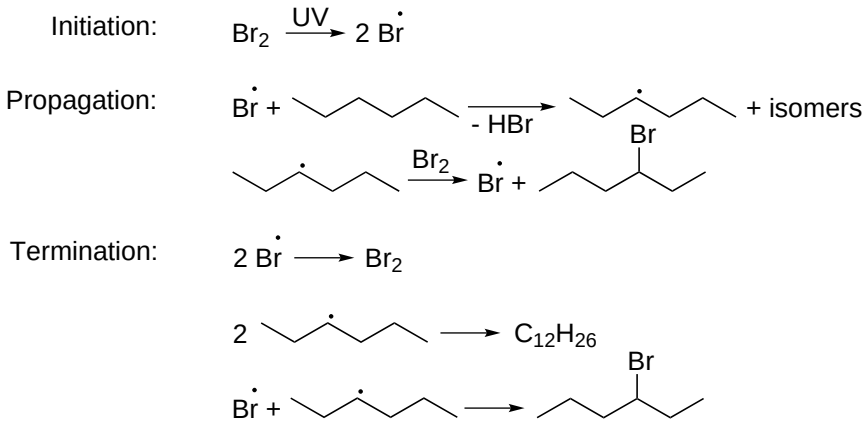
Scheme 25 - Grafting-onto possibilities of 10-undecenoic derived poly(2-oxazoline).

For example, the poly(2-oxazoline) derived from 10-undecenoic acid can be very efficiently post-modified with thiol-ene addition reactions using a slight excess of thiol under UV irradiation. Thereby, complete conversion of the double bonds was achieved using various thiols.[80, 108] Also, it was shown that the terminal double bond can be hydroborylated using 9-borabicyclo[3.3.1]nonane.[109] The resulting modified polymers can be converted to the terminal alcohols by oxidation and basic cleavage in a straightforward manner, where the polymeric backbone remains untouched. Furthermore, it has been shown that different acrylates can be grafted-onto the poly(2-oxazoline) derived from 10-undecenoid acid using the Hoveyda-Grubbs metathesis catalyst 2nd generation (HG II) in an olefin cross-metathesis reaction.[110]

Herein, acrylates with different functional groups such as hydroxyl-, alkyl-, fluorinated- or PEG-acrylates have been successfully grafted-onto the aliphatic side chains. All of these grafting-onto reactions were performed with only a small amount of polymer-polymer coupling as side reaction using relatively low catalyst loadings of 5 mol% HG II and an excess of acrylates.

1.3.3. Regioselective radical chlorination of saturated fatty acids

A well-known possibility for the modification of alkanes is the radical halogenation. The radical reaction is usually performed with alkanes (for example *n*-hexane) and a halogen such as chlorine or bromine. The reaction itself proceeds *via* a radical mechanism, where first the halogen is cleaved into two radicals, for example by UV irradiation. Then, the respective halogen radicals can react with the alkane in a radical chain mechanism, wherein the halogen radical first abstracts a hydrogen atom from the alkane to generate a carbon radical. This carbon radical can then react with either a halogen radical to form the halogenated product and to terminate the chain, with a halogen to also form the halogenated product and another halogen radical or also with another carbon radical to homo-couple and terminate the radical chain reaction (Scheme 26).



Scheme 26 - Schematic overview of the radical bromination of *n*-hexane.

One of the main drawbacks of the radical halogenation is the poor regioselectivity. Because of this, a statistical product mixture is obtained. In fact, because of the stabilizing inductive effect of the alkyl chains, internal carbon radicals are more stable and thus preferentially formed. However, the radical halogenation is an interesting concept, also for the modification of saturated fatty acids, when performed in a

regioselectively manner. In this context, Schäfer and coworkers have introduced an interesting strategy for a more regioselective radical chlorination of saturated fatty acids.[111] In order to obtain an improved selectivity, the free carboxylic acids were absorbed on alumina. Thereby, the chain parts close to the carboxylic acid function were "shielded" from halogenation. However, for short chain fatty acids such as hexanoic or octanoic acid, no regioselectivity was observed, whereas for long chain fatty acids such as stearic acid, a good regioselectivity for the radical chlorination was observed (Figure 2). All in all, the observed selectivity is highly dependent on the reaction temperature and the chlorinating agent (in this report either gaseous chlorine or *t*-butyl hypochlorite) used.

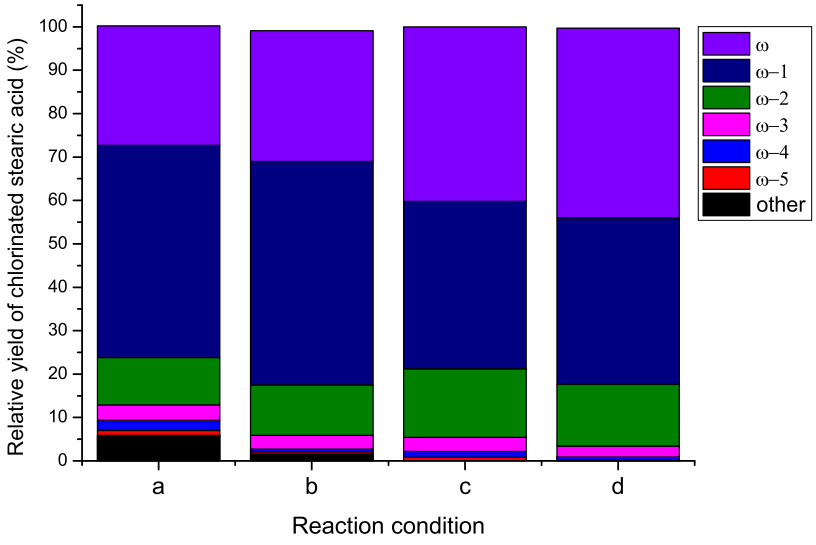


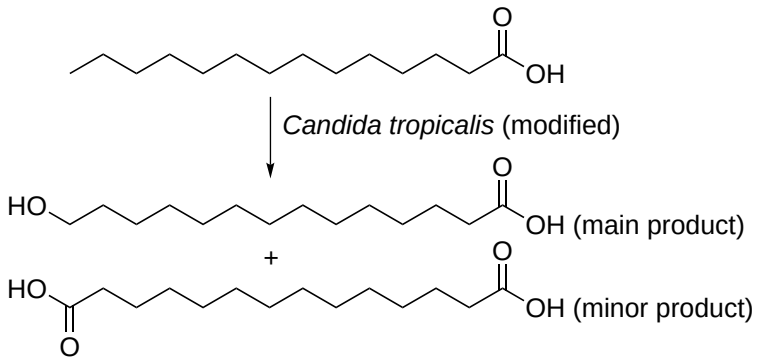
Figure 2 - Product distribution of the chlorination of stearic acid using different reaction conditions with a: *t*-BuOCl at -20 °C, b: *t*-BuOCl at -35 °C, c: Cl_2 at -20 °C and d: Cl_2 at -35 °C.[111]

As it is obvious from Figure 2, the reaction has a good selectivity for the *ω*- to *ω*-2 position of stearic acid. As mentioned already, only a poor selectivity was obtained for shorter fatty acids. The authors postulate that the reason for the obtained selectivity lies in the hydrophobic interactions of the fatty acid chains, which

increase with the longer carbon chain. Because of these hydrophobic interactions and the resulting assembly of the fatty acids, the “shielding” of the chain parts closer to the carboxylic acids is supposed to be increased. However, although this method is an interesting technique for the preparation of *ω*-selective halogenated fatty acids, the reaction procedure has diverse drawbacks. For instance, the overall conversions of the fatty acids are rather low, ranging from 30-45 % for the reactions presented in Figure 2. This may be due to the fact that only 1.0 equivalents of the chlorine-agent was employed in order to inhibit multiple chlorination. Additionally, the reaction is typically carried out in tetrachloromethane, a highly toxic solvent which does not comply to the principles of green chemistry.[112] Most important, although a quite good regioselectivity is achieved, still a mixture of isomers is obtained which cannot be used for the preparation of well-defined monomers. If, for example, the halogenated fatty acids should be converted to unsaturated fatty acids by elimination of the chlorine and subsequent olefin self-metathesis, diesters ranging from C_{30} to C_{34} would be obtained assuming that only the most common isomers would be employed. It has already been shown that polyesters derived from a mixture of diesters with different chain lengths results in poorer thermal properties compared to polyesters from well-defined monomers.[67] Thus, it appears that the presented method is not ideal for the preparation of monomers derived from saturated fatty acids.

1.3.4. Biochemical synthesis of hydroxy fatty acids and their polymers

Apart from the double bond, the most common functional group within a fatty acid chain is the hydroxyl group. Although there is only one hydroxyl fatty acid (HFA) which is naturally produced on a large scale, namely ricinolic acid, many other HFAs are known.[113] HFAs play an important role as precursors for bio-degradable polymers or as additives in cosmetics. Interestingly, many HFAs show biological acitivities.[114-115] Usually, HFAs are prepared *via* a microbial pathway and occur as *α*-HFAs, *β*-HFAs, internal HFAs or terminal HFAs. Furthermore, fatty acids with more than one hydroxyl group are known. However, most of these compounds are not interesting in terms of polymer synthesis since *ω*-functionalized fatty acids are preferentially used for the preparation of linear, non branched polymers, which exhibit improved thermal properties. In this context, Gross and coworkers have prepared a modified yeast of the strain *Candida tropicalis,* which is capable to perform a selective *ω*-oxidation of saturated fatty acids to yield the *ω*-hydroxy fatty acid by a fermentation process (Scheme 27).[116]

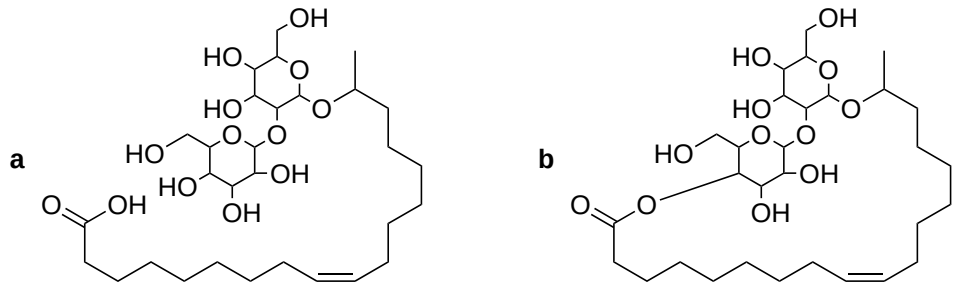


Scheme 27 - Conversion of tetradecanoic acid by modified *candida tropicalis.*

In contrast to the earlier reported transformation *via* isomerization of a double bond and subsequent reaction, no regioisomers were obtained. In an upscale test reaction employing tetradecanoic acid, the only side product was the *α*,*ω*-diacid. The

conversion of the substrate was very good yielding a total of 174 g/L of the desired product and only 6.1 g/L of the diacid from altogether 200 g/L tetradecanoic acid after 148 hours. The produced *ω*-hydroxy tetradecanoic acid can afterwards be polymerized directly to yield the polyester 14 with high molecular weights and a melting transition of approximately 95 °C.[117-118] In addition, the *ω*-hydroxy tetradecanoic acid was used as a co-monomer for the preparation of a poly(butyl-terephthalate) (PBT) co-polymer which showed significantly different thermal and mechanical properties.[119] For instance, the melting transitions of the prepared copolymers were significantly lowered with increasing content of *ω*-hydroxy tetradecanoic acid. Furthermore, the elasticity was highly improved with increased contents of *ω*-hydroxy tetradecanoic acid which was measured by elongation at break values.

Another interesting class of HFAs are sophorose lipids, or more generally glycolipids (Scheme 28). Such compounds are well known and can be prepared by fermentation of the corresponding fatty acid with sugars and different yeast strains, e.g. *Candida bombicola*.[120-121] Thereby, the desired product can be obtained on a large scale of up to 400 g/L. These compounds are usually employed as bio-surfactants since they significantly lower the surface tension and represent a very valuable and important renewable alternative for petroleum-based surfactants, which are still preferably used. Furthermore, these sophorose lipids are also known to have biological activities.[122-124]

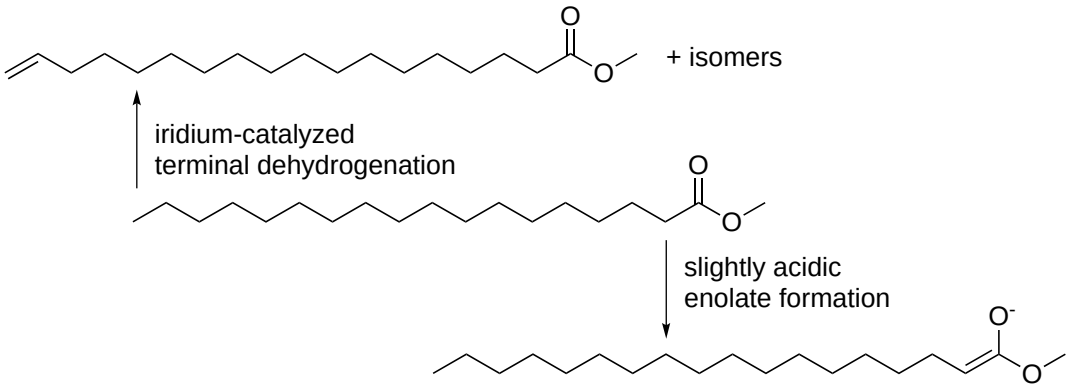


Scheme 28 - Sophorose lipids derived from oleic acid in the (a) free acid and (b) lactonic form.

However, with regard to polymer chemistry, only the ROMP of sophorose lipids has been studied, yet.[125-126] On the other hand, no AA- or AB-type monomers derived from sophorose lipids have been described in the literature, although these compounds offer an interesting platform for the preparation of renewable monomers. The use of sophorose lipids for monomer synthesis will be discussed in chapter 3.3.2.

2. Motivation of this work

As it has been described in the introduction and several reviews, numerous derivatization strategies of fatty acids are known and reported.[69, 127] However, most of the investigated reactions and modification of fatty acids make use of the double bond within the fatty acid chain. Therefore, these derivatization reactions are limited to unsaturated fatty acids. The modification possibilities of saturated fatty acids, on the other hand, are quite limited and not fully explored. However, saturated fatty acids have two chemically specific positions within the aliphatic chain, which are, at least in principle, selectively accessible for diverse modifications (Scheme 29).



Scheme 29 - Possible modifications of methyl stearate.

For instance, the *α*-position of the ester is slightly acidic and can be deprotonated by strong bases to form the corresponding enolate as a reactive intermediate. Employing this enolate for further reactions such as Michael-additions, nucleophilic additions, or coupling-reactions could be particularly useful. The modifications of unsaturated fatty acids at the *α*-position to prepare monomers are of specific interest since the thereof derived polymers still have the unsaturation of the aliphatic chain, allowing further modification of the synthesized polymers. Herein, a selective post-polymerization functionalization by e.g. olefin (cross)-metathesis or thiol-ene addition

can be utilized to achieve a targeted design of the thermal and mechanical properties of the respective polymers.

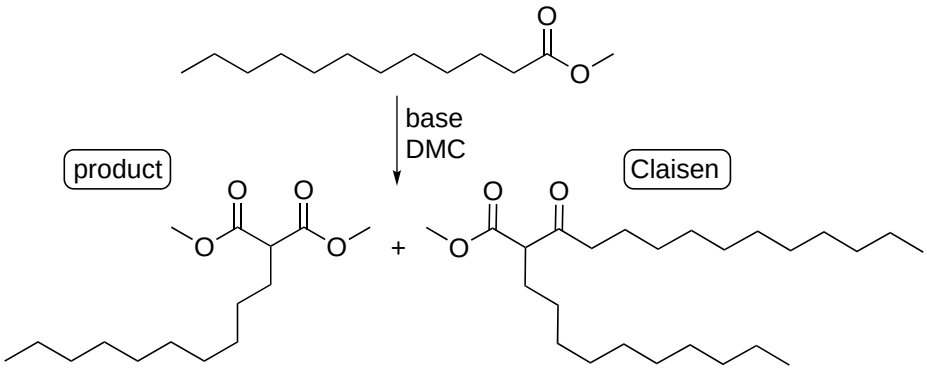
The other chemically specific position of saturated fatty acids aliphatic chains is the terminal CH_3-group. For alkanes, the terminal methyl-groups can be selectively dehydrogenated using iridium-pincer compounds yielding *α*-olefins and regioisomers.[128-129] The corresponding reaction with saturated fatty acids would yield long-chained *ω*-unsaturated fatty acids than can be transformed into long chain monomers and the respective polyamides and polyesters. Furthermore, the terminal CH_3-group can be addressed biochemically as it has been discussed above.

According to the principles of green and sustainable chemistry,[112] the aim of this doctoral thesis is to investigate the aforementioned possibilities of the derivatization of saturated fatty acids and therefore the use of saturated fatty acids as renewable feedstock to prepare diverse monomers. Additionally, the obtained monomers based on modified saturated FAMEs should be polymerized and analyzed with respect to molecular weight and thermal properties.

3. Results and discussion

3.1. Malonate derivatives from fatty acid methyl esters*

The first idea for a selective derivatization of saturated FAMEs was the preparation of malonate derivatives by deprotonation of the *α*-position of the ester with a strong base in DMC as reactive solvent. Once the enolate of the ester is formed, it should either react with another FAME to undergo a Claisen-condensation reaction[130] or in a nucleophilic manner with DMC to form the desired malonate (Scheme 30). Thereby, it is worth mentioning that DMC can be considered as a “green solvent” since it is relatively safe compared to other organic solvents and can be synthesized from carbon monoxide or dioxide and methanol.[131-132]



Scheme 30 - Preparation of malonates from FAMEs.

In order to achieve the selective formation of the desired malonates, it was necessary to find optimal reaction conditions to obtain a high conversion and good product selectivity at the same time, thus suppressing the Claisen-condensation as side-reaction. Therefore, reaction parameters like the employed base, temperature, reaction time, equivalents of DMC, and additives were evaluated.

* The work of this chapter has been partially published:
N. Kolb, M. A. R. Meier, Monomers and their polymers derived from saturated fatty acid methyl esters and dimethyl carbonate, *Green Chem*., 2012, **14**, 2429-2435
N. Kolb, M. A. R. Meier, Grafting onto a renewable unsaturated polyester *via* thiol–ene chemistry and cross-metathesis, *Eur. Polym. J*., 2013, **49**, 843-852

Once reaction conditions are optimized, the respective malonates of saturated FAMEs, ranging from C_8 (methyl octanoate) to C_{18} (methyl stearate), could be synthesized and tested for their polymerization behavior for both the preparation of polyesters and polyamides. Furthermore, this reaction should also be applied to castor-oil derived methyl undec-10-enoate in order to obtain a malonate derivative with a terminal double bond in the aliphatic chain, which still would be present after the polymerization reaction and therefore can be used for post-polymerization modifications. Besides, with the malonate derived from methyl undec-10-enoate, the preparation of AB_2-type malonates should be easily possible by modification of the terminal double bond, for example by using thiol-ene addition reactions.

3.1.1. Synthesis of malonate derivatives from FAMEs

The first challenge of this study was to find suitable conditions for the synthesis of malonate derivatives from saturated FAMEs in DMC. Therefore, strong bases were required in order to efficiently deprotonate the *α*-position of the ester. Also, an excess of DMC was necessary in order to suppress the Claisen-condensation as side-reaction.

In an initial investigation of the reaction conditions, it was found that the best base for this reaction is NaH. Other bases like sodium hydroxide, potassium hydroxide, potassium carbonate or trimethylamine resulted in no or very low conversion. When LDA (2M in THF) was used, the reaction proceeded but only with comparably low yields, since after a short reaction time the reaction mixture became gel-like and stirring was thus hindered. The best results (73.7 % GC-conversion with 62.1 % product selectivity) were obtained with 2.0 eq. of LDA in 2.0 eq. of DMC at 60 °C. Employing a high DMC concentration of 10.0 eq, only 53.0 % conversion was obtained with a product selectivity of 66.6 %, according to GC analysis. Moreover, the Claisen-condensation was considerably promoted by using LDA as a base, most probably because of a faster and more efficient deprotonation.

The reaction conditions were then further investigated and optimized using NaH as base. NaH was used in the range of 1.0-3.0 eq. and DMC from 5.0-20.0 eq. During these investigations, it was also observed that anhydrous DMF considerably accelerates the deprotonation and therefore DMF was added to

most reactions (compare Table 1) as an additive. This increased the conversion significantly (Table 1, entries 2 and 3). Since similar reactions are carried out in pure DMF,[133] this can be argued with a better solvation of the hydride anions and therefore increased reactivity of the base. However, doubling the concentration of DMF had no considerable effect on the conversion (Table 1, entry 5). It was also observed that the reaction proceeded up to 90 % conversion with 3.0 eq. NaH in 5.0 eq. DMC. However, a significant amount of the Claisen-condensation side-product was also obtained under these conditions (Table 1, entry 4). This was successfully suppressed by employing a larger excess of DMC of 10 or 20 equivalents (Table 1, entries 6 and 7, respectively). However, due to the large dilution, the reaction yields were lower. This problem was solved by prolonging the reaction time to 8 hours; under these conditions, also 2.5 eq. of base gave very good product conversion with almost no Claisen-condensation side-product (Table 1, entries 10 and 11, respectively). Thus, the optimal conditions were found to be 2.5 eq. NaH in 20.0 eq. DMC with 1.0 eq. DMF as an additive at 60 °C for at least 8 hours reaction time, yielding almost quantitative conversions in GC analysis (Table 1, entry 11). In terms of sustainability and safety, the use of an excess of NaH could be considered as drawback of this reaction. This excess, however, was required since the malonate derivatives are more acidic than the starting esters and thus preferentially deprotonated. Hence, base loadings lower than 2.0 eq. resulted in very low conversions (Table 1, entry 12).

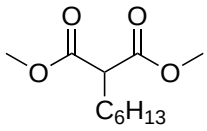
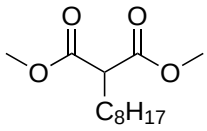
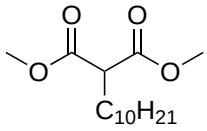
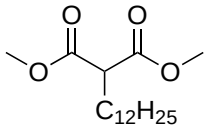
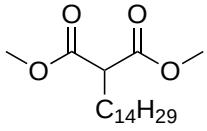
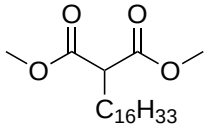
Table 1 – Results of the reaction condition screening for the synthesis of malonates from FAMEs.

Entry	NaH (eq.)	DMC (eq.)	DMF (eq.)	Time (h)	Conv. (%, GC)	Product (%, GC)	Claisen (%, GC)
1	1.0	5.0	None	6.0	4.7	56.7	43.3
2	2.0	5.0	None	6.0	22.7	62.4	37.6
3	2.0	5.0	1.0	6.0	63.1	71.0	29.0
4	3.0	5.0	1.0	6.0	95.5	85.6	14.4
5	3.0	5.0	2.0	6.0	93.6	91.7	8.3
6	3.0	10.0	1.0	6.0	90.3	95.0	5.0
7	3.0	20.0	1.0	6.0	46.8	100.0	0.0
8	2.0	10.0	1.0	8.0	79.7	100.0	0.0
9	2.0	20.0	1.0	8.0	74.5	100.0	0.0
10	2.5	10.0	1.0	8.0	97.6	97.7	2.3
11	2.5	20.0	1.0	8.0	97.2	99.0	1.0
12	1.5	10.0	1.0	10.0	29.8	100.0	0.0

With these results in hand, the next step was the synthesis of the malonate derivatives of different saturated fatty acids (C_8-C_{18}) in higher scale for the further characterizations and polymerization reactions (Table 2). For monomers **1**-**4**, a reaction time of 8 hours gave an almost quantitative conversion, similarly to the small-scale reactions. However, for malonates **5** and **6**, the reaction time required to obtain similar results was 12 hours. This might be explained by the lower solubility with the increase of the aliphatic chain length and/or steric hindrance. All malonate derivatives were purified by vacuum distillation to give the desired products with a good purity and yields varying in the range of 59 % to 82 % (Table 2). Nevertheless, with long-chain fatty acids, the purification of the products was far more challenging

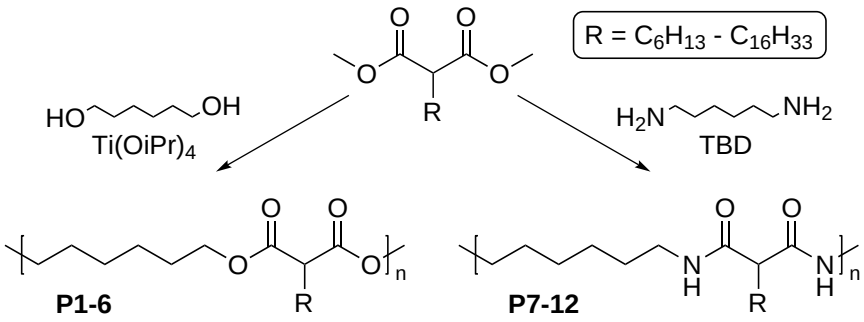
since their chemical and physical properties were almost the same compared to the starting material. Therefore, the isolated yields, with an acceptable purity, were only about 60 % for **5** and **6**.

Table 2 - Isolated yields of saturated FAME-derived malonates.

Entry	Product	Isolated yield (%)
1		72.9
2		72.7
3		81.3
4		81.6
5		59.1
6		61.1

3.1.2. Polymerization reactions of fatty-acid derived malonates

Once the malonate synthesis from saturated FAMEs was optimized, the next step was to polymerize the obtained monomers to polyesters and polyamides in order to investigate their polymerization behaviour and the thermal properties of the corresponding polymers (Scheme 31).



Scheme 31 – Polymers derived from malonate derivatives 1-6.

First, the preparation of polyesters from **3** and 1,6-hexanediol as comonomer giving PE 6,3 derivatives with aliphatic side-chains was investigated. In the beginning, three different polymerization catalysts were tested, namely *p*-TsOH, TBD and Ti(O*i*Pr)$_4$. Using relatively high concentrations of 10 mol% catalysts relative to the employed monomers, for all three catalysts comparable results at 80 or 100 °C (Table 3, entries 1-6) were observed. On the other hand, when the catalyst loading was reduced to 2 mol%, only Ti(O*i*Pr)$_4$ gave promising results, whereas TBD and *p*-TsOH gave only oligomers under similar conditions (Table 3, entries 7-9). Therefore, Ti(O*i*Pr)$_4$ was chosen as the polycondensation catalyst. Further studies showed that the aforementioned catalyst performs best with a concentration of 1 mol% at 120 °C yielding a high molecular weight polymer with the expected PDI value of ~2 (Table 3, entry 14). For a reaction temperature of 100 °C, the molecular weights were significantly lower (Table 3, entry 11). Surprisingly, it seems that higher

concentrations of the catalyst had a reverse effect on the polymerization, which also resulted in higher PDI values (Table 3, entries 5, 8 and 13).

Table 3 - Condition screening for the preparation of PE 6,3 from monomer 3.

Entry	Temp. (°C)	Cat.	mol%	M_n (kDa)	M_w (kDa)	PDI
1	80	TBD	10.0	4.0	6.0	1.50
2	80	$Ti(OiPr)_4$	10.0	3.7	7.1	1.94
3	80	*p*-TsOH	10.0	1.6	2.2	1.40
4	100	TBD	10.0	4.6	7.1	1.55
5	100	$Ti(OiPr)_4$	10.0	4.8	14.1	2.93
6	100	*p*-TsOH	10.0	4.8	8.6	1.78
7	100	TBD	2.0	No polymer		
8	100	$Ti(OiPr)_4$	2.0	15.2	44.0	2.89
9	100	*p*-TsOH	2.0	No polymer		
11	100	$Ti(OiPr)_4$	1.0	11.8	24.6	2.08
12	100	$Ti(OiPr)_4$	0.5	14.5	29.3	2.02
13	120	$Ti(OiPr)_4$	2.0	17.0	50.8	2.99
14	120	$Ti(OiPr)_4$	1.0	22.1	44.6	2.02
15	120	$Ti(OiPr)_4$	0.5	15.7	33.9	2.17

With these results in hand, the polycondensation reactions were carried out on a larger scale (5.0 mmol of the respective monomer) with slightly optimized reaction conditions (Scheme 31 left; see chapter 5.3 for details). Consequently, the monomers were dissolved after mixing in 2 mL THF in order to homogenize the reaction mixture. The crude and precipitated polymers, respectively, were analyzed *via* GPC after 24 h. The number average molecular weights (M_n) of the resulting polyesters were between 9-17 kDa (Table 4 and Figure 3).

Table 4 - Molecular weight distribution and thermal behavior of P1-P6, respectively.

Entry	M_n (kDa)	M_w (kDa)	PDI	T_m (°C)	T_g (°C)
P1	16.0	23.8	1.49	-	-65.1
P2	11.1	19.3	1.73	-	-68.0
P3	12.2	24.1	1.97	-35.7	-
P4	9.4	17.4	1.84	-6.4	-
P5	12.8	28.3	2.21	11.4	-
P6	17.0	32.0	1.88	26.8	-

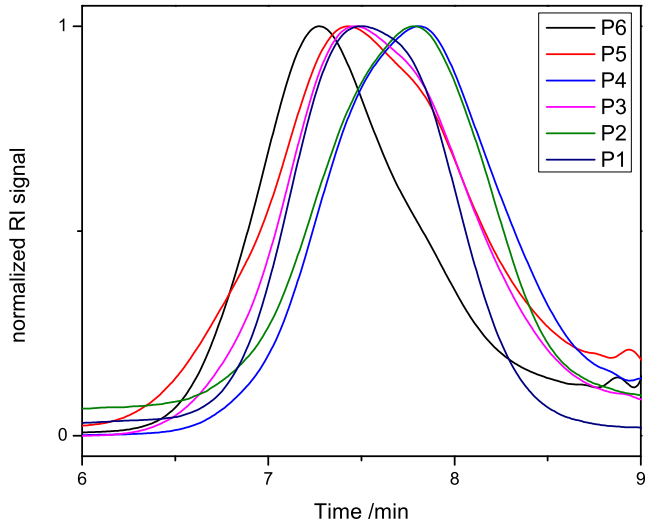


Figure 3 - Molecular weight distribution of P1-6.

Except for **P6**, which showed properties of a rubbery material, all polyesters were yellowish, highly viscous and sticky materials, which were well soluble in many common organic solvent such as acetone, toluene, chloroform, dichloromethane or DMF.

The thermal properties of the precipitated polyesters were studied by DSC analysis within a temperature range from -75 to 200 °C (Table 4 and Figure 4). As expected, polyesters **P1** and **P2** did not exhibit any melting transition within that range but glass transitions. The longer the aliphatic side-chains of the polyesters, the higher the

melting point of the resulting polymers, ranging from -35.7 to 26.8 °C. **P6** is the only polyester that was obtained as a solid at room temperature, but it was still very tacky and rubbery. The obtained results from the DSC analysis suggest that the side-chain length and the resulting non-polar interactions are the main driving force for the crystallinity of the obtained poly(malonates).

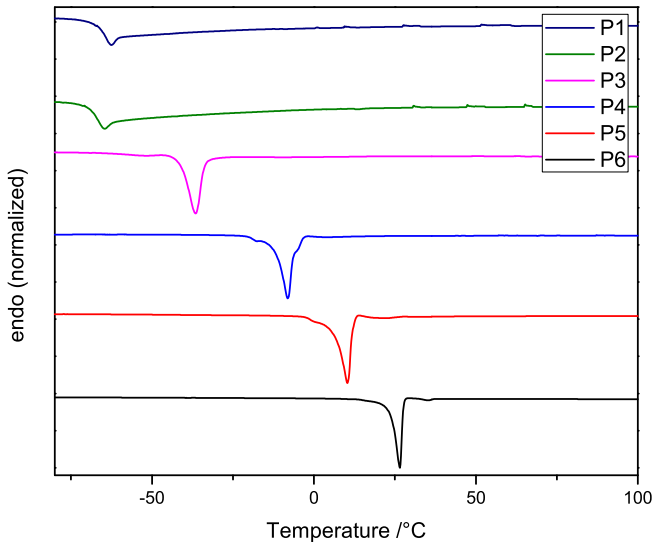


Figure 4 - DSC analysis of P1-6; data is shown from the 2nd scan.

Having established some basic properties of the poly(malonates), comparatively, the preparation of malonate derived polyamides was investigated. In this aspect, 1,6-hexanediamine was used as comonomer with 5 mol% of TBD as catalyst since this compound has proven as an ideal catalyst for the preparation of polyamides.[61] Unlike polyesters, in general the synthesis of polyamides is quite challenging because of the bad solubility of the resulting polymers and the usual high melting points. Therefore, the polyamide synthesis was performed in *o*-xylene as solvent to keep the mixture stirrable as long as possible. Also, the temperature was increased steadily in 3 steps from 120 to 180 °C (see chapter 5.3 for details) along with the

change from a stream of argon to high vacuum (~ 2 mbar). After the polymerization, the polymers were transparent, colourless to yellowish melts, which were dissolved in HFIP and precipitated into ice-cold diethyl ether. It is noteworthy that the longer the side-chain got, the worse the polyamides were soluble in HFIP. Aside from HFIP, the polyamides were only soluble in boiling DMSO and DMF. Both the crude polymers and precipitated samples were analyzed by GPC in HFIP eluent. It was apparent that the side-chain length had a strong effect on the polymerization rate and thus the molecular weight (Table 5 and Figure 5). While **P7** had a molecular weight of almost 16 kDa, the polyamide with the longest side-chains **P12** had only a molecular weight of about 5 kDa. It can be considered that this is because of the bad solubility of the polyamides in general and the even worse solubility with a longer side-chain. This also did not change with higher temperatures and longer reaction times what was tested for polyamides **P7** and **P11** where the optimized procedure was modified to 20 hours of heating at 200 °C as the last step. The molecular weights changed only marginally *(M_n* of 18.6 kDa for **P7** and 8.6 kDa for **P11** for the precipitated polymers) with almost no change in the PDI value.

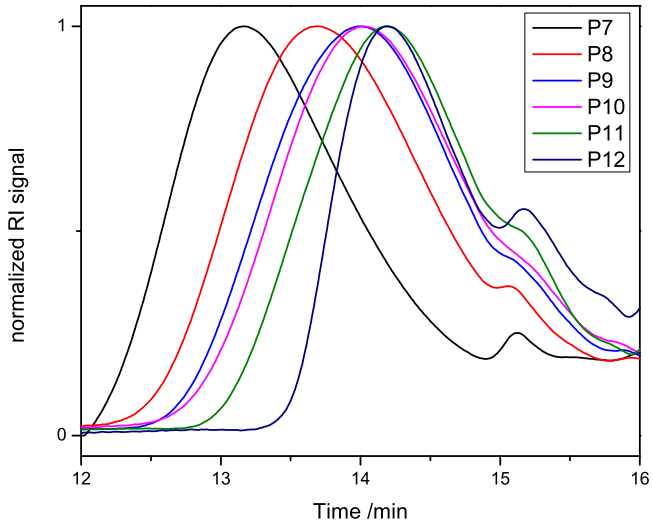


Figure 5 - Molecular weight distribution of P7-12.

Table 5 - Molecular weight distribution and thermal behavior of P7-P12.

Entry	M_n (kDa)	M_w (kDa)	PDI	T_m (°C)
P7	15.4	23.2	1.51	128.8
P8	8.9	13.2	1.48	113.6
P9	8.4	11.6	1.38	139.2
P10	8.3	11.7	1.41	128.2
P11	6.9	9.4	1.36	140.6
P12	7.0	7.9	1.13	158.5

Likewise as for the polyesters **P1-P6**, the DSC analysis of the precipitated polyamides was carried out from -75 to 200 °C. It was found that the best results were obtained with a relatively high heating rate of 20 °C/min since with slower heating rates, the peaks could not be identified clearly.

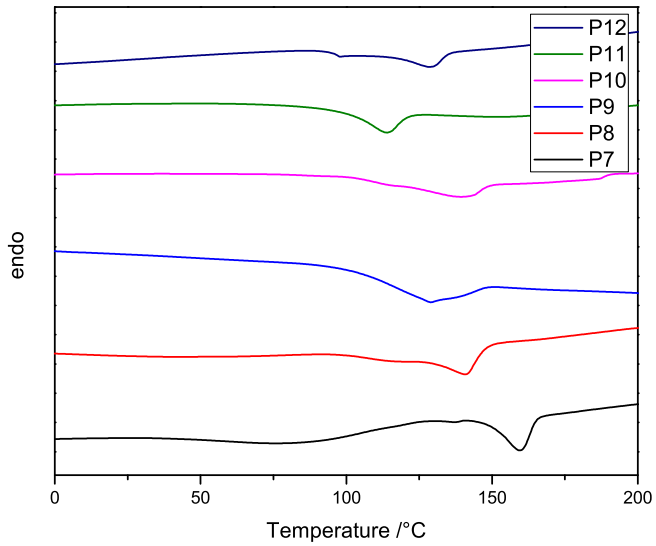


Figure 6 - DSC analysis of P7-12.

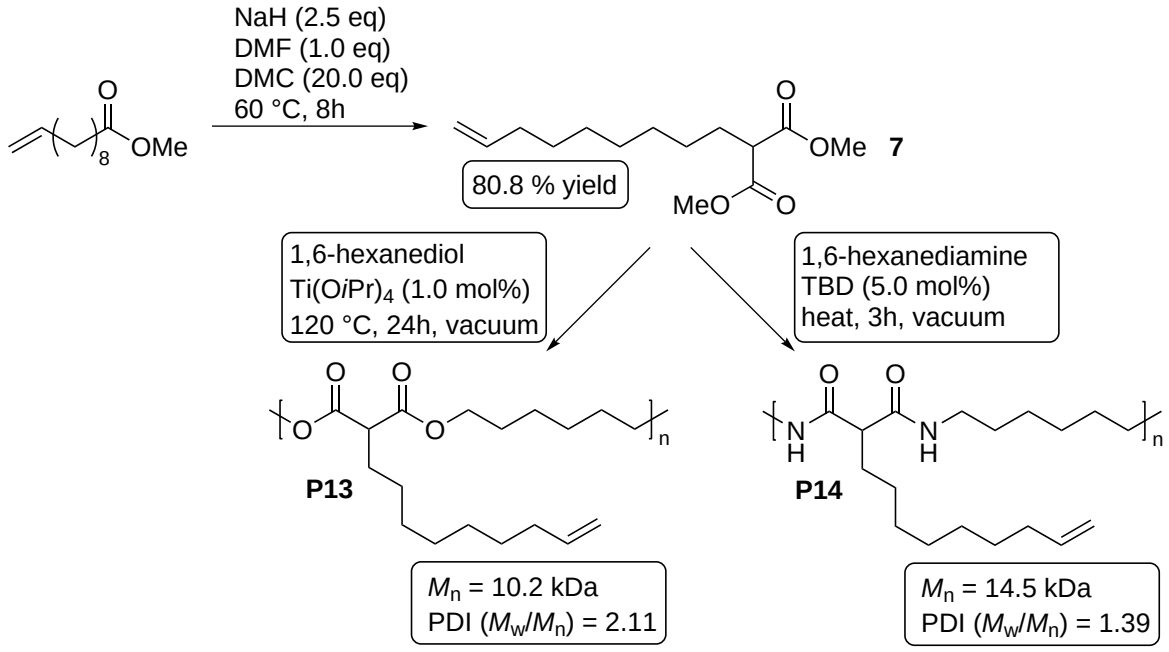
The precipitated polyamides were found to be high melting polymers with melting points ranging from 120 to 160 °C (Table 5 and Figure 6) resulting from the strong hydrogen bonding interactions. Interestingly, it was observed that for **P8** with an 8-carbon side-chain, the melting point was the lowest, whereas for the other polyamides the melting points increased with longer side-chains. Likewise, the melting point of **P7**, with a 6-carbon side-chain, is significantly higher than for **P8**. This shows the important impact of the aliphatic side-chain on the ability to crystallize for the polyamide. It can be considered that with longer side-chains, the non-polar interactions contribute to a better packing and therefore higher crystallinity. In addition, below a certain length (in this case C_6 for **P7**), shortening the chain length contributes to the crystallinity of the polyamide because of the less steric hindrance of the side-chains. **P7** is also the only polyamide sample which shows a clear T_g.

Furthermore, it is noteworthy that ^{1}H-NMR analysis of the polyamides was not possible because of their bad solubility. Experiments to derivatize the polyamides

with TFAA in order to solubilize them in chloroform [61] or similar solvents seemed successful but the respective ^{1}H-NMR spectra were not possible to be fully interpreted. Albeit, the most important signals were possible to be assigned which confirmed the general structure of the polyamides **P7-12**.

3.1.3. Dimethyl malonate and polymers from methyl undec-10-eneoate

After having successfully prepared the poly(malonates) and poly(malonamides) derived from saturated FAMEs, it was of interest if the malonate preparation can also be applied to unsaturated FAMEs. Therefore, the synthesis of a malonate derivative from unsaturated fatty acids and its polymerization was investigated (Scheme 32). As model substance, the castor oil derived 10-undecenoic acid [50] was chosen since it features a terminal double bond, which offers manifold opportunities for subsequent grafting onto chemistry. For the malonate synthesis, the earlier described reaction conditions were used with 2.5 equivalents of NaH and 1.0 equivalent DMF in 20.0 equivalents of DMC as reactive solvent. This reaction yields the malonate derivative **7** in 80.8 % yield on a multiple gram scale (0.10 mol set-up, 20.7 g yield). The polymerization of the resulting malonate monomer was then carried out with 1,6-hexanediol and 1.0 mol% titanium isopropoxide under bulk conditions applying a high vacuum at 120 °C.

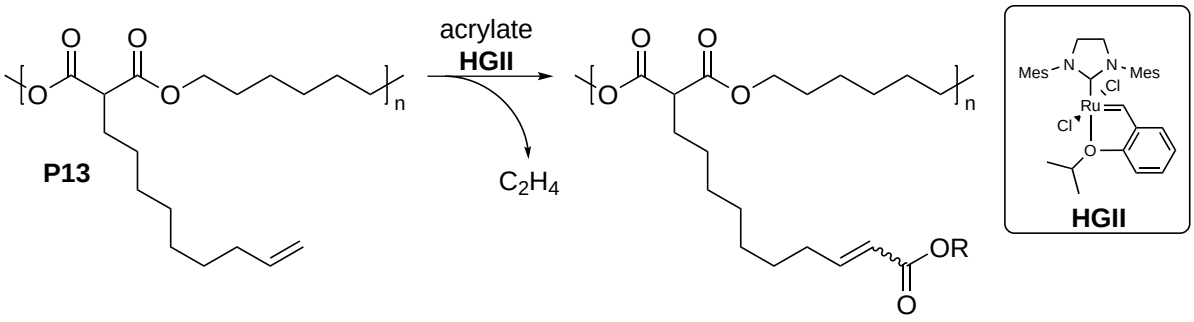


Scheme 32 - Preparation of P13 and P14 from methyl undec-1-enoate.

The obtained polymer was dissolved in a small quantity of THF and precipitated in ice-cold methanol. It is worth mentioning that, although the terminal double bond is thermodynamically less stable than an internal one, no double bond isomerization was observed during the malonate synthesis or the polymerization. The resulting poly(malonate) **P13** was obtained with an average molecular weight of 10.2 kDa as a yellow, highly viscous oil. DSC studies showed a glass-transition of this polymer at -74.1 °C which corresponds with the earlier studies on saturated poly(malonates). Aside from the poly(malonate), the analogous poly(malonamide) was also prepared with 1,6-hexanediamine as comonomer (**P14**). Unfortunately, since the fatty-acid derived poly(malonates) were almost insoluble in any common solvent, this polymer was not suitable to be studied with respect to grafting-onto reactions.

3.1.4. Grafting-onto poly(malonates) *via* olefin cross-metathesis

First, the modification of **P13** *via* ruthenium-catalyzed cross-metathesis was tested (Scheme 33) with acrylates (electron-deficient type II olefins), which exhibits excellent cross-metathesis selectivity with terminal double bonds (electron-rich type I olefins).[57] Also, the Hoveyda-Grubbs catalyst 2nd generation (**HG II**) was chosen as catalyst, since this catalyst gave best results in earlier studies on the cross-metathesis of methyl 10-undecenoate with methyl acrylate (MA).[58]



Scheme 33 - Grafting-onto reaction *via* cross-metathesis.

The first experiments were carried out on a 0.5 mmol scale, respective to the repeating unit of **P13** (155 mg) in 1 mL of DCM with 1 mol% catalyst loading and 5.0 to 10.0 equivalents of MA. Although a complete conversion of the terminal double bonds was achieved, GPC analysis showed coupling of the polymer *via* self-metathesis (Table 6, entries 1-2). Therefore, the reaction was tested under bulk conditions with 10.0 equivalents of MA to avoid DCM as solvent and suppress the polymer-polymer coupling side-reaction. These conditions resulted in complete conversion of the terminal double bond without any cross-linking (Table 6, entry 3). Interestingly, employing 5.0 equivalents of MA under bulk conditions, only 67 % conversion was achieved and polymer-polymer coupling took place in a considerable amount (Table 6, entry 4). On the other hand, reducing the catalyst

loading to 0.5 mol% also resulted in comparatively lower conversions of only 83 % (Table 6, entry 5). Therefore, bulk conditions with 10 equivalents of the respective acrylate and 1.0 mol% of the **HG II** catalyst at 40 °C were used as optimized reaction conditions for further cross-metathesis modifications.

Table 6 - Reaction condition screening for cross-metathesis reactions after 2 h reaction time.

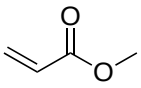
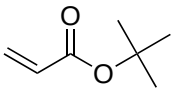
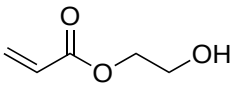
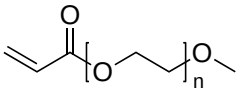
Entry	**HGII** (mol%)[a]	DCM (mL)	MA (eq)	Conv. (%)[b]	SM[c]
1	1.0	1.0	5.0	Quant.	Yes
2	1.0	1.0	10.0	Quant.	Yes
3	1.0	None	10.0	Quant.	No
4	1.0	None	5.0	67 %	Yes
5	0.5	None	10.0	83 %	No

[a]Respective per repeating unit; [b] Calculated *via* ^{1}H-NMR integration in $CDCl_3$; [c] determined *via* GPC

With the optimized reaction conditions in hand, the cross-metathesis of **P13** was investigated applying different acrylates on a 1.0 mmol scale of the monomer repeating unit. In addition to MA, *t*-butyl acrylate (bearing the possibility of simple modification to the free acid), hydroxy-ethyl acrylate (HEA), and PEG acrylate (M_n ~ 480 Da) were employed. With methyl- and *t*-butyl acrylate, the reaction proceeded without coupling and with good to very high conversions after 3 hours (Table 7, entries 1 and 2). With HEA, however, the reaction did not proceed as satisfying as with the other acrylates since only 83 % conversion was achieved even after 6 hours reaction time (Table 7, entry 3). It can be considered that this is because of the free hydroxyl groups, which can lead to catalyst degradation. This was already reported for other ruthenium-based metathesis catalysts.[134-135] However, also with HEA, no polymer-polymer coupling was observed from GPC analysis. With PEG acrylate on the other hand, the reaction proceeded very fast with complete conversion after only 1 hour (Table 7, entry 4). Unfortunately, the internal conjugated

double bond of the PEG modified polymer **P18** tends to cross-link very easily during the work up procedure and drying. Therefore, **P18** had to be handled as a solution in THF containing BHT as a radical inhibitor. The ^{1}H-NMR spectra of **P13** and metathesis modified polymers **P15-P18** are shown in Figure 8. It is clear to observe that the initial signals for the terminal double bond at 4.9 and 5.7 ppm, respectively, disappear almost completely except for HEA-modified polymer **P17**. Additionally, it is obvious that no polymer-polymer coupling occurs which would result in signals for internal olefins at around 5.3 ppm.

Table 7 - Grafting-onto reactions with different acrylates.

Entry	Acrylate	Time (h)	Degree of functionalization[a]	M_n (kDa)	M_w (kDa)	PDI
P15		3	> 95 %	12.4	27.0	2.18
P16		3	> 99 %	13.6	2.8	1.97
P17		6	~ 83 %	11.4	24.1	2.12
P18		1	> 99 %	24.8	39.6	1.60

[a] Calculated from ^{1}H-NMR integration in $CDCl_3$

As seen from the PDI values shown in Table 7 and GPC chromatograms of the respective polymers (Figure 7), side-reactions are held very low during the cross-metathesis reactions.

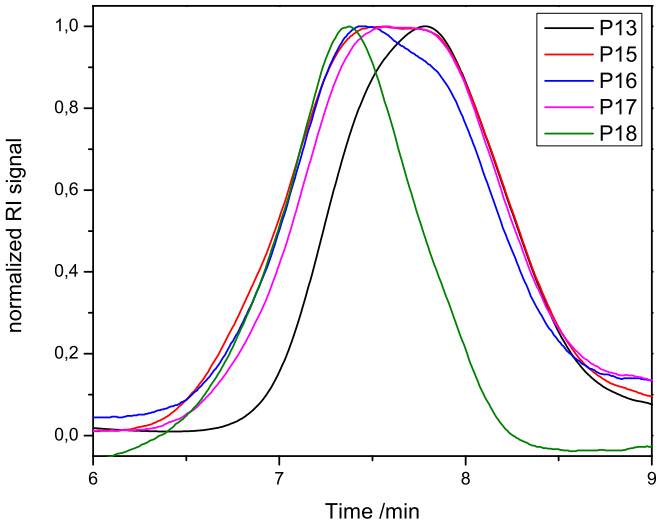


Figure 7 - GPC traces of olefin-metathesis functionalized polymers P15-18.

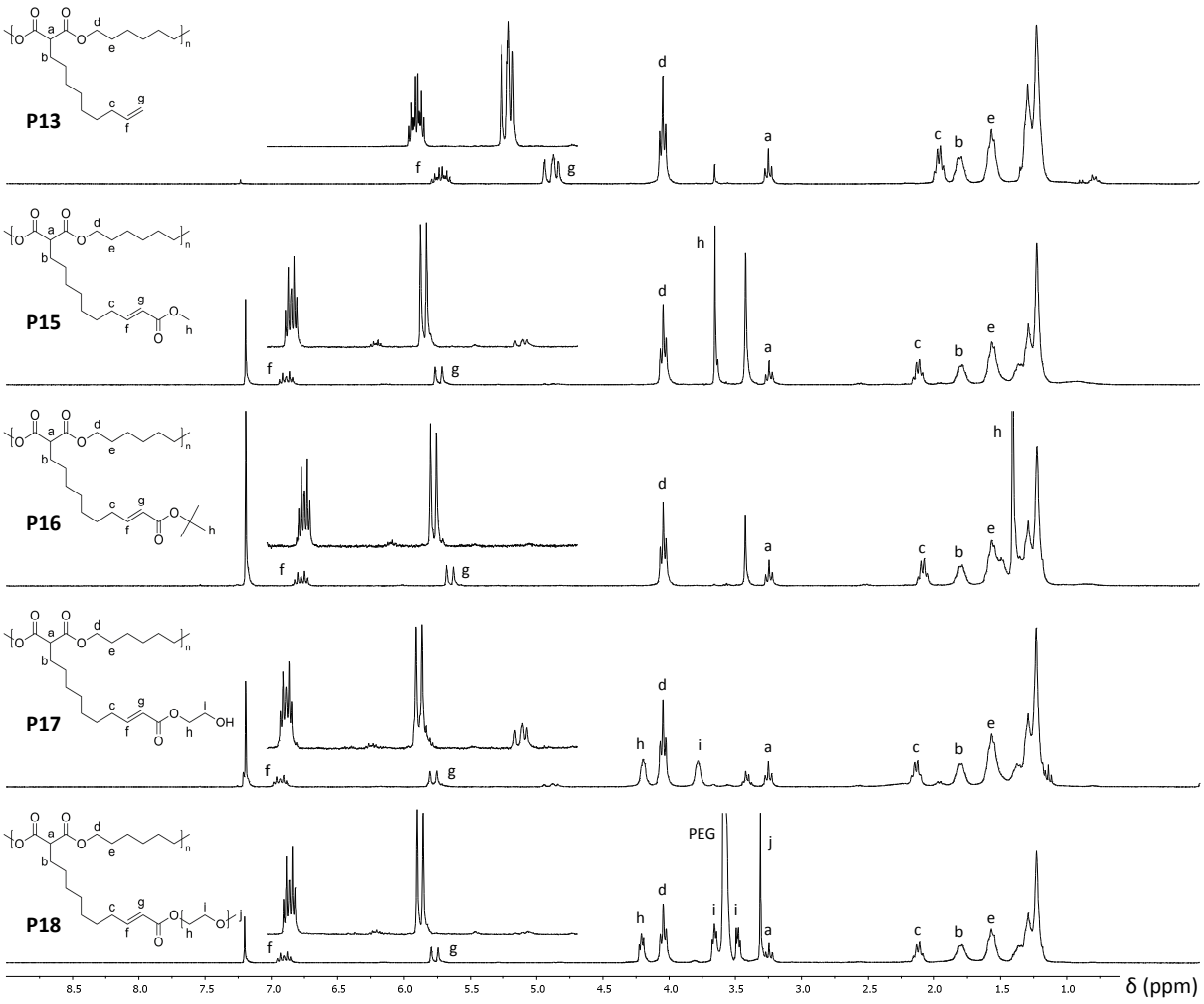


Figure 8 - ^{1}H-NMR spectra of P13 and P15-18, respectively, in $CDCl_3$.

The thermal properties of all olefin-metathesis modified polymers were analyzed by differential scanning calorimetry (Figure 9). In contrast to the starting polymer **P13** with a T_g value of -74.1 °C, polymers **P15-P7**, which were grafted with short acrylates, have slightly higher T_g values (compare Figure 9). Methyl- and *t*-butyl-acrylate modified polymers **P15** and **P16** have almost similar T_g values of -50.8 °C and -51.2 °C, respectively. HEA-modified polymer **P17** has a significantly lower T_g value of -59.2 °C. PEG-modified polymer **P18**, on the other hand, exhibits the expected thermal properties of a semi-crystalline polymer with a T_g value of -59.0 °C, a clear crystallization point at -43.6 °C and the melting transition T_m at -1.9 °C.

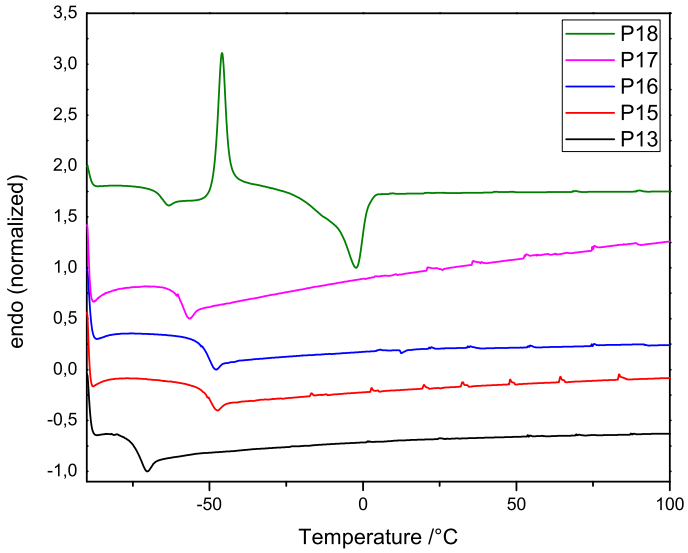
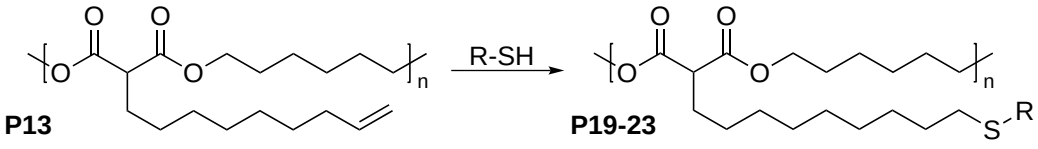


Figure 9 - DSC analysis of P15-18 from 2nd heating scans.

3.1.5. Grafting-onto poly(malonates) *via* thiol-ene addition reactions

Having shown the modification possibilities *via* cross-metathesis, the next grafting-onto technique to be tested was the post-polymerization functionalization of **P13** *via* thiol-ene addition reactions (Scheme 34).[73]



Scheme 34 - Grafting-onto P13 by thiol-ene addition reactions.

It is long known that thiols can add to terminal double bonds by radical initiation or even initiator-free in an anti-Markovnikov manner.[71] The first studies to graft thiols on **P13** were carried out on a 0.5 mmol scale respective to the repeating unit of **P13** in 0.5 mL THF under UV irradiation without any initiator at room temperature for 4 hours employing various amounts of 2-mercaptoethanol as a model thiol compound. These initiator-free reactions proceeded very poorly with low conversion for 1-2 equivalents of thiol (Table 8, entries 1-3) and good conversions of more than 90 % for a 3-fold excess of thiol (Table 8, entry 4). With these results in hand, DMPA was tested as a radical initiator under UV irradiation, also at room temperature. With a loading of 5.0 mol% DMPA, the reaction proceeded with quantitative conversion of the double bond after only 1 hour without observed polymer-polymer coupling (Table 8, entries 5, 6 and 8). Lowering the concentration of DMPA to 2.0 mol% gave only 60 % conversion (Table 8, entry 7). Therefore, 5 mol% of DMPA were used with equimolar amounts of the respective thiol in a 1M THF solution for further modifications. Similar studies were performed in higher dilutions, with larger thiol-

loadings or at higher temperatures usually giving quantitative conversions of the double bonds.[82-84]

Table 8 - Reaction condition screening for the thiol-ene addition of 2-mercaptoethanol on P13.

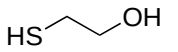
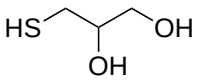
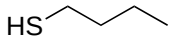
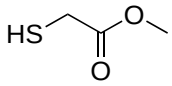
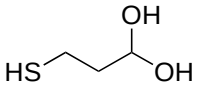
Entry	Thiol (eq.)[a]	DMPA (mol%)[a]	Time (h)	Conv. (%)[b]
1	1.0	-	4.0	~ 55 %
2	1.5	-	4.0	~ 55 %
3	2.0	-	4.0	~ 61 %
4	3.0	-	4.0	~ 90 %
5	1.0	5.0	4.0	Quant.
6	1.0	5.0	2.0	Quant.
7	1.0	2.0	2.0	~ 60 %
8	1.0	5.0	1.0	Quant.

[a]Respective per repeating unit; [b] Calculated *via* ^{1}H-NMR integration in $CDCl_3$

In order to investigate the scope of the thiol-ene addition reaction as a grafting-onto technique, different thiols bearing different functional groups, such as hydroxyl groups, esters or carboxylic acids (Table 9) were employed using the aforementioned optimized conditions. For all thiols used, the reaction proceeded with quantitative consumption of the double bond within one hour as verified by ^{1}H-NMR analysis. Furthermore, ^{1}H-NMR analysis and GPC data (Figure 10) suggested that polymer-polymer coupling was very low (< 5 % as measured *via* GPC-integration) and no side-reactions, such as a radical-initiated ring-closure of the side-chains, occurred. However, it is worth to mention that the GPC results in THF as solvent showed shoulders for all thiol-ene modified polymers. It can be considered that this is due to column interactions of the introduced functional groups, since such interactions and shoulders did not occur when DMAc is used as GPC eluent. However, with DMAc it

was not possible to analyze polymer **P23**. Therefore, polymer **P23** was analyzed with THF as GPC-solvent.

Table 9 - Grafting-onto P13 by thiol-ene addition reactions.

Entry	Thiol	Degree of functionalization[a]	M_n (kDa)	M_w (kDa)	PDI
P19		> 99 %	17.2	30.6	1.79
P20		> 99 %	19.1	33.1	1.73
P21		> 99 %	9.9	14.7	1.48
P22		> 99 %	14.7	22.7	1.55
P23		> 99 %	13.9	29.9	2.14

[a] Calculated *via* ^{1}H-NMR integration in $CDCl_3$

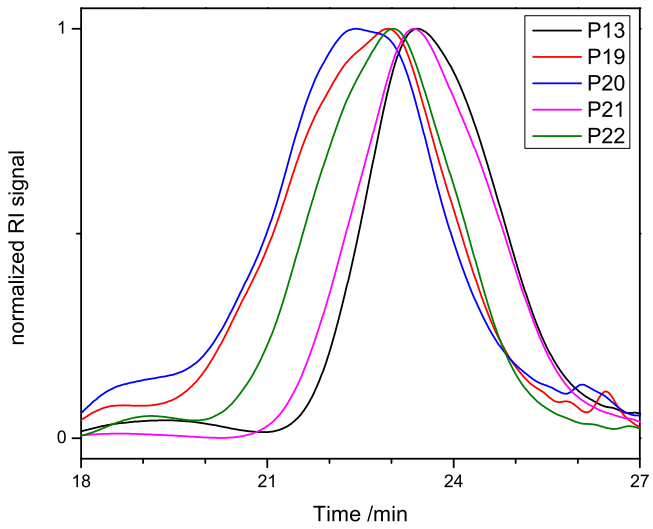
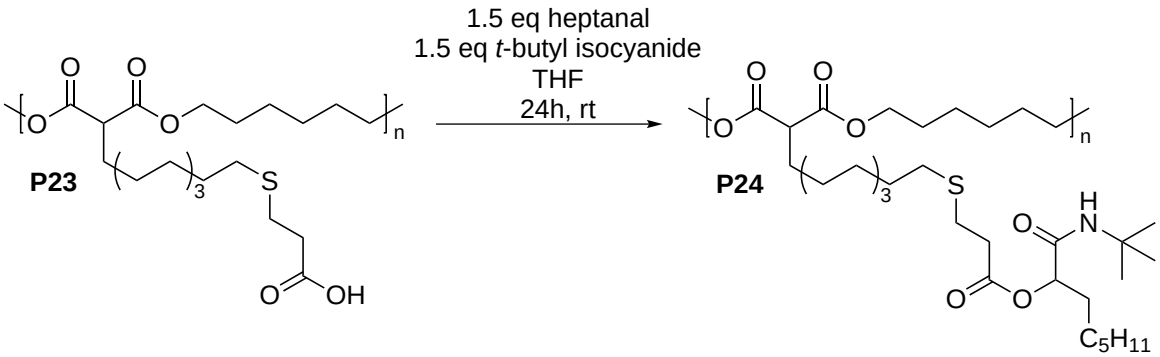


Figure 10 - GPC traces (in DMAC) of P19-22 after precipitation.

In order to broaden the scope of the thiol-ene addition as a grafting-onto reaction, **P23**, bearing free carboxylic acids, was used for a further grafting-onto reaction. Therefore, the Passerini multi-component reaction, which is a 3-component reaction of a carboxylic acid, an aldehyde and an isocyanide, was used.[136] Since its discovery in 1921 by Mario Passerini, the Passerini multi-component reaction has become a very useful tool in organic chemistry for various purposes.[137] Thanks to its great synthetic potential, the Passerini reaction can be used for the synthesis of renewable monomers, as a polymerization method and for grafting onto reactions on polymeric structures under very mild conditions at room temperature.[138] In this context, the idea was to modify the starting polymer **P13** *via* thiol-ene addition of 3-mercaptopropionic acid (**P23**) and subsequently use the pendant carboxylic acids of the resulting polymer for a Passerini reaction without further purification steps in a one-pot reaction (Scheme 35). For the thiol-ene addition, the already established procedure was employed; thus subsequently, *t*-butyl isocyanide and heptanal were added as model substrates, since these compounds would lead to characteristic signals in the ^{1}H-NMR spectra ($CDCl_3$; δ = 1.29 ppm for *t*-butyl and 0.80 ppm for terminal CH_3). Employing 1.0 eq. of the isocyanide and aldehyde, only ~ 80 % conversion was achieved after 24h at room temperature. For 1.1 as well as 1.2 equivalents of isocyanide and aldehyde, respectively, approximately 88 % conversions were obtained under otherwise not modified conditions. However, complete conversion of the carboxylic acid was achieved when employing 1.5 equivalents of the reagents, which was verified by ^{1}H-NMR analysis. The resulting polymer was precipitated in cold *n*-hexane to obtain it in > 95 % yield. Also, GPC analysis clearly showed a very efficient reaction proceeding without any noticeable side-reaction (Figure 11). The presence of the shoulders in the GPC spectra was previously discussed and could be

assigned to interactions with the column on the THF-GPC system. Furthermore, it was observed that the obtained polymer **P24** seems to cross-link when it is stored dry at room temperature.



Scheme 35 - Grafting onto P23 *via* Passerini multicomponent reaction.

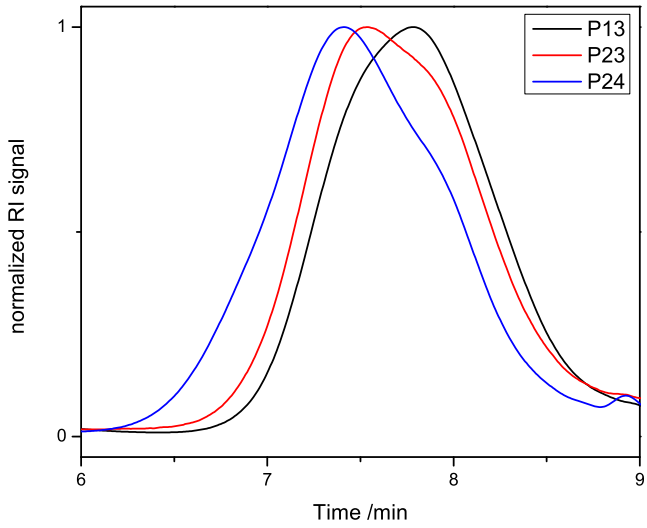


Figure 11 - GPC traces (in THF) of polymers P23 and P24 after precipitation.

The thiol-ene modified polymers **P19-24** exhibit the expected thermal behavior (Figure 12) as measured with DSC analysis. Polymers **P19** and **P20**, which bear one and two hydroxyl groups in the side-chain, respectively, have a higher T_g value of -54.6 or -46.0 °C than the starting polymer **P13** with -74.1 °C. The 1-butanethiol

modified polymer **P21** showed a clear melting transition at -41.7 °C. These results are in accordance with the earlier findings that longer aliphatic side-chains in the polyesters increase the melting point. Polymers **P22** and **P23** exhibit T_g values of -63.6 or -40.9 °C, respectively. Finally, the Passerini-modified polymer **P24** exhibits the highest T_g value of -29.8 °C which can be explained by the strong hydrogen-bonds from the Passerini-product.

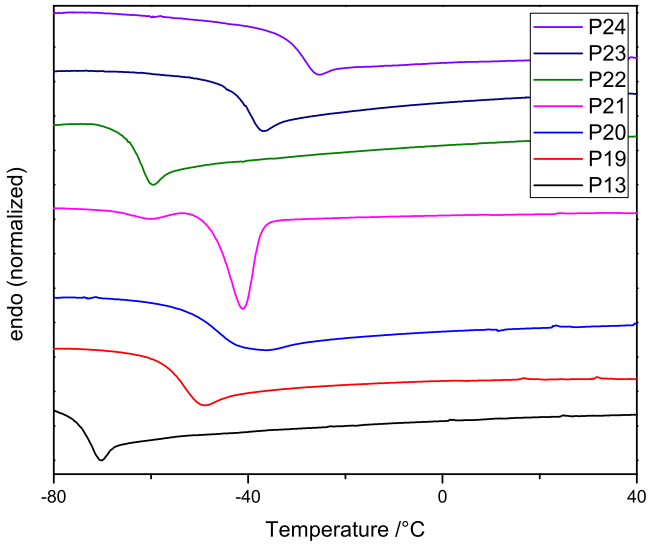
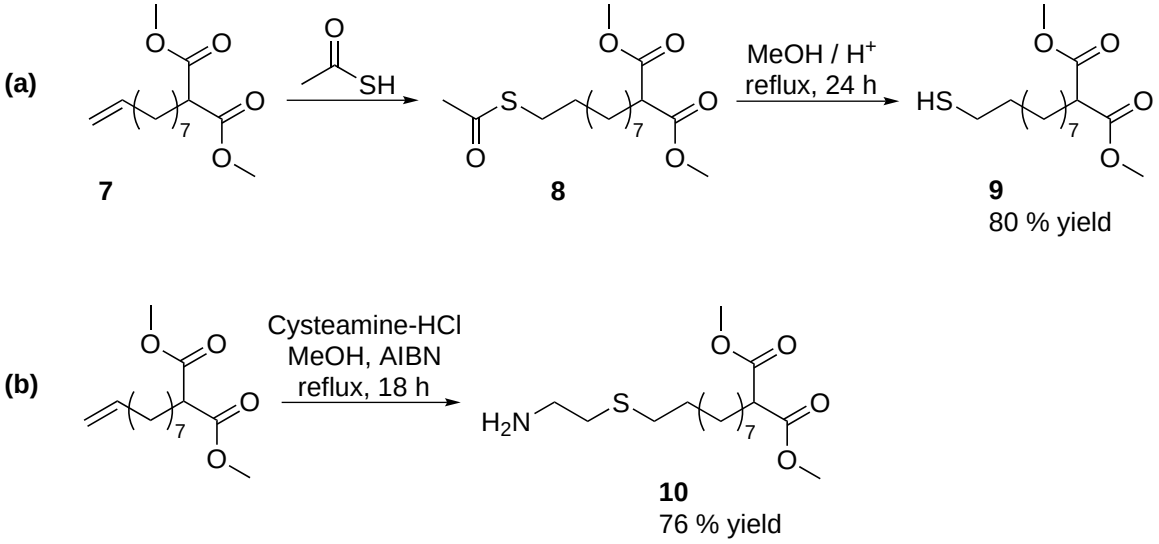


Figure 12 - DSC analysis of polymers P19-24 with results from 2nd heating scans.

3.1.6. Synthesis and polymerization of AB_2-type malonate derivatives

Another possible use for the malonate derivative from methyl undec-10-enoate (**7**) is the preparation of AB_2-type monomers by thiol-ene addition reactions. Thereby, several different monomers are possible to prepare such as *ω*-hydroxy, *ω*-amino or *ω*-mercapto-malonates. In order to test their behavior as AB_2-type monomers, the *ω*-mercapto- (**9**) and *ω*-amino-malonate (**10**) were synthesized from **7** as presented in Scheme 36.

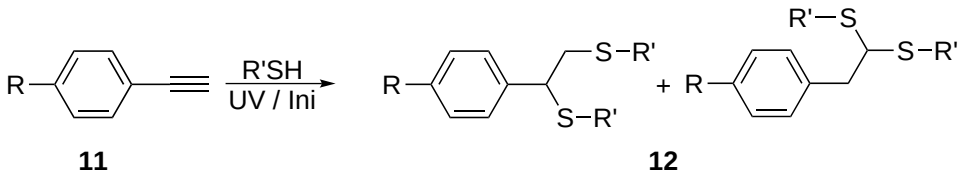


Scheme 36 - Synthesis of AB_2-type malonates from 7.

For the preparation of **9**, a two-step approach was used (Scheme 36**a**). Thereby, the first step was the thiol-ene addition of 1.1 equivalents thioacetic acid with **7** in order to obtain a thio-ester (**8**) in quantitative yield. By this reaction, the double bond was consumed completely after 3 hours. The obtained thio-ester can afterwards easily be cleaved by either basic saponification or transesterification with methanol under acetic conditions yielding the desired thiol **9** and methyl acetate as by-product. With this strategy, highly pure monomer **9** was obtained in a total yield of 80 % after 2 steps. For the synthesis of the *ω*-amino-malonate **10** (Scheme 36**b**), cysteamine

hydrochloride was used for the thiol-ene addition in methanol. In this reaction, the thiol-ene addition was initiated with AIBN at reflux conditions, since otherwise the cysteamine hydrochloride was not fully soluble. Also, earlier experiments have shown that under such conditions, the maximum conversion and yield was obtained.[76] Performing this reaction, **10** was obtained after 18 hours reaction time and subsequent work-up in 76 % yield and high purity.

With AB_2-monomer **9** in hand, its thiol-ene and thiol-yne reaction behavior was investigated. The main interest was to use **9** as a branching molecule for the preparation of dendrimers; therefore it was tested with a phenylacetylene-derived dendrimeric core-molecule (Scheme 37, kindly donated by the group of Prof. Bräse).



11 **12**

Scheme 37 - Thiol-ene addition reaction on phenylacetylene-based cores.

However, it is apparent that although the synthesis of **9** worked well, the prepared thiol **9** does not exhibit efficient thiol-ene behavior compared to commercially available compounds like methyl thioglycolate (Me-TG). This was verified by GPC analysis of the prepared first-generation dendrimers (Figure 13).

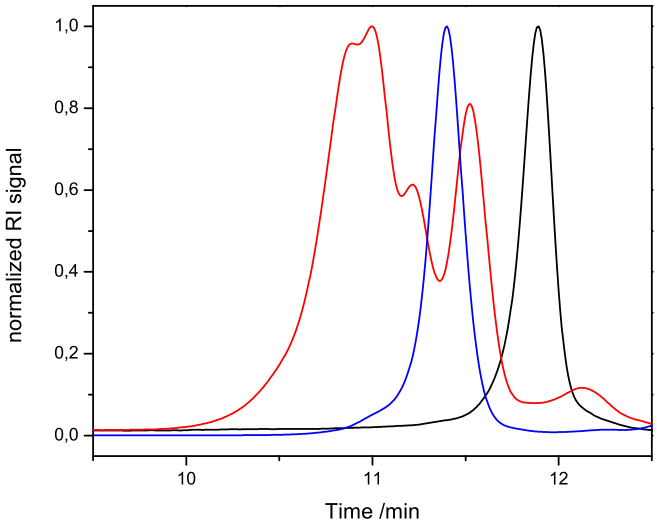
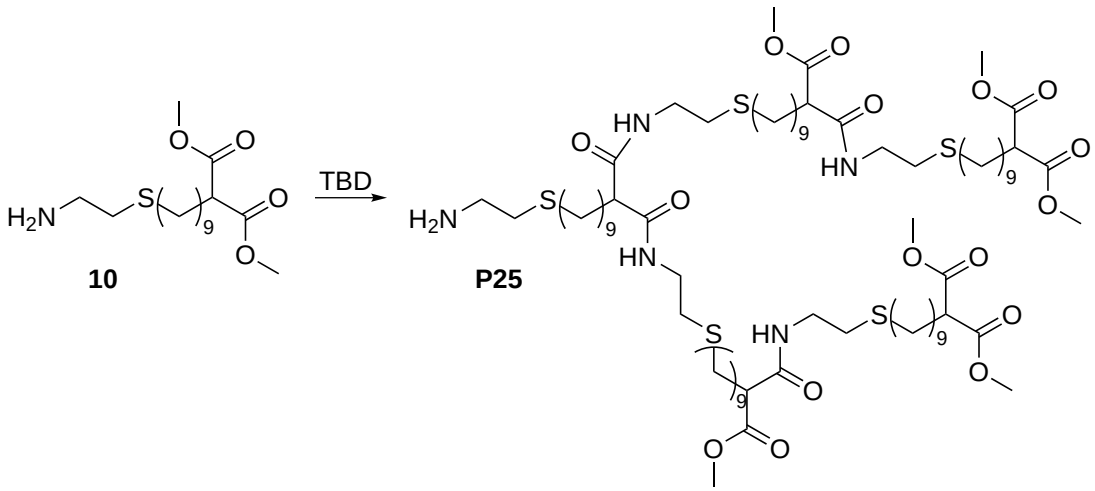


Figure 13 – GPC traces in THF of crude mixtures from thiol-yne additions onto 11 (black line) using compound 9 (red line) and commercially available methyl-thioglycolate (blue line).

After these somewhat disappointing results, the next aim was to investigate the self-polymerization of the *ω*-amino malonate **10**. A direct polymerization of this compound would yield a hyperbranched polyamide (**P25**) with a high content of residual methyl-esters (Scheme 38). Because of the high stability of the amide-bond, these methyl-esters should be selectively accessible and cleavable without destruction of the polymeric backbone.



Scheme 38 - Possible branched polyamide P25 derived from 10.

In this context, the hyperbranched polyamide **P25** was first prepared by direct polymerization of **10** catalyzed by 5 mol% TBD at 160 °C for 4 hours under vacuum. During the reaction, a reddish, gel-like material formed, which was insoluble in nearly every organic solvent. In HFIP, the compound was slightly soluble allowing GPC measurements. These measurements showed clearly that a polymer was obtained with a satisfying average molecular weight of M_n = 7.56 kDa, but a relatively high PDI of 3.50 (Figure 14). However, this PDI was somewhat expected since this reaction cannot be considered as a classical polycondensation. In addition, although a polymer was clearly obtained, the resulting ^{1}H-NMR was not possible to analyze and did not exhibit all signals, which were expected for the product formation. It was also tried to selectively cleave the methyl-esters by various methods, such as saponification with sodium or potassium hydroxide or lithium bromide. However, in all cases, a completely insoluble material was obtained. Because of this low solubility, another trial to polymerize **10** was performed by using a core-molecule (trimesic acid methyl ester, 1:7 ratio of core to **10**) in order to limit the possible molecular weight of the polymer. Compared to the core-free polymerization, although GPC data showed a lower molecular weight, the polymer was still almost insoluble and the ^{1}H-NMR also was misleading. Therefore, no further experiments with the AB_2-type malonates were performed.

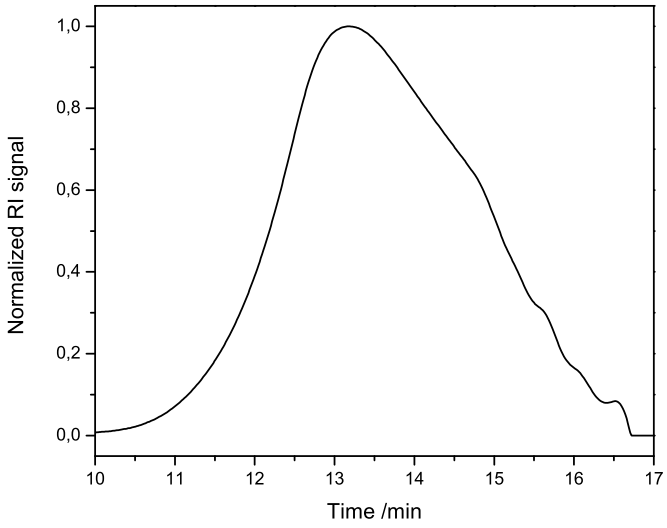
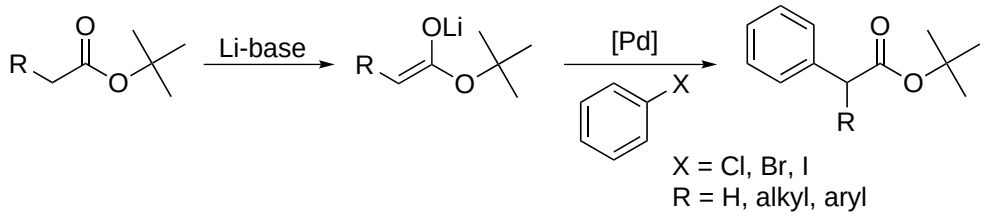


Figure 14 - GPC traces (crude, in HFIP) of P25 after a core-free polymerization of 10 catalyzed by TBD.

3.2. *α*-Arylation of *t*-butyl fatty acid esters[†]

Apart from the preparation of malonates, another possibility to use the *α*-acidity of fatty acids is the arylation reaction. In this reaction, a *t*-butyl ester is deprotonated at the *α*-position employing a strong lithium-base. After the enolate formation, this reactive intermediate is coupled with aryl halides using palladium catalysts (Scheme 39).



Scheme 39 - Schematic overview of the *α*-arylation reaction.

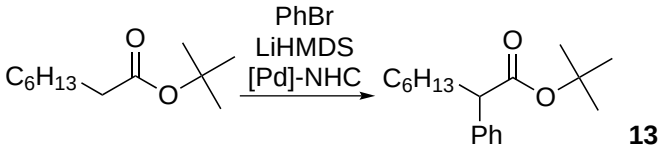
Such reactions have been studied intensively for short-chain esters, mainly *t*-butyl acetate, whereas the main application of these reactions is the synthesis of drugs such as Ibuprofen and similar compounds.[139-145] However, the reaction should be applicable also to long-chain fatty acid esters.

Therefore, the potential to derivatize saturated fatty acids *via* *α*-arylation reactions was investigated. Thereby, a main focus was the arylation reaction with 1,4-dibromobenzene in order to obtain aryl-bridged diesters, which would offer an access for the preparation of partially renewable polymers or for the synthesis of gemini surfactants.

[†] The work of this chapter has been partially published:
N. Kolb, R. Hofsäß, M. A. R. Meier, α-Arylation of saturated fatty acids, *Eur. J. Lipid Sci. Tech.,* 2013, **115**, 729-734

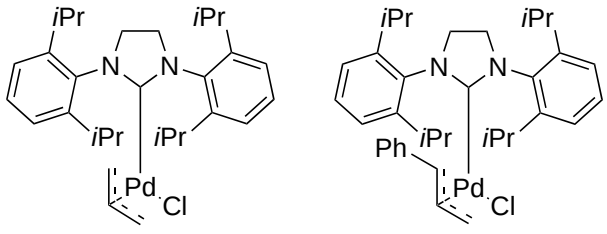
3.2.1. Reaction-condition screening and preparation of aryl-bridged diesters

As described before, the *α*-arylation reaction has been widely studied with short-chain esters, mainly *t*-butyl acetate.[139] Therefore, results reported by Hartwig and coworkers, who studied the reaction conditions intensively with respect to the used base, solvents and ligands, were adapted.[145] The first studies were carried out with *t*-butyl octanoate and bromobenzene to test the arylation activity of long-chain aliphatic esters in general (Scheme 40). It should be noted that the stable and bulky *t*-butyl esters were crucial for the reaction, since otherwise side-reactions like the Claisen-condensation are taking place. Therefore, unsurprisingly, test reactions with other fatty acid esters (methyl- or isopropyl-octanoate) did not result in any product formation.



Scheme 40 - *α*-arylation of *t*-butyl octanoate with bromobenzene.

As catalysts, NHC-ligated palladium complexes **NHC-1** and **NHC-2** (Scheme 41) were used, which are commercially available, air-stable and known to give the highest yields in the *α*-arylation of *t*-butyl acetate with aryl bromides.

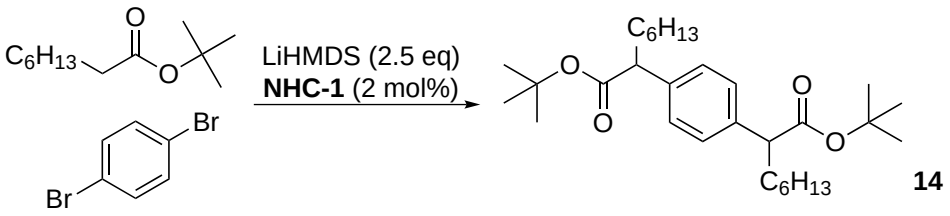


NHC-1 **NHC-2**

Scheme 41 - NHC-palladium catalysts employed for the arylation reactions.

The first set of experiments for the arylation of *t*-butyl octanoate was carried out with both catalysts at room temperature for 4 hours and high loadings of catalysts (10.0 mol% per ester). Under these conditions, the conversion of the starting material was quantitative with a product selectivity of approximately 70 % for both catalysts as quantified *via* GC measurements. Reducing the amounts of the catalyst to 5.0 mol% resulted in a conversion of the starting ester of 97.9 % and a change in the product selectivity to 84.0 % for **NHC-1**, whereas both conversion and product selectivity remained unchanged for **NHC-2**. Further decrease in the loading of the catalyst (2.0 mol%) resulted in slightly lower conversions of 95.6 % for **NHC-2** and 81.2 % for **NHC-1**, respectively. However, the product selectivity increased to 75.0 % for **NHC-2** and dropped to only 70.4 % for **NHC-1**. This unexpected low product selectivity for catalyst loading of 2.0 mol% remained the same after 6 hours reaction time. However, raising the temperature to 40 °C, a quantitative conversion of the starting material was achieved for both catalysts even with 2.0 mol% loading and a good product selectivity of 79.0 % for **NHC-1** was detected. For **NHC-2** on the other hand, the product selectivity dropped to only 21.7 % at the applied higher temperature. Moreover, increasing the temperature to 60 or even 80 °C resulted in even worse product selectivity, because of side-reactions and most probably the low stability of the formed enolate. Therefore, all further reactions were performed using **NHC-1** with 2.0 mol% catalyst loading and 40 °C for 6 hours. It is necessary to mention that during the performed reaction condition screenings, a relatively poor reproducibility was encountered for some of the reactions, showing more than 10 % difference for the product selectivity as detected by GC measurements. However, with the optimized reaction conditions, the reaction was possible to be reproduced with a maximum of 5.0-10.0 % error in both conversion and product selectivity, as observed

by GC analysis. Therefore, the next goal was the synthesis of renewable diesters by arylation of fatty acids with 1,4-dibromobenzene (Scheme 42).

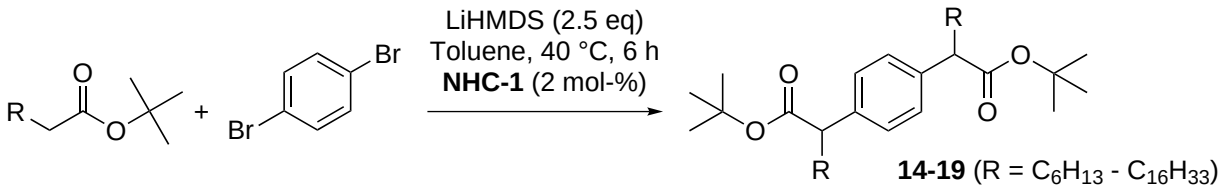


Scheme 42 - Test-reaction for the arylation of *t*-butyl octanoate.

These investigations were started by testing the reaction of *t*-butyl octanoate with 1,4-dibromobenzene using 2.0 mol% of **NHC-1**. Only 0.45 equivalents of 1,4-dibromobenzene were used in order to ensure complete consumption of the aromatic compound and 2.5 equivalents of the base, both respectively to the ester. This reaction led to complete conversion of the starting material with a product selectivity of 88.0 % after 4 hours, which was quite satisfying. With these results in hand, the upscaling of this reaction to a 10 mmol scale, respectively to the starting ester, was carried out (Table 10). In order to ensure a complete conversion, the reaction time was extended to 6 hours, where a higher product formation was observed by ^{1}H-NMR. All other reaction parameters were kept unchanged.

In order to obtain pure compounds, purification *via* column chromatography was crucial for all synthesized diesters. The products were obtained as white to yellowish, waxy compounds in the range of 60 to 80 % yield. All compounds were able to be recrystallized from acetone.

Table 10 - Synthesis and isolated yields of aryl-bridged diesters 14-19 from saturated FAMEs.



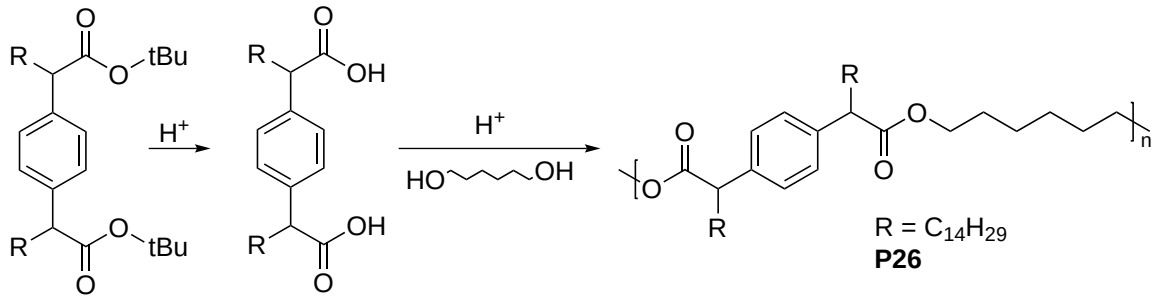
14-19 (R = C_6H_{13} - $C_{16}H_{33}$)

Entry	Product	R =	Isolated yield [%][a]
1	**14**	C_6H_{13}	83.4
2	**15**	C_8H_{17}	59.9
3	**16**	$C_{10}H_{21}$	65.6
4	**17**	$C_{12}H_{25}$	61.9
5	**18**	$C_{14}H_{29}$	67.1
6	**19**	$C_{16}H_{33}$	72.4

Reaction conditions: fatty acid *t*-butyl ester (10.0 mmol) with 1.07 g 1,4-dibromobenzene (4.50 mmol) and 115 mg (2.0 mol%) catalyst NHC-1 in 25 mL LiHMDS (1M in toluene, 2.5 eq.); [a] The products were isolated by column chromatography with a solvent gradient from *n*-hexane:acetone 99:1 to 97:3.

3.2.2. Polymerization reactions of aryl-bridged diesters

After having obtained the aryl-bridged diesters **14-19**, the next aim was the preparation of polyesters directly from the synthesized *t*-butyl diester using 1,6-hexanediol as comonomer. For this purpose, the polymerization behavior of **18** with 1,6-hexanediol was tested using different catalysts such as Ti(O*i*Pr)$_4$ and Sn(Oct)$_2$ or the organic catalyst TBD, which all have been used for polyester synthesis before.[60-61, 79, 146-147] However, all of these catalysts remained inactive for the *t*-butyl esters. It can be considered that the reason for this matter is the steric hindrance of the *t*-butyl esters. To accomplish a successful polymerization, sulfuric acid was used in different concentrations as catalyst, which first led to a cleavage of the *t*-butyl ester followed by acid catalyzed esterification (Scheme 43).



Scheme 43 – Polymerization trials of aryl-bridged diester 18 with sulfuric acid to P26.

Unfortunately, also this method resulted only in oligomers of low molecular weight (Figure 15). This might be explained with the low stability of esters towards strong acids, especially in high temperatures.[66]

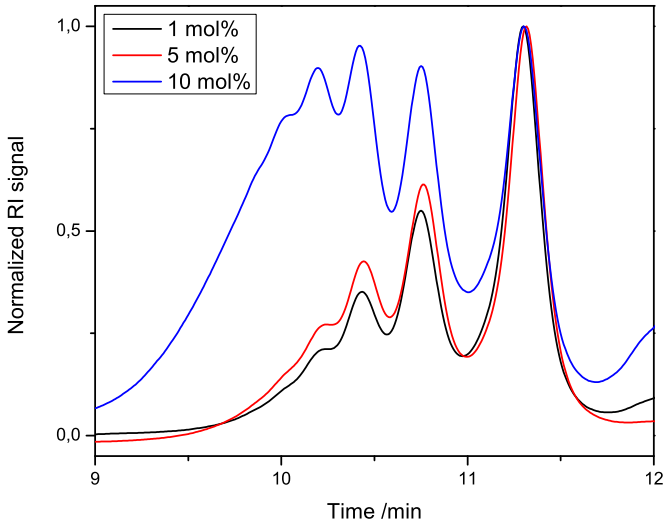
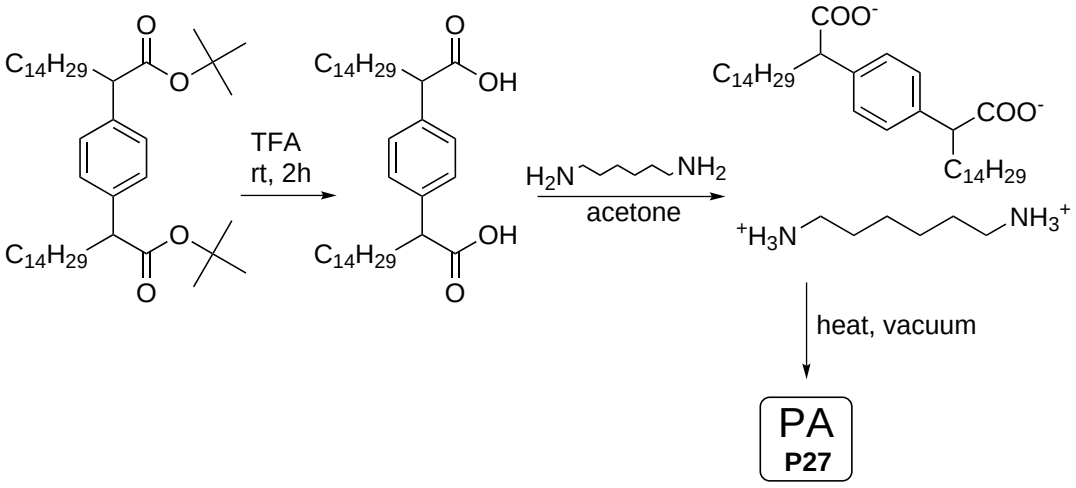


Figure 15 - GPC traces in THF of polyester P26 prepared from 18 and 1,6-hexanediol by catalytic amounts of sulfuric acid.

Somewhat disappointed by these results, the next interest was the preparation of polyamides with 1,6-hexanediamine, with **18** as the model monomer. Considering that the *t*-butyl ester seemed too bulky for a successful polymerization, a 2-step approach was employed (Scheme 44).



Scheme 44 - Preparation of polyamides from free diacids.

Therefore, the diesters were deprotected first using TFA in DCM. This reaction proceeded very well yielding the free carboxylic acids in quantitative yields after

2 hours reaction time at room temperature. The used reagents can be easily evaporated afterwards; therefore no further purification was necessary. In the second step, the free carboxylic acid was dissolved in acetone and mixed with 1,6-hexanediamine in a 1:1 ratio. An immediate formation of a precipitate was observed, which was insoluble in boiling acetone. After removal of the solvent and washing with acetone, the precipitate was heated to different temperatures under high vacuum for 18 hours. The precipitate melted at a temperature of approximately 180 °C, and thus the polymerization was performed at considerably higher temperatures, namely 220, 240 and 280 °C for 18 hours. At higher temperatures, undesirable side-reactions took place resulting in completely insoluble, black, coal-like solids in both cases. At 220 °C however, it was possible to solubilize the obtained compound in boiling DMF for precipitation in ice-cold water. The obtained brownish powder was surprisingly insoluble in the standard polyamide-solvent HFIP, but very well soluble in THF. GPC analysis of this compound showed a polymer, but unfortunately with a rather low average molecular weight of M_n = 5.1 kDa and incomplete polymerization as seen from the GPC traces (Figure 16).

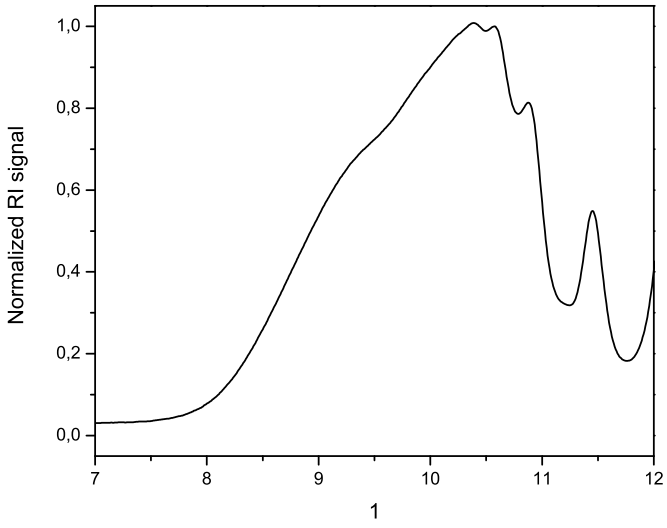
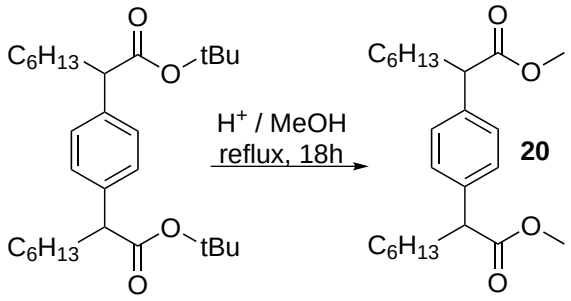


Figure 16 - GPC traces of a precipitated polyamide P27 prepared by heating the free acid of 18 and 1,6-hexanediamine under vacuum.

The next approach to polymerize the aryl-bridged diesters was the transesterification of **14** to the methyl ester **20** (Scheme 45) and its subsequent polymerization.



Scheme 45 - Preparation of methyl-diester 20.

For these experiments, the earlier reported conditions for the synthesis of poly(malonates) and poly(malonamides) were used, namely 1 mol% Ti(O*i*Pr)$_4$ as catalyst for polyester synthesis and 5 mol% TBD for the synthesis of polyamides with 1,6-hexanediol and 1,6-hexanediamine, respectively.[146] The methyl-diester **20** was synthesized easily by refluxing **14** in methanol together with 2 mol% sulfuric acid over

night, filtering the mixture over basic alumina and evaporation of the solvents. The preparation of the polyester **P28** was then performed at 120 °C, first with a stream of argon for 1 hour and subsequent 18 hours under high vacuum, using 1 mol% $Ti(OiPr)_4$. Unfortunately, only oligomers were obtained also in this case (Figure 17). For the synthesis of polyamide **P29**, a gradient heating was performed starting at 120 to 200 °C with a temperature raise of 20 °C every 30 minutes under a stream of argon. Afterwards, the mixture was heated to 200 °C applying high vacuum for 4 hours. For this reaction, GPC analysis (also in THF) revealed only oligomers as well (Figure 17).

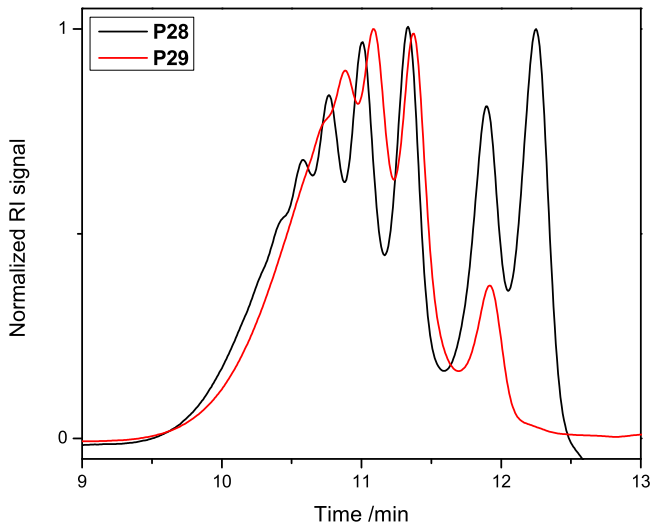
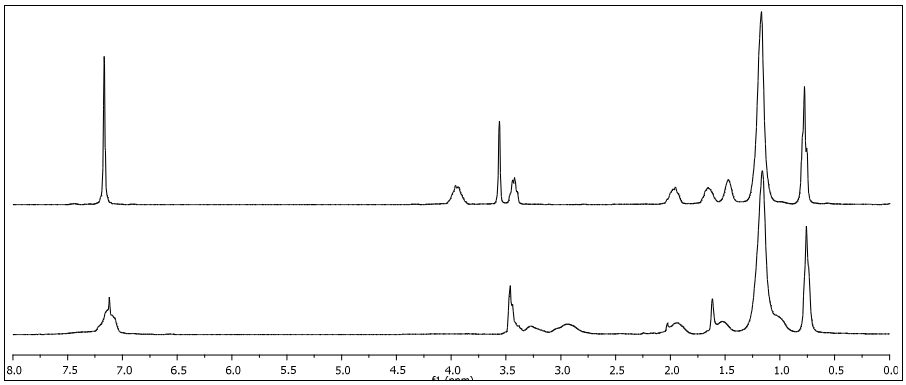


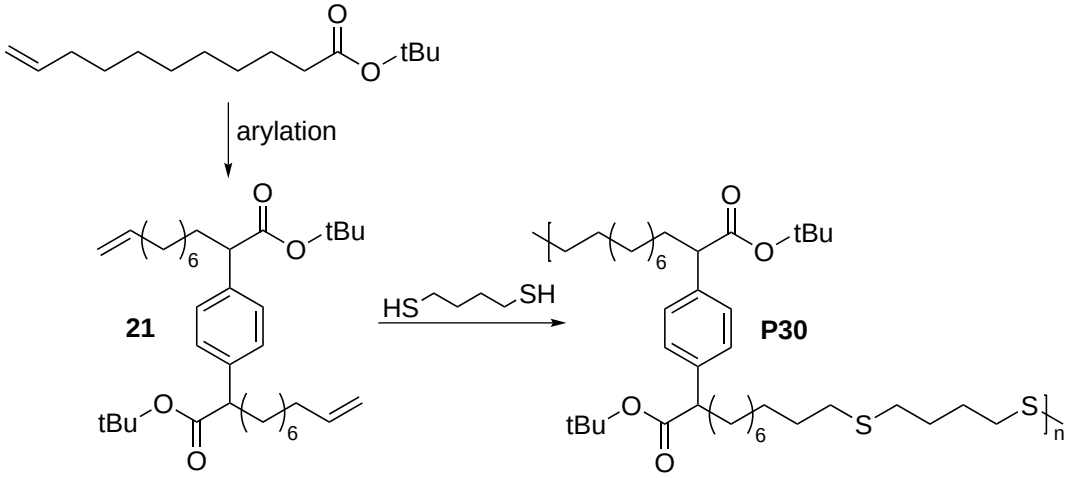
Figure 17 – GPC traces in THF of polyester P28 and polyamide P29.

Also, ^{1}H-NMR analysis of the resulting oligomers showed approximately 40 % residual, unreacted methyl ester (Scheme 46). These data suggest that the reason for this very low transesterification/transamidation and polymerization activity results from the steric hindrance of the employed monomers. Therefore, no further trials for the polymerization of the aryl-bridged diesters **14-20** were performed.



Scheme 46 - ^{1}H-NMR of P28 (top) and P29 (bottom) prepared from 20 with residual methyl ester.

However, it must be noted that the *α*-arylation reaction can also be performed with *t*-butyl undec-10-enoate yielding a diester with 2 terminal double bonds (**21**, Scheme 47). Although some double bond isomerization was observed, the reaction works considerably well offering the aryl-bridged diester in 64 % yield after column chromatography.



Scheme 47 - Preparation of P30 by thiol-ene addition.

This monomer can be co-polymerized with dithiols, for example 1,4-butanedithiol, to yield **P30**. This polymerization works considerably well under UV irradiation with DMPA as catalyst at room temperature for 4 hours. However, GPC analysis (Figure 18) revealed a PDI of approximately 3, which is too high for a conventional polycondensation reaction. This suggests an inhomogeneous polymerization mixture

and/or side-reactions. In addition, after precipitation, the resulting polymer was hardly soluble in any organic solvent which suggests undesired cross-linking reactions. In general, the aforementioned polymer would contain esters or carboxylic acids within its chain, thus providing access to polymers with a rather inert backbone and high grafting-onto possibilities. However, due to the side-reactions occurring during polymerization and the preparation of the monomer, which were not in line with the terms of green chemistry, the synthesis and consequent modification of **P30** was not followed.

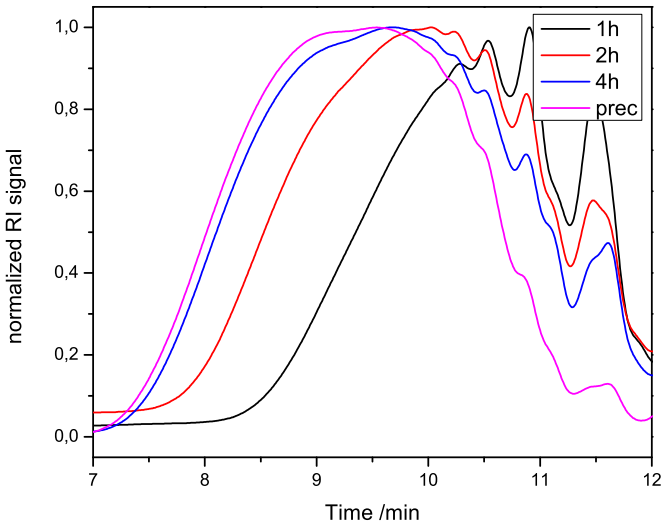
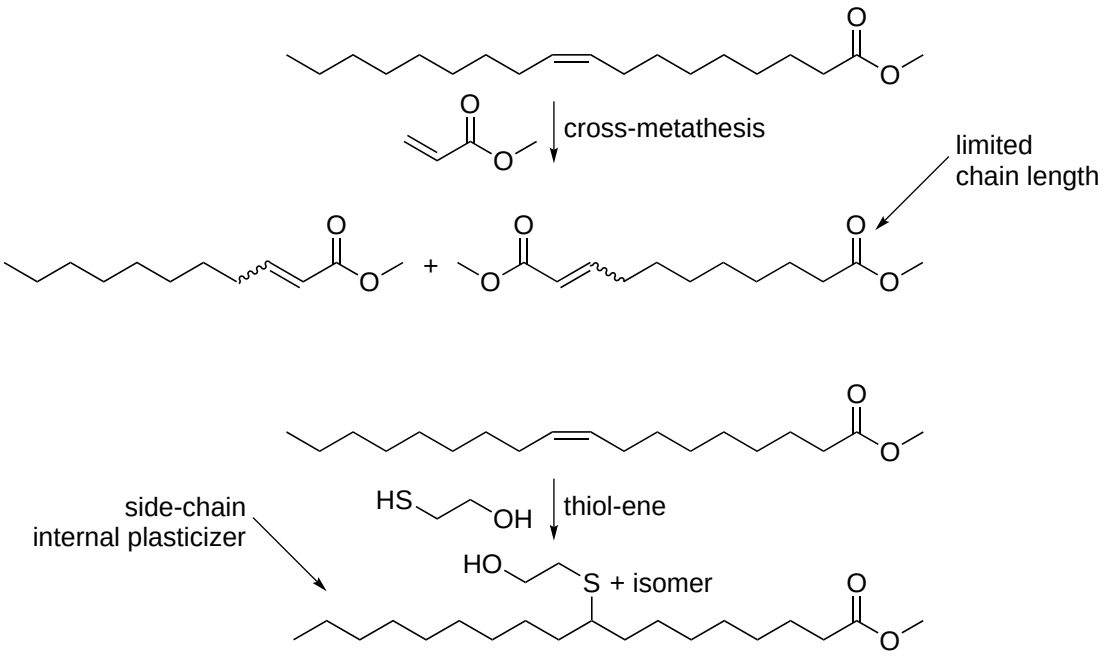


Figure 18 – GPC traces in THF of polymer P30 prepared by thiol-ene addition reaction.

3.3. Preparation of omega-unsaturated long-chain fatty acids[‡]

As it was already mentioned before (compare Chapter 1.3), numerous reactions have been reported in order to derivatize fatty acids towards renewable monomers. Apart from the use of the *α*-acidity, the double bond was used for these reactions (Scheme 48). However, the double bond was usually used at the specific position of the fatty acid chain where it naturally occurs. This limits the chain lengths of the resulting monomers for olefin (cross-) metathesis reactions. For thiol-ene addition reactions on the other hand, a pending, aliphatic chain will be present in the monomer and resulting polymer, which can act as an internal softener thus limiting the possible applications of the respective polymers.



Scheme 48 - Possible derivatizations of methyl-oleate towards monomers.

Therefore, for the synthesis of long-chain *ω*-unsaturated FAMEs, the double bond needs to be either isomerized towards the chain end or it has to be introduced at the

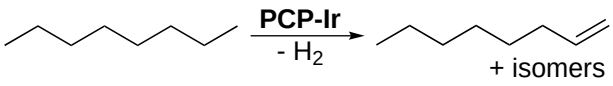
[‡] The work of this chapter has been partially submitted for publication:
N. Kolb, M. Winkler, C. Syldatk, M. A. R. Meier, *Eur. Poly. J*, submitted

chain end of saturated fatty acids by a dehydrogenation process. Such a dehydrogenation reaction has been presented for alkanes in order to prepare *α*-olefins and respective isomers by iridium-catalysis.[128] If such a reaction would be applicable towards saturated fatty acids, the respective *ω*-unsaturated fatty acids could be modified by self-metathesis to yield long-chain *α*,*ω*-diesters with chain lengths of up to C_{34}, mainly derived from stearic acid. The thereof resulting polymers would be interesting in terms of a renewable substitute for polyethylene, since it has been shown that the thermal properties of long-chain polyesters come close to those of high-density polyethylene.[60, 92-93, 96]

However, if such a derivatization would not be possible using iridium catalysts, those FAMEs could also be prepared from fatty acids, which were obtained *via* biotechnology routes. It is long known that the yeast *Candida brobicila* can oxidize fatty acids at the *ω*-1 position in order to prepare so-called sophorose lipids.[121] Also, *ω*-hydroxy fatty acids from biochemically transformations[116] are commercially available and should be possible to use for the preparation of *ω*-unsaturated FAMEs by employing straight forward organic chemistry.

3.3.1. Terminal dehydrogenation of fatty acids

Carbon-hydrogen bonds are among the most stable bonds in organic chemistry, making these bonds almost chemically inert. Therefore, one of the biggest challenges to date is to selectively activate carbon-hydrogen bonds, for example in alkanes. Within this context, pincer-ligated iridium (**PCP-Ir**) catalysts have been presented, which have the ability to dehydrogenate alkanes towards alkenes, both with and without a hydrogen acceptor. Thereby, it is of high importance that these catalysts have an unusual selectivity for *α*-olefins when linear alkanes are used for the dehydrogenation reaction (Scheme 49).[128-129]

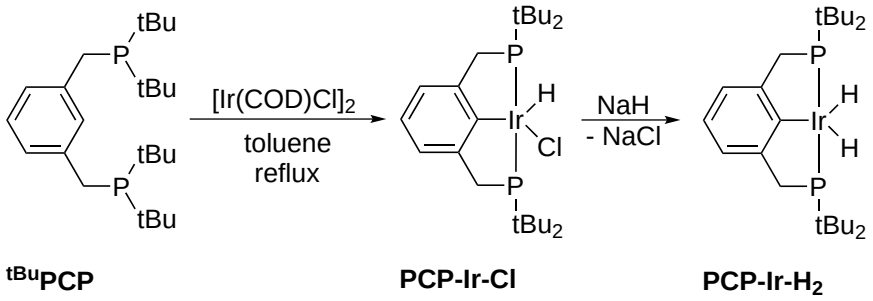


Scheme 49 - Dehydrogenation of *n*-octane.

However, these catalysts have also the tendency to isomerize double bonds; therefore, also the respective isomers are formed. Furthermore, it was shown that the dehydrogenation reaction of cyclic alkanes, for example cyclooctane, worked much better than for linear alkanes. Also, the dehydrogenation without a hydrogen acceptor worked hardly for linear alkanes but fairly good for cyclic ones.

Therefore, the first approach for the preparation of FAMEs with a terminal unsaturation was carried out with the above mentioned iridium pincer compounds. The commercially available ligand **^{tBu}PCP** was used for the catalyst synthesis along with *bis*(1,5-cyclooctadiene)diiridium(I)-dichloride as metal source in refluxing toluene for 18 hours (Scheme 50).[148] The reaction has to be carried out under inert conditions, since otherwise the phosphines oxidize easily and therefore cannot be

used as ligands anymore. After the complete reaction, the solvent can easily be removed under reduced pressure to yield the pre-catalyst **PCP-Ir-Cl** in >90 % purity as calculated from ^{1}H-NMR integration. Furthermore, the pre-catalyst is stable towards air and water and can therefore be handled without special care.

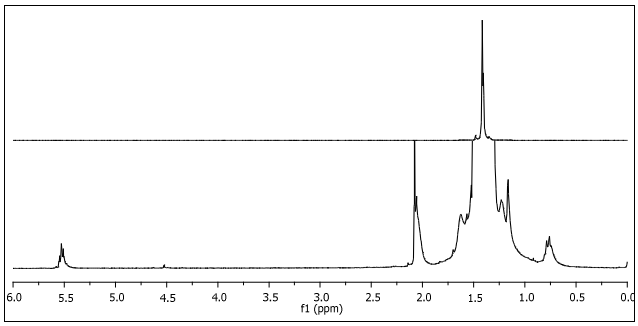


Scheme 50 - Synthesis of iridium-based dehydrogenation catalyst PCP-Ir-H_2.

The activated form of the catalyst (**PCP-Ir-H_2**) can be obtained by addition of a strong base, such as NaH or potassium *t*-butoxide.[149-151] However, it is known that the active form of the catalyst has the tendency to form a nitrogen bridged dimer with an unusual high stability, which results in a complete loss of the catalytic activity.[152] Therefore, the catalyst either needs to be stored under argon or has to be prepared *in situ*.

The tests for the catalytic activity in general were performed by *in situ* generation of the catalyst with COA as cyclic alkane as well as tetradecane as linear alkane. For the dehydrogenation of COA, 15.0 mmol alkane were used with 3.0 mmol TBE as hydrogen acceptor and 0.01 mmol **PCP-Ir-Cl** as catalyst with 1.2 mg NaH as activator. The mixture was stirred under argon at 150 °C for 4 hours. Afterwards, the crude mixture was analyzed *via* ^{1}H-NMR showing clearly the formation of internal double bonds and an approximately TON of 20 (Scheme 51). For tetradecane, on the other hand, 10.0 mmol alkane were employed with 1.0 mmol hydrogen acceptor and

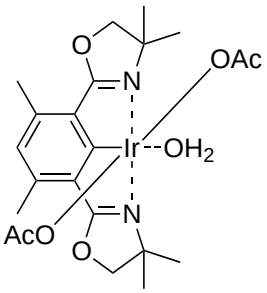
otherwise similar conditions. Two hydrogen acceptors were used, which have been already reported in the literature, TBE and 1-decene, which both worked very well but in both cases the double bond isomerized within the chain.[153] The TONs were approximately 15 for TBE as hydrogen acceptor and 30 for 1-decene.



Scheme 51 - ^{1}H-NMR spectra in $CDCl_3$ of cyclooctane before (top) and after (bottom) the dehydrogenation reaction with different zoom factors; on the lower spectrum, hydrogen signals for cyclooctene are visible at ~ 5.5 ppm for the internal double bonds and ~ 2.0 ppm for *α*-hydrogens next to the double bonds.

Although it was only possible to determine the TON by ^{1}H-NMR having a considerable error, these data show clearly that the dehydrogenation reaction with the synthesized iridium-catalysts worked fairly well. Therefore, the next step was to investigate whether or not saturated fatty acids can be dehydrogenated using such compounds. Unfortunately, it turned out that activated iridium-pincer dehydrogenation catalysts have the tendency to coordinate towards carbonyl functionalities. As a result of this coordination, the dehydrogenation activity is complete lost, which has been published earlier.[154] Therefore, it seems that it is not possible to synthesize *ω*-unsaturated FAMEs by this method. However, a new generation of such compounds has been introduced, which are acetate-ligated and still have a dehydrogenation activity (Scheme 52).[155] Although this dehydrogenation is only performed stoichiometrically, it seems promising that it might be possible to

dehydrogenate saturated FAMEs with iridium complexes. However, this reaction was not investigated.

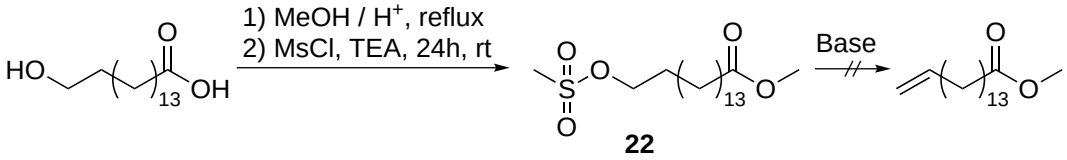


Scheme 52 - New acetate-coordinated iridium complex for dehydrogenation reactions.

Because of these somewhat disappointing results, biochemically modified fatty acids were tested for the preparation of long-chain diesters in the next chapter.

3.3.2. Preparation of *ω*-unsaturated, long-chain FAMEs

In order to investigate the synthesis of long-chain diesters, biotechnologically derived *ω*-hydroxy fatty acids were tested. For this purpose, the commercially available *ω*-hydroxy palmitic acid was used first. The idea was to transform the *ω*-hydroxyl function into a mesylate followed by an elimination to prepare the *ω*-unsaturated FAME, which can be utilized for a self-metathesis (SM) reaction to obtain the desired C_{30} diester (Scheme 53).

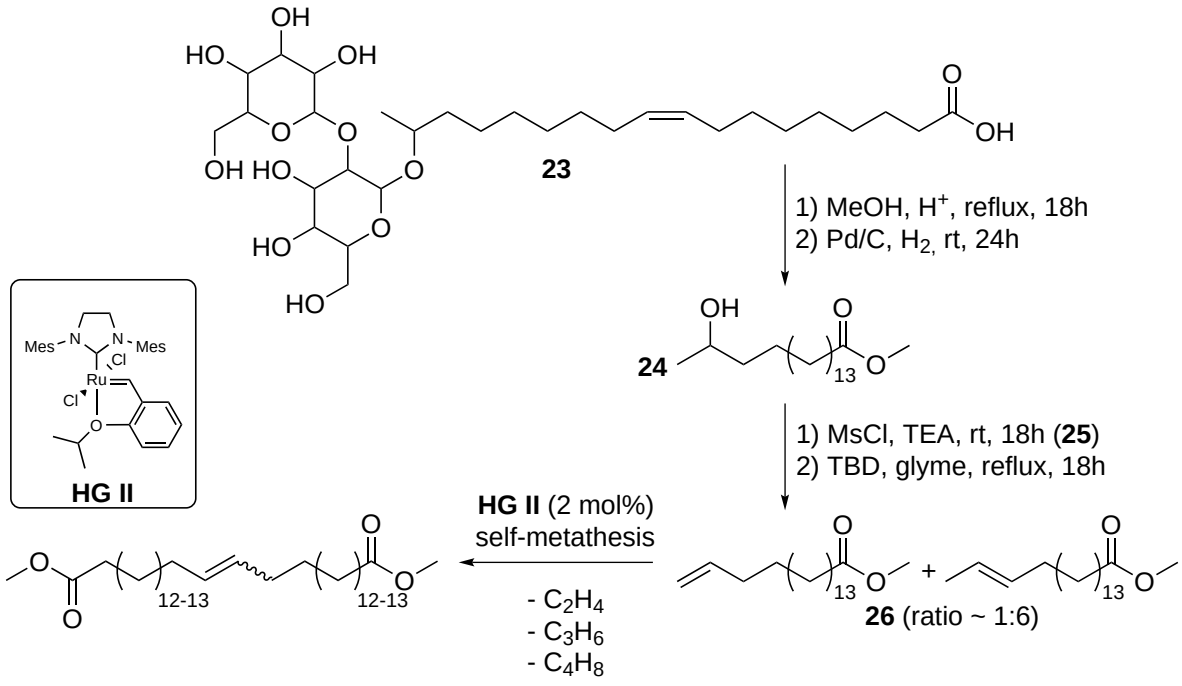


Scheme 53 – Synthesis of a C_{16} *ω*-unsaturated FAME derived from *ω*-hydroxy palmitic acid.

After simple esterification with methanol under acetic conditions and subsequent reaction with mesyl chloride, the desired mesylate (**22**) was obtained in 85 % yield and high purity after recrystallization from hot methanol. With this compound in hand, generation of the terminal double bond was tested by elimination reactions using strong bases such as potassium *tert*-butoxide in THF or DMSO, or organic bases like TBD or DBU, combined with sodium iodide, which is reported to eliminate tosylates very efficiently.[156] However, the elimination reaction towards the *ω*-unsaturated fatty acid was not successful in any of the performed experiments, since only low conversions were obtained. The highest conversion (15 % terminal double bond) was achieved with 4.0 eq. of KOtBu and 3.0 eq. of sodium iodide in refluxing glyme for 5 hours.

To obtain better results, sophorose lipids (**23**),[120-121] another biotechnologically derived fatty acid derivative, were used for further studies, since they can be

transformed into FAMEs having a *ω*-1 hydroxyl group by straightforward acidic cleavage of the disaccharide. The sophorose lipids were prepared directly from rapeseed oil using a known literature procedure.[157] Since a secondary alcohol is present, the elimination reaction should be facilitated using the above discussed synthetic strategy (Scheme 54). It is worth mentioning that such sophorose lipids are composed of a mixture of different compounds having saturated and unsaturated fatty acids. Also, short-chain *α*,*ω*-diesters and *ω*-hydroxy fatty acids as by-products were identified in the sophorose lipids used.



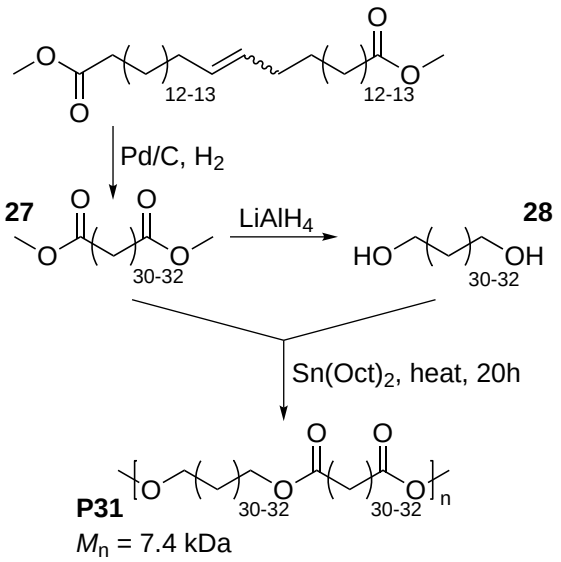
Scheme 54 - Preparation of a C_{32} diester from sophorose lipids.

The cleavage of the disaccharide and simultaneous esterification was achieved by refluxing 12.5 g of the sophorose lipid (approx. 20 mmol) in 150 mL methanol with 2 v% concentrated sulfuric acid for 18 hours. Afterwards, the product was dried under reduced pressure and suspended in dichloromethane, leading to a precipitation of the sugar, which can then be filtered off yielding a mixture of *ω*/*ω*-1-hydroxy saturated and unsaturated methyl esters derived from oleic acid and some short-

chained *α*,*ω*-diesters. In the next step, hydrogenation of the double bonds was performed in ethyl acetate under a hydrogen atmosphere (1 bar) and palladium on activated choral (2 mol% Pd) at room temperature over-night. After removal of the Pd/C catalyst by filtration and evaporation of the solvent, the desired C_{18} *ω*-1-hydroxy ester (**24**) was obtained. It is worth to mention that $^{1}H/^{13}C$-NMR and mass analysis of intermediate product was performed with small quantities of each synthesized compound, but to improve the overall yield, all further reactions were carried out using the crude reaction products since none of the by-products affected the reactions carried out afterwards.

The mesylate **25** was prepared by mixing the hydroxy-fatty acid (**24**) with triethylamine and mesyl chloride in dichloromethane. After the reaction, the crude product can be isolated by simple evaporation of the solvent and washing with diluted hydrochloric acid. The mesylate (**25**) was then used in elimination reactions employing non-nucleophilic bases. Similarly as described above, potassium *t*-butoxide and the organic bases TBD, DBU or DABCO were tested under different conditions. Potassium *t*-butoxide provided a very high selectivity towards the *α*-olefins (usually 10:1 in THF solution), but unfortunately it also offered only limited conversions (max. 60 mol% double bond in final product with 4.0 eq KO*t*Bu at 80 °C). Addition of sodium iodide increased the amount of double bond to 70 %, but was accompanied with a decreased selectivity (60 % terminal olefin). On the other hand, the amine bases TBD and DBU provided very high conversions of up to 90 %, but only a very poor selectivity towards the terminal olefins (80-95 % of *ω*-1 olefins) was observed. However, since a high conversion of the substrate was more desirable, TBD was used as base for further studies (4 equivalents and 3 equivalents sodium iodide as additive in glyme) as it was similarly reported for the elimination of

tosylates.[156] During the elimination step, the methyl ester was partially cleaved. Therefore, esterification of the elimination products with methanol was necessary to obtain the *ω*- and *ω*-1 unsaturated FAMEs (**26**). The obtained mixture of unsaturated FAMEs was then used for a self-metathesis reaction with 2 mol% of the Hoveyda-Grubbs 2nd generation catalyst and 5 mol% *p*-benzoquinone in order to inhibit isomerization of the double bond. The reaction was performed in dichloromethane at 40 °C for 4 hours under a gentle stream of argon and quenched by addition of an excess (respective to the catalyst) of ethyl-vinyl-ether. The crude reaction mixture was directly hydrogenated using palladium on choral (2 mol%) as catalyst and 20 bar hydrogen pressure in dichloromethane at 50 °C for 18 hours (Scheme 55). After the reaction, the Pd/C catalyst was filtered off and product **27** was recrystallized from boiling methanol. Intensive washing of the product with cold methanol gave the $C_{32\text{-}34}$ diester (**27**) in high purity and an overall yield of usually 0.80 – 1.20 gramm (approx. 10 wt% of the starting sophorose lipid).



Scheme 55 - Preparation of C_{32} diester and diol and its polymerization.

The conversion of the $C_{32\text{-}34}$ diesters towards the respective diols (**28**) was accomplished by employing a reported reduction with lithium aluminium hydride. [158]

To ensure a complete reaction, an excess of 3.0 eq lithium aluminium hydride per ester was used to obtain **28** in ~ 65 % yield and high purity.

3.3.3. Preparation and properties of $PE_{32\text{-}34:32\text{-}34}$

With both monomers in hand, polycondensation experiments were carried out adapting known polycondensation catalysts such as TBD (5 mol%), $Ti(OiPr)_4$ or $Sn(Oct)_2$ (5 mol%) at different temperatures applying high vacuum (Scheme 55). The best results for the polyester preparation experiments were obtained with $Sn(Oct)_2$ as catalyst with a concentration of 5 mol% applying a temperature gradient from 120 to 170 °C and 20 hours reaction time. The resulting polymer (**P31**) was dissolved in warm toluene and precipitated in THF to yield **P31** in 72 % yield. By this reaction, an average molecular weight of M_n = 7.4 kDa was obtained with a PDI of ~ 2 without low molecular-weight side-products. In general, purification of the resulting polymer is challenging because of the low solubility of the respective monomers or oligomers. DSC analyses of the polymer samples showed a melting transition of 109 °C (Figure 19). The observed melting point is slightly lower than expected, if compared to already reported long-chain polyesters. From the report of Mecking and coworkers, a melting point in the range of 111-115 °C would be expected.[96] However, taking into consideration that a mixture of monomers ranging from C_{32} to C_{34} was used, the slightly reduced melting point can be explained. For instance, it is well known that a broad distribution of chain-lengths within a polyester can largely influence the thermal properties of the resulting polymer.[67]

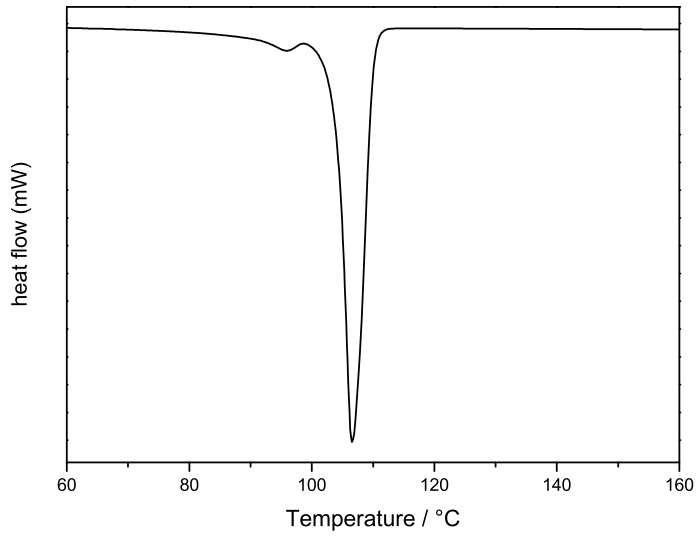


Figure 19 - Thermal analysis of polymer P31 prepared with 5 mol% TBD.

In general, these results show that biotechnologically derived fatty acid derivatives can be used for the straightforward preparation of polymers. Because of their unusually long aliphatic chain, the resulting polyester has interesting thermal properties resulting in a high melting point of 109 °C. This result adds to the manifold possibilities in the derivatization of fatty acids for the synthesis of high-performance polymers derived from renewable resources.

4. Conclusion remarks and outlook

Within this thesis, several methods to derivatize (saturated) fatty acids towards renewable and sustainable monomers were investigated and evaluated. Thereby, the greatest attention was drawn on the utilization of the slight *α*-acidity of esters.

It has been shown (Chapter 3.1) that FAMEs can be easily converted to the respective malonate derivatives using NaH as base in DMC as reactive solvent. These malonate derivatives can afterwards be easily co-polymerized with either 1,6-hexanediol to yield polyesters or 1,6-hexanediamine to prepare polyamides, respectively. The properties of these polymers were studied with respect to the molecular weight distribution and thermal behavior. Thereby, it was apparent that the aliphatic side-chain of the FAME-derived malonates had an important influence on the thermal properties since it acts as an internal plasticizer. Because of this characteristic, such compounds could find a possible application as plasticizers for commercially used polyesters.

In addition, it has been shown that the synthesis of FAME-derived malonates can be carried out with unsaturated fatty acids such as methyl undec-10-enoate. By use of this monomer, a polymer can be obtained where terminal double bonds are present within the side-chains. It was shown that these double bonds can easily be modified after the polymerization by both, thiol-ene addition reactions and olefin cross-metathesis using different acrylates as grafting-onto techniques. Consequently, it was possible to selectively change the thermal properties of the respective polymers. Furthermore, by using the Passerini multicomponent reaction in a one-pot

procedure, it was possible to graft a complex synthetic architecture onto the polymer in high yield and quantitative conversion. Having this in mind, it should also be possible to use the rather similar Ugi multicomponent reaction as a grafting-onto technique as future work. This would be interesting since some products derived from the Ugi reaction are used for medical purposes.[159-161] In this context, it might be possible to use this easy, one-pot technique for the preparation of a polymeric drug-carrier with the active species directly attached to the polymer chain. However, this has not been proven yet and is only thinkable in the distant future.

Another possible route to derivatize fatty acids has been presented with the *α*-arylation reaction (Chapter 3.2). To achieve this reaction, the fatty acid *t*-butyl ester was deprotonated using LiHMDS as a strong base. It has been shown that the thereof generated enolate can be coupled with 1,4-dibromobenzene using palladium-NHC catalysts. By this route, aryl-bridged diesters were obtained in yields ranging from 60 to 80 % in high purity after column chromatography. Unfortunately, these prepared diesters from saturated fatty acids were not possible to polymerize using various different polycondensation reactions. However, it has been shown that the reaction can also be applied to *t*-butyl undec-10-enoate which yields an aryl-bridged diester with 2 terminal double bonds. This monomer can be polymerized by thiol-ene addition reactions, for example with 1,4-butanedithiol. Although the resulting polymer had a high PDI which suggests undesired side-reactions, it was shown that it is possible to polymerize this double unsaturated diester. The thereby prepared polymer had a relatively inert backbone and possesses two *t*-butyl esters per monomer unit which could be easily accessible for grafting-onto reactions. However,

first experiments in order to investigate these possibilities were unsuccessful since they resulted in completely insoluble materials.

The last project within this thesis was the preparation of long-chain *ω*-unsaturated FAMEs (Chapter 3.3). Therefore, the potential to selectively dehydrogenate the FAMEs using iridium pincer catalysts were tested. Unfortunately, it turned out that the current iridium-based dehydrogenation catalysts coordinate to carbonyl bonds, which completely inhibits the dehydrogenation activity of the catalyst. Because of this reason, further investigations for selective dehydrogenations were not performed. However, another route to *ω*-unsaturated FAMEs is to use biochemically modified fatty acids such as commercially available *ω*-hydroxy fatty acids or sophorose lipids. Thereby, it has been shown that sophorose lipids can be converted to the respective *ω*- and *ω*-1 unsaturated fatty acids using basic organic chemistry. These products can afterwards be easily converted to long-chain diesters and diols having C_{32} to C_{34} carbon chains. These monomers can be polymerized by TBD catalysis yielding a $C_{32\text{-}34:32\text{-}34}$ polyester with a melting point of 109 °C and a molecular weight of M_n = 7.4 kDa. These results show that fatty acids give the opportunity for the preparation of high-performance polyesters which can substitute polyethylene.

To sum up, with the malonate preparation, this thesis features the first general method for the selective derivatization of saturated and unsaturated fatty acids towards renewable diesters. Also, another method for the *α*-functionalization of fatty acids is presented as well as an investigation for the preparation of long-chain polyesters derived from biochemically modified fatty acids. These results show the high potential of fatty acids to act as renewable alternatives in polymer chemistry.

Unfortunately, the herein presented methods for the *α*-functionalization use excessive amounts of base and for the *α*-arylation, high catalyst loadings of 2 mol% are required. These aforementioned reasons limit the possible uses of these reactions dramatically. In order to be able to apply the herein presented reactions, catalytically reactions are crucial for a real green approach and economically arguable products. This is also valid for the preparation of the long-chain diesters as a possible substitute of polyethylene. Considering the low price of polyethylene and the relatively complicated route from the sophorose lipid towards the polymer, it is clear to see that these highly interesting compounds need to be prepared in an easier and more economic way.

Last but not least, it has been shown that fatty acids are a highly interesting platform chemical with countless possible modifications and that the fatty-acid derived products can be considered as an alternative for polymers based on fossil-resources.

5. Experimental part

5.1. Materials and methods

Unless otherwise noted, all solvents and reagents were used as received without further purification steps. All used chemicals were purchased from Sigma Aldrich, Fisher Scientific or Strem. Furthermore, unless otherwise noted, all reactions were carried out under atmospheric conditions.

For reaction condition screenings and polymerization reactions, Radleys Carousel™ 12 Plus tubes (RR98072, Radleys Discovery Technologies, UK) were used; for large-scale synthesis, a Radleys Carousel™ 6 Plus (Radleys Discovery Technologies, UK) equipped with 250 mL round bottom flasks was used.

Nuclear magnetic resonance (**NMR**) measurements were performed on a Bruker AVANCE DPX system at 300 MHz for ^{1}H-NMR and 75 MHz for ^{13}C-NMR. The chemical shifts (δ) are given in ppm relative to tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard.

Polymer molecular weight analysis by gel permeation chromatography (**GPC**) was performed on four different systems. For polyesters **P1-6**, **P13**, all samples from the alpha-arylation reactions, metathesis-modified polymers **P15-18** and Passerini-polyesters **P23-24**, a LC-20A system from Shimadzu was used, which was equipped with an SIL-20A autosampler and an RID-10A refractive index detector in THF with a flow rate of 1 mL/min at 50 °C. The analysis was performed on the following column

system: PLgel 5 µm MIXED-D column (Varian, 300mm × 7.5mm, 10 000 Å) with a SDV gel 5 µm pre-column (PSS, 50 mm x 8.0 mm).

For polyamide samples (**P7-12** and **P14**), a Tosoh EcoSEC HLC-8320 GPC system with HFIP containing 0.1 wt% potassium trifluoroacetate as the solvent was used. The solvent flow was 0.40 mL/min at 30 °C. The analysis was performed on a 3-column system: PSS PFG Micro precolumn (3.0 x 0.46cm, 10.000Å), PSS PFG Micro (25.0 x 0.46cm, 1000Å) and PSS PFG Micro (25.0 x 0.46cm, 100Å). Both systems were calibrated with linear poly(methyl methacrylate) standards with molecular weights ranging from 102 – 981 000 Da obtained from PSS (Polymer Standard Service).

For polyesters which were modified with thiol-ene addition reactions (**P19-22**), a Polymer Laboratories PL-GPC 50 Plus Integrated System equipped with an autosampler and a differential refractive index detector running in *N,N*-dimethylacetamide (DMAc) containing 0.03 wt% lithium bromide at a flow rate of 1 mL/min at 50 °C was used. The analysis was performed on the following column system: PLgel 5 µm MixedC column (300 × 7.5 mm) with a PLgel 5 µm bead-size guard column (50 × 7.5 mm). The DMAc-GPC was calibrated with linear poly(styrene) standards with molecular weights ranging from 160 to 6000000 Da, obtained from PSS (Polymer Standard Service).

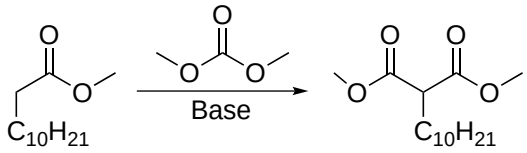
For polyester **P31**, a Polymer Laboratories 220 system equipped with Olexis columns with RI, viscosity and light-scattering detectors was used. The GPC measurements were carried out in 1,2,4-trichlorobenzene at 160 °C with a flow rate of 1.0 ml/min.

Differential scanning calorimetry (**DSC**) experiments were carried out under a nitrogen atmosphere with indicated heating rates (usually 10 °C/min) using a DSC821e (Mettler Toledo) calorimeter up to a temperature of 200 °C. The average sample mass was in the range of 20-30 mg. The data from second heating scans are reported.

Gas chromatography (**GC**) analysis of synthesized compounds was performed on a Bruker 430 GC instrument equipped with a capillary column FactorFour^{TM} VF-5 ms (30.0m × 0.25mm × 0.25µm), using flame ionization detection. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C/min to 220 °C, hold for 4 min, ramp at 15 °C/min to 300 °C, hold for 2 min, ramp at 15 °C/min to 325 °C, hold for 3 min. The injector transfer line temperature was set to 220 °C. Measurements were performed in split–split mode using hydrogen as the carrier gas (flow rate 30 mL/min).

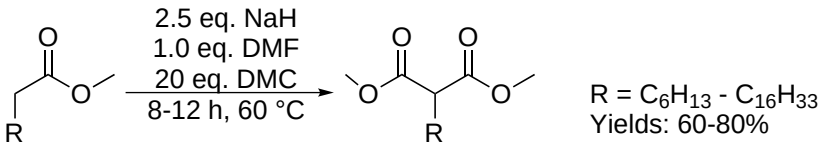
5.2. Condition screening and preparation of fatty-acid derived malonates

Condition screening malonate synthesis from methyl dodecanoate



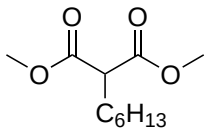
In a typical experiment, 0.50 mL of methyl dodecanoate (2.0 mmol) were mixed with different amounts of DMC and NaH. For most reactions, DMF was added as an additive. The suspensions were then heated to 60 °C for different reaction times. To quench the reaction, 10 mL of diluted hydrochloric acid was added resulting in an immediate separation of the organic phase. The conversions were then analyzed by GC of the organic phase without the use of an internal standard. For detailed amounts and results see Table 1.

General procedure for upscale synthesis of malonate derivatives (Procedure A)



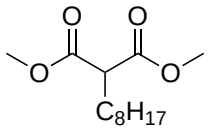
For large scale synthesis of the malonate derivatives, 0.1 mol of the FAME was mixed with 170 mL DMC (20.0 eq), 10.0 g NaH (2.5 eq) and 7.7 mL DMF (1.0 eq). The mixtures were heated to 60 °C for 8 h, in case of methyl palmitate and stearate for 12 h. To quench the reaction, the suspensions were added slowly to 200 mL diluted hydrochloric acid. The organic phase was separated and concentrated under reduced pressure. Thus, non-reacted DMC could be recovered. All malonate derivatives were isolated by high vacuum distillation.

Synthesis of dimethyl 2-hexylmalonate (1)



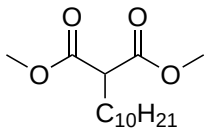
Following procedure A, 15.8 g (72.9 %) of the product were obtained as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (s, 6H, OC*H*$_3$), 3.29 (t, *J* = 7.5 Hz, 1H, $CH_3OOCCHRCOOCH_3$), 1.82 (m, *β*-H), 1.22 (m, 8H, chain), 0.80 (t, *J* = 6.4 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.81 (*C*$OOCH_3$), 52.21 (CH_3OOC-*C*HR-$COOCH_3$), 51.59 (COO*C*H_3), 31.38 (*C*H_2), 28.74 (*C*H_2), 27.18 (*C*H_2), 22.40 (*C*H_2), 13.85 (*C*H_3); MS (EI): *m/z* = 217.2 ($[M + H]^+$, calc. 217.14).

Synthesis of dimethyl 2-octylmalonate (2)



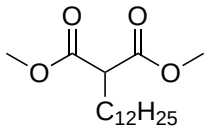
Following procedure A, 17.7 g (72.7 %) of the product were obtained as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (s, 6H, OC*H*$_3$), 3.28 (t, *J* = 7.5 Hz, 1H, $CH_3OOCCHRCOOCH_3$), 1.82 (m, 2H, *β*-H), 1.21 (m, 12H, chain), 0.80 (t, *J* = 6.4 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.82 (*C*$OOCH_3$), 52.21 (CH_3OOC-*C*HR-$COOCH_3$), 51.60 (COO*C*H3), 31.71 (*C*H_2), 29.39 – 28.94 (*C*H_2), 28.76 (*C*H_2), 27.23 (*C*H_2), 22.53 (*C*H_2), 13.93 (*C*H_3); MS (EI): *m/z* = 245.2 ($[M + H]^+$, calc. 245.17).

Synthesis of dimethyl 2-decylmalonate (3)



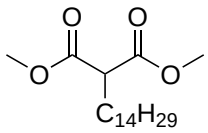
Following procedure A, 22.1 g (81.3 %) of the product were obtained as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.61 (s, 6H, OC*H*$_3$), 3.24 (t, *J* = 7.5 Hz, 1H, $CH_3OOCCHRCOOCH_3$), 1.78 (m, 2H, β-H), 1.15 (s, 16H, chain), 0.77 (t, *J* = 6.2 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.64 (*C*$OOCH_3$), 52.03 (CH_3OOC-*C*HR-$COOCH_3$), 51.47 ($COOCH_3$), 31.75 (*C*H_2), 29.80 – 28.82 (*C*H_2), 28.68 (*C*H_2), 27.17 (*C*H_2), 22.51 (*C*H_2), 13.86 (*C*H_3); MS (EI): *m/z* = 273.3 ($[M + H]^+$, calc. 273.21).

Synthesis of dimethyl 2-dodecylmalonate (4)



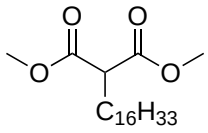
Following procedure A, 24.5 g (81.6 %) of the product were obtained as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 6H, OC*H*$_3$), 3.30 (t, *J* = 7.5 Hz, 1H, $CH_3OOCCHRCOOCH_3$), 1.84 (m, 2H, β-H), 1.22 (s, 20H, chain), 0.82 (t, *J* = 6.5 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.76 (*C*$OOCH_3$), 52.16 (CH_3OOC-*C*HR-$COOCH_3$), 51.59 ($COOCH_3$), 31.83 (*C*H_2), 29.79 – 28.83 (*C*H_2), 28.75 (*C*H_2), 27.24 (*C*H_2), 22.58 (*C*H_2), 13.95 (*C*H_3); MS (EI): *m/z* = 300.3 ([M], calc. 300.23).

Synthesis of dimethyl 2-tetradecylmalonate (5)



Following procedure A, 19.4 g (59.1 %) of the product were obtained as a white wax. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 6H, OC*H*$_3$), 3.29 (t, *J* = 7.5 Hz, 1H, $CH_3OOCCHRCOOCH_3$), 1.82 (m, 2H, *β*-H), 1.18 (s, 24H, chain), 0.81 (t, *J* = 6.4 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.97 (*C*$OOCH_3$), 52.40 (CH_3OOC-*C*HR-$COOCH_3$), 51.72 ($COOCH_3$), 31.91 (*C*H_2), 29.86 – 28.99 (*C*H_2), 28.85 (*C*H_2), 27.33 (*C*H_2), 22.67 (*C*H_2), 14.09 (*C*H_3); MS (EI): *m/z* = 328.3 ([M], calc. 328.23).

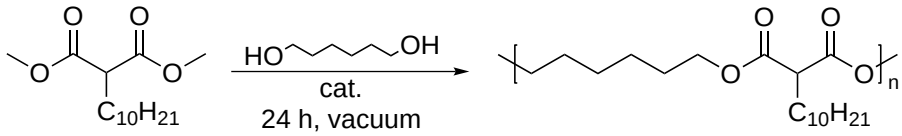
Synthesis of dimethyl 2-hexadecylmalonate (6)



Following procedure A, 21.8 g (61.1 %) of the product were obtained as a white wax. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (s, 6*H*, OCH_3), 3.28 (t, *J* = 7.5 Hz, 1H, $CH_3OOCCHRCOOCH_3$), 1.82 (m, 2H, *β*-*H*), 1.18 (s, 28H, chain), 0.80 (t, *J* = 6.0 Hz, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, CDCl3) δ 169.84 (*C*OOCH3), 52.25 (CH3OOC-*C*HR-$COOCH_3$), 51.64 ($COOCH_3$), 31.88 (*C*H_2), 29.84 – 28.94 (*C*H_2), 28.80 (*C*H_2), 27.29 (*C*H_2), 22.63 (*C*H_2), 14.02 (*C*H_3); MS (EI): *m/z* = 356.3 ([M], calc. 356.29).

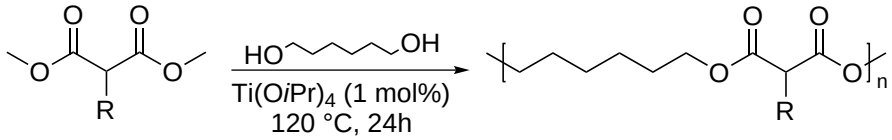
5.3. Preparation of poly-malonates and -malonamides

Condition screening for polyester synthesis



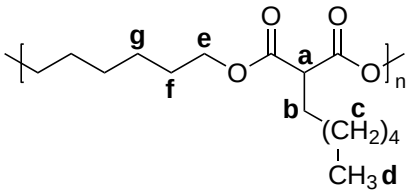
In a typical reaction, 0.5 mL dimethyl 2-decylmalonate (**2**, 2.0 mmol) were mixed with 236 mg 1,6-hexanediol (2.0 mmol) and different catalysts in different amounts. The mixtures were then heated to different temperatures for 24h and subsequently analyzed by GPC without precipitation. For detailed amounts and results see Table 3.

Polymerization of polyesters P1-6 (Procedure B)



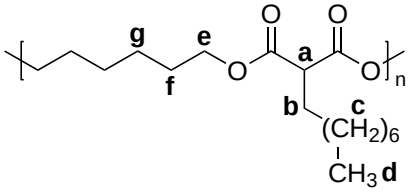
After optimizing the polyester condensation, the reaction conditions were adapted with little modifications on a large scale with different malonates. In a typical reaction, 5.0 mmol malonate derivative (**1-6**) was mixed with 591 mg 1,6-hexanediol (5.0 mmol) and 15.0 µL $Ti(OiPr_4)$ (1 mol%). Afterwards, 2.0 mL THF was added to homogenize the mixture which was consequently heated to 120 °C for 1 h under a argon stream where the THF evaporated after 1-2 minutes and afterwards 23 h under high vacuum. After the complete reaction, the polymers were dissolved in THF and precipitated in methanol at room temperature. Because of the good solubility and due to the sticky nature of all polymers, the isolation of the precipitated polyesters was not complete. Therefore, no yields can be supported for the preparation of **P1-6**.

Preparation of poly(hexyl 2-hexylmalonate) (P1)



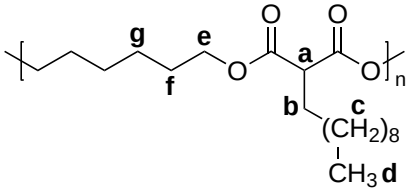
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.6 Hz, 4H, **e**), 3.25 (t, *J* = 7.5 Hz, 1H, **a**), 1.81 (m, 2H, **b**), 1.56 (m, 4H, **f**), 1.29 (s, 4H, **g**), 1.22 (s, 8H, **c**), 0.80 (t, *J* = 6.4 Hz, 3H, **d**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.55 (*C*OOR), 65.09 (**e**), 52.03 (**a**), 31.49 - 22.48 (chain), 13.98 (**d**).

Preparation of poly(hexyl 2-octylmalonate) (P2)



^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.5 Hz, 4H, **e**), 3.25 (t, *J* = 7.4 Hz, 1H, **a**), 1.81 (m, 2H, **b**), 1.57 (m, 4H, **f**), 1.29 (s, 4H, **g**), 1.19 (s, 12H, **c**), 0.81 (t, *J* = 6.4 Hz, 3H, **d**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.55 (*C*OOR), 65.09 (**e**), 52.03 (**a**), 31.78 - 22.60 (chain), 14.04 (**d**).

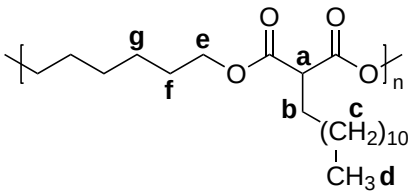
Preparation of poly(hexyl 2-decylmalonate) (P3)



^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.6 Hz, 4H, **e**), 3.25 (t, *J* = 7.5 Hz, 1H, **a**), 1.81 (m, 2H, **b**), 1.57 (m, 4H, **f**), 1.29 (s, 4H, **g**), 1.18 (s, 16H, **c**), 0.81 (t, *J* = 6.1 Hz,

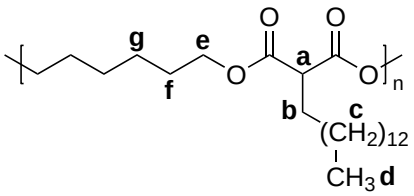
3H, **d**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.56 (*C*OOR), 65.10 (**e**), 52.05 (**a**), 31.87 - 22.65 (chain), 14.07 (**d**).

Preparation of poly(hexyl 2-dodecylmalonate) (P4)



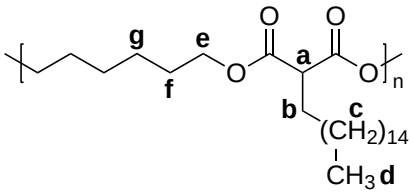
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.6 Hz, 4H, **e**), 3.25 (t, *J* = 7.5 Hz, 1H, **a**), 1.81 (m, 2H, **b**), 1.57 (m, 4H, **f**), 1.29 (s, 4H, **g**), 1.18 (s, 20H, **c**), 0.81 (t, *J* = 6.4 Hz, 3H, **d**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.55 (*C*OOR), 65.08 (**e**), 52.04 (**a**), 31.89 - 22.65 (chain), 14.07 (**d**).

Preparation of poly(hexyl 2-tetradecylmalonate) (P5)



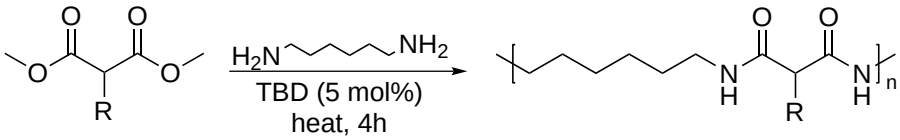
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.4 Hz, 4H, **e**), 3.25 (t, *J* = 7.3 Hz, 1H, **a**), 1.80 (s, 2H, **b**), 1.57 (s, 4H, **f**), 1.29 (s, 4H, **g**), 1.18 (s, 24H, **c**), 0.81 (t, *J* = 6.1 Hz, 3H, **d**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.55 (*C*OOR), 65.09 (**e**), 52.05 (**a**), 31.90 - 22.66 (chain), 14.08 (**d**).

Preparation of poly(hexyl 2-hexadecylmalonate) (P6)



^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, J = 6.4 Hz, 4H, **e**), 3.25 (t, J = 7.3 Hz, 1H, **a**), 1.82 (s, 2H, **b**), 1.57 (s, 4H, **f**), 1.30 (s, 4H, **g**), 1.18 (s, 28H, **c**), 0.81 (t, J = 6.0 Hz, 3H, **d**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.52 (*C*OOR), 65.06 (**e**), 52.01 (**a**), 31.90 - 22.66 (chain), 14.07 (**d**).

Preparation of poly(malonamides) (P7-12)

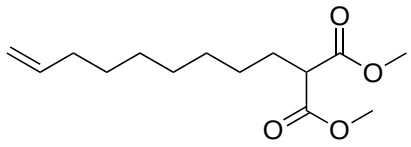


In a typical experiment, 2.0 mmol malonate derivative was mixed with 232.0 mg 1,6-hexanediamine (2.0 mmol) and 14.0 mg TBD (5 mol%). 2.0 mL *o*-xylene were added. Afterwards, the mixture was heated to 120 °C under a stream of argon for 90 minutes. After this time, the mixtures became gel-like or solid. Therefore, the temperature was increased to 140 °C for additional 30 minutes and then to 180 °C for 30 more minutes. Afterwards, the mixture was heated at 180 °C for 90 more minutes under high vacuum. The polymers were then dissolved in HFIP and precipitated in diethyl ether at room temperature.

For NMR analysis, ~ 20 mg of the precipitated polymers were mixed with 0.7 mL $CDCl_3$ and 0.1 mL TFAA to solubilize them. As mentioned before, the resulting ^{1}H-NMR spectra could not be interpreted completely.

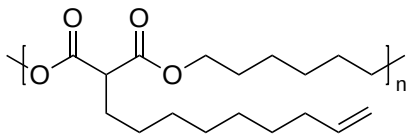
5.4. Grafting-onto reactions

Synthesis of dimethyl 2-(non-8-en-1-yl)malonate (7)



Following the general procedure A, 22.3 mL methyl 10-undecenoate (0.10 mol) were mixed with 7.70 mL DMF (1.0 eq) and 10.0 g NaH (60 wt% dispersion in mineral oil, 0.25 mmol, 2.5 eq.) in 170 mL DMC (2.0 mol, 20 eq.). The suspension was stirred at 60 °C for 8 hours. To stop the reaction, the suspensions were added slowly to 200 mL diluted hydrochloric acid. The organic phase was isolated and concentrated under reduced pressure. Distillation under high vacuum gave the product as a colorless oil with 80.8 % yield (20.7 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, CH_2=C*H*R), 4.95 – 4.77 (m, 2H, CH_2=CHR), 3.65 (s, 6H, COOCH_3), 3.28 (t, J = 7.5 Hz, 1H, C*H*R(COOMe)$_2$), 1.95 (dd, J = 13.4, 6.4 Hz, 2H, CH_2=CH-CH_2R), 1.83 (m, 2H, CH_2), 1.26 (m, 10H, chain); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.73 (*C*OOCH$_3$), 138.86 (CH_2=*C*HR), 114.06 (*C*H_2=CHR), 52.17 (COO*C*H$_3$), 51.54 (CH_3OOC-*C*HR-COOCH$_3$), 33.62 - 27.18 (chain); MS (EI): *m/z* = 256.2 ([M], calc. 256.17).

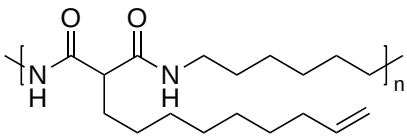
Preparation of the starting poly(malonate) (P13)



Following the general procedure B, 25.6 g dimethyl 2-(non-8-en-1-yl)malonate (**7**, 0.10 mol) was mixed with 11.8 g 1,6-hexanediol (0.10 mol) in a 100 mL Schlenk

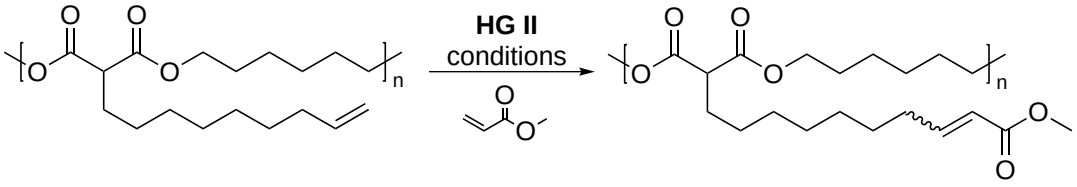
flask. The mixture was heated to 120 °C, then 295 µL Ti(O*i*Pr)$_4$ (284 mg, 1.0 mol%) was added. Afterwards, the reaction was heated at 120 °C for one hour with a stream of argon and afterwards high vacuum was applied for 23 hours. After 24 hours reaction time, the polymer was dissolved in 30 mL THF and precipitated in 500 mL ice-cold methanol and kept at -4 °C for 2 hours. After carefully decanting of the solvent, the polymer was washed twice with ice-cold methanol. The pure polymer was obtained with 22.3 g (71,9 % yield) as a yellow, highly viscous material. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, CH_2=C*H*R), 4.97 – 4.78 (m, 2H, C*H*$_2$=CHR), 4.05 (t, J = 6.6 Hz, 4H, RCOOC*H*$_2$R), 3.25 (t, J = 7.5 Hz, 1H, C*H*R(COOMe)$_2$), 1.96 (dd, J = 13.7, 6.8 Hz, 2H, CH_2=CH-C*H*$_2$R), 1.81 (m, 2H, CH_2), 1.57 (m, 4H, $COOCH_2$-C*H*$_2$-R), 1.26 (d, J = 20.2 Hz, 14H, chain).

Preparation of undecenoic-derived poly(malonamide) (P14)



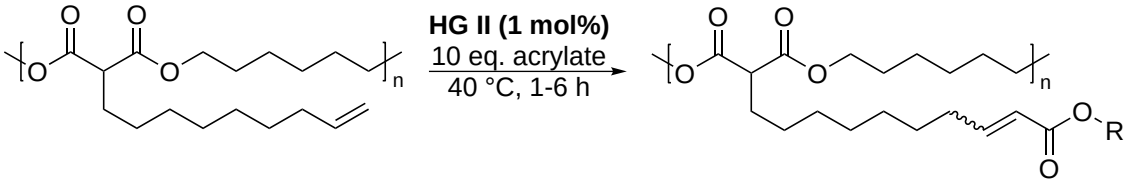
10.2 g dimethyl 2-(non-8-en-1-yl)malonate (**7**, 40.0 mol) were mixed with 4.65 g 1,6-hexanediamine (40.0 mmol) and 0.3 g TBD (5 mol%) in a 100 mL Schlenk flask. The mixture was homogenized with 40 mL *o*-xylene. Afterwards, the polymerization was carried out using a heating gradient from 120 to 180 °C as for the preparation of saturated poly(malonamides). After the reaction, the polymer was dissolved in 80 mL boiling DMSO and precipitated in 400 mL cold water. Afterwards, the polymer was filtered off and washed twice with 150 mL methanol. After intensive drying using high vacuum, 10.66 g of the polymer were obtained as a white powder (87 % yield). Because of its bad solubility, no NMR measurements were possible of the resulting polymer.

Condition screening for cross-metathesis of P13 with methyl acrylate



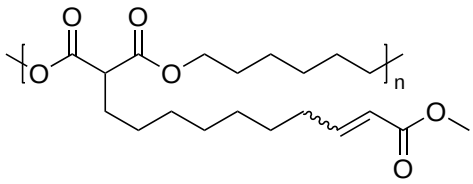
155 mg polymer **P13** (corresponds to 0.50 mmol repeating units) were dissolved in various amounts of methyl acrylate and optional DCM as solvent. Afterwards, various amounts of **HG II** catalyst were added and the mixture was stirred at 40 °C. After 2 hours, the reaction was quenched by addition of 10 µL ethyl vinyl ether. The crude reaction mixture was analyzed by ^{1}H-NMR and THF-GPC. The conversion was calculated by ^{1}H-NMR integration.

General procedure (C) for cross-metathesis modifications



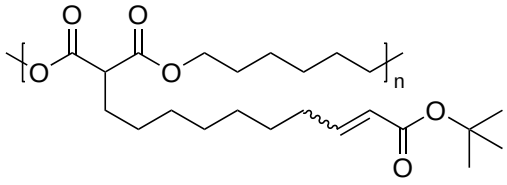
310 mg polymer **P13** (corresponds to 1.00 mmol repeating units) were dissolved in 10 equivalents of the respective acrylate and 6.2 mg **HG II** (1 mol%) was added. The mixture was stirred at 40 °C for various times. Afterwards, the reaction was stopped by addition of 20 µL ethyl vinyl ether and analyzed by ^{1}H-NMR and THF-GPC.

Cross-metathesis with methyl acrylate (P15)



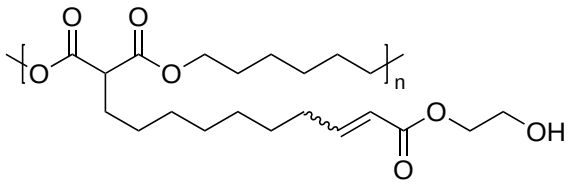
Following the general procedure C, 310 mg **P13** were dissolved in 900 µL methyl acrylate (10.0 mmol, 10.0 eq.) together with 6.2 mg **HG II** (1 mol%) and stirred at 40 °C for 3 hours. After the reaction was stopped, the crude polymer was precipitated in ice-cold methanol (271 mg, 73.6 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (dt, J = 15.5, 6.9 Hz, 1H, acrylate β-H), 5.74 (d, J = 15.7 Hz, 1H, acrylate α-H), 4.05 (t, J = 6.7 Hz, 4H, RCOOCH_2R), 3.65 (s, 3H, COOCH_3), 3.25 (t, J = 7.5 Hz, 1H, CHR(COOMe)$_2$), 2.18 – 2.05 (m, 2H, acrylate γ-CH_2), 1.79 (m, 2H, CH_2), 1.57 (m, 4H, $COOCH_2$-CH_2-R), 1.23 (m, 14H, chain).

Cross-metathesis with *t*-butyl acrylate (P16)



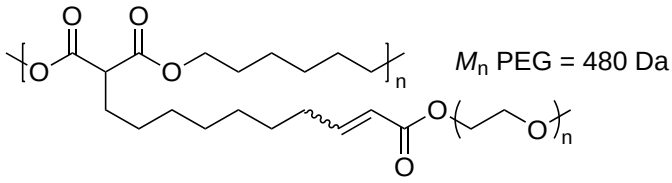
Following the general procedure C, 310 mg **P13** were dissolved in 1.45 mL *t*-butyl acrylate (10.0 mmol, 10.0 eq.) together with 6.2 mg **HG II** (1 mol%) and stirred at 40 °C for 3 hours. After the reaction was stopped, the crude polymer was precipitated in ice-cold methanol (141 mg, 34.4 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (dt, J = 15.4, 6.9 Hz, 1H, acrylate β-H), 5.65 (d, J = 15.6 Hz, 1H, acrylate α-H), 4.05 (t, J = 6.6 Hz, 4H, RCOOCH_2R), 3.25 (t, J = 7.5 Hz, 1H, CHR(COOMe)$_2$), 2.08 (dd, J = 13.6, 6.7 Hz, 2H, acrylate γ-CH_2), 1.81 (m, 2H, CH_2), 1.57 (m, 4H, $COOCH_2$-CH_2-R), 1.41 (s, 9H, COOC(CH_3)$_3$), 1.26 (m, 14H, chain).

Cross-metathesis with 2-hydroxyethyl acrylate (P17)



Following the general procedure C, 310 mg **P13** were dissolved in 1.15 mL 2-hydroxyethyl acrylate (10.0 mmol, 10.0 eq.) together with 6.2 mg **HG II** (1 mol%) which resulted in a turbid mixture that was stirred at 40 °C for 6 hours. After the reaction was stopped, the crude polymer was precipitated in ice-cold *n*-hexane (278 mg, 69.8 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (dt, J = 15.5, 6.9 Hz, 1H, acrylate β-H), 5.78 (d, J = 15.7 Hz, 1H, acrylate α-H), 4.20 (s, 2H, COOCH_2CH$_2$OH), 4.05 (t, J = 6.5 Hz, 4H, RCOOCH_2R), 3.78 (s, 2H, COOCH$_2$CH_2OH), 3.25 (t, J = 7.4 Hz, 1H, CHR(COOMe)$_2$), 2.13 (dd, J = 12.2, 5.5 Hz, 2H, acrylate γ-CH_2), 1.81 (m, 2H, CH_2), 1.57 (m, 4H, COOCH$_2$-CH_2-R), 1.26 (m, 14H, chain).

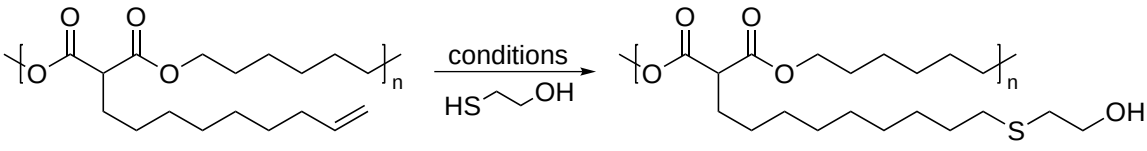
Cross-metathesis with PEG acrylate (P18)



Following the general procedure C, 310 mg **P13** were dissolved in 4.4 mL PEG acrylate (10.0 mmol, 10.0 eq.) together with 6.2 mg **HG II** (1 mol%) and stirred at 40 °C for 1 hour. After the reaction was stopped, the crude polymer was precipitated in ice-cold diethyl ether. The exact weight of polymer could not be measured since it tended to polymerize upon complete drying. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (dt, J = 15.3, 6.9 Hz, 1H, acrylate β-H), 5.77 (d, J = 15.6 Hz, 1H, acrylate α-H), 4.25 - 4.14 (m, 2H, COOCH_2CH$_2$OR), 4.04 (t, J = 6.6 Hz, 4H, RCOOCH_2R),

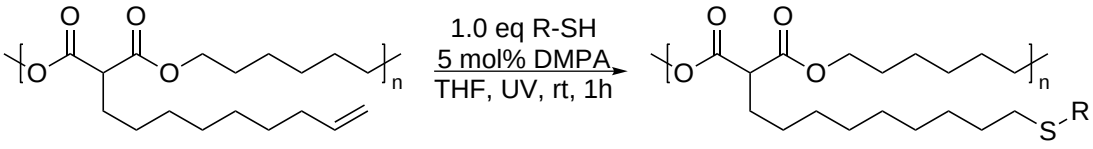
3.68 - 3.64 (m, 2H, $COOCH_2CH_2OR$), 3.58 (s, 28H, PEG CH_2), 3.50 – 3.45 (m, 2H, PEG CH_2), 3.31 (s, 3H, PEG-OCH_3), 3.25 (t, J = 7.5 Hz, 1H, $CHR(COOMe)_2$), 2.12 (dd, J = 13.6, 6.7 Hz, 2H, acrylate γ-CH_2), 1.81 (m, 2H, CH_2), 1.57 (m, 4H, $COOCH_2$-CH_2-R), 1.36 (m, 2H, chain), 1.29 (m, 4H, chain), 1.23 (m, 8H, chain).

Condition screening with 2-mercaptoethanol



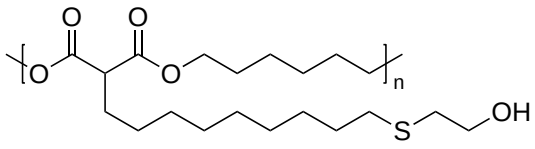
155 mg **P13** (0.50 mmol) were dissolved in 0.5 mL THF with optional DMPA as photoinitiator and various amounts of 2-mercaptoethanol. The mixtures were then stirred for different times at room temperature and continuously analyzed by ^{1}H-NMR. The conversion was determined by ^{1}H-NMR integration of the terminal double bonds.

General procedure (D) for thiol-ene additions



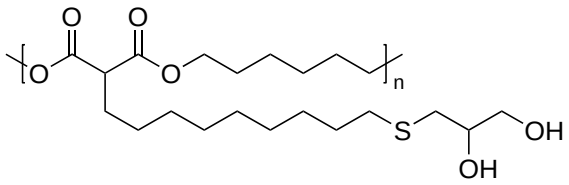
620 mg **P13** (2.0 mmol) were dissolved in 2 mL THF with 25.6 mg DMPA (5 mol%) and 1.0 equivalent of the respective thiol. The mixtures were stirred at room temperature under UV irradiation (365 nm) for 1 hour.

Thiol-ene addition of 2-mercaptoethanol (P19)



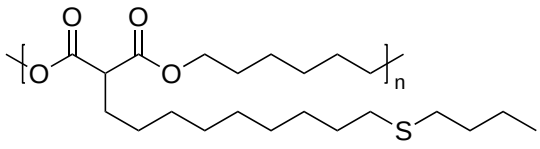
Following the general procedure D, 620 mg **P13** were dissolved in 2 mL THF with 25.6 mg DMPA and 140 µL 2-mercaptoethanol and stirred under UV irradiation for 1h. Afterwards, the polymer was precipitated in ice-cold *n*-hexane (550 mg, 70.9 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, J = 6.6 Hz, 4H, RCOOCH_2R), 3.65 (t, J = 6.0 Hz, 2H, RCH_2SCH_2-CH_2OH), 3.25 (t, J = 7.5 Hz, 1H, CHR(COOMe)$_2$), 2.66 (t, J = 6.0 Hz, 2H, RCH_2SCH_2-CH_2OH), 2.45 (t, J = 7.3 Hz, 2H RCH_2SCH_2-CH_2OH), 2.11 (s, 2H, CH_2), 1.82 (m, 2H, CH_2), 1.57 (s, 6H, chain), 1.25 (m, 16H, chain).

Thiol-ene addition of thioglycerol (P20)



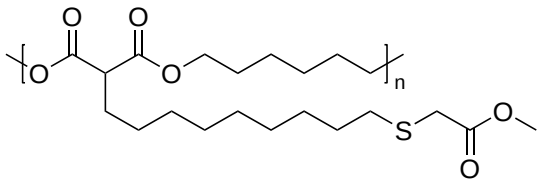
Following the general procedure D, 620 mg **P13** were dissolved in 2 mL THF with 25.6 mg DMPA and 173 µL thioglycerol and stirred under UV irradiation for 1h. Afterwards, the polymer was precipitated in ice-cold *n*-hexane (627 mg, 68.2 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, J = 6.5 Hz, 4H, RCOOCH_2R), 3.74 – 3.63 (m, 2H, HOCH_2-CHOH-CH_2SCH_2R), 3.56 – 3.46 (m, 1H, $HOCH_2$-CHOH-CH_2SCH_2R), 3.26 (t, J = 7.4 Hz, 1H, CHR(COOMe)$_2$), 2.68 – 2.51 (m, 2H, $HOCH_2$-CHOH-CH_2SCH_2R), 2.51 – 2.42 (m, 2H, $HOCH_2$-CHOH-CH_2SCH_2R), 1.80 (m, 2H, CH_2), 1.57 (m, 6H, chain), 1.25 (m, 16H, chain).

Thiol-ene addition of *n*-butanethiol (P21)



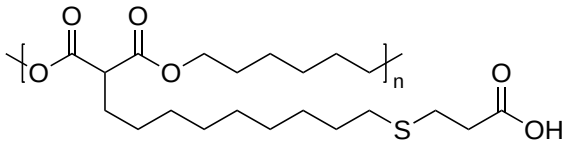
Following the general procedure D, 620 mg **P13** were dissolved in 2 mL THF with 25.6 mg DMPA and 215 µL *n*-butanethiol and stirred under UV irradiation for 1h. Afterwards, the polymer was precipitated in ice-cold methanol (493 mg, 61.6 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, J = 6.7 Hz, 4H, RCOOCH_2R), 3.25 (t, J = 7.5 Hz, 1H, CHR(COOMe)$_2$), 2.43 (t, J = 8.6 Hz, 4H, RCH_2SCH_2R), 1.79 (m, 2H, CH_2), 1.65 – 1.47 (m, 8H, chain), 1.42 – 1.18 (m, 18H, chain), 0.85 (t, J = 7.2 Hz, 3H, CH_3).

Thiol-ene addition of methyl thioglycolate (P22)



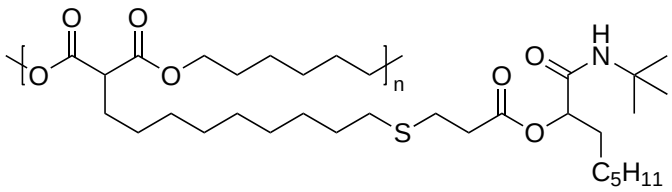
Following the general procedure D, 620 mg **P13** were dissolved in 2 mL THF with 25.6 mg DMPA and 179 µL methyl thioglycolate and stirred under UV irradiation for 1h. Afterwards, the polymer was precipitated in ice-cold methanol (528 mg, 61.4 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, J = 6.7 Hz, 4H, RCOOCH_2R), 3.67 (s, 3H, COOCH_3), 3.25 (t, J = 7.5 Hz, 1H, CHR(COOMe)$_2$), 3.16 (s, 2H, SCH_2COOMe), 2.61 – 2.48 (m, 2H, CH_2), 1.79 (m, 2H, CH_2), 1.53 (m, 6H, chain), 1.25 (m, 16H, chain).

Thiol-ene addition of 3-mercaptopropionic acid (P23)



Following the general procedure D, 620 mg **P13** were dissolved in 2 mL THF with 25.6 mg DMPA and 175 µL 3-mercaptopropionic acid and was stirred under UV irradiation for 1h. Afterwards, the polymer was precipitated in ice-cold *n*-hexane (415 mg, 49.9 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.53 (s, 1H, COO*H*), 4.05 (t, *J* = 6.4 Hz, 4H, RCOOC*H*$_2$R), 3.26 (t, *J* = 7.5 Hz, 1H, C*H*R(COOMe)$_2$), 2.70 (m, 2H, RCH$_2$SC*H*$_2$CH$_2$COOH), 2.59 (t, *J* = 7.2 Hz, 2H, RCH$_2$SCH$_2$C*H*$_2$COOH), 2.46 (t, *J* = 6.8 Hz, 2H, RC*H*$_2$SCH$_2$CH$_2$COOH), 1.80 (m, 2H, C*H*$_2$), 1.65 – 1.45 (m, 8H, chain), 1.25 (m, 16H, chain).

Passerini reaction of P23, heptanal and *t*-butyl isocyanide (P24)

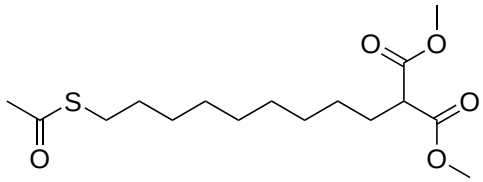


For the Passerini reaction, the crude reaction mixture resulting from the preparation of **P23** was taken and mixed with 340 µL *t*-butyl isocyanide (3.0 mmol, 1.5 eq.) and 417 µL heptanal (3.0 mmol, 1.5 eq.). The mixture was stirred at room temperature for 24 hours. Afterwards the polymer was precipitated in ice-cold *n*-hexane (1.18 g, 96.2 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (s, 1H, N*H*), 5.01 (t, *J* = 6.0 Hz, 1H, C*H*R$_3$), 4.05 (t, *J* = 6.6 Hz, 4H, RCOOC*H*$_2$R), 3.25 (t, *J* = 7.5 Hz, 1H, C*H*R(COOMe)$_2$), 2.83 – 2.68 (m, 2H, RCH$_2$SC*H*$_2$CH$_2$COOR), 2.63 (t, *J* = 6.4 Hz, 2H, RCH$_2$SCH$_2$C*H*$_2$COOR), 2.47 (t, *J* = 7.3 Hz, 2H, RC*H*$_2$SCH$_2$CH$_2$COOR), 1.79 (m, 4H,

2x CH_2), 1.54 (m, 6H, chain), 1.33 – 1.18 (m, 33H, RC(C*H*$_3$)$_3$ + chain), 0.79 (t, *J* = 6.0 Hz, 3H, CH_3).

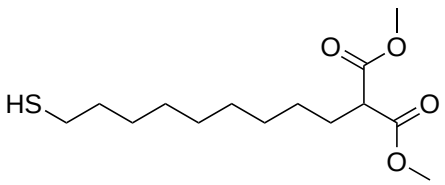
5.5. Experimental procedures regarding AB_2-type malonates

Synthesis of dimethyl 2-(9-(acetylthio)nonyl)malonate (8)



2.56 g of **7** (10.0 mmol) were mixed with 0.79 mL thioacetic acid (11.0 mmol, 1.1 eq.) and 128 mg DMPA (5 mol%) under bulk conditions. Afterwards, the mixture was stirred at room temperature under UV irradiation until GC and ^{1}H-NMR analysis showed a quantitative consumption of the starting material (3 hours). For work-up, the product was intensively dried under reduced pressure to remove the excess thioacetic acid. The product **8** was obtained as colorless oil in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 6H, COOC*H*$_3$), 3.29 (t, *J* = 7.6 Hz, 1H, *α-H*), 2.79 (t, *J* = 7.3 Hz, 2H, CH_3COS-C*H*$_2$-CH_2-), 2.25 (s, 3H, C*H*$_3$COS-CH_2-CH_2-), 1.82 (m, 2H, CH_3COS-CH_2-C*H*$_2$-), 1.48 (dt, *J* = 14.6, 7.4 Hz, 2H, *β-H*), 1.20 (s, 12H, chain); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.06 (s, *C*H_3COS-CH_2-CH_2-), 169.96 (s, *C*$OOCH_3$), 52.43 (s, COO*C*H_3), 51.69 (s, *α-C*H), 30.63 - 27.29 (chain); MS (FAB): *m/z* = 333.2 ($[M + H]^+$, calc. 333.17).

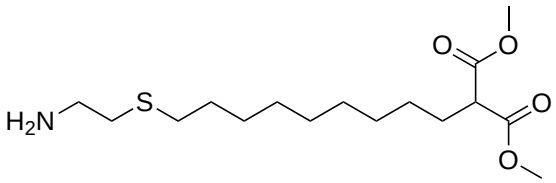
Synthesis of dimethyl 2-(9-mercaptononyl)malonate (9)



For the synthesis of **9**, the crude product from the synthesis of dimethyl 2-(9-(acetylthio)nonyl)malonate (**8**, about 10.0 mmol) was dissolved in 20 mL methanol

with 0.1 mL concentrated sulfuric acid. The mixture was refluxed for 20 hours. Afterwards, 100 mL water were added to the reaction mixture and the product was extracted with 3 times 50 mL DCM to obtain the product in good purity and 2.33 g (8.0 mmol, 80 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 6H, COOCH_3), 3.29 (t, J = 7.5 Hz, 1H, α-H), 2.45 (dt, J = 14.7, 7.4 Hz, 2H, HS-CH_2-CH_2-), 1.82 (d, J = 6.5 Hz, 2H, β-H), 1.52 (t, J = 10.9 Hz, 2H, HS-CH_2-CH_2-), 1.20 (s, 12H, chain); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.92 (s, COOCH$_3$), 52.40 (s, COOCH$_3$), 51.66 (s, α-CH), 33.99 - 27.27 (chain), 24.59 (HS-CH$_2$-); MS (FAB): m/z = 291.2 ([M + H]$^+$, calc. 291.16).

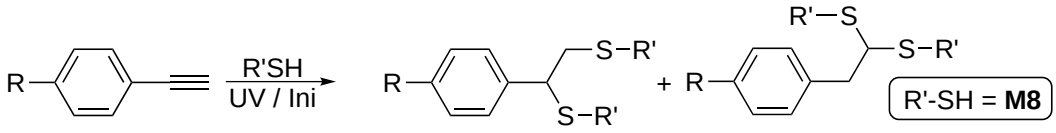
Synthesis of dimethyl 2-(9-((2-aminoethyl)thio)nonyl)malonate (10)



2.56 g of **7** (10.0 mmol) were mixed with 1.4 g cysteamine hydrochloride (12.0 mmol, 1.2 eq.) in 10 mL methanol with 82 mg AIBN (5 mol%). The mixture was stirred at 80 °C for 16 hours. Afterwards, 100 mL DCM were added and the excess cysteamine was extracted with a basic potassium carbonate solution (3 x 50 mL) and water (2 x 100 mL). Afterwards, the solvent was removed under reduced pressure and the product was dried under high vacuum to obtain 2.53 g of **10** (76 % yield) as a yellowish oil in high purity. It seems that the product tends to polymerize while stored in dryness at 4 °C after several weeks. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 6H, COOCH_3), 3.29 (t, J = 7.5 Hz, 1H, α-H), 2.80 (t, J = 6.3 Hz, 2H, H_2N-CH_2-), 2.54 (t, J = 6.3 Hz, 2H, H_2N-CH_2-CH_2-S-CH_2-), 2.48 – 2.37 (m, 2H, H_2N-CH_2-CH_2-S-CH_2-),), 1.82 (m, 2H, β-H), 1.49 (m, 2H, chain), 1.42 (s, 2H, -NH_2), 1.20 (s, 12H, chain);

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.93 (s, *C*OOMe), 52.41 (s, COO*C*H_3), 51.66 (s, *α-C*H), 42.53 - 27.27 (chain); MS (FAB): *m/z* = 334.3 ([M + H]$^+$, calc. 334.20).

Example for the thiol-yne addition of 9 to phenylacetylene derivative 11



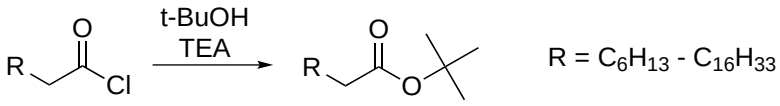
52 mg tetrakis(4-ethynylphenyl)methane (**11**, 0.125 mmol, 0.50 mmol acetylene) were mixed with 1.16 g of **9** (4.0 mmol, 8.0 eq. thiol / acetylene) and 26 mg DMPA (5 mol%) in 2.0 mL DMF. The mixture was stirred at room temperature under UV irradiation for 8 hours. After the reaction, the crude product **12** was precipitated by addition into *n*-hexane under intensive stirring. GPC analysis of the product showed insufficient product formation (see Figure 13). Also, ^{1}H-NMR analysis of the product was not possible due to numerous unidentified signals.

Preparation of a branched polyamide by homo-polymerization of 10 (P25)

333 mg of **10** (1.0 mmol) were mixed together with 7 mg TBD (5 mol%) and homogenized in 2 mL acetone. Afterwards, the mixture was heated, first for 1 hour at 120 °C with a stream of argon passing by to remove the acetone and then for 4 hours at 160 °C applying high vacuum. During this time, the product **P25** was formed as a reddish, gel-like and tacky material which was basically insoluble in any organic solvent except for HFIP and slightly in boiling DMF. Because of its bad solubility, no ^{1}H-NMR data can be provided of the polymer.

5.6. Preparation and polymerization of aryl-bridged diesters

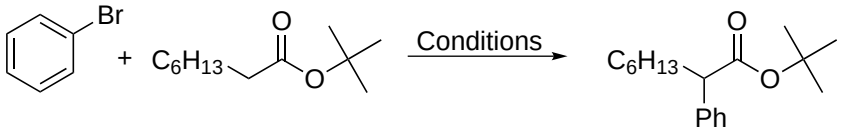
Synthesis of fatty-acid *t*-butyl esters



$R = C_6H_{13} - C_{16}H_{33}$

The *t*-butyl esters, which were necessary for the arylation reactions, were synthesized from the reaction of the corresponding acid chloride in a 1:1 mixture of *t*-butanol and triethylamine (5.0 eq. each) at 60 °C for 4 hours. After the reaction was completed, the product was extracted in diethyl ether, filtered over basic alumina oxide and then purified by high vacuum distillation (C_8-C_{14}) or recrystallization from *n*-hexane (C_{16}-C_{18}), yielding the esters in very high purity and an average yield of 50 to 60 %. It is noteworthy that the arylation reaction did not proceed well when the starting material was not filtered through basic alumina oxide, most probably because of residual free carboxylic acids, although no signal was observed in ^{1}H-NMR spectra.

Condition screening for the *α*-arylation of *t*-butyl octanoate with bromobenzene

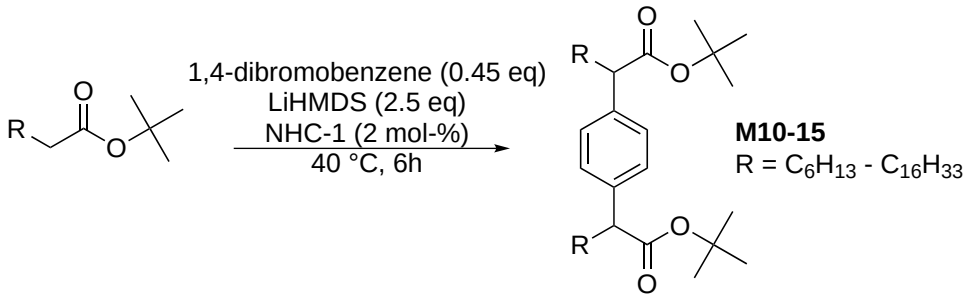


13

In order to investigate the reaction conditions for the arylation of *t*-butyl fatty acids, 115 µL *t*-butyl octanoate (0.5 mmol) were mixed with varying amounts of bromobenzene, palladium NHC catalysts (**NHC-1** and **NHC-2**) and LiHMDS as base in a carousel flask. The mixtures were stirred for different times and different temperatures. Afterwards, diluted hydrochloric acid was added, the product extracted

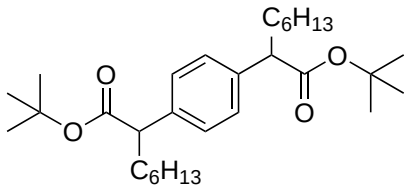
in diethyl ether and concentrated under reduced pressure. The product formation of **13** was analyzed by GC measurements.

Synthesis of aryl-bridged diesters 14-19 (Procedure E)



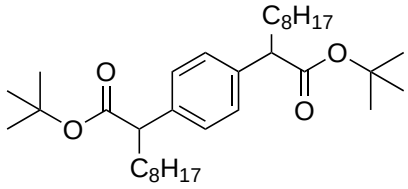
10.0 mmol of the fatty acid *t*-butyl ester was mixed with 1,07 g 1,4-dibromobenzene (4.5 mmol, 4.5 eq) and 115 mg allyl[1,3-*bis*(2,6-diisopropylphenyl)-2-imidazolidinylidene]chloropalladium(II) (**NHC-1**, 0.20 mmol, 2 mol%) in a dry 50 mL round bottom flask. Afterwards, 25 mL LiHMDS (1.0 M in toluene, 2.5 eq) were added and the mixture was heated to 40 °C. The mixture was stirred for 6 hours where it usually turned dark red after approximately 30 minutes. To stop the reaction, the mixture was added to diluted hydrochloric acid where it was extracted with dichloromethane. After evaporation of the solvent, the products were purified by silica gel column chromatography using a solvent gradient from *n*-hexane:acetone 99:1 to 97:3.

Di-*t*-butyl 2,2'-(1,4-phenylene)dioctanoate (14)



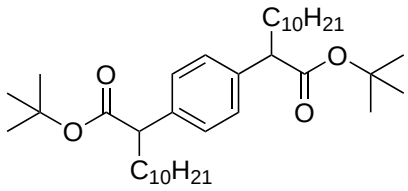
Following the general procedure E, 1.78 g (83.4 %) of **14** was obtained as a yellowish solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.14 (s, 4H, aryl-*H*), 3.36 – 3.25 (m, 2H, α-H), 1.90 (m, 2H, β-H), 1.60 (m, 2H, β-H), 1.30 (s, 18H, *t*Bu), 1.17 (s, 16H, chain), 0.78 (t, *J* = 6.6 Hz, 6H, R-CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 173.58 (R*C*OO*t*Bu), 139.06 (aromatic *C*-$C_{\alpha\text{-Ester}}$), 128.17 (aromatic *C*-H), 80.57 (ROO*C*$(CH_3)_3$), 52.72 (α-C), 34.02 (chain), 32.03 (chain), 29.43 (chain), 27.98 (ROOC(*C*$H_3)_3$), 22.94 (chain), 14.19 (R-*C*H_3); MS (FAB): *m/z* = 363.3 ([M - 2 x *t*Bu + H]$^+$, calc. 363.25).

Di-*t*-butyl 2,2'-(1,4-phenylene)didecanoate (15)



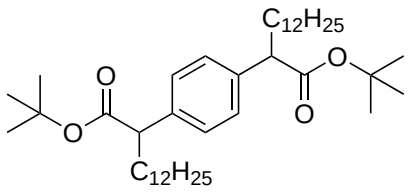
Following the general procedure E, 1.43 g (59.9 %) of **15** was obtained as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.14 (s, 4H, aryl-*H*), 3.39 – 3.24 (m, 2H, α-H), 1.88 (m, 2H, β-H), 1.60 (m, 2H, β-H), 1.30 (s, 18H, *t*Bu), 1.18 (s, 24H, chain), 0.79 (t, *J* = 6.1 Hz, 6H, R-CH_3); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 173.59 (R*C*OO*t*Bu), 139.06 (aromatic *C*-$C_{\alpha\text{-Ester}}$), 128.16 (aromatic *C*-H), 80.57 (ROO*C*$(CH_3)_3$), 52.73 (α-C), 34.02 (chain), 32.22 (chain), 29.67 (chain), 29.23 (chain), 28.00 (chain), 23.03 (chain), 14.23 (R-*C*H_3); MS (FAB): *m/z* = 419.4 ([M – 2 x *t*Bu + H]$^+$, calc. 419.31).

Di-*t*-butyl 2,2'-(1,4-phenylene)didodecanoate (16)



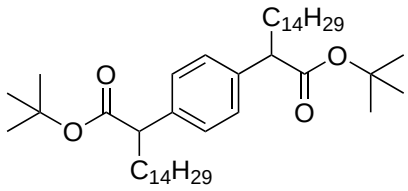
Following the general procedure E, 1.73 g (65.6 %) of **16** was obtained as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2) *δ* 7.14 (s, 4H, aryl-*H*), 3.38 – 3.24 (m, 2H, *α*-H), 1.87 (m, 2H, *β*-H), 1.56 (m, 2H, *β*-H), 1.30 (s, 18H, *t*Bu), 1.17 (s, 32H, chain), 0.79 (t, *J* = 6.5 Hz, 6H, R-C*H*$_3$); ^{13}C NMR (75 MHz, CD_2Cl_2) *δ* 173.59 (R*C*OO*t*Bu), 139.06 (aromatic *C*-C$_{\alpha\text{-Ester}}$), 128.16 (aromatic *C*-H), 80.57 (ROO*C*(CH$_3$)$_3$), 52.73 (*α*-C), 34.02 (chain), 32.28 (chain), 30.19 – 29.38 (chain), 28.00 (chain), 23.06 (chain), 14.24 (R-C*H*$_3$); MS (FAB): *m/z* = 475.4 ([M – 2 x *t*Bu + H]$^+$, calc. 475.38).

Di-*t*-butyl 2,2'-(1,4-phenylene)ditetradecanoate (17)



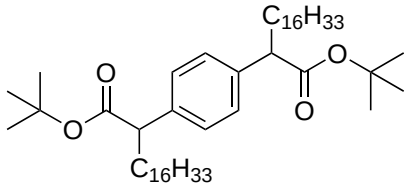
Following the general procedure E, 1.79 g (61.9 %) of **17** was obtained as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2) *δ* 7.14 (s, 4H, aryl-*H*), 3.36 – 3.25 (m, 2H, *α*-H), 1.89 (m, 2H, *β*-H), 1.60 (m, 2H, *β*-H), 1.28 (s, 18H, *t*Bu), 1.17 (s, 40H, chain), 0.80 (t, *J* = 6.3 Hz, 6H, R-C*H*$_3$); ^{13}C NMR (75 MHz, CD_2Cl_2) *δ* 173.59 (R*C*OO*t*Bu), *δ* 139.06 (aromatic *C*-C$_{\alpha\text{-Ester}}$), 128.16 (aromatic *C*-H), 80.57 (ROO*C*(CH$_3$)$_3$), 52.73 (*α*-C), 34.02 (chain), 32.30 (chain), 30.62 – 29.59 (chain), 28.01 (chain), 23.07 (chain), 14.25 (R-*C*H$_3$); MS (FAB): *m/z* = 531.5 ([M – 2 x *t*Bu + H]$^+$, calc. 531.44).

Di-*t*-butyl 2,2'-(1,4-phenylene)dipalmitate (18)



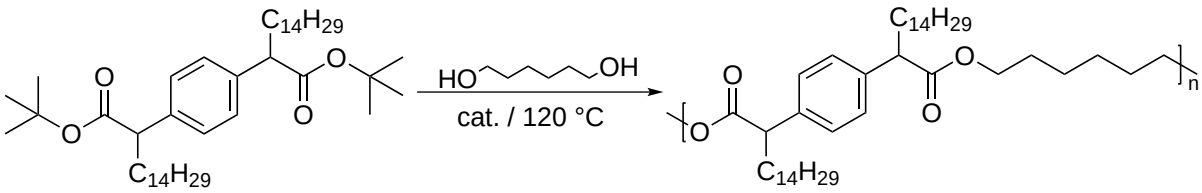
Following the general procedure E, 2.11 g (67.1 %) of **18** was obtained as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.14 (s, 4H, aryl-*H*), 3.33 – 3.28 (m, 2H, α-H), 1.90 (m, 2H, β-H), 1.57 (m, 2H, β-H), 1.28 (s, 18H, *t*Bu), 1.18 (s, 48H, chain), 0.79 (t, *J* = 6.3 Hz, 6H, C*H*$_3$); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 173.59 (R*C*OO*t*Bu), δ 139.06 (aromatic *C*-C$_{\alpha\text{-Ester}}$), 128.16 (aromatic *C*-H), 80.58 (ROO*C*(CH$_3$)$_3$), 52.72 (α-C), 34.03 (chain), 32.31 (chain), 30.39 – 29.55 (chain), 28.05 (chain), 23.07 (chain), 14.26 (R-*C*H$_3$); MS (FAB): *m/z* = 587.5 ([M – 2 x *t*Bu + H]$^+$, calc. 587.50).

Di-*t*-butyl 2,2'-(1,4-phenylene)distearate (19)



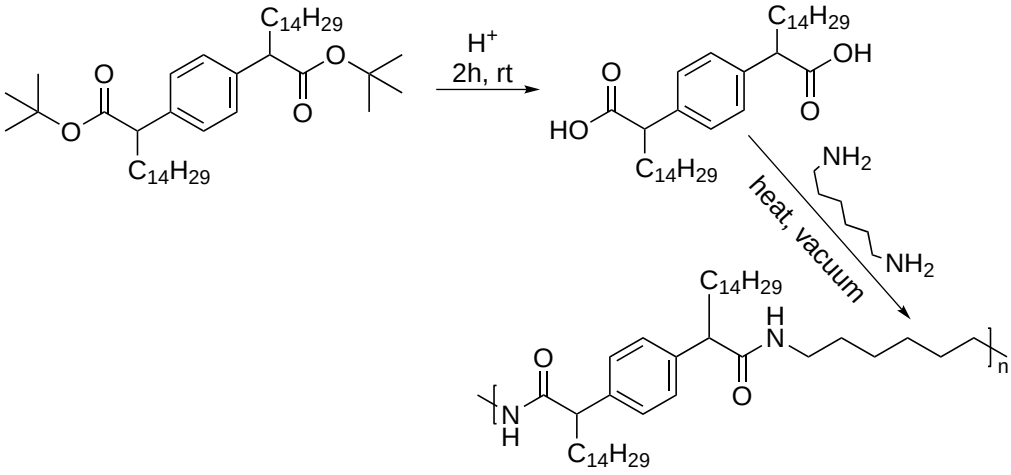
Following the general procedure E, 2.46 g (72.4 %) of **19** was obtained as a white solid. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.14 (s, 4H, aryl-H), 3.31 (t, *J* = 7.7 Hz, 2H, α-H), 1.91 (m, 2H, β-H), 1.56 (m, 2H, β-H), 1.30 (s, 18H, *t*Bu), 1.18 (s, 56H, chain), 0.77 (t, *J* = 6.5 Hz, 6H, R-C*H*$_3$); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 173.60 (R*C*OO*t*Bu), 139.05 (aromatic *C*-C$_{\alpha\text{-Ester}}$), 128.16 (aromatic *C*-H), 80.58 (ROO*C*(CH$_3$)$_3$), 52.73 (α-C), 34.02 (chain), 32.31 (chain), 30.26 – 29.47 (chain), 28.01 (chain), 23.07 (chain), 14.26 (R-*C*H$_3$); MS (FAB): *m/z* = 643.5 ([M – 2 x *t*Bu + H]$^+$, calc. 643.57).

Condition screening of polyester synthesis (P26) from 18



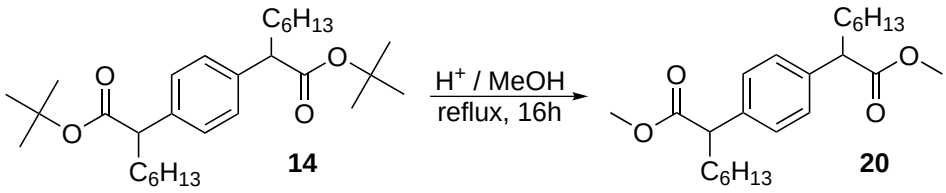
349 mg of **18** (0.50 mmol) were mixed with 59.1 mg 1,6-hexanediol (0.50 mmol, 1.0 eq) in 1 mL acetone. Afterwards, the polymerization catalyst ($Ti(OiPr)_4$, $Sn(Oct)_2$ or H_2SO_4) was added using different amounts and the mixture was stirred at 120 °C, first for one hour with a stream of argon and afterwards 18 hours in high vacuum. The crude reaction mixture was analyzed *via* GPC.

Preparation of polyamide P27 from 18



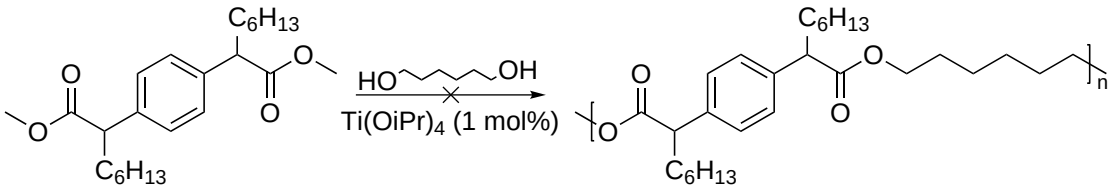
349 mg **18** (0.50 mmol) were solved in 5 mL of a 4:1 mixture of dichloromethane and trifluoroacetic acid. Afterwards, the solution was stirred at room temperature for 2 hours when cleavage of the *t*-butyl ester was complete. Then, the solvents were evaporated and the residue solved in 2 mL acetone and 58 mg 1,6-hexanediamine in 2 mL acetone were added. An immediate salt formation was observed. Then, the mixture was heated slowly to different temperatures, first in an open vessel for evaporation of the solvent and then applying high vacuum for 18 hours.

Synthesis of dimethyl 2,2'-(1,4-phenylene)dioctanoate (20) from 14



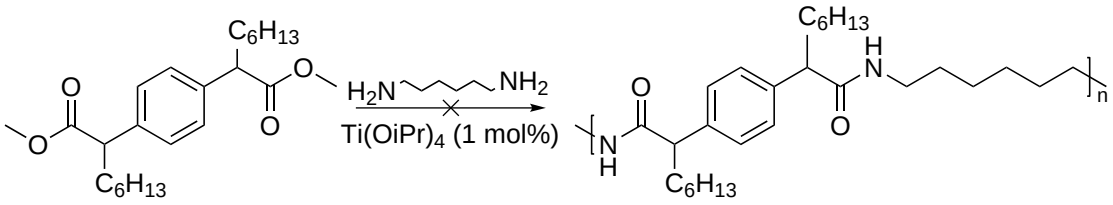
948 mg **14** (2.0 mmol) were dissolved in 30 mL methanol with 40 µL sulfuric acid (about 30 %). The mixture was refluxed for 16 hours, filtered through a pad of basic alumina oxide, washed with methanol and concentrated in high vacuum to obtain the product as yellow oil in quantitative yield and high purity from ^{1}H-NMR. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.15 (s, 4H, aryl-*H*), 3.54 (s, 6H, COOC*H*$_3$), 3.44 (t, *J* = 7.7 Hz, 2H, *α-H*), 1.96 (m, 2H, *β*-H), 1.64 (m, 2H, *β*-H), 1.17 (s, 16H, chain), 0.78 (t, *J* = 6.6 Hz, 6H, R-C*H*$_3$); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 174.74 (*C*OOMe), 138.73 (aromatic *C*-C$_{\alpha\text{-Ester}}$), 128.41 (aromatic *C*-H), 52.10 (COO*C*H$_3$), 51.54 (*C*OOCH$_3$), 33.93 (chain), 31.98 (chain), 29.38 (chain), 27.86 (chain), 22.93 (chain), 14.17 (R-*C*H$_3$). MS (FAB): *m/z* = 391.3 ([M + H]$^+$, calc. 391.26).

Preparation of polyester P28 from 20



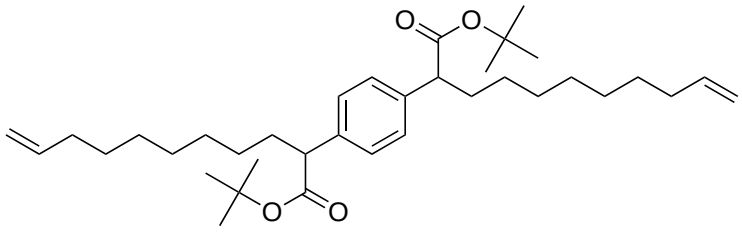
195 mg **20** (0.50 mmol) were mixed with 59.1 mg 1,6-hexanediol (0.50 mmol) in 1 mL acetone. Afterwards, 1,5 µL Ti(O*i*Pr)$_4$ (1,42 mg, 1 mol%) were added and the mixture was heated to 120 °C, first for one hour with a stream of argon passing by and then 18 hours applying high vacuum. GPC-analysis of the crude reaction mixture showed only oligomer formation.

Preparation of polyamide P29 from 20



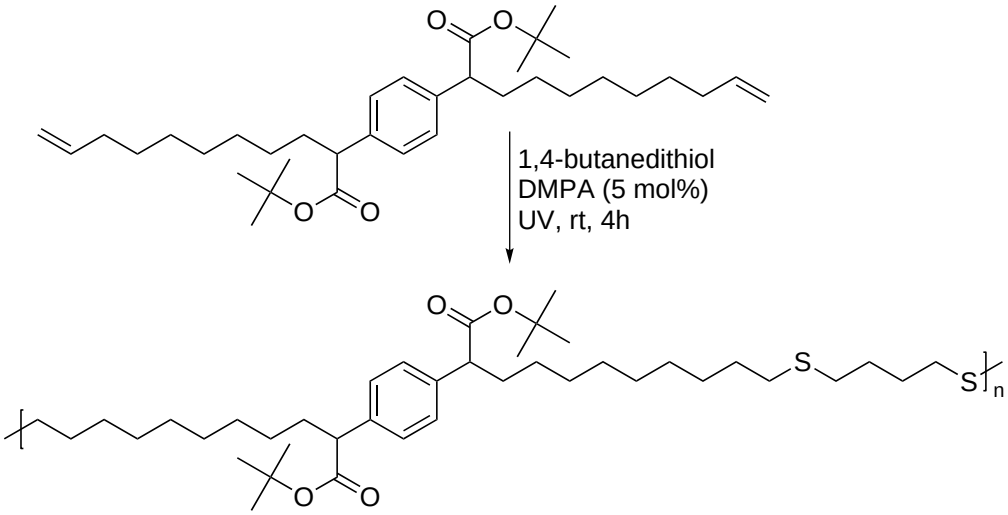
195 mg **20** (0.50 mmol) were mixed with 58 mg 1,6-hexanediamine (0.50 mmol) in 5 mL toluene. Afterwards, 3.5 mg TBD (5 mol%) were added and the mixture was heated from 120 °C to 200 °C at a rate of 40 °C each hour. In the end, the mixture was heated at 200 °C with high vacuum for 4 hours. GPC-analysis showed only oligomer formation.

Di-*t*-butyl 2,2'-(1,4-phenylene)*bis*(undec-10-enoate) (21)



Following the general procedure E, 1.59 g (63.7 %) of **21** was obtained as a colorless oil. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.14 (s, 4H, aryl-H), 5.74 (ddd, *J* = 23.7, 13.5, 6.7 Hz, 2H, CH_2=C*H*R), 4.86 (dd, *J* = 20.9, 12.0 Hz, 4H, CH_2=CHR), 3.37 – 3.23 (m, 2H,, *α*-H), 2.01 – 1.89 (m, 6H, *β*-H + CH_2=CH-CH_2-R), 1.55 (s, 2H, *β*-H), 1.30 (s, 18H, *t*Bu), 1.19 (s, 20H, chain); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 173.57 (R*C*OO*t*Bu), 139.65 (CH_2=*C*HR), 139.05 (aromatic *C*-$C_{\alpha\text{-Ester}}$), 128.16 (aromatic *C*-H), 114.18 (*C*H_2=CHR), 80.59 (ROO*C*$(CH_3)_3$), 52.72 (*α*-C), 34.07 (chain), 29.49 (chain), 28.00 (chain); MS (FAB): *m/z* = 443.4 ([M – 2 x *t*Bu + H]$^+$, calc. 443.32).

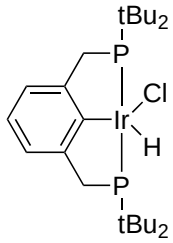
Preparation of P30 by thiol-ene polymerization of 21 and 1,4-butanedithiol



544 mg **21** (1.0 mmol) were mixed with 122 mg 1,4-butanedithiol (117 µL, 1.0 mmol) and 13 mg DMPA (0.05 mmol, 5 mol%) in 1 mL THF. The mixture was stirred at room temperature under UV irradiation (365 nm) for 4 hours with GPC measurements after 1, 2 and 4 hours (Figure 18). For precipitation, the polymer **P30** was directly dropped into ice-cold methanol. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (s, 4H, aryl-*H*), 3.32 (t, *J* = 7.6 Hz, 2H, *α*-H), 2.53 – 2.36 (m, 8H, -C*H*$_2$-S-C*H*$_2$-), 1.92 (m, 2H, *β*-H), 1.52 (m, 10H, β-H + -C*H*$_2$-CH$_2$-S-), 1.31 (s, 18H, *t*Bu-ester), 1.18 (s, 24H, chain).

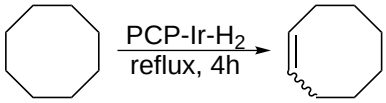
5.7. Experimental procedures for the preparation of long chain polyesters

Synthesis of 2,6-*bis*[(di-*t*-butylphosphino)methyl]phenyl-chlorohydridoiridium (PCP-Ir-Cl)



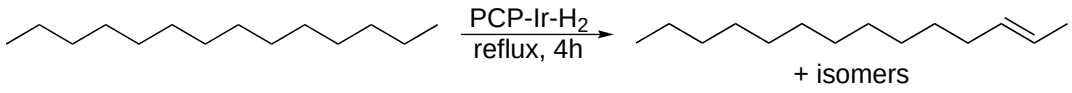
In an argon-filled glovebox, 434 mg 1,3-*bis*(di-*t*-butylphosphinomethyl)benzene (**^{tBu}PCP**, 1.1 mmol) were mixed with 336 mg *bis*(1,5-cyclooctadiene)diiridium(I) dichloride ($[Ir(COD)Cl]_2$, 0.5 mmol, 1.0 mmol iridium) in a 25 mL Schlenk-flask. Afterwards, 10 mL dry and degassed toluene was added and the mixture refluxed for 16 hours, still under argon. Afterwards, the solvent was evaporated and the product dried under high vacuum. Thereby, 714 mg (quantitative yield) of a reddish powder was obtained with a purity of approximately 90 % which was analyzed from ^{1}H-NMR integration of the hydride signal. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (d, J = 7.4 Hz, 2H, aryl-*H*), 6.66 (t, J = 7.4 Hz, 1H, aryl-*H*), 3.35 – 3.10 (m, 4H, CH_2), 1.29 (dd, J = 13.2, 6.5 Hz, 36H, $C(CH_3)_3$), -43.52 (t, J = 12.5 Hz, 1H, Ir-*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.92 (s, *aryl*-H), 151.83 (t, J = 8.5 Hz, *aryl*-CH_2), 122.64 (s, *aryl*-H), 120.89 (t, J = 7.9 Hz, *aryl*-Ir), 37.70 (t, J = 10.2 Hz, $C(CH_3)_3$), 35.37 – 34.55 (m, $C(CH_3)_3$), 29.99 (t, J = 2.4 Hz, $C(CH_3)_3$), 29.22 (t, J = 2.4 Hz, $C(CH_3)_3$), 27.11 (s, aryl-CH_2-P-); MS (FAB): m/z = 586.1 ([M – HCl], calc. 586.25).

Catalytic dehydrogenation of cyclooctane using PCP-Ir-H_2



6 mg **PCP-Ir-Cl** (0.01 mmol) were solved in 2.0 mL cyclooctane (15.0 mmol) with 0.39 mL TBE (3.0 mmol) as hydrogen acceptor. Afterwards, the mixture was degassed intensively and argon was added. Under the argon atmosphere, 1.2 mg NaH as activator was added and the mixture was refluxed under argon for 4 hours. It is noteworthy that immediately after addition of the activator, the solution turned intensive dark red. After 4 hours, the reaction was cooled with a stream of argon passing by in order to remove TBE and TBA. Afterwards, the mixture was analyzed *via* ^{1}H-NMR to test for dehydrogenation activity. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (m, 2H, -CH_2-C*H*=C*H*-CH_2-), 2.08 (m, 4H, -CH_2-C*H*$_2$-CH=CH-), 1.55 – 1.29 (m, 615H, COA and chain).

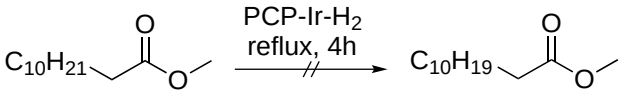
Catalytic dehydrogenation of tetradecane using PCP-Ir-H_2



6 mg **PCP-Ir-Cl** (0.01 mmol) were solved in 2.6 mL tetradecane (10.0 mmol) with 0.13 mL TBE (1.0 mmol) as hydrogen acceptor. Afterwards, the mixture was degassed intensively and argon was added. Under the argon atmosphere, 1.2 mg NaH as activator was added and the mixture was refluxed under argon for 4 hours where it turned dark red immediately after addition of the activator. After 4 hours, the reaction was cooled with a stream of argon passing by in order to remove TBE and TBA. The mixture was analyzed *via* ^{1}H-NMR to test for dehydrogenation activity. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.42 – 5.19 (m, 2H, internal double bond), 2.03 – 1.77

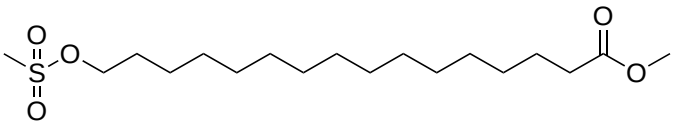
(m, 4H, *α*-C*H*$_2$ to double bond), 1.29 – 1.08 (m, 640H, chain), 0.81 (t, *J* = 6.6 Hz, 159H, -C*H*$_3$).

Trial for the catalytic dehydrogenation of methyl dodecanoate using PCP-Ir-H$_2$



6 mg **PCP-Ir-Cl** (0.01 mmol) were dissolved in 2.45 mL methyl dodecanoate (10.0 mmol) with 0.39 mL TBE (3.0 mmol) as hydrogen acceptor. Afterwards, the mixture was degassed intensively and argon was added. Under the argon atmosphere, 1.2 mg NaH as activator was added and the mixture was refluxed under argon for 4 hours. It is noteworthy that in contrast to the dehydrogenation of alkanes, the mixture turned yellowish after addition of the activator. After 4 hours, the reaction was cooled with a stream of argon passing by in order to remove TBE and TBA. The mixture was analyzed *via* ^{1}H-NMR to test for dehydrogenation activity. However, the ^{1}H-NMR showed clearly only the starting material (methyl dodecanoate) without any double bond formation.

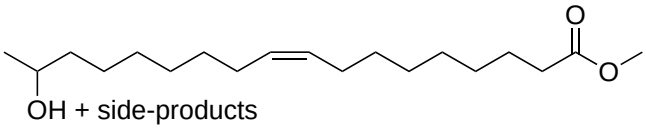
Synthesis of methyl 16-((methylsulfonyl)oxy)hexadecanoate (22)



2.29 g methyl 16-hydroxypalmitate (8.0 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. Afterwards the reaction was stirred at room temperature for 4 hours. Afterwards the solvent was removed under reduced pressure and the product

washed with 3 x 50 mL diluted hydrochloric acid. For purification the product was recrystallized from hot methanol to yield 2.48 g (6.8 mmol, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 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 174.41 (*C*$OOCH_3$), 70.31 (CH_3-SO_2-*C*H_2-), 51.50 (COO*C*H_3), 37.41 - 25.03 (chain); HRMS (FAB): $C_{18}H_{36}O_5S$ $[M+H]^+$ calc. 365.2362 found 365.2366

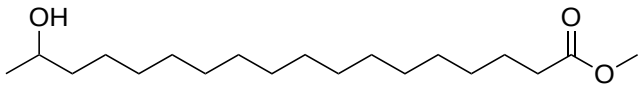
Preparation of methyl 17-hydroxyoctadec-9-enoate from sophorose lipids



12.5 g sophorose lipid (approx. 20.0 mmol) was suspended in 150 mL methanol with 3 mL concentrated sulfuric acid. The mixture was refluxed for 18 hours. Afterwards, the mixture was filtered over basic alumina and concentrated under reduced pressure to obtain a brownish, crystalline material. Then, 150 mL DCM were added resulting in an immediate precipitation of the cleaved sugar, which can then be filtered off. The sugar was afterwards washed with DCM until it became colorless. Removal of the DCM gave 4.96 g of a fatty acid mixture containing the *ω*-1 hydroxy saturated and unsaturated FAME and short-chain fatty acid *α*,*ω*-diesters. ^{1}H-NMR analysis shows approximately 50 % unsaturated ester and approximately 60 % desired *ω*-1 hydroxy FAMEs. The reaction product was directly used for the hydrogenation reaction without work-up. ^{1}H-NMR (300 MHz, $CDCl_3$, mixture of products) δ 5.36 – 5.22 (m, -CH_2-C*H*=C*H*=CH_2-), 3.79 – 3.68 (m, CH_3-C*H*OH-CH_2-), 3.64 – 3.57 (s, COOC*H*$_3$), 2.25 (t, J = 7.5 Hz, *α-H* Me-Ester), 1.98 (m, -C*H*$_2$-CH=CH=C*H*$_2$-),), 1.53 (m, *β-H*

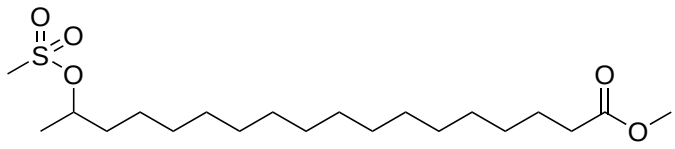
Me-Ester), 1.45 – 1.16 (m, chain), 1.12 (d, *J* = 6.2 Hz, C*H*$_3$-CHOH-). MS (FAB): m/z = 313.1 ([M + H]$^+$, calc. 312.27).

Synthesis of methyl 17-hydroxyoctadecanoate (24)



For the hydrogenation of the reaction mixture derived from the esterification of the sophorose lipids all products (4.96 g, from approx. 20 mmol sophorose lipid, about 60 % purity) were dissolved in 50 mL ethyl acetate together with 428 mg palladium on choral (2 mol% palladium). The mixture was stirred at room temperature under a hydrogen atmosphere (1 atm) for 24 hours. Afterwards, the choral was filtered off, the solvent removed under reduced pressure and the product dried under vacuum. Yield: 3.19 g (10.15 mmol). ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 3.79 – 3.65 (m, 1H, CH_3-C*H*OH-CH_2-), 3.60 (s, 3H, COOC*H*$_3$), 2.23 (t, J = 7.5 Hz, 2H, *α-H*), 1.52 (m, 2H, *β-H*), 1.36 (s, 2H, CH_3-CHOH-C*H*$_2$-), 1.20 (s, 24H, chain), 1.12 (d, J = 6.2 Hz, 3H, C*H*$_3$-CHOH-CH_2-); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 174.33 (*C*OOCH$_3$), 68.21 (CH_3-*C*HOH-CH_2-), 51.38 (COO*C*H$_3$), 39.33 - 24.91 (chain), 23.40 (*C*H$_3$-CHOH-CH_2-); MS (FAB): m/z = 315.2 ([M + H]$^+$, calc. 314.28).

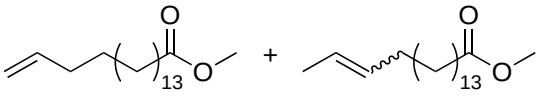
Synthesis of methyl 17-((methylsulfonyl)oxy)octadecanoate (25)



1.26 g pure methyl 17-hydroxyoctadecanoate (4.0 mmol) was dissolved in 20 mL DCM with 2.8 mL triethylamine (20.0 mmol, 5.0 eq.). Afterwards 0.93 mL mesyl chloride (12.0 mmol, 3.0 eq.) were added while the mixture was cooled on ice.

Afterwards, the mixture was stirred for 30 more minutes on ice and then at room temperature over-night. The DCM was then removed under reduced pressure and the product washed 3 times with diluted hydrochloric acid. Afterwards, the product was recrystallized from boiling methanol. Yield: 1.28 g (3.26 mmol, 82 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.72 (m, 1H, CH_3-C*H*(OSO_2CH_3)-CH_2-), 3.59 (s, 3H, COOC*H*$_3$), 2.93 (s, 3H, -OSO_2C*H*$_3$), 2.23 (t, J = 7.5 Hz, 2H, *α-H*), 1.75 – 1.46 (m, 4H, *β-H* + CH_3-CH(OSO_2CH_3)-C*H*$_2$-), 1.35 (d, J = 6.2 Hz, 3H, C*H*$_3$-CH(OSO_2CH_3)-CH_2-), 1.18 (s, 22H, chain); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.31 (*C*OOCH_3), 80.44 (CH_3-*C*H(OSO_2CH_3)-CH_2-), 51.40 (COO*C*H$_3$), 38.61 - 24.93 (chain), 21.17 (*C*H$_3$-CH(OSO_2CH_3)-CH_2-). MS (FAB): m/z = 393.4 ($[M + H]^+$, calc. 392.26).

Preparation of methyl octadec-16/17-enoate (26)

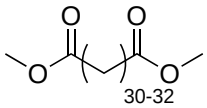


ratio ~ 1:6

784 mg methyl 17-((methylsulfonyl)oxy)octadecanoate (2.0 mmol) were dissolved in 60 mL glyme with 0.90 g sodium iodide (6.0 mmol, 3.0 eq.) and 1.11 g TBD (8.0 mmol, 4.0 eq.). The mixture was refluxed for 18 hours. Afterwards, the reaction was quenched by addition to 100 mL diluted hydrochloric acid and the product extracted with dichloromethane. Then, the product was dissolved in 30 mL methanol with 0.2 mL sulfuric acid and refluxed for 6 hours in order to regain the methyl-ester. The mixture was then filtered over basic alumina and concentrated under vacuum to obtain the desired product in quantitative yield and approximately 75 % double bond formation with a ratio of *α*:*α*-1 olefins of 1:5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (m, 0.14H, CH_2=C*H*-CH_2-), 5.51 – 5.31 (m, 1.40H, CH_3-C*H*=C*H*-CH_2-), 5.05 – 4.87 (m, 0.28H, C*H*$_2$=CH-CH_2-), 3.65 (s, COOC*H*$_3$, 3H), 2.29 (t, J = 7.6 Hz, 2H, *α-H*),

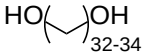
2.10 - 1.89 (m, 2H, *β-H*), 1.61 (m, 4H, *α-H* to double bonds), 1.24 (m, chain); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 174.33 (*C*$OOCH_3$), 131.68 (CH_3-CH=*C*H-CH_2-), 124.48 (CH_3-*C*H=CH-CH_2-), 51.40 (COO*C*H_3), 34.06 - 24.89 (chain), 17.89 (*C*H_3-CH=CH-CH_2-). MS (FAB): m/z = 297.2 ($[M + H]^+$, calc. 296.28).

Synthesis of C_{32}-C_{34} diester by self-metathesis and hydrogenation (27)



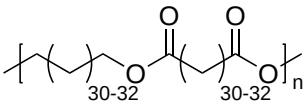
For the self-metathesis reaction, the crude reaction product from the elimination reaction was used; 297 mg (approx. 1.0 mmol) were dissolved in 3 mL DCM with 14 mg Hoveyda-Grubbs 2nd generation catalyst (2.0 mol%) and 5.4 mg *p*-benzoquinone (5.0 mol%). The mixture was heated to 40 °C for 4 hours under a stream of argon. Afterwards, the reaction was quenched by addition of 20 µL ethyl-vinyl-ether and the solvent was removed under reduced pressure. The crude product was then dissolved in 10 mL DCM with 30 mg palladium on choral (1 mol% palladium) and stirred at 50 °C under a 20 bar hydrogen atmosphere in a pressure reactor for 24 hours. Afterwards, the choral was filtered off and washed intensively with DCM. The product was obtained after removal of the solvent as a white powder, which can be easily recrystallized from boiling methanol or acetone. ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 3.60 (s, 6H, COOCH_3), 2.23 (t, J = 7.5 Hz, 4H, *α-H*), 1.60 – 1.50 (m, 4H, *β-H*), 1.18 (s, 52H, chain); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 173.29 (*C*$OOCH_3$), 50.39 (COO*C*H_3), 33.10 - 23.95 (chain). MS (FAB): m/z = 315.2 ($[M + H]^+$, calc. 314.3). MS (FAB): m/z = 538.3 ([M C_{32}], calc. 538.50; m/z = 553.5 ($[M + H\ C_{33}]^+$, calc. 552.51).

Synthesis of C_{32-34} diol with lithium aluminium hydride (28)



For the preparation of **28**, 800 mg 27 (approx. 1.5 mmol) were dissolved in 50 mL dry THF and 9 mL of a 1M solution of lithium aluminium hydride in THF was added. An immediate gas evolution was observed. The mixture was then refluxed for 18 hours and afterwards quenched by slow addition of water until no more gas evolution was observed. The mixture was filtered over basic alumina and washed intensively with warm THF and DCM. After evaporation of the solvent, the product was obtained as a white powder (480 mg, approx. 1.0 mmol, 66 % yield). ^{13}C NMR of the product was not possible due to its low solubility. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55 – 3.44 (m, 4H, *α-H*), 1.53 – 1.40 (m, 4H, *β-H*), 1.18 (s, 56H, chain); m/z = 483,5 ($[M + H\ C_{32}]^+$, calc. 482.51.

Preparation of long-chain polyester $PE_{32-34:32-34}$ (P31) with $Sn(Oct)_2$



For preparation of **P31**, 54 mg **27** and 48 mg **28** (both 0.1 mmol) were mixed with 1.6 µL $Sn(Oct)_2$ (5 mol%). Afterwards, the mixture was melted at 120 °C for 2 hours under a stream of argon, then at 150 °C for 4 hours applying high vacuum and in the end for 14 hours at 170 °C, also applying high vacuum. For precipitation, **P31** was dissolved in 3 mL warm toluene and added into room-temperature THF to yield 69.3 mg **P31** (72 %) as a white powder. ^{1}H-NMR was only possible at higher temperatures of 60 °C in d_6-benzene with 10 vol% TFA as additive. ^{1}H NMR (600 MHz, C_6D_6) δ 3.94 (t, *J* = 6.7 Hz, 4H, -CH_2-COO-C*H*$_2$-), 2.13 (t, *J* = 7.5 Hz, 4H, -C*H*$_2$-COO-CH_2-), 1.47 (m, 8H, *β-H*s), 1.35 (s, 112H, chain).

6. Index of contents

6.1. List of tables

6.2. List of schemes

6.3. List of figures

6.4. List of abbreviations

AIBN	Azobisisobutyronitrile
BHT	Butylated hydroxytoluene
CDI	Carbodiimide
COA	Cyclooctane
COE	Cyclooctene
DCM	Dichloromethane
DMAC	N,N-Dimethylacetamide
DMC	Dimethyl carbonate
DMF	N,N-Dimethylformamide
DMPA	2,2-Dimethoxy-2-phenylacetophenone
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
FAME	Fatty acid methyl ester
GC	Gas chromatography
GPC	Gel permeation chromatography
HEA	Hydroxy ethylacrylate
HFA	Hydroxy fatty acid
HFIP	Hexafluoroisopropanol
LDA	Lithium diisopropylamide
LiHMDS	Lithium *bis*(trimethylsilyl)amide
NaH	Sodium hydride (used as a 60 wt% dispersion in mineral oil)
NHC	N-heterocyclic carbene
NMR	Nuclear magnetic resonance

PBT	Poly(butyl-terephthalate)
PLA	Poly(lactic acid)
PEG	Polyethylene glycol
PET	Poly(ethylene-terephthalate)
PDI	Poly-dispersity index
PRA	Poly(ricinolic acid)
ROMP	Ring-opening metathesis polymerization
$Sn(Oct)_2$	Tin(II) 2-ethylhexanoate
TBA	*t*-Butyl ethane
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TBE	*t*-Butyl ethene
THF	Tetrahydrofuran
$Ti(O\mathit{i}Pr)_4$	Titanium (VI) isopropoxide
TON	Turnover number
UV	Ultraviolet

6.5. Literature and references

1. U. S. E. I. Administration, International Energy Statistics, www.eia.gov, Accessed 03.07.2013, 2013.
2. R. T. Mathers, *J. Polym. Sci. Part A: Polym. Chem.*, 2012, **50**, 1-15.
3. S. Kim and B. E. Dale, *Biomass Bioenergy*, 2004, **26**, 361-375.
4. M. Balat and H. Balat, *Appl. Energ.*, 2009, **86**, 2273-2282.
5. M. Iwamoto, K. Kasai and T. Haishi, *ChemSusChem*, 2011, **4**, 1055-1058.
6. Y. Hu, N. Zhan, C. Dou, H. Huang, Y. Han, D. Yu and Y. Hu, *Biotech. J.*, 2010, **5**, 1186-1191.
7. D. Tilman, J. Hill and C. Lehman, *Science*, 2006, **314**, 1598-1600.
8. K. Madhavan Nampoothiri, N. R. Nair and R. P. John, *Bioresour. Technol.*, 2010, **101**, 8493-8501.
9. P. Mercier, L. Yerushalmi, D. Rouleau and D. Dochain, *J. Chem. Technol. Biotechnol.*, 1992, **55**, 111-121.
10. D. X. Zhang and M. Cheryan, *Biotechnol. Lett.*, 1991, **13**, 733-738.
11. R. P. John, D. Gangadharan and K. Madhavan Nampoothiri, *Bioresour. Technol.*, 2008, **99**, 8008-8015.
12. G. Reddy, M. Altaf, B. J. Naveena, M. Venkateshwar and E. V. Kumar, *Biotechnol. Adv.*, 2008, **26**, 22-34.
13. D. Garlotta, *J. Polym. Environ.*, 2001, **9**, 63-84.
14. A. P. Gupta and V. Kumar, *Eur. Poly. J.*, 2007, **43**, 4053-4074.
15. N. W. LLC, About Natureworks, http://www.natureworksllc.com/About-NatureWorks-LLC, 08.07.2013.
16. M. Rose and R. Palkovits, *Macromol. Rapid Commun.*, 2011, **32**, 1299-1311.
17. R. M. Rasal, A. V. Janorkar and D. E. Hirt, *Prog. Polym. Sci.*, 2010, **35**, 338-356.
18. D. W. Grijpma and A. J. Pennings, *Macromol. Chem. Phys.*, 1994, **195**, 1633-1647.
19. D. W. Grijpma and A. J. Pennings, *Macromol. Chem. Phys.*, 1994, **195**, 1649-1663.
20. A. O. Helminen, H. Korhonen and J. V. Seppälä, *Macromol. Chem. Phys.*, 2002, **203**, 2630-2639.
21. E. M. Frick, A. S. Zalusky and M. A. Hillmyer, *Biomacromolecules*, 2003, **4**, 216-223.
22. M. L. Robertson, J. M. Paxton and M. A. Hillmyer, *ACS Appl. Mater. Interfaces*, 2011, **3**, 3402-3410.
23. W. Luo, S. Li, J. Bei and S. Wang, *J. Appl. Polym. Sci.*, 2002, **84**, 1729-1736.
24. O. Martin and L. Avérous, *Polymer*, 2001, **42**, 6209-6219.
25. R. A. Quirk, M. C. Davies, S. J. B. Tendler and K. M. Shakesheff, *Macromolecules*, 2000, **33**, 258-260.
26. R. A. Quirk, M. C. Davies, S. J. B. Tendler, W. C. Chan and K. M. Shakesheff, *Langmuir*, 2001, **17**, 2817-2820.
27. K. Cai, K. Yao, X. Hou, Y. Wang, Y. Hou, Z. Yang, X. Li and H. Xie, *J. Biomed. Mater. Res.*, 2002, **62**, 283-291.
28. R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004, **4**, 835-864.
29. K. A. Athanasiou, G. G. Niederauer and C. M. Agrawal, *Biomaterials*, 1996, **17**, 93-102.

30. T. Kasuga, Y. Ota, M. Nogami and Y. Abe, *Biomaterials*, 2000, **22**, 19-23.
31. S. Fredenberg, M. Wahlgren, M. Reslow and A. Axelsson, *Int. J. Pharm.*, 2011, **415**, 34-52.
32. L. Mialon, A. G. Pemba and S. A. Miller, *Green Chem.*, 2010, **12**, 1704-1706.
33. I. A. Pearl, *J. Am. Chem. Soc.*, 1942, **64**, 1429-1431.
34. P. Rodrigues Pinto, E. Borges da Silva and A. Rodrigues, in *Biomass Conversion*, eds. C. Baskar, S. Baskar and R. S. Dhillon, Springer Berlin Heidelberg, 2012, ch. 12, pp. 381-420.
35. H. Kang, R. Liu and Y. Huang, *Polym. Int.*, 2013, **62**, 338-344.
36. M. C. Gortari and R. A. Hours, *Biotechnological processes for chitin recovery out of crustacean waste: A mini-review*, 2013.
37. D. Klemm, B. Heublein, H.-P. Fink and A. Bohn, *Angew. Chem. Int. Ed.*, 2005, **44**, 3358-3393.
38. M. Sasaki, Z. Fang, Y. Fukushima, T. Adschiri and K. Arai, *Ind. Eng. Chem. Res.*, 2000, **39**, 2883-2890.
39. S. C. Fox, B. Li, D. Xu and K. J. Edgar, *Biomacromolecules*, 2011, **12**, 1956-1972.
40. D. Roy, M. Semsarilar, J. T. Guthrie and S. Perrier, *Chem. Soc. Rev.*, 2009, **38**, 2046-2064.
41. D. Roy, J. T. Guthrie and S. Perrier, *Macromolecules*, 2005, **38**, 10363-10372.
42. H. Lönnberg, L. Fogelström, L. Berglund, E. Malmström and A. Hult, *Eur. Poly. J.*, 2008, **44**, 2991-2997.
43. H. Lönnberg, Q. Zhou, H. Brumer, T. T. Teeri, E. Malmström and A. Hult, *Biomacromolecules*, 2006, **7**, 2178-2185.
44. H. Dong, Q. Xu, Y. Li, S. Mo, S. Cai and L. Liu, *Colloids Surf., B*, 2008, **66**, 26-33.
45. Q. Yan, J. Yuan, F. Zhang, X. Sui, X. Xie, Y. Yin, S. Wang and Y. Wei, *Biomacromolecules*, 2009, **10**, 2033-2042.
46. D. L. Berthier, A. Herrmann and L. Ouali, *Polym. Chem.*, 2011, **2**, 2093-2101.
47. H. Kang, R. Liu, H. Sun, J. Zhen, Q. Li and Y. Huang, *J. Phys. Chem. B*, 2011, **116**, 55-62.
48. S. Ifuku and J. F. Kadla, *Biomacromolecules*, 2008, **9**, 3308-3313.
49. WORLD OILS & FATS 2009, http://econ.mpob.gov.my/economy/annual/stat2009/World6.3.pdf, Accessed 24.06.2013.
50. H. Mutlu and M. A. R. Meier, *Eur. J. Lipid Sci. Technol.*, 2010, **112**, 10-30.
51. M. Genas, *Angew. Chem.*, 1962, **74**, 535-540.
52. P. Welters, *Biospektrum*, 2012, **18**, 550-552.
53. R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2006, **45**, 3760-3765.
54. T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2000, **34**, 18-29.
55. P. Jean-Louis Hérisson and Y. Chauvin, *Makromol. Chem.*, 1971, **141**, 161-176.
56. R. H. Grubbs, *Tetrahedron*, 2004, **60**, 7117-7140.
57. A. K. Chatterjee, T.-L. Choi, D. P. Sanders and R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 11360-11370.
58. A. Rybak and M. A. R. Meier, *Green Chem.*, 2007, **9**, 1356-1361.
59. A. Rybak, P. A. Fokou and M. A. R. Meier, *Eur. J. Lipid Sci. Technol.*, 2008, **110**, 797-804.
60. C. Vilela, A. J. D. Silvestre and M. A. R. Meier, *Macromol. Chem. Phys.*, 2012, **213**, 2220-2227.

61. H. Mutlu and M. A. R. Meier, *Macromol. Chem. Phys.*, 2009, **210**, 1019-1025.
62. T. Jacobs, A. Rybak and M. A. R. Meier, *Appl. Catal., A*, 2009, **353**, 32-35.
63. X. Miao, P. H. Dixneuf, C. Fischmeister and C. Bruneau, *Green Chem.*, 2011, **13**, 2258-2271.
64. S. Warwel, C. Demes and G. Steinke, *J. Polym. Sci. Part A: Polym. Chem.*, 2001, **39**, 1601-1609.
65. D. M. Ohlmann, N. Tschauder, J.-P. Stockis, K. Gooßen, M. Dierker and L. J. Gooßen, *J. Am. Chem. Soc.*, 2012, **134**, 13716-13729.
66. O. Turunc and M. A. R. Meier, *Green Chem.*, 2011, **13**, 314-320.
67. P. A. Fokou and M. A. R. Meier, *J. Am. Chem. Soc.*, 2009, **131**, 1664-1665.
68. A. Rybak and M. A. R. Meier, *ChemSusChem*, 2008, **1**, 542-547.
69. U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schäfer, *Angew. Chem. Int. Ed.*, 2011, **50**, 3854-3871.
70. S. Chikkali and S. Mecking, *Angew. Chem. Int. Ed.*, 2012, **51**, 5802-5808.
71. T. Posner, *Chem. Ber.*, 1905, **38**, 646-657.
72. C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, 1959, **81**, 1144-1148.
73. O. Türünç and M. A. R. Meier, *Eur. J. Lipid Sci. Technol.*, 2013, **115**, 41-54.
74. U. Biermann, W. Butte, R. Koch, P. A. Fokou, O. Türünç, M. A. R. Meier and J. O. Metzger, *Chem. Eur. J.*, 2012, **18**, 8201-8207.
75. C. E. Hoyle and C. N. Bowman, *Angew. Chem. Int. Ed.*, 2010, **49**, 1540-1573.
76. O. Turunc, M. Firdaus, G. Klein and M. A. R. Meier, *Green Chem.*, 2012, **14**, 2577-2583.
77. M. Desroches, S. Caillol, R. Auvergne, B. Boutevin and G. David, *Polymer Chemistry*, 2012, **3**, 450-457.
78. M. Desroches, S. Caillol, R. Auvergne and B. Boutevin, *Eur. J. Lipid Sci. Technol.*, 2012, **114**, 84-91.
79. O. Türünç and M. A. R. Meier, *Macromol. Rapid Commun.*, 2010, **31**, 1822-1826.
80. K. Kempe, R. Hoogenboom and U. S. Schubert, *Macromol. Rapid Commun.*, 2011, **32**, 1484-1489.
81. A. S. Goldmann, A. Walther, L. Nebhani, R. Joso, D. Ernst, K. Loos, C. Barner-Kowollik, L. Barner and A. H. E. Müller, *Macromolecules*, 2009, **42**, 3707-3714.
82. C. Boyer, A. Granville, T. P. Davis and V. Bulmus, *J. Polym. Sci. Part A: Polym. Chem.*, 2009, **47**, 3773-3794.
83. N. ten Brummelhuis, C. Diehl and H. Schlaad, *Macromolecules*, 2008, **41**, 9946-9947.
84. L. M. Campos, K. L. Killops, R. Sakai, J. M. J. Paulusse, D. Damiron, E. Drockenmuller, B. W. Messmore and C. J. Hawker, *Macromolecules*, 2008, **41**, 7063-7070.
85. A. Dondoni, *Angew. Chem. Int. Ed.*, 2008, **47**, 8995-8997.
86. K. L. Killops, L. M. Campos and C. J. Hawker, *J. Am. Chem. Soc.*, 2008, **130**, 5062-5064.
87. P. Antoni, M. J. Robb, L. Campos, M. Montanez, A. Hult, E. Malmström, M. Malkoch and C. J. Hawker, *Macromolecules*, 2010, **43**, 6625-6631.
88. G. Lligadas, J. C. Ronda, M. Galià and V. Cádiz, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 2111-2124.
89. K. Y. Ghebreyessus and R. J. Angelici, *Organometallics*, 2006, **25**, 3040-3044.
90. A. Behr, D. Obst and A. Westfechtel, *Eur. J. Lipid Sci. Technol.*, 2005, **107**, 213-219.

91. M. R. L. Furst, R. L. Goff, D. Quinzler, S. Mecking, C. H. Botting and D. J. Cole-Hamilton, *Green Chem.*, 2012, **14**, 472-477.
92. F. Stempfle, D. Quinzler, I. Heckler and S. Mecking, *Macromolecules*, 2011, **44**, 4159-4166.
93. D. J. Cole-Hamilton, *Angew. Chem. Int. Ed.*, 2010, **49**, 8564-8566.
94. C. Jiménez-Rodriguez, G. R. Eastham and D. J. Cole-Hamilton, *Inorg. Chem. Commun.*, 2005, **8**, 878-881.
95. P. Roesle, C. J. Dürr, H. M. Möller, L. Cavallo, L. Caporaso and S. Mecking, *J. Am. Chem. Soc.*, 2012, **134**, 17696-17703.
96. F. Stempfle, P. Ortmann and S. Mecking, *Macromol. Rapid Commun.*, 2013, **34**, 47-50.
97. Goo, D. M. Ohlmann and M. Dierker, *Green Chem.*, 2010, **12**, 197-200.
98. S. Cermak and T. Isbell, *J. Am. Oil Chem. Soc.*, 2000, **77**, 243-248.
99. H. Mutlu and M. A. R. Meier, *J. Polym. Sci. Part A: Polym. Chem.*, 2010, **48**, 5899-5906.
100. A. Chernykh, S. Alam, A. Jayasooriya, J. Bahr and B. J. Chisholm, *Green Chem.*, 2013.
101. R. Hoogenboom, *Eur. J. Lipid Sci. Technol.*, 2011, **113**, 59-71.
102. G. Çayli and M. A. R. Meier, *Eur. J. Lipid Sci. Technol.*, 2008, **110**, 853-859.
103. S. K. Joshi and P. C. Chatterjee, *J. Am. Oil Chem. Soc.*, 1978, **55**, 607-609.
104. S. Khalkar, D. Bhowmick and A. Pratap, *J. Oleo Sci.*, 2013, **62**, 167-173.
105. T.-L. Choi and R. H. Grubbs, *Angew. Chem.*, 2003, **115**, 1785-1788.
106. S. A. Harrison and D. H. Wheeler, *J. Am. Chem. Soc.*, 1951, **73**, 839-842.
107. J. M. Rodriguez-Parada, M. Kaku and D. Y. Sogah, *Macromolecules*, 1994, **27**, 1571-1577.
108. A. Gress, A. Völkel and H. Schlaad, *Macromolecules*, 2007, **40**, 7928-7933.
109. G. Cai and M. H. Litt, *J. Polym. Sci. Part A: Polym. Chem.*, 1996, **34**, 2689-2699.
110. L. M. de Espinosa, K. Kempe, U. S. Schubert, R. Hoogenboom and M. A. R. Meier, *Macromol. Rapid Commun.*, 2012, **33**, 2023-2028.
111. L. Hinkamp, H. J. Schäfer, B. Wippich and H. Luftmann, *Liebigs Ann. Chem.*, 1992, **1992**, 559-563.
112. J. C. W. P. T. Anastas, *Green Chemistry: Theory and Practice*, Oxford University Press, 1998.
113. Y. Cao and X. Zhang, *Appl. Microbiol. Biotechnol.*, 2013, **97**, 3323-3331.
114. S. Arias, A. Sandoval, M. Arcos, L. M. Cañedo, B. Maestro, J. M. Sanz, G. Naharro and J. M. Luengo, *Microb. Biotechnol.*, 2008, **1**, 170-176.
115. Á. Sandoval, E. Arias-Barrau, F. Bermejo, L. Cañedo, G. Naharro, E. Olivera and J. Luengo, *Appl. Microbiol. Biotechnol.*, 2005, **67**, 97-105.
116. W. Lu, J. E. Ness, W. Xie, X. Zhang, J. Minshull and R. A. Gross, *J. Am. Chem. Soc.*, 2010, **132**, 15451-15455.
117. C. Liu, F. Liu, J. Cai, W. Xie, T. E. Long, S. R. Turner, A. Lyons and R. A. Gross, *Biomacromolecules*, 2011, **12**, 3291-3298.
118. L. Chen, L. Fei, C. Jiali, X. Wenchun, E. L. Timothy, S. R. Turner, L. Alan and A. G. Richard, in *Biobased Monomers, Polymers, and Materials*, American Chemical Society, 2012, vol. 1105, ch. 9, pp. 131-150.
119. A. Celli, P. Marchese, S. Sullalti, J. Cai and R. A. Gross, *Polymer*, 2013, **54**, 3774-3783.
120. I. N. A. Van Bogaert, J. Zhang and W. Soetaert, *Proc. Biochem.*, 2011, **46**, 821-833.

121. I. A. Van Bogaert, K. Saerens, C. De Muynck, D. Develter, W. Soetaert and E. Vandamme, *Appl. Microbiol. Biotechnol.*, 2007, **76**, 23-34.
122. H. Isoda, D. Kitamoto, H. Shinmoto, M. Matsumura and T. Nakahara, *Biosci. Biotechnol. Biochem.*, 1997, **61**, 609-614.
123. S. Singh, P. Patel, S. Jaiswal, A. A. Prabhune, C. V. Ramana and B. L. V. Prasad, *New J. Chem.*, 2009, **33**, 646-652.
124. A. Azim, V. Shah, G. F. Doncel, N. Peterson, W. Gao and R. Gross, *Bioconjugate Chem.*, 2006, **17**, 1523-1529.
125. W. Gao, R. Hagver, V. Shah, W. Xie, R. A. Gross, M. F. Ilker, C. Bell, K. A. Burke and E. B. Coughlin, *Macromolecules*, 2006, **40**, 145-147.
126. Y. Peng, J. Decatur, M. A. R. Meier and R. A. Gross, *Macromolecules*, 2013, **46**, 3293-3300.
127. M. A. R. Meier, J. O. Metzger and U. S. Schubert, *Chem. Soc. Rev.*, 2007, **36**, 1788-1802.
128. J. Choi, A. H. R. MacArthur, M. Brookhart and A. S. Goldman, *Chem. Rev.*, 2011, **111**, 1761-1779.
129. M. C. Haibach, S. Kundu, M. Brookhart and A. S. Goldman, *Acc. Chem. Res.*, 2012, **45**, 947-958.
130. R. R. Briese and S. M. McElvain, *J. Am. Chem. Soc.*, 1933, **55**, 1697-1700.
131. P. Tundo and M. Selva, *Acc. Chem. Res.*, 2002, **35**, 706-716.
132. J.-C. Choi, L.-N. He, H. Yasuda and T. Sakakura, *Green Chem.*, 2002, **4**, 230-234.
133. H. E. Zaugg, D. A. Dunnigan, R. J. Michaels, L. R. Swett, T. S. Wang, A. H. Sommers and R. W. DeNet, *J. Am. Chem. Soc.*, 1961, **26**, 644-651.
134. D. Banti and J. C. Mol, *J. Organomet. Chem.*, 2004, **689**, 3113-3116.
135. M. B. Dinger and J. C. Mol, *Organometallics*, 2003, **22**, 1089-1095.
136. M. Passerini and L. Simone, *Gazz. Chim. Ital.*, 1921, **51**, 126-129.
137. L. Banfi and R. Riva, in *Organic Reactions*, John Wiley & Sons, Inc., 2004.
138. O. Kreye, T. Tóth and M. A. R. Meier, *J. Am. Chem. Soc.*, 2011, **133**, 1790-1792.
139. F. Bellina and R. Rossi, *Chem. Rev.*, 2009, **110**, 1082-1146.
140. T. Hama and J. F. Hartwig, *Org. Lett.*, 2008, **10**, 1545-1548.
141. T. Hama and J. F. Hartwig, *Org. Lett.*, 2008, **10**, 1549-1552.
142. T. Hama, X. Liu, D. A. Culkin and J. F. Hartwig, *J. Am. Chem. Soc.*, 2003, **125**, 11176-11177.
143. D. A. Culkin and J. F. Hartwig, *Acc. Chem. Res.*, 2003, **36**, 234-245.
144. W. A. Moradi and S. L. Buchwald, *J. Am. Chem. Soc.*, 2001, **123**, 7996-8002.
145. M. Jørgensen, S. Lee, X. Liu, J. P. Wolkowski and J. F. Hartwig, *J. Am. Chem. Soc.*, 2002, **124**, 12557-12565.
146. N. Kolb and M. A. R. Meier, *Green Chem.*, 2012, **14**, 2429-2435.
147. J. Trzaskowski, D. Quinzler, C. Bährle and S. Mecking, *Macromol. Rapid Commun.*, 2011, **32**, 1352-1356.
148. C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, **0**, 1020-1024.
149. I. Göttker-Schnetmann, P. S. White and M. Brookhart, *Organometallics*, 2004, **23**, 1766-1776.
150. I. Göttker-Schnetmann, P. White and M. Brookhart, *J. Am. Chem. Soc.*, 2004, **126**, 1804-1811.
151. B. Punji, T. J. Emge and A. S. Goldman, *Organometallics*, 2010, **29**, 2702-2709.

152. D. W. Lee, W. C. Kaska and C. M. Jensen, *Organometallics*, 1998, **17**, 1-3.
153. F. Liu, E. B. Pak, B. Singh, C. M. Jensen and A. S. Goldman, *J. Am. Chem. Soc.*, 1999, **121**, 4086-4087.
154. D. Morales-Morales, Red, oacute, R. n, Z. Wang, D. W. Lee, C. Yung, K. Magnuson and C. M. Jensen, *Can. J. Chem.*, 2001, **79**, 823-829.
155. K. E. Allen, D. M. Heinekey, A. S. Goldman and K. I. Goldberg, *Organometallics*, 2013, **32**, 1579-1582.
156. P. Phukan, M. Bauer and M. E. Maier, *Synthesis*, 2003, **2003**, 1324-1328.
157. H.-J. Daniel, M. Reuss and C. Syldatk, *Biotechnol. Lett.*, 1998, **20**, 1153-1156.
158. H. Mutlu, Hofsa, R. E. Montenegro and M. A. R. Meier, *RSC Advances*, 2013, **3**, 4927-4934.
159. C. C. Musonda, D. Taylor, J. Lehman, J. Gut, P. J. Rosenthal and K. Chibale, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 3901-3905.
160. I. Ugi and S. Heck, *Comb. Chem. High Throughput Screening*, 2001, **4**, 1-34.
161. C.-Y. Tsai, W. K. C. Park, G. Weitz-Schmidt, B. Ernst and C.-H. Wong, *Bioorg. Med. Chem. Lett.*, 1998, **8**, 2333-2338.

7. Appendix

7.1. List of publications and conference contributions

Publications in peer-reviewed journals:

1. N. Kolb, M. A. R. Meier: Monomers and their polymers derived from saturated fatty acid methyl esters and dimethyl carbonate, *Green Chem.,* 2012, **14**, 2429-2435
2. N. Kolb, M. A. R. Meier: Grafting onto a renewable unsaturated polyester *via* thiol–ene chemistry and cross-metathesis, *Eur. Poly. J.,* 2013, **49**, 843-852
3. N. Kolb, R. Hofsäß, M. A. R. Meier: *α*-Arylation of saturated fatty acids, *Eur. J. Lipid Sci. Tech.,* 2013, **115***,* 729-734
4. N. Kolb, M. Winkler, C. Syldatk, M. A. R. Meier: Long-chain polyesters and polyamides from biochemically derived fatty acids, *Eur. Poly. J.*, submitted

Selected poster-presentations as conference contributions:

1. N. Kolb, M. A. R. Meier: Monomere aus nachwachsenden Rohstoffen: C-H Aktivierung gesättigter Fettsäuren, GDCH Wissenschaftsforum, September 4-7 2011, Bremen, Germany
2. N. Kolb, M. A. R. Meier: Monomers from renewable resources: C-H functionalization of saturated fatty acids, International Green Catalysis Symposium, March 7-9 2012, Rennes, France
3. N. Kolb, M. A. R. Meier: Monomers from renewable resources: C-H functionalization of saturated fatty acids, 5th Workshop on Fats and Oils as

Renewable Feedstock for the Chemical Industry, March 18-20 2012, Karlsruhe, Germany

4. N. Kolb, M. A. R. Meier: Malonate derivatives and their polymers prepared from fatty acid methyl esters and dimethyl carbonate, GDCH Fachtagung Nachhaltige Chemie, September 16-18 2012, Kaiserslautern, Germany
5. N. Kolb, M. A. R. Meier: Malonate derivatives and their polymers prepared from fatty acid methyl esters and dimethyl carbonate, Macro BeGe 2012, December 3-4 2012, Houffalize, Belgium
6. N. Kolb, M. A. R. Meier: *α*-arylation of saturated fatty acids, 6th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry, March 17-19 2013, Karlsruhe, Germany
7. N. Kolb, M. A. R. Meier: Malonate derivatives and their polymers prepared from fatty acid methyl esters and dimethyl carbonate, Sustainable Polymers, May 20-23 2013, Safety Harbor, Florida, USA

7.2. Curriculum vitae Nicolai Kolb

Personal data:

Name:	Nicolai Kolb
Date of birth:	January 20th 1987
Place of birth:	Berlin-Zehlendorf
Nationality:	German

Educational steps:

10/2010 – 10/2013 Karlsruher Institut für Technologie (KIT)

Expected degree: Ph. D. (Dr. rer. nat.)

Field of study: Organic Chemistry / Polymer Chemistry

Supervisor: Prof. Dr. Michael A. R. Meier

Topic of thesis: *Monomers from Renewable Resources: C-H Functionalization of Saturated Fatty Acids*

09/2009 – 08/2010 State University of New York in Stony Brook (SUNY)

Degree: Master of Science (M. Sc.) Grade: 1.5

Field of study: Chemistry / Molecular Biology

Supervisor: Prof. Dr. Eckard Wimmer

Topic of thesis: *Genetic analyses of the terminal protein (VPg) and of spacer II in the 5'-nontranslated region of poliovirus RNA*

10/2006 – 08/2009 Freie Universität Berlin

Degree: Bachelor of Science (B. Sc.) Grade: 2.1

Field of study: Chemistry

Supervisor: Prof. Dr. Beate Koksch

Topic of thesis: Kinetic studies on native ligation using α-helical coiled-coil forming peptides

08/1999 – 07/2006 Schadow-Gymnasium Berlin-Zehlendorf

Allgemeine Hochschulreife Grade: 2.6

08/1993 – 07/1999 Schweizerhof-Grundschule Berlin-Zehlendorf

Working experience:

01/2010 – 01/2010 Tutor

Tutor at the State University of New York

Lab course basic Organic Chemistry

10/2008 – 07/2009 Tutor

Tutor at the Freien Universität Berlin

Lab course Organic Chemistry for Veterinarians and Biologists

08/2008 – 09/2008 BASF SE Ludwigshafen

Internship during the Bachelors degree

Voluntary work:

10/2004 – 07/2006	Elected representative of the pupils of a school Schulsprecher am Schadow-Gymnasium Berlin
10/2004 – 07/2005	Participation in local educational political committees Management of the „*Landesschülerausschusses Berlin*“ Head of the „*Bezirksschülerausschuss Zehlendorf*“

Scholarships:

DAAD Travel grant

Conference „Sustainable Polymers“

Mai 20-23 2013 in Safety Harbor, Florida, USA

Ph.D. scholarship

Deutsche Bundesstiftung Umwelt (DBU)

Ph.D. stipend for 3 years

Scholarship for graduate program abroad

Schimmelpfennig-Lange-Stiftung

Partial scholarship for the Master’s program at the SUNY Stony Brook