Sustainable, efficient approaches to renewable platform chemicals and polymers

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

M.Sc. Hatice Mutlu

aus

Kircali, Bulgaria

Dekan: Prof. Dr. M. Bastmeyer
Referent: Prof. Dr. M. A. R. Meier
Korreferent: Prof. Dr. C. Barner-Kowollik
Tag der mündlichen Prüfung: 19.04.2012

Die vorliegende Arbeit wurde von Juli 2008 bis Februar 2012 unter Anleitung von Prof. Dr. Michael A. R. Meier an der Hochschule Emden/Leer (von Juli 2008 bis August 2009), der Universität Potsdam (von September 2009 bis Dezember 2011) und am Karlsruher Institut für Technologie (KIT, von January 2011 bis Februar 2012) - Universitätsbereich angefertigt.

Sevdiklerime…

Abstract

Environmental concerns, such as pollution and decreases in natural resources, have led to an increased demand for renewable materials in recent years. Adoption of efficient approaches, like metal-free organocatalysis, olefin metathesis and thiol-ene coupling, both in academic and industrial research, offers the potential of increased sustainability, comparatively lower production costs (besides olefin metathesis), and more environmentally benign processes. Thus, the following work is performed with the attempt to meet both, making use of oils as renewable feedstock, in this case mainly plant oil derived platform chemicals, and using sustainable, efficient approaches as valuable synthetic tools.

Kurzzusammenfassung

Ökologische Bedenken, wie Umweltverschmutzung und der Rückgang der natürlichen Ressourcen, haben in den letzten Jahren zu einer gestiegenen Nachfrage nach nachwachsenden Rohstoffen geführt. Die Anwendung effizienter synthetischer Methoden, wie etwa metallfreie Organokatalyse, Olefinmetathese und Thiol-En-Kupplung, sowohl in akademischer als auch industrieller Forschung, haben das Potenzial zu mehr Nachhaltigkeit, vergleichsweisen niedrigeren Produktionskosten und umweltfreundlicheren Prozessen beizutragen. Aus diesem Grund hat die vorliegende Arbeit als Ziel sowohl die Nutzung nachwachsender Rohstoffe, in diesem Fall vor allem von Pflanzenöl und davon abgeleiteten Plattform Chemikalien, als auch der Anwendung nachhaltiger und effizienter Methoden als wertvolle synthetische Werkzeuge zu veranschaulichen.

Content

1 Introduction

Oil, the history of which dates over five thousand years ago, when oil seeping up through the ground was used in waterproofing boats, paints, lighting and even for medication;[1] is a wide ranging term that includes many substances and forms of liquids. On the other hand, the modern crude oil history is known since the 19th century, with the discovery and the subsequent commercialization. Furthermore, since World War II, chemistry has become dependent on crude oil, especially naphta, which is a side stream of the production of fuels from crude oil. Thus, along being the dominant source of energy, crude oil is a vital source of a wide range of raw materials required for manufacturing the ubiquitous plastics and other products that are involved in every level of life in our modern society. However, the tremendous growth of the petrochemical industry in the 20th century slowed down with the re-gained importance of bio-based products. Moreover, not only the challenge of a globalized economy and the awareness of the depletion of fossil resources, but also the desire to reduce the global warming due to the carbon dioxide emissions has directed the attention of researchers to the use of biomass as a source of energy and raw material for value-added commodity and speciality products. Thus, "sustainable (green) chemistry" rose as an innovative, multi-disciplinary field to cover the research about developing environmentally benign and crude oil-independent methods.[2] In parallel, by introducing “The 12 principles of Green Chemistry”,[3] Anastas and Warner made incredible impact to the Brundtland-report,[2] thus emphasizing that a sustainable development has to be addressed in a technological, social and economical context (Figure 1.1) and particularly revealed the basic twelve rules that chemists and others should apply in the design of new methods or in improving existing methods to decrease their impact on the environment and on human health.

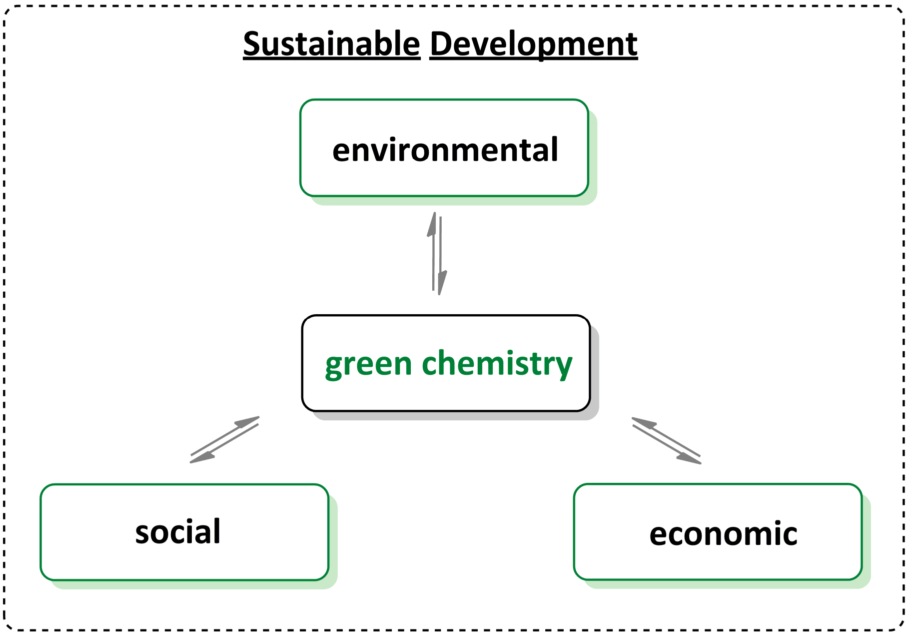


Figure 1.1: The complete integration of green chemistry within sustainable development.

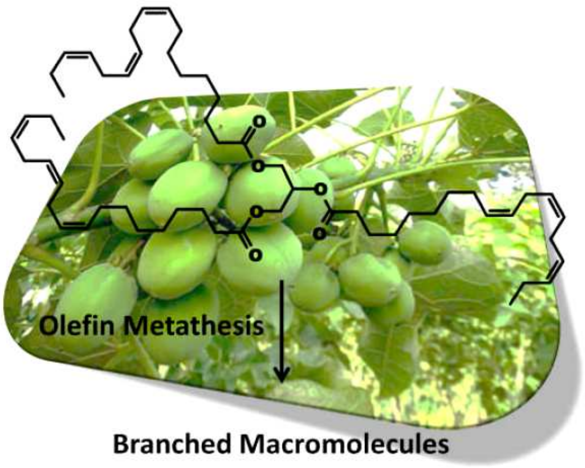
To achieve the goal of sustainable development and thus to improve the greenness of a method, the following major objectives can be pointed out from these twelve principles:

- Maximize waste and energy saving
- Use renewable feedstocks in a sustainable fashion as often as possible
- Minimize of used toxic reactants and solvents
- Use catalytic (and other efficient) chemical reactions

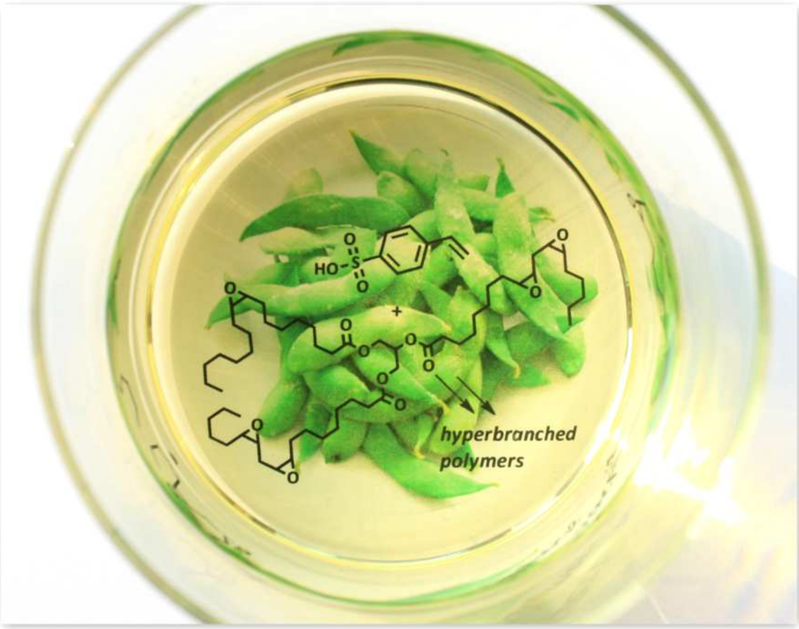
Nowadays, these principles are aiming to motivate chemistry at all levels: industry, basic research, education and public perception, thus encompassing several fields of activity. Key areas for application of these principles are: renewables, catalysis, polymers, solvents, analytical methods and new synthetic pathways.

Following the emergence of developing and modifying sustainable methods and taking into account the structural diversity of plant oils and thereof derived platform chemicals, the present thesis describes new ways for value creation from plant oils within different synthetic approaches. Among them, the synthesis of polymers is an active and important research field with the objective of minimizing the strong dependence of the polymer industry on fossil-derived raw materials. On the one hand, the direct utilization of plant oil triglycerides for polymer synthesis was investigated:

- Regarding the direct use of plant oils, it has been shown that *plukenetia conophora* oil can be used for the synthesis of hyperbranched polyesters, with interesting rheological properties, *via* olefin metathesis (acyclic triene metathesis, ATMET) polymerization.

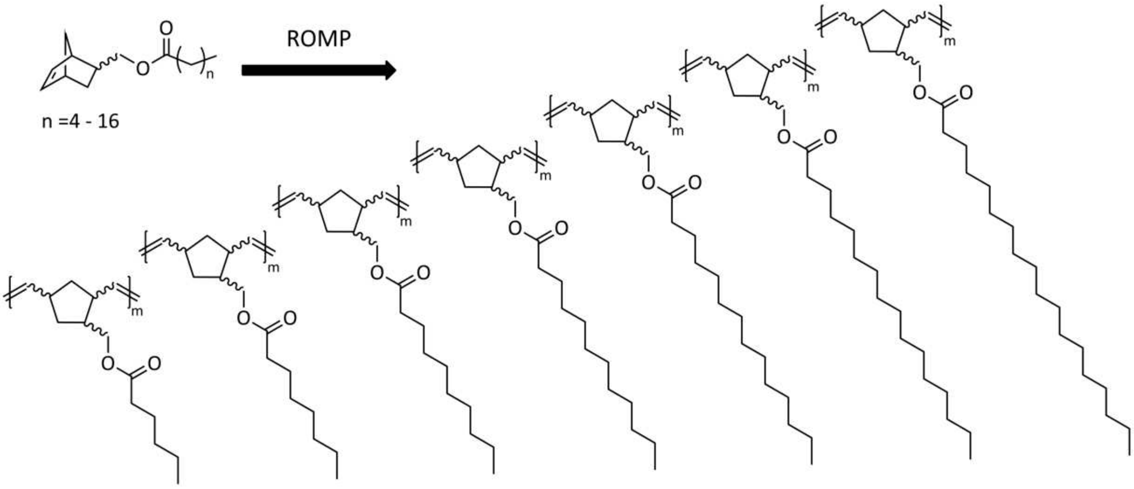


- In a different approach, the introduction of styrene moieties into the structure of sunflower oil has been used to obtain a multifunctional monomer for the synthesis of hyperbranched polymers also *via* ATMET.

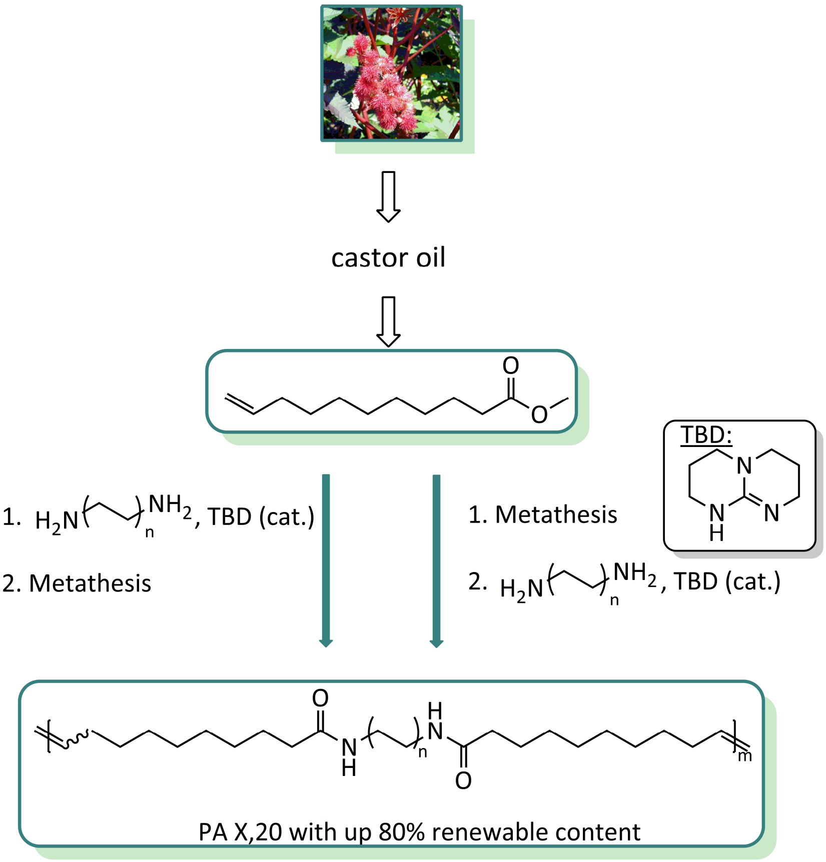


On the other hand, plant oil derived platform chemicals such as fatty acids, esters and alcohols were shown to be versatile building blocks for the synthesis of polymers:

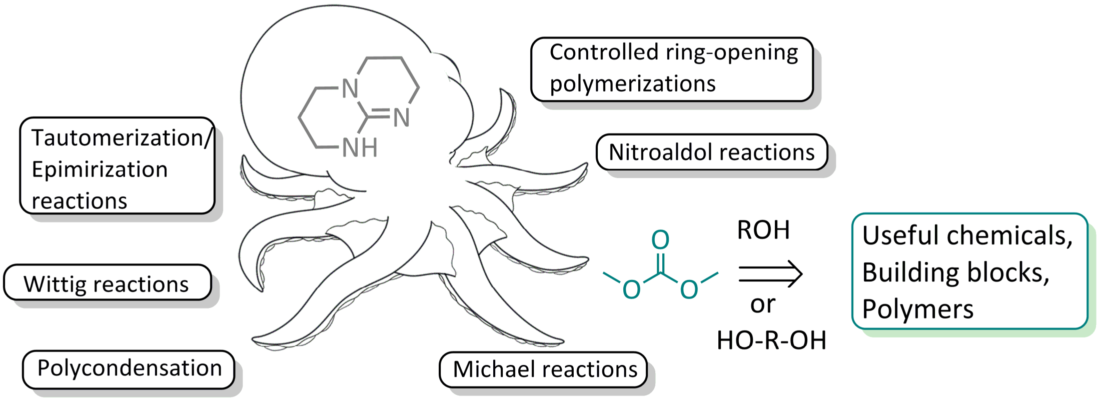
- Different monomers for ring-opening metathesis polymerization (ROMP) have been prepared and polymerized by functionalization of a hydroxyl containing norbornene with different fatty acids.



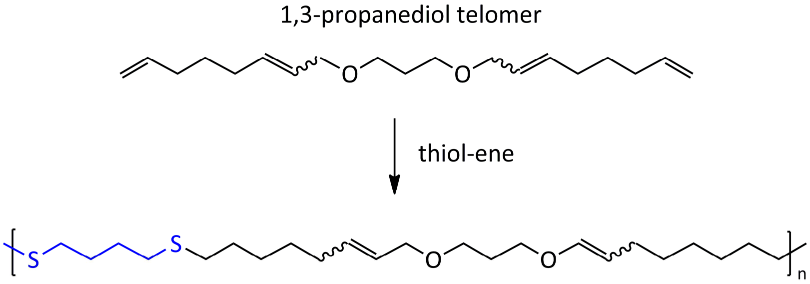
- The synthesis of fatty acid-based polyamides has been studied following two different approaches: acyclic diene metathesis (ADMET) polymerization of amide-based dienes, and TBD-catalyzed polycondensation of fatty diester and diamines.



- TBD has been efficiently applied as catalyst for the synthesis of carbonate and carbamate-based building blocks as well as renewable polycarbonates from castor oil derivative, (*E*) icos-10-ene-1,20-diol, and dimethyl carbonate. In addition, for the first time, ADMET polymerization has been successfully applied for the polycarbonate synthesis of terpene-based monomers containing trisubstituted terminal-olefins.



- The applicability of 1,3-propanediol-based telomers, in particular α,ω–diene ones, has been extended for the first time to the synthesis of polymers following two different approaches: ADMET polymerization and thiol-ene polyaddition.



2 Bio-based resources and their efficient utilization: Plant oils as alternative to crude oil

A current challenge of the chemical industry is to design sustainable processes. From that point of view, agricultural and forestal raw materials, such as plant oils, starch, sugar, cellulose, fibers, and other agricultural resources are obvious candidates for a sustainable chemical production with regard to the advantage of a low-carbon economy. It is noteworthy that some of these feedstocks have already been used for centuries. Until the beginning of the 20th century, all materials, fuels and chemicals, such as dyes, fibers, medicine, clothes and organic solvents were made from bio-based resources.[4] On the other hand, renewable raw materials might be a limited resource. However, in contrast to fossil resources that have required millions of years for their formation, renewable raw materials can be produced every year (such as oils from oilseed crops) or within a few years (e.g. in the case of forestation), thus not endangering the management and utilisation of natural renewable resources and providing a continuous supply for required raw materials. Table 2.1 gives an overview of industries and material uses of some of the most commonly used renewable raw materials (in alphabetical order).[5]

Table 2.1: Commonly used renewable materials (in alphabetical order) and respectively the industries involved and fields of application.[5]

Raw material	Resources	Types of industry	Applications
Natural fibers	Europe: Hemp, flax, nettle, cotton Imported: cotton, kenaf, jute, sisal, ramie	Textile industry, pulp and paper industry, plastic industry	Textiles, technical textile, nonwovens (e.g. insulating materials), fiber reinforced plastics, paper
Plant oils	Europe: rape, sunflower, olive; Imported: soybean, palm oil	Chemical industry, pharmaceutical industry, technical industry, plastics industry	Lubricants, surfactants, binders, paint additives, polymers, polymer additives, linoleum, glycerol
Sugar	Europe: Sugar beet. Imported: sugar cane	Chemical industry (fermentation), pharmaceutical industry, plastic industry	Bulk chemicals, fine chemicals, polymers, pharmaceuticals, bioethanol
Starch	Wheat, potato, maize, other cereals	Pulp and paper industry, chemical industry (fermentation), pharmaceutical industry, plastic industry	Paper starch, glues, binders, chemicals, cosmetics, textile starch, bioethanol, polymers
Wood	Europe: Soft wood, hard wood. Imported: tropical hard wood	Pulp and paper industry, timber industry, plastic industry	Construction wood, packaging furniture, paper, cellulose

A comprehensive industrial survey revealed that the total use of renewable raw materials (without wood) in Europe was about 9 million tonnes in the last years.[5] While other industries processed 2.65 million tons, the chemical industry used 6.4 million tonnes of renewables: divided into oils and fats (31%), starch (35%), sugar (14%), natural cellulose fibres (16%) and other (4%) (Figure 2.1).

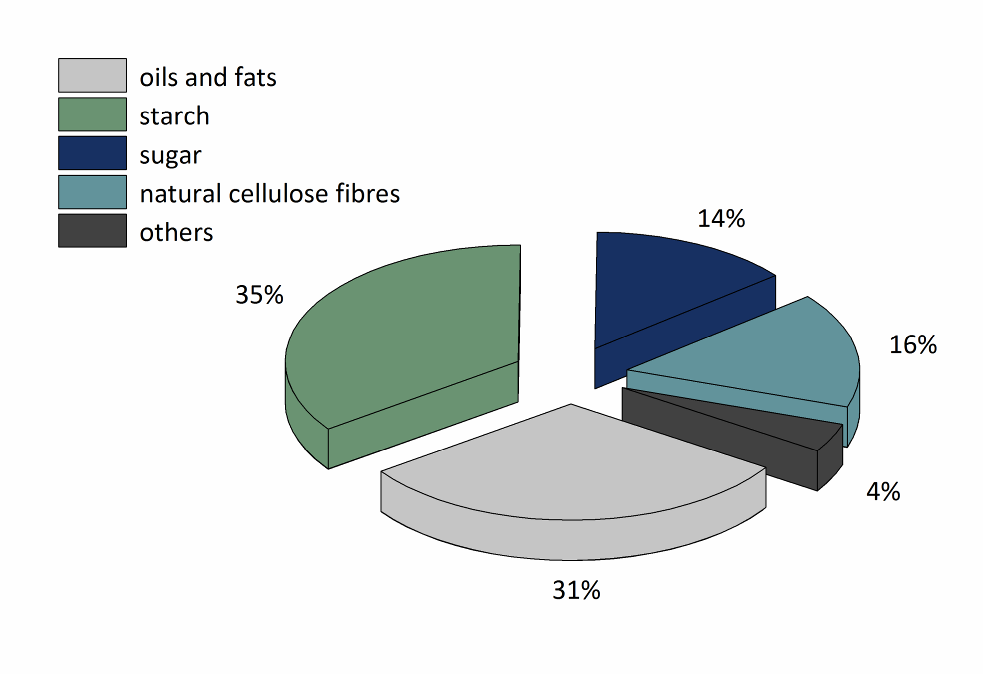


Figure 2.1: Renewable raw materials distribution in the chemical industry.[5]

One can consider that new challenges would require new tools to tackle them. However, as a matter of fact, raw material familiarity is an important component in the shift of the industry from non-renewables to renewables. The technology and equipment present in the chemical industry can be adapted to use the derived building blocks from the non-fossil-based sources. Especially, the fatty acid structure undoubtedly contributes to the greater relative amounts of renewable raw materials consumed by the chemical industry. Fatty acids and derivatives, in contrast to the highly oxygenated structure of carbohydrates, represent a class of hydrocarbons and are more closely related to petrochemicals, and thus well suited for many transformations already applied by the chemical industry. Fatty acids are primarily obtained from natural oils and fats. Evidently, an enormous amount of plant-based fats and oils are produced annually. The annual global production of the major plant oils in 2010/11 amounted 147 million tons.[6] The main component of plant oil is triglyceride

(98%), beside for some oils like cashew nutshell oil. Depending on the oils source used (Table 2.2), the fat splitting process can lead to a wide variety of fatty acids (saturated or unsaturated fatty acids shown in Figure 2.2 and Table 2.3), each possessing different types of functional groups (-OH, epoxides, triple bonds and etc.). On the other hand, the content of the different fatty acids in the plant oils can be modified by breeding or genetic modification of crops.[7]

Table 2.2: The broad range of oil sources that could conceivably be used to supply the oleochemical industry.

Animal fats	Butter, edible tallow, inedible tallow and grease, Lard
Edible plant oils	Canola, Corn, Cotonseed, Olive, Peanut, Safflower, Sesame, Soybean, Sunflower
Industrial oils	Castor, Linseed, Oiticica, Rapeseed, Tall, Tung
Marine oils	Fish, Menhaden, Sperm
Palm oils	Babassu, Coconut, Palm

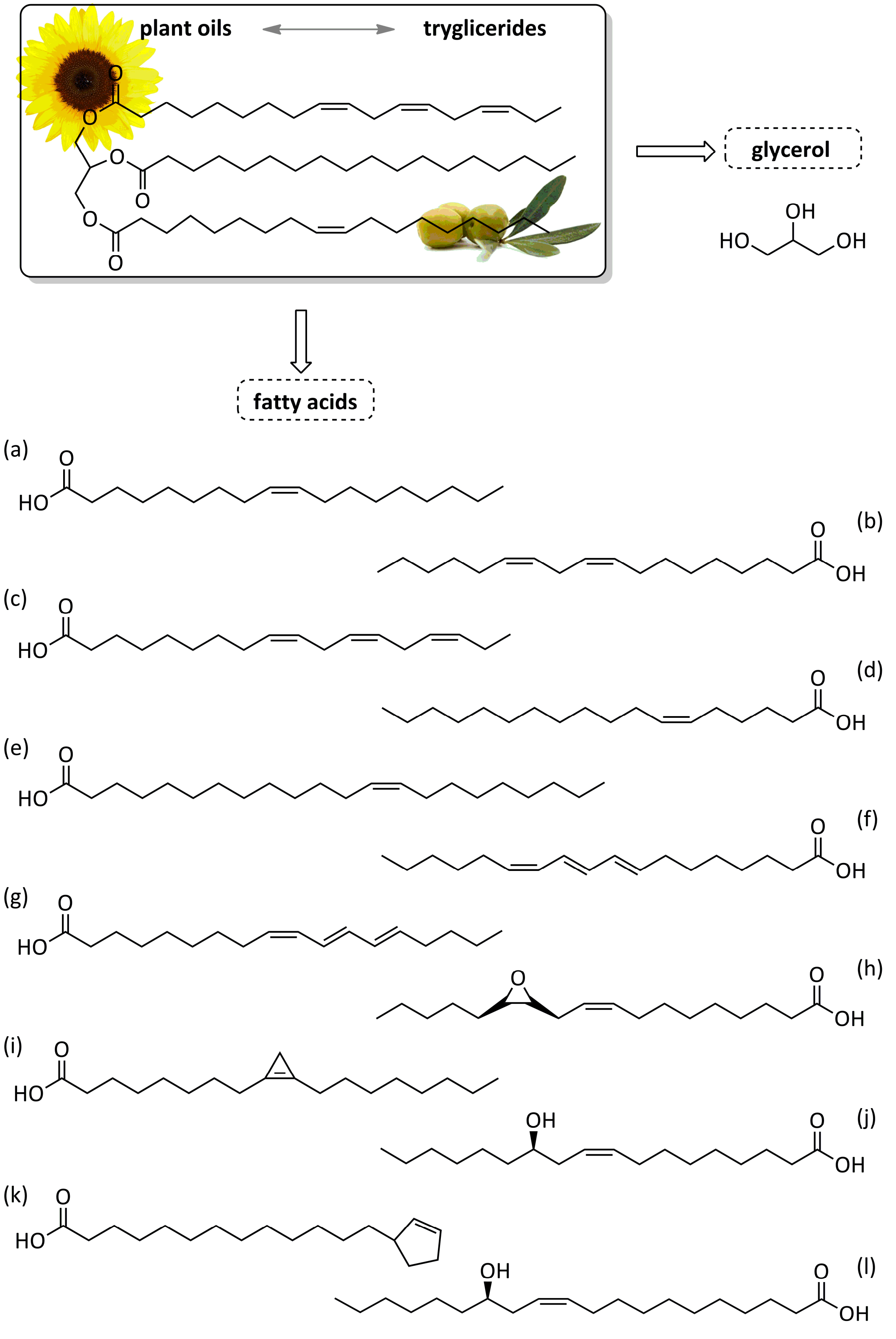


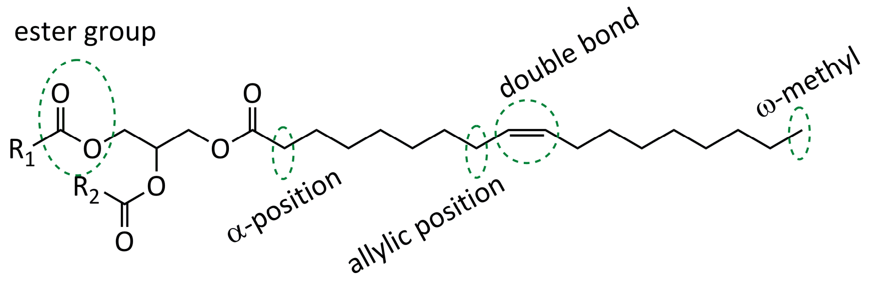
Figure 2.2: Structures of some usual and unusual fatty acids derived from different plant oils: (a) oleic acid, (b) linoleic, (c) linolenic, (d) petroselinic, (e) erucic, (f) calendic, (g) α-eleostearic, (h) vernolic, (i) sterculic, (j) ricinoleic, (k) chaulmoogric and (l) lesquerolic.

Table 2.3: Fatty acid content of the major commodity oils (wt%). **C**: number of carbon atoms. **DB**: number of double bonds.

Fatty acid	**C:DB**	**Castor**[a)]	**Corn**	**Cotton seed**	**Linseed**	**Olive**	**Palm**	**Soybean**	**Sunflower**	**High oleic**
Palmitic	16:0	0.9	10.9	21.6	5.5	13.7	44.4	11.0	6.1	6.4
Stearic	18:0	0.8	2.0	2.6	3.5	2.5	4.1	4.0	3.9	3.1
Oleic	18:1	2.9	25.4	18.6	19.1	71.1	39.3	23.4	42.6	82.6
Linoleic	18:2	4.5	59.6	54.4	15.3	10.0	10.0	53.2	46.4	2.3
Linolenic	18:3	0.6	1.2	0.7	56.6	0.6	0.4	7.8	1.0	3.7
DB/Triglyceride		-	4.5	3.9	6.6	2.8	1.8	4.6	-	3.0

a) castor oil contains ricinoleic acid in the range of 87.7-90.4%.

Due to the aforementioned different functional groups on the fatty acids, which can be used to introduce new functionality and then further be modified, there is a wealth of possible fine chemicals, monomers, and polymers that can be produced from plant oils.[8] Typically, five chemically reactive sites can be identified on a fatty acid for further modification (Figure 2.3, R_1 and R_2 chains correspond to fatty alkyl chains). The possible chemical transformations depending on the reacting functional group are listed in Figure 2.3.



ester group

- hydrolysis
- transesterification
- alcoholysis
- saponification
- reduction
- amidation
- halogenation

double bond

- epoxidation
- hydrogenation
- oxidation (vicinyl-dihydroxylation)
- ozonolysis
- addition reactions
- Friedel-Crafts alkylation
- sulfonation
- metathesis
- isomerization
- pericyclic reactions
- carbonylation
- auto-oxidation
- thiol-ene coupling
- photo peroxidation

α-position

- α-sulfonation
- α-halogenation
- acylation
- alkylation
- Claisen condensation
- dimerization

allylic position

- allyl-halogenation
- allyl-hydroperoxidation
- allyl-hydroxylation
- electrochemical acetylation

ω-position

- ω-oxidation

Figure 2.3: Illustration of a generic triglyceride with its reactive sites and the consequent possible transformations of each chemically active point.

However, the state of the art in chemical modification of plant oils focuses almost entirely on simple, cumulative changes at the acyl group of the fatty acid. Indeed, a literature[8,9] survey clearly indicated that, regarding the industrial uses of oils and fatty acids, most of the classical and well-established transformations are directed to the carboxyl and ester groups, and relatively little are carried at the side chain. With the implementation of these conventional reactions at the carboxy group, fatty acids are mainly transformed to fatty alcohols,[10] soaps,[11] esters,[12] thioesters,[13] hydrazides,[14] amides[15] or amines.[16] While this is generally not a new approach regarding the reactivity of the ester group, there have been several useful new developments. For instance, recently an outstanding dimeric complex of Ru and Os was reported as homogeneous efficient catalyst for the hydrogenation of triglycerides, thus allowing the synthesis of unsaturated fatty alcohols directly from olive oil in almost quantitative yields (Figure 2.4).[17]

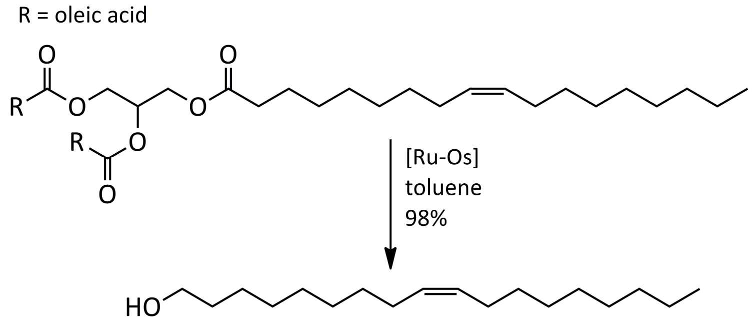


Figure 2.4: Direct synthesis of fatty alcohols from triglycerides under neutral conditions using a novel complex of Ru and Os as a catalyst.[17]

In the last two decades, extensive research, both in academic and industry has been performed regarding the selective functionalization of the alkyl chain of fatty compounds, and great attention was given especially to the C=C double bond. Remarkably, only very few reactions utilizing the double bond of unsaturated fatty compounds are currently applied in the chemical industry: hydrogenation, ozone cleavage, or epoxidation being the most prominent examples.

The epoxidation of unsaturated fatty acids and triglycerides with the so called Prilezhaef reaction[18] generates products with increased polarity and reactivity. In a typical epoxidation reaction, the olefinic double bonds of the unsaturated fatty acids are oxidized by a short chain percarboxylic acid to epoxides. The epoxidation reaction can be promoted either by enzymatic[19] or usual organic catalysts either in homogeneous or heterogeneous fashion.[20] The conversion of various triglycerides and fatty acids to epoxides actually dates to 1940s.[21] It is worth mentioning that nowadays epoxidized soybean oil (ESO) and different products based on epoxidized derivatives of fats and oils are already commercially available. For example, currently, fatty acid epoxides are predominantly employed as PVC-plasticizers and stabilizers due to their ability to scavenge free HCl thus slowing down PVC degradation. Moreover, vernonia oil, a naturally occuring epoxidized vegetable oil, was used as a renewable raw material for the synthesis of novel symmetric and asymmetric bolaamphiphilic compounds with potential application in drug delivery.[22] Beyond this, the epoxide rings can undergo electrophilic or nucleophilic ring-opening reactions to generate other chemical functions such as alcohol,[23] azide,[24] and carbonate[25] (some representative reactions are shown in Figure 2.5). Hence, they represent valuable raw materials for the production of various polyurethanes.[26] Although the synthesis of soybean oil-based carbonate (CSO) required 70 h,[25a,27] it was employed as a synthetic building block for the synthesis of isocyanate-free polyurethanes as well as polyesters which showed better bio-degradation behavior than other polyurethane systems. Since CSO has the potential to replace petroleum in the synthesis of biodegradable polymers, its synthesis has been recently improved. Erhan *et al*. uitilized supercritical CO_2 as a solvent, thus enabling the synthesis of the material in ~ 1/3 of the reaction time reported in the literature.[27d]

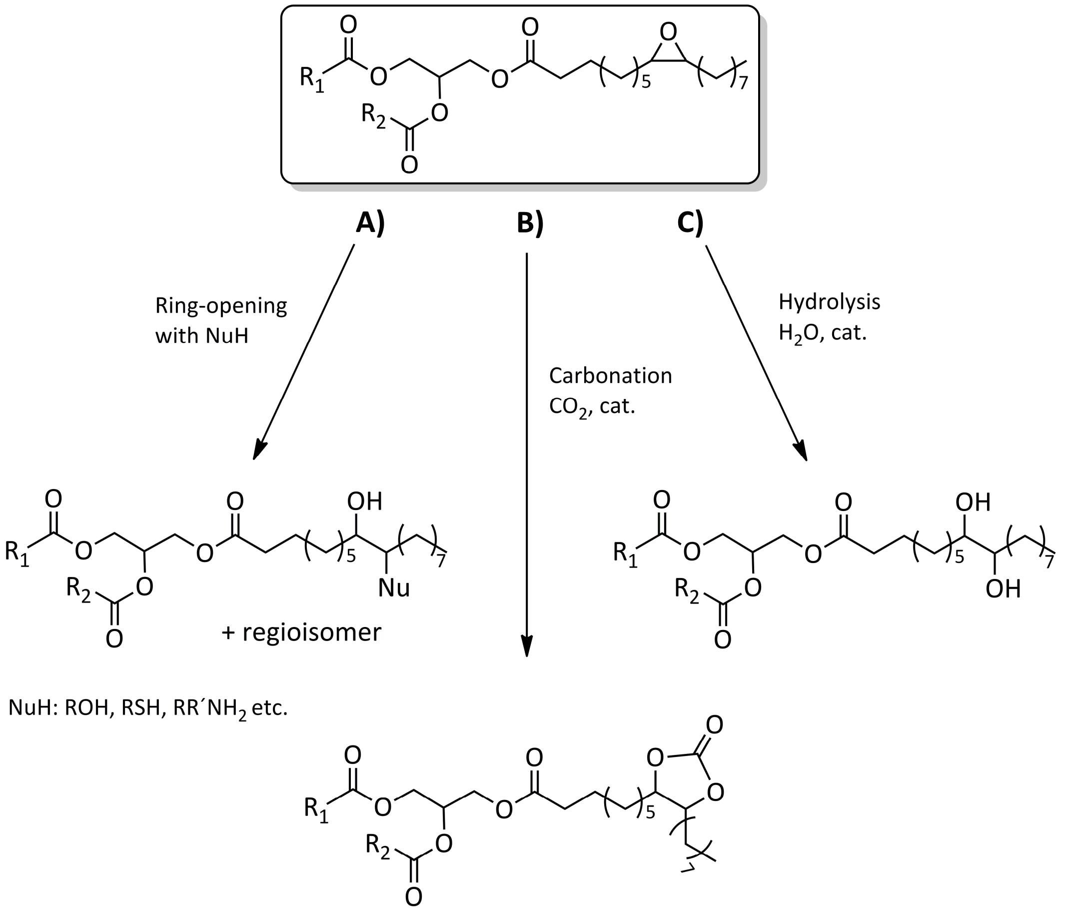


Figure 2.5: Summary of some common functionalizations on epoxidized vegetable oils: **A)** epoxide ring-opening reactions in the presence of different nucleophiles: **B)** direct carbonation of epoxidized oil in the presence of CO_2 and a suitable catalyst; **C)** hydrolysis of epoxidized oil generating hydroxylated vegetable oil.

Radical, electrophilic, nucleophilic, as well as pericyclic additions to the C=C double bond of a readily accessible unsaturated fatty acid led to a large number of novel oleochemicals with interesting characteristics (Figure 2.6).[8f,28] For instance, formaldehyde addition in an ene reaction onto unsaturated fatty acids in the presence of stoichiometric amounts of dimethylaluminium chloride (Me_2AlCl) [or ethylaluminium dichloride ($EtAlCl_2$)] generates a hydroxyl-carboxylic acid which, in turn is of interest as polyester component (Pathway **C** in Figure 2.6)

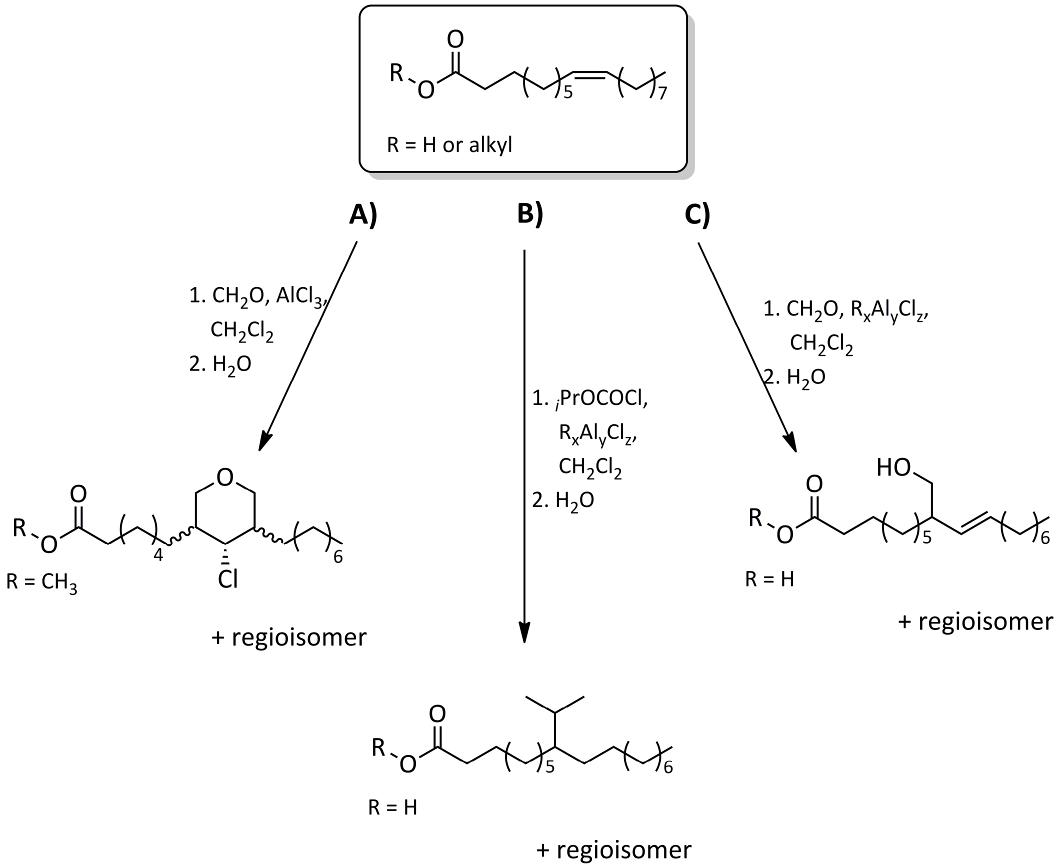


Figure 2.6: Some representative Lewis acid induced electrophilic addition reactions to the double bonds to afford: **A)** 4-chlorotetrahydropyrans; **B)** alkylated products (in this case: 9- and 10-isopropyloctadecanoic acid); **C)** *β,γ* -unsaturated oxocarboxylic acid.

Another interesting and complex reaction of multiple C=C double bonds is the dimerization reaction.[29] Different homogeneous and heterogeneous catalysts can be employed at relatively high reaction temperatures to yield a fatty acid dimer which can be further reduced into fatty diol dimers. Such materials are valuable monomers for specialty polymers, for instance to reduce the brittleness of polymers or introduce a higher hydrophobicity to materials.

Naturally occuring fatty acids generally have the *cis* configuration and interest has been nowadays growing regarding the potential impact of *trans* fatty acids upon health. Thus, the *cis*-*trans* isomerization of double bonds is employed to convert the less thermodynamically stable *cis*-isomer into the more stable *trans*-isomer.[30] Thyil radicals, produced from the homolysis of mercaptanes or sulfides, are suitable for this reaction. The well-known example of this of type transformation is the *cis-trans* isomerization of oleic acid (*cis*-9-octedecenoic acid) to ~ 80% *trans*-9-octadecenoic acid at 30 °C in the presence of active radicals generated from β-mercaptopropionic acid or diphenyl sulfide activated by UV light.[31] On the other hand, in order to generate a conjugated arrangement of isolated, multiple C=C double bonds, alkaline hydroxides in alcoholic solution, nickel/activated coal and iron pentacarbonyl [$Fe(CO)_5$] are examples of suitable catalysts.[32]

By combining double-bond migration with an irreversible reaction step that selectively removes certain double-bond isomers from the equilibrium, new synthetic transformations for fatty acid derivatives can be accomplished (Figure 2.7).[33] In this way, mixtures of double-bond isomers are selectively converted into valuable, terminally functionalized products. Hence, diverse functional groups can be introduced selectively at the terminal position of the alkyl chain, taking advantage of both the lower electron density and lower steric hindrance of terminal olefins relative to all other isomers [Figure 2.7, A)]. For example, [$Ir(COE)_2Cl]_2$/dppe as a catalysts promoted both the isomerization of the double bond from the 9,10-position of methyl oleate to the terminal position and the subsequent selective hydroboration of this isomer gave, in 45% yield, a product with terminal (C18 position) boronate ester group.[33a] Moreover, the resulting linear boronate of methyl oleate can be further converted into high-value-added chemicals, such as alcohol, amine, aldehyde, and alkyl halide. Along this, recently, the synthesis of 18-formyl stearic acid methyl ester, α,ω-bifunctional product containing both ester and aldehyde groups, was reported from unsaturated fatty acid methyl esters under hydroformylation conditions by using a rhodium catalyst bearing a sterically demanding phosphite ligand. Cole-Hamilton and colleagues were able to demonstrate the synthesis of dialkyl dicarboxylates by isomerising alkoxycarbonylation in the presence of a palladium-based catalyst system.[33b]

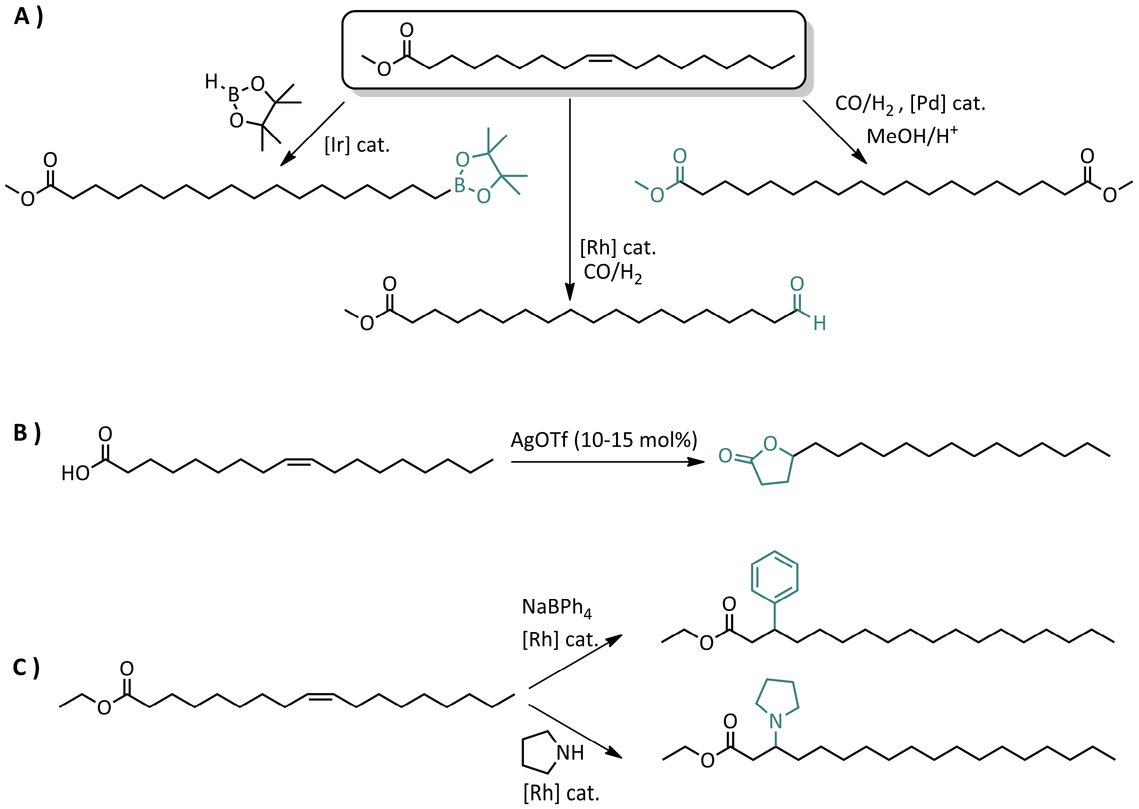
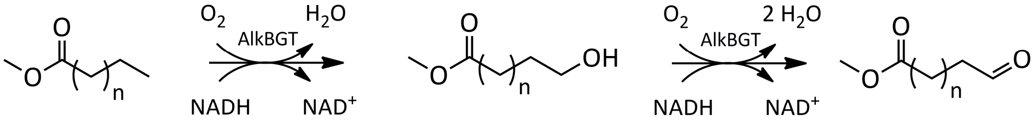


Figure 2.7: Examples of transition metal catalyzed double bond isomerizing tandem reaction in oleic acid derivatives: **A)** selective ω-functionalization of methyl oleate to yield ω-boronate, ω-aldehyde and dialkyl dicarboxylate derivatives, respectively; **B)** direct synthesis of long-chain γ-lactones from oleic acid; **C)** transformation of ethyl oleate to β-substituted esters.

On the other hand, a silver(I)-based catalytic system was employed in a one-step isomerization-γ-lactonization tandem process, which allowed the direct conversion of unsaturated fatty acids into the corresponding γ-lactones in good yields [in Figure 2.7, B)].[34] In addition, the successful combination of isomerization and conjugate addition of aryl and nitrogen nucleophiles in the presence of a rhodium/phosphite system yielded valuable β-functionalized compounds.[35] It was observed that the initial position of the double bond was not of relevance for the efficiency of the transformation. Although, as the number of possible double-bond isomers increased with growing chain length, even ethyl oleate, with a rather low concentration of the required α,β-unsaturated isomer in the equilibrium mixture, was selectively converted to the desired product.

In the context of double bond transformation, olefin metathesis and thiol-ene additions are considered as alternative and efficient processes, which contribute not only to a more feasible synthesis of plant oil-based polymers, but also to broaden the application possibilities of plant oils. Accordingly, these two reactions will be described separately in Chapter 3 since olefin metathesis and thiol-ene chemistry are employed as important synthetic methods and as polymerization techniques in this thesis.

The ω-functionalization at the alkyl or alkenyl chains in fatty acids and derivatives could be highly desirable and of general economic interest, as they would lead to oleochemicals with new properties or serve as building blocks for polymer synthesis. However, the unreactive character of the sp^3 C-H bonds makes the alkyl chain of fatty acid methyl esters barely accessible for almost any selective functionalization by chemical means. For example, the ω-CH_3 has the highest dissociation energy for the C-H bond, however, it exhibits the lowest steric hindrance for chemical reactions. Hence, multi-step processes including dehydrogenation, separation, and finally oxyfunctionalization are necessary to obtain the desired oxygenates.[36] As an alternative, biocatalysts can be applied for the direct and selective oxyfunctionalization of inert C-H bonds.[37] Accordingly, in recent work, a biocatalytic procedure was shown to be efficient for the selective functionalization of the ω-position of fatty acid methyl esters with medium length alkyl chains specifically (Figure 2.8).[38]



AlkBGT = alkane monooxygenase gene

Figure 2.8: General scheme of the ω–oxyfunctionalization of fatty acid methyl ester using a biocatalyst containing alkane monooxygenase genes.[38]

In theory, all typical substitution reactions of aliphatic petrochemicals should be applicable on the saturated hydrocarbon chain of fatty acids and derivatives. In this line, Hinkamp *et al.*[39] were able to report the chlorination of stearic acid with high selectivity in the (ω-2), (ω-1) and ω-positions of the corresponding free fatty acid by absorbing the fatty acid on alumina, thus allowing it to react with gaseous chlorine or *t*-BuOCl at 20 and – 35 °C.

In contrary to the ω-position, the α-position of fatty acid derivatives is activated either by the neighbor carboxyl or ester group, thus it is feasible to perform several selective modifications[40] on this reactive site, such as α−sulfonation, α-halogenation (Hell-Volhard-Zelinsky reaction), Claisen condensation, alkylation, acylation and addition of carbonyl compounds.

Taking the advantage of the naturally occurring functional groups present in triglycerides and the aforementioned further chemical modifications on the active sites, the application of plant oils and their derivatives in polymer chemistry has become an important research area in constant growth. The polymerization attempts of triglycerides, which are multifunctional monomers, usually ended up with the synthesis of cross-linked[41] polymers along linear and hyperbranched[42] ones.

In addition to above mentioned transformation of typical fatty acids and derivatives, there are some readily available fatty acids that offer different substitution patterns. Nowadays, the only commercial source of such different substituted fatty acid is castor oil,[43] naturalized and cultivated all around the world in temperate zones. Like other plant oils, castor oil is a triacylglycerol composed of various fatty acids and glycerol. The fatty acids consist of up to 90% ricinoleic acid and varying small amounts of saturated and unsaturated fatty acids.[44] The high content of ricinoleic acid is the reason for the high value of castor oil and its versatile application possibilities in the chemical industry. The pyrolysis of castor oil (Figure 2.9) splits the ricinoleate molecule to form heptaldehyde and undecenoic acid, as well as light gases and few percent of free fatty acids (saturated and unsaturated) from C10 to C18.[43,45] The two products, heptaldehyde and 10-undecenoic acid are important raw materials for cosmetics (C11 and C7 aldehydes are used in soaps, shampoos, talcum powders and perfume formulations), pharmaceuticals, and polymeric compounds.[44] Furthermore, heptaldehyde is used as a solvent for rubber, resins, and plastics, and 10-undecenoic acid can be directly used for applications as bactericides and fungicides.[44] In addition, 10-undecenoic acid was shown to be a valuable precursor for the synthesis of antitumor compounds and antibiotics,[46] but most importantly, 10-undecenoic acid is one of the oldest renewable building blocks, being used in the industry as a Nylon 11 precursor.

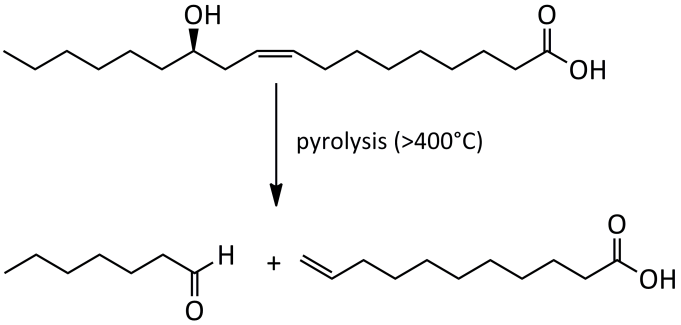


Figure 2.9: The synthesis of the two of the most common industrial platform chemicals derived from castor oil *via* pyrolysis: heptaldehyde and 10-undecenoic acid.[43,44,45]

On the other hand, ricinoleic acid can be polymerized with polyols in the presence of immobilized lipases from *Candida Antarctica B* and *Rhizomucor miehei* under solvent free conditions at 70 °C to yield poly(ricinoleic acid)-based star polymers.[47] In addition castor oil was modified with acrylic acid, acryloyl chloride, and α,α′-dimethyl benzyl isocyanate (TMI). The acrylated castor oil derivatives were found to cross-link *via* radical photopolymerization, whereas the castor oil-TMI adduct was cross-linked *via* cationic polymerization.[48] In addition, by taking the advantage of the hydroxyl group, castor oil was employed in the synthesis of wide variety of polyurethane products, ranging from coatings, cast elastomers, thermoplastic elastomers, rigid foams, semi-rigid foams, sealants and adhesives to flexible foams;[8b,49] clearly showing that castor oil is and will be one of the most promising renewable raw materials for the chemical and polymer industries.

3 Efficient approaches for carbon-carbon and carbon-hetero atom bond formations

Maximizing the benefits of sustainable chemistry requires the development of innovative methods and/or the modification of the already existing procedures towards higher efficiency in terms of resources, and more benefit to the environment.[2,3] Moreover, in a broader sense to favour research in academia as well as in industry. Such approaches include, for example, catalytic procedures.[50,51] With regard to waste minimization, energy saving and atom efficiency catalysis is essential.[3,50] Thus, catalytic methods offer an efficient strategy and represent a key technology for to advance of sustainable/green chemistry.[52] Especially, the use of transition-metals as catalysts[53] has brought a dramatic revolution in synthetic organic chemistry, particularly in carbon–carbon bond forming reactions. Nowadays, nucleophilic displacements, radical additions or organometallic couplings are the most useful chemical methods for the preparation of this type of bond.[54] Moreover, among the various types of transition metal catalyzed C-C bond forming reactions, olefin metathesis,[55] a C=C double bond breaking and reforming sequence, has become one of the most important synthetic organic tools in recent years, owing to the wide range of transformations that are possible with commercially available and easily handled catalysts.[56-62] Clean reactions with minimal waste and by-products drawn on the olefin metathesis to be categorized as potential sustainable method which is easily applicable either in the synthesis of “small” or “macro” molecules.[62,63]

Concurrently, metal-free catalysis[64] represents an attractive option in organic synthesis as alternative green approach by complementing environmental acceptability within widespread resources. Thus, during the past decades there was considerable effort directed toward the development of synthetic methodologies based on metal-free catalysts of high performance.[65,66] In particular, organic catalysts are in many cases complementary to metal or enzyme catalysts. Recent reports highlight the advantages of organocatalytic approaches, especially in biomedical or microelectronic[67] applications where the presence of metal residues in the final material can be deleterious to their end use. In this aspect, the bifunctional character and high basicity of guanidines[68] make them a common tool for the synthetic organic chemist for a variety of base participative organic transformation.

On the other hand, Sharpless and co-workers introduced in 2001 the concept of click chemistry as an additional concept involving a set of highly efficient carbon-carbon and carbon-heteroatom bond formation reactions.[69] Click systems are advantageous from the standpoint of starting with readily accessible starting materials, and resulting in products with high yields that can be isolable by non-chromatographic methods. Thus, the attention of these reactions is focused on the easy production of properties rather than on challenging structures. With this idea behind, the click philosophy has received widespread attention by researchers in different fields and inspired the publication of hundreds of papers in areas such as materials and polymer science, nanotechnology, drug delivery and the pharmaceutical sciences in general.[70] Initially, the Cu(I)-catalyzed azide-alkyne cycloaddition attracted most of the attention in the field, however, many other reactions are consistent with the click philosophy. Most of these reactions were firmly established before the click concept was proposed. This is the case for the Michael addition and Diels-Alder cycloaddition, which have been traditionally used for decades. At the same time, the introduction of the click concept has attracted renewed interest on efficient classical transformations.

3.1 Olefin metathesis

Among the large number of organic and organometallic reactions allowing the formation of carbon-carbon bonds, olefin metathesis has found its place in organic synthesis as well as polymer science as a very versatile tool that allows transformations that were not (or hardly) possible before.[55,62] Olefin metathesis, or trans-alkylidenation, is a chemical reaction that involves the rearrangement of alkene fragments by the scission of carbon-carbon double bonds, thus coupling, cleaving, ring-closing, ring-opening, or polymerizing olefinic molecules (Figure 3.1). Moreover, the reversible nature of the process is a reason for the formation of equilibrium mixtures of starting materials and products. Thus, the driving force behind this reaction is either the release of ring strain, the formation of a stable ring, or the formation of volatile co-products (mainly ethylene). The extension of this reaction to triple bonds was made possible and termed as ene-yne and alkyne metathesis.[71] In addition, advantages including the creation of fewer side products and non-hazardous wastes make this reaction an alternative sustainable process. Evidently, the importance of the development of metathesis methods in organic synthesis was recognized by the award of the Nobel Prize in Chemistry for 2005 jointly to Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock.

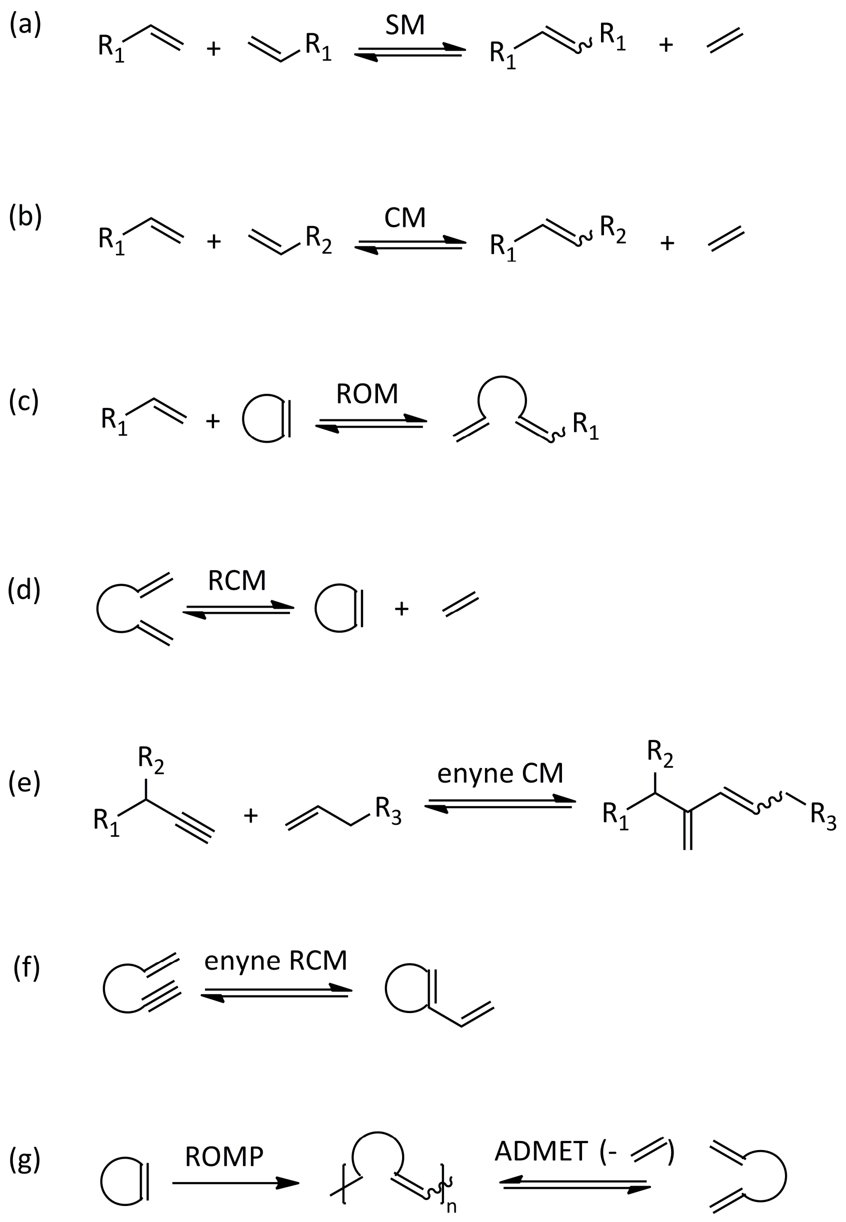
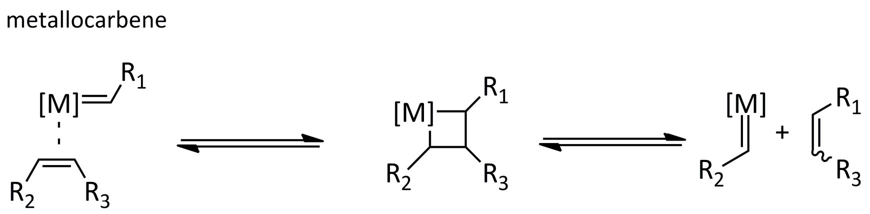


Figure 3.1: Types of transition metal-catalyzed olefin metathesis transformations: (a) self-metathesis (SM), (b) cross-metathesis (CM), (c) ring-opening metathesis (ROM), (d) ring-closing metathesis (RCM), (e) enyne cross-metathesis (enyne ROM), (f) enyne ring-closing metathesis (enyne RCM), (g) metathesis polymerizations, respectively ring-opening (ROMP) and acyclic diene metathesis (ADMET) polymerizations.

Although the olefin metathesis reaction was reported as early as 1955 in a Ti(II)-catalyzed polymerization of norbornene,[72] it took approximately 15 years till Hérisson and Chauvin envisioned the today's still accepted mechanism for the first time (Figure

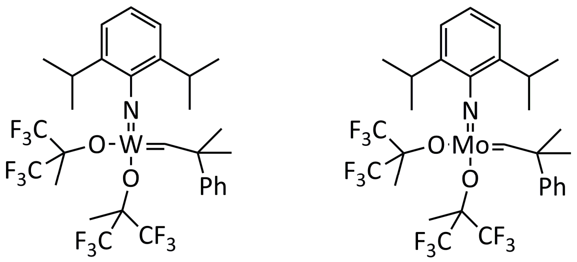
3.2).[73] According to this mechanism, a metallacyclobutane intermediate is formed *via* the [2+2] cycloaddition of an olefinic double bond with a metallocarbene, and the consequent cycloreversion of the metallacyclobutane in the opposite sense leads to a new olefin and a metal alkylidene. Investigations performed by Casey,[74] Katz[75] and Grubbs[76] helped to unlock the key to the reaction, thus providing experimental evidences for the validity of the mechanism. Notably, Casey and co-workers were the first to show that an exchange between a metal carbene and an olefin occurs as a fundamental step in the olefin metathesis.[74] The contributions by Katz *et al.* were mainly focused on the kinetics of the reaction, while Grubbs used isotopically labeled olefins to track the exchange of the groups.



[M] = represents transition metal and ancillary ligands
R = hydrogen, alkyl or aryl group

Figure 3.2: The generally accepted mechanism for olefin metathesis postulated by Hérisson and Chauvin in 1971.[73]

The proposed mechanism introduced new essential ideas for the development of new catalysts, thus many transition metals have been investigated considering their applicability in olefin metathesis either in homogeneous or heterogeneous fashion. Initially, poorly defined group VIII multicomponent catalysts, such as $Mo(CO)_6$/alumina, WCl_6/Bu_4Sn, MoO_3/SiO_2 and $WOCl_4/EtAlCl_2$,[77] which did not possess an alkylidene fragment, were employed until the mid of 1970s. It is now established that ill-defined catalysts form the active alkylidene *in situ* either after the addition of a carbene source or by coordination of the substrate to the coordinative unsaturated complex with subsequent 1,2-hydrogen shift. While these catalysts were generally cheap and readily commercially available, the lack of initiation efficiency (especially in polymerization reactions) triggered researchers to look for more efficient ones. Hence, reports of well-defined early and late transition metal akylidenes as metathesis catalysts began to appear in the literature.[59,78] In 1986, the first well-characterized, highly active, neutral tungsten (**C1**) and molybdenum (**C2**) alkylidene complexes were synthesized by Schrock and co-workers (Figure 3.3).[79]



C1 **C2**

Figure 3.3: First well-defined catalysts developed by Schrock.[79]

Even though **C1** and **C2** were employed both in the metathesis of different olefins and the ROMP of functionalized norbornene to polynorbornene with low polydispersities,[80] the low stability of these catalysts in combination with their limited functional group tolerance was still a major drawback.

Alternatively, the coordination chemistry of ruthenium (Ru-) complexes progressed, and features like high electron transferability, low redox potentials, stability of reactive metallic species, metallacycles, and metal carbenes of Ru had opened the way for a broad variety of catalytic transformations. Thus, in 1992, Grubbs and co-workers synthesized a Ru-complex *via* reaction of $RuCl_2(PPh_3)_3$ with phenyldiazomethane and tricyclohexylphosphine. This well-defined Ru-catalyst, named as the first generation Grubbs catalyst (**C3** in Figure 3.4), is known as remarkably tolerant towards many organic functional groups.[81] Hence, it is widely used in organic syntheses under a variety of reaction conditions, including protic media. Consequently, Hermann and co-workers contributed to the improvement of the performance of **C3** by reporting on the synthesis of mononuclear as well as binuclear *N*-heterocyclic carbene (NHC)-based Ru-alkylidenes.[82] Although NHCs are considered to be analogous to tertiary phosphine ligands, complex **C4** (Figure 3.4), which resulted from the replacement of one tricyclohexylphosphine by a (NHCs), often perform superior to **C3** in terms of catalytic activity and stability. The introduction of a chelating isopropoxybenzylidene moiety in this catalyst by Hoveyda and co-workers (Hoveyda-Grubbs 2nd generation catalyst, **C5** in Figure 3.4), and the design of the fast initiating bromo-pyridine catalysts (known as third generation Grubbs catalyst, **C6**, Figure 3.4) are other notable historical developments in the progression of olefin metathesis catalysts.[83] While **C5** affords superior stability, **C6** has greatly benefited polymer synthesis in materials application especially with the synthesis of well-defined polymers with low polydispersity values *via* ROMP. So far, to tailor the applicability of metathesis catalysts, **C7** (known as Zhan-1B catalyst) was developed by Prof. Zhan based on the modification of the structure of **C5**, as an efficient and air stable catalyst giving rise to different synthetic possibilities.[84] With the introduction of strong electron withdrawing group *para* to the ligatating *i*PrO in **C5**, the chelation between *i*PrO and Ru is weakened thus facilitating initiation of the catalytic cycle.

Since then, significant progress has been made to understand both catalyst and substrate structural features, and more importantly, their interactions. As a result of this continuous improvement, nowadays, many different catalysts exist with activities that are tuned towards a variety of specific applications. Very recently, a modified catalyst showed great promise in the *Z*-selective olefin metathesis (**C8**, in Figure 3.4).[85]

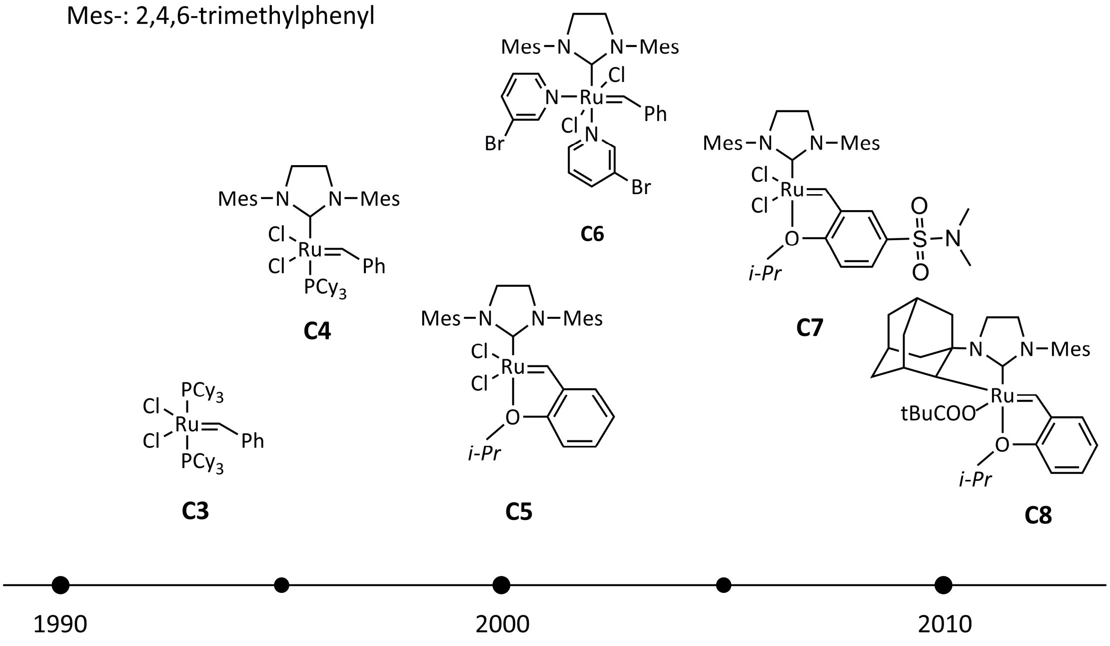
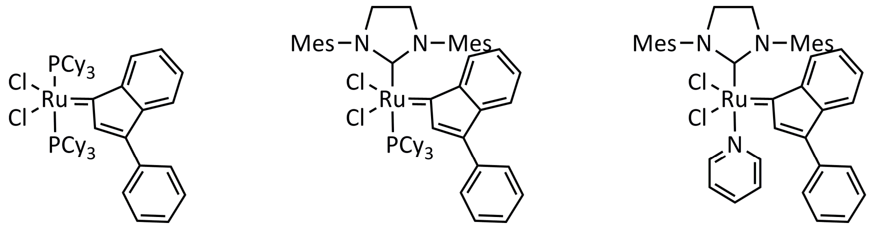


Figure 3.4: The development of Ru-based olefin metathesis catalysts.

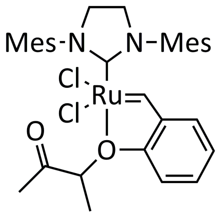
Dixneuf, Fürstner, Hill and Nolan developed a parallel system to first, second and third generation Grubbs catalysts, where the benzylidene ligand is replaced by an indenylidene one (Figure 3.5).[86]



C9 **C10** **C11**

Figure 3.5: Ru-indenylidene analogues (**C9**, **C10** and **C11**) of Ru-benzylidene catalysts **C3**, **C4** and **C6**.[86]

The feasibility of the olefin metathesis reaction has led to search for more stable and active Ru catalytic systems. Moreover, it is known that the catalytic activity and latency of a metathesis catalyst is affected either by direct substitution of the chelating heteroatom or by proper functionalization of the chelating benzylidene ether (like in the case of **C7**, Figure 3.4).[87] Thus, encouraged by the success of a method based on proper functionalization of the chelating benzylidene ether, Grela and co-workers[88] investigated the effect of modifying **C5** by introducing a donor group (in this case keto group) as a terminal substituent of the benzylidene ether. Accordingly, it was observed that, the keto functionalized Hoveyda-Grubbs 2nd generation catalyst (**C12**, Figure 3.6) exhibited higher performance than the unmodified **C5** in RCM and CM, for both standard and challenging substrates.



C12

Figure 3.6: New precatalyst generated from monofunctionalized styrenyl ethers; ketyl functionalized Hoveyda-Grubbs 2nd generation catalyst.[88]

Many review articles[89,56] on olefin metathesis have appeared in the last years; some of them concerned a particular group of compounds like carbohydrates, peptides, or fatty acids. An attractive application of alkene metathesis deals with the transformation of plant oil derivatives into added-value molecules.[7e] For instance, recently, the transformation of plant oil unsaturated acid derivatives into α,ω-bifunctional linear molecules[90] with potential as surfactants or monomers, precursors of polyesters,[91] and polyamides[92] has been successfully accomplished. The cross-metathesis of plant oil unsaturated acids and esters with acrylonitrile in the presence of Ru-alkylidene complexes such as **C3** and **C5** catalysts has just allowed the direct access to linear α,ω-nitrile acid/ester derivatives,[93] some known precursors of polyamides.[92d]

Apart from the synthesis of high-added value molecules, olefin metathesis has turned to be a powerful polymerization technique for the synthesis of various functionalized polyalkenes, alternating block-copolymers, telechelic, and even hyperbranched polymers.[94] ROMP and ADMET are attractive synthetic tools for polymer chemist since these polymerizations can be performed under extremely mild and user-friendly conditions. The general structures of the polymers obtained by ADMET and ROMP are illustratable in the same fashion [compare Figure 3.1, (g)], however each requires a different set of considerations for successful polymerization.[94]

Acyclic diene metathesis (ADMET) polymerization is a step-growth polymerization driven by the release of a condensate, usually ethylene.[95] ADMET is typically performed on α,ω-dienes to produce well-defined and strictly linear polymers with unsaturated polyethylene backbones. The mechanism of the ADMET polymerization cycle is well established (Figure 3.7).[96]

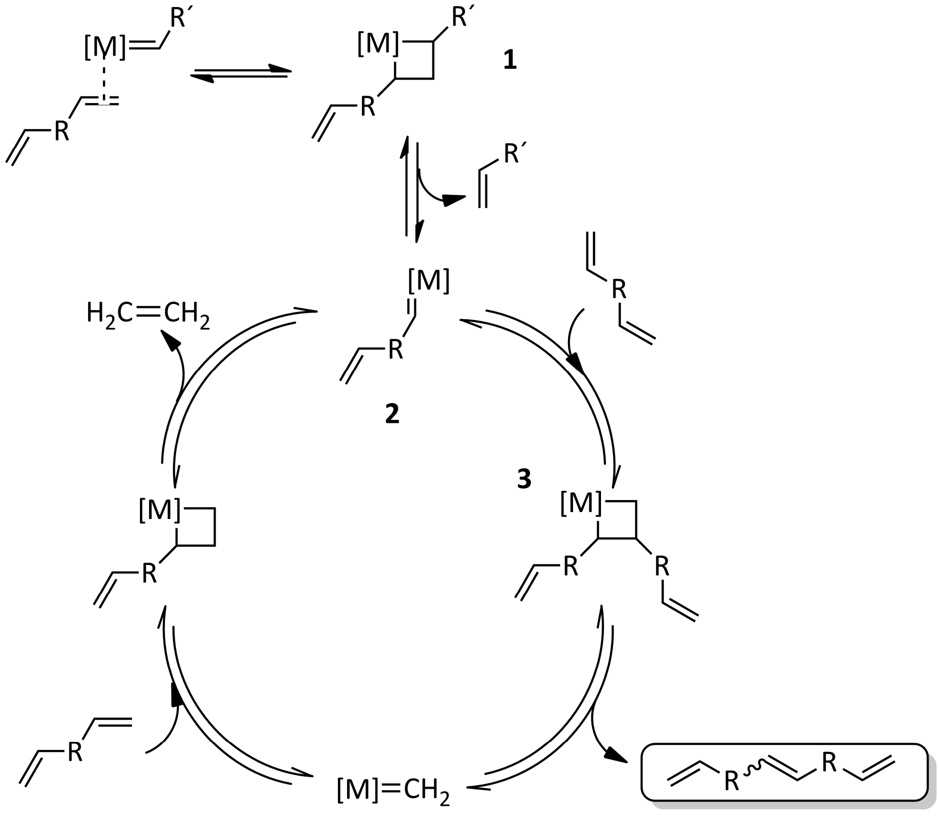


Figure 3.7: Generally accepted mechanism of ADMET polymerization.[96]

The olefin coordinates to the metal centre followed by formation of a metallacyclobutane intermediate (**1**). At this point, the productive cleavage of **1** leads to the formation of the metathesis active alkylidene complex (**2**). Subsequent reaction with the double bond of another monomer produces the metallacyclobutane ring (**3**), which subsequently leads to polymer formation. The cycle proceeds with coordination of another diene or growing polymer, followed by productive cleavage, and release of ethylene. Since all the species involved in this catalytic cycle are in equilibrium, in order to shift it towards polymer formation, ethylene is usually removed from the reaction mixture by applying vacuum or by using a constant flow of an inert gas, such as nitrogen or argon.

Regarding other experimental issues, ADMET polymerizations, just like any other step-growth polymerization, are preferably performed in bulk to avoid the formation of cyclic oligomers. However, as the polymerization proceeds and high molecular weights are achieved, the viscosity increases impeding stirring and making an efficient ethylene removal difficult. For this reason, depending on the monomer properties, the use of solvents can be necessary to reach high conversions. In these cases, non-volatile solvents such as toluene or *o*-xylene are preferred. Already the first reports on ADMET highlighted the mild reaction conditions required to polymerize non-functionalized α,ω-dienes as a main advantage of this technique. Nowadays, the availability of robust and versatile metathesis catalysts permits the ADMET polymerization of a wide variety of functionalized α,ω-dienes at low temperatures. It is essential to the success of ADMET polymerizations to prevent side reactions. This can be realized by choosing a suitable catalyst and suitable reaction conditions. Each type of catalyst system has strengths and weaknesses, thus the choice particularly depends on the functional groups of the diene to be polymerized and other factors like the melting point or solubility of the monomers. For instance, increasing the steric hindrance of the olefins leads to decreased metathesis rates.[97] Sterically hindered and electronically deactivated substrates are often rather difficult to polymerize with **C4**, however the activity of **C5** has often surpassed that of Schrock type Mo-based metathesis catalyst.[98,99] This clearly indicates that the functional group tolerance is partly dependent on the central metal, while it can be improved by ligand design.[100]

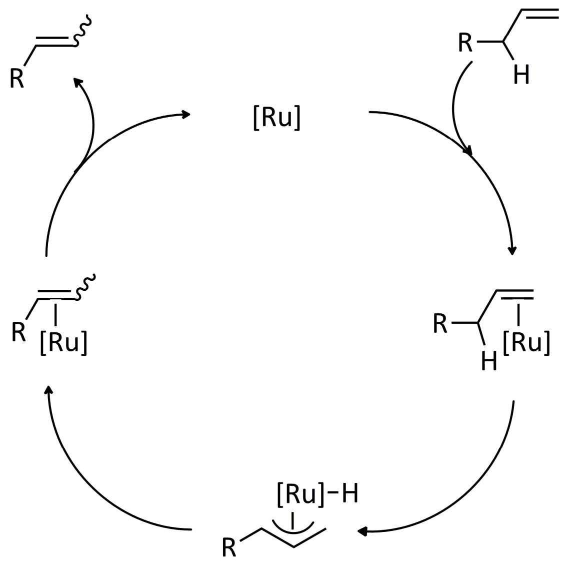
As already indicated above, the key to improved functional group tolerance in olefin metathesis was the development of catalysts that react preferentially with olefins in the presence of heteroatomic functionalities. Being less oxophilic, well defined Ru catalyst systems developed by Grubbs and co-workers have thus been used to polymerize monomers containing ketones,[101] alcohols,[59] esters,[102,103] ethers,[104] silyl chlorides, siloxanes,[105] amides,[106,107] and carboxylic acids.[103] Additionally, these complexes allowed solution ADMET polymerization of amino acid containing monomers.[108]

ADMET does not always produce defined polymeric architectures when olefin isomerization competes with metathesis chemistry, an issue that has been related to catalyst chemistry.[109,110] As a result, double bond isomerization side-reactions have been the subject of extensive research. Double bonds can migrate (isomerize) along the polymer backbone and/or in the monomer during olefin metathesis and, as a result, the repeat unit structure of the produced polymer can become irregular with respect to carbon chain length and double bond position.

Many heterogeneous and homogeneous organometallic complexes were reported to promote the olefin isomerization.[109,110] Although the exact mechanism for the Ru catalyzed olefin metathesis was not established, two major mechanisms were proposed for transition metal catalyzed isomerization of olefins.[110] As one of the two prevalent pathways, the π-allyl mechanism (intramolecular 1,3-hydrogen shift) is less common (Figure 3.8, **A**). The key step in this pathway is supposed to be the oxidative addition of an activated allylic carbon-hydrogen bond of the olefin substrate to a transition metal complex (in this case Ru-based metal complex in Figure 3.8, **A**) with the formation of a π-allyl metal hydride intermediate. By reductive elimination of the olefin from this intermediate, the isomerization would be observed if the hydrogen shifts to the α-carbon instead of returning to the γ-carbon (in the case of terminal alkene, as depicted in Figure 3.8, **A**). The other established pathway for olefin isomerization is the metal hydride addition/β elimination mechanism (alkyl mechanism or 1,2-hydrogen shift) (Figure 3.8, **B**).[110] In this mechanism, free olefin coordinates to a kinetically stable metal hydride species to give a π-complex. Subsequent insertion (hydrometalation) into the metal-hydride bond yields a σ-alkyl complex. Formation of the secondary metal alkyl followed by β-elimination yields isomerized olefins and regenerates the initial metal hydride by dissociation of the isomerized alkene. Considering the research performed upon the mechanistic investigations of olefin metathesis, it could be concluded that the π–allyl metal hydride mechanism is the more likely mechanism for Ru catalyzed metathesis reactions.

Two decades ago, some reports assumed that isomerization might result during the purification of the final metathesis product by distillation.[111] Fürstner and co-workers isolated a Ru-dihydride complex, $RuCl_2(PCy_3)_2(H)_2$, that they proposed to be responsible for the isomerization, presumably through a hydride mechanism.[112] Furthermore, Sutton *et al.* suggested that impurities in the metathesis catalyst lead to the isomerization.[113] Recent studies showed that Ru-hydride species, either formed *in situ* from the decomposition of the Ru-metathesis catalyst or present as impurities in the original catalyst, are responsible for the isomerization process.[110] For instance, mechanistic investigations of the thermal decomposition of the second generation catalyst from Grubbs (**C4**) clearly showed that heating the catalyst results in the formation of a binuclear Ru-hydride complex, which is most likely responsible for the isomerization.[114] During the last decade, several strategies have been reported that can reduce the amount of olefin isomerization side reactions. For instance, phenylphosphoric acid[115] and benzoquinones[116] have been reported to efficiently suppress olefin isomerization side reactions during metathesis reactions. Moreover, tin and iron halogenides have been reported to not only enhance the metathesis activity of Grubbs type catalysts, but also to reduce or even completely suppress the isomerization side reactions.[117] In order to be able to quantify the actual amount of isomerization during ADMET polymerizations, a strategy to analyze the monomer repeat units after ADMET polymerization by GC-MS was recently developed.[118] Within this study not only the quantification of side reactions was possible, but also the polymerizations procedures were developed using second generation catalysts that allowed for the preparation of well-defined polymers with very little isomerization.

A) π-Allyl hydride mechanism



B) Hydrometalation/β-hydride elimination mechanism

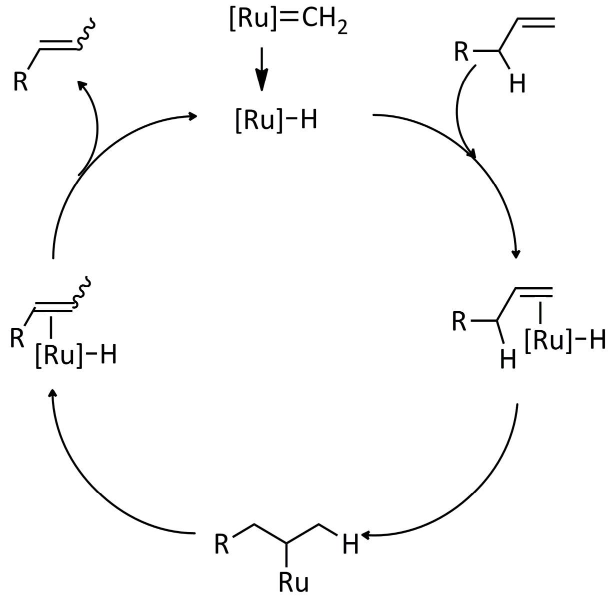


Figure 3.8: Two possible mechanistic pathways of metal catalyzed olefin isomerization:[110] **A)** π-allyl hydride mechanism (up); **B)** hydrometalation/β-hydride mechanism (down).

The discovery and use of both the Schrock and Grubbs metathesis catalysts opened the way for the synthesis of various polymer architectures and functionalities *via*

ADMET.[59,94,95,100-108] Consequently, broad ranges of novel polymers with designed architectures can be prepared that are difficult or impossible to synthesize *via* other routes. A variety of telechelic polymers has been prepared, both directly and by the ADMET depolymerization of unsaturated polymers,[119] and some of these were used for the synthesis of segmented and ABA-type block copolymers.[120] Furthermore, ADMET enabled synthetic routes to perfectly linear polyethylene and to a variety of alkyl branched and functionalized polyethylenes with precisely placed pendant groups along the hydrocarbon backbone.[94] Graft copolymers with "perfect comb" structures are also accessible through ADMET polymerization.[121] Many representative examples of these diverse materials with defined architectures were surveyed with recent reviews published by Meier *et.al* and Wagener *et al.*[94]

The alternative reaction, the so-called ROMP,[122] involves a chain-growth polymerization of cyclic olefins to linear unsaturated polymers as illustrated in Figure 3.1, (g). Several industrial processes involving ROMP have been developed and brought into practice, such as the ROMP of cyclooctene, norbornene and dicyclopentadiene, leading to useful polymers.[123]

An important feature that distinguishes ROMP from typical olefin addition polymerizations is that in ROMP any unsaturation associated with the monomer is conserved as it is converted to polymer.

The mechanism for ROMP in the presence of **C4** is based on the general mechanism proposed by Chauvin (Figure 3.9).[73] Initially, a 14 electron complex dissociated from the metathesis initiator (**C4**) undergoes [2+2] cycloaddition to give a metallacyclobutane intermediate, which rapidly undergoes [2+2] cycloreversion to produce a ring opened product. This sequence is highly thermodynamically favoured due to the relief of the ring strain of the initial monomer. This intermediate contains the catalytically active Ru-alkylidene and undergoes further reactions until the monomer is completely consumed. Subsequent quenching with ethyl vinyl ether[124] results in a polymer and an alkoxycarbene complex.

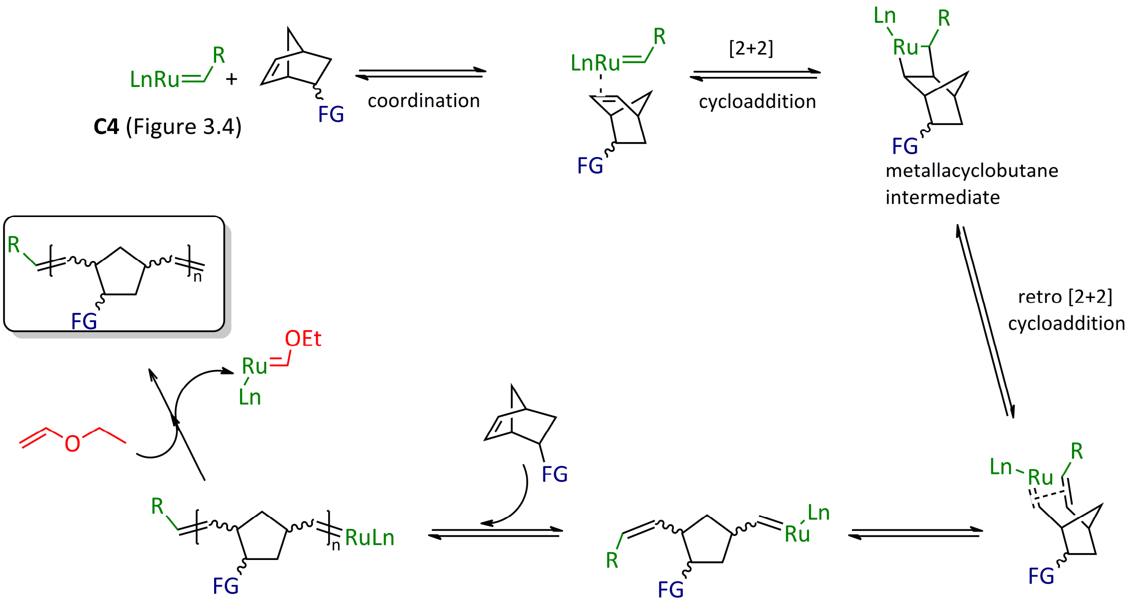


Figure 3.9: A general mechanism for **C4** mediated ROMP based on Chauvin´s mechanism.[73]

Regarding metal-mediated ROMP reactions, some features are considered as quite prominent in the polymerization and on the final product, respectively.[122] For instance, ROMP reactions are generally reversible like most olefin metathesis reactions. However, ROMP polymerization reactions can be equilibrium-controlled and the position of the equilibrium (monomer vs. polymer) can be predicted by considering the thermodynamics of the polymerization. Thus, the driving force is the release of the ring strain; in other words, cyclic, bicyclic, and polycyclic olefins having a more negative ΔG value of polymerization due to their increased ring strain are especially prone to polymerize *via* ROMP.[125] For instance, cyclohexene, with a very little enthalpic driving force, does not undergo ROMP.[126] On the other hand, the temperature and concentration at which the ROMP is conducted have an additional strong influence over the outcome of the reaction.[127] Generally, the highest monomer concentration at the lowest possible temperature results in a successful ROMP reaction.

Among other living/controlled polymerization techniques, living ROMP (LROMP) has recently emerged as a powerful tool for the polymer chemist due to the absence of side reactions which can occur in conventional ROMP, such as chain termination and chain transfer.[128] As a consequence, the synthesis of well-defined polymers with controlled molecular weight and narrow PDI can be accomplished. The introduction of well-defined catalysts that mediate living ROMP has pushed the frontier of living polymerization.[83] In this context, Grubbs-type catalysts (**C4**, **C5** and **C6** in Figure 3.4) have been proven to be particularly useful in ROMP due of their high tolerance toward air, moisture, and functional groups.[83c,129] ROMP performed in the presence of slow initiating 2nd generation catalysts (**C4** and **C5**) is fast but uncontrolled; on the other hand, the 3rd generation dipyridine analogue **C6** displays both high reactivity and precise specification of chain lenghts, with PDIs as low as 1.02.[83c] For example, the LROMP of cyclobutenecarboxamide (a glycine derivative) in the presence of **C6** generated amino acid functionalized polymers (PDIs ranging from 1.2 to 1.6.) with a stereoregular backbone, and moreover these polymers showed excellent prospects for applications in both materials and chemical biology (Figure 3.10).[130]

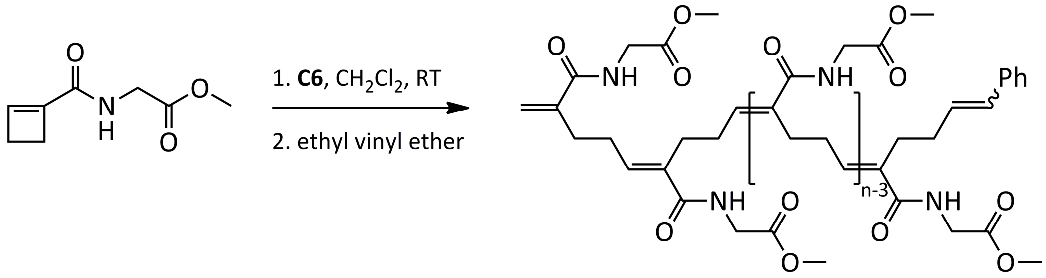


Figure 3.10: Regio- and stereoselective ROMP of glycine-derived cyclobutene.[130]

In recent years, Ru-indenylidene complexes have been intensively investigated as the promising alternative to the Grubbs type benzylidene derivatives in all areas of olefin metathesis. In line with this, the scope of **C11** (Figure 3.5) in the living/controlled ROMP of norbornene-type monomers was demonstrated.[131]

Regarding the stereochemistry of ROMP polymers, it was considered that the above mentioned Ru-based initiators gave only exclusively *trans* polymers,[132] while Grubbs *et al.* has recently demonstrated that classic Ru-catalysts (for example **C4**) can give polymers with unexpectedly high *cis* selectivity in certain situations (48 - 96%).[133] It was observed that the *cis* content in the final polymer varied significantly with the monomer structure: bicyclic monomers resulting in high *cis* content in contrast to monocyclic monomers.

Living ROMP reactions are commonly quenched deliberately through the addition of a specialized reagent.[124] The function of this reagent is either to selectively remove and deactivate the transition metal from the end of the growing polymer chain (i.e. ethyl vinyl ether) or install a known functional group in place of the metal.[134] Vinylene carbonate and 3H-furanone, as examples of unsaturated lactones, are alternative quenching agents for ROMP. By using those, aldehyde and carboxylic acid end-groups can be introduced.

In the search for high performance polymer architectures, norbornene and its functionalized derivatives have become the monomers of choice for living ROMP due to commercial availability, low cost, and general ease of synthesis.[135] Moreover, the high ring strain[136] (about 27.2 kcal/mol) allows for efficient polymerization, and furthermore, certain substituents on the norbornene can prevent secondary metathesis of the polymer backbone.

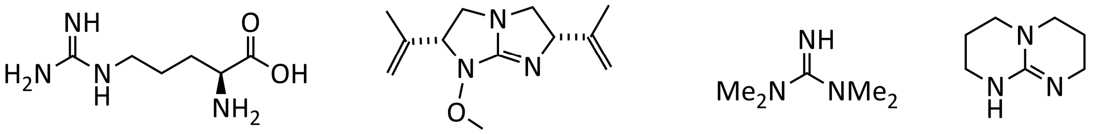
In line with green/sustainable chemistry, the integration of renewable monoterpenes (such as limonene oxide or β-pinene) in the ROMP polymerization of dicyclopentadiene (another commonly used ROMP monomer) allowed the synthesis of hyperbranched polymers[137] or thermosets.[138] In the latter case, the presence of β-pinene, during the ROMP of dicyclopentadiene altered the degree of cross-linking and plasticized the thermoset, thus creating a sustainable method for altering the physical properties (modulus and glass transition temperatures) of thermosets.

Literature survey revealed many review articles focused on ROMP and LROMP.[89d,94b,122b,139] For instance, Grubbs *et al*. covered the fundamental aspects of living ROMP and briefly traced its historical development from a catalyst-design perspective.[122b] Additionally, they illustrated the utility of living ROMP in the preparation of macromolecular materials with advanced structures and functions. On the other hand Slugovc and co-workers presented the current state of research in ROMP reactions initiated by Ru-benzylidene and indenylidene complexes, emphasizing the use of ROMP reactions employing sustainable substrates.[94b] In addition, the usefulness of combining ROMP with other synthetic techniques such as RAFT, ATRP or click chemistry was highlighted.[94b] On the other hand, Nguyen *et al*. outlined the promising emergence of ROMP-derived amphiphilic block copolymers containing therapeutic agents, their assembly into polymer nanoparticles, together with their modification for the targeting group attachment.[139]

3.2 Guanidines as efficient and promising organocatalysts

Although chemical transformations employing organic catalysts have been reported over the past century, the sudden "birth" and the rapid growth of this field dates back to the 1990s.[66b,140] However, it took 10 more years until the term "organocatalysis" was introduced to the chemical literature and since then, it is accepted as one of the main branches of catalysis. Although organocatalysis offers economic, environmental and scientific benefits, the significant advantages are in terms of operational simplicity and potential for new synthetic possibilities. Along this, of particular importance is the often lower toxicity of the used catalysts. Hence, several publications that give a comprehensive overview of organocatalysis are available.[66,141]

The guanidine functional group, which is frequently found in bioactive compounds, either from natural sources[142] or of synthetic origin,[143] constitutes an attractive building block not only in total synthesis, but also for the design of new materials (Figure 3.11).[144] Recently, guanidines and guanidinium salts are additionally employed as ionic liquids and encountered in coordination chemistry as guanidinium counter cations, as chelate guanidinate, and as neutral guanidine ligands with different metals.[145] Special interest in guanidine originates also from its activity as strong neutral organic base, which in turn arises from the resonance stabilization of their conjugated acids.



L-Arginine (±)-isoalchorneine TMG TBD

Figure 3.11: Examples of guanidines either from natural source or of synthetic origin: the amino acid arginine (L-Arginine), (±) isoalchorneine, 1,1,3,3-tetramethylguanidine (TMG) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), respectively.

Modifications on the guanidine skeleton by the introduction of chirality into the molecule are a widely and easily applied approach for the synthesis of a variety of guanidine bases. The driving force behind some of the major advances made in the development of bicyclic guanidines is the synthesis of both inorganic and organic solid-supported derivatives.[146]

The tetrasubstituted bicyclic guanidine TBD (Figure 3.12) represents the most widely used member of the family of bicyclic guanidines,[147] which have been previously utilized as organocatalysts in many transformations for the synthesis of fine chemicals,[68b,148] and the polymerizations of diverse monomers, either *via* polycondensation[149] or (controlled) ring-opening polymerization (Figure 3.12).[150]

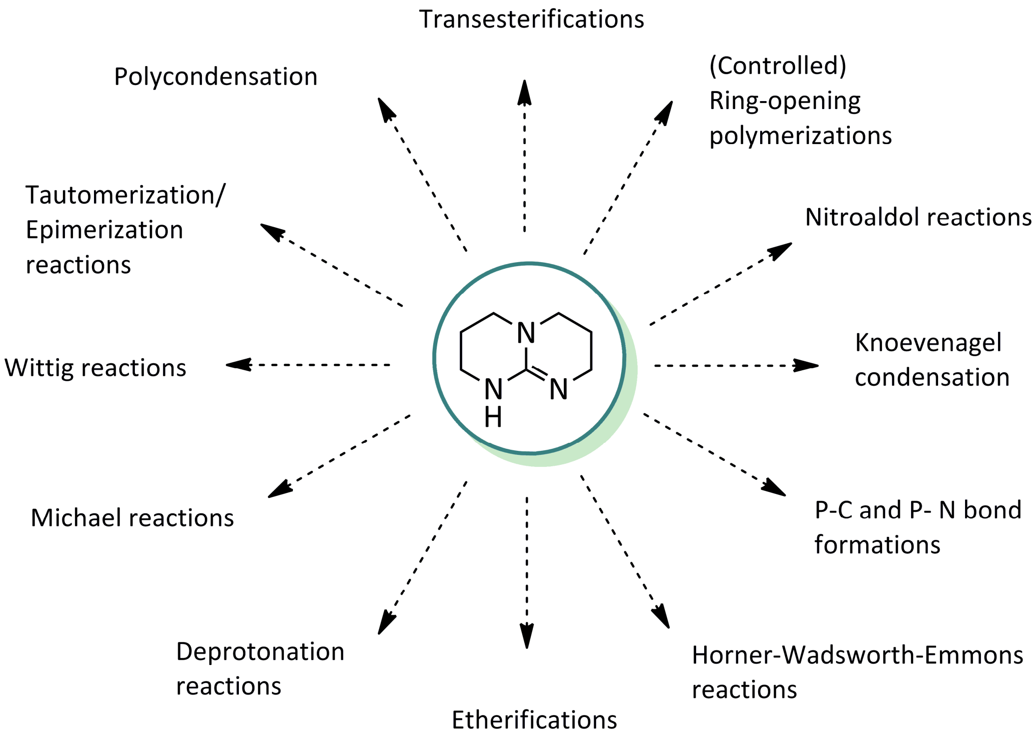


Figure 3.12: Scope of TBD reactivity.[145,148,150]

Additionally, the green aspects of TBD-promoted chemistry have been explored by examining the potential for catalysis under solvent-free conditions. For example, Waymouth *et al.* have shown that the secondary amides from vinyl, benzyl and ethyl esters, as well as primary amides can be afforded in the presence of TBD under bulk conditions.[147] Furthermore, the same researchers have also shown that TBD is additionally an efficient catalyst for transesterifications and for the ring-opening polymerization of cyclic esters such as lactide, δ-valerolactone, and ε-caprolactone.[147] Extension to other monomer systems has been established, including the polymerization of cyclic carbosiloxanes,[151] trimethylene carbonate,[152] and other substituted cyclic carbonate monomers. The flexibility of the TBD organocatalytic system was demonstrated with the formation of organic-inorganic hybrid materials involving the graft polymerization of ε-caprolactone onto a polysilsesquioxane.[153] Regarding the mechanistic investigations of the polymerization, comparative experiments and NMR analyses indicated that the NH proton is vital to the high activity and stereoselectivity. Based on X-ray diffraction analysis of both guanidine and adducts, a preliminary mechanism has been proposed to illustrate a dual activating mode (Figure 3.13).[150]

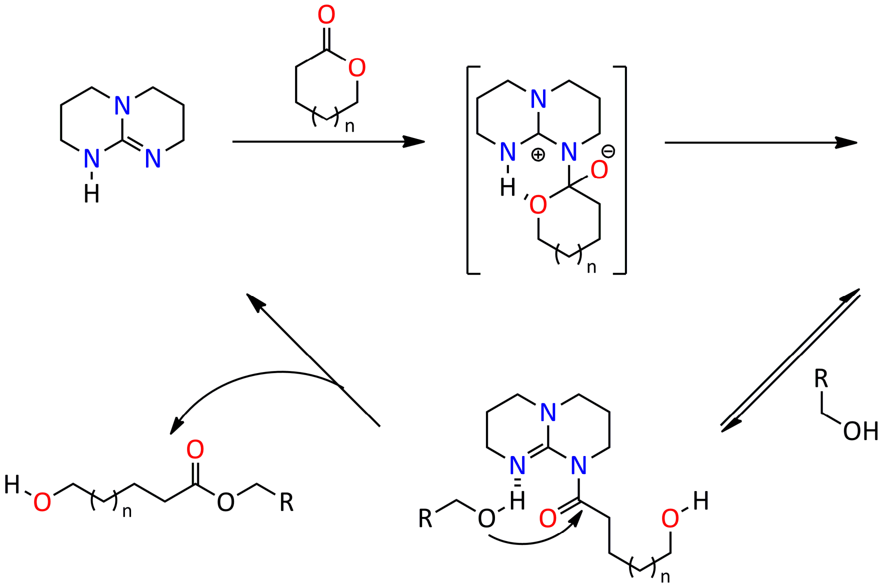
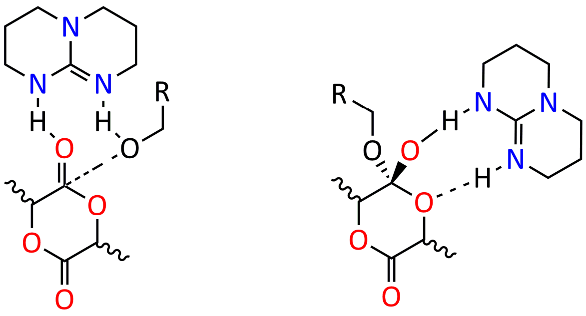


Figure 3.13: The acetyl transfer: an initially proposed mechanism by which TBD catalyzes ring-opening polymerization of lactide.[150]

Based on observations from a bifunctional thiourea amine system, an alternative system was proposed.[154]



intermediate (A) intermediate (B)

Figure 3.14: Reaction intermediate predicted by computational studies.[154]

Accordingly, the dual activation of the monomer and alcohol occurs only through hydrogen bonding to the guanidine, giving intermediates (A) and (B) in Figure 3.14. This is energetically preferred over the acetyl transfer pathway, and furthermore the theoretical results were consistent with the experimental data.

In line of sustainable chemistry, an important target is the utilization of TBD along renewable resources (such as plant oils or CO_2) as a carbon resource. Hence, in 1996, Costa and co-workers showed that TBD catalyses the reaction of acetylinic amines with CO_2 to form 5-methylene-oxazolidin-2-ones.[155] Although no mechanism was proposed for the role of the guanidine catalysts, it was found that the rate of reaction was independent of the pK_a of the catalyst. Another report has shown that TBD catalyzes the synthesis of propylene carbonate from propylene glycol and carbon dioxide.[156] In addition, TBD was employed as an excellent catalyst for polycondensation reactions thus leading to terpene-based polyesters (Figure 3.15)[149] and isocyanate-free, well-defined, bio-based segmented polyurethanes.[157] Recently, Hillmyer *et al.* demonstrated the controlled ring-opening transtesterification polymerization of a monomer produced from renewable resources in the absence of solvents, and at moderate temperatures, using TBD.[158]

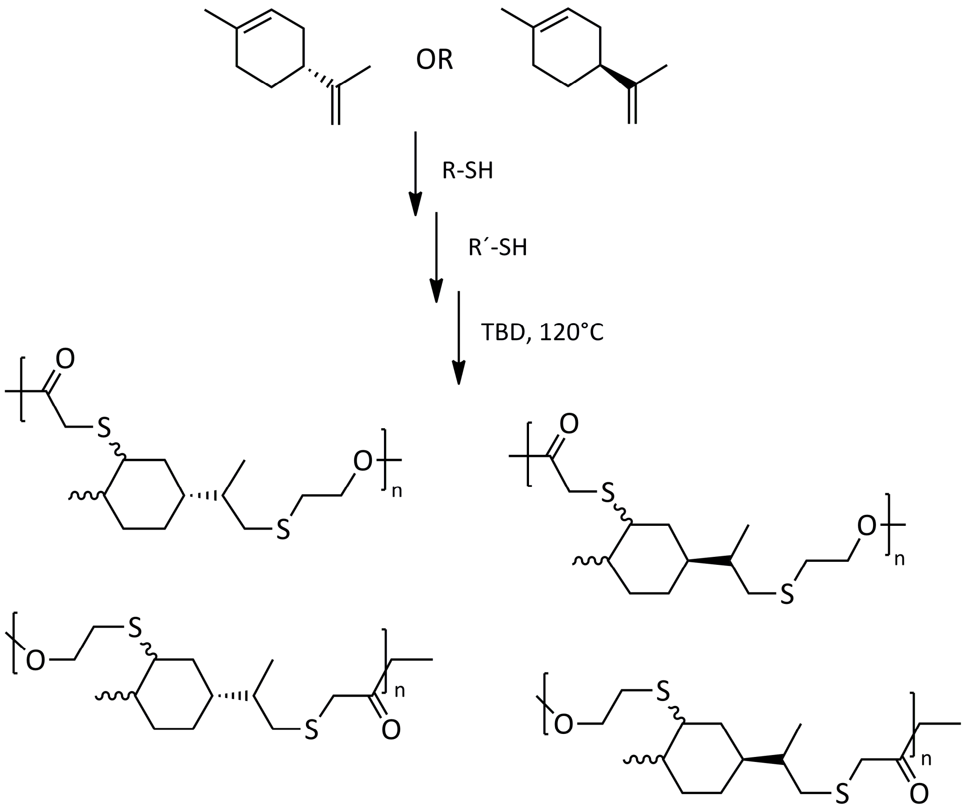


Figure 3.15: Bio-based polyesters obtained *via* TBD mediated homopolymerization of terpene-derived heterodifunctional monomers.[149b]

Due to its hydrophilic nature, TBD also plays an important role in the stabilisation of protein conformations through hydrogen bonding and in the mediation of solubility of natural products. The lability of the NH atom of TBD has been exploited in an isotope exchange reaction.[159] Using 4´-methoxyacetophenone as a test substrate and a catalyst loading of 30% at room temperature, the total incorporation yield for TBD was 92% after 0.5 h. Besides this, TBD is considered as a very interesting agent in designing molecular systems for crystal engineering and for studies of the proton transfer reactions and formation of hydrogen-bonded chains with phenols and C-H acids.[160]

The existing chemistry for the synthesis[161] of non-functionalized bicyclic guanidines requires multi-steps or it is based on the use of expensive starting reagents (Figure 3.16, A). A simple one-pot method was published in 1986,[162] hence this procedure led to the commercial availability of TBD, driven by an interest in the utilization of these compounds for many applications. Despite the good yield provided by this method, the generation of toxic intermediates and the formation of hydrogen sulfide have motivated the search for more environmentally-friendly synthesis methods. Therefore, recently, a greener method was developed for the synthesis of TBD (Figure 3.16, B).[163] According to this method, TBD was generated easily by the condensation reaction of TMG (or cyanamide) with bis(3-aminopropyl)amine at reaction temperature in the range of 130-170 °C. The noteworthy advance of this approach was the high purity of the TBD (>95%), obtained in one step without any additional purification. Moreover, it was shown that the addition of strong acids up to 1.0 equivalent of the amount of triamine drastically improved the yields of TBD versus the likely occurring side reaction; the polyimine formation. Furthermore, it was observed that all guanidine moiety-containing structures (besides melamine) can produce a cyclic guanidine. The authors concluded that the major driving force for the reactions was the constant removal of volatile amines (dimethylamine in the case of TMG) from the reaction mixture. Accordingly, the formation of TBD starts with the substitution of a nitrogen atom in the guanidine with a nitrogen atom, from the triamine, followed by a number of further substitutions with formation both TBD and oligomeric products.

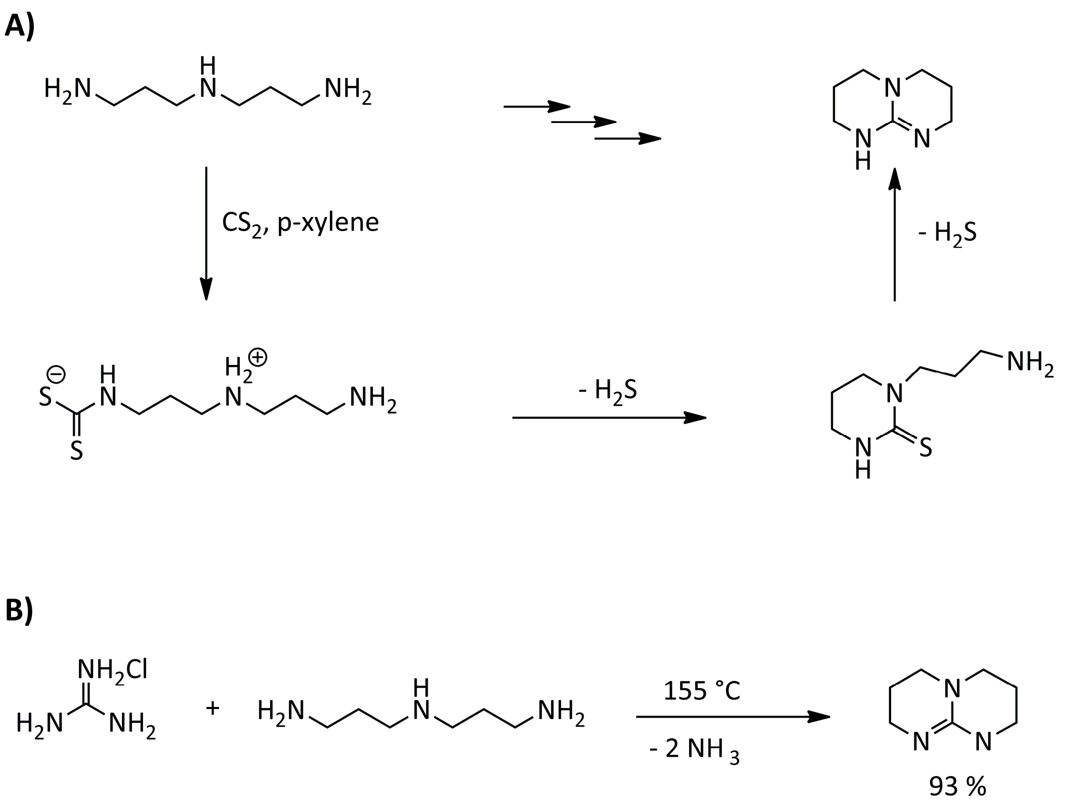


Figure 3.16: Schematic representation of methods for the synthesis of TBD: **A)** the commercially adapted[162] and **B)** recently proposed "green" approach,[163] respectively.

In summary, along the aforementioned advantages over more traditional catalysts, the ease of handling and mildness of reaction conditions certainly make TBD a catalyst of choice for many applications.

3.3 Thiol-ene reaction

Researchers are continuously seeking the development of highly efficient and orthogonal reactions that do not require any metal catalyst in order to contribute to a sustainable chemistry. This has created a trend toward the convergence of synthetic organic techniques within the 12 principles of Green Chemistry. Along this trend, in 2001, Sharpless and co-workers introduced the term "click chemistry" to define a set of nearly perfect reactions that resemble natural biochemical ligations.[69] Thus, in order to a reaction to be considered as a click, certain requirements which should be fulfilled, such as simplicity, high reactivity, and broad variety of available reagents applicable in wide scope of reactions.[69]

Given that there have been a number of outstanding reviews written on polymer synthesis *via* click chemistry for different applications,[69,164] a brief introduction of the employed reactions and summary of the very recent developments in thiol-ene coupling is aimed within the following paragraphs.

Whilst commonly copper (I)-catalyzed alkyne–azide cycloaddition (CuAAC) is highlighted as click chemistry,[69] the concept is not limited to the CuAAC reaction, and involves many reactions with distinct mechanisms and conditions [Figure 3.17, (a)].

However, due to the toxicity of copper and the inherent danger of working with azides, a growing interest has rose in the development of copper and azide-free chemistry. Regarding this, Schubert *et al*. published an overview of the latest achievements in metal-free click chemistry.[165] Within the past decade, Bertozzi and co-workers have developed the reaction of azides with cyclooctyne derivatives[166] referred to as strain-promoted azide-alkyne coupling (SPAAC) [Figure 3.17, (b)]. With this contribution, it was clearly observed that the cyclooctyne derivatives greatly increased the reactivity of azide–alkyne cycloadditions in the absence of copper, particularly when difluorinated. However, the complex synthesis of the difluorinated cyclooctynes remains a limitation.[167] The well-known Diels-Alder reaction, first reported by Otto Diels and Kurt Alder in 1928,[168] which is a highly selective [4 + 2] cycloaddition between an electron-rich diene and an electron-poor dienophile, is another commonly applied example of click chemistry [Figure 3.17, (c)]. Contrary to other click reactions, which result in carbon-heteroatom bonds, DA click cycloadditions result in new carbon-carbon bonds in a “reagent-free” manner that does not require catalyst, photoinitiator, or radical initiation, however, with the drawback of relatively longer reaction times.[169]

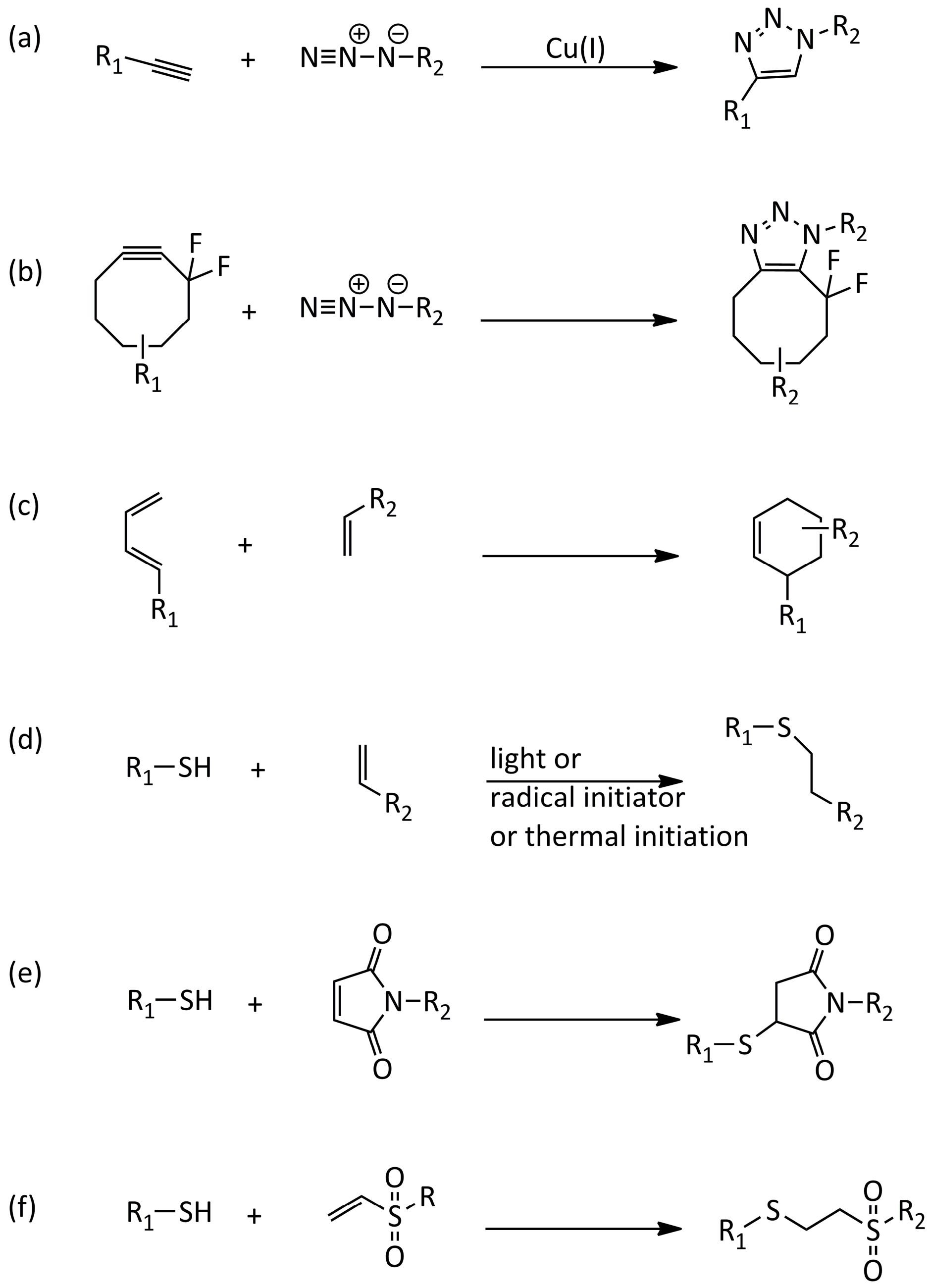


Figure 3.17: (a) copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC), (b) azide-alkyne coupling (SPAAC), (c) Diels-Alder (DA) cycloaddition, (d) radical-mediated thiol-ene coupling, (e) thio-Michael addition to maleimides, and (f) to vinyl sulfones.

Thiols have been used in diverse chemical reactions for well over a century; on the other hand practical considerations regarding the utilized thiols include such as odor, the storage and shelf life stability. However, with the improved synthetic methods, these challenges have been overcome and features such as wide accessibility made thiols to good candidates for the click reactions. Consequently, reactions such as nucleophilic substitutions, thio-Michael additions, and radical thiol-ene couplings are considered as other highly efficient transformations that fulfil the click criteria [Figure 3.17, (d)-(f)].[170,171] The history of Michael type addition of thiols to α,β-unsaturated carbonyl compounds dates back to 1940s,[172] and to this day, it continues to be a versatile tool within different fields of organic chemistry. The reaction rates of this versatile approach depend on the nucleophilicity of the thiol component.[171] While thiol-maleimide [Figure 3.17, (e)] is a relevant example for protein conjugation,[173] the vinyl sulfone-thiol click reaction [Figure 3.17, (f)][70d] is serving as an important cross-linking mechanism for the synthesis of enzyme-degradable hydrogels. On the other hand, the hydrothiolation of a C=C bond [Figure 3.17, (d)], which is already known since a century,[174] has been limited to the synthesis of simple thioethers and to kinetic studies for a long time.[175] However, it re-emerged as a powerful approach with the first implementation in polymer science by means of preparing near-perfect networks and films.[176] Schlaad and co-workers were the first to name the radical-mediated thiol-ene reaction as a click reaction,[177] when they investigated the radical addition of hydrophilic and hydrophobic thiols (like mercaptan) onto the poly[2-(3-butenyl)-2-oxazoline] homo- and copolymers. In this way, the thiol-ene coupling was utilized as a versatile tool for the synthesis of tailor-made polymers.

The free-radical chain mechanism was established as the initial mechanism of thiol-ene coupling by Kharasch and co-workers.[178] Hence, typically, the thiol-ene reaction is conducted through generation of a thiyl radical from a thiol, either thermally, radically or by light initiation. Subsequently, the thiyl radical adds to the alkene in an anti-Markovnikov fashion to give an alkyl radical that, by abstraction of a hydrogen radical from the thiol, leads to the final thioether and a new thiyl radical, thus maintaining the propagation of the radical chain (Figure 3.18). In addition, to this well-established mechanism, there is a comprehensive literature on the reaction pathways and kinetics of thiols.[179]

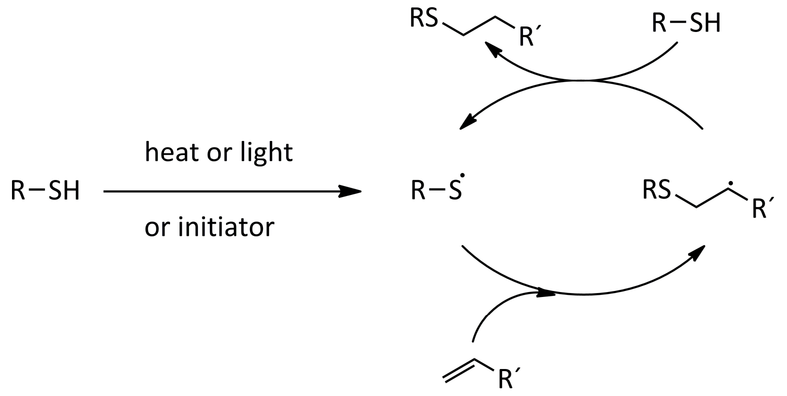


Figure 3.18: Mechanism of thiol-ene coupling induced either thermally, by light or with initiator.[178]

Notably, the thio-ene coupling can be employed under aerobic conditions with total atom economy and rapid kinetics, and without expensive and potentially toxic metal-based catalysts. Moreover, it is highly tolerant to a wide range of functional groups. Of special relevance is that thiol-ene reactions can be initiated by irradiation at a wavelength close to visible light, or can even be performed without any initiator.[149a]

As aforementioned, the free-radical addition of thiols to double bonds is a highly efficient tool in many areas of chemistry, being used for polymerizations, curing reactions, and for the modification of polymers.[180] A remarkable example was reported by Hawker *et al.*, who synthesized dendrimers up to fourth generation employing sequential thiol-ene "click" reactions and esterifications under solvent free conditions, without deoxygenation, and by 30 min irradiation with a hand-held UV-lamp (λ = 365 nm).[181] Most importantly, the dendrimer obtained after each thiol-ene coupling step was purified by simple precipitation.

In addition to the fossil-based fine chemicals, monomers and polymers that possess double bonds, vegetable oils and derivatives can be addressed as additional reactants for thiol-ene coupling. The double bonds of vegetable oils are electron-rich, thus enabling radical addition of various molecules, especially of thiols; however, when compared to olefins with terminal unsaturations, the reaction rates are slower[183] The literature survey exposes many references to reactions of fats with thiols,[182]such as the synthesis of α,ω-dicarbonylic oleic acid derivatives through thiol-ene additions using thiols and dithiols. In addition, several works were focused on the oligomerization[183] or cross-linking reactions with polyfunctional thiols.[184] Recently, the synthesis of telechelic alcohols from allyl 10-undecenoate by thiol-ene coupling with mercaptoethanol was afforded.[185] In this way, a series of telechelics with molecular weights ranging from 1.0 to 3.0 kDa and with hydroxyl, carboxyl, or trimetoxysilyl end-groups were synthesized. Meier *et al.* performed the thiol-ene addition to functionalize methyl 10-undecenoate, a derivative of castor oil, with mercaptoethanol or 1-thioglycerol (Figure 3.19).[149a] Hence, the resulting monomers were polymerized to yield polyesters with molecular weights ranging from 4.0 to 10.0 kDa. This technique was also adapted to the synthesis of di/tri-carboxylic acids used as polyanhydride precursors.[186] Moreover, the thiol-ene functionalization was also carried out onto polyoxazoline to yield polyols with controlled molecular weight and hydroxyl content.[187] In addition, the synthesis of fatty polyols as precursors for polyurethane synthesis was accomplished with the thiol-ene coupling of 2-mercaptoethanol directly on unsaturated triglycerides.[188] Recently, an UV-initiated thiol-ene coupling was carried out for the synthesis of a polyamine from an unsaturated vegetable oil and cysteamine chloride.[189]

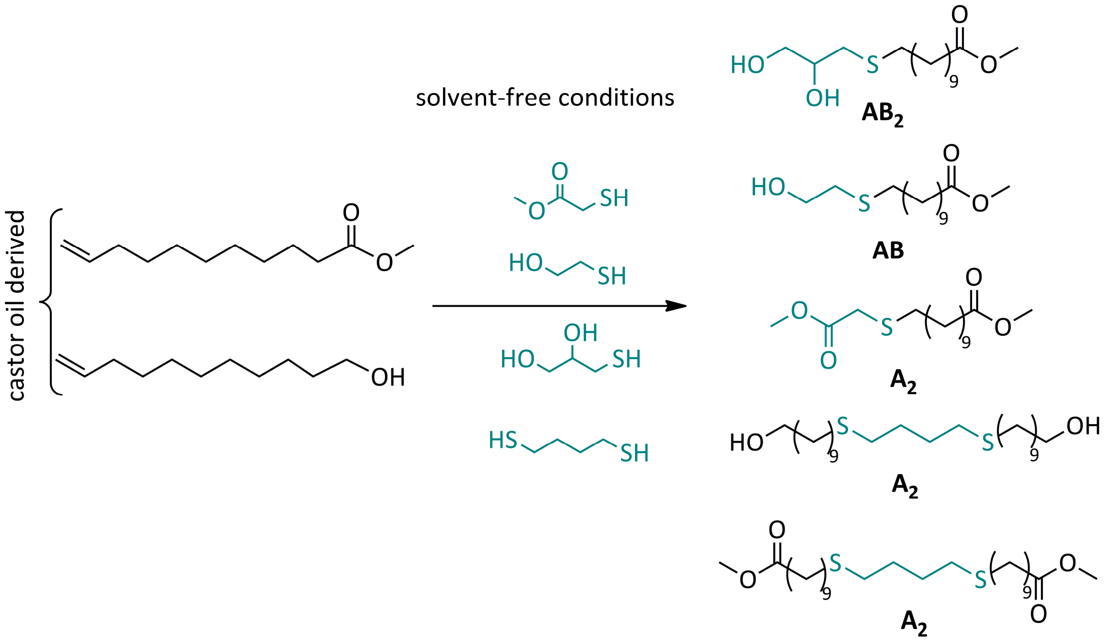


Figure 3.19: Fatty acid-based precursors for polyester synthesis via thiol-ene chemistry.[149a]

Meier et al. copolymerized fatty acid derivatives with ferulic acid (as a representative of renewable polyphenolics) derivatives in different ratios *via* thiol-ene addition with 1,4-butanedithiol.[190] The thermal analysis of the final copolymers revealed high glass transition temperature values, derived from the incorporation of high amounts of the ferulic acid derivative in the final copolymer composition.

Last but not least, polyhedral oligomeric silsesquioxanes containing thiol groups were introduced into acrylated castor oil, thus to develop a novel photocured hybrid material *via* thiol-ene chemistry with the potential in applications such as coatings.[191]

The examples described above clearly indicate that thiol–ene chemistry can be considered as an efficient tool for the synthesis of fine chemicals and monomers, as well as for the synthesis and modification of polymers derived either from natural or fossil-based sources.

4 Main Part

4.1 Acyclic Triene Metathesis (ATMET) Polymerization of *plukenetia conophora oil*: branched polymers by direct polymerization of renewable resources

Introduction

The most straightforward way of using plant oils as raw materials for the synthesis of polymers is their direct polymerization. For this purpose, the reactivity of the functional groups contained in the fatty acid alkyl chains can be used, and since plant oils are composed of triglycerides, the polymers derived from them are generally cross-linked or hyperbranched. Some popular oils like sunflower, linseed, soybean and rubber seed, which contain a variable number of double bonds in the fatty chains, have been used for the preparation of different polymers varying from alkyds,[192] polyepoxides,[193] polyesteramides[194196] or polyurethanes.[197199] On the other hand, castor oil has been used as natural polyol in the formulation of polyurethanes with good water resistancy and flexibility, however, its low functionality and the low reactivity of the secondary alcohol groups lead to semi-flexible and semi-rigid materials.[49] Furthermore, castor oil is an industrially relevant oil and its derivatives have recently received much attention as building blocks for a large variety of different polymers.[44] However, due to the competitive use of some of the mentioned oils, the use of commercially less developed oils might provide an opportunity to develop new value added products. *Plukenetia conophora* (PKC) is a climbing shrub that is common in the South-western part of Nigeria, Cameroon, Gabon, Sierra Lone and Benin Republic.[200] The seeds are eaten like walnuts and the leaves are also edible. Furthermore, the seeds, which contain about 50% oil, are also traditionally used for curing headache.[200] The physico-chemical characterization of the seed oil[201] has shown that it is best employed for industrial rather than for edible purposes. Moreover, PKC oil, which consists of 98.0% unsaturated fatty acids made up of mainly 70.3% of linolenic acid, has been reported to belong to the drying oil group and might be a substitute for linseed oil (Table 4.1).[201]

Table 4.1: Typical *plukenetia conophora oil* composition.[201]

Fatty acid	Mol percentage (%)[201]
Palmitic	0.8
Stearic	0.6
Oleic	10.7
Linoleic	17.0
Linolenic	70.3

Over the last 20 years, researchers have investigated the synthesis of highly branched three-dimensional macromolecular architectures, since these are considered candidates for tailor made materials with high performance and/or novel functionality due to their unusual and unique physical and chemical characteristics.[202] Several reviews have been written on the topic discussing interesting details on the history and current trends in hyperbranched polymers.[202204] Generally, this type of polymers can be synthesized by step-growth polymerization of multifunctional monomers,[202, 203,205-207] copolymerization of conventional monomers *via* self-condensing vinyl polymerization,[208,212] or copolymerization of vinyl monomers in the presence of multifunctional vinyl co-monomers.[213,214] “Living”/controlled radical polymerization approaches have also been used to synthesize a variety of hyperbranched molecules with controlled compositions and variable functionality.[215,220] Recently, Gorodetskaya *et al.* have introduced the acyclic diene metathesis (ADMET) polymerization as an alternative method for the synthesis of hyperbranched macromolecules of AB_n monomers with one terminal and two or more acrylic olefins,[221] an approach that was used short after by Xie *et al.*[222] for the synthesis of hyperbranched *azo*-polymers. Building on these findings, Meier and co-workers reported the first synthesis of star-shaped polymers *via* ADMET using Hoveyda-Grubbs 2nd generation catalyst (**C5**). This was possible by polymerization of a castor oil-based AB monomer containing a terminal double bond and an acrylate in the presence of glycerol triacrylate as core molecule. Moreover, the molecular weight was efficiently controlled by choosing the desired monomer/core molecule ratio. Work in the same group dealt with the development of a simple way to synthesize branched macromolecules from an A_3 monomer derived from castor oil. This monomer, a triglyceride containing three terminal olefins, was polymerized *via* olefin metathesis in a procedure that was termed acyclic triene metathesis (ATMET) polymerization. Moreover, cross-linking was prevented by adding methyl acrylate as chain-stopper, which thus remained at the end groups providing a direct access to end-functionalized hyperbranched polyesters.[223] Larock and co-workers applied the olefin metathesis directly on the commercially available unsaturated plant oils in the presence of 0.1 mol% Grubbs 1st generation catalyst (**C3**).[224] Furthermore, Meier and co-workers reported the solvent-free ATMET synthesis of highly branched and functionalized polyesters taking commercially available native high oleic sunflower oil (over 92% of oleic acid, monounsaturated).[225]

In view of the high oil content of the seed, the fatty acid composition of the oil and in line with our interest of using renewable feedstock, the aim of this work is to continue investigations regarding the opportunities of using metathesis polymerization for the synthesis and characterization of highly branched polymers by direct ATMET polymerization of PKC oil.

Results and discussion

The pioneering work of Boelhouwer and co-workers opened a new route towards producing many valuable chemicals *via* the metathesis of fatty acids and derivatives of commonly available plant oils.[226] In this respect, self-metathesis and acyclic diene metathesis polymerization of plant oils have been widely reported in the literature.[223,227-229] However, little is reported on the direct polymerization of plant oils *via* metathesis. Considering this, *Plukenetia conophora* oil (**PKCO**), a highly polyunsaturated seed oil consisting of about 70% linolenic acid, has the potential to be polymerized *via* ATMET (Figure 4.1). From a chemistry point of view all different double bonds of **1**, as shown in Figure 4.1, have very similar reactivity. Thus, since olefin metathesis is an equilibrium reaction, when a metathesis catalyst is added to **1**, an equilibrium of oligomers of **1** should be formed as schematically outlined in Figure 4.1. The first step of this step-growth polymerization is the formation of a dimer, such as **2,** and an alkene as condensation product. If not the ω–9 double bonds are reacting as depicted in Figure 4.1, but two ω–3 double bonds of the triglycerides react, a lower molecular weight condensation product (3-hexene in this case) with lower boiling point is formed. Of course, all intermediate situations are also occuring and thus five different dimers and also five different condensation products can be formed. For example, the cross-metathesis of a ω–3 double bond of a linoleic acid moiety with a ω–9 double bond of an oleic moiery can form 3-dodecene. Moreover, self- metathesis of linoleic acid residues will result in the formation of 1,4-cyclohexadiene *via* ring-closing metathesis.[230]

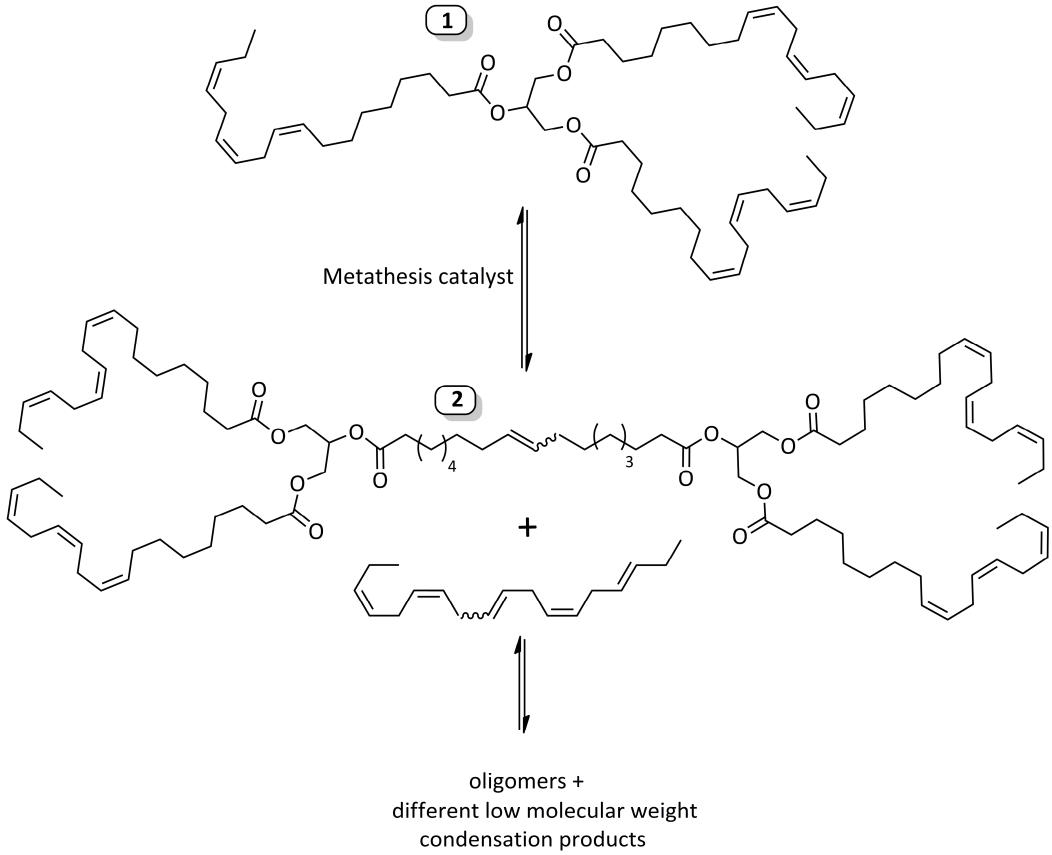


Figure 4.1: Major triglyceride of *Plukenetia conophora* oil and the schematic representation of oligomerization and polymerization of **1**.

These considerations are important for the further discussion, since this behaviour is very different from the recently reported polymerization of high oleic sunflower oil, where only 9-octadecene can be formed as a condensate.[225] In sharp contrast, the possible formation of 1,4-cyclohexadiene and 3-hexene in equlibrium during the polymerization of **PKCO** allows for an easy removal of these condensation products due to their low boiling points and in consequence simplifies the polymerization procedure and does not require high vacuum. The ADMET polymerizations of PKCO were performed in collaboration with C. O. Akintayo.

PKCO was polymerized *via* olefin metathesis under different conditions using different metathesis catalysts in order to study the molecular weight variations of the resulting polymer. Since the catalyst has a prominent effect in olefin metathesis reactions, initial studies have been focussed on the evaluation of the different Ru-benzylidene and indenylidene catalysts (Table 4.2).

Table 4.2: Polymer characteristics at different reaction condition using different metathesis catalysts.

Sample	Catalyst[a) b)]	T (°C)	M_w[c)] (kDa)	Mn[c)] (kDa)	PDI[c)] (M_w/M_n)	Conversion[c)] (%)
P1	**C5**	70	28.7	7.3	3.94	86.0
P2	**C5**	90	28.8	7.4	3.90	80.3
P3	**C4**	70	19.2	6.5	2.95	84.5
P4	**C4**	90	19.9	6.6	3.02	85.6
P5	**C11**	70	11.7	5.1	2.30	81.0
P6	**C11**	90	14.2	5.5	2.58	82.4
P7	**C12**	70	15.0	5.4	2.78	85.8
P8	**C12**	90	15.1	6.1	2.48	86.0
P9	**C12**	110	26.2	6.7	3.91	88.3

a) 1.5 mol% catalyst/triglyceride; b) Additional conditions applied during polymerization: N_2 purging for 10 minutes during the polymerization; c) data obtained from GPC performed in THF relative to PMMA calibration.

Recently, investigations performed by Meier and co-workers based on the ATMET of the unsaturated model trygliceride glyceryl triundec-10-enoate and high oleic sunflower oil, have revealed that the best results concerning reaction conditions and yields were obtained using the Hoveyda-Grubbs 2nd generation catalyst (**C5**).[223,225] Thus, the ATMET of **PKCO** has first been carried out in bulk in the presence of 1.5 mol% **C5** at different reaction conditions (compare entries 1-2 in Table 4.2). The increase of reaction temperature from 70 to 90 °C had a marginal effect on the reaction (compare Table 4.2, entries 1 and 2). According to GPC analysis, conversions of the investigated polymerization reactions were all >80% (Table 4.2 and Figure 4.2).

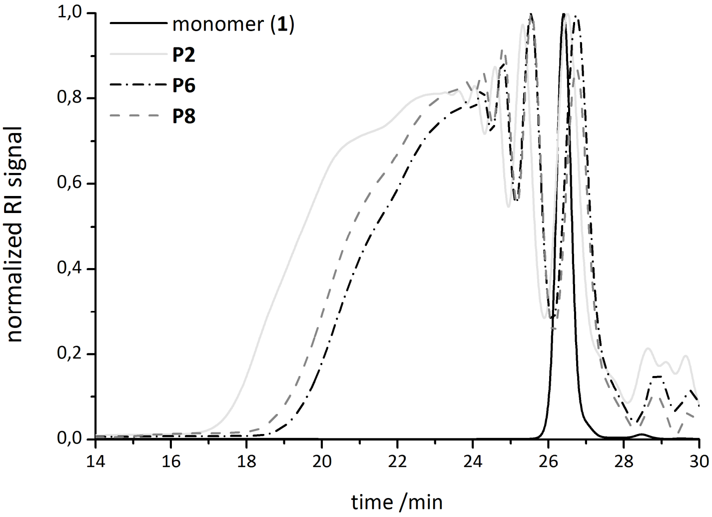


Figure 4.2: GPC traces of crude reaction mixtures obtained from monomer **1**, and polymers **P2**, **P6**, and **P8**.

Subsequently, **C4** was tested for the polymerization of **1** (compare **P3** and **P4** in Table 4.2). Unlike **P1** and **P2**, the polymers obtained from the ATMET reaction of **PKCO** with **C4** possessed similar M_n values and lower PDI indexes, indicating more defined structures. Also with this catalyst quite high conversion could be obtained. Along with the well known Ru-benzylidene catalysts, the activity of Ru-indenylidene-based catalysts $M3_1$ (**C11**) and $M5_1$ (**C12**) were examined. These catalysts led to the formation of polymers, but the molecular weights were somewhat lower. It is interesting to note that in case of **C11** at 70 °C, a rather defined branched polymer was obtained having a PDI value of only 2.3 (compare Table 4.2, **P5**). In an attempt to further increase the molecular weight of the hyperbranched macromolecules, all catalysts were also investigated at 90 °C. However, this further increase of the polymerization temperature only resulted in slightly increased molecular weights for **C11** and **C12**. On the other hand, when **C12** was investigated at 110 °C, a clear increase in the molecular weight was observed on increasing the temperature from 70 °C to 110 °C. Moreover, it is important to point out here that no gelation was observed for any of these reactions, most likely due to the presence of about 11% of oleic acid in **PKCO**, which gives the high boiling 9-octadecene as condensation product, which is not removed during the polymerization. Thus, 9-octadecene remains in the polymerization mixture and can still participate in metathesis reactions, thus effectively acting as a chain stopper. Moreover, the presence of small amounts of saturated fatty acids will also efficiently act as chain stoppers.

Figure 4.3 shows the ^{1}H NMR spectrum of polymer **P2**. Notably the spectrum of the branched polymers is similar to its monomer (**PKCO**) as their structures are similar; the spectra thus only differ in the peak intensities. Interestingly, the bisallylic hydrogens at 2.8 ppm in the pure PKCO have disappeared after the reaction. This can easily be explained by the formation of 1,4-cyclohexadiene as condensate during metathesis of linoleic and linolenic acid derivatives.[230] Moreover, one could expect that the resonance signals at 0.98 ppm of protons corresponding to ω-1 terminal methylene group of linoleate will diminish due to the formation of 3-hexene as a condensate. On the other hand, the ^{1}H NMR spectra of **P2** shows two new overlapping peaks -two triplets- around 0.95 ppm, which might correspond to the *cis* and *trans* configurations of the possible end-group **EG$_1$** as represented in Figure 4.4. The presence of this end group was confirmed with ^{13}C NMR and additional 2D-NMR, ^{1}H,^{1}H-COSY and heteronuclear multiple-quantum correlation spectrum (HMQC) experiments. The double bond has a marked influence on the easily recognized ω-1 to ω-3 signals. Furthermore, it is well know that if the the double bond is sufficiently far from the acyl function and from the end methyl group in any unsaturated trigyleride, the two olefinic carbon atoms have the same chemical shift. In our case, for the another possible end group **EG$_3$** shown in Figure 4.4, these olefinic carbons were observed in ^{13}C NMR at ~ 129.7 and 130.1 ppm for *cis* and *trans*, respectively. On the other hand, in case of end group **EG$_1$**, the olefinic group positioned at carbon ω-3 has two chemical shifts; thus ω-3 and ω-4 carbons show resonances at 131.9 and 129.1 ppm, respectively. Moreover, resonances arising from the carbon atoms adjacent to the double bond indicate the position of the double bond. Thus, the allylic carbon ω-2 in **EG$_1$** appears at 20.4 ppm in comparison to allylic carbons in **EG$_2$** and **EG$_3$** which appear at ~27 ppm.

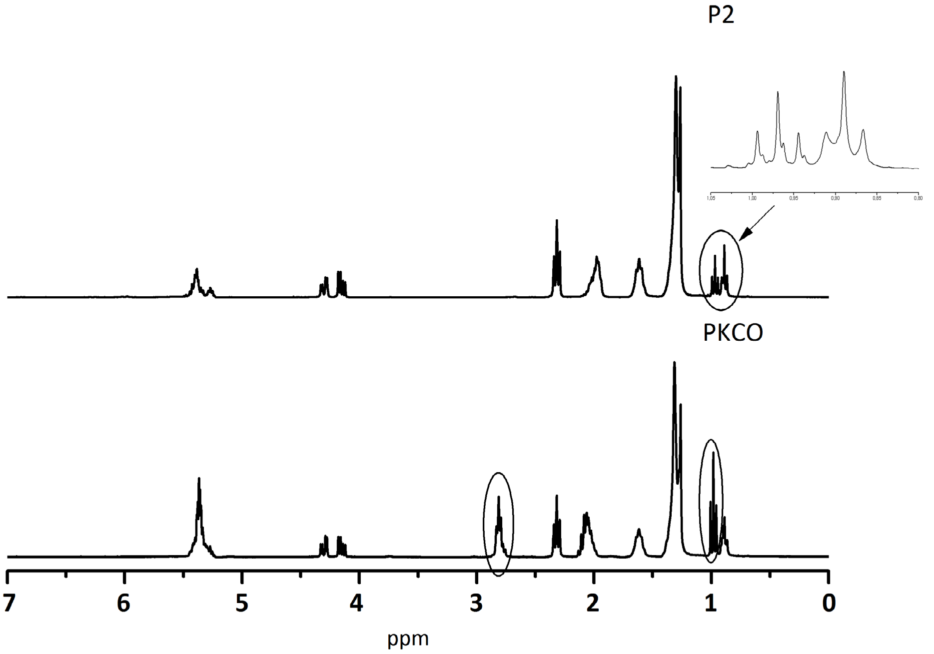


Figure 4.3: ^{1}H NMR spectra of the product obtained from the ATMET polymerization of **1** (**PKCO**) in the presence of **C5** (top, **P2**, see Table 2) and pure **PKCO** (bottom).

Additionally, the chemical structures of the hyperbranched macromolecules were also analyzed by GC-MS after a transesterification reaction of the polymer with methanol. The GC-MS profile of **P2** after this degradation *via* transesterification clearly reveals the ester corresponding to **EG$_1$** (methyl 9-dodecenoate), which showed the molecular ion at 213 *m/z* at 8.4 min retention time (Figure 4.5). Furthermore, in the view of the GC-MS results of the transesterification reaction of **P2,** the possible repeating unit and the end groups of the hyperbranched structures were proposed (Figure 4.4). These results confirm that oleic acid residues acted as chain-stoppers and are present as end-groups in the prepared polymers. Moreover, the presence of **EG₁** confirms ring-closing metathesis reactions to form 1,4-cyclohexadiene as a condensate.

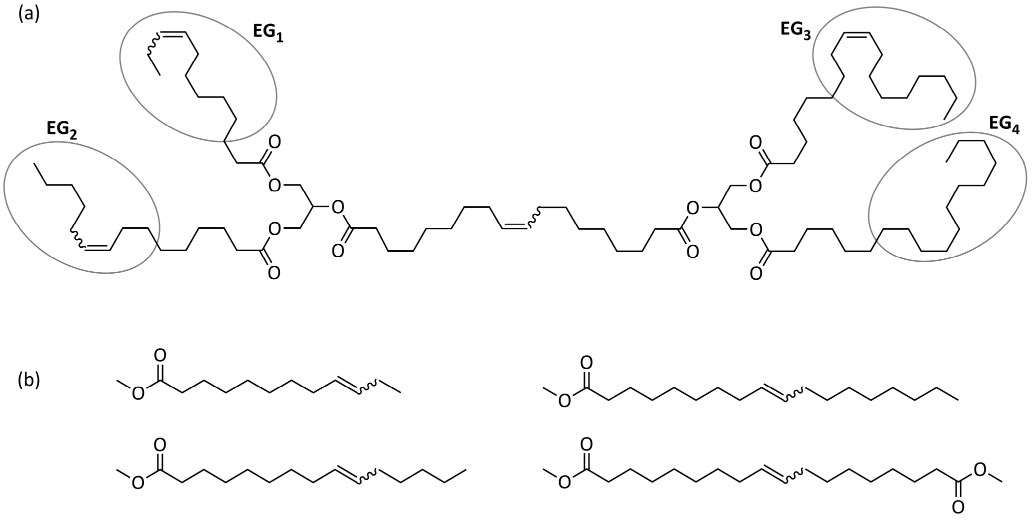


Figure 4.4: Schematic illustration of: a) the possible end groups by ATMET and consequent secondary metathesis reactions; b) the major methanol transesterification products of **P2**.

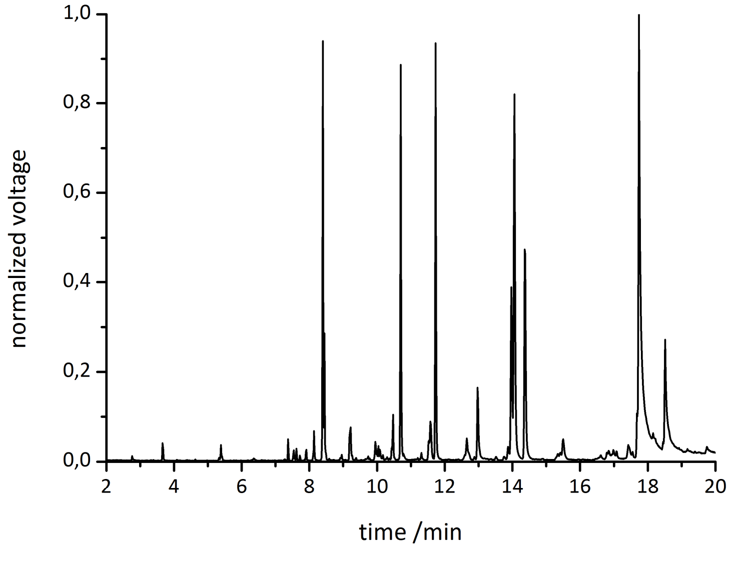


Figure 4.5: GC-MS profile of transesterified **P2.**

NMR spectroscopy is an important tool for the characterization of the hyperbranched structures, since detailed analysis of the spectra permits calculation of the degree of polymerization. Thus, in order to determine the degree of polymerization, the crucial point is to determine the ratio of terminal methyl protons of the fatty acid chain *E* (–CH_3, Figure 4.3, 0.89-0.98 ppm) and glycerol units *G* (-CH_2O-, Figure 4.3, 4.15-4.30 ppm). In the case of pure **PKCO** oil, *E* = 3 and *G* = 1, and thus, the ratio *E/G* equals 3. Furthermore, as more triglyceride molecules react with each other without intramolecular cyclization, the ratio of *E* to *G* should decrease and ultimately reach a 1:1 ratio for an idealized macromolecular structure with increase in molecular weight. Thus, considering this idealized polymerization, the ratio of *E/G* should follow the general rule *(x+2):x*, where *x* is the degree of polymerization of **PKCO**.[225] Analysis of the data in Table 4.3 indicated that the highest degree of polymerization was observed for **P9**, which was synthesized in the presence of **C12** at 110 °C. Indeed, this result is consistent with the GPC results (compare Table 4.2, **P9**). On the other hand, intramolecular cyclization can be expected during the polymerization of **PKCO**, as also reported in the literature.[223-225] If there was at least one macrocycle in the structure due to the possible ring-closing metathesis between the internal double bonds, the ratio of *E/G* will be *x:x*, and in case of two intramolecular cycles: *(x+2):x* and so on. Thus, the calculated DPs in Table 4.3 are most likely heavily underrepresented.

Table 4.3: Characterization of branched macromolecules obtained from ATMET.

Entry	***E/G*1)**	***DP*b)**
P1	1.56	3.6
P2	1.64	3.1
P3	1.76	2.6
P4	1.50	4.0
P5	1.80	2.5
P6	1.75	2.7
P7	1.61	3.3
P8	1.68	3.0
P9	1.44	4.6

a) Ratio of end groups *E* (-CH_3) and glycerol units *G* determined by ^{1}H NMR; b) Degree of polymerization of **PKCO** estimated from the ratio *E/G=(x+2):x*, where *x = DP*.

The behavior of these polymers as highly branched macromolecules can be conclusively confirmed by the specific solution properties. Thus, DLS and SLS were used as complementary methods to characterize the dilute solution properties of the hyperbranched macromolecules. Static light scattering (SLS) was performed with **P2** in order to get more information about the weight average molar mass of this sample. Initially, refractive index increment (d*n*/d*c*) analyses were performed for **P2** in toluene, THF and DMAc, since it was necessary to determine these values for the purpose of precise SLS measurements. The obtained value in toluene was quite low, -0.014 mL/g, and since *dn/dc* was lower than 0.050 mL/g, the intensity of the scattered light was too low. On the other hand the *dn/dc* value of **P2** in DMAc was measured as 0.036 mL/g. Since the intensity of the scattered light did not change with scattering angle, the measurements for **P2** were performed at the angle of 90°. However, an evaluation of the Zimm plot for **P2** was not possible. The polydisperse nature of the solvent/solute system may have contributed to the abnormal shape of the Zimm plots from the static data. As expected, SLS measurements are more sensible to the presence of the aggregates, which leads to a larger intensity of the scattered light and consequently to the higher values of the weight average molar mass.

DLS was then used to investigate the size of the macromolecules and the influence of different types of solvents on the hydrodynamic radius of the sample in the solution and to study the ability of aggregate formation in THF, toluene and DMAc. From the results obtained by the intensity, volume, and number distribution it can be observed that the presence of the aggregates can be detected in the sample both in THF and toluene solutions. The size distribution histogram of **P2** in THF showed a bimodal distribution. The presence even of the small amount of the aggregates led to the high scattering of the light, which further induced the appearance of the second distribution of the peaks in the graph for the intensity distribution. A similar behaviour, with even higher aggregate size, was observed from the results obtained for **P2** in toluene. On the other hand, when the analysis was performed in DMAc as a solvent, the presence of aggregates was not detected in the number distribution of **P2,** from which it is possible to determine the number of molecules of different sizes (Figure 4.6). The NICOMP calculation revealed that these particles have a mean diameter of 6 nm (99.5% in the present DLS sample of **P2)**. The volume of this specific molecule was calculated from the volume distribution as 86.1%.

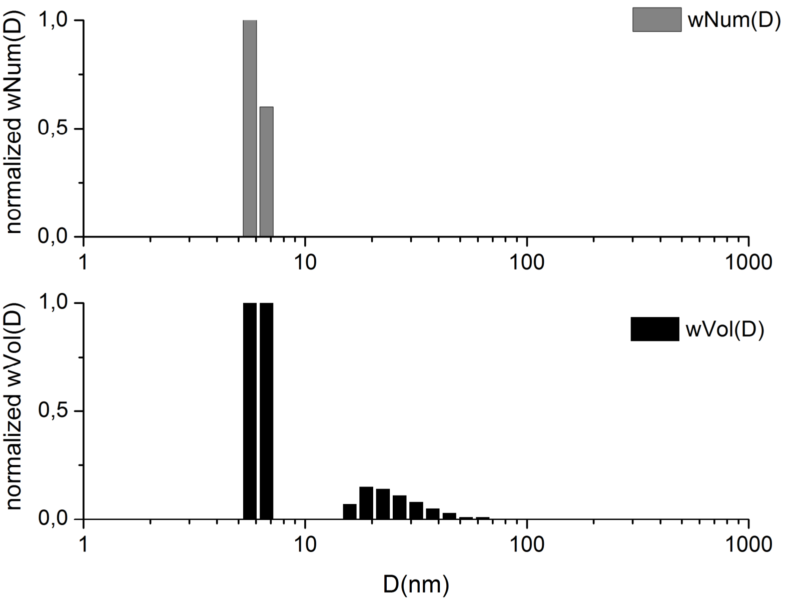


Figure 4.6: Number and volume distributions of **P2** in DMAc solution at 25 °C by DLS analysis with an advanced evaluation method.

The dimensionless shape parameter ρ defined as $\rho = R_g/R_h$, is often used to describe the structure of macromolecules in solution.[231] The type of structure (sphere, rigid rod, flexible coil), the nature of the solvent, the segment density in the polymer chain and the dispersity of the system are important parameters are influencing the value of ρ. Many previous experimental results have verified that the ρ value is in the range of 1.50−1.70 for flexible linear polymers in a good solvent,[231] whereas the value is 0.78 for a homogeneous sphere. On the basis of a Kirkwood approximation for the hydrodynamic interaction,[42] the ρ parameter for hyperbranched structures was theoretically predicted as 1.22. In our case, the value of ρ was 0.50, suggesting that **P2** does not possess a high degree of branching.

Hyperbranched polymers find potential applications in drug delivery, coatings and as rheology modifiers for processing,[232,233] this serves as a strong driving force for studying the rheology of the synthesized polymers. Thus, rheological experiments were performed on **P2** as a model compound. An important first step in performing dynamic rheological characterization is to determine the linear viscoelastic (LVE) region of materials in which dynamic rheological parameters are independent of applied strains. In order to determine the LVE region for **P2**, dynamic strain sweep experiments were performed at 0.1, 1.0 and 10.0 Hz from 1 to 1000% strain amplitude. Figure 4.7 shows the strain dependence of storage (*G*′) and loss moduli (*G*″) of **P2** at 25 °C with a frequency of 1.0 Hz. The LVE region is valid for the whole strain amplitude measured. No non-linear behaviour, e.g. shear-thinning, occurs. Due to the difference of *G″* and *G′* of about two decades, the sample behaves predominantly viscous. Thus, the structural character of **P2** can be determined by comparing the *G´* and *G´´*. The frequency dependence of the storage and loss modulus of **P2** measured by dynamic frequency sweep experiments within LVE range is depicted in Figure 4.8. For low frequencies, vanishing values for the storage modulus *G*′ were obtained, at the limit of the sensitivity of ARES-G2 rheometer indicative of the dominant viscous response of the material. Besides this, **P2** showed no crossover in *G´* and *G´´* at higher frequency values, indicating that there is no transition from viscous-like deformation behaviour to a more elastic one.

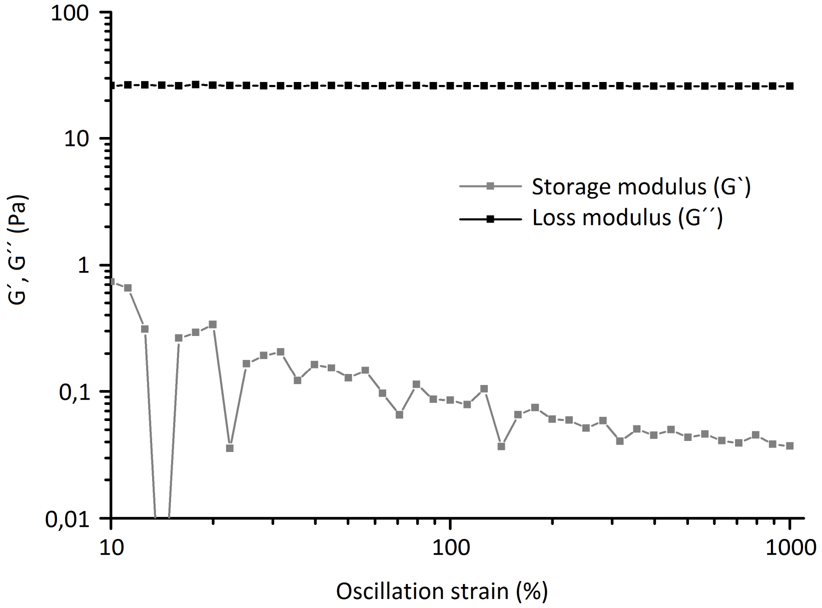


Figure 4.7: Strain dependence of storage modulus (grey line) and loss modulus (black line) of **P2** at 25 °C and 1.0 Hz.

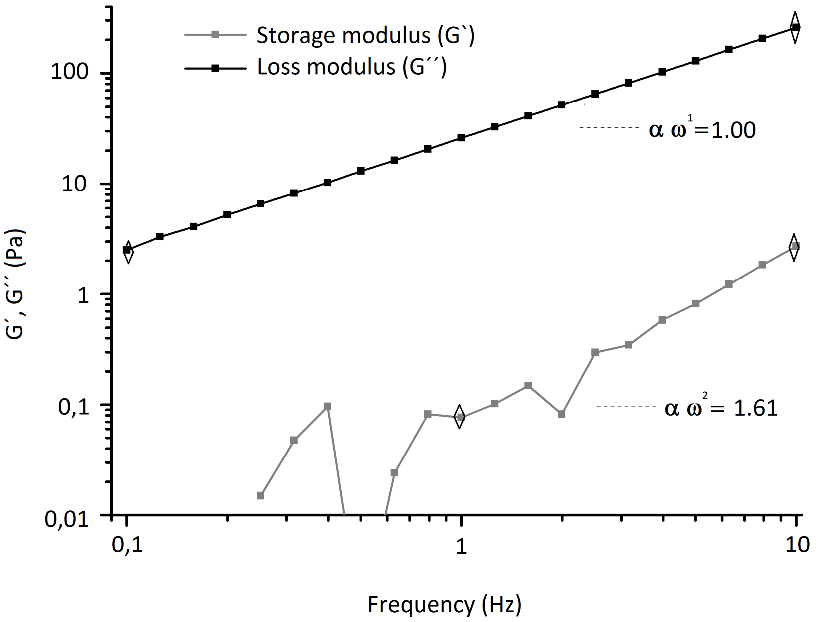


Figure 4.8: Frequency dependence of *G′* and *G′′* for **P2** measured at 25 °C applying f = 0.1-10.0 Hz, γ_0 = 100%.

Polymer **P2** showed a Newtonian behavior, i.e. the melt viscosity was not affected by the shear rate within the shear range tested, which indicates an absence of chain entanglements. This behavior was also justified with the continuous constant loss modulus over a wide frequency range with a slope of 1.00, which was 1-2 decades higher than the storage modulus. Moreover, it has already been reported that the lack of entanglement of the dendritic macromolecules leads to their Newtonian behaviour.[234] The viscosity of the polymer was determined by steady shear measurements (shear rate from 0.05-10 s^{-1}) as 4.1 Pa-s.

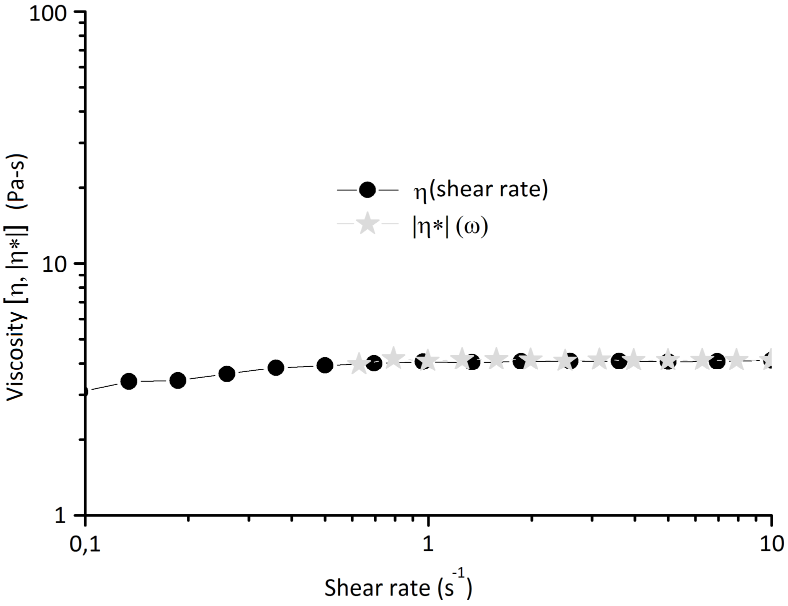


Figure 4.9: Comparison of η and |η*| for polymer **P2** at 25 °C.

Another commonly reported rheological feature of dendritic polymers is the possible correlation between the oscillatory viscoelastic properties and steady shear viscosity. Cox and Merz gave one very simple rule, known as the Cox–Merz rule, which predicts that complex viscosity, $\eta^*(\omega)$, and steady shear viscosity, $\eta(\dot{\gamma})$; are the same value at the same deformation rate.[235] To test the applicability of the Cox-Merz rule in this present investigation, the shear viscosity and the complex viscosity, which were obtained at 25 °C, were compared for **P2** (Figure 4.9). The result given in Figure 4.9 agreed well with only a slight deviation, indicating that the investigated polymers are indeed rheologically simple and not cross-linked.

Hyperbranched polymers are usually formed by very short and dense branches, which completely prevent crystallization and molecular entanglement.[236] On the other hand, it has been reported that hyperbranched polyesters terminated with long-enough alkyl chains not only have a lower T_g, but show several different crystalline phases since the length of the linear parts is sufficient for formation of crystalline domains.[237] The performed X-ray studies by Hult *et al.* on AB_2 monomer-based hyperbranched polyesters showed that hyperbranched macromolecules with long terminal alkyl chains crystallize *via* intramolecular interactions, whereas in the case of hyperbranched polyesters with shorter alkyl chains the crystallization takes place intermolecularly by the interpenetration of end-groups from adjacent molecules.[238]

Table 4.4: Thermal results of all prepared polymers.

Entry	T_g (°C)[a)]	T_m (°C)[a)]	$T_{5\% \text{ loss}}$ (°C)[b)]
P1	-64.3	-0.2	292.0
P2	-61.5	-0.9	330.5
P3	-52.1	-0.8	314.6
P4	-57.9	-0.1	309.8
P5	-60.4	-6.1	297.0
P6	-64.1	-1.5	318.0
P7	-49.1	-0.3	301.0
P8	-	-1.9	324.0
P9	-66.5	0.5	316.5

[a)]DSC data; [b)] Onset degradation temperature (5% weight loss)

In our case, the DSC analyses showed melting peaks during the second heating scans for all polymers (Table 4.4). Among all polymers, **P5** showed the lowest melting transition temperature at -6 °C. The rest of the polymers, regardless of structural variations for this series of samples, had melting transitions in the range of -1.9 °C.

From the results in Table 4.4, it can be seen that these hyperbranched polymers display acceptable thermal stability under nitrogen. Under the given experimental conditions a measurable mass loss ($T_{5\% \text{ loss}}$) of the polymers starting between 290 and 330 °C was detected. Therefore, it can be concluded that in these samples, below 290 °C, no measurable amount of evaporable compounds were present. As already mentioned, the consequence of intramolecular metathesis reactions during the polymerization is the formation of the cyclic structures. However, these small molecules are most likely evaporated at the temperature used in the polymerization reactions (compare Table 4.3 and Table 4.4).

Conclusions

The presented approach thus allows the preparation of polymeric materials that are fully along the lines of green chemistry. These imperfectly branched, dendritic structures were shown to have special structural and rheological properties that might lead to potential applications in various areas, such as rheology modifiers and drug deliver

4.2 Acyclic Triene Metathesis (ATMET) polymerization of soybean oil modified with 4-vinylbenzene sulfonic acid

Introduction

Although plant oils naturally contain functional groups such as double bonds and hydroxyl groups, their reactivity towards polymerization is often limited. For this reason, the introduction of polymerizable functional groups in their structure opens the way to a wider range of plant oil-based polymeric materials. Among many different efficient approaches that use the reactivity of double bonds, the epoxidation is one of the most used ones. This reaction is performed industrially with H_2O_2 and acetic or formic acid in the presence of strong mineral acids (H_2SO_4 or H_3PO_4),[239] but also other catalysts can be employed with better results in low-scale reactions such as methyltrioxorhenium,[240] ammonium molybdate,[241] ion exchange resins[242] or Venturello's catalyst.[243] Phase transfer catalysts such as quaternary ammonium tetrakis(diperoxotungsto) phosphates[244] and crown ethers[245] improve the selectivity and increase both conversion and yield. Furthermore, the lipase-catalyzed chemoenzymatic epoxidation is a highly efficient alternative that works at mild temperatures.[246] Moreover, since the enzymes can be immobilized in cross-linked supports, their removal from the reaction mixture *via* filtration of the reaction mixture is straightforward and allows for catalyst recycling.

The oxirane rings of epoxidized plant oils are highly reactive towards nucleophiles and thus can be used to introduce polymerizable groups. Moreover, once the epoxides are opened, the hydroxyl functionalities formed can be used for further functionalization or left in the structure to provide specific properties to the final polymers. Thus, as an example, epoxidized soybean oil (ESO) has been converted to its acrylate ester with acrylic acid, to its cinnamate ester with cinnamic acid, and to its maleate ester with monomethyl maleate among other transformations. These esters can be free-radically polymerized or copolymerized with reactive diluents, such as styrene, to give thermoset resins having mechanical properties that are similar to those of commercially successful polyester and vinyl ester resins.[247-250]

The reaction of different epoxy compounds with arene sulfonic acid yielding 1-arylsulfanyloxy-2-alkonols has been reported in literature.[251-253] Thus, in this work, a new triglyceride-based monomer was synthesized by the reaction of ESO with 4-vinylbenzene sulfonic acid (4VBSA, Figure 4.10). The product, 1-(4-vinylbenzene sulfonyl)oxy-2-alkonols of epoxidized soybean oil (SESO), contains styrenic moieties that can be polymerized in the presence of metathesis initiators *via* ATMET (Figure 4.11). As mentioned in Chapter 3, the Grubbs 1st generation catalyst (**C3**) is highly reactive but lacks functional group tolerance. Therefore, the 2nd generation catalysts such as Grubbs 2nd generation (**C4**), Hoveyda-Grubbs 2nd generation (**C5**) catalysts, and **C12** are usually better suited for ADMET polymerization of functionalized monomers.[254] Motivated by the well-known good characteristics of the ADMET reaction, it was reasoned that SESO would be well suited to synthesize vegetable oil-based polymers *via* this method. Compared to the direct ATMET polymerization of *Plukenetia conophora* oil, the approach proposed here, which is based on the previous modification of the plant oil's structure, presents both disadvantages and advantages. On one side, the epoxidation and ring-opening reactions are extra steps before the polymerization, however, this modifications allow the introduction of functional groups that otherwise would not be possible.

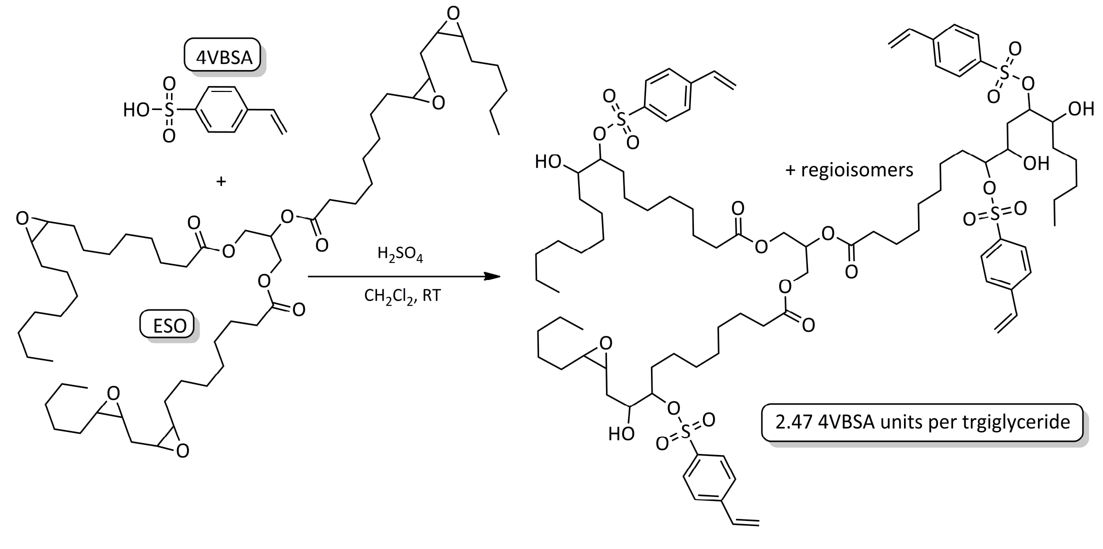


Figure 4.10: Schematic representation of the new monomer and its polymerizations.

Result and discussion

In order to determine whether catalysts **C3**-**C5** and **C12** tolerate the functional groups present on SESO, a monofunctional model compound was synthesized by reaction of epoxidized methyl oleate (EMO) with 4VBSA. This monomer (SEMO) contains all the functional groups in SESO and can be used as ^{1}H-NMR model. ADMET dimerization of SEMO proceeded as expected and a singlet peak at ~7.00 ppm corresponding to the vinyl protons in the ^{1}H-NMR verified the production of SEMO dimer. The reaction is shown in Figure 4.11.

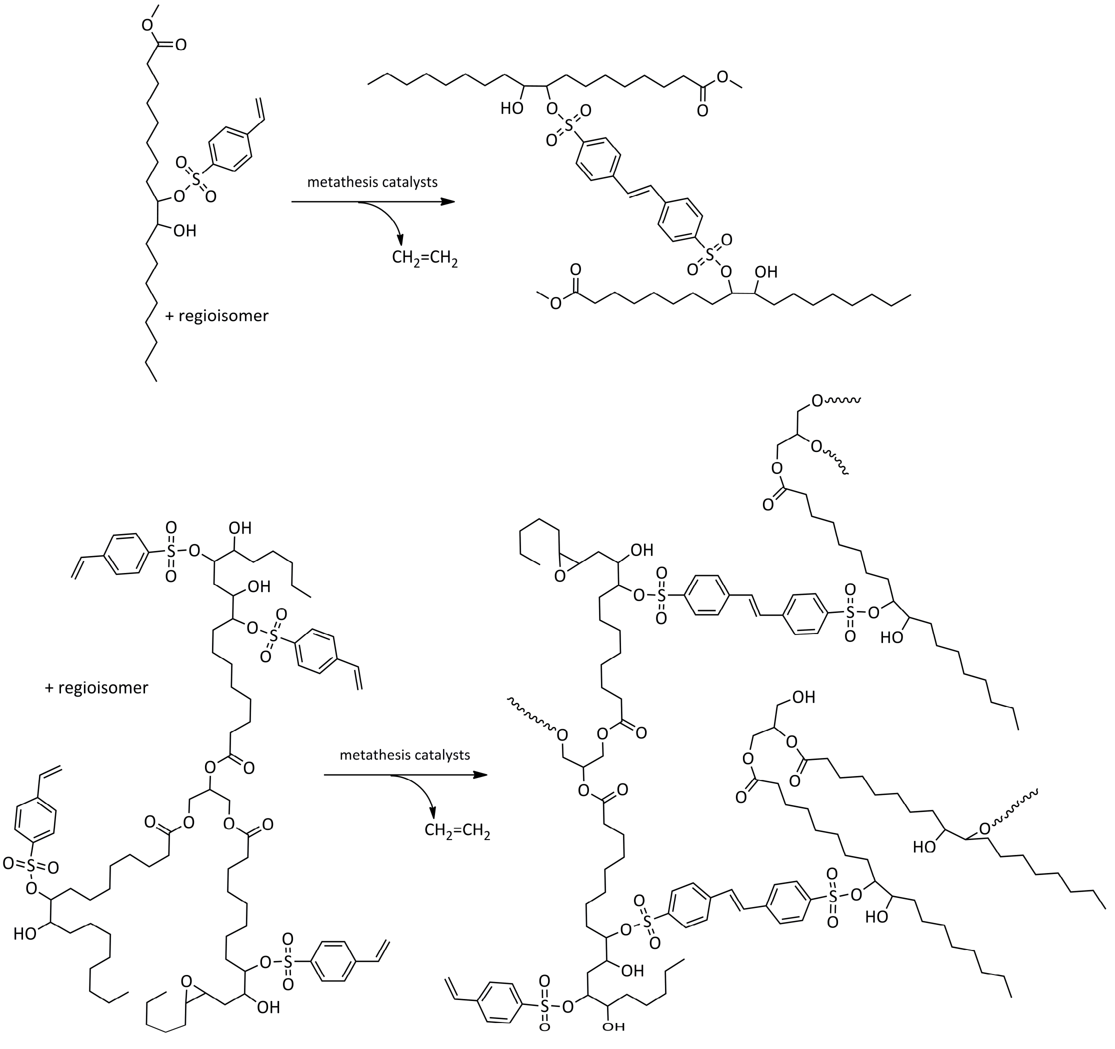


Figure 4.11: ADMET dimerization of SEMO and ADMET polymerization of SESO.

Table 4.5: ADMET polymerization of SESO: conditions, yields, and thermal properties.

Entry	Catalyst (mol%/double bond)	T (°C)	Conditions	time	Yield %	T_g (°C)
P1	**C3**, 0.5 mol%	40	CH_2Cl_2	19 h	65.4	-12.5
P2	**C4**, 0.5 mol%	40	CH_2Cl_2	18 h	79.4	-11.9
P3	**C5**, 0.5 mol%	40	CH_2Cl_2	12 h	80.3	-11.3
P4	**C12**, 0.5 mol%	40	CH_2Cl_2	10 h	81.4	-11.6
P5	**C5**, 0.5 mol%	115	Bulk	15 min	87.2	-1.6
P6	**C12**, 0.5 mol%	115	Bulk	30 min	84.5	-1.5

The ADMET reaction of SESO was carried out in solvent (CH_2Cl_2) at 40 °C, since the neat viscous monomer was immiscible with the any of the catalyst at that temperature. It was already reported that high viscosity, due to the absence of solvent can be a limiting factor, as the efficiency of ethylene removal is critical toward the success and extent of polymerization.[16] Catalysts **C3**-**C5** and **C12** were used for these polymerizations, to be able to compare the activity of catalysts of different generations. The results of this screening are summarized in Table 4.5. During these polymerization reactions, a continuous viscosity increase was observed. The GPC chromatogram in Figure 4.12 shows the gradual increase of the molecular weight during the synthesis of **P1** (Table 4.5, entry 1). After 2 hours of reaction time, the polymer products were no longer completely soluble in THF, thus no further analysis *via* GPC was possible.

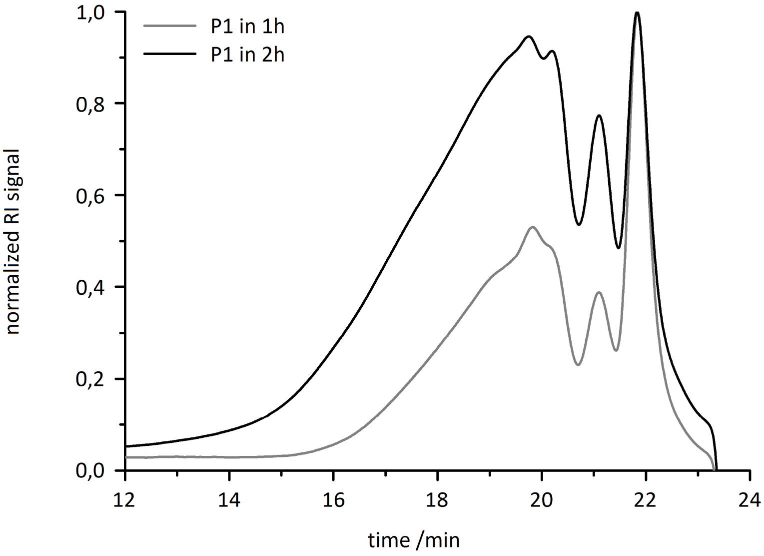


Figure 4.12: GPC data for P1 in 1 and 2 h reaction time.

Table 4.5 shows that **C3** gave the lowest conversion most probably due to its limited functional group tolerance. The use of the more stable catalysts **C4**, **C5** and **C12** provided more satisfactory results in short reaction times. The ^{1}H NMR spectra of the soluble part (oligomers and unreacted monomer) of the obtained polymers showed in all cases a distinct singlet for the double bond conjugated to the benzene rings at ~ 7.10 ppm, which clearly indicated the on-going polymerization.

The reactivity of the monomer used towards ADMET was also investigated under bulk conditions. It was observed that due to the high melting point of the monomer, a reaction temperature of 115 °C was required and this high temperature was incompatible with the thermal stability of **C3** and **C4**. However **C5** and **C12** showed better stability and provided good results under these conditions Bulk polymerization proceed at a much faster rate than solution polymerization, due to the higher temperature used.

An insoluble network polymer was obtained in the ATMET polymerizations of SESO with catalysts **C3**-**C5** and **C12**. Although all performed polymerizations would ultimately result in similar polymer networks, the rates of polymerization may be different. Thus, the polymerizations in solvent most likely show a lower conversion of functional groups, leading to more flexible and less cross-linked polymer networks, and thus to lower T_gs (Table 4.5).

Conclusions

A new polymerizable triglyceride-based monomer was synthesized by the addition of 4-vinylbenzene sulfonic acid to epoxidized soybean oil triglycerides. This new monomer was polymerized *via* ATMET and the final properties of these polymers were investigated. The second generation metathesis catalysts **C4**, **C5** and **C12** outperformed the first generation catalyst **C3** at 40 °C in DCM, probably due to the low tolerance of the latter to the sulfonyl groups of SESO. The polymerization time can be reduced from several hours to minutes by working in bulk; however, in this case higher temperatures are needed (115 °C) to provide homogeneity to the reaction mixture. The resulting polymers have glass transition temperatures close below ambient temperature.

4.3 Living Ring-Opening Metathesis Polymerization (ROMP) of fatty acid derived monomers

Introduction

The development of synthetic methodologies to produce macromolecules with defined structures is a major goal in polymer chemistry. Controlled/living polymerization techniques that enable control over the molecular weight through variation of the monomer/initiator ratio ([M]/[I]) and/or the monomer conversion have been widely applied for the synthesis of well-defined polymers.[255257] ROMP, as an example of a powerful tool for polymer synthesis,[94b] is a highly functional group tolerant polymerization technique that allows for the facile introduction of many different functional groups to a polymer main- or side-chain.[258-260] Since the rate of initiation is faster or comparable to propagation and secondary metathesis reactions are minimized, very narrow molecular weight distributed polymers can be prepared with this type of polymerizations.[128,261] As already mentioned in Chapter 3, the well-defined transition metal alkylidenes Grubbs 2nd generation (**C4**) and Hoveyda-Grubbs 2nd generation (**C5**) catalysts, are particularly useful in initiating ROMP. However, the ROMP with slow initiating 2nd generation catalysts is fast but uncontrolled, thus resulting in ill-defined polymeric materials with respect to molecular weight distributions. With the introduction of the pyridine-based Grubbs 3rd generation initiators (**C6** as representative example) that combine high activity, complete initiation, high functional group tolerance and low sensitivity towards moisture and oxygen, new synthetic strategies emerged allowing the synthesis of well-defined polymers by controlled/living ROMP.[260]

Regarding the use of plant oil-based monomers, Larock and co-workers have performed the non-living ROMP of norbornenyl anhydride-functionalized castor oil/cyclooctene[262] and Dilulin (a norbornenyl-functionalized linseed oil)/dicyclopentadiene.[263] Both systems afford green thermosets and provide a promising new route to bio plastics from bio renewable resources. Moreover, the synthesis of ester-functionalized poly(norbornene)s *via* ROMP was already reported using Grubbs 1st generation catalyst (**C3**).[264] High molecular weights and yields were observed, but these polymers possessed relatively high polydispersity indices (PDIs) of ~2.1, pointing to a non-living ROMP. The authors attributed this to the low functional group tolerance of **C3**. The synthesis of copolymers of norbornene derivatives with an ester group and CO, using cationic Pd compounds as a catalyst *via* vinyl addition polymerization was also reported.[265] The number average molecular weights (M_n) of the synthesized polymers ranged from 3800 to 5300, and the glass transition temperature (T_g) varied from -32 to 117 °C, revealing that the presence of linear long side chains remarkably decreased the T_g value of the norbornene copolymers. Considering the drawbacks of the previous research performed on the vinyl and ROMP with norbornenes bearing ester groups, this section deals with a synthetic approach towards polynorbornenes functionalized with fatty acids varying from 6 to 18 carbons. The approach involves the esterification of a hydroxy-functional norbornene monomer with fatty acids of different chain lengths and their subsequent controlled/living ROMP with 3-bromopyridine-based catalyst **C6**. All synthesized polymers were characterized by GPC and NMR. Furthermore, the effects of the fatty acid chain length on the polymerization process, and the thermal properties of the resulting polymers have been extensively investigated.

Results and discussion

Monomers synthesis

Functional poly(norbornene)s are of particular interest because of their unique physical properties. Functionalization of commercially available *exo,endo*-5-norbornene-2-methanol (NBM) was carried out *via* 1,1'-Carbonyldiimidazole (CDI) assisted esterification with different chain length fatty acids (varying from 6 to 18 carbons, see Figure 4.13) to give the corresponding alkyl ester containing norbornenes (Figure 4.13). Although greener and more sustainable one step transesterification methods of NBM with FAMEs can be envisaged (e.g. using TBD, p-toluensulfonic acid or other catalysts), the observed presence of side reactions during such transesterification reactions clearly revealed the mild CDI coupling approach as the method of choice. CDI is a well-known coupling agent and has been widely used in peptide coupling, small molecule synthesis and also to prepare polymers.[266] Advantages of this reagent include its ease of handling and its relatively low toxicity. During this *in situ* activation, only imidazole, CO_2, and the reactive intermediate carboxylic acid diimidazole were formed.[267] The intermediate was easily converted with the norbornene-2-methanol to the resulting pure fatty acid functionalized norbornene-based monomers in high isolated yields. No side reactions were observed.

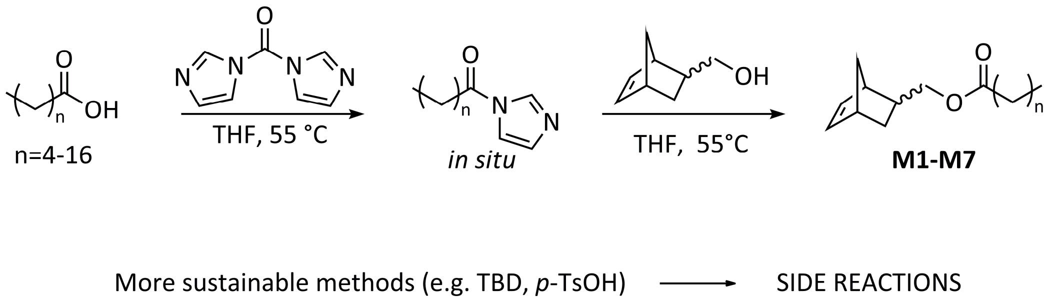


Figure 4.13: Synthetic representtaion of CDI activation of fatty acids and subsequent coupling to NBM to yield monomers **M1**-**M7**.

ROMP of monomers M1-M7

Grubbs 3rd generation catalyst **C6** was used to polymerize monomers **M1**-**M7** (Figure 4.13). Reactions were carried out in degassed dichloromethane DCM and THF with various monomer-to-initator ratios at room temperature with a monomer concentration of 0.064M (Table 4.6).

Table 4.6: Results of the ROMP of **M1-M7** using catalyst **C6**. [a] Results are representative for at least duplicated experiments; [b] Monomer-to-initiator (**C6**) ratio; [c] isolated by precipitating in methanol; [d] determined by GPC in THF relative to PMMA standards; [e] assuming full monomer conversions.

Entry[a]	Monomer	[M]/[I][b]	Yield (%)[c]	M_n(obs.) (kDa)[d]	M_n (theo.) (kDa)[e]	PDI
P1	**M1**	50	92	10.6	11.1	1.17
P2	**M1**	100	95	20.5	22.2	1.19
P3	**M1**	200	93	43.2	44.5	1.16
P4	**M2**	50	90	11.5	12.5	1.18
P5	**M2**	100	91	22.0	25.0	1.25
P6	**M2**	200	93	46.5	50.0	1.21
P7	**M3**	50	89	12.0	14.0	1.2
P8	**M3**	100	93	25.3	27.9	1.18
P9	**M3**	200	93	50.0	55.7	1.15
P10	**M4**	50	92	16.2	15.3	1.25
P11	**M4**	100	94	34.1	30.7	1.13
P12	**M4**	200	92	65.0	61.3	1.16
P13	**M4**	400	95	140.0	122.6	1.14
P14	**M4**	100+300	95	138.0	122.6	1.11

Cont. Table 4.6: Results of the ROMP of **M1-M7** using catalyst **C6**. [a] Results are representative for at least duplicated experiments; [b] Monomer-to-initiator (**C6**) ratio; [c] isolated by precipitating in methanol; [d] determined by GPC in THF relative to PMMA standards; [e] assuming full monomer conversions.

Entry[a]	Monomer	[M]/[I][b]	Yield (%)[c]	M_n(obs.) (kDa)[d]	M_n (theo.) (kDa)[e]	PDI
P15	**M5**	50	92	18.0	16.7	1.09
P16	**M5**	100	92	36.2	33.5	1.12
P17	**M5**	200	93	64.0	67.0	1.11
P18	**M6**	50	93	25.8	18.1	1.13
P19	**M6**	100	93	40.8	36.3	1.14
P20	**M6**	200	91	70.3	72.6	1.15
P21	**M6**	500	95	165.0	181.3	1.26
P22	**M7**	50	76	18.7	19.5	1.05
P23	**M7**	100	70	36.5	39.0	1.06
P24	**M7**	200	83	75.0	78.0	1.09

The solvent mixture of THF and DCM was necessary, since polymerizations in pure DCM and THF were not progressing in a living manner (see also discussion below). Polymerizations were quenched with an excess of ethyl vinyl ether, monitored by GPC and showed a rapid and quantitative reaction. The obtained M_n values showed degrees of polymerization consistent with the monomer to initiator ratio and most polymerizations were complete in less than one minute. It was observed that the polymerization proceeded in a living fashion (e.g. low polydispersity indices of 1.06-1.25; see also discussion below). These results were in contrast to those already reported in the literature, where broad polydispersities of typically 1.9, 2.1 and 2.2 were observed for polymers derived from **M2**, **M3** and **M4**, respectively.[264,265] It can thus be concluded that the polymerizability of the monomers largely depends on the bulkiness of the substituent and the applied solvents.

In order to determine the effect of changing the polymerization conditions on the secondary metathesis reactions occurring during the course of the reaction, a time and solvent study using 200 equivalents of monomer **M4** to catalyst **C6** was performed. A change in the solvent of the reaction had remarkable effects. Samples of **M4** in DCM, solvent mixtures of EtOH:DCM and THF:DCM were polymerized under ambient and nitrogen atmosphere, and terminated at different times (Figure 4.14).

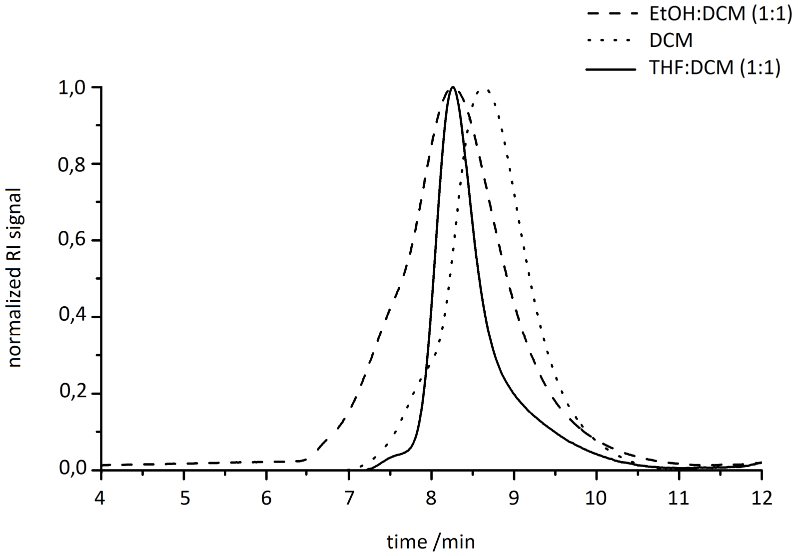


Figure 4.14: GPC traces of polymerizations of monomer **M4** performed in different reaction solvents: EtOH:DCM (dashed line), DCM (dotted lined) and THF:DCM (solid line) quenched after 15 seconds reaction time with ethyl vinyl ether (results were obtained with GPC operating with one column system).

After a 15 second reaction time in DCM under nitrogen flow, a broadly dispersed high molecular weight polymer was obtained, which clearly indicates that under this reaction conditions secondary metathesis reactions compete with chain propagation. On the other hand, when EtOH was used as co-solvent together with DCM, chain termination was observed as side reaction (Figure 4.14, dashed line). However, in a THF:DCM solvent mixture, the reaction was completed after 15 seconds and only a minor high molecular weight shoulder was observed in GPC. After an additional 15 minutes reaction time, the polydispersity did not broaden and no higher molecular weight species appeared, indicating a controlled/living polymerization without competing chain transfer reactions. Along the same lines, it was already reported that changing the reaction solvent to a more coordinating solvent, such as THF, can limit or even prevent secondary metathesis reactions.[268,269] When the monomer concentration was lowered to 0.01 M in a THF:DCM solvent mixture, no effects on the product yields, molecular weights, or PDI values for **M4** were observed. Furthermore, increasing the reaction temperature from 25 °C to 45 °C in THF:DCM gave a polymer with a similar M_n but a considerably broader PDI of 1.32. These results suggest that chain transfer or backbiting occurs at higher temperatures for monomer **M4.**

Encouraged by the obtained narrow PDI values, we examined whether the molecular weights are controlled by the stochiometry of the reaction. Representative graphs of M_n versus [M]/[I] feed ratios for monomer **M4** are presented in Figure 4.15, clearly showing linear relationships. Together with the observed low PDI values these results indicate that the performed polymerizations were indeed living.

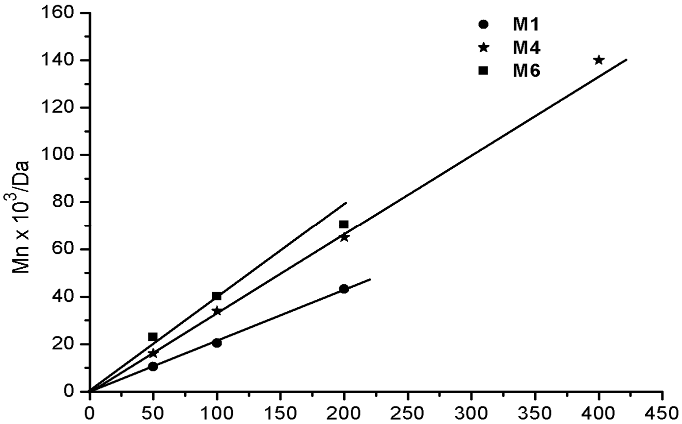


Figure 4.15: Plot of M_n versus DP (based on the results listed in Table 4.6) for the ROMP of **M1**, **M4** and **M6** with **C6** in THF: DCM=1:1 at 25 °C.

To further investigate the livingness of these polymerizations, a kinetic study of **M4** revealed a linear correlation of –ln([M^t]/[M^0]) vs. time (Figure 4.16) for **M4**, thus confirming the constant number of propagating species throughout the reaction and the livingness of the polymerization.

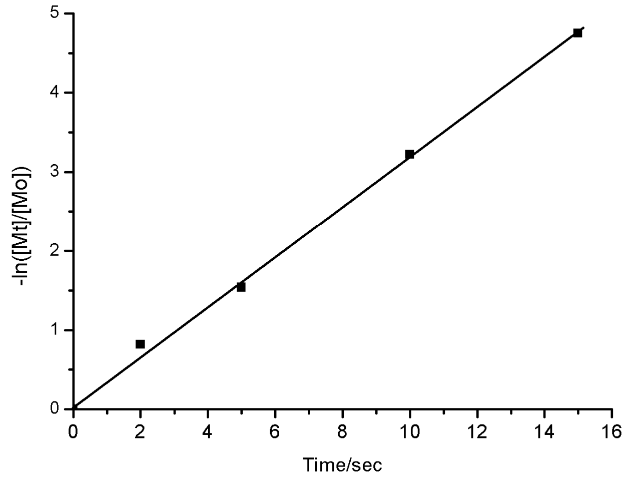


Figure 4.16: First-order kinetic plot (-ln ([M^t]/[M^o]) vs. time) for ROMP of **M4** with an aimed DP of 100.

However, for longer fatty acid substituted norbornenes, such as **M7**, at higher [M]/[I] ratios, the polymerization stalled at approximately 76% conversion (compare also behavior of **M6** in Figure 4.15). The monomer chain length seems to be a critical factor for the observed conversions, probably due to the steric hindrance during the propagation step. Thus, reaction conditions that afford higher conversions of **M7** were investigated. Due to the high activity of **C6** and low critical monomer concentration of norbornene, the ROMP of **M6** and **M7** can be performed at very low concentrations ([M_0] = 0.02M) to keep a relatively low viscosity of the solution throughout the polymerization. When the initial monomer concentration was decreased from [M_0] = 0.064M to [M_0] = 0.02M, the molecular weight stayed consistent, and the observed conversions and isolated yields remained high. Figure 4.17 represents the GPC traces of polymers of **M6** obtained in diluted reaction conditions with different molecular weights, clearly revealing that it was possible to obtain narrowly distributed polymers over a wide range of molecular weights, further indicating the control over the polymerization.

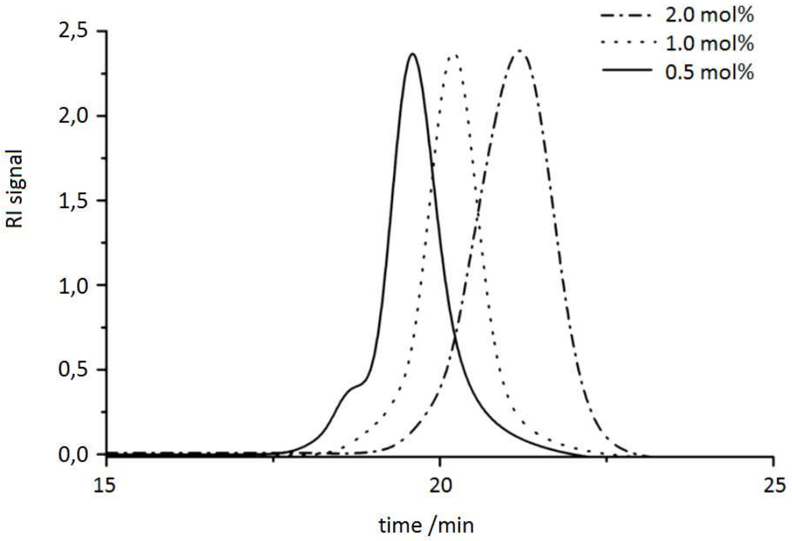


Figure 4.17: GPC traces of polymers of different molecular weights obtained by ROMP of **M6**.

To further proof that our polymerizations fulfill the criteria of a living polymerization, a representative two-step polymerization sequence was carried out for **M4**, the monomer with intermediate length of the alkyl side chain. A 100:1 [M]/[I] ratio of monomer **M4** was thus first polymerized to completion and allowed to stir for an additional 5 minutes. Subsequently, an additional 300 equivalents of monomer were added. Figure 4.18 depicts the results of this chain-extension experiment. A well-defined monodisperse final polymer (Table 4.6, entry 14, M_n = 138 x 10^3, PDI = 1.11) was thus obtained, and the complete molecular weight distribution of the original polymer (Table 4.6, entry 11, M_n = 34.1 x 10^3, PDI = 1.13) shifted to higher molecular weights. No fractions of low-molecular weight polymers were observed by GPC after chain-elongation, indicating that no chain termination reactions occurred in the course of the sequential addition of the monomer. Both chain termination and chain transfer would produce nonliving polymer chains that would not increase in molecular weight upon further addition of fresh monomer. Identical results were observed for monomer **M1,** with the shortest length of alkyl side branch. These findings, together with the findings discussed above, clearly proved the controlled/living character of our polymerization reactions.

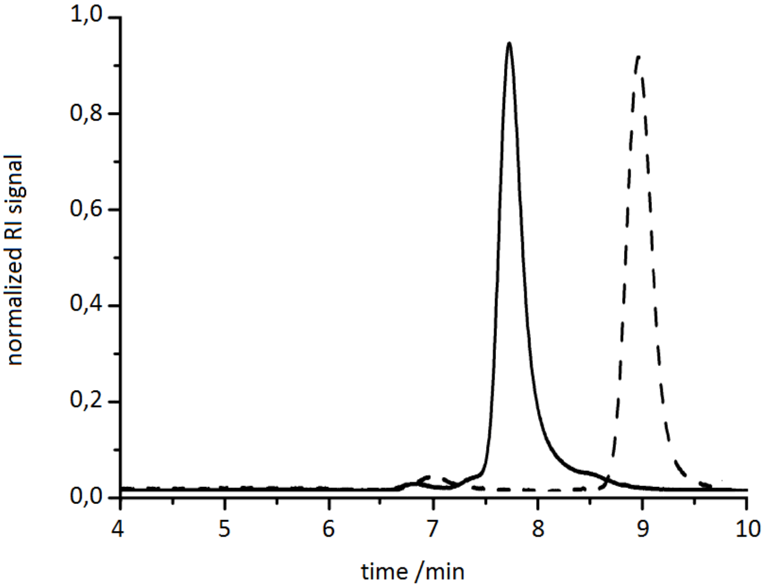


Figure 4.18: GPC traces of the chain-extensoin experiment using **M4** with **C6** in THF:DCM= 1:1 at 25 °C (entries 11 and 14, table 4.6).

The polymerization of all monomers, like all other poly(norbornene)s synthesized *via* ROMP, could also be monitored *via* ^{1}H NMR spectroscopy (Figure 4.19). The alkene proton signals of the strained norbornene ring at approximately δ = 6.0 ppm shifted upfield to approximately δ = 5.0-5.2 ppm upon ring-opening and subsequent polymerization. This greatly facilitated the monitoring the progress of the polymerization. ^{1}H NMR spectroscopy proved that all the monomers had been quantitatively converted into polymers over various polymerization times and confirmed the structure of the polymers.

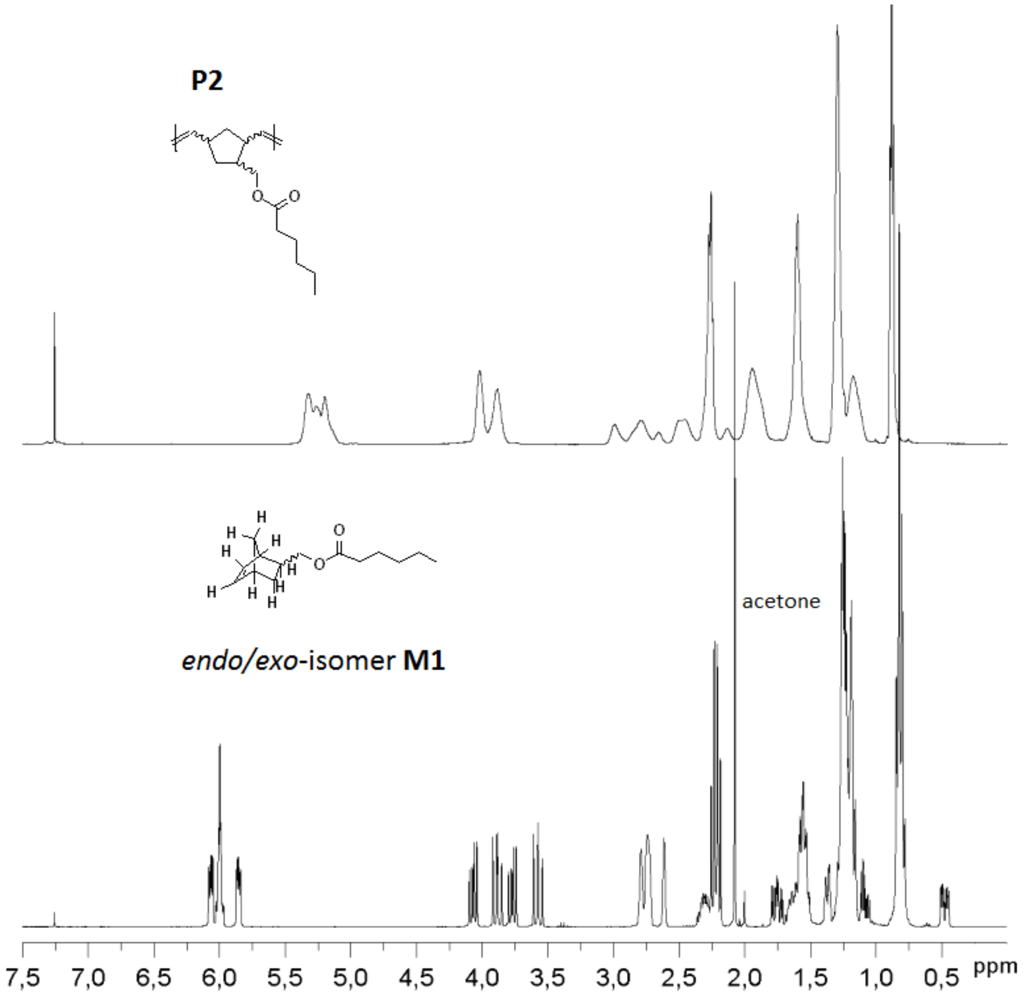


Figure 4.19: ^{1}H NMR spectry of **M1** and the corresponding polymer **P2** (compare Table 4.6).

Thermal properties

Finally, thermal investigations by DSC and TGA of the prepared polymers were performed. The thermal stabilities of the polymers were studied by TGA under nitrogen atmosphere with a 10 °C/min heating rate. It was observed that, independently of the monomers, the temperature corresponding to 5% weight loss for all polymers was around 325 °C, indicating good thermal stability of the prepared polymers. Moreover, DSC studies revealed a decreasing T_g with increasing alkyl chain lengths of the studied monomers. The thermal properties of the prepared polymers are summarized in Table 4.7. It can be concluded that the alkyl side chains behave like an internal plasticizer, thus lowering the T_g. Moreover, only polymers with a side chain of 14 or more carbon atoms started to crystallize. The latter effect is in good agreement with other polymers bearing fatty acid side chains. As the length of the pendant alkyl chain increases, the crystallization might be increasingly hindered, thus leading to the observed decrease in the T_m and crystallinity of the polymers.

Table 4.7: Thermal properties of the prepared well defined renewable polymers.

Polymer	**T_g (°C)**	**T_m (°C)**
P2	102	-
P5	84	-
P8	54	-
P11	35	-
P16	26	29.8
P19	10	15.3
P23	-32	5.9

Conclusions

The synthesis and ROMP of fatty acid functionalized norbornenes was developed and studied. This approach was used for the preparation of polymers with a high level of structural control at the repeating unit level as well as over polymer molecular weight and polydispersity. Using different chain length fatty acids as grafts thus allowed us to study structure property relations within this series of defined polymers. Moreover, the study broadens the applicability of fatty acid derived renewable polymers and demonstrates their broad range of achievable polymer properties.

4.4 Studies on the activity and selectivity of indenylidene-based metathesis catalysts during ADMET polymerization

Introduction

As already described in Chapter 3, double bond migration is an important side reaction of Ru-catalyzed metathesis reactions. Early reports on this class of olefin isomerization described its occurrence with substrates containing allylic oxygen or nitrogen functional groups in combination with first generation catalysts.[111,270-273] Later, the degradation product of Grubbs 1st generation catalyst (**C3**) was found to catalyze double bond migration,[274] and this side reaction was also demonstrated in the presence of 2nd generation catalysts on a broad variety of substrates, competitively, and in some cases prior to olefin metathesis.[113,275-278] A number of further publications addressed this problem discussing two possible reaction pathways and their corresponding mechanisms: the π-allyl metal hydride and the metal hydride addition-elimination mechanisms.[110a,111,113,273,275-278,] In most cases, isomerization was attributed to the presence of a Ru-hydride species,[275,113] a conclusion that was supported by mechanistic investigations. It was also reported that a proper selection of solvents and additives can eliminate isomerization (see Chapter 3).

In the context of ADMET, isomerization from terminal to internal olefin, followed by a productive metathesis step with a terminal olefin, would liberate an α-olefin such as propene or 1-butene, as opposed to the ethylene liberated from a conventional ADMET reaction of two terminal olefins (Figure 4.20).[94c] Release of these higher condensate molecules would decrease the mass yield of the polymer and, if olefin isomerization occurs in a similar timescale as metathesis, this would result in polymers with ill-defined repeat units, thus also affecting the physical properties of the polymer. Noteworthy, **C3** was found not to promote double bond migration during ADMET.[279]

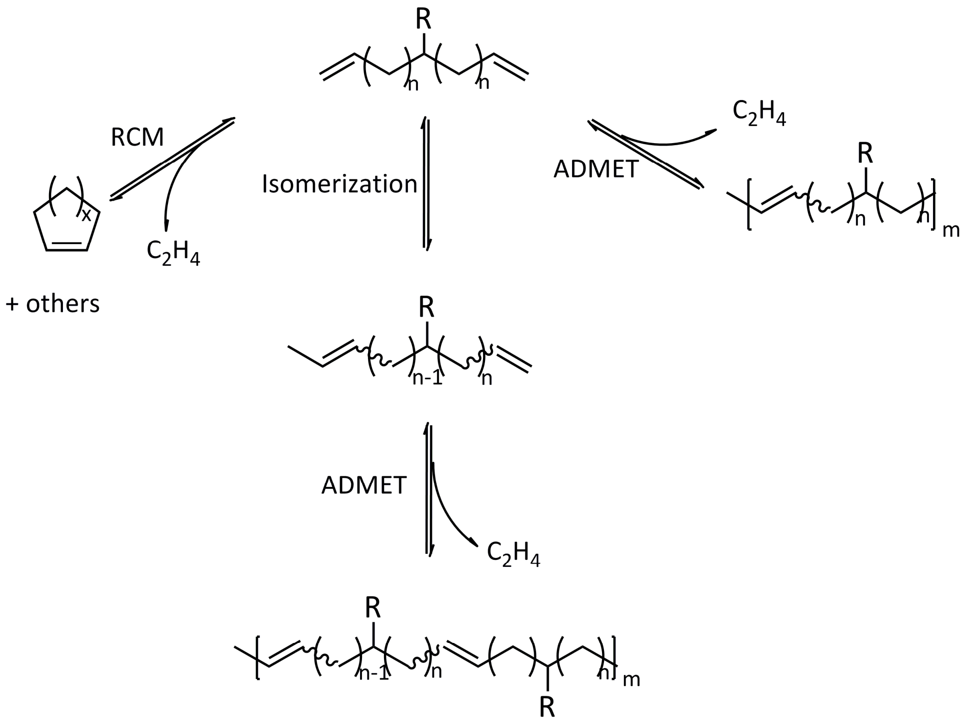


Figure 4.20: Olefin isomerization during ADMET polymerization.

In model studies carried out with simple olefins, Wagener and co-workers could show that while Grubbs 1st generation and Schrock´s molybdenum alkylidene catalysts (**C2**) did not produce appreciable double bond isomerization, Grubbs 2nd generation catalyst (**C4**) presented significant isomerization activity, which was greatly reduced at temperatures below 30 °C.[278,280] These studies were further complemented and confirmed by MALDI analysis of an aminoacid polymer synthesized with **C4**.[281]

Meier and Fokou performed a detailed study of the dependence of double bond migration on the temperature, catalyst, and ADMET polymerization conditions.[279] Thus, the tendency of **C4** to promote double bond migration was found to increase at high temperatures, i.e. 100 °C. Several second generation metathesis catalysts were subsequently studied in ADMET polymerizations.[282] All investigated catalysts showed high degrees of isomerization at 80 °C. The addition of **BQ** efficiently reduced olefin isomerization when added before the catalyst, which indicates that catalyst decomposition begins as soon as the catalyst is added to the reaction mixture at high reaction temperatures. The effects of nitrogen purging and higher temperatures in the presence of **BQ** were also investigated, revealing that nitrogen purging did not significantly change the result, or reduced the degree of isomerization in some cases.

Presently, there is a lack of knowledge on the double bond migration activity of commonly used metathesis catalysts during ADMET polymerizations. Among the numerous metathesis initiators available, this study is focused on the application of the less investigated indenylidene Ru-based catalysts **C10**, **C11**, and **C12**[283] in ADMET polymerization, and on their tendency to yield isomerized products under different reaction conditions.

These indenylidene Ru-complexes provide an attractive alternative to the Ru-benzylidene compounds. It has been shown that all indenylidene Ru-catalysts display higher resistance to demanding reaction conditions (temperature and functional group tolerance) compared to their Ru-benzylidene counterparts.[129d,131,284,] In addition, good catalytic activities in the RCM of linear dienes[284-287] and the ROMP of cycloolefins[129d,131] have been reported. RCM studies using diethyl diallylmalonate and diallyl tosylamine as substrates showed an appreciable catalytic activity and selectivity for the 2nd generation 16-electron Ru-indenylidene complex (**C10**).[291] High temperatures allow for better ligand dissociation, and hence for a higher initiation rate of **C10** in RCM.[285,287] Moreover, good activities have been obtained in the self-metathesis reaction of undecylenic aldehyde, a renewable building block derived from castor oil pyrolysis.[92b] Research performed by Monsaert *et al.* illustrated that **C11** gives high conversions in the ROMP of 1,5-cyclooctadiene, and conversions of up to 80% in the RCM of diethyl diallylmalonate in short reaction times (5-10 min), thus being superior to the benzylidene analogue.[287]

Recently, Grela and co-workers compared the performance of several Ru-indenylidene complexes with Grubbs and Hoveyda-Grubbs type catalysts in olefin metathesis reactions.[292] In contrast to Grubbs and Hoveyda-Grubbs catalysts, **C10** was found practically inactive in the room temperature RCM of diethyl diallymalonate using catalyst loadings as low as 0.05 mol%. However, conversions dramatically increased when the reaction temperature was increased to 70 °C. In addition, application of **C10** to challenging substrates such as diethyldi(methallyl)malonate in fluorinated aromatic hydrocarbon solvents resulted in a remarkable enhancement of the catalytic activity. Moreover, this approach was successfully extended to the RCM of natural products and the synthesis of trisubstituted alkenes *via* cross-metathesis.[293]

In the following lines, the performance of **C10**, **C11** and **C12** in ADMET polymerization is described and their double bond migration activities are studied in relation with the reaction conditions.

Results and discussion

To date, only one example of ADMET polymerization with an *in situ* generated Ru-indenylidene catalyst has been reported.[289] The related arene Ru-indenylidene complex (Figure 4.21) was generated *in situ* from [RuCl(p-cymene)(=C=C=CPh$_2$)(PCy$_3$)][CF$_3$SO$_3$], as the catalyst precursor and HOSO$_2$CF$_3$, and applied in the ADMET of 1,9-decadiene to yield a polymer with 94% conversion in 12 h at 0 °C.

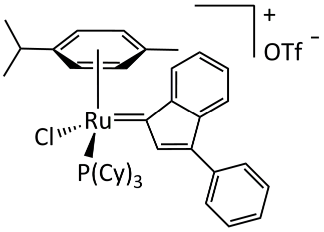


Figure 4.21: Representative scheme for the *in situ* generated Ru-indenylidene.[289]

The α,ω-diene used in the ADMET polymerizations was synthesized following a procedure adapted from the literature using 1,3-propanediol, which can be prepared from glycerol, and 10-undecenoic acid,[44a] commercial derivative of castor oil (Figure 4.22). A set of ADMET polymerizations was used to evaluate the performance of complexes **C10**, **C11** and **C12** at four different temperatures (60, 80, 100 and 120 °C), under bulk conditions, for 5 h reaction time, and constant catalyst loading (200:1=monomer **1**: catalyst). This provided a broad data set to evaluate the catalytic systems tested (Table 4.8 and Table 4.9, respectively). The activity of these catalysts was compared to the Hoveyda-Grubbs 2nd generation catalyst (**C5**), which was previously examined in ADMET polymerizations of the same monomer.[282] In all cases, continuous nitrogen purging was applied throughout the polymerizations and polymerizations were run in duplicate to obtain a reliable set of data.

Moreover, the resulting ADMET polymers were transesterified with methanol to yield α,ω-diesters. The resulting structures represent monomer units from the polymers, and thus provide direct information about the extent of isomerization. Further analysis of the transesterification mixtures with GC-MS allowed the quantification of double bond migration during ADMET (Figure 4.22). For polymerizations in which isomerization does not occur, would result, after transesterification, in a GC-MS spectrum consisting of one single peak representing the unsaturated C-20 repeating unit of the studied polymers (compare Figure 4.22). On the other hand, the occurrence of double bond migration during ADMET would result in a mixture of α,ω-diesters diesters with different chain lengths. The molecular weight of the isomerized diesters vary by multiples of 14 g/mol (one methylene group), corresponding to the differences in mass between the olefin molecules released during the ADMET polymerization. In this case, the GC-MS spectrum would consist of a distribution of different peaks.

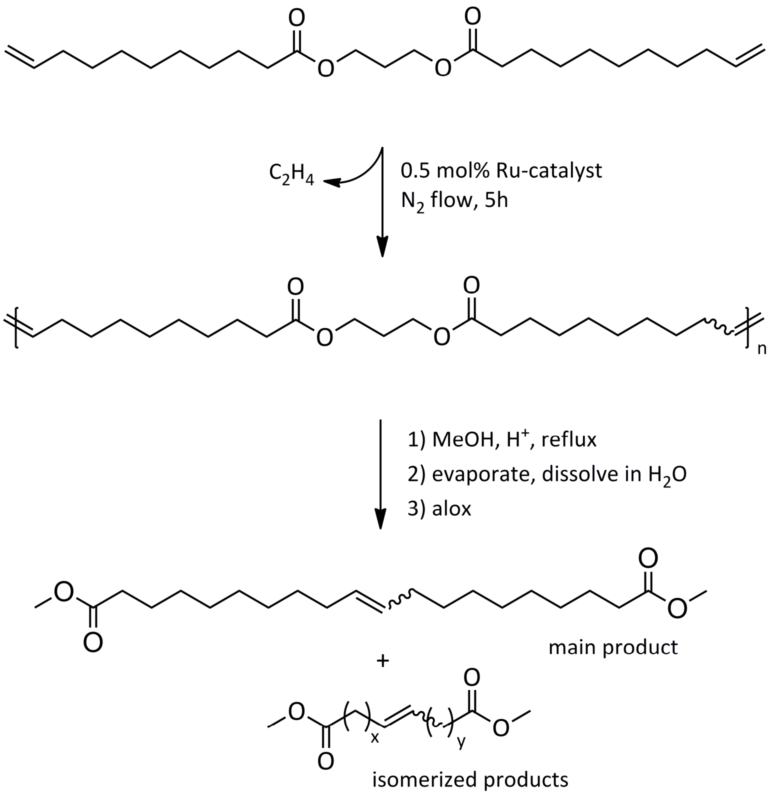


Figure 4.22: Synthesis of the studied α,ω-diene, its ADMET polymerization, and strategy to evaluate isomerization side reactions.

The analytic data of the polymers synthesized is summarized in Tables 4.8 and 4.9 and selected GPC traces are depicted in Figure 4.23. Except for the cases in which only oligomers were obtained, monomer conversion was quantitative as determined by the total disappearance of the monomer signal in the GPC traces of the reaction mixtures. The runs at 60 °C showed that, among **C10**, **C11** and **C12** (compare entries 1, 3 and 5 in Table 4.8, respectively; and Figure 4.22), **C10** led to the highest molecular weight of around 10.0 kDa, with a moderate isomerization degree of 36.3% (Table 4.8, entry 1). Interestingly, at this temperature **C11** showed a considerably low degree of isomerization of 9.91%, however we were able to obtain just oligomers (M_n 1700 Da). Another goal in this research was to suppress the isomerization side reaction and thus to synthesize well defined polyesters. Benzoquinones are very effective additives for the prevention of the olefin isomerization.[116] Thus, we performed the same set of experiments in the presence of **BQ**, and observed that the degree of isomerization was significantly reduced for **C10,** from 36.3% to 0.7% of degree of isomerization**.** However, this decrease in the isomerization degree was accompanied with reduced molecular weights for all studied catalysts. In the worst case of **C11**, the molecular weight was reduced by factor of 3 (compare entries 3 and 4 in Table 4.8).

Table 4.8: Overview of polymerization and the isomerization results of the corresponding polymers at 60 and 80 °C.

Entry	Polymer	Cat % (0.5 mol%)	T (°C)	Conditions[a)]	Iso %[b)]	M_n (kDa)[c)]	PDI
1	**P1**	**C10**	60		36.3	10.5	2.00
2	**P2**	**C10**	60	**BQ** (1.0 mol%)	0.70	8.3	2.05
3	**P3**	**C11**	60		9.91	1.7	1.16
4	**P4**	**C11**	60	**BQ** (1.0 mol%)	NI[d)]	2.2	1.36
5	**P5**	**C12**	60		69.6	8.0	1.60
6	**P6**	**C12**	60	**BQ** (1.0 mol%)	63.9	4.2	1.76
7	**P7**	**C10**	80		63.9	14.0	1.92
8	**P8**	**C10**	80	**BQ** (1.0 mol%)	74.2	14.0	2.09
9	**P9**	**C11**	80		41.9	14.2	1.90
10	**P10**	**C11**	80	**BQ** (1.0 mol%)	28.6	9.2	1.90
11	**P11**	**C12**	80		91.4	11.9	1.80
12	**P12**	**C12**	80	**BQ** (1.0 mol%)	59.2	11.3	1.93

[a)] Additional conditions applied during polymerization: **BQ**: amount of benzoquinone in % respective to monomer; [b)] % amount of isomerized diesters observed with GC-MS after transesterification of the respective polymer [c)] GPC was performed in THF, containing BHT, with PMMA calibration; [d)] NI: no isomerization.

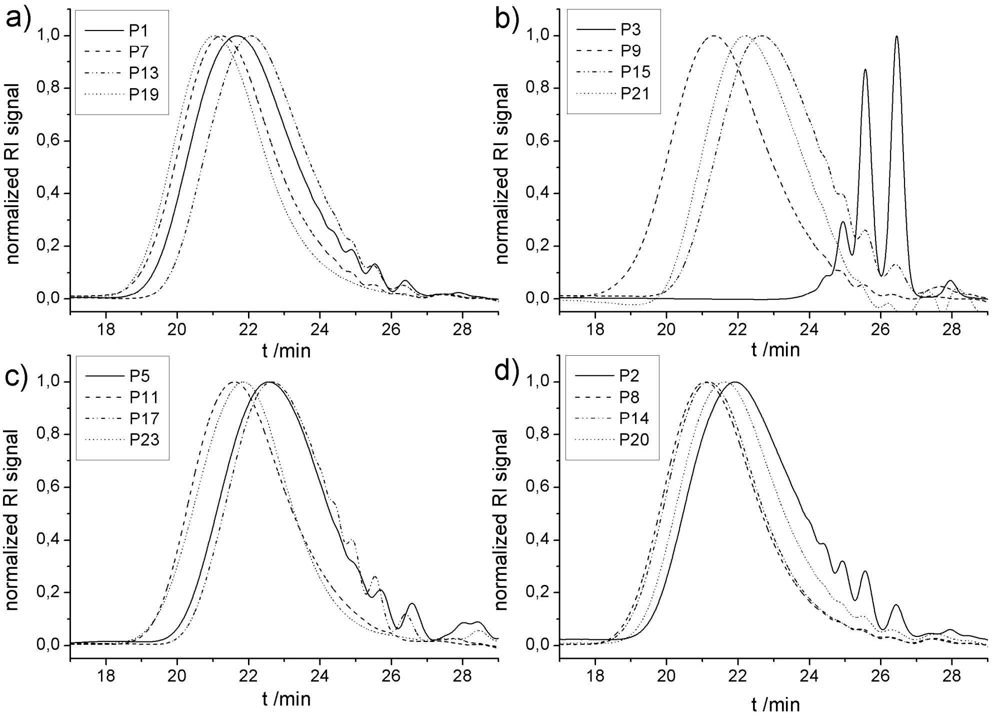


Figure 4.23: GPC traces of the polymerizations performed at 60, 80, 100 and 120 °C in presence of a) 0.5 mol% **C10**, b) 0.5 mol% **C11**, c) 0.5 mol% **C12**, and d) 0.5 mol% **C10** with 1 mol% **BQ**.

When the polymerization temperature was increased to 80 °C higher molecular weight polymers were obtained with all studied catalysts. For instance, **C11** produced a polymer with more than double molecular weight when increasing the reaction temperature from 60 to 80 °C. Furthermore, the increase of the temperature led to an increase in the amount of the isomerization for all of the catalysts. Concerning the isomerization inhibition effect of **BQ** on the catalyst, the effect was significant (factor of 1.5) for **C11** and **C12**, whereas **BQ** was ineffective in the presence of **C10**. In case of **C12**, the molecular weights of the corresponding polymers synthesized with and without **BQ** were similar, with a lower isomerization value for **P12**, as expected. Surprisingly, **C10** showed higher isomerization degrees in the presence of **BQ** at 80 °C.

In an attempt to further increase the molecular weights of the obtained polyesters; all catalysts were also investigated at 100 °C (Table 4.9). Surprisingly, this further increase of the polymerization temperature led to lower molecular weights for all studied catalysts. Quite interestingly, at that temperature the most significant inhibition effect of **BQ** on the degree of isomerization was observed for **C2** (compare entries 15 and 16 in Table 4.9), however just yielding oligomers. Similarly as for the results at 80 °C, when we used **C10** and **BQ**, we observed the increase of isomerization degree along the almost same M_n value (Table 4.9, entries 13 and 14). On the other hand, **C12** revealed the same tendency as at 80 °C. The obtained polymers possessed lower isomerization percentage, and quite high molecular weight values.

Furthermore, the catalysts **C10**, **C11,** and **C12,** together with **C5** as a comparison, were investigated at 120 °C (Table 4.9, entries 19, 21, 23, and 25). All complexes provided comparatively high molecular weights, following the order **C10** (~17000 Da) > **C11** (13000 Da) > **C12** (12200 Da) > **C5** (10500 Da). Regardless of the catalyst, all the polymers at that temperature possessed high isomerization values. Subsequently, we tried to reduce the amount of isomerization by performing the same set of reactions in the presence of **BQ** (Table 4.9, entries 20, 22, 24 and 26). The isomerization degree was slightly reduced when using **C10** (Figure 4.24a), and the most prominent effect of **BQ** was observed again for **C11** (Figure 4.24b); however, this time the polymerization in the presence of **BQ** resulted in polymer with M_n of 8500 Da, compared to the results at lower temperatures. Interestingly, the polymerization with **C12** in the presence of **BQ** followed the same tendency like at 100 °C and resulted in higher molecular weight polymer in comparison to the polymerization without **BQ**, whereas the isomerization remained high (Table 4.9, entries 23 and 24).

Table 4.9: Overview of polymerization and the isomerization results of the corresponding polymers at 100 and 120 °C.

Entry	Polymer	Cat % (0.5 mol%)	T (°C)	Conditions[a)]	Iso %[b)]	M_n (kDa)[c)]	PDI
13	**P13**	**C10**	100		79.3	10.0	1.79
14	**P14**	**C10**	100	**BQ** (1.0 mol%)	81.6	11.3	1.74
15	**P15**	**C11**	100		53.6	9.0	1.85
16	**P16**	**C11**	100	**BQ** (1.0 mol%)	0.80	4.5	1.60
17	**P17**	**C12**	100		55.2	6.7	1.72
18	**P18**	**C12**	100	**BQ** (1.0 mol%)	37.2	10.2	1.92
19	**P19**	**C10**	120		89.4	16.7	1.80
20	**P20**	**C10**	120	**BQ** (1.0 mol%)	73.0	11.0	1.83
21	**P21**	**C11**	120		83.7	13.0	1.66
22	**P22**	**C11**	120	**BQ** (1.0 mol%)	16.0	8.5	1.78
23	**P23**	**C12**	120		87.4	12.2	1.73
24	**P24**	**C12**	120	**BQ** (1.0 mol%)	73.8	14.9	1.73
25	**P25**	**C5**	120		80.5	10.4	1.93
26	**P26**	**C5**	120	**BQ** (1.0 mol%)	66.5	12.0	1.67

[a)] Additional conditions applied during polymerization: **BQ**: amount of benzoquinone in % respective to monomer; [b)] % amount of isomerized diesters observed with GC-MS after transesterification of the respective polymer [c)] GPC was performed in THF, containing BHT, with PMMA calibration.

In the already mentioned work by Fokou and Meier, Hoveyda-Grubbs 2nd generation catalyst (**C5**) was shown to provide polymers with molecular weights M_n of 8.0 kDa at 80 °C, and 8.8 kDa at 100 °C. The isomerization degrees were found to be 24% and 20% respectively.[282] Herein we have demonstrated that **C5** can be applied at a higher temperature (120 °C), in the presence of **BQ** (1.0 mol%), and low amount of catalyst (0.5 mol%), thus yielding a polymer with M_n of 12000 Da. However, at 120 °C the amount of isomerization was high with and without **BQ** (entries 25 and 26, Table 4.9). These results, along with the results mentioned in our previous work, proved that **C5** can be used in a quite broad temperature range.

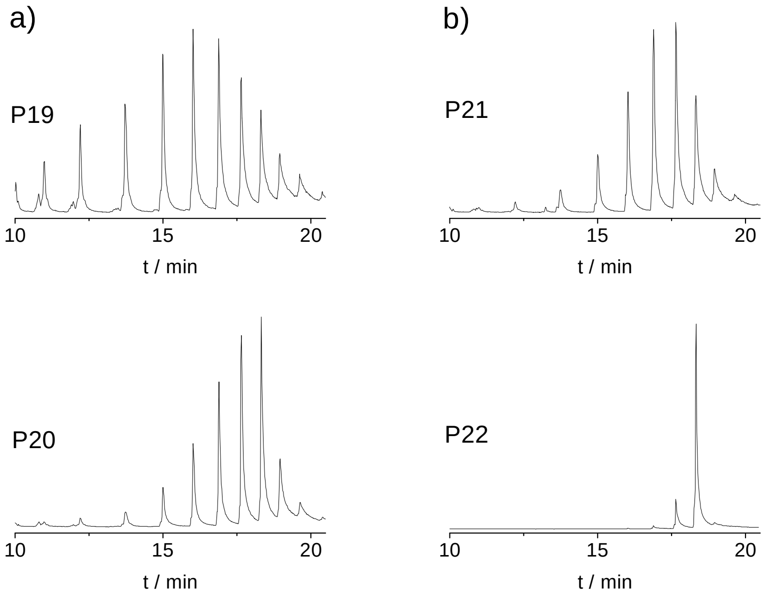


Figure 4.24: GC-MS study of the acid-catalyzed degradation products of polymers **P19**, **P20**, **P21**, and **P22**.

As a summary, the tendency found for the activity of these catalysts as a function of the temperature was not linear. A clear increase in the activities was observed when increasing the temperature from 60 °C to 80 °C, however, when the temperature was increased to 100 °C a general activity decrease was observed for all catalysts, and finally the activity increased again when performing the reactions at 120 °C. As the temperature is increased the activity of the catalyst increases, however, its degradation might also be accelerated. At 100 °C, the degradation of the catalyst could be predominant, thus resulting in lower molecular weights. On the other hand, when the temperature is raised to 120 °C, the catalysts degradation could be compensated by an extremely fast initiation and short-term propagation promoted by the high temperature, giving as a result high molecular weights before catalysts degradations take place. This argumentation is speculative, but in order to provide some data to support this idea, we decided to examine the progress of the polymerization at different times for **C10** at 80, 100 and 120 °C. We took samples at 5, 15, 30, and 120 minutes for each temperature and analyzed them by GPC (Figure 4.25). As predicted from the arguments above, the propagation observed for the polymerization at 80 °C was slower than that at 100 °C at short times, however, the polymerization stalled at 100 °C, maybe due to catalyst degradation, yielding lower molecular weights. Furthermore, the propagation in the initial steps for the polymerization at 120 °C was found to be the fastest, leading to high molecular weight species in short times before catalyst degradation became predominant.

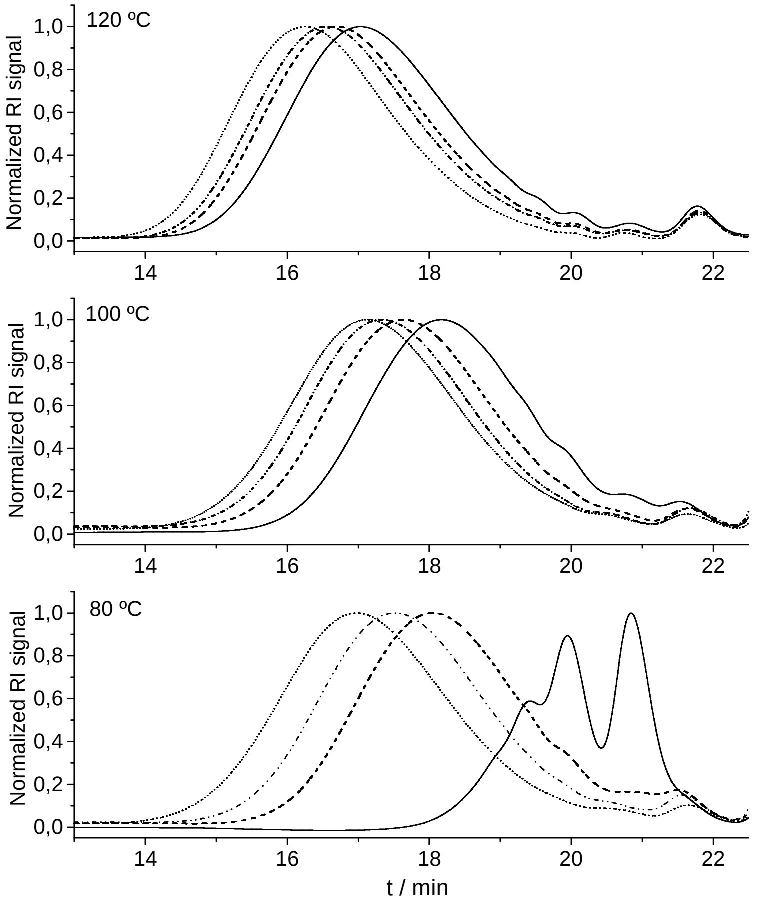


Figure 4.25: GPC traces of polymerizations performed with **C1** at 80, 100, and 120 °C. Samples taken at 5 min (——), 15 min (–), 30 min (– · ·), and 120 min (-).

Olefin isomerization occurring during ADMET polymerization leads to macromolecules with ill-defined structures. Depending on the isomerization degree, the physical properties of the polymers are correspondingly affected. A different insight into the effect of the isomerization ratio on the thermal properties of the polymers can be achieved by differential scanning calorimetry (DSC) analysis of the synthesized polymers. The thermal behavior of two polymers with similar M_n, synthesized at same temperature with and without **BQ** was studied by DSC (Figure 4.26). Polymer **P12** (Table 4.8, entry 12), possessing a lower degree of isomerization, exhibited a quite sharp T_m peak at 47 °C. On the other hand, the DSC trace of polymer **P11** (Table 4.8, entry 11), with higher isomerization degree, presented multiple peak melting transitions at lower temperatures resulting from its ill-defined repeat unit structure. These results show that, even if the addition of **BQ** does not completely avoid isomerization in most of the herein presented examples, polymers with a higher structural regularity can be obtained by using **BQ**.

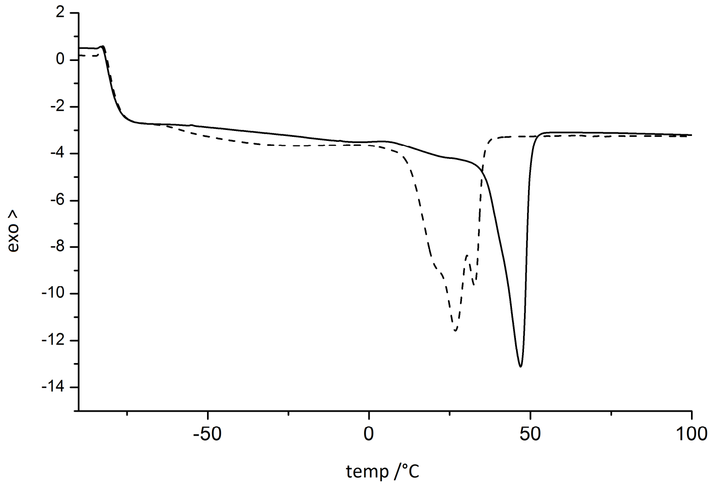


Figure 4.26: DSC traces of ADMET polymers **P11** and **P12** (Table 4.8, entries 11 and 12, respectively).

Conclusion

In summary, the indenylidene Ru-complexes provided an attractive alternative to the benzylidene compounds and allowed preparing polyesters of up to 17.0 kDa *via*

ADMET polymerization, even at elevated temperatures with enhanced activity. Unfortunately, the attempt to synthesize regular polymer architectures through addition of **BQ** and thus to prevent the isomerization reaction was not possible with these catalyst. Nevertheless, these results should be regarded as first experimental data set on these catalysts and further improvement, building upon these results, can be expected in the future.

4.5 Synthesis of castor oil-derived unsaturated PA X,20 *via* metathesis and catalytic amidation

Introduction

Aliphatic polyamides (PA) are important engineering materials that are widely applied due to their excellent properties, such as a high modulus, good toughness, relatively high melting points and heat resistance, abrasion resistance, as well as chemical inertness.[294] The mainly applied methods for their synthesis include the polycondensation of *ω*-aminocarboxylic acids, the polycondensation of aliphatic diamines and dicarboxylic acids (or their derivatives), or the ring-opening polymerization of lactams.[295] As an alternative, recently, a new polymerization reaction in the presence of dearomatized Ru-pincer complexes emerged as a synthetically useful and general method for the preparation of a variety of polyamides under mild, neutral conditions, using non-toxic reagents, not requiring preactivation of the substrates, and generating no waste.[296] In the case of renewable polyamides, the most prominent example of industrially produced, 100% bio-based, polyamide is the AB-type polyamide-11.[8a] In contrast, the synthesis of 100% bio-based AABB type polyamides is not expected in the near future due to the non-availability of bio-based diamines. However, research on routes to obtain diacids from glucose (adipic acid) or vegetable oils (azelaic acid, sebacic acid) for the production of partially bio-based polyamides-6,6, -6,9, and -6,10 are currently investigated. Adipic acid, for instance, can be obtained from glucose *via* fermentation with modified *E. coli.*[297] The resulting intermediate, *cis,cis*-muconic acid, was then chemically hydrogenated to adipic acid at elevated pressure. Production of nylon X,6 from the derived adipic acid and a diamine would then follow a conventional step growth polymerization. In contrast to the fermentation pathway to adipic acid from glucose, azelaic acid and sebacic acid can be produced *via* oxidative cleavage of oleic acid and alkaline pyrolysis of castor oil, respectively.[8a,298]

Among various polycondensation methods, acyclic diene metathesis (ADMET) is useful for the synthesis of a variety of polymer architectures that would otherwise be difficult to obtain.[95] Due to the development of functional group tolerant metathesis catalysts, it is now possible to polymerize various *α,ω*-dienes bearing ether, ester, ketone, acetal, alcohol, amino acid, boronate and carboxylic acid functional groups *via* ADMET polymerization.[102,106,299-304] However, attempts to polymerize amide containing *α,ω*-dienes were less successful until now. Tastard *et al.* described the indirect polymerization of a variety of amide containing *α,ω*-dienes by first performing a ring-closing metathesis (RCM) reaction at high dilution in chloroform or THF with 1.0 mol% of the Grubbs 2nd generation catalyst (**C4**) to obtain an amide containing macrocycle in moderate to good yields.[305] These macrocyles were then further polymerized by an entropically driven ring-opening polymerization (ED-ROMP) using 0.5 mol% of the same catalyst, to give the final polyamides (including PA 8,20). The properties of the resulting polymers were not described. Moreover, the direct ADMET polymerization of amide containing *α,ω*-dienes was investigated in this study revealing that only oligomers were formed with 1.0 mol% of **C4** after 4 days of reaction time.[305] Moreover, many different types of long chain aliphatic polyamides obtained by conventional melt polycondensation are described in the literature. For instance, the long chain diacids octadec-9-enedioic acid,[306] eicosanedioic acid,[307,308] 1,16-octadecane diacid[309] and 1,14-hexadecane diacid[310] were polymerized with various aliphatic diamines, ranging from 2 to 12 methylene units. The resulting polymers showed good thermal properties. For instance, the melting temperature (T_m) of these polyamides increased along with an increase of the relative amide group density, whereas the decomposition temperature showed no obvious trends with respect to increasing diamine chain length.

The main goal of this study is to describe the synthesis of novel unsaturated polyamides that can be obtained from plant oil derivatives *via* two different approaches, each involving one metathesis step.[62] First, long chain aliphatic α,ω-dienes with two symmetrically spaced amide segments were polymerized *via* ADMET. Secondly, *E*-dimethyl-eicos-10-enedioate **2** was polymerized with different aliphatic diamines using strong organic bases, such as TBD, as catalysts. The monomer **2** is a bio-based unsaturated monomer and was obtained *via* self-metathesis of methyl-10-undecenoate, a castor oil derived platform chemical. Both reaction pathways led to unsaturated PA X,20 and the two different routes were investigated, optimized and compared to one another. Moreover, the properties of the resulting polyamides were investigated revealing that these long-chain polyamides are well applicable as engineering plastics and that their properties depend on the structure of the applied monomers, as expected.

Results and discussion

The main objective of the present study was to investigate the synthesis of PA X,20 from renewable resources *via* two routes and to compare these routes to one another (compare Figure 4.27). Both routes rely on methyl-10-undecenoate **1** that can be obtained from castor oil by pyrolysis and is thus a renewable building block that does not interfere with food or feed. Although **3a-3d** are at present petroleum based the desired polymers **5a-d** have a renewable percentage varying from 70 to 80% by mass, depending on the used diamine.

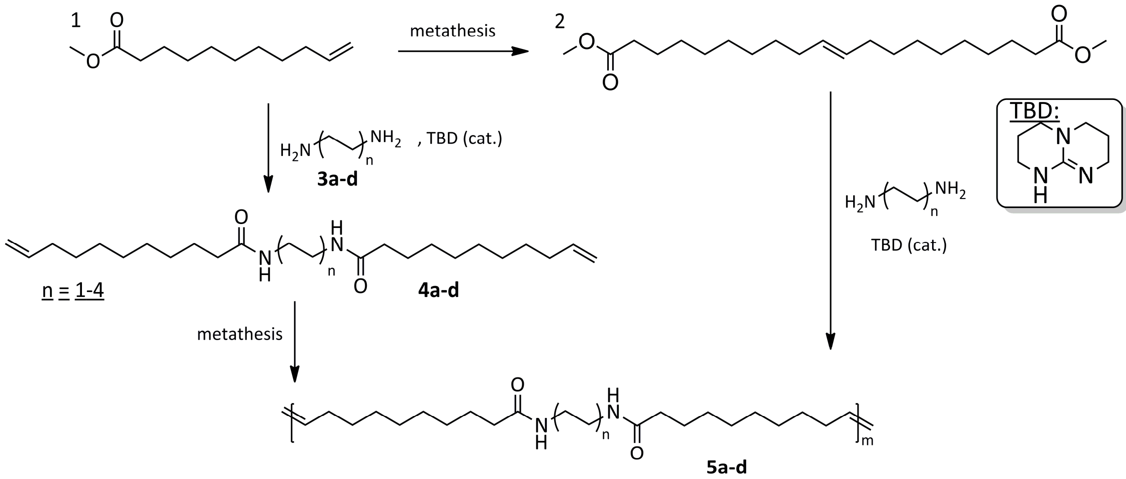


Figure 4.27: Schematic representation of the two different investigated routes to obtain PA X,20 from renewable resources; note: depending on the applied synthesis route the double bonds of polymers **5** will be either a *cis*/*trans* mixture (ADMET) or solely E configured (route *via* monomer **2**).

Both routes involve one metathesis step and one catalytic amidation step, only in reverse order. Thus, the first route is based on the synthesis of ADMET monomers **4a-d**. These α,ω-dienes were obtained from **1** and different chain length diamines (**3a-3d**; Figure 4.27). The strong organic bases DBN, DBU, and TBD were tested as catalyst at three different temperatures (25, 75 and 100 °C) and different amounts (1, 2.5, 5, 7.5 and 10.0 mol%) for the solvent-free amide synthesis revealing that TBD at 75 °C and 7.5 mol% was best suited for this reaction, since these conditions provided the highest conversions of methyl 10-undecenoate to the corresponding monomers **4a-4d** as observed by GC, IR and ^{1}H NMR investigations. A larger quantity of TBD and/or higher temperature did not improve the observed yields. After this optimization procedure, the desired monomers **4a-4d** could be obtained in high yields and purities in a simple and reproducible catalytic one step reaction. The thus obtained *α,ω*-diene monomers were soluble in dimethyl formamide (DMF) and o-xylene (after applying sonication) and slightly soluble in dimethyl sulfoxide (DMSO) and dimethyl acetamide (DMAc). The ADMET polycondensation of **4a-4d** was then investigated with 2nd generation catalysts **C4** and **C5**, since these catalysts are highly tolerant to functional groups, oxygen and small amounts of moisture, and can be applied at higher temperatures.[59,311] Most often, ADMET polymerizations are performed using neat liquid monomers, however the investigated amide containing monomers were all crystalline solids with high melting points that unfortunately required the use of solvent for these polymerizations. Typically, **C4** and **C5** are soluble in dichloromethane, toluene or THF, and metathesis reactions are carried out in these solvents at temperatures ranging from room temperature to about 80 °C.[312] However, the synthesized α,ω-diene monomers **4a-d** were insoluble in all of these solvents and their ADMET polycondensations had to be carried out with minimal amounts of DMF to assure a homogeneous reaction mixture. These ADMET reactions were tested with up to 10% of **C4** and **C5** and all polymerizations were monitored by GPC. It was observed that, even after 24 hours reaction at 80 °C, during which the ethylene was removed by a continuous nitrogen flow, neither of these catalysts yielded polymers, and unreacted monomers were recovered. Further increasing the reaction temperature did not change this situation. However, attempts to perform the polymerization in o-xylene revealed better results. The diamide monomers **4c** and **4d** both reacted in the presence of **C5** (5.0 mol%) in o-xylene at 80 °C gave polymers **5c** and **5d**, respectively. Moreover, monomer **4d** also polymerized in the presence of **C4** (5.0 mol%) and the obtained polymers showed higher molecular weights in comparison to polymerization with **C5**. Higher catalyst loadings of 10.0 mol% of **C4** and **C5** for both monomers **4c** and **4d**, did not lead to higher molecular weights. In contrast, any attempt to polymerize monomers **4a** and **4b** *via* ADMET failed completely. The unreactivity of the latter monomers was attributed to the significantly lower solubility in o-xylene. Moreover, one can conclude that DMF is an unsuitable or at least nonpreferential solvent for ADMET (and other metathesis reactions), most likely due to its coordinative character. The results obtained from these ADMET polymerization are summarized in Table 4.10 and clearly show that this route to renewable PA X,20 is feasible, but unsatisfactory since not all monomers can be polymerized and low molecular weight polymers were obtained.

Table 4.10: Results obtained from the ADMET polymerization of monomers of **4a-d** with o-xylene as a solvent at 80 °C.

Polyamide	**Catalyst (mol%)**	**M_n (GPC)**	**M_w/M_n (GPC)**
8,20 (**5d**)	**C4** (5.0)	6000	2.11
8,20 (**5d**)	**C4** (10.0)	6800	1.98
8,20 (**5d**)	**C5** (5.0)	4900	1.87
8,20 (**5d**)	**C5** (10.0)	5500	2.23
6,20 (**5c**)	**C5** (5.0)	4000	1.98
6,20 (**5c**)	**C5** (10.0)	4100	2.01

Our alternative route for the synthesis of unsaturated PA X,20 involves the self-metathesis of **1** in the presence of **C4** to yield **2** and the subsequent catalytic amidation of this monomer with aliphatic diamines (Figure 4.27). The self-metathesis of **1** could be performed with very low amounts of catalyst under bulk conditions, as expected. This is a first important advantage of the second route, since the use of solvent for the metathesis step can be avoided and only low amounts of precious metathesis catalyst are required. Both aspects are also important in terms of a lower environmental impact of the second route. The subsequent catalytic amidation polymerizations of **2** with **3a-d** showed noticeable differences in term of thermal behavior of the obtained polymers compared to the polymers synthesized *via* ADMET polymerization, already indicating their higher molecular weight. Classic procedures to prepare long chain aliphatic PAs are the melt polycondensation at high temperature of carboxylate/ammonium salts formed beforehand or the reaction of the respective acid chlorides with the diamines. The main disadvantages of these procedures are the requirement of high reaction temperatures (180-300 °C) and the application of acid chlorides, respectively. Moreover, side reactions, such as transamidation, as well as oxidative and thermal decomposition can be observed, which almost always occur during melt condensation. The required efficient removal of the produced side products, water and HCl, are additional disadvantages.[295] In contrast, our catalytic amidation shows good product yields and no salt is produced, the only by-product being methanol (and the catalyst).

In our approach two different routes were studied and optimized: the one step-heating (A) and the three step-heating catalytic amidation (B). For the A process various reaction temperatures were tested (60, 75, 100, 125 and 150 °C). IR and GPC analysis were used to identify the most suitable reaction temperature. For all reaction temperatures, a decrease of the ester group peak (1740 cm^{-1}) and an increase of the amide peaks (3306 and 3080 cm^{-1}) was observed by IR with increasing reaction time. For the lower reaction temperatures (60 and 75 °C) the conversion of the ester peak into amide peaks was slow and the molecular weights obtained from GPC analysis were comparatively low. The higher temperatures showed considerably better conversions and higher molecular weights, whereby 150 °C provided the best results. Further increasing the temperature above 150 °C did not improve the results. Moreover, the IR spectra of the polymers prepared at 150 °C revealed full conversion of the ester and therefore, this reaction temperature was used for all further experiments. Thus, monomer **2** was reacted with different diamines **3a-3d** at 150 °C in the presence of TBD as a catalyst. Three different amounts of catalyst were tested: 5.0, 7.5 and 10.0 mol%. TBD was chosen as the catalyst for these polymerizations, since it provided the best results for the synthesis of monomers **4a-d**. Since **4a-d** can be considered as model compounds of polymers **5a-d**, we expected a similar behavior during these polymerizations. All polymerizations were performed under bulk conditions and a continuous flow of nitrogen to facilitate the removal of methanol. Solvent-free conditions were chosen to avoid solvent waste, to enhance conversions, and to avoid the formation of cyclic structures. The analytic results of the polymers with the highest obtained molecular weights *via* this route are summarized in Table 4.11. Similarly like for route A, the three step-heating amidation B was performed in bulk and under nitrogen flow, but three different temperatures (75, 100 and 150 °C) were applied stepwise. The B route was tested in order to reduce the evaporation of the lower molecular weight diamines at the beginning of the reaction at the high polymerization temperatures. Higher molecular weight polymers were obtained *via* route A, with the exception of the most volatile diamine **3a**. This behavior can for example be observed if GPC traces of the unsaturated PA 8,20 prepared *via* the two different routes are compared (Figure 4.28).

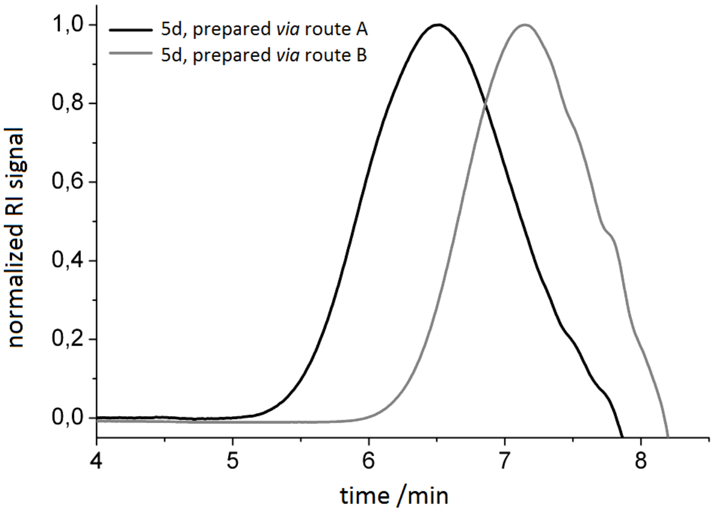


Figure 4.28: GPC traces of crude reaction mixtures of trifluoroacetylated **5d** prepared *via* the two different routes A and B.

Additionally to the reaction temperature, the catalyst loading was of great importance. When route A was applied, the optimal catalyst loading in terms of observed molecular weights decreased with increasing diamine chain length. The results obtained after optimizing the polymerizations *via* the two different routes are summarized in Table 4.11. It should be mentioned here that the GPC results presented in Table 4.11 are relative to polymethycrylate standards and that the molecular weights are of the solubilized polymers (modification with TFAA). Therefore, the molecular weights are expected to be quite off their absolute values. However, this simple method was a valuable tool to optimize different reaction conditions and the results should be valid at least relative to each other. Moreover, the results clearly show that route A is, at least for long chain diamines and diesters, a simple and reproducible laboratory technique suitable for the preparation of polymers with considerable molecular weights that can be used for structure confirmation and for the evaluation of basic material properties.

Table 4.11: Results obtained from the catalytic amidation polymerizations of monomers **2** with diamines **3a-d**.

Polyamide	Route	TBD (mol%)	M_n (GPC)	M_w/M_n (GPC)
8,20 (**5d**)	A	5.0	14700	2.4
8,20 (**5d**)	B	10.0	6000	2.0
6,20 (**5c**)	A	5.0	11300	2.3
6,20 (**5c**)	B	7.5	8200	1.9
4,20 (**5b**)	A	10.0	9300	2.0
4,20 (**5b**)	B	7.5	6300	1.9
2,20 (**5a**)	A	7.5	5300	1.9
2,20 (**5a**)	B	10.0	5500	2.3

The polyamides with the highest obtained molecular weights were then used for structural and thermal characterization. The GPCs of these polymers are depicted in

Figure 4.29 showing that symmetrical molecular weight distributions were obtained for **5b-5d**, whereas **5a** mainly consisted of oligomers. These polymers were also investigated by ^{1}H NMR in a $CDCl_3$/TFAA solvent mixture. All peak assignments were based on the literature and on the comparison of polyamide spectra with those of their trifluoroacetylated model compounds **4a-d**.[306,310,313]

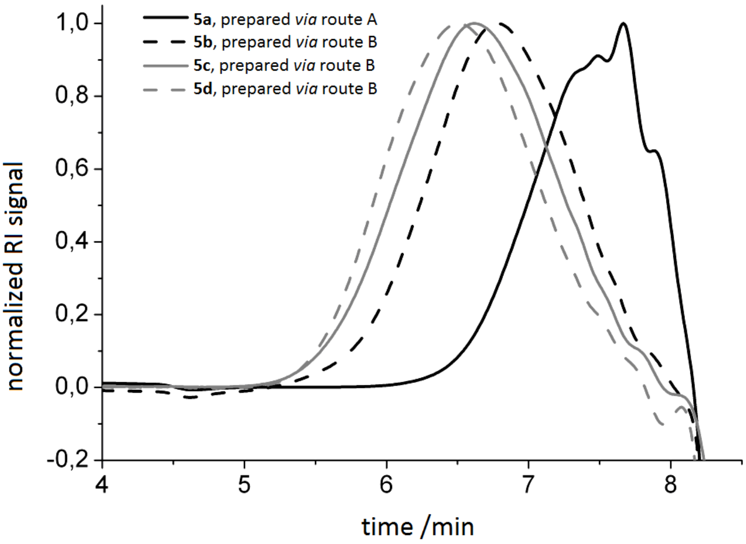


Figure 4.29: GPC traces of trifluoroacetylated **5a-5d** obtained by optimized reaction conditions.

As an example of these NMR investigations, the ^{1}H NMRs of monomer **4d** and polymer **5d** are presented in Figure 4.30. No end-group signals stemming from trifluoroacetylated amine or carboxylic acid derivatives could be detected in the polymer spectrum indicating its high molecular weight.

The ^{1}H NMR spectrum of polymer **5d** showed an internal olefin peak at 5.38 ppm and the methylene groups in α position to the carbonyl of trifluoroacetylated amide linkages at 2.8 ppm as typical signals for monomer **2**. The signal at 3.7 ppm corresponds to the protons in α position to the nitrogen atom of the diamine unit. All other signals could also easily be identified and thus the ^{1}H NMR of the investigated polymers clearly confirmed their structure. However, a small signal at 2.4 ppm was observed in the ^{1}H NMR of all polymers that could not be properly assigned despite all efforts. Similar signals could also not be assigned in literature examples.[306,310]

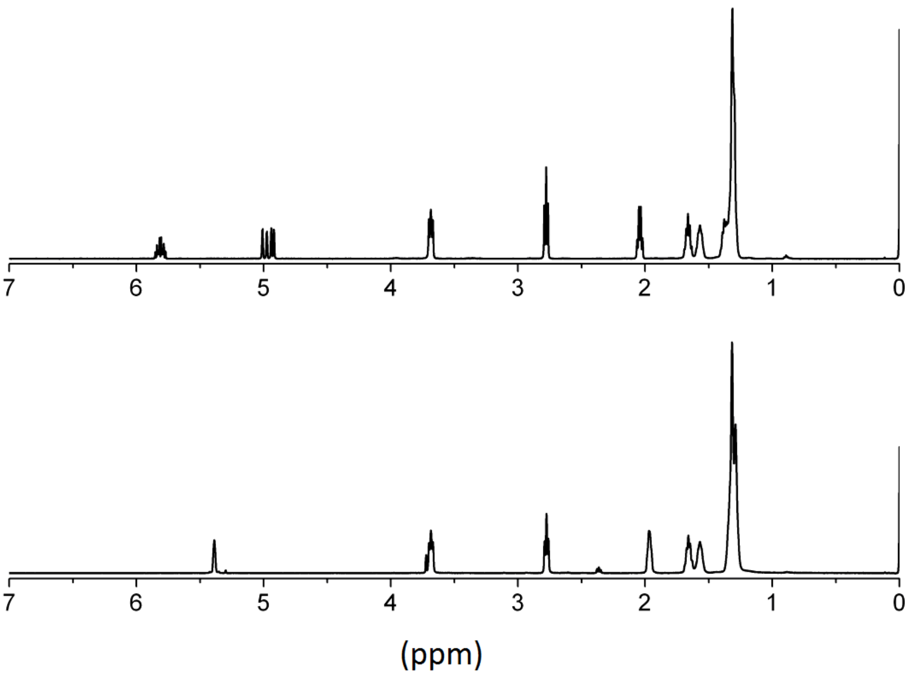


Figure 4.30: ^1H NMR spectra of trifluoroacetylated monomer **4d** (top) and polymer **5d** (bottom).

DSC studies showed a broadened endotherm in the second heating run with a shoulder on the high temperature side for PA 2,20, PA 4,20 and PA 6,20. For PA 8,20 a single endotherm was observed. According to previous reports on polyamides thermal properties, the low temperature endothermal peak originates from the melting of the thin lamellae crystals in the semicrystallized polymers and the high temperature one is attributed to the melting of the thick lamellae crystals or the recrystallized parts during the heating process.[314,315] Not surprisingly, PA 2,20 exhibited the highest melting temperature (T_m) in comparison to the other prepared PAs because of the shorter diamine segment and thus the higher amide group content. In general, the thermal properties (compare Table 4.12) are in the expected range and it is also worth mentioning that our E-configured unsaturated PA 8,20 (T_m = 180 °C) showed a slightly higher melting point compared to that of the polyamide synthesized from Z-octadec-9-enedioic acid, PA 8,18 (T_m = 169 °C).[313] This is most likely a result of a better crystallization due to (i) the better crystal fitting of the E configuration and (ii) the length of the diacid monomer unit.

Moreover, the TGA data (Table 4.12) indicate a good thermal stability for all polyamides under consideration. Except for PA 2,20, all polymers have a decomposition onset temperature, T_d, of 400 °C or higher. The somewhat poorer stability of PA 2,20 can most likely be related to the low molecular mass of this polymer.

Table 4.12: Thermal properties of the synthesized renewable polyamides X,20.

Polyamide	T_m **(°C)**	T_d **(°C)**
8,20 (**5d**)	180	416
6,20 (**5c**)	193	404
4,20 (**5b**)	222	400
2,20 (**5a**)	226	370

Conclusion

It has been demonstrated that the self-metathesis of monomer **2** and its subsequent polymerization with diamines using TBD as a catalyst is a straightforward method for the preparation of aliphatic polyamides, at least on lab scale. This route was superior to the also investigated ADMET polymerization of monomers **4a-d** and has some advantages (e.g. avoiding of acid chlorides) over conventional polyamide synthesis techniques. The obtained polymers showed good properties indicating their potential use as engineering plastics. Moreover, our studies clearly demonstrated that the described unsaturated polyamides can be obtained from renewable resources and demonstrate a new example of the use of plant oil derivatives in polymer science.

4.6 Synthesis of carbonate-based polymers and building blocks

Introduction

Unsymmetric and symmetric organic carbonates are important intermediates for the chemical industry (Figure 4.31). They can, for instance, act as useful protecting groups of alcohols and phenols, since they are more stable than the corresponding esters under basic conditions.[316] Additionally, organic carbonates have found application as monomers for organic glasses and as solvents, for instance, in the manufacture of lithium batteries.[317] Although the remarkable importance of aryl and alkyl carbonates in various fields as chemical intermediates is well documented by the presence of a large number of patents[318] and articles[317,319] in the literature, very few carbonates are available commercially. The conventional methods for the preparation of organic carbonates suffer from disadvantages and still require the use of toxic reagents,[319,320] such as phosgene, dimethyl sulfate, pyridine and carbon monoxide. Most commonly, chloroformate esters obtained from phosgene and alcohols were proposed as safer substituent.[321] However, the methods based on phosgene produce a high quantity of chloride salts as side products and phosgene istself is of course highly toxic.

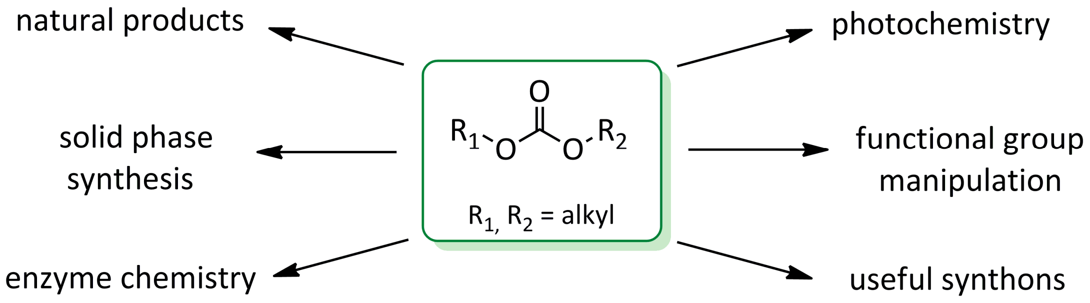


Figure 4.31: General view regarding carbonate applications in organic synthesis.

Furthermore, the selective synthesis of unsymmetric organic carbonates was accomplished using alkyl halides, either *via* the alkylation of metal carbonate with various alkyl halides and sulfonates in ionic liquids,[322] or by inorganic catalysts (e.g. Cs_2CO_3) based coupling of alcohols, carbon dioxide and alkyl halides.[323] Thus, bearing in mind these drawbacks, it seems advisable to develop more convenient and environmentally benign catalytic systems for the synthesis of carbonates.[146,324]

Along with this idea, the organic carbonate interchange reaction can be proposed as the most pursued eco-friendly “carbonylation” route to produce unsymmetric as well as symmetric carbonates in the presence of organic, metal-free catalyst, and dimethyl carbonate (DMC). Since DMC can be synthesized using CO_2 as building block,[325] and features high biodegradability and low toxicity, it incorporates several of the fundamental aspects of green chemistry (Figure 4.32).[3] In particular, DMC has been proposed as a substitute of dimethyl sulphate, methyl halides and phosgene and reacts either as methoxycarbonylating or as a methylating agent, depending on the reaction conditions.[324,326]

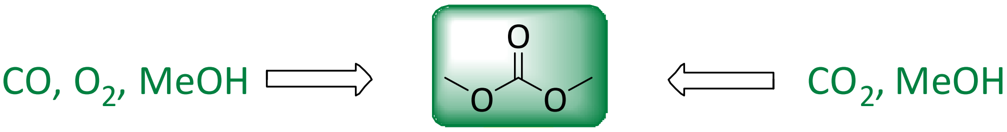


Figure 4.32: Phosgeneless routes to dimethyl carbonate.[325]

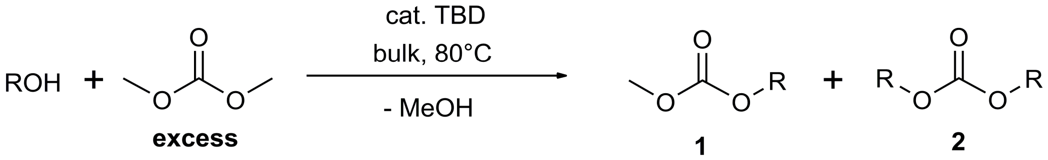
The carbonate interchange reaction was investigated by many researchers,[319] however, since this reaction is an equilibrium reaction, sophisticated procedures, high temperatures (>100 °C) and rather complicated heterogeneous catalysts systems (including MCM-41-TBD,[146]Mg/La metal oxide,[324e] CsF/α-Al_2O_3,[324b] nano-crystalline MgO[327] and metal–organic frameworks[328]) have been applied to shift the equilibrium towards the desired product. Furthermore, although unsymmetric organic carbonates, compared to symmetric ones, are more useful synthons, the synthetic routes are becoming even more complex. On the other hand, organocatalysts are steadily approaching the performance of organometallic catalysts and enzymes. Therefore, in order to develop a sustainable and selective unsymmetric organic carbonate synthesis, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) can be proposed as an alternative catalyst.

Concerning polymers, it is well know that carbonate linkages within the backbone structure introduce a spectrum of properties, such as reduced biodegradation time and enhanced mechanical performance.[329] Moreover, symmetric organic carbonates, especially long-chain ones, find application in lubricant, cosmetic, plasticizer and fuel compositions.[330] For all these reasons, the development of new phosgene- and metal-free synthetic routes to polycarbonates and low molecular weight organic carbonates is of major interest. Thus, the following discussion will be focused on the reactivity of DMC in the presence of commercially available TBD at low catalyst loadings (1.0 mol%), which allowed us to set up a simple and mild approach to the synthesis ofa wide range of symmetric and unsymmetric carbonates, as well as polycarbonates from different renewable diols. The synthesis of castor oil and citronellol derived symmetric α,ω-diene carbonates, and their further polymerization *via* ADMET will also be described.[94c]

Results and discussion

Unsymmetric organic carbonate synthesis

As discussed in the introduction, most of the catalytic systems for the synthesis of organic carbonates require the toxic and hazardous reagent phosgene at some stage. In order to address this problem, several groups used dimethyl or diethyl carbonate as a substituent for phosgene. In addition to this, organocatalysis has the potential to make current chemical processes more environmentally benign by avoiding the use of toxic transition metal catalysts. Among a wide variety of existing organocatalysts, TBD displays an outstanding catalytic performance in condensation reactions. Thus, the solvent-free direct condensation of alcohols and dimethyl carbonate, using TBD as homogeneous organocatalyst, was studied (Figure 4.33). It should be noted that although DMC is used in excess, both the monoaddition and the diaddition products can be expected.



ROH = 1°-, 2°- or less-reactive 3° alcohols

Figure 4.33: The solvent-free, direct condensation of an alcohol and dimethyl carbonate in the presence of TBD in homogeneous fashion.

First, it was important to set the proper reaction temperature, since, as aforementioned, DMC exhibits a versatile and tuneable chemical reactivity that depends on the experimental conditions, especially on the reaction temperature. Although there is no clear cut-off, it is known that in the presence of nucleophiles at the reflux temperature (T ~ 90 °C), DMC acts as a methoxycarbonylating agent, and at higher temperatures acts primarily as a methylating agent.[324] Furthermore, high temperatures favour the elimination of CO_2 from the organic carbonate, thus facilitating the formation of the corresponding ether. In this case, we found that the best results in terms of yield and selectivity were achieved by performing the reactions at 80 °C.

A number of different alcohols were chosen to evaluate the scope of the reaction; the first experiments were carried out using a simple primary alcohol (1-octanol) in order to optimize the reaction conditions. In a typical experiment, an excess of DMC was reacted with the alcohol in the presence of TBD. The product distribution was monitored by GC and GC-MS analysis and in some cases by NMR. The results obtained from these experiments are summarized in Table 4.13. While investigating the effect of the DMC/alcohol ratio at 80 °C using a catalyst loading of 1.0 mol% (to alcohol), it became clear that the rate of the reaction was somewhat reduced if the DMC/alcohol ratio was increased to 12/1 (Table 4.13, entry 4); in other words, the use of a larger excess of DMC did not further improve the yield of the reaction. It was thus necessary to reach a compromise between the amounts of unsymmetric and symmetric carbonate (undesirable product in this case) obtained in the reaction. Thus, we chose a DMC/ROH ratio of 5/1 as the one providing the best relation between yield of unsymmetric carbonate and excess of DMC, and at the same time the lowest amount of symmetric carbonate. Moreover, longer reaction times did not improve the conversion, since the competitive formation of the symmetric carbonates began to be more pronounced.

In order to enhance the selectivity, different catalyst amounts of TBD in the presence of constant molar ratio of DMC/ROH (5/1) were investigated. For example, catalyst loadings greater than 1.0 mol% led to rapid reaction; the reaction was complete in 15 min at a catalyst loading of 5.0 mol% (Table 4.13, entry 5).

Table 4.13: Carbonylation of 1-octanol under different reaction conditions.

Entry	DMC/ROH	TBD (mol%)	time	conversion (%)[a)]	selectivity (%)[b)]
1	3/1	1.0	1 h	96	83
2	5/1	1.0	1 h	>98	95
3	10/1	1.0	1 h	97	97
4	12/1	1.0	1 h	96	98
5	5/1	5.0	15 min	>98	91
6	5/1	0.5	1 h 30 min	>98	93
7[c)]	5/1	1.0	15 min	>98	89
8[d)]	5/1	1.0	30 min	>98	92

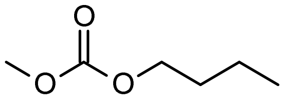
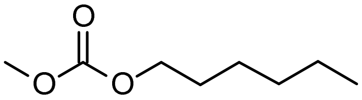
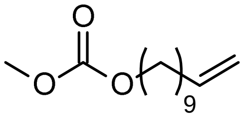
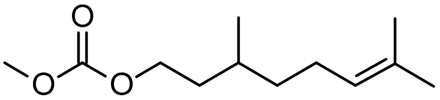
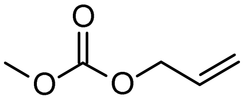
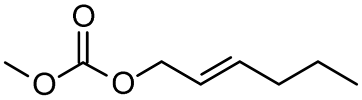
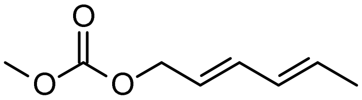
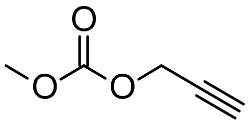
[a)] Conversions were calculated by GC-FID analysis using tetradecane as internal standard; [b)] The selectivity towards the unsymmetric carbonate; [c)] Reaction performed under continuous flow of Argon; [d)] Reaction carried out in the presence of molecular sieves 4Å.

In this case, the selectivity for the desired unsymmetric carbonate was 91%; higher catalyst loadings only marginally improved this result. On the other hand, decreasing the catalyst loading to 0.5 mol% did not result in comparably better selectivity (compare entries 2 and 6 in Table 4.13). 1.0 mol% TBD loading thus seemed to be a good compromise in terms of conversion and selectivity. It is well known that the removal of methanol strongly determines the efficiency of TBD-catalyzed transesterification; consequently, a model reaction was carried out under fixed reaction conditions (DMC/ROH = 5/1, 1.0 mol% TBD, 80 °C) applying a continuous stream of an inert gas or molecular sieves to remove the released methanol, respectively (entry 6 and entry 7 in Table 4.13). From these results, it became evident that no clear increase in the rate of the reaction took place in any of both cases. However, the selectivity in both the continuous gas flow and addition of molecular sieves reactions decreased due to the formation of the symmetric carbonate.

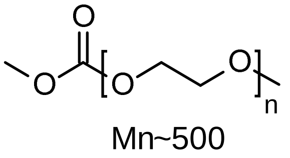
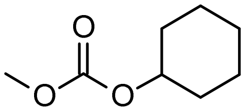
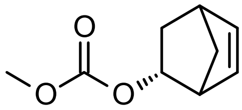
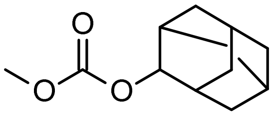
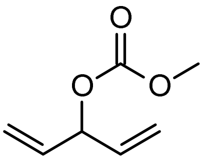
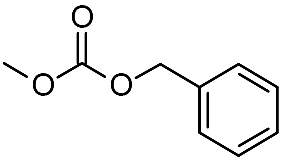
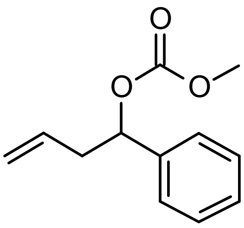
The same experimental conditions were adopted for the synthesis of the corresponding unsymmetric carbonates, presented in Table 4.14, in order to evaluate potential differences in the reactivity of different alcohols. Alkyl methyl carbonates (n = 3-5), especially butyl methyl carbonate, are suitable as co-solvents in lithium-ion batteries.[331] Thus, a clean and quantitative alternative synthesis of butyl methyl carbonate is a matter of interest. In accordance, butyl methyl carbonate was synthesized in relatively short time and with 91% selectivity.

Catalytic cross-coupling reactions of allylic and propargylic compounds are used as a intermediates for the formation of carbon-carbon and carbon-hetero atom bonds;[332] for this reason we investigated the usefulness of our approach for the synthesis of unsymmetric allylic and propargylic carbonates. Initial attempts were performed to synthesize the unsymmetric carbonates of primary alcohol derivatives (Table 4.14, entries 5-7). After optimization, the maximum conversion for the synthesis of allyl methyl carbonate was 88% with a DMC/ROH molar ratio of 7.5/1 in 1 h, with quite high selectivity (94%). Prolonging the reaction times resulted in the formation of the symmetric product. Applying high molar ratios of DMC/ROH (such as 10/1, 15/1 and 20/1) did not result in higher conversions. However, these results (88% conversion, 94% selectivity) are very useful for synthetic procedures and are by far less toxic than usually applied synthetic routes (i.e. the use of chloroformates).

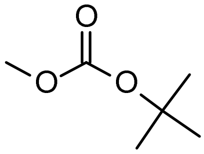
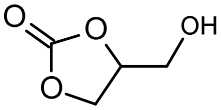
Table 4.14*:* Synthesis of various unsymmetric carbonates *via* TBD catalysed transesterification of DMC.

Entry[a)]	**Product**	**DMC/ ROH**	**time**	**conversion (%)**[b)]	**selectivity (%)**[b)]
1		5/1	30 min	98	91
2		5/1	30 min	99	93
3		5/1	2 h	98	97
4		5/1	30 min	99	97
5		7.5/1	1 h	88	94
6		5/1	40 min	98	94
7		5/1	2 h	98	92
8[c)]		7.5/1	6 h	80	94

Cont. Table 4.14: Synthesis of various unsymmetric carbonates *via* TBD catalysed transesterification of DMC.

Entry[a)]	**Product**	**DMC/ ROH**	**time**	**conversion (%)**[b)]	**selectivity (%)**[b)]
9	 Mn~500	5/1	5 h	99	98
10[d)]		5/1	3 h	98	97
11		5/1	20 h	98	99
12		5/1	4 h	98	98
13		5/1	4 h	98	97
14		7.5/1	8 h	99	97
15		5/1	3 h	99	94

Cont. Table 4.14: Synthesis of various unsymmetric carbonates *via* TBD catalysed transesterification of DMC.

Entry[a]	Product	DMC/ ROH	time	conversion (%)[b]	selectivity (%)[b]
16[e]		7.5/1	48 h	86	99
17		5/1	20 min	99	96

[a] all reactions were carried out with 15 mmol of the corresponding alcohol and 0.15 mmol (1.0 mol%) of TBD unless stated otherwise; [b] conversions and selctivity were calculated for crude reaction mixtures *via* ^{1}H NMR (300 MHz) and /or GC and GC-MS with tetradecane as internal standard; [c] 5.0 mol% catalyst was used instead of 1.0 mol% TBD; [d] molecular sieves were added; [e] 10.0 mol% catalyst was used instead of 1.0 mol% TBD.

Moreover, the tendency of substituted allylic alcohols to afford better yields than the allyl alcohol was remarkable (compare results in entry 5 and 6 in Table 4.14). It should also be noted that divinyl carbinol (Table 4.14, entry 13), a prochiral and *bis*-allylic alcohol, provided the desired product with relatively good conversion and selectivity within 4 h. Further, the carbonylation of propargyl alcohol proved to be more difficult; only a higher molar ratio of DMC/ROH (7.5/1) in combination with a higher catalyst loading (5.0 mol% TBD) resulted in a satisfactory conversion (entry 8, Table 4.14).

Besides this, another interesting example was the carbonylation of poly(ethylene glycol) methyl ether (mPEG-OH, M_n ~ 500 Da). The covalent modification of biological macromolecules and surfaces for many pharmaceutical and biotechnical applications is accomplished by the coupling of PEG to the peptide or protein.[333] Hence, an important aspect in this process is the incorporation of various PEG functional groups, like anhydrides, chloroformates and carbonates, which can easily conjugate to the protein.

Within this in mind, mPEG-OH was successfully carbonated to the corresponding unsymmetric organic carbonate (entry 9, Table 4.14) with quantitative conversion and high selectivity.

The behaviour of a few representative and less reactive secondary alkyl and aryl alcohols was also studied (Table 4.14, entries 10-15). All substrates were transformed to the corresponding unsymmetric carbonates in comparably good selectivity to the previously reported methods. Also in the case of the chiral, homoallylic, secondary alcohol, 4-phenyl-1-buten-4-ol (entry 15, Table 4.14), almost quantitative conversion was obtained. Of special note is that the *tert*-butyl methyl carbonate (entry 16, Table 4.14), which is useful as octane enhancer for gasoline,[319] was selectively obtained in 86% conversion within 48 h. Although it was necessary to use a molar ratio DMC/ROH of 7.5/1 and catalyst loading of 10.0 mol%, the procedure is still advantageous in comparison to the method employing inorganic base (cesium carbonate) with phase transfer catalyst (PEG-2000) under pressure at 125 °C, in which the final yield was just 43%.[334] Additionally to all these monoalcohols, a potential renewable platform molecule for synthesis, glycerol, was tested as well under the specified conditions: DMC/ROH molar ratio 5/1 and 1.0 mol% TBD (Table 4.14, entry 17). When the reaction was conducted for 20 min, the synthesis of glycerol carbonate with conversion of glycerol of >99.9% and selectivity of 96% was observed.

Polycarbonate synthesis *via* TBD mediated polycondensation

After proving the carbonylation efficiency of TBD as organocatalyst for the synthesis of several unsymmetric organic carbonates, the next step was to test the activity of TBD in the polymerization of DMC with diols of different chain lengths. Aliphatic polycarbonates are important precursors for the preparation of novel polyurethanes and are conventionally synthesized either by polycondensation of phosgene with diols, or by the transesterification of five-membered cyclic carbonate with selected diols through heterogeneous or lipase-based catalysis.[329] In addition to the growing interest in the synthesis of aliphatic polycarbonates for fiber and film forming applications, aliphatic polycarbonates have attracted increasing attention as degradable biomaterials in recent years because of the non-production of acid components upon *in vivo* implantation. Moreover, the use of renewable diols is desirable, and for this reason, one of the chemical precursors used for the synthesis of aliphatic polycarbonates was 1,3-propanediol (**D1**), which can be obtained from renewable resources through economical and sustainable processes such as microbial fermentation.[335] 1,6-Hexanediol (**D2**) and the fatty acid derived (*E*) icos-10-ene-1,20-diol (**D3**) were also investigated as alternative diols. Industrially, 1,6-hexanediol is prepared by the hydrogenation of adipic acid and since the first pilot plant producing adipic acid *via* a fermentation process using non-food, plant-based feedstock was recently set up, **D2** can be considered as (potentially) biomass derived as well.[336]

TBD catalyzed polycondensation between DMC and the respective diol occurred in two steps: (a) hydroxyl and carbonate end groups reacted with the elimination of alcohol (MeOH) to yield the oligomers; (b) transesterification between two carbonate end groups with elimination of DMC. A representative procedure for the synthesis of polymers is depicted in Figure 4.34.

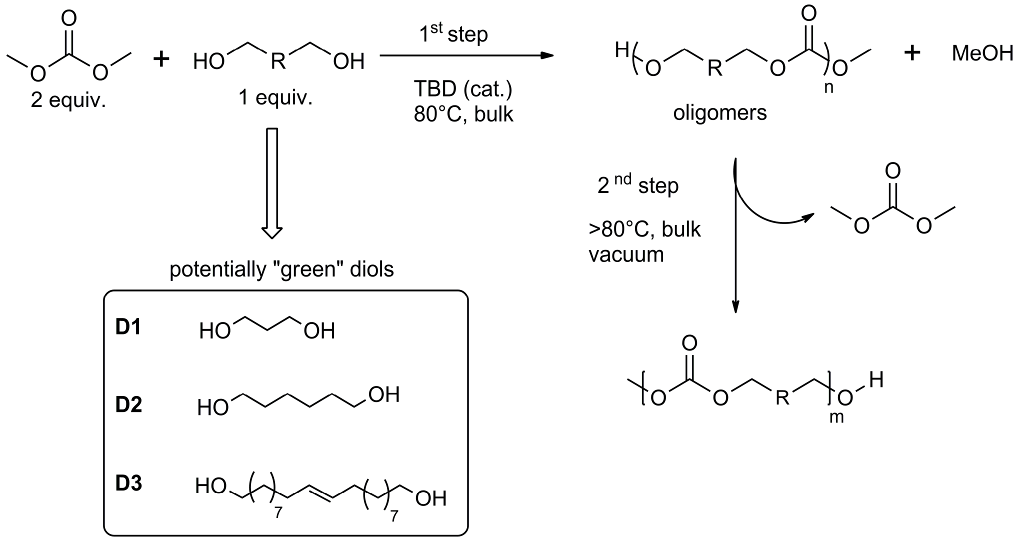


Figure 4.34: One-pot two-step polymerization *via* TBD catalyzed carbonylation of DMC in the presence of renewable diols**.**

Based on the results obtained for the synthesis of the unsymmetric carbonates, the initial polymerization attempts were performed with 1.0 mol% TBD related to the diol molecule. Solvent-free conditions were chosen to avoid solvent waste, enhance conversions, and reduce the formation of cyclic structures. Whereas conventional catalytic polycondensation reactions of AA-BB type monomers require 1:1 feed ratio, the 1st step (Figure 4.34) was performed under atmospheric pressure at 80 °C in bulk using a DMC/diol molar ratio of 2/1. In this way, we prevented the loss of DMC that would shift the reaction stoichiometry. Furthermore, in this type of polymerizations, low DMC feed ratios yield low molecular weight chains with hydroxyl terminal groups.[337] However, with sufficient excess of DMC, chain growth would continue by the reactions occurring both between hydroxyl and methyl carbonate as well as between two terminal methyl carbonate groups (with release of DMC). On the other hand, if the DMC/ROH ratio is quite high, *i.e*. using a 4 to 1 stoichiometry, the terminal groups of the polymer would entirely be methyl carbonate moieties and thus the polymerization rate would be quite slow. In summary, for the propagation to continue, a substantial fraction of chain ends must be methyl carbonate moieties.

To favour the formation of the oligomers, continuous argon flow was applied within the first step. Online monitoring by GPC and/or NMR was performed on the crude reaction samples. From these results (Table 4.15), it was clearly observed that the time required for this reaction step was determined by the chain length of the employed diol. For the diol with shortest chain, **D1**, the transesterification reaction (1st step in Figure 4.34) took ~1 h, and for **D3**, this was 4 h. Once a sufficient amount of oligomers was formed, in an effort to facilitate the polymerization by removing the unreacted DMC and methanol produced by the condensation reactions and to reach high molecular weight, the reaction temperature was increased to 90 °C with reduced pressure.

Table 4.15: Results for the synthesis of aliphatic carbonates *via* the polycondesation reaction of DMC and three renewable diols in the presence of 1.0 mol% TBD.

Entry	**Diol**	**first step[a)]** **time / T** **M_n[b)](kDa) / PDI(M_w/M_n)**	**second step** **time / T** **Mn[b)](kDa) / PDI(M_w/M_n)**
P1	**D1**	1 h / 80 °C 1.2 / 1.97	3 h / 90 °C 3.5 / 2.16
P2	**D2**	2 h / 80 °C 2.4 / 2.40	1 h / 90 °C 12 h / 100 °C 7.5 / 2.15
P3	**D3**	4 h / 80 °C 3.2 / 2.39	1 h / 90 °C 12 h / 100 °C 15.5 / 1.85

[a)] first step performed at 80 °C in bulk under continuous flow of argon; [b)] data obtained from GPC performed in THF relative to PMMA calibration.

The crucial point in the second step was to determine the final temperature till which the polymerization could be carried out. We clearly observed that the M_n and the yield of polymers synthesized with **D1** decreased with increasing temperature. Performing the reaction at 100 °C for 1 h under vacuum resulted in markedly decrease in M_n from 3.5 kDa to 2.6 kDa. This could be ascribed to the evaporation of oligomers of **D1** and thermal degradation of the final polymer under these conditions. Therefore, 90 °C was the best poylmerization temperature for **D1**. In contrast, 90 °C was inefficient to yield high molecular weight polymers with **D2** and **D3**; thus, the reaction temperature was increased to 100 °C under vacuum. After 12 hours at 100 °C under continuous vacuum the final M_n value for **P2** was still not high, indicating that these reaction conditions are not efficient for **D2**. On the other hand, for **P3** in Table 4.15 under the preliminary polymerization conditions and consistent with chain growth was the observation that, by using a 2/1 DMC/**D3** feed, the PDI value decreases from 2.39 to 1.85 throughout the course of the second step. This trend could be attributed to the longer reaction times at 100 °C, which permitted the low molar mass products to diffuse to catalyst and form products of higher molecular weight, thereby reducing the low molecular weight fraction and decreasing the PDI.

In order to further improve the M_n values for the polymer synthesized with **D2**, the temperature was hourly increased to 150 °C during the second polymerization stage, which resulted in significatly improved molecular weight (Table 4.16).

In further experiments, we observed that the polymerizations of **D1** and **D2** were also promoted by lower loadings of TBD (Table 4.16). By minimizing the catalyst loading to 0.5 mol%, formation of polymer with M_n of 33.0 kDa for **D2** was accomplished (Table 4.16, entry 3). Figure 4.35 shows the GPC chromatograms of the polymers synthesized with **D2** in the presence of 0.5 and 1.0 mol% TBD, respectively (compare **P6** and **P4**, Table 4.18). These results represented a significant improvement with regards to previously reported result for the same polymer, where 11.0 kDa were obtained *via* the polymerization of diethyl carbonate with 1,6-hexanediol catalyzed by immobilized *Candida antarctica* Lipase B.[329] In line with these observations, increasing the catalyst loading to 5.0 mol% resulted in a decrease of the M_n values both for **D1** and **D2**.

Table 4.16: Optimized reaction conditions for the polymerization of **D1** and **D2** with different catalyst loadings.

Entry	Diol / TBD (mol%)	first step[a) time / T	first step[a) M_n[b)(kDa) / PDI(M_w/M_n)	second step time / T	second step M_n[b)(kDa) / PDI(M_w/M_n)
P4	**D2** /1.0	1 h / 80 °C	13.5 / 2.18	1 h / 90 °C 1 h / 100 °C 1 h / 120 °C 1 h / 140 °C 1 h / 150 °C	16.2 / 2.15
P5	**D1** /0.5	1 h / 80 °C	3.0 / 2.17	3 h / 90 °C	5.9 / 1.97
P6	**D2** /0.5	2 h / 80 °C	5.2 / 2.31	1 h / 90 °C 1 h / 100 °C 1 h / 120 °C 1 h / 140 °C 1 h / 150 °C	33.0 / 1.94
P7	**D1** /5.0	1 h / 80°C	2.8 / 1.91	3 h / 90°C	5.9 / 1.97

[a)] first step performed at 80 °C in bulk under continuous flow of argon; [b)] data obtained from GPC performed in THF relative to PMMA calibration.

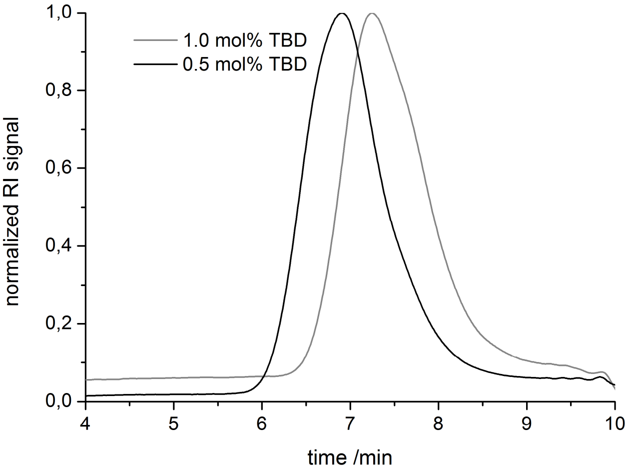


Figure 4.35: GPC chromatogram for the polymers of **D2** with two different catalyst loadings, respectively 0.5 and 1.0 mol% TBD.

Furthermore, a closer look at the polymerization results *via* NMR revealed an interesting fact regarding the obtained molecular structure of the final polymer synthesized from **D1**. It became evident that in the presence of high TBD loadings, the terminal methyl carbonates are cleaved, and as a consequence of this the formation of terminal allyl carbonate group was observed. This clearly provided an explanation for the decrease of the M_n in the presence of 5.0 mol% of TBD. Figure 4.36 shows, in its inset, the ^{1}H NMR spectrum of the precipitated polymers obtained from **D1** in the presence of different amounts of TBD, in which the effect of catalyst loading on the formation of the aforementioned cleavage can be clearly observed. Indeed, this cleavage, leads to a allyl carbonate function displaying a different reactivity that might be further exploited in another context. Evidently, it should be noted that the polymers obtained from **D1** in the presence of TBD are classified as poly(trimethylene carbonate), and the proposed method can substitute the traditional synthesis by ring-opening polymerization of 1,3-dioxan-2-one, which on the other hand is obtained by refluxing 1,3-propanediol in an excess of diethyl carbonate.

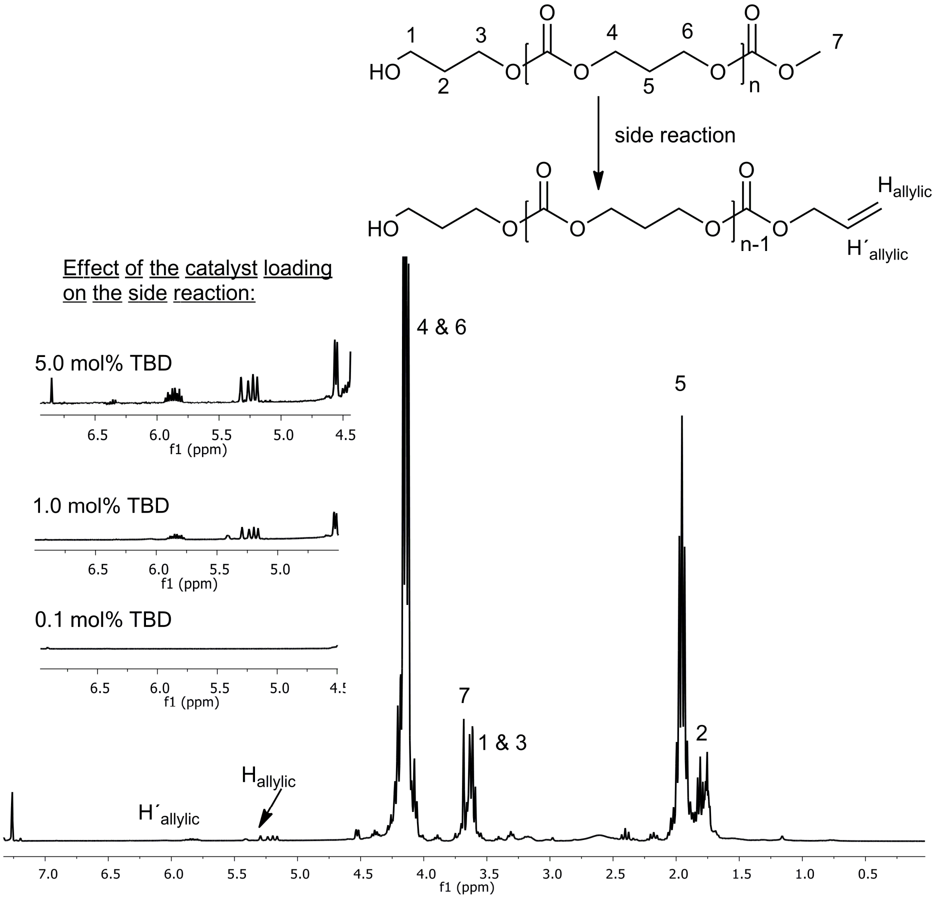


Figure 4.36: ^{1}H NMR spectra of polymers synthesized with **D1** in the presence of 0.1, 0.5, 1.0 and 5.0 mol% TBD, thus revealing the effect of TBD on the possible side reaction: cleavage of terminal methyl carbonate.

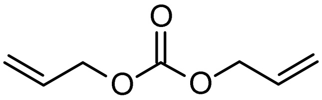
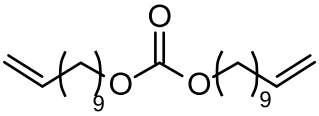
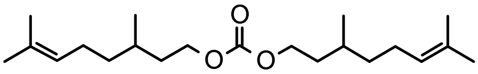
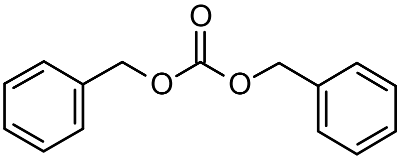
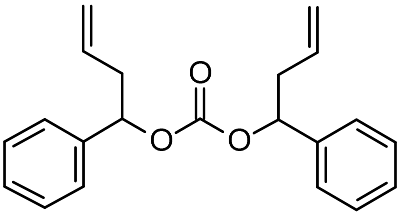
Moreover, decarboxylation is a side reaction which is known to commonly occur during the synthesis of polycarbonates at high reaction temperature.[338] It is noteworthy to mention that we did not observe the corresponding signals in our NMR spectra, indicating that TBD does not cause such side reactions (at least within our temperature limits).

Symmetric organic carbonate synthesis and subsequent ADMET studies of representative monomers

As an extension, we turned our attention to the utilization of this approach for the synthesis of symmetric organic carbonates, which possess terminal double bonds and can thus be employed as monomers in olefin metathesis polymerization. 10-Undecen-1-ol and citronellol are two biomass derived alcohols and thus the final symmetric organic carbonates can be considered as renewable building blocks for the synthesis of aliphatic bio-based linear polycarbonates. In addition, to assess the scope of the symmetric organic carbonate synthesis, the reactivity of allyl alcohol, benzyl alcohol and the chiral, homoallylic, secondary alcohol, 4-phenyl-1-buten-4-ol, were investigated. It is worth to highlight the simplicity of the reaction, which was performed under solventless conditions by mixing (at room temperature) DMC and the corresponding alcohol in ratio of 2.1/1, along with a catalytic amount (1.0 mol%) of the guanidine base TBD and subsequent heating to 80 °C.

The synthetic results of the reactions are presented in Table 4.17. Generally speaking, this reaction gave very good conversions with all tested alcohols allowing us to obtain the corresponding symmetric organic carbonates as the only product. No product arising from the methylation of the alcohol was observed under these reaction conditions. However, as was anticipated, in the case of benzyl alcohol the reaction was slower and afforded the desired product only after 45 h. Moreover, the carbonate interchange reaction of citronellol with DMC led to a new terpenoid, which could be further investigated as a potential monomer for olefin metathesis polymerization.

Table 4.17: Selected results for the synthesis of symmetric organic carbonates at 80 °C.

Entry[a)]	Product	Time (h)	conversion (%)[b)]	selectivity (%)[b)]
1		16	99	99
2	**M1** 	14	99	99
3	**M2** 	12	99	99
4		45	99	99
5		8	99	99

[a)] all reactions were carried out with molar ratio DMC/ROH of 1/2.1 and 15 mmol of the corresponding alcohol in the presence of 1.0 mol% of TBD under bulk with continuous Argon stream unless stated otherwise; [b)] conversions were calculated for crude reaction mixtures *via* ^{1}H NMR (300 MHz) and /or GC/GC-MS with tetradecane as internal standard.

ADMET polymerization allows the polymerization of α,ω-diene monomers bearing a wide variety of functionalities (see Chapter 3). Thus, the product of diaddition of 10-undecen-1-ol to DMC (**M1**, see Table 4.17) was used for polycarbonate synthesis *via* ADMET polymerization. In order to study the molecular weight variations of the resulting polymers, the first experiments (Table 4.18) were performed in bulk at 80 °C under continuous vacuum for 1 h using three different metathesis catalysts: Grubbs 2nd generation catalyst (**C4**), Hoveyda-Grubbs 2nd generation catalyst (**C5**) and Zhan 1B catalyst (**C7**) (Figure 4.37). The precise control of the backbone functionality can be interrupted with the possible side reaction: olefin isomerisation of the terminal double bonds. Thus, benzoquinones (especially 1,4-benzoquinone, **BQ**), which are very effective additives for the prevention of the olefin isomerization[116] were added to the reaction mixture prior to the catalyst addition. The analytic data of the polymers synthesized is summarized in Table 4.18 and selected GPC traces are depicted in Figure 4.37. Monomer conversion was quantitative as determined by the complete disappearance of the monomer signal in the GPC traces of the reaction mixtures. The results clearly indicated that **M1** can be successfully polymerized in the presence of 0.2 mol% **C7**, reaching M_n values of 27.5 kDa.

Table 4.18: Selected results for ADMET of **M1** at 80 °C with three different catalysts.

Entry	**Catalyst (mol%)**	**M_n[b)](kDa) / PDI(M_w/M_n)**
P8	**C4** (0.2)	9.5 / 1.60
P9	**C5** (0.2)	13.5 / 1.73
P10	**C7** (0.2)	27.5 / 1.92

a) data obtained for crude reaction mixtures from GPC performed in THF relative to PMMA calibration.

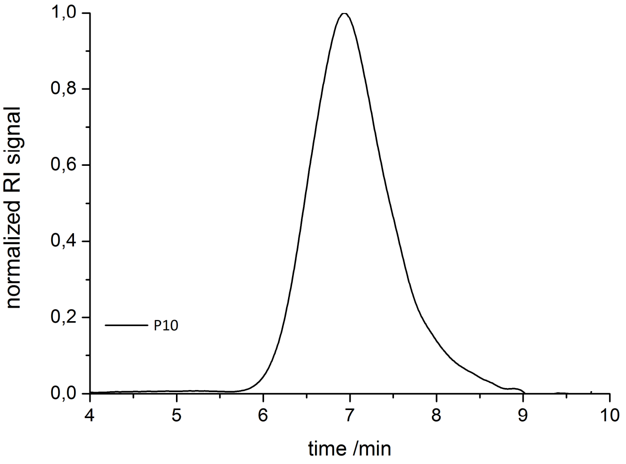


Figure 4.37: GPC data of ADMET polymer for **M1** synthesized in the presence of **C7**.

Nowadays, of great interest is the applicability of terpenes as renewable raw materials for the synthesis of new chemical intermediates *via* different chemical transformations.[339] Apart from this, a considerable number of terpene derivatives have been tested as polymer precursors, using different polymerization mechanisms.[340] Wagener and co-workers investigated the reactivity of 1,1-disubstituted and trisubstituted olefins towards ADMET in the presence of the highly active Lewis acid free Schrock alkylidenes type catalyst.[341] However, all attempts to polymerize failed; the tungsten-based catalyst was unable to promote metathesis chemistry with any of the mentioned substituted olefins. On the other hand, the molybdenum-based catalyst afforded the metathesis of 1,1-disubstituted alkenes but only through cross-metathesis with internal olefins, which were no more than disubstituted. Having in hand the symmetric organic carbonate monomer **M2** (Table 4.17, entry 3), synthesized with the aforementioned method from citronellol and DMC in the presence of TBD, some test experiments were performed. Hence, considering the enhanced difficulty for the challenging polymerization of **M2**, the highly active **C7** was the catalyst of choice. The initial screening showed that high temperature was necessary to achieve high conversion. Consequently, the reaction was directly attempted under solvent free conditions at 90 °C with 1.0, 2.5 and 5.0 mol% **C7** and the respective **BQ** amount (2.0 equivalents to the catalyst) was added prior the catalyst addition. As already reported, vacuum or continuous gas flow is a requirement for a successful release of ethylene during the olefin metathesis polymerization reactions. However, in case of the ADMET polymerization of **M2**, tetramethylethylene is the condensate. Therefore, to further accelerate the release of this compound (boiling point = 73 °C), continuous vacuum was employed. Our results indicated that 1.0 and 2.5 mol% **C7** were inefficient to polymerize (compare results in Table 4.19) **M2** and that the used amounts of **BQ** were not enough to prevent the isomerization occurring during the ADMET reactions of the respective this diene (observed by GC-MS and NMR, Figure 4.38). On the other hand, a catalyst loading of 5.0 mol% **C7,** together with 20.0 mol% of **BQ,** was efficient enough to yield a methyl-branched, unsaturated hydrocarbon polymer (**P14** in Table 4.19). The GPC chromatogram of the precipitated polymer is represented in Figure 4.39. The GPC monitoring of the reaction revealed that the present reaction conditions provided a polymer in 75% yield with 89% monomer conversion within 4 h.

Table 4.19: Selected results for ADMET of **M2** with **C7** at 90 °C.

Entry	**C7 (mol%) / BQ (mol%)**	**M_n ^a)^(kDa) / PDI(M_w/M_n)**
P11	1.0 / 2.0	0.6 / 1.19
P12	2.5 / 5.0	1.6 / 1.75
P13	5.0 / 10.0	4.1 / 1.86
P14	5.0 / 20.0	7.9 / 1.81

a) data obtained for crude reaction mixtures from GPC performed in THF relative to PMMA calibration.

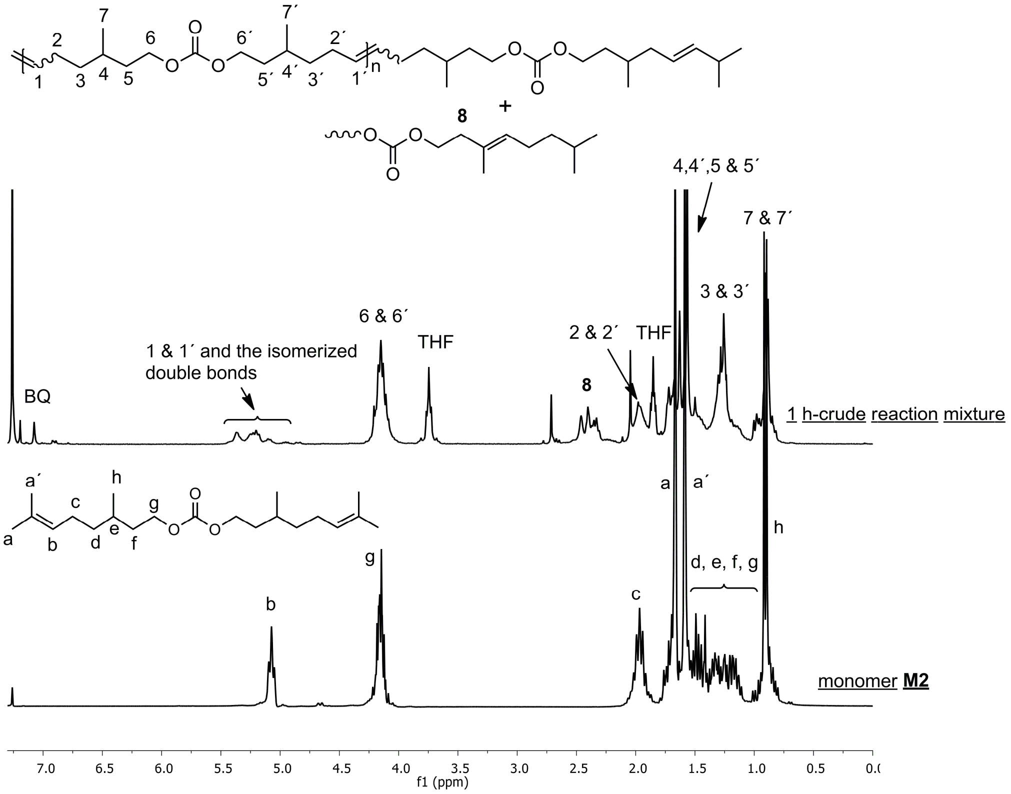


Figure 4.38: The olefin isomerization observed during the polymerization of **M2** in the presence of **C7** (Table 4.19, entry **P13**).

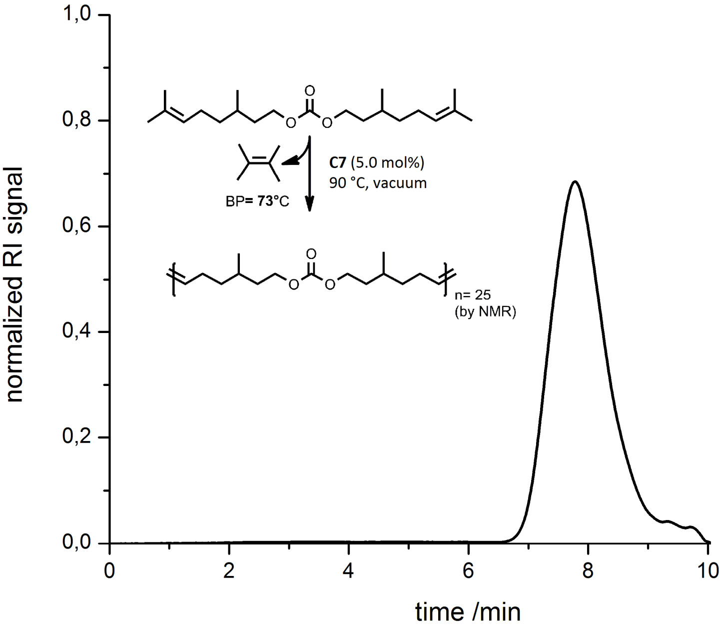


Figure 4.39: GPC data for the precipitated polymer **P14** (table 4.19).

Conclusions

The herein reported method, which is very easy to implement and incorporates many features of green chemistry, such as clean synthesis and the use of less toxic reactants, permits the synthesis of unsymmetric carbonates from the parent alcohols under solvent-free conditions with good selectivity. The influence of several reaction parameters such as amount of DMC, catalyst loading and reaction time on the reaction efficiency are discussed. Furthermore, the process opens new ways for a flexible utilisation of renewable resources for non-food value-added products, since we have shown the transformation of a variety of renewable alcohols into polycarbonates *via* ADMET polymerization and *via* classic polycondensation.

4.7 On the polymerization behavior of telomers: Metathesis *versus* thiol-ene chemistry

Introduction

Within the scope of efficient and environmentally friendly processes for the production of building blocks, the addition of nucleophiles to olefins and alkynes represent typical examples of 100% atom-efficient reactions. Among these reactions, the telomerization reaction,[342] a synthetic methodology originally discovered by Smutny in 1967,[343] is reported to provide linear dimerization products of 1,3-dienes (such as 1,3-butadiene and isoprene) *via* 1,6 or 3,6-addition of an appropriate nucleophile (e.g. alcohols,[344] water,[345] amines and ammonia,[346] sugar[347] and polyols,[348] starch[349] and carbon dioxide[350]) in good yields for countless applications. This valuable process enables, for instance, the synthesis of intermediates for natural products or fine chemicals synthesis[351] and the preparation of amphiphilic compounds that find use as surfactants or emulsifiers if the proper diene/nucleophile combination is selected.[352] In addition, if the applicability of telomers, in particular α,ω-diene ones, could be extended to polymerization reactions, this would open up new opportunities for building high molecular weight and value-added materials. To date, studies reporting the use of telomers as monomers for polymer synthesis are rare. The only example is the copolymerization of ethylene with 2,7-octadienyl methyl ether, a mono-telomer available by the telomerization of 1,3-butadiene with methanol and palladium catalysts.[353] However, di-telomers have not been yet regarded as monomers for the synthesis of polymers. Since di-telomers contain internal and terminal double bonds, both ADMET and thiol-ene polyaddition are in principle suitable polymerization techniques.

Thus, in order to broaden the application possibilities of butadiene telomers, we report here a comparative study on the polymerization of α,ω-diene telomers using these two straightforward and simple chemical pathways as versatile tools to convert such valuable monomers into potentially useful macromolecular materials.

Results and discussion

The di-telomers used in this study were synthesized by Andrei N. Parvulescu, Pieter C. A. Bruijnincx and Bert M. Weckhuysen, from the Utrecht University. The Pd-catalyzed telomerization of 1,3-butadiene (readily available and relatively cheap) with renewable 1,3-propanediol, a 100% atom-efficient process, is an elegant way to synthesize the herein studied monomers with minimum environmental impact.[354] It must be pointed out that 1,3-propanediol can be obtained directly either from corn or any plant oil as a renewable raw material,[355] and thus the telomerization process can be in principle be integrated in a 100% biomass-based synthesis platform as long as butadiene is obtained from renewable sources, for instance from bio-ethanol.[356] With the application as surfactant precursor in mind, previous studies were aimed at optimizing conditions for formation of the mono-telomer of 1,3-propanediol.[354] However, as the di-telomer product was required for our polymerization studies, the telomerization conditions were adapted by our colleages from the University of Utrech. They used a larger excess of butadiene (1,3-butadiene:1,3-propanediol molar ratio of 6:1) and a longer reaction time at 80 °C under solvent-free conditions. Using the Pd/TOMPP complex as telomerization catalyst, the di-telomers were obtained with full conversion of the diol substrate and a yield of 92%. Telomerization products are almost inevitably obtained as a mixture of the linear (1-addition product) and branched (3-addition) octadienes. Thus, we received three different di-ethers with different linear/branched ratios as shown in Figure 4.40.

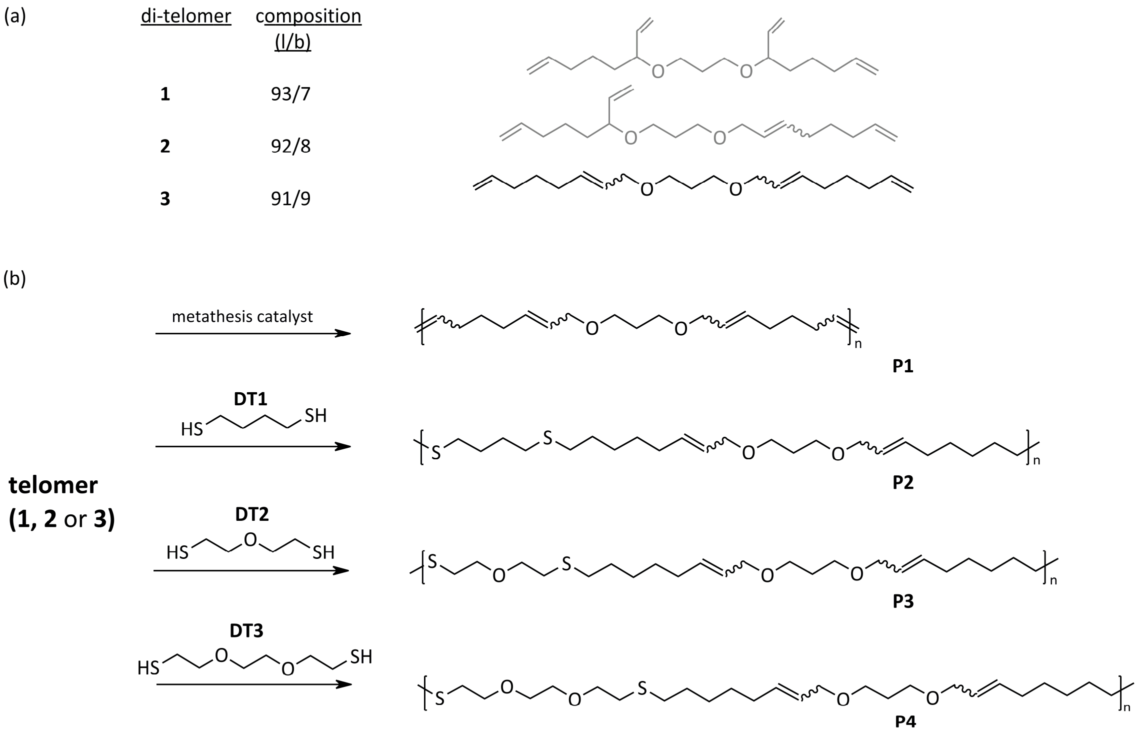


Figure 4.40: a) Di-telomer composition as obtained *via* GC-MS and NMR analysis; b) schematic representation of the applied polymerization techniques and idealized products.

ADMET Polymerizations

The efficacy of the telomers (**1**, **2** and **3**) as monomers was evaluated using two polymerization methods. The first route focuses on the reactivity of the di-telomers in the presence of metathesis catalysts. As mentioned in the introduction, it is well known that, in addition to the construction of many complex and important low molecular weight molecules, the metathesis reaction has enabled the synthesis of diverse polymers.[357] So far, concerning the transformation of the hydrophobic chain of different mono-telomers [such as (*E*)-1-phenoxy-2,7-octadiene or the (peracetylated)octadienylether of xylose], the activity of several Ru-based Grubbs 1st and 2nd generation catalysts, as well as Re- and W-based complexes, has been investigated.[358] In those cases where Ru-based catalysts were used, compounds corresponding to a metathesis involving internal double bonds were observed. However, up to date olefin metathesis has not been applied to di-telomers. As the di-telomers can be considered α,ω-dienes, they would be suitable monomers for ADMET polymerization. Nevertheless, di-telomers also possess internal double bonds and thus cannot be considered traditional α,ω-dienes, but participation of the internal olefins in ADMET would nonetheless still lead to polymer formation. Therefore, the ADMET reactions of monomers **1**, **2** and **3** were investigated (Figure 4.40). The readily available Ru-based metathesis catalysts should be more suitable for these di-telomers, given their functional group tolerance.[94a,c] In order to study the scope and limitations of the ADMET polymerization, extensive optimization studies involving changes of catalyst, temperature and substrate (the effect of l/b ratio) were carried out. Since ADMET polymerization is ideally performed in bulk monomer to maximize monomer concentration and favor formation of polymer,[103] the reactions were performed under solvent-free conditions. Moreover, ADMET chemistry relies on ethylene removal, which drives the reaction in this step-growth polymerization.[95] Therefore, unless otherwise specified, a continuous gas flow (argon or nitrogen) was applied throughout the reactions, which were run for 4 h. Furthermore, all results presented stem from at least two individual reactions. Monitoring of these reactions by GPC and NMR provided the necessary insights to fully understand the polymerization behavior of these new monomers. The primary screening of the ADMET reaction of telomers **1**, **2** and **3** was focused on the effects of catalyst loading and temperature on the conversion to the desired polymer. The crucial point in this study was to retain the internal double bonds of the monomers unreacted. Ru-benzylidene metathesis catalysts are known to have better activities at mild temperatures.[78a] Furthermore, low reaction temperatures reduce the extent of the possible isomerization during ADMET. Thus, the efficiency of some classical metathesis catalysts such as Grubbs 1st (**C3**) and 2nd (**C4**) generations were initially compared at 40 °C with monomer **1**, which possesses the highest l/b ratio (Table 4.20 and Table 4.21). When 0.2 mol% **C3**, one of the most widely studied metathesis catalysts, in relation to the di-telomer was used (Table 4.20, entry **1**), **1** was recovered along with 30% dimeric product. Since further gradual increasing of the catalyst loading up to 2.0 mol% (entries 2-6) did not significantly change this result, a catalyst loading of 0.4 mol% **C3** was chosen for exploring the effect of the temperature on **C3**. Although it has been reported that **C3** does hardly show any side reactions up to a polymerization temperature of 90 °C,[279,282] temperatures higher than 70 °C were not applied due to the occurrence of catalyst decomposition in the current system.[359] Therefore, in attempts to favor higher conversions, the reaction temperature was varied between 50 and 70 °C. However, the higher reaction temperature was found not to have a considerable effect on the polymerization reaction, as evidenced by GPC (Table 4.20, compare entries 7-9). Moreover, also longer reaction times did not result in higher molecular weights, leading us to conclude that **C3**, at least under the applied bulk conditions, is unsuitable for the polymerization of these telomers.

Table 4.20: Selected results of ADMET studies of telomer **1** in the presence of **C3** at different reaction temperatures after 4 h reaction time.

Entry[a)]	**Catalyst (mol%)**	**T (°C)**	**M_w[b)] (Da)**	**PDI[b)] (M_w/M_n)**
1	**C3** (0.2)	40	600	1.35
2	**C3** (0.4)	40	650	1.27
3	**C3** (0.8)	40	650	1.32
4	**C3** (1.0)	40	700	1.26
5	**C3** (1.6)	40	750	1.48
6	**C3** (2.0)	40	820	1.50
7	**C3** (0.4)	50	830	1.50
8	**C3** (0.4)	60	750	1.48
9	**C3** (0.4)	70	690	1.42

[a)] Additional conditions applied during polymerization: argon was applied for 4 h, unless otherwise specified; [b)] GPC was performed crude reaction samples, quenched with ethyl vinyl ether, in THF, containing BHT, with PMMA calibration; M_w is the weight average molecular weight detected *via* GPC.

The catalyst screening showed that **C4** (0.4 mol%) was more effective at low temperature, with better consumption of **1** (entries 1, 3 and 4, Table 4.21). However, neither this catalyst afforded high molecular weight polymers. Efforts to increase the molecular weight by increasing the catalyst amount from 0.4 to 2.0 mol% at 40 °C showed similar trends as in the case of **C4**.

Hoveyda-Grubbs 2nd generation catalyst **C5** possesses metathesis efficiency similar to Grubbs 2nd generation catalyst (**C4**), but with different substrate specificity. Under the initial conditions (i.e., at 40 °C and 0.4 mol% of catalyst) only 50% of oligomer formation with 35% monomer recovery was observed together with 15% undefined low molecular weight product formation (GPC data). Thus, high catalyst loadings were used to improve the yield of high molecular weight products. Reactions of **1** with loadings of 0.4, 0.8, 1.0 and 2.0 mol% of **C5** gave low-molecular-weight oligomers with conversions increasing with the catalyst loading (up to 80% at 2.0 mol% of **C5**). Encouraged by this result, the ADMET reaction of **1** in the presence of 1.0 mol% of **C5** was performed at 80 °C, a typical polymerization temperature for ADMET reactions. The results of this experiment indicated high activity of **C5** after 4 h at 80 °C. However, even at 90% conversion, appreciably high molecular weights were not achieved. On the other hand, unidentified low molecular weight products were observed at higher retention times by GPC. The use of 2.0 mol% **C5** resulted in lower conversion of **1** with high amount of undefined small product formation (detected by GPC). A switch to another metathesis catalyst with chelating alkylidene ligand, **C4**, gave similar results at 80 °C with loadings of 1.0 mol% as with **C5** (cf. entries 8 and 12 in Table 4.21).

Table 4.21: Selected results of ADMET studies of telomer **1** in the presence of **C4, C5** and **C12** at different reaction temperatures after 4 h reaction time.

Entry	Catalyst (mol%)	Conditions[a)]	T (°C)	M_w[b)] (Da)	PDI[b)] (M_w/M_n)
1	**C4** (0.4)	-	40	2200	1.82
2	**C4** (0.4)	**BQ** (0.8 mol%)	40	750	1.39
3	**C4** (0.4)	-	60	1500	1.64
4	**C4** (0.4)	-	80	890	1.54
5	**C5** (0.4)	-	40	1100	1.69
6	**C5** (2.0)	-	40	1900	1.74
7	**C5** (2.0)	**BQ** (4.0 mol%)	40	4650	1.98
8	**C5** (1.0)	-	80	1900	1.75
9	**C5** (1.0)	**BQ** (2.0 mol%)	80	4000	2.01
10	**C5** (1.0)	**BQ** (8.0 mol%)	80	4900	2.65
11[c)]	**C5** (1.0)	**BQ** (8.0 mol%)	80	5600	2.17
12	**C12** (1.0)	-	80	1750	1.78
13	**C12** (1.0)	**BQ** (8.0 mol%)	80	1950	1.84
14[c)]	**C12** (1.0)	**BQ** (8.0 mol%)	80	5450	2.33
15[d)]	**C5** (1.0)	**BQ** (8.0 mol%)	80	9400 (6350)[e)]	5.73 (2.48)[e)]
16[d)]	**C12** (1.0)	**BQ** (8.0 mol%)	80	3800 (2750)[e)]	2.71 (2.50)[e)]

[a)] Additional conditions applied during polymerization: argon was applied for 4 h, unless otherwise specified; **BQ**: amount of benzoquinone in % with respect to monomer; [b)] GPC was performed to crude reaction samples, quenched with ethyl vinyl ether, in THF, containing BHT, with PMMA calibration; M_w is the weight average molecular weight detected *via* GPC; [c)] vacuum was applied for 4 h instead of gas flow; [d)] reactions were performed for 48 h with continuous argon flow for the first 4 h; [e)] GPC data for crude reaction samples after 24 h, quenched with ethyl vinyl ether, in THF, containing BHT, with PMMA calibration.

After these studies, it became apparent that the reason for the inability to achieve a higher degree of polymerization could be the *in situ* isomerization of the double bonds during metathesis.[110a,111,278,360] Previous studies showed that, depending on the nature of the reacting olefinic partners, the reaction conditions, as well as the nature of the catalyst, double bond isomerization reactions may occur.[116] Double bond isomerization occurs as result of Ru-hydride formation, which can be suppressed by the addition of hydride scavengers, e.g., 1,4-benzoquinone (**BQ**).[116] Thus, catalysts **C4, C5** and **C12** were examined with the same set of experiments in the presence of **BQ**. Rather unexpectedly, the inclusion of **BQ** did not show efficient isomerization inhibition at 40 °C for **C4**; in contrast, a drop of the molecular weight was detected, as observed by GPC (Table 4.21, entries 1 and 2). On the other hand, at 80 °C with a loading of 1.0 mol% **C5** and 8.0 mol% **BQ**, an increase of the molecular weight up to 4.9 kDa was observed (entry 10, Table 4.21). To investigate whether the **BQ** addition would favor an increase in molecular weight through longer reaction times, reactions 10 and 13 in Table 4.21 were reproduced and run for 48 h with initial argon flow for 4 h (entries 15 and 16, respectively). The GPC data of the reactions showed the catalysts to be still active even after 24 h in the presence of **BQ** with the molecular weight values clearly increasing.

Since the kinetics during ADMET are dictated by the removal of ethylene, a possible reason why ADMET mainly produced low molecular weight polymers, even in the presence of the isomerization inhibitor, could be inefficient ethylene removal. Therefore, an efficient ethylene removal by applying vacuum, instead of inert gas flow, was investigated. Indeed, when ADMET was performed under vacuum for 4 h in case for **C5** (entry 11, Table 4.21), the efficiency was substantially improved. For catalyst **C12**, the effect of applied vacuum was more pronounced (compare entries 13 and 14, Table 4.21), showing higher monomer conversions (monitored *via* NMR and GPC). Moreover, when the reactions represented at entries 11 and 13 in Table 4.21 were run over night (after applying vacuum for 4 h), the final products were highly viscous, sticky materials, soluble in chloroform.

Monomer **1** is a mixture of linear and branched telomers with an l/b ratio of 93/7. Since the branched monomers possess 3 or 4 terminal double bonds, they act as branching points leading to the formation of hyperbranched structures. In order to get a more accurate picture of both the mechanism and the scope and limits of the reaction, the other two monomers **2** and **3**, which possess lower l/b ratio, were reacted under the optimized conditions: 1.0 mol% **C5** (or **C12**) at 80 °C under vacuum for 4 h. The results presented in Table 4.22 show a clear tendency for both catalysts (**C5** and **C12**): the molecular weights increase with the branching ratio of the monomers, which supports the polymerizations to highly branched systems and is due to the presence of a higher amount of more reactive terminal double bonds. Furthermore, the same set of experiments was performed for 24 h, with continuous vacuum for the first 4 h. The results of this set are also in line with the formation of hyperbranched structures. Furthermore, in the case of monomers **2** and **3**, the higher content of branched telomers led to gelation caused by cross-linking. Once cross-linked, the characterization of these materials (entries 3 and 4 in Table 4.22) was troublesome as they were no longer soluble in any common solvents such as THF, $CHCl_3$, DMSO and DMF.

Table 4.22: ADMET screening of monomers **2** and **3** at 80 °C with 1.0 mol% **C5** (or **C12**) and 8.0 mol% **BQ**.

Entry	**Monomer**	**Catalyst (mol%)**	**T (°C)**	**$M_w$$^{a)}$ (Da)**	**PDI$^{a)}$ (M_w/M_n)**
1	**2**	**C5** (1.0)	80	5350	4.35
2	**2**	**C12** (1.0)	80	4950	3.85
3	**3**	**C5** (1.0)	80	3500	5.84
4	**3**	**C12** (1.0)	80	4220	3.61

Additional reaction conditions applied during polymerization: vacuum was applied for 4 h, unless otherwise specified; [a)] GPC was performed to crude reaction samples, quenched with ethyl vinyl ether, in THF, containing BHT, with PMMA calibration; M_w is the weight average molecular weight detected *via* GPC.

Presumably, in the reactions performed with constant flow of argon, the failure in directing the reaction of monomer **1** towards high molecular weight was due to other interfering intra- and intermolecular metathesis reactions. The intramolecular metathesis of a α,ω-diene could yield ethylene and an unsaturated carbocycle (or heterocycle) *via* ring-closing metathesis (RCM), whereas the intermolecular reaction would result in the release of ethylene with oligomer or polymer formation *via* ADMET. The GPC traces for almost all products in Table 4.21 and Table 4.22 were multimodal, with several distinct peaks in the low molecular weight range, suggesting that low molecular weight cyclic products were formed along with linear chains. Thus, to gain more evidence whether the RCM was occurring, control experiments under dilute solvent conditions (dichloromethane as solvent) with two different catalyst amounts (0.4 and 5.0 mol% **C4** or **C5** per **1**) were performed. Surprisingly, even under the dilute solvent conditions, oligomer formation as well as RCM took place in the first 30 min of the reactions (under continuous gas flow). To better understand the polymerization mechanism of monomer **1**, ^{1}H NMR analysis was performed at different reaction times with additional 2D-NMR, ^{1}H,^{1}H-COSY, and heteronuclear multiple-quantum correlation (HMQC) experiments to confirm the structures drawn in Figure 4.41. The NMR analysis of both control experiments and ADMET polymerizations at different reaction times clearly showed that RCM of the terminal and internal double bonds did take place (with release of cyclopentene, see Figure 4.41), yielding a mixture of products (RCM products and new monomer structure suitable for further ADMET). Cyclopentene and 1,6-heptadiene were collected from the ADMET reaction as distillate. Along with these compounds, a ring-opening metathesis compound (dimer) was observed in the distillate as determined by ^{1}H NMR and GC-MS. The isolated mixture of cyclopentene and 1,6-heptadiene amounted to 1/5th of the total reaction mixture. The rate and the yield of RCM reaction depended on the reaction conditions, e.g. whether argon flow or vacuum was applied; under vacuum, the RCM was observed only in the first 5 min of the reaction. However, with a continuous gas flow, the RCM occurred for approximately 45 min. The formation of the ring-closing product between the terminal and internal double bond was evidenced by ^{1}H NMR, which showed a decrease of the terminal double bond proton resonances at 5.81 [5, in Figure 4.41, a)] and 4.97 ppm (4) and the appearance of new terminal double bond protons at

5.91 (1) and 5.20 ppm (2) belonging to the allylic ether. Furthermore, it was observed that the products from step (a) in Figure 4.41 subsequently reacted *via* ADMET, either with themselves or with unreacted monomers, thus giving a mixture of products as shown in Figure 4.41b. These metathesis reactions led to polymer formation (as observed by GPC); however, ^{1}H NMR analysis of the products also revealed that further double bond isomerization took place (Figure 4.42). The vinyl ether signals observed (hydrogens 1, 2, 3, and 4 in Figure 4.42), which have similar intensities as the signals belonging to the internal olefins formed by direct ADMET, illustrate this. The isomerization of the allylic (ether) double bonds to the vinyl position gave a 1:1 mixture of *trans* (1 and 2 in Figure 4.42) and *cis* (3 and 4) isomers. While this can be considered a non-disturbing side reaction in most polymerizations, the isomerization of allyl ethers to vinyl ethers has to be considered as it can lead to slow catalyst deactivation (ethyl vinyl ether[124] is the typical reagent used to quench metathesis reactions catalyzed with Ru-alkylidenes). Moreover, a small amount of terminal double bond isomerization was also observed (Figure 4.42). Along with the aforementioned points, in ADMET polymerization, the polymerizability of a monomer can be limited by the number of methylene spacers between the olefin and the ether oxygen.[104,361] Thus, it could be that, to some extent, also the so-called “negative neighbouring group effect” is a reason for the somewhat poor polymerization results. Moreover, in some cases, self- and cross-metathesis reactivity was observed for monomers with only one methylene spacer present.[362] Finally, oligomerization of diallylic ethers has been reported before.[302] All this contributes to the observed rather poor polymerizability of the di-telomers *via* ADMET.

In summary, although it is possible to react the monomers with low catalyst loadings and relatively low temperatures *via* metathesis, the presence of branched telomers in the monomer mixture caused cross-linking at high monomer conversions. Moreover, ADMET was not sufficiently regioselective, allowing RCM events to take place. In addition, olefin isomerization events led to vinyl ether moieties within the polymer backbones.

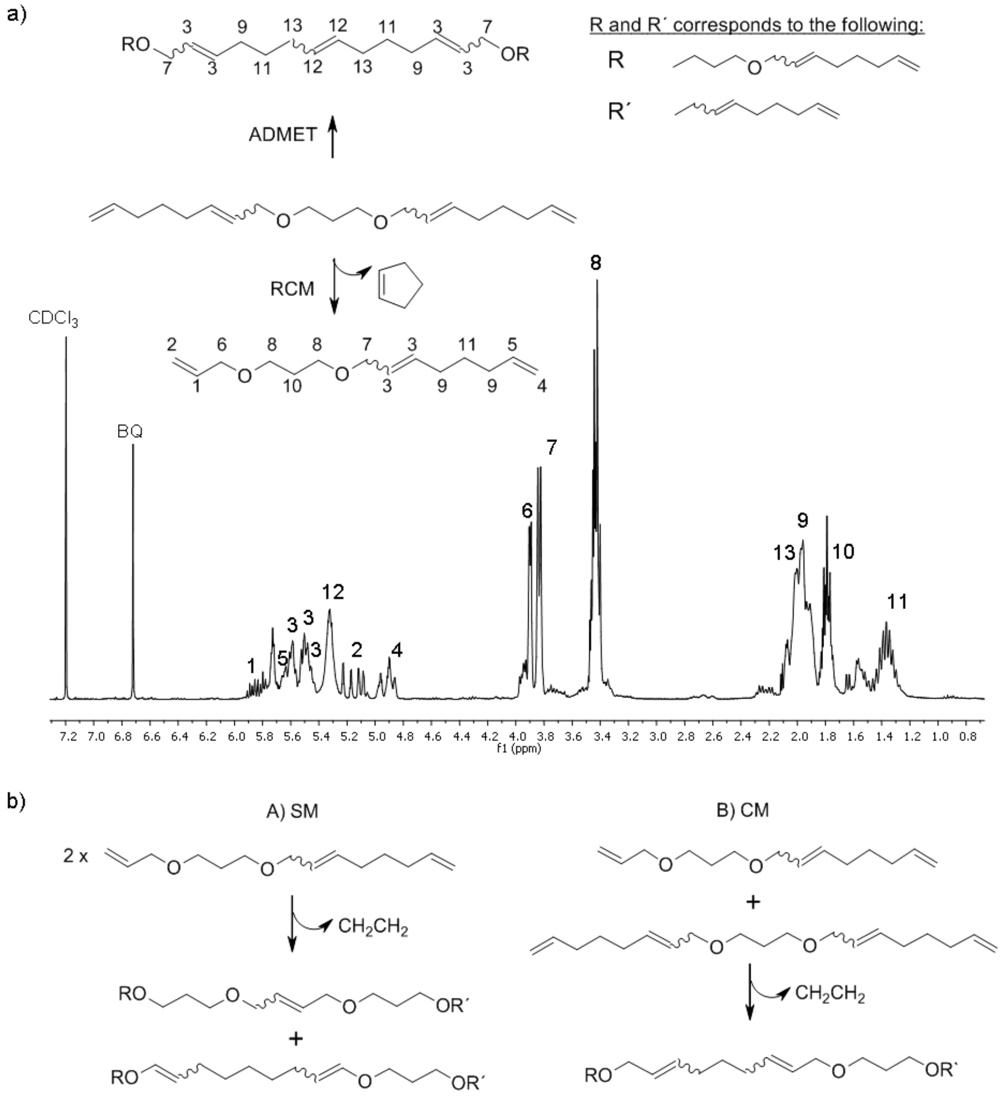


Figure 4.41: Study of the polymerization mechanism by means of NMR analysis: a) initial reactions observed (first 30 min of ADMET reaction) (entry 11, Table 4.21); b) subsequent reactions of RCM product.

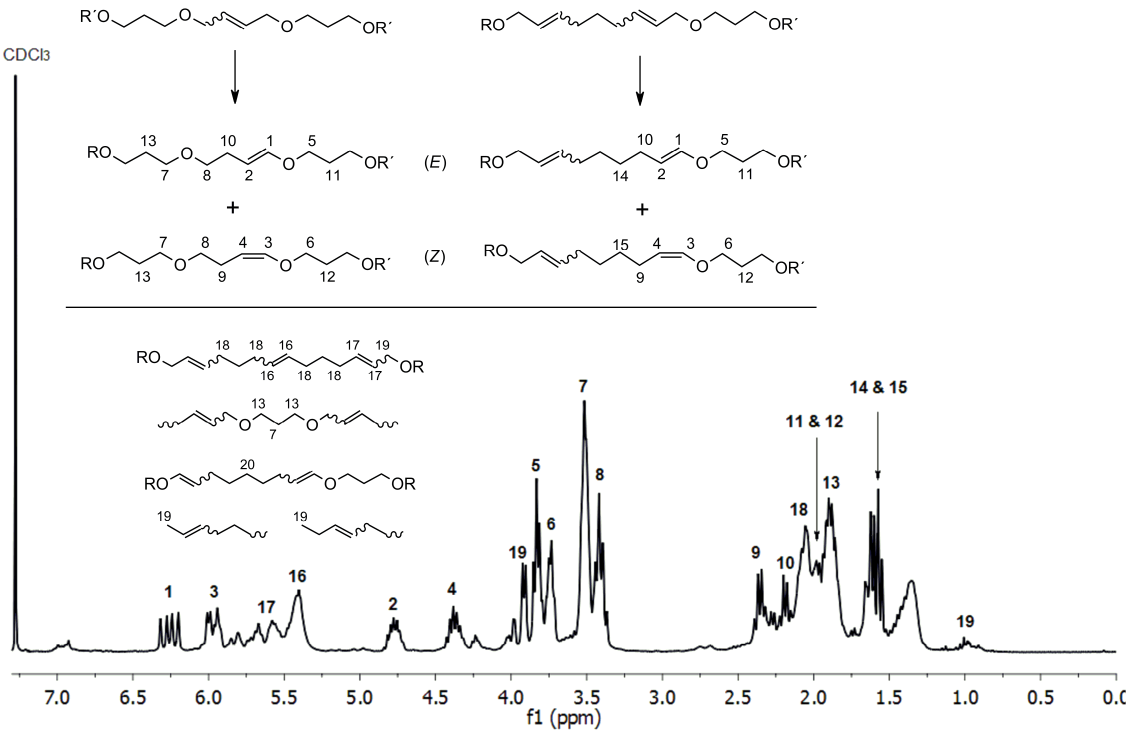


Figure 4.42: NMR spectra of a sample of the crude reaction mixture of entry 11, Table 4.21, taken after 2 h, showing the isomerization occurring during the ADMET reaction.

Thiol-ene polymerizations

Thiols have a strong tendency to react with terminal double bonds in radical-initiated reactions. Therefore, in order to establish an alternative polymerization pathway for monomers **1**, **2** and **3**, the transformation of the di-telomers was also investigated in the presence of thiols as comonomers.

Initially, the model compound 1-octanethiol was reacted with telomer **1** under radical-initiated (model reaction A) or thermally induced (model reaction B) conditions using a molar ratio of 4:1 (thiol:**1**). Although low temperatures are generally favorable for thiol-ene additions, elevated reaction temperatures are required to avoid high viscosity or crystallization during polymerization. Furthermore, it was shown that in dithiol/diene mixtures, which are free of oxygen, radicals can also form spontaneously under initiator-free conditions.[363] Therefore, the model reaction was carried out at 70 °C without initiator. Although Hawker and colleagues showed that thiol-ene coupling reactions do not strictly require deoxygenation[181,364] when performed under solvent-free conditions, both model reactions were nonetheless kept under vacuum (200 mbar) for 5 min prior to exposing to heat and/or addition of initiator in order to remove oxygen, which is an efficient radical scavenger in these types of reactions.[364] The dithioether generated from the reaction performed in the presence of the radical initiator (**AIBN**) was the expected anti-Markovnikov diaddition product (Figure 4.43). As illustrated by the disappearance of the protons associated with the terminal double bonds (5.78 and 4.96 ppm) and homoallylic (1.46 ppm) signals, and the appearance of proton signals corresponding to the thioether product (methylenes in α- 2.52 ppm and β-position δ1.60 ppm to the sulphur atom), the conversion was found to be essentially quantitative after 1 h at 75 °C (for complete description of the NMR data see the experimental section). Interestingly, the ^{1}H NMR spectra displayed also new significant signals at δH 6.20 (d, J=12.6 Hz, 1H_{trans}), 5.91 (dd, J=6.2, 1.3 Hz, 1H_{cis}), 4.81-4.68 (m, 1H_{trans}) and 4.37-4.25 (m, 1H_{cis}) due to a migration of the internal allyl ether double bonds to the vinylic position (*cis*- and *trans*-isomers were observed), along with a corresponding decrease of the integral value of the internal double bond signal (Figure 4.43). The thermally-induced reaction without added initiator, on the other hand, resulted in a lower yield (90%) (model reaction B) after a significantly longer reaction time (20 h) at 70 °C. However, in this case, the aforementioned internal double bond migration occured to a much lesser extent; just 3% internal allyl ether double bond migration was detected in contrast to 27% migration in case of model reaction A (compare results in Figure 4.43). While the extent of olefin migration may not be substantial under standard thiol-ene addition conditions, its occurrence is of considerable fundamental importance, since it involves hydrogen atom transfer between thiyl and allylic species.[365]

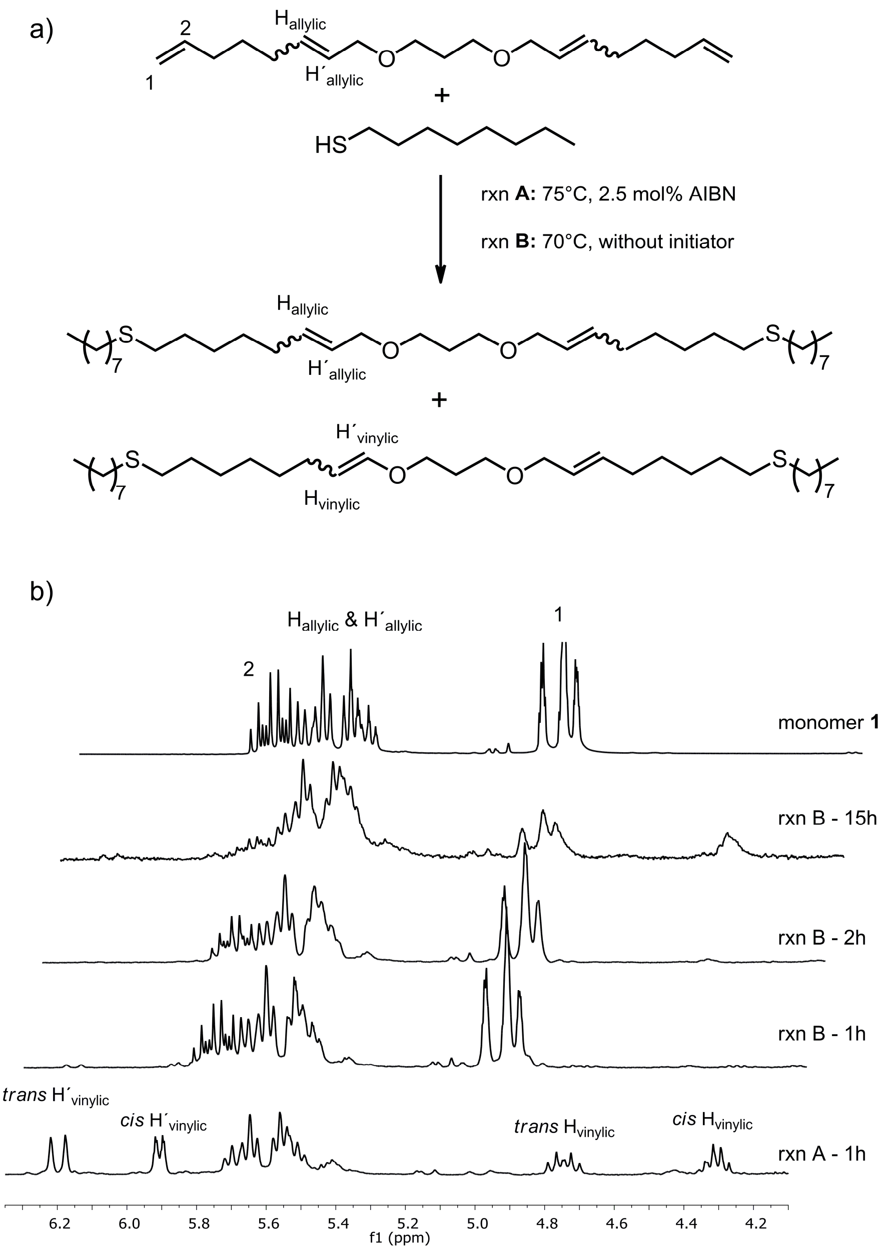


Figure 4.43: a) Schematic representation of the model reactions mimicking the products from thiol-ene polymerization. b) ^{1}H NMR spectra (CDCl$_3$; 300 MHz) comparison of the model thiol-ene reactions A and B with the corresponding monomer: di-telomer **A** (black line, crude reaction mixture of model reaction A, 1 hour, with **AIBN**; blue line, crude reaction mixture of model reaction B, 1 hour, without **AIBN**; light grey line, model reaction B, 2 hour; dark grey line, model reaction B, 15 h; red line, monomer: di-telomer **A**).

Thiols are efficient hydrogen donors, and since C-H bonds are stronger than S-H bonds [bond dissociation energy (BDE) = 91 kcal/mol],[366] thiyl radicals are usually regarded as unreactive with respect to hydrogen abstraction. Hydrogen atom transfer reactions are usually very sensitive to enthalpic polar effects, however. It was indeed reported that thiyl radicals can abstract hydrogen atoms from thermodynamically favorable allylic systems[365] in water/alcohol mixtures as well as from other C-H activated compounds.[367] Since an allylic C-H bond is unusually weak (BDE = 82 kcal/mol),[366] the free radical abstraction of such hydrogens is easier than for non-allylic hydrogens. The migration of the double bond could thus be explained by the mechanism proposed in Figure 4.44. This involves a favorable allylic hydrogen abstraction, followed by trapping of either the intermediate allylic radical or the more stable additional resonance form [step (b) in Figure 4.44] by a thiol to regenerate the initial structure or to form the internal vinyl ether (in the latter case). It should be noted that the hydrogen atom transfer between the electron-rich C-H bond in the di-telomer and the electrophilic thiyl radical is favored, if there is an appropriate polarity match between radical and the alkene [step (a) in Figure 4.44].[368] The same assumption could be applied for step (c) (Figure 4.44), where the hydrogen atom is transferred from the electrophilic thiol, acting here as a hydrogen atom donor, to the nucleophilic carbon centred radical.

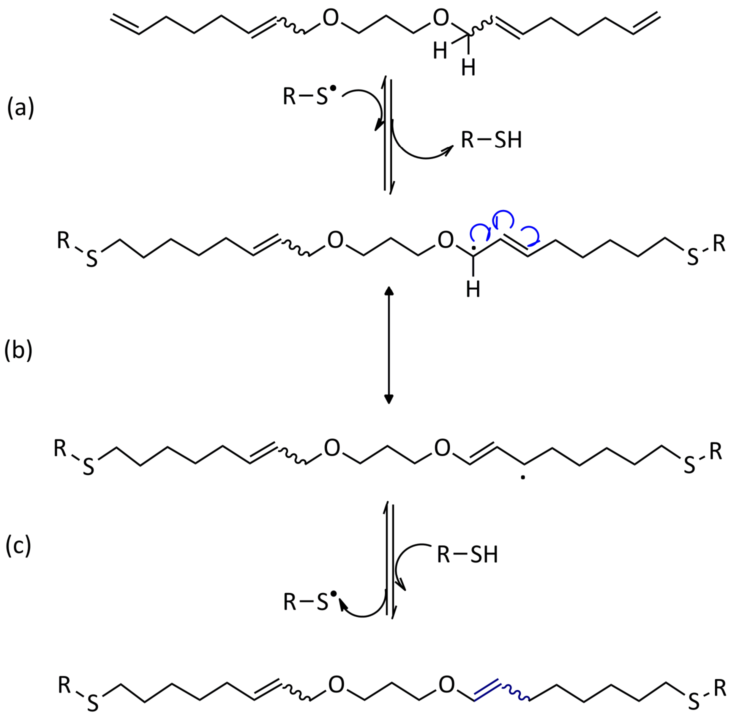


Figure 4.44: Thiyl radical-mediated olefin migration.

The model study thus shows that the use of radical initiator shortens the reaction time and results in double bond migration. This migration, leads to a vinyl ether function displaying a different reactivity that might be further exploited in another context.

Encouraged by the successful model study, and in order to demonstrate the feasibility of di-telomers in thiol-ene polymerizations, three different dithiols were investigated: 1,4-butanedithiol (**DT1**), 2-mercaptoethyl ether (**DT2**) and 3,6-dioxa-1,8-octane-dithiol (**DT3**), under comparable conditions, in the absence or presence of radical initiator. Compared to the model reactions, the synthesis of polymers could present a number of additional challenges regarding efficiency. Although the internal double bonds of the di-telomers showed quite low reactivity at 70 °C during the model studies, the polymerizations were conducted at three different temperatures in order to obtain more detailed information about the effect of the temperature on the reactivity of the internal double bonds. Monomer **1**, possessing the highest l/b ratio [Figure 4.40, a)], was used in the initial optimization studies. The polymerizations were followed by GPC and NMR. The reactions were run until a viscosity increase was qualitatively observed, and then quenched by cooling to room temperature and diluted with an excess of THF to avoid cross-linking. All of the major impurities, including excess reactant and the initiator residue, were easily removed by repeated precipitation, and no chromatography was required.

Monomer **1** was polymerized at 35, 50 and 70 °C with **DT1**, first without the initiator **AIBN**. The GPC analysis showed that, even after 72 h at 35 °C, the thiol-ene reaction did not occur as efficiently as expected, and only low-molecular-weight oligomers (molecular weight < 3000 Da) were formed (Table 4.23, entry 1). Generally, the results confirmed the internal double bonds to be less reactive than the terminal ones, which is known from literature and is a result of the reversibility of the C-S bond formation.[369] The NMR data of the reaction run at 50 °C (Table 4.23, entry 2) revealed characteristic peaks attributed to the formation of thioether bonds as well as the repeat units of thiol monomer and signals from the telomer backbone, which indicated that the reaction occurred. Moreover, the data shows that the internal double bonds remain almost unreacted. When the reaction was performed at 70 °C (Table 4.23, entry 3), a successful polyaddition was observed; however, prolonging the reaction times (more than 24 h) resulted in gelation. As with the model reactions described above, in the experiments performed at 50 and 70 °C, the internal double bond migration from the allylic to vinylic position was again observed.

Table 4.23: Reaction conditions and analytical data of selected thiol-ene polymerizations.

Entry	Monomer : Thiol (ratio)	T (°C)	Reaction time (h)	M_w [a] (Da)	PDI[a] (M_w/M_n)
1[b]	1 : DT1 = 1:1	35	24 (72)	2200	1.85
2	1 : DT1 = 1:1	50	48	19820	5.60
3[c]	1 : DT1 = 1:1	70	24	124200	27.00
4	1 : DT2 = 1:1	35	72	49900	9.88
5	1 : DT2 = 1:1	50	96	48100	6.40
6	1 : DT2 = 1:1	70	56	40200	9.46
7	1 : DT3 = 1:1	50	48	53800	8.61
8	1 : DT1 = 1:0.95	50	72	6400	2.91
9	1 : DT1 = 0.95:1	50	56	20300	5.08
10	1 : DT2 = 1:0.95	50	96	20600	3.61
11	1 : DT2 = 0.95:1	50	96	480000	53.0
12	1 : DT1 = 1:1 (2.5 mol% **AIBN**)	75	1	12100	3.22
13	1 : DT2 = 1:1 (2.5 mol% **AIBN**)	75	1	13200	5.01
14	1 : DT3 = 1:1 (2.5 mol% **AIBN**)	75	1	32600	5.74
15	1 : DT3 = 1:1 (1.0 mol% **AIBN**)	75	4	8400	2.49

Additional conditions applied during polymerization: reaction mixtures were degassed *via* 3 times 200 mbar vacuum and subsequent Ar purge, unless otherwise specified; [a]GPC was performed to crude reaction samples in THF, containing BHT, with PMMA calibration; M_w is the weight average molecular weight detected *via* GPC.; [b]reaction was performed for 72 h, however there was no difference between the GPC data of 24 and 72 h; [c]GPC data is for the corresponding soluble part of the crude reaction mixture

To explore the influence of the dithiol’s structure on the reactivity of **1**, **DT2** was selected as it contains an ether group and thus resembles more the structure of the 1,3-propandiol di-telomers. The reactions were conducted in analogy to those with **DT1**. Online GPC monitoring of the reactions revealed that the conversion of the di-telomer and of the dithiol were better in comparison to **DT1** [Figure 4.45, a)].

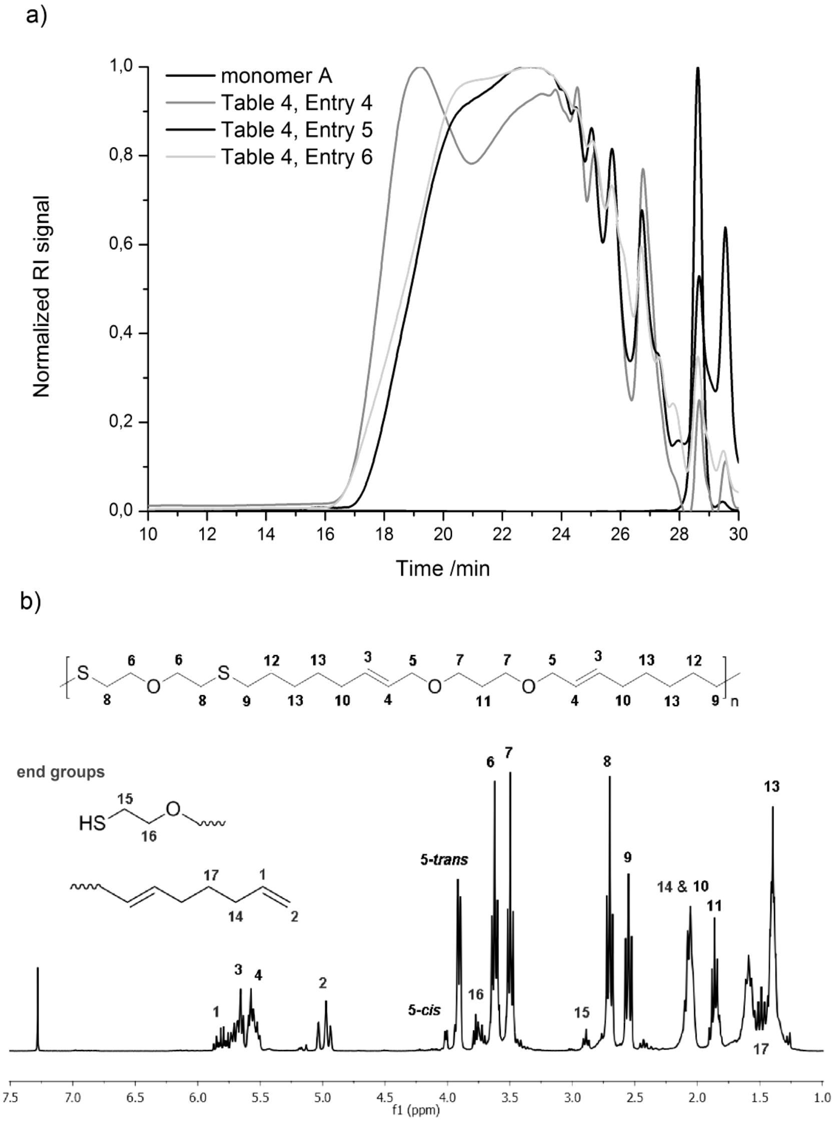


Figure 4.45: a) Crude GPC chromatograms and b) representative NMR data of the thiol-ene reaction product of **DT2** at three different temperatures (35, 50, and 70 °C). (The GPC data was obtained from SEC system with method A).

The ^{1}H NMR spectra of entries 4, 5 and 6 (Table 4.23) showed little variation [Figure 4.45, b)]. As a common feature, the internal double bonds did not react, as calculated by comparison of the integrals of the characteristic multiplet centred at ~5.53 ppm (^{1}H of the internal double bond), and the triplet at ~3.50 ppm (4H from the 1,3-propanediol core of monomer **A**, which should not vary throughout the reaction). On the other hand, the integral value of the terminal double bond peak at ~4.95 ppm decreased, confirming the successful thiol-ene coupling. The conversion of the terminal double bonds could be calculated from the characteristic multiplet centered at 4.95 ppm and the triplet at 3.50 ppm. The product obtained at 50 °C showed 75% conversion of terminal double bonds, while the products obtained at 35 and 70 °C showed 84 and 82% conversion, respectively. The polymerization at 35 °C gave the highest conversion of terminal double bonds, but it also resulted in an inhomogeneous molecular weight distribution (compare Figure 4.45). On the other hand, the polymerization at 70 °C gave a higher terminal double bond conversion than at 50 °C, but since the increase both in terminal double bond conversion and in molecular weight (GPC) was small, 50 °C was taken as temperature for further optimization of the reaction conditions. In the initial experiments, the dithiol amount used was calculated considering the di-telomer samples as pure linear di-telomers. To account for the small percentage of branched di-telomers present [Figure 4.40, a)], the effect of varying the di-telomer/dithiol ratio, from 1:1 to 0.95:1 and to 1:0.95, on the polymerizations at 50 °C was studied. Since the branched telomers contain extra terminal double bonds that can more easily react with the dithiols, an increase in the thiol ratio should favor branching reactions and thus should lead to higher molecular weights and higher PDIs (entry 11, Table 4.23). This was confirmed by the GPC traces of **DT1** (Table 4.23, entries 2, 8 and 9) and **DT2** (Table 4.23, entries 5, 10 and 11). The GPC analysis of the samples from the reaction of **1** with slight excess of thiol **DT2** (0.95:1) indeed showed an increase of molecular weight compared to the 1:1 reaction (75% conversion), which was in accordance with the observed 82% conversion of terminal double bonds (determined by ^{1}H NMR); however, ^{1}H NMR analysis also revealed 8% conversion of the internal olefins. Excess of di-telomer (1:0.95) resulted in a drop of conversion of the terminal double bonds to 70%, again in accordance with the lower M_w observed by GPC. These results demonstrate that variation in the temperature did not have a pronounced effect on the reactivity of the internal olefins, but a small excess of dithiol did have a considerable effect on the molecular weights.

Next, **DT3** was tested in the thiol-ene polymerization of the di-telomers. The third dithiol tested, was expected to have a positive effect on the polymerization results in terms of improved compatibility (miscibility) between both monomers (1:1 ratio at 50 °C, Table 4.23, entry 7). The GPC data of the 24 h crude reaction mixture revealed 92% monomer conversion to the polymer. The higher double bond conversion (80% by ^{1}H NMR) obtained at short reaction time further confirmed the improved polymerization compared to **DT1** and **DT2**.

Since the thermally induced thiol-ene polymerization reactions needed long polymerization times (at least 48 h), **AIBN** was applied as radical initiator (2.5 mol% to di-telomer molecule) to reduce the reaction time. The **AIBN**-initiated polymerizations were completed in 1 hour (reaction mixture was not stirring anymore) with conversions of 95% for entry 14, Table 4.23 (by GPC). As with the previously obtained products, the polymers were completely soluble, although dissolution took time (around 6 h for the polymer with the highest molecular weight). The difference in solubility was attributable to the molecular weight difference. Since the high concentrations of radicals present in the reaction mixture increases the probability of side reactions, also lower **AIBN** loadings were tested for monomer **1**. From NMR and GPC analysis, it became clear that an initiator loading of 1.0 mol% already results in 95% conversion (by GPC, no carbons corresponding to the end groups detected in ^{13}C NMR). Almost no double bond migration is observed by ^{1}H NMR, thus more well-defined polymers were synthesized (Table 4.23, entry 15). In the same fashion, additional experiments were performed with monomer **2** and **3** in order to study the effect of the l/b ratio on the polymerizations performed in the presence of **AIBN**. Indeed, the higher the branching ratio, the higher the molecular weight and also the less well-defined structures with broad PDI values were obtained.

Both the thermally and radical-induced thiol-ene reactions were initially affected by difficulties in reaching the quantitative conversions targeted for polymer synthesis. However, variation of the di-telomer to dithiol ratio and the type of dithiol, led to optimized reaction conditions allowing for the formation of high molecular weight products. Very interestingly, the three dithiols yielded thermoplastic polysulfides of different structures, which could be shaped as transparent and colorless films by casting THF solutions (graphical abstract and Figure 4.46). To ascertain the thermal properties of the obtained thiol−ene polymers, DSC analysis was performed. The majority of the samples, even when subjected to different heating rates during DSC analysis, did not show any thermal transition in the studied temperature range (from −75 to +250 °C). However, a small T_g at 99 °C (at 20 °C/min) was observed for the polysulfide from entry 2, Table 4.23, suggesting that the rest of polysulfides possibly have T_gs in the same range, but are not detectable by DSC (Figure 4.46). It should be noted that the ditelomers monomers have no detectable glass or melting transitions in the studied temperature range and that the investigated polymer (entry 2, Table 4.23) can be reshaped by redissolution and solvent casting for several times, suggesting that it is not cross-linked. From the TGA analysis performed on the same polymer, it could be seen that the polymers display acceptable thermal stability under nitrogen. Under the given experimental conditions 5% mass loss of the polymer was detected at 306 °C.

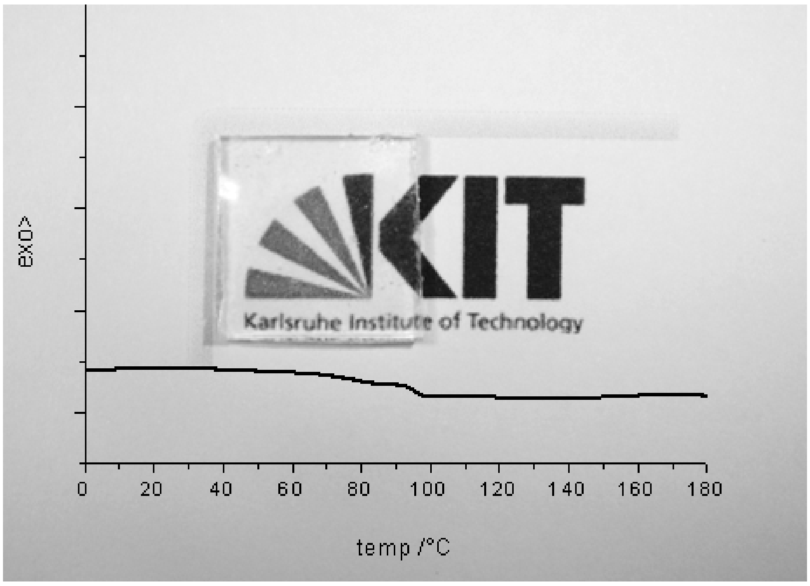


Figure 4.46: DSC chromatogram of for the polysulfide from entry 2, Table 4.23.

Conclusions

The potential of di-telomers obtained from 1,3-propanediol as monomers for the synthesis of polymers *via* ADMET and thiol-ene polymerizations has been assessed. Regarding the ADMET pathway, it was shown that the products obtained were different depending on the method used to remove the released ethylene. When a flow of argon was used, mostly ring-closing metathesis products were obtained together with oligomers. On the other hand, when vacuum was applied low molecular weight polymers were obtained in a ring-closing metathesis-ADMET-olefin isomerization sequence. The thiol-ene polyaddition with different dithiols led to higher molecular weights than ADMET polymerization. The polymerizations in the presence of a radical initiator (**AIBN**) were considerably faster than the thermally initiated ones. In both cases, isomerization of the allyl ether to vinyl ether was observed, although in a more prominent fashion in the presence of **AIBN**. The high molecular weight polymers obtained *via* the thiol-ene route showed interesting application possibilities and behaved as shapeable and completely transparent thermoplastics.

5 Experimental section

5.1 Characterization methods

The analytical techniques employed in the development of this thesis, together with the technical specifications of the equipment used are listed below.

Thin layer chromatography (TLC)

Thin layer chromatography (TLC) was performed on silica gel TLC-cards (layer thickness 0.20 mm, Fluka). The compounds were visualized by using as developing solution the permanganate reagent, prepared as follows: potassium permanganate (3 g) + potassium carbonate (20 g) + 5% aqueous NaOH (5 mL) + water (300 mL).

Nuclear magnetic resonance (NMR) spectroscopy

^{1}H-NMR and ^{13}C-NMR spectra were recorded on different spectrometers:
A) Bruker AVANCE DPX spectrometer operating at 300 MHz.

B) Bruker AVANCE DPX spectrometer operating at 400 MHz.

C) Bruker AVANCE DPX spectrometer operating at 500 MHz.

D) Varian 400-MHz spectrometer (Waltham, MA).

$CDCl_3$ or DMSO-*d*6 were used as solvents depending on the samples solubility. Chemical shifts (δ) are reported in parts per million (ppm) relative to the internal standard tetramethylsilane (TMS, δ = 0.00 ppm). For the analyses of the polymers, the relaxation time (d1) was set to 5 seconds in order to obtain reliable integration values.

Gas chromatography (GC)

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

Gas chromatography-Mass spectroscopy (GC-MS)

GC-MS (EI) chromatograms were recorded using two different equipments:
A) Varian 431-GC instrument with a capillary column FactorFourTM VF- 5ms (30 m × 0.25 mm × 0.25 µm), and a Varian 210-MS detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scans × s^{-1}. Measurements were performed in the split–split mode (split ratio 50:1) using helium as carrier gas (flow rate 1.0 ml×min^{-1}). Different oven temperature programs were used: initial temperature 95 °C, hold for 1 min, ramp at 15 °C × min^{-1} to 200 °C, hold for 2 min, ramp at 15 °C × min^{-1} to 325 °C, hold for 5 min. The injector's transfer line temperature was set to 250 °C.

B) VARIAN 3900 GC instrument with a capillary column FactorFour^{TM} VF- 5ms (30 m × 0.25 mm × 0.25 µm) and a Saturn 2100T ion trap mass detector in the presence of tetradecane as an internal standard. Scans were performed from 40 to 650 m/z at rate of 1.0 scans x s^{-1}. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C x min^{-1} to 200 °C, hold for 2 min, ramp at 15 °C x min^{-1} to 325 °C, hold for 5 min. The injector's transfer line temperature was set to 250 °C.

Measurements were performed in the split–split mode (split ratio 50:1) using helium as carrier gas (flow rate 1.0 mL x min^{-1}).

Mass spectrometry (MS)

Mass spectra (ESI) were recorded on a VARIAN 500-MS ion trap mass spectrometer with the TurboDDS^{TM} option installed. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the drying gas. Helium served as cooling gas for the ion trap and collision gas for MS^n. Nitrogen was generated by a nitrogen generator Nitrox from Dominick Hunter.

Electron spray ionization mass spectra (ESI-MS) were recorded on a Micromass Q-TOF instrument and high resolution mass spectra (HRMS) with electron impact ionization (EI) were recorded on a GC-TOF.

Size exclusion chromatography (SEC)

Polymer molecular weights were determined using an SEC System LC-20 A from Shimadzu equipped with a DGU-20A$_3$ degassing unit, a SIL-20A auto sampler, a CTO-20A oven, and a RID-10A refractive index detector. THF stabilized with 250 ppm of BHT was used as eluent at a flow rate of 1 mL × min^{-1} and a temperature of 50 °C. Different column systems were used:

A) One PSS SDV column (5 µm, 300 mm × 7.5 mm).

B) Two PSS SDV columns (5 µm, 300 mm × 7.5 mm).

C) Three PSS SDV columns (5 µm, 300mm x 7.5mm).

D) PLgel 5µm MIXED-D column (Polymer Laboratories, 300 × 7.5mm).

E) PLgel 5 µm MIXED-D column (Varian, 300 mm x 7.5 mm) with PSS SDV gel pre-column (5 µm, 50 mm x 8.0 mm).

All determinations of molar mass were performed relative to PMMA standards (Polymer Standards Service, M_p 1100–981.000 Da).

Differential scanning calorimetry (DSC)

DSC experiments were carried out with two different systems:

A) DSC 1 STAR^e system (Mettler Toledo) calorimeter with autosampler under a constant nitrogen flow of 10 mL × min^{-1} using 40 or 100 μL aluminum crucibles.

B) DSC821e (Mettler Toledo) calorimeter under a constant nitrogen flow of 10 mL × min^{-1} using 40 μL aluminum crucibles.

The melting temperature, T_m, is reported as the minimum of the endothermic peak of the second heating scan unless annealing was used as a pretreatment. The glass transition temperature, T_g, is reported as the midpoint of the step change of the heat capacity in the second heating scan.

Thermogravimetric analysis (TGA)

TGA was performed on a TGA/SDTA851e instrument (Mettler Toledo) under nitrogen atmosphere at a heating rate of 10 °C × min^{-1}. The weights of the samples were in the range of 8-10 mg. The decomposition onset temperature, T_d, was recorder as the temperature at which a 5% loss in weight occurred.

Static light scattering (SLS)

SLS was performed using a MALLS-detector (multi-angle laser light scattering detector) SLD 7000 from Polymer Standards Service GmbH (PSS), Mainz, Germany. The polymer was dissolved in DMAc. The required *dn/dc* values where measured in the same solvent with a refractometer *dn/dc* 2010 also from PSS, Mainz, Germany. Typically six concentrations of the polymer from 2-12 mg × mL^{-1} were used to determine *dn/dc*-values and SLS measurements.

Dynamic light scattering (DLS)

Hydrodynamic radii where determined with a NICOMP 380 DLS spectrometer (Particle Sizing Systems, Santa Barbara, USA). The measurements where performed in automatic mode and evaluated with a standard Gaussian and an advanced evaluation method, the latter using an inverse Laplace algorithm to analyze for multimodal distributions. *N*,*N*-dimethyl acetamide (DMAc) was used as solvent at a temperature of 23 °C resulting in a viscosity of 0.553 cP for the solvent, received from an interpolation of literature data.[370-372] Prior to the light scattering measurements the sample solutions of polymer **P2** in DMAc (0.1 mg × mL^{-1}) were filtered using Millipore Teflon filters with a pore size of 0.45 µm.

Rheology

Rheological measurements were conducted for oscillatory and steady shear on an ARES G2 strain controlled rotational rheometer from TA Instruments in cone plate geometry (25 mm, 0.02 rad) at room temperature (25 °C). The temperature was controlled with a force convection oven. Dynamic strain sweep experiments were performed at 0.1, 1 and 10 Hz from 1 to 1000% strain amplitude (γ_o). A dynamic frequency sweep test was conducted from 0.1-10 Hz at 100% strain amplitude (γ_o).

5.2 Acyclic Triene Metathesis (ATMET) polymerization of *plukenetia conophora* oil

Materials

Plukenetia conophora seeds, which were collected during the raining season, were bought from Erekesan Market in Ado Ekiti, Nigeria, then milled on a C&N Junior laboratory mill size 5 (Christy and Norris Limited Engineers, Chemlsford, England) and extracted using n-hexane in a Soxhlet apparatus.

[1,3-*bis*(2,4,6 trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1H-inden-1-ylidene)(pyridyl)ruthenium(II) (Umicore M3$_1$, **C11**) and [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-[2-(1-methylacetoxy)phenyl]methyleneruthenium(II) (Umicore M5$_1$, **C12**)were kindly donated by Umicore, [1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxy-phenylmethylene)ruthenium (Hoveyda-Grubbs 2nd generation catalyst, **C5**), benzylidene [1,3-*bis*-(2,4,6-trimethylphenyl) imidazolidinylidene]dichloro (tricyclohexylphosphine)ruthenium (Grubbs 2nd generation catalyst, **C4**), n-hexane and ethyl vinyl ether (99%) were obtained from Aldrich. All reagents were used without further purification.

Specifications on the analytical methods

NMR: Spectrometers A and B.

SEC: Column systems B and C.

DSC: System A. Meassurements performed at a heating rate of 10 °C × min^{-1} up to 180 °C with samples in the range of 8–15 mg.

Synthetic procedures

ATMET polymerization of *Plukenetia conophora* with different metathesis catalysts

Plukenetia conophora oil (0.5 g, 0.598 mmol) was added into a 3 mL conical vial with screw cap and septum. Different amount of catalysts (**C4**, **C5**, **C11** or **C12**) were added separately. The influence of the reaction conditions on the obtained molecular weight was studied (Table 2). After 6 h reaction, the residue was dissolved in THF and the metathesis reaction was stopped by adding ethyl vinyl ether (500-fold excess to the catalyst) and stirring for 30 minutes at room temperature. The crude product mixtures were analyzed by ^{1}H, ^{13}C NMR spectroscopy, as well as GPC analysis. Prior to the rheological experiments, **P2** was precipitated in cold MeOH on ice bath and afterwards dried at the oven at 50 °C as a viscous material.

Representative transesterification of the obtained polymer P2 and GC-MS analysis

The respective polymer (30 mg), excess methanol (4 mL) and concentrated sulphuric acid (5 drops) were added to a carousel reaction tube, stirred magnetically, and refluxed at 85 °C for 5 h. At the end of the reaction, the excess of methanol was removed under reduced pressure. Then, the residue was dissolved in diethyl ether and filtered over a small column of basic aluminum oxide. Subsequently, a GC-MS sample was prepared by taking 500 µL of this solution and diluting it with methanol (500 µL).

5.3 Acyclic Triene Metathesis (ATMET) polymerization of soybean oil modified with 4-vinylbenzene sulfonic acid

Materials

ESO (Paraplex G-62) having 4.2 mole epoxy groups per mole of triglyceride was purchased from C.P. HALL COMPANY (Chicago, USA), Sodium 4-vinylbenzene sulfonate,

Al_2O_3, $NaHCO_3$ and Na_2SO_4 were purchased from Merck (Darmstadt, Germany), THF was purchased from J.T.Baker (Deventer Holland), sulphuric acid (98%, Sigma-Aldrich), benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs 1st generation cataylst, **C3**), (1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium(II) (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene)ruthenium(II) (Grubbs 2nd generation catalyst, **C4**), [1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(o-isopropoxy-phenylmethylene)ruthenium (Hoveyda-Grubbs 2nd generation catalyst, **C5**), 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(2-(1-methylacetoxy)phenyl]methyleneruthenium(II) (Umicore $M5_1$, **C12**) and ethyl vinyl ether obtained from Sigma-Aldrich (Milwaukee, WI).

Specifications on the analytical methods

NMR: Spectrometers A and D.

SEC: Column system B.

DSC: System B. Meassurements performed at a heating rate of 10 °C × min^{-1} with samples in the range of 7-10 mg.

Synthetic procedures

Synthesis of 1-(4-vinylbenzene sulfonyl)oxy-2-alkonols of epoxidized soybean oil (SESO)

2.5 g Sodium 4-vinylbenzene sulfonate (12.6 mmol) and 3.0 g ESO (containing 12.6 mmol epoxy groups) were added to 100 mL CH_2Cl_2. The mixture was stirred for 10 minutes at room temperature and then 2 mL of 98% H_2SO_4 (36.8 mmol excess) was added to the mixture dropwise in 2 hours. The reaction was completed after 2 hours. Na_2SO_4 by-product was removed from the solution by a simple filtration. CH_2Cl_2 layer was washed successively with water, 5% $NaHCO_3$ (aq.) solution and water in order to remove excess H_2SO_4 and 4-vinylbenzene sulfonates. The aqueous layers were discarded while the CH_2Cl_2 was filtered through a short Al_2O_3 column to remove any residual H_2SO_4 and 4-vinylbenzene sulfonates. The CH_2Cl_2 solution was dried and the solvent was evaporated. 4.0 g of a light yellow viscous product was obtained.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 0.9 (-CH_3), 1.2–1.6 (-CH_2-), 2.3 (-CH_2-(C=O)-), 3.5 (-O-CH_2-CH-), 3.6-3.8 (-OH), 4.2 (-CH_2OH-CH_2-O-), 4.9(-CH_2-CH(-O-)CH_2-), 5.3 (-CH_2-CH(-O-)CH_2-), 5.5 (CH_2=CH-Ar), 5.9 (CH_2=CH-Ar), 6.7 (CH2=CH-Sty), 7.5 (Ar-H), 7.8 (Ar-H)
^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 14.1 (-CH_3), 22.6 (-CH2-CH3), 24.7 (-CH_2-CH_2-(C=O)-) , 29.6-31.8 (-CH_2-), 34.0 (-CH_2-(C=O)-), 62.7 (-OCH_2-CH_2-O-), 68.8 (-OCH_2-(CH_2-O-)-CH_2O-), 72.1 (-S-OCH_2-CHOH-) (-CHOH-CHOH-), 85.6 (-S-OCH_2-CHOH-), 118.4 (CH_2=CH-Ar), 126.6 (meta-C (Ar)), 128.0 (orto-C (Ar)), 135.1 (CH_2=CH-Ar), 143.4 (para-C, ipso-C (Ar)), 173.3 (-CH2-(C=O)-)
IR (Film) (cm^{-1}): 3000-3600 (br, OH), 3087-3063 (w, -OSO_3-), 2927 (s, CH), 2855 (s, CH), 1741 (s, C=O), 1658 (m, -C=C- Ar), 1630-1596 (m, -HC=CH-), 1461 (m, CH_2, Def.), 1397 (w, SO), 1362 (m, S=O, Strech.), 1214 (m, C-O-C, Def.), 1190-1186-1714 (s, CO, Def.; C-O-C, Def.), 1139 (w, C-O-C, Def.), 1099 (w, C-O-C, Def.), 1050 (w, SO), 910 (m, Ar-SO), 846 (w, Ar-SO coordinated water), 663 (m, Ar), 561 (s, Ar)

Synthesis of methyl 10-hydroxy-9-(4-vinylphenylsulfonyloxy)octadecanoate (SEMO)

Methyl oleate was first epoxidized following a literature method[25]. The epoxidized methyl oleate (3 g, 9.6 mmol) and sodium 4-vinylbenzene sulfonate (1.979 g, 9.6 mmol) were added to 50 mL CH_2Cl_2. The mixture was stirred for 10 minutes at room temperature and then 1.6 mL of H_2SO_4 (98%, 28.8 mmol) was added to the mixture dropwise in 1 h. The reaction was completed in 1 h. Na_2SO_4 was removed by filtration. The CH_2Cl_2 was washed successively with water, 5% $NaHCO_3$ (aq.) solution and water in order to remove excess H_2SO_4 and 4-vinylbenzene sulfonates. The aqueous layers were discarded while the CH_2Cl_2 was filtered through a short Al_2O_3 column to remove any residual H_2SO_4 and 4-vinylbenzene sulfonates. The organic layer was dried over molecular sieves (4 Å, beads), filtered and the solvent was evaporated to obtain a light yellow viscous oil in a quantitative yield (4.52 g, ~95%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 0.89 (-CH_3), 1.2–1.6 (-CH_2-), 2.3 (-CH_2-(C=O)-), 3.4 (-OH), 3.7 (-O-CH_3), 4.8 (-CH_2-CH(-O-)CH_2-), 5.5 (CH_2=CH-Ar), 5.9 (CH_2=CH-Ar), 6.7 (CH2=CH-Sty), 7.6 (Ar-H), 7.9 (Ar-H)

General procedure for self-metathesis of SEMO

To 0.1 g of SEMO (0.02 mmol) in a 3 mL conical vial with screw cap and septum, 0.5 mol% of the corresponding Ru catalyst was added at 40 °C reaction temperature under continuous nitrogen flow for 4 h. The reaction mixture was dissolved in 1 mL THF and quenched by addition of ethyl vinyl ether. The final reaction mixture was analyzed by ^{1}H NMR without further purification.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 0.89 (-CH_3), 1.2–1.6 (-CH_2-), 2.3 (-CH_2-(C=O)-), 3.4 (-OH), 3.7 (-O-CH_3), 4.8 (-CH_2-CH(-O-)CH_2-), 7.0 (-CH=CH-), 7.8 (Ar-H), 7.9 (Ar-H).

General Procedure for ATMET polymerization

To 0.1 g of SESO (0.067 mmol, containing 0.16 mmol vinyl groups) in a 3 mL conical vial with screw cap and septum, 0.5 mol% of the corresponding Ru catalyst was added at the desired reaction temperature (see Table 1.) under continuous nitrogen flow. Methanol (10 mL) was added to the reaction mixture to precipitate out the polymer and the polymerizations were quenched by addition of ethyl vinyl ether. The solid product was filtered and extracted with diethyl ether to remove unreacted monomers, non-cross-linked oligomers, or both. The final polymer was dried at 50 °C for 4 hours. Conditions, catalysts and yields are given in Table 1.

5.4 Living Ring-Opening Metathesis Polymerization (ROMP) of fatty acid-derived monomers

Materials

Bicyclo[2.2.1]hept-5-ene-2-methanol (5-norbornene-2-methanol, NBM, Aldrich, 98%, mixture of *endo* and *exo*), ethyl vinyl ether (Aldrich, 99%), 1,1'-carbonyl diimidazole (CDI, Fluka, 98%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Aldrich, 98%), tetradecane (Aldrich, ≥99.5%), tetrahydrofuran (THF, anhydrous, ≥99.9%, contains 250 ppm BHT as inhibitor, Aldrich), dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine)ruthenium(II) (Grubbs 3rd generation catalyst, **C6**, Aldrich) were used as received. Fatty acids were kindly donated by Cognis Oleochemicals. Dichloromethane (technical grade) was distilled and stored over molecular sieves (4 Å) prior to use.

Specifications on the analytical methods

NMR: Spectrometers A and C.

SEC: Column systems A and C.

DSC: System B. Meassurements performed at a heating rate of 20 °C × min^{-1} up to 150 °C with samples in the range of 4-10 mg.

GC-MS: equipment B.

Synthetic procedures

Monomer synthesis (M1-M7)

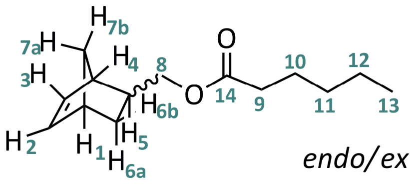
Bicyclo [2.2.1] hept-5-ene-2-methyl hexanoate (M1)

Caproic acid (2.426 g, 20.8 mmol) was reacted in a 100 mL round bottom flask with 1.2 equivalents of CDI (4.047 g, 25 mmol) using THF (25 mL) as solvent at 55 °C. The reaction was monitored by GC-MS and TLC. It was found that fatty acid, independent of the chain length, was completely converted to the intermediate acylimidazole after approximately 2 h. Subsequently, 1.2 equivalents of NBM (85% *endo*, 15% *exo,* 2.751 g, 22.88 mmol) was slowly added to the reaction mixture and the stirring was continued. The progress of the reaction was monitored by GC-MS. After an additional 16 h of stirring at 55 °C, the reaction was stopped and the solvent was evaporated. Diethyl ether was used to extract the desired product from the residue. The organic phase was subsequently washed with saturated $NaHCO_3$ (aq) and water twice, then dried over anhydrous Na_2SO_4. After the extraction, the solvent was evaporated. The product was further purified by column chromatography with basic alumina using hexane: diethyl ether (8:2) as eluent. The solvent was removed *in vacuo* and the desired product was obtained as analytically pure compound in 99.8% (4.62 g) yield as colorless viscous oil.

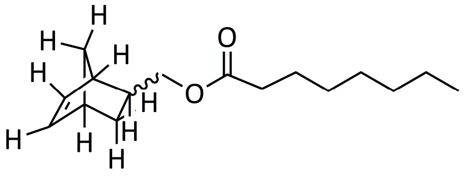
^{1}H NMR (300 MHz, *CDCl₃*, δ in ppm) (Figure 5.1): 6.07 (dd, *J* = 3.03 and 5.7 Hz, 0.85H, H_{endo2}), 6.0 (m, 0.3H, H_{exo2} and H_{exo3}), 5.86 (dd, *J* =2.88 and 5.70 Hz, 0.85H, H_{endo3}), 3.9-4.07 (ddd, *J* = 7.83, 10.89 and 19,99 Hz, 0.3H, H_{exo8}), 3.58-3.77 (ddd, *J* = 8.11, 10.73 and 20.15 Hz, 1.7H, H_{endo8}), 2.79 (s, 0.85H, H_{endo4}), 2.74 (m, H_{endo1} and H_{exo4}), 2.61 (s, 0.15H, H_{exo1}), 2.32 (m, 0.85H, H_{endo5}), 2.22 (dd, *J* = 7.42 and 13.86 Hz, 2H, H_9), 1.71 (ddd, *J* = 5.97, 4.82, 3.38 Hz, 0.85H, H_{endo6b}), 1.64 (m, 0.15H, H_{exo5}), 1.56 (m, 2H, H_{10}), 1.37 (m, 0.85H, H_{endo7b};), 1.15−1.25 (m, 5.3H, H_{exo6b}, H_{endo7a}, H_{exo7a}, H_{exo7b}, and $H_{11\text{-}12}$), 1.09 (ddd, *J* = 2.55, 5.19 and 11.74 Hz, 0.15H, H_{exo6a}), 0.81 (t, *J* = 6.69, 6.69 Hz, 3H, H_{13}), 0.48 (ddd, *J* = 2.60, 4.40 and 11.69 Hz, 0.85H, H_{endo6a}) (Figure 5.1). MS (ESI-positive): *m/z* = 245.2 ($[M+Na]^+$, calc. 245.3).

Bicyclo [2.2.1] hept-5-ene-2-methyl octanoate (M2)

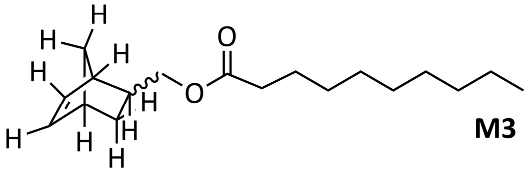
Monomer **M2** was synthesized applying a similar procedure as described for the preparation of **M1** starting with 3 g (20.8 mmol) of caprylic acid. The desired product was collected in 97.7% (5.09 g) yield as colorless viscous oil. ^{1}H NMR shifts and coupling constants were identical with compound **M1**, the intensity of δ = 1.15−1.25 corresponds to 9.3H (m, H_{exo6b}, H_{endo7a}, H_{exo7a}, H_{exo7b}, and $\text{-}(CH_2)_4\text{-}CH_3$). MS (ESI-positive): *m/z* = 273.2 ($[M+Na]^+$, calc. 273.4).



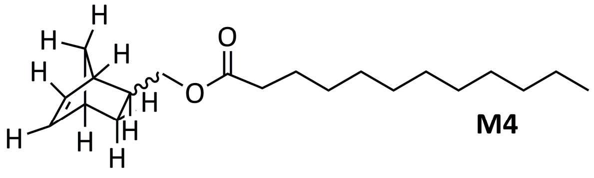
endo/*exo*-isomer **M1**



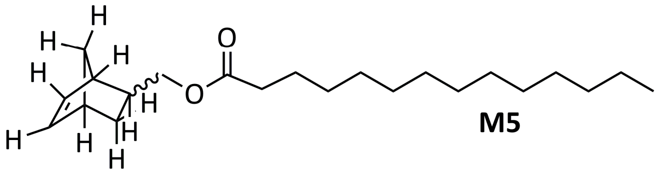
M2



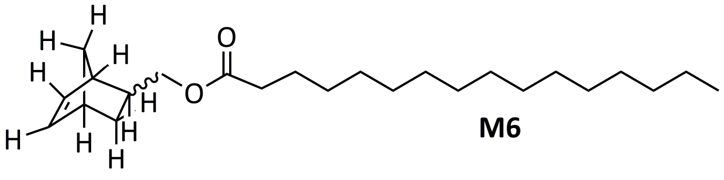
M3



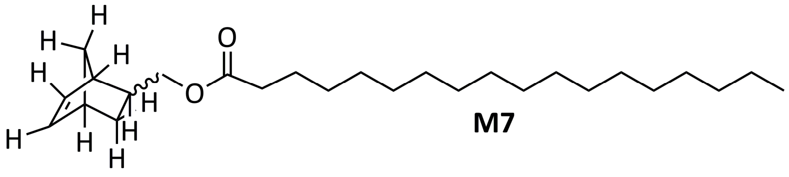
M4



M5



M6



M7

Figure 5.1: Structures of monomers **M1-M7**.

Bicyclo [2.2.1] hept-5-ene-2-methyl decanoate (M3)

Monomer **M3** was synthesized applying a similar procedure as described for the preparation of **M1** starting with 3.597 g (20.8 mmol) of capric acid. The desired product was collected in 81.2% (4.703 g) yield as colorless viscous oil. ^{1}H NMR shifts and coupling constants were identical with compound **M1**, the intensity of δ = 1.15−1.25 corresponds to 13.3H (m, H_{exo6b}, H_{endo7a}, H_{exo7a}, H_{exo7b}, and -$(CH_2)_6$-CH_3). MS (ESI-positive): *m/z* = 301.3 ($[M+Na]^+$, calc. 301.4).

Bicyclo [2.2.1] hept-5-ene-2-methyl dodecanoate (M4)

Monomer **M4** was synthesized applying a similar procedure as described for the preparation of **M1** starting with 4.167 g (20.8 mmol) of lauric acid. The desired product was collected in 85.8% (5.45 g) yield as colorless viscous oil. ^{1}H NMR shifts and coupling constants were identical with compound **M1**, the intensity of δ = 1.15−1.25 corresponds to 17.3H (m, H_{exo6b}, H_{endo7a}, H_{exo7a}, H_{exo7b}, and -$(CH_2)_8$-CH_3). MS (ESI-positive): *m/z* = 329.3 ($[M+Na]^+$, calc. 329.5).

Bicyclo [2.2.1] hept-5-ene-2-methyl tetradecanoate (M5)

Monomer **M5** was synthesized applying a similar procedure as described for the preparation of **M1** starting with 4.750 g (20.8 mmol) of myristic acid. The desired product was collected in 78.4% (5.453 g) yield as colorless viscous oil. ^{1}H NMR shifts and coupling constants were identical with compound **M1**, the intensity of δ = 1.15−1.25 corresponds to 21.3H (m, H_{exo6b}, H_{endo7a}, H_{exo7a}, H_{exo7b}, and -$(CH_2)_{10}$-CH_3) MS (ESI-positive): *m/z* = 357.3 ($[M+Na]^+$, calc. 357.6).

Bicyclo [2.2.1] hept-5-ene-2-methyl hexadecanoate (M6)

Monomer **M6** was synthesized applying a similar procedure as described for the preparation of **M1** starting with 5.3338 g (20.8 mmol) of palmitic acid. The desired product was collected in 82.2% (6.2 g) yield as colorless viscous oil. ^{1}H NMR shifts and coupling constants were identical with compound **M1**, the intensity of δ = 1.15−1.25 corresponds to 25.3H (m, H_{exo6b}, H_{endo7a}, H_{exo7a}, H_{exo7b}, and -$(CH_2)_{12}$-CH_3). MS (ESI-positive): *m/z* = 385.4 ($[M+Na]^+$, calc. 385.6).

Bicyclo [2.2.1] hept-5-ene-2-methyl octadecanoate (M7)

Monomer **M7** was synthesized applying a similar procedure as described for the preparation of **M1** starting with 5.940 g (20.8 mmol) of stearic acid. The desired product was collected in 73.1% (5.938 g) yield as white solid. ^{1}H NMR shifts and coupling constants were identical with compound **M1**, the intensity of δ= 1.15−1.25 corresponds to 29.3H (m, H_{exo6b}, H_{endo7a}, H_{exo7a}, H_{exo7b}, and -(CH_2)$_{14}$-CH$_3$). MS (ESI-positive): *m/z* = 413.4 ([M+Na]$^+$, calc. 413.7).

Metathesis Polymerization of Monomers M1-M7

If not otherwise mentioned, all polymerization reactions were carried out under ambient atmosphere. For a polymerization aiming at 100 repeating units ([M]/[I] ratio: 100/1), a typical polymerization procedure was as follows: A 3 mL conical vial (Supelco) was charged with 0.128 mmol of the respective monomer (**M1-M7**), 1 mL of THF, 0.8 mL of DCM, and a magnetic stirrer. A stock solution of catalyst (0.00128 mmol of **C6** in 0.1 mL of DCM) was rapidly and completely added to the vigorously stirring monomer solution *via* syringe in ambient atmosphere. After stirring at 25 °C for 1 min, ethyl vinyl ether (~ 0.1 mL) was added and the reaction was allowed to stir for 30 min at room temperature. The residue was then precipitated by drop-wise addition of the reaction mixture into 20 mL of vigorously stirred cold MeOH in an ice bath. The polymers were washed multiple times with MeOH. Depending on the monomer applied, polymers were precipitated as sticky rubbery materials to white solids.

5.5 Studies on the activity and selectivity of indenylidene-based metathesis catalysts during ADMET polymerization

Materials

10-undecenoic acid (Sigma-Aldrich, 98%), 1,3-propanediol (Sigma-Aldrich, 99.6%), *p*-toluenesulfonic acid monohydrate (Sigma-Aldrich, 98.5%), ethyl vinyl ether (Sigma-

Aldrich, 99%), sulfuric acid (Fluka, 95–97%), 1,4-benzoquinone (Fluka, 98%), (1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro-(3-phenyl-1H-inden-1-ylidene)(tricyclohexylphosphine)ruthenium(II) (Umicore M2, **C10**), (1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro-(3-phenyl-1H-inden-1-ylidene) (pyridyl)ruthenium(II) (Umicore M3$_1$, **C11**), (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(2-(1-methylacetoxy)phenyl]methyleneruthenium(II) (Umicore M5$_1$, **C12**) (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene)ruthenium(II) (Hoveyda-Grubbs 2nd generation catalyst, **C5**, Sigma-Aldrich).

Specifications on the analytical methods

NMR: Spectrometers A and C.

SEC: Column system C.

DSC: System B. Meassurements performed at heating rates of 5, 10 and 20 °C × min^{-1} up to 150 °C with a sample mass of approximately 4 mg.

GC-MS: Equipment A.

Synthetic procedures

Synthesis of 1,3-propylene diundec-10-enoate (1)

50.00 g (0.27 mol) of 10-undecenoic acid, 8.4 g (0.11 mol) of 1,3-propanediol and 3 g (0.0157 mol) of *p*-toluensulfonic acid were placed in a round-bottomed flask provided with a magnetic stirrer and a Dean-Stark apparatus. Then, 200 mL of toluene were added and the resulting reaction mixture was heated to reflux. Water was collected as the reaction proceeded and once the reaction was completed, the reaction mixture was allowed to cool down. Toluene was removed under reduced pressure and the residue was filtered through a short pad of basic aluminium oxide using hexane as eluent. After removing the hexane, the crude product was dissolved in diethyl ether

(200 mL) and washed with two times with water (200 mL). The organic fraction was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The desired product was isolated in 87% yield (39 g).

^{1}H NMR ($CDCl_3$): δ=5.85–5.76 (m, 2H, 2x-C*H*=CH_2), 5.00–4.91 (m, 4H, 2xCH=CH_2), 4.15 (t, 4H, J=6.1 Hz, 2xCH_2OCO-), 2.30 (t, 4H, J=7.3 Hz,CH_2COO–), 2.00 (m, 4H, 2xCH_2–CH=CH2), 1.99–1.94 (m, 2H, J=6.1 Hz, C$H_2$$CH_2$OCO–), 1.64–1.58 (m, 4H, 2xC$H_2$$CH_2$COO–), 1.38–1.34 (m, 4H, 2xCH_2) 1.29–1.24 (br.s, 16H, 2x[4CH_2]) ppm.
^{13}C NMR (CDCl3): δ=173.6 (s, –*C*OO–), 139.0 (s, –*C*H=CH_2), 114.1 (s, –CH=CH_2), 60.7 (s, CH_2OCO–), 34.1 (s, CH_2), 33.7 (s, CH_2), 29.2 (s, CH_2), 29.1 (s, CH_2), 29.0 (s, CH_2), 28.8 (s, CH_2), 24.8 (s, CH_2) ppm. MS (EI): *m/z*=408 $[M]^+$, calc. 408.3239.

ADMET polymerization (P1-P26)

To 1 g (2.45 mmol) of 1,3-propylene diundec-10-enoate in a tube equipped with a screw, 0.5 mol% of the corresponding Ru catalyst, (**C10**: 11.6 mg (0.0122 mmol), **C11**: 9.1 mg (0.0122 mmol), **C12**: 8 mg (0.0122 mmol) and **C5**: 7.7 mg) was added at the desired reaction temperature (60-120 °C). In some cases, 1.0 mol% of **BQ** was added to the reaction mixture 10 min before addition of the catalyst. Reactions were carried out in parallel using a carousel reaction station from Radleys. The stirring was continued at the selected temperature under a continuous flow of nitrogen for 5 h. After 5 h reaction time, the reaction mixture was dissolved in 1 mL of THF and the polymerization was quenched by addition of 1 mL of ethyl vinyl ether and stirring for 30 min at room temperature. The product was purified by precipitation into cold methanol. Final polymer molecular weights were determined after precipitation using GPC system.

Transesterification of the obtained polymers (P1-P26) and GC-MS analysis

The respective polymer (30 mg), excess methanol (4 mL) and concentrated sulphuric acid (5 drops) were added to a carousel reaction tube, stirred magnetically, and refluxed at 85 °C for 5 h. At the end of the reaction, the excess of methanol was removed under reduced pressure. Then, the residue was dissolved in diethyl ether and filtered over a small column of basic aluminum oxide. Subsequently, GC-MS samples were prepared by taking 500µL of this solution and diluting it with methanol (500µL). The percentage of olefin isomerization was calculated based on the areas of the peaks belonging to the isomerized diesters.

5.6 Synthesis of castor oil-derived unsaturated PA X,20 *via* metathesis and catalytic amidation

Materials

10-Undecenoic acid (Aldrich, 98%), 1,2-Diamonoethane (EDA; Aldrich, 98%), 1,4-Diaminobutane (DAB; Aldrich, 98%), 1,6-Hexanediamine (HMDA; Aldrich, 98%), 1,8-Diaminooctane (OMDA; Aldrich, 98%), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD; Aldrich, 98%), benzylidene [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (Grubbs 2nd generation catalyst, **C4**, Aldrich), (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene)ruthenium (Hoveyda-Grubbs 2nd generation catalyst, **C5**, Aldrich), trifluoroaceticanhydride (TFAA; Fluka, 99%). Methyl-10-undecenoate was synthesized by esterification with methanol from corresponding 10-undecenoic acid according to standard laboratory procedures.

Specifications on the analytical methods

NMR: Spectrometer C.

SEC: Column system D. Polyamide samples had to be derivatized for GPC analysis according to the following modified literature procedure:[373,374] small amounts of sample (10-20 mg) were weighed into GPC vials. 50 µl of dichloromethane and 50 µl of TFAA were then added to the vial and the sample was sealed and kept until the polymer dissolved. Once a clear solution was obtained, the vials were opened and the solutions were diluted with 900 µl of THF resulting in sample concentrations of ~ 1 mg × mL^{-1}. Each solution was prepared immediately prior to analysis.

DSC: System B. Meassurements performed at a heating rate of 10 °C × min^{-1} up to 280 °C with a sample mass of approximately 5 mg.

Synthetic procedures

Synthesis of monomers

E-dimethyl-eicos-10-enedioate (2)

2 was prepared according to a modified literature procedure.[90a] 60.0 g (302 mmol) of **1** were heated to 40 °C. 50 mg (0.059 mmol = 0.02 mol%) of **C4** were then added under a nitrogen atmosphere and the reaction was continued under vacuum (20 mbar) for 7 h. After cooling to room temperature, the reaction mixture was treated with 500 mL hexane and 30 g of silica at room temperature for 6 h. The silica was filtered off and the solvent was removed *in vacuo* to yield the crude product (90% purity by GC). The *trans* product was then isolated by recrystallization from methanol (34.2 g, 57%). Melting point: 45.5 °C. Analytic data is in accordance with the literature.[90a]

N,N'-(ethane-1,2-diyl)diundec-10-enamide (4a)

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD; 0.06195 g, 0.445 mmol, 7.5 mol%) was added to a mixture of methyl-10-undecenoate (1.764 g, 8.896 mmol, 2.5 equiv) and 1,2-Diamonoethane (0.214 g, 3.56 mmol, 1 eq.) in a 100 mL round bottom flask and stirred magnetically at 75 °C overnight under a continuous flow of nitrogen in order to remove the produced methanol. At the end of the reaction, the mixture was cooled to room temperature and the white solid was washed with methanol to remove the catalyst and unreacted ester. The solvent was removed *in vacuo*. The product was obtained as an ivory solid (1.235 g, 70%), m.p.: 147.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$/TFAA, δ): 5.82 (m, 2H), 4.99 (m, 4H), 3.99 (s, 4H), 2.78 (t, J = 7.5 Hz, 4H), 2.05 (dd, J = 14.3 and 7.0 Hz, 4H), 1.66 (m, 4H), 1.31 (m, 20H). MS (ESI-positive, MeOH): m/z 415.5 ([M+Na]$^+$, calc. 415.3).

N,N'-(butane-1,4-diyl)diundec-10-enamide (4b)

Diene **4b** was prepared by reaction of 1,4-Diaminobutane with methyl-10-undecenoate applying a similar procedure as described for the preparation of diene **4a**. The product was obtained as a white solid (1.323 g, 75%), m.p.: 144.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$/TFAA, δ): 5.82 (m, 2H), 4.96 (m, 4H), 3.73 (m, 4H), 2.79 (t, J = 7.5 Hz, 4H), 2.05 (dd, J = 14.3 and 7.0 Hz, 4H), 1.66 (m, 4H), 1.62 (m, 4H), 1.35 (m, 20H). MS (ESI-positive, MeOH): m/z 443.5 ($[M+Na]^+$, calc. 443.4).

N,N'-(hexane-1,6-diyl)diundec-10-enamide (4c)

Diene **4c** was prepared by reaction of 1,6-Hexanediamine with methyl-10-undecenoate applying a similar procedure as described for the preparation of diene **4a**. The product was obtained as a white solid (1.570 g, 89%), m.p.: 137.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$/TFAA, δ): 5.84 (m, 2H), 4.92 (m, 4H), 3.69 (m, 4H), 2.79 (t, J = 7.4 Hz, 4H), 2.05 (m, 4H), 1.66 (m, 4H), 1.59 (m, 4H), 1.35 (m, 24H).

MS (ESI-positive, MeOH): m/z 449.2 ($[M+H]^+$, calc. 449.4).

N,N'-(octane-1,8-diyl)diundec-10-enamide (4d)

Diene **4d** was prepared by reaction of 1,8-Diaminooctane with methyl-10-undecenoate applying a similar procedure as described for the preparation of diene **4a**. The product was obtained as a white solid (1.588 g, 90%), m.p.: 134.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$/TFAA, δ): 5.82 (m, 2H), 4.97 (m, 4H), 3.69 (m, 4H), 2.78 (t, J = 7.5 Hz, 4H), 2.04 (m, 4H), 1.66 (m, 4H), 1.57 (m, 4H), 1.35 (m, 28H).
MS (ESI-positive, MeOH): m/z 499.4 ($[M+Na]^+$, calc. 499.6).

Synthesis of polyamides

Catalytic amidation

Catalytic amidation polymerizations were carried out in 3 mL conical vials (Supelco) equipped with screw cap and septa. Monomer **2** (0.2 g, 0.543 mmol, 1 eq) was mixed with diamine (**3a-3d**, 1 eq) and degassed under nitrogen for 1 h. TBD (5.0, 7.5 or 10.0 mol%) was then added to the reaction mixture. The reaction mixture was then flushed with nitrogen for 10 minutes at RT under magnetic stirring, since TBD is hygroscopic, sensitive to CO_2 and humidity.[375] For route A, the stirring was continued at 150 °C with a continuous flow of nitrogen overnight. For route B, the stirring was continued at 75 °C for 2 h. Then the reaction temperature was increased to 100 °C. After being kept for 2 h at 100 °C, the reaction temperature was adjusted to 150 °C and kept for an additional 2 h under these conditions. The resulting polymers were then trifluoroacetylated and subsequently precipitated in order to remove the catalyst from the reaction mixture.

ADMET polymerization

Polymerization were carried out in a 3 mL conical vial (Supelco) equipped with screw cap and septa under nitrogen atmosphere. **C4** or **C5** were added to pre-degassed solution of **4a-d** (0.25 mmol) in o-xylene (0.25 mL), and the resulting mixture was kept stirring in an oil bath at 80 °C under a continuous flow of nitrogen. Catalyst concentrations were varied from 1.0 to 10.0 mol%. After 4 h reaction time, the polymerization was quenched by adding ethyl vinyl ether (0.1 mL). The resulting mixture was concentrated with a rotary evaporator and the residue was washed with DMF and subsequently dried to isolate the polymer.

5.7 Synthesis of carbonate-based polymers and building blocks

Materials

All alcohols (analytical grade), glycerol (≥99%), dimethyl carbonate (DMC, 99%), 1,5,7-triazobicyclo[4.4.0]dec-5-ene (TBD, 98%), 1,4-benzoquinone (**BQ**, ≥98%), ethyl vinyl ether (99%), tetradecane (>99%), pyrrolidine (>99.5%), benzylidene[1,3-*bis*-(2,4,6-trimethylphenyl)imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (Grubbs 2nd generation catalyst, **C4**), [1,3-*bis*-(2,4,6-trimethylphenyl)-2-

imidazolidinylidene]dichloro(o-isopropoxy-phenylmethylene)ruthenium (Hoveyda-Grubbs 2nd generation catalyst, **C5**) were obtained from Aldrich. 1,3-*bis*-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-yliden[2-(isopropoxy)-5-N,N-dimethylaminosulfonyl)phenyl] methylene ruthenium (II) dichloride (Zhan catalyst, **C7**, 96%) was delivered from ABCR. Poly(ethylene glycol) methyl ether (mPEG-OH, M_n~500 Da) was purchuased from Fluka. All reagents were used without further purification. (*E*) Icos-10-ene-1,20-diol (**D3**) was prepared according to the procedure reported by Meier and co-workers.[149b] Solvents for chromatography were technical grade.

Specifications on the analytical methods

NMR: Spectrometer A.

GC-MS: Equipment A. Two different oven programs: Method A - the oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C × min^{-1} to 200 °C, hold for 2 min, ramp at 15 °C × min^{-1} to 325 °C, hold for 5 min. Method B - the oven temperature was: initial 35 °C, hold for 2 min, ramp at 10 °C × min^{-1} to 150 °C, hold for 1 min. The injector's transfer line temperature was set to 250 °C.

SEC: Column system E.

Synthetic procedures

All reactions and polymerizations were perfromed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK).

Synthesis and characterization of unsymmetric organic carbonates

Tetradecane (10.0 mol% relative to the alcohol) was used as internal standard and the conversion, selectivity and yield were calculated with respect to the alcohol. In a typical procedure, a mixture of the alcohol (15.0 mmol) and the corresponding amount DMC (see Table 2 in the main text) was added to the carousel tube and stirred magnetically at 80°C for a couple of minutes. After taking a t = 0 min sample, if not otherwise specified, 0.15 mmol TBD was added to the carousel tube (see Table 2 in the main text for additional information). The reactions were sampled and analysed by GC, GC-MS and NMR in specific time intervals, thus the product distribution and conversion being determined. After a defined time, the heating was stopped and the recation mixtures were allowed to cool to room temperature. The crude reaction mixture was purified by column chromatography to obtain the pure product. In cases when the product was a mixture of the unsymmetric and symmetric organic carbonate mixture, fractional destillation was applied.

Model compound - methyl octyl carbonate: after purification with column chromotography (*n*-hexane/ethyl acetate = 9:1) methyl octyl carbonate was obtained as colourless oil in a yield of 95%. The ^{1}H and ^{13}C NMR spectra were in accordance with the already reported one.[376]

Characterization of the unsymmetric carbonates.

Butyl methyl carbonate (Table 4.16, entry 1)**:** colourless liquid, *n*-hexane/ethyl acetate = 2/1, yield = 85%.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.11 (m, 2H, -CH_2-O-), 3.77 (s, 3H, -O-CH_3), 1.73–1.46 (m, 2H, -CH_2-CH_2-CH_3), 1.43–1.15 (m, 2H, -CH_2-CH_2-CH_3), 0.87 (t, *J* = 6.6 Hz, 3H, -CH_3).
^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.7 (-OCO_2-), 69.1 (-CH_2-O-), 54.9 (-O-CH_3), 28.9 (-CH_2-CH_2-CH_3), 18.8 (-CH_2-CH_2-CH_3), 13.5 (-CH_3).
MS (EI) of $C_6H_{12}O_3$ $[M+H]^+$ calc. 133.08 found 133.2

Hexyl methyl carbonate (Table 4.16, entry 2): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 89%

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.22–3.98 (m, 2H, -CH_2-O-), 3.77 (s, 3H, -O-CH_3), 1.77–1.49 (m, 2H, aliphatic -CH_2-), 1.46–1.16 (m, 6H, aliphatic -CH_2-), 0.87 (t, *J* = 6.6 Hz, 3H, -CH_3).
^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.9 (-OCO_2-), 68.2 (-CH_2-O-), 54.6 (-O-CH_3), 31.6

(aliphatic -*C*H_2-), 28.6 (aliphatic -*C*H_2-), 25.3 (aliphatic -*C*H_2-), 22.5 (aliphatic -*C*H_2-), 13.9 (-*C*H_3).

HRMS of $C_8H_{16}O_3$ $[M+H]^+$ calc. 161.11 found 161.30

Methyl undec-10-en-1-yl carbonate (Table 4.16, entry 3): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 93%.

^{1}H NMR(300 MHz, $CDCl_3$, δ in ppm): 5.80 (ddt, *J* = 16.9, 10.2 and 6.7 Hz, 1H, CH_2=C*H*-), 5.03–4.82 (m, 2H, C*H*$_2$=CH-), 4.11 (t, *J* = 6.7 Hz, 2H, -C*H*$_2$-O-), 2.07–1.96 (m, 2H, CH_2=CH-C*H*$_2$-), 1.69–1.57 (m, 2H, -C*H*$_2$-CH_2-O-), 1.42–1.18 (m, 12H, aliphatic -C*H*$_2$-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.8 (-O*C*O_2-), 139.1 (CH_2=*C*H-), 114.1 (*C*H_2=CH-), 68.2 (-C*H*$_2$-O-), 54.5 (-O*C*H_3), 33.8 (CH_2=CH-*C*H_2-), 29.4-25.6 (aliphatic-*C*H_2-).

HRMS of $C_{13}H_{24}O_3$ $[M+H]^+$ calc. 229.18 found 229.10

3,7-dimethyloct-6-en-1-yl methyl carbonate (Table 4.16, entry 4): colourless liquid, *n*-hexane/ethyl acetate = 9/1, yield = 94%.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.18–4.95 (m, 1H, -*H*C=C(CH_3)$_2$), 4.28–4.04 (m, 2H, -O-C*H*$_2$-), 3.86 (s, 3H, -O-C*H*$_3$), 1.94 (pt, *J* = 13.1, 6.6 Hz, 2H, -C*H*$_2$-HC=C(CH_3)$_2$), 1.78–1.08 (m, 11H), 0.91 (d, *J*=6.4 Hz, 3H, -CH(C*H*$_3$)-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.9 (-O*C*O_2-), 131.3 (-HC=*C*(CH_3)$_2$), 124.5 (-H*C*=C(CH_3)$_2$), 66.6 (-O-*C*H_2-), 54.6(O-*C*H_3), 36.9 (-*C*H_2-CH_2-HC=C(CH_3)$_2$), 35.6 (CH_3O-C(O)$_2$-CH_2-*C*H_2-), 29.3 (-CH_2-*C*H(CH_3)-CH_2-), 25.6 (-$C_{isomer}H_2$-HC=C(CH_3)$_2$), 25.3 (-$C_{isomer}H_2$-HC=C(CH_3)$_2$), 19.3 (-HC=C(*C*H_3)$_2$), 17.6 (-HC=C(*C*H_3)$_2$).

HRMS of $C_{12}H_{22}O_3$ $[M+H]^+$ calc. 215.16 found 215.20

Allyl methyl carbonate (Table 4.16, entry 5): colourless oil, *n*-hexane/ethyl acetate = 15/1, yield = 80%.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 6.06–5.77 (m, 1H, CH_2=C*H*-), 5.38–5.21 (m, 2H, C*H*$_2$=CH-), 4.60 (dd, *J* = 5.7 and 1.3 Hz, 2H, -C*H*$_2$-O-), 3.68 (s, 3H, -O-C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.7 (-O*C*O_2-), 131.7 (CH_2=*C*H-), 118.5 (*C*H_2=CH-), 68.5 (-*C*H_2-O-), 54.9 (-O-*C*H_3).

MS (EI) of $C_{12}H_{22}O_3$ $[M+H]^+$ calc. 117.05 found 117.20

Methyl *trans*-2-hexen-1-yl carbonate (Table 4.16, entry 6): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 92%.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.97–5.32 (m, 2H, -C*H*=C*H*-), 4.54 (ddd, *J* = 19.6, 10.3, 4.2 Hz, 2H, -CH_2-O-), 3.76 (s, 3H, -O-CH_3), 2.17–1.87 (m, 2H, -CH_2-CH=CH-), 1.50–1.27 (m, 2H, -CH_2-CH_2-CH=CH-), 0.90 (t, 3H, -CH_3).
^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.8 (-O*C*O_2-), 137.4 (-CH=*C*H-CH_2-OCO_2-), 123.5 (-*C*H=CH-CH_2-OCO_2-), 68.9 (-*C*H_2-O-), 54.8 (-O-*C*H_3), 34.4 (-*C*H_2-CH=CH-), 22.1 (-CH_2-CH_2-CH=CH-), 13.7 (CH3-).
HRMS of $C_8H_{12}O_3$ $[M]^+$ calc. 158.09 found 158.20

Methyl *trans*-2,4-hexadien-1-yl carbonate (Table 4.16, entry 7): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 89%.
^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 6.40–5.93 (m, 2H, -CH=C*H*-C*H*=CH-), 5.86–5.54 (m, 2H, -C*H*=CH-CH=C*H*-), 4.72–4.52 (m, 2H, -CH_2-O-) 3.77 (s, 3H, -O-CH_3), 1.87–1.65 (m, 3H, -CH_3).
^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.6 (-O-*C*H_3), 135.5 (-CH=*C*H-CH=CH-CH_3), 131.6 (-CH=CH-CH=*C*H-CH_3), 130.3 (-CH=CH-CH=*C*H-CH_3), 122.9 (*C*H=CH-CH=CH-CH_3), 68.2 (-*C*H_2-O), 54.7 (-O-CH3), 18.1 (-*C*H_3).
HRMS of $C_8H_{12}O_3$ $[M]^+$ calc. 156.08 found 156.10

Methyl propargyl carbonate (Table 4.16, entry 8): yellowish oil, *n*-hexane/ethyl acetate = 15/1, yield = 75%.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.68–4.64 (m, 2H, -CH_2-O-), 3.75 (s, 3H, -O-CH_3), 2.52–2.48 (m, 1H, *H*C≡C-).
^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.1 (-O*C*O_2-), 76.9 (HC≡*C*-, overlapping with $CDCl_3$), 75.6 (HC≡C-), 55.1 (-*C*H2-O-), 55.0 (-O-*C*H3).
MS (EI) $C_5H_6O_3$ $[M+H]^+$ calc. 115.04 found 115.20

Methyl poly(ethylene glycol) methyl ether carbonate (Table 4.16, entry 9): excess of DMC carbonate was removed *via* extraction of the crude reaction mixture with hexane; the highly viscous product was dried under vacuum thus yielding 94% viscous colourless oil.

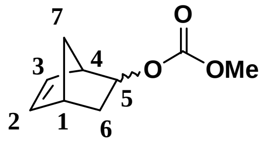
^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 4.30- 4.20 (m, 2H, -C*H*$_2$-O-C(O)O-CH$_{3\mathit{end\ group}}$), 3.76 (s, 1H, -CH$_2$-O-C(O)O-C*H*$_{3\mathit{end\ group}}$), 3.72-3.49 (m, repeating unit -O-C*H*$_2$-C*H*$_2$-O-), 3.35 (s, 3H, -CH$_2$-O-C*H*$_{3\mathit{end\ group}}$).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 156.8 (-O*C*O$_2$-), 71.9 (-O-CH$_2$-*C*H$_2$-O-CH$_{3\mathit{end\ group}}$), 70.6 (repeating unit -O–*C*H$_2$-*C*H$_2$-O-), 70.4 (-O-*C*H$_2$-CH$_2$-O-CH$_{3\mathit{end\ group}}$), 68.9 (-*C*H$_2$-CH$_2$-O-C(O)O-CH$_{3\mathit{end\ group}}$), 66.9 (-*C*H$_2$-O-C(O)O-CH$_{3\mathit{end\ group}}$), 58.9 (-CH$_2$-O-*C*H$_{3\mathit{end\ group}}$), 54.6 (-C(O)O-*C*H$_{3\mathit{end\ group}}$).

HRMS [M+H]$^+$ found 575.5

Cyclohexyl methyl carbonate (Table 4.16, entry 10): colourless liquid, *n*-hexane/ethyl acetate = 9/1, yield = 93%. Spectroscopic properties were in agreement with those reported in the literature.[377]

Bicyclo[2.2.1]hept-5-en-2-yl methyl carbonate (Table 4.16, entry 11): colourless liquid, *n*-hexane/ethyl acetate = 4/1, yield = 95%.



^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 6.36–6.27 (m, 1H, H^2), 6.00–5.92 (m, 1H, H^3), 5.25–5.15 (m, 1H, H^5), 3.72 (s, 3H, OMe), 3.18–3.12 (m, 1H, H^4), 2.85–2.78 (m, 1H, H^1), 2.16–2.08 (m, 1H, H^6), 1.48–1.43 (m, 1H, H^7), 1.29 (d, *J* = 8.9 Hz, 1H, $H^{7'}$), 1.03–0.95 (m, 1H, $H^{6'}$).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 154.20 (CO), 139.97 ($C^{2'}$), 137.28 (C^2), 130.87 ($C^{3'}$), 129.79 (C^3), 77.54 ($C^{5'}$), 77.23 (C^5), 53.02 (OMe′), 52.98 (OMe), 46.11 (C^7), 45.86 ($C^{7'}$), 44.67 ($C^{4'}$), 44.31 (C^4), 40.75 (C^1), 39.07 ($C^{1'}$), 33.01 (C^6, $C^{6'}$).

HRMS of $C_{12}H_{18}O_3$ [M]$^+$ calc. 168.08 found 168.80

2-Adamantyl methyl carbonate (Table 4.16, entry 12): recrystalized from MeOH, yield = 93%.

^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm) 4.86–4.67 (m, 1H, -C*H*-O-C(O)O-), 3.76 (s, 3H, C*H$_3$*-O-C(O)O-), 2.17–1.96 (m, 2H), 1.92–1.66 (m, 8H), 1.53 (t, *J* = 16.1 Hz, 4H).
^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 155.3 (-O*C*O$_2$-), 81.1 (-C*H*-O-C(O)O-), 54.4 (-O-*C*H$_3$), 37.3 (2C), 36.3 (2C), 31.8, 31.5, 28.8, 27.1, 26.9.
HRMS of $C_{12}H_{18}O_3$ $[M+H]^+$ calc. 211.13 found 211.00

Methyl-1,4-pentadien-3-yl carbonate (Table 4.16, entry 13): colourless oil, *n*-hexane/ethyl acetate = 15/1, yield = 89%.

^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 5.94–5.69 (m, 2H, CH$_2$=C*H*-), 5.46 (dt, *J*=11.6 and 8.3 Hz, 1H, -C*H*-O-), 5.38–5.13 (m, 4H, C*H$_2$*=CH-), 3.75 (s, 3H, -O-C*H$_3$*).
^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 156.4 (-O*C*O$_2$-), 134.6 (CH$_2$=*C*H-), 118.1 (*C*H$_2$=CH-), 79.1 (-*C*H$_2$-O-), 54.8 (-O-*C*H$_3$).

Benzyl methyl carbonate (Table 4.16, entry 14): colourless oil, *n*-hexane/ethyl acetate = 9/1, yield = 93%. Spectroscopic properties were in agreement with those reported in the literature.[378]

Methyl (1-phenylbut-3-en-1-yl) carbonate (Table 4.16, entry 15): colourless oil, *n*-hexane/ethyl acetate = 5/1, yield = 90%.

^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 7.49–7.27 (m, 10H, aromatic –C*H*-), 5.87–5.57 (m, 1H, CH$_2$=C*H*-), 5.29–4.99 (m, 3H, C*H$_2$*=CH- and CH$_2$=CH-CH$_2$-C*H*-), 3.69 (s, 3H, -OC*H$_3$*), 2.99–2.42 (m, 2H, CH$_2$=CH-C*H$_2$*-CH-).
^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 155.0 (-O*C*O$_2$-), 139.4 (aromatic –*C*H-), 132.8 (CH$_2$=*C*H-), 128.4 (aromatic –*C*H-), 128.1 (aromatic –*C*H-), 126.4 (aromatic –*C*H-), 118.3 (*C*H$_2$C=H-), 79.3 (-*C*H-O-), 54.6 (-*C*H$_2$-O-), 40.7 (CH$_2$=CH-*C*H$_2$-).
HRMS of $C_{12}H_{14}O_3$ $[M+H]^+$ calc. 207.10 found 207.10

tert-Butyl methyl carbonate (Table 4.16, entry 16): colourless liquid, *n*-hexane/ethyl acetate = 10/1, yiled = 82%.

^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 3.74 (s, 3H, -O-C*H$_3$*), 1.43 (s, 9H, C-(C*H$_3$*)$_3$).
^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 155.6 (-O*C*O$_2$-), 81.1 (-*C*-(CH$_3$)$_3$), 55.9 (-C*H$_2$*-O-), 28.4 (-C-(*C*H$_3$)$_3$).
MS (EI) of $C_6H_{12}O_3$ $[M+H]^+$ calc. 133.08 found 133.10

Glycerol carbonate (Table 4.16, entry 17): colourless oil, *n*-hexane/ethyl acetate = 1/25, yield = 95%.

^{1}H NMR (300 MHz, DMSO-*d6*, δ in ppm): 5.28 (dd, *J* = 7.2, 3.8 Hz, 1H, *H*O-CH$_2$-CH-) 4.80 (ddd, *J* = 11.6, 5.9, 3.0 Hz, 1H, HO-CH$_2$-C*H*-), 4.49 (td, *J* = 8.3, 2.9 Hz, 1H, -O-C*H$_2$*-CH-), 4.28 (dd, *J* = 8.1, 5.8 Hz, 1H, -O-C*H$_2$*-CH-). 3.67 (ddd, *J* = 12.6, 5.4, 2.7 Hz, 1H, HO-C*H$_2$*-CH-), 3.50 (ddd, *J* = 12.6, 5.6, 3.3 Hz, 1H, HO-C*H$_2$*-CH-).
^{13}C NMR (75 MHz, DMSO-*d6*, δ in ppm): 155.3 (-O*C*O$_2$-), 77.1 (HO-CH$_2$-*C*H-), 65.9 (HO-*C*H$_2$-CH-), 60.6 (-O-*C*H$_2$-CH-).
MS (EI) of $C_4H_6O_4$ $[M+H]^+$ calc. 119.03 found 119.01

One pot two-step polymerization *via* TBD mediated polycondesation

Polymers in Table 3, 4 and 5 were synthesized following a two-step polycondensation of DMC with **D1**, **D2** and **D3** (Scheme 2 in the main text), respectively, in the melt. In a typical experiment 2.7 gr (35.0 mmol) of DMC and 1.0 equvialent (17.5 mmol) of the corresponding “potential” green diols (**D1**, **D2** or **D3**) were introduced into a carousel tube. The reaction was equipped with magnetic stirring and a screw cap with a septum. The mixture was homogenized at room temperature for 10 min and the specific amount of TBD (0.1, 0.5, 1.0 and 5.0 mol% to the alcohol) was added and the reaction which was equipped with argon purge and heated at 80 °C. Once the sufficient amount of oligomers was obtained, vacuum was applied (10^{-2} bar) and the temperature was increased to 90 °C to facilitate the polymerization by removing both unreacted DMC and methanol released in the condensation reactions. The reactions were kept at 90 °C for 1 h except for **D1**. The temperature of the reactions for **D2** and

D3 were gradually increased to 150 °C over a period of *ca* 3 h and maintained at this temperature for 1 h to allow complete removal of the methanol and DMC. The reaction of **D1** was kept at 90 °C at continuous vacuum for 3 h in total. After completion, the reaction mixtures were dissolved in THF and the obtained polymers were precipitated in ice cold MeOH in yields ranging from 75 to 95%.

P3 (89%): ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.41–5.28 (m, -C*H*=C*H*-), 4.11 (t, *J* = 6.7 Hz, $-CH_2-O-$), 1.98 (t, *J* = 14.6 Hz, $-CH=CH-CH_2-$), 1.72–1.53 (m, $-CH_2-CH_2-O-$), 1.40–1.21 (m, aliphatic $-CH_2-$).

P5 (82%): ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.25–4.03 (m, $-O-CH_2-CH_2-CH_2-O-$), 3.66–3.56 (m, $-OH_{\textit{end group}}$), 2.03–1.87 (m, H, $-O-CH_2-CH_2-CH_2-O-$), 1.85–1.72 (m, 1H).

P6 (89%): ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 4.19–3.92 (m, $-O-CH_2-$), 1.73–1.48 (m, $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$), 1.47–1.21 (m, $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$).

Synthesis and characterization of the symmetrical organic carbonates

Reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). Tetradecane (10.0 mol% relative to the alcohol) was used as internal standard, and the conversion, selectivity and yield were calculated with respect to the limiting reactant (in this case: DMC)

Typical procedure - Diallyl carbonate (Table 4.19, entry 1): 871 mg of allyl alcohol (15.0 mmol) was mixed with 643 mg of DMC (7.14 mmol) into a carousel reaction tube. To this mixture, 10.0 mg of TBD (1.0 mol%) was added at 80 °C. The reaction was stirred under contionuos argon purge until completion as confirmed by TLC. The heating was stopped and the reaction mixtures were allowed to cool to room temperature. The crude reaction mixture was filtered through a short pad of silica gel with *n*-hexane/ethyl acetate = 9/1 to give a light yellow liquid in 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.94 (ddd, *J* = 16.2, 11.0, 5.8 Hz, 2H, $CH_2=CH-$), 5.42–5.19 (m, 4H, $CH_2=CH-$), 4.64 (dd, *J* = 5.7 and 1.3 Hz, 4H, $-CH_2-O-$).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.7 ($-OCO_2-$), 131.7 ($CH_2=CH-$), 118.1 ($CH_2=CH-$), 68.5 ($-CH_2-O-$).

MS (EI) of $C_7H_{10}O_3$ $[M]^+$ calc. 142.06 found 142.10

Characterization of the symmetrical carbonates

Di(undec-10-en-1-yl) carbonate (**M1,** Table 4.19, entry 2): purified over short pad of silica with *n*-hexane to give a colourless liquid in 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.80 (ddt, *J* = 16.9, 10.2 and 6.7 Hz, 2H,$CH_2=CH$-), 5.03–4.82 (m, 4H, CH_2=CH-), 4.11 (t, *J* = 6.7 Hz, 4H, -CH_2-O-), 2.07–1.96 (m, 4H, CH_2=CH-CH_2-), 1.69–1.57 (m, 4H, -CH_2-CH_2-O-), 1.42–1.18 (m, 24H, aliphatic -CH_2-).
^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.4 (-O*C*O_2-), 139.1 (CH_2=*C*H-), 114.1 (*C*H_2=CH-), 67.9 (-CH_2-O-), 33.8 (CH_2=CH-*C*H_2-), 29.4–25.7 (aliphatic -*C*H_2-).
HRMS of $C_{23}H_{42}O_3$ $[M+H]^+$ calc. 367.32 found 367.30

Di(3,7-dimethyloct-6-en-1-yl) carbonate (**M2,** Table 4.19, entry 3): purified over short pad of silica (*n*-hexane/ethyl acetate = 9/1), colourless oil in 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.08 (t, *J* = 7.0 Hz, 2H, -*H*C=C$(CH_3)_2$), 4.25–4.07 (m, 4H, -O-CH_2-), 1.94 (pt, *J* = 13.1, 6.6 Hz, 4H, -CH_2-HC=C$(CH_3)_2$), 1.77–1.53 (m, 16H), 1.53–1.11 (m, 6H), 0.91 (d, *J* = 6.4 Hz, 6H-CH(CH_3)-).
^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.4 (-O*C*O_2-), 131.3 (-HC=*C*$(CH_3)_2$), 124.5 (-H*C*=C$(CH_3)_2$), 66.4 (-O-*C*H_2-), 37.0 (-*C*H_2-CH_2-HC=C$(CH_3)_2$), 35.5 (CH_3O-C$(O)_2$-CH_2-*C*H_2-), 29.2 (-CH_2-*C*H(CH_3)-CH_2-), 25.7 (-$C_{isomer}H_2$-HC=C$(CH_3)_2$), 25.3 (-$C_{isomer}H_2$-HC=C$(CH_3)_2$), 19.3 (-HC=C$(CH_3)_2$), 17.6 (-HC=C$(CH_3)_2$).
HRMS of $C_{21}H_{38}O_3$ $[M+H]^+$ calc. 339.29 found 339.20

Dibenzyl carbonate (Table 4.19, entry 4): purified with extraction using *n*-hexane to yield a solid at RT (93%).

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 7.54–7.30 (m, 10H), 5.22 (s, 4H).
^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 155.0 (-O*C*O_2-), 135.1 (aromatic *C*H), 128.4 (aromatic *C*H), 69.6(-*C*H_2-O-).

HRMS of $C_{15}H_{14}O_3$ $[M+H]^+$ calc. 243.10 found 243.10

Di(1-phenylbut-3-en-1-yl) carbonate (Table 4.19, entry 5): purified over short pad of silica (*n*-hexane/ethyl acetate = 5/1); colourless oil in 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 7.49–7.27 (m, 10H, aromatic C*H*), 5.87–5.57 (m, 2H, CH_2=C*H*-), 5.29–4.99 (m, 6H, CH_2=CH- and CH_2=CH-CH_2-C*H*-), 2.99–2.42(m, 4H, CH_2=CH-CH_2-CH-).
^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm): 153.9 (-O$C_{isomer}$$O_2$-), 153.8 (-O$C_{isomer}$$O_2$-), 139.4 (aromatic *C*H), 139.3 (aromatic CH), 132.8 (CH_2=C_{isomer}H-), 132.7 (CH_2=C_{isomer}H-), 128.4-126.3 (aromatic *C*H), 118.2 ($C_{isomer}$$H_2$C=H-), 118.1 ($C_{isomer}$$H_2$C=H-), 79.2 (-$C_{isomer}$H-O-), 79.1 (-$C_{isomer}$H-O), 40.7 ($CH_2$=CH-$C_{isomer}$$H_2$-), 40.6 ($CH_2$=CH-$C_{isomer}$$H_2$-).
HRMS of $C_{21}H_{22}O_3$ $[M+H]^+$ calc. 323.16 found 323.20

ADMET polymerization of M1 with different metathesis catalysts

Reactions were carried out in parallel using a carousel reaction station^{TM} RR98072 (Radleys Discovery Technologies, UK). In a representative polymerization 500 mg (1.37 mmol) of **M1** and 0.4 mol% **BQ** were added to a carousel tube equipped with a screw at the reaction temperature of 80 °C and let to stir magnetically for 10 min. Then, 0.2 mol% of the corresponding Ru catalyst (**C4**, **C5** or **C7**) was added to the reaction mixture. After 1 h reaction under continuous vacuum, the reaction mixtures were allowed to cool to room temperature, the residue was dissolved in THF and the metathesis reaction was stopped by adding ethyl vinyl ether (500-fold excess to the catalyst) and stirring for 30 minutes at room temperature. Polymers were precipitated in cold MeOH on ice bath.

P10 (85%): ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.44–5.30 (m, -C*H*=C*H*-), 4.12 (dt, *J* = 9.7, 6.5 Hz, -CH_2-O-), 2.05–1.87 (m, -CH=CH-CH_2-), 1.73–1.54 (m, aliphatic -CH_2-), 1.27 (s, aliphatic -CH_2-).

ADMET polymerization of M2

Reactions were carried out in parallel using a carousel reaction station^{TM} RR98072 (Radleys Discovery Technologies, UK). In a representative polymerization 500 mg (1.48 mmol) of **M1** and different amounts of **C7** were added separately to a carousel tube equipped with a screw at 90 °C. The influence of the amount of the **BQ**, added 10 min prior to the catalyst addition, on the obtained molecular weight was studied. After 4 h reaction under continuous vacuum, the reaction mixtures were allowed to cool to room temperature, then the residue was dissolved in THF and the metathesis reaction was stopped by adding ethyl vinyl ether (500-fold excess to the catalyst) and stirring for 30 minutes at room temperature. Polymers were precipitated in ice cold MeOH.

P14 (75%) ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm): 5.46–4.96 (m, -C*H*=C*H*-), 4.14 (dt, *J* = 13.3, 6.6 Hz, -CH_2-O-), 2.48–2.15 (m, -CH=CH-$C_{isomerized}H_2$-), 2.14–1.80 (m, -CH=CH-CH_2-), 1.80–1.40 (m, aliphatic -CH_2-), 1.38–1.04 (m, aliphatic -CH_2-), 1.04–0.72 (m, -CH_3).

5.8 On the polymerization behavior of telomers: Metathesis *versus* thiol-ene chemistry

Materials

All chemicals were used as received: $Pd(dba)_2$ (dba, bis(dibenzylideneacetone) (Aldrich), TOMPP (tris-(*ortho*-methoxyphenyl)phosphine), 1,3-propanediol (> 99%, Fluka), 1,3-butadiene (Linde Gas), 1,4-benzoquinone (**BQ**, >99%, Aldrich), 1-octanethiol (>98.5%, Aldrich), 1,4-butanedithiol (**DT1**, >97%, Aldrich), 2-mercaptoethyl ether (**DT2**, >95%, Aldrich), 3,6-dioxa-1,8-octane-dithiol (**DT3**, >95%, Aldrich), benzylidene-*bis*(tricyclohexylphosphine) dichlororuthenium (Grubbs 1st generation catalyst, **C3**, Aldrich), benzylidene [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine) ruthenium (Grubbs 2nd generation catalyst, **C4**, Aldrich), (1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*isopropoxyphenylmethylene) ruthenium (Hoveyda–

Grubbs 2nd generation catalyst, **C5**, Aldrich), [1,3-*bis*(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro [2-(1-methylacetoxy)phenyl]methylene ruthenium(II) (Umicore $M5_1$, **C12**), ethyl vinyl ether (99%, Aldrich), 2,2'-azobis(2-methylpropionitrile) (**AIBN**, 98%, Aldrich) was used after recrystallization from methanol. All solvents (technical grade) were used without purification.

Specifications on the analytical methods

NMR: Spectrometers A and B.

SEC: Column systems B, C and E.

DSC: System A. Meassurements performed at a heating rate of 10 °C × min^{-1} up 250 °C with samples in the range of 8-15 mg.

Synthetic procedure

Thiol-ene model reaction for di-telomers

The thiol-ene model reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). Into a reaction tube, 0.5 g (1.71 mmol) of the di-telomer and 1.0 g 1-octanethiol (6.84 mmol) were introduced and degassed *via* 3 times 200 mbar vacuum and subsequent argon purge. The reaction were conducted either radically (model reaction A) or thermally induced (model reaction B) under solvent-free conditions at the desired reaction temperature (75 and 70 °C for the respective model reactions A and B). In the case of radical initiated reactions, 2.5 mol% (0.04 mmol) of **AIBN** was added to the reaction mixture. The reactions were followed with TLC with hexane-ethyl acetate (15:1, v:v) as eluent. Moreover, the monomer conversion was calculated from integration of corresponding ^{1}H NMR signals. A relaxation time (d1) of 5 s was used in the ^{1}H NMR analyses in order to obtain reliable integral values. The reaction products were purified by column chromatography with hexane-ethyl acetate (15:1, v:v) as eluent.

^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm) 6.20 (d, -CH=C*H*-O-CH$_2$-, *J*=12.6 Hz, 1H$_{trans}$), 5.91 (dd, -CH=C*H*-O- CH$_2$-, *J*=6.2, 1.3 Hz, 1H$_{cis}$), 5.72-5.62 (m, -C*H*=CH-CH$_2$O- $_{trans\text{-isomer}}$, -C*H*=CH$_2$ $_{\text{branched telomer}}$), 5.58-5.48 (m, -CH=C*H*-CH$_2$-O- $_{trans\text{-isomer}}$, -C*H*=C*H*-CH$_2$-O- $_{cis\text{-isomer}}$), 5.17-5.11 (m, -CH=CH_2 $_{\text{branched telomer}}$), 4.81-4.68 (m, -C*H*=CH- O-CH$_2$-, 1H$_{trans}$), 4.37-4.25 (m, -C*H*=CH-O-CH$_2$-, 1H$_{cis}$), 3.99 (d, *J* = 4.8 Hz, -CH=CH-CH_2-O- $_{cis\text{-isomer}}$), 3.89 (d, *J* = 5.9 Hz, -CH=CH-CH_2-O- $_{trans\text{-isomer}}$), 3.79-3.64 (m, -CH=CH-O-CH_2-CH$_2$-CH_2-O-), 3.48 (t, *J* = 6.4 Hz, -O-CH_2-CH$_2$-CH_2-O-), 2.57-2.46 (m, -CH$_2$-S-CH$_2$-), 2.10-1.98 (m, -CH_2-CH=CH-), 1.90-1.79 (m, -O-CH$_2$-CH_2-CH$_2$-O-, -CH=CH-O-CH$_2$-CH_2-CH$_2$-O-), 1.67-1.52 (m, -S-CH$_2$-CH_2-CH$_2$-), 1.42-1.31 (m, -CH$_2$-), 0-92-0.84 (t, -CH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm) 146.18 (-CH=*C*H-O-CH$_2$- $_{cis\text{-}isomer}$), 144.99 (-CH=*C*H-O-CH$_2$-$_{trans\text{-}isomer}$), 134.31 (-*C*H=CH-CH$_2$-O- $_{trans\text{-isomer}}$), 134.17 (-*C*H=CH-CH$_2$-O- $_{cis\text{-isomer}}$), 126.95 (-CH=*C*H-CH$_2$O- $_{cis\text{-isomer}}$), 126.80 (-CH=*C*H-CH$_2$O- $_{trans\text{-isomer}}$), 106.78 (-*C*H=*C*H-O-CH$_2$-$_{cis\text{-}isomer}$), 104.09 (-*C*H=*C*H-O-CH$_2$-$_{trans\text{-}isomer}$), 74.88 (-CH=CH-O-*C*H$_2$-CH$_2$-*C*H$_2$-O-), 71.80 (-CH=CH-*C*H$_2$-O- $_{trans\text{-isomer}}$), 67.38 (-O-*C*H$_2$-CH$_2$-CH_2-O-), 66.65 (-CH=CH-*C*H$_2$-O- $_{cis\text{-isomer}}$), 32.35 (-*C*H$_2$-S-CH$_2$-), 32.29 (-CH$_2$-S-*C*H$_2$-), 32.15 (-*C*H$_2$-CH=CH-O-), 31.93 (-*C*H$_2$-CH=CH-CH$_2$-O-), 30.37 (-O-CH$_2$-*C*H$_2$-CH$_2$-O-), 30.13 (-CH=CH-O-CH$_2$-*C*H$_2$-CH$_2$-O-), 29.79 (-S-CH$_2$-CH$_2$-CH$_2$-*C*H$_2$-), 29.72 (-S-CH$_2$-*C*H$_2$-CH$_2$-), 28.90 (-S-CH$_2$-CH$_2$-*C*H$_2$-), 28.67 (-*C*H$_2$-CH$_2$-CH$_2$=CH-), 28.4 (-*C*H$_2$-CH$_2$-CH$_2$-CH$_3$), 22.27 (-*C*H$_2$-CH$_3$), 14.14 (*C*H$_3$).

Polymerization reactions

General procedure for ADMET polymerizations

The ADMET reactions were performed in a carousel reaction station^{TM} RR98072 (Radleys Discovery Technologies, UK). Di-telomer **1**, **2** or **3** (0.5 g, 1.71 mmol) was added into the carousel tube. Different amounts of catalysts **C3**, **C4**, **C5** or **C12** were added separately. The influence of the reaction conditions on the obtained molecular weight was studied (Tables 1, 2 and 3). Ethylene gas (byproduct) was removed by applying gas or vacuum continuously. The reactions were cooled down to room temperature and quenched in THF by adding ethyl vinyl ether (500-fold excess to the catalyst) with stirring for 30 min at room temperature. Samples were taken periodically to determine the monomer conversion and the molar mass (distribution) of the resulting polymers using ^{1}H, ^{13}C NMR spectroscopy, as well as GPC analysis. The final reaction mixtures were precipitated in ice cold methanol. The yields varied in the range of 50-85%.

General procedure for thiol-ene polymerizations

The thiol-ene polymerization reactions were performed in a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK). Into a reaction vessel 0.5 g (1.71 mmol) of the di-telomer (**1**, **2** or **3**) and the corresponding dithiol compound (see Table 4) were introduced and degassed *via* 3 times 200 mbar vacuum and subsequent Ar purge. Afterwards, the reaction was let to stir magnetically (500 rpm) at the desired reaction temperature (35–70 °C) till the reaction became very viscous and could not *be* stirred anymore (Table 4.23). In some cases, desired amounts of **AIBN** (1.0-2.5 mol%) were added to the reaction mixture and reacted at 75 °C (Table 4.23). The final reaction mixtures were precipitated in ice cold methanol. The yields varied in the range of 70-92%.

Spectroscopic data of representative thiol-ene polymers

P2: ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 5.85-5.72 (m, -C*H*=CH_2), 5.72-5.62 (m, -C*H*=CH-CH_2-O-$_{trans\text{-isomer}}$, -C*H*=$CH_{2\ \text{branched telomer}}$), 5.58-5.48 (m, -CH=C*H*-CH_2-O- $_{trans\text{-isomer}}$, -C*H*=C*H*-CH_2-O- $_{cis\text{-isomer}}$), 5.17-5.11 (m, -CH=C$H_{2\ \text{branched telomer}}$), 5.01-4.92 (m, -CH=C$H_2$), 3.99 (d, *J* = 4.8 Hz, -CH=CH-CH_2-O- $_{cis\text{-isomer}}$), 3.89 (d, *J* = 5.9 Hz, -CH=CH-CH_2-O- $_{trans\text{-isomer}}$), 3.48 (t, *J* = 6.4 Hz, -O-CH_2-CH_2-CH_2-O-), 2.57-2.46 (m, -CH_2-S-CH_2-, -CH_2-SH $_{\text{end group}}$), 2.10-1.98 (m, 1H, -CH_2-CH=CH-), 1.90-1.79 (m, 1H, -O-CH_2-CH_2-CH_2-O-, -CH_2-CH_2-SH $_{\text{end group}}$), 1.74-1.63 (m, -S-CH_2-CH_2-CH_2-CH_2-S-), 1.63-1.52 (m, 1H, -S-CH_2-CH_2-CH_2-), 1.52-1.42 (m, -CH_2-CH_2-CH=CH_2 $_{\text{end group}}$), 1.42-1.31 (m, -CH_2-).

^{13}C NMR (75 MHz, $CDCl_3$, δ in ppm) 138.80 (-*C*H=CH_2), 134.31 (-*C*H=CH-CH_2-O- $_{trans\text{-isomer}}$), 134.17 (-*C*H=CH-CH_2-O- $_{cis\text{-isomer}}$), 126.95 (-CH=*C*H-CH_2-O- $_{cis\text{-isomer}}$), 126.80 (-CH=*C*H-CH_2-O- $_{trans\text{-isomer}}$), 114.73 (-CH=*C*H_2), 71.80 (-CH=CH-*C*H_2-O- $_{trans\text{-isomer}}$), 67.38 (-O-CH_2-CH_2-CH_2-O-), 66.65 (-CH=CH-*C*H_2-O- $_{cis\text{-isomer}}$), 33.40 (-*C*H_2-CH=CH_2), 33.22 (-CH_2-CH_2-

SH), 32.35 (-*C*H$_2$-S-CH$_2$-), 32.29 (-CH$_2$-S-*C*H$_2$-), 31.93 (-*C*H$_2$-CH=CH-), 30.37 (-O-CH$_2$-*C*H$_2$-CH$_2$-O-), 29.72 (-S-CH$_2$-*C*H$_2$-CH$_2$-), 28.95 (-S-CH$_2$-*C*H$_2$-*C*H$_2$-CH$_2$-S-), 28.90 (-S-CH$_2$-CH$_2$-*C*H$_2$-), 28.67 (-*C*H$_2$-CH$_2$-CH=CH-), 28.47 (-*C*H$_2$-CH$_2$-CH=CH$_2$), 24.41 (HS-*C*H$_2$-CH$_2$-).

P3: ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm) 5.85-5.71 (m, -C*H*=CH$_2$), 5.71-5.61 (m, -C*H*=CH-CH$_2$-O- $_{\mathit{trans}\text{-isomer}}$, -C*H*=CH$_2$ $_{\text{branched telomer}}$), 5.58-5.48 (m, -CH=C*H*-CH$_2$-O- $_{\mathit{trans}\text{-isomer}}$, -C*H*=C*H*-CH$_2$-O- $_{\mathit{cis}\text{-isomer}}$), 5.17-5.11 (m, -CH=C*H*$_2$ $_{\text{branched telomer}}$), 5.01-4.92 (m, -CH=C*H*$_2$), 3.99 (d, *J* = 4.9 Hz, -CH=CH-C*H*$_2$-O- $_{\mathit{cis}\text{-isomer}}$), 3.89 (d, *J* = 6.1 Hz, -CH=CH-C*H*$_2$-O- $_{\mathit{trans}\text{-isomer}}$), 3.70 (t, *J* = 6.6 Hz, –O-C*H*$_2$-CH2-SH $_{\text{end group}}$), 3.60 (t, *J* = 6.6 Hz, -S-CH$_2$-C*H*$_2$-O-C*H*$_2$-), 3.47 (t, *J* = 6.4 Hz, -O-C*H*$_2$-CH$_2$-C*H*$_2$-O-), 2.87 (t, *J* = 6.6 Hz, –O-CH$_2$-C*H*$_2$-SH $_{\text{end group}}$) 2.68 (t, *J* = 6.9 Hz, -S-C*H*$_2$-CH$_2$-O-), 2.53 (t, *J* = 7.4 Hz, -S-C*H*$_2$-CH$_2$-CH$_2$-), 2.10-1.98 (m, 1H, -C*H*$_2$-CH=CH-), 1.88-1.79 (m, 1H, -O-CH$_2$-C*H*$_2$-CH$_2$-O-), 1.64-1.52 (m, 1H, -S-CH$_2$-C*H*$_2$-CH$_2$-), 1.52-1.42 (m, -C*H*$_2$-CH$_2$-CH=CH$_2$ $_{\text{end group}}$), 1.42-1.33 (m, -CH$_2$-).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm) 138.81 (-*C*H=CH$_2$), 134.30 (-*C*H=CH-CH$_2$-O- $_{\mathit{trans}\text{-isomer}}$), 134.21 (-*C*H=CH-CH$_2$-O- $_{\mathit{cis}\text{-isomer}}$), 126.91 (-CH=*C*H-CH$_2$-O- $_{\mathit{cis}\text{-isomer}}$), 126.78 (-CH=*C*H-CH$_2$-O- $_{\mathit{trans}\text{-isomer}}$), 114.74 (-CH=*C*H$_2$), 71.80 (-CH=CH-*C*H$_2$-O- $_{\mathit{trans}\text{-isomer}}$), 70.87 (-S-CH$_2$-*C*H$_2$-O-*C*H$_2$-CH$_2$-S-), 69.40 (-O-*C*H$_2$-CH$_2$-SH), 67.37 (-O-C*H*$_2$-CH$_2$-C*H*$_2$-O-), 67.30 (-O-C*H*$_2$-CH$_2$-C*H*$_2$-O-), 66.63 (-CH=CH-*C*H$_2$-O- $_{\mathit{cis}\text{-isomer}}$), 33.40 (-*C*H$_2$-CH=CH$_2$), 32.74 (-S-*C*H$_2$-CH$_2$-O-CH$_2$-*C*H$_2$-S-), 32.33 (-CH$_2$-S-*C*H$_2$-), 31.70 (-*C*H$_2$-CH=CH-), 30.35 (-O-CH$_2$-*C*H$_2$-CH$_2$-O-), 29.79 (-S-CH$_2$-*C*H$_2$-CH$_2$-), 28.87 (-S-CH$_2$-CH$_2$-*C*H$_2$-), 28.59 (-*C*H$_2$-CH$_2$-CH=CH-), 28.53 (-O-CH$_2$-*C*H$_2$-SH), 28.44 (-*C*H$_2$-CH$_2$-CH=CH$_2$).

P4: ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm) 5.87-5.72 (m, -C*H*=CH$_2$), 5.72-5.63 (m, -C*H*=CH-CH$_2$-O- $_{\mathit{trans}\text{-isomer}}$, -C*H*=CH$_2$ $_{\text{branched telomer}}$), 5.59-5.50 (m, -CH=C*H*-CH$_2$-O- $_{\mathit{trans}\text{-isomer}}$, -C*H*=C*H*-CH$_2$-O- $_{\mathit{cis}\text{-isomer}}$), 5.18-5.12 (m, -CH=C*H*$_2$ $_{\text{branched telomer}}$), 5.03-4.93 (m, -CH=C*H*$_2$), 4.00 (d, *J* = 4.8 Hz, -CH=CH-C*H*$_2$-O- $_{\mathit{cis}\text{-isomer}}$), 3.90 (d, *J* = 5.9 Hz, -CH=CH-C*H*$_2$-O- $_{\mathit{trans}\text{-isomer}}$), 3.74 (t, *J* = 6.7 Hz, –O-C*H*$_2$-CH2-SH $_{\text{end group}}$), 3.66-3.60 (m, -C*H*$_2$-O-C*H*$_2$-C*H*$_2$-O-C*H*$_2$-), 3.49 (t, *J* = 6.4 Hz, -O-C*H*$_2$-CH$_2$-C*H*$_2$-O-), 2.89 (t, *J* = 6.7 Hz, –O-CH$_2$-C*H*$_2$-SH $_{\text{end group}}$) 2.70 (t, *J* = 7.0 Hz, -S-C*H*$_2$-CH$_2$-O-), 2.53 (t, *J* = 7.3 Hz, -S-C*H*$_2$-CH$_2$-CH$_2$-), 2.09-1.99 (m, -C*H*$_2$-CH=CH-), 1.90-1.80 (m, -O-CH$_2$-C*H*$_2$-CH$_2$-O-), 1.64-1.53 (m, -S-CH$_2$-C*H*$_2$-CH$_2$-), 1.53-1.43 (m, -C*H*$_2$-CH$_2$-CH=CH$_2$ $_{\text{end group}}$), 1.43-1.33 (m, -CH$_2$-).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm) 134.45 (-*C*H=CH-CH$_2$-O- $_{\textit{cis}\text{-isomer}}$), 134.24 (-*C*H=CH-CH$_2$-O- $_{\textit{trans}\text{-isomer}}$), 126.77 (-CH=*C*H-CH$_2$-O- $_{\textit{trans}\text{-isomer}}$), 126.44 (-CH=*C*H-CH$_2$-O- $_{\textit{cis}\text{-isomer}}$), 71.76 (-CH=CH-*C*H$_2$-O- $_{\textit{trans}\text{-isomer}}$), 71.19 (-S-CH$_2$-*C*H$_2$-O-CH$_2$-CH$_2$-O-*C*H$_2$-CH$_2$-S-), 70.43 (-S-CH$_2$-CH$_2$-O-*C*H$_2$-*C*H$_2$-O-CH$_2$-CH$_2$-S-), 67.34 (-O-*C*H$_2$-CH$_2$-*C*H$_2$-O-), 32.68 (-S-*C*H$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-*C*H$_2$-S-), 32.28(-S-*C*H$_2$-CH$_2$-CH$_2$-), 31.28 (-*C*H$_2$-CH=CH-), 30.32 (-O-CH$_2$-*C*H$_2$-CH$_2$-O-), 29.79 (-S-CH$_2$-*C*H$_2$-CH$_2$-), 28.84 (-S-CH$_2$-CH$_2$-*C*H$_2$-), 28.56 (-*C*H$_2$-CH$_2$-CH=CH-).

6 Summary and outlook

Within this thesis, a variety of examples of the utilization of renewable resources for the synthesis of organic building blocks and polymers have been described. Special attention has been given to plant oils and thereof derived platform chemicals, which have been successfully used as precursors of monomers for the synthesis of linear and hyperbranched polymers such as polyesters, polyamides or polycarbonates. For this purpose, olefin metathesis has been shown as a suitable chemical transformation for monomer synthesis and for the polymerization of renewable monomers *via* ADMET and ATMET. In this aspect, and due to its simplicity, the direct polymerization of naturally occurring *Pluketenia Conophora* oil *via* ATMET to obtain hyperbranched polyesters is remarkable. Moreover, a thorough study of their properties suggested that these hyperbranched polymers may find application as rheology modifiers and in drug delivery. In a different approach, epoxidized soybean oil (SESO) was used as starting material, which provides access to wider functionalization possibilities by ring-opening of the oxirane functionalities. A new triglyceride derivative containing 4-vinylbenzene sulphonic acid moieties synthesized from SESO was polymerized *via* ATMET, and the properties of the resulting cross-linked materials were evaluated. Also of interest is the first successful living ROMP of fatty acid-based norbornenes, which led to polymers with controlled molecular weights and low polydispersities. This work supposed one of the first reports on the controlled/living polymerization of fatty acid-based monomers, and set a starting point for further investigations on the synthesis, properties and applications of this kind of polymers. Further work on ADMET polymerization consisted of a study of the performance of three Ru-based indenylidene catalysts, which up to that date had not been applied with this purpose. Moreover, their tendency to promote double bond migration during ADMET was evaluated, and it could be concluded that these catalysts have a high double bond migration activity even in the presence of 1,4-benzoquinone, an additive that efficiently reduces this side-reaction in the case of conventional Ru-based catalysts. The functional group tolerance of Ru-based metathesis catalysts was demonstrated with the polymerization of castor oil and citronellol derived α,ω-dienes containing carbonate functionalities. As a result, polycarbonates with M_n of 27.5 and 7.9 kDa respectively were obtained, which, in the latter case, was surprisingly high considering that the polymerization involves the metathesis of trisubstituted olefins.

The bicyclic guninide base organocatalyzed reaction of dimethyl carbonate (green carbonylating agent) and alcohols with a wide variety of structures was shown to be a very efficient and selective method for the synthesis of symmetric and unsymmetric carbonates. A TBD loading of 1.0 mol% was sufficient to give conversions between 88% and 99% and selectivities between 91 and 99%. Moreover, DMC was reacted with different diols in the presence of 1.0 mol% of TBD yielding polycarbonates with M_n up to 33.0 kDa. Taking into account that DMC can be obtained *via* phosgene-free methods, the low price of TBD, and the simplicity of this reaction protocol, it is possible to consider its large-scale applicability.

Telomers, which are industrially relevant compounds can be produced in large scale and find a number of applications. However, they had never been used as monomers for polymer synthesis. Di-telomers obtained from 1,3-butadiene containing terminal and internal double bonds, were used as monomers for ADMET and thiol-ene polymerization. Efficient ethylene removal with vacuum was necessary to induce ADMET polymerization and avoid competitive RCM; however, also low molecular weight oligomers were obtained in a ring-closing metathesis-ADMET-olefin isomerization sequence. Thiol-ene polyaddition was successful, and the addition of **AIBN** was found to strongly accelerate the polymerization rate, but at the same time it promoted double bond migration. As a result, colourless and transparent shapeable thermoplastics were obtained.

The data summarized above demonstrate the effort dedicated in the development of environmentally friendly methodologies for the production of organic building blocks and polymers. All procedures exhibit some interesting advantages over the traditional synthetic routes within the minimisation of waste production and the concomitant benefit of using safer reagents. Thus, within this work, we have contributed to the production of monomers and polymers by sustainable reactions with fatty acid derivatives.

On the other hand, we can also consider that much work will soon follow this direction due to the vast, yet unexplored, possibilities of the aforementioned sustainable and efficient methods in combination with fatty acids, and other renewable platform chemicals. In addition, the versatility of plant oils as precursors of diverse materials has been, and is still nowadays proved with the development of synthetic strategies leading to new polymeric materials. Clearly, an immense amount of work is still left to be done to both improve current sustainable/green approaches and develop new ones.

7 List of abbreviations

2D-NMR:	wo-dimensional nuclear magnetic resonance
4VBSA:	4-vinylbenzene sulphonic acid
ADMET:	Acyclic diene metathesis
AIBN:	Azobisisobutyronitrile
ATMET:	Acyclic triene metathesis
BHT:	Butylated hydroxytoluene
BQ:	1,4-benzoquinone
CDI:	1,1'-Carbonyldiimidazole
CM:	Cross-metathesis
COSY:	Correlation spectroscopy (2D-NMR)
DBN:	1,5-Diazabicyclo[4.3.0]non-5-ene
DBU:	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM:	Dichloromethane
DLS:	Dynamic light scattering
DMAc:	*N,N´*-dimethylacetamide
DMC:	Dimethylcarbonate
DMF:	Dimethylformamide
DMSO:	Dimethylsulfoxide

DP:	Degree of polymerization
DSC:	Differential scanning calorimetry
ED-ROMP:	Entropically driven ring-opening metathesis polymerization
EMO:	Epoxidized methyl oleate
ESI-MS:	Electrospray ionization mass spectrometry
ESO:	Epoxidized soybean oil
FAME:	Fatty acid methyl ester
G':	Storage modulus
G'':	Loss modulus
GC:	Gas chromatography
GC-MS:	Gas chromatography coupled with mass spectrometry
GPC:	Gel permeation chromatography
HMQC:	Heteronuclear multiple quantum coherence (2D-NMR)
HRMS:	High resolution mass spectrometry
IR:	Infrared (spectroscopy)
LROMP:	Living ring-opening metathesis polymerization
LVE:	Linear viscoelastic (region)
[M]/[I]:	monomer-to-initiator molar ratio
M_n:	Number average molecular weight,
MO:	Methyl oleate
M_w:	Weight average molecular weight,
NBM:	5-Norbornene-2-methanol
NHC:	*N*-heterocyclic carbene
NMR:	Nuclear magnetic resonance (spectroscopy)
PA:	Polyamide
PDI:	Polydispersity index (M_w/M_n)

PEG:	Poly(ethylene glycol)
PKCO:	*Plukenetia conophora* oil
PMMA:	Poly(methyl methacrylate)
RCM:	Ring-closing metathesis
ROM:	Ring-opening metathesis
ROMP:	Ring-opening metathesis polymerization
ROP:	Ring-opening polymerization
SEC:	Size exclusion chromatography
SEMO:	methyl 10-hydroxy-9-(4-vinylphenylsulfonyloxy)octadecanoate
SESO:	1-(4-vinylbenzene sulfonyl)oxy-2-alkonols of epoxidized soybean oil
SLS:	Static light scattering
SM:	Self-metathesis
TBD:	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TFAA:	Trifluoroacetic anhydride
T_d:	Thermal decomposition temperature
T_g:	Glass transition temperature
TGA:	Thermogravimetric analysis
THF:	Tetrahydrofuran
TLC:	Thin-layer chromatography
T_m:	Melting temperature
TMS:	Tetramethylsilane
TOMPP:	Tris(2-methoxyphenyl) phosphine

8 *Curriculum Vitae*

Personal Data

Nationality: Bulgarian and Turkish

Date of Birth: December 5th, 1981

Place of Birth: Kircali, Bulgaria

Education

07.2008 – 02.2012: Ph.D degree (*magna cum laude*) under supervision of Prof. Michael A. R. Meier at Karlsruhe Institute of Technolgy, Karlsruhe, Germany. Dissertation title: “Sustainable, efficient approaches to renewable chemicals and polymers”.

2005 – 2008: M.Sc. degree at the Department of Chemistry, Bogazici University, Istanbul, Turkey. Dissertation title: “Polymerization of plant oil with *p*-dinitrosobenzene” with Prof. Selim H. Küsefoglu.

2000 – 2005: Marmara University, B.S. degree from Chemistry Department, Istanbul, Turkey. Bachelor thesis: “Investigation of different applications of Matrix Assisted Laser Desorption Ionization Time of Flight Spectroscopy” with Prof. Adnan Aydin.

Working Experience

2012 – Research Assistant, Karlsruhe Institute of Technology, Karlsruhe, Germany.

2011 – 2012: Research Assistant, Karlsruhe Institute of Technology, Karlsruhe, Germany.

2008 – 2011: Research Assistant, Hochschule Emden/Leer, Emden, Germany.

2004 – 2005: Undergraduate Research Assistant, Marmara University, Istanbul, Turkey.

2004: Summer Internship, Department of Chemistry Laboratory, Ministry of Agriculture and Rural Affairs, Istanbul, Turkey.

Summer Internship, Quality Control Laboratory, Merter Koska Food Industry and Trade Co. Inc., Istanbul, Turkey.

2003: Summer Internship, Quality Control Laboratory, Aroma – Polifarma Pharmaceutical Manufacturing Co. Inc., Istanbul, Turkey.

Summer Internship, Research and Development Laboratory, Polisan Dye Industry and Trade Co. Inc., Kocaeli, Turkey.

Publications

H. Mutlu, J. Ruiz, S. C. Solleder, M. A. R. Meier, TBD catalysis with dimethyl carbonate: a fruitful and sustainable alliance, *Green Chem.* **2012**, *14*, doi:10.1039/C2GC35191A.

H. Mutlu, A. N. Parvulescu, P. C. A. Bruijnincx, B. M. Weckhuysen, M. A. R. Meier, On the polymerization behavior of telomers: metathesis *versus* thiol-ene chemistry, *Macromolecules* **2012**, *45*, 1866-1878.

C. O. Akintayo, H. Mutlu, M. Kempf, M. Wilhelm, M. A. R. Meier, Acyclic Triene Metathesis (ATMET) Polymerization of *Plukenetia conophora oil*: branched polymers by direct polymerization of renewable resources, *Macromol. Chem. Phys.* **2011**, *213*, 87-96.

C. Öztürk, H. Mutlu, M. A.R. Meier, S. H. Küsefoğlu, 4-Vinylbenzenesulfonic acid adduct of epoxidized soybean oil: synthesis, free-radical and ADMET polymerizations, *Eur. Polym. J.* **2011**, *47*, 1467-1476.

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

H. Mutlu, L. Montero de Espinosa, M. A. R. Meier, Acyclic Diene Metathesis (ADMET): a versatile tool for the construction of (defined) polymer architectures, *Chem. Soc. Rev.* **2011**, *40*, 1404–1445.

H. Mutlu, M. A. R. Meier, Ring-opening metathesis polymerization of fatty acid derived monomers, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 5899-5906.

H. Mutlu, M. A. R. Meier, Castor oil as a renewable resource for the chemical industry, *Eur. J. Lipid Sci. Technol.* **2010**, *112*, 10-30.

H. Mutlu, M. A. R. Meier, Unsaturated PA X,20 from renewable resources *via* metathesis and catalytic amidation, *Macromol. Chem. Phys.* **2009**, *210*, 1019-1025.

H. Mutlu, S. H. Küsefoglu, Synthesis and characterization of polymers from soybean oil and p-dinitrosobenzene, *J. Appl. Polym. Sci.* **2009**, *113*, 1925-1934.

Talks

H. Mutlu, M. A. R. Meier, *9th Euro Fed Lipid Congress, "Oils, Fats and Lipids for a Healthy and Sustainable World"* **2011**, *18-21 September*, Rotterdam, The Netherlands, “Living ring--opening metathesis polymerization of partially renewable monomers”.

H. Mutlu, M. A. R. Meier, *15th Annual Green Chemistry & Engineering Conference and 5th International Conference on Green and Sustainable Chemistry* **2011**, *21-23 June*, Washington DC, USA, “Living ring-opening metathesis polymerization of partially renewable monomers”.

H. Mutlu, M. A. R. Meier, *Nachwuchsgruppentreffen* **2010**, *26-27 May*, Oberhausen, Germany, “Polyamides and polynorbornenes from plant oils”.

Selected poster presentations

H. Mutlu, M. A. R. Meier, *15th Annual Green Chemistry & Engineering Conference and 5th International Conference on Green and Sustainable Chemistry* **2011**, *21-23 June*, Washington DC, USA, “Toward "green" polycarbonates *via* ADMET and thiol-ene polymerizations”.

H. Mutlu, M. A. R. Meier, *Macro2010: 43rd IUPAC World Polymer Congress* **2010**, *11-16 July*, Glasgow, UK, “Unsaturated PA X,20 from renewable resources *via* metathesis and catalytic amidation”.

H. Mutlu, M. A. R. Meier, *Macro2010: 43rd IUPAC World Polymer Congress* **2010**, *11-16 July*, Glasgow, UK, “Ring-opening metathesis polymerization of fatty acid derived monomers”.

H. Mutlu, M. A. R. Meier, *Frontiers in Polymer Science* **2009**, *7-9 June*, Mainz, Germany, “PA X,20 from renewable resources *via* metathesis and catalytic amidation”.

H. Mutlu, M. A. R. Meier, *2nd Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry* **2009**, *22-24 March*, Emden, Germany, “PA X,20 from renewable resources *via* metathesis and catalytic amidation”.

Travel grant:

Fellowship of the German Chemical Society (GDCh) for the participation on the Conference *15th Annual Green Chemistry & Engineering Conference and 5th International Conference on Green and Sustainable Chemistry* **2011**, *21-23 June,* Washington DC, USA.

Conference report: C. J. Meier, R. Döpp, C. Federsel, M. R. Königs, E. Merkul, H. Mutlu, T. vom Stein, O. Türünç, *Nachr. Chem.,* **2011**, *59*.

9 Acknowledgments

To find suitable words to acknowledge everyone who supported and helped me throughout these last years is not less difficult than the research process itself. Within the following lines I would like to express my indebtedness to a few of the many.

At first, I would like to say “Danke schön” for “everything” to my promoter, Michael Meier. Mike, this “everything”, initially, involves the opportunity to work with you in Emden, Potsdam and Karlsruhe, thus letting me to see and discover almost whole Germany. All has been an invaluable experience, but most importantly, I am grateful for your consistent support, both moral and substantial (even in the moments when I did not deserve it☺) and for many other uncountable things. Along this, I would like to express that without the support of Prof. Dr. Selim Küsefoglu, I would not be able to meet Mike and to be where I am right now.

I would like to say thank you for the nice and efficient collaborations to Prof. Dr. Bert M. Weckhuysen, Dr. Pieter C. A. Bruijnincx and Dr. Andrei N. Parvulescu from Utrecht; Dr. Cecilia Akintayo from Nigeria, and Dr. Cem Öztürk and Prof. Dr. Selim Küsefoglu from Turkey.

Furthermore, I would like to thank the members of the defence committee, Prof. Dr. Christopher Barner-Kowollik, Prof. Dr. Helmud Ehrenberg and Prof. Dr. Anne Ulrich for taking part in my defence.

As I mentioned there are so many people in whole Germany (also in Turkey and some in Spain) to whom I am grateful for the moments which we shared, and for the support which I received from them.

Especially, thanks to Anastasiya, Tina and Patrice during the first months in Emden. Of course, I should not forget Thao, it was pleasure to share not only the hood, but also my room with you. Guy Bertrand, you made me laugh and gave the spirit to dance at any moment during the nine months that we worked together in Emden. Dominik and Manuela, thanks to both of you for improving my German☺

And of course Potsdam´ leute… I should say that the 15 months which I spent in Potsdam were incredible in every aspect. To meet and get to know people like

Katharina, Bettina, Marie, Julia, Zoran, Urska, Kenny, Lucia, Alex made my life completely different and better than ever.

Especially Katharina, I don't know how to express my indebtedness to you… You are meine liebe Katharina…Along you, Liebe Katharina, I would like to say thank you to your whole family, Sylvia, Peter and Oma Hilde for the endless support. All you, you let me feel as a part of your family...

Quique, the three months with you in Potsdam were my longest party time☺ I think I have never been partying for so long time☺

Nade and Natalia, as my mum is saying my two Spanish sisters, I guess I could not express what you both mean for me, I think you know it already…

Lucia, without you, adjusting to the lab in Potsdam would not have been easy, thanks one more time…

Karlsruhe´ leute: Nicolai, Olli, Kaichen, Matthias, Winnie, Madlenchen, Sarah, Susanne, Johal, Maulidan, Ansgar, Wiebke thanks for suffering me under any circumstances in these last 14 months of my PhD process, you are a great team, it is a pleasure to work with you. Also thanks for my great F1 bolide☺

Oguz, tesekkür ederim.

Aylin´im sana da tesekkür ederimm guzel zamanlarimiz icin…

Pinar, canim, sensiz hicbir isin ustesinden gelemezdim Karlsruhe´de. Karsiliksiz yardimlarin icin ne kadar tesekkür etsem azdir…

Yifeng, you are on of the special friends although you are so far away…

Kizlar, canolarim, size de ne kadar tesekkür etsem azdir. Bu kadar uzakta olmamiza ragmen, desteginizi herzman hissettim ve hissedecegimi de biliyorum. Iyi ki hayatimdasiniz, iyi ki canlarimsiniz…Seviyorum sizi…

Herr Montero, what should I write for you, to be honest I do not know…For sure I should say thank you for being next to me at any happy, sad, hard moment under any circumstances. You mean a lot for me. Although we had and we are having bad moments, we always found a way to make it better…Gracias…Along you, I want to say thank you to Nieves, Paco and Cecilia…

Muttim, Babam, Kardesim-canim Loch Nesim, Nenem, Dedem, Daykom, Ayse ablam, Halam, Behcet enistem, Hulicik, Hazel ablamm… kisacasi sevgili ailem, sizlere ne kadar tesekkür etsem azdir. Iyiki sizin Ati´nizim☺

Thanks (Danke Schön, Gracias, Tesekkürler) to all of you☺

Hatis (HM) ☺

10 References

---

[1] www.rigjobs.co.uk.

[2] The Brundtland Commission, formally the World Commission on Environment and Development (WCED). Convened by the United Nations in 1983.

[3] P. T. Anastas, J. C. Warner *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998, p. 30.

[4] L. D. Gomez, C. G. Steele-King, S. J. McQueen-Mason *New Phytol* 2008, 178, 473.

[5] A. Jering, J. Günther, A. Raschka, M. Carus, S. Piotrowski, L. Scholz ETC/SCP report 1/ 2010, 2010.

[6] United States Department of Agriculture, Oilseeds: World Markets and Trade Monthly Circular http://www.fas.usda.gov/psdonline/circulars/oilseeds.pdf.

[7] P. N. Mascia, J. Scheffran, J. M. Widholm (Eds.) *Plant Biotechnology for Sustainable Production of Energy and Co-Products, Series: Biotechnology in Agriculture and Forestry, Vol. 66,* Springer-Verlag, Heidelberg, 2010, p. 57

[8] (a) M. A. R. Meier, J. O. Metzger, U. S. Schubert *Chem Soc Rev* 2007, 36, 1788. (b) V. Sharma, P. P. Kundu *Prog Polym Sci* 2008, 33, 1199. (c) A. Gandini *Macromolecules* 2008, 41, 9491. (d) J. C. Ronda, G. Lligadas, M. Galia, V. Cadiz *Eur J Lipid Sci Technol* 2011, 113, 46. (e) L. Montero de Espinosa, M. A. R. Meier *Eur Polym J* 2011, 47, 837. (f) U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger, H. J. Schäfer *Angew Chem Int Ed* 2011, 50, 3854.

[9] (a) F. D. Gunstone *Eur J Lipid Sci Technol* 2001, 103, 307. (b) C. Scrimgeour *Chemistry of Fatty Acids.* In: *Bailey's Industrial Oil and Fat Products*, Sixth Ed., F. Shahidi (Ed.), John Wiley &

Sons, 2005, p. 1. (c) M. Dierker, H. J. Schäfer *Eur J Lipid Sci Technol* 2010, 112, 122. (d) H. G. Hauthal *Tenside Surfact Deterg* 2008, 45, 30. (e) K. Hill *Pure Appl Chem* 2007, 79, 1999. (f) G. Knothe, J. T. P. Derksen (Eds.) *Recent Developments in the Synthesis of Fatty Acid Derivatives*, AOCS Press, Champaign, 1999. (g) U. Tornvall, R. Hatti-Kaul *Lipid Technol* 2007, 19, 84.

[10] U.R. Kreutzer *J Am Oil Chem Soc* 1984, 61, 343.

[11] B. Hedman, P. Piispanen, El-Q. Alami, T. Norin *J Surfact Deterg* 2003, 6, 47.

[12] (a) P. Bondioli *Top Catal* 2004, 27, 77. (b) J. M. Marchetti, A. F. Errazu *Biomass Bioenergy* 2008, 32, 892. (c) A. Takagaki, M. Toda, M. Okamura, J. N. Kondo, S. Hayashi, K. Domen, M. Hara *Catal Today* 2006, 116, 157. (d) WO Pat. 2008135665, 2008.

[13] US Pat. 4 566 878, 1986.

[14] S. Tolowal, K. Jadav, K Patel *Indian J Pharm Sci* 2009, 71, 144.

[15] (a) WO Pat. 2007019063, 2007. (b) US Pat. 6 369 007, 2002.

[16] J. Barrault, Y. Pouilloux *Catal Today* 1997, 37, 137.

[17] D. Spasyuk, S. Smith, D. G. Gusev *Angew Chem Int Ed* 2012, *doi: 10.1002/ange.201108956.*

[18] N. Prileschajew *Ber Dtsch Chem Ges* 1909, 42, 4811.

[19] G. J. Piazza, T. A. Foglia *J Am Oil Chem Soc* 2005, 82, 481.

[20] Selected examples for epoxidation of fatty acids with conventional organic catalysts: (a) E. Poli, J-M. Clacens, J. Barraulta, Y. Pouilloux *Catal Today* 2009, 140, 19. (b) P. Jiang, M. Chen, Y. Dong, Y. Lu, X. Ye, W. Zhang *J Am Oil Chem Soc* 2010, 87, 83. (c) A. Campanella, M. A. Baltanas, M. C. Capel-Sanchez, J. M. Campos-Martin, J. L. G. Fierro *Green Chem* 2004, 6, 330.

[21] (a) D. Swern, G. N. Billen, T. W. Findley, J. T. Scanlan *J Am Chem Soc* 1945, 67, 1786. (b) T. W. Findley, D. Swern, J. T. Scanlan *J Am Chem Soc* 1945, 67, 412.

[22] S. Grinberg, N. Kipnis, C. Linder, V. Kolot, E. Heldman *Eur J Lipid Sci Technol* 2010, 112, 137.

[23] Z. S. Petrovic, A. Guo, W. Zhang *J Polym Sci Part A: Polym Chem* 2000, 38, 4062.

[24] A. Biswas, B.K. Sharma, J.L. Willett, A. Advaryu, S.Z. Erhan, H.N. Cheng *J Agric Food Chem* 2008, 56, 5611.

[25] (a) B. Tamami, S. Sohn, G. L. Wilkes *J Appl Polym Sci* 2004, 92, 883. (b) N. Man, S. K. Mendon, J. W. Rawlins, S. F. Thames *J Am Oil Chem Soc* 2008, 85, 791. (c) Z. Li,; Y. Zhao, S. Yan, X. Wang, M. Kang, J. Wang, H. Xiang *Catal Lett* 2008, 123, 246.

[26] M. F. Desroches, M. Escouvois, R. Auvergne, S. Caillol, B. Boutevin *Polym Rev* 2012, 52, 38.

[27] (a) US Pat. 2004074352, 2004. (b) R. L. Shogren, Z. Petrovic, Z. Liu, S. Z. Erhan *J Polym Environ* 2004, 12, 173. (c) K. M. Doll, S. Z. Erhan *Green Chem* 2005, 7, 849.

[28] (a) U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J.O. Metzger, M. Rüsch gen. Klaas, H. J. Schäfer, M.P. Schneider *Angew Chem Int Ed* 2000, 39, 2206.(b) U. Biermann, J.O. Metzger *Topics in Catalysis* 2004, 38, 3675. (c) J. O. Metzger *Eur J Lipid Sci Technol* 2009, 111, 865. (d) U. Biermann, S. Fürmeier, J. O. Metzger *New chemistry of oils and fats.* In: *Oleochemical Manufacture and Applications,* F. D. Gunstone, R. J. Hamilton (Eds.), Sheffield Academic Press and CRC Press, 2001.

[29] P. M. Tolvanen, P. Maki-Arvela, N. Kumar, K. Eranen, R. Sjoholm, J. Hemming, B. Holmbom, T. Salmi, D. Y. Murzin *Appl Catal A: Gen* 2007, 330, 1.

[30] A.E. Rheineck in: *Progress in the chemistry of fats and other lipids*, *Vol 5*, Pergamon Press New York, 1958.

[31] H.W. Kircher *J Am Oil Chem Soc* 1964, 41, 351.

[32] (a) P. L. Nichols Jr., S. F. Herb, R. W. Riemenschneider *J Am Chem Soc* 1951, 73, 247. (b) J.S. Shepard, J.S. Showell *J Am Oil Chem Soc* 1969, 46, 479. (c) F. Destaillats, P. Angers *Lipids* 2002, 37, 435.

[33] (a) K. Y. Ghebreyessus, R. J. Angelici *Organometallics* 2006, 25, 3040. (b) A. Behr, D. Obst, A. Westfechtel *Eur J Lipid Sci Technol* 2005, 107, 213. (c) C. Jimnez-Rodriguez, G. R. Eastham, D. J. Cole-Hamilton *Inorg Chem Commun* 2005, 8, 878.

[34] L. J. Gooßen, D. M. Ohlmann, M. Diecker *Green Chem* 2010, 12, 197.

[35] D. M. Ohlmann, L. J. Gooßen, M. Diecker *Chem Eur J* 2011, 17, 9508

[36] J. A. Labinger, J. E. Bercaw *Nature* 2002, 417, 507.

[37] B. Bühler, A. Schmidt *J Biotechnol* 2004, 113, 183.

[38] M. Schrewe, A. O. Magnusson, C. Willrodt, B. Bühler, A. Schmid *Adv Synth Catal* 2011, 353, 3485.

[39] L. Hinkkamp, H.J. Schäfer, B. Wippich *Liebigs Ann Chem* 1992, 559.

[40] (a) US Pat. 1 916 442, 1933. (b) A. J. Stirton *J Am Oil Chem Soc* 1962, 39, 490. (c) H. B. Watson *Chem Rev* 1930, 7, 180. (d) L. Claisen *Ber Dtsch Chem Ges* 1887, 20, 655. (e) P. E.

Pfeffer, L. S. Silbert *J Org Chem* 1972, 37, 1256. (f) M. W. Rathke, J. Deitch *Tetrahedron Lett* 1971, 2953.

[41] F. S.Güner, Y. Yağcı, A. T. Erciyes *Prog Polym Sci* 2006, 31, 633.

[42] M. A. R. Meier *Macromol Chem Phys* 2009, 210, 1073.

[43] (a) K. T. Achaya *J Am Oil Chem Soc* 1971, 48, 758. (b) F. C. Naughton *J Am Oil Chem Soc* 1974, 51, 65.

[44] H. Mutlu, M. A. R. Meier *Eur J Lipid Sci Technol* 2010, 112, 10.

[45] G. Das, R. K. Trivedi, A. K. Vasishtha *J Am Oil Chem Soc* 1989, 66, 938.

[46] M. Van der Steen, C. V. Stevens, Y. Eeckhout, L. De Buyck, F. Ghelfi, F. Roncaglia E*ur J Lipid Sci Technol* 2008, 110, 846.

[47] A. R. Kelly, D. G. Hayes *J Appl Polym Sci.* 2006, 101, 1646.

[48] (a) H. Pelletier, A. Gandini *Eur J Lipid Sci Technol* 2006, 108, 411. (b) H. Pelletier, M. N. Belgacem, A. Gandini *J Appl Polym Sci* 2006, 99, 3218.

[49] Z.S. Petrovic *Polym Rev* 2008, 48, 109.

[50] C. G. Freyschlag, R. J. Madix *Mater Today* 2011, 14, 134.

[51] G. Centi, S. Perathoner *Catalysis Today* 2003, 77, 287.

[52] P. Anastas, N. Eghbali *Chem Soc Rev* 2010, 39, 301.

[53] (a) I. J. S. Fairlamb *Annu Rep Prog Chem Sect B* 2003, 99, 104. (b) J. A. Gladyzs *Chem Rev* 2011, 111, 1167.

[54] (a) E. Negishi *Acc Chem Res* 1982, 15, 340. (b) D. J. Hart *Science* 1984, 223, 883. (c) J. Iqbal, B. Bhatia, N. K. Nayyar *Chem Rev* 1994, 94, 519. (d) B. Cornils, W. A. Herrmann *Applied Homogeneous Catalysis with Organometallic Compounds*, Wiley-VCH, Weinheim, 2000.

[55] R. H. Grubbs, R. R. Schrock, A. Fürstner (Eds.) *Advanced synthesis and catalysis, Olefin metathesis*, *Vol. 349,* Wiley-VCH, Weinheim, 2007, p. 1.

[56] S. P. Nolan, H. Clavier *Chem Soc Rev* 2010, 39, 3305.

[57] M. Schuster, S. Blechert *Angew Chem Int Ed* 1997, 36, 2036.

[58] A. Fürstner *Angew Chem Int Ed* 2000, 39, 3012.

[59] T. M. Trnka, R. H. Grubbs *Acc Chem Res* 2001, 34, 18.

[60] S. Connor, S. Blechert *Angew Chem* 2003, 115, 1944.

[61] R. H. Grubbs *Tetrahedron* 2004, 60, 7117.

[62] A. Rybak, P. A. Fokou, M. A. R. Meier *Eur J Lipid Sci Technol* 2008, 110, 797.

[63] R. L. Pederson, I. M. Fellows, T. A. Ung, H. Ishihara, S. P. Hajela *Adv Synth Catal* 2002, 344, 728.

[64] (a) G. Bredig, P. S. Fiske *Biochem Z* 1912, 46, 7. (b) U. Eder, G. Sauer, R. Weichert *Angew Chem Int Ed* 1971, 10, 496. (c) Z. G. Hajos, D. R. Parrish *J Org Chem* 1974, 39, 1615.

[65] Recent overview about the organocatalysis in: “Organocatalysis” special issue: B. List (Ed.) *Chem Rev* 2007, 107, 5413.

[66] (a) S. Bertelsen, K. A. Jorgensen *Chem Soc Rev* 2009, 38, 2178. (b) D. W. C. MacMillan *Nature* 2008, 455, 304.

[67] S. H. Kim, F. Nederberg, L. Zhang, C. G. Wade, R. M. Waymouth, J. L. Hedrick *Nano Lett* 2008, 8, 294.

[68] (a) T. Ishikawa, T. Kumamoto *Synthesis* 2006, 5, 737. (b) M. P. Coles *Chem Commun* 2009, 3659. (c) J. E. Taylor, S. D. Bull, J. M. J Williams *Chem Soc Rev* 2012, *doi: 10.1039/C2CS15288F.*

[69] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew Chem Int Ed* 2001, 40, 2004.

[70] (a) P. Wu, W. Fokin *Aldrichimica Acta* 2007, 40, 7. (b) M. Meldal, C. W. Tornøe *Chem Rev* 2008, 108, 2952. (c) R. K. Iha, K. L. Wooley, A. M. Nyström, D. J. Burke, M. J. Kade, C. J. Hawker *Chem Rev* 2009, 109, 5620. (d) M. van Dijk, D. T. S. Rijkers, R. M. J. Liskamp, C. F. van Nostrum, W. E. Hennink *Bioconjugate Chem* 2009, 20, 2001. (e) E. Lallana, A. Sousa-Herves, F. Fernandez-Trillo, R. Riguera, E. Fernandez-Megia *Pharm Res* 2012, 29, 1.

[71] (a) A. Fürstner, P. W. Davies *Chem Commun* 2005, 2307. (b) H. Villar, M. Frings, C. Bolm *Chem Soc Rev* 2007, 36, 55. (c) M. Mori *Materials* 2010, 3, 208. (d) C. Fischmeister, C. Bruneau *Beilstein J Org Chem* 2011, 7, 156.

[72] A. W. Anderson, M. G. Merckling *Chem Abstr* 1955, 50, 3008i.

[73] J-L. Hérisson, Y. Chauvin *Makromol Chem* 1971, 141, 161.

[74] C. P. Casey, T. J. Burkhardt *J Am Chem Soc* 1974, 96, 7808.

[75] T. J. Katz, J. McGinnis *J Am Chem Soc* 1975, 97, 1592.

[76] (a) R. H. Grubbs, P. L. Burk, D. D. Carr *J Am Chem Soc* 1975, 97, 3265. (b) R. H. Grubbs, D. D. Carr, C. Hoppin, P. L. Burk *J Am Chem Soc* 1976, 98, 3478.

[77] N. Calderon, H. Y. Chen, K.W.Scott *Tett Lett* 1967, 34, 3327.

[78] (a) G. C. Vougioukalakis, R. H. Grubbs *Chem Rev* 2010, 110, 1746. (b) C. Samojłowicz, M. Bieniek, K. Grela *Chem Rev* 2009, 109, 3708.

[79] J. S. Murdzek, R. R. Schrock *Organometallics* 1987, 6, 1373.

[80] J. S. Murdzek, R. R. Schrock *Macromolecules* 1987, 20, 2640.

[81] (a) G. C. Fu, S. T. Nguyen, R. H. Grubbs *J Am Chem Soc* 1993, 115, 9856. (b) T. D. Clark, M. R. Ghadiri *J Am Chem Soc* 1995, 117, 12364. (c) S. T. Diver, S. L. Schreiber *J Am Chem Soc* 1997, 119, 5106.

[82] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann *Angew Chem Int Ed* 1998, 37, 2490.

[83] (a) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. *J Am Chem Soc* 2000, 122, 8168. (b) M. S. Sanford, J. A. Love, R. H. Grubbs *Organometallics* 2001, 20, 5314. (c) J. L. Love, J. P. Morgan, T. M. Trnka, R. H. Grubbs *Angew Chem Int Ed* 2002, 41, 4025.

[84] (a) CN Pat. 1907992A. (b) US Pat. App. 20070043180-A1, 2007. (c) WO Pat. App. 2007003135-A1, 2007.

[85] K. Endo, R. H. Grubbs *J Am Chem Soc* 2011, 133, 8525.

[86] (a) F. Boeda, H. Clavier, S. P. Nolan *Chem Commun* 2008, 2726. (b) R. Castarlenas, C. Vovard, C. Fischmeister, P. H. Dixneuf *J Am Chem Soc* 2006, 128, 4079.

[87] Y. Vidavsky, A. Anaby, N. G. Lemcoff *Dalton Trans* 2012, 41, 32.

[88] M. Bieniek, C. Samojzowicz, V. Sashuk, R. Bujok, P. Sledz, N. Lugan, G. Lavigne, D. Arlt, K. Grela *Organomettalics* 2011, 30, 4144.

[89] (a) S. Kotha, K. Lahiri *Synlett* 2007, 2767. (b) C. Coperet *Beilstein J Org Chem* 2011, 7, 13. (c) H. M. A. Hassan *Chem Commun* 2011, 46, 9100. (d) S. Sutthasupa, M. Shiotsuki, F. Sanda *Polymer J* 2010, 42, 905. (e) A. Aljarilla, J. C. Lopez, J. Plumet *Eur J Org Chem* 2010, 6123. (f) X. Wu, M. Tamm *Beilstein J Org Chem* 2011, 7, 82. (g) S. Monsaert, V. Lozano, R. Drozdzak, P. Van

der Voort, F. Verpoort *Chem Soc Rev* 2009, 38, 3360. (h) M. R. Buehmeiser *Chem Rev* 2009; 109, 303.

[90] (a) A. Rybak, M. A. R. Meier *Green Chem* 2007, 9, 1356. (b) A. Rybak, M. A. R. Meier *Green Chem* 2008, 10, 1099. (c) T. Jacobs, A. Rybak, M. A. R. Meier *Appl Catal A: Gen* 2009, 353, 32.

[91] D. Quinzler, S. Mecking *Chem Commun* 2009, 5400.

[92] (a) R. Malacea, C. Fischmeister, C. Bruneau, J.-L. Dubois, J.-L. Couturier, P. H. Dixneuf *Green Chem* 2009, 11, 152. (b) X. Miao, C. Fischmeister, C. Bruneau, P. H. Dixneuf, *ChemSusChem* 2009, 2, 542. (c) WO Pat. App. 2008/053113A1, 2008. (d) WO Pat. App. 2008/104722A2, 2008.

[93] X. Miao, P. H. Dixneuf, C. Fischmeister, C. Bruneau *Green Chem* 2011, 13, 2258.

[94] (a) K. L. Opper, K. B. Wagener *J Polym Sci Part A: Polym Chem* 2011, 49, 821 and references cited therein. (b) A. Leitgeb, J. Wappel, C. Slugovc *Polymer* 2010, 51, 2927. (c) H. Mutlu, L. Montero de Espinosa, M. A. R. Meier *Chem Soc Rev* 2011, 40, 1404.

[95] T. W. Baughman, K. B. Wagener *Adv Polym Sci* 2005, 176, 1.

[96] K. B. Wagener, J. M. Boncella, J. G. Nel *Macromolecules* 1991, 24, 2649.

[97] M. Ulman, R. H. Grubbs *Organometallics*, 1998, 17, 2482.

[98] A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubb *J Am Chem Soc* 2000, 122, 3783.

[99] C. W. Bielawski, R. H. Grubbs *Angew Chem Int Ed* 2000, 39, 2903.

[100] K. B. Wagener, D. W. Smith Jr. *Macromolecules* 1991, 24, 6073.

[101] K. B. Wagener, J. T. Patton, M. D. E. Forbes, T. L. Myers, H. D. Maynard *Polym Int* 1993, 32, 411.

[102] M. D. Watson, K. B. Wagener *Macromolecules* 2000, 33, 3196.

[103] M. D. Watson, K. B. Wagener, *Macromolecules* 2000, 33, 8963.

[104] K. B. Wagener, K. Brzezinska, J. D. Anderson, T. R. Younkin, K. Steppe, W. DeBoer, *Macromolecules* 1997, 30, 7363.

[105] K. R. Brzezinska, K. B. Wagener, G. T. Burns *J Polym Sci A: Polym Chem* 1999, 37, 849.

[106] T. E. Hopkins, J. H. Pawlow, D. L. Koren, K. S. Deters, S.M. Solivan, J. A. Davis, F. J. Gomez, K. B. Wagener *Macromolecules* 2001, 34, 7920.

[107] T. E. Hopkins, J. H. Pawlow, F. Tep, K. B. Wagener *Polym Prep (Am Chem Soc Div Polym Sci)* 2002, 43, 281.

[108] T. E. Hopkins, K. B. Wagener *Macromolecules* 2004, 37, 1180.

[109] R. H. Crabtree *The organometallic Chemistry of Transition Elements*, 4th ed., Wiley, Newyork, 2005, pp. 239-241.

[110] (a) B. Schmidt *Eur J Org Chem* 2004, 1865. (b) B. Schmidt *Chem Commun* 2004, 742.

[111] H. D. Maynard, R. H. Grubbs *Tetrahedron Lett* 1999, 40, 4137.

[112] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel *Chem Eur J* 2001, 7, 3236.

[113] A. E. Sutton, B. A. seigal, D. F. Finnegan, M. L. Snapper *J Am Chem Soc* 2002, 124, 13390.

[114] S. H. Hong, M. W. Day, R. H. Grubbs *J Am Chem Soc* 2004, 126, 7414.

[115] (a) P. Formentin, N. Gimeno, J. H. G. Steinke, R. Vilar *J Org Chem* 2005, 70, 8235. (b) N. Gimeno, P. Formentín, J. H. G. Steinke, R. Vilar *Eur J Org Chem* 2007, 918.

[116] S. H. Hong, D. P. Sanders, C. W. Lee, R. H. Grubbs *J Am Chem Soc* 2005, 127, 17160.

[117] W. H. Meyer, A. E. McConnell, G. S. Forman, C. L. Dwyer, M. M. Kirk, E. L. Ngidi, A. Blignaut, D. Saku, A. M. Z. Slawin *Inorg Chim Acta* 2006, 359, 2910.

[118] P. A. Fokou, M. A. R. Meier *J Am Chem Soc* 2009, 131, 1664.

[119] J. C. Marmo, K. B. Wagener *Macromolecules* 1993, 26, 2137.

[120] K. R. Brzezinska, T. J. Deming *Macromolecules* 2001, 34, 4348.

[121] P. M. O´Donnel, K. R. Brzezinska, D. Powell, K. B. Wagener *Macromolecules* 2001, 34, 6845.

[122] (a) N. Calderon *J Macromol Sci Rev Macromol Chem* 1972, 7, 105. (b) C. W. Bielawski, R. H. Grubbs *Prog Polym Sci* 2007, 32, 1.

[123] J. Mol *J Mol Catal A: Chem* 2004, 213, 39.

[124] M. S. Sanford, M. Ulman, R. H. Grubbs *J Am Chem Soc* 2001, 123, 749.

[125] L. Delaude, D. Jan, F. Simal, A. Demonceau, A. F. Noels *Macromol Symp* 2000, 153, 133.

[126] S. Gutierrez, A. Fulgencio, M. A. Tlenkopatchev *J Chem Thermodyn* 2006, 38, 383.

---

[127] A. D. Benedicto, J. P. Claverie, R. H. Grubbs *Macromolecules* 1995, 28, 500.

[128] O. W. Webster *Science* 1991, 251, 887.

[129] (a) B. M. Novak, W. Risse, R. H. Grubbs *Adv Polym Sci* 1992, 102, 47. (b) K. Nomura, M.M. Abdellatif *Polymer* 2010, 51, 1861. (c) T.-L. Choi, R.H. Grubbs *Angew Chem Int Ed* 2003, 42, 1743. (d) P. de Fremont, H. Clavier, V. Monetmbault, L. Fontaine, S. P. Nolan *J Mol Catal A: Chem* 2008, 283, 108.

[130] J. C. Lee, K. A Parker, N. S. Sampson *J Am Chem Soc* 2006, 128, 4578.

[131] D. Burtscher, C. Lexer, K. Mereiter, R. Winde, R. Karch, C. Slugovc *J Polym Sci Part A: Polym Chem* 2008, 46, 4630.

[132] (a) L. Delaude, A. Demonceau, A. F. Noels *Macromolecules* 1999, 32, 2091. (b) V. Amir-Ebrahimi, D. A. Corry, J. G. Hamilton, J. M. Thompson, J. J. Rooney *Macromolecules* 2000, 33, 717. (c) (a) L. Delaude, A. Demonceau, A. F. Noels *Macromolecules* 2003, 36, 1446. (d) L. H. Peeck, S. Leuthäusser, H. Plenio *Organometallics* 2010, 29, 4339.

[133] B. K. Keitz, A. Fedorov, R. H. Grubbs *J Am Chem Soc* 2012, 134, 2040.

[134] S. Hilf, R. H. Grubbs, A. F. M. Kilbinger *J Am Chem Soc* 2008, 130, 11040.

[135] C. Janaik, P. Lassahn *Macromol Rapid Commun* 2001, 22, 479.

[136] P. von R. Schleyer, J. E. Williams Jr., K. R. Blanchard *J Am Chem Soc* 1970, 92, 2377.

[137] R. T. Mathers, K. Damodaran, M. G. Rendos, M. S. Lavrich *Macromolecules* 2009, 42, 1512.

[138] J. M. Delancey, M. D. Cavazza, M. G. Rendos, C. J. Ulisse, S. G. Palumbo, R. T. MathersJ *Polym Sci Part A: Polym Chem* 2011, 49, 3719.

[139] D. Smith, E. B. Pentzer, S. T. Nguyen *Polymer Rev* 2007, 47, 419.

[140] D. Seebach *Angew Chem Int Ed* 1990, 29, 1320.

[141] B. List *Adv Synth Cat* 2004, 346, 1021

[142] (a) M. El-Naggar, M. Conte, R. J. Capon *Org Biomol Chem* 2010, 8, 407. (b) I. B. Seiple, S. Su, I. S. Young, C. A. Lewis, J. Yamaguchi, P. S. Baran *Angew Chem Int Ed* 2010, 49, 1095. (c) R. G. S. Berlinck, A. C. B. Burtoloso, M. H. Kossuga *Nat Prod Rep* 2008, 25, 919.

[143] J. Magano *Chem Rev* 2009, 109, 4398.

[144] T. Ishikawa *Superbases for Organic Synthesis* John Wiley & Sons, Chippenham, 2009.

[145] (a) M. P. Coles *Dalton Trans* 2006, 985. (b) S. H. Oakley, D. B. Soria, M. P. Coles, P. B. Hitchcock *Polyhedron* 2006, 25, 1247.

[146] S. Carloni, D. E. De Vos, P. A. Jacobs, R. Maggi, G. Sartori, R. Sartorio *J Catal* 2002, 205, 199.

[147] (a) M. K. Kiesewetter, M. D. Scholten, N. Kirn, R. L. Weber, J. L. Hedrick, R. M. Waymouth *J Org Chem* 2009, 74, 9490. (b) I. Kaljurand, A. Kuett, L. Soovaeli, T. Rodima, V. Maeemets, I. Leito, I. A. Koppel *J Org Chem* 2005, 70, 1019.

[148] For selected examples of TBD catalyzed reactions, see: (a) D. Simoni, M. Rossi, R. Rondanin, A. Mazzali, R. Baruchello, C. Malagutti, M. Roberti, F. P. Invidata *Org Lett* 2000, 2, 3765. (b) D. Simoni, R. Rondanin, M. Morini, R. Baruchello, F. P. Invidata *Tetrahedron Lett* 2000, 41, 1607. (c) O. Mahé, D. Frath, I. Dez, F. Marsais, V. Levacher, J.-F. Briere *Org Biomol Chem* 2009, 7, 3648. (d) J. Ma, X. Zhang, N. Zhao, A. S. N. Al-Arifi, T. Aouak, Z. A. Al-Othman, F. Xiao, W. Wei, Y. Sun *J Mol Catal A: Chem* 2010, 315, 76. (e) A. Horvath *Tetrahedron Lett* 1996, 37, 4423. (f) W. Ye, J. Xu, C.-T Tan, C.-H. Tan *Tetrahedron Lett* 2005, 46, 6875. (g) R. Ballini, D. Fiorini, R. Maggi, P. Righi, G. Sartori, R. Sartorio *Green Chem* 2003, 5, 396. (h) C. Ghobril, C. Sabot, C. Mioskowski, R. Baati Eur *J Org Chem* 2008, 4104.

[149] (a) O. Türünç, M. A. R. Meier *Macromol Rapid Commun* 2010, 31, 1822. (b) M. Firdaus, L. Montero de Espinosa, M. A. R. Meier *Macromolecules* 2011, 44, 7253.

[150] (a) R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, R. M. Waymouth, J. L. Hedrick *J Am Chem Soc* 2006, 128, 4556. (b) N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer, J. L. Hedrick *Chem Rev* 2007, 107, 5813. (c) A. P. Dove *Chem Commun* 2008, 6446. (d) M. L. Foresti, M. L. Ferreira *Macromol Rapid Commun* 2004, 25, 2025.

[151] B. G. G. Lohmeijer, G. Dubois, F. Leibfarth, R. C. Pratt, F. Nederberg, A. Nelson, R. M. Waymouth, C. Wade, J. L. Hedrick *Org Lett* 2006, 8, 4683.

[152] F. Nederberg, B. G. G. Lohmeijer, F. Leibfarth, R. C. Pratt, J. Choi, A. P. Dove, R. M. Waymouth, J. L. Hedrick *Biomacromolecules* 2007, 8, 153.

[153] M. Kashio, T. Sugizaki, S. Yamamoto, T. Matsuoka, O. Moriya *Polyme*r 2008, 49, 3250.

[154] (a) L. Simon, J. M. Goodman *J Org Chem* 2007, 72, 9656. (b) A. Chuma, H. W. Horn, W. C. Swope, R. C. Pratt, L. Zhang, B. G. G. Lohmeijer, C. G. Wade, R. M. Waymouth, J. L. Hedrick, J. E. Rice *J Am Chem Soc* 2008, 130, 6749.

[155] M. Costa, G. P. Chiusoli, M. Rizzardi *Chem Commun* 1996, 1699.

[156] S. Huang, J. Ma, J. Li, N. Zhao, W. Wei, Y. Sun *Catal Commun* 2008, 9, 276.

[157] D. Tang, D.-J. Mulder, B. A. J. Noordover, C. E. Koning *Macromol Rapid Commun* 2011, 32, 1379.

[158] M. T. Martello, A. Burns, M. Hillmyer *ACS Macro Lett* 2012, 1, 131.

[159] C. Sabot, K. A. Kumar, C. Antheaume, C. Mioskowski *J Org Chem* 2007, 72, 5001.

[160] G. Wojciechowski, G. Schroeder, G. Zundel, B. Brzezinski *J Phys Chem* 2000, 104, 7469.

[161] A. F. McKay, M.-E. Kreling *Can J Chem* 1957, 35, 1438. (b) F. P. Schmidtchen *Chem Ber* 1980, 113, 2175.

[162] EP Pat. 198680, 1986.

[163] S. Usachev, A. Gridnev *Synth Commun* 2011, 41, 3683.

[164] (a) P. L. Golas, K. Matyjaszewski *Chem Soc Rev* 2009, 39, 1338. (b) D. Fournier, R. Hoogenboom, U. S. Schubert *Chem Soc Rev* 2007, 36, 1369. (c) H. W. Binder, R. Sachsenhofer *Macromol Rapid Commun* 2007, 28, 15. (d) C. M. Nimmo, M. S. Shoichet *Bioconjugate Chem* 2011, 22, 2199.

[165] C. R. Becer, R. Hoogenboom, U. S. Schubert *Angew Chem Int Ed* 2009, 48, 4900.

[166] N. J. Agard, J. A. Prescher, C. R. Bertozzi *J Am Chem Soc* 2004, 126, 15046.

[167] J. M. Baskin, J. A. Prescher, S. T. Laughlin, N. J. Agard, P. V. Chang, I. A. Miller, A. Lo, J. A. Codelli, C. R. Bertozzi *Proc Natl Acad Sci USA* 2007, 104, 16793.

[168] O. Diels, K. Alder *Justus Liebigs Ann Chem* 1928, 460, 98.

[169] C. M. Nimmo, S. C. Owen, M. S Shoichet *Biomacromolecules* 2011, 12, 824.

[170] B. D. Mather, K. Viswanathan, K. M. Miller, T. E. Long *Prog Polym Sci* 2006, 31, 487.

[171] C. E. Hoyle, A. B. Lowe, C. N. Bowman *Chem Soc Rev* 2010, 39, 1355.

[172] C. D. Hurd, L. L. Gershbein *J Am Chem Soc* 1947, 69, 2328.

[173] B. D. Polizzotti, B. D. Fairbanks, K. S. Anseth *Biomacromolecules* 2008, 9, 1084.

[174] T. Posner *Ber Chem Gesellschaf* 1905, 38, 646.

[175] X.-F. Wang, Q.-L. Hua, Y. Cheng, X.-L. An, Q.-Q. Yang, J.-R. Chen, W.-J. Xiao *Angew Chem Int Ed* 2010, 49, 8379.

[176] (a) J. Shin, H. Matsushima, J. Chan *Macromolecules* 2009, 42, 3294. (b) J. Carioscia, J. Stansbury, C. Bowman *Polymer* 2007, 48, 1526.

[177] A. Gress, A. Volkel, H. Schlaad *Macromolecules* 2007, 40, 7928.

[178] M. S. Kharasch, A. T. Read, F. R. Mayo *Chem Ind* 1938, 57, 752.

[179] (a) K. S. Anseth, C. M. Wang, C. N. Bowman *Macromolecules* 1994, 27, 650. (b) M. Claudino, M. Johansson, M. Jonsson *Eur Polym J* 2010, 46, 2321. (c) B. S. Chiou, R. J. English, S. A. Khan *Macromolecules* 1996, 29, 5368.

[180] (a) R. L. A. David, J. A. Kornfield, *Macromolecules* 2008, 41, 1151. (b) C. Nilsson, N. Simpson, M. Malkoch, M. Johansson, E. Malmstrom *J Polym Sci Part A: Polym Chem* 2008, 46, 1339. (c) A. Dondoni *Angew Chem Int Ed* 2008, 47, 8995.

[181] K. L. Killops, L. M. Campos, C. J. Hawker *J Am Chem Soc* 2008, 130, 5062.

[182] N. H. Koenig, D. Swern *J Am Chem Soc* 1957, 79, 362.

[183] J. Samuelsson, M. Jonsson, T. Brinck, M. Johansson *J Polym Sci Part A: Polym Chem* 2004, 42, 6346.

[184] M. Black, J. W. Rawlins *Eur Polym J* 2009, 45, 1433.

[185] C. Lluch, J. C. Ronda, M. Galia, G. Lligadas, V. Cadiz *Biomacromolecules* 2010, 11, 1646.

[186] C. Lluch, J. C. Ronda, M. Galia, G. Lligadas, V. Cadiz *Macromol Rapid Commun* 2011, 32, 1343.

[187] E. Del Rio, G. Lligadas, J. C. Ronda, M. Galia, V. Cadiz *J Polym Sci Part A: Polym Chem* 2011, 49, 3069.

[188] M. F. Desroches, S. Caillol, V. Lapinte, R. Auvergne, B. Boutevin *Macromolecules* 2011, 44, 2489.

[189] M. Stemmelen, F. Pessel, V. Lapinte, S. Caillol, J. P. Habas, J. J. Robin *J Polym Sci Part A: Polym Chem* 2011, 49, 2434.

[190] O. Kreye, T. Toth, M. A. R. Meier *Eur Polym J* 2011, 47, 1804.

[191] A. Luo, X. Jiang, H. Lin, J. Yin *Green Chem* 2011, 21, 12753.

---

[192] C. Wang, F. N. Jones *J Appl Polym Sci* 2002, 78, 1698.

[193] J. John, M. Bhattacharya, R. B. Turner *J Appl Polym Sci* 2002, 86, 3097.

[194] S. Ahmad, S. M. Ashrat, F. Naqvi, S. Yadav, A. Hasnat *Prog Org Coat* 2003, 42, 95.

[195] T. K. Roy, V. M. Mannavi *J Sci Ind Res* 1993, 56, 1661.

[196] D. A. Raval, V. M. Manari *Res Ind* 1993, 38, 129.

[197] S. Ahmad, S. M. Ashrat, E. Ashraf, E. Sharmi , F. Yafar, A. Hasnat *Prog Cryst Growth Charact Mater* 2002, 45, 83.

[198] S. Ahmad, S. M. Ashraf, A. Hasnat, S. Yadaf, A. Jamal *J Appl Polym Sci* 2001, 82, 1855.

[199] M. Alam, E. Sharmin, S. M Ashraf, S Ahmad *Prog Org Coat* 2004, 50, 224.

[200] G. L. Webster *Ann Missouri Bot Gard* 1994, 81, 93.

[201] E. T. Akintayo, E. Bayer *Bioresource Technol* 2002, 85, 95.

[202] C. Gao, D. Yan *Prog Polym Sci* 2004, 29, 183.

[203] B. I. Voit, A. Lederer *Chem Rev* 2009, 109, 5924.

[204] M. Seiler *Fluid Phase Equilib* 2006, 241, 155.

[205] K. W. Wolf, H. Frey *Macromolecules* 2009, 42, 9443.

[206] C. Gottschalk, H. Frey *Macromolecules* 2006, 39, 1719.

[207] C. Y. Hong, Y. Z. You, D. C. Wu, Y. Liu, C. Y. Pan *J Am Chem Soc* 2007, 129, 5354.

[208] J. M. J. Frechet, M. Henmi, I. Gitsov, S. Aoshima, M. R. Leduc R. B. Grubbs *Science* 1995, 269, 1080.

[209] C. J. Hawker, J. M. J. Frechet, R. B. Grubbs, J. Dao *J Am Chem Soc* 1995, 117, 10763.

[210] K. Matyjaszewski, S. G. Gaynor, A. Kulfan, M. Podwika *Macromolecules* 1997, 30, 5192.

[211] K. Matyjaszewski, S. G. Gaynor, A. H. E. Müller *Macromolecules* 1997, 30, 7034.

[212] P. F. W. Simon, A. H. E. Müller, T. Pakula *Macromolecules* 2001, 34, 1677.

[213] B. Liu, A. Kazlauciunas, J. T. Guthrie, S. Perrier *Macromolecules* 2005, 38, 2131.

[214] B. Liu, A. Kazlauciunas, J. T. Guthrie, S. Perrier *Polymer* 2005, 46, 6293.

[215] T. Otsu *J Polym Sci Part A: Polym Chem* 2000, 38, 2121.

[216] C. J. Hawker, A. W. Bosman, E. Harth *Chem Rev* 2001, 101, 3661.

[217] K. Matyjaszewski, J. Xia *Chem Rev* 2001, 101, 2921.

[218] M. Kamigaito, T. Ando, M. Sawamoto *Chem Rev* 2001, 101, 3689.

[219] M. Ouchi, T. Terashima, M. Sawamoto *Chem Rev* 2009, 109, 4963.

[220] H. Chaffey-Millar, M. H. Stenzel, T. P. Davis, M. L. Coote, C. Barner-Kowollik *Macromolecules* 2006, 39, 6406.

[221] I. A. Gorodetskaya, T. L. Choi, R. H. Grubbs *J Am Chem Soc* 2007, 129, 12672.

[222] L. Ding, L. Zhang, H. Han, W. Huang, C. Song, M. Xie, Y. Zhang *Macromolecules* 2009, 42, 5036.

[223] P. A. Fokou, M. A. R. Meier *Macromol Rapid Commun* 2008, 29, 1620.

[224] M. D. Refvik, R. C. Larock, Q. Tian *J Am Oil Chem Soc* 1999, 76, 93.

[225] U. Biermann, J. O. Metzger, M. A. R. Meier *Macromol Chem Phys* 2010, 211, 854.

[226] C. Boelhouwer, J. C. Mol *J Am Oil Chem Soc* 1984, 61, 425.

[227] L. R. Tsai, Y. Chen *Macromolecules* 2008, 41, 5098.

[228] M. Haussler, R. Zheng, J. W. Y. Lam, H. Tong, H. Dong, B. Z Tang *J Phys Chem B* 2004, 108, 10645.

[229] J. A. Orlicki, J. L. Thompson, L. J. Markoski, K. N. Sill, J. S. Moore *J Polym Sci Part A: Polym Chem* 2002, 40, 936.

[230] E. Verkuijlen, C. Boelhouwer *J Chem Soc, Chem Commun* 1974, 793.

[231] S. Park, T. Chang, I. C. H. Park *Macromolecules* 1991, 24, 5729.

[232] Y. Hong, S. J. Coombs, J. J. Cooper-White, M. E. Mackay, C. J. Hawker, E. Malmström, N. Rehnberg *Polymer* 2000, 41, 7705.

[233] D. Schmaljohann, L. Häβler, P. Pötschke, B. I. Voit, P.E. Frolehling, B. Mostert, J. A. Loontjens *Macromolecules* 1999, 32, 6333.

[234] C. J. Hawker, P. J. Farrington, M. E. Mackay, K. L. Wooley, J. M. J. Fréchet *J Am Chem Soc* 1995, 117, 4409.

[235] W. P. Cox, E. H. Merz *J Polym Sci* 1958, 28, 619.

[236] G. L. Baker, Vogel, B. V. Erin, M. R. Smith *Polym Rev* 2008, 48, 64.

[237] D. Schmaljohann, L. Häβler, P. Pötschke, B. I. Voit, J. A. Loontjens *Macromol Chem Phys* 2000, 201, 49.

[238] E. Malmstrom, M. Johansson, A. Hult *Macromol Chem Phys* 1996, 197, 3199.

[239] Z.S. Petrovic, A. Zlatanic, C.C. Lava, S. Sinadinovic-Fiser *Eur J Lipid Sci Technol* 2002, 104, 293.

[240] A.E. Gerbase, J.R. Gregorio, M. Martinelli, M.C. Brasil, A.N.F. Mendes *J Am Oil Chem Soc* 2002, 79, 179.

[241] US Pat. 5 081 267, 1992

[242] S. Sinadinovic-Fiser, M. Jankovic, Z.S. Petrovic *J Am Oil Chem Soc* 2001, 78, 725.

[243] J. A. Sherringham, A. J. Clark, B.R.T. Keene *Lipid Technol* 2000, 12, 129.

[244] K. Zou, M. D. Soucek *Macromol Chem Phys* 2005, 206, 967.

[245] S. Chakrapani, J. V. Crivello *J Macromol Sci Part: A Pure Appl Chem* 1998, 35, 691.

[246] T. Vlček, Z. S. Petrović *J Am Oil Chem Soc* 2006, 83, 247

[247] US Pat. 4 119 640, 1978.

[248] US Pat. 6 121 398, 2000.

[249] H. Esen, S. H. Kusefoglu *J Appl Polym Sci* 2003, 89, 3882.

[250] H. Esen, S. H. Kusefoglu, R. P. Wool *J Appl Polym Sci* 2006, 103, 626.

[251] K. Ogawa, T. Terada, Y. Muranaka, T. Hamawaka, S. Hashimoto, S. Fujii *Chem Pharm Bull* 1986, 34, 1118.

[252] K. Ogawa, T. Terada, Y. Muranaka, T. Hamawaka, S. Hashimoto, S. Fujii *Chem Pharm Bull* 1986, 34, 3252.

[253] K. Ogawa, S. Ohta, M. Okamoto *Synthesis* 1987, 3, 281.

[254] P. P. Matloka, K. B. Wagener *J Mol Catal A: Chem* 2006, 257, 89.

[255] M. Szwarc *Nature* 1956, 178, 1168.

[256] M. Szwarc, M. Levy *J Am Chem Soc* 1956, 78, 2656.

[257] M. Szwarc *Adv Polym Sci* 1983, 49, 1.

[258] M. R. Buchmeiser *Chem Rev* 2000, 100, 1565.

[259] C. Slugovc, S. Demel, S. Riegler, J. Hobosch, F. Stelzer *J Mol Catal A: Chem* 2004, 213, 107.

[260] T.- L. Choi, R. H. Grubbs *Angew Chem* 2003, 115, 1785.

[261] R. P. Quirk, B. Lee *Polym Int* 1992, 27, 359.

[262] P. H. Henna, R. C. Larock *Macromol Mater Eng* 2007, 292, 1201.

[263] P. H. Henna, R. C. Larock *J Appl Polym Sci* 2009, 112, 1788.

[264] D.-J. Liaw, T.-P. Chen, C.-C. Huang *J Polym Sci Part A: Polym Chem* 2005, 43, 4233.

[265] D.-J. Liaw, J.-S. Tsai, H.-C. Sang *J Polym Sci Part A: Polym Chem* 1998, 36, 1785.

[266] F. M. Houlihan, F. Bouchard, J. M. J. Frechet, C. G. Wilson *Macromolecules* 1986, 19, 13.

[267] H. A. Staab *Angew Chem* 1962, 74, 407.

[268] C. W. Bielawski, R. H. Grubbs *Macromolecules* 2001, 34, 8838.

[269] J. B. Matson, R. H. Grubbs *Macromolecules* 2008, 41, 5626.

[270] S. J. Miller, H. E. Blackwell, R. H. Grubbs *J Am Chem Soc* 1996, 118, 9606.

[271] D. Bourgeois, A. Pancrazi, L. Ricard, J. Prunet *Angew Chem Int Ed* 2000, 39, 725.

[272] S. D. Edwards, T. Lewis, R. J. K Taylor *Tetrahedron Lett* 1999, 40, 4267.

[273] B. Schmidt, H. Wildemann *J Org Chem* 2000 ,65, 5817.

[274] M. B. Dinger, J. C. Mol *Adv Synth Catal* 2002, 344, 671.

[275] A. Fürstner, O. R. Thiel, L. Ackermann, H. J. Schanz, S. P. Nolan *J Org Chem* 2000, 65, 2204.

[276] J. C. Sworen, J. H. Pawlow, W. Case, J. Lever, K. B. Wagener *J Mol Cat* 2002, 194, 69.

[277] D. Bourgeois, A. Pancrazi, S. P. Nolan, J. Prunet *J Organomet Chem* 2002, 643, 247.

[278] S. E. Lehman, J. E. Schwendeman, P. M. O'Donnell, K. B. Wagener *Inorg Chim Acta* 2002, 345, 190.

[279] P. A. Fokou, M. A. R. Meier *J Am Chem Soc* 2009, 131, 1664.

[280] F. C. Courchay, J. C. Sworen, K. B. Wagener *Macromolecules* 2003, 36, 8231.

[281] V. I. Petkovska, T. E. Hopkins, D. H. Powell, K. B. Wagener *Macromolecules* 2005, 38, 5878.

[282] P. A. Fokou, M. A. R. Meier *Macromol Rapid Commun* 2010, 31, 368.

[283] WO Pat. App. 2007034552, 2007.

[284] L. Jafarpour, H. J. Schanz, E. D. Stevens, S. P. Nolan *Organometallics* 1999, 18, 5416.

[285] J. Broggi, C. A. Urbina-Blanco, H. Clavier, A. Leitgeb, C. Slugovc, A. M. Z. Slawin, S. P. Nolan *Chem Eur J* 2010, 16, 9215.

[286] H. Clavier, J. L. Petersen, S. P. Nolan *J Organomet Chem* 2006, 691, 5444.

[287] S. Monsaert, R. Drozdzak, V. Dragutan, I Dragutan, F. Verpoort Eur *J Inorg Chem* 2008, 432.

[288] T. Opstal, F. Verpoort *Angew Chem Int Ed* 2003, 42, 2876.

[289] P. Castarlenas, P. H. Dixneuf *Angew Chem Int Ed* 2003, 42, 4524.

[290] O. Adekunle, S. Tanner, W. H. Binder *Beilstein J Org Chem* 2010, 6, 59.

[291] H. Clavier, S. P. Nolan *Chem Eur J* 2007, 13, 8029.

[292] M. Bieniek, A. Michrowska, D. L. Usanov, K. Grela *Chem Eur J* 2008, 14, 806.

[293] C. Samojlowicz, M. Bieniek, A. Zarecki, R. Kadyrov, K. Grela *Chem Commun* 2008, 6282.

[294] M. I. Kohan (Ed.) *Nylon plastics handbook*, Hanser, New York, 1995.

[295] D. Braun (Ed.) *Polymer Synthesis: Theory and Practice; Fundamentals, Methods, Experiments,* Springer-Verlag, Berlin, 2005.

[296] B. Gnanaprakasam, E. Balaraman, C. Gunanathan, D. Milstein *J Polym Sci Part A: Polym Chem* 2012, *doi: 10.1002/pola.25943*.

[297] W. Niu, K. M. Draths, J. W. Frost *Biotechnol Prog* 2002, 18, 201.

[298] D. S. Ogunniyi *Bioresour Technol* 2006, 97, 1086.

[299] K. Brzezinska, K. B. Wagener *Macromolecules* 1991, 24, 5273.

[300] M. D. Watson, K. B. Wagener *Macromolecules* 2000, 33, 5411.

[301] A. Rybak, M. A. R. Meier *ChemSusChem* 2008, 1, 542.

[302] K. Brzezinska, P. S. Wolfe, M. D. Watson, K. B. Wagener *Macromol Chem Phys* 1996, 197, 2065.

[303] D. J. Valenti, K. B. Wagener *Macromolecules* 1998, 31, 2764.

[304] P. S. Wolfe, K. B. Wagener *Macromolecules* 1999, 32, 7961.

[305] C. Y. Tastard, P. Hodge, A. Ben-Haida, M. Dobinson *React Funct Polym* 2006, 66, 93.

[306] C. Bennett, L. J. Mathias *Macrom Chem Phys* 2004, 205, 2348.

[307] X. Cui, D. Yan *J Appl Polym Sci* 2004, 93, 2066.

[308] Y. Huang, W. Li, D. Yan *Polym Bull* 2002, 49, 111.

[309] X. Cui, W. Li, D. Yan, C. Yang, G. Di Silvestro *J Appl Polym Sci* 2005, 98, 1565.

[310] W. Li, D. Yan *J Appl Polym Sci* 2003, 88, 2462.

[311] D. Astruc *New J Chem* 2005, 29, 42.

[312] J. E. Schwendeman, A. C. Church, K. B. Wagener *Adv Synth Catal* 2002, 344, 597.

[313] F. Pardal, S. Salhi, B. Rousseau, M. Tessier, S. Claude, A. Fradet *Macromol Chem Phys* 2008, 209, 64.

[314] Y. J. Li, X. Y. Zhu, G. H. Tian, D. Y. Yan, E. Zhou *Polym Int* 2001, 50, 677.

[315] Y. J. Li, D. Y. Yan, X. Y. Zhu *Eur Polym J* 2001, 37, 1849.

[316] T. W. Greene, P. G. M. Wuts *Protective Groups in Organic Synthesis*, 3rd ed., Wiley, New York, 1999.

[317] J. P. Parrish, R. N- Salvatore, K. W. Jung *Tetrahedron* 2000, 56, 8207, and references cited therein.

[318] Some examples of patents that appeared recently follow: (a) WO Pat. 2005028415, 2005. (b) JP Pat. 2005126496, 2005. (c) WO Pat. 2005000783, 2005. (d) JP Pat. 2004010491, 2004. (e) JP Pat. 2004107241 2004. (f) WO Pat. 2004016577, 2004.

[319] A.-A. G. Shaikh, S. Siviram *Chem Rev* 1996, 96, 951 and references cited therein.

[320] A. F. Hegarty in *Comprehensive Organic Chemistry*, I. O. Sutherland (Ed.), Pergamon, London, 1979.

[321] L. Cotarca, P. Delogu, A. Nardelli, V. Sunjic *Synthesis* 1996, 553.

[322] Y. R. Jorapur, D. Y. Chi *J Org Chem* 2005, 70, 10774.

[323] S.-I. Kim, F. Chu, E. E. Dueno, K. W. Jung *J Org Chem* 1999, 64, 4578; R. N. Salvatore, V. L. Flanders, D. Ha, K. W. Jung *Org Lett* 2000, 2, 2797.

[324] Some selected references follow: (a) P. Tundo, M. Selva *Acc Chem Res* 2002, 35, 706. (b) B. Veldurthy, J. M. Clacens, F. Figueras *Eur J Org Chem* 2005, 1972. (c) P. Tundo, L. Rossi, A. Loris *J Org Chem* 2005, 70, 2219. (d) B. Veldurthy, F. Figueras *Chem Commun* 2004, 734. (e) M. Verdecchia, M. Feroci, L. Palombi, L. Rossi *J Org Chem* 2002, 67, 8287. (f) M. O. Bratt, P. C. Taylor *J Org Chem* 2003, 68, 5439. (g) R. N. Salvatore, F. Chu, A. S. Nagle, E. A. Kapxhiu, R. M. Cross, K. W. Jung *Tetrahedron* 2002, 58, 3329. (h) R. Srivastava, D. Srinivas, P. Ratnasamy *Appl Catal A* 2005, 289, 128.

[325] S. Sakai, T. Fujinami, S. Furusawa *Nippon Kagaku Kaishi* 1975, 1789.

[326] N. Keller, G. Rebmann, V. Keller *J Mol Catal A: Chem* 2010, 317, 1.

[327] M. L. Kantam, U. Pal, B. Sreedhar, B. M. Choudary *Adv Synth Catal* 2007, 349, 1671.

[328] Y.-X. Zhou, S.-G. Liang, J.-L. Song, T.-B. Wu, S.-Q Hu, H.-Z. Liu, B.-X. Han *Acta Phys Chim Sin* 2010, 26, 1.

[329] Z. Jiang, C. Liu, R. A. Gross *Macromolecules* 2008, 41, 4671; T. Yu, J. Ren, S. Gu, M. Yang *Polym Int* 2009, 58, 1058.

[330] (a) US Pat. 5 391 311, 1995. (b) WO Pat. 2003005981, 2003. (c) US Pat. 4 403 056, 1983.

[331] J. Vetter, P. Novak *J Power Sources* 2003, 119-121, 338.

[332] J. Tsuji *Palladium Reagents and Catalysts, New Perspectives for the 21st Century*, Willey, UK, Chichester, 2004.

[333] M. J. Roberts, M. D. Bentley, J. M Haris *Adv Drug Deliv Rev* 2002, 54, 459.

[334] US Pat. 5 206 408, 1993.

[335] H. Beiebl, K.Menzel, A. P. Zeng, W. D. Decker *Appl Microbiol Biotechnol* 1999, 52, 289; H. Huang, C. S. Gong, G. T. Tsao *Appl Microbiol Biotechnol* 2002, 98, 687.

[336] http://renewablechemicals.agra-net.com/2011/12/verdezyne-opens-renewable-adipic-acid-pilot-plant-in-california/

[337] Z. Jiang, C. Liu, W. Xie, R. A. Gross *Macromolecules* 2007, 40, 7934.

[338] T. Ariga, T. Takata, T. Endo *Macromolecules* 1997, 30, 737.

[339] K. Tiefenbacher, J. Mulzer *Angew Chem Int Ed* 2008, 47, 6199; F. Grellepois, B. Crousse, D. Bonnet-Delpon, J-P. Begue *Org Lett* 2005, 7, 5219; K. Mori *Tetrahedron* 2009, 65, 2798.

[340] S. J. Hou, X. Gong, W. K. Chan *Macromol Chem Phys* 1999, 200, 100.

[341] J. Konzelman, K. B. Wagener *Macromolecules* 1995, 28, 4686.

[342] A. Behr, M. Becker, T. Beckmann, L. Johnen, J. Leschinski, S. Reyer *Angew Chem Int Ed* 2009, 48, 3598 and references cited therein.

[343] E. J. Smutny *J Am Chem Soc* 1967, 89, 6793.

[344] (a) R. Jackstell, S. Harkal, H. Jiao, B. Spannenberg, D. Rottger, F. Nierlich, M. Elliot, S. Niven, K. Cavell, O. Navarro, M. Viciu, S. P. Nolan, M. Beller *Chem Eur J* 2004, 10, 3891. (b) M. J.-L. Tschan, E. J. Garcia-Suarez, Z. Freixa, H. Launay, H. Hagen, J. Benet-Buchholz, P. W. N. M. van Leeuwen *J Am Chem Soc* 2010, 132, 6463.

[345] B. I. Lee, K. H. Lee, S. Lee *J Mol Catal A: Chem* 2000, 156, 283.

[346] (a) A. Behr, L. Johnen, A. J. Vorholt *ChemCatChem* 2010, 2, 1271. (b) A. Grotevendt, M. Bartolome, A. Spannenberg, D. J. Nielsen, R. Jackstell, K. J. Cavell, L. A. Oro, M. Beller *Tetrahedron Lett* 2007, 48, 9203. (c) T. Prinz, B. Driessen-Hölscher *Chem Eur J* 1999, 5, 2069.

[347] (a) V. Desvergnes-Breuil, C. Pinel, P. Gallezot *Green Chem* 2001, 3, 175. (b) B. Estrine, S. Bouquillon, F. Henin, J. Muzart *Appl Organomet Chem* 2007, 21, 945.

[348] (a) A. Behr, M. Urschey *Adv Synth Catal* 2003, 345, 1242. (b) R. Palkovits, I. Nieddu, R. J. M. Klein Gebbink, B. M. Weckhuysen *ChemSusChem* 2008, 1, 193. (c) A. Grotevendt, R. Jackstell, D. Michalik, M. Gomez, M. Beller *ChemSusChem* 2009, 2, 63.

[349] J. Mesnager, C. Quettier, A. Lambin, F. Rataboul, A. Perrard C. Pinel *Green Chem* 2010, 12, 475.

[350) A. Behr, P. Bahke, B. Klinger, M. Becker *J Mol Catal A: Chem* 2007, 267, 149.

[351] (a) A. Rodriguez, M. Normen, B. W. Spur, J.-J. Godfroid, T. H. Lee Eur *J Org Chem* 2000, 2991. (b) J. Tsuji, Y. Kobayashi, T. Takahasi *Tetrahedron Lett* 1980, 21, 483. (c) J. Tsuji, I. Shimizu, H. Suzuki, Y. Naito *J Am Chem Soc* 1979, 101, 5070. (d) J. Tsuji, H. Yasuda, T. Mandai *J Org Chem* 1978, 43, 3606. (e) J. Tsuji, T. Mandai *Tetrahedron Lett* 1978, 19, 1817. (f) J. Tsuji, K. Mizutani, I. Shimizu, K. Yamamoto *Chem Lett* 1976, 773.

[352] (a) W. von Rybinski, K. Hill *Angew Chem* 1998, 110, 1394; *Angew Chem Int Ed* 1998, 37, 1328. (b) DE Pat. 4 242 467, 1992. (c) WO Pat. 199013531, 1990; [*Chem Abstr* 1991, 115, 137003].

[353] M. Fernandes, W. Kaminsky *Macromol Chem Phys* 2009, 210, 585.

[354] (a) R. Palkovits, A. N. Parvulescu, P. J. C. Hausoul, C. A. Kruithof, R. J. M. Klein Gebbink, B. M. Weckhuysen *Green Chem* 2009, 11, 1155. (b) P. J. C. Hausoul, P. C. A. Bruijnincx, R. J. M. Klein Gebbink, B. M. Weckhuysen *ChemSusChem* 2009, 2, 855. (c) R. Palkovits, I. Nieddu, C. A. Kruithof, R. J. M. Klein Gebbink, B. M. Weckhuysen *Chem Eur J* 2008, 14, 8995. (d) P. J. C. Hausoul, A. N. Parvulescu, M. Lutz, A. L. Spek, P. C. A. Bruijnincx, R. J. M. Klein Gebbink, B. M. Weckhuysen *Angew Chem Int Ed* 2010, 49, 7972.

[355] G. A. Kraus *CLEAN – Soil, Air, Water* 2008, 36, 648 and references therein.

[356] T. J. Korstanje, J. T. B. H. Jastrzebski, R. J. M. Klein Gebbink *ChemSusChem* 2010, 3, 695.

[357] (a) Y. Chauvin *Angew Chem Int Ed* 2006, 45, 3741. (b) R. R. Schrock *Angew Chem Int Ed* 2006, 45, 3748. (c) R. H. Grubbs *Angew Chem Int Ed* 2006, 45, 3760. (d) A. H. Hoveyda, A. R. Zhugralin *Nature* 2007, 450, 243. (e) C. P. Casey *J Chem Educ* 2006, 83, 192.

[358] (a) C. Damez, S. Bouquillon, F. Hénin, J. Muzart *Eur J Org Chem* 2006, 20, 4565. (b) S. C. R. Bouquillon *Chimie* 2011, 14, 716.

[359] M. Ulman, R. H. Grubbs *J Org Chem* 1999, 64, 7202.

[360] (a) A. Michaut, J. Rodriguez *Angew Chem Int Ed* 2006, 45, 5740. (b) M. Tori, R. Mizutani Molecules 2010, 15, 4242.

[361] J. T. Patton, J. M. Boncella, K. B. Wagener *Macromolecules* 1992, 25, 3862.

[362) Y. A. Lin, J. M. Chalker, B. J. Davis *J Am Chem Soc* 2010, 132, 16805.

[363] E. Klemm, S. J. Sensfuss *Macromol Sci- Chem* 1991, 28, 875.

[364] C. D. Heidecke, T. K. Lindhorst *Chem Eur J* 2007, 13, 9056.

[365] (a) L. Lunazzi, G. Placucci, L. Grossi *J Chem Soc, Chem Commun* 1979, 12, 533. (b) C. Schoeneich, K.-D. Asmus, U. Dillinger, F. Bruchhausen *Biochem Biophys Res Commun* 1989, 161, 113.

[366] D. F. McMillen, D. M. Golden *Ann Rev Phys Chem* 1982, 33, 493 and references cited therein.

[367] (a) R. Zhao, J. Lind, G. Merenyi, T. E. Eriksen *J Am Chem Soc* 1994, 116, 12010. (b) M. J. Robins, G. J. Ewing *J Am Chem Soc* 1999, 121, 5823. (c) T. Nauser, C. Schoneich *J Am Chem Soc* 2003, 125, 2042.

[368] B. P. Roberts *Chem Soc Rev* 1999, 28, 25.

[369] T. M. Roper, C. A. Guymon, E. S. Jönsson, C. E. Hoyle *J Polym Sci Part A: Polym Chem* 2004, 42, 6283.

[370] J. A. Riddick, W. B. Bunger in: *Techniques of Chemistry*, *Vol. 2,* A. Weissberger (Ed.), 3rd ed., Wiley, New York, 1970, p. 450.

[371] H. Iloukhani, H. A. Zarei, M. Behroozi *J Mol Liq* 2007, 135, 141.

[372] J. G. Baragi, M. I. Aralaguppi, T. M. Aminabhavi, M. Y. Kariduraganavar, S. S. Kulkarni *J Chem Eng Data* 2005, 50, 917.

[373] E. Jacobi, H. Schuttenberg, R.C. Schulz *Macromol Chem Rapid Commun* 1980, 1, 397.

[374] H. Schuttenberg, R.C. Schulz *Angew Chem* 1976, 88, 848.

[375] A. Huczynski, B. Brzezinski *Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons, 2008.

[376] P. Tundo, F. Aricò, A. E. Rosamilia, Sofia Memoli *Green Chem* 2008, 10, 1182.

[377] Y.Terui, K. Tori, N. Tsuji *Tetrahedron Lett* 1976, 17, 621.

[378] M. Selva, C. A. Marques, P. Tundo *J Chem Soc Perkin Trans 1* 1995, 1889-1893.

Eigenständigkeitserklärung gemäß Abs.5 §11 der Studienprüfungsordnung

Hiermit versichere ich, dass ich die vorliegende Doktorarbeit selbständig verfasst habe. Ich versichere, dass ich keine anderen als die angegebenen Quellen benutzt und alle wörtlich oder sinngemäß aus anderen Werken übernommene Aussagen als solche gekennzeichnet habe, und dass die eingereichte Arbeit weder vollständig noch in wesentlichen Teilen Gegenstand eines anderen Prüfungsverfahren gewesen ist.

Karlsruhe, den 24.09.2012 Hatice Mutlu