Application of Catalytic Ester Reductions in Polymer Chemistry

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One of the beautiful things about science is that it allows us to bumble along, getting it wrong time after time, and feel perfectly fine as long as we learn something each time.

Martin A. Schwarz

Die vorliegende Arbeit wurde von November 2014 bis Juli 2018 unter Anleitung von Prof. Dr. Michael A. R. Meier am Karlsruher Institut für Technologie (KIT) angefertigt.

Hiermit erkläre ich wahrheitsgemäß, dass ich die vorliegende Doktorarbeit selbstständig angefertigt und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt sowie die wörtlich oder inhaltlich übernommenen Stellen als solche kenntlich gemacht und die Satzung des Karlsruher Instituts für Technologie (KIT) zur Sicherung guter wissenschaftlicher Praxis in der jeweils gültigen Fassung beachtet habe. Des Weiteren erkläre ich, dass ich mich derzeit in keinem laufenden Promotionsverfahren befinde, und auch keine vorausgegangenen Promotionsversuche unternommen habe.

Ort, Datum Unterschrift

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Abstract

Polyethers are amongst the most diverse polymers in terms of potential applications, yet the synthesis of aliphatic polyethers is limited to ring-opening polymerization of epoxides or tetrahydrofuran. In this thesis, the range of available polyethers was significantly broadened by introducing the direct reduction of polyesters to polyethers as synthesis method. Due to the versatility of polyesters — especially with regards to length and structure of the backbone — this synthetic approach leads to the preparation of various polyethers, unreported to-date, although they are simple in molecular structure. Full conversion of the ester groups was confirmed by ^{1}H-NMR and IR spectroscopy as well as SEC-ESI mass spectrometry. Degradation of polyethers with four or more methylene groups between functional groups was minimal, as shown by GPC- and NMR end group- analyses. Mechanistic studies revealed that the reduction occurs at random positions in the polymer chain and, by thermal analysis, basic material properties of the novel polyethers were established. Gallium bromide, the catalyst for the reduction, was introduced as a possible catalyst for the controlled ring-opening polymerization of lactones keeping its activity after polymerization and ultimately leading to a one-pot, two-step procedure for the production of polyethers from cyclic esters. In a second approach, the same reduction was applied to synthesize fatty acids based ω,ω'-unsaturated diene ethers, which were polymerized afterwards by thiol-ene or ADMET polymerizations and modified post-polymerization by oxidation or hydrogenation, respectively. To prove the utility of the polyethers in their most common application — the production of polyurethanes — while keeping in mind principles of sustainability, the conversion of their hydroxy end groups to amine end groups was investigated, to obtain prepolymers for non-isocyanate polyurethanes. A novel procedure utilizing ε-caprolactam to produce ester-amines was established achieving quantitative conversion. Moreover, a sustainable comonomer, namely erythritol bis(carbonate), was obtained from the renewable sugar substitute erythritol by transesterification with dimethyl carbonate. The literature procedure for this transformation was improved significantly in terms of temperature, pressure, reaction time, conversion, simplicity of the workup and recyclability of reactants.

Zusammenfassung

Polyether gehören zu den vielfältigsten Polymeren hinsichtlich ihrer Anwendung und nichtsdestotrotz ist die Synthese von aliphatischen Polyethern auf Ringöffnungspolymerisation von Epoxiden oder Tetrahydrofuran beschränkt. In dieser Arbeit wurde durch die Einführung der direkten Reduktion von Polyestern zu Polyethern als Synthesemethode das Spektrum der verfügbaren Polyether signifikant erweitert. Durch die Vielseitigkeit der Polyester – insbesondere bezüglich der Länge und Struktur des Polymerrückgrats – führte dieser Ansatz zur Synthese verschiedenster Polyether, die trotz ihrer einfachen molekularen Struktur bislang unbekannt sind. Der vollständige Umsatz der Estergruppen wurde durch ^{1}H-NMR und IR Spektroskopie sowie SEC-ESI Massenspektrometrie nachgewiesen. Der Abbau der Polymerkette konnte für Polyether mit vier oder mehr Methylengruppen bei einem Minimum gehalten werden. Mechanistische Untersuchungen ergaben, dass die Reduktion an zufälligen Stellen in der Polymerkette abläuft und mittels thermischer Analyse konnten die grundlegenden Materialeigenschaften der neuartigen Polyether bestimmt werden. Galliumbromid, der Katalysator für die Reduktion, wurde als möglicher Katalysator für die kontrollierte Ringöffnungspolymerisation von Lactonen eingeführt. Dadurch, dass Galliumbromid seine katalytische Aktivität nach der Polymerisation beibehält, konnte letztlich eine Eintopfreaktion in zwei Schritten für die Herstellung von Polyethern aus zyklischen Estern durchgeführt werden. In einem zweiten Ansatz wurden mittels der gleichen Reduktion fettsäurebasierte *ω*,*ω*'-ungesättigte Dienether hergestellt. Die erhaltenen Monomere wurden mittels Thiol-En- oder ADMET- Reaktion polymerisiert und jeweils durch Oxidation oder Hydrierung nach der Polymerisation modifiziert. Um der Nutzen der Polyether in ihrer häufigsten Anwendung — der Herstellung von Polyurethanen — zu belegen und zudem noch Prinzipien der Nachhaltigkeit zu beachten, wurde die Umsetzung ihrer Hydroxy- zu Amin- Endgruppen untersucht, um Präpolymere für die Herstellung von isocyanatfreien Polyurethanen zu erhalten. Es konnte eine neue Methode zur Herstellung von Ester-Aminen mittels *ε*-Caprolactam etabliert und quantitativer Umsatz erreicht werden. Außerdem konnte ein nachwachsendes Comonomer, Erythritbis(carbonat), aus dem erneuerbaren Zuckerersatzstoff Erythrit durch Umesterung mit Dimethylcarbonat erhalten werden. Die Literaturmethode dieser Reaktion konnte signifikant hinsichtlich Temperatur, Druck, Reaktionszeit, Umsatz,

Einfachheit der Aufreinigung und Wiederverwertung der Reagenzien verbessert werden.

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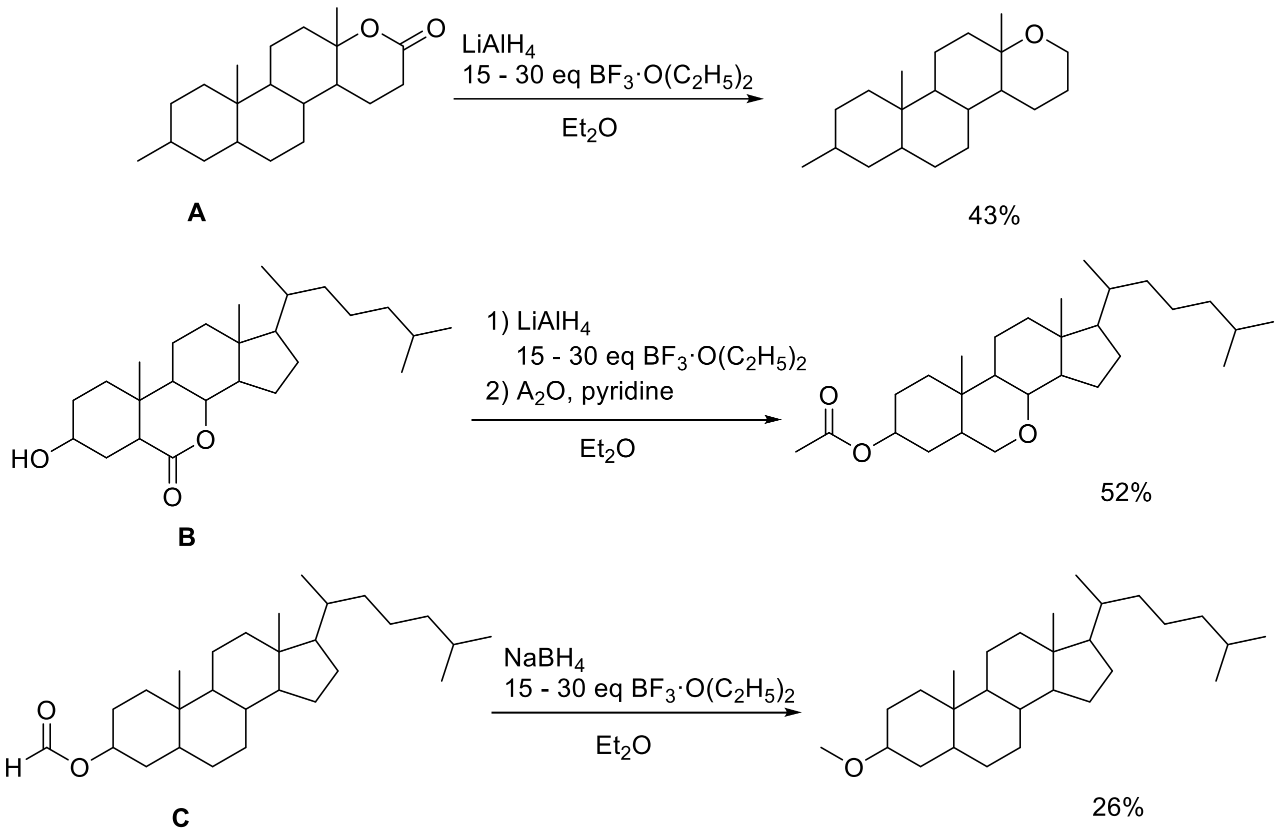
1 Introduction

Polyethers have numerous applications, for instance in material science for the production of segmented polyurethanes[1] or block copolymers,[2] in medical chemistry for drug delivery systems[3] or hydrogels as scaffolds for tissue engineering,[4] but also in most commercial water based products as surfactants, stiffening agents, antifoaming agents and many more.[5] However, their commercial production is limited to ring-opening polymerizations of epoxides or tetrahydrofuran, which severely limits the possible monomer feedstock. Currently, commercial polyethers are all based on more and more depleting fossil resources. The synthesis of renewable polyethers exhibiting more structural diversity would be of high interest. With regard to lower molecular weight organic ethers, J. O. Metzger *et al.* recently reported on a highly efficient reduction of esters to the corresponding ethers.[6,7] This quantitative transformation achieved high yields and exhibits several traits of sustainability as it can be run at room temperature, without solvent, the catalyst is used in very little amounts of less than 1 mol% and the reducing agent — albeit used in 10% excess — can be regarded as by-product of the silicon industry.[8] They applied this reduction mostly on derivatives of fats and oils, a renewable resource that exhibits one major advantage: With the breeding of new crops, unlike any other agricultural product, plant oils are chemically defined and available in high purity after simple extraction.[9] The synthesis of polymers derived from fats and oils was topic of intensive research during the last decade (discussed in section 2.5), although only very little focus was placed on polyethers derived from fats and oils. In contrast, many different routes for the synthesis of fatty acid derived polyesters were investigated, mostly with the aim of substituting polyethylene with long-chain aliphatic polyesters.[10] However, to date very little is known about long-chain aliphatic polyethers. Another focus in recent years was the synthesis of non-isocyanate polyurethanes (NIPUs). Polyethers are well known for their excellent properties as soft segment in polyurethanes, yet very little of their application in NIPUs is reported. The reason might be that the typical hydroxy-end groups of polyethers are not suited for NIPU synthesis and there are almost no suitable sustainable transformations of hydroxy- end-groups to NIPU compatible amine groups.

2 Theoretical background and state of the art

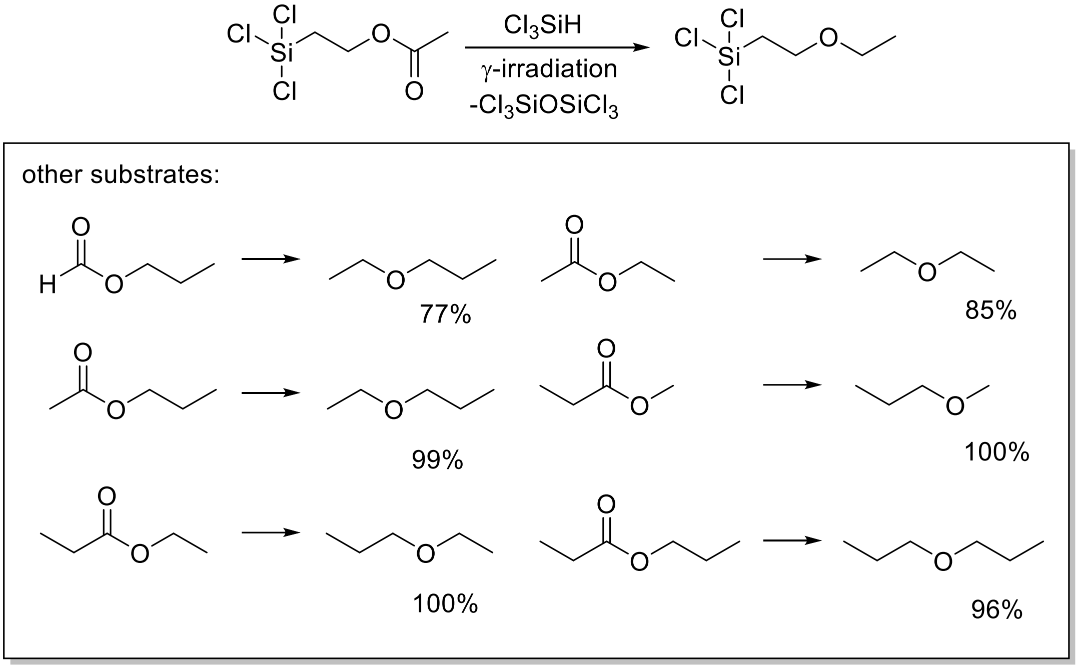
2.1 Reduction of esters to ethers

The reduction of esters to ethers is a comparably uncommon organic reaction, which dates back to 1960 and the reports of G. R. Pettit *et al.*.[11,12,13] Utilizing a large excess of boron trifluoride diethyl etherate, they were able to reduce the ester groups in several steroids to ether groups with the standard reducing agents $LiAlH_4$ or $NaBH_4$.



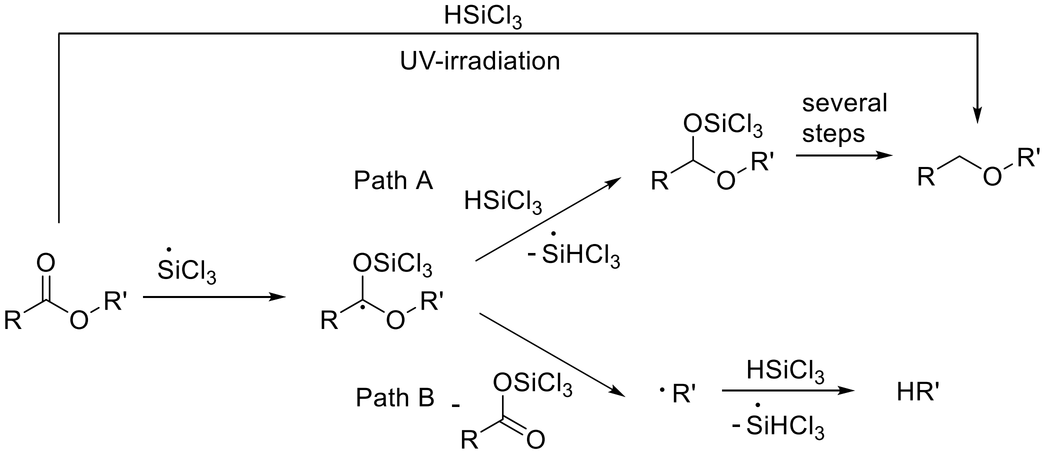
*Scheme 1: First reduction of an ester to an ether on steroids.[11,12] The reduction of the lactone in **B** is followed by an esterification with Ac_2O and only the total yield of the synthesis is given in literature.*

J. Tsurugi *et al.* reported on the reduction of esters with trichlorosilane under *γ*-irradiation in 1969 achieving quantitative yields (Scheme 2).[14] They expanded the concept to different lactones (*γ*-butyro-, *δ*-valero-, *ε*-capro-) and also substituted lactones achieving yields of up to 100%. *β*-Propiolactone could not be reduced to oxetane, which was ascribed to high ring-strain and ring-opening.[15] Similar conditions could be used to reduce acetals.[16] In fact, according to mechanistic studies on methyl acetate, intermediates of the reaction seem to be of acetal type. Thus, a free-radical chain mechanism *via* these intermediates was proposed.[17]



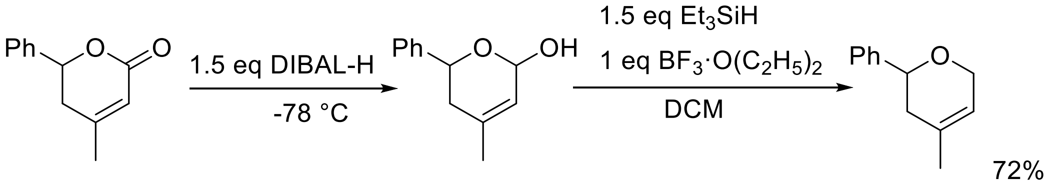
Scheme 2: *The reduction of esters with trichlorosilane under γ-irradiation by J. Tsurugi et al..*[14,16]

In 1975, S. W. Baldwin *et al.* reported on the UV-induced reduction of esters to ethers also utilizing trichlorosilane as reducing agent.[18] Their study revealed that a competitive reaction under these conditions is the formation of the deoxygenated alkane (Scheme 3), which is mostly controlled by the nature of R'. Primary acetates gave the lowest and tertiary acetate the highest amount of deoxygenation, yielding the respective alkane.



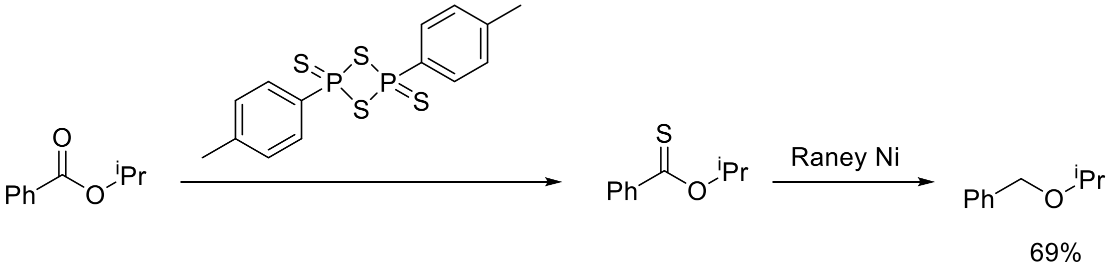
Scheme 3: Proposed mechanism for the reduction of esters to ethers via trichlorosilane and UV-irradiation and competing deoxygenation.[18]

In 1981, G. A. Kraus and coworkers reported on a two-step procedure for the reduction of lactones to ethers (Scheme 4).[19] In the first step, the lactone was reduced to the lactol, which was afterwards reduced to the ether with triethylsilane as reducing agent and stoichiometric amounts of borontrifluoride etherate achieving overall yields of different lactones in between 50 and 88%.



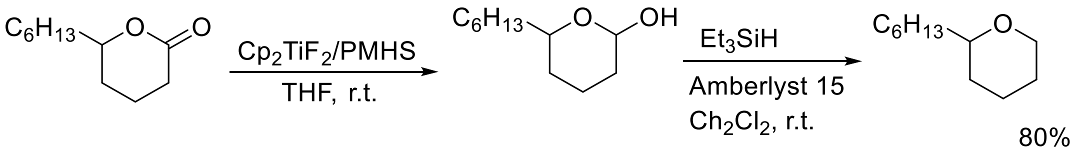
Scheme 4: Two step procedure for the reduction of lactones to ethers using DIBAL-H, triethylsilane and borontrifluoride etherate.[19]

Another two-step procedure was reported by J. S. Bradshaw *et al.* in 1981. In the first step, the ester is thionated using 2,4-bis (4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's Reagent) followed by desulfination with Raney nickel at -10 to -30 °C achieving yields between 6 and 69% depending on the substrate (Scheme 5).[20]



Scheme 5: Two-step procedure by J. S. Bradshaw et al. to synthesize ethers from esters using 2,4-bis (4-methoxyphenyl) -1,3,2,4-dithiadiphosphetane 2,4-disulfide followed by desulfination with Raney nickel.

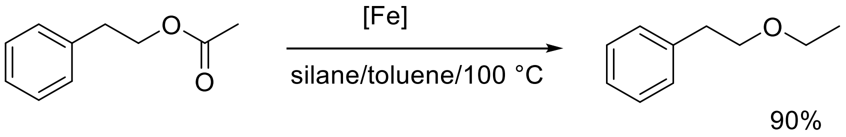
In 1995, A. R. Cutler *et al.* reported the first catalytic procedure on several different aliphatic, aromatic, linear, branched or cyclic esters to the respective ethers.[21] They utilized $PhSiH_3$ and 1.5 – 3 mol% of $(CO)_4MnC(O)CH_3$ catalyst and achieved yields between 5 and 96% depending on the substrate within less than 1h reaction time. Interestingly, only straight-chain esters yielded the corresponding ethers without any side products, while other esters gave mixtures of their ether and the alkoxysilanes. In 1998, another two-step procedure for lactones was reported by S. L. Buchwald *et al.* describing a reduction to the lactol first and to the cyclic ether, subsequently.[22] The initial step is catalyzed by titanocene difluoride (CP_2TiF_2) with polymethylhydrosiloxane (PMHS) as reducing agent. In the second step, the acidic Amberlyst 15 resin is added to a solution of the lactol and triethylsilane in dichloromethane achieving overall yields between 67 and 94% for different lactones.



Scheme 6: Two step procedure for the synthesis of cyclic ethers from lactones by S. L. Buchwald and coworkers.[22][22]

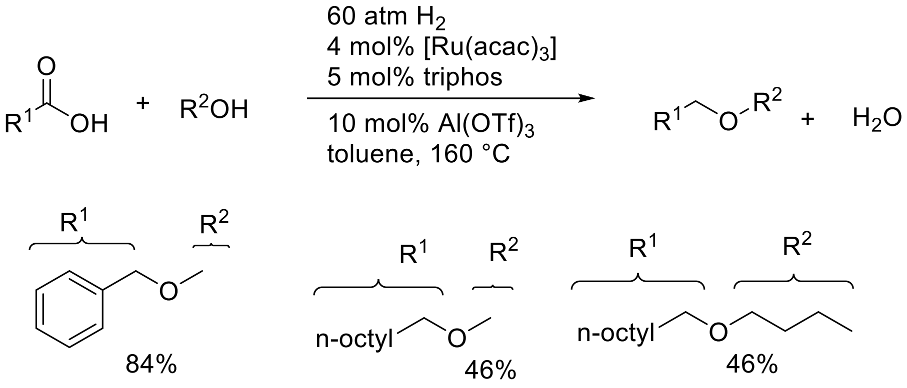
In 2001, K. Homma *et al.* utilized an excess of 3 eq silver trifluoromethanesulfonate (AgOTf), 3.0 eq trimethylsilyl trifluoromethanesulfonate (TMSOTf), 1.5 eq $TiCl_4$, and 5 eq Et_3SiH as reducing agent for the synthesis of several ethers from the respective esters in up to 89% yield. In 2002, H. Nagashima reported on a procedure utilizing only 1 mol% of (μ^3,η^2:η^3:η^5-acenaphthylene)$Ru_3(CO)_7$ as catalyst and $HSiMe_2Et$ as reducing agent to synthesize different aliphatic, aromatic, cyclic and acyclic ethers. The selectivity towards alcohol or ether of this procedure strongly depends on the substrates. Interestingly, also carboxylic acids or tertiary amides were reduced to alcohols or tertiary amines.[23] In 2007, the same group reported on the reduction of secondary amides with the same catalyst.[24]

In 2012, M. Beller *et al.* described $Fe_3(CO)_{12}$ as efficient catalyst for the reduction of esters to ethers using silanes as reducing agent (Scheme 7).[25] On the example of 2-phenylethyl acetate the type of catalyst, silane and solvent were optimized. Other iron salts and complexes apart from $Fe_3(CO)_{12}$, *e.g.* Zn(II)- and Cu(II)-based catalysts, did not give any conversion of the substrate. Other silanes (*i.e.* Ph_2MeSiH, Et_3SiH, PMHS or $(EtO)_2MeSiH$) gave no or significantly less yield than TMDS. In terms of solvent, dioxane gave only 61% yield, while *p*-xylene gave, similarly to toluene, 90% yield. By variation of the substrate, 19 aromatic or aliphatic esters could be reduced and in none of the cases alcohol formation was observed. Already in 2009, the same group utilized this catalyst to reduce tertiary carboxamides to tertiary amines.[26]



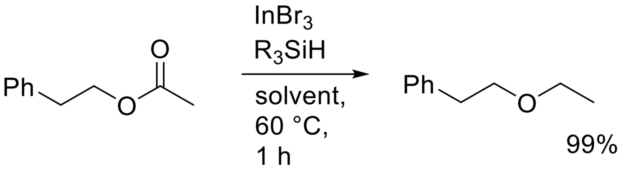
Scheme 7: Catalytic reduction of esters to ethers with silanes catalyzed by an iron catalyst.[25]

In 2015, the same group reported a major breakthrough as they applied hydrogen as reducing agent and directly coupled carboxylic acids with alcohols and reduced them in a one-pot procedure to the ethers (Scheme 8).[27] Moreover, a direct application on various aliphatic and aromatic lactones, linear esters, and one diester in the presence of a dual Ru-Al catalyst system was possible. The reactivity order was observed to be aliphatic γ-lactones > aliphatic *δ*-lactones > aromatic *γ*-lactones ≫ linear esters.



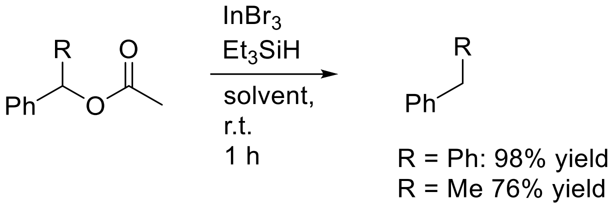
Scheme 8: Direct reductive coupling of ester and primary alcohols by M. Beller and coworkers.[27]

In 2007, N. Sakai *et al.* reported on the catalytic reduction of esters using $InBr_3$ as catalyst.[28] On phenethyl acetate as model compound, they compared different reaction conditions (Scheme 9). In terms of solvent, they concluded that chloroform gives a better yield than benzene or toluene, while in THF or acetonitrile no or very low conversion can be observed. Other indium salts such as $InCl_3$, $In(OTf)_3$ or $In(OAc)_3$ gave no conversion. Et_3SiH was most efficient as reducing agent, while $PhMe_2SiH$ gave slightly lower conversion and $(EtO)_3SiH$ gave almost no conversion.



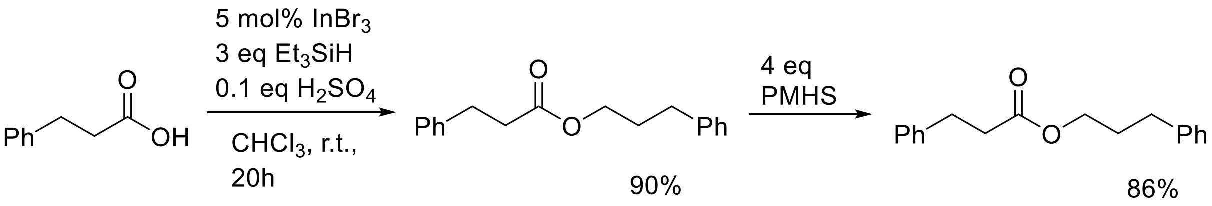
Scheme 9: Catalytic reduction of esters to ethers with $InBr_3$ as catalyst.[28]

Interestingly, if the reaction of secondary acetates was carried out at room temperature, deacetoxylation of the starting material took place forming either diphenylmethane or ethylbenzene (Scheme 10). Additionally, other carbonyl compounds were examined for the reduction. Thioacetate or amides did not yield the desired sulfide or secondary amine. However, tertiary amides could be reduced to form a tertiary amine in up to 90% isolated yield.[29] Moreover, ketones condensed to the symmetrical ether product in 88% yield. Carboxylic acids underwent reduction to the alcohol in 32% yield along with the silyl ether product. In 2011, this procedure could be improved to yield up to 99% of the alcohol.[30] Aromatic carboxylic acids could be reduced to the alcohol. However, they underwent a reductive substitution with other aromatic compounds to produce diphenylmethanes.



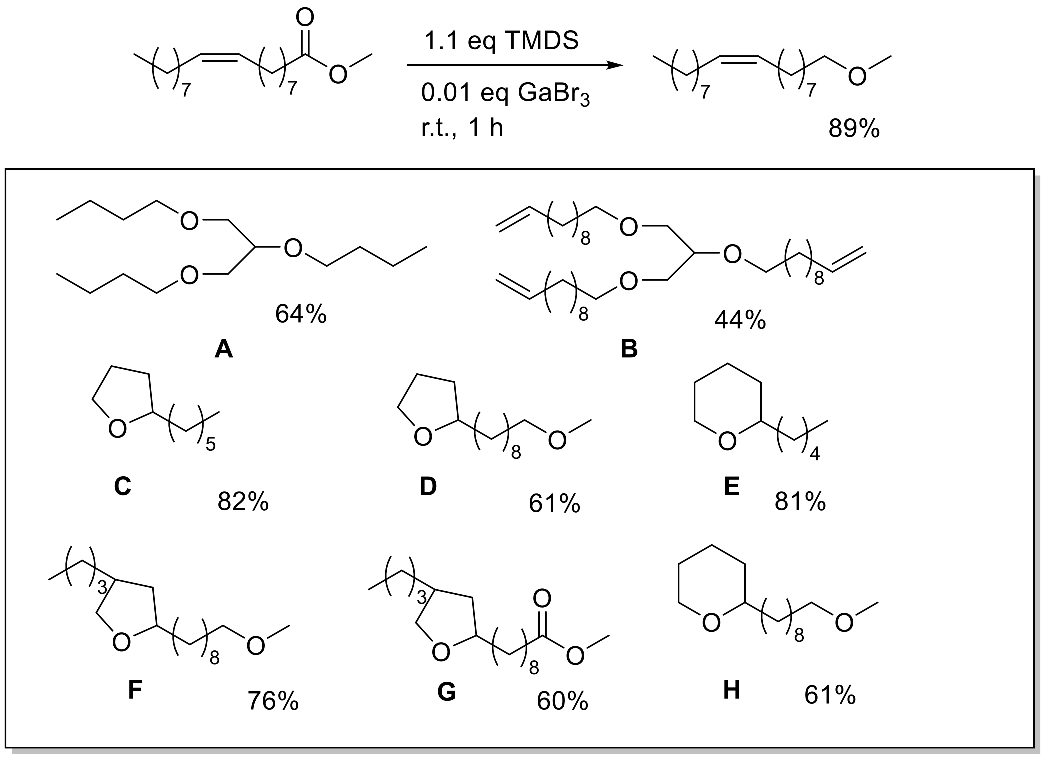
Scheme 10: Deacetoxylation of the ester instead of reduction to the ether.[30]

In 2011, another interesting approach from the same group was the reductive esterification by a combination of catalysts involving $InBr_3$ and sulfuric acid as well as Et_3SiH as reducing agent (Scheme 11).[31] In a second step, without purification PMHS could be added to the mixture directly reducing the ester to the symmetric ether. The utility of this approach was expanded in 2012 by several substrates.[32]



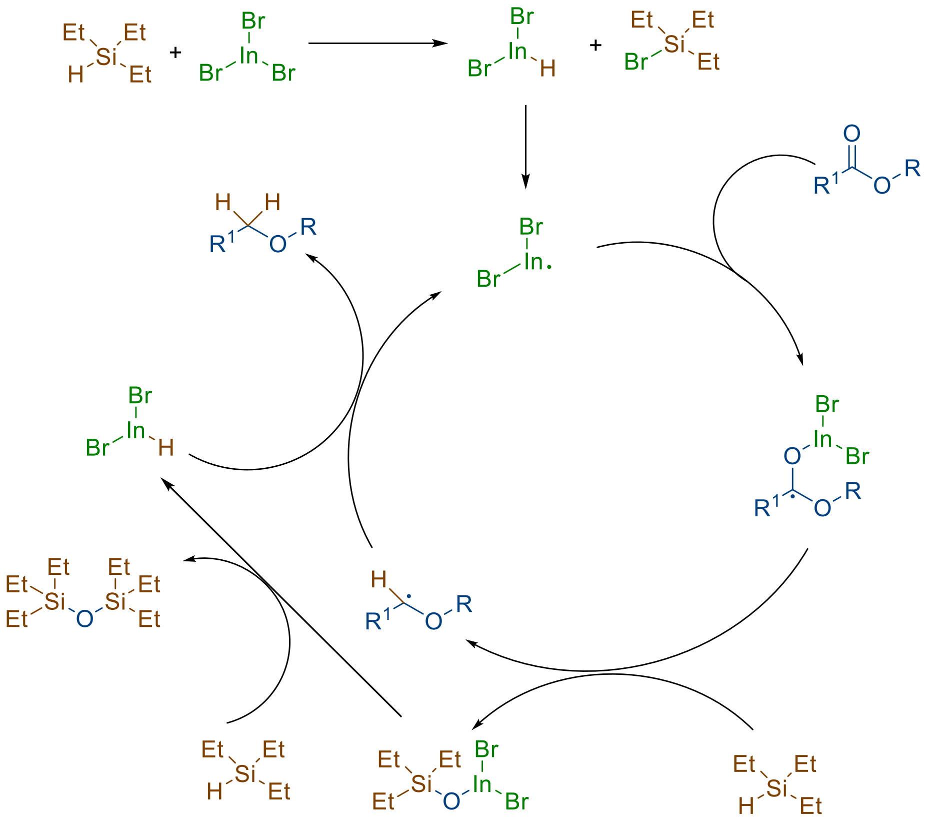
Scheme 11: Reductive esterification catalyzed by $InBr_3$ with Et_3SiH as reducing agent and H_2SO_4 as promoter.[31][31]

In 2014, J. O. Metzger *et al.* reported on the catalytic reduction of high oleic sunflower oil to glyceryl trioleyl ether utilizing $GaBr_3$ or $InBr_3$ as catalyst and TMDS as reducing agent. There were several significant improvements compared to the procedure of N. Sakai *et al.* and M. Beller *et al.*. Instead of 60 °C or 100 °C reaction temperature and chloroform or toluene as solvent, the reaction was performed at room temperature without solvent. The catalyst concentration in the previous procedures was 5 mol% $InBr_3$ or 10 mol% $Fe_3(CO)_{12}$ and could be lowered to 0.5 – 1 mol% $GaBr_3$ per ester group still reaching quantitative conversion after stirring at room temperature or slightly elevated temperatures after 30 minutes. Only about 7 % of the side reaction to oleyl alcohol could be observed, compared to 20 % when using $InBr_3$. The reaction could be expanded to several other cyclic or acyclic substrates (Scheme 12).[6] The reduction of the lactone moiety was preferred compared to a linear ester, which could be observed by employing substochiometric amounts of reducing agent (Scheme 12, example **G**).



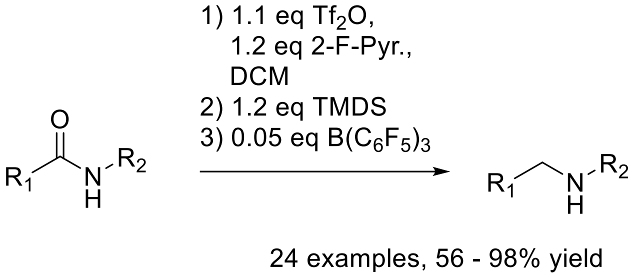
Scheme 12: GaBr₃ catalyzed reduction of esters to ethers with TMDS as reducing agent.[6]

The mechanism of the reduction with InBr₃ was proposed in 2007 by N. Sakai and coworkers, however no conclusive evidence was provided yet (Scheme 13).[28]



Scheme 13: Proposed mechanism of the InBr₃ catalyzed reduction of esters to ethers by Sakai et al.[28]

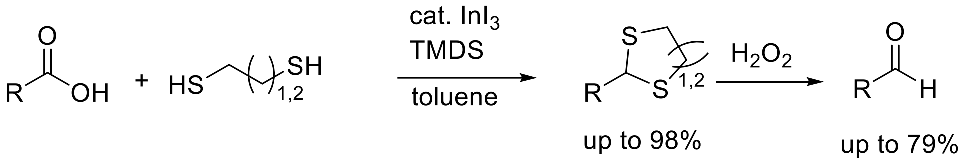
First, a transmetalation between Et_3SiH and $InBr_3$ takes place, followed by radical formation and subsequent abstraction of hydrogen by the radical intermediate and formation of the ether product. The $InBr_2$-radical species is finally regenerated and can react with another ester molecule. Apart from the reduction of esters to ethers, the (metal) catalyzed reduction with silanes has many other applications on different types of substrates. In 2016, P.-Q. Huang *et al.* reported on the one-pot catalytic reduction of amides to secondary amines activated by triflic anhydride, catalyzed by tris(pentafluorophenyl)boron with TMDS as reducing agent (Scheme 14).[33]



Scheme 14: One-pot catalytic reduction of amides to secondary amines using TMDS as reducing agent. Tf_2O = triflic anhydride, 2-F-Pyr. = 2-fluoropyridine, $B(C_6F_5)_3$) = tris(pentafluorophenyl)boron.

Tris(pentafluorophenyl)boron was already reported in 2014 simultaneously by A. Adronov *et al.*[34] and T. Cantat *et al.*[35] to be catalytically active in the reduction of secondary, tertiary, and even primary *N*-phenyl amides with TMDS. In 2016, Y. Motoyama *et al.* reported that tertiary carboxamides can effectively be reduced by TMDS utilizing simple commercial palladium on carbon (Pd/C) as catalyst achieving up to 99% yield.[36] Secondary amides could not be reduced with this catalyst system. H. Adolfsson *et al.* reported on $Mo(CO)_6$ being able to also reduce secondary amides. The reaction could be controlled to give the respective aldehydes at lower temperatures and tertiary amines at higher temperatures.[36] In 2015, N. Sakai *et al.* utilized InI_3 and could show the effectiveness of the transformation on 27 examples of secondary amides, which were reduced to the secondary amines. Reexamination of their earlier results from 2007 revealed, that the transformation is also possible with $InBr_3$, however yields are much lower.[37] Several other catalytic systems are available for the reduction of amides to amines utilizing silanes as reducing agent and were reviewed in 2015 by H. Nagashima.[38]

In 2017, N. Sakai *et al.* reported on the reductive dithioacetalization with InI_3 and TMDS followed by oxidative desulfurization.[39]



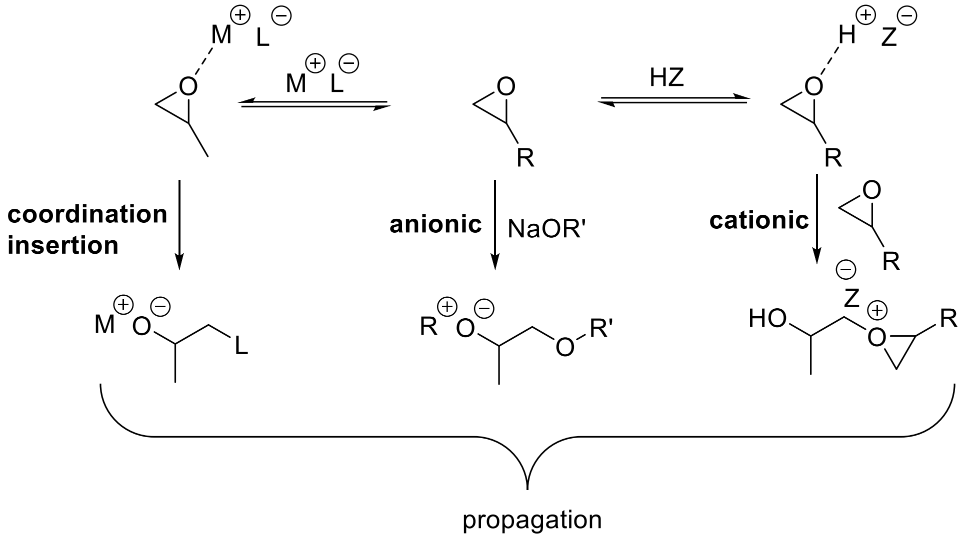
Scheme 15: InI_3 catalyzed one-pot reductive dithioacetalization with InI_3 and TMDS followed by oxidative desulfurization.[39]

The same group reported on the synthesis of symmetric thioethers from aldehydes employing elemental sulfur and TMDS as reagents and InI_3 as catalyst.[40,41] Moreover, the InI_3/TMDS system could be applied to reduce nitrobenzenes to anilines, as shown on 22 examples[40] and on the reductive monoalkylation of electron-rich benzenes with aliphatic carboxylic acids and molecular iodine.[42] Many other types of reduction can be realized with TMDS and different catalysts, which was reviewed by G. L. Larson *et al.* in 2016.[43]

.

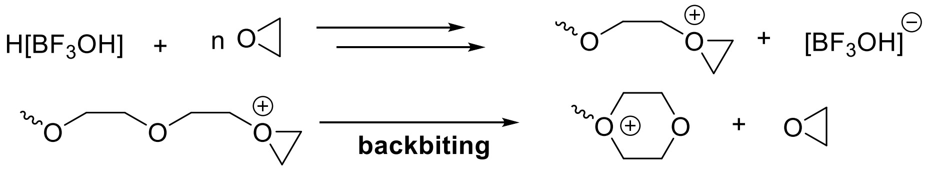
2.2 Polyethers

Polyethers constitute a widely known class of polymers with their main representatives being poly(ethylene oxide), PEO; poly(propylene oxide), PPO; and poly(tetramethylene oxide), PTMO. PEO and PPO are available in a broad range of molecular weights up to several million g mol^{-1} and change in their physical properties from liquids to soft waxes and even to thermoplastic, tough materials at high molecular weights. The hydroxy end groups of typical polyethers offer much potential for further chemical modification or polymerization, *e.g.* in segmented polyurethanes in which they usually form the “soft segment”. Other functional groups such as isocyanate,[44] vinyl,[45] allyl or propenyl esters,[46] carboxyl,[47] amine,[48] azide,[49] or thiol[50] can be introduced by termination of the polymerization or post-polymerization modification with different moieties. Isocyanate-terminated polyethers are marketed as Adiprene (Du Pont) and Vibrathane (Uniroyal) precursors for curing polyols to produce elastomers.[5] A very unique behavior in terms of solubility can be observed for PEO, which is in contrast to other polyethers is highly water-soluble in practically all concentrations and exhibits very low immunogenicity, antigenicity and toxicity. An explanation for this feature is the unique distances of the oxygen atoms, which can result in a specific coupling and chain packing in a tetrahedral coordination.[51] Polyethers are typically obtained *via* or coordination insertion, anionic, cationic or activated monomer ring opening polymerization (ROP) from epoxides (Scheme 16). The mechanism of anionic ROP was first established 1940 on the example of PEO by P. J. Flory predicting a Poisson-type distribution for a living chain-growth process.[52,53] For anionic polymerization of propylene oxide and higher alkylidene oxides an elimination side reaction from the methyl group and consequently chain transfer to the monomer limits the achievable molecular weight with highly basic initiator systems. This side reaction can be overcome to a great extent by employing caesium alkoxides or counterion complexation with crown ethers and keeping the reaction temperature low.[53] Cationic polymerization plays an important role for PTMO, since, generally four-membered cyclic ethers polymerize by the cationic mechanism only.[53] For PEO and PPO cationic polymerizations are rarely used due to the backbiting mechanism of the active oxonium ion shown in Scheme 17 on the example of PEO. The intramolecular nucleophilic attack of an oxygen atom competes with the intermolecular attack of the oxygen atom in the cyclic monomer leading to the formation of 1,4-dioxane or crown ether structures as side product.



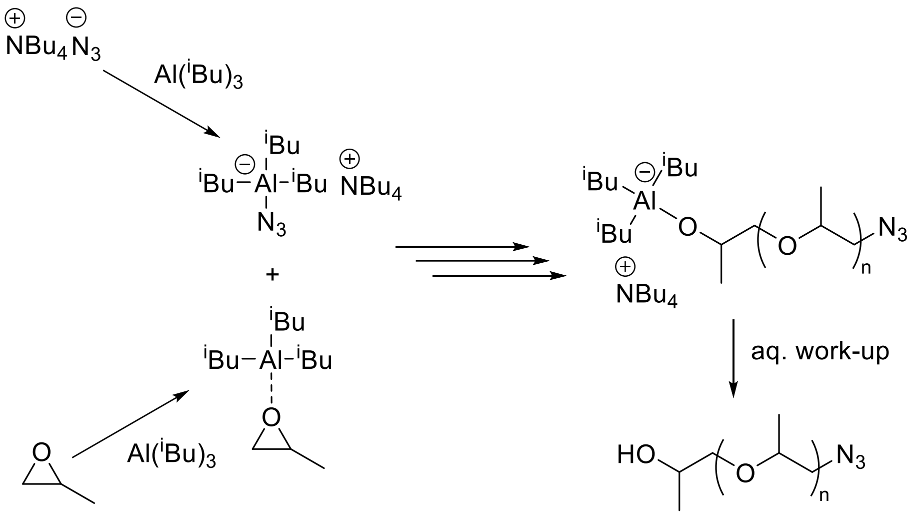
Scheme 16: Different types of initiation of the ring-opening polymerization of epoxides.[5]

The presence of alcohols as initiators leads to the "activated monomer" mechanism and backbiting can mostly be avoided as the active center (*i.e.* positive charge) is located on the monomer instead of the polymer chain.[53]



Scheme 17: Backbiting mechanism in cationic ring-opening polymerization of ethylene oxide.[53]

Utilizing Lewis acids instead of Brønsted Acids leads to the formation of an "ate complex" between the Lewis acid (catalyst, $^{i}Bu_3Al$ in Scheme 18) and a weak nucleophile (initiating species, NBu_4N_3 in Scheme 18).[53,54] Note that the Lewis acid to initiator ratio must be more than one to implement an activation of the monomer and additional formation of the "ate" complex.[53] The coordination insertion polymerization is — similarily to the activated monomer mechanism — utilizing a metal, that exhibits Lewis acidity to activate the monomer (*e.g.* Ca, Zn, and Al) with the only difference that the initiator is not added separately and stems from the ligands (*e.g.* alkoxides) of the metal-complex.[55] Polymerization of propylene oxide and longer 1,2-alkylidene oxides results in two different modes of ring-opening and three kinds of monomer unit connections (head-to-tail, head-to-head, tail-to-tail). Due to steric reasons, anionic polymerization largely results in head-to-tail connections, whereas irregular combinations of head-to-tail, head-to-head and tail-to-tail linkages are obtained by cationic polymerization. To achieve high stereoselectivity numerous metal catalysts have been investigated focusing mostly on the porphyrin, calixarene or salen complexes of aluminum, zinc, iron and cobalt.[53]

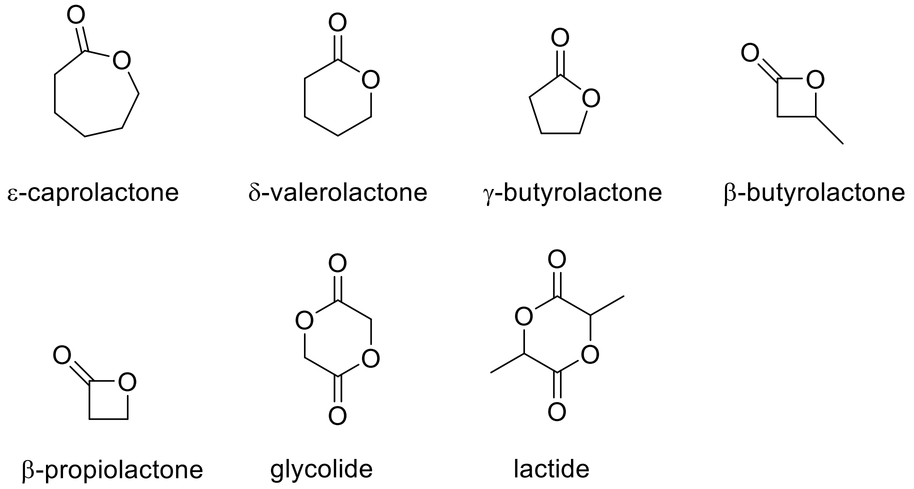


Scheme 18: Activated-monomer mechanism of the polymerization of propylene oxide with tetrabutylammonium azide (NBu_4N_3) as initiator and trisisobutylaluminum ($Al(^iBu)_3$) as catalyst.[49,53,54]

PEO was already obtained as early as 1863 by C.-A. Wurtz utilizing alkali hydroxides or zinc chloride.[53,56] In 1930, it was commercialized based on the addition of EO to ethylene glycol under basic conditions and within the 1940s wide applications were developed ranging from surfactants, adhesives, lubricants to pharmaceutics and prepolymers for polyurethane foams. The name poly(ethylene glycol) is typically used for lower molecular weight polymers below 30 kDa while for higher molecular weights the polymer is referred to as PEO or poly(oxyethylene) (POE).[53] Various copolymers of ethylene oxide and propylene oxide have been synthesizes in random, block, and graft form.[57] Random copolymers can be prepared from mixtures of monomers, while block copolymers are prepared by alternately feeding the two monomers.[5] ABA block copolymers can be easily prepared by letting *e.g.* poly(1-propline)[58] or poly(ε-caprolactone)[59] grow from hydroxyl-terminated PEO. Polyethers are susceptible to autooxidation and form hydroperoxides similar to typical small organic molecule ethers (*i.e.* diethyl ether or tetrahydrofuran). Hence, heavy metal ions, strong acids, and ultraviolet light leads to degradation of the polymer chain.[60]

2.3 Ring-Opening Polymerization of Cyclic Esters

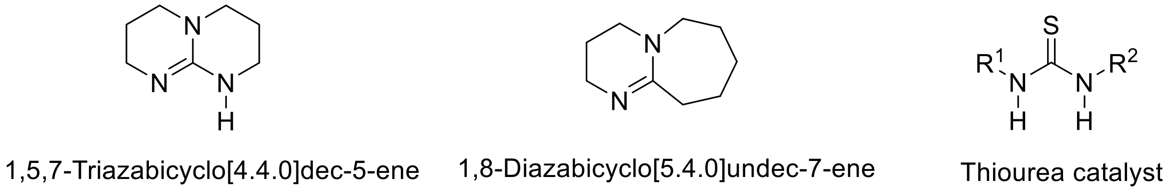
In comparison with polycondensation, ring-opening polymerization of cyclic esters (lactones) has smaller choice of monomer feedstock, thus providing less variety in its range of functional polymers. However, in return it offers a high degree of control of the average molecular weight of the obtained polyester, since ROP displays many of the characteristics of a living polymerization and typically higher molecular weights are achievable. Moreover, a high degree of end-group control is possible and block copolymers are accessible by chain extension.[61] Similarly to epoxides ROP of lactones can proceed *via* coordination insertion, anionic, cationic or activated monomer ring opening polymerization. The competition of pure cationic (active chain-end) and activated monomer (cationic) ring opening polymerization was investigated by M. A. Hillmyer on the example of 2-methyl-1,3-dioxan-4-one. Without external initiator, the polymerization proceeding *via* active chain-end gave similar backbiting side reaction as they can be observed for the cationic polymerization of epoxides.[62] Typical commercial monomers for ROP of lactones are *ε*-caprolactone, *δ*-valerolactone, *γ*-butyrolactone, *β*-butyrolactone, *β*-propriolactone, glycolide and lactide (Scheme 19).



Scheme 19: Commercial lactone monomers available for ROP.

The thermodynamic polymerizability of lactones is strongly related to their ring-size. While the ROP of 3 – 14 membered rings is enthalpically favored, which is related to their ring-strain, it is entropically disfavored, which means that both standard state enthalpy and entropy are negative and the ratio of the two is proportional to the ceiling temperature (T_C).[63] Due to low ring-strain, *δ*-valerolactone and *γ*-butyrolactone are nearly incapable of polymerization under typical conditions. Substituted *δ*-valerolactones exhibit actually more ring-strain than their unsubstituted counterpart, which is suspected to be largely because of unfavorable interactions between the alkyl substituents and hydrogen atoms across the ring (transannular strain). However, their polymerization is typically 2 – 3 times more entropically disfavored, which leads to a lower ceiling temperature than for unsubstituted lactones.[63] For good polymerizability of *δ*-valerolactone, an *α*-substituent has the least entropically unfavorable impact on the polymerization. For substituents in *δ*-position it was additionally observed that polymerization rates are typically much lower than for monomers with substituents in other positions or the unsubstituted monomer, which was ascribed to a lower reactivity of the propagating secondary alcohol.[63] For substituted *ε*-caprolactone monomers less extensive studies of the effect of alkyl substituents have been performed, however in principle similar results are to be expected.

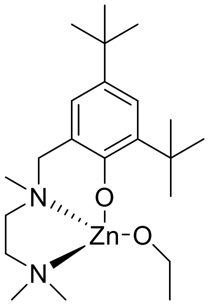
Kinetic polymerizability and polymerization rates are not necessarily linked to thermodynamic parameters and mostly dependent on the catalyst used. Apart from traditional transesterification catalysts as *e.g.* Sn(Oct)$_2$, modern organocatalysts such as 1,8-diazabicycloundec-7-ene (DBU) became increasingly popular as they are easy to use and highly active (Scheme 20).[64] However, despite being able to catalyze the polymerization of lactide, DBU has shown to be inactive for polymerization of *ε*-caprolactone and *δ*-valerolactone or large ring lactones such as *ω*-pentadecalactone.[65] The combination of a thiourea derived cocatalyst (Scheme 20) and DBU promotes the reaction rate by dual activation of monomer and initiator and polymerizations finally enabling these transformations.[64] Moreover, a thiourea catalyst was designed, in which another amine moiety is included having the dual catalysis within one molecule.[66]



Scheme 20: Common organocatalysts active in transesterifications.

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) is also able to undergo a dual-activation by itself and performs well for these transformations without additives.[65] The sterically hindered *δ*-decalactone could be polymerized utilizing TBD as catalyst achieving average molecular weights up to $M_n = 80{,}000\ \mathrm{g\ mol^{-1}}$ ($Đ_M = 1.20$) at room temperature.[67] However, when using TBD in the ROP of small ring lactones the polymerization is hard to control as it proceeds within seconds and transesterifications are taking place at high conversions.[64]

For the polymerization of ε-caprolactone, a variety of catalysts have been reported, based on metal complexes of *e.g.* aluminium,[68–70] titanium,[71] or enzyme catalysis.[72] The polymerization of 6-methyl-ε-caprolactone, which can be obtained by Baeyer-Villiger oxidation of 2-methylcyclohexanone, has been reported using tin,[73,74] aluminum,[68] and enzymatic catalysts,[75] achieving high molecular weights of up to 150,000 g mol^{-1} and narrow dispersities of less than 1.2.[73] Sterically even more demanding substrates, such as *(−)*-menthide (isopropyl substituent)[76] or carvomenthide (methyl substituent),[77] were polymerized obtaining molecular weights up to 91,000 g mol^{-1} using a Zn alkoxide (Scheme 21) or diethyl zinc catalyst, respectively. The combination of Lewis acids and base dual catalysis — even though widely exploited in organic chemistry — was rarely explored for ROP of lactones in polymer chemistry until recently.[78,79] Examples for earlier reports are the polymerization of lactide with aluminium isopropoxide/4-picoline,[80] $Sn(Oct)_2$/4-picoline,[81] NHCs/$SnCl_2$,[82] NHCs/$Ti(Cl)(OPri)_3$,[83] $NEt_3/InCl_3$ (described in detail below),[84,85] [Zn^{2+}]/PMP (Zn-catalyst shown in Scheme 21),[86] $Zn(C_6F_5)_2$/PMP.[87] A. P. Dove *et al.* investigated several Lewis acid-Base combinations and revealed an order of activity of $MgX_2 \gg YCl_3 \gg AlCl_3$ and $MgI_2 > MgBr_2 > MgCl_2$ for the investigated Lewis acids.[78]



Scheme 21: Novel Zn-complex highly active for ROP.

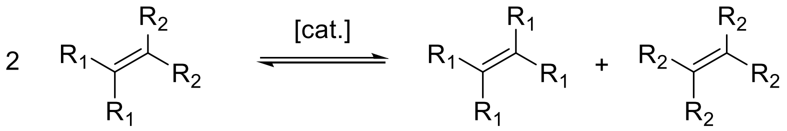
Group III metals have been extensively studied for ROP of lactones. Especially alkoxide complexe are effective catalysts for ROP of a variety of cyclic esters.[88] It has been revealed that an electronegative bromine substituent on the supporting ligands retards the overall reaction rate.[89] Even though stronger Lewis acids increase the reactivity of the monomer, they might also form a stronger binding to the growing alkoxide chain retarding transfer of the alkoxide to the carbonyl of the monomer.[70]

Other aluminium catalysts have been developed, mostly as complexes with ligands such as the salen ligand.[90] In recent years, also indium-,[91,92,92,93,93,94] and to a lesser extent gallium-complexes[94,95] received attention for ROP. In 2010, W. B. Tolman *et al.* utilized a catalytic system prepared *in situ* from $InCl_3$ or $InBr_3$, benzyl alcohol, and triethylamine to polymerize lactide.[84] Interestingly, as they replaced $InCl_3$ with $GaCl_3$ or $AlCl_3$ no polymerization occurred. Utilizing 3-diethylamino-1-propanol instead of benzyl alcohol, and triethylamine led to a high degree of stereoselectivity from a mixed *D,L*-lactide feedstock. In the absence of benzyl alcohol, InX_3, or NEt_3, polymerizations did not proceed indicating that the catalytic species is derived from all three components. Employing the same catalyst system on *ε*-caprolactone instead of lactide, M_n = 32,000 g mol^{-1} ($Đ_M$ = 1.16) could be achieved after 24 h reaction time with an initiator : monomer ratio of 1 : 100. For the polymerization of 6-methyl-ε-caprolactone, a higher temperature of 60 °C instead of room temperature was necessary to achieve M_n = 20,200 g mol^{-1} ($Đ_M$ = 1.30) applying the same conditions as for ε-caprolactone.[85] P. Mehrkhodavandi *et al.* synthesized various aluminum, gallium and indium complexes with salen and other ligands and compared their activity to the $GaCl_3$/BnOH/NEt_3 three-component system.[96] In their study they revealed that gallium complexes are far less active in polymerizations than their indium analogues, although they revealed that indium halide complexes are less Lewis acidic than their aluminum and gallium analogues.[96] This result fits well with the results on alkoxides with different Lewis acidities mentioned above. Moreover, in contrast to the $InCl_3$/BnOH/NEt_3 system, they could also detect no activity of the $GaCl_3$/BnOH/NEt_3 system for the polymerization of lactide after several days reaction time at room temperature.

2.4 Metathesis

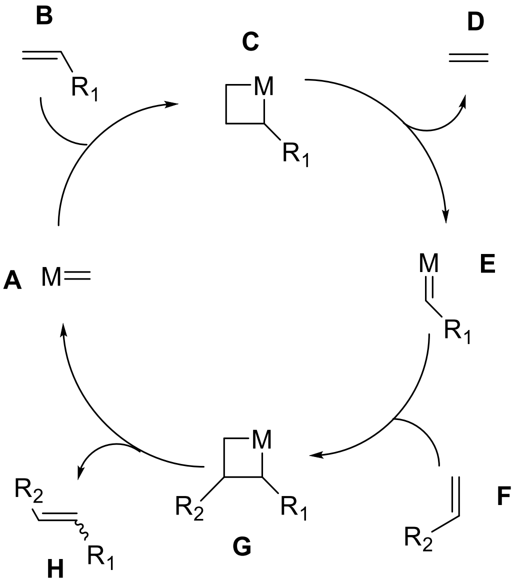
2.4.1 Mechanism and catalysts

One major challenge in organic synthesis is the formation of carbon–carbon bonds. Out of the many techniques available in that area, olefin metathesis is among those with the most utility and universality.[97] The importance of olefin metathesis is reflected by the 2005 Nobel Prize to Grubbs, Schrock, and Chauvin for their pioneering work in this area.[98] The word metathesis is derived from the Greek word “μετάθεσις” and means “change places”. Olefin metathesis can formally be regarded as the exchange of the two “carbenes” of an olefin with those of another olefin molecule (Scheme 22), a principle which can be extended to the exchange of the “carbynes” of alkyne molecules.[97]



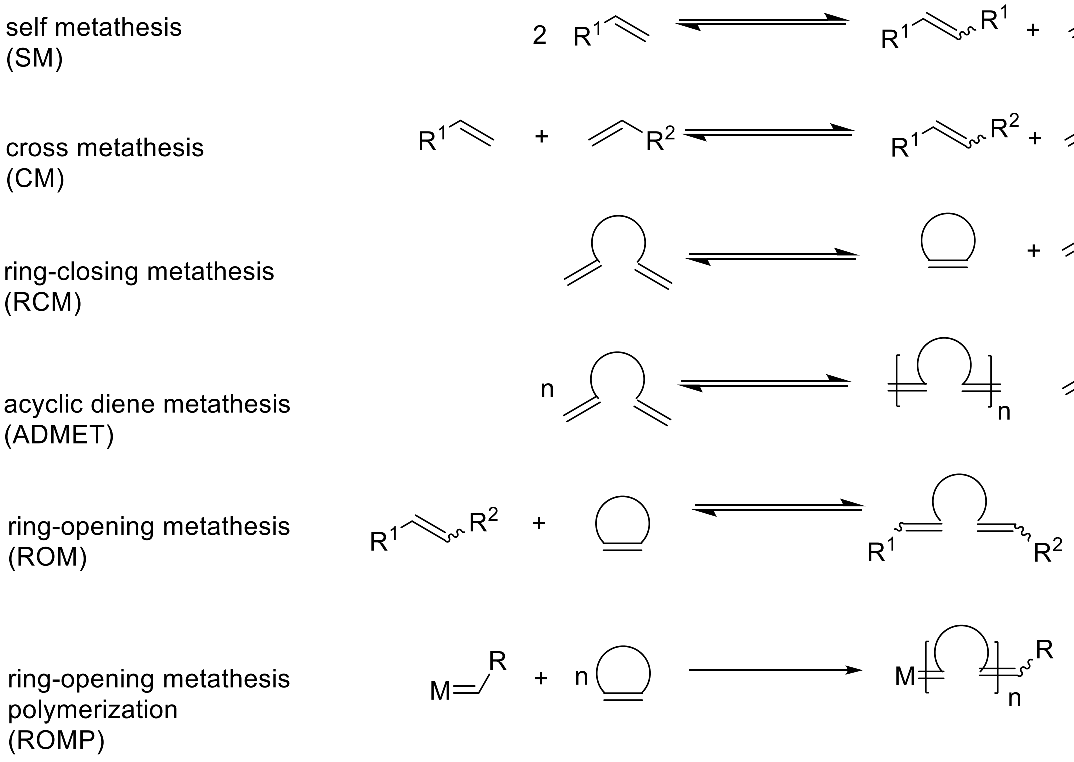
Scheme 22: General scheme of metathesis reactions.[97]

The mechanism of olefin metathesis was proposed by Chauvin and his student Hérisson and published in 1971.[99,100]



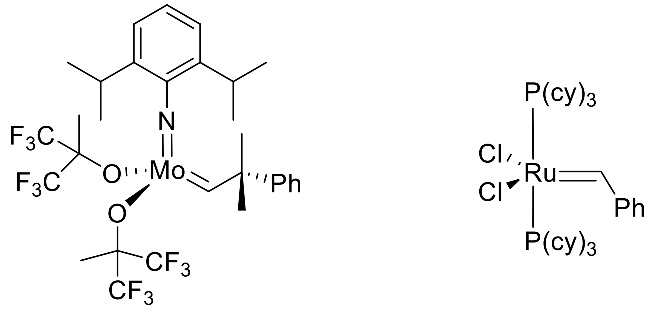
Scheme 23: Cyclic representation of the Chauvin mechanism in a cross metathesis reaction.[99,100] All steps are reversible (not explicitly shown).

The mechanism involves a metal–carbene species ***A*** (Scheme 23), the coordination of an alkene ***B*** onto the metal atom (not shown), followed by the formation of a metallacyclobutane intermediate ***C***, and finally the resolution of the metallacyclobutane. This releases an olefin ***D*** and forms a new metal-alkylidene ***E***, which can again react with an olefin ***F*** to metallacyclobutane ***G*** releasing olefin ***H*** to form metal–carbene ***A***.[97] Commonly six different types of metathesis reactions are distinguished (Scheme 24). Intermolecular reactions of two noncyclic olefins are described as self-metathesis (SM) or cross metathesis (CM). Dienes can react inter- or intramoleculary giving either cycles (ring-closing metathesis, RCM) or polymers (acyclic diene metathesis, ADMET), which depends mostly on the concentration of the reactants. By the removal of possible volatile side products (typically ethylene) the reaction equilibrium can be driven towards the desired product. The reversal of RCM in the presence of a second acyclic olefin is typically driven by the release of ring-strain and called ring-opening metathesis (ROM). Without a second acyclic olefin the ring-opening results in a chain-reaction and the formation of polymers (ring-opening metathesis polymerization - ROMP).[101]



Scheme 24: Different types of metathesis reactions.[97]

Early metathesis reactions were based on catalysts such as $M(CO)_6$ (M = Mo or W) (1956), or heterogeneous catalysts as Re_2O_7 on alumina or silica (1964) until Schrock synthesized the first isolated metal–alkylidene complex, $[\mathrm{Ta{=}CH{}^{t}Bu(CH_2{}^{t}Bu)_3}]$ (1974).[98] Grubbs identified the first unimolecular ruthenium–carbene metathesis catalyst $[\mathrm{Ru{=}\ CHPh(PR_3)_2Cl_2}]$ in 1992. Until now, many further advancements were made. The most basic differentiation in homogeneous metathesis catalysis is between Schrock type catalysts and Grubbs-type catalysts.[98] Schrock catalysts are typically molybdenum and tungsten–alkylidene complexes in a pseudotetrahedral geometry of the general formula $[\mathrm{M({=}CHCMe_2Ph)(N{-}Ar)(OR_2)}]$. R and Ar are bulky groups controlling the electron density at the metal center M, which is either Mo or W (example in Figure 1). The absence of a proton at the *β*-carbon of the carbene prevents deactivation *via β*-elimination. Moreover, due to the provided steric hindrance by the ligands, bimolecular decomposition is avoided. They are considered 14-electron complexes as the imido ligand donates its electron pair to the metal center to form a pseudo triple bond. As a result, due to their electron deficient character, these complexes are air and moisture sensitive.[102] Grubbs type catalysts are typically ruthenium based 16-electron carbene complexes. The most prominent example $[\mathrm{Ru({=}CHPh)Cl_2(PCy_3)_2}]$ (Figure 1) is known as the first-generation Grubbs catalyst (**G-I**) and even today it is the metathesis catalyst most used by organic chemists.[97]

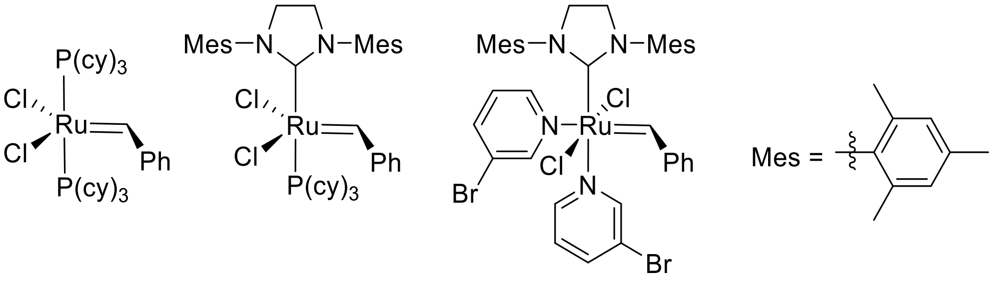


Prototype of Schrock's catalysts

Grubbs 1st generation catalyst

*Figure 1: Most prominent examples of Schrock's catalysts (1990) and the Grubbs 1st generation catalyst (**G-I**).*

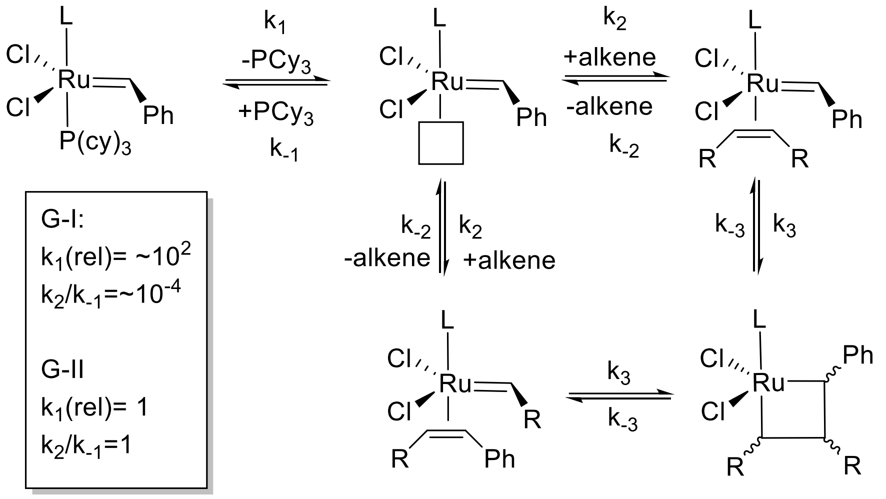
Comparing Schrock type catalysts with Grubbs type catalysts, both types have their own advantages and disadvantages concerning catalytic activity, selectivity, functional group tolerance and stability. In a very general consideration, Schrock catalysts have an advantage regarding the activity due to their high reactivity. The selectivity (*e.g.* E/Z) is highly dependent on specific substrate catalyst interactions and the type of metathesis reaction, thus generalizations are difficult to make. Still, since in tungsten and molybdenum imidoalkylidene catalysts the attached ligands do not dissociate from the tetrahedral metal center during the catalytic cycle, precise control of activity and selectivity of the catalyst is possible. Although Schrock catalysts are already remarkably versatile, ruthenium-based catalysts have an advantage regarding functional group tolerance. Schrock catalysts are compatible with ethers, epoxides, acetals, ketones, esters, secondary and tertiary amines, amides, carbamates, silanes, sulphides and disulphides. They do not tolerate carboxylic acids, aldehydes, most alcohols and primary amines.[102] In addition, their widespread use is limited due to their sensitivity to moisture and oxygen. In sustainable chemistry using renewable resources, it is often difficult to guarantee a highly pure feedstock and Grubbs catalysts might be better suited for this type of application. During the last decades, starting from the Grubbs 1st generation catalyst several improvements were made, although the basic structure still resembles the original complex. Arguably one of the most significant improvements was made by Grubbs in 1999, substituting one of the tricyclohexylphosphine ligands with the bulky *N*-heterocyclic carbene (NHC) ligand H_2IMes to obtain the Grubbs 2nd generation catalyst (**G-II**, Figure 2).[103]



G-I **G-II** **G-III**

Figure 2: Most commonly used commercial Grubbs catalysts

This resulted in a significant increase in stability, as carbenes are strong Lewis bases and behave as excellent σ-donors and poor π-acceptors. The resulting metal–carbon bonds are usually less labile than the related metal–phosphine bonds.[103] Furthermore, also the activity of the catalyst was increased significantly. An explanation for the different reactivity of the 1st and 2nd generation Grubbs catalysts was first assumed to be a faster phosphine dissociation through a higher electronic *trans*-influence. In fact, the dissociation of the phosphine ligand is two orders of magnitude higher for the 1st generation catalyst (Scheme 25, k_1). However, the ratio of the partitioning (k_2/k_{-1}) between the coordination of the alkene substrate (k_2) and the return to the resting state of the catalyst (k_{-1}) is believed to be four orders of magnitude greater for **G-II** than for **G-I**. In other words, the better reactivity of the 2nd generation Grubbs catalysts is due to an increased affinity towards olefins of the NHC-substituted ruthenium species.[103,104] Further modifications of the ligands by Grubbs and co-workers led to the development of the Grubbs 3rd generation catalyst (**G-III**, Figure 2) bearing two pyridine ligands.[105]



Scheme 25: Catalytic mechanisms of the Grubbs 1st generation catalyst in comparison to the Grubbs 2nd generation catalyst. L=respective ligands shown previously.[103,104]

A distinctive feature of this catalyst is its fast initiation rate, which is reflected in the reaction of **G-III** with ethyl vinyl ether being at least six orders of magnitude higher than the corresponding initiation rate of second-generation catalyst **G-II**. The fast initiation is specifically useful for ROMP to produce polymers with very narrow dispersities and for the synthesis of block copolymers.[106]

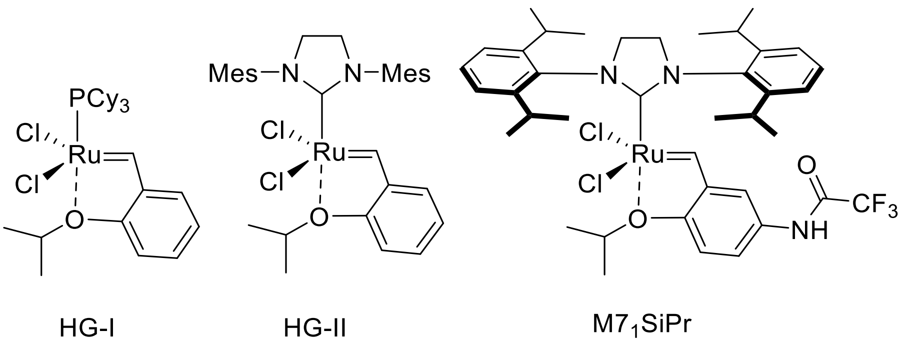
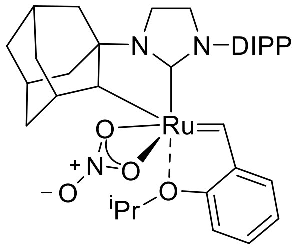


*Figure 3: Hoveyda-Grubbs 1st generation (**HG-I**) and Hoveyda-Grubbs 2^2nd generation catalyst (HG-II) and Umicore M7₁ SiPr catalyst (**M7₁**).*

Another significant development in the improvement of Grubbs catalysts was the introduction of chelating benzylidene ligands by Hoveyda in 1997.[107] The synthesis of the Hoveyda-Grubbs 1st generation catalyst (**HG-I**, Figure 3) proceeds through a reaction of 2-isopropoxyphenyldiazomethane with $RuCl_2(PPh_3)_3$ followed by phosphine exchange, resulting in a catalyst that is much more robust to air and moisture than typical Grubbs catalysts.[108] Particularly metathesis reactions involving highly electron-deficient substrates show improved results with Hoveyda-type catalysts.[109] The Hoveyda-Grubbs 2nd generation catalyst (**HG-II**, Figure 3) combines the advantages of NHC ligand and chelating benzylidene ligands. Plenty of further modifications of the **HG-II** catalyst are available and promise an even better stability and activity, as for example the Umicore M7$_1$ SiPr catalyst (**M7$_1$SiPr**, Figure 3).[110] The electron withdrawing group in *para* position decreased its donor properties and facilitates opening of the chelate ring, required for the initiation process.[108] Initially, another advantage of this catalyst was assumed to be its ability to be recovered due to a "boomerang" mechanism.[111] However, a study by H. Plenio and co-workers from 2010 suggests no evidence supportive of a significant contribution of a release-return mechanism. Instead, re-isolation of the Grubbs–Hoveyda complex after olefin metathesis reactions is primarily caused by incomplete activation of the initial Grubbs–Hoveyda complex.[112] One of the big challenges throughout the decades has been diastereocontrol of the double bond formed during an olefin metathesis reaction. While Schrock-type catalysts can easily achieve good metathesis results when modified with bulky ligands,[113] introduction of very large ligands on ruthenium catalysts has a number of disadvantages. As ruthenium catalysts are inherently less reactive than their early-metal counterparts, large ligands tend to have an adverse effect on metathesis activity,[114] in some cases accompanied by an increase in side reactions, such as olefin migration.[115] Moreover, as already mentioned previously, ruthenacycles are highly dynamic, even at low temperatures, compared to tungsta- and molybdacycles. In consequence it is difficult to design ligands that can influence the geometry of the important intermediates.[114] However, the development of a novel chelated metathesis catalyst (Figure 4) in 2013 led to unpreceded Z-selectivities of over 95% in RCM, SM and CM, comparable to those of Z-selective Schrock catalysts and turnover numbers (TONs) of up to 7400.[116] Apart from changing the substituents on the carbene framework of the typical NHCs, cyclic alkyl amino carbenes (CAACs) were discovered as another family of stable carbenes (*e.g.*, Figure 5, **E2**, **E4**). It was discovered that the CAAC catalysts displayed improved conversion to the Z-olefin relative to that observed using the classical NHC- and phosphine-based systems.[117]

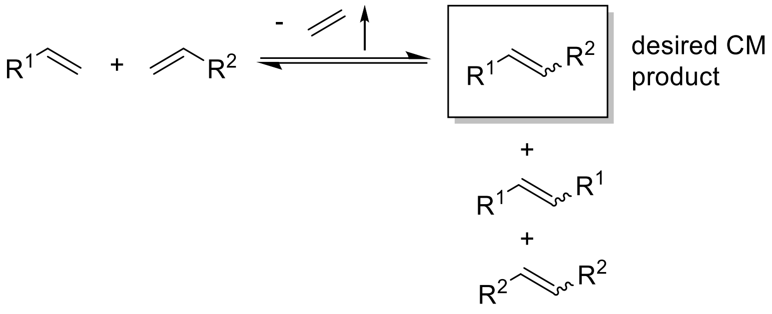


DIPP = 2,6-diisopropylphenyl

Figure 4: Novel chelated ruthenium-based metathesis catalyst bearing an N-2,6-diisopropylphenyl group displaying near-perfect selectivity for the Z-olefin (>95%).

Additionally, they have been identified as most active and selective metathesis catalyst for formation of terminal olefins, *e.g.* in the ethenolysis of methyl oleate. A detailed discussion of ethenolysis reactions is given in the following section.

2.4.2 Cross metathesis



$R_1 : R_2$	CM product selectivity
1 : 1	50%
2 : 1	66%
4 : 1	80%
10 : 1	91%
20 : 1	95%

Scheme 26: Statistical distribution of CM products.[118]

One of the most important characteristics of metathesis reactions is their reversibility. To prevent the formation of solely statistic product mixtures, the release of the volatile side product allows to drive the reaction to completion. As a result, preferably substrates with a terminal double bond are subjected to metathesis reactions. In CM another problem arises, as the yield is often limited by self-metathesis as side reaction leading to a maximum of 50% yield of the desired CM product.[118] There are a few solutions to this problem. An excess of one of the reactants can lead to a significant increase in selectivity (see Scheme 26). Another possibility is to modify the reactivity of one of the partners by either electronic or steric factors.[118,119] Typically, four different types of olefins are differentiated according to their reactivity (fast homodimerization – type I, slow homodimerization – type II, no homodimerization – type III, spectators to CM – type IV, see Table 1).

Table 1: Olefin reactivity categories for selective cross metathesis.[118]

Olefin type	Grubbs II	Grubbs I	Schrock
Type I (fast homodimerization)	terminal olefins, allylic alcohols, allylic esters, allyl boronate esters, allyl halides, styrenes (no large ortho substituent), allyl phosphonates, allyl silanes, allyl phosphine oxides, allyl sulphides, protected allyl amines	terminal olefins, allylic alcohols, allylic esters, allylic ethers, allyl boronate esters, allyl halides	terminal olefins, allyl silanes
Type II (slow homodimerization)	styrenes (large ortho substituent), acrylates, acrylamides, acrylic acid, acrolein, vinyl ketones, unprotected 3° allylic alcohols, vinyl epoxides, 2° allylic alcohols, perfluorinated alkane olefins	styrene, 2° allylic alcohols, vinyl dioxolanes, vinyl boronates	styrene, allyl stannanes
Type III (no homodimerization)	1,1-disubstituted olefins, non-bulky trisubst. olefins, vinyl phosphonates, phenyl vinyl sulfonate, 4° allylic carbons, 3° allylic alcohols	vinyl siloxanes	3° allyl amines, acrylonitrile
Type VI (spectators to CM)	vinyl nitro olefins, trisubstituted allyl alcohols	1,1-disubstituted olefins, disubst. α, β-unsaturated carbonyls, 4° allylic carbon-containing olefins, perfluorinated alkane olefins, 3° allyl amines (protected)	1,1-disubstituted olefins

A reaction between two olefins of different types (preferably type I and type III) leads to a more selective cross metathesis even with a 1 : 1 ratio of the reactants. To prevent self-metathesis of the more reactive olefin an excess of the unreactive olefin further benefits the reaction. When using a type III olefin that does not undergo SM the excess can be recovered after the reaction.

2.4.3 Ethenolysis

The ethenolysis of methyl oleate is an industrially potentially important method that converts naturally produced seed oils into lighter, carbon-containing fragments for biofuels and other valuable commercial products and was extensively studied in literature.[120] Earlier investigations of the ethenolysis focused mainly on heterogeneous catalysis utilizing Re_2O_7 on alumina-supported catalyst,[121] methyltrioxorhenium on silica-alumina (CH_3ReO_3/Al_2O_3-SiO_2),[122] or Re_2O_7 on silica-alumina impregnated with B_2O_3 and activated with $SnMe_4$ ($Re_2O_7/SiO_2.Al_2O_3/B_2O_3$-$SnBu_4$).[123]

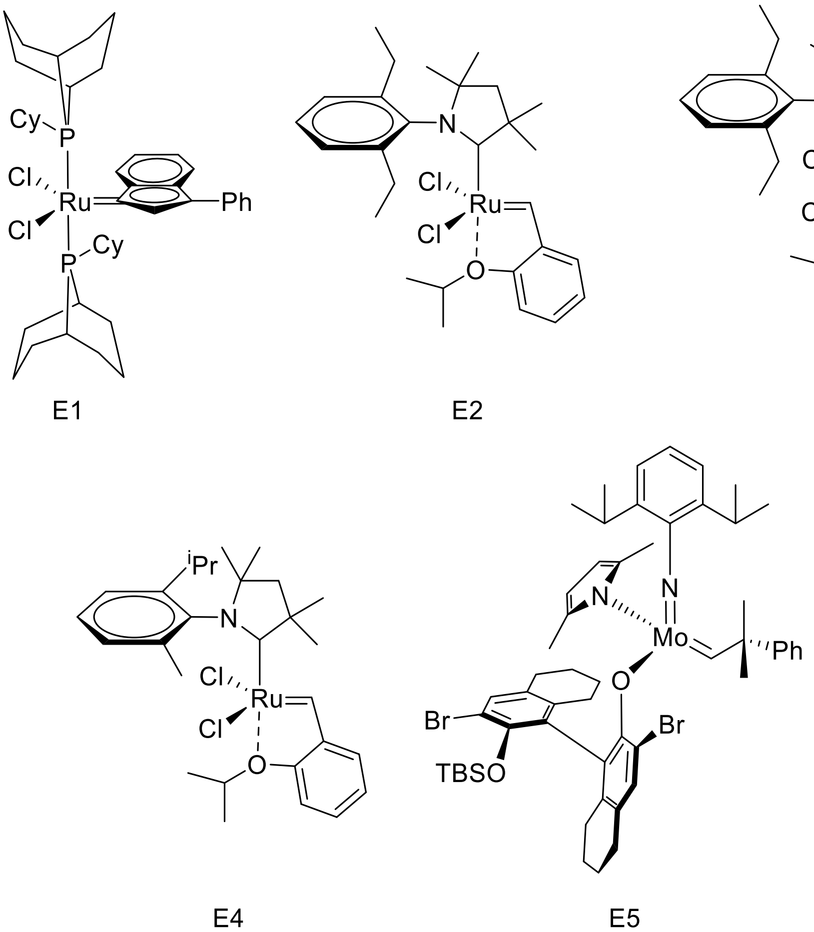
In 2004, B. R. Maughon *et al.* did an extensive optimization study of the ethenolysis of methyl oleate utilizing the **G-I** catalyst (Figure 2).[124] A variation of the catalyst loading yielded turnover numbers (TONs) of over 15,000 for a catalyst concentration of 0.001 mol%, although the conversion only reaches <20% (Table 1, entry A). For a catalyst loading of 0.022 mol% a TON of 3010 and conversions up to 82% were achieved (Table 1, entry B). The selectivity towards ethenolysis compared to self-metathesis gets significantly lower with higher conversions, which can be prevented by employing a higher ethylene pressure (Table 2, entry B and C). P. H. Dixneuf *et al.* demonstrated up to 97% GC yield of methyl decanoate utilizing **HG-I** (Figure 3) as catalysts.[125] They found that the **HG-I** catalyst is highly selective at 20°C, however it leads to double bond migration at higher temperatures (Table 2, entry D and E). Moreover, they found out that the reaction can be run in ionic liquids with up to 95% conversion and only trace amounts of self-metathesis product. The reaction mixture can be reused after extraction of the product, however the conversion decreases after the fourth run to 45% (Table 2, entry F and G). Although these results seem promising, the use of 2.5 mol% catalyst for experiments in toluene and up to 5 mol% catalyst for experiments in ionic liquids can be seen critically as the higher catalyst concentration counteracts the benefit of easy recovery. G. S. Forman *et al.* achieved up to 64% conversion and 98% selectivity with 0.005 mol% of the phoban-indenylidene ruthenium catalyst **E1** (Figure 5, Table 2 entry H).[126] R. L. Pederson *et al.* performed an extensive study on the ethenolysis of neat methyl oleate varying different metathesis catalysts, ethylene pressure, temperature and time. Interestingly, they found out that the 2nd generation NHC-based catalysts **G-II** and **HG-II** were less selective toward ethenolysis than their first-generation equivalents (Table 2, entry K – M). Still, increasing the temperature improved the conversion to 68% and the yield to 32% (Table 2, entry N). Further improvement was achieved by the cyclic (alkyl)(amino)carbene (CAAC)-based ruthenium catalyst **E2** mentioned in the last section.

Table 2: Comprehensive overview of selected ethenolysis reactions (homogeneous catalysis) in literature.

Entry	Catalyst	Eq. cat [mol%]	Solvent	p [bar]	T [°C]	C [%]	Y [%]
A[124]	**G-I**	0.001	toluene	4.14[d]	30	20	19
B[124]	**G-I**	0.022	toluene	4.14[d]	30	75	64
C[124]	**G-I**	0.022	toluene	16.5[d]	30	82	79
D[125]	**HG-I**	2.5	toluene	10[d]	20	97	97
E[125]	**HG-I**	2.5	toluene	10[d]	70	97	97[a]
F[125]	**HG-I**	5	ionic liq.[g]	10[d]	20	95	95
G[125]	**HG-I**	5[b]	ionic liq.[g]	10[d]	20	45	45
H[126]	**E1**	0.005	neat	10[d]	50	64	62
I[127]	**E2**	0.005	toluene[c]	4.14[d]	40	80	70
J[128]	**G-I**	0.01	neat	10.3[d]	40	58	54
K[128]	**HG-I**	0.01	neat	10.3[d]	40	51	48
L[128]	**G-II**	0.01	neat	10.3[d]	40	64	28
M[128]	**HG-II**	0.01	neat	10.3[d]	40	60	20
N[128]	**HG-II**	0.01	neat	10.3[d]	60	68	32
O[128]	**E2**	0.01	neat	10.3[d]	40	73	53
P[128]	**E2**	0.001	neat	10.3[d]	40	42	35
Q[129]	**E3**	0.005	neat	10.3[d]	40	48	46
R[130]	**E4**	0.0003	neat	10.3[d]	40	59	54
S[130]	**E4**	0.0001	neat	10.3[e]	40	-	13
T[130]	**E4**	0.0001	neat	10.3[f]	40	-	34
U[131]	**E5**	0.02	neat	10.1[d]	RT	95	95

[a] three different isomers because of double bond migration, [b] 4th run utilizing a recycled catalyst solvent mixture, [c] flow reactor system, [d] purity of the ethylene <99.95% [e] purity of the ethylene: 99.95%, [f] purity of the ethylene 99.995%; [g] [bdmim]- [NTf$_2$].

CAAC ligands, which are known to be more electron donating than their *N*-heterocyclic carbene counter-parts, are expected to increase electron density at the ruthenium and stabilize the otherwise highly reactive and electron-deficient methylidene intermediate.[130] The catalyst exhibits longer lifetimes in cross-metathesis reactions because of its stability to existing as a methylidene. Utilizing only 0.01 mol% of catalyst **E2** they achieved conversions up to 73% and GC yields up to 53% at 10 bar ethylene pressure and remarkably, only 0.001 mol% catalyst loading still gave a GC yield of 35% (Table 2, entry O and P).[117,128] R. H. Grubbs *et al.* designed catalyst **E3**, which was even better achieving 48% conversion and 46% yield with only 0.005 mol% concentration exhibiting a remarkable selectivity.[129] Moreover, they performed the ethenolysis of methyl oleate in microfluidic, dual-phase system with up to 80% conversion and 70% yield with only 0.005 mol% of **E2** proving the efficiency of the reaction including the possibility of a convenient scale-up (Table 2 entry I).[127] Using **E4** (Figure 5) R. H. Grubbs *et al.* recently achieved TONs of more than 100.000 at a catalyst loading of only 3 ppm with a yield of 54% and a conversion of 59% (Table 2, entry R).[130] At a catalyst loading of 1 ppm the purity of the ethylene was of high importance as an increase of purity from 99.95 to 99.995% increased the yield from 13 to 34% (Table 2, entry S and T).



E1 E2 E3

E4 E5

Figure 5: Different metathesis catalysts showing excellent performance in ethenolysis reactions.

In 2009 R. R. Schrock *et al.* showed that in comparison to Grubbs-type catalysts Schrock catalysts can be even more efficient for the ethenolysis of methyl oleate as was shown.[131] With an imido alkylidene monoaryloxide monopyrrolide complex of molybdenum (Figure 5, **Mo1**) up to 95% yield and over 99% selectivity were achieved at room temperature, under neat conditions at 10 bar ethylene pressure.

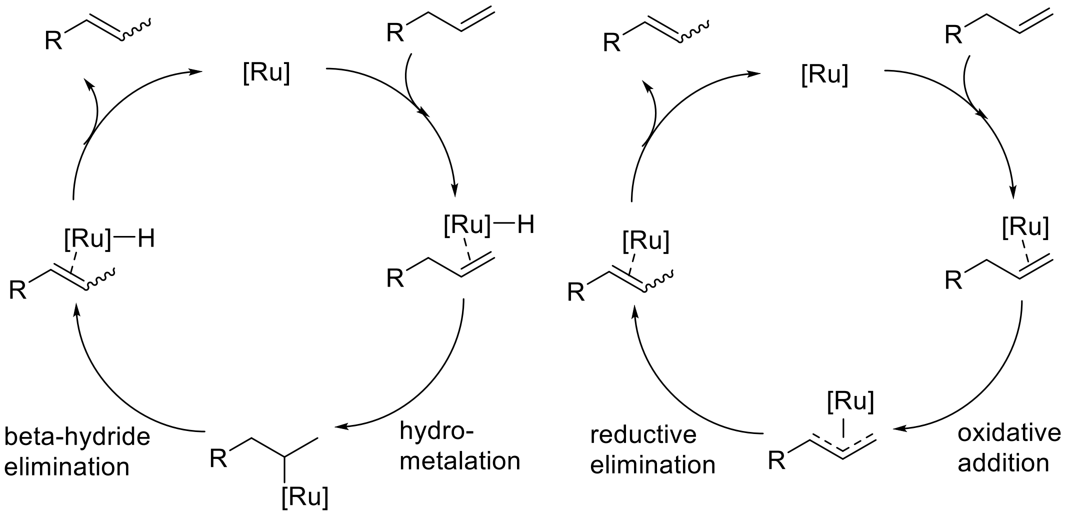
As mentioned above, the ethylene purity seems to play an important role, especially at low catalyst loadings. In a recent review from 2017, E. L. Scott *et al.* compiled the highest TON for each catalyst per publication.[120] The authors concluded that impurities from the ethylene feed have a bigger influence on the TON than the catalyst used, as increases in TON using purer ethylene are significantly larger than the increases obtained by novel catalysts. For example, for 99.9% pure ethylene, catalyst **E5** (Figure 5) leads to a TON of 35.000, which is only slightly higher than the TON of 24.800 obtained with the traditional **G-I**. Other impurities can originate from the solvent or feedstock. For example, toluene is known to often include traces of morpholine,[132] which degrades catalysts containing a phosphine group. The phosphine undergoes displacement by an amine, followed by an attack of the ruthenium alkylidene species by the phosphine.[133] In renewable feedstocks containing double bonds, a major contributor to degradation of metathesis catalysts are hydroxyperoxides, which are gradually formed over time.[120] Pre-treatment of the feedstock with magnesium silicate has been identified by R. L. Pederson *et al.* as comparably cheap method to remove peroxides and increase catalyst performance.[134] Alternatively, treatment with Al_2O_3 at 200 °C was shown to be effective in the ethenolysis of oleonitrile removing both, peroxides and water.[135]

2.4.4 ADMET polymerizations

Metathesis reactions involving α,ω-dienes can lead to either RCM in high dilution or ADMET polymerizations in more concentrated mixtures. ADMET is a step-growth polymerization and the final molecular weight is described as a function of conversion by the Carothers equation.[136]

$$X_n = \frac{1}{1-p}$$

Where X_n is the degree of polymerization and p is the conversion. This equation reveals that, in order to obtain high molecular weights, a conversion of >99% is necessary. One major problem of ADMET polymerizations is the isomerization of double bonds at higher temperatures by either β-hydride elimination (Scheme 27, left) or intramolecular 1,3-hydrogen shift (Scheme 27, left). To avoid the isomerization, **G-I** or Schrock-catalysts, which are known for very little double bond isomerization, are typically utilized.[137] If the high functional group tolerance of ruthenium is needed and the **G-I** catalyst is not active enough, 2nd generation catalysts together with additives such as phenylphosphoric acid[138] or tin and iron halides[139] are used, which scavenge the ruthenium hydride species held responsible for the isomerization reactions. In particular 1,4-bezoquinone has been extensively applied and is likely to be reduced to hydroquinones by any ruthenium hydride species that is formed,[136,140] although the specific mechanism was not investigated yet.



Scheme 27: Proposed mechanisms for the Isomerization of the terminal double bond by either β-hydride elimination (left) or intramolecular 1,3-hydrogen shift (right).[141]

Due to the possibility to polymerize monomers with various functional groups and structures, ADMET has been applied to produce a variety of polymers and different applications. Wagener and co-workers have systematically studied the effect of both the position and nature of the branch group in branched polyethylene (PE) followed by exhaustive hydrogenation. For this purpose, linear ADMET PE[142] as well as alkyl-,[143] hydroxy-,[144] acetate-,[145] phenyl-,[146] fluoro-,[147] chloro-,[146,148] bromo-,[149] methoxy- or ethoxy-,[150] carboxylic acid-,[151] sulfonic acid ethyl ester-,[152] phosphonic acid-,[153] and PEG-[154] branched ADMET polymers have been prepared. The hydrogenation step typically can be performed in a tandem reaction in case of **G-I** or **G-II** as catalysts.[155] Moreover, silica gel can be added to the completed homogeneous polymerization converting the metathesis catalyst to a highly efficient heterogeneous olefin hydrogenation catalyst. Alternatively, hydrogenation over Pd/C[146] or Wilkinson's catalyst $RhCl(PPh)_3$[156] have proved particularly effective. The substrate scope of ADMET is not only limited to functional group side chains, but also the backbone can include several different types of functional groups and therefore give different types of polymers. Among the most important polymer classes synthesized by ADMET are polyethers,[157] polyacetals,[158] polyesters,[159,160] polycarbonates,[161,162] polyketones,[159] polycarbosilanes and -siloxanes,[163] polyamides[164] and polyurethanes.[164] The synthesis of polyamines[165] and polythioethers[166] was accomplished with Schrock's catalyst, as Grubbs catalysts tend to form complexes with the substrate.[136] The variety and functional group tolerance of ADMET polymerizations is impressive, however sufficient "spacing" is required between the active terminal olefin and the heteroatom for successful polymerization to occur. This is known as the "negative neighboring group effect" and it was determined that for esters and for ethers two methylene spacers from the functional group to the double bond are required.[136,167]

2.5 Polymers derived from fats&oils

Fats and oils represent one of the most interesting classes of renewables for the synthesis of sustainable monomers and polymers, as they are available in high amounts and their long aliphatic chain contributes as major elements to the polymer backbone.[168] Within the past eight years, several reviews discussed their application in polymer science.[169] In particular biotechnological (especially oxy-) modifications of fatty acids have been topic of intensive research.[170] For example, genetically modified *escherichia coli* strains can produce polyhydroxyalkanoates (PHA), such as polyhydroxybutyrate (PHB),[171] which is utilized in this thesis (section 4.1.2), but can also modify longer fatty acid chains.[172]

Classic ‘chemical’ modifications of fats&oils are in the focus of recent research, as well. The most common reaction described using fats and oils is their epoxidation and use in thermosetting materials. These thermosets have several advantages as *e.g.* purity of the reactants is of minor importance and waste vegetable oil can be used maintaining decent material properties.[173] However, compared to thermosets, thermoplastic polymers have several advantages mostly related to processing and recyclability. Modifications leading to thermoplastic polymers will be discussed in the next section, since thermoplastic polymers are the focus of this thesis.

2.5.1 Thermoplastic polymers[i]

A. Llevot, P.-K. Dannecker, M. von Czapiewski, L. C. Over, Z. Soyler, Meier, Michael A. R., *Chem-Eur J.* **2016**, *22*, 11510.

Most of the modifications are carried out on double bonds of unsaturated crude oils or of their fatty acid derivatives (general overview of important transformations see Scheme 28). In contrast to unsaturated fatty acid methyl esters (FAMEs), saturated FAMEs are more challenging to modify. One method is to exploit their *α*-acidity for the direct transformation into malonate derivatives, followed by their polymerization to polyesters and polyamides exhibiting long aliphatic pending chains.[175]

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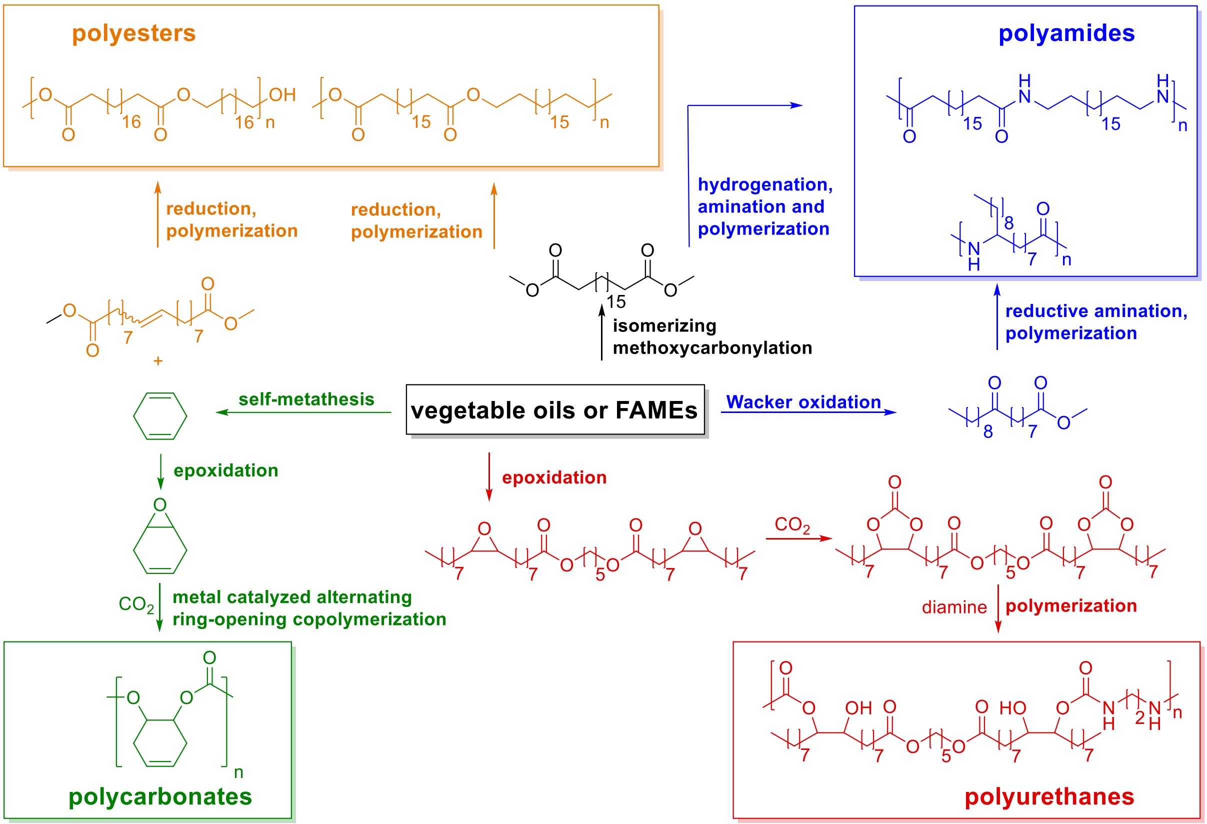
[i] parts of this section were published in[174] (A. Llevot, P.-K. Dannecker, M. von Czapiewski, L. C. Over, Z. Soyler, Meier, Michael A. R., *Chem-Eur J.* **2016**, *22*, 11510.). Here, an updated version of the article is presented.



Scheme 28: Different sustainable routes to utilize FAMEs for the synthesis of different polymer classes of thermoplastic materials.[174]

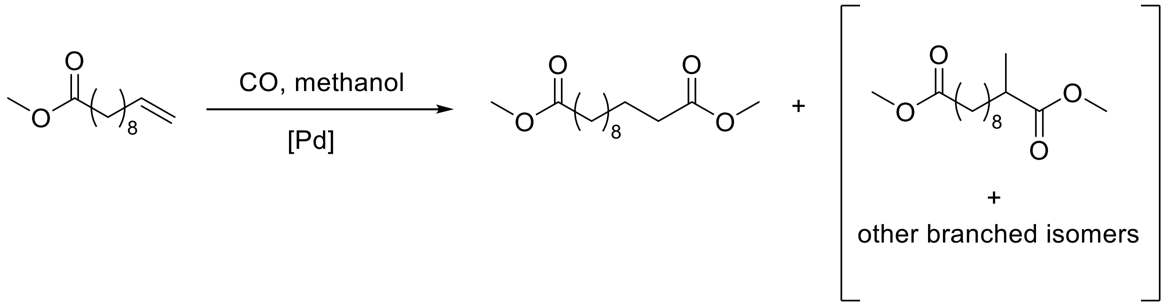
Among the different methodologies employed to react a double bond, the thiol-ene addition was progressively established as a convenient method to produce polyesters, polyamides, polythioethers, telechelic diols and polyols for polyurethane synthesis (discussed in detail in section 2.5.2). [176–180]

Metathesis, as a highly efficient catalytic reaction, is frequently used for the synthesis of sustainable polymers. Either *α,ω*-bifunctional bio based monomers, such as diacids or diols, are synthesized by self- or cross-metathesis, or dienes are directly polymerized by acyclic diene metathesis (ADMET) polymerizations yielding polymers with diverse structures, such as polycarbonates, polyethers, polyesters, polyamides or polyurethanes (discussed in detail in section 2.5.3).[164,181,182,183] The efficiency of metathesis is driven by the removal of by-products (*e.g.* ethylene). M. A. R. Meier *et al.* synthesized long-chain polyesters *via* the self-metathesis of a mixture of polyunsaturated FAMEs,[184] which was recently also applied and further investigated by S. Şehitoğlu and co-workers utilizing different metathesis catalysts as well as homobimetallic ruthenium complexes.[185] The renewable cyclohexadiene (CHD) by-product was further epoxidized by C. K. Williams *et al.* and employed in a metal catalyzed alternating ring-opening copolymerization (ROCOP) with carbon dioxide

(CO_2) in order to produce renewable polycarbonates.[186] The production of polycarbonates from CO_2 enables to consume a greenhouse gas to synthesize value added products. The state of the art on this topic was recently reviewed by B. A. Wasmi *et al*. elsewhere.[187]

Different sustainable oxidation pathways were described on vegetable oil derivatives to produce bifunctional bio-based monomers. The Wacker oxidation is a palladium(II) catalyzed functionalization of olefins, which does not need a co-catalyst if performed in dimethylacetamide.[188] M. A. R. Meier *et al.* reported it as an environmentally benign oxyfunctionalization of FAMEs with a low catalyst loading, which features the complete recycling of the solvent–catalyst mixtures, and a straightforward isolation of the keto-fatty acid product.[189] Moreover, the Schenck-Ene reaction was used to oxidize fatty acids and their derivatives.[190] V. Cádiz *et al.* demonstrated that this procedure can be applied to high-oleic sunflower oil to obtain a regioisomeric mixture of enones by treatment with acetic anhydride and pyridine or tertiary amines, which was further employed to produce thermosets.[191] Finally, the sustainable potential of ozonolysis as highly efficient method to oxyfunctionalize FAMEs was recently optimized by Y. Pouilloux *et al*.[192] The reaction was carried out without solvent, at room temperature, in the presence of Pd/C and hydrogen with a yield and purity over 90%.

In 2016, A. Vorholt and co-workers reported about the hydroesterification of methyl 10-undecenoate utilizing palladium / 1,2-bis(di-tert butylphosphino)methyl)benzene / methanesulfonic acid catalysis in a recyclable thermomorphic multicomponent solvent system, achieving yields up to 79% and a high regioselectivity of 94% to the linear product (Scheme 29).[193]



Scheme 29: Hydroesterification products of methyl 10-undecenoate reported by Vorholt and co-workers.[193]

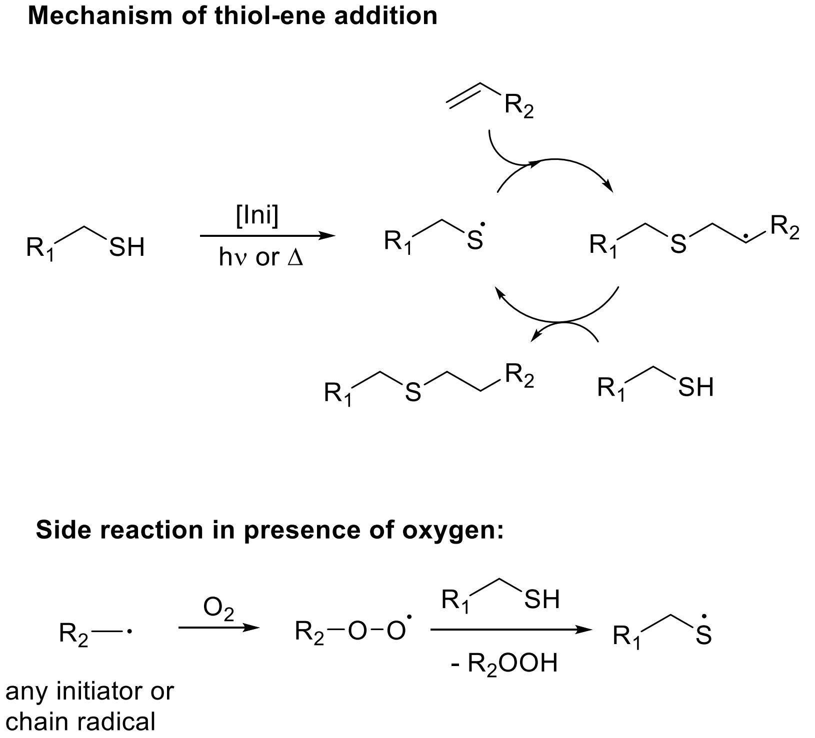
The isomerizing methoxycarbonylation constitutes a different approach to obtain bifunctional fatty acid derived monomers and was first reported by Cole-Hamilton and co-workers.[194] Using a palladium(II) catalyst modified with the diphosphine dtbpx at 80 °C and 30 bar of carbon monoxide and methanol, methyl oleate was converted into the linear *α,ω*-diester dimethyl 1,19-nonadecanedioate. This approach received further attention from S. Mecking *et al.,* who improved the reaction by using [(dtbpx)Pd(OTf)$_2$] as a defined catalyst precursor and afterwards synthesized polyesters on a preparative scale.[195] Recently, the same group expanded the concept and demonstrated that instead of alcohols, water can be used as nucleophile, directly yielding α,ω-dicarboxylic acids with high conversions and selectivities of >90% for the linear product.[196] In 2016, they reviewed the different possibilities to synthesize fatty acid derived long-chain aliphatic polymers by polycondensation approaches.[10] They gave a comprehensive account of the monomer syntheses, preparation, physical properties, morphologies, mechanical behavior, and degradability of long-chain polyester, polyamides, polyurethanes, polyureas, polyacetals and polycarbonates. In 2006, D. Milestein *et al.* described a ruthenium PNN complex that catalyzes the hydrogenation of esters to alcohols in high yields under neutral conditions using molecular hydrogen.[197]

In addition to oxidation reactions, aminations are often carried out in order to obtain desired monomers. Aminations of alcohols are discussed in detail in section 2.6.1.

Comparing the different approaches to modify renewables, for an overall sustainable process, catalytic transformations are required to replace traditional procedures using stoichiometric amounts of poorly atom-economic reagents.

2.5.2 Vegetable oil-based Thiol-Ene Polymers

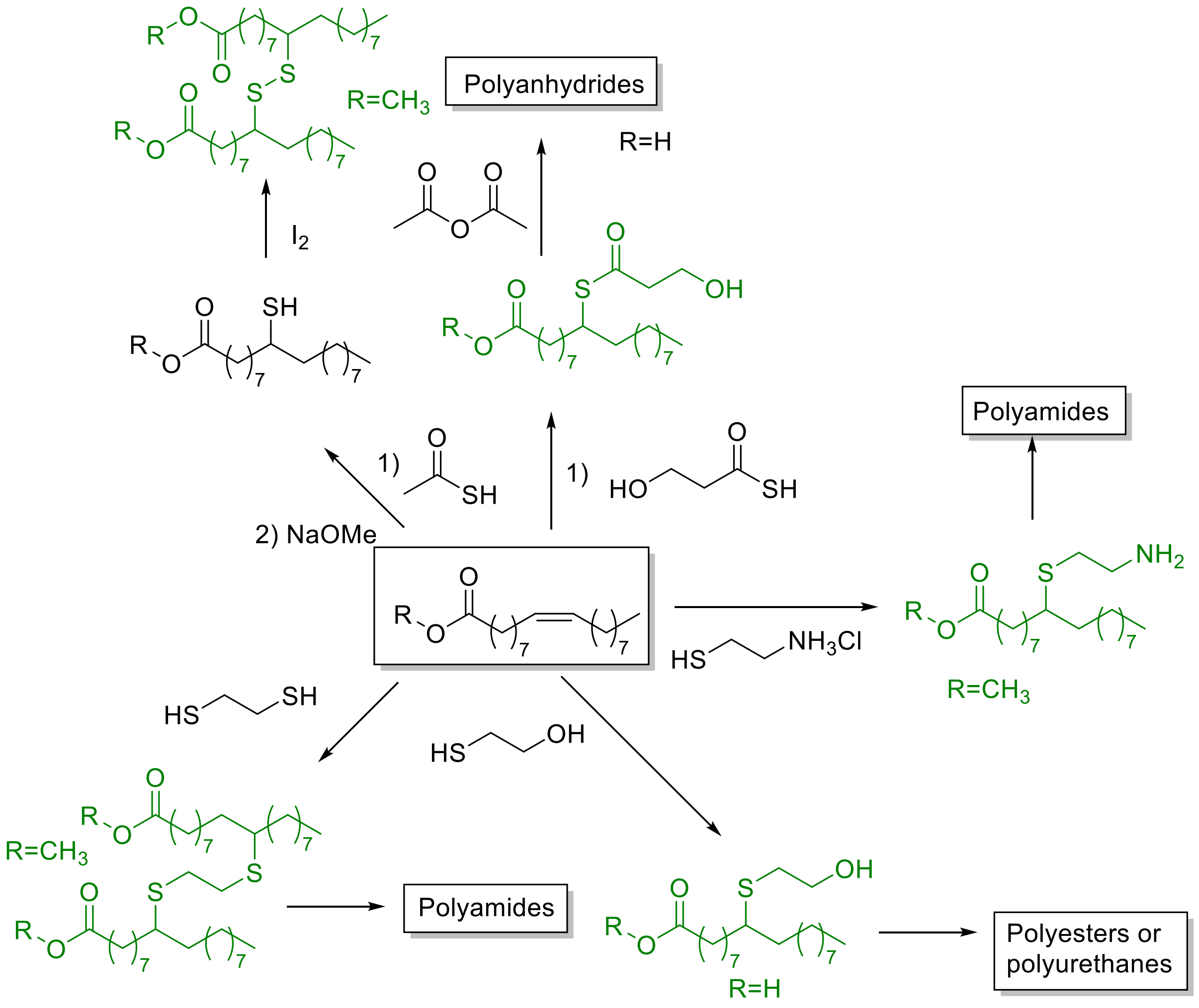
The earliest report on thiol-ene additions dates back to 1905 from T. Posner.[198] Since then, the thiol-ene addition has found numerous applications and became a powerful tool in synthetic organic chemistry, which is partly related to the fact that under certain conditions the reaction is considered a *click* reaction by some authors, as it is claimed to be relatively tolerant towards air and moisture (provided the concentration of oxygen does not approach that of the thiol).[199] Still, especially for polycondensations an inert atmosphere is recommended as oxygen leads to the formation of disulphides or peroxides,[200,201] which impacts the stoichiometry of the reaction and influences the molecular weight that can be obtained, although some authors claim that it does not impede a step growth polymerization mechanism even though they observed disulfide linkage in the obtained thioethers.[202]



Scheme 30: General mechanism of the thiol-ene reaction and illustration of a possible inhibition caused by oxygen.[201]

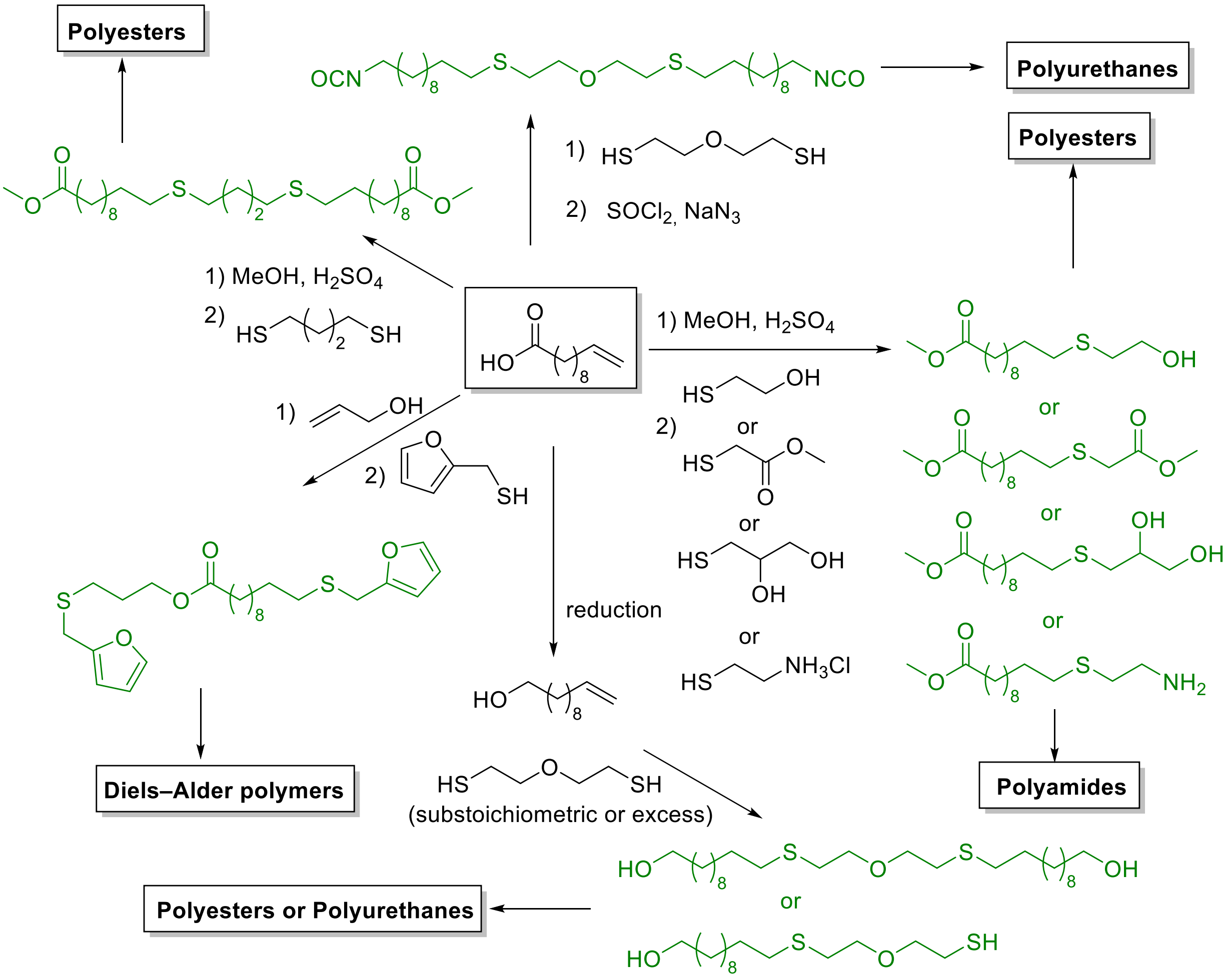
The mechanism of radically initiated thiol-ene additions typically follows the reaction cycle presented in Scheme 30. The initiator, *e.g.* DMPA or AIBN, which typically decompose under the influence of UV irradiation or heat respectively (AIBN can also photolytically cleave),[203] forms a radical species. Afterwards, initiation occurs *via* hydrogen abstraction from a thiol functional group (Scheme 30) or addition to an ene functional group (not depicted in mechanism). Propagation proceeds by either thiol or acrylic radical addition to acrylate functional groups or chain transfer from acrylic radicals to thiol functional groups.[201] In 2016, L. Lecamp *et al.* studied thiol-ene chemistry of vegetable oils and their derivatives under UV light and air, reaching the conclusion that several oxidation processes, such as peroxidation and ozonolysis occur as side reaction.[204]

As double bonds are readily available for modification in many fatty acid derived substrates, thiol-ene additions are a valuable tool in oleochemistry. Thiol-ene additions to internal double bonds, as they are typically occurring in natural fatty acids are, in contrast to additions to terminal double bonds, reversible and offer less potential for direct polymerizations due to the low efficiency of the reaction. Nevertheless, modifications of fatty acids such as oleic acid (and their methyl esters) are possible (Scheme 31).



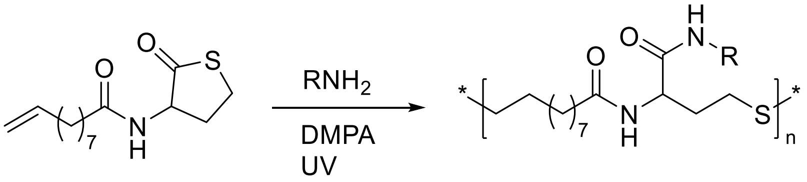
Scheme 31: Different thiol-ene additions to methyl oleate.

N. H. Koenig *et al.* prepared dimer fatty acids by the addition of thioacetic acid to methyl oleate followed by ester cleavage and coupling to the disulphide (Scheme 31, top left).[205] The addition of 3-mercaptopropionic acid to methyl oleate was performed in 2011 by V. Càdiz *et al.* followed by heating with acetic anhydride to form polyanhydrides.[206] In 2016, M. A. R. Meier and co-workers used 1,2-ethanedithiol to dimerize methyl oleate and polymerize it afterwards to produce copolyamides (Scheme 31, bottom left).[207]

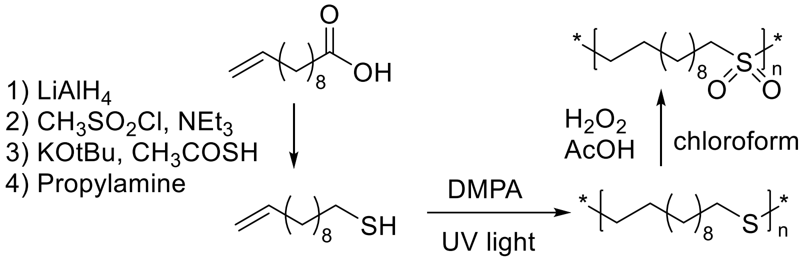


Scheme 32: Different thiol-ene additions to 10-undecenoic acid.

In 2011, R. Auvergne and co-workers evaluated the model reaction of 2-mercaptoethanol with oleic acid and the synthesis of a polyol from the reaction of the thiol with rapeseed oil.[180] In 2012, H. Cramail *et al.* described an extensive study to produce polyols from methyl oleate and 10-methyl undecenoate *via* thiol-ene addition and other fatty acid derivatives.[208] 10-Undecenoic acid, which can be obtained from castor oil by vacuum pyrolysis,[209] is a key component in many transformations as it contains a terminal double bond and its synthesis is comparably cheap. In 1991, Boutevin and co-workers prepared a diisocyanate by coupling 10-undecenoic acid with 2,2'-oxybis(ethane-1-thiol) and subsequent treatment with thionyl chloride and sodium azide (Scheme 32, top middle).[210] Moreover, the addition of 2,2'-oxybis(ethane-1-thiol), either in excess or in substoichiometric amounts, yielded the mercapto-alcohol[211] or the diol respectively (Scheme 32, bottom right).[212] Other approaches to obtain diols for polyurethane synthesis by thiol-ene addition have been realized, most noteworthy from V. Cádiz *et al*.[179] and H. Cramail and co-workers.[213] In 2010 Meier *et al.* performed the first systematic modification of methyl 10-undecenoate and obtained several monomers suitable for polycondensation by the addition of 2-mercaptoethan-1-ol, methyl 2-mercaptoacetate or 3-mercaptopropane-1,2-diol (Scheme 32, right).[176][176] In 2012, they expanded the approach with the addition of cysteamine hydrochloride to methyl undecenoate (Scheme 32, right) as well as methyl oleate (Scheme 31, right).[214] Moreover, dimerization of methyl undecenoate with 1,4-butanediol gave a dimethyl ester suitable for polymerization (Scheme 32, top left).[176][176] A. Gandini *et al.* reported another interesting application with the synthesis of polymers having thermoreversible character. The monomers were obtained by thiol-ene addition of furan-2-ylmethanethiol and polymerized in combination with maleimides.[215] An interesting approach was presented in 2014 by F. E. Du Prez *et al.* who performed a one pot thiol-ene polymerization of a renewable AB′ monomer with simultaneous introduction of amide side groups.[216] In 2013 the same group polymerized an AB-type monomer derived from 10-undecenoic acid to obtain a polythioether without additional functionalities and modified the thioether after polymerization by oxidation with H_2O_2 in chloroform (Scheme 34).[217]

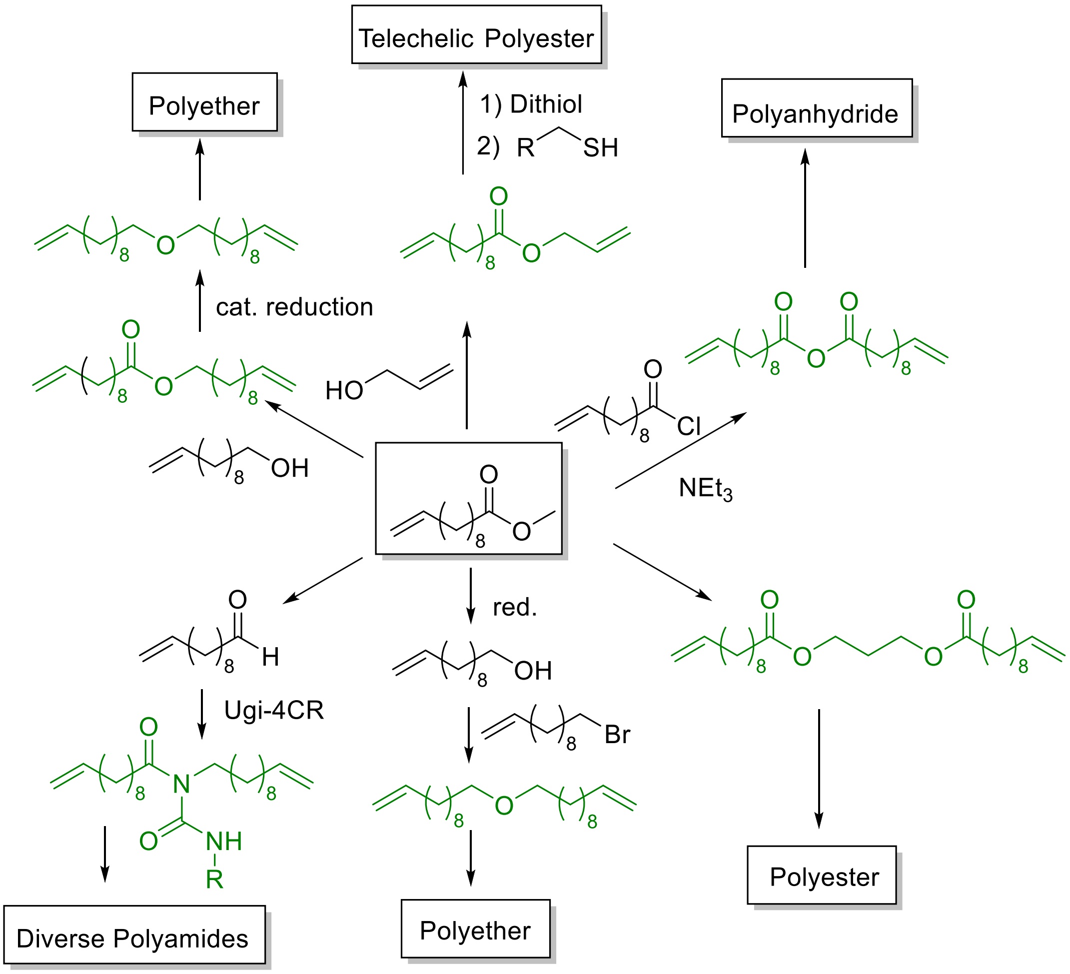


Scheme 33: One-pot stepwise photopolymerization of 10-undecenoylthiolactonamide, yielding linear polyamide structures with adjustable side chains.[216]



Scheme 34: Polythioethers from 10-undecenoic acid and post-polymerization oxidation to the polysulfone.[217]

Another possibility is to utilize the thiol-ene reaction as polymerization method and include other desired functionalities in a α,ω-diene structure. G. Lligadas and co-workers prepared the allyl ester of 10-methyl undecenoate, polymerized it with a dithiol and end-capped it with another thiol to obtain a telechelic polyester (Scheme 35, top middle).[218] Condensation of 10-methyl undecenoate with its acid chloride derivative (Scheme 35, top right) or with 1,3-propanediol (Scheme 35, bottom right) resulted in two monomers with anhydride and ester moieties, and the monomers were subsequently polymerized *via* both thiol-ene or ADMET polymerization reactions.[219] In 2011, M. A. R. Meier *et al.* reported the syntheses of diene monomers from 10-undecenol, bearing either no other functional group (not depicted) or a symmetrical ether with two linear C11 chains (Scheme 35, bottom middle), which were thiol-ene or ADMET polymerized in the next step.[220] Utilizing the Ugi-four component reaction M. A. R. Meier *et al.* described in 2012 an approach to synthesize poly-1-(alkyl-carbamoyl)carboxamides containing diverse amide side groups.[221]



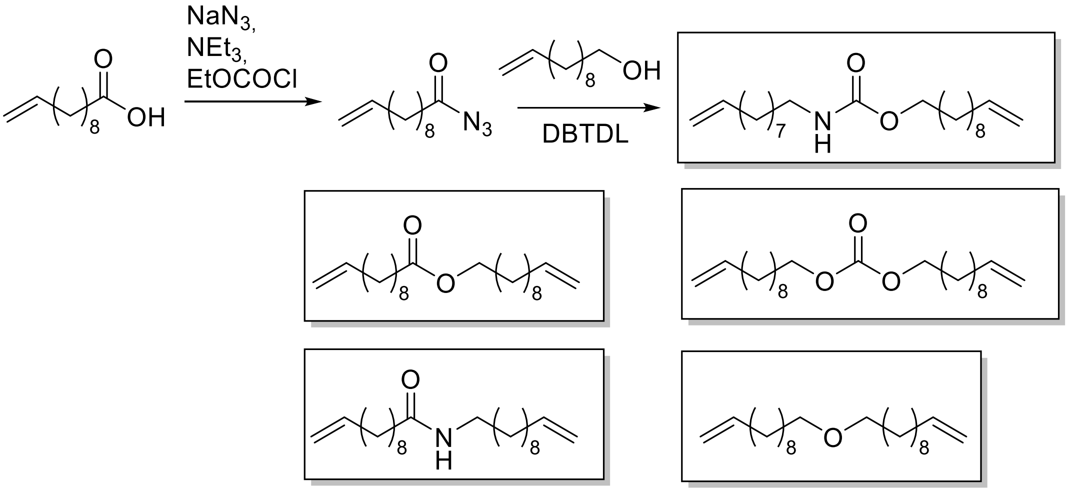
Scheme 35: Fatty acid derived monomers for thiol-ene polymerization. The polymerizations were carried out in each case with commercial dithiols.

In 2014, M. A. R. Meier *et al.* already utilized the catalytic reduction of esters to ethers, which is main topic of this thesis, to reduce the condensation product of 10-methyl undecenoate and 10-undecenol and polymerize it further by thiol-ene polymerization (Scheme 35, top left). Details regarding this synthesis are discussed in the results and discussion part (4.2.3 and 4.2.4).[222] Despite the atom economy of thiol-ene polymerizations, typical commercial thiols are not derived from renewables and not produced in a sustainable fashion. J. O. Metzger *et al.* recently described the synthesis of limonene and fatty acid derived sustainable thiols by the addition of thioacetic acid to dienes at room temperature, under solvent and initiator free conditions, followed by transesterification with methanol using TBD as organocatalyst.[222]

2.5.3 Vegetable oil-based ADMET Polymers

ADMET polymerizations fulfill many criteria of sustainability as they are efficient catalytic reactions and can be performed without solvent. Unsaturated fatty acids are already for a long time a regularly used substrate in ADMET polymerizations. In 2006, P. Hodge and co-workers utilized undecyl undecenoate in ADMET polymerizations even though the main focus of their work was the depolymerization afterwards in high dilution by ring-closing metathesis.[223] In 2008, M. A. R. Meier and co-workers optimized the polymerization of undecyl undecenoate by using different metathesis catalysts in different concentrations as well as a chain-stopper to control the molecular weight.[182] S. Mecking and co-workers compared this ADMET polymer in 2011 with the polyester 20,20 obtained by self-metathesis and polycondensation, and concluded that the polyester obtained by ADMET has a lower melting point due to isomerization.[224] In 2015, H. Cramail and co-workers copolymerized undecenyl undecenoate with dimers obtained from abietic acid, a resource from tall oil or pines, employing ADMET methodology. Moreover, in 2017 the same group copolymerized undecyl undecenoate with α,ω-unsaturated trehalose diesters glycolipids and their solution self-assembly was investigated by dynamic light scattering (DLS) in water.[225] An interesting approach was pursued by F. E. Du Prez *et al.,* who polymerized several 10-undecenoic acid based monomers and post-polymerization modified the resulting ADMET polymers with substituted TAD (triazoline-3,5-dione) compounds to ultimately obtain a crosslinked material with a triazolinedione crosslinker.[226] Apart from ADMET polymerizations, it is also possible to polymerize fatty acid derived trifunctional alkenes *via* acyclic triene metathesis (ATMET), which was demonstrated by M. A. R. Meier *et al.* in 2008 on glyceryl triundec-10-enoate.[227] The concept was further expanded to high-oleic sunflower oil[228] and to the synthesis of polyols for shape memory polyurethanes.[229] An interesting approach was pursued by V. Cádiz *et al.* in 2015, who utilized a 10-undecenoic acid derived benzoxazine-containing diene monomer to synthesize thermoplastic prepolymers that can yield thermosets after undergoing thermally activated ring opening polymerization.[230] In 2009, M. A. R. Meier *et al.* produced α,ω-unsaturated amide monomers for ADMET polymerization by converting 2 equivalents of 10-methyl undecenoate with different diamines, although the approach to first employ self-metathesis and polymerize the diester afterwards was more efficient in the synthesis of polyamides.[183] In 2013, H. Cramail *et al.* utilized ADMET polymerizations to produce renewable polyurethanes. Again starting from

10-undecenoic acid, a urethane containing α,ω-diene was synthesized and polymerized exploiting the Curtius rearrangement (Scheme 36).[161] It is particularly interesting for this thesis, that they were able to synthesize different types of very high molecular weight polymers up to M_n=52,000 g mol^{-1} by employing polarclean, a “green” and nontoxic high boiling point solvent.



Scheme 36: Depiction of 10-undecenoic derived dienes and synthesis of urethane containing α,ω-diene.

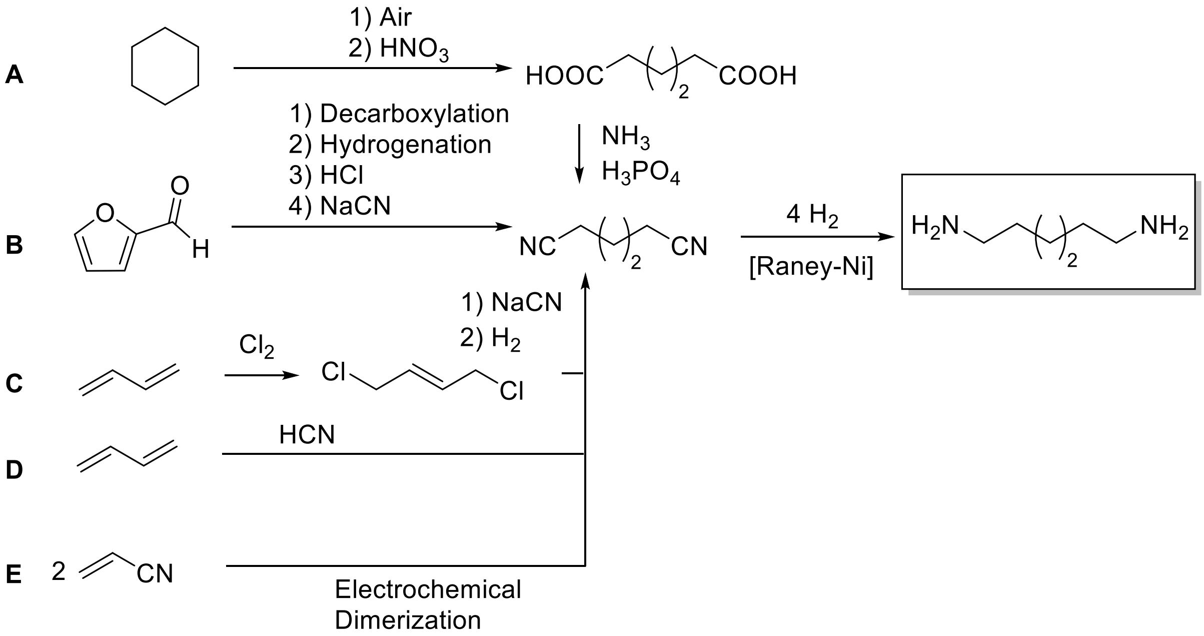
In 2014, the same group reduced ricinoleic acid to the diol and produced after transesterification with 10-methyl undecenoate and ADMET polymerization long-chain branched aliphatic polyesters.[231] An interesting approach was pursued by Z.-C. Li *et al.* who transesterified itaconic acid with 10-undecenol obtaining a polymer that can be modified by Michael addition after the ADMET polymerization.[232] ADMET polymerizations can also be run in miniemulsion as it was shown by M. A. R. Meier *et al.* in 2014, obtaining average molecular weight up to 15 kDa (M_n).[233]

2.6 Non-Isocyanate Polyurethanes (NIPUS)

A major focus of oleochemistry based polymer research in recent years was the synthesis of polyols as precursor for polyurethanes.[234] However, this approach itself is insufficient, since the necessary isocyanates are classically synthesized from phosgene. A first step towards more sustainable polyurethanes was the synthesis of isocyanates using the Curtius rearrangement to avoid the use of phosgene, even though it has to be viewed critically, as it proceeds *via* toxic acyl azides.[235] Sustainable polyurethanes with backbones similar to the petroleum-based ones can be produced by transurethanization of carbamates.[236] Moreover, a sustainable synthesis of bio-based carbamates was performed by Lossen rearrangement of hydroxamic acids, which are activated *in situ* by dialkyl carbonates in the presence of catalytic amounts of tertiary amine bases (0.1–0.4 eq.).[237] Still, NIPU synthesis from *bis*-cyclic carbonates (bCC) and diamines is arguably the most promising approach,[238] which is discussed in more detail in section 2.6.3.

2.6.1 Amines from alcohols

Industrially relevant commercial diamines are typically produced by hydrogenation of nitriles, as *e.g.* 1,6-hexamethylenediamine from adiponitrile.[239]



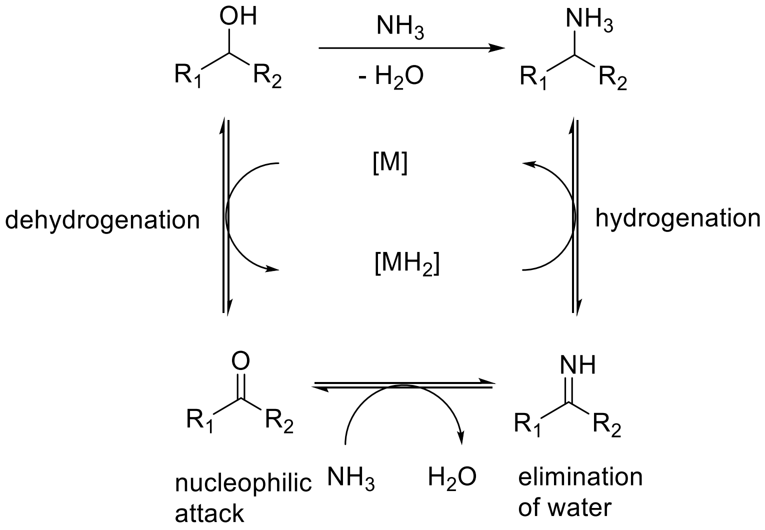
Scheme 37: Different industrial routes to 1,6-hexamethylenediamine.

From 1949 to 1961, DuPont produced adiponitrile from the renewable furfural (**B**, Scheme 37), but abandoned this process because tetrahydrofuran, the key intermediate, became available from petrochemical C4 hydrocarbons or acetylene and formaldehyde (Reppe process).[240] Until the late 1990s, another process commercialized by DuPont employed adipic acid made from cyclohexane and proceeded with the conversion of the diacid *via* vapor-phase dehydration of the ammonium salt in the presence of phosphoric acid or a boron–phosphorus catalyst (**A**, Scheme 37).

Table 3: Different commercially relevant diamines and their source.[241]

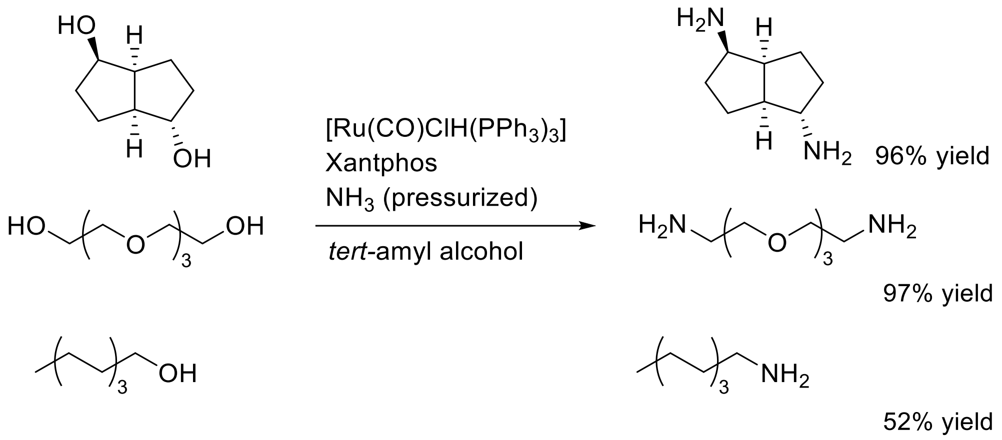
Diamine	Source
1,4-Butanediamine	Acrylonitrile, HCN and propene
1,6-Hexanediamine	butadiene, propene
2-Methylpentamethylenediamine	butadiene
4,4′-Diaminodicyclohexylmethane	aniline and formaldehyde
m-Xylylenediamine	m-xylene
2,2,4-Trimethylenehexamethylenediamine	acetone
2,4,4-Trimethylenehexamethylenediamine	butadiene
1,12-Dodecanediamine	butadiene
C36-Priamine	oleic and linoleic acids

From 1951 to 1983, DuPont operated a butadiene chlorination process, in which sodium cyanide was used to convert intermediate 1,4-dichloro-2-butene to 3-hexenedinitrile, followed by hydrogenation to adiponitrile (**C**, Scheme 37). This method was abandoned after developing a process for the catalytic addition of hydrogen cyanide to butadiene was developed (**D**, Scheme 37). A route developed by Monsanto in 1965 is the electrochemical dimerization of acrylonitrile (produced by ammoxidation of propene) at the cathode in an electrolytic cell. Nowadays, only route **D** and **E** starting from butadiene or acrylonitrile are still in operation.[242] Most industrially used diamines are based on fossil resources (Table 3).[241] Typically, aldehydes and ketones are used in the synthesis of amines *via* reductive amination with hydrogen, but not for the production of diamines.[243] The synthesis of amines by nucleophilic substitution of alkyl halides is, apart from ethylenediamine, industrially of minor importance due to the lack of cheap staring materials, corrosion and product-quality problems that arise in the processing of halides and the need to dispose of the formed salt.[244] Nowadays, the conversion of alcohols to amines is the most common process for the preparation of lower alkylamines. The catalysts used are mainly based on nickel, cobalt, copper, or iron and to a lesser extent platinum or palladium with promoters, such as Ag, Zn, In, Mn, Mo, and alkali metals on solid Al_2O_3, SiO_2, or ZrO_2 supports. In this reaction, the product always consists of a mixture of primary, secondary, and tertiary amines, because the primary amine formed initially is more nucleophilic than ammonia and can react further with one or two molecules of the alcohol. Moreover, the latter reactions are exothermic, while the former is close to thermoneutral, which further promotes the reaction to secondary or tertiary amines. A two- to eightfold excess of ammonia is used to shift the equilibrium towards the primary amines. Hydrogen is not required as a direct reactant, however in its absence imines, enamines, and even nitriles are formed.[244]



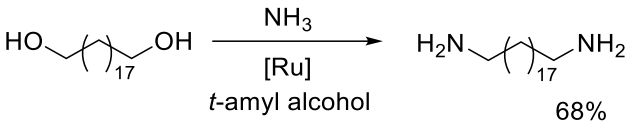
Scheme 38: Catalytic amination of alcohols via borrowing-hydrogen strategy.[246]

D. Milstein and co-workers developed a homogeneous pathway of the selective synthesis of primary amines from primary alcohols using ammonia gas and a ruthenium PNP pincer complex as catalyst.[247] In 2010, Beller *et al.*[246,248] as well as Vogt *et al.* went one step further and independently reported the synthesis of primary amines from secondary alcohols utilizing the combination of $[Ru_3(CO)_{12}]$ and commercially available CataCXiumPCy as catalyst.[248,250]



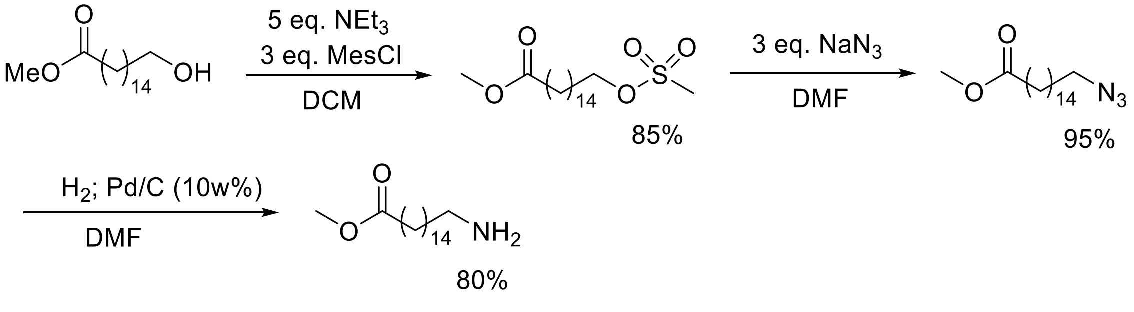
Scheme 39: Several examples of the direct amination of alcohols using ammonia.[246]

Köckritz *et al.* demonstrated a very good example in terms of sustainability by applying the isomerizing methoxycarbonylation as well as Milstein's catalyst in the synthesis of nonadecane-1,19-diamine from high-oleic sunflower oil (Scheme 40).[245][245]



Scheme 40: Direct amination of nonadecane-1,19-diamine using ammonia and Milstein's catalyst. [245][245]

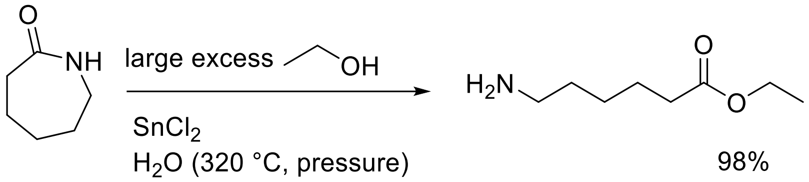
The reaction proceeds by the so-called "borrowing-hydrogen" methodology. In the first step, a catalytic dehydrogenation of the alcohol takes place to give the corresponding carbonyl compound and hydrogen. Subsequent formation of the imine and final hydrogenation leads to the desired amination product.[246] This methodology has been optimized and can be applied to various monofunctional or difunctional alcohols (Scheme 39). While this catalytic amination is certainly efficient, the yields for longer aliphatic alcohols (*e.g.* Scheme 39, bottom 52%; Scheme 40 68%) are far from quantitative, which makes this method not suitable for end group modification.



Scheme 41: Synthesis of methyl-16-aminohexadecanoate from methyl 16-hydroxypalmitate.[253]

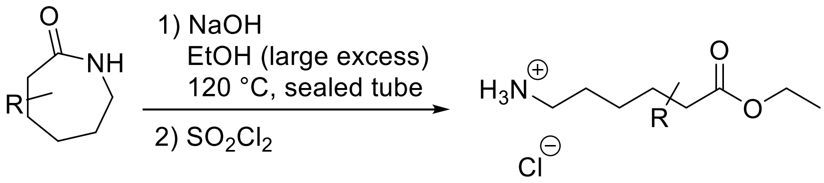
On a laboratory scale, the conversion of hydroxy groups to amines can be achieved by first synthesizing the methyl sulfone ester (good leaving group), nucleophilic substitution with sodium azide and reduction with hydrogen catalyzed by Pd/C (Scheme 41).[253] However, the overall yield of this 3-step synthesis is only 65%, which is again too inefficient for end-group modification.

A highly interesting transformation is the selective ring-opening of *ε*-caprolactam (CPL) to an ester-amine. This reaction is barely described in literature. In 2013, L. Y. Dai and co-workers heated a CPL : $SnCl_2$: water : ethanol mixture (molar ratio 0.15 : 1 : 56 : 28) to 320 °C in a pressure reactor to produce “near critical water” and obtained ethyl-6-aminohexanoate in a yield of up to 98% (Scheme 42).[249][249] This synthesis is very selective; however, it is most likely not applicable to water-insoluble alcohols. Moreover, the selectivity is with respect to the CPL and not the alcohol and consequently end groups and diols cannot be modified selectively.



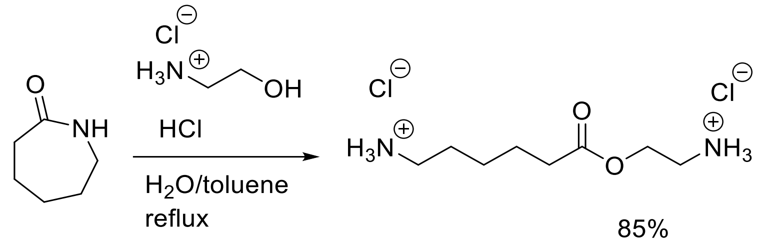
Scheme 42: Synthesis of ethyl-6-aminohexanoate in “near critical water”.[249][249]

In 2016, Y. Fu *et al.* reported on a „directing group in decarboxylative cross-coupling: copper catalyzed site-selective C−N bond formation from nonactivated aliphatic carboxylic acids” and in the process of obtaining their starting materials also utilized the ring-opening of caprolactam derivatives in a multi-step synthesis to obtain an intermediate (Scheme 43).[251][251] Again, the reaction uses a large excess of alcohol to achieve a selective ring-opening without polymerization. Unfortunately, the synthesis is not described in detail in the supporting information and no specifics for the yields of the reaction step are given.



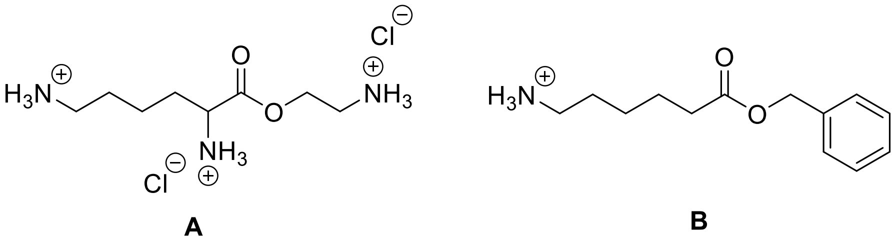
Scheme 43: Base-catalyzed ring-opening of caprolactam derivatives in ethanolic sodium hydroxide solution.[251][251]

Covestro (former Bayer MaterialScience) filed a patent in 2012 about the alcoholysis of amides to produce ester containing isocyanates.[254] They introduced concentrated HCl gas in a mixture of *ε*-caprolactam and water (1.3 eq) and removed the water by azeotropic distillation with toluene, while still keeping a constant HCl introduction in the mixture and obtained the product in 85% yield.



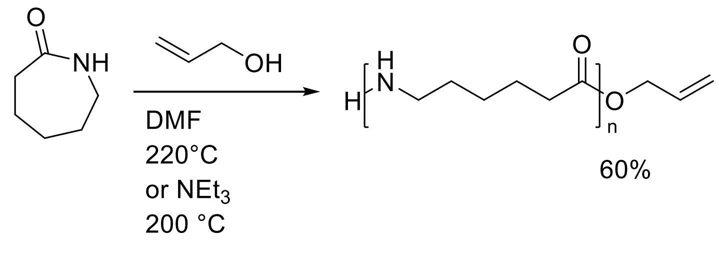
Scheme 44:Acid-catalyzed aminolysis of amides to produce diamines.[254]

Toray Industries from Japan already filed a similar patent for the synthesis of a triamine in 1986, although the exact reaction conditions are difficult to assess as the patent is not translated to English (Scheme 45, **A**).[252][252]



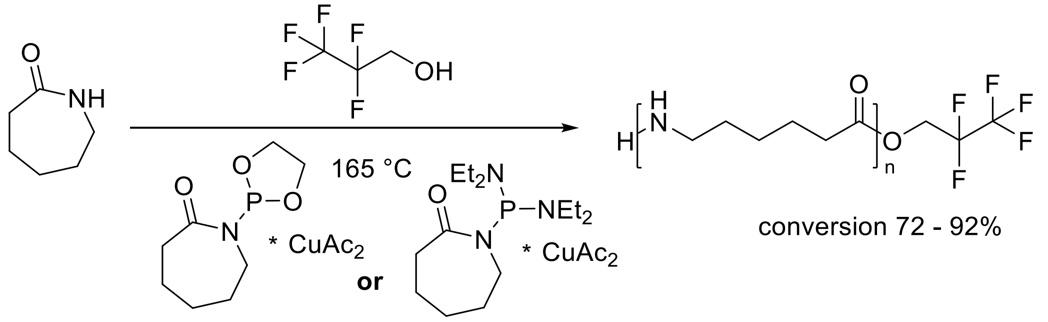
Scheme 45: Products of the alcoholysis of ε-caprolactam of different patented procedures.[252][252]

In 2014, Sunny Pharmtech Inc. from Taiwan filed a patent titled “method of making 6-aminocaproic acid from *ε*-caprolactam as active pharmaceutical ingredient”. They describe an example of first synthesizing 6-amino-hexanoic acid by acidic hydrolysis of *ε*-caprolactam and simple esterification with benzyl alcohol by classic Fischer esterification (Scheme 45, **B**), which cannot be considered as a direct selective ring-opening of *ε*-caprolactam.



Scheme 46: Alcoholysis of ε-caprolactam under basic conditions.[255]

In 2002, N. A. Storozhakova *et al.* utilized allyl alcohol under basic conditions for the alcoholysis of *ε*-caprolactam.[256] However, they only obtained 60% yield of an oligomer mixture, which was only characterized by IR- and elemental analysis. According to their study, aliphatic alcohols, in particular propyl and butyl alcohols almost do not react with lactam under these conditions. The same group reported on the reaction of *ε*-caprolactam with polyfluorinated alcohols and diacetatobis(ε-caprolactam)copper as catalyst in 2007.[257,258] They achieved conversions of 72 – 92% and obtained an oligomer mixture.



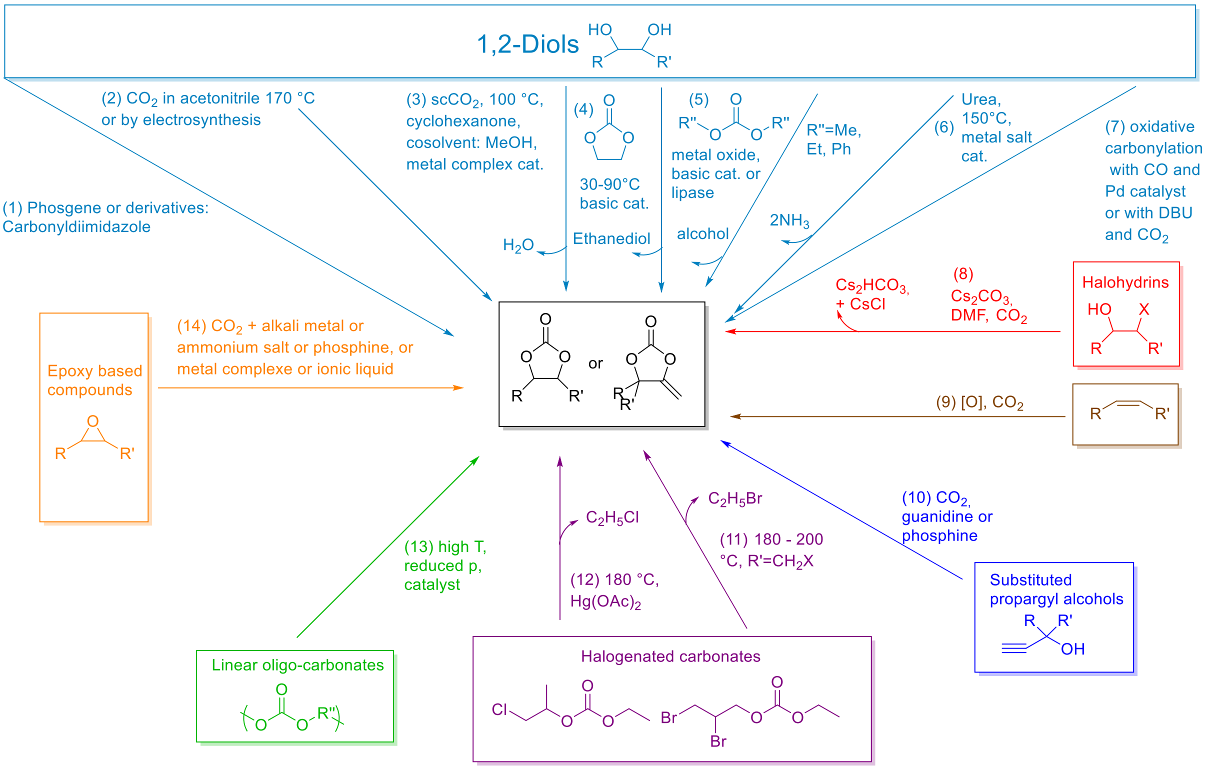
Scheme 47: Alcoholysis of ε-caprolactam polyfluorinated alcohols and diacetatobis(ε-caprolactam)copper as catalyst.[258]

2.6.2 Five-membered carbonates

In 2015, H. Cramail and coworkers reviewed the different synthesis methods of five-membered cyclic carbonates (Scheme 48).[259] The first route for the synthesis of five-membered carbonates is on the example of ethylene carbonate and involves phosgenation by phosgene or triphosgene (Scheme 48, (1)), which is due to obvious reasons not suitable for a sustainable synthesis, as the original purpose of NIPUs is to avoid phosgene.[260] Most sustainable approaches are typically based on either insertion of CO_2 into epoxides (Scheme 48, (14)), which are synthesized from renewable resources containing double bonds or from 1,2-diols (Scheme 48, (1) – (7)).

For some carbonates, such as *e.g.* glycerol carbonate, the direct synthesis from the 1,2-diol and supercritical CO_2 ($_{sc}CO_2$) has been established,[261] although the reaction is currently still not feasible on an industrial scale due to low conversions (32%).[259] Another method utilizing supercritical CO_2 was reported by M. Aresta *et al.* first obtaining the ketal of cyclohexanone and 1,2-ethanediol followed by transition-metal complex catalyzed carbonate formation in $_{sc}CO_2$ (Scheme 48, (3)) or with CO_2 in organic solvents.[262] Other methods involving pressurized CO_2 and 1,2-diols are performed in acetonitrile at 170 °C and catalyzed by metallic acetates (Scheme 48, (2)),[263] by electrosynthesis (Scheme 48, (2)),[264] or with DBU in dibromomethane (Scheme 48, (7)).[265] The carbonate interchange reaction between 1,2-diols and ethylene carbonate (Scheme 48, (4)) or linear carbonates (dimethyl carbonate, diethyl carbonate or diphenyl carbonate) is another interesting approach, which will be discussed in more detail in a later paragraph of this section.[266] Another approach is the transesterification with urea and ZnO or various other solid catalysts.[267] Very interesting is the oxidative carbonylation with carbon monoxide using for instance palladium-based catalysts,[268] which is also the established synthesis of most basic linear carbonates. Alternatively to a two-step procedure (first synthesizing the epoxide and insertion of CO_2 afterwards), olefins can be directly converted by oxidative carboxylation with a catalytic system of $MoO_2(acac)_2$ – quaternary ammonium salt and *tert*-butyl hydroperoxide as an oxidant in an one-pot multistep process (Scheme 48, (9)).[269] Other methods available for this oxidative carboxylation were reviewed in 2011 by J. Sun and coworkers.[270] Methods involving other starting materials are of minor importance, *e.g.* from halohydrins (Scheme 48, (8)),[270] substituted propargyl alcohols

(Scheme 48, (10)),[271] halogenated carbonates (Scheme 48, (11, 12)),[272] or linear oligo-carbonates (Scheme 48, (13)).[273]

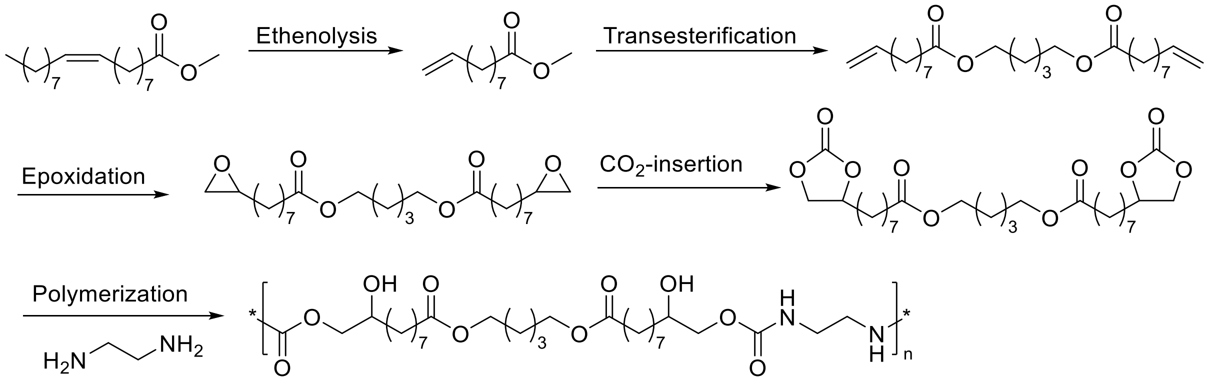


Scheme 48: Different methods for the synthesis of 5-membered cyclic carbonates reviewed by H. Cramail and coworkers.[259]

Six- or seven- membered cyclic carbonates can be obtained from 1,3-diols or 1,4 diols by similar means as five-membered cyclic carbonates. While they provide a better reactivity due to a lower thermodynamic stability (six-membered cyclic carbonates react up to 60 times faster, seven-membered cyclic carbonates react up to 2,400 times faster),[238] the synthesis of six- or seven- membered carbonates is much harder for exactly the same reason.[274] Still, K. Tomishige *et al.* reported a particularly efficient catalyst (CeO_2) with high yields for six- membered carbonates (62−>99%) from CO_2 and diols in 2014.[275] However, a high excess (10 times) of 2-cyanopyridine was needed to remove water from the reaction mixture and obtain a high selectivity.

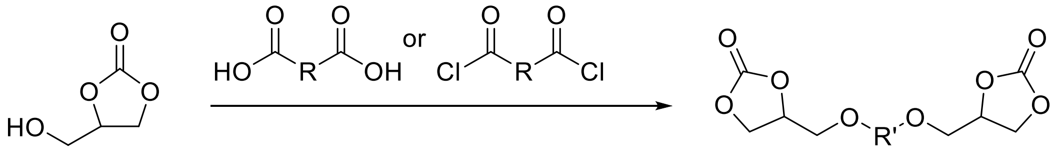
2.6.3 *Bis*-cyclic carbonates and their polymerization with diamines

Various renewable resources were explored for the synthesis of bCCs. An attractive route is the reaction of epoxidized plant oil precursors with CO_2. H. Cramail *et al.* reported the carbonation of different fatty acid derived epoxide monomers (Scheme 49).[276] Especially the solubility of supercritical CO_2 in the respective vegetable oil derivatives as a function of temperature and pressure is of high importance and was studied in detail and the concept was expanded on several substrates.[277]



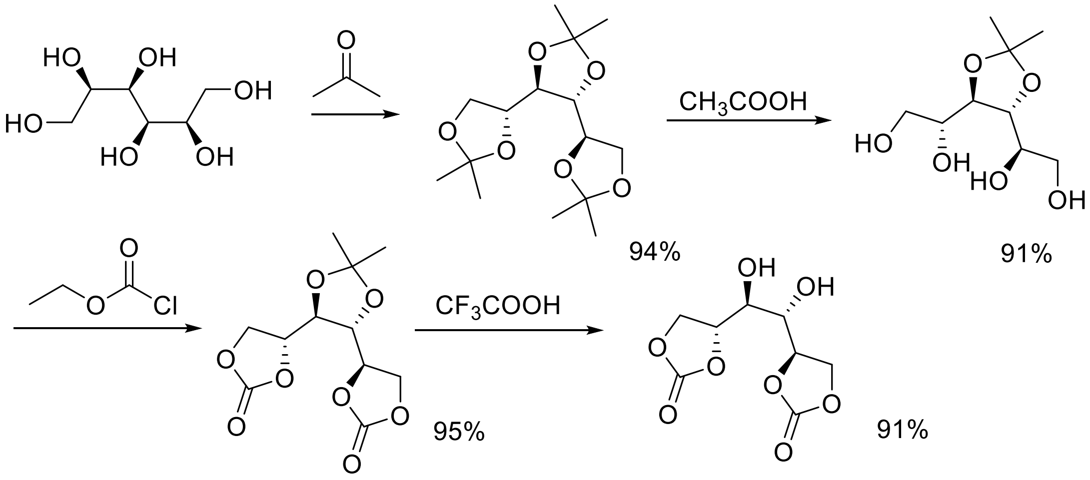
Scheme 49: Example for fatty acid derived NIPUs derived from methyl oleate.[276]

Starting from glycerol carbonate, several routes to bio-based bCCs are possible. For example esterification with coupling agents[278] or acid chlorides.[279]



Scheme 50: Synthesis of bCCs from glycerol carbonate by esterification.

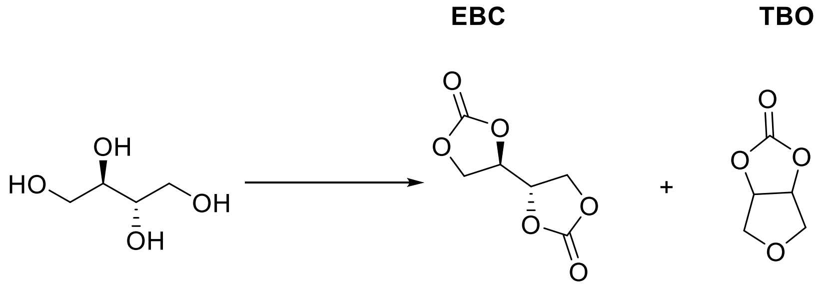
By further derivatization of glycerol carbonate, dimerization can also be achieved by other means, such as *e.g.* thiol-ene reactions.[280] G. Prömpers *et al.* synthesized D-mannitol-1,2:5,6-dicarbonate in a four-step synthesis utilizing a protection deprotection strategy and achieving a high overall yield of 74% (see Scheme 51).[281]



Scheme 51: Four-step synthesis of D-mannitol-1,2:5,6-dicarbonate.

R. Mülhaupt *et al.* converted limonene into a bCC in 2012 and polymerized it afterwards with several commercial diamines.[282] Utilizing an glycidylation with epichlorohydrin followed by CO_2-insertion, several renewable substrates such as isosorbide[283] or vanillin[284] were converted to bCCs.

In 2012, G. Rokicki *et al.* reported the first synthesis of erythritol bis(carbonate) (EBC) from erythritol as a side reaction of the “intramolecular etherification of five-membered cyclic carbonates bearing hydroxyalkyl groups”.[285] They utilized an excess of dimethyl carbonate (DMC) at 70 °C and 226 mbar with K_2CO_3 as catalyst, only obtaining the EBC in 5% yield and mostly obtaining (1*R*,5*S*)-2,4,7-trioxa-3-oxy-bicyclo[3.3.0]octane (Scheme 52, TBO, conditions A).



Conditions A: 10 eq DMC, 0.1 eq K_2CO_3, THF; yield 5%

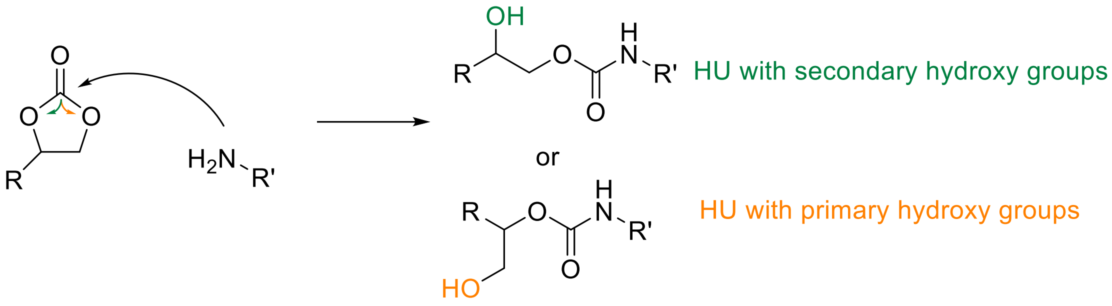
Conditions B: 2.1 eq DPC, 0.01 eq $Zn(OAc)_2$, DMSO; yield 80 - 90%

Scheme 52: Synthesis of erythritol bi(carbonate); conditions A (G. Rokicki et al.*);[285] conditions B (R. Mülhaupt* et al.*);[286] DMC = dimethyl carbonate, DPC = diphenyl carbonate,*

In 2017, based on these results, R. Mülhaupt *et al.* used diphenyl carbonate (DPC) instead of DMC at 120 °C and 30 mbar in DMSO with $Zn(OAc)_2$ as catalyst, thus avoiding the intramolecular etherification and obtaining EBC in 80 – 90% yield

(Scheme 52, conditions B).[286] Moreover, they also synthesized EBC from butadiene by epoxidation and CO_2-insertion, a process that was already patented in 1960 by Union Carbide Whelan.[287] Utilizing different commercial diamines, polyurethanes were prepared in solution (DMSO) and by melt-phase polyaddition using a twin-screw miniextruder with weight-average molar masses of up to 44 kg mol^{-1}. Combining flexible and rigid diamines segmented PHU thermoplastics with properties varying from hard to semicrystalline, amorphous, flexible, and soft were produced.

The kinetics of the addition of amines to five-membered carbonates have been studied by several groups.[259] At higher temperatures, the reaction progresses faster,[259] but at temperatures above 100°C, another amine molecule is able to react with the hydroxyurethane to yield a substituted urea. At 150 °C, CO_2-evolution occurs and alkylation reactions take place.[286,288] An increase of conversion and yield can be observed if the reaction is performed in toluene instead of DMSO,[289] however in bulk even better conversions can be observed.[259] The mechanism oft the addition of amines to cyclic carbonates affords either primary or secondary hydroxy groups in the polymer backbone (Scheme 53).[259]



Scheme 53: Different possibilities of the ring-opening of a monosubstituted five-membered carbonate. HU=Hydroxyurethane.

Typically, secondary hydroxyl groups are formed preferably as investigated by Steblyanko *et al.*, who studied the reaction of glycerine carbonate benzoate with benzyl amine at room temperature and received a ratio of primary : secondary hydroxyl group of 18% : 82%.[290] The ratio seems to be independent of the reaction temperature, however it is depended on the solvent, as *e.g.* in DMSO the isomer with a secondary OH-group is formed less than in toluene.[291] The structure of the amine is also important and it was revealed that *e.g.* hexylamine forms a higher amount of secondary OH-groups compared to benzylamine.[291] Moreover, longer alkyl chains on the amine afford more of the isomer bearing primary hydroxy groups compared to shorter alkyl chains.[292] Another influence is the structure of the substituent of the carbonate. More electron withdrawing substituents favor the formation of the secondary hydroxy groups and increase the overall reactivity of the carbonate towards amines.[289] For example, in the reaction between diethyltriamine and carbonated epichlorohydrin, exclusively secondary hydroxy groups are formed.[293] Usually no catalysts are required for the polymerization. However, strong non-nucleophilic bases such as TBD, DBU, 1,4-diazabicyclo[2.2.2]octane (DABCO), piperazine or triethylamine, as well as Lewis acids can have a positive effect on the reaction rate.[259,294]

3 Aim of the thesis

In this thesis, two different approaches of utilizing the $GaBr_3$-catalyzed reduction of esters for the synthesis of polyethers are introduced. In the first approach, polyesters with different structures and lengths of the aliphatic segment are synthesized, based on renewable resources, by either polycondensation of dimethyl esters and diols or ring-opening polymerization of lactones. The reduction of these polyesters to polyethers is optimized, in terms of conversion of ester groups and suppression of possible side reactions (*i.e.* reduction to the alcohol). The obtained polyethers are analyzed regarding their chemical structure, average molecular weight and thermal properties and are compared to the respective polyesters they are derived from.

In the second approach, *ω,ω'*-unsaturated esters are synthesized from plant oils and plant oil derivatives. For this purpose, the ethenolysis of methyl oleate and the transesterification of the obtained *ω*-unsaturated methyl ester with diols is initially optimized. Afterwards, the *ω,ω'*-unsaturated esters are reduced to the respective ethers and polymerized by ADMET or thiol-ene polymerization, obtaining polyethers and poly(ether-thioethers). For thiol-ene polymerizations, the *ω,ω'*-unsaturated ethers are first converted to the respective dithiols to obtain suitable comonomers. After the optimization of the polymerizations, the ADMET or thiol-ene polymers are modified by hydrogenation and oxidation, respectively, to improve their material properties. The polymers are compared regarding their thermal properties and molecular weight.

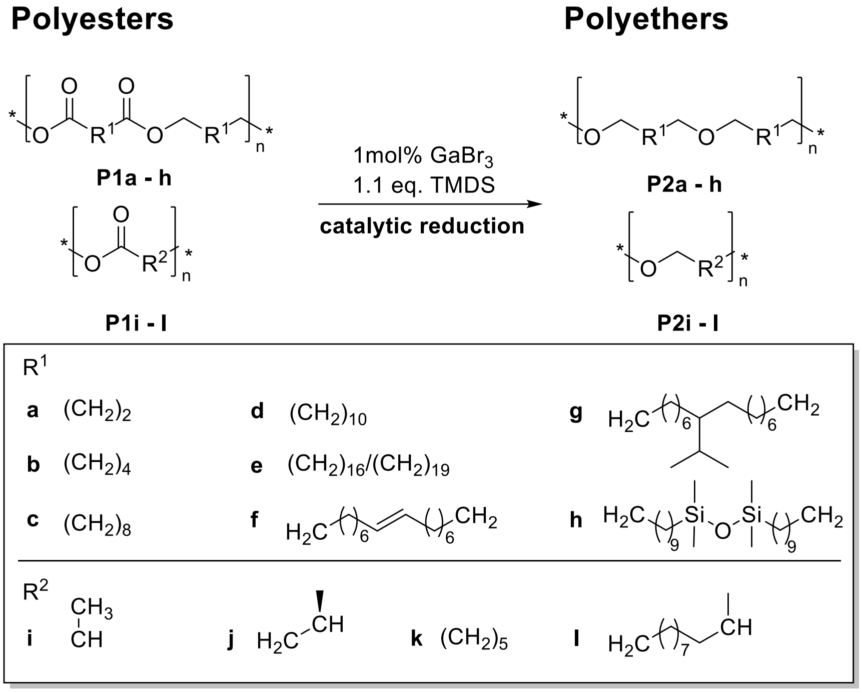
Finally, the polyethers synthesized in the first approach are modified to form polyether-diamine prepolymers. Therefore, a quantitative conversion of the hydroxy- end to amine end groups is necessary and the synthesis is optimized. The synthesis of erythritol bis(carbonate) is optimized to obtain a suitable comonomer and lastly both monomers are utilized for the preparation of non-isocyanate polyurethanes.

4 Results and Discussion

4.1 Polymer Approach - Renewable polyethers via $GaBr_3$ catalyzed reduction of polyesters[i]

P.-K. Dannecker, U. Biermann, M. von Czapiewski, J. O. Metzger, M. A. R. Meier, *Angew. Chem. Int. Ed.* **2018**, *57*, 8775–8779; *Angew. Chem.* **2018**, *130*, 8911–8915.

In the polymer approach, the $GaBr_3$/TMDS system is applied to predominantly renewable polyesters as a new route for the synthesis of polyethers (Scheme 54). Polyesters **P1a**-**h** were prepared from the respective dimethyl esters and their corresponding diols, polyesters **P1i** and **P1k** from L-lactide and ε-caprolactone by ring-opening polymerization, respectively, and **P1l** from methyl 10-hydroxyundecanoate. Poly[(*R*)-3-hydroxybutanoate] **P1j** is produced by *cupriavidus necator* bacteria and was obtained commercially.



*Scheme 54: Catalytic reduction of renewable polyesters **P1a**-**h** (obtained from the respective dimethyl esters and diols), **P1i** and **P1k** (obtained by ring-opening polymerization of L-lactide and ε-caprolactone, respectively), **P1j** (natural origin) and **P1l** (obtained from methyl 10-hydroxyundecanoate) to polyethers **P2a**-**l**.*

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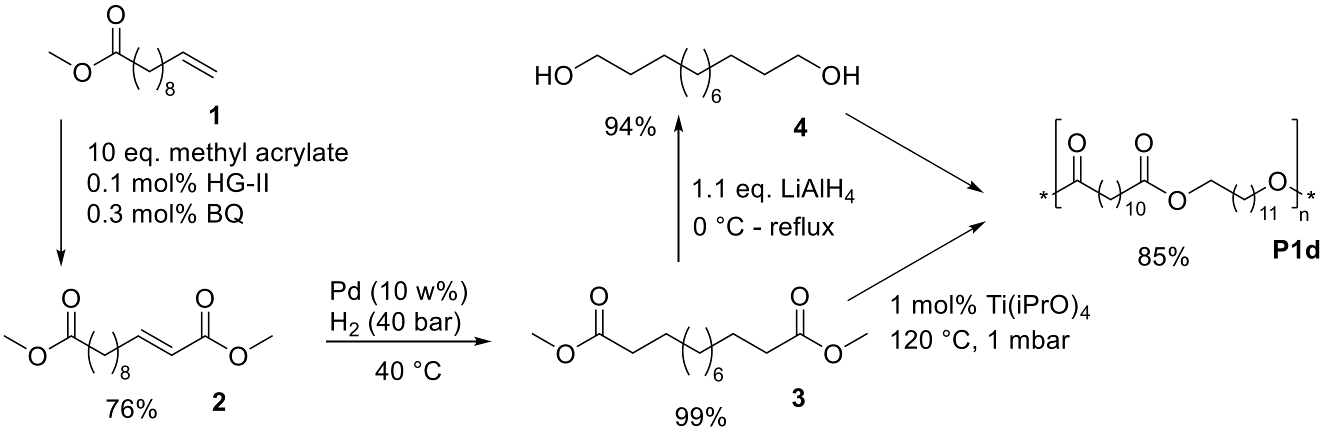
[i] Part of this chapter was published in: Patrick-Kurt Dannecker, Ursula Biermann, Marc v. Czapiewski, Jürgen O. Metzger, Michael A. R. Meier, *Angew. Chem. Int. Ed.* ***2018**, 57, 8775–8779; Angew. Chem. **2018**, 130, 8911–8915.*

4.1.1 Polyester synthesis

4.1.1.1 Polyesters by polycondensation of diols and dimethyl esters

To prepare non-commercial monomers **3**, **4**, **8**, **9**, **10**, **11**, **12**, **13**, **14** and **15** for the subsequent synthesis of polyesters **P1d** – **P1h**, different routes starting from fatty acid derived substrates were pursued.



*Scheme 55: Synthesis of monomers **19** and **20** for polyester **P1d**. Methyl undecenoate **17** was used in a cross-metathesis reaction with methyl acrylate to obtain **18**. Dimethyl ester **19** was obtained after hydrogenation followed by reduction using $LiAlH_4$ to obtain diol **20**.*

For the synthesis of polyester **P1d**, methyl undecenoate **1** was reacted in a cross-metathesis reaction with methyl acrylate in excess (10 eq.) to obtain dimethyl ester **2** in a yield of 76% after purification by column chromatography.

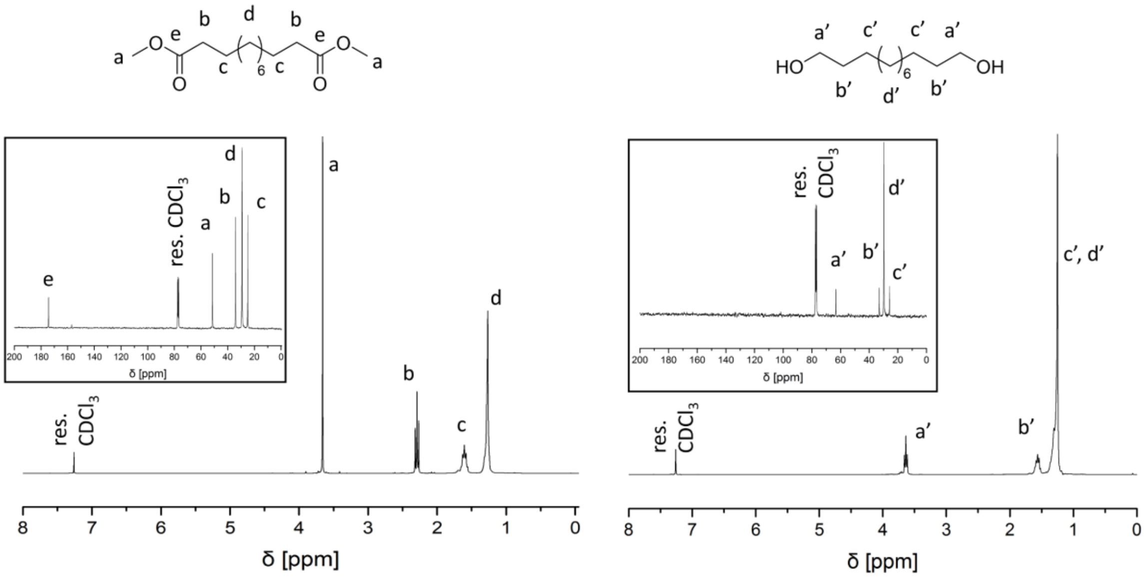


*Figure 6: ^1H- and ^{13}C-NMR spectra in $CDCl_3$ of dimethyl ester **3** (left) and diol **4** (right).*

Hydrogenation, using 40 bar hydrogen pressure and palladium on charcoal as catalyst, gave dimethyl ester **3** in quantitative yield. The catalyst was removed by simple filtration. Diol **4** was obtained after reduction with $LiAlH_4$ (1.1 eq., 10 % excess) and purification by column chromatography in 94% yield. The purity of the compounds was confirmed by ^{1}H- and ^{13}C-NMR-spectroscopy (Figure 6). For dimethyl ester **3**, a characteristic singlet ***a*** can be observed at a chemical shift of 3.66 ppm for the methoxy group and a triplet at 2.30 ppm for methylene group ***b*** in α-position to the ester. For diol **4**, methylene group ***a'*** in α-position to the alcohol can be discerned as triplet at 3.66 ppm. For both, diol and dimethyl ester, methylene groups ***c*** and ***c'*** are shifted towards the high field in the ^{13}C-NMR spectrum at 25.0 and 25.5 ppm, respectively, which was confirmed by 2D-NMR-spectroscopy (HSQC, COSY). Diol **4** and dimethyl ester **3** were polymerized afterwards in a polycondensation using TBD as catalyst at 120 °C and reduced pressure to remove the volatile side product methanol. Polyester **P1d** was obtained in a yield of 85 % after precipitation in methanol. GPC analysis in HFIP (this polyester was insoluble in THF at room temperature) revealed a molecular weight of M_n=9,300 g mol^{-1} with $Đ$=2,86 (Figure 7, right). In the ^{1}H-NMR spectrum (Figure 7), the ester bond characteristic triplets ***a*** and ***b*** can be assigned at 3.98 and 2.22 ppm, respectively. Signals of the methoxy end group (3.60 ppm, singlet) and of the -CH_2-OH end group (3.57 ppm, triplet) overlap and end group analysis reveals a molecular weight of M_n=8,700 g mol^{-1} assuming a 1:1 ratio of both end groups. To obtain polyester **P1e**, a procedure developed in the Meier group in 2013 was followed.[184]

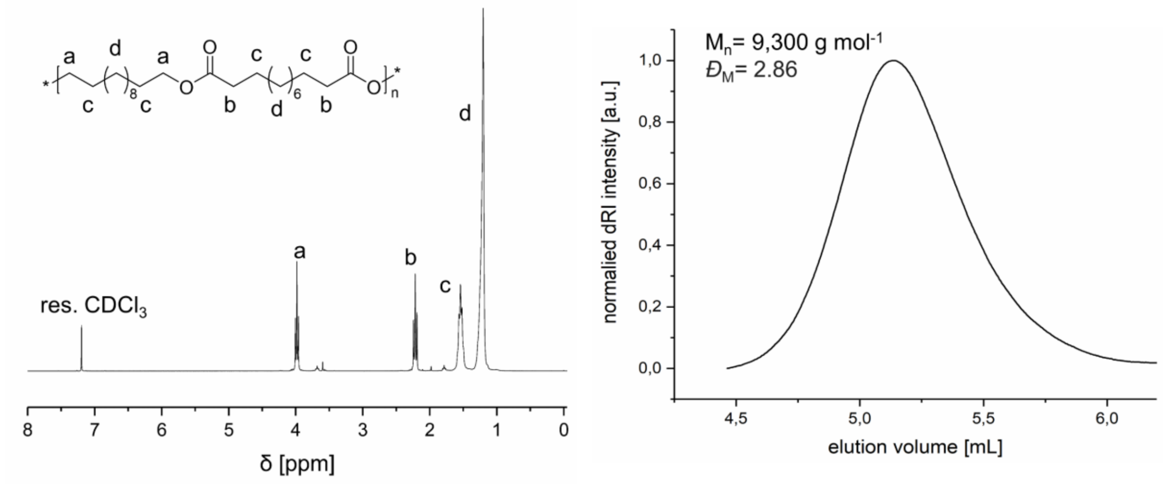
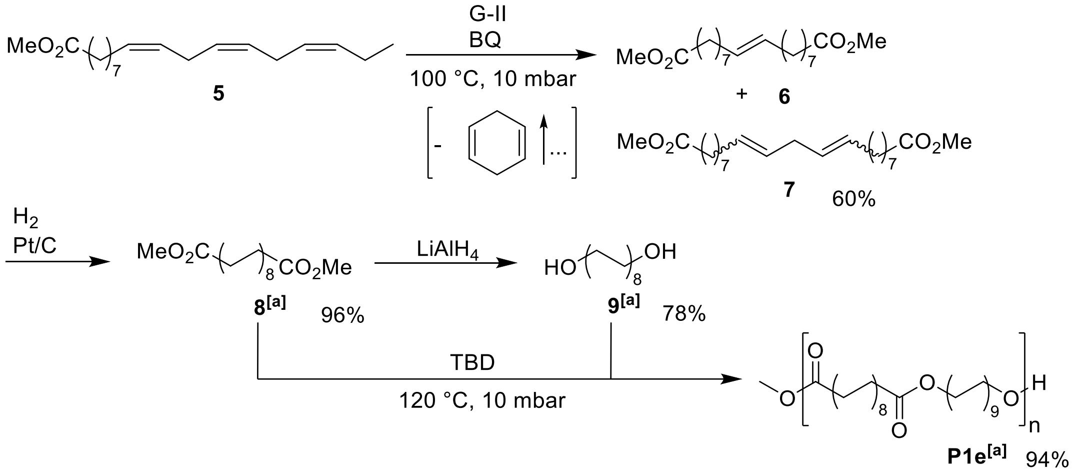


*Figure 7: ^{1}H-NMR spectrum (left) in $CDCl_3$ and GPC chromatogram (right) of polyester **P1d**.*

By self-metathesis of polyunsaturated fatty acid methyl esters (FAMEs, mostly containing methyl linolenate **5**), dimethyl ester mixture **6** + **7** was be obtained. To shift the reaction equilibrium, volatile side products (*i.e.* cyclohexadiene or hex-3-ene) were removed under reduced pressure during the reaction. After purification by column chromatography dimethyl ester **6** and **7** were obtained in 60 % yield in a ratio of 63:37. Following the self-metathesis, similar to the synthesis of polyester **P1d** shown previously, dimethyl ester mixture **6** and **7** was hydrogenated, reduced to the diol and polymerized afterwards (Scheme 56).



*Scheme 56: Self-metathesis of methyl linolenate **5**, followed by hydrogenation of dimethyl ester mixture **6** and **7**, reduction to diol **9** and polymerization of diol and dimethyl ester to polyester **P1e**. [a]simplified structure, C21-dimethyl ester is not shown.*

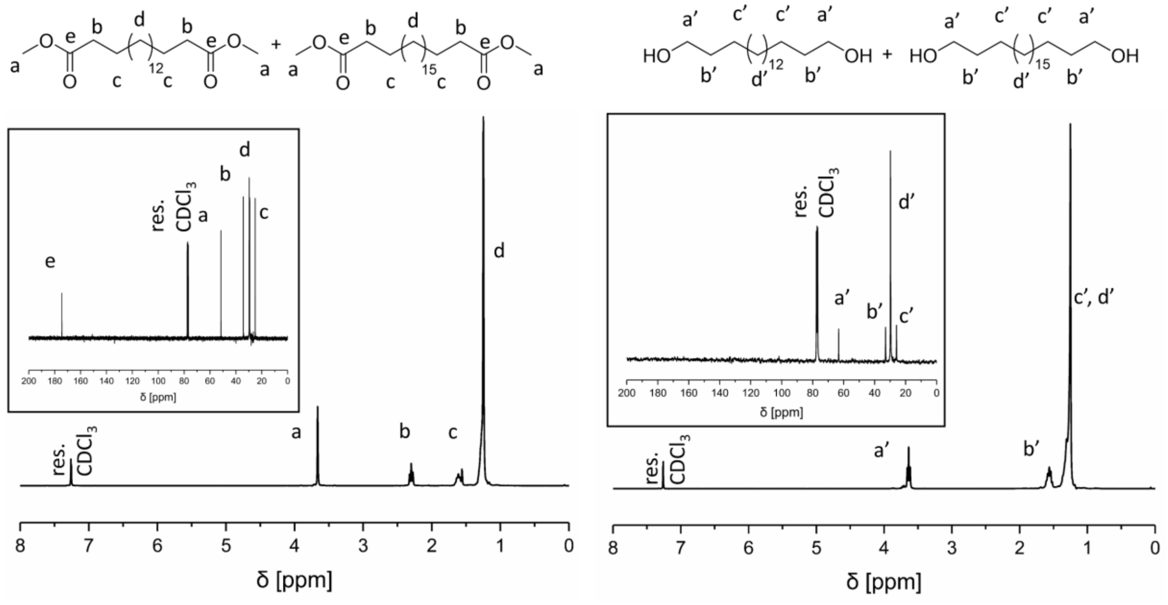
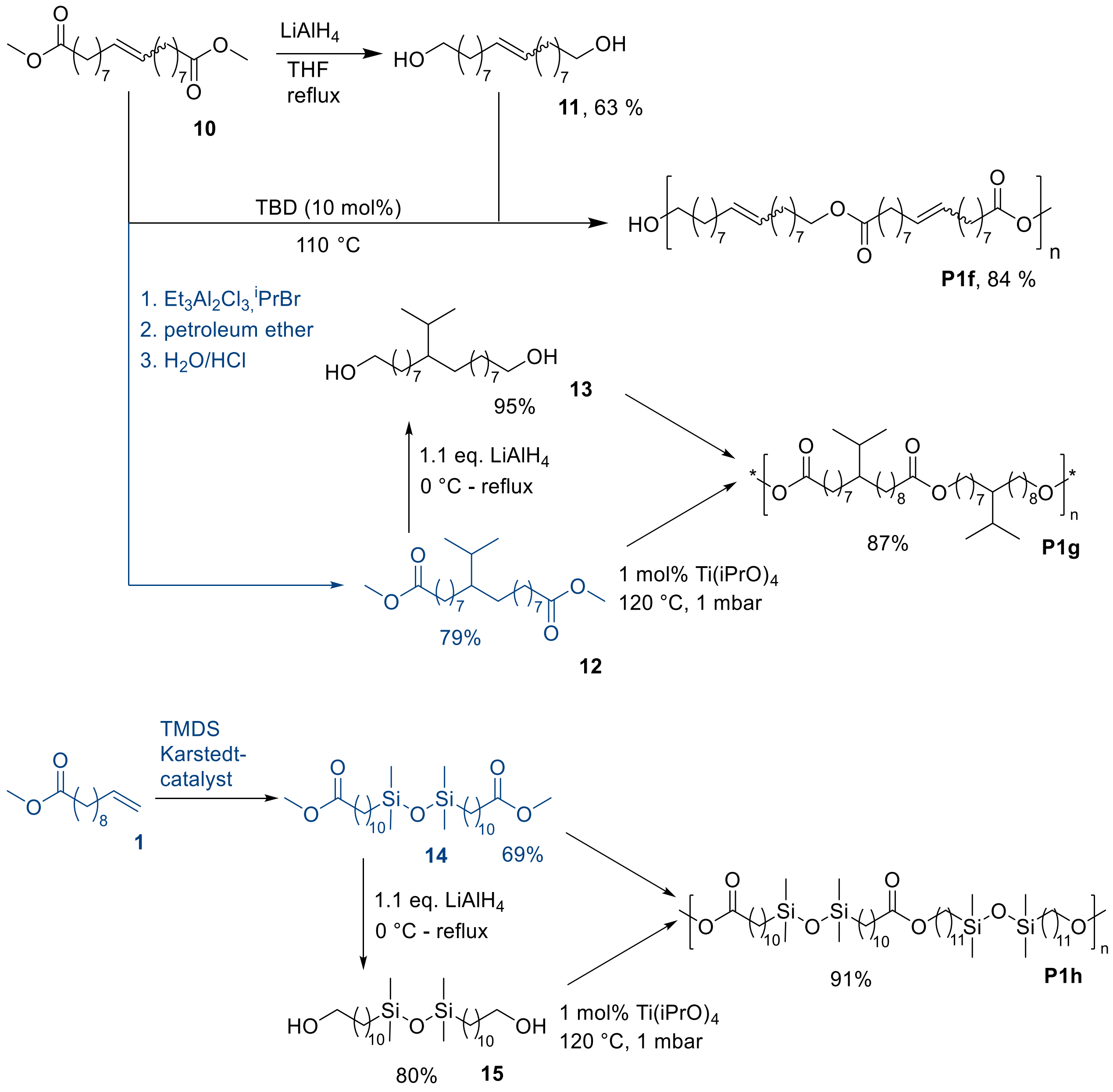


*Figure 8: ^{1}H- and ^{13}C-NMR spectra in $CDCl_3$ of dimethyl ester **8** (left) and diol **9** (right).*

In ^{1}H- and ^{13}C-NMR-spectroscopy, the signals for dimethyl ester **8** and diol **9** can be assigned in a similar fashion as for dimethyl ester **3** and diol **4** (Figure 8). For the polycondensation, the same conditions were applied as for **P1d**. The resulting polyester **P1e** is insoluble in common organic solvents at room temperature and could not be analyzed by ^{1}H-NMR-spectroscopy or GPC analysis. To produce soluble aliphatic long chain polyesters, **P1f** – **P1h** containing solubilizing groups were thus synthesized (Scheme 57).



*Scheme 57: Synthesis of FAME based polyesters **P1f** – **P1h**. Steps shown in blue were performed by the project partner.*[i]

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[i] Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

For the synthesis of polyester **P1f**, pure methyl ester **10** (in contrast to the mixture of **2**+**3** for the synthesis of **P1e**) was obtained as side product of the ethenolysis of methyl oleate (monomer approach, discussed in detail in section 4.2.1). It was directly reduced to diol **11** without prior hydrogenation with a yield of 63 % after column chromatography. Polyester **P1g** was obtained by alkylation with $Et_2Al_2Cl_3$ and isopropyl bromide[1] and purified by short-path vacuum distillation (79% yield).[295] Similarly to the previous dimethyl ester, **12** was reduced to the diol **13** (95% yield) and polymerized under reduced pressure to **P1g** (87% yield after precipitation in MeOH at -10 °C). For the synthesis of **P1h** methyl undecenoate **1** was dimerized by hydrosilylation of methyl undecenoate **14** in the presence of the Karstedt catalyst according to a method described by Katir *et al.*[296] and obtained in a yield of 69%.[i] Reduction to the corresponding diol (69% yield) and subsequent polymerization resulted in **P1f** (Scheme 57, 91% yield after precipitation in MeOH at -10 °C).

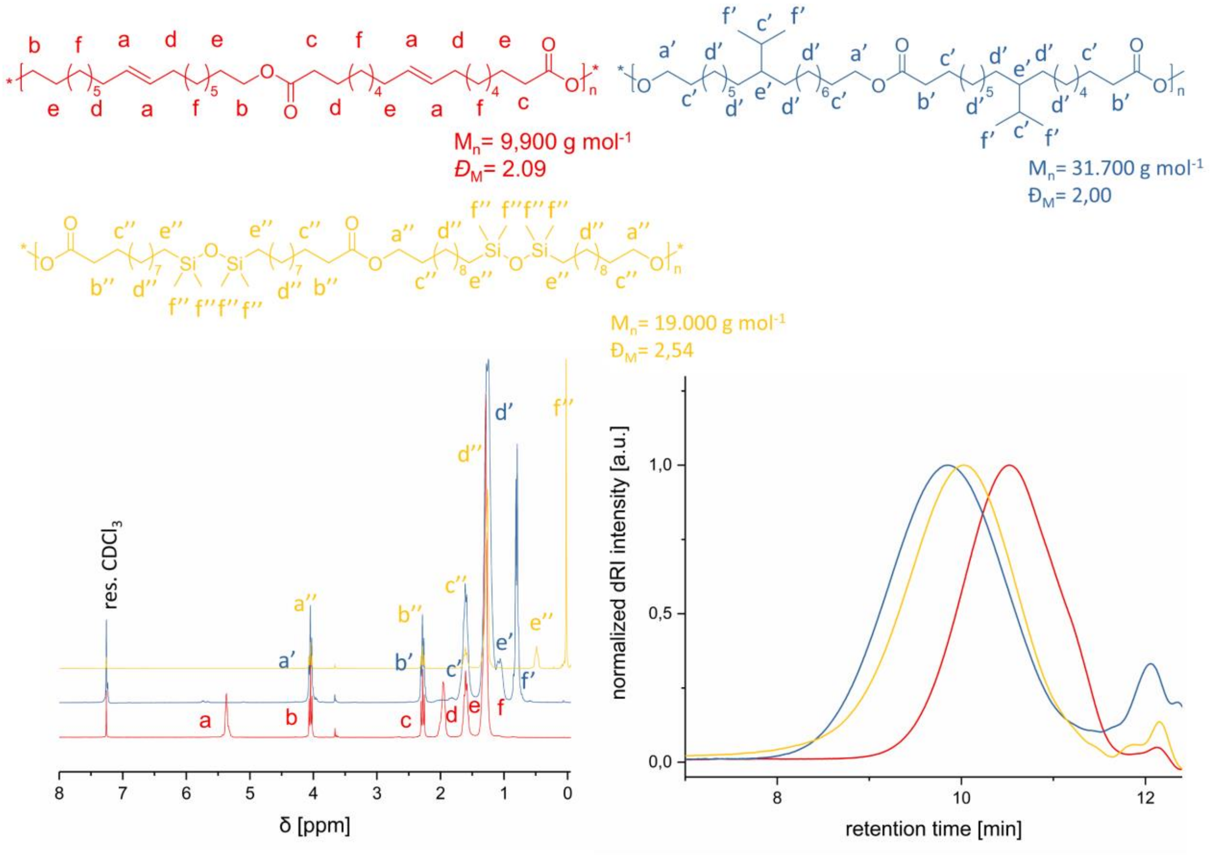

*Figure 9: Stacked ^{1}H-NMR spectra and GPC chromatograms of polyester **P1f** (red), **P1g** (blue) and **P1h** (yellow).*

In ^{1}H-NMR-spectroscopy (Figure 9, left side), the signal for the internal double bond of **P1f** can be observed as multiplet at 5.47 – 5.24 ppm. For all polyesters **P1f** – **h**, the

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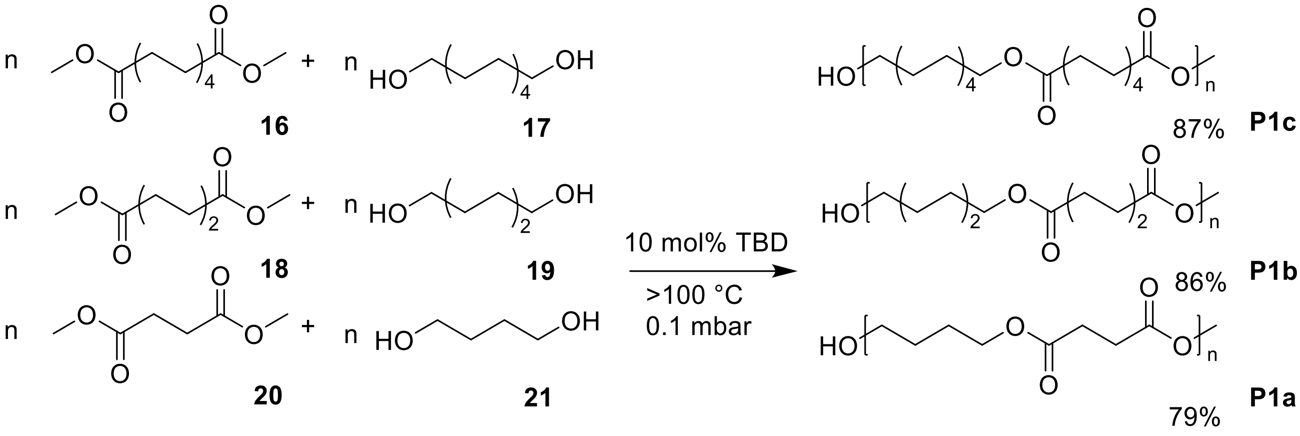
[i] Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

ester bond gives characteristic triplets at 4.04 ppm and 2.28 ppm. Additionally, for polyester **P1g**, multiplet ***c'*** can be discerned at 1.92 – 1.70 ppm (shifted to the low field as confirmed by COSY and HSQC, in ^{13}C-NMR however shifted to the high field at 27.9 ppm). An unexpected chemical shift can be observed for CH-proton ***e'***, which can be identified in the ^{1}H-NMR spectrum as multiplet in the high field at 1.13 – 0.99 ppm, by correlating in the ^{13}C NMR spectrum to a signal in the low field at 43.8 ppm. For polyester **P1h**, the methylene group ***e''*** in α-position to the silyl group is identified as multiplet at 0.58 – 0.43 ppm. Moreover, methyl groups ***f''*** are visible as sharp singlet at 0.02 ppm. The number average molecular weights according to NMR end group analysis (M_n=9,400 g mol^{-1} (**P1f**), M_n=13,100 g mol^{-1} (**P1g**), M_n=8,300 g mol^{-1} (**P1h**)) are in case of **P1g** and **P1h** largely different from the GPC measurements (Figure 9, right side) (M_n=9,300 g mol^{-1}, $Đ_M$ =2,86 (**P1f**), M_n=31.700 g mol^{-1}, $Đ_M$=2,00 (**P1g**) to M_n=19.000 g mol^{-1}, $Đ_M$=2,54 (**P1h**)), which might indicate that that the PMMA standards used for GPC-calibration are not well suited for this type of polymer.



*Scheme 58: Synthesis of polyesters **P1a** – **P1c** from renewable or potentially renewable diols and dimethyl esters.*[297]

Polyesters **P1c**, **P1b** and **P1a** were synthesized from commercial, renewable or potentially renewable diols and dimethyl esters, again using TBD as catalyst at elevated temperatures and reduced pressure giving yields in between 79 and 87% after precipitation in methanol.[298]

After synthesizing polyesters **P1a** – **P1h**, the conversion of the respective polymerizations can be calculated by using carothers' equation.

$$DP = \frac{1}{1 - C}$$

DP: degree of polymerization;

p: conversion.

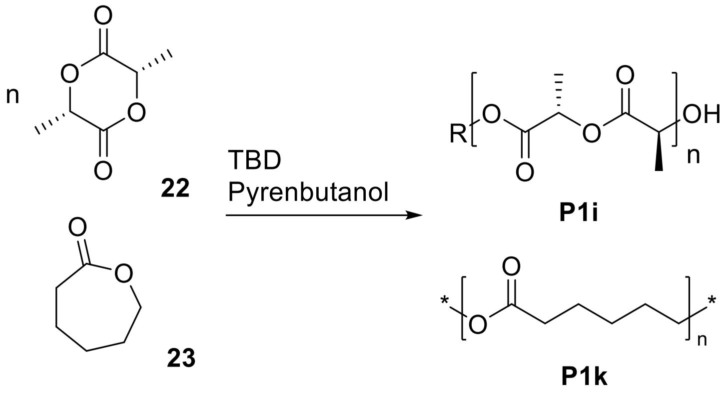
Table 4: Summary of all synthesized AABB-type polyesters. Number average molecular weight M_n, degree of polymerization (DP), Yield (Y) and the via carothers equation obtained conversions (C) are shown.

Polymer	**M_n [g mol^{-1}]**	**$Đ_M$**	**DP[c]**	**C [%][e]**	**Y [%]**
P1a	4,900[b]	1.83	57	98.2	79
P1b	7,500[b]	1.62	66	98.5	86
P1c	15,000[b]	1.75	88	98.9	87
P1d	9,300[b]	2.86	47	97.9	85
P1e	-[d]	-[d]	-[d]	-[d]	99
P1f	9,900[a]	2.09	35	97.1	84
P1g	31,700[a]	2,00	98	99.0	87
P1h	19,000[a]	2.54	43	97.7	91

[a] determined by GPC analysis in THF; [b] determined by GPC analysis in HFIP; [c] degree of polymerization M_n/M_0, M_0=average molecular weight of diol and diacid component; [d] insoluble in HFIP; [e] calculated by carothers equation M_n.

4.1.1.2 Polyesters by ring-opening polymerization of lactones

Polylactide **P1i** and polycaprolactone **P1k** were obtained by ring-opening polymerizations of lactide and *ε*-caprolactone.



*Scheme 59: Ring-opening polymerizations of lactide **22** and ε-caprolactone **23**.*

Both polymerizations were performed in dichloromethane with TBD as catalyst and pyrenebutanol as initiator. Due to the high activity of TBD as well as high reactivity of *L*-lactide **22**, the polymerization to **P1i** was very fast (<15 s, >50% conversion) and difficult to control. Nevertheless, in both cases narrow molecular weight distributions ranging from 1.09 – 1.69 could be obtained by variation of the monomer to initiator ratio and quenching of the reaction after 30 s (for **P1i**) or 8 h (for **P1k**) using benzoic acid.

Poly(lactide) **P1i**	Initiator [mol%]	M_n [g mol^{-1}]	$Đ_M$
P1i.1	0.2	45,800	1.09
P1i.2	0.4	28,400	1.12
P1i.3	0.6	9,600	1.69

Poly(*ε*-caprolactone) **P1k**	Initiator [mol%]	M_n [g mol^{-1}]	$Đ_M$
P1k.1	0.0625	15,400	1.13
P1k.2	0.125	11,450	1.12
P1k.3	0.25	8,800	1.13
P1k.4	0.5	4,400	1.09

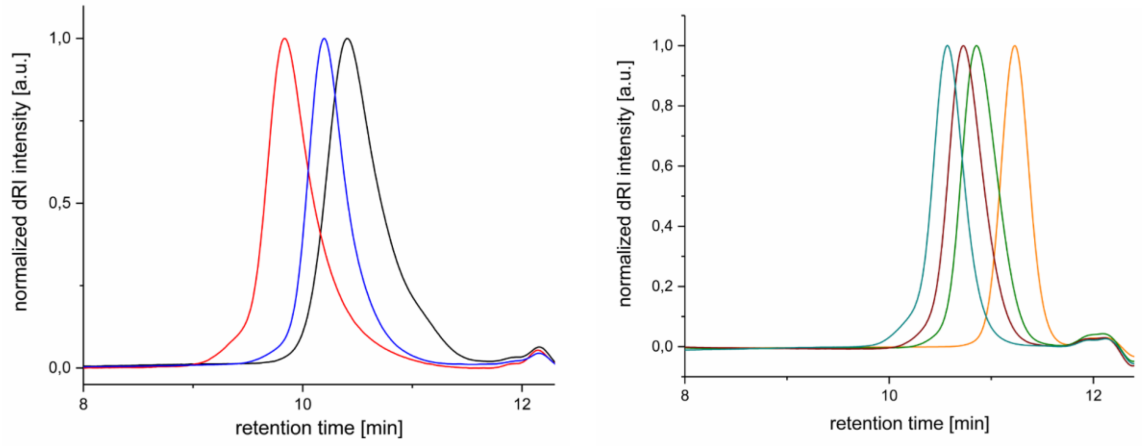
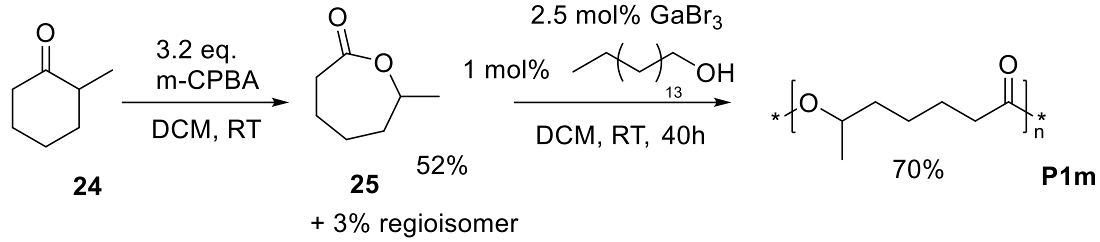


*Figure 10: GPC chromatograms for polyesters **P1i.1** – **P1i.3** and **P1k.1** – **P1k.4**.*



*Scheme 60: Baeyer-Villinger Oxidation of methyl-cyclohexanone **24** and polymerization to poly(methyl-caprolactone) **P1m**.*[i]

Additionally, methyl-ε-caprolactone **24** was synthesized by Baeyer-Villinger Oxidation (52% yield after column chromatography) of methyl-cyclohexanone and polymerized afterwards to polyester **P1m**.[1] Interestingly, the monomer did not polymerize using TBD as catalyst even after 20 h of reaction time or an elevated reaction temperature of 40 °C. An explanation for this behavior might be steric hindrance due to methyl group preventing TBD from coordinating to the ester group. As an alternative catalyst, which has not yet been described for ring-opening polymerizations in the literature, $GaBr_3$ was employed in 1.0, 2.5 and 5.0 mol% catalyst concentration. Monitoring of the reaction progress by GPC-analysis revealed a continuous increase in molecular weight during the first 20 h up to 3,100 ($Đ_M$=1.66, 1.0 mol% $GaBr_3$), 3,400 ($Đ_M$=1.70, 2.5 mol% $GaBr_3$), 3,000 ($Đ_M$=1.89, 5.0 mol% $GaBr_3$) for the respective catalyst concentrations and a constant M_n afterwards until 210 h reaction time. The obtained molecular weight was considerably lower than the targeted M_n of 12,800 g mol^{-1} and further investigation is required to study this effect. Applying the same conditions to ε-caprolactone **23** the maximum M_n is reached after 40 h: 9,750 ($Đ_M$=1.17, 1.0 mol% $GaBr_3$), 13,050 ($Đ_M$=1.08, 2.5 mol% $GaBr_3$), 8,700 ($Đ_M$=1.19, 5.0 mol% $GaBr_3$). Afterwards, the molecular weight was declining for all catalyst concentrations, which might be explained by the flask not being sealed well enough and traces of water getting into the reaction mixture. Interestingly, a higher catalyst concentration does not notably promote the reaction rate and there is no apparent correlation to the obtained M_n. Nevertheless, the M_n after 40 h fits rather well to the theoretical M_n for this initiator concentration at 100% conversion (11,400 g mol^{-1}). Therefore, $GaBr_3$ could be introduced as new catalyst for ring-opening polymerizations of lactones with a high level of possible control due to its long reaction time. Typical Lewis acid based catalyst

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[i] Carried out by Andreas Ganzbuhl in the Bachelor thesis "Catalytic reduction of sustainable A-B-type polyesters to polyethers" (under lab-supervision of Patrick-Kurt Dannecker). Specifics are given in the experimental part.

systems known up to now mostly rely on a combination and dual catalysis with a Lewis base.[78]

4.1.2 Reduction of polyesters to polyethers[i]

While the successful reduction of esters to ethers on small organic molecules was already demonstrated,[6,7] a transfer of this reaction to polymers is highly demanding. For instance, even a slight amount of the reduction of an ester group to an alcohol instead of an ether, a side reaction, that has been observed, would lead to a significant degradation of the polymer chain. In order to avoid this side reaction as far as possible, the reaction conditions were optimized and applied for most of the polyesters: 2 mmol of the polyester were dissolved in CH_2Cl_2, 1-2 mol % of $GaBr_3$ (based on one ester group) were added and 4.4 mmol of TMDS (1.1 eq. per ester unit) served as reductant.[ii] The mixture was stirred at room temperature overnight. To remove the formed polysiloxane, typically, the polyethers were purified by simple precipitation in hexane or petroleum ether achieving yields between 83% and 92% for polyethers **P2b**–**e**, **P2g**, **P2k** and **P2l**. For polyethers **P2a**, **P2f, P2h**, **P2i** and **P2j**, lower yield of 66%, 50%,42%, 34% and 74% were achieved, respectively, which might be attributed to a higher solubility of the polyethers and thus more difficult precipitation, but possibly also to some degradation (**P2i**, **P2j**). As confirmed by ^{1}H NMR-spectroscopy, a quantitative reduction of the ester groups (>99%) was achieved for **P2a** – **P2d** and **P2f** – **P2l**. IR spectroscopy confirms this quantitative reduction. Polyester **P1e** – at room temperature insoluble – was reacted at 60°C in toluene. A conversion of ~90% of the ester groups could be achieved according to IR spectroscopy. Table 5 gives a comprehensive overview of the molecular weights of the different polyesters and the respective polyethers.

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[i] Part of this chapter was published in: Patrick-Kurt Dannecker, Ursula Biermann, Marc v. Czapiewski, Jürgen O. Metzger, Michael A. R. Meier, *Angew. Chem. Int. Ed.,* DOI: 10.1002/anie.201804368.

[ii] Most reductions carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg) and analysed by Patrick-Kurt Dannecker. Detailed differentiation in experimental part.

*Table 5: Complete overview of polyesters **P1a** – **P1l** and polyethers **P2a** – **P2l**. Molecular weights, percentage of reduced ester groups and yields of the reduction.*

Polyester	M_n [g mol^{-1}] (DP[h])	Đ	T_m [°C]	M_n[g mol^{-1}] (NMR)[j]	Polyether	M_n [g mol^{-1}] (DP[h])	Đ	T_m [°C]	M_n [g mol^{-1}] (NMR)[k]	Red.[%][c]	Red.[%][d]	Y[%][e]
P1a	4,900[b] (57)	1.83	102.0	2,200	**P2a**	3,300[b] (46)	1.43	35.8	1,200	>99	97	66
P1b	7,500[b] (66)	1.62	41.9	3,900	**P2b**	7,600[b] (76)	1.67	37.8	2,600	>99	>99	83
P1c	15,000[b] (88)	1.75	67.3	8,800	**P2c**	12,900[b] (83)	3.22	64.0	3,900	>99	99	88
P1d	9,300[b] (47)	2.86	86.6	8,700	**P2d**	6,800[b] (37)	1.97	85.3	4,000	>99	95	90
P1e	-[f]	-[f]	101.6	-	**P2e**	- [f]	- [f]	96.6	- [f]	-[f]	90	92
P1f	9,900[a] (35)	2.09	64.6	9,400	**P2f**	6,000[a] (23)	3.48	67.7	3,100	>99	-[g]	50
P1g	31,700[a] (98)	2,00	-66,8[i]	13,100	**P2g**	-[c]	-[c]	-66,3[i]	6,500	>99	97	93
P1h	19,000[a] (43)	2.54	-5.1	8,300	**P2h**	23,100[a] (54)	32.2	0.6	3,500	>99	97	42
P1i	28.400[a] (394)	1,12	46.3[i]	26,300[l]	**P2i**	300[a] (5)	1,50	-	400[m]	>99	-[p]	34
P1j	197,100[b] (2289)	2.54	172.0	-	**P2j**	800[a] (11)	1.38	-73,9[i]	850[m]	>99	-[p]	73
P1k.1	15,400[a] (134)	1.13	54.6	8,400[o]	**P2k.1**	9,150[a] (91)	1.79	49.1	5,650[o]	>99	>99	85
P1l	7,900[a] (43)	2.05	-58,0[i]	8,100[n]	**P2l**	8,200[a] (48)	2,01	-69,0[i]	-[q]	>99	98	83

[a] determined by GPC in THF; [b] determined by GPC in HFIP; [c] percentage of ester groups reduced determined by NMR-spectroscopy; [d] percentage of ester groups reduced determined by IR spectroscopy, normalized to CH stretching vibration at 2930 cm^{-1}; [e] yield after precipitation; [f] no data, because of insolubility in THF, HFIP or $CHCl_3$; [g] not determined due to superimposition of C=O vibration and C=C vibration; [h] DP (degree of polymerization): M_n/M_0, for polyesters M_0 is the average molecular weight of the diacid and diol component; [i] glass transition; [j] due to overlap of -COO-CH_3 and -CH_2-OH end groups estimated with the assumption of a 1:1 ratio of methyl ester end group and OH end group; [k] estimated by normalization -OCH_3 and -CH_2-OH end groups; [l] estimated by normalization to pyrene butanol end group; [m] estimated by normalization to -CH-OH end group; [n] estimated by normalization to -COO-CH_3 end group; [o] estimated by normalization to -CH_2-OH and/or pyrene butanol end group; [p] all vibrations are changing significantly before and after reduction: conversion cannot be determined; [q] not determined due to overlap of -OCH_3 end group and -CH-O-CH_2 ether signal.

The reduction of the polyesters resulted in many cases in an increased dispersity, which can be explained by some degradation as mentioned above, thus an increasing quantity of lower molecular weight species. A typical example for this behavior is polycaprolactone **P1k**, which was polymerized in a controlled fashion and shows a broadening of the dispersity from 1.13 to 1.79 after reduction. To investigate the influence of the molecular weight on the reduction, polycaprolactones with different molecular weights ranging from 4,400 to 15,400 g mol^{-1} were reduced (Table 6, Figure 11). Polyethers **P2k.1-4** have a lower average molecular weight than that of the parent polyester, which can be expected as, even though the reduction shows remarkable selectivity, a slight amount of side reaction to the alcohol (and thus chain cleavage) remains.

Table 6: GPC and NMR end group analysis of poly(ε-caprolactone) ***P1k*** *before and after reduction.*

Polyester	**M_n [g mol^{-1}][a] (DP[c])**	**Đ**	**M_n[g mol^{-1}] (NMR)[b]**	**Polyether**	**M_n [g mol^{-1}][a] (DP[c])**	**Đ**	**M_n[g mol^{-1}] (NMR)[b]**
P1k.1	15,400 (134)	1.13	8,400	**P2k.1**	9,150 (91)	1.79	5,650
P1k.2	11,450 (100)	1.12	4,900	**P2k.2**	7,700 (77)	2.27	4,600
P1k.3	8,800 (77)	1.13	4,300	**P2k.3**	7,650 (76)	1.56	4,450
P1k.4	4,400 (38)	1.09	2,750	**P2k.4**	4,300 (43)	1.32	2,100

[a] determined by GPC in THF; [b] estimated by normalization to -CH$_2$-OH and/or pyrene butanol end group; [c] DP (degree of polymerization).

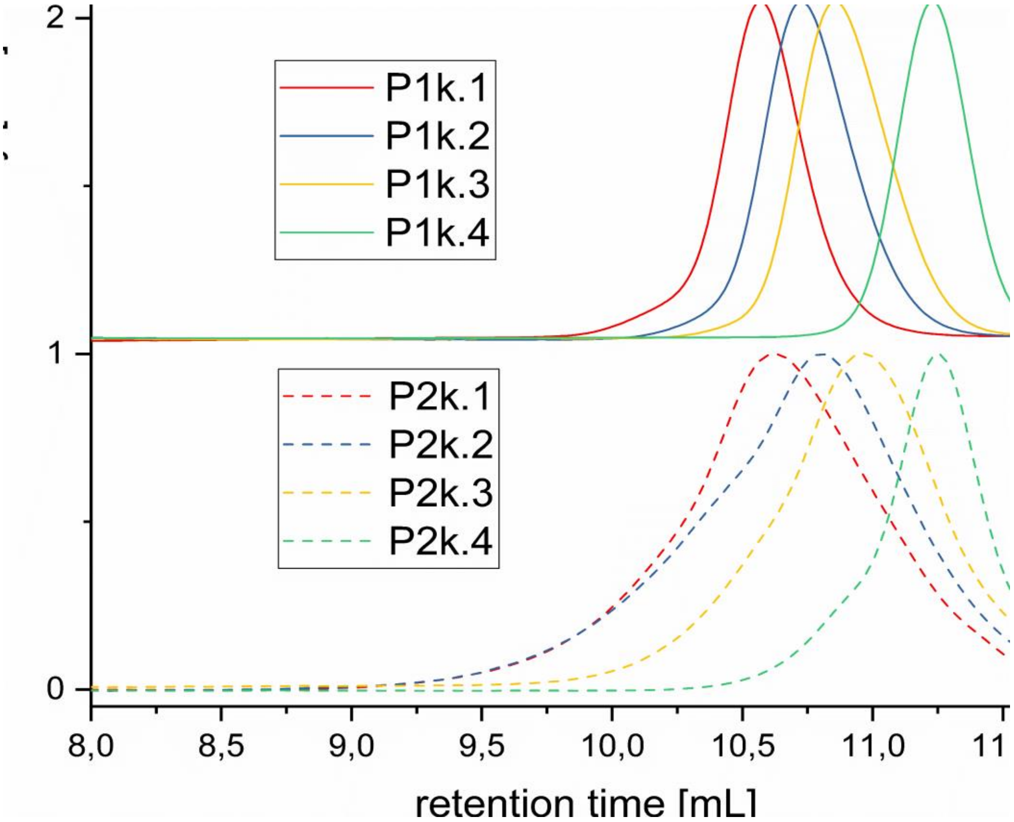


Figure 11: GPC chromatogram of polyethers ***P2k.1*** *–* ***P2k.4****.*

As it can be expected, this effect is more pronounced for higher molecular weights. For some of the other polyethers, (see i.e. shifted SEC-trace of **P2b** in Figure 12), SEC seems to reveal higher molecular weights than that of the parent polyester. Due to the mechanistically highly unlikely formation of higher molecular weights (i.e. chain-chain coupling), a change in hydrodynamic volume due to decreased solubility of the polyether in comparison to the polyester seems more reasonable to explain these results.

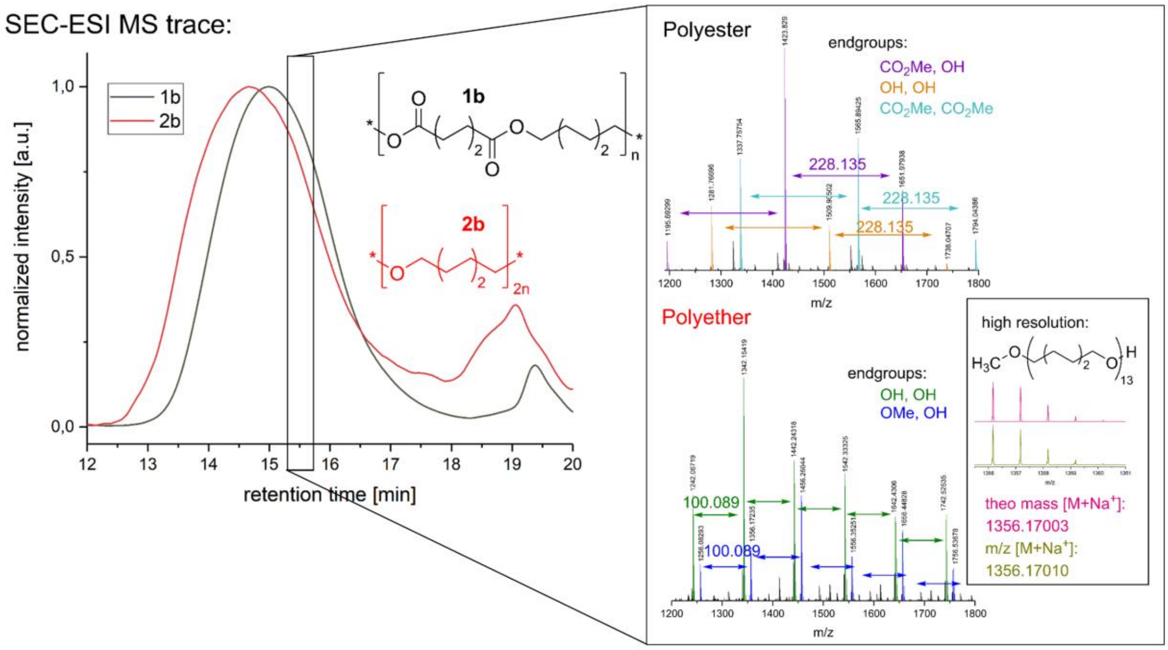


Figure 12: SEC-ESI MS analysis of polyester ***P1b*** *(black) and polyether* ***P2b*** *(red). The mass spectrum was obtained at a retention time interval of 15.3 - 15.8 min (indicated by a black box in the chromatogram).*

Further confirmation of a solvent/solubility effect is the observed increase in molecular weight for **P2b** compared to **P1b** when measured in THF (Figure 2, **P1b**: M_n = 6,300 g mol^{-1}, $Đ$ = 1.67, **P2b**: M_n = 7.300 g mol^{-1}, $Đ$ = 1.71), in contrast to a constant molecular weight when measured in HFIP (see Table 5, **P1b**: M_n = 7,500, $Đ$ = 1.62, **P2b**: M_n = 7.600 g mol^{-1}, $Đ$ = 1.67). The ^{1}H-NMR and IR spectra of polyester **P1c** before and after reduction to polyether **P2c** are exemplarily shown in Figure 13. Full conversion can be observed in the NMR spectrum, as the integrals for the characteristic triplets for CH$_2$-groups ***c*** (2.28 ppm) and ***d*** (4.04 ppm) of the polyester decreased (>99%) after reduction and a new triplet corresponding to the CH$_2$ group ***c'*** of the polyether appears at 3.38 ppm. Moreover, a slight shift can be observed for multiplet ***b*** to ***b'*** from 1.51 – 1.69 to 1.45 – 1.67 ppm, while signals ***a*** and ***a'*** for the remaining CH$_2$-groups can be assigned at 1.14 – 1.41 ppm. The triplet at 3.64 ppm can be assigned to the -C*H$_2$*-OH end group and at 3.66 ppm a singlet can be assigned to the methyl ester group for the polyester, which changes after reduction to a methoxy signal at 3.35 ppm. Average molecular weight determination by end group analysis is difficult due to partly overlapping signals, but the spectra reveal polyethers with two hydroxy end groups or a hydroxyl, possibly silylated, and a methoxy end group.

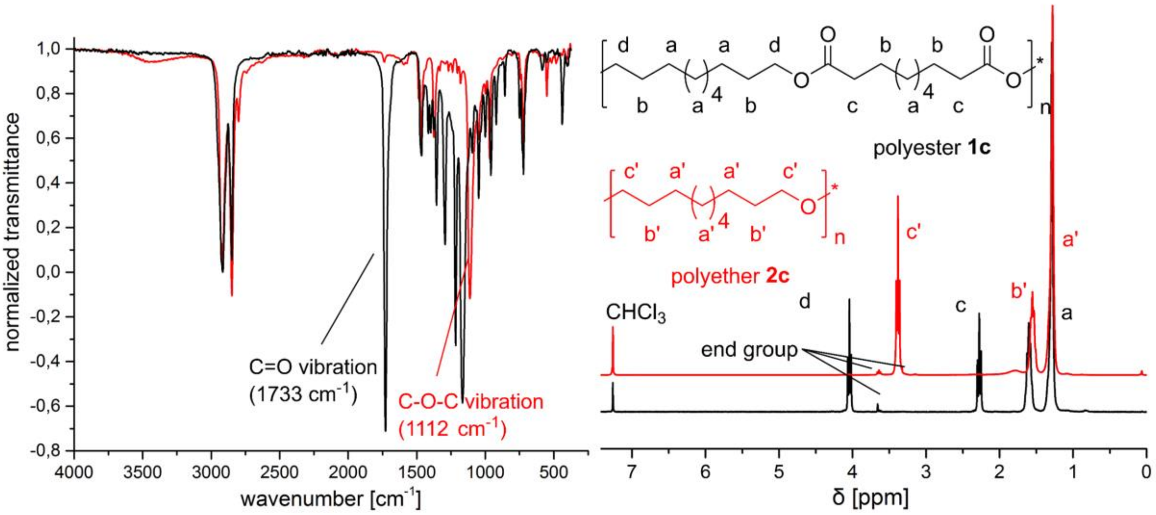


*Figure 13: ^{1}H-NMR spectrum (right side) and IR spectrum (left side) of polyester **P1c** (black) and the respective polyether **P2c** (red).*

The data also shows that most polyester chains are cleaved on average one time. In general, the average molecular weight determined by GPC analysis was significantly higher than the estimated molecular weights by NMR end group analysis. At 0.07 ppm, a singlet can be assigned to remaining <0.5 wt% silyl species in the polymer (Figure 13). In the corresponding IR-spectrum, the signal intensity of the carbonyl vibration of the ester at a wavenumber of 1733 cm^{-1} is reduced (>99%) after the reduction, confirming the conversion determined by ^{1}H NMR. Additionally, at a wavenumber of 1112 cm^{-1}, a signal belonging to the ether vibration can be observed after reduction. SEC analysis coupled with ESI-mass spectrometry (shown in Figure 12 on the example of **P1b** and **P2b**) further confirms the success of the reductions. Oligomers with 5-7 repeating units and different end groups could be assigned to the structure of polyester **P1b** and oligomers with 11-17 repeating units to polyether **P2b** in the same mass range of m/z 1200 – 1800. The example of a polyether with 13 repeating units and OH as well as OMe end-groups is shown in Figure 12 in high resolution. The theoretical mass [M+Na]$^+$ = 1356.17003 together with the calculated isotope pattern both fit to the measured mass of m/z [M+Na]$^+$ = 1356.17010 and the observed isotope pattern, clearly confirming the assigned structures. Polyethers **P2a** – **P2h** were in general less soluble in common organic solvents than the respective polyesters. An example of this observation is polyether **P2g**, which in contrast to polyester **P1g** does not dissolve in THF.

To investigate the influence of the end groups on the reduction, a low molecular weight version of polyester **P1c** was prepared using an excess of diol (1.26 eq) to ensure only OH-end groups (**P1c.1**).

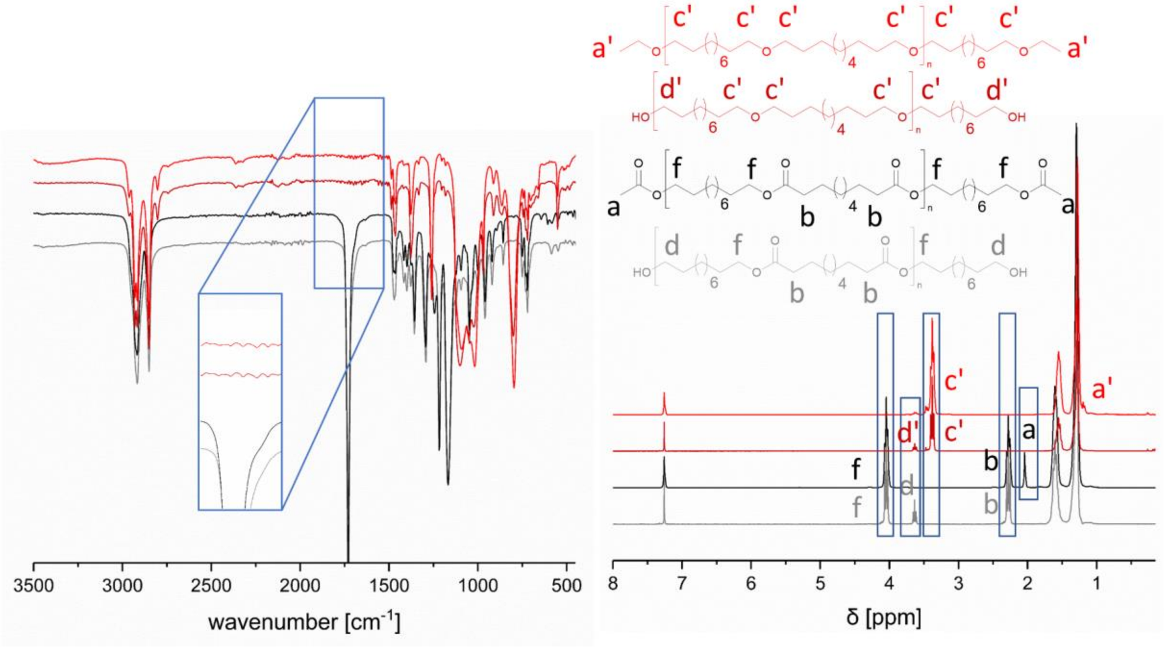


*Figure 14: IR and ^{1}H-NMR spectra of polyester **P1c.1, P1c.2** and polyether **P2c.1, P2c.2** bearing specific end groups. Hydroxy terminated polyester (grey), acetoxy terminated polyester (black), hydroxy terminated polyether (dark red), ethyl ether terminated polyether (red).*

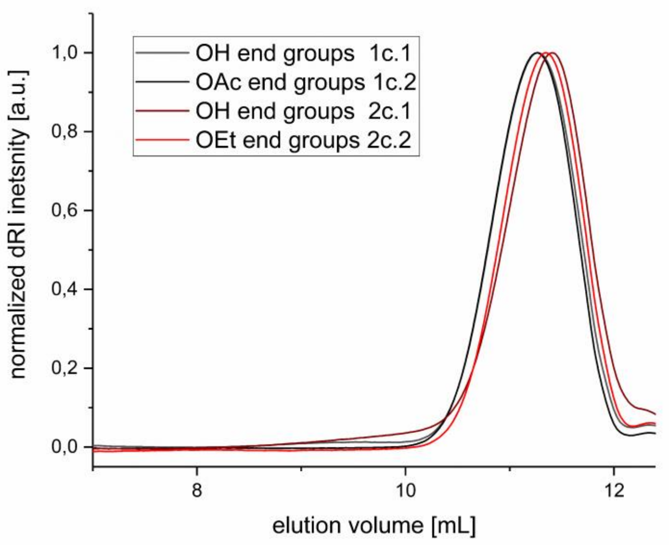


*Figure 15: GPC chromatograms of polyester **P1c.1, P1c.2** and polyether **P2c.1, P2c.2** bearing specific end groups. Hydroxy terminated polyester (grey), acetoxy terminated polyester (black), hydroxy terminated polyether (dark red), ethyl ether terminated polyether (red).*

Moreover, the OH-end groups were acetylated using acetyl chloride ensuring OAc-end groups (**P1c.2**). In both cases, the polyester could be reduced quantitatively to polyethers **P2c.1** and **P2c.2** as confirmed by IR- and NMR-spectroscopy (Figure 14). The M_n of polyester **P1c.1** (2,500 g mol^{-1} (NMR), 4,550 g mol^{-1} (GPC)), **P1c.2** (2,550 g mol^{-1} (NMR), 4,900 g mol^{-1} (GPC)) had a similar decrease for polyether **P2c.1** (1,700 g mol^{-1} (NMR), 3,700 g mol^{-1} (GPC)) and **P2c.2** (1,650 g mol^{-1} (NMR), 4,050 g mol^{-1} (GPC)). It must be noted that the signal of the $O\text{-}CH_2\text{-}C\mathit{H_3}$ end group of **P2c.2** overlaps to a certain extend with signal ***a*** (aliphatic methylene groups) and consequently integration is highly inaccurate in this case. These results indicate that OH-end groups do not significantly influence the here presented reduction procedure. In order to investigate if the mechanism of the reduction occurs predominantly statistical or block-wisely, partially reduced **2a**-**c** (4-8% reduced groups, using 0.1 eq. TMDS) were cleaved and afterwards transesterified with methanol and TBD. Investigation of the obtained fragments by SEC-ESI MS analysis (see section 0 in experimental part) revealed a statistical mechanism as no higher molecular weight polyether fragments could be identified, which would suggest a reduction starting from the end-groups.

For the reduction of (L)-polylactide **P1i**, instead of 1 mol% catalyst $GaBr_3$ and 1.1 eq. reducing agent TMDS per ester group, 5 mol% $GaBr_3$ and 5 eq. TMDS were required for full conversion of the ester groups. Interestingly, polypropylene glycol **P2i** might still have a defined stereochemistry as the reduction does not involve the stereocenter. However, due to the cleavage reaction and very low molecular weight, the ^{13}C-NMR spectrum of **P2i** shows several peaks of different oligomers and isotacticity cannot be proven at this stage (see Figure 16).

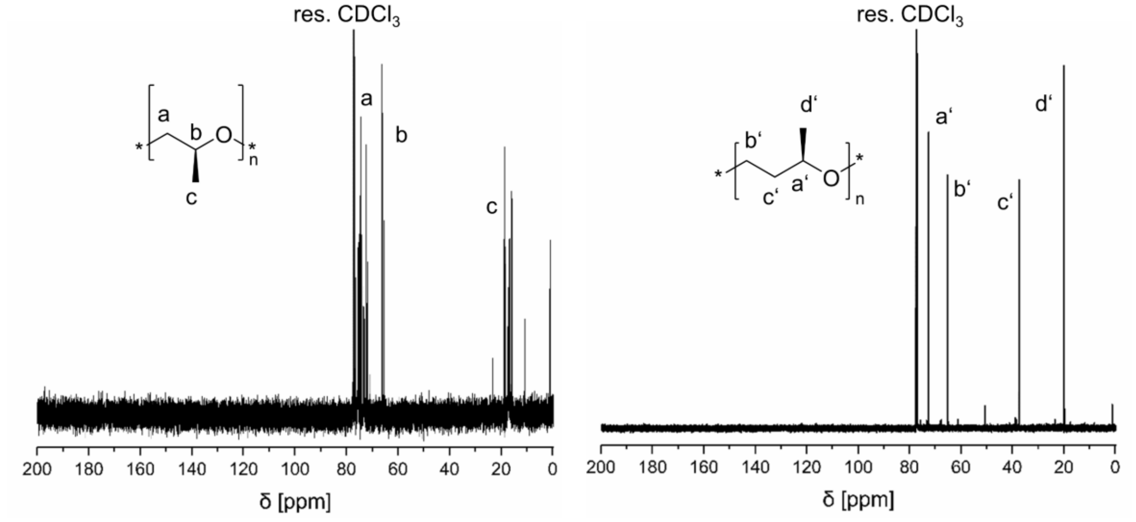


*Figure 16: ^{13}C-NMR spectrum of (S)-polypropyleneoxide **P2i** (left) and poly(oxy-1-methyl-propylene) **P2j** (right).*

In contrast, poly(oxy-1-methyl-propylene) **P2j** is a stereo- and regiochemically defined oligoether with sharp peaks at chemical shift of 72.4 (-OCHCH$_3$), 65.1 (-OCH$_2$), 37.3 (-OCH$_2$*C*H$_2$-), 19.8 (-CH$_3$) in good agreement with literature (Figure 16).[299,300] In the typical synthesis of **P2j** by cationic polymerization of 2-methyloxacyclobutane, a mixture of head-to-head, tail-to-tail, and head-to-tail additions is obtained.[299] Although the molecular weights of the here obtained **P2i** (M_n = 0,300 g mol^{-1}) and **P2j** (M_n = 0,800 g mol^{-1}) are rather low, they might still be used as a polyols for the synthesis of polyurethanes. The more pronounced degradation for polyethers **P2i** and **P2j** might be related to the close distance in between the ester groups. As comparison, the GaBr$_3$ catalyzed reduction of triglycerides, having respective neighbouring oxygen atoms, showed about 7% reduction per ester unit to the alcohol,[7] which is in agreement to the reduction of **P1i** and **P1j**. An influence of the methyl group in α-position to the ester functionality can be excluded, as the reduction of **P1l** to **P2l** did not result in excessive cleavage. The result of the GPC analysis of polypropylene oxide **P2i** was confirmed by mass spectrometry (ESI-MS), showing the main peak at m/z = 315.2354 ($C_{15}H_{32}LiO_6$) corresponding to five monomer-units (Figure 17).

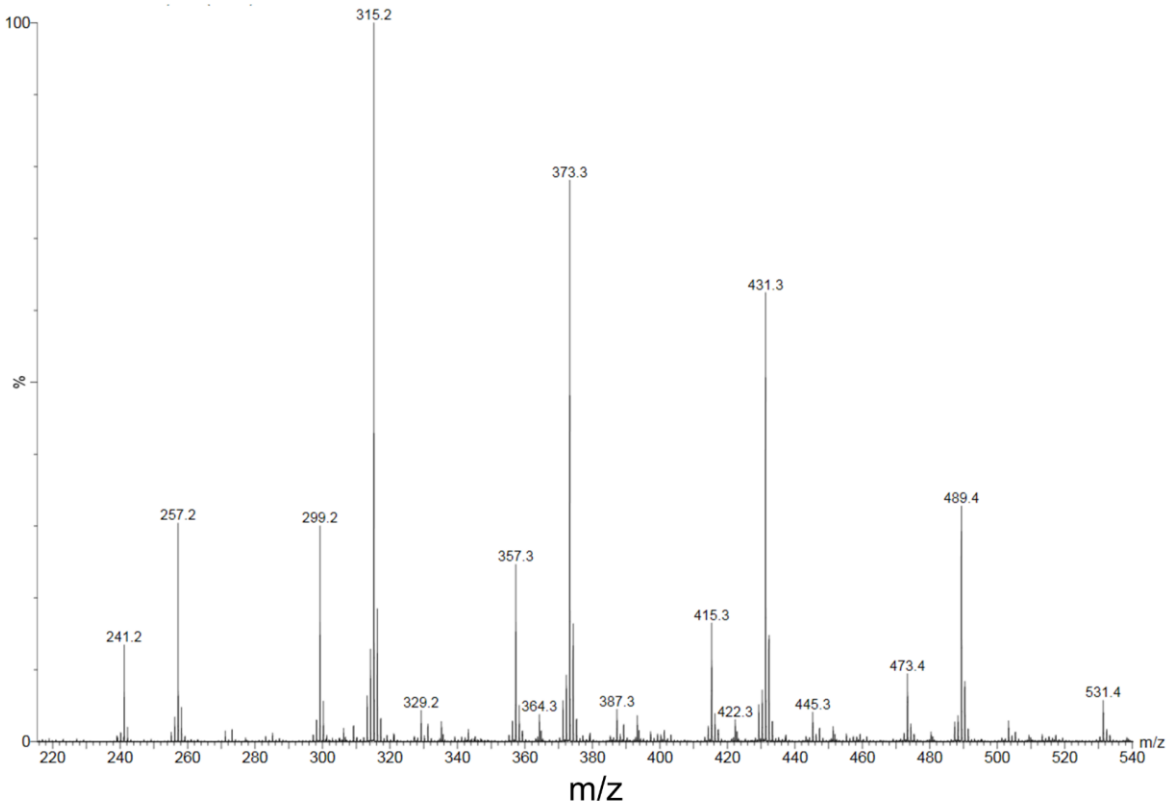
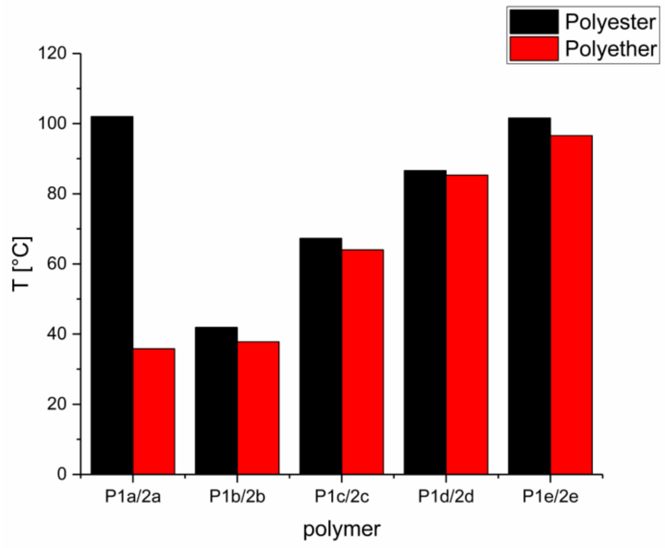


*Figure 17: ESI-MS spectrum m/z = 220 – 540 of polypropylene oxide **P2i**.*

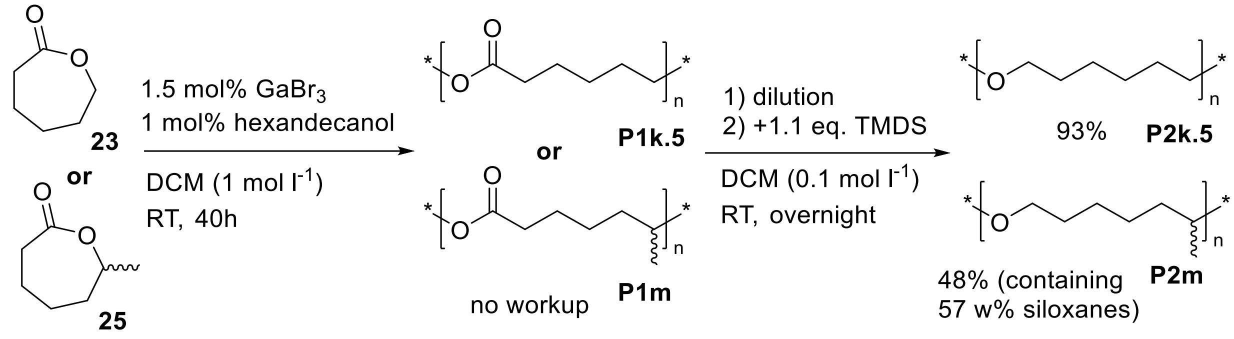
Since some of the prepared polyesters and all polyethers (except **P2a**, which can be obtained by ring opening polymerization of THF) are novel or in case of **P2b** and **P2c** only known as oligomers,[301] their thermal properties were studied in order to establish their basic material properties. The comparison of the melting points of the different polyesters and polyethers shows interesting results (Table 5). A direct comparison of polyesters and the thereof derived reduced polyethers reveals lower melting points for the polyethers. This difference increases with a smaller distance in between the ester/ether groups. This is an expected, yet interesting to confirm observation for this set of AA-BB type polyesters with even numbers of carbon atoms and the thereof derived polyethers. For polyesters **P1f** – **P2l** and polyethers **P2f** – **P2l**, the interpretation of the change in thermal behavior is not as straightforward. A slight increase in melting point can be observed for polyester **P1f** and **P1h** (64.6 °C and -5.1 °C) to polyether **P2f** and **P2h** (67.7 °C and 0.6 °C). The isopropylated polyester **P1g** and polyether and **P2g** show a glass transition at -66.8 °C and -66.3 °C due to their bulky side-chains that also prevent crystallization and thus increase solubility. Polyester **P1k** and polyether **P2k** show a glass transition at -58,0 °C and -69,0 °C. Comparing the melting point of polyether **P2a** (35.8 °C) with its commercial counterpart PTMO (31.3 °C) of similar molecular weight reveals good agreement.



Polyester	T_m [°C]	Polyether	T_m [°C]
P1a	102.0	**P2a**	35.8
P1b	41.9	**P2b**	37.8
P1c	67.3	**P2c**	64.0
P1d	86.6	**P2d**	85.3
P1e	101.6	**P2e**	96.6

*Figure 18: Comparison of melting point of polyesters **P1a** – **P1e** and polyethers **P2a** – **P1e**.*

One disadvantage of the $GaBr_3$ catalyzed reduction of polyesters as a general synthesis method of polyethers is certainly the need of an additional step after polymerization to the polyester. Typically, to remove the catalyst of the polyesterification, an additional precipitation/workup step is necessary. As shown in section 4.1.1.2 $GaBr_3$ could efficiently catalyze ring-opening polymerizations as well, thus allowing a one-pot two-step cascade synthesis.



*Scheme 61: One-pot two-step cascade synthesis of **P2k.5** and **P2m** without workup after ROP to the polyester.* [i]

Confirming this idea, indeed, after polymerization of *ε*-caprolactone to **P1k.5** in dichloromethane (1 mol l^{-1}) utilizing 1.5 mol% $GaBr_3$ and 1 mol% Initiator (1-hexandecanol) at room temperature and 40 h reaction time, 1.1 eq. TMDS was added after dilution to 0.1 mol l^{-1}. The reaction was stirred overnight and the ester groups were reduced quantitatively. After precipitation in cold methanol, **P2k.5** was obtained in a yield of 93% and a molecular weight of M_n = 6.400 g mol^{-1}, $Đ$ = 1.97. The two-step cascade polymerization and reduction were also applied to poly(6-methyl-caprolactone) **P1m**, however with an overall yield of 48% (still containing 57 w% siloxanes) and comparably low molecular weight (M_n = 2.850 g mol^{-1}, $Đ$ = 2.30) the reaction still needs to be optimized and **P2m** cannot be compared to the other polyethers yet.

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[i] Carried out by Andreas Ganzbuhl in the Bachelor thesis “Catalytic reduction of sustainable A-B-type polyesters to polyethers” (under lab-supervision of Patrick-Kurt Dannecker). Specifics are given in the experimental part.

4.1.3 Sustainability of the reduction

Several aspects of this method include principles of sustainability. Compared to typical polyethers, the method does not involve highly flammable or explosive and toxic gases as ethylene oxide or propylene oxide and the process can be regarded as comparably safe. Moreover, the reaction is carried out at room temperature and most importantly the polyesters are typically obtained from renewable resources.

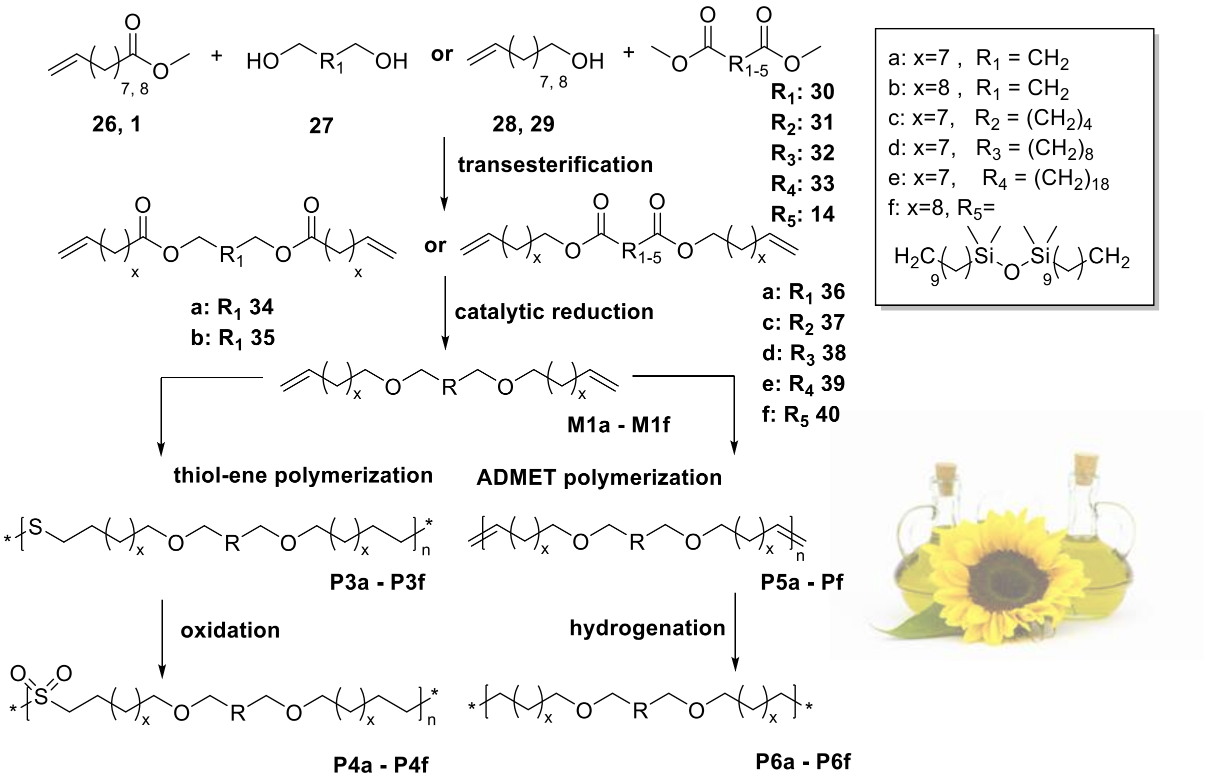
However, a major problem of the reduction is the use of CH_2Cl_2 as solvent and the precipitation in petrol ether as both are toxic and generate much waste. Moreover, stoichiometric amounts of reducing agent TMDS are used and the reaction suffers from a poor E-factors (E) overall. The Williamson Ether Synthesis is another possibility to form unusual polyethers, although it has yet to be successfully applied in the synthesis of aliphatic polyethers. A direct comparison can be made for the literature known synthesis of aromatic polyethers, more specifically the condensation of 1,4-dichlorobut-2-ene (DCB) and bisphenol A (BPA),[302] which still gives an atom economy (AE) of 75%. In comparison, the reduction of poly(1,10-decamethylene sebacate) **P1c** gives an AE of only 52%. Comparing the much more conclusive E-factors of the actual procedures, the polycondensation of DCB and BPA has a higher E-factor (E=336) compared to the reduction of **P1c** (E=152). As the procedures are however not optimized regarding an economic use of solvent for reaction and workup, these numbers only represent a first indication. TMDS ca be regarded as by-product of the silicon industry[8] and as a consequence the poor AE is less of a concern compared to *e.g.* for other highly valuable reactants resulting in inorganic salt waste. Another aspect is that the sustainability of a post-polymerization modification itself is low as in any case an additional step is involved. Addressing this issue, it was demonstrated that in case of ring-opening polymerizations it is possible to directly reduce the polyester without additional workup between polymerization and reduction.

Another point is the abundancy of gallium (15 ppm in earth’s crust), which is scarce compared to aluminum (8.23%) or iron (5.63%), still, it is more abundant than boron (10 ppm) or thallium (8.3 ppm) and 300 times more abundant than indium (50 ppb).[303] The toxicity of gallium and its salts is barely studied, since gallium is barely used in industry apart from the semiconductor and solar cell production, where indoor GaAs particulate levels are high. In this case, arsenic is of far higher concern and isolated effects of Ga are difficult to assess. Medical literature reports very little information about the toxicology of gallium in humans and only two cases of Ga poisoning are documented in the medical literature. The first involves a chemistry research associate who developed neurological sequelae after exposure to fumes from a vial of gallium fluoride crystals (1972).[304] The second case is a study from 2011 titled “Gallium poisoning: A rare case report”, in which a chemistry student was exposed to aqueous residues of originally Ga_2Cl_4 in the eye and experienced symptoms of typical heavy metal poisoning.[305] Based on animal studies, gallium is a poison by subcutaneous and intravenous routes and harmful if inhaled or swallowed. However, all in all, the toxicity of gallium salts is considered very low as they are hydrolyzed to form insoluble hydroxides, which are un-absorbable and become colloidal in biological tissues.[305]

To conclude, there are several aspects which need to be improved regarding the sustainability of the reaction. While TMDS and $GaBr_3$ are arguably sustainable reagents, the toxic solvents CH_2Cl_2 and petrol ether are a major problem. Only if TMDS was directly applied without solvent and the formed polysiloxanes would be left within the product, the reaction can be regarded as relatively sustainable.

4.2 Monomer approach - aliphatic long chain polyethers by catalytic reduction and polymerization of ω,ω’-unsaturated esters derived from fatty acids

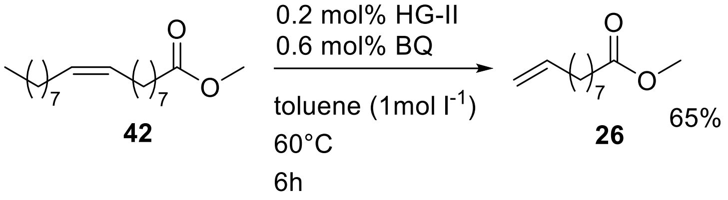
In the monomer approach ω,ω’-unsaturated esters were produced by known transformations, such as the ethenolysis of methyl oleate, followed by transesterification with 1,3-propanediol. Afterwards, the catalytic reduction with $GaBr_3$ was used to produce the respective ω,ω’-unsaturated ether monomers, which were polymerized by either ADMET- or thiol-ene polymerizations and post-polymerization modified by hydrogenation or oxidation, respectively. In this fashion, six different fatty acid derived monomers were polymerized and modified resulting in 24 different polymers, which were compared in melting point and other properties. A brief overview of the reaction pathways is shown in Scheme 62.



Scheme 62: General reaction scheme and overview of the different monomers and polymers synthesized by the monomer route. The monomers and thiol-ether bonds are symmetric, thus the AABB-type thiol-ene polymer can be shown in an abbreviated form.

4.2.1 Ethenolysis of methyl oleate

The first step in the synthesis of ω,ω'-unsaturated monomers from fats and oils is to obtain fatty acid methyl esters (FAMEs) containing terminal double bonds. The conversion of the naturally occurring internal double bonds can, in case of ricinoleic acid, be achieved by a retro-Alder-Ene reaction under vacuum pyrolysis to 10-undecenoic acid.[209][209] For other unsaturated fats & oils, ethenolysis is typically used. Here, the ethenolysis to obtain 9-methyl decenoate from methyl oleate utilizing commercially available standard catalysts, was optimized.



Scheme 63: Optimized reaction conditions for the ethenolysis of methyl oleate (non-1-ene and self-metathesis byproducts not shown).

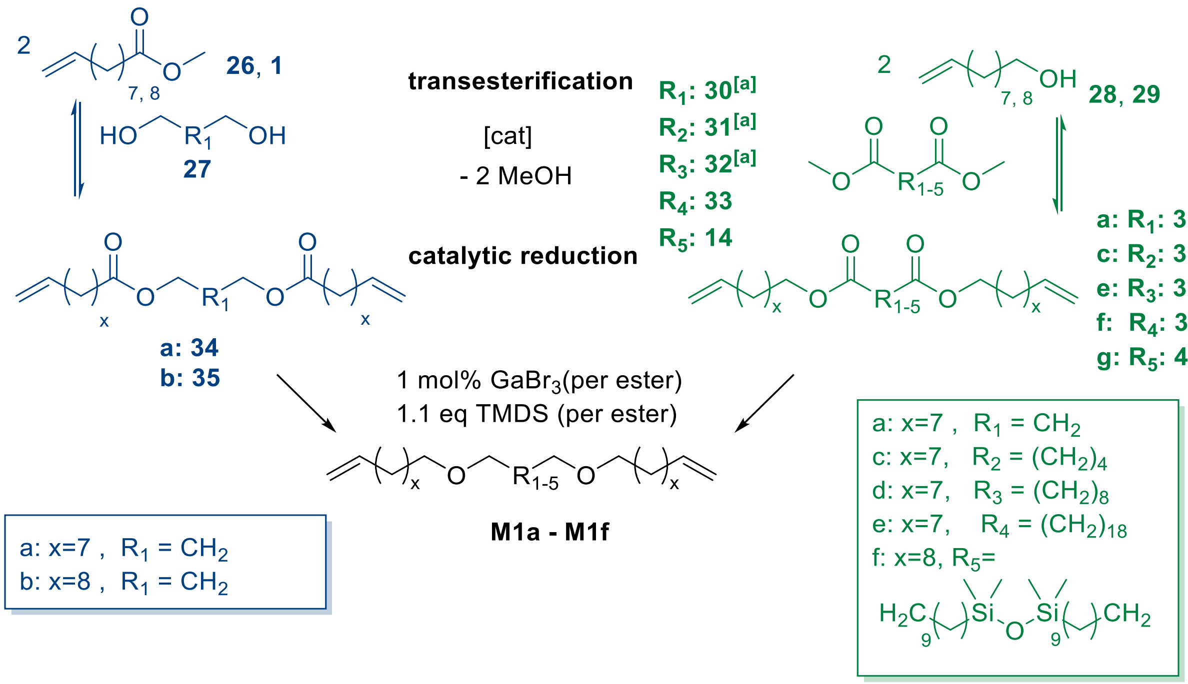
Table 7: Comparison of the conversion and product ratio of the ethenolysis of methyl oleate varying reaction time, temperature, catalyst, amount of catalyst and solvent.

Entry	Cat.	Cat. [mol%]	t [h]	T [°C]	Conc. [mol L^{-1}][c]	Conversion [%][a]	Product ratio [%][b]
A	G-I	0.2	2.5	60	1	78	99
B	G-II	0.2	2.5	60	1	78	65
C	HG-II	0.2	2.5	60	1	85	73
D	HG-II	0.2	6	60	1	91	91
E	HG-II	0.2	6	80	1	90	89[e]
F	HG-II	0.2	6	80	-[d]	84	74
G	HG-II	0.2	6	60	0.3	95	67
H	HG-II	0.2	6	RT	0.3	81	78
I	HG-II	0.1	6	60	0.3	82	66

*All reactions were carried out at 15 bar ethylene pressure; catalysts: Grubbs Catalyst 1st Generation (**G-I**), Grubbs Catalyst 2nd Generation (**G II**) and Hoveyda-Grubbs Catalyst 2nd Generation (**HG-II**); [a] determined via GC (tetradecane as internal standard); [b] (Pr/(SM+Pr); Pr = product, SM = self-metathesis side product, [c] solvent: toluene, [d]no solvent, [e] 7% side product due to isomerization of the double bond.*

The ethenolysis was optimized regarding reaction time, temperature, catalyst, amount of catalyst and solvent (Table 7). The optimization study was kept very brief, as the ethenolysis of methyl oleate is widely known in literature.[120] All experiments were carried out at 15 bar ethylene pressure, since B. R. Maughon *et al.* revealed that the selectivity towards the ethenolysis product decreases rapidly with increasing conversion and this effect can be minimized by using higher ethylene pressure of 15 bar or more.[124] As starting conditions, a substrate concentration of 1 mol l^{-1} in toluene, a catalyst concentration of 0.2 mol% and a reaction time of 2.5 h at 60 °C were chosen. Comparing the **G-I**, **G-II** and **HG-II** catalysts (entry A-C), it could be shown that the **HG-II** catalyst (entry C) exhibits the highest conversion (85%). **G-I** and **G-II** catalysts both have similar conversions of 78%. However, the **G-II** catalyst, exhibiting a product ratio of 65% (comparing product and self-metathesis side product) and shows a lower selectivity than the **G-I** catalyst (99% product ratio). These findings are in agreement with the results of Y. Schrodi *et al.*, who achieved significantly lower yield and selectivity with H_2IMes-based catalysts **G-II** and **HG-II**. Nevertheless, a higher conversion was prioritized, and the optimization was continued with the **HG-II** catalyst as the self-metathesis side product **10** was required in large quantities for the polymer approach (section 4.1.1.1). A longer reaction time of 6 h instead of 2.5 h increased the conversion and product ratio both to 91% (entry D). Increasing the temperature from 60 °C to 80 °C slightly lowered the selectivity of the ethenolysis as the product ratio decreases from 91% to 89% (entry E). Additionally, isomerization of the double bond (up to 7%) takes place at 80 °C, compared to less than 1% at 60 °C. The use of toluene as solvent is beneficial regarding both conversion and selectivity, as without solvent (entry F) the conversion is only 84% and the product ratio is 74%. Moreover, a lower concentration of 0.3 mol L^{-1} instead of 1 mol L^{-1} increased the conversion from 90% to 95%, while the product ratio decreased significantly (67%, entry G). By lowering the reaction temperature to room temperature, conversion and product ratio decreased to 81% and 78% (entry H). Furthermore, a decrease of catalyst concentration from 0.2 mol% to 0.1 mol% also decreased the conversion to 82% and the product ratio to 66% (entry I). As a result of this optimization study, the upscaling of the reaction was performed using a catalyst concentration of 0.2 mol% at 60 °C in toluene (1 mol L^{-1}) and a reaction time of 6h. Still, having the overall sustainability in mind, for an industrial application a different compromise using less catalyst, no solvent or a lower temperature might be more appropriate. Without special pre-treatment of technical methyl oleate (90% purity), a yield of 65% was achieved for 9-methyl decenoate **26**. For purification, the catalyst was removed by column chromatography as otherwise isomerization occurs during distillation at high temperatures. In contrast to typical literature procedures much higher catalyst concentrations were required.[128] These results can be explained by insufficient purity of the technical grade methyl oleate used in this procedure compared to highly pure, pretreated methyl oleate (>99% purity) and solvent. R. L. Pederson *et al.* suggest organic hydroperoxides, which can be formed in natural oils by oxidative ageing, to be responsible for catalyst poisoning and pretreatment of the feedstock with magnesium silicate.[134] Another possible contamination are traces of morpholine present in toluene, which are known to be responsible for degradation of metathesis catalysts.[120] In their comprehensive review of the ethenolysis of biomass, E. L. Scott *et al.* concluded that the purity of the ethylene and the feedstock has a much higher influence on the efficiency of the reaction than the catalyst, which is illustrated by the fact that **G-I** is still among the best performing catalysts, even though a variety of new catalysts are available.[120]

4.2.2 Transesterification to produce ω,ω'-unsaturated esters and reduction to the corresponding ω,ω'-unsaturated ether monomers



Scheme 64: Two different transesterification routes, either by transesterification of ω-unsaturated fatty acid methyl esters and diols (blue) or diethyl esters and ω-unsaturated alcohols (green), leading to ω,ω'-diene esters. Methanol/ethanol can be removed from the reaction to shift the equilibrium. Afterwards, the ω,ω'-diene esters are reduced to ω,ω'-diene ethers. Dimethyl ester ***14*** *was synthesized by hydrosilylation as shown in section 4.1.1. [a] Diethyl esters used instead of dimethyl esters.*

To produce ω,ω'-diene esters **34** – **40** from fatty acid derivatives, two routes are possible and were both pursued (Scheme 64). Either ω-unsaturated FAMEs and diols or dimethyl/ diethyl-esters and ω-unsaturated alcohols can be transesterified. The yield of the reaction was increased by utilizing a slight excess (1.1 eq) of the monofunctional component. Sodium methanolate was used as catalyst at 50 °C under nitrogen atmosphere. In this way, 7 different ω,ω'-unsaturated esters were produced (Scheme 65).[i]

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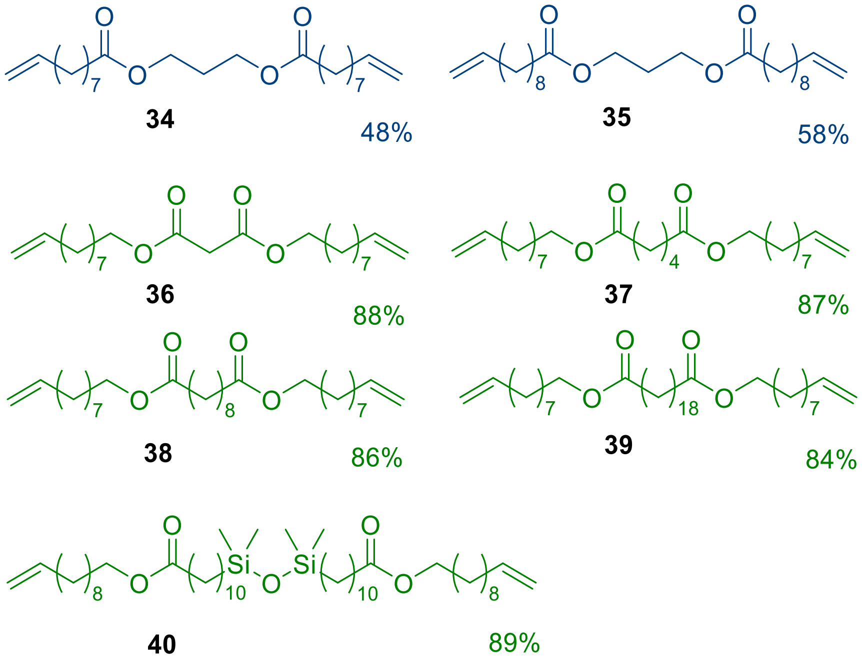
[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).



Scheme 65: Different ω,ω'- unsaturated diene esters either by transesterification of ω-unsaturated fatty acid methyl esters and diols (dark blue) or dimethyl/ diethyl- esters and ω-unsaturated alcohols (green) and yields of the respective transesterifications.

Afterwards, the ω,ω'-unsaturated esters were reduced to the ω,ω'-unsaturated ethers. Conveniently, the different routes of transesterification can yield the same ω,ω'-unsaturated ether as it is shown for **M1a** (Scheme 64), which was obtained by either reducing **34** or **36**. Comparing the yields of the different routes, the yield of the transesterification of diethyl or diethyl esters and ω-unsaturated alcohols (87 – 89%) is superior to the yields of transesterification reactions involving FAMEs and diols (48 – 59%). In a direct comparison between **34** (48% yield) and **36** (88% yield), the approach using diethyl malonate and 9-decenol clearly gives better yields than the one using methyl 9-decenoate and 1,3-propanediol. As alternative to the procedure utilizing sodium methanolate, TBD was evaluated as catalyst because of the advantage, that it can be used without relying on Schlenk-technique.[i] The reaction was carried out at 60 °C, with 5 mol% TBD and 2.2 equivalents (10% excess) methyl 10-undecenoate **1** (Scheme 66).

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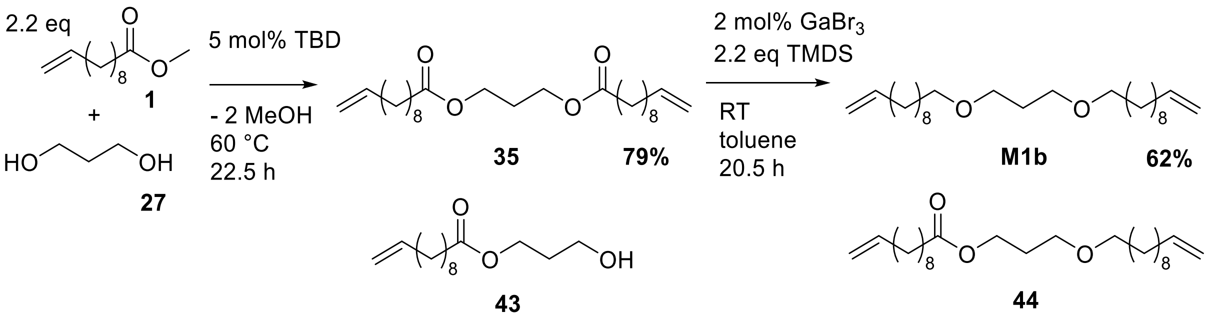
[i] Carried out by Alexandra Sink in the Bachelor thesis "Neue katalytische Wege zu biobasierten Polyethern" (under lab-supervision of Patrick-Kurt Dannecker). Specifics are given in the experimental part.



Scheme 66: Scheme of the transesterification of methyl 10-undecenoate and 1,3-propanediol and reduction afterwards.

Methanol was distilled off, which was assisted by a light airflow through the mixture. Monitoring of the reaction progress (Figure 19) revealed that the monofunctional intermediate 3-hydroxypropyl undec-10-enoate **43** is formed very quickly within the first 30 minutes, until it is present in the mixture with a ratio of up to 25% and reaches a plateau at 200 min reaction time. At the same time, product formation is comparably slow reaching only a ratio of 29%. The reaction slows down considerably and in between 400 and 1400 min, the product ratio increases slowly from 44% to 63%, while still 25% starting material **1** and 12% intermediate **43** remain.

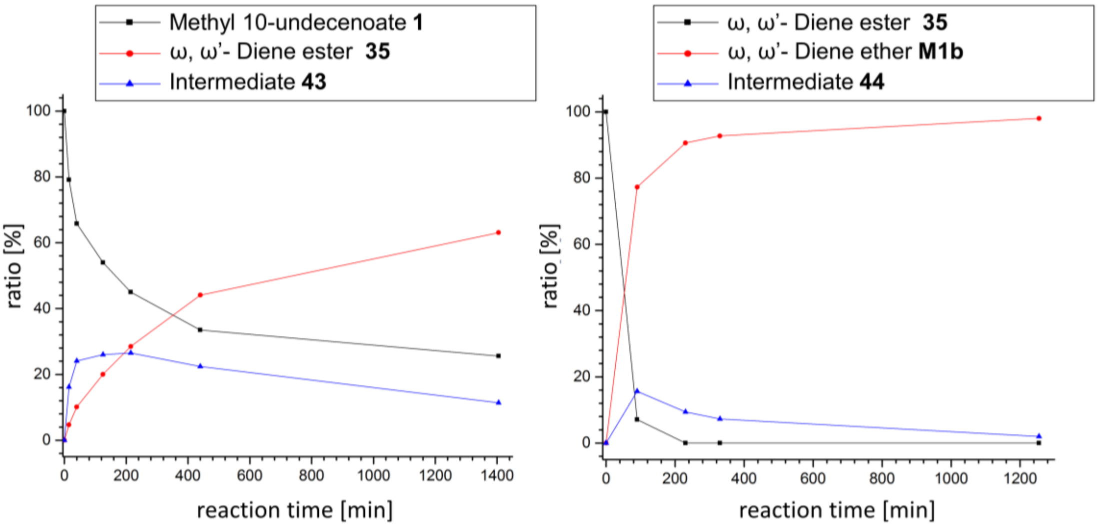


*Figure 19: Reaction process of the transesterification of methyl 10-undecenoate **1** and 1,3-propanediol **27** (left side) and reaction progress of the reduction of diene ester **35** to diene ether **M1b** (right side). The ratio in [%] was estimated by GC-FID analysis without calibration.* [i]

It should be noted that **1** was used in excess (10%) and would be present in the reaction mixture even at 100% conversion. After purification by column

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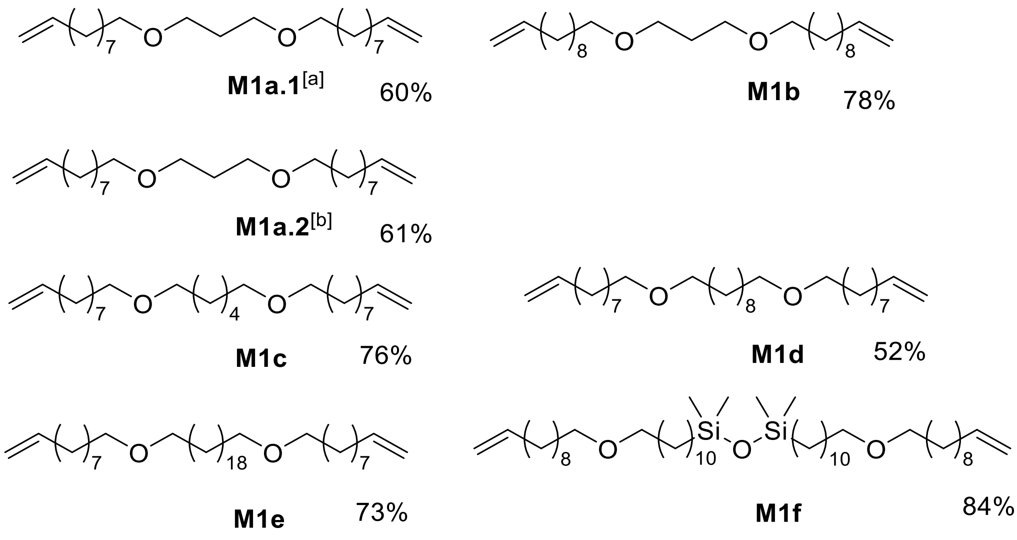
[i] Carried out by Alexandra Sink in the Bachelor thesis "Neue katalytische Wege zu biobasierten Polyethern" (under lab-supervision of Patrick-Kurt Dannecker). Specifics are given in the experimental part.

chromatography, propane-1,3-diyl bis(undec-10-enoate) **35** was isolated in a yield of 79%. In comparison to the yield of 59% for the procedure utilizing sodium methanolate, the procedure with TBD as catalyst and continuous removal of the formed methanol by airflow-assisted distillation is clearly superior.

Afterwards, **35** was reduced to the corresponding polyether monomer **M1b** by applying the catalytic reduction with 2 mol% $GaBr_3$ (1 mol% per ester group) as catalyst and 2.2 eq TMDS (1.1 eq per ester group) as reducing agent. The reaction was carried out at room temperature for a reaction time of 20.5 h. Compared to the previous procedure for the monomers **34** – **40**, toluene was chosen as a solvent to minimize the reduction to the alcohol as side reaction and facilitate separation. GC analysis revealed a fast reaction as **36** is completely consumed after 240 minutes. At the same time, intermediate **44** with only one reduced ester group is still present in an amount of 7%. However, after 1250 minutes, the product **M1b** is present in the reaction mixture for 98%, reaching almost quantitative yield. As there were no traces of alcohol side products due to overreduction found, it can be confirmed that the reaction is remarkably selective under the applied conditions. The purification of the product is challenging, as polysiloxanes produced by the polymerization of the reducing agent TMDS must be separated. By column chromatography utilizing a gradient of cyclohexane → mixture of cyclohexane / ethyl acetate 10:1 → dichloromethane the amount of remaining polysiloxanes could be reduced to 0.38 w% and the product **M1b** was obtained in a yield of 62%.



Scheme 67: Yields of the different ω,ω'-unsaturated diene ethers after the catalytic reductions.[a] ***M1a.1*** *synthesized from* ***35****,* ***M1a.2*** *synthesized from* ***37****.*

Alternatively, in a more sustainable procedure, **M1a** – **M1f** were reduced without the addition of a solvent.[i] By purifying the substrates through short-path vacuum (Kugelrohr) distillation instead of column chromatography the polysiloxane side product could be removed in a sustainable way without much product loss resulting in yields between 60 and 84% (Scheme 67).

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[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

4.2.3 Conversion of ω,ω'- unsaturated diene ethers to dithiols

As already discussed in section 2.5.2, thiol-ene reactions are considered as a versatile tool in polymer science since they are efficient, selective and widely applicable. They can be used in monomer synthesis, thiol-ene polymerizations or post-polymerization modifications. To polymerize monomers **M1a** – **M1f** *via* thiol-ene polymerization, an additional dithiol is required. Typically, commercial dithiols mostly derived from fossil resources, as *e.g.* 1,4-butanedithiol or 2,2′-(ethylenedioxy)diethanethiol are used for such purposes. A more sustainable alternative is to convert renewable dienes to the respective dithiols. Already in 1957, C. S. Marvel and L. E. Olson converted *D*-limonene to a dithiol *via* addition of thioacetic acid and basic cleavage of the thioesters afterwards.[306] In their procedure, they added an excess of thioacetic acid (1.25 eq per double bond) without external heating or cooling, however in a slow rate to prevent an increase of the temperature above 90 °C by the exothermic reaction. This led to a mixture of monofunctionalized and bifunctionalized substrate (0.21:1). Afterwards, cleavage of the thioester through basic hydrolysis in water for 48 h led to the dithiol. In our group, we improved this procedure by cleaving the dithio ester catalytically with TBD as catalyst in methanol. In this way, the reaction time could be lowered to 16 h to give full conversion of the substrate.[222] In the case of di-10-undecenyl ether, the reaction time of the addition was only 1 h. In this work, the same conditions were applied to monomers **M1a** – **M1f**, which are structurally similar to di-10-undecenyl ether (Scheme 68). First, the reaction was optimized on monomer **M1a**.[i] In contrast to di-10-undecenyl ether, the conversion reached only 75% and did not increase after 1 h of stirring at room temperature. To improve the conversion, the reaction was carried out in a microwave reactor and after 1 h reaction time at 80 °C, full conversion of the double bond could be reached for **M1a** – **M1f**. In order to avoid deactivation of the catalyst TBD, which is applied in the next reaction step, a complete removal of thioacetic acid was necessary. Evaporation of thioacetic acid under reduced pressure turned out to be a facile method to give quantitative yield without further workup. In the next step, the dithio esters were cleaved by transesterification with methanol under reflux conditions overnight to yield **M2a** – **M2f**. To prevent the formation of disulphides, the reaction was carried out under argon atmosphere.

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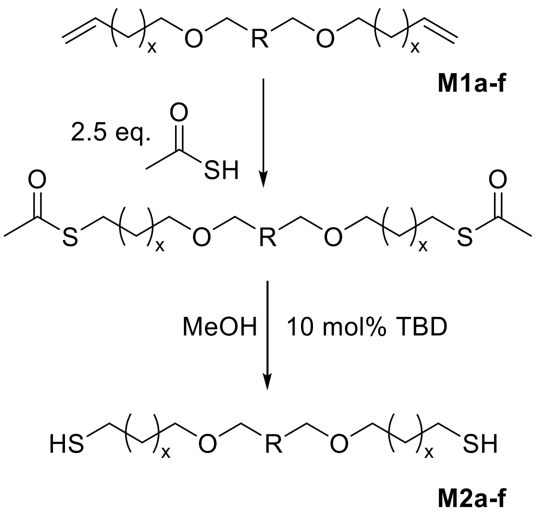
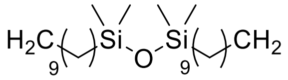
[i] Carried out by Fabian R. Blößer in the Vertieferarbeit "Polyethers by reduction of esters" (under lab-supervision of Patrick-Kurt Dannecker). None of the here presented molecules stem from this work.

Afterwards, methanol and the formed methyl acetate were removed under reduced pressure and the crude product was purified by column chromatography achieving yields from 57 to 81%. The purity of the products was confirmed by ^{1}H-NMR-spectroscopy (Figure 20).



	yield [%]
a: x=7 , R = CH_2	**80**
b: x=8 , R = CH_2	**57**
c: x=7, R = $(CH_2)_4$	**81**
d: x=7, R = $(CH_2)_8$	**70**
e: x=7, R = $(CH_2)_{18}$	**57**
f: x=8, R= 	**63**

*Scheme 68: Synthesis of dithiols from ω,ω'- unsaturated diene ethers **M1a** – **M1f** by addition of thioacetic acid (2.5 eq., 1.25eq. per double bond) and cleavage afterwards by TBD and methanol.*

In the ^{1}H-NMR spectra for all dithiols **M2a** – **M2f**, methylene group ***b*** adjacent to the ether bond can be discerned as triplet at a chemical shift in the range of 3.36 to 3.40 ppm. For dithiols **M2a** and **M2b**, due to the proximity of the second ether group, an additional triplet for methylene group ***a*** is present in the range of 3.46 to 3.48 ppm. The methylene group ***c*** correlates for all dithiols to a quartet at 2.50 ppm. For **M2a** and **M2b**, methylene group ***d*** gives a quintet in the range of 1.81 to 1.83 ppm. Methylene groups ***e*** in β-position to the ether or thiol groups can be observed as multiplet between 1.74 and 1.45 ppm. The signal of the -SH proton ***f*** overlaps with the aliphatic region (methylene groups ***e***), which can be confirmed in COSY (COrrelated SpectroscopY) experiments. For **M2f**, the methylene group ***h*** adjacent to the silyl-group can be assigned to a triplet at 0.49 ppm and the methyl groups ***j*** give a sharp singlet at 0.02 ppm.

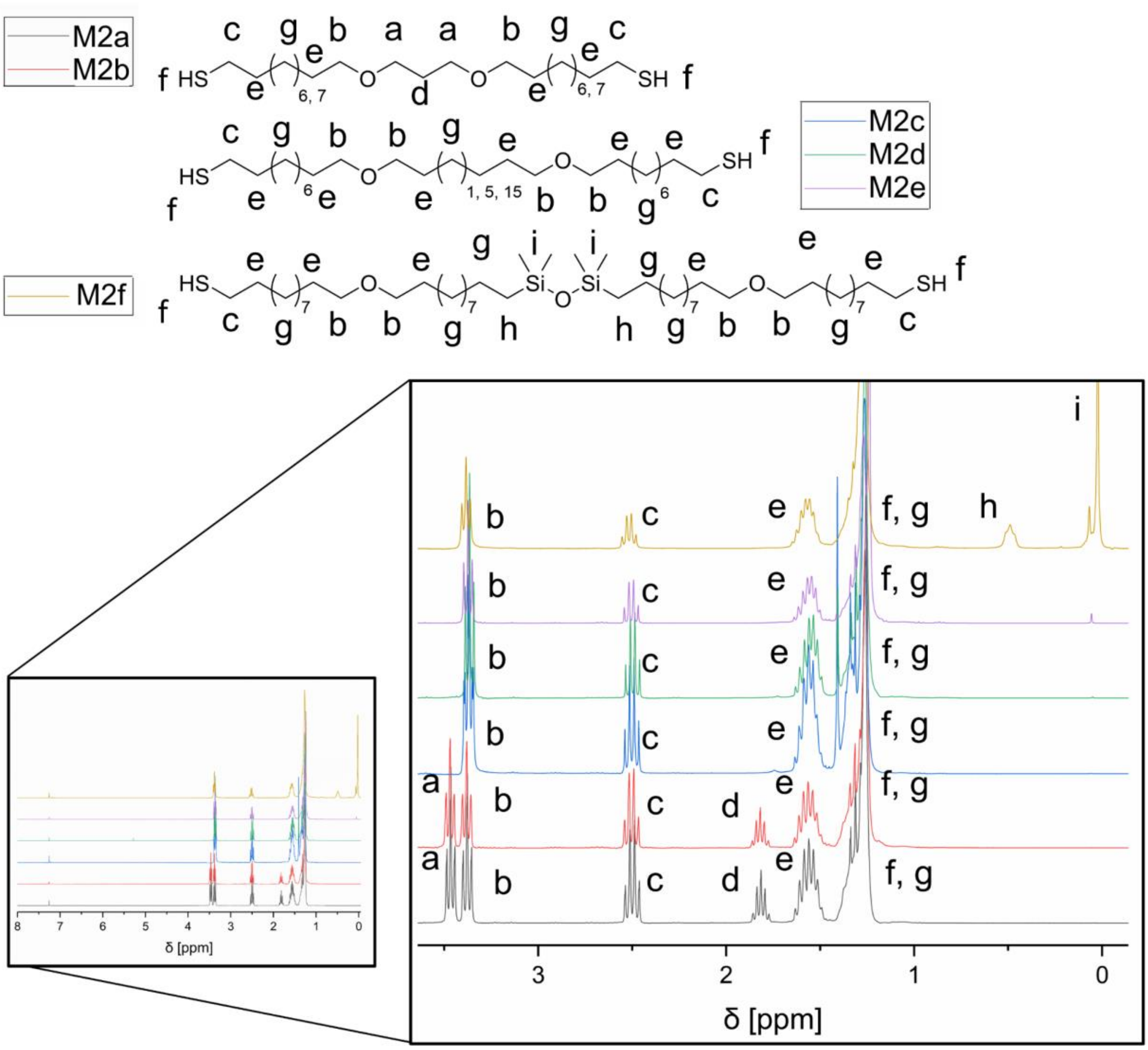


*Figure 20: ^{1}H-NMR spectra of monomers **M2a-f** after purification.*

*Table 8: Different melting points of ω,ω'-unsaturated diene ethers **M1a** – **M1f** and dithiols **M2a** – **M2f**.*

Monomer	**T_m [°C]**	**Monomer**	**T_m [°C]**
M1a	-8.3	M2a	23.0
M1b	14.1	M2b	31.8
M1c	16.8	M2c	43.0
M1d	30.0	M2d	54.6
M1e	55.2	M2e	70.5
M1f	10.3	M2f	35.7

Measured by DSC on the first heating scan (as side reactions happen and for some monomers the second peak consists of a double peak).

4.2.4 Thiol-ene polymerizations of ω,ω'-unsaturated diene ethers

As discussed in chapter 2.5.2 there are many examples of thiol-ene polymerizations of long-chain α,ω-unsaturated monomers. Typically, two different types of initiation are differentiated: thermal or UV-initiation. The most commonly used thermal initiator is azoisobutyronitrile (AIBN), while the most commonly used UV-initiator is 2,2-dimethoxy-2-phenylacetophenone (DMPA). A quick optimization was performed using the synthesis of **P3c** as example, as the polymer should exhibit a higher crystallinity than **P3a** and **P3b** due to the longer aliphatic segment in between the ether groups, however, compared to **P3d** and **P3e** it should still be well soluble and easily analyzable. At first, to prevent waste, the polymerization was performed without solvent in melt at 80 °C. AIBN was used as initiator (2.5 mol%) and the mixture was stirred in the microwave for 5 h. Under these conditions, the obtained number average molecular weight was low (M_n = 950 g mol^{-1}, $Đ_M$ = 2.20), which might be attributed to poor mixing because of the high viscosity, that can be found slightly above the melting point of the polymer (T_m = 74.6 °C). To lower the viscosity the reaction was carried out at 110 °C utilizing 1,1′-azobis(cyclohexanecarbonitrile) (ACHN, 10 h half life time at 88 °C)[307] instead of AIBN (10 h half life time at 65 °C).[307] The obtained M_n was still rather low (M_n = 2,000 g mol^{-1}, $Đ_M$ = 5.11). The use of a solvent seemed necessary to provide a homogeneous mixture and in general milder conditions. A non-toxic, more sustainable alternative to typical solvents as THF or dichloromethane is 2-methyltetrahydrofuran (2-Methyl-THF). 2-Methyl-THF can be obtained from furfural and levulinic acid by catalytic reduction. Furfural and levulinic acid are in turn produced by the dehydration of C5 sugars in biomass.[308] Another advantage of 2-methyl-THF is the higher boiling point (78 – 80 °C) compared to THF (65 – 67 °C), which allows for higher reaction temperatures. Additionally, 2-methyl-THF exhibits a far lower toxicity, which makes it suitable for application in pharmaceutical products.[309] At 80 °C in the microwave AIBN gave a higher molecular weight (M_n = 9,350 g mol^{-1}, $Đ_M$ = 2.58) than ACHN at 110 °C (M_n = 5,700 g mol^{-1}, $Đ_M$ = 1.88) after 5 h reaction time. Interestingly, photoinitiation with DMPA (2.5 mol%) at room temperature gave a significantly higher molecular weight (M_n = 15,350 g mol^{-1}, $Đ_M$ = 3.11), even though the mixture solidified after 10 min and was not stirred anymore. As a result of the optimization, the polymers **P3a** (M_n = 15,650 g mol^{-1}, $Đ_M$ = 2.76), **P3b** (M_n = 15,450 g mol^{-1}, $Đ_M$ = 3.69), and **P3f** (polymer insoluble in THF at RT) were similarly obtained using the optimized conditions with DMPA as initiator at room temperature. In contrast, due to the high crystallinity of the monomers **M1d**, **M1e**, **M2d** and **M2e**, which is indicated by their high melting point (Table 8), they could not be dissolved in THF at room temperature and thus polymerization was carried out by thermal initiation with AIBN at 80 °C in the microwave. Polymers **P3d**, **P3e** and **P3f** were not soluble in THF or HFIP and the average molecular weight (M_n) could not be obtained by GPC analysis. After polymerization, the reaction mixtures were typically precipitated either directly in cold methanol (**P3a** and **P3b**) or first heated to dissolve the dispersed polymer that already precipitated during the polymerization. In Figure 21 (right side) GPC chromatograms of thiol-ene polymer **P3c** before and after precipitation are shown. M_n seems to increase after precipitation, which is related to the removal of oligomers and cyclic compounds (91% yield after precipitation). Similar increases of molecular weight for polythioethers after drying have been reported in literature.[310] In Figure 21 (left side), the ^{1}H-NMR spectrum of **P3c** is depicted. Methylene groups ***a*** adjacent to the ether bond can be discerned as triplet at a chemical shift of 3.38 ppm. Another triplet can be observed at 2.49 ppm belonging to methylene groups ***b*** adjacent to the thioether bond. Methylene groups **c** in *β*-position to the ether or thioether can be discerned as multiplet at 1.79 – 1.46 ppm. The remaining methylene groups ***d*** are identified as a multiplet at 1.45 – 1.14 ppm.

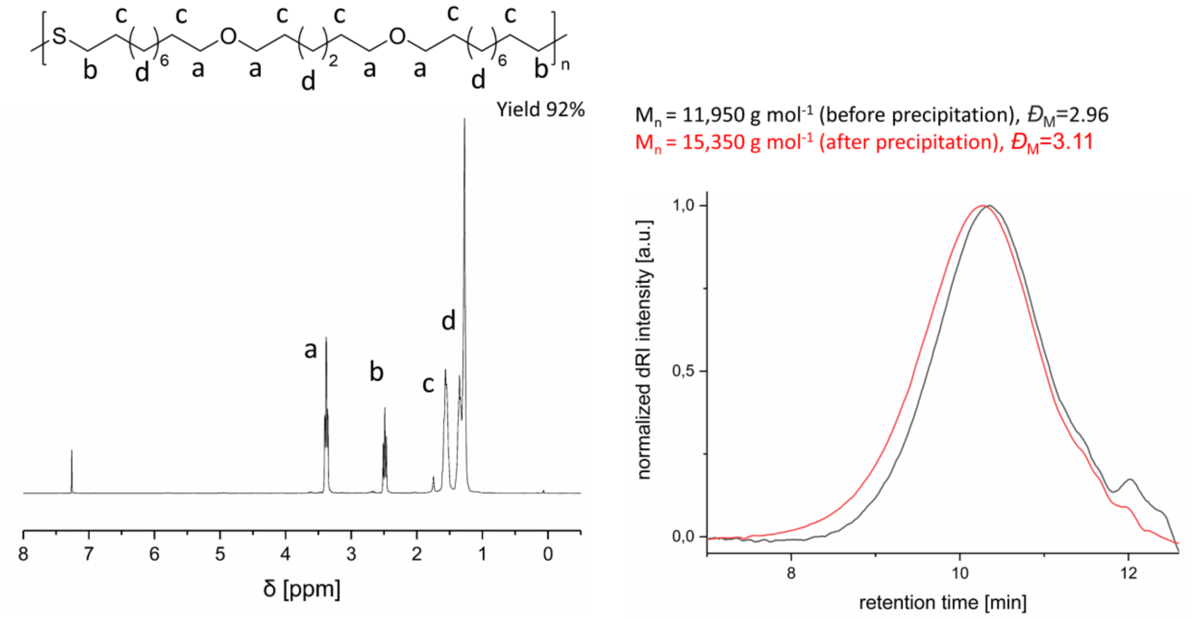


*Figure 21: ^{1}H-NMR analysis of **P3c** and GPC-analysis before and after precipitation. Due to the symmetry of the monomers and thiol-ether bond, the AABB-type polymer can be shown in an abbreviated form.*

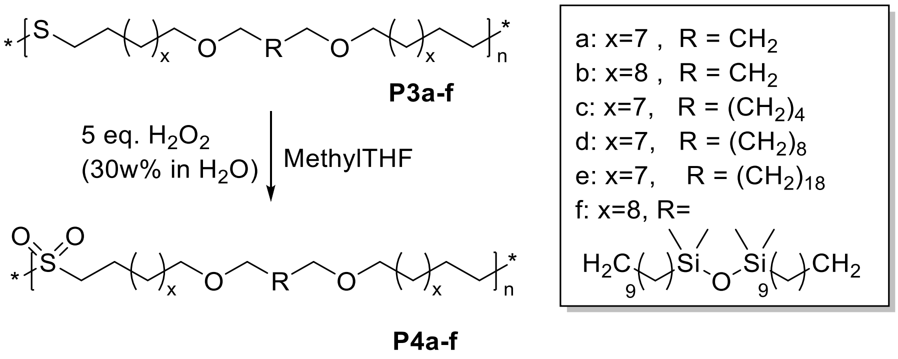
End group analysis of the remaining signal of the terminal double bond suggests an average molecular weight of (M_n = 28,600 g mol^{-1}) assuming an 1 : 1 ratio of thiol and terminal alkene. This approximation was necessary as the thiol end group (-CH_2-SH, quartet, 2.50 ppm) overlaps with the -CH_2-S-CH_2- signal (triplet, 2.49 ppm). For **P3a** and **P3b**, the -HC=CH$_2$ end group was not visible in ^{1}H-NMR-spectroscopy, suggesting a very high molecular weight. **P3d**, which is not soluble in THF at room temperature and could not be analyzed by GPC analysis, dissolves in chloroform and according to end group analysis revealed a comparably low average molecular weight (M_n = 4,100 g mol^{-1}). A possible explanation is the lower efficiency of the thermal initiation, as it could not be polymerized at room temperature by UV-initiation as mentioned above. **P3e** was neither soluble in chloroform nor in THF and no indication of the molecular weight could thus be obtained. More information on the molecular weight of the thiol-ene polymers could be obtained after oxidation and subsequent GPC analysis of the oxidized polymers in HFIP, which is discussed in the next section (4.2.5). A comprehensive overview of the thiol-ene polymers **P3a** – **P3g** as well as the oxidized thiol-ene polymers **P4a** – **P4g**, ADMET polymers **P5a** – **P5g** and hydrogenated ADMET polymers **P6a** – **P6g**, which are discussed in the later sections, is given in Table 9.

Table 9: Overview of all optimized thiol-ene, oxidized thiol-ene ADMET and hydrogenated ADMET, polymers (average molecular weights (M_n) and dispersities (Đ$_M$) obtained by GPC-measurements and melting points (T_m) obtained by DSC-analysis).

	Thiol-ene polymer (P3a – P3g)			**Ox. thiol-ene polymer (P4a – P4g)**			**ADMET polymer (P5a – P5g)**			**Hyd. ADMET polymer (P6a – P6g)**
Entry	**M_n [g mol^{-1}]**	**Đ$_M$**	**T_m [°C]**	**M_n [g mol^{-1}]**	**Đ$_M$**	**T_m[b] [°C]**	**M_n [g mol^{-1}]**	**Đ$_M$**	**T_m [°C]**	**T_m [°C]**
a	15,650	2.76	65.9	19,500	1.71	101.8	20,650	2.85	25.5	69.4
b	15,450	3.69	66.6	13,450	1.67	106.9	22,900	2,09	36.1	76.3
d	15,350	3.11	74.6	13,050	1.52	104.6	31,800	2.20	49.4	83.6
e	-[a]	-[a]	78.0	7,350	2.03	104.1	19,800	2.56	59.6	88.2
f	-[a]	-[a]	67.3	-[a]	-[a]	93.5	-[a]	-[a]	76.0	99.8
g	-[a]	-[a]	64.0	-[a]	-[a]	65.8	-[a]	-[a]	14.3	38.0

Ox. thiol-ene polymer = oxidized thiol-ene polymer; hydr. ADMET polymer = hydrogenated ADMET polymer; [a] insoluble in THF or HFIP at room temperature, [b] two close melting peaks (explanation in continuous text), minimum of second peak (higher temperature).

4.2.5 Oxidation of the thiol-ene polymers



Scheme 69: Reaction scheme of the oxidation of thiol-ene polymers ***P3a*** *–* ***P3g****.*

To improve the material properties, thiol-ene polymers **P3a** – **P3f** were oxidized by aqueous H_2O_2-solution (5 eq. per sulfur atom), a known process to convert thioethers to sulfoxides and sulfones.[222] The reaction was run overnight in THF at reflux conditions. Afterwards, the mixture was precipitated in water : methanol with a ratio 7 : 3 and the polymers were obtained in a yield of 77 – 83% for **P4a** – **P4e** and 56% for **P4f**. The conversion of the thioether groups was investigated by IR-spectroscopy and for **P4a** – **P4d** by ^{1}H-NMR-spectroscopy. **P4e** and **P4f** were insoluble in chloroform and other common solvents at room temperature and could not be analyzed by ^{1}H-NMR-spectroscopy. The molecular weight distribution of the in HFIP soluble polymers **P4a**, **P4b**, **P4c** and **P4d** was investigated by GPC analysis. Moreover, DSC analysis was performed to investigate differences in thermal behavior. In the IR-spectra of **P4b** (Figure 22, full spectrum (left side) an enlarged area of 1430 cm^{-1} – 460 cm^{-1} (right side) before oxidation (red) and after oxidation (blue)), a new vibration at 1018 cm^{-1} (sulfoxide specific IR absorption) and 1245, 1266, 1287, 1324 cm^{-1} (sulfone specific IR absorptions) confirm the formation of a polysulfone. The evaluation of IR-spectra of **P4a** and **P4c** – **P4f** gives similar results (Figure 22, left side), although the evaluation for **P4f** is not entirely conclusive as silyl ether specific absorptions overlap with most sulfoxide and sulfone specific IR absorptions.

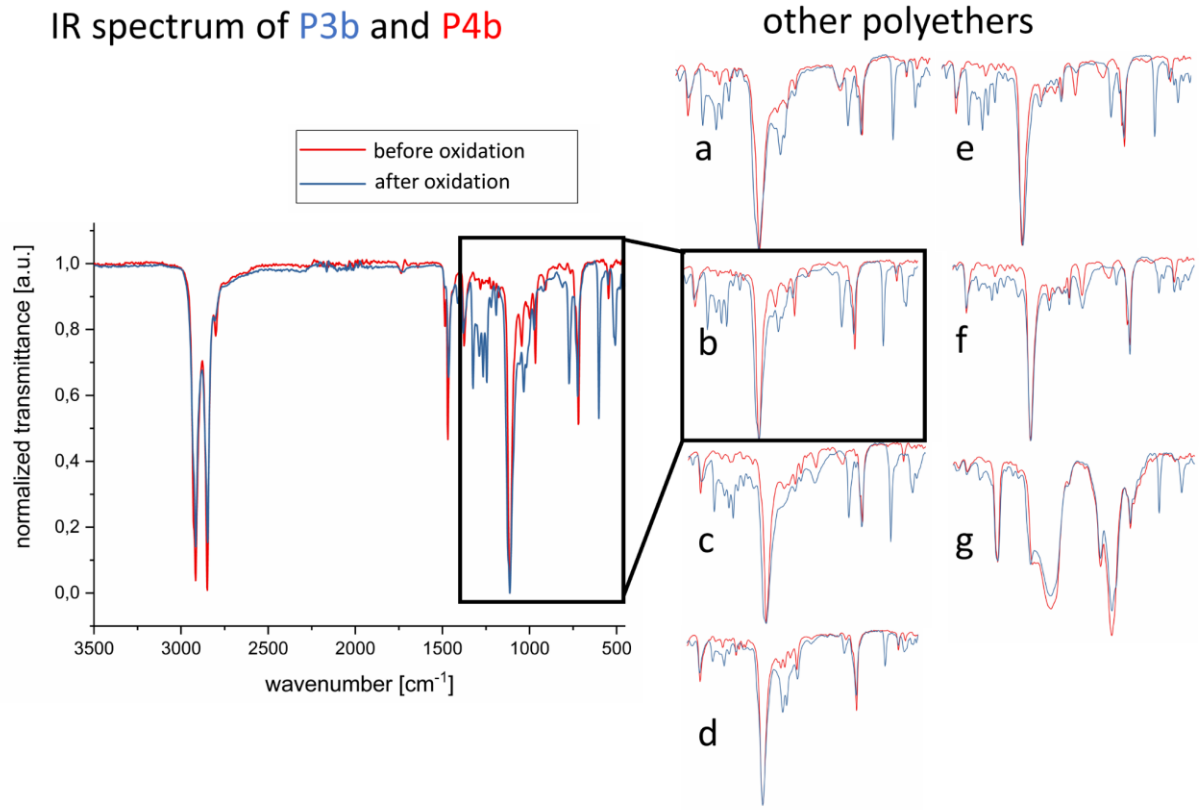


Figure 22: IR spectrum of the thiol-ene polymers before (red) and after (blue) oxidation. On the right side the relevant area of 1430 cm^{-1} – 460 cm^{-1} of the sulfoxide and sulfone specific IR-absorptions is shown. The IR spectra were normalized to the ether vibration at 1110 cm^{-1}.

In the ^{1}H-NMR spectra of the in chloroform soluble oxidized thiol-ene polymers **P4a, P4b**, **P4c**, **P4d**, the triplet at 2.49 ppm specific for the methylene group adjacent to the thiol-ether (Figure 23) is not discernible anymore, which confirms full conversion of the thiol-ether groups. At 2.91 – 2.81 ppm, a new multiplet can be confirmed for the methylene group adjacent to the sulfone. However, the integral (3.03 for **P4c**, normalized to the ether of one abbreviated repeating unit) does not fit to the expected 4 protons. A different, broad multiplet at 2.74 – 2.48 ppm can be discerned with an integral of 1.17, which either hints at a signal splitting due to hindered rotation of the methylene groups or an incomplete oxidation and an additional sulfoxide species. Signal splitting is in this case unlikely as without ring formation or stiff groups like amides, the long aliphatic chains should not be hindered in their rotation and an incomplete oxidation seems more likely. Aliphatic thioether compounds in literature[312] only slightly differ in their ^{13}C-NMR signal for the methylene group adjacent to sulfones or sulfoxides (<1 ppm), which can also be observed in this case (Figure 23, HSQC right side) and strongly suggests an incomplete oxidation and mixture of sulfones and sulfoxides for **P4a** (61% sulfone)**, P4b** (72% sulfone) and **P4c** (36% sulfone). Only in case of **P4d** a quantitative oxidation to the sulfone was possible.

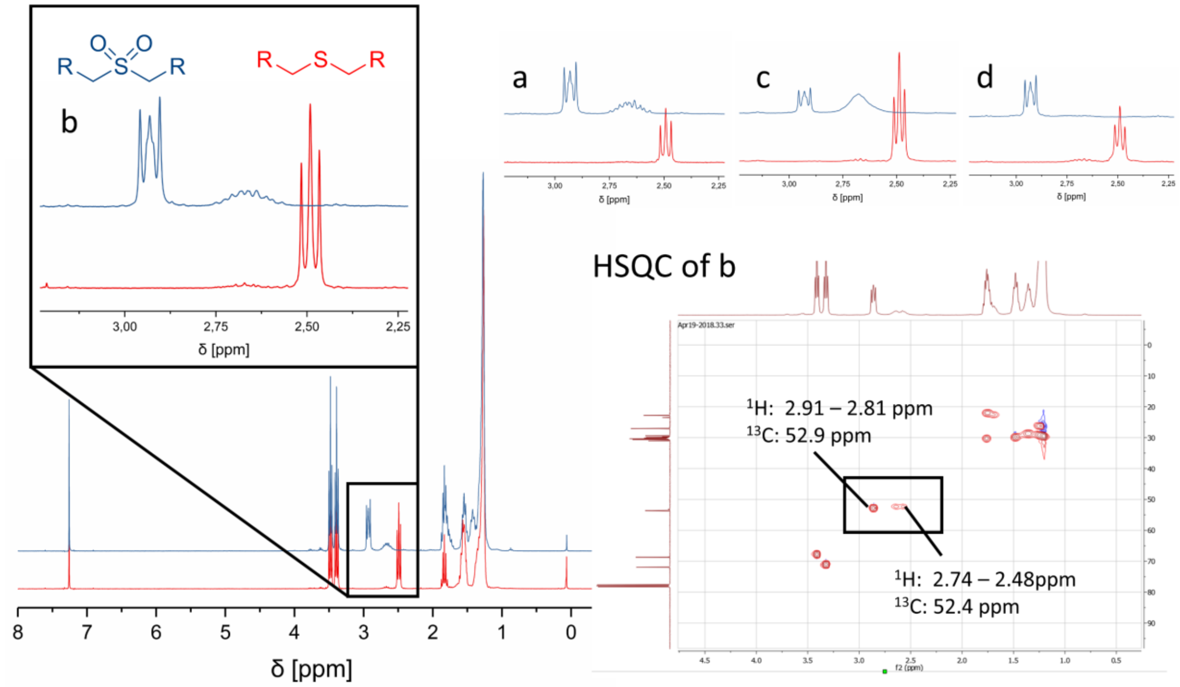


*Figure 23: Full ^{1}H NMR spectrum of **P3b** (left) before oxidation and the resulting **P4b** after oxidation. On the right side a HSQC spectrum of **P4b** is shown and the significant magnification of the relevant area of the spectra of **P4a**, **P4c** and **P4d**.*

DSC analysis of polymers **P4a – P4f** (Table 9) revealed that the melting point was increased significantly for all strictly aliphatic thioethers. The increase for more aliphatic polymers **P4c** – **P4e** was found to be in a range of 26 – 30 °C, whereas the increase for less aliphatic polymers **P4a** and **P4b** was between 36 – 40 °C. This general trend seems reasonable, as the influence of the oxidation should increase with a higher functional group density, a trend which can also be seen for the hydrogenations of the ADMET polymers, which is discussed in section 4.2.7. Interestingly, the melting point for silylated **P4f** barely increased from 64.0 to 65.8 °C. In general, in DSC analysis of **P4a** – **P4e** two close melting peaks were discernible (exemplary DSC graph for **P4c** in Figure 24), which is common for oxidized thiol-ene polymers and known from literature.[178] Such behavior is indicative for the recrystallization of different crystal forms in polar polymeric materials and also observed for nylon-6.6.[313] Another explanation is exothermic decomposition of the sulfoxide bond by reverse cycloaddition, although this reaction is typically only favored next to electron withdrawing groups.[314] Still, ^{1}H-NMR-spectroscopy after heating the sample to 120 °C overnight shows a significant increase of the sulfone signal at 2.91 – 2.81 ppm (integral of 2.40 to 3.19 for **P4a**), a slight decrease of the sulfoxide signal at 2.74 – 2.48 ppm (integral of 1.57 to 1.36 for **P4a**) and a new broad singlet emerging at 2.50 – 2.21 ppm (integral 1.35) confirming some degradation. The number average molecular weight (M_n) of the oxidized thiol-ene polymers **P4a**, **P4b**, **P4c** and **P4d** (not soluble in THF, soluble in HFIP) is comparable to **P3a**, **P3b**, **P3c** and **P3d**, although the dispersities are far lower.

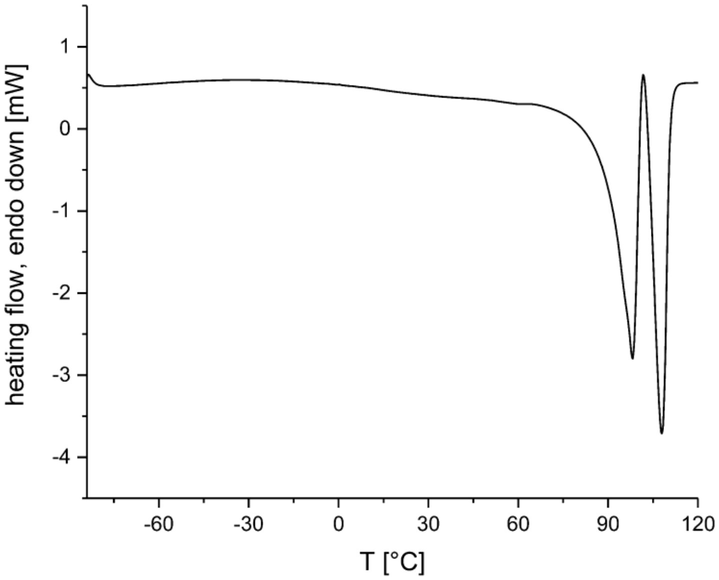
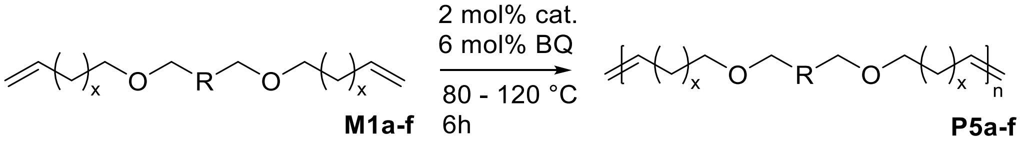


Figure 24: Exemplary DSC graph (second heating scan) of ***P4c****. Explanation for the double peak in the continuous text.*

4.2.6 ADMET polymerizations of ω,ω'-unsaturated diene ethers

A basic catalyst screening was conducted on the example of monomers **M1b** and **M1c** to investigate the activity of different metathesis catalysts towards the polymerization of the synthesized ω,ω'-unsaturated diene ethers (Scheme 70).



Scheme 70: General reaction scheme of the optimization for ADMET polymerizations.

In all reactions benzoquinone (6 mol%) was added to suppress isomerization. The reactions were initially carried out at 80 °C. However, as the mixtures became exceedingly viscous and difficult to stir, the temperature was increased to 120 °C after 2 h. To guarantee a good removal of the ethylene side product, reduced pressure of 700 – 20 mbar was applied (pressure was decreased within the first minutes of the reaction in a rate of ~100 mbar/min) and the stirring was regulated during the reaction to be as high as possible. A comparison between **G-II**, **HG-II** and **Um7₁** catalyst (Table 10, entry A-C, Figure 25) shows that the **HG-II** performs better than the other metathesis catalysts. This observation might be explained by a better stability of the **HG-II** catalyst at the reaction temperature or a better tolerance towards the monomer and slight polysiloxanes impurities. In general, ADMET polymerizations can be conducted without solvent if the melting point of the monomer is not too high (<100°C), which is certainly the most sustainable way to perform the reaction. However, for the mostly aliphatic long-chain monomers **M1c** – **M1f**, stirring the highly viscous reaction mixture at temperatures that do not heavily decompose the catalyst, becomes difficult. As a result, the dispersity of the polymer becomes increasingly high, which can be observed on the example of **P5c** (Table 11, entry A-C). H. Cramail and co-workers demonstrated that methyl-5-(dimethylamido)-2-methyl-5-oxopentanoate (polarclean), an eco-friendly water-soluble solvent with a high boiling point, can be utilized in ADMET polymerizations achieving high molecular weights.[161] According to their findings and set of monomers, the **G-II** catalyst gave only oligomers in polarclean, while the **HG-II** catalyst gave far higher molecular weights than both catalysts without solvent. This study confirms these findings, as monomers **M1b** and **M1c** gave higher molecular weights in polarclean than without solvent (Table 10 and Table 11, entry D). In case of monomer **M1c**, which gives a highly viscous reaction mixture without solvent, the utilization of polarclean resulted in a significant increase of molecular weight from 9,000 g mol^{-1} to 31,800 g mol^{-1} and a decrease of dispersity from 3.45 to 2.20 (compare Table 11, entry C and D).

*Table 10: Optimization of the ADMET-polymerization of monomer **M1b**.*

Entry	Catalyst	Solvent	M_n [g mol^{-1}]	$Đ_M$
A	G-II	-	6,000	3.10
B	M7$_1$[a]	-	5,500	2.74
C	HG-II	-	16,000	2.20
D	HG-II	polarclean	22,900	2.09

[a] end temperature 140 °C instead of 120 °C.

*Table 11: Optimization of ADMET-polymerizations of monomer **M1c**.*

Entry	Catalyst	Solvent	M_n [g mol^{-1}]	$Đ_M$
A	G-II	-	13,300	4.09
B	M7$_1$[a]	-	7,250	3.53
C	HG-II	-	9,000	3.45
D	HG-II	polarclean	31,800	2.20

[a] end temperature 140 °C instead of 120 °C.

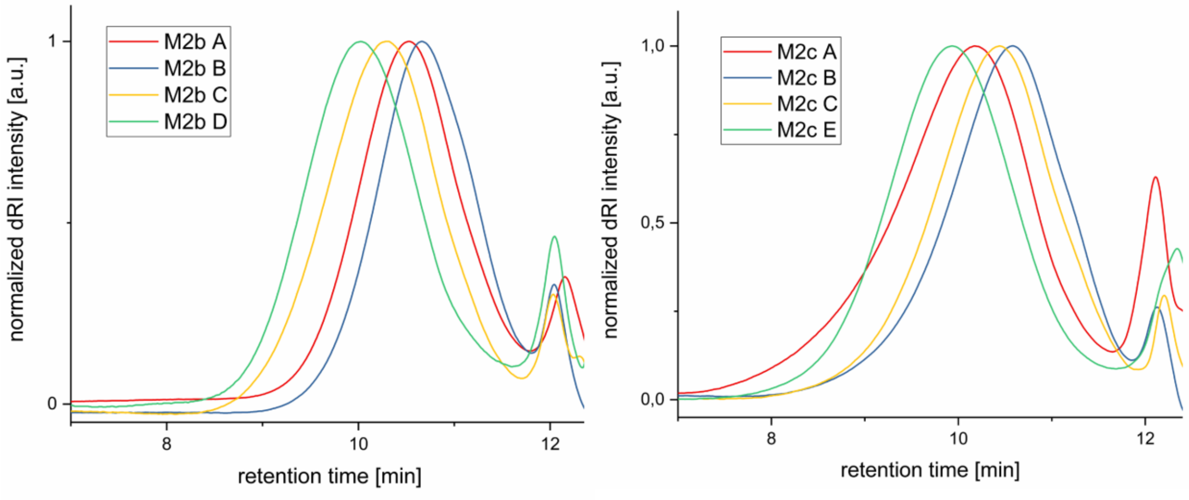


*Figure 25: GPC traces of the optimization reactions for the ADMET polymerization of **M1b** and **M1c**.*

To separate the solvent polarclean and the residual monomer or macrocycles from the desired ADMET polymers, the mixtures of ADMET polymers **P5a** – **P5f** were precipitated in cold methanol after polymerization. In Figure 26, the ^{1}H-NMR spectrum of the purified polymer **P5b** and the GPC chromatograms before and after precipitation are shown. In the ^{1}H-NMR spectrum, no end group signals were found suggesting high molecular weight. At a chemical shift of 5.41 – 5.30 ppm, a multiplet can be assigned to signal ***a*** of the double bond of the ADMET polymer.

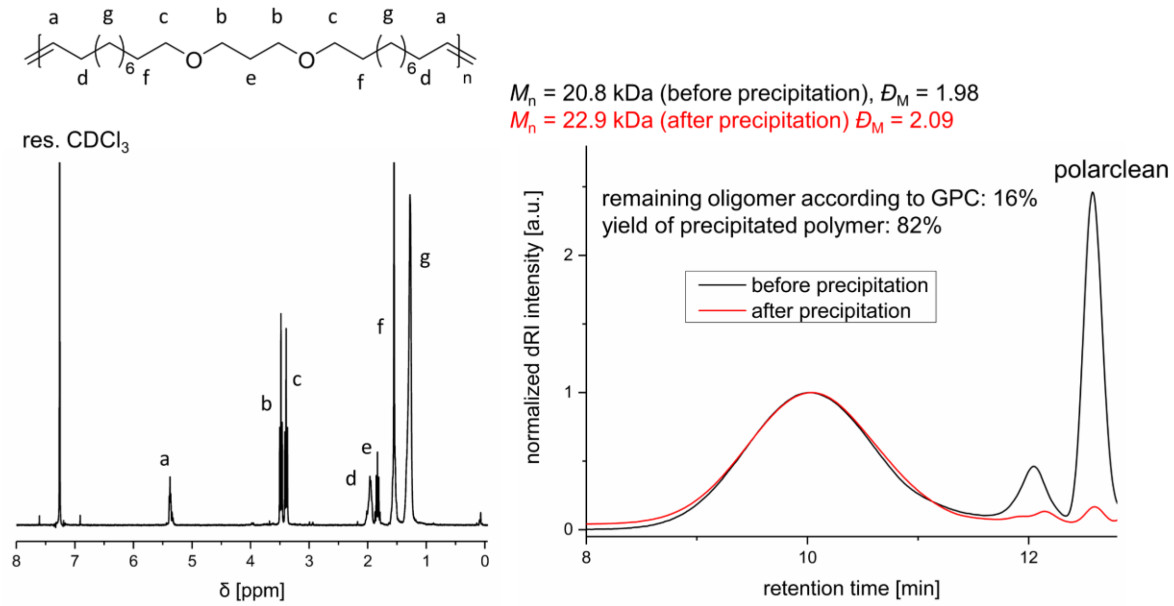


*Figure 26: ^{1}H-NMR spectrum of **P3b** and corresponding GPC chromatogram of before and after precipitation.*

The methylene groups ***b*** and ***c*** adjacent to the ether bond can be identified as triplets at 3.48 and 3.39 ppm. Methylene group ***d*** next to the double bond can be assigned to the multiplet at 2.05 – 1.90 ppm. Methylene group ***e*** next to methylene group ***b*** can be identified as quintet at 1.83 ppm. The rest of the methylene groups can be assigned to multiplet ***f*** at 1.62 – 1.49 ppm and multiplet ***g*** at 1.39 – 1.20 ppm. The GPC trace (Figure 26, right) shows that polarclean and residual monomer or macrocycles at 12.0 min and 12.3 min are removed. Integral of the removed residual monomer or macrocycles at 12.0 min, compared to the main peak, roughly fits to the observed loss of yield after precipitation (18%).

4.2.7 Hydrogenation of ADMET polymers

To improve the material properties, ADMET polymers **P5a** – **P5f** were hydrogenated using Shvo's catalyst (Figure 27) and hydrogen. The reaction was carried out well above the melting point of the ADMET polymers at 100 °C in toluene at 40 bar hydrogen pressure overnight.

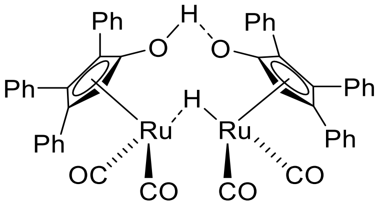


Figure 27: Shvo's catalyst.

After hydrogenation, polyethers **P6a** – **P6f** were insoluble in all common organic solvents at room temperature. To confirm the success of the hydrogenations, the IR-spectra of polyethers **P5a** – **P5f** and **P6a** – **P6f** were compared (Figure 28).

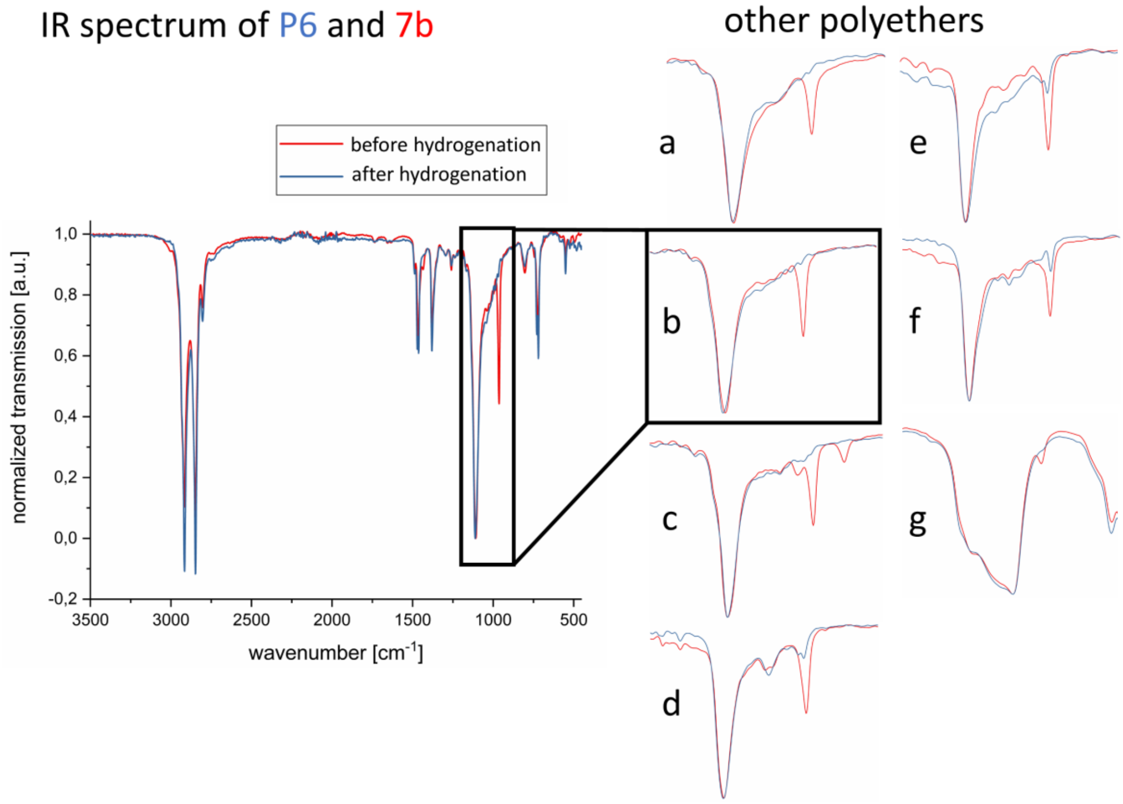
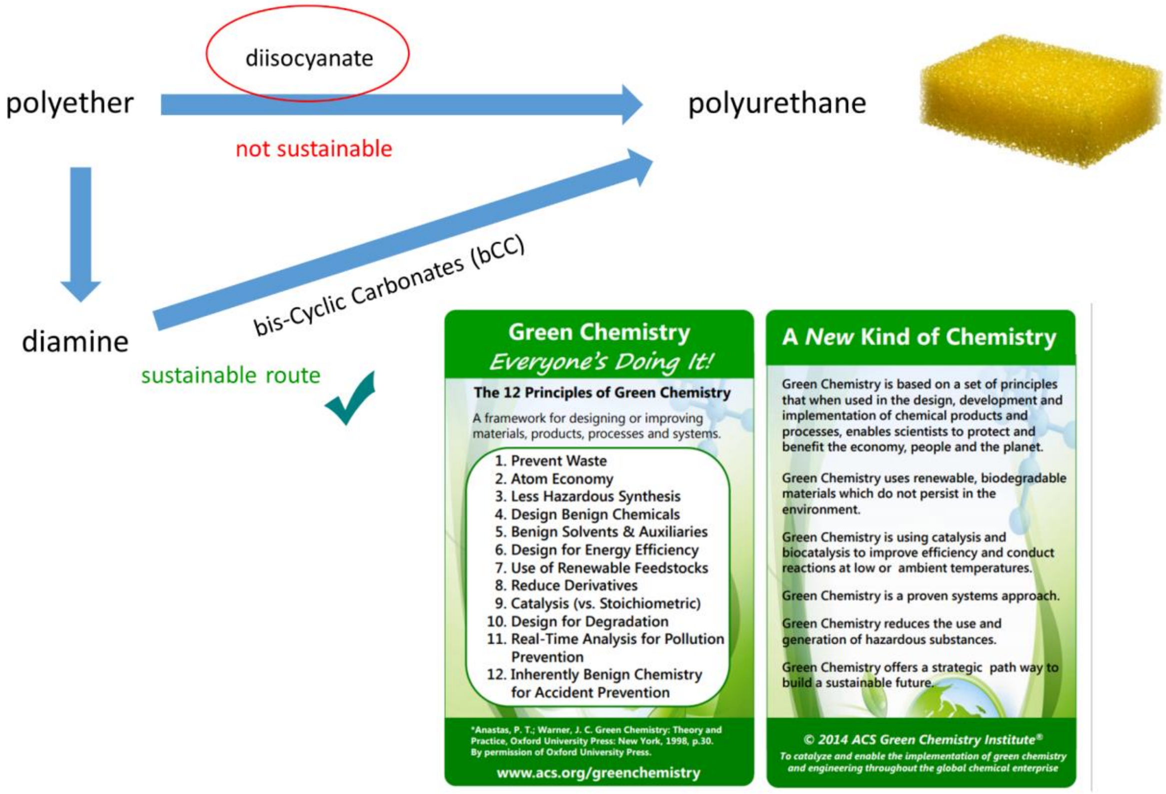


*Figure 28: IR spectrum of polyether before (**P5b**) and after (**P6b**) hydrogenation (right side). On the left side the relevant area of 1200 cm^{-1} – 900 cm^{-1} of the vibration of the double bond is shown. The IR spectra were normalized to the ether vibration at 1110 cm^{-1}.*

The vibration correlating to the double bond at a wavenumber of 963.2 cm^{-1} is decreasing significantly and for polyethers **P5a** and **P5b** the polymers were hydrogenated quantitatively to **P6a** and **P6b**. For polyethers **P6d** – **P6e**, a small residual peak indicates incomplete conversion, which might be explained by the increasing aliphatic nature and insolubility of the polymer at the employed reaction conditions. For polyether **P5f**, the broad silyl ether vibration at 1018.1 cm^{-1} overlaps significantly with the vibration of the double bond at 966.7 cm^{-1} and even though the peak of the double bond seems to disappear, it is difficult to claim full conversion. Another indication for the successful hydrogenation of the ADMET polymers is an increase in the melting points. A comprehensive overview of the melting points of **P5a** – **P5e** and **P6a** – **P6e** is given in Table 9. The most pronounced increase in melting point can be observed for **P5a** (~44 °C, 25.5 to 69.4 °C). A slightly lower increase can be found for **P5b**, which consists of two additional methylene groups per monomer (~40 °C, 36.1 to 76.3 °C). **P5c**, similar to **P5a**, though with three additional methylene groups between the ether bonds, exhibits an increase of (~34 °C, 49.4 to 83.6). **P5d**, having five additional methylene units compared to **P5a**, has a lower increase of (~29 °C, 59.6 to 88.2). The melting point of mainly aliphatic **P5e** increases by (~24 °C, 76.0 to 99.8 °C). Silylated polyether **P5f** in general exhibits a very low melting point, but also shows an increase of (~24 °C, 14.3 to 38.0 °C). In general, the melting point of ADMET polymers **P5** from shorter chain monomers is lower than that of monomers consisting of more methylene units. After hydrogenation the melting points increase, which further confirms the success of the reaction. The relative increase ranging from 24 to 44 °C is higher for shorter monomers.

4.3 Non-Isocyanate Polyurethanes from Renewable long-chain Polyether Diols and Erythritol Bis(carbonate)



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*Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30. By permission of Oxford University Press.

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Figure 29: Sustainable and non-sustainable routes to polyurethanes from polyethers.[i]

Most commonly, polyethers are applied as polyols for the production of segmented polyurethanes (PUs). Typically, soft and hard segments are differentiated. The soft segment consists of either polyethers or polyesters, whereas the hard segments are based on the reaction of diisocyanates and a diamine chain extender. As the soft and hard segments are immiscible, the polymer chains undergo phase separation, which can lead to the formation of thermoplastic elastomers. By adjusting the chemical nature and respective amounts of reagents, it is possible to obtain a wide range of materials with different properties.[315] Due to the limited variety of commercial polyethers, the variation of the chemical nature of polyether segments is challenging.

The easiest way to obtain polyurethanes from such polyethers is a polymerization with diisocyanates as co-monomer (Figure 29). However, the use of isocyanates is not

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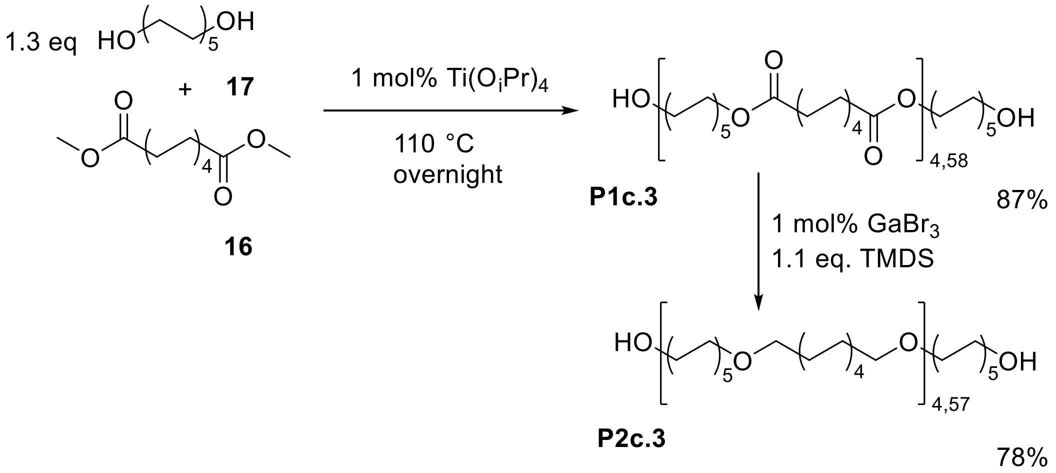
[i] The 12 Principles of Green Chemistry Pocket Guide : https://www.acs.org/content/dam/acsorg/greenchemistry/resources/the-12-principles-of-green-chemistry-pocket-guide.pdf (access date: 15.04.2018)

considered sustainable. Therefore, as an alternative route, the diol can be converted to a diamine first and subsequently polymerized by using a bCC as co-monomer to obtain hydroxypolyurethanes, the most common subclass of NIPUs.

4.3.1 Synthesis of a novel polyether segment to be used in NIPUS

The novel polyethers that can be obtained *via* the $GaBr_3$-catalyzed reduction of esters offer a large potential for the variation of the soft segment and thus the properties of PUs or NIPUs. Most of the polyesters reduced in section 4.1.1 have methyl ester and OH-end groups, ultimately leading to methoxy and OH-end groups after reduction. For the use as prepolymers in the production of polyurethanes, it is essential to have only OH- and no methoxy end groups in the polymer. This can either be achieved by the polymerization of acids instead of methyl ester components, as the acid functionality is also reduced to the alcohol. Another option is the use of an excess of diol from the beginning, thus ensuring that only OH-end groups exist after polymerization. Ring-opening polymerizations can also lead exclusively to OH-end groups by initiating the polymerization with a diol instead of a monofunctional alcohol.



Scheme 71: Polymerization of dimethyl sebacate and an excess of 1,10-decanediol to obtain decamethylene sebacate ***P1c.3*** *with only OH-end groups, which was reduced to polyether* ***P2c.3*** *afterwards.*

Here, the approach to use an excess of diol component was chosen on the example of C10 polyester **P1c** (see section 4.1.1.1) to yield **P1c.3** (Figure 30), which was already polymerized in this fashion previously (**P1c.1**). The reaction was repeated on larger scale and the resulting product **P1c.3** was subsequently reduced to the corresponding polyether **P2c.3** (Scheme 71), which was confirmed by ^{1}H-NMR spectroscopy (Figure 30). Full conversion can be confirmed by the decrease of the triplet at 4.05 ppm specific for the ester bond and the formation of a new triplet at 3.33 ppm specific for the ether (further discussed for **P1c.1** in section 4.1.2). According to end group analysis of the ^{1}H-NMR-specta no degradation can be observed, as the degree of polymerization remains constant after reduction (M_n=1,600 g mol^{-1}, DP=10.3) compared to before (M_n=1,750 g mol^{-1}, DP=10.3). In addition, the molecular weight according to GPC analysis remains roughly the same (M_n=3,350 g mol^{-1} after reduction compared to M_n=3,300 g mol^{-1} before reduction).

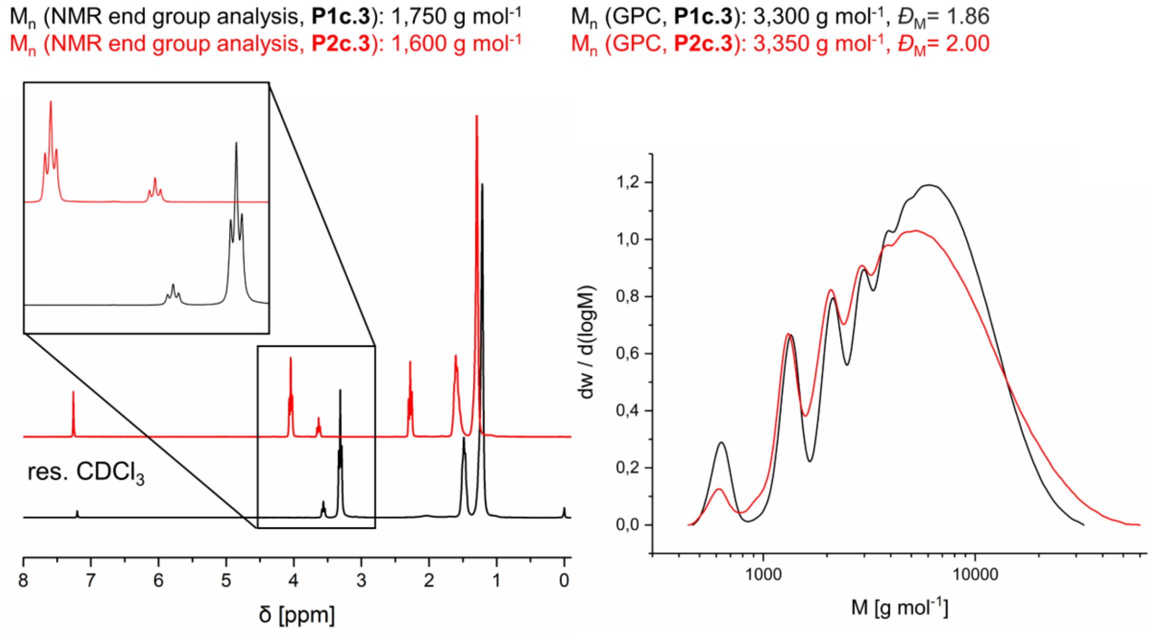
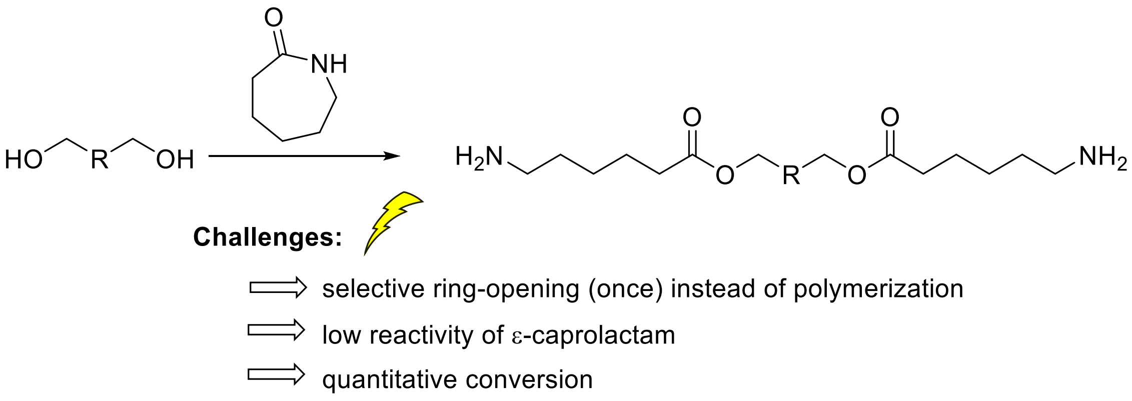


*Figure 30: ^{1}H-NMR spectra and GPC analysis (in chloroform) of polyester **P1c.3** (black) and polyether **P2c.3** (red).*

4.3.2 An efficient, novel conversion of hydroxy groups to amines

The obtained telechelic polyether might be polymerized using diisocyanates, however, as mentioned previously, a more sustainable method is the conversion to a diamine followed by the polymerization with bis-cyclic carbonates as co-monomers.



Scheme 72: Novel approach for the synthesis of diamines from diols with ε-caprolactam.

The conversion of hydroxy groups to amine groups is hard to be achieved quantitatively. The direct amination of alcohols described by M. Beller *et al.* works almost quantitatively for some diols as *e.g.* isosorbide or tetraethylene glycol.[246] However, as already described in (2.6.1), alcohols with longer aliphatic chains seem to result in bad yields, ultimately preventing them to be used in end group functionalization. To quantitatively convert the OH-end groups to amine groups, another approach was chosen, which to the best of our knowledge has yet to be studied in scientific literature (Scheme 72): The selective, acid catalyzed ring-opening of *ε*-caprolactam (CPL) without further polymerization. However, this reaction posed some challenges. Typically, CPL is used in polymerizations and a selective ring-opening is only possible if the reactivity of the formed amine as a nucleophile is inhibited. Moreover, CPL - due to its stable amide bond - is a comparably unreactive compound that requires harsh conditions to react quantitatively. To overcome those challenges specific reaction conditions are required. For selectivity, either the nucleophilicity of the hydroxy group has to be enhanced compared to the amine group formed after the reaction, or the nucleophilicity of the amine group has to be decreased. By using a stoichiometric amount of a strong acid, the latter can be achieved as the formed amine is protonated and cannot react further. To increase the low reactivity of CPL and achieve quantitative conversion, harsh conditions as *e.g.* a high temperature without solvent are beneficial.

As model substrate for the optimization of this reaction, 1,10-decanediol was chosen, as it is the formal monomer unit of **P2c.3**, thus having similarities in its chemical characteristics and solubility. The choice of acid catalyst was motivated by the idea of having a cheap, commercially available, strong acid which is still comprised of an organic rest to provide some extent of solubility. Therefore, *p*-toluene sulfonic acid (TsOH) was tested for its reactivity. Per hydroxy group, 1.5 eq TsOH and a slight excess (1.1 eq) of *ε*-caprolactam were heated to 130 °C (slightly above the melting temperature of TsOH) and stirred for 24 h. After 2 h, 16 h and 24 h, samples for ^{1}H-NMR analysis were taken. Figure 31 shows the ^{1}H-NMR spectrum after 16 h reaction time and illustrates the different characteristic signals for product **45**, side products and reactants. Product formation could easily be monitored by the comparison of the triplet ***a*** at 3.99 ppm characteristic for ester bonds compared to the residual triplet ***b*** at 3.34 ppm. A different triplet **c** at 3.32 ppm is specific for ether by-product **47** formation, an expected side reaction of alcohols at harsh acidic conditions.

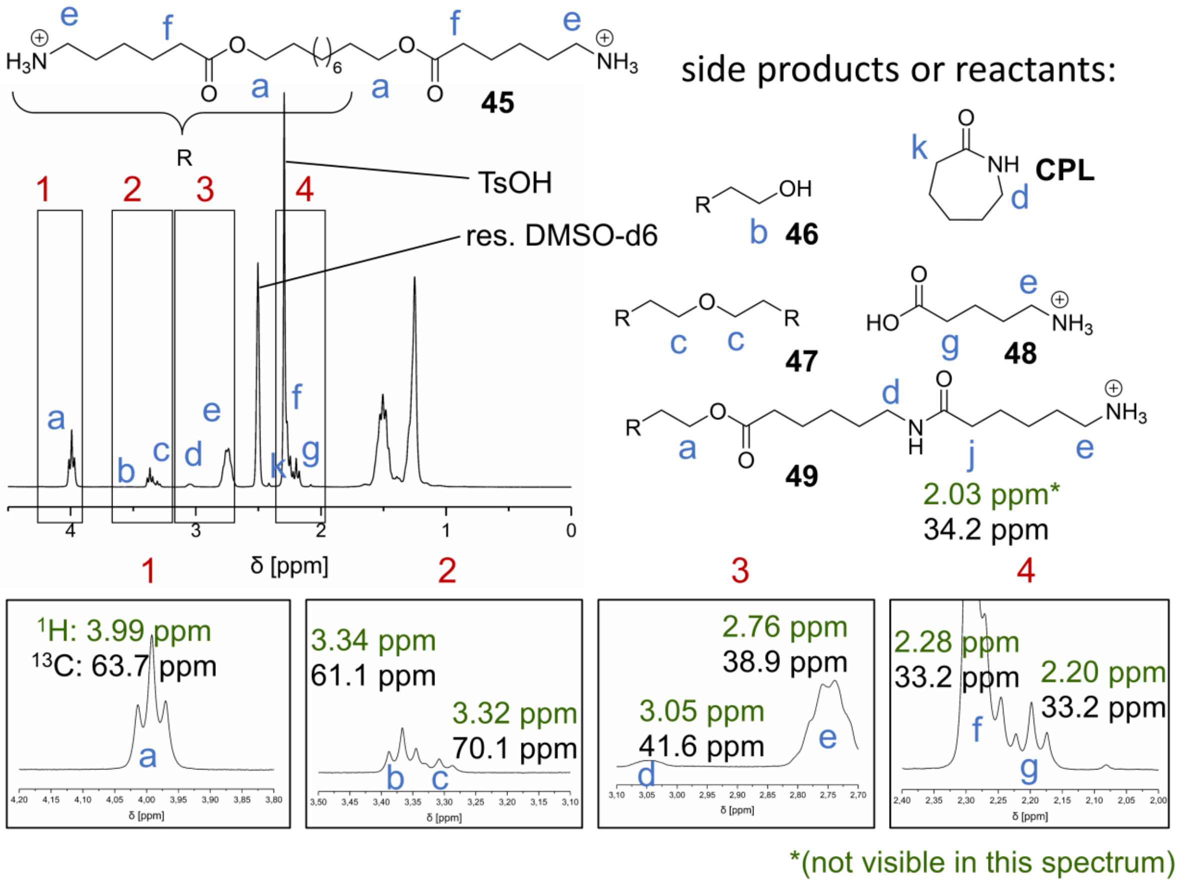


Figure 31: ^{1}H-NMR of the product, side products and reactants of the reaction of ε-caprolactam with 1,10-decanediol catalyzed by TsOH after 16 h reaction time. For the relevant signals, the chemical shifts of ^{1}H-NMR (green) and ^{13}C-NMR (black) are assigned. Signals of the side product ***49*** *are not visible in this spectrum, still the chemical shift for methylene group* ***j*** *is included from other spectra.*

At 3.05 ppm, the methylene group ***d*** in *α*-position to the amide in the reactant CPL as well as the oligoamide side product **49** can be observed. The methylene group in α-position to the carbonyl of the amide group can be observed as multiplet ***k*** for ε-caprolactam at 2.33 – 2.23 ppm, while it can be seen as multiplet ***j*** for the oligoamide side product **49** at 2.05 – 2.00 ppm. The methylene group ***e*** attached to the newly formed ammonium group can be distinguished as multiplet at 2.84 – 2.68 ppm. Triplet ***f*** in α-position to the newly formed ester at 2.28 ppm overlaps with the methyl group signal of the TsOH catalyst and cannot be clearly distinguished. Interestingly, residual water (TsOH is only available as monohydrate) also acted as nucleophile and contributed to an opening of *ε*-caprolactam to side product **48**, which can be identified by another triplet ***g*** of the formed carboxylic acid at 2.20 ppm. Not all signals are baseline separated, however a rough estimation of the conversion and selectivity of the reaction could still be given as all products and side products give unique and clearly identifiable signals. Therefore, the reaction was optimized at 130 °C without solvent regarding reaction time, amount of acid, type of acid and amount of CPL (Table 12). The conversion and two different selectivities were compared: Selectivity S (1) gives information about the hydroxy groups successfully converted to the ester compared to the side reaction to ether **47** or methyl sulfonate (a side reaction that was observed in case pure MsOH was used instead of a mixture of acids). Selectivity S (2) additionally informs about the polyamide side product **49**. However, this is not entirely comparable, as the polyamide is not necessarily attached to the diol, it can also be formed from side product **48** that further oligomerized. Entries 1 – 3 display the reaction of 3 eq. TsOH (≙ 1.5 eq. per hydroxy group) and 2.2 eq. CPL (≙ 1.1 eq. per hydroxy group). It became apparent that after 2 h reaction time the conversion is still rather low (32%). However, after 16 h already 79% conversion was achieved. The reaction did proceed further and reached a conversion of 94% after 42 h. At this point, the CPL was entirely consumed, forming either the product **45** or the side product **48**. The selectivity of the reaction decreased due to ether formation in the acidic environment after most of the CPL was consumed. Exact stoichiometric or substoichiometric amounts of acid (entry 4 – 6) increased the selectivity S (1) and comparably less ether was formed. However, the reaction did not proceed further after 4 h (entry 9 – 11, entry 14 – 16) and stopped at 34 – 48% conversion.

Table 12: Optimization of the acid catalyzed reaction of 1,10-decanediol and ε-caprolactam (CPL).

Entry	t[h]	Acid	CPL [eq]	C [%][h]	S (1) [%][i]	S (2) [%][j]
1	2	3 eq. TsOH	2.2	32	100	100
2	16	3 eq. TsOH	2.2	79	95	95
3	42	3 eq TsOH	2.2	94	92	92
4	4	1 eq. TsOH	2.2	44	100	100
5	4	1.5 eq. TsOH	2.2	-[k]	100	100
6	4	2 eq. TsOH	2.2	59	99	99
7	4	3 eq. TsOH	2.2	55	98	98
8	4	4 eq. TsOH	2.2	55	97	97
9	9	1 eq. TsOH	2.2	40	100	93
10	9	1.5 eq. TsOH	2.2	46	100	97
11	9	2 eq. TsOH	2.2	77	98	95
12	9	3 eq. TsOH	2.2	81	93	93
13	9	4 eq. TsOH	2.2	78	88	88
14	24	1 eq. TsOH	2.2	34	100	85
15	24	1.5 eq. TsOH	2.2	48	100	93
16	24	2 eq. TsOH	2.2	43	100	94
17	24	3 eq. TsOH	2.2	92	90	85
18	24	4 eq. TsOH	2.2	87	87	87
19[a]	4	3 eq. TsOH	2.2	55	97	97
20[b]	4	3 eq. TsOH	2.2	59	98	98
21[c]	4	3 eq. TsOH	2.2	57	89	89
22[d]	4	3 eq. TsOH	2.2	43	100	100
23[a]	8	3 eq. TsOH	2.2	81	95	95
24[b]	8	3 eq. TsOH	2.2	71	96	96
25[c]	8	3 eq. TsOH	2.2	74	90	90
26[d]	8	3 eq. TsOH	2.2	55	100	100
27	24	3 eq. TsOH	4	77	100	93
28	3	3 eq. MsOH	2.2	70	75[e]	75[e]
29	8	1.5 eq. MsOH + 1.5 eq. TsOH	2.2	81	95	95
30	24	1.5 eq. MsOH + 1.5 eq. TsOH	2.2	90	93	93
31	8	1.5 eq. MsOH + 1.5 eq. TsOH	4	85	100	95
32	24	1.5 eq. MsOH + 1.5 eq. TsOH	4	87	100	91
33[f]	32	2 eq. MsOH + 1.5 eq. TsOH	4	98	100	90
34[f]	35	2 eq. MsOH + 1.5 eq. TsOH	4	98	100	90
35	24	3 eq. MsOH + 1.5 eq. TsOH	4	99	100	95
36[g]	32	3 eq. MsOH + 1.5 eq. TsOH	4	99	100	92

All reactions were performed at 130 °C without solvent; acid and ε-caprolactam were premixed before the addition of the diol; equivalents are relative to 1 eq 1,10-decanediol, e.g. 2.2 eq. CPL relate to 1.1 eq. per hydroxy group; [a] additional silica as drying agent; [b] additional Na_2SO_4 as drying agent; [c] TsOH, diol and Na_2SO_4 heated for 1 h at 130 °C before addition of ε-caprolactam; [d] TsOH predried with molecular sieves (4 Å) for 1 h at 130 °C before addition of ε-caprolactam; [e] additional methane sulfone ester side product; [f] additional 0.5 eq. MsOH after 22 h; [g] big batch compared to test reactions; [h] the (functional group) NMR-conversion C was determined by applying the following ratio after normalization (ether+methyl sulfone ester+ester)/(ether+methyl sulfone ester+ester+alcohol); [i] the NMR-selectivity S (1) was determined by the following ratio after normalization (ester/(ether+methyl sulfone ester+ester)); [j] the NMR-selectivity S (2) was determined by the following ratio after normalization (ester/(ether+methyl sulfone ester+ester+amide); [k] cannot be determined due to overlapping broad acid peak.

In a repetition of the experiment using 3 eq. TsOH, a similar reaction progress was observed after 9 h compared to 16 h in the previous reaction (compare entry 2: C = 79%, S (1) = 95%; entry 12: C = 81%, S (1) = 93%). Between 24 h and 42 h, the progress in conversion was minimal (compare entry 17: C = 92%, S (1) = 90%; entry 3: C = 94%, S (1) = 92%). In a direct comparison between 3 and 4 eq. TsOH after 4 h reaction time, no difference was observed (compare entry 7 and 8). However, after 9 h until the end of the reaction at 24 h, the reaction employing less acid gave a higher conversion and selectivity (compare entry 12: C = 81%, S (1) = 93%; entry 13: C = 78%, S (1) = 88%; entry 17: C = 92%, S (1) = 90%; entry 18: C = 87%, S (1) = 87). The main reason for the incomplete conversion is the formation of the **48** side product from CPL and water, which consumes CPL as well as the acid. In contrast, the side reaction to the ether **47** might even be desirable, as the original aim of this project is to generate polyethers with amine end groups. To remove the water from TsOH and possibly even force the ether formation to **47** by removing water formed by the condensation to the ether, several drying agents were added to the reaction mixtures. To start with, activated silica beads were added as drying agent (entry 19 and 23). Moreover, Na_2SO_4 powder was added to the reaction mixture (entry 20 and 24). Additionally, Na_2SO_4 powder was added 1 h before the addition of CPL to precondense the diol to an oligoether (entry 21 and 25). Finally, TsOH was pre-dried in melt for 1 h with activated molecular sieves at 130 °C before the reaction was started (entry 22 and 26). In all cases, the conversion was worse or similar to experiments without drying agents, thus indicating their ineffectiveness in removing the water in a heavily acidic environment. Most probably $NaHSO_4$ is formed, which is less active as an acid and catalyst. Moreover, the addition of drying agents led to less effective stirring, which might further explain the lower conversions. In entry 28, methane sulfonic acid (MsOH) was utilized instead of TsOH. MsOH gave a higher conversion than TsOH (compare entry 7: C = 55%, S (1) = 99%; entry 29: C = 70%, S (1) = 75), though additionally the methane sulfone ester was formed. Interestingly, a 1:1 mixture of MsOH and TsOH gave similar results compared to TsOH (compare entry 12 and entry 17 with entry 29 and 30) with only 2.2 eq CPL. However, using 4 eq CPL and the mixture of acids gave far better results than with TsOH only (compare entry 27: C = 77%, S (1) = 100%; entry 32: C = 87%, S (1) = 100%).

Moreover, MsOH has several advantages:

- Since it is a liquid, it can be handled more easily, not only in industrial applications.[311][311]
- The molar mass of MsOH (96.1 g mol^{-1}) is far lower compared to TsOH (172.2 g mol^{-1}) as it has a lower carbon content (TOC), resulting in less waste, considering its use in excess in this reaction.
- MsOH is less corrosive than TsOH and, compared to H_2SO_4, has no oxidizing properties.[311][311]
- MsOH is biodegradable and toxicologically unproblematic[316]
- MsOH can be produced industrially from sulfur trioxide and methane at low temperatures of 30 – 60 °C.[317]

By adding 0.5 eq MsOH to the reaction after 24 h (compare entry 32 and 33), the conversion could be increased from 87% to 98%. Increasing the content of MsOH from the beginning gave a similar result (3 eq : 1.5 eq of MsOH : TsOH, total amount of acid 2.25 eq per OH-group) and a conversion of 99% and a selectivity S (1) of 100% could be achieved after 24 h.

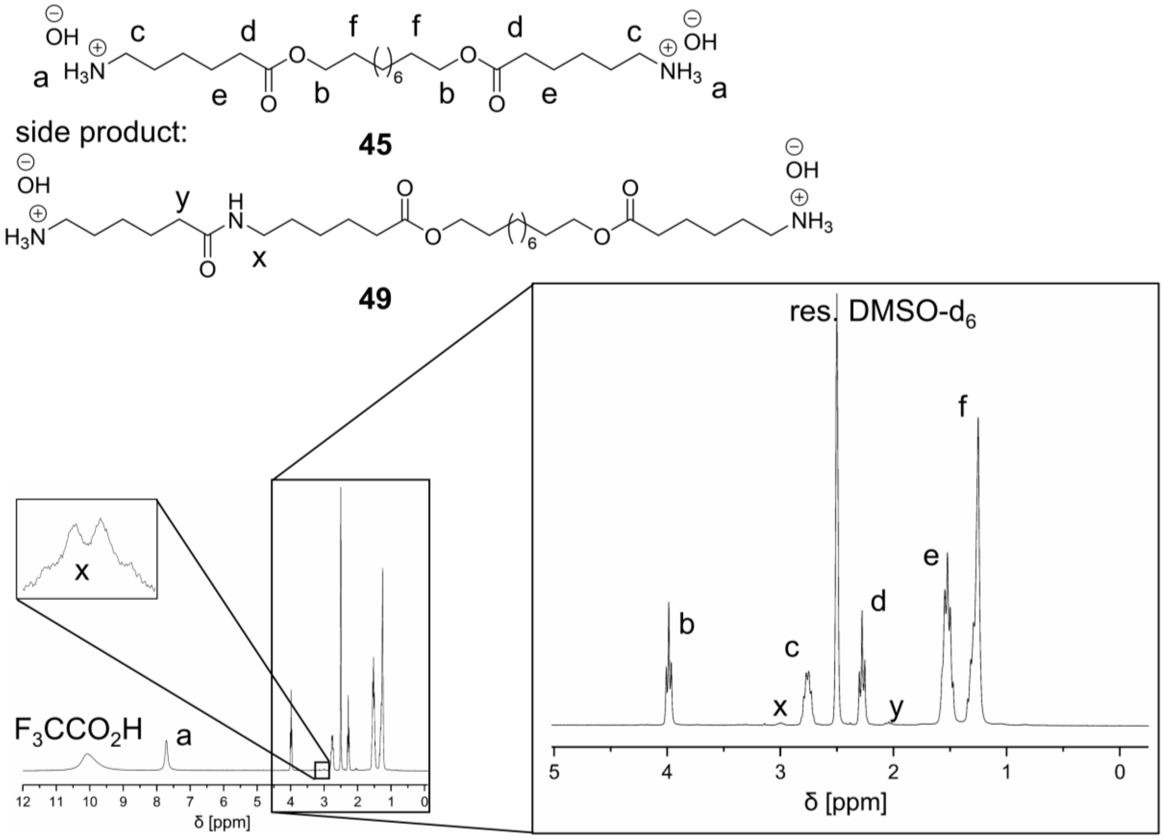


*Figure 32: ^{1}H-NMR of diamine **45** after aqueous workup.*

After the optimization of the reaction conditions, the reaction could be scaled up from 0.75 g 1,10-decanediol to 12 g without any loss of reactivity (compare entry 35 and 36). The further workup was a simple washing of the solid reaction mixture with 1 M aqueous sodium carbonate solution (3×) and water (2×), since, conveniently the acid, CPL and side product **48** are soluble in water. As the diamine product presumably forms the ammonium hydroxide salt in aqueous solution, trifluoroacetic acid was added to the ^{1}H-NMR sample to solubilize the compound. The ammonium protons could be assigned to a broad singlet at 7.71 ppm (confirmed by COSY). The integrals of the triplets characteristic for the ester at 3.99 ppm and 2.28 ppm (4.00, 4.06) fit exactly to the integrals of the sextet at 2.76 ppm (4.05) belonging to the CH_2-group next to the amine, thus confirming the amine formation. Roughly 6% of the side product **49** were identified by the characteristic signals at 3.05 – 2.94 ppm and 2.05 – 2.00 ppm. However, the side product is also a diamine and therefore does not influence the application for NIPUs. The yield of the reaction was 106% of the theoretical yield after drying. Considering the additional molecular weight of the caprolactam included in side product **D5**, the yield was still 105% of the possible theoretical yield.

Since no additional signals were detected in the ^{1}H-NMR spectrum, an organic impurity can be excluded. A reasonable assumption is, that the product contains water chemically bound as ammonium salt, which cannot be removed under reduced pressure. Mass spectrometry (ESI) confirms product formation (401.33603 ($M+H^+$), and formation of the side product **49** (514.42005 ($M+H^+$)). However, no further oligomers were detected. To confirm the reactivity of the amine with carbonates, ethylene carbonate was heated in excess with product **45** and the result was compared with the product of ethylene carbonate and hexamethylenediamine. The ^{1}H-NMR spectrum of the obtained product **50**, matched for the relevant signals ***a***, ***b***, ***d***, ***e*** and ***f*** the spectrum of model compound **51** (Figure 33, COSY and HSQC confirm the signal assignment). This confirmed the reactivity of **45** towards carbonates in the desired fashion. Further confirmation of the amine functionality could be obtained by TLC straining with ninhydrin solution, which indicates amines by a red coloring. Ammonium salt **45** was only sparsely soluble in methanol (~1 mg mL^{-1}) and not soluble in other organic solvents without the addition of acid. Another test reaction was performed in MeOD (0.3 mol L^{-1}) by adding 1.1 eq. isobutyraldehyde to 50 mg substrate. After 10 min of stirring at room temperature the substrate dissolved and ^{1}H-NMR-spectroscopy confirmed the formation of the imine **52** (see Figure 34).

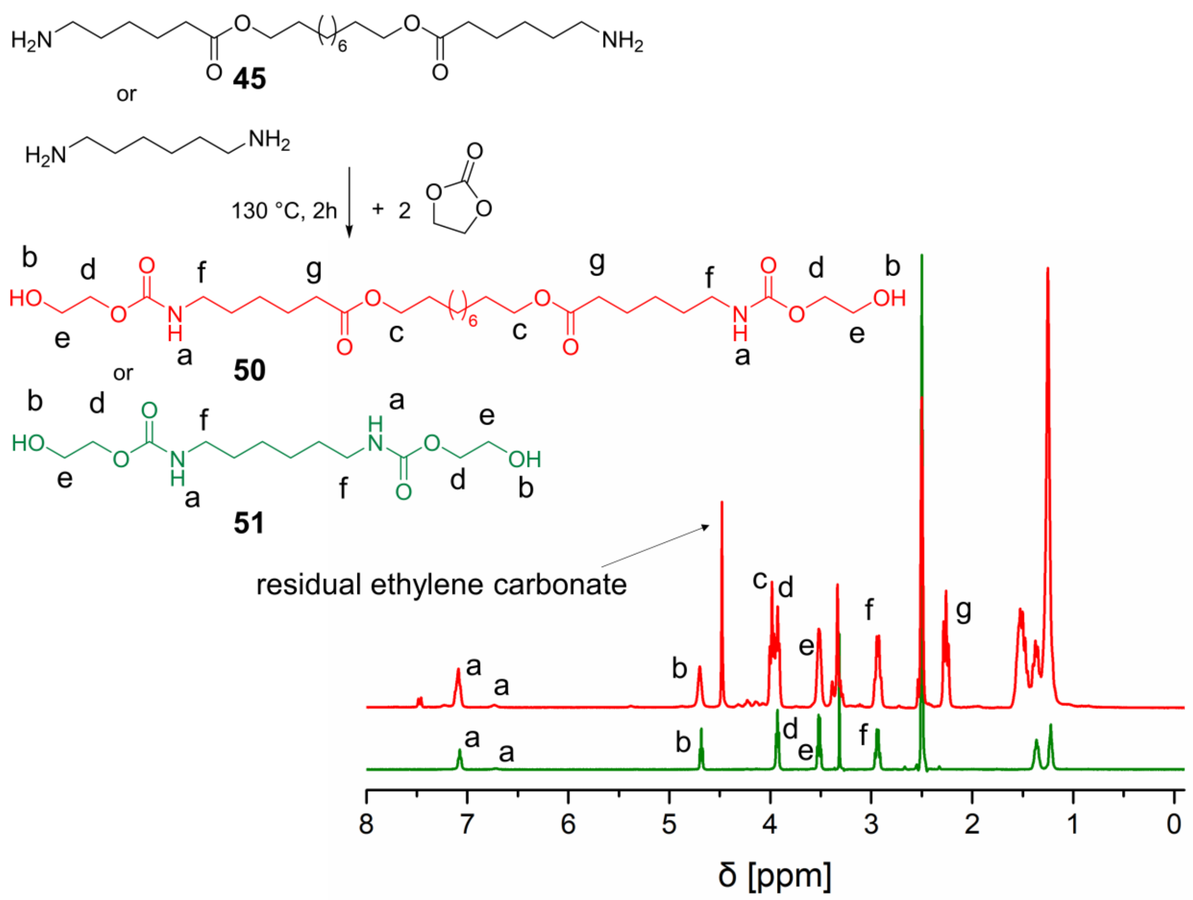


Figure 33: Test of the reactivity of the amine in the ring-opening reaction of ethylene carbonate.

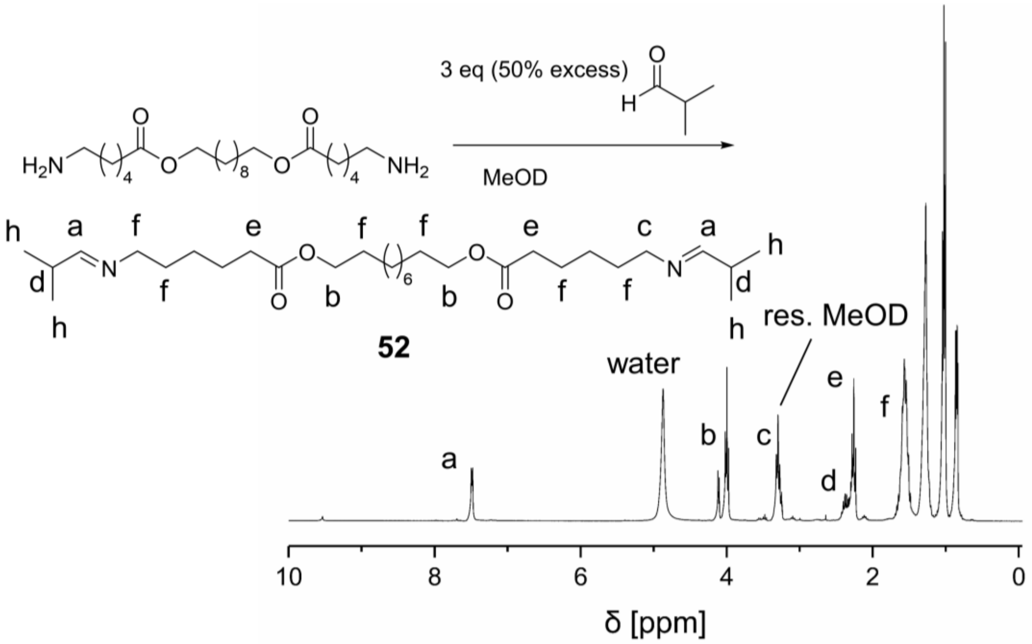
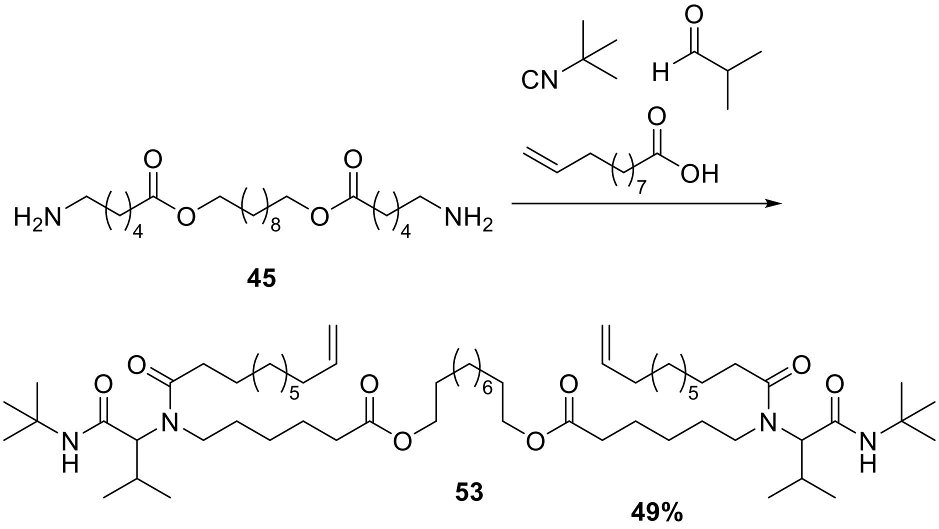


Figure 34: ^{1}H-NMR spectrum of the crude reaction mixture of isobutyraldehyde with diamine D5 in MeOD.

Additionally, it could be shown that diamine **45** can react in an Ugi-Reaction (Scheme 73) achieving a yield of 49% after column chromatography. The structure of the product was confirmed by ^{1}H-NMR-spectroscopy. In Figure 35, additionally the coupling of the characteristic signals with the respective ^{13}C-NMR signals is assigned. Interestingly, for signal ***e*** no ^{13}C-NMR coupling could be observed. However, the integrals of all signals fit well to the respective number of protons and the chemical shift characteristic for methylene groups in *α*-position to peptoid groups also fits to the shift of signal ***e***. Overall, by the synthesis of diene **53**, the amine reactivity of **45** could be further demonstrated. Additionally, **53** might also be used as a monomer itself, as it contains two terminal double bonds, which enable *e.g.* thiol-ene or ADMET polymerizations.



*Scheme 73: Ugi-reaction of diamine **45** with isobutyraldehyde, tert-butylisocyanide and 10-undecenoic acid.*

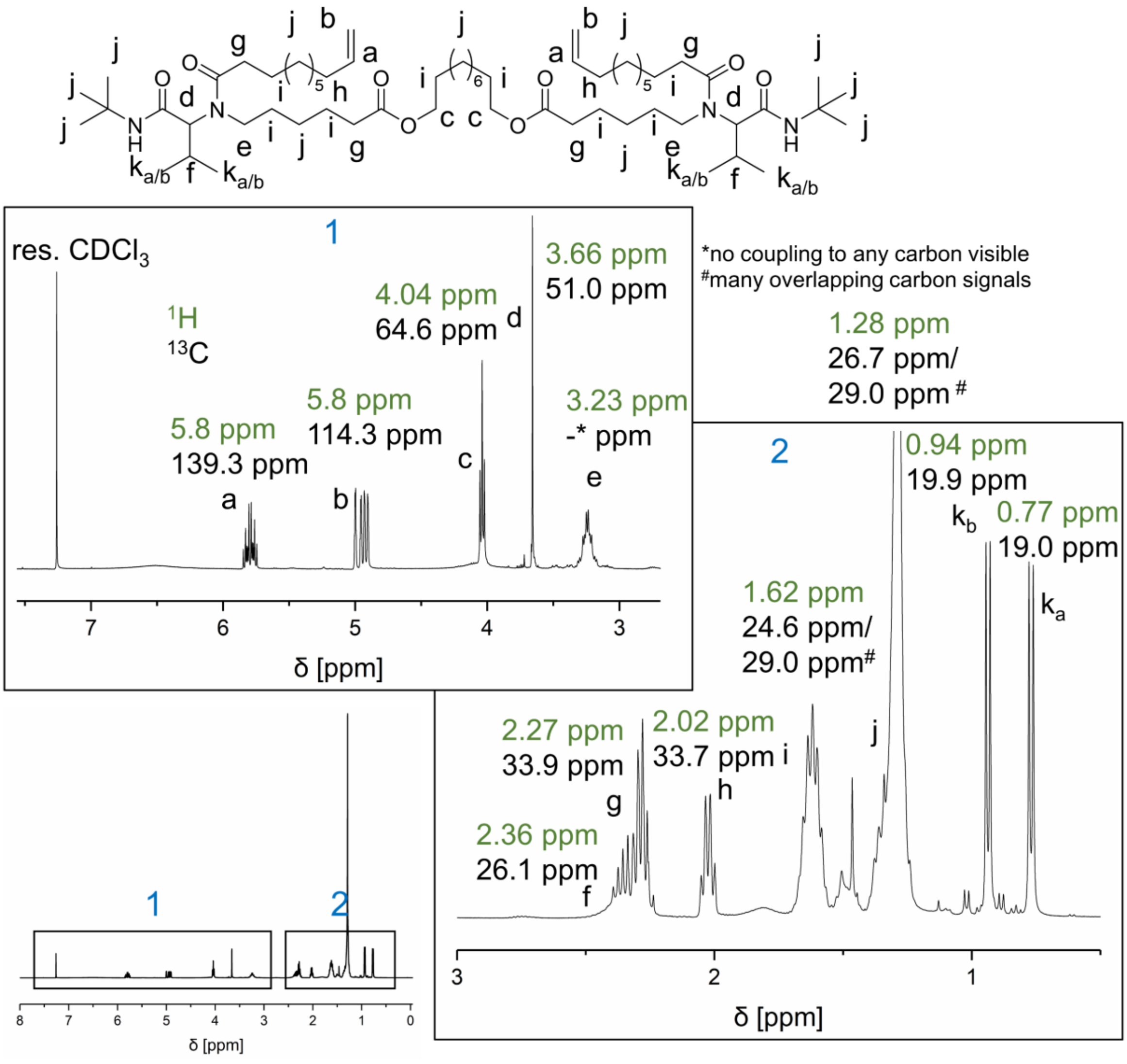


*Figure 35: ^{1}H NMR spectrum of Ugi product **53**. ^{1}H NMR signals (green) are shown with the respective ^{13}C NMR signals for the respective carbon coupling in HSQC.*

After verifying the reactivity of the model diamine **45**, the functionalization was further transferred to the previously synthesized polyether **P2c.3**. Applying the same conditions as for **45** (Table 12), entry 36), polyether diamine **54** was obtained in a yield of 95%. Although GPC (Figure 36, right) analysis suggests some degradation because of a decrease in molecular weight from M_n=3,350 g mol^{-1} to M_n=2,100 g mol^{-1}, in ^{1}H-NMR-spectroscopy (Figure 36, left) no relevant degradation and full conversion was observed, as the ratio of the integral of ***a*** and the integral of ***b*** to ether signal ***c*** are roughly the same. Although at 3.62 ppm seemingly a residual signal of ***b*** is left, this peak probably constitutes a satellite peak of the ether signal, as in a similar distance from the ether peak (3.38 ppm) another signal can be observed in the high field at 3.16 ppm, which is also present in the **P2c.3**.

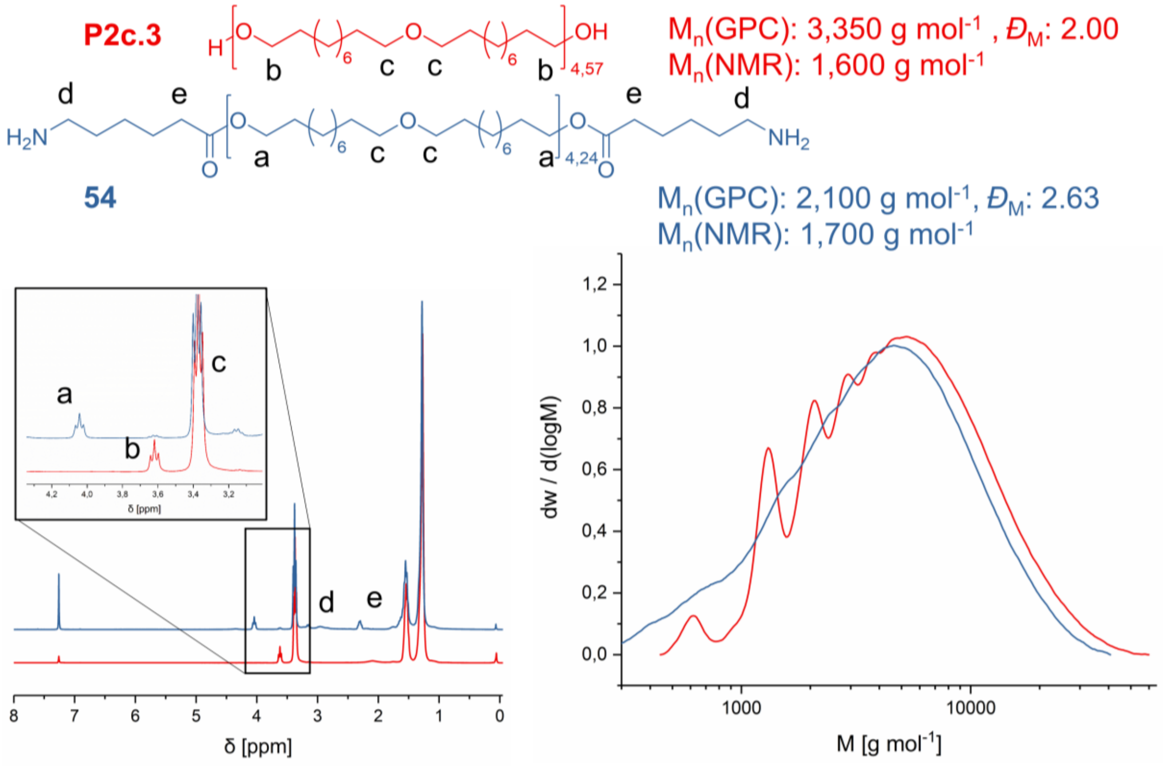


*Figure 36: ^{1}H NMR spectra (left) and GPC traces (right) of **P2c.3** before modification (red) and **54** after modification (blue) to a diamine.*

In addition to modifying polyether **P2c.3**, the modification of polyester **P1c.3** was attempted as well. Again, the same conditions as for **45** (Table 12, entry 36) were applied, reaching a yield of 66%. Similar to the reaction before, GPC (Figure 37, right) analysis suggests some degradation from M_n=3,300 g mol^{-1} to M_n=1,750 g mol^{-1}, however this time ^{1}H-NMR spectroscopy is difficult to interpret. The most reliable signal ***a*** for the estimation of the yield at 4.04 ppm overlaps with signals of the polyester backbone. Full conversion cannot be confirmed as signal ***b*** is overlapping with an unidentified broad singlet at 3.56 ppm. The integral of the multiplet ***c*** in *α*-position to the newly formed amine at 2.68 – 2.92 ppm is only half as much (1.92) as it would be for full conversion (4.00) assuming no degradation. Overall, the conversion of the polyester as well as a possible degradation or preservation of the molecular weight could not be confirmed for this synthesis.

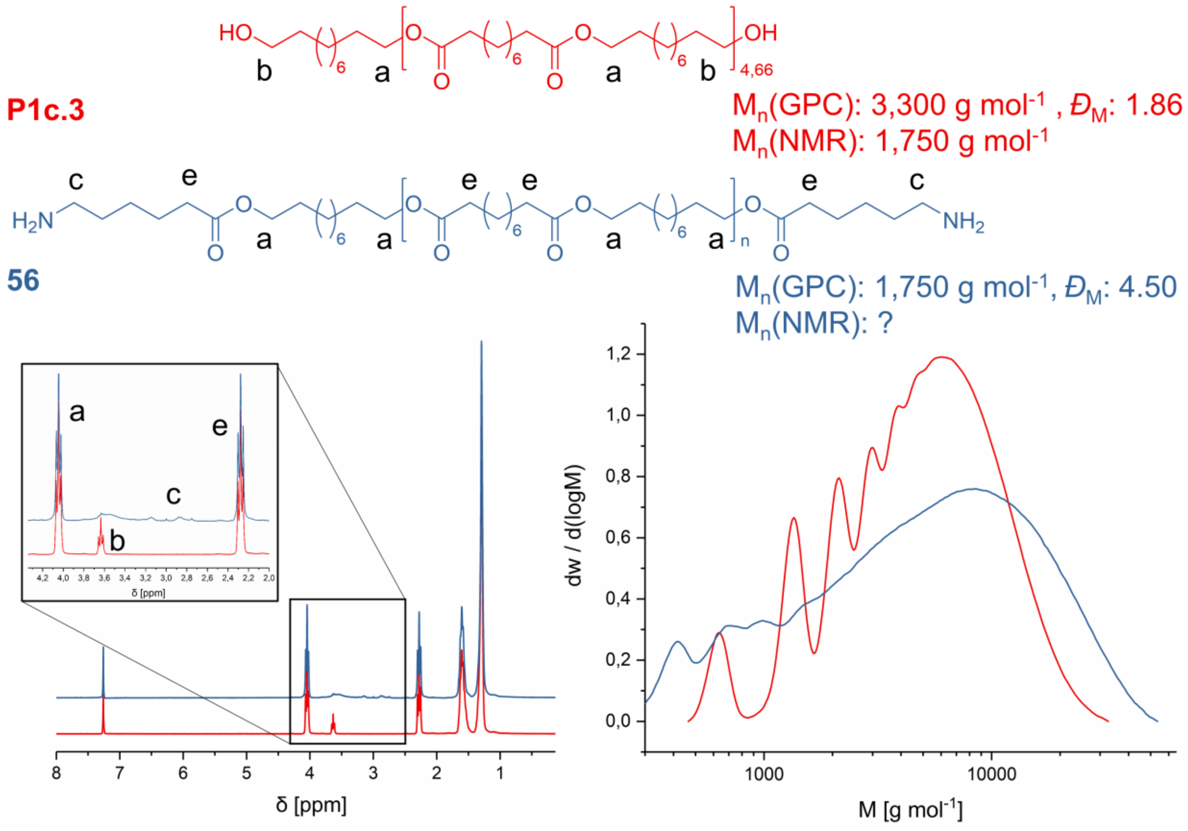
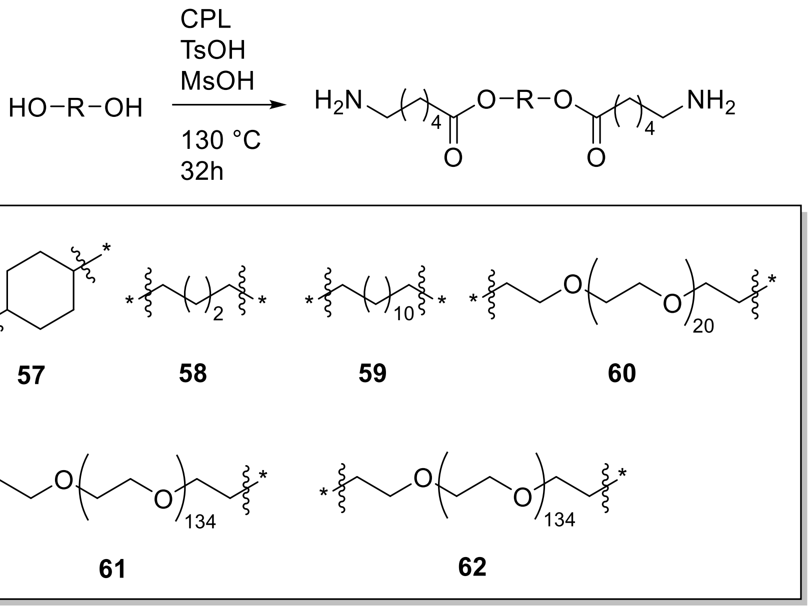


*Figure 37: ^{1}H NMR spectra (left) and GPC traces (right) of **P1c.3** before modification (red) and **DP1c.3** after modification (blue) to a diamine.*

To increase the substrate scope of the reaction other diols were tested for this modification. Applying 1,12-dodecanediol for the synthesis of diamine **59** similar to the reaction of **45**, full conversion could be obtained. After workup, 98% yield was obtained, in this case containing 22% of the oligoamide side product. In the synthesis of the diamine **57** from 1,4-cyclohexanediol with the same conditions, again full conversion of the hydroxy groups could be observed. However, as expected for secondary alcohols, up to 12.5 % of the hydroxyl groups were consumed in an elimination generating a double bond (as observed by ^{1}H-NMR-spectroscopy and verified by HSQC and COSY spectra) and the product was not isolated. In addition, for 1,4-butanediol to diamine **59** full conversion could be observed after 30 h reaction time. However, as the product in this case is water-soluble and the workup is not possible with a simple washing procedure, the product was not isolated.



Scheme 74: Reaction of diols to diamines by ring opening of CPL: Increase in substrate scope.

The modification of PEG would be of high interest as well, since it is one of the most commonly used diols to produce segmented polyurethanes. For this purpose, PEG-1000, PEG-6000 and PEG-10000 were exposed to the optimized reaction conditions to obtain diamines **60**, **61** and **62**. It was more challenging to monitor the conversion for this reaction, since the quartet of the -CH_2-OH end group at 3.4 ppm (recorded in dry DMSO-d_6) is rather small and overlaps partly with the main peak **c** of PEG in the ^{1}H-NMR spectrum at 3.60 ppm. Nevertheless, full conversion was observed as the signal at 3.4 ppm could not be detected anymore and the typical signal ***a*** for the ester group at 4.15 – 4.23 ppm was discernible (Figure 38). Moreover, signal ***b*** with a similar integral could be observed at 3.66 – 3.71 ppm, which could be assigned to the methylene group in β-position of the ester. At 2.32 ppm, a triplet was assigned to the methylene group ***e*** in α-position to the carbonyl functionality of the ester. The typical signal for the methylene group ***d*** in *α*-position to the amine could be discerned at 2.71 ppm. If the integral of the main peak ***c*** is set to 81.8 for comparison (which is the same value as before modification), a lower value of only 2.75 instead of 4.00 is obtained as integral for signal ***a***, which indicates incomplete conversion. Due to the water solubility of PEG the workup of the reaction had to be modified and included liquid phase extraction using dichloromethane and 1M Na$_2$CO$_3$ solution. Even though the high content of Na$_2$CO$_3$ prevented most of the PEG from being separated, lower molecular weight chains might still have been lost. On the other hand, the final yield for **60** was 99%, which does not confirm this theory. For PEG-Diamines **61** and **62**, similar conversions could be observed, although the integration was difficult due to the little amount of end groups and results are less reliable. Interestingly, the yield after extraction of CPL, TsOH and MsOH for the higher molecular weight PEGs was lower (87% for **61**, 79% for **62**).

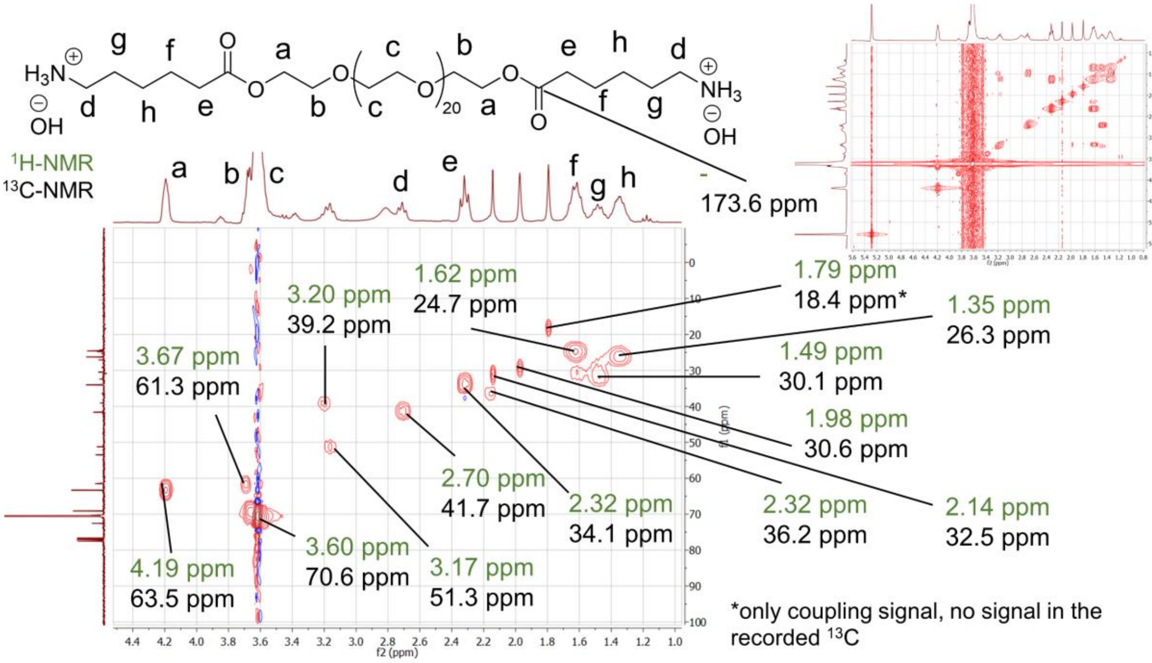
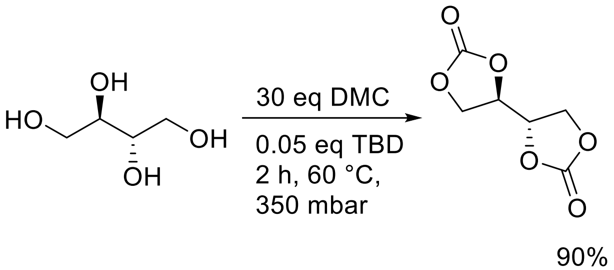


*Figure 38: HSQC NMR spectrum of PEG diamine **60** recorded in $CDCl_3$. The chemical shift for the cross peaks (taken from the 1D-spectra after confirmation of the coupling) is given in green (¹H-NMR) and black (¹³C-NMR). The COSY spectrum is shown in the top right corner.*

4.3.3 A more sustainable synthesis of erythritol bis(carbonate)

In literature, many different methods for the synthesis of bis-cyclic carbonates (bCCs) are known (see section 2.6.3). One method of preparation involves 5-membered carbonate formation by transesterification using 1,2-diols and carbonates such as dimethyl carbonate (DMC) or diphenyl carbonate (DPC) and Lewis acid or base catalysis. Having two of the 1,2-diol functionalities in one molecule can lead to bCCs. The conversion of erythritol - a renewable polyol typically used as sugar substitute - to erythritol bis(carbonate) (EBC) was observed as a side reaction (10% yield) in the reaction of dimethyl carbonate with erythritol using K_2CO_3 as base. Main product of the reaction was the cyclic ether formed by the intramolecular elimination of CO_2 and methanol after the addition of the carbonate.[285][285] R. Mülhaupt *et al.* found conditions to prevent this ether formation by employing diphenyl carbonate (DPC) in DMSO with $Zn(OAc)_2$ as catalyst and 19 h reaction time.[286] However, DPC is far less sustainable than DMC.



63

EBC

Scheme 75: Novel procedure for the synthesis of erythritol bis(carbonate) ***EBC****.*

Aside from the classic unsustainable phosgenation of alcohols, both can be produced by oxidative carbonylation from the respective alcohol and carbon monoxide.[318] However, while phenol is typically produced in the cumene process from fossil benzene and propene,[319] methanol can be obtained via various different routes from renewables (*e.g.* from bio-derived synthesis gas or methane).[320] Moreover, the process of the oxidative carbonylation of methanol is more efficient and involves cheaper catalysts (copper instead of palladium) and auxiliaries than the one of phenol. Industrially, the oxidative carbonylation of phenol is barely realized, while for methanol this route is long since established.[318] R. Mülhaupt *et al.* claimed that erythritol bis(carbonate) cannot be synthesized efficiently by using DMC. Still, during this thesis conditions were found for its efficient, selective and high yielding synthesis directly with DMC without additional solvent. Erythritol **63** was barely soluble in DMC, however at

60 °C, still a small amount went into solution. By utilizing the organocatalyst TBD, **63** is successfully transesterified without observing any side reactions *via* GC-MS. The orientation of the hydroxy groups combined with an overall shift in equilibrium prevented the formation of other carbonates. By removing the methanol under reduced pressure, the final product **EBC** precipitated from the reaction mixture with >90% yield. The methanol could already be removed during the reaction by applying reduced pressure shifting the overall equilibrium and shortening the reaction time. After completion, the product was simply filtered off and the mother liquor, which still contained DMC, the catalyst or dissolved trace amounts of product could be reused in another reaction. The recovery of the reaction mixture was performed four times and a new batch of reactant **63** added to the recovered mixture each time. In contrast to the reaction run for 2 h achieving >90% yield a shorter reaction time of 1 h was chosen. The yields of the respective recovery experiments are presented in Table 13. As the reaction time was shorter, the yield of the first reaction for the recovery cycles was far lower than for the previously optimized reaction. However, with the next batch of freshly added erythritol the yield increased and reached more than 100% due to residual reactant **63** in the recovered reaction mixture. Even after storage of the reaction mixture overnight (reaction 4) the catalyst was still active and showed no signs of degradation. Interestingly, by letting the reaction continue without filtration of the precipitated product for 6h, the catalyst appears to be degrading as the mixture turns yellow and finally dark red.

In total, an average yield per cycle of 87% was achieved compared to 90% of the single reaction with 2 h reaction time, however by continuing with further cycles the total yield might increase further. Additionally, the reaction time for each cycle could be optimized further preventing degradation of the catalyst while still obtaining a higher yield.

Table 13: Experiments regarding the recovery of the reaction mixture

Reaction cycle	**Yield [%]**	**m [g]**
1[a]	57	1.64
2	66	1.90
3	105	3.00
4[b]	105	2.99
5	100	2.84

Theoretical yield: 2.85 g; each time the same amount of erythritol was added to the recovered mother liquor and DMC was refilled to the original volume; [a] original reaction with fresh chemicals; [b] the mother liquor was stored overnight at -15 °C.

Typically, after simple filtration, the product was already highly pure. Still, in case of remaining reactant or catalyst, the impurities might simply be removed by washing the product with water. In the ^{1}H-NMR spectrum (Figure 39), three distinct peaks can be observed as the methylene group of signal **b** undergoes diastereotopic signal splitting due to hindered rotation, which can be confirmed by HSQC as signals b_1 and b_2 both couple with the same carbon at 64.7 ppm. The shifts of the ^{1}H-NMR spectrum were in accordance with literature data, even though a false peak assignment was found in literature and no 2D or ^{13}C NMR spectra were recorded.[286]

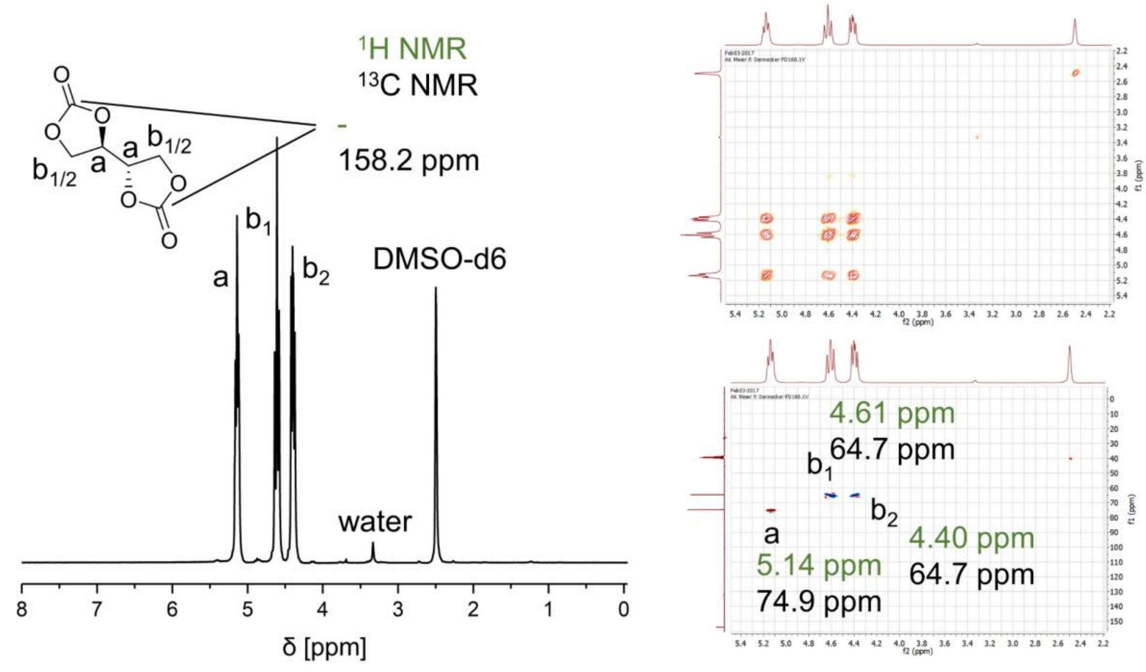


Figure 39: ^{1}H-NMR, HSQC and COSY of erythritol bis(carbonate). Chemical shifts of the ^{1}H NMR are depicted in green, correlated shifts of the ^{13}C-NMR in black.

The simplicity of the synthesis and workup coupled with its sustainability clearly highlight the advantages compared to the literature procedure.

Table 14: Comparison of literature procedure and new procedure for the synthesis of erythritol bis(carbonate).

	Literature	**New procedure**
Solvent	DMSO	DMC
Carbonyl source	DPC	DMC
Reaction temperature	120 °C	60 °C
Reaction time	19 h	2 h
Pressure	30 mbar	350 mbar
Workup	recrystallization in acetone	direct filtration of the pure product
Catalyst	$Zn(OAc)_2*2H_2O$	TBD
Recycling	not possible	reaction mixture directly reusable without any purification.
Yield	80 – 90%	90%

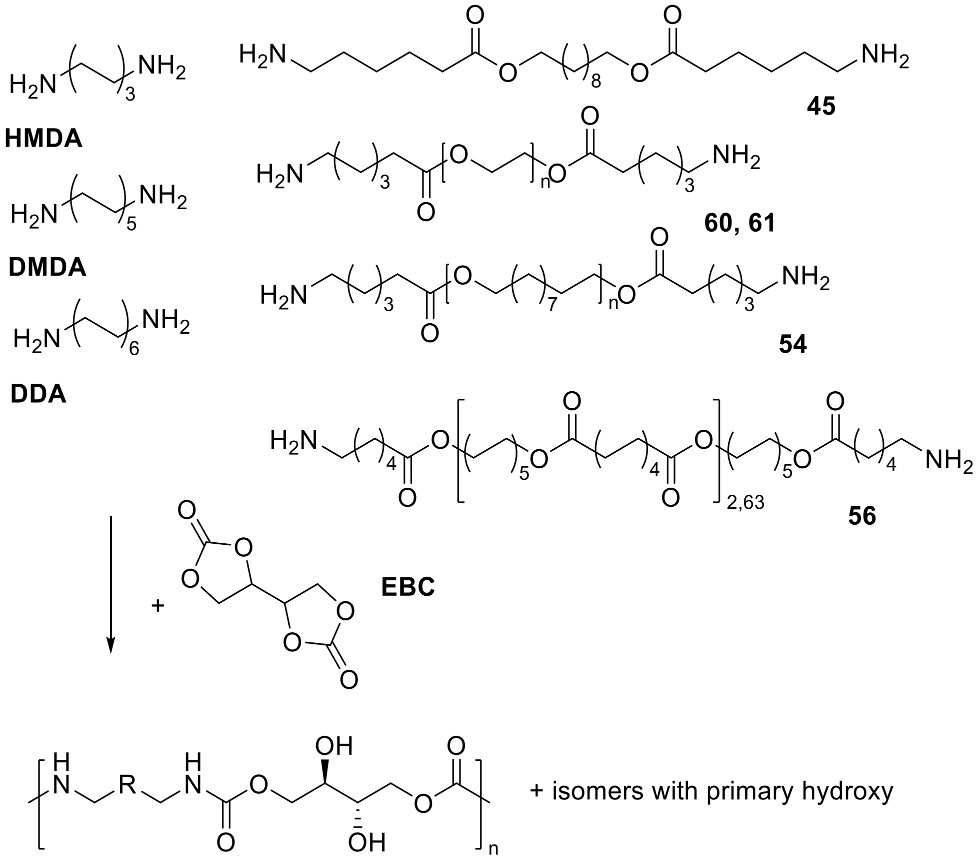
DMSO, the solvent for the literature procedure, achieves a total rating of “some issues” on in GSK’s solvent sustainability guide, while DMC is among the few solvents with “few issues”.[321] DPC is, as previously mentioned, a less sustainable carbonyl source compared to DMC. The reaction temperature for the new procedure is far lower (60°C compared to 120 °C) and in fact ideal for industrial processes. In industry, control of the reaction temperature is required and possibly expensive cooling is necessary if the reaction conditions require room temperature. As a consequence, a moderate amount of heating is, in fact, ideal. A shorter reaction time (2 h instead of 19 h) brings obvious advantages as well as a moderate (350 mbar) instead of a high (30 mbar) vacuum. In fact, the reaction worked just as selective without any vacuum, however the product did not precipitate if a considerable amount methanol was present. The catalyst TBD is more expensive than $Zn(Ac)_2*2H_2O$ (0.16 € g^{-1}, *product number 383058-500G* compared to 6.80 € g^{-1}, *product number 345571-5G*; Sigma Aldrich; checked 06.05.2018), but as it can be recovered and reused the overall price might not be much higher. The workup consists of a simple filtration compared to a recrystallization, which requires solvent, as well. This directly results in additional waste, as it cannot be reused or recycled.

4.3.4 Polymerization to NIPUs

Industrially, polymerizations to segmented polyurethanes are typically performed by melt processing of diisocyanates and short-chain diols, such as butanediol together with flexible long-chain diols such as polyester or polyether diols.[286] To efficiently substitute this process with bis-cyclic carbonates and diamines the polymerization to NIPUs should preferably be performed without solvent. R. Mülhaupt *et al.* concluded that melt-phase EBC polyaddition with diamines is competitive with conventional reactive processing of polyurethane thermoplastics using isocyanates. During processing, they used additives such as DABCO catalyst, phosphite processing stabilizer (Irgafos168), phenolic antioxidant (Irganox1010), and the corresponding stabilizer blend (50 wt % Irganox1010/50 wt % Irgaphos168). Utilizing various diamines in different ratios (1,6-hexamethylenediamine (HMDA), 1,12-dodecamethylenediamine (DDA), 2,2-dimethyl-4-methylhexamethylenediamine (TMHMDA), isophoronediamine (IPDA) and dimer fatty acid-based diamidoamine DFS-1,6-AA, obtained by end-capping dimer fatty acid with HMDA) they obtained molecular weights of M_n=2,200 g mol^{-1} – 12,400 g mol^{-1} with dispersities between 2.14 and 4.20. Additionally, by polymerization in DMSO of only EBC and HMDA, 1,8-octamethylenediamine (OCDA), and DDA they obtained more defined, linear polyurethanes with molecular weights between M_n=9,700 g mol^{-1} and 10,000 g mol^{-1} and dispersities between 2.4 and 3.1. The molecular weight was measured in DMAc after acetylation of the polyurethanes.

To test the reactivity of the EBC synthesized in this work, first the already known polymerization of EBC and DDA was performed without solvent at 100 – 150 °C (slow heating within the first hour) overnight. However, GPC analysis (in HFIP) revealed low molecular weights (M_n < 4,000 g mol^{-1}). An explanation for the low molecular weight might be insufficient mixing of the two components as both solids are only melting during polymerization and give a very viscous mixture difficult to stir as additionally, the melting point of the polyurethane is 141 °C according to literature.[286] A higher reaction temperature is not feasible, as above 140 °C several side reactions accompanied by evolution of carbon dioxide compete with the urethane formation.[286] Therefore, the polymerization of EBC simply in melt without additives and simultaneous extrusion is not possible and the polymerization has to be conducted in solution or an extruder. As an alternative, the polymerization was conducted in DMSO

(1 mol L^{-1}). First, again the commercial diamines HMDA, DMDA (1,10-decamethylenediamine) and DDA were tested for reactivity and compared to literature data (Table 15).



Scheme 76: Polymerization of different commercial and synthesized diamines. R stems from the respective diamine unit.

The obtained results for the polymerizations were significantly lower in molecular weight compared to literature, even though the same conditions were applied (Table 15). Major difference to literature was the method of GPC-analysis: In literature, polyurethanes were acetylated afterwards and measured in DMAc, which might influence the measured molecular weight. In this work, the polyurethanes were directly measured in HFIP.

Table 15: Comparison of literature results of the polymerization of EBC and different commercial diamines with the obtained results applying the same conditions.

Diamine	**M_n [g mol^{-1}] (lit.)[a]**	**$Đ_M$ (lit.)**	**M_n [g mol^{-1}][b]**	**$Đ_M$**
HMDA	9,700	2.4	7,850	1.33
DMDA	-	-	6,350	1.83
DDA	10,000	3.1	5,800	1.63

[a] GPC of acetylated polyurethanes measured in DMAc, [b] GPC of polyurethanes measured in HFIP.

To improve the molecular weight, the polymerization of HMDA and EBC was alternatively conducted in toluene at 120 °C in a pressure tube using Schreiner's Thiourea catalyst (Figure 40).

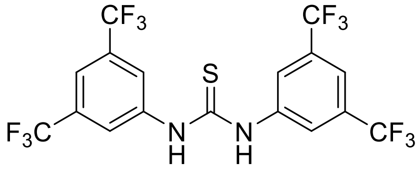


Figure 40: Schreiner's Thiourea catalyst.

The substrate did not dissolve in toluene before and also during polymerization, nevertheless an average molecular weight of M_n=6,750 g mol^{-1}, $Đ_M$=3.35 could be obtained. Diamine **45** was also polymerized in DMSO achieving a lower molecular weight than the commercial diamines (M_n=4,050, $Đ_M$=1.68, Table 16, entry A). Performing the reaction without solvent resulted in an insoluble material, which could not be analyzed (Table 16, entry B). Performing the reaction with additionally 5 mol% TBD as catalyst resulted in a marginal improvement of the molecular weight (M_n=4,400 g mol^{-1}, $Đ_M$=1.78, Table 16, entry C).

Table 16: Different conditions for the polymerization of diamine ***D1*** *and EBC.*

Entry	T [°C]	t [h]	Solvent[a]	Cat.[b]	M_n [g mol^{-1}][c]	$Đ_M$	Y [%]
A	100 °C	15	DMSO	-	4,050	1.68	53
B	150	15	-	-	-[d]	-	quant.
C	RT	15	DMSO	TBD	1,750	1.28	68
D	100 °C	15	DMSO	TBD	4,400	1.78	51
E	RT	15	DMF	TBD	1,900	1.20	59
F	100 °C	15	DMF	TBD	3,200	1.83	76
G	100 °C	15	DMF	-	3,400	1.75	81
H	100 °C	15	DMF/DMSO	TBD	3,550	1.68	98
I	100 °C	15	DMF/DMSO	-	3,600	1.78	58
J	RT	15	DMF/DMSO	TBD	1,850	1.12	64
K	100 °C	15	DMF/toluene	TBD	3,700	1.88	65
L	100 °C	15	DMF/toluene	-	4,950	1.91	92
M	RT	15	DMF/toluene	TBD	1,850	1.22	76

[a] concentration 1 mol L^{-1}, ratio of mixed solvents 1:1; [b] catalyst concentration 5 mol%; [c] measured by GPC analysis in DMF after precipitation in water; [d] insoluble in common organic solvents.

The use of different solvents and their mixtures (DMF, toluene, DMSO) did not result in significantly higher molecular weights, (Table 16, entry D – M). Reactions at room temperature instead of 100 °C only yielded an average molecular weight of $M_n < 2{,}000$ g mol^{-1}, Table 16 entry C, E, J, M). The polymerizations of modified oligoethers **54** and **56** resulted in an insoluble residue and could not be analyzed. Reactions of modified PEGs **60** (M_n=2,400 g mol^{-1}, $Đ_M$=1.46 before polymerization, M_n=3,000 g mol^{-1}, $Đ_M$=1.57 after polymerization) and **61** (M_n=8,400 g mol^{-1}, $Đ_M$=1.57 before polymerization, M_n=7,400 g mol^{-1}, $Đ_M$=1.73 after polymerization) with EBC did not result in any increase in molecular weight.

5 Conclusion and Outlook

Two different approaches to utilize the catalytic reduction of esters to ethers applying $GaBr_3$ as catalyst and TMDS as reducing agent were pursued to produce polyethers. Moreover, the application of the obtained polyethers for non-isocyanate polyurethane (NIPU) synthesis was investigated.

In the first approach, it was demonstrated that polyesters can be reduced to polyethers and thereby a novel polyether synthesis method was introduced. The polyesters were obtained from (potentially) renewable resources. For this purpose, either diols and dimethyl esters were polymerized by polycondensation or cyclic esters were polymerized by ring-opening polymerization. Non-commercial monomers were synthesized by different means, such as metathesis, hydrogenation, alkylation, hydrosilylation, reduction and Baeyer–Villiger oxidation. The reduction of the polyesters was optimized and ester groups were quantitatively reduced, as confirmed by NMR and IR spectroscopy as well as mass spectrometry, while degradation of the polymer chain was minimal for polyethers with four or more methylene groups between functional groups. Thus, various novel polyethers as well as poly(tetramethylene oxide) and poly(propylene oxide) oligomers were obtained. End group modification could prove that a moderate amount of hydroxy end groups does not have a significant influence on the reduction. Mechanistic studies revealed that the reduction occurs at random positions in the polymer chain. For ring-opening polymerizations of cyclic esters, $GaBr_3$ could be introduced as new catalyst, which offers a high degree of control due to long reaction times and limited transesterifications leading to backbiting. The catalyst remained active after polymerization and was able to catalyze the reduction to the polyether after addition of the reducing agent, thus providing a one-pot, two-step procedure for the synthesis of uncommon polyethers. Finally, a comparison of the thermal properties of the different polyesters and polyethers revealed interesting structure-property relationships.

In the second approach, the catalytic reduction was applied to fatty acid derived *ω,ω'*-unsaturated diene esters to synthesize in total six different *ω,ω'*-unsaturated diene ethers, which served as monomers in thiol-ene and ADMET polymerizations. To obtain the *ω,ω'*-unsaturated diene ethers, the ethenolysis of methyl oleate and transesterification reactions were optimized. For thiol-ene polymerizations, methyl-THF was introduced as sustainable solvent. For ADMET polymerization, the eco-friendly polarclean was used as solvent confirming the results from H. Cramail *et al.*, who introduced this solvent for ADMET polymerization of other monomers. The thiol-ene and ADMET polymerizations were optimized and number average molecular weights up to M_n = 31,800 g mol^{-1} were obtained. Thiol-ene polymers were oxidized to poly(ether sulfones) and ADMET polymers were hydrogenated to obtain saturated polyethers ultimately improving the material properties. The melting points of 24 polymers were compared, revealing an increase after modification which was related to the density of modified functional groups. To confirm the chemical structure, IR-spectroscopy was performed on all polymers and ^{1}H-NMR spectroscopy was performed on all chloroform-soluble polymers.

Finally, hydroxy- terminated oligoethers obtained by the first approach were modified to synthesize diamines for NIPU synthesis. For this purpose, a novel method of converting hydroxy- groups to ester-amines with *ε*-caprolactam was introduced and the reaction was optimized on the example of 1,10-decanediol, ultimately obtaining over 99% conversion and more than 99% selectivity towards diamines. The workup procedure consisted of a simple washing procedure obtaining quantitative yields, thus providing overall a selective, facile and novel methodology. The reactivity of the obtained amine was investigated by several model reactions, *i.e.* imine formation, a Ugi-reaction and ring-opening of ethylene carbonate. The diamine synthesis was expanded to several monomeric and oligomeric diols, thus proving its versatility. For the synthesis of the bio-derived, sustainable comonomer, erythritol bis(carbonate), the sustainability and simplicity of the synthesis procedure was significantly improved compared to literature. A more sustainable solvent (DMC instead of DMSO) was chosen, running the reaction at lower temperatures (60 °C instead of 120 °C) and higher pressures (350 mbar instead of 30 mbar), thus achieving full conversion in shorter reaction times (2 h instead of 19 h) followed by a facile and direct filtration of the precipitated product, that allows for the reaction mixture to be reused. In this fashion, 90% yield of the pure product was achieved (compared to a similar yield of 80 – 90% in literature) and the reaction was easily scaled up to a 30 g scale synthesis. Afterwards, the obtained diamine as well as commercial diamines and erythritol bis(carbonate) were polymerized achieving moderate average molecular weights of M_n = 5,000 g mol^{-1} – 10,000 g mol^{-1}.

It would be of high interest to expand the herein presented novel procedures and methods to other monomers, polymers and substrates. Moreover, the sustainability of the reduction of polyesters could potentially be improved, *e.g.* in terms of solvent selection and workup. Additionally, the molecular weight of the herein obtained polyurethanes can be further improved by additional optimization of the polymerization procedure.

6 Experimental Part

6.1 Materials & Methods

6.1.1 Materials

The following chemicals were used as received: Poly[(*R*)-3-hydroxybutanoate] (Sigma Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, Sigma Aldrich), decane-1,10-diol (98%, Aldrich), dimethyl sebacate (99%, Sigma Aldrich), titanium(IV) isopropoxide (97%, Aldrich), hexane-1,6-diol (99%, Sigma Aldrich), succinic acid (≥99%, Sigma Aldrich), dimethyl adipate (≥99%, Sigma Aldrich), trimethyl orthoformate (99%, Sigma Aldrich), (1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)ruthenium (Hoveyda-Grubbs catalyst of the 2nd generation, Sigma Aldrich), 1,4-benzoquinone (>99%, Sigma Aldrich), ethyl vinyl ether (99%, Sigma Aldrich), palladium on activated charcoal (10% Pd, Sigma Aldrich), lithium aluminium hydride solution (1M in THF, Sigma Aldrich), silica gel 60 (0.035 – 0.070, Sigma-Aldrich), chloroform-*d* ($CDCl_3$, 99.8 atom-% D, Euriso-Top), dimethyl sulfoxide-d_6 (99.8 atom-% D, Euriso-Top). $GaBr_3$ (99.999%, Sigma Aldrich) and 1,1,3,3-tetramethyldisiloxane (97%, Sigma Aldrich), ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) (Chemtura Holdings GmbH, Bergkamen, Germany), 2-bromopropane (dried over molecular sieve, Aldrich), *m*-chloroperoxybenzoic acid (≤77%, Sigma Aldrich), *(3S)-cis*-3,6-dimethyl-1,4-dioxane-2,5-dione (L-Lactide, 98%, Sigma Aldrich), *ε*-caprolactone (97%, Sigma Aldrich), 4-(pyren-1-yl)butan-1-ol (99%, Sigma Aldrich), oleic acid (90%, Sigma Aldrich), 1,3-propanediol (98%, Sigma Aldrich), thioacetic acid (96%, Sigma Aldrich), hydrogen peroxide (30% (w/w) in H_2O, Sigma Aldrich), Shvo's Catalyst (98%, Sigma Aldrich), methanesulfonic acid (≥99.0%, Sigma Aldrich), *p*-toluenesulfonic acid monohydrate (≥98.5%, Sigma Aldrich), 1,12-dodecanediol (99%, Sigma Aldrich), *meso*-erythritol (>99.0%, TCI), hexamethylenediamine (98% Sigma Aldrich), 1,10-diaminodecane (97%, Sigma Aldrich), 1,12-diaminododecane (98%, Sigma Aldrich) polyethylene glycol (average M_n 1,000; 6,000; 10,000, Sigma Aldrich). All solvents were used without any kind of purification unless otherwise noted. Water was deionized by passing through columns packed with ion exchange resins.

6.1.2 Characterization methods

Analytical GC was performed on a Carlo Erba GC series 4160 with a FID detector and fused silica capillary column DB1, 29 m, 0.25 mm.

GC-MS (electron impact (EI)) measurements were performed on the following system: a Varian 431 GC instrument with a capillary column FactorFour VF-5 ms (30 m × 0.25 mm × 0.25 mm) and a Varian 210 ion trap mass detector. Scans were performed from 40 to 650 *m*/*z* at rate of 1.0 scans s^{-1}. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 15 °C min^{-1} to 220 °C, hold for 4 min, ramp at 15 °C min^{-1} to 300 °C, hold for 2 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in the split – split mode (split ratio 50:1) using helium as carrier gas (flow rate 1.0 mL min^{-1}).

NMR spectra (300 MHz for ^{1}H- and at 75 MHz for ^{13}C-measurements) were recorded on a Bruker AVANCE DPX spectrometer operating at 300 K. NMR spectra (500 MHz for ^{1}H- and at 75 MHz for ^{13}C-measurements) were recorded on a Bruker DRX 500 spectrometer operating at 300 K. For all NMR-spectra the residual non-deuterated solvent (^{1}H NMR) or $CDCl_3$ (^{13}C NMR) signal was used as internal standard.

Polymers were characterized on two different SEC systems. Polymers soluble in THF were characterized on a SEC System LC-20A (Shimadzu) equipped with a SIL-20A autosampler and RID-10A refractive index detector (flow rate 1.0 mL min^{-1}) at 50 °C. The analysis was performed on the following column system: main-column PSS SDV analytical (5.0 µm, 300 mm × 8.0 mm, 10000 Å) with a PSS SDV analytical precolumn (5.0 µm, 50 mm × 8.0 mm). For the calibration, narrow linear poly(methyl methacrylate) standards (Polymer Standards Service PPS, Germany) ranging from 1100 to 981000 Da were used. Polymers soluble in 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) containing 0.1 wt.% potassium trifluoroacetate were characterized on a Tosoh EcoSEC HLC-8320 SEC. The solvent flow was 0.40 mL min^{-1} at 30 °C. The analysis was performed on a three column system: PSS PFG Micro precolumn (3.0 × 0.46 cm, 10,000 Å), PSS PFG Micro (25.0 × 0.46 cm, 1000 Å) and PSS PFG Micro (25.0 × 0.46 cm, 100 Å). The system was calibrated with linear poly(methyl methacrylate) standards (Polymer Standard Service, M_p 102 – 981000 Da).

The thermal properties of the prepared polymers were studied by differential scanning calorimetry (DSC) with a Mettler Toledo DSC stare system operating under nitrogen atmosphere using about 5 mg of the respective polymer for the analysis. The glass transition (T_g) and melting point (T_m) were recorded on the second heating scan by using the following method: cooling to - 85 °C, heating from - 85 °C to 120 °C at 10 °C min^{-1}, cooling from 120 °C to - 85 °C at 10 °C min^{-1} and heating from - 85 °C to 120 °C at 10 °C min^{-1}. The melting temperature is recorded as the minimum (endothermic transitions are represented downwards) of the endothermic melting peak.

Infrared spectra (IR) were recorded on a Bruker Alpha-p instrument in a frequency range from 3998 to 374 cm^{-1} applying KBr and ATR technology.

Electron Ionization (EI) and Fast atom bombardment (FAB) mass spectra were recorded on a *Finnigan MAT 95* instrument. The protonated molecular ion is expressed by the term: $[M+H]^+$

ESI-MS spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe to record high resolution electrospray ionization – MS (ESI-MS). Calibration was carried out in the m/z range of 74 – 1.822 using premixed calibration solutions (Thermo Fisher Scientific). A constant spray voltage of 4.7 kV and a dimensionless sheath gas of 5 were employed. The S-lens RF level was set to 62.0, while the capillary temperature was set to 250 °C. All samples were dissolved at a concentration range of 0.05 – 0.01 mg mL^{-1} in a mixture of THF and MeOH (3:2) doped with 100 µmol sodium trifluoroacetate and injected with a flow of 5 µL min^{-1}.

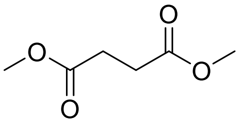
All thin layer chromatography experiments were performed on silica gel coated aluminium foil (silica gel 60 F254, Aldrich). Compounds were visualized by irradiation with a UV-lamp or by staining with Seebach-solution (mixture of phosphomolybdic acid hydrate, cerium(IV)sulphate, sulfuric acid and water). The hydrogenations were either performed in a high-pressure laboratory reactor BR-100 or BR-300 from the company Berghof with a maximum operating pressure of 200 bar.

Size exclusion chromatography-electrospray ionization mass spectrometry (SEC-ESI MS) spectra were recorded on a LTQ Orbitrap XL Q Exactive mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the *m/z* range 74 - 1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 4.6 kV, a dimensionless sheath gas of 8, and a dimensionless auxiliary gas flow rate of 2 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0, respectively. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a thermostated column department (TCC 3000SD). Separation was performed on two mixed bed size exclusion chromatography columns (Polymer Laboratories, Mesopore 250 × 4.6 mm, particle diameter 3 µm) with precolumn (Mesopore 50 × 4.6 mm) operating at 30 °C. THF at a flow rate of 0.30 mL min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to (an UV-Detector (VWD 3400 RS), and) a RI detector (RefractoMax520, ERC, Japan) in a setup described earlier.[322] 0.27 mL min^{-1} of the eluent were directed through the RI-detector and 30 µL min^{-1} infused into the electrospray source after postcolumn addition of a 100 µM solution of sodium iodide in methanol at 20 µL min^{-1} by a micro- flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 50 µL aliquot of a polymer solution with a concentration of 2 mg mL^{-1} was injected onto the HPLC system.

6.2 Procedures for Polymer Approach - Renewable polyethers via $GaBr_3$ catalyzed reduction of polyesters

6.2.1 Monomers

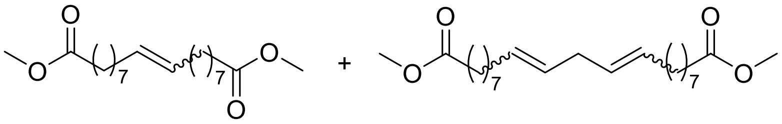
Dimethyl succinate (20)



To a stirred solution of succinic acid (30.4 g, 254 mmol) in methanol (144 ml, 114 g, 3.56 mol), trimethoxymethane (18.5 ml, 13.5 g, 127 mmol) and sulfuric acid (5.78 ml, 7.97 g, 81.0 mmol) were added. The mixture was stirred at 70 °C for 10 h. Afterwards, the mixture was extracted three times with Et_2O. The combined organic layers were washed three times with water, dried over sodium sulfate and concentrated *in vacuo*. After purification by distillation (90 °C, 28 mbar), the product was obtained as colourless liquid (26.1 g, 179 mmol, 70%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.71 (s, 6 H, -CO-OC*H*$_3$), 2.65 (s, 4 H, -C*H*$_2$-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 172.7 (-*C*O-OCH$_3$), 51.8 (-CO-O*C*H$_3$), 28.9 (-*C*H$_2$-COO-); HRMS (EI) of $C_6H_{10}O_4$ $[M]^+$ *m/z* calc. 146.0574, found 146.0573; IR (ATR): *v* = 2954.7, 1730.4, 1472.9, 1436.7, 1360.0, 1322.5, 1199.5, 1155.5, 1027.9, 997.8, 956.6, 845.0, 804.3, 646.0, 564.8, 398.2 cm^{-1}.

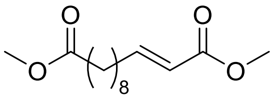
Dimethyl octadec-9-enedioate (C_{18}) (6) / dimethyl henicosa-9,12-dienedioate (C_{21}) (7)



The synthesis was carried out adapted to a literature procedure.[3] Methyl linolenate (16.7 mL, 15.0 g, 51.3 mmol) was added to a 100 mL round bottom flask equipped with a distillation bridge, vacuum pump and a magnetic stirrer. The methyl linolenate was stirred at 100 °C and 1 mbar for 10 min. Then, *p*-benzoquinone (17.0 mg, 0.154 mmol) was added and stirred for another 10 min at the same conditions before adding Grubbs Catalyst 2nd Generation (48 mg, 0.0560 mmol, 1.1 µmol). Additional catalyst (22.0 mg, 0.026 mmol) and *p*-benzoquinone (5.50 mg, 0.0510 mmol) were added after 14 h and the reaction was run overnight. The desired product was isolated by column chromatography (*n*-hexane : EtOAc 19:1) together with the dimethyl henicosa-9,12-dienedioate side product in a ratio of 63:37 as yellow viscous oil (5.22 g, 60%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 5.49 – 5.30 (m, 2 H (C_{18})/ 4 H (C_{21}), -C*H*=C*H*-), 3.66 (s, 6 H, -CO-OC$\mathit{H_3}$), 2.70 – 2.61 (m, 2 H, (C_{21}), =CH-C$\mathit{H_2}$-CH=), 2.30 (t, *J* = 7.5 Hz, 4 H, C$\mathit{H_2}$-COO-), 1.85 – 2.13 (m, 4 H, -C$\mathit{H_2}$-CH=), 1.71 – 1.48 (m, 4 H, -C$\mathit{H_2}$-CH_2-COO-), 1.43 – 1.14 (m, 16 H, -CH_2-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 174.4 (-*C*O-OCH_3), 133.5 – 128.5 (-*C*H=*C*H-; C_{18}/C_{21} *E/Z*-isomers), 51.5 (-CO-O*C*H_3), 35.7 (=CH-*C*H_2-CH=, C_{21} *E/Z*-isomers), 34.2 (-*C*H_2-COO-), 32.6 (-*C*H_2-CH=), 29.6 – 29.0 (-*C*H_2-), 25.0 (-*C*H_2-CH_2-COO-); HRMS (FAB) of $C_{20}H_{37}O_4$ $[M+H]^+$ *m/z* calc. 341.2686, found 341.2684; IR (ATR): *v* = 2923.0, 2852.2, 1736.8, 1434.3, 1359.5, 1243.4, 1194.4, 1168.0, 967.0, 879.8, 724.0 cm^{-1}.

Dimethyl (E)-dodec-2-enedioate (2)



In a 250 mL round-bottom flask methyl undec-10-enoate (15.0 g, 75.6 mmol), methyl acrylate (68.5 ml, 65.1 g, 756 mmol), and *p*-benzoquinone (0.049 g, 0,454 mmol) were mixed and degassed for 15 min. Hoveyda–Grubbs catalyst 2nd Gen. (95.0 mg, 0.151 mmol) was added. The mixture was stirred for 1 h at 50 °C under constant Ar-flow. The reaction was quenched with ethyl vinyl ether (2.00 ml, 1.51 g, 20.9 mmol). The excess methyl acrylate was removed under reduced pressure. The product was purified by column chromatography (cyclohexane/EtOAc 10:1) and obtained as a white waxy solid (14.7 g, 76%).

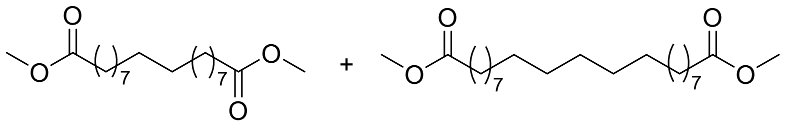
^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 6.94 (dt, *J* = 15.6 Hz, 1.3 Hz, 1 H, -C*H*=CH-CO_2-), 5.79 (dd, *J* = 15.6 Hz, 1.3 Hz, 1 H, =C*H*-CO_2-CH_3), 3.70 (s, 3 H, =CH-CO_2-C$\mathit{H_3}$), 3.64 (s, 3 H, -CO_2-C$\mathit{H_3}$), 2.21 – 2.35 (m, 2 H, -C$\mathit{H_2}$-CO_2-), 2.09 – 2.21 (m, 2 H, -C$\mathit{H_2}$-CH=), 1.50 – 1.69 (m, 2 H, -C$\mathit{H_2}$-CH_2-CO_2-), 1.34 – 1.49 (m, 2 H, -C$\mathit{H_2}$-CH_2-CH=), 1.17 – 1.33 (m, 8 H, -C$\mathit{H_2}$-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 174.4 (-*C*O_2-CH_3), 167.3 (=CH-*C*O_2-CH_3), 149.8 (-*C*H=CH-CO_2-), 120.9 (=*C*H-CO_2-CH_3), 51.5 (-CO_2-CH_3), 34.2 (-*C*H_2-CO_2-), 32.3 (-*C*H_2-CH=), 29.2 (-CH_2-), 28.1 (-*C*H_2-CH_2-CH=), 25.0 (*C*H_2-CH_2-CO_2); HRMS (EI) of $C_{14}H_{25}O_4$ $[M+H]^+$ *m/z* calc. 257.1747, found 257.1747; IR (ATR):

v = 2928.0, 2855.4, 1722.8, 1656.5, 1435.2, 1312.9, 1268.1, 1194.9, 1170.3, 1135.1, 1110.0, 1038.7, 979.7, 850.9, 719.3, 437.8 cm^{-1}.

6.2.1.1 General procedure for hydrogenation of dimethyl esters

In a Teflon reactor tube inlet, the dimethyl ester, palladium on activated charcoal (10 wt.%) in ethyl acetate were pressurized with hydrogen (40 bar) and stirred at 40 °C until full conversion of the double bond was achieved. Afterwards, the catalyst was filtered off, the solvent withdrawn *in vacuo* and the desired product obtained without further purification.

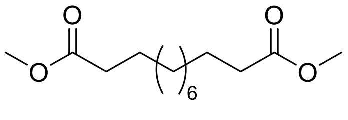
Dimethyl octadecanedioate(C18)/dimethyl henicosanedioate(C21) (8)



The product was obtained as a white powder (4.59 g, 96%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.66 (s, 6 H, -CO-OCH_3), 2.30 (t, *J* = 7.5 Hz, 4 H, -CH_2-COO-), 1.69 – 1.51 (m, 4 H, CH_2-CH_2-COO-), 1.25 (s, 24 H (C_{18})/ 30 H (C_{21}), -CH_2-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 174.45 (-CO-OCH_3), 51.53 (-CO-OCH_3), 34.18 (-CH_2-COO-), 29.8 – 29.3 (-CH_2-), 25.1 (-CH_2-CH_2-COO-); HRMS (FAB) of $C_{20}H_{39}O_4$ $[M]^+$ *m/z* calc. 343.2843, found 343.2841; IR (ATR): *v* = 2914.6, 2846.8, 1736.4, 1472.2, 1461.6, 1435.8, 1378.1, 1237.5, 1210.4, 1167.3, 1109.8, 985.9, 882.6, 729.8, 719.0 cm^{-1}.

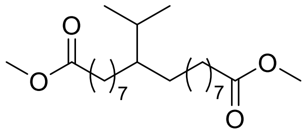
Dimethyl dodecanedioate (3)



The product obtained as a white powder (5.19 g, 99%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.66 (s, 6 H, -CO_2-CH_3), 2.30 (t, *J* = 7.5 Hz, 4 H, -CH_2-CO_2-), 1.70 – 1.52 (m, 4 H, -CH_2-CH_2-CO_2-), 1.38 – 1.21 (m, 12 H, -CH_2-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 174.3 (-CO_2-CH_3), 51.5 (-CO_2-CH_3), 34.2 (-CH_2-CO_2-), 29.4 (-CH_2-), 29.3 (-CH_2-), 25.0 (CH_2-CH_2-CO_2); HRMS (EI) of $C_{14}H_{26}O_4$ $[M]^+$ *m/z* calc. 258.1826, found 258.1824; IR (ATR): *v* = 2916.4, 2848.1, 1737.2, 1472.9, 1463.4, 1435.0, 1411.4, 1381.7, 1370.2, 1333.1 1267.7, 1237.0, 1203.7, 1154.9, 1072.2, 1061.0, 1037.0, 1005.2, 972.1, 898.7, 882.1, 796.6, 734.1, 720.5, 700.7, 587.8, 501.2, 465.9 cm^{-1}.

Dimethyl 9-isopropyloctadecanedioate (12) [i]



The hydroalkylation of dimethyl octadec-9-enedioate followed the general protocol given in [4].

Dimethyl octadec-9-enedioate (3.07 g, 9.00 mmol) was degassed in a Schlenk flask (25 mL), flushed with nitrogen (3 freeze-thaw cycles) and slightly heated in a water bath until it was liquid. The reaction was carried out under nitrogen atmosphere. $Et_3Al_2Cl_3$ (4.1 mL, 4.48 g, 18 mmol) was dropped to the stirred diester allowing the temperature to increase to a maximum of 50°C (cooling with water bath to approximately 20°C). 2-Bromopropane (2.50 mL, 3.27 g, 27.0 mmol) was added dropwise via a syringe with septum under formation of gas. After about 1.5 h 2-bromopropane was completely added and GC analysis showed only a small amount of 3-4 % of remaining substrate. The sample was stirred overnight and then dropped into a mixture of diethyl ether (150 mL) and aqueous HCl solution (50 mL, 10 %). Strong stirring of the sample gave two clear phases. After separation the organic layer was washed neutral with H_2O (3 x) and dried over Na_2SO_4. After filtration the solvent was removed *in vacuo* and the sample applied to "Kugelrohr distillation" (185°C, 2x10^{-3} mbar) yielding 2.7 g (79 %) of pure alkylation product.

^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) = 3.61 (s, 6 H, -OCH_3), 2.26 (t, *J* = 7.8 Hz, 4 H, -CH_2CO-), 1.62 (m, bs, 5 H, -$COCH_2C\mathit{H_2}$-, -$C\mathit{H}CH_3$), 1.37 – 0.90 (m, 23 H, -CH_2-, -$C\mathit{H}CH_2$-), 0.79 (d, *J* = 7.2 Hz, 6 H, $C\mathit{H}_3CH$-); ^{13}C-NMR ($CDCl_3$, 125.75 MHz): δ (ppm) = 174.3 (C=O), 51.4 (-OCH_3), 43.7 (-$\mathit{C}HCH_2$), 34.1 (-$\mathit{C}H_2CO$-), 30.5-29.9, 29.5, 29.2, 27.7, 19.8 ($\mathit{C}H_3CH$-).

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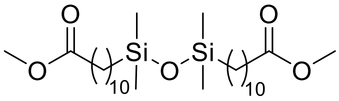
[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

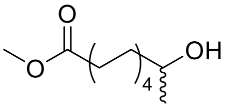
Dimethyl 11,11'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)diundecanoate[i] (14)



The synthesis of the silylated diester followed lit.[5] using a modified method. Methyl 10-undecenoate (4.95 g, 25 mmol) and TMDS (1.34 g, 10.0 mmol) were degassed in a 25 mL Schlenk flask and flushed with nitrogen (3 freeze-thaw cycles). Karstedt's catalyst (10 µL) was added and the mixture was heated at 50°C without using any solvent for 24 h. The sample was cooled to r.t., dissolved in 150 mL of diethyl ether, washed with H_2O and dried over Na_2SO_4. After filtration the solvent was removed *in vacuo* and the sample applied to "Kugelrohrdistillation" (230°C, 1x10^{-3} mbar) yielding 4.5 g (69 %) of the silylated product.

The ^1H and ^{13}C NMR spectra were in agreement with those given in lit.[5]

Methyl 10-hydroxyundecanoate[ii]



Methyl 10-oxoundecanoate (2.00 g, 9.34 mmol), obtained by the Wacker-Oxidation of methyl undec-10-enoate,[6] was dissolved in 20 mL dichloromethane / methanol (9:1 v/v). After addition of sodium borohydride (177 mg, 4.67 mmol), the reaction mixture was stirred over night at room temperature. The crude mixture was washed with sodium hydrogen carbonate solution, brine, and water. The water phase was extracted with dichloromethane (3 x 5 mL) and the combined organic phases were dried over sodium sulphate and evaporated to dryness to afford 10-hydroxyundecanoate **5** as colorless liquid in quantitative yield (> 99%, 2.01 g).

The ^1H and ^{13}C NMR spectra were in agreement with those given in lit.[6]

6.2.1.2 General procedure for the reduction of dimethyl esters to diols

The dimethyl ester (1.00 eq) was dissolved in anhydrous THF. At 0 °C $LiAlH_4$-solution (1.10 eq) was added carefully under vigorous stirring. After complete addition of $LiAlH_4$, the reaction mixture was stirred for additional 2.5 h at reflux temperature. The reaction

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[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).
[ii] Carried out by Dr. Marc von Czapiewski (KIT, group of Prof. M. A. R. Meier)

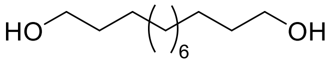
was cooled to room temperature and quenched with saturated NaCl-solution until gas generation stopped. The cloudy mixture was extracted two times with THF. Afterwards the aqueous phase was acidified with aqueous H_2SO_4 solution (10 wt.%) and extracted two times with EtOAc. The combined organic phases were washed with saturated $NaHCO_3$ solution, dried over sodium sulfate, and concentrated *in vacuo*.

Octadecane-1,18-diol(C_{18}) and henicosane-1,21-diol(C_{21}) mixture (9)

The product was isolated without further purification as a white solid (1.02 g, 79%).

^{1}H-NMR (DMSO-d$_6$, 300 MHz): δ (ppm) = 3.64 (t, *J* = 6.6 Hz, 4 H, -CH_2-OH), 1.69 – 1.51 (m, 4 H, CH_2-CH_2-OH), 1.45 – 1.17 (m, 28 H(C_{18})/ 34 H (C_{21}), -CH_2-), ^{13}C-NMR (DMSO-d$_6$, 75 MHz): δ (ppm) = 63.3 (-*C*H_2-OH), 33.0 (-*C*H_2-CH_2-OH), 29.8 (-*C*H_2-), 25.9 (-*C*H_2-CH_2-CH_2-OH); HRMS (FAB) of $C_{18}H_{39}O_2$ $[M+H]^+$ *m/z* calc. 287.2945, found 287.2947; IR (ATR): *v* = 3262.7, 2914.5, 2846.8, 1471.3, 1461.7, 1406.5, 1122.2, 1057.4, 932.8, 879.1, 729.8, 719.1, 681.9, 541.5, 459.5 cm^{-1}.

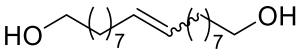
Dodecane-1,12-diol (4)



After purification by recrystallization in MeOH, the product was obtained as white powder (3.68 g, 94%).

^{1}H-NMR (DMSO-d$_6$, 300 MHz): δ (ppm) = 4.32 (t, *J* = 5.1 Hz, 2 H, -OH), 3.66 (dt, *J* = 3.2 Hz, 11.7 Hz, 4 H, -CH_2-OH), 1.46 – 1.33 (m, 4 H, -CH_2-CH_2-OH), 1.16 – 1.32 (m, 16 H, -CH_2-); ^{13}C-NMR (DMSO-d$_6$, 75 MHz): δ (ppm) = 60.7 (-*C*H_2-OH), 32.6 (-*C*H_2-CH_2-OH), 29.1 (-*C*H_2-), 25.5 (-*C*H_2-CH_2-CH_2-OH); HRMS (EI) of $C_{12}H_{27}O_2$ $[M+H]^+$ *m/z* calc. 203.2006, found 203.2006; IR (ATR): *v* = 3403.0, 3340.1, 2919.7, 2889.7, 2848,4, 1480.1, 1460.6, 1364.2, 1348.9, 1308.2, 1057.3, 1039.1, 990.3, 728.4, 710.6, 514.2, 487.9 cm^{-1}.

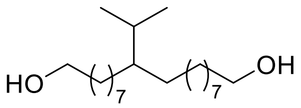
Octadec-9-ene-1,18-diol (11)



The product was purified by column chromatography (ethyl acetate/cyclohexane 1:5) and isolated as a white solid (6.52 g, 68%).

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) = 5.44 – 5.28 (m, 2 H, -C*H*=C*H*-), 3.61 (t, *J* = 6.6 Hz, 4 H, -C*H*$_2$-OH), 2.06 – 1.91 (m, 4 H, -C*H*$_2$-CH=), 1.91 – 1.72 (m, 2 H, -OH), 1.65 – 1.44 (m, 4 H, -C*H*$_2$-CH$_2$-OH), 1.42 – 1.17 (s, 20 H, -C*H*$_2$-); ^{13}C-NMR (CDCl$_3$, 75 MHz): δ (ppm) = 130.5 – 130.0 (-CH=CH-; E/Z-isomers), 63.2 (-*C*H$_2$-OH), 32.9 (-*C*H$_2$-CH=CH-), 32.7 (-*C*H$_2$-CH$_2$-OH), 29.7 – 29.2 (-*C*H$_2$-), 27.3 (-*C*H$_2$-CH$_2$-CH=CH-), 25.9 (-*C*H$_2$-); HRMS (FAB) of C$_{18}$H$_{37}$O$_2$ [M+H]$^+$ *m/z* calc. 285.2788, found 285.2786; IR (ATR): *v* = 3263, 3235, 2917, 2847, 1460, 1131, 1059, 1007, 966, 941, 878, 665 cm^{-1}.

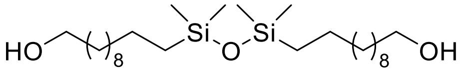
9-Isopropyloctadecane-1,18-diol (13)



After purification by column chromatography (cyclohexane/EtOAc 1:1) the product was obtained as colourless liquid (1.16 g, 95%).

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) = 3.62 (t, *J* = 6.6 Hz, 4 H, -C*H*$_2$-OH), 1.92 – 1.70 (m, 1 H, CH-C*H*), 1.69 – 1.48 (m, 4 H, C*H*$_2$-CH$_2$-OH), 1.45 – 1.14 (m, 26 H, -C*H*$_2$-), 1.13 – 0.99 (m, 1 H, -C*H*-CH-), 0.80 (d, *J* = 6.9 Hz, 6 H, -CH$_3$); ^{13}C-NMR (CDCl$_3$, 75 MHz): δ (ppm) = 63.2 (-*C*H$_2$-OH), 43.8 (CH-*C*H), 32.9 (-*C*H$_2$-CH$_2$-OH), 30.6 (-*C*H$_2$-), 30.3 (-*C*H$_2$-), 29.8 (-*C*H$_2$-), 30.2 (-*C*H$_2$-), 29.6 (-*C*H$_2$-), 29.4 (-*C*H$_2$-), 27.9 (-*C*H-CH), 25.9 (-*C*H$_2$-CH$_2$-CH$_2$-OH), 19.4 (-*C*H$_3$); HRMS (FAB) of C$_{21}$H$_{44}$O$_2$ [M+H]$^+$ *m/z* calc. 328.3336, found 328.3337; IR (ATR): *v* = 3327.2, 2922.5, 2852.8, 1463.5, 1384.0, 1366.6, 1122.2, 1055.4, 721.0 cm^{-1}.

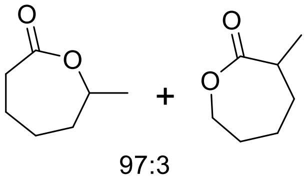
11,11'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(undecan-1-ol) (15)



After purification by column chromatography (gradient cyclohexane/EtOAc 4:1 → 1:2) the product was obtained as colorless liquid (1.06 g, 79%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.64 (t, *J* = 6.6 Hz, 4 H, -CH_2-OH), 1.68 – 1.49 (m, 4 H, -C*H*$_2$-CH_2-OH), 1.37 (bs, 2 H, -OH), 1.36 – 1.19 (m, 32 H, -CH_2-), 0.57 – 0.43 (m, 4 H, -C*H*$_2$-$SiMe_2$-O), 0.02 (s, 12 H, Si(C*H*$_3$)$_2$); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 63.2 (-*C*H$_2$-OH), 33.6 (-*C*H$_2$-), 33.0 (-*C*H$_2$-), 29.8 (-*C*H$_2$-), 29.6 (-*C*H$_2$-), 25.9 (-*C*H$_2$-), 23.4 (-*C*H$_2$-), 18.5 (-*C*H$_2$-$SiMe_2$-O), 0.5 (Si(*C*H$_3$)$_2$); IR (ATR): *v* = 3320.3, 2920.6, 2852.3, 1464.4, 1408.7, 1250.9, 1049.7, 787.5, 703.4, 631.1, 419.6 cm^{-1}.

7-methyloxepan-2-one[i] (25)



14.5 g 2-methylcyclohexanone (130 mmol, 1.00 eq) was dissolved in 600 mL DCM and cooled in an ice bath to 0 °Celsius. 71 g *m*-chloroperoxybenzoic acid (414 mmol, 3.20 eq) was slowly added to the solution before it was stirred at room temperature for 20 hours. The solution was cooled down again to 0 °C before salts remaining in the solution were separated by filtration through CELITE®. DCM was evaporated under reduced pressure and the yellowish residue was dissolved in EtOAc. The solution was washed with 10% $Na_2S_2O_5$ solution (500 mL), saturated Na_2CO_3 solution (2x500 mL) and saturated NaCl solution (2x500 mL). The organic layer was dried over $MgSO_4$ before the solvent was evaporated under reduced pressure. Purification was carried out by column chromatography (silica gel, cyclohexane: ethyl acetate 3:1). Methyl-ε-caprolactone was obtained as a yellow liquid with a yield of 53% (8.8 g, 68.7 mmol).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.53 – 4.33 (m, 1H, C*H*-), 2.63 (m, 2H, -C*H*$_2$-CO-), 2.80 – 2.46 (m, 3H, -C*H*$_2$*(A)*-, diastereotopic splitting), 2.03 – 1.79 (m, 3H, -C*H*$_2$*(B)*-, diastereotopic splitting), 1.34 (d, J = 6.4 Hz, 3H, C*H*$_3$-) ppm; ^{13}C-NMR

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[i] Carried out by Andreas Ganzbuhl in the Bachelor thesis “Catalytic reduction of sustainable A-B-type polyesters to polyethers” (under lab-supervision of Patrick-Kurt Dannecker).

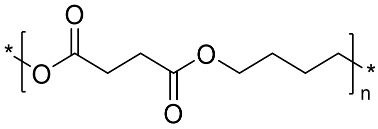
($CDCl_3$, 75 MHz) δ (ppm) = 176.03 (*C*O), 76.4 (-O-*C*H-), 36.6 (-*C*H_2-) , 35.3 (-*C*H_2-), 28.6 (-*C*H_2-), 28.2 (-*C*H_2-), 23.3 (-*C*H_2-), 22.9 (-*C*H_3-); IR (ATR): *v* = 2933.2, 1720.2, 1449.5, 1346.1, 1330.1, 1279.9, 1255.0, 1238.5, 1174.4, 1136.7, 1097.9, 1072.6, 1014.4, 984.3, 937.4, 858.5, 692.9, 560.8, 532.2, 442.3; HRMS (ESI) of $C_7H_{13}O_2$ $[M+H]^+$ *m/z* calc. 129.0910, found 129.0908, IR v = 2976.3 (CH_3-), 2933.7 (CH_2-), 2863.2 (CH-), 1719.0 (-CO-O-C-) cm^{-1}.

6.2.2 Polymers

6.2.2.1 Polyester

All polycondensations were performed in a Radleys Discovery Technologies carousel reaction station TM RR98072 connected to a vacuum pump.

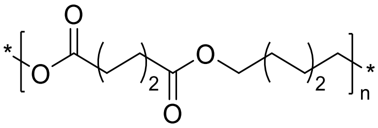
Poly(1,4-butylene succinate) (P1a)



A mixture of dimethyl succinate (4.24 g, 29.0 mmol), butane-1,4-diol (2.62 g, 29.0 mmol) and titanium(IV) isopropoxide (85.0 µl, 83.0 mg, 0.290 mmol) was heated in a carousel reactor tube to 120 °C under constant stirring (500 rpm). Afterwards the pressure was reduced gradually to 360 mbar over a period of 10 min. Under these conditions, the mixture was stirred overnight (100 rpm). The crude polymer was dissolved in hot THF and precipitated in MeOH at r.t. obtaining a white powder (3.93 g, 79%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.23 – 3.98 (m, 4 H, -C*H_2*-OOC-), 3.69 (s, -COO-CH_3, end group), 3.67 (t, *J* = 6.7 Hz, -C*H_2*-OH, end group), 2.75 – 2.50 (m, 4 H, -C*H_2*-COO-), 1.83 – 1.52 (m, 4 H, -C*H_2*-CH_2-OOC-); IR (ATR): *v* = 2944.6, 1711.5, 1471.9, 1446.7, 1425.2, 1386.9, 1328.5, 1311.3, 1207.0, 1153.2, 953.4, 918.5, 805.5, 652.4, 568.6, 395.2 cm^{-1}; T_m = 102.0 °C.

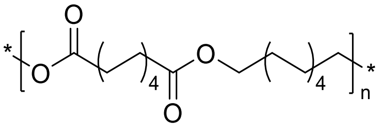
Poly(1,6-hexamethylene adipate) (P1b)



A mixture of dimethyl adipate (3.42 g, 19.6 mmol), hexane-1,6-diol (2.32 g, 19.6 mmol) and titanium(IV) isopropoxide (58.0 µl, 56.0 mg, 0.196 mmol) was heated in a carousel reactor tube to 120 °C under constant stirring (500 rpm). Afterwards the pressure was reduced gradually to 360 mbar over a period of 10 min. Under these conditions, the mixture was stirred overnight (100 rpm). The crude polymer was dissolved in hot THF and precipitated in MeOH at r.t. obtaining a white powder (4.28 g, 86%).

^{1}H-NMR ($\mathrm{CDCl_3}$, 500 MHz): δ (ppm) = 4.05 (t, J = 6.7 Hz, 4 H, -CH_2-OOC), 3.67 (s, -COO-$\mathrm{CH_3}$, end group), 3.64 (t, J = 6.7 Hz, -CH_2-OH, end group), 2.40 – 2.22 (m, 4 H, -CH_2-COO), 1.78 – 1.49 (m, 8 H, -CH_2-$\mathrm{CH_2}$-OOC, -CH_2-$\mathrm{CH_2}$-COO-), 1.47 – 1.27 (m, 4 H, -CH_2-); IR (ATR): v = 2933.8, 2864.8, 1724.6, 1463.5, 1414.9, 1398.1, 1368.4, 1256.0, 1161.4, 1077.3, 1041.3, 968.1, 910.1, 737.3, 583.0, 416.2 cm^{-1}; T_m = 41.9 °C.

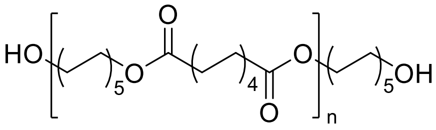
Poly(1,10-decamethylene sebacate) (P1c)



A mixture of dimethyl sebacate (5.00 g, 21.7 mmol), decane-1,10-diol (3.78 g, 21.7 mmol) and TBD (302 mg, 2.17 mmol) was heated in a carousel reactor tube to 150 °C under constant stirring (500 rpm). Afterwards the pressure was reduced gradually to 1 mbar over a period of 10 min. Under these conditions, the mixture was stirred for 2.5 h (100 rpm). The crude polymer was dissolved in hot THF and precipitated in MeOH at r.t. obtaining a white powder (6.43 g, 87%).

^{1}H-NMR ($\mathrm{CDCl_3}$, 500 MHz): δ (ppm) = 4.04 (t, J = 6.7 Hz, 4 H, -CH_2-OOC-), 3.66 (s, -COO-$\mathrm{CH_3}$, end group), 3.64 (t, J = 6.7 Hz, -CH_2-OH, end group), 2.28 (t, J = 7.5 Hz, 4 H, -CH_2-COO-), 1.71 – 1.49 (m, 8 H, -CH_2-$\mathrm{CH_2}$-OOC-, -CH_2-$\mathrm{CH_2}$-COO-), 1.41 – 1.14 (m, 20 H, -CH_2-); IR (ATR): v = 2915.8, 2849.6, 1728.3, 1465.1, 1415.8, 1397.8, 1356.1, 1293.3, 1216.5, 1166.2, 1094.8, 1047.8, 999.9, 958.9, 920.1, 856.9, 749.7, 721.1, 584.4, 438.8 cm^{-1}; T_m= 64.5 °C.

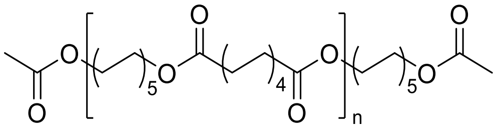
Poly(1,10-decamethylene sebacate) – OH end groups (P1c.1)



Stoichiometry: Dimethyl decanedioate (5.00 g, 21.7 mmol), decane-1,10-diol (4.77 g, 27.4 mmol); Catalyst used: titanium(IV) isopropoxide. The crude polymer was dissolved in hot THF and precipitated in MeOH at r.t. obtaining a white powder (6.02 g, 72%).

^{1}H-NMR (CDCl$_3$, 500 MHz): δ (ppm) = 4.04 (t, *J* = 6.7 Hz, 4 H, -C*H$_2$*-OOC-), 3.63 (t, *J* = 7.5 Hz, 4 H, -C*H$_2$*-OH end group), 2.28 (t, *J* = 7.5 Hz, 4 H, -C*H$_2$*-COO-), 1.72 – 1.49 (m, 8 H, -C*H$_2$*-CH$_2$-OOC-, -C*H$_2$*-CH$_2$-COO-), 1.46 – 1.17 (m, 20 H, -C*H$_2$*-); IR (ATR): *v* = 2916.6, 2850.8, 1729.8, 1470.6, 1417.1, 1400.7, 1378.1, 1357.5, 1293.7, 1244.4, 1217.6, 1168.3, 1094.2, 1049.8, 999.9, 960.6, 919.4, 857.7, 750.8, 719.9, 586.2, 438.1 cm^{-1}.

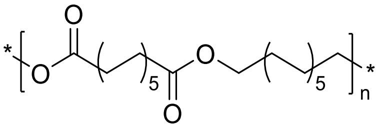
Poly(1,10-decamethylene sebacate) – OAc end groups (P1c.2)



Poly(1,10-decamethylene sebacate) with OH end groups (1.50 g, 0.646 mmol) and pyridine (0.94 ml, 11.6 mmol) were suspended in dichloromethane (12 ml) to give a white suspension. After slow addition of acetyl chloride (0.413 ml, 0.456 g, 5.81 mmol) the mixture was stirred under reflux for 2.5 h. After cooling down the mixture was precipitated in cold MeOH and the product was obtained as white powder (1.43 g, 92%).

^{1}H-NMR (CDCl$_3$, 500 MHz): δ (ppm) = 4.05 (t, *J* = 6.7 Hz, 4 H, -C*H$_2$*-OOC-), 2.28 (t, *J* = 7.5 Hz, 4 H, -C*H$_2$*-COO), 2.04 (s, 6 H, -OOC-CH$_3$ (end group)), 1.70 – 1.51 (m, 8 H, -C*H$_2$*-CH$_2$-OOC, -C*H$_2$*-CH$_2$-COO-), 1.41 – 1.18 (m, 20 H, -C*H$_2$*-); IR (ATR): *v* = 2916.6, 2850.8, 1729.8, 1466.5, 1417.1, 1398.6, 1357.5, 1293.7, 1244.4, 1217.6, 1168.3, 1094.2, 1046.9, 999.6, 958.5, 919.4, 857.7, 750.8, 722.0, 643.8, 608.8, 582.1, 549.2, 440.2 cm^{-1}.

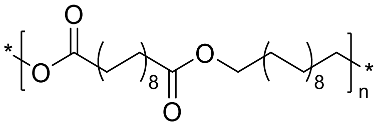
Poly(1,12-dodecamethylene dodecanedioate) (P1d)



A mixture of dimethyl dodecanedioate (1.60 g, 6.20 mmol), decane-1,10-diol (1.25 g, 6.20 mmol) and titanium(IV) isopropoxide (18.1 µl, 17.6 mg, 0.0620 mmol) was heated in a carousel reactor tube to 110 °C under constant stirring (500 rpm). Afterwards the pressure was reduced gradually to 1 mbar over a period of 10 min. Under these conditions, the mixture was stirred overnight (100 rpm). The crude polymer was dissolved in hot THF and precipitated in MeOH at r.t. obtaining a white powder (2.10 g, 85%).

^{1}H-NMR (CDCl$_3$, 500 MHz): δ (ppm) = 4.05 (t, *J* = 6.7 Hz, 4 H, -CH_2-OOC-), 3.66 (s, -COO-CH$_3$, end group), 3.64 (t, *J* = 6.7 Hz, end group), 2.28 (t, *J* = 7.6 Hz, 4 H, -CH_2-COO-), 1.69 – 1.46 (m, 8 H, -CH_2-CH$_2$-OOC-, -CH_2-CH$_2$-COO-), 1.34 – 1.13 (m, 28 H, -CH_2-); IR (ATR): *v* = 2876.8, 2006.2, 1537.7, 1445.6, 1386.5, 1351.5, 1300.9, 1246.5, 1193.0, 1112.6, 1083.1, 1045.1, 1010.2, 975.3, 932.9, 838.5, 782.9, 657.2 cm^{-1}; T_m= 86.6 °C.

Poly(1,18-octadecamethylene octadecanedioate-co-1,21-heneicosamethylene heneicosanedioate) (P1e)

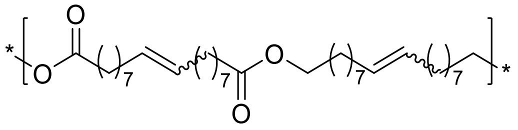


simplified structure

A mixture of dimethyl octadecanedioate (C18 : C21 = 63 : 37, 260 mg, 0.762 mmol), octadecane-1,18-diol (C18 : C21 = 63 : 37, 218 mg, 0.762 mmol) and TBD (10.6 mg, 0.0760 mmol) was heated in a carousel reactor tube to 120 °C under constant stirring (500 rpm). Afterwards the pressure was reduced gradually to 1 mbar over a period of 10 min. Under these conditions, the mixture was stirred for 6.5 h (100 rpm). The crude polymer was dissolved in hot toluene and precipitated in MeOH at r.t. obtaining a white powder (451 mg, 99%), which is insoluble in most common organic solvents at r.t..

IR (ATR): *v* = 2914.0, 2846.5, 1733.8, 1462.8, 1414.2, 1165.5, 1058.6, 955.2, 919.0, 729.3, 719.5 cm^{-1}; T_m = 101.6 °C.

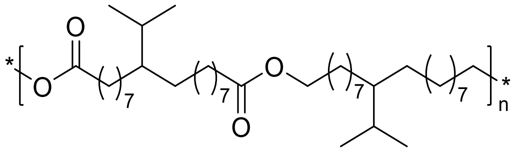
Poly(octadec-9-ene octadec-9-enedioate) (P1f)



A mixture of dimethyl octadec-9-enedioate (770 mg, 2.26 mmol), octadec-9-ene-1,18-diol (643 mg, 2.26 mmol) and TBD (31.0 mg, 0.226 mmol) was heated in a carousel reactor tube to 110 °C under constant stirring (500 rpm). Afterwards the pressure was reduced gradually to 20 mbar over a period of 10 min. Under these conditions, the mixture was stirred for 8 h (100 rpm). The crude polymer was dissolved in hot toluene and precipitated in MeOH at r.t. obtaining a white powder (1.10 g, 84%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) = 5.47 – 5.24 (m, 4 H, -CH=CH-), 4.04 (t, *J* = 6.7 Hz, 4 H, -CH_2-OOC-), 3.66 (s, -COO-CH_3, end group), 3.65 – 3.61 (m, -CH_2-OH, end group) 2.28 (t, *J* = 7.5 Hz, 4 H, -CH_2-COO-), 2.10 – 1.87 (m, 8 H, -CH_2-CH=CH-), 1.76 – 1.49 (m, 8 H, -CH_2-CH_2-OOC, -CH_2-CH_2-COO-), 1.46 – 1.16 (m, 34 H, -CH_2-); IR (ATR): *v* = 2918.1, 2849.9, 1731.3, 1465.3, 1399.0, 1349.2, 1291.9, 1254.8, 1211.5, 1176.5, 1095.7, 1072.7, 961.5, 920.0, 721.8, 583.6, 516.6, 442.2 cm^{-1}; T_m = 64.6 °C.

Poly(9-isopropy l-1,18- octadecamethylene 9-isopropyloctadecane dioate) (P1g)

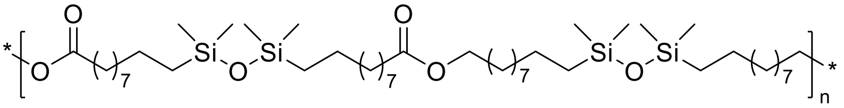


A mixture of dimethyl 9-isopropyloctadecanedioate (585 mg, 1.52 mmol), 9-isopropyloctadecane-1,18-diol (500 mg, 1.52 mmol) and titanium(IV) isopropoxide (4.46 µl, 4.32 mg, 0.0150 mmol) was heated in a carousel reactor tube to 110 °C under constant stirring (500 rpm). Afterwards the pressure was reduced gradually to 3 mbar over a period of 25 min. Under these conditions, the mixture was stirred for 8 h (100 rpm). The crude polymer was dissolved in hot THF and precipitated in MeOH at -10 °C obtaining a colorless sticky polymer (858 mg, 87%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.05 (t, *J* = 6.7 Hz, 4 H, -CH_2-OOC-), 3.66 (s, -COO-CH_3, end group), 3.66 – 3.62 (m, -CH_2-OH, end group), 2.28 (t, *J = 7.4 Hz*, 4 H, -CH_2-COO-), 1.74 – 1.50 (m, 10 H, -CH_2-CH_2-OOC-, -CH_2-CH_2-COO-, CH-C*H*), 1.43 – 0.96 (m, 50 H, -CH_2-, -C*H*-CH-), 0.91 – 0.71 (m, 12 H, -CH-CH_3); IR (ATR): *v* =

2879.6, 1974.6, 1596.4, 1406.1, 1330.3, 1220.9, 1130.6, 1095.2, 803.1 cm^{-1}; T_g= -66.8 °C.

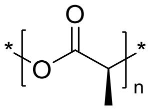
Poly(11,11'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(undecamethylene) 11,1'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(undecanoate)) (P1h)



A mixture of dimethyl 11,11'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(undecanoate) (553 mg, 1.12 mmol), 11,11'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(undecan-1-ol) (500 mg, 1.12 mmol) and titanium(IV) isopropoxide (3.28 µl, 3.18 mg, 0.0110 mmol) was heated in a carousel reactor tube to 120 °C under constant stirring (500 rpm). Afterwards the pressure was reduced gradually to 4 mbar over a period of 10 min. Under these conditions, the mixture was stirred for 8 h (100 rpm). The crude polymer was dissolved in hot THF and precipitated in MeOH at -10 °C obtaining a colorless sticky polymer (906 mg, 91%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.05 (t, J = 6.7 Hz, 4 H, -CH_2-O-), 3.66 (s, -$COOCH_3$, end group), 3.66 – 3.62 (m, -$\mathrm{C}H_2$-OH, end group) 2.29 (t, J = 7.5 Hz, 4 H, -CH_2-COO-), 1.70 – 1.53 (m, 8 H, -$\mathrm{C}H_2$-CH_2-OH), 1.41 – 1.13 (m, 64 H, -CH_2-), 0.58 – 0.43 (m, 8 H, -CH_2-$SiMe_2$-O-), 0.02 (s, 24 H, Si($\mathrm{C}H_3$)$_2$); IR (ATR): v = 2920.9, 2852.8, 1737.5, 1464.3, 1250.5, 1169.8, 1049.0, 837.7, 789.0, 704.1 cm^{-1}; T_m= -5.1 °C.

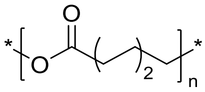
Poly-(L)-lactide (P1i)



(3S,6S)-3,6-dimethyl-1,4-dioxane-2,5-dione (1.25 g, 8.67 mmol) was dissolved in 11.5 mL dry DCM, and 0.6 mL of a standard solution of 4-(pyren-1-yl)butan-1-ol (14.4 mg, 0.0525 mmol) in DCM (0.0875 mol/l) was added to give a colorless solution. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (2.42 mg, 0.0174 mmol) was added in 0.2 mL DCM. After 15 seconds, the reaction was quenched by the addition of benzoic acid (53.0 mg, 0.434 mmol) in 1 mL DCM and precipitated in cold Et_2O to give the product as a white powder (0.700 g, 56%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) = 5.16 (q, *J = 7.1 Hz*, 1 H, -C*H*-CH_3), 1.58 (d, *J = 7.1 Hz*, 3 H, -CH-C*H₃*); IR (ATR): *v* = 2997.4, 2946.0, 1747.8, 1454.5, 1383.5, 1359.1, 1180.3, 1129.0, 1082.0, 920.7, 871.0, 755.0, 692.7, 448.1 cm^{-1}; T_g= 46.3 °C.

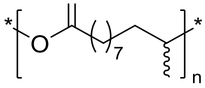
Polycaprolactone (P1k)



In a dried Schlenk-flask ε-caprolactone (4.85 ml, 5.00 g, 43.8 mmol) was dissolved in 20 mL dry CH_2Cl_2 to give a colorless solution. (1.00/0.5/0.25/0.125 mL, 0.219/0.110/0.0550/0.0275 mmol) of a standard solution of 4-(pyren-1-yl)butan-1-ol in CH_2Cl_2 (0.219 mol/l) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (90 mg, 0,647 mmol) in CH_2Cl_2 were added. The mixture was stirred for 8 h 45 min at r.t. and quenched by the addition of 1 mL of a solution of benzoic acid (267 mg, 2.19 mmol). After precipitation in MeOH a white powder (0.562/1.21/1.32/1.63 g, 11/24/26/33 %) was obtained. Molecular weights were not targeted by reaching a predetermined conversion and only by the variation of the monomer:initiator ratio.

^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.06 (t, *J = 6.7 Hz*, 2 H, -C*H_2*OOC), 2.30 (t, 2 H, *J = 7.5 Hz*, -C*H_2*-CO_2-), 1.56 – 1.76 (m, 4 H, -C*H_2*-), 1.28 – 1.49 (m, 4 H, -C*H_2*-); IR (ATR): *v* = 2943.9, 2864.8, 1721.2, 1470.5, 1418.7, 1365.1, 1292.8, 1176.5, 1107.3, 1065.1, 1043.7, 960.2, 933.7, 731.3, 710.5, 453.1 cm^{-1}; T_m= 54.6 °C.

Poly(10-hydroxyundecanoate)[i] (P1l)



The synthesis was performed according to literature.[6] Methyl 10-oxoundecanoate (200 mg, 0.925 mmol) and titanium(IV) isopropoxide (2.7 µl, 2.6 mg, 9.1 µmol) were dissolved in 1.0 mL of tetrahydrofuran (THF). Then the reaction mixture was stirred for two hours at 120 °C. Subsequently, vacuum was applied and the reaction mixture was stirred for 24 h at 120 °C. Afterwards, the crude polymer was dissolved in THF and added dropwise into cold methanol, the precipitated polymer was filtered off, dried *in vacuo,* and obtained as colorless viscous liquid (130 mg, 76%).

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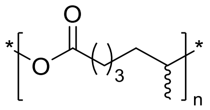
[i] Carried out by Dr. Marc von Czapiewski (KIT, group of Prof. M. A. R. Meier)

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 4.92 – 4.79 (1 H, m, >CH-CH_3), 3.61 – 3.68 (3 H, s, CH_3OOC, end group), 2.21 (2 H, t, J = 7.5 Hz, -C*H*$_2$-CO_2-), 1.64 – 1.47 (2 H, m, -C*H*$_2$-), 1.46 – 1.35 (4 H, m, -C*H*$_2$-), 1.24 (8 H, m, -C*H*$_2$-), 1.18 – 1.11 (3 H, m, -C*H*$_3$); IR (ATR): *v* = 2924.8, 2854.1, 1729.0, 1461.7, 1337.4, 1376.4, 1244.0, 1176.0, 1128.4, 1101.3, 1072.1, 1025.5, 982.7, 944.1, 855.0, 723.5, 591.9, 426.8 cm^{-1}, T_g = -58.0 °C.

Poly(methyl-ε-caprolactone) [i] *(P1m)*

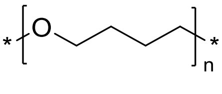


1.00 g methyl-ε-caprolactone (7.80 mmol, 1.00 eq, 1.028 mL), 18.9 mg hexanedecan-1-ol (0.078 mmol, 0.01 eq), 36.2 mg $GaBr_3$ (0.117 mmol, 0.015 eq) and 3.9 mL of DCM (99.8% anhydrous) were added under argon counter current into a dried Schlenck-flask and then stirred under argon protective atmosphere at room temperature for 40 hours. Purification was achieved by precipitation of the crude-product in cold petroleum ether (-78 °C). Poly(6-methylcaprolactone) was obtained as slightly yellow highly viscous liquid with a yield of 70% (703 mg, 5.46 mmol).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) = 4.88 (dd, J = 12.6 Hz, 6.3 Hz, 1H, -O-CH-), 2.26 (t, J = 7,5Hz, 2H, -OC-CH_2-R), 1.64 (m, 2H, -OC-R-CH_2-), 1.19 (d, J = 6.2 Hz, 3H, -CH_3), 1.33 (m, 2H, -CH_2-) , IR (ATR): *v* = 2933.4, 2863.4, 1725.8, 1456.7, 1376.0, 1172.6, 1129.5, 1087.9, 953.4; no T_g or T_m detected between -85 and 120 °C.

6.2.3 Polyethers

Poly(oxy-1,4-butylene) [ii] (P2a)



Polyester **1a** (0.400 g, 2.0 mmol) was dissolved in CH_2Cl_2 (20 mL) and after 10 min. of stirring $GaBr_3$ (23.9 mg, 0.077 mmol) was added. After dropwise addition (syringe pump, 3.2 µL/min.) of TMDS (0.78 mL, 4.4 mmol) the sample was stirred overnight at

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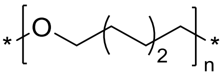
[i] Carried out by Andreas Ganzbuhl in the Bachelor thesis “Catalytic reduction of sustainable A-B-type polyesters to polyethers” (under lab-supervision of Patrick-Kurt Dannecker).
[ii] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

r.t.. Then the sample was diluted with petroleum ether (40 mL) and kept in the refrigerator overnight at - 20°C. The precipitate was filtered off (glass frit), washed with petroleum ether (3 x 20 mL) and dried *in vacuo*. Yield: 188.5 mg (66 %, containing 3 % of silyl species).

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 3.70 – 3.63 (m, -CH_2OH, end group), 3.64 – 3.33 (m, 4 H, -CH_2O-), 3.31 (s, -OCH_3, end group), 1.75 – 1.45 (m, 2 H, -OCH_2CH_2-); IR (ATR): 3409.8, 2936.9, 2852.0, 1654.4, 1445.9, 1366.1, 1258.6, 1207.6, 1101.2, 800.4 cm^{-1}; T_m= 35.8 °C.

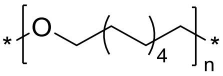
Poly(oxy-1,6-hexamethylene) [i] (P2b)



Polyester **1b** (0.46 g, 2.0 mmol) was dissolved in CH_2Cl_2 (10 mL) and after 10 min. of stirring $GaBr_3$ (16.8 mg, 0.054 mmol) was added. After dropwise addition (syringe pump, 13 µL/min.) of TMDS (0.78 mL, 4.4 mmol) the sample was stirred overnight at r.t.. Then the sample was diluted with petroleum ether (40 mL) and kept in the refrigerator overnight at - 20°C. The precipitate was filtered off (glass frit), washed with petroleum ether (3 x 20 mL) and dried *in vacuo*. Yield: 331.6 mg (83 %, containing 4 % of silyl species).

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 3.67 – 3.61 (m, -CH_2OH, end group), 3.37 (t, J = 6.7 Hz, 4 H, -CH_2O-), 3.31 (s, -OCH_3, end group), 1.65 – 1.49 (m, 4 H, -OCH_2CH_2-), 1.41 – 1.23 (m, 4 H, -CH_2-); IR (ATR): 2930.4, 2854.9, 2800.9, 1488.2, 1465.6, 1375.5, 1260.8, 1226.4, 1194.7, 1107.3, 1038.0, 980.0, 800.8, 726.1, 521.8, 503.3 cm^{-1}; T_m = 37.8 °C.

Poly(oxy-1,10-decamethylene) [i](P2c)



Polyester **1c** (0.68 g, 2.0 mmol) was dissolved in CH_2Cl_2 (20 mL) and after 20 min. of stirring, $GaBr_3$ (21.7 mg, 0.07 mmol) was added. After dropwise addition (syringe pump, 3.2 µL/min.) of TMDS (0.78 mL, 4.40 mmol) the sample was stirred overnight at r.t.. The solvent was removed *in vacuo*, the residue was pestled, admitted to petroleum

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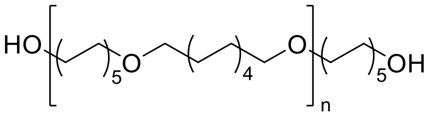
[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

ether (40mL) and stirred again overnight. After filtration over a glass frit the solid was stirred in petroleum ether (40 mL) again for another 3 h to remove polysiloxanes completely. The polyether was filtered off (glass frit), washed with petroleum ether (3 x 20 mL) and dried *in vacuo*. Yield: 548.6 mg (88 %, containing 1 % of silyl species).

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 3.69 – 3.63 (m, -CH_2OH, end group); 3.37 (t, *J* = 6.8 Hz, 4 H, $-CH_2O-$), 3.31 (s, $-OCH_3$, end group), 1.73 – 1.43 (m, 4 H, -OCH_2CH_2-), 1.43 – 1.03 (m, 12 H, -CH$_2$-); ^{13}C-NMR: (125.7 MHz, $CDCl_3$): δ (ppm) = 71.0 ($-OCH_2-$), 29.7 (-*C*H$_2$-), 29.5 (-*C*H$_2$-), 26.2 (-*C*H$_2$-); IR (ATR): 2915.6, 2848.8, 2800.3, 1593.2, 1486.3, 1468.2, 1375.4, 1238.7, 1180.5, 1112.1, 1048.3, 968.7, 719.3, 550.7, 409.3 T_{m}= 64.7 °C.

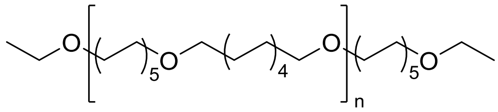
Poly(oxy-1,10-decamethylene) - OH end groups (P2c.1)



Polyester **1c.2** (0.5 g, 2.15 mmol) bearing OH end groups was degassed in a Schlenk flask. CH_2Cl_2 (21 mL) was added and after 20 min. of stirring, $GaBr_3$ (11.5 mg, 0.037 mmol) was added. After dropwise addition (syringe pump, 7 mL h^{-1}) of TMDS (0.60 mL, 3.30 mmol) the sample was stirred over the weekend at r.t.. The solvent was removed *in vacuo* giving quantitative yield and all analysis was performed without prior separation of the polysiloxanes side product.

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 3.63 (t, -CH_2OH, end group); 3.38 (t, J = 6.7 Hz, 4 H, $-CH_2O-$), 1.68 – 1.45 (m, 4 H, -OCH_2CH_2-), 1.42 – 1.11 (m, 12 H, -CH$_2$-); IR (ATR): 2929.0, 2916.6, 2850.8, 2801.4, 1593.2, 1487.1, 1464.5, 1376.0, 1260.8, 1102.4, 1022.2, 968.7, 913.3, 800.1, 719.9, 551.2 cm^{-1}.

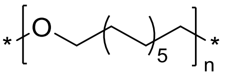
Poly(oxy-1,10-decamethylene) - OEt end groups (P2c.2)



Polyester **P1c.2** (0.5 g, 2.08 mmol) bearing OAc end groups was degassed in a Schlenk flask. CH_2Cl_2 (21 mL) was added and after 20 min. of stirring $GaBr_3$ (9.4 mg, 0.030 mmol) was added. After dropwise addition (syringe pump, 7 mL h^{-1}) of TMDS (0.60 mL, 3.30 mmol), the sample was stirred over the weekend at r.t.. The solvent was removed in vacuo giving quantitative yield and all analysis was performed without prior separation of the polysiloxanes side product.

1H-NMR: (500 MHz, CDCl3): δ (ppm) = 3.38 (t, J = 6.7 Hz, 4 H, $-CH_2O-$), 1.71 – 1.42 (m, 4 H, $-OCH_2CH_2-$), 1.42 – 1.21 (m, 12 H, $-CH_2-$), 1.20 (t, J = 6.7 Hz, $-O-CH_2-CH_3$, end group); IR (ATR): 2916.6, 2850.8, 2801.4, 1485.0, 1464.5, 1376.0, 1258.8, 1090.1, 1020.2, 968.8, 863.9, 798.1, 719-9, 551.2 cm^{-1}.

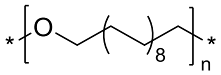
Poly(oxy-1,12-dodecamethylene)[i] (P2d)



Polyester **1d** (1.31 g, 3.30 mmol) was dissolved in CH_2Cl_2 (25 mL) and after 5 min. of stirring $GaBr_3$ (25.4 mg, 0.082 mmol) was added. After dropwise addition of TMDS (1.28 mL, 7.30 mmol, cooling by water bath) the sample was stirred overnight at r.t.. Then the viscous material was diluted with CH_2Cl_2 (150 mL) and stirred until dispersion was obtained. After filtration (glass frit) the solid was washed with CH_2Cl_2 (50 mL) and dried *in vacuo*. Yield: 1.09 g (90 %, containing 2 % of silyl species)

^1H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 3.69 – 3.60 (m, $-CH_2OH$, end group), 3.37 (t, *J* = 6.8 Hz, 4 H, $-CH_2O-$), 3.32 (s, $-OCH_3$, end group), 1.64 – 1.47 (m, bs, 4 H, $-OCH_2CH_2-$), 1.41 – 1.14 (m, 16 H, $-CH_2-$); IR (ATR): 2924.0, 2852.6, 1720.6, 1463.2, 1371.8, 1338.8, 1260.4, 1092.1, 802.2 cm^{-1}; T_m = 85.3 °C.

Poly(oxy-1,18-octadecamethylene-co-1,21-heneicosamethylene) (P2e)



simplified structure

In a 100 mL round-bottomed flask, polyester **1e** (300 mg, 0.531 mmol) was suspended in 30 mL of toluene. Afterwards, $GaBr_3$ (4.93 mg, 0.0160 mmol) and TMDS (206 µl, 157 mg) were added and the mixture was stirred for 20 h at 60 °C. The reaction mixture was concentrated *in vacuo* and precipitated in cold MeOH obtaining a white solid (262 mg, 92%), which is not soluble in common organic solvents at r.t..

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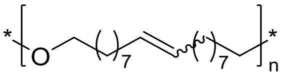
[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

IR (ATR): v = 2914.8, 2846.8, 1736.7, 1462.6, 1374.0, 1258.9, 1167.0, 1097.7, 1021.3, 910.3, 798.5, 729.0, 719.4, 542.5 cm^{-1}; T_m= 96.6 °C.

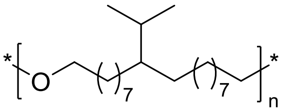
Poly(oxy-1,18-octadec-9-ene) [i] (P2f)



Polyester **1f** (0.28 g, 0.500 mmol) was dissolved in CH_2Cl_2 (10 mL) and after 20 min. of stirring $GaBr_3$ (10.9 mg, 0.035 mmol) was added. After dropwise addition of TMDS (195 µL, 1.10 mmol) the sample was stirred overnight at r.t.. The solvent was removed *in vacuo*, the residue was pestled, added to petroleum ether (20mL) and heated under reflux for 3.5 h. After filtration over a glass frit 208.3 mg of a white solid (50 %, containing 4 % of silyl species) were obtained.

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 5.49 – 5.20 (m, 2 H, -CH=CH-), 3.69 – 3.57 (m, -CH_2OH, end group), 3.38 (t, J = 6.7 Hz, 4 H, -CH_2O-), 3.32 (s, -OCH_3, end group), 2.22 – 1.79 (m, 4 H, -CH=CHCH_2-), 1.74 – 1.44 (m, 4 H, -OCH_2CH_2-), 1.44 – 1.02 (m, 20 H, -CH_2-); IR (ATR): 2918.1, 2849.4, 1732.1, 1468.4, 1378.7, 1260.5, 1097.8, 1022.7, 962.8, 865.4, 800.6, 720.2; T_m= 64.7 °C.

Poly(oxy-9-isopropyl-1,18-octadecamethylene) [i](P2g)



Polyester **1g** (0.36 g, 0.56 mmol) was dispersed in CH_2Cl_2 (10 mL) and slightly heated until a solution was obtained. $GaBr_3$ (11.1 mg, 0.036 mmol, 6.37 mol%) was added while cooling the sample with a water bath. After dropwise addition of TMDS (0.22 mL, 1.22 mmol) the sample was stirred overnight r.t.. The solvent was removed *in vacuo*, the residue dissolved in acetone (40 mL) and again stirred overnight. After filtration, the solid was washed with acetone and dried *in vacuo* (25 mbar). Yield: 0.32 g (93 %, containing 2 % of silyl species).

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 3.59 (t, J = 6.6 Hz, -CH_2OH, end group), 3.39 (t, J = 6.8 Hz, 4 H, -CH_2O-), 3.33 (s, -OCH_3, end group), 1.73 – 1.62 (m, 1 H, -C$H$$CH_3$), 1.62 – 1.50 (m, 4 H, -OCH_2CH_2-), 1.44 – 0.96 (m, 27 H, -CH_2-, -C$H$$CH_2$-), 0.81 (d, J

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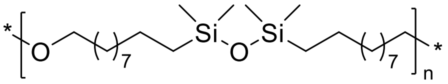
[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

= 6.8 Hz, 6 H, CH_3); IR (ATR): 2922.2, 2852.0, 1739.5, 1463.9, 1366.4, 1260.8, 1112.3, 802.9, 721.4 cm^{-1}; T_g= -69 °C.

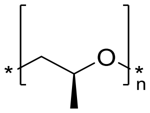
Poly(oxy-10,10'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(decamethylene)[i] (P2h)



Polyester **1h** (0.40 g, 0.45 mmol) was dissolved in CH_2Cl_2 (10 mL) and after 10 min. of stirring $GaBr_3$ (6.0 mg, 0.02 mmol, 4.44 %) was added while cooling the sample with a water bath. After dropwise addition of TMDS (0.18 mL, 1.0 mmol) the sample was stirred overnight at r.t.. The solvent was removed *in vacuo* and the residue dissolved in acetone (20 mL). After stirring the sample overnight and filtration the obtained white solid was dried *in vacuo* (25 mbar). Yield: 0.37 g (41.9 %, containing 10 % of silyl species).

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 3.61 (t, J = 6.7 Hz, -CH_2OH, end group), 3.39 (t, J = 6.8 Hz, 4 H, -CH_2O-), 3.33 (s, -OCH_3, end group), 1.74 – 1.49 (m, 4 H, -OCH_2CH_2-), 1.47 – 1.19 (m, 32 H, -CH_2-), 0.49 (t, J = 7.7 Hz, 4 H, -CH_2Si-), 0.02 (s, 12 H, -$SiCH_3$); IR (ATR): 2921.2, 2852.5, 1464.6, 1409.2, 1251.9, 1044.1, 837.9, 792.5, 703.5 cm^{-1}; T_m= 0.6 °C.

(S)-Polypropyleneoxide[i] (P2i)



Polyester **1i** (1.08 g, 15.0 mmol) was dissolved in CH_2Cl_2 (10 mL), $GaBr_3$ (235.1 mg, 0.76 mmol, 5.07 mol%) was added and the sample was stirred for 30 min. at r.t. and then cooled to 0°C. After dropwise addition of TMDS (13.25 mL, 75.0 mmol) the sample was stirred overnight at r.t.. CH_2Cl_2 (30 mL) was added and the sample was washed with HCl (10%) and afterwards with H_2O (3x) and dried over Na_2SO_4. After filtration the solvent was removed *in vacuo* and the residue dissolved in a mixture of MeOH (20 mL) and H_2O (2 mL) and extracted with 4 mL of petroleum ether (5x) to remove polysiloxane. The methanolic layer was concentrated *in vacuo*, the residue dissolved

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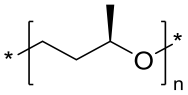
[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

in a mixture of MeOH (5 mL) and H_2O (0.5 mL) and extracted again with petroleum ether (1 mL) for several times until most of the polysiloxane was removed. The methanolic layer was dried over Na_2SO_4 and after filtration the solvent was removed *in vacuo* (25 mbar). Yield: 0.29 g (34 %, containing 6 % of silyl species).

^{1}H-NMR: (300 MHz, $CDCl_3$): δ (ppm) = 4.03 – 3.83 (m, -$C\mathit{H}OH$, end group), 3.82 – 2.91 (m, 3 H, -CH_2O-, CHO-), 1.58 – 1.45 (m, -$CH_3C\mathit{H_2}$-, end group), 1.31 – 0.92 (m,3 H, -$CHC\mathit{H_3}$), 0.85 (t, *J* = 7.5 Hz, $C\mathit{H_3}CH_2$-, end group); IR (ATR): 3420.6, 3045.6, 2952.3, 2173.2, 1429.0, 1202.7, 968.5, 882.4, 769.6, 688.3 cm^{-1}; HR-MS/ESI $C_{15}H_{32}LiO_6$: calc. 315.2359, found 315.2354, HR-MS/ESI $C_{15}H_{32}LiO_5$: calc. 299.2410, found 299.2409. About 20% reduction of the secondary OH-group was observed giving CH_3CH_2 endgroup.

Poly(oxy-1-methyl-propylene)[i] (P2j)



Polyester **1j** (0.344 g, 4.0 mmol) was dissolved in CH_2Cl_2 (10 mL) and $GaBr_3$ (30.8 mg, 0.099 mmol, 2.48 mol%) was added. After stirring of the sample for 30 min. at r.t. TMDS (0.78 mL, 4.4 mmol, syringe pump, 3.2 µL/ min.) was added and the sample was stirred overnight at r.t.. The solvent was removed *in vacuo* and the residue, after dilution in 2 mL diethyl ether, was applied to column chromatography (25x1.5 cm, silica gel 60, elution with 250 mL of petroleum ether/diethyl ether 1:1 and 300 mL of methanol). The methanolic fraction was concentrated and dried *in vacuo* (25 mbar) yielding 0.21 g (73 %) of polyether **2j** as white powder.

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 3.78 – 3.69 (m, -CHOH, end group), 3.67 – 3.61 (m, -CH_2OH, end group), 3.51 (dt, *J* = 5.9 Hz, 6.9 Hz, 1H, -$CH_{2(a)}O$-), 3.45 (dt, *J* = 5.9 Hz, 7.0 Hz, 1H, -$CH_{2(b)}O$-), 3.40 – 3.30 (m, 1H, -CHO-), 1.78 – 1.65 (m, 1H, -$C\mathit{H}_{2(a)}CH$-), 1.64 – 1.54 (m, 1H, $C\mathit{H}_{2(b)}CH$-), 1.10 (d, *J* = 6.5 Hz, 3 H, -$CHC\mathit{H_3}$); ^{13}C-NMR: (125.7 MHz, $CDCl_3$): δ (ppm) = 72.4 (-$O\mathit{C}HCH_3$), 65.06 (-OCH_2), 37.3 (-$OCH_2\mathit{C}H_2$-), 19.8 (-CH_3), in agreement with Lit.[8]; IR (ATR): 2965.3, 2928.6, 2863.9,

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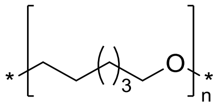
[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

1738.8, 1476.5, 1450.3, 1372.3, 1338.6, 1259.6, 1136.6, 1072.3, 1014.7, 913.9, 801.4, 465.2, 401.3 cm^{-1}.

Poly(oxy-1,6-hexamethylene) [i] (P2k)

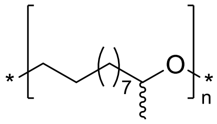


Polyester **1k.1** (0.34 g, 3.0 mmol) was dissolved in CH_2Cl_2 (10 mL) and after 10 min. of stirring $GaBr_3$ (11.0 mg, 0.035 mmol, 1.18 mol%) was added while cooling the sample (water bath). Then TMDS (0.59 mL, 3.3 mmol) was added dropwise and the sample was stirred overnight at r.t.. The solvent was removed *in vacuo* and the residue dissolved in petroleum ether (20 mL). After storage of the sample at -20° C for 24 h, the obtained white solid was filtered off, washed with petroleum ether and dried *in vacuo* (25 mbar). Yield: 0.29 g (85 %, containing 4 % of silyl species).

Polyesters **1k.2-4** were reduced analogously giving polyethers **2k.2-4**.

^{1}H-NMR: (300 MHz, $CDCl_3$): δ (ppm) = 3.64 (t, J = 6.6 Hz, $-CH_2OH$, end group), 3.38 (t, J = 6.7 Hz, 4 H, $-CH_2O-$), 1.78 – 1.50 (m, 4 H, $-OCH_2CH_2-$), 1.47 – 1.19 (m, 4 H, $-CH_2-$); IR (ATR): 2931.6, 2856.4, 2802.0, 1488.8, 1376.2, 1329.1, 1261.5, 1195.2, 1108.3, 1038.5, 980.3, 804.2, 726.4, 521.4 cm^{-1}; T_m= 49.1 °C.

Poly(oxy-1-methyl-decamethylene) [i](P2l)



Polyester **1k** (1.10 g, 6.0 mmol) was dissolved in CH_2Cl_2 (9 mL) and after 10 min. of stirring $GaBr_3$ (24.4 mg, 0.078 mmol, 1.31 mol%) was added while cooling the sample (water bath). Then TMDS (1.17 mL, 6.60 mmol) was added dropwise and the sample was stirred overnight at r.t.. The solvent was removed *in vacuo* and the residue was dissolved in diethyl ether (80 mL). The organic layer was washed with diluted HCl (10%) and NaCl solution / H_2O until neutral. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The residue was dissolved in petroleum ether (5 mL) and after addition of acetone (15 mL), while stirring the sample, a white

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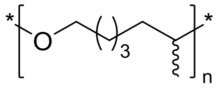
[i] Carried out by Dr. Ursula Biermann (Carl von Ossietzky Universität Oldenburg).

solid precipitated which, after filtration, was dried *in vacuo* (25 mbar). Yield: 0.85 g (83 %, containing 9 % of silyl species).

^{1}H-NMR: (300 MHz, $CDCl_3$): δ (ppm) = 3.84 – 3.75 (m, 1H, >C*H*OH, end group), 3.54 – 3.40 (m, 1H, >CHO-), 3.39 – 3.26 (m, 2H, $-CH_2O-$), 1.81 – 1.46 (m, 4H, $-OCH_2CH_2-$), 1.42 – 1.20 (m, 12H, $-CH_2-$), 1.11 (d, J = 6.1 Hz, 3H, $-CH_3$); IR (ATR): 2924.0, 2852.6, 1463.2, 1371.8, 1338.8, 1260.4, 1092.1, 802.2, 721.6 cm^{-1}; T_g= -69,0 °C.

Poly(oxy-1-methyl-hexamethylene [i] (P2m)



703 mg poly(6-methyl-caprolactone) **3** (5.46 mmol, 1.00 eq) and 25.0 mg $GaBr_3$ (0.082 mmol, 0.015 eq) and 27.3 ml DCM (99.8% anhydrous) were added under argon counter current into a dried Schlenk-flask. 1.06 mL TMDS (807 mg, 6.01 mmol, 1.1 eq) was added slowly under argon counter current into the Schlenck-flask. The mixture was then stirred for 17 hours at room temperature. Purification was achieved through precipitation of the crude-product in cold petroleum ether (-78 °C). The respective reduced polyether was obtained as milky-white highly viscous liquid with a yield of 44% (270 mg, 2.42 mmol, still containing 57 w% siloxanes).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 3.60 – 3.23 (m, 3H, -O-C*H*-, $-O-CH_2-$), 1.70 – 1.24 (m, 6H, $-CH_2-$), 1.17 – 1.07 (m, 3H, $-CH_3$); IR (ATR): v = 2962.2, 1412.0, 1258.0, 1013.9, 863.4, 792.8, 701.4, 401.1; T_g= -52.2 °C.

6.2.4 Synthesis, cleavage and analysis of partly reduced polyesters P2a.part, P2b.part, P2c.part

Procedure

For the synthesis of party reduced polyethers **2a.part**, **2b.part 2c.part** the same procedure as for **2a**, **2b** and **2c** was applied using 0.1 eq TMDS instead of 1 eq. For the ester cleavage of partly reduced polyesters, 10 mg **2a.part**, **2b.part** or **2c.part** was dispersed in 1.5 mL methanol in a pressure tube. TBD (10 mol%) was added and the mixture was stirred at 95 °C overnight. Methanol was evaporated under reduced pressure, the mixture was analyzed by NMR-spectroscopy to confirm (89% **2a.part**,

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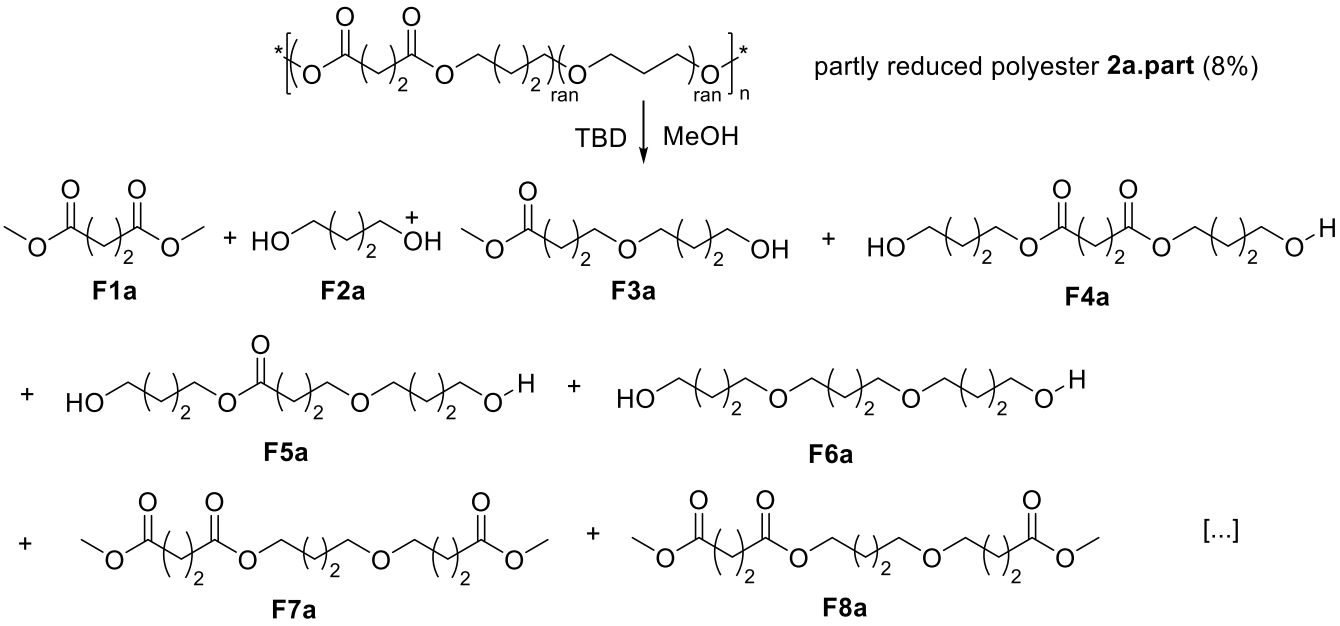
[i] Carried out by Andreas Ganzbuhl in the Bachelor thesis “Catalytic reduction of sustainable A-B-type polyesters to polyethers” (under lab-supervision of Patrick-Kurt Dannecker).

93 % **2b.part**, 92% **2c.part**) conversion of the ester group to methylester fragments and finally the mixture was analyzed by SEC-ESI-MS.

Analysis of the fragments by SEC-ESI MS



Scheme 77: Cleavage of partly reduced polyester ***P2a.part*** *(8% according to ^{1}H-NMR spectroscopy) by transesterification with methanol. Isomers of the given structures with the ester bond at different positions are possible; ran= random.*

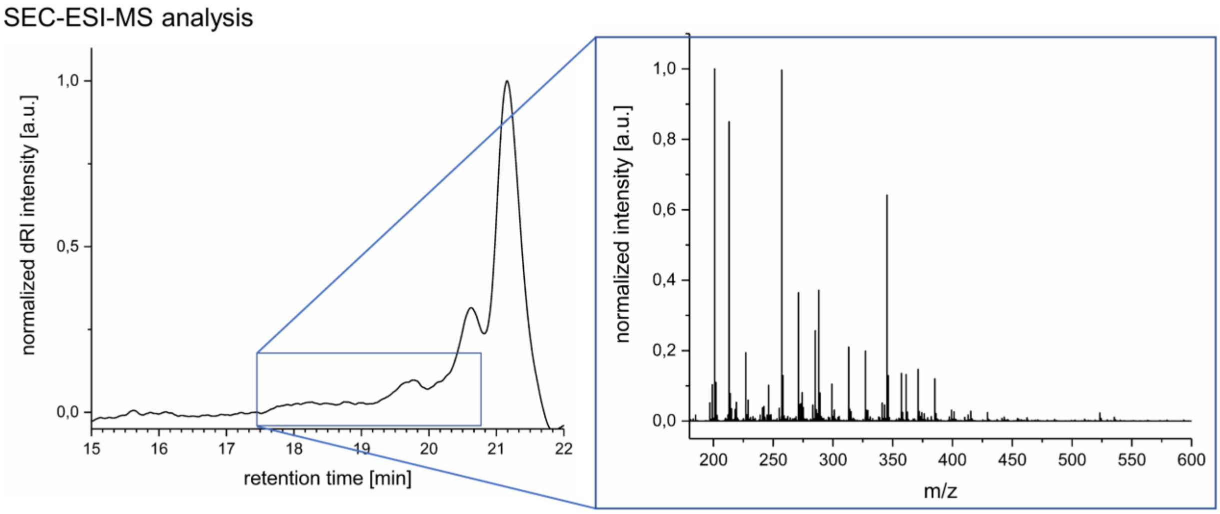
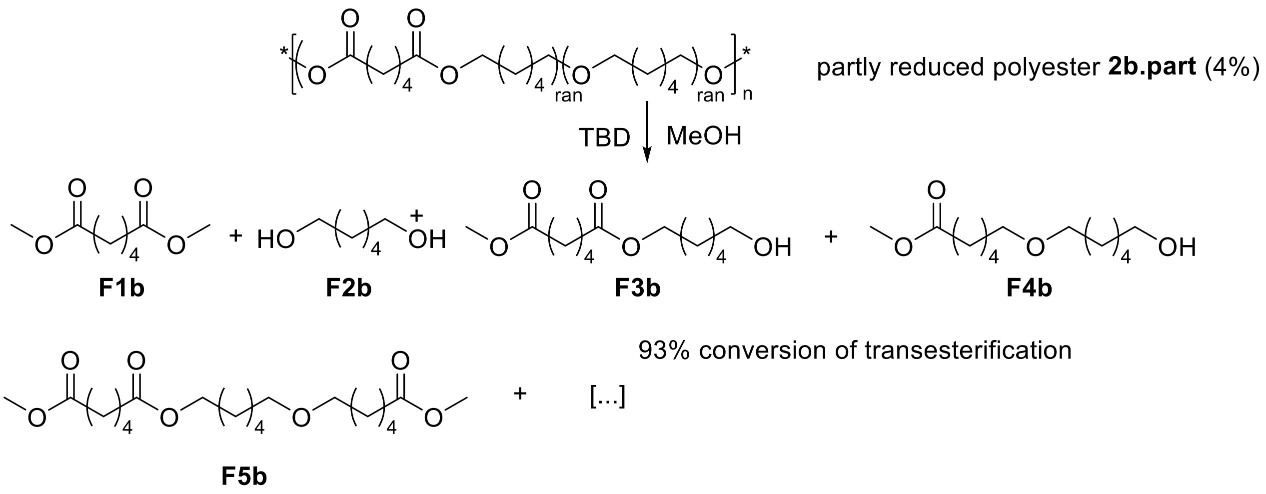


Figure 41: SEC-ESI-MS analysis of the obtained mixture of the cleavage of partly reduced polyester ***P2a.part****. The mass spectrum was obtained by integration between 17.49 and 20.68 min of the chromatogram (excluding the monomer peak at 21.16 min). Background peaks: 201.09, 229.08, 288.13, 245.20, 361.20, 408.28, 454.37, 510.43, 523.30.*

Table 17: SEC-ESI-MS analysis of the fragments of the cleavage of partly reduced polyester ***P2a.part*** *by transesterification with methanol. Main fragments are highlighted and assigned to structures* ***F1a*** *–* ***F8a****.*

	Fragment	**Groups reduced**	**Mass [m/z][g]**	**Formula**	**Retention time[d] [min]**	**Rel. intensity [%]**
Dimer[c]		0	227.09	$C_9H_{16}NaO_5$	19.11	19.4
	F3a	***1***	***213.11***	***$C_9H_{18}NaO_4$***	***19.12***	***85.0***
		2[e]	199.13	$C_9H_{20}NaO_3$	not found	not found
		1[f]	199.09	$C_8H_{16}NaO_4$	18.95	10.3
		2[f]	185.12	$C_8H_{18}NaO_3$	19.07	1.6
Trimer[a]	***F4a***	***0***	***285.13***	***$C_{12}H_{22}NaO_6$***	***18.35***	***25.2***
	F5a	***1***	***271.15***	***$C_{12}H_{24}NaO_5$***	***18.35***	***36.4***
	F6a	***2***	***257.17***	***$C_{12}H_{26}NaO_4$***	***18.38***	***100***
Trimer[b]		0	341.12	$C_{14}H_{22}NaO_8$	18.79	5.2
	F7a	***1***	***327.14***	***$C_{14}H_{24}NaO_7$***	***18.88***	***19.9***
	F8a	***2***	***313.16***	***$C_{14}H_{26}NaO_6$***	***18.92***	***19.8***
		3[e]	299.18	$C_{14}H_{28}NaO_5$	not found	not found
		4[e]	285.20	$C_{14}H_{30}NaO_4$	not found	not found
		1[f]	313.13	$C_{13}H_{22}NaO_7$	19.64	4.3
		2[f]	299.15	$C_{13}H_{24}NaO_6$	18.83	6.8
		3[f]	285.17	$C_{13}H_{26}NaO_5$	18.83	11.1
		4[f, e]	271.19	$C_{13}H_{28}NaO_4$	not found	not found
Tetramer[c]		0	399.16	$C_{17}H_{28}NaO_9$	18.14	3.1
		1	385.18	$C_{17}H_{30}NaO_8$	18.12	12.0
		2	371.20	$C_{17}H_{32}NaO_7$	18.13	14.7
		3	357.23	$C_{17}H_{34}NaO_6$	18.30	13.5
		4[e]	343.25	$C_{17}H_{36}NaO_5$	not found	not found
		1[f]	371.17	$C_{16}H_{28}NaO_8$	17.96	1.5
		2[f]	357.19	$C_{16}H_{30}NaO_7$	18.05	2.7
		3[f]	343.21	$C_{16}H_{32}NaO_6$	18.04	4.5
		4[f]	329.23	$C_{16}H_{34}NaO_5$	18.00	3.0
Pentamer[a]		0	457.20	$C_{20}H_{34}NaO_{10}$	not found	not found
		1	443.23	$C_{20}H_{36}NaO_9$	17.59	1.1
		2	429.25	$C_{20}H_{38}NaO_8$	17.74	2.4
		3	415.27	$C_{20}H_{40}NaO_7$	17.74	2.7
		4	401.29	$C_{20}H_{42}NaO_6$	17.84	2.6
Pentamer[b]		0	513.19	$C_{22}H_{34}NaO_{12}$	not found	not found
		1	499.22	$C_{22}H_{36}NaO_{11}$	not found	not found
		2	485.24	$C_{22}H_{38}NaO_{10}$	17.97	0.3
		3	471.26	$C_{22}H_{40}NaO_9$	17.97	0.3
		4	457.28	$C_{22}H_{42}NaO_8$	18.06	0.2
		5[e]	443.30	$C_{22}H_{44}NaO_7$	not found	not found
		6[e]	429.32	$C_{22}H_{46}NaO_6$	not found	not found
		1[f]	485.20	$C_{21}H_{34}NaO_{11}$	not found	not found
		2[f]	471.22	$C_{21}H_{36}NaO_{10}$	not found	not found
		3[f]	457.24	$C_{21}H_{38}NaO_9$	17.84	0.3
		4[f]	443.26	$C_{21}H_{40}NaO_8$	18.11	0.4
		5[f]	429.28	$C_{21}H_{42}NaO_7$	not found	not found
		6[f]	415.30	$C_{21}H_{44}NaO_6$	not found	not found

[a] 2x OH end groups; [b] 2x COOMe end groups; [c] 1x OH 1x COOMe end groups; [d] retention time shown for which peak is most intense; [e] only possible at the chain end with at least one OMe end group; [f] in this case only possible by overreduction to the alcohol; [g] calculated mass and obtained mass do not differ in at least the shown accuracy of $\Delta m/z < \pm 0.01$.



Scheme 78: Cleavage of partly reduced polyester ***P2b.part*** *(4% according to ^{1}H-NMR spectroscopy) by transesterification with methanol. Isomers of the given structures with the ester bond at different positions are possible; ran= random.*

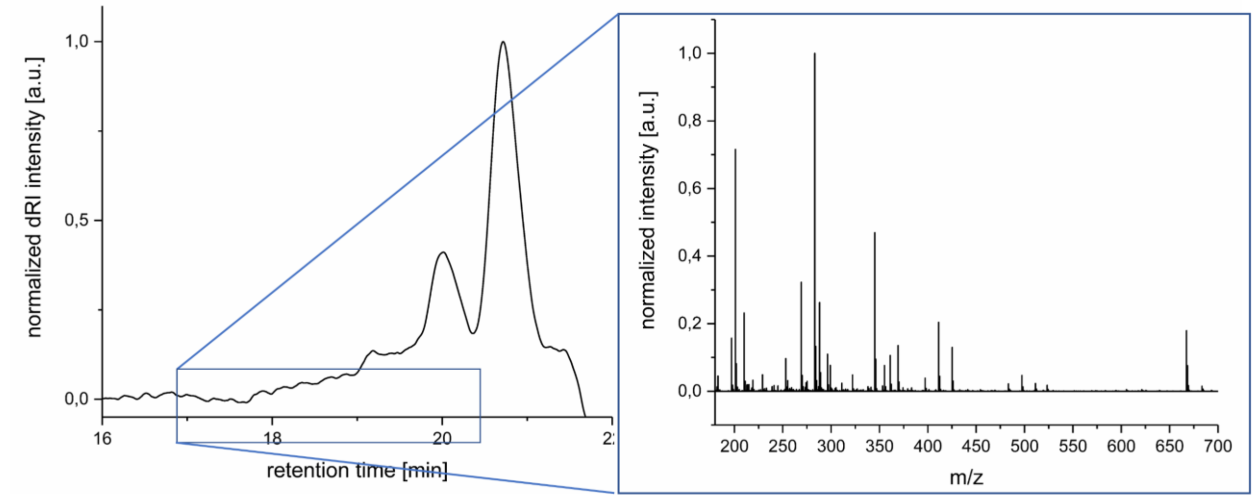
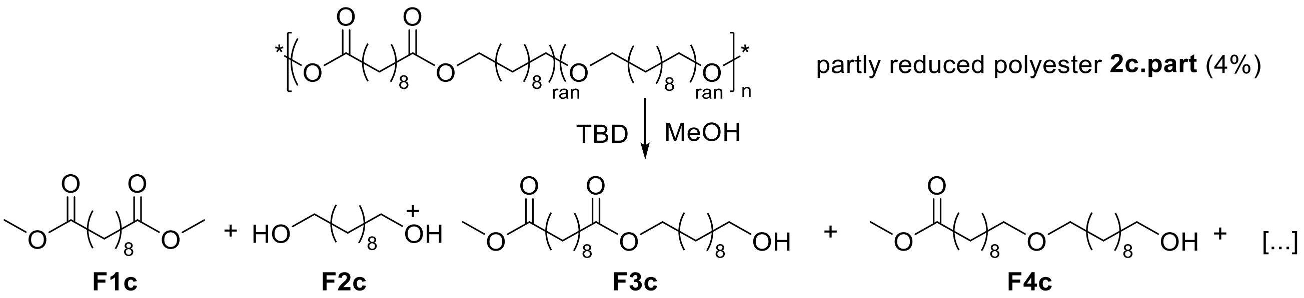


Figure 42: Cleavage of partly reduced polyester ***P2b.part*** *(4% according to ^{1}H-NMR-spectroscopy) by transesterification with methanol and SEC-ESI-MS analysis of the obtained mixture. The mass spectrum was obtained by integration between 16.96 and 20.42 min of the chromatogram (excluding the monomer peak at 20.71 min of monomer). background peaks: 201.09, 229.08, 288.13, 245.20, 361.20, 408.28, 454.37, 510.43, 523.30. The main products of the cleavage (monomers* ***18*** *and* ***19****; M+Na$^+$ 113.05 and 169.05 Da).*

Table 18: SEC-ESI-MS analysis of the fragments of the cleavage of partly reduced polyester ***P2b.part*** *by transesterification with methanol. Main fragments are highlighted and assigned to structures* ***F1b*** *–* ***F5b****.*

	Fragment	Groups reduced	Mass [m/z][g]	Formula	Retention time[d] [min]	Rel. intensity [%]
Dimer[c]	***F3***	***0***	***283.15***	**$C_{13}H_{24}NaO_5$**	***18.57***	***100***
	F4	***1***	***269.17***	**$C_{13}H_{26}NaO_4$**	***19.37***	***31.8***
		2[e]	255.19	$C_{13}H_{28}NaO_3$	not found	not found
		1[f]	255.16	$C_{12}H_{24}NaO_4$	18.44	16.9
		2[f]	241.18	$C_{12}H_{26}NaO_3$	not found	not found
Trimer[a]		0	369.23	$C_{18}H_{34}NaO_6$	17.94	13.5
		1	355.25	$C_{18}H_{36}NaO_5$	18.06	7.6
		2	341.27	$C_{18}H_{38}NaO_4$	18.06	1.2
Trimer[b]		0	425.22	$C_{20}H_{34}NaO_8$	18.10	13.0
	F5	***1***	***411.24***	**$C_{20}H_{36}NaO_7$**	***18.39***	***20.4***
		2	397.26	$C_{20}H_{38}NaO_6$	18.43	3.9
		3[e]	383.28	$C_{20}H_{40}NaO_5$	not found	not found
		4[e]	369.30	$C_{20}H_{42}NaO_4$	not found	not found
		1[f]	397.22	$C_{19}H_{34}NaO_7$	18.07	3.0
		2[f]	383.24	$C_{19}H_{36}NaO_6$	18.08	1.0
		3[f]	369.26	$C_{19}H_{38}NaO_5$	not found	not found
		4[f, e]	355.28	$C_{19}H_{40}NaO_4$	not found	not found
Tetramer[c]		0	511.29	$C_{25}H_{44}NaO_9$	17.56	2.3
		1	497.31	$C_{25}H_{46}NaO_8$	17.56	4.7
		2	483.33	$C_{25}H_{48}NaO_7$	17.61	2.2
		3	469.35	$C_{25}H_{50}NaO_6$	17.56	0.3
		4[e]	455.37	$C_{25}H_{52}NaO_5$	17.72	0.2
		1[f]	441.36	$C_{24}H_{50}NaO_5$	17.90	0.4
		2[f]	483.29	$C_{24}H_{44}NaO_8$	17.29	0.3
		3[f]	469.31	$C_{24}H_{46}NaO_7$	17.29	0.2
		4[f]	455.33	$C_{24}H_{48}NaO_6$	not found	not found
Pentamer[a]		0	597.36	$C_{30}H_{54}NaO_{10}$	not found	not found
		1	583.38	$C_{30}H_{56}NaO_9$	17.07	0.2
		2	569.40	$C_{30}H_{58}NaO_8$	17.16	0.1
		3	555.42	$C_{30}H_{60}NaO_7$	not found	not found
		4	541.44	$C_{30}H_{62}NaO_6$	not found	not found
Pentamer[b]		0	653.35	$C_{32}H_{54}NaO_{12}$	not found	not found
		1	639.37	$C_{32}H_{56}NaO_{11}$	17.29	0.2
		2	625.39	$C_{32}H_{58}NaO_{10}$	17.32	0.3
		3	611.41	$C_{32}H_{60}NaO_9$	not found	not found
		4	597.43	$C_{32}H_{62}NaO_8$	not found	not found
		5[e]	583.45	$C_{32}H_{64}NaO_7$	not found	not found
		6[e]	569.48	$C_{32}H_{66}NaO_6$	not found	not found
		1[f]	625.36	$C_{31}H_{54}NaO_{11}$	not found	not found
		2[f]	611.38	$C_{31}H_{56}NaO_{10}$	not found	not found
		3[f]	597.40	$C_{31}H_{58}NaO_9$	not found	not found
		4[f]	583.42	$C_{31}H_{60}NaO_8$	not found	not found
		5[f]	569.44	$C_{31}H_{62}NaO_7$	not found	not found
		6[f]	555.46	$C_{31}H_{64}NaO_6$	not found	not found

[a] 2x OH end groups; [b] 2x COOMe end groups; [c] 1x OH 1x COOMe end groups; [d] retention time shown for which peak is most intense; [e] only possible at the chain end with at least one OMe end group; [f] in this case only possible by overreduction to the alcohol; [g] calculated mass and obtained mass do not differ in at least the shown accuracy of $\Delta m/z < \pm 0.01$.



partly reduced polyester **2c.part** (4%)

92% conversion of transesterification

*Scheme 79: Cleavage of partly reduced polyester **P2c.part** (4% according to ¹H-NMR-spectroscopy) by transesterification with methanol. Isomers of the given structures with the ester bond at different positions are possible; ran= random.*

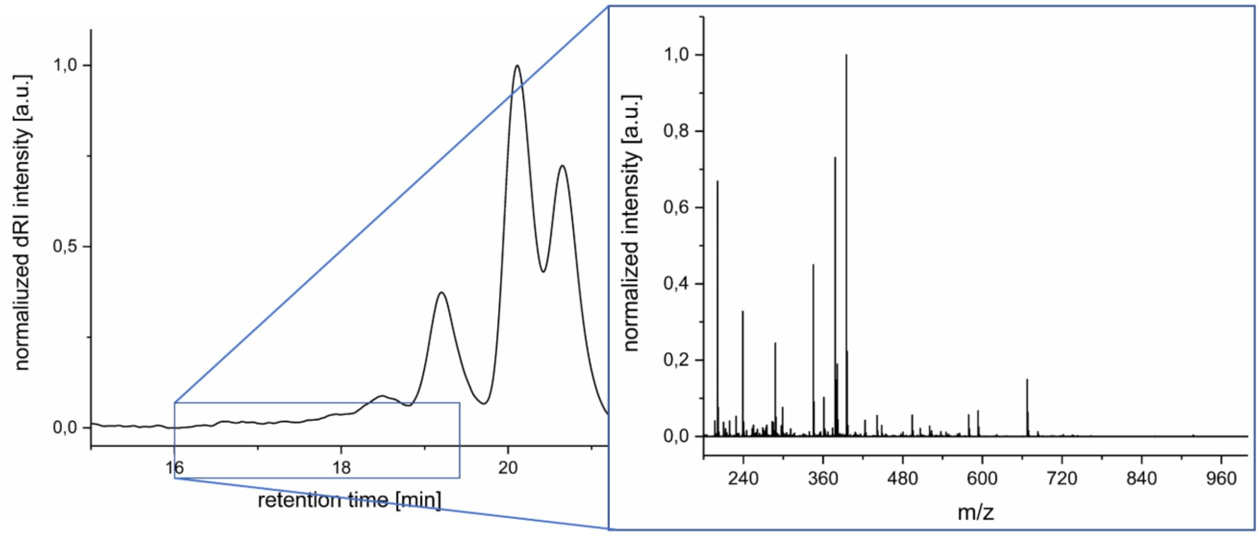


*Figure 43: Cleavage of partly reduced polyester **P2c.part** (4% according to ¹H-NMR-spectroscopy) by transesterification with methanol and SEC-ESI-MS analysis of the obtained mixture. The mass spectrum was obtained by integration between 16.06 and 19.74 min of the chromatogram (excluding the monomer peak at 20.11 min of monomer). background peaks: 201.09, 229.08, 288.13, 245.20, 345.20, 361.20, 408.28, 454.37, 510.43, 523.30, 667.42, 683.41.*

*Table 19: SEC-ESI-MS analysis of the fragments of the cleavage of partly reduced polyester **P2c.part** by transesterification with methanol. Main fragments are highlighted and assigned to structures **F1c** – **F4c**.*

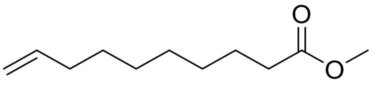
	Fragment	Groups reduced	Mass [m/z][g]	Formula	Retention time[d] [min]	Rel. intensity [%]
Dimer[c]	***F3c***	***0***	***395.28***	***$C_{21}H_{40}NaO_5$***	***18.70***	***79.4***
	F4c	***1***	***381.30***	***$C_{21}H_{42}NaO_4$***	***18.67***	***18.9***
		2[e]	367.32	$C_{21}H_{44}NaO_3$	not found	not found
		1[f]	353.30	$C_{20}H_{42}NaO_3$	18.38	0.4
		2[f]	367.28	$C_{20}H_{40}NaO_4$	17.68	1.2
Trimer[a]		0	537.41	$C_{30}H_{58}NaO_6$	17.12	1.3
		1	523.43	$C_{30}H_{60}NaO_5$	17.14	1.4
		2	509.45	$C_{30}H_{62}NaO_4$	17.16	0.2
Trimer[b]		0	593.40	$C_{32}H_{58}NaO_8$	17.22	6.7
		1	579.42	$C_{32}H_{60}NaO_7$	17.50	5.6
		2	565.44	$C_{32}H_{62}NaO_6$	17.71	0.8
		3[e]	551.47	$C_{32}H_{64}NaO_5$	not found	not found
		4[e]	537.49	$C_{32}H_{66}NaO_4$	not found	not found
		1[f]	565.41	$C_{31}H_{58}NaO_7$	17.15	0.6
		2[f]	551.43	$C_{31}H_{60}NaO_6$	17.17	0.2
		3[f]	537.45	$C_{31}H_{62}NaO_5$	not found	not found
		4[f, e]	523.47	$C_{31}H_{64}NaO_4$	not found	not found
Tetramer[c]		0	735.54	$C_{41}H_{76}NaO_9$	16.73	0.4
		1	721.56	$C_{41}H_{78}NaO_8$	16.78	0.4
		2	707.58	$C_{41}H_{80}NaO_7$	16.70	0.2
		3	693.60	$C_{41}H_{82}NaO_6$	not found	not found
		4[e]	679.62	$C_{41}H_{84}NaO_5$	not found	not found
		1[f]	665.61	$C_{40}H_{82}NaO_5$	not found	not found
		2[f]	707.54	$C_{40}H_{76}NaO_8$	not found	not found
		3[f]	693.56	$C_{40}H_{78}NaO_7$	not found	not found
		4[f]	679.59	$C_{40}H_{80}NaO_6$	not found	not found
Pentamer[a]		0	877.67	$C_{50}H_{94}NaO_{10}$	not found	not found
		1	863.70	$C_{50}H_{96}NaO_9$	not found	not found
		2	849.72	$C_{50}H_{98}NaO_8$	not found	not found
		3	835.74	$C_{50}H_{100}NaO_7$	not found	not found
		4	821.76	$C_{50}H_{102}NaO_6$	not found	not found
Pentamer[b]		0	933.66	$C_{52}H_{94}NaO_{12}$	not found	not found
		1	919.69	$C_{52}H_{96}NaO_{11}$	not found	not found
		2	905.71	$C_{52}H_{98}NaO_{10}$	not found	not found
		3	891.73	$C_{52}H_{100}NaO_9$	not found	not found
		4	877.75	$C_{52}H_{102}NaO_8$	not found	not found
		5[e]	863.77	$C_{52}H_{104}NaO_7$	not found	not found
		6[e]	849.79	$C_{52}H_{106}NaO_6$	not found	not found
		1[f]	905.67	$C_{51}H_{94}NaO_{11}$	not found	not found
		2[f]	891.69	$C_{51}H_{96}NaO_{10}$	not found	not found
		3[f]	877.71	$C_{51}H_{98}NaO_9$	not found	not found
		4[f]	863.73	$C_{51}H_{100}NaO_8$	not found	not found
		5[f]	849.75	$C_{51}H_{102}NaO_7$	not found	not found
		6[f]	835.77	$C_{51}H_{104}NaO_6$	not found	not found

[a] 2x OH end groups; [b] 2x COOMe end groups; [c] 1x OH 1x COOMe end groups; [d] retention time shown for which peak is most intense; [e] only possible at the chain end with at least one OMe end group; [f] in this case only possible by overreduction to the alcohol; [g] calculated mass and obtained mass do not differ in at least the shown accuracy of Δm/z < ±0.01.

6.3 Procedures for: Monomer Approach - Aliphatic long chain polyethers by catalytic reduction and polymerization of ω,ω'-unsaturated esters derived from fatty acids

6.3.1 Monomer synthesis

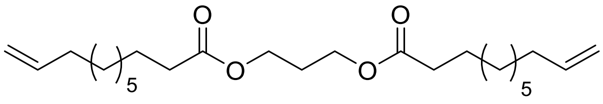
Ethenolysis of methyl oleate - methyl dec-9-enoate (26)



In a Teflon reactor tube inlet, technical grade methyl oleate (5.76 mL, 5.00 g, 16.9 mmol), p-benzoquinone (10.9 mg, 0.101 mmol) and Hoveyda–Grubbs catalyst 2nd gen. (21.0 mg, 0.034 mmol) were dissolved in 17.0 mL toluene, pressurized with ethylene (15 bar) and stirred for 6 h at 60 °C. Afterwards the reaction was quenched with ethyl vinyl ether (0.2 mL) and the solvent was removed *in vacuo*. After removal of 1-decene at r.t. and 0.001 mbar, the catalyst was removed by filtration through silica gel in a mixture of 19:1 cyclohexane:EtOAc. The product was separated by distillation (48 °C, 0.03 mbar) and obtained as colorless liquid (1.92 g, 65%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, -C*H*=CH_2), 5.07 – 4.83 (m, 2H, -CH=CH_2), 3.66 (s, 3H, -COOCH_3), 2.30 (t, *J* = 7.5 Hz, 2H, -CH_2-COO), 2.13 – 1.93 (m, 2H, -CH_2-CH=CH_2), 1.74 – 1.48 (m, 2H, -CH_2-CH_2-COO-), 1.46 – 1.19 (m, 8H, -CH_2-); ^{13}C-NMR ($CDCl_3$, 75 MHz): 174.2 (C=O), 139.0 (-*C*H=CH_2), 114.19 (-CH=*C*H_2), 51.4 (-*C*H_2-OOC-), 34.1 (-*C*H_2COO-), 33.8 (-*C*H=CH_2), 29.1 (-CH_2), 28.9 (-CH_2), 24.9 (-*C*H_2-CH_2-OOC-); HRMS (EI) $C_{11}H_{20}O_2$ $[M]^+$ *m/z* calc. 184.1458, found 184.1460; IR (ATR): *v* = 3075.6, 2924.9, 2853.4, 1738.0, 1639.2, 1434.5, 1358.4, 1244.4, 1195.4, 1166.9, 993.2, 907.9, 724.5, 635.4 cm^{-1}.

Synthesis of ω,ω'-diene ester[i] (35)



A mixture of methyl-10-undecenoate (26.7 g, 135 mmol, 2.21 eq.) and 1,3-propanediol (4.69 g, 61.6 mmol, 1.00 eq.) was heated to 60 °C under constant stirring. Afterwards, TBD (0.428 g, 3.73 mmol, 0.05 eq.) was added to the mixture and the mixture was stirred at 60 °C under constant air-flow through the mixture. During the reaction the two phases of the mixture combined. Leftover reactants were removed under reduced pressure (65°C, 1,0*10^{-3} mbar) and the crude product was purified by column chromatography (cyclohexane/EE 10:1, R$_f$ = 0,31 (CH/EE 30:1)) yielding a colorless liquid (20,0 g, 79%).

^{1}H-NMR (CDCl$_3$, 300MHz) δ (ppm) = 5.89 – 5.67 (m, 2H, -C*H*=CH$_2$), 5.02 – 4.85 (m, 4H, -CH=CH_2), 4.13 (t, *J*= 6.3 Hz, 4H, -CH_2-OOC-), 2.27 (t, *J*= 7.5 Hz, 4H, -CH$_2$COO-), 2.10 – 1.97 (m, 4H, -CH_2-CH=), 1.97 – 1.89 (m, 2H, -O-CH$_2$-CH_2-), 1.70 - 1.51 (m, 4H, -OOC-CH$_2$-CH_2-), 1.42 - 1.15 (m, 20H, -CH$_2$-) ppm; ^{13}C (CDCl$_3$, 75MHz) δ= 173.8 (CO), 139.2 (-*C*H=CH$_2$), 114.2 (-CH=*C*H$_2$), 60.9 (-*C*H$_2$-OOC-), 34.3 (-*C*H$_2$COO-), 33.9 (-*C*H$_2$-CH=), 29.4-29.0 (-*C*H$_2$-), 28.2 (-*C*H$_2$-), 25.0 (-*C*H$_2$-CH$_2$COO-); HRMS (FAB) C$_{25}$H$_{44}$O$_4$ [M + H]$^+$ m/z calc. 408.3234, found 408.3234; IR (ATR): *v* = 2924.8, 2854.9, 1736.0, 1641.3, 1460.3, 1162.1, 1046.9, 993.5, 909.1, 724.0, 635.6 cm^{-1}.

6.3.1.1 *Synthesis of ω,ω'-diene esters 34 – 40 by transesterification with sodium methanolate*

All transesterification with sodium methanolate as catalyst were carried out by the project partner Dr. Ursula Biermann (University of Oldenburg) and are not included in this experimental section.

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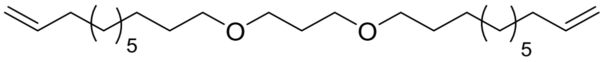
[i] Carried out by Alexandra Sink in the Bachelor thesis “Neue katalytische Wege zu biobasierten Polyethern” (under lab-supervision of Patrick-Kurt Dannecker).

Synthesis of ω,ω‘-diene ether[i] (M1b)



Utilizing Schlenk technique, $GaBr_3$ (0.128 g, 0.414 mmol, 0.011 eq.) was dissolved in 25 mL dry toluene. TMDS (10.9 g, 81.9 mmol, 2.20 eq.) was dissolved in 10 mL toluene and added to the mixture with a flow rate of 50 mL h^{-1}. The reaction was stirred for 20.5 h at room temperature. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (3x, cyclohexane / EE 30:1, dichloromethane / methanol 98.5 : 1.5, cyclohexane : dichloromethane 100% CH→ 8:1 → 1:1→100% DCM, R_f = 0,31 (CH/EE 30:1), R_f = 0,38 (DCM/MeOH 98,5:1,5), R_f = 0,36 (DCM 100%)) yielding a colorless liquid (8.56 g, 62%).

^{1}H-NMR ($CDCl_3$, 300MHz) δ (ppm) = 5.89 – 5.72 (m, 2H, -C*H*=CH$_2$), 5.06 – 4.86 (m, 4H, -CH=CH_2), 3.52 – 3.44 (t, *J*= 6.4 Hz, 4H, -CH_2-O), 3.43 – 3.35 (t, J=6.7 Hz, 4H, -CH_2-O) 2.04 (q, *J*= 6.9 Hz, 4H, -CH_2-CH=), 1.83 (p, *J*=6.4 Hz, 2H, -O-CH$_2$-CH_2-), 1.62 – 1.49 (m, 4H, O-CH$_2$-CH_2-), 1.42 – 1.20 (m, 24H, -CH$_2$-) ppm; ^{13}C ($CDCl_3$, 75MHz) δ (ppm) = 138.9 (-*C*H=CH$_2$), 113.8 (-CH=*C*H$_2$), 70.8 (-*C*H$_2$-O-), 67.5 (-*C*H$_2$-O-), 33.5 (-*C*H$_2$COO-), 29.9 (-*C*H$_2$-), 29.5-28.7 (-*C*H$_2$-), 25.9 (-*C*H$_2$-); HRMS (FAB) $C_{25}H_{48}O_2$ [M + H]$^+$ m/z: calc. 380.3649, found. 380.3648; IR (ATR): *v* = 2922.8 (CH$_2$), 2852.9 (CH$_2$), 1641.3, 1464.5 (CH$_2$), 1367.8, 1112.7 (COC), 991.4, 907.1 (CH=CH$_2$), 719.9 (CH$_2$) cm^{-1}.

Synthesis of ω,ω‘-diene ethers M1a – M1f by catalytic reduction without solvent

All catalytic reductions without solvent were carried out by the project partner Dr. Ursula Biermann (University of Oldenburg) and are not included in this experimental section.

6.3.2 Conversion to Dithiols

6.3.2.1 General Method

The respective ω, ω‘-diene ether (1.00 mmol, 1.00 eq.) and thioacetic acid (3.00 mmol, 3.00 eq.) were heated for 2 h in a microwave reactor. The crude product was checked for full conversion of the double bond by NMR-spectroscopy and excess of thioacetic

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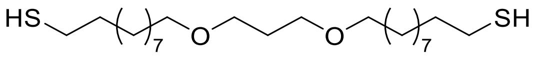
[i] Carried out by Alexandra Sink in the Bachelor thesis “Neue katalytische Wege zu biobasierten Polyethern” (under lab-supervision of Patrick-Kurt Dannecker).

acid was removed *in vacuo* to obtain the pure dithio ester without further purification. The dithio ester was dispersed in methanol, triazabicyclodecene (TBD, 0.100 mmol, 0.100 eq.) was added and the mixture was heated to reflux overnight under Ar-atmosphere. The solvent and during the reaction formed methyl acetate were removed *in vacuo* and the crude product was purified by column chromatography.

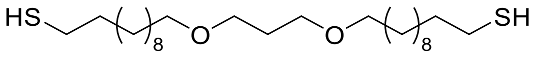
10,10'-(propane-1,3-diylbis(oxy))bis(decane-1-thiol) (M2a)



Reactants: **3a** (10.0 g, 28.4 mmol, 1.00 eq), thioacetic acid (6.48 g, 85.0 mmol, 3.00 eq). The product was obtained as white powder (9.58 g, 80%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.46 (t, *J* = 6.4 Hz, 4H, -CH_2-O-), 3.38 (t, *J* = 6.7 Hz, 4H, -CH_2-O-), 2.50 (q, *J* = 7.4 Hz, 4H, -CH_2-S-), 1.81 (p, *J* = 6.4 Hz, 2H, O-CH_2-CH_2-CH_2-O-), 1.66 – 1.44 (m, 8H, -CH_2-CH_2-O-, -CH_2-CH_2-S-), 1.43 – 1.17 (m, 26H, -CH_2-, -S*H*); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 71.10 (-*C*H_2-O-), 67.8 (-*C*H_2-O-), 34.1 (-*C*H_2-CH_2-S-), 30.2 (O-CH_2-*C*H_2-CH_2-O), 29.8 (-*C*H_2-CH_2-O), 29.6 (-*C*H_2-), 29.1 (-*C*H_2-), 28.5 (-*C*H_2-), 26.3 (-*C*H_2-), 24.7 (-*C*H_2-S); HRMS (ESI) of $C_{23}H_{48}O_2S_2Na$ $[M+Na]^+$ *m/z* calc. 443.2989, found 443.2977; IR (ATR): v = 2926.0, 2853.6, 2161.6, 2028.0, 1464.7, 1369.2, 1300.4, 1112.9, 722.0 cm^{-1}.

11,11'-(propane-1,3-diylbis(oxy))bis(undecane-1-thiol) (M4b)

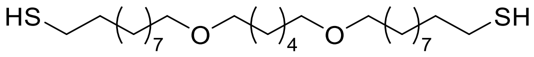


Reactants: **3b** (4.00 g, 10.5 mmol, 1.00 eq.), thioacetic acid (2.40 g, 31.5 mmol, 3.00 eq.). The product was obtained as a white powder (2.71 g, 57%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.47 (t, *J* = 6.4 Hz, 4H, -CH_2-O-), 3.38 (t, *J* = 6.7 Hz, 4H, -CH_2-O-), 2.50 (q, *J* = 7.4 Hz, 4H, -CH_2-S-), 1.82 (p, *J* = 6.4 Hz, 2H, O-CH_2-CH_2-CH_2-O-), 1.66 – 1.45 (m, 8H, -CH_2-CH_2-O, -CH_2-CH_2-S-), 1.42 – 1.16 (m, 30H, -CH_2-, -S*H*); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 71.2 (-*C*H_2-O-), 67.9 (-*C*H_2-O-), 34.2 (-*C*H_2-CH_2-S-), 30.3 (-O-CH_2-*C*H_2-CH_2-O-), 29.9 (-*C*H_2-CH_2-O-), 29.6 (-*C*H_2-), 29.2 (-*C*H_2-), 28.5 (-*C*H_2-), 26.3 (-*C*H_2-), 24.8 (-*C*H_2-S-); HRMS (ESI) of $C_{25}H_{52}O_2S_2Na$

[M+Na]$^+$ *m/z* calc. 471.3301, found 471.3289; IR (ATR): *v* = 2916.6, 2850.0, 1488.5, 1469.2, 1372.0, 1346.4, 1237.5, 1115.5, 939.9, 717.1 cm^{-1}.

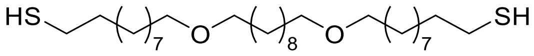
10,10'-(hexane-1,6-diylbis(oxy))bis(decane-1-thiol) (M4c)



Reactants: **3c** (15.0 g, 39.0 mmol, 1.00 eq.), thioacetic acid (8.68 g, 114 mmol, 3.00 eq.). The product was obtained as a white powder (14.2 g, 81 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.45 – 3.27 (m, 8H, -C*H*$_2$-O-), 2.50 (q, *J* = 7.4 Hz, 4H, -C*H*$_2$-S-), 1.69 – 1.45 (m, 12H, -C*H*$_2$-CH$_2$-O, -C*H*$_2$-C*H*$_2$-S-), 1.45 – 1.17 (m, 30H, -S*H*, -C*H*$_2$-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 71.1 (-*C*H$_2$-O-), 71.0 (-*C*H$_2$-O-), 34.2 (-*C*H$_2$-CH$_2$-S-), 29.9 (O-CH$_2$-*C*H$_2$-CH$_2$-O), 29.6 (-*C*H$_2$-CH$_2$-O), 29.2 (-*C*H$_2$-), 28.5 (-*C*H$_2$-), 27.0 (-*C*H$_2$-), 26.3 (-*C*H$_2$-), 26.2 (-*C*H$_2$-), 24.8 (-*C*H$_2$-S); HRMS (EI) of $C_{26}H_{54}O_2S_2Na$ [M+Na]$^+$ *m/z* calc. 485.3457, found 485.3445; IR (ATR): *v* = 2916.9, 2849.8, 2802.3, 2538.0, 1488.7, 1470.2, 1376.7, 1313.6, 1280.9, 1251.5, 1224.1, 1200.0, 1113.3, 1051.0, 1037.2, 1020.0, 993.8, 969.0, 727.7, 544.2, 513.6, 476.5 cm^{-1}.

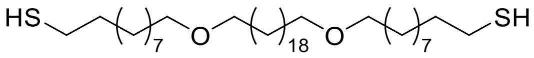
10,10'-(decane-1,10-diylbis(oxy))bis(decane-1-thiol) (M4d)



Reactants: **3d** (5.0 g, 11.1 mmol, 1.00 eq.), thioacetic acid (2.53 g, 33.3 mmol, 3.00 eq.). The product was obtained as a white powder (4.03 g, 70 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.36 (t, *J* = 6.7 Hz, 8H, -C*H*$_2$-O-), 2.50 (q, *J* = 7.4 Hz, 4H, -C*H*$_2$-S-), 1.66 – 1.46 (m, 12H, -C*H*$_2$-CH$_2$-O, -C*H*$_2$-C*H*$_2$-S-), 1.43 – 1.17 (m, 38H, -S*H*, -C*H*$_2$-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 71.0 (-*C*H$_2$-O-), 70.6 (-*C*H$_2$-O-), 34.1 (-*C*H$_2$-CH$_2$-S-), 29.9 (O-CH$_2$-*C*H$_2$-CH$_2$-O-), 29.6 (-*C*H$_2$-CH$_2$-O-), 29.2 (-*C*H$_2$-), 28.4 (-*C*H$_2$-), 27.1 (-*C*H$_2$-), 26.7 (-*C*H$_2$-), 26.2 (-*C*H$_2$-), 25.9 (-*C*H$_2$-), 24.7 (-*C*H$_2$-S); HRMS (ESI) of $C_{30}H_{62}O_2S_2Na$ [M+Na]$^+$ *m/z* calc. 541.4083, found 541.4070; IR (ATR): *v* = 2915.5, 2848.9, 1469.5, 1377.9, 1114.5, 966.7, 727.8, 547.3 cm^{-1}.

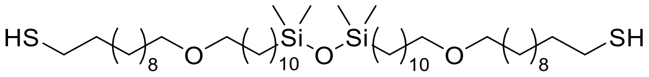
10,10'-(icosane-1,20-diylbis(oxy))bis(decane-1-thiol) (M4e)



Reactants: **3e** (2.0 g, 3.38 mmol, 1.00 eq.), thioacetic acid (0.773 g, 10.2 mmol, 3.00 eq.). The product was obtained as a white powder (1.27 g, 57%).

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) = 3.37 (t, *J* = 6.7 Hz, 8H, -C$\mathit{H_2}$-O-), 2.50 (q, *J* = 7.4 Hz, 4H, -C$\mathit{H_2}$-S-), 1.66 – 1.47 (m, 12H, -C$\mathit{H_2}$-CH$_2$-O, -C$\mathit{H_2}$-C$\mathit{H_2}$-S-), 1.44 – 1.14 (m, 58H, -S*H*, -C$\mathit{H_2}$-); ^{13}C-NMR (CDCl$_3$, 75 MHz): δ (ppm) = 71.0 (-*C*H$_2$-O-), 34.1 (-*C*H$_2$-CH$_2$-S-), 30.4 (-O-CH$_2$-*C*H$_2$-), 29.8 (-*C*H$_2$-), 29.6 (-*C*H$_2$-), 29.3 (-*C*H$_2$-), 28.5 (-*C*H$_2$-), 28.1 (-*C*H$_2$-), 27.1 (-*C*H$_2$-), 26.8 (-*C*H$_2$-), 26.3 (-*C*H$_2$-), 24.7 (-*C*H$_2$-S); HRMS (ESI) of $C_{40}H_{82}O_2S_2Na$ [M+Na]$^+$ *m/z* calc. 681.56484, found 681.56274; IR (ATR): *v* = 2915.9, 2848.2, 2801.7, 1487.1, 1470.8, 1377.1, 1313.8, 1282.2, 1253.2, 1223.1, 1117.2, 1043.6, 1011.8, 995.6, 962.0, 729.4, 719.7, 541.5, 445.0 cm^{-1}.

11,11'-(((1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(undecane-11,1-diyl))bis(oxy))bis(undecane-1-thiol) (M4f)



Reactants: **3f** (750 mg, 0.962 mmol, 1.00 eq.), thioacetic acid (220 mg, 2.89 mmol, 3.00 eq.). The product was obtained as a white, sticky residue (513.5 mg, 63%).

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) = 3.38 (t, *J* = 6.7 Hz, 8H, -C$\mathit{H_2}$-O-), 2.52 (q, *J* = 7.4 Hz, 4H, -C$\mathit{H_2}$-S-), 1.73 – 1.46 (m, 12H, -C$\mathit{H_2}$-CH$_2$-O, -C$\mathit{H_2}$-C$\mathit{H_2}$-S-), 1.44 – 1.12 (m, 62H, -S*H*, -C$\mathit{H_2}$-), 0.49 (t, *J* = 7.3 Hz, 4H, -C$\mathit{H_2}$-Si), 0.02 (s, 12H, Si-C$\mathit{H_3}$) ^{13}C-NMR (CDCl$_3$, 101 MHz): δ (ppm) = 71.1 (-*C*H$_2$-O-), 34.2 (-*C*H$_2$-CH$_2$-S-), 33.6 (-CH$_2$-), 30.0 (O-CH$_2$-*C*H$_2$-), 29.8 (-*C*H$_2$-), 29.8 (-*C*H$_2$-), 29.8 (-*C*H$_2$-), 29.7 (-*C*H$_2$-), 29.7 (-*C*H$_2$-), 29.6 (-*C*H$_2$-), 29.2 (-*C*H$_2$-), 28.5 (-*C*H$_2$-), 26.4 (-*C*H$_2$-), 26.4 (-*C*H$_2$-), 24.8 (-*C*H$_2$-), 23.5 (-*C*H$_2$-), 18.6 (*C*H$_2$-Si), 0.55 (-Si(*C*H$_3$)$_2$-).; HRMS (ESI) of $C_{48}H_{102}O_3S_2Si_2Na$ [M+Na]$^+$ *m/z* calc. 869.6701, found 869.6673; IR (ATR): *v* = 2917.1, 2884.4, 1463.2, 1374.8, 1250.4, 1169.3, 1119.1, 1068.9, 966.8, 846.7, 794.7, 779.6, 720.2, 705.6, 539.2, 457.1 cm^{-1}.

6.3.3 Thiol-ene polymerizations

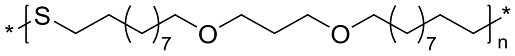
6.3.3.1 General method for UV-initiation

The respective ω, ω‘-diene ether (1.00 mmol, 1.00 eq.), ω, ω‘-dithiol (1.00 mmol, 1.00 eq.) and 2,2-dimethoxy-1,2-diphenylethan-1-one (DMPA, 0.025 mmol, 0.025 eq.) were dissolved in 2-Methyl THF (1 mL). Under vigorous stirring the mixture was irradiated with UV light (254 nm and 365 nm) for 5 h. The polymer was obtained after precipitation of the hot reaction mixture in methanol.

6.3.3.2 General method for thermal initiation

The respective ω, ω‘-diene ether (1.00 mmol, 1.00 eq.), ω, ω‘-dithiol (1.00 mmol, 1.00 eq.) and 1,1′-azobisisobutyronitrile (AIBN, 0.025 mmol, 0.025 eq.) were dissolved in 2-Methyl THF (1 mL). Under vigorous stirring, the mixture was heated to 80 °C for 5 h in a microwave reactor. The polymer was obtained after precipitation of the hot reaction mixture in methanol.

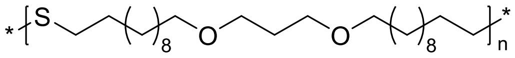
Thiol-ene polymer (P3a)



UV-initiation, Reactants: **M1a** (335 mg, 0.951 mmol, 1.00 eq.) and **M2a** (400 mg, 0.951 mmol, 1.00 eq.). The polymer was obtained as a white powder (603.5 mg, 82 %).

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) = 3.48 (t, *J* = 6.4 Hz, 8 H, -CH_2-O-), 3.39 (t, *J* = 6.7 Hz, 8 H, -CH_2-O-), 2.54 – 2.44 (m, 8 H, -CH_2-S-), 1.83 (p, *J* = 6.5 Hz, 4 H, -O-CH$_2$-CH_2-CH$_2$-O-), 1.63 – 1.49 (m, 16 H, -CH_2-CH$_2$-O, -CH_2-CH_2-S-), 1.43 – 1.21 (m, 48 H, -CH_2-); IR (ATR): *v* = 2917.5, 2849.9, 2806.4, 1468.5, 1381.3, 1261.0, 1222.7, 1109.3, 1004.2, 973.8, 802.8, 719.0, 550.4, 510.7 cm^{-1}, T_m= 65.9 °C.

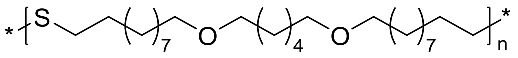
Thiol-ene polymer (P3b)



UV-initiation, Reactants: **M1b** (339 mg, 0.891 mmol, 1.00 eq.) and **M2b** (400 mg, 0.891 mmol, 1.00 eq.). The polymer was obtained as a white powder (703 mg, 95 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.48 (t, J = 6.4 Hz, 8 H, -CH_2-O-), 3.39 (t, J = 6.7 Hz, 8 H, -CH_2-O-), 2.58 – 2.40 (m, 8 H, -CH_2-S-), 1.83 (p, J = 6.4 Hz, 4 H, -O-CH_2-CH_2-CH_2-O), 1.68 – 1.47 (m, 16 H, -CH_2-CH_2-O, -CH_2-CH_2-S-), 1.43 – 1.17 (m, 56 H, -CH_2-); IR (ATR): v = 2917.7, 2849.8, 1469.2, 1381.1, 1260.7, 1110.4, 975.0, 802.8, 719.5, 550.3 cm^{-1}, T_m= 66.6 °C.

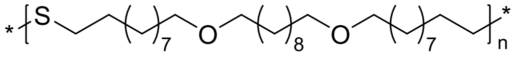
Thiol-ene polymer (P3c)



UV-initiation, Reactants: **M1c** (341 mg, 0.864 mmol, 1.00 eq.) and **M2c** (400 mg, 0.864 mmol, 1.00 eq.). The polymer was obtained as a white powder (682 mg, 92 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.38 (t, J = 6.7 Hz, 16 H, -CH_2-O-), 2.49 (t, J = 7.4 Hz, 8 H, -CH_2-S-), 1.79 – 1.46 (m, 24 H, -CH_2-CH_2-O-, -CH_2-CH_2-S-), 1.45 – 1.14 (m, 56 H, -CH_2-); IR (ATR): v = 2917.4, 2850.2, 2801.6, 1486.7, 1468.5, 1375.9, 1281, 1224.9, 1037.1, 1020.8, 969.4, 719.0, 543.4, 514.4 cm^{-1}, T_m= 74.6 °C.

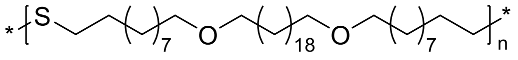
Thiol-ene polymer (P3d)



Thermal initiation, Reactants: **M1d** (347 mg, 0.771 mmol, 1.00 eq.) and **M2d** (400 mg, 0.771 mmol, 1.00 eq.). The polymer was obtained as a white powder (593 mg, 79 %).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.38 (t, J = 6.7 Hz, 16 H, -CH_2-O-), 2.49 (t, J = 7.4 Hz, 8 H, -CH_2-S-), 1.70 – 1.45 (m, 24 H, -CH_2-CH_2-O-, -CH_2-CH_2-S-), 1.43 – 1.16 (m, 72 H, -CH_2-); IR (ATR): v = 2916.2, 2848.4, 2799.5, 1470.5, 1376.0, 1118.8, 1042.9, 962.9, 911.4, 803.1, 719.8, 540.8 cm^{-1}, T_m= 78.0 °C.

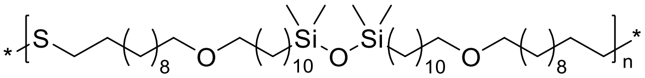
Thiol-ene polymer (P3e)



Thermal initiation, Reactants: **M1e** (359 mg, 0.607 mmol, 1.00 eq.) and **M2e** (400 mg, 0.607 mmol, 1.00 eq.). The polymer was obtained as a white powder (681 mg, 90 %) insoluble in THF or $CHCl_3$ at room temperature.

IR (ATR): *v* = 2916.2, 2848.4, 2799.5, 1470.5, 1376.0, 1118.8, 1042.9, 962.9, 911.4, 803.1, 719.8, 540.8 cm^{-1}, T_m= 67.3 °C.

Thiol-ene polymer (P3f)



Thermal initiation, Reactants: **M1f** (46.4 mg, 0.0595 mmol, 1.00 eq.) and **M2f** (50.4 mg, 0.0595 mmol, 1.00 eq.). The product was obtained as a colorless, sticky polymer and was not further purified due to its insolubility (96.1 mg, 99 %).

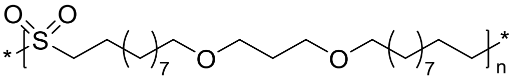
IR (ATR): *v* = 2918.0, 2850.3, 1467.6, 1375.0, 1252.1, 1038.6, 839.4, 794.5, 719.5, 540.0 cm^{-1}, T_m= 64.0 °C.

6.3.4 Oxidized thiol-ene polymers

6.3.5 General method for oxidation

The respective thiol-ene polymer (1.00 mmol, 1.00 eq.) was suspended in THF. An aqueous hydrogen peroxide solution (30% H_2O_2 in H_2O, 10.0 mmol, 5 eq. per sulfur atom) was added and the mixture was heated to 90 °C overnight. The hot mixture was precipitated in methanol:water mixture 7:3 at room temperature.

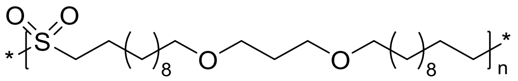
Oxidized thiol-ene polymer (P4a)



Reactants: **P3a** (200 mg, 0.259 mmol, 1.00 eq.), hydrogen peroxide solution (0.264 mL, 0.293 g, 2.59 mmol, 10 0 eq.). The polymer was obtained as a white powder (171 mg, 79 %)

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.48 (t, *J* = 6.4 Hz, 8 H, -C*H*$_2$-O-), 3.39 (t, *J* = 6.7 Hz, 8 H, -C*H*$_2$-O-), 3.00 – 2.50 (m, 8 H, -C*H*$_2$-SO$_2$-), 1.91 – 1.68 (m, 12H, -C*H*$_2$-CH$_2$-SO$_2$-, O-CH$_2$-C*H*$_2$-CH$_2$-O), 1.64 – 1.49 (m, 8 H, C*H*$_2$-CH$_2$-O-), 1.49 – 1.19 (m, 48 H, -C*H*$_2$-); IR (ATR): *v* = 2916.7, 2848.2, 1464.9, 1412.4, 1380.1, 1325.0, 1273.9, 1252.5, 1225.6, 1112.3, 1029.8, 805.1, 772.8, 723.5, 601.5, 550.2, 516.8, 460.4 cm^{-1}, T_m= 101.8 °C.

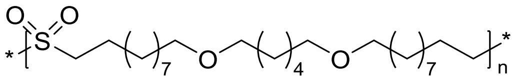
Oxidized thiol-ene polymer (P4b)



Reactant: **P3b** (200 mg, 0.241 mmol, 1.00 eq.), hydrogen peroxide solution (0.246 mL, 0.273 g, 2.41 mmol, 10.0 eq.). The polymer was obtained as a white powder (165 mg, 77 %)

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) = 3.48 (t, *J* = 6.4 Hz, 8 H, -CH_2-O-), 3.39 (t, *J* = 6.7 Hz, 8 H, -CH_2-O-), 3.01 – 2.55 (m, 8 H, -CH_2-SO$_2$-), 1.90 – 1.68 (m, 12H, -CH_2-CH$_2$-SO$_2$-, O-CH$_2$-CH_2-CH$_2$-O), 1.63 – 1.48 (m, 8 H CH_2-CH$_2$-O-), 1.48 – 1.17 (m, 56 H, -CH_2-); IR (ATR): *v* = 2915.9, 2847.4, 1464.4, 1412.6, 1380.1, 1324.7, 1288.3, 1266.8, 1245.6, 1191.7, 1033.4, 974.2, 772.9, 723.4, 602.1, 550.2, 508.3, 451.0 cm^{-1}, T_m= 106.9 °C.

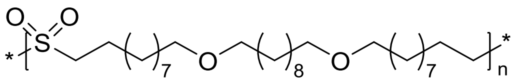
Oxidized thiol-ene polymer (P4c)



Reactant: **P3c** (200 mg, 0.225 mmol, 1.00 eq.), hydrogen peroxide solution (0.197 mL, 0.219 g, 2.25 mmol, 10.0 eq.). The polymer was obtained as a white powder (179 mg, 83 %)

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) = 3.38 (t, *J* = 6.7 Hz, 16H, -CH_2-O-), 3.00 – 2.53 (m, 8H, -CH_2-SO$_2$-), 1.91 – 1.67 (m, 8H, -CH_2-CH$_2$-SO$_2$-), 1.66 – 1.48 (m, 16H, CH_2-CH$_2$-O), 1.49 – 1.19 (m, 56 H, -CH_2-); IR (ATR): *v* = 2916.9, 2849.2, 1727.7, 1467.5, 1377.6, 1323.1, 1274.6, 1225.0, 1113.1, 1029.0, 1012.7, 967.1, 770.4, 720.9, 599.1, 543.3, 518.7 cm^{-1}, T_m= 104.6 °C.

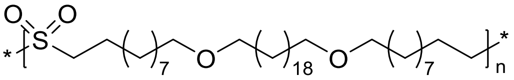
Oxidized thiol-ene polymer (P4d)



Reactant: **P3d** (200 mg, 0.206 mmol, 1.00 eq.), hydrogen peroxide solution (0.211 mL, 0.234 g, 2.06 mmol, 10.0 eq.). The polymer was obtained as a white powder (165 mg, 77 %)

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.38 (t, J = 6.7 Hz, 16 H, -CH_2-O-), 3.01 – 2.50 (m, 8 H, -CH_2-SO_2-), 1.91 – 1.67 (m, 8 H, -CH_2-CH_2-SO_2-), 1.65 – 1.48 (m, 16 H, CH_2-CH_2-O-), 1.48 – 1.18 (m, 72 H, -CH_2-); IR (ATR): v = 2916.8, 2848.9, 1466.4, 1414.0, 1376.0, 1326.7, 1273.1, 1251.3, 1224.4, 1115.5, 1048.2, 966.1, 772.1, 722.5, 608.1, 511.0 cm^{-1}, T_m= 104.1 °C.

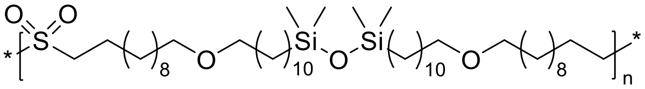
Oxidized thiol-ene polymer (P4e)



Reactant: **P3e** (200 mg, 0.206 mmol, 1.00 eq.) hydrogen peroxide solution (0.163 mL, 0.181 g, 1.60 mmol, 10.0 eq.). The polymer was obtained as an insoluble white powder (149 mg, 71 %).

IR (ATR): v = 2915.4, 2848.5, 1469.7, 1376.2, 1273.2, 1117.5, 1042.6, 962.5, 909.3, 773.0, 718.8, 602.2, 540.3, 516.2 cm^{-1}, T_m= 93.5 °C.

Oxidized thiol-ene polymer (P4f)



Reactant: **P3f** (50 mg, 0.031 mmol, 1.00 eq.), hydrogen peroxide solution (0.031 mL, 0.035 g, 0.307 mmol, 10.0 eq.). The polymer was obtained as an insoluble white powder (29.3 mg, 56 %).

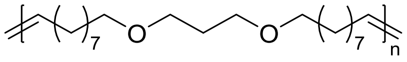
IR (ATR): v = 2916.1, 2849.5, 1734.0, 1468.5, 1417.5, 1377.0, 1324.2, 1252.3, 1120.3, 1030.3, 839.6, 793.8, 719.8, 603.9, 513.5, 456.5 cm^{-1}, T_m= 65.8 °C.

6.3.6 ADMET polymerizations

6.3.6.1 General method for ADMET polymerization

p-Benzoquinone (3.24 mg, 0.03 mmol, 0.06 eq.) and the respective diene (0.5 mmol, 1.00 eq.) were dissolved in 0.2 mL dry polarclean. HG-II catalyst (6.28 mg, 0.02 mmol, 0.02 eq.) was added at 85 °C. The pressure was reduced to 40 mbar within 10 minutes. After 6h the reaction was quenched with ethyl vinyl ether and the mixture was precipitated in methanol cooled with dry ice.

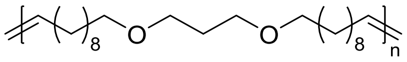
ADMET polymer (P5a)



Reactant: **M1a** (176 mg, 0.5 mmol, 1.00 eq.). The product was obtained as a gray, sticky residue (148 mg, 91%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 5.58 – 5.15 (m, 2 H, -*H*C=C*H*-), 3.48 (t, *J* = 6.4 Hz, 4 H, -CH_2-O-), 3.39 (t, *J* = 6.6 Hz, 4 H, -CH_2-O-), 2.09 – 1.89 (m, 4 H, -CH_2-*CH*=), 1.83 (p, *J* = 6.4 Hz, 2 H, O-CH_2-CH_2-CH_2-O), 1.68 – 1.47 (m, 4 H, -CH_2-CH_2-O), 1.42 – 1.18 (m, 20 H, -CH_2-); IR (ATR): *v* = 2921.9, 2851.6, 1735.1, 1651.9, 1462.9, 1398.3, 1367.9, 1260.7, 1110.6, 965.7, 802.9, 722.1 cm^{-1}, T_m= 25.5 °C.

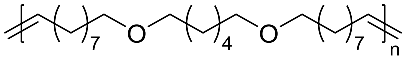
ADMET polymer (P5b)



Reactant: **M1b** (190 mg, 0.5 mmol, 1.00 eq.). The product was obtained as a gray, sticky residue (145 mg, 82%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 5.41 – 5.30 (m, 2 H, - C*H*=), 3.48 (t, *J* = 6.4 Hz, 4 H, -CH_2-O-), 3.39 (t, *J* = 6.7 Hz, 4 H, -CH_2-O-), 2.05 – 1.90 (m, 4 H, -CH_2-*CH*=), 1.83 (p, *J* = 6.4 Hz, 2 H, O-CH_2-CH_2-CH_2-O-), 1.62 – 1.49 (m, 4 H, -CH_2-CH_2-O), 1.39 – 1.20 (m, 24 H, -CH_2-); IR (ATR): *v* = 2918.0, 2849.4, 2803.7, 1466.6, 1380.0, 1259.5, 1107.5, 963.7, 803.3, 720.8, 550.6 cm^{-1}, T_m = 36.1 °C.

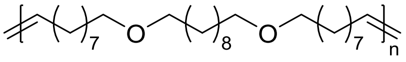
ADMET polymer (P5c)



Reactant: **M1c** (197 mg, 0.5 mmol, 1.00 eq.). The product was obtained as a gray, sticky residue (179 mg, 92%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) =5.47 – 5.25 (m, 2 H, -C*H*=), 3.38 (t, *J* = 6.7 Hz, 8 H, -CH_2-O-), 2.09 – 1.81 (m, 4 H, -CH_2-*CH*=), 1.72 – 1.45 (m, 8 H, CH_2-CH_2-O-), 1.47 – 1.18 (m, 24 H, -CH_2-); IR (ATR): *v* = 2919.7, 2849.7, 2799.6, 1733.7, 1649.1, 1485.7, 1464.9, 1375.8, 1260.3, 1111.8, 1037.4, 964.4, 803.5, 722.9, 542.5, 384.3 cm^{-1}, T_m= 49.4 °C.

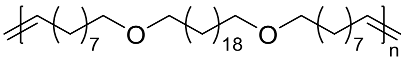
ADMET polymer (P5d)



Reactant: **M1d** (225 mg, 0.5 mmol, 1.00 eq.). The product was obtained as a gray, sticky residue (108 mg, 51%).

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) = 5.59 – 5.19 (m, 2H, -CH=), 3.38 (t, J = 6.7 Hz, 8H, -CH_2-O-), 2.13 – 1.84 (m, 4H, -CH_2-CH=), 1.74 – 1.44 (m, 8H, CH_2-CH$_2$-O), 1.44 – 1.18 (m, 32H, -CH_2-); IR (ATR): v = 2917.7, 2849.0, 2799.2, 1734.8, 1649.4, 1485.3, 1466.7, 1374.9, 1262.0, 1114.5, 964.5, 803.1, 721.3, 547.6, 382.1 cm^{-1}, T_m= 59.6 °C.

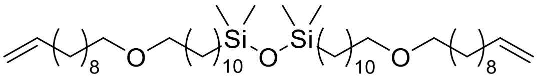
ADMET polymer (P5e)



Reactant: **M1e** (296 mg, 0.5 mmol, 1.00 eq.). The product was obtained as a gray, sticky residue (245 mg, 87%).

IR (ATR): v = 2916.6, 2848.2, 2798.7, 1733.0, 1649.9, 1464.2, 1375.0, 1261.3, 1115.0, 963.6, 801.6, 720.5, 540.8 cm^{-1}, T_m=76.0.

ADMET polymer (P5f)



Reactant: **M1f** (398 mg, 0.5 mmol, 1.00 eq), the product was insoluble in THF. Residues of polarclean, catalyst and *p*-benzoquinone were removed by washing with methanol. The product was obtained as a sticky grey polymer (385 mg, quant.).

IR (ATR): v = 2921.8, 2852.4, 1736.4, 1655.1, 1463.5, 1257.6, 1017.8, 838.8, 793.5, 703.4, 384.3 cm^{-1}, T_m= 14.3 °C.

6.3.7 Hydrogenations of ADMET polymers

6.3.7.1 General method for hydrogenations

The respective ADMET polymer (1.00 mmol, 1.00 eq) was dispersed in toluene (12 mL) in an autoclave. Shvo's Catalyst (0.01 mmol, 0.01 eq per double bond) was added and the mixture was stirred at 100 °C and 40 bar hydrogen pressure overnight.

After cooling down to 50 °C, the mixture was precipitated in methanol (100 mL) cooled with dry ice. The product was filtered off.

Hydrogenated ADMET polymer P6a

Reactant: **P5a** (70.0 mg, 0.216 mmol, 1.00 eq). The polymer was obtained as a grey powder (51.1 mg, 73%).

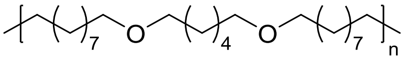
IR (ATR): *v* = 2915.8, 2848.1, 2803.3, 1463.8, 1380.0, 1259.7, 1111.8, 803.2, 719.5, 550.9 cm^{-1}, T_{m}= 69.4 °C.

Hydrogenated ADMET polymer P6b

Reactant: **P5b** (70.0mg, 0.199 mmol, 1.00 eq). The polymer was obtained as a grey powder (43.3 mg, 62%).

IR (ATR): *v* = 2915.8, 2848.0, 2803.7, 1462.9, 1380.4, 1259.2, 1111.6, 803.5, 729.8, 719.2, 551.1, 410.4 cm^{-1}, T_{m}= 76.3 °C.

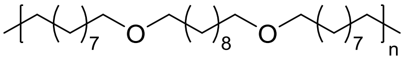
Hydrogenated ADMET polymer P6c



Reactant: **P5c** (4.00 g, 10.9 mmol, 1.00 eq). The polymer was obtained as a grey powder (2.95 g, 73%).

IR (ATR): *v* = 2916.9, 2848.3, 2799.3, 1485.7, 1470.1, 1375.5, 1189.3, 1112.2, 1031.3, 968.8, 805.7, 720.2, 544.2, 416.4, 390.4 cm^{-1}, T_{m}= 83.6 °C.

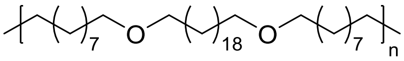
Hydrogenated ADMET polymer P6d



Reactant: **P5d** (70.0 mg, 0.166 mmol, 1.00 eq). The polymer was obtained as a grey powder (42.0 mg, 60%).

IR (ATR): *v* = 2917.6, 2848.6, 2798.9, 1733.6, 1647.2, 1485.0, 1463.3, 1374.6, 1261.0, 1113.6, 966.4, 804.0, 720.6, 547.6, 383.7 cm^{-1}, T_m= 88.2 °C.

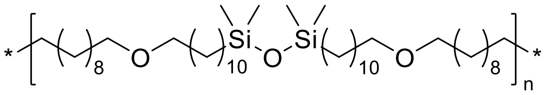
Hydrogenated ADMET polymer P6e



Reactant: **P5e** (70.0 mg, 0.126 mmol, 1.00 eq). The polymer was obtained as a grey powder (30.8 mg, 44%).

IR (ATR): *v* = 2916.9, 2848.4, 2798.9, 1733.3, 1647.6, 1463.5, 1375.2, 1261.6, 1115.3, 963.4, 802.4, 720.5, 542.1 cm^{-1}, T_m= 72.2 °C.

Hydrogenated ADMET polymer P6f



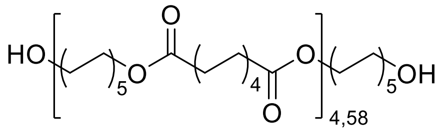
Reactant: **P5f** (337 mg, 0.448 mmol, 1.00 eq). The product was obtained as a grey sticky polymer (284 mg, 84%).

IR (ATR): *v* = 2918.7, 2850.8, 1466.5, 1256.7, 1018.1, 794.0, 719.9 cm^{-1}, T_m= 38.0 °C.

6.4 Procedures for: Non-Isocyanate Polyurethanes from Renewable long-chain Polyether Diols and Erythritol Bis(carbonate)

6.4.1 Polyether synthesis

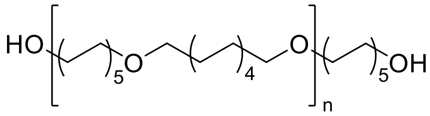
Poly(1,10-decamethylene sebacate) – OH end groups P1c.3



Dimethyl decanedioate (12.0 g, 52.7 mmol, 1.00 eq.), decane-1,10-diol (11.8 g, 67.7 mmol, 1.30 eq.) and titanium(IV) isopropoxide (148 mg, 0.0521 mmol, 0.01 eq.) were heated for 8 h at 5 mbar. The crude polymer was dissolved in hot THF and precipitated in MeOH at r.t. obtaining a white powder (19.3 g, 87%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ (ppm) = 4.04 (t, *J* = 6.7 Hz, 4 H, -CH_2-OOC-), 3.63 (t, *J* = 7.5 Hz, 4 H, -CH_2-OH end group), 2.28 (t, *J* = 7.5 Hz, 4 H, -CH_2-COO), 1.72 – 1.49 (m, 8 H, -CH_2-CH_2-OOC-, -CH_2-CH_2-COO-), 1.46 – 1.17 (m, 20 H, -CH_2-); IR (ATR): *v* = 2916.6, 2850.8, 1729.8, 1470.6, 1417.1, 1400.7, 1378.1, 1357.5, 1293.7, 1244.4, 1217.6, 1168.3, 1094.2, 1049.8, 999.9, 960.6, 919.4, 857.7, 750.8, 719.9, 586.2, 438.1 cm^{-1}.

Poly(oxy-1,10-decamethylene) - OH end groups P2c.3



Poly(1,10-decamethylene sebacate) **P1c.3** (15.0 g, 44.1 mmol, 1.00 eq.) was degassed in a Schlenk flask. CH_2Cl_2 (140 mL) was added and after 20 min. of stirring, $GaBr_3$ (230 mg, 0.743 mmol, 0.017 eq.) was added. After dropwise addition the sample was stirred for 12 h at r.t.. The solvent was removed *in vacuo* and the mixture was precipitated from DCM in methanol (1x) and afterwards in petrolether at -60 °C (4x). The product was obtained as a white powder (10.7 g, 78%).

^{1}H-NMR: (500 MHz, $CDCl_3$): δ (ppm) = 3.63 (t, *J* = 6.7 Hz, -CH_2OH, end group); 3.38 (t, *J* = 6.7 Hz, 4 H, -CH_2O-), 1.68 – 1.45 (m, 4 H, -OCH_2CH_2-), 1.42 – 1.11 (m, 12 H, -

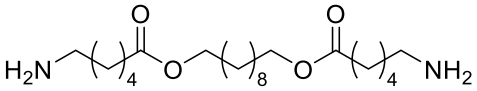
CH_2-); IR (ATR): 2929.0, 2916.6, 2850.8, 2801.4, 1593.2, 1487.1, 1464.5, 1376.0, 1260.8, 1102.4, 1022.2, 968.7, 913.3, 800.1, 719.9, 551.2.

6.4.2 Diamine synthesis

6.4.2.1 General procedure

MsOH (3.00 mmol, 3.00 eq.), TsOH (1.50 mmol, 1.50 eq.) and ε-caprolactam (4.00 mmol, 4.00 eq.) and the respective diol (1.00 mmol, 1.00 eq.) were heated overnight at 130 °C under N_2 atmosphere. After checking for full conversion (NMR-spectroscopy) the mixture was cooled down to room temperature. Water insoluble substrates were directly washed with Na_2CO_3 solution (3x) and water (2x) to separate the acids and remaining excess of ε-caprolactam.

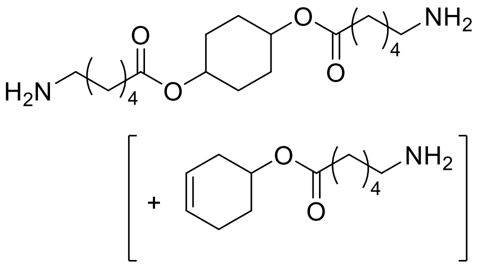
Decane-1,10-diyl bis(6-aminohexanoate) (45)



Reactants: MsOH (19.8 g, 207 mmol, 3.00 eq.), TsOH (19.7 g, 103 mmol, 1.50 eq.), *ε*-caprolactam (31.2 g, 275 mmol, 4.00 eq.), 1,10-decanediol (12.0 g, 68.9 mmol, 1.00 eq.). The crude product was washed with 100 mL Na_2CO_3 solution (1 M, 3x) and 100 mL water (2x) and obtained after filtration as a white solid (29.6 g, 106%, still containing chemically bound water e.g. as ammonium hydroxide).

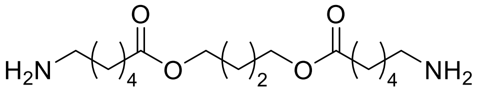
^{1}H-NMR (DMSO-d_6 + 1 drop of TFA, 300 MHz): δ (ppm) = 7.71 (bs, 6H, -NH_3^+), 3.99 (t, *J* = 6.6 Hz, 4H, -CH_2-O-CO-), 2.86 – 2.68 (m, 4H, -CH_2-NH_3^+), 2.28 (t, *J* = 7.3 Hz, 4H, -CH_2-COO-), 1.63 – 1.42 (m, 12H, -CH_2-CH_2-COO-, -CH_2-CH_2-NH_3^+, -CH_2-CH_2-O-CO-), 1.38 – 1.15 (m, 16H, -CH_2-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 172.9 (-*C*O-O-), 63.9 (-*C*H_2-O-CO-), 38.8 (-*C*H_2-NH_3^+), 33.3 (-*C*H_2-COO-), 30.0 (-*C*H_2-), 28.7 (-*C*H_2-), 28.3 (-*C*H_2-), 26.8 (-*C*H_2-), 25.5 (-*C*H_2-), 25.4 (-*C*H_2-), 24.0 (-*C*H_2-); HRMS (ESI) of $C_{22}H_{45}N_2O_4$ $[M+H]^+$ *m/z* calc. 401.33738, found 401.33603; HRMS (ESI) of $C_{22}H_{46}N_2O_5Na$ [M+H_2O+Na^+]: calc. 441.32989 found 441.36747; HRMS (ESI) of $C_{28}H_{56}N_3O_5$ (side product) $[M+H]^+$ *m/z* calc. 514.42145, found 514.42005; IR (ATR): *v* = 2913.7, 1851.0, 1729.9, 1571.6, 1437.3, 1408.4, 1271.9, 1236.4, 1173.2, 1033.3, 960.2, 903.6, 865.9, 816.9, 718.8, 687.0, 568.1, 471.6, 423.8 cm^{-1}.

Cyclohexane-1,4-diyl bis(6-aminohexanoate) (57)



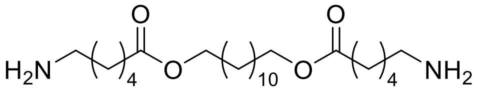
Reactants: MsOH (1.27 g, 13.2 mmol, 2.05 eq.), TsOH (1.84 g, 9.68 mmol, 1.50 eq.), *ε*-caprolactam (2.92 g, 25.8 mmol, 4.00 eq.), cyclohexane-1,4-diol (0.75 g, 6.46 mmol, 1.00 eq.). The conversion was checked by NMR-spectroscopy and the product was not isolated.

Butane-1,4-diyl bis(6-aminohexanoate) (58)



Reactants: MsOH (1.64 g, 17.1 mmol, 2.05 eq.), TsOH (2.37 g, 12.48 mmol, 1.50 eq.), *ε*-caprolactam (3.77 g, 33.3 mmol, 4.00 eq.), butane-1,4-diol (0.75 g, 8.32 mmol, 1.00 eq.). The conversion was checked by NMR-spectroscopy and the product was not isolated.

Tetradecane-1,14-diyl bis(6-aminohexanoate) (59)

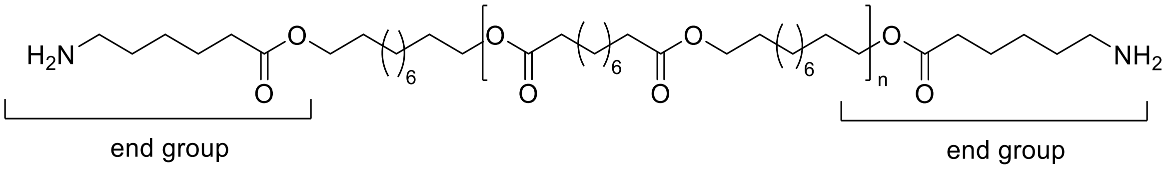


Reactants: MsOH (4.38 g, 45.6 mmol, 3.08 eq.), TsOH (4.23 g, 22.2 mmol, 1.50 eq.), ε-caprolactam (6.71 g, 39.3 mmol, 4.00 eq.), 1,12-dodecanediol (3.00 g, 68.9 mmol, 1.00 eq.). The crude product was washed with 50 mL Na_2CO_3 solution (1 M, 3x) and 50 mL water (2x) and obtained after filtration as a white solid (6.73 g, 105%, still containing chemically bound water e.g. as ammonium hydroxide).

^{1}H-NMR (DMSO-d$_6$ + 1 drop of TFA, 300 MHz): δ (ppm) = 7.67 (bs, 6H, -NH_3^+), 3.97 (t, *J* = 6.7 Hz, 4H, -C*H$_2$*-O-CO-), 2.86 – 2.63 (m, 4H, -C*H$_2$*-NH_3^+), 2.27 (t, *J* = 7.2 Hz, 4H, -C*H$_2$*-COO-), 1.67 – 1.41 (m, 12H, -C*H$_2$*-CH_2-COO-, -C*H$_2$*-CH_2-NH_3^+, -C*H$_2$*-CH_2-O-CO-), 1.41 – 1.10 (m, 20H, -CH_2-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 172.9 (-COO-

), 63.8 (-*C*H_2-OOC-), 38.8 (-*C*H_2-NH_3^+, overlaps with DMSO signal, identified in HSQC), 33.4 (-*C*H_2-COO-), 29.1 (-*C*H_2-), 28.8 (-*C*H_2-), 28.3 (-*C*H_2-), 26.8 (-*C*H_2-), 25.6 (-*C*H_2-), 25.5 (-*C*H_2-), 25.4 (-*C*H_2-), 24.0 (-*C*H_2-); HRMS (ESI) of $C_{22}H_{45}N_2O_4$ $[M+H]^+$ *m/z* calc. 429.36868, found 429.36740; IR (ATR): v = 3456.7, 2914.3, 2850.4, 1729.6, 1619.2, 1540.7, 1476.5, 1396.4, 1366.1, 1272.5, 1236.3, 1173.9, 1027.5, 966.1, 846.7, 817.6, 717.4, 574.5, 452.8, 397.3 cm^{-1}.

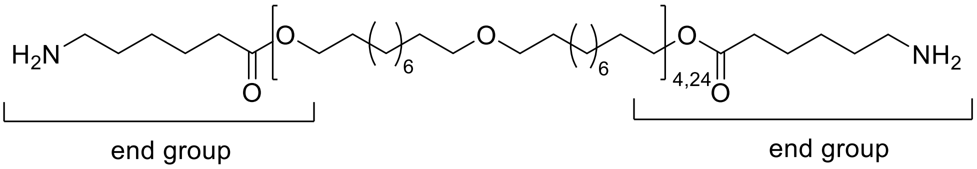
Poly(1,10-decamethylene sebacate)-diyl bis(6-aminohexanoate) (56)



Reactants: MsOH (0.546 g, 5.68 mmol, 2.05 eq.), TsOH (0.79 g, 4.19 mmol, 1.50 eq.), ε-caprolactam (1.25 g, 7.49 mmol, 4.00 eq.), poly(1,10-decamethylene sebacate) (3.00 g, 2.72 mmol, 1.00 eq.). The crude product was washed with 50 mL Na_2CO_3 solution (1 M, 3x) and 50 mL water (2x) and obtained after filtration as a white solid (2.38 g, 66%).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 4.44 (bs, 4H, NH_2), 4.04 (t, *J* = 6.8 Hz, 4H, -CH_2-OOC-), 3.62 (t, *J* = 6.5 Hz, residual unconverted end group), 2.86 – 2.68 (m, -CH_2-NH_3^+, end group), 2.27 (t, *J* = 7.5 Hz, 4H, -CH_2COO-), 1.74 – 1.42 (m, 8H, -CH_2-CH_2-COO, -CH_2-CH_2-O-CO-, (-CH_2-CH_2-NH_3^+ end group)), 1.42 – 1.08 (m, 24H, -CH_2-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 174.1 (-*C*OO-), 71.1 (-*C*H_2-OOC-), 64.7 (-*C*H_2-OOC-), 39.9 (-*C*H_2-NH_3^+, end group), 34.0 (-*C*H_2-COO-), 30.1 (-*C*H_2-), 29.9 (-*C*H_2-), 29.6 (-*C*H_2-), 26.3 (-*C*H_2-); IR (ATR): v = 2916.3, 2850.3, 1728.8, 1561.3, 1471.9, 1398.3, 1356.1, 1293.4, 1216.5, 1166.5, 1047.1, 999.9, 958.5, 920.0, 857.4, 749.8, 721.4, 567.8, 438.6 cm^{-1}.

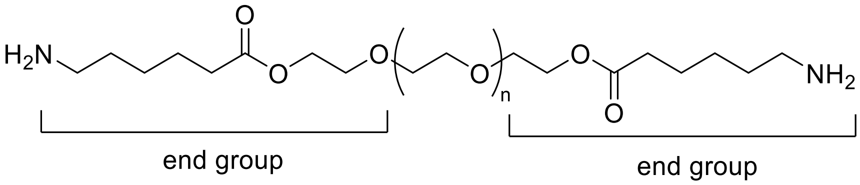
Poly(oxy-1,10-decamethylene)-diyl bis(6-aminohexanoate) (54)



Reactants: MsOH (0.369 g, 3.84 mmol, 2.05 eq.), TsOH (0.534 g, 2.81 mmol, 1.50 eq.), ε-caprolactam (0.847 g, 7.49 mmol, 4.00 eq.), poly(oxy-1,10-decamethylene) (3.00 g, 1.87 mmol, 1.00 eq.). The crude product was washed with 50 mL Na_2CO_3 solution (1 M, 3x) and 50 mL water (2x) and obtained after filtration as a white solid (3.24 g, 95%).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 3.98 (t, *J* = 6.8 Hz, -C*H₂*-O-CO-, end group), 3.31 (t, *J* = 6.7 Hz, 4H, -CH_2-O-), 2.99 – 2.68 (m, -C*H₂*-NH_3^+, end group), 2.33 – 2.17 (m, -C*H₂*-COO-, end group), 1.67 – 1.41 (m, 4H, -C*H₂*-CH_2-COO- end group, -C*H₂*-CH_2-NH_3^+ end group, -C*H₂*-CH_2-O-CO-, end group, -C*H₂*-CH_2-O-), 1.36 – 1.00 (m, 24H, -CH_2-); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 174.1 (-*C*OO-, end group), 71.1 (-*C*H_2-OOC-, end group), 64.7 (-*C*H_2-O-), 39.9 (-*C*H_2-NH_3^+, end group), 34.0 (-*C*H_2-COO-, end group), 30.1 (-*C*H_2-), 29.9 (-*C*H_2-), 29.6 (-*C*H_2-), 26.3 (-*C*H_2-); IR (ATR): *v* = 2917.0, 2849.9, 2800.5, 1735.0, 1647.7, 1468.4, 1375.5, 1179.4, 1114.4, 1047.9, 968.9, 719.9, 550.4, 398.4 cm^{-1}.

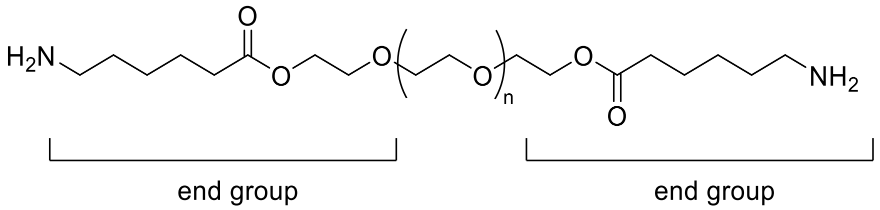
PEG1000-diyl bis(6-aminohexanoate) (60)



Reactants: MsOH (0.600 g, 6.23 mmol, 2.05 eq.), TsOH (0.867 g, 4.56 mmol, 1.50 eq.), ε-caprolactam (1.38 g, 12.2 mmol, 4.00 eq.), PEG1000 (3.00 g, 3.04 mmol, 1.00 eq.). The crude product was dissolved in 200 mL dichloromethane washed with 50 mL Na_2CO_3 solution (1 M, 3x) and 50 mL brine (2x), the aqueous phase was extracted with 100 mL DCM and the solvent was removed under reduced pressure. The residue was precipitated from 4 mL DCM in 200 mL cold Et_2O (-60°C) and the product was obtained as brown solid (3.68 g, 99%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 4.23 – 4.12 (m, -CH_2-O-CO-, end group), 3.71 – 3.64 (m, -CH_2-CH_2-O-CO-, end group), 3.62 – 3.45 (m, 4 H, O-CH_2-CH_2-O-,), 2.86 – 2.63 (m, -CH_2-NH_3^+, end group), 2.30 (t, *J* = 7.4 Hz, -CH_2-COO-, end group), 1.70 – 1.51 (m, 8H, -CH_2-CH_2-COO-, -CH_2-CH_2-NH_3^+, end group), 1.51 – 1.25 (m, -CH_2-, end group); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 173.6 (-*C*O-O-), 70.5 (O-CH_2-CH_2-O) 63.5 (-CH_2-O-CO-), 61.3 (-O-CH_2-CH_2-O-CO-), 41.7 (-CH_2-NH_3^+), 34.1 (-CH_2-COO-), 30.0 (-CH_2-), 26.3 (-CH_2-), 24.7 (-CH_2-); IR (ATR): *v* = 3320.8, 2859.8, 1730.4, 1634.6, 1544.0, 1467.3, 1342.6, 1279.2, 1239.6, 1143.8, 1105.6, 962.3, 841.2, 717.3, 527.8, 453.6, 396.2 cm^{-1}.

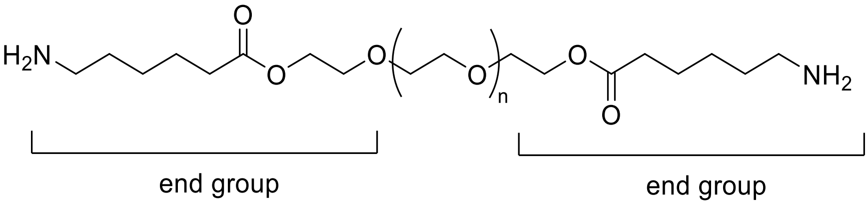
PEG6000-diyl bis(6-aminohexanoate) (61)



Reactants: MsOH (0.199 g, 1.24 mmol, 2.05 eq.), TsOH (0.173 g, 1.00 mmol, 1.50 eq.), ε-caprolactam (0.274 g, 2.42 mmol, 4.00 eq.), PEG6000 (3.00 g, 0.606 mmol, 1.00 eq.). The crude product was dissolved in 200 mL dichloromethane washed with 50 mL Na_2CO_3 solution (1 M, 3x) and 50 mL brine (2x), the aqueous phase was back extracted with 100 mL DCM and the solvent was removed under reduced pressure. The residue was precipitated from 4 mL DCM in 200 mL cold Et_2O (-60°C) and the product was obtained as brown solid (3.14 g, 87%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 4.33 – 4.09 (m, -CH_2-O-CO-, end group), 3.73 – 3.66 (m, -CH_2-CH_2-O-CO-, end group), 3.62 – 3.39 (m, 4 H, O-CH_2-CH_2-O-,), 2.88 – 2.50 (m, -CH_2-NH_3^+, end group), 2.49 – 2.30 (m, -CH_2-COO-, end group), 1.76 – 1.52 (m, 8H, -CH_2-CH_2-COO-, -CH_2-CH_2-NH_3^+, end group), 1.50 – 1.21 (m, -CH_2-, end group); IR (ATR): *v* = 2881.8, 1649.3, 1466.1, 1359.3, 1340.1, 1279.0, 1239.6, 1146.1, 1101.4, 1059.2, 946.1, 841.2, 528.3 cm^{-1}.

PEG10000-diyl bis(6-aminohexanoate) (62)

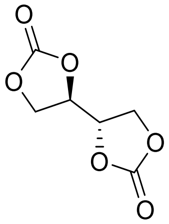


Reactants: MsOH (0.059 g, 0.614 mmol, 2.05 eq.), TsOH (0.085 g, 0.449 mmol, 1.50 eq.), ε-caprolactam (0.136 g, 1.20 mmol, 4.00 eq.), PEG10000 (3.00 g, 0.299 mmol, 1.00 eq.). The crude product was dissolved in 200 mL dichloromethane, washed with 50 mL Na_2CO_3 solution (1 M, 3x) and 50 mL brine (2x), the aqueous phase was back extracted with 100 mL DCM and the solvent was removed under reduced pressure. The residue was precipitated from 4 mL DCM in 200 mL cold Et_2O (-60°C) and the product was obtained as brown solid (3.14 g, 87%).

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 4.26 – 4.13 (m, -C*H₂*-O-CO-, end group), 3.79 – 3.66 (m, -CH_2-CH_2-O-CO-, end group), 3.62 – 3.44 (m, 4 H. O-CH_2-CH_2-O-,), 2.99 – 2.73 (m, -CH_2-NH_3^+, end group), 2.50 – 2.39 (m, -CH_2-COO-, end group), 1.70 – 1.51 (m, 8H, -CH_2-CH_2-COO-, -CH_2-CH_2-NH_3^+, end group), 1.55 – 1.16 (m, -CH_2-, end group); IR (ATR): *v* = 2879.8, 1466.2, 1359.4, 1340.5, 1279.0, 1240.0, 1146.2, 1096.6, 1059.1, 946.3, 841.1, 528.7 cm^{-1}.

6.4.3 Bis(carbonate) synthesis

Erythritol bis(carbonate) – standard procedure (EBC)



In a 500 mL flask, erythritol (24.0 g, 197 mmol, 1.00 eq) and TBD (1.37 g, 9.83 mmol, 0.05 eq.) were dispersed in 393 mL DMC and heated to 60 °C for 2 h at the rotary evaporator at 350 mbar. The crystalline erythritol dissolved completely after 30 min and after 2 h a white precipitate was formed. The product was filtered off after the mixture was cooled down to room temperature and washed with water yielding a white powder (30.7 g, 90%).

Erythritol bis(carbonate) – procedure for recycling of the reaction mixture

In a 50 mL flask, erythritol (2 g, 16.4 mmol, 1.00 eq) and TBD (114 mg, 0.820 mmol, 0.05 eq.) were dispersed in 33 mL DMC and heated to 60 °C for 1 h at the rotary evaporator at 350 mbar. The crystalline erythritol dissolved completely after 30 min and after 1 h the white precipitate was filtered off, after the mixture cooled down to room temperature. The powder was washed with DMC and the mother liquor was reused for another batch, for which the same procedure was applied.

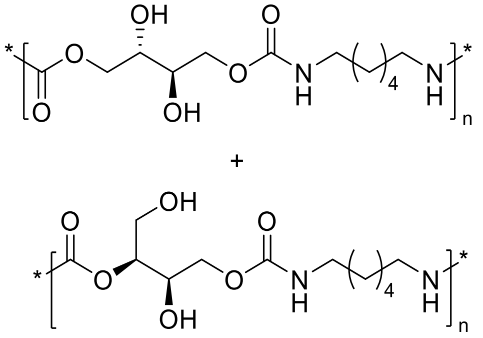
Yields:

Reaction cycle	Yield [%]	m [g]
1[a]	57	1.64
2	66	1.90
3	105	3.00
4[b]	105	2.99
5	100	2.84

^{1}H-NMR (DMSO-d_6, 300 MHz): δ (ppm) = 5.25 – 5.07 (m, 2H, CH), 4.69 – 4.52 (m, 2H, CH_2(a), diastereotopic signals), 4.47 – 4.31 (m, 2H, C*H*$_2$, diastereotopic signals); ^{13}C-NMR (DMSO-d_6, 75 MHz): δ (ppm) = 158.2 (*C*O), 74.9 (*C*H), 64.7 (-*C*H$_2$-); IR (ATR): *v* = 1803.7, 1779.0, 1545.5, 1476.1, 1381.2, 1299.6, 1206.5, 1144.6, 1067.0, 1030.9, 978.1, 896.2, 771.8, 739.1, 719.1, 532.1, 384.9 cm^{-1}.

6.4.4 Polymerizations

Polyurethane derived from HMDA and EBC – in DMSO



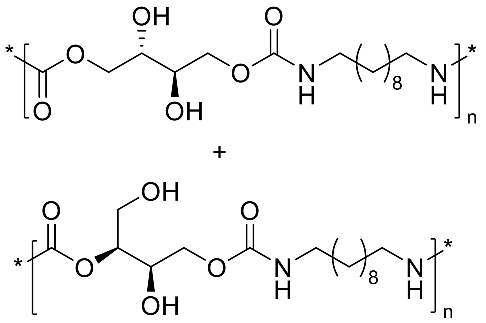
DMA (334 mg, 2.87 mmol, 1.00 eq.) and EBC (500 mg, 2.87 mmol, 1.00 eq.) were dispersed in 2.9 mL DMSO. The mixture was stirred at 120 °C overnight. The product was obtained as brown solid after precipitation in water (712 mg. 85%).

Polyurethane derived from HMDA and EBC – in toluene

HMDA (336 mg, 2.87 mmol, 1.00 eq.) and EBC (500 mg, 2.87 mmol, 1.00 eq.) were dispersed in 1.4 mL toluene in a pressure tube. Schreiner's Thiourea catalyst (13.6 mg, 0.026 mmol, 0.9 mol%) was added and the mixture was stirred at 120 °C overnight. The product was obtained as brown solid after filtration (825 mg. 99%).

^{1}H-NMR (DMSO-d_6, 300 MHz): δ (ppm) = 7.24 – 6.91 (m, 2 H, $NH_{(A)}$ signal splitting), 6.83 – 6.66 (m, 2 H, $NH_{(B)}$ signal splitting), 5.09 – 4.44 (m, 2H, -OH), 4.22 – 4.06 (m, NHCOO-CH_2), 4.01 – 3.68 (m, -CH-OH, sec. hydroxy), 3.64 – 3.45 (m, HO-CH_2-CH-, prim. hydroxy; ratio prim. hydroxy : sec. hydroxy 1.00 : 1.04), 3.07 – 2.81 (m, 4 H, -CH_2-NH-CO-), 1.52 – 1.07 (m, 8 H, -CH_2-), signal assignment was done according to lit.[286][286] and was not confirmed by 2D-NMR spectroscopy; IR (ATR): *v* = 3329.8, 2934.2, 1686.5, 1531.1, 1462.2, 1342.0, 1254.8, 1144.6, 1064.1, 892.0, 775.4, 618.9 cm^{-1}, T_m = 126.9 °C.

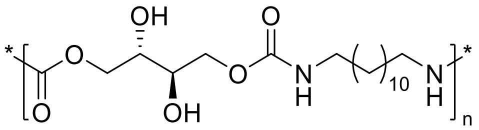
Polyurethane derived from DMA and EBC



DMA (495 mg, 2.87 mmol, 1.00 eq.) and EBC (500 mg, 2.87 mmol, 1.00 eq.) were dispersed in 2.9 mL DMSO. The mixture was stirred at 120 °C overnight. The product was obtained as brown solid after precipitation in water (867 mg. 87%).

^{1}H-NMR (DMSO-d$_6$, 300 MHz): δ (ppm) = 7.19 – 6.94 (m, 2 H, NH$_{(A)}$ signal splitting), 6.82 – 6.65 (m, 2 H, NH$_{(B)}$ signal splitting), 5.07 – 4.41 (m, 2H, -OH), 4.19 – 4.06 (m, NHCOO-CH$_2$-), 4.04 – 3.67 (m, -CH-OH, sec. hydroxy), 3.69 – 3.42 (m, HO-CH_2-CH-, prim. hydroxy; ratio prim. hydroxy : sec. hydroxy 1.10 : 1.00), 3.05 – 2.84 (m, 4 H, -CH_2-NH-CO-), 1.52 – 1.07 (m, 16 H, -CH_2-), signal assignment was done according to lit.[286][286] and was not confirmed by 2D-NMR spectroscopy; IR (ATR): ν = 3330.7, 2921.3, 2851.0, 1687.1, 1529.8, 1466.9, 1244.1, 1145.9, 1011.9, 952.1, 892.0, 776.3, 622.1 cm^{-1}, T$_g$ = 37 °C.

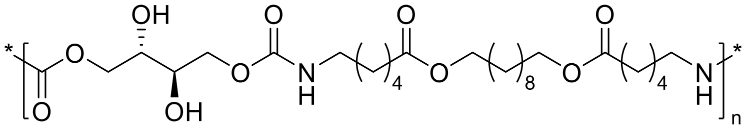
Polyurethane derived from DDA and EBC – in DMSO



DMA (575 mg, 2.87 mmol, 1.00 eq.) and EBC (500 mg, 2.87 mmol, 1.00 eq.) were dispersed in 2.9 mL DMSO. The mixture was stirred at 120 °C overnight. The product was obtained as brown solid after precipitation in water (807 mg. 75%).

^{1}H-NMR (DMSO-d$_6$, 300 MHz): δ (ppm) = 7.16 – 6.90 (m, 2 H, NH$_{(A)}$ signal splitting), 6.77 – 6.61 (m, 2 H, NH$_{(B)}$ signal splitting), 5.07 – 4.46 (m, 2H, -OH), 4.22 – 4.06 (m, NHCOO-CH$_2$-), 4.04 – 3.72 (m, -CH-OH, sec. hydroxy), 3.69 – 3.42 (m, HO-CH_2-CH-, prim. hydroxy; ratio prim. hydroxy : sec. hydroxy 1.01 : 1.00), 3.07 – 2.81 (m, 4 H, -CH_2-NH-CO-), 1.52 – 1.07 (m, 20 H, -CH_2-), signal assignment was done according to lit.[286][286] and was not confirmed by 2D-NMR spectroscopy; IR (ATR): *v* = 3327.7, 2919.1, 2850.1, 1687.0, 1531.1, 1467.2, 1241.7, 1146.6, 1058.5, 892.2, 776.6, 720.4, 619.6 cm^{-1}, T$_m$ = 126.9 °C.

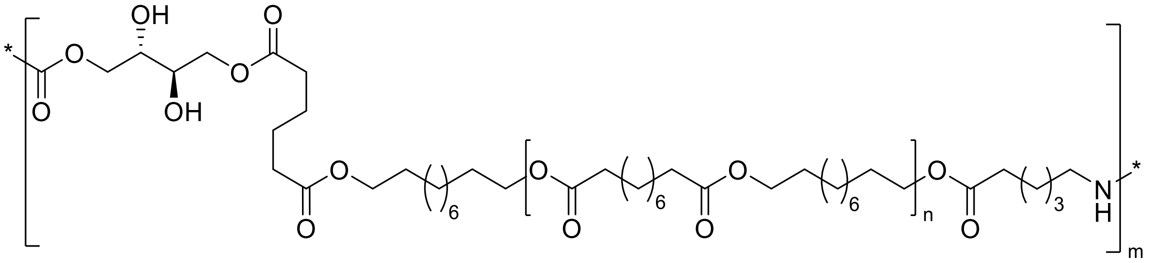
Polyurethane derived from decane-1,10-diyl bis(6-aminohexanoate) and EBC



Decane-1,10-diyl bis(6-aminohexanoate) **45** (300 mg, 0.576 mmol, 1.00 eq.) and EBC (100 mg, 0.576 mmol, 1.00 eq.) were dispersed in 1.9 mL of the respective solvent mixture. The mixture was stirred at 100 °C overnight. The product was obtained as brown solid after precipitation in water (yield for DMF/toluene mixture: 381 mg. 92%, other yields in Table 16), which is insoluble in chloroform or DMSO.

IR (ATR): *v* = 3337.9, 2919.0, 2852.2, 1725.9, 1687.6, 1532.3, 1465.7, 1417.2, 1357.2, 1256.6, 1167.2, 1065.4, 1034.4, 1004.4, 891.2, 777.4, 729.4, 621.5 cm^{-1}, T$_m$ = 79.1 °C.

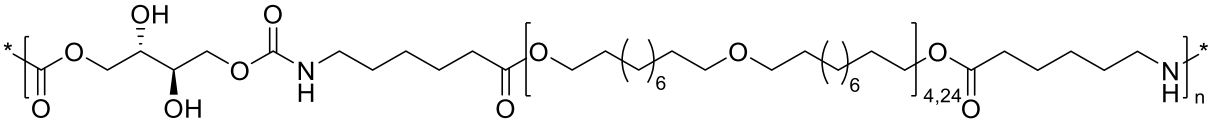
Polyurethane derived from poly(1,10-decamethylene sebacate)-diyl bis(6-aminohexanoate)



Poly(1,10-decamethylene sebacate)-diyl bis(6-aminohexanoate) **56** (300 mg, 0.229 mmol, 1.00 eq.) and EBC (39.9 mg, 0.229 mmol, 1.00 eq.) were dispersed in 0.6 mL DMSO. The mixture was stirred at 100 °C overnight. The product was obtained as brown solid after precipitation in water (203 mg, 60%), which is insoluble in HFIP, THF or chloroform.

IR (ATR): *v* = 3358.2, 2919.0, 2851.1, 1793.0, 1728.7, 1535.4, 1465.0, 1397.9, 1355.9, 1293.5, 1216.7, 1165.5, 1084.0, 1047.3, 1000.6, 958.4, 920.3, 857.3, 772.6, 721.6, 582.6, 438.5 cm^{-1}, T$_m$ = 74.9 °C.

Polyurethane derived from poly(oxy-1,10-decamethylene)-diyl bis(6-aminohexanoate)



Poly(1,10-decamethylene sebacate)-diyl bis(6-aminohexanoate) **54** (300 mg, 0.229 mmol, 1.00 eq.) and EBC (39.9 mg, 0.229 mmol, 1.00 eq.) were dispersed in 0.6 mL DMSO. The mixture was stirred at 100 °C overnight. The product was obtained as brown solid after precipitation in water (238 mg, 85%), which is insoluble in HFIP, THF or chloroform.

IR (ATR): v = 3356.4, 2917.1, 2850.1, 2800.4, 1733.6, 1541.7, 1468.0, 1374.4, 1259.9, 1169.8, 1111.7, 1046.5, 968.5, 802.6, 719.8, 549.4 cm^{-1}, T_m = 69.4 °C.

7 Appendix

7.1 Abbreviations

(dtbpx)Pd(OTf)$_2$	Bis(trifluoromethanesulfonato){1,2-bis(di-tert-butylphosphinomethyl)benzene)}palladium(II)
[bdmim]- [NTf$_2$]	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
2-Methyl-THF	2-Methyltetrahydrofuran
Ac_2O	Acetic anhydride
ACHN	1,1′-Azobis(cyclohexanecarbonitrile)
ADMET	Acyclic diene metathesis
AE	Atom economy
AgOTf	Silver trifluoromethanesulfonate
AIBN	Azobisisobutyronitrile
ATMET	Acyclic triene metathesis
bCC	*bis*-Cyclic carbonates
BnOH	Benzyl alcohol
BPA	Bisphenol A
C	Conversion
CAAC	Cyclic (alkyl)(amino)carbene
Cat.	Catalyst
CHD	Cyclohexadiene
CM	Cross metathesis
COSY	Correlation spectroscopy
Cp_2TiF_2	Difluorobis(cyclopentadienyl)titanium
CPL	*ε*-Caprolactam
DABCO	1,4-Diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicycloundec-7-ene
DCB	1,4-Dichlorobut-2-ene
DCM	Dichloromethane
DDA	1,12-Dodecamethylenediamine
DFS-1,6-AA	Dimer fatty acid-based diamidoamine
DIBAL-H	Diisobutylaluminium hydride
DIPP	2,6-diisopropylphenyl
$Đ_M$	Dispersity
DMAc	Dimethylacetamide
DMC	Dimethyl carbonate
DMDA	1,10-Decamethylenediamine
DMF	Dimethylformamide
DMPA	2,2-Dimethoxy-2-phenylacetophenone

DMSO	Dimethyl sulfoxide
DP	Degree of polymerization
DPC	Diphenyl carbonate
DSC	Differential scanning calorimetry
E	E-factors
EBC	Erythritol bis(carbonate)
EI	Electron Ionization
EO	Ethylene oxide
Eq	Equivalents
Et	Ethyl
Et_2O	Diethyl ether
FAB	Fast atom bombardment
FAME	Fatty acid methyl ester
GC	Gas chromatography
GC-MS	Gas chromatography–mass spectrometry
G-I	Grubbs 1st generation catalyst
G-II	Grubbs 2nd generation catalyst
G-III	Grubbs 3rd generation catalyst
GPC	Gel permeation chromatography
HFIP	Hexafluoroisopropanol
HG-I	Hoveyda-Grubbs 1st generation catalyst
HG-II	Hoveyda-Grubbs 2nd generation catalyst
HMDA	1,6-hexamethylenediamine
HSQC	Heteronuclear single quantum correlation
IMes	1,3-Dimesitylimidazol-2-ylidene
IPDA	Isophoronediamine
^iPr	Isopropyl
IR	Infrared
$M7_1$	Umicore catalyst $M7_1$
Me	Methyl
MeOH	Methanol
MS	Mass spectrometry
MsOH	Methane sulfonic acid
NHC	*N*-Heterocyclic carbene
NIPU	Non-isocyanate polyurethane
NMR	Nuclear magnetic resonance
OCDA	1,8-Octamethylenediamine
p	Pressure
PE	Poly(ethylene)
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)

PHA	Poly(hydroxyalkanoates)
PHB	Poly(hydroxybutyrate)
PHU	Poly(hydroxy urethane)
PMHS	Poly(methylhydrosiloxane)
PMP	1,2,2,6,6-Pentamethylpiperidine
POE	Poly(oxyethylene)
Polarclean	Methyl-5-(dimethylamido)-2-methyl-5-oxopentanoate
PPO	Poly(propylene oxide)
Pr	Product
PTMO	Poly(tetramethylene oxide)
PU	Polyurethane
RCM	Ring-closing metathesis
ROCOP	Ring-opening copolymerization
ROM	Ring-opening metathesis
ROMP	Ring-opening metathesis polymerization
ROP	Ring-opening polymerization
$Ru(acac)_3$	Ruthenium(III) acetylacetonate
$_{SC}CO_2$	Supercritical CO_2
SEC-ESI MS	Size-exclusion chromatography electrospray ionization mass spectrometry
SiPr	1,3-Bis(2,6-diisopropylphenyl)imidazolinium
SM	Self metathesis
$Sn(Oct)_2$	Tin(II) 2-ethylhexanoate
T	Temperature
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TBO	(1R,5S)-2,4,7-Trioxa-3-oxy-bicyclo[3.3.0]octane
THF	Tetrahydrofuran
Ti(^{i}PrO)	Titanium isopropoxide
TLC	Thin-layer chromatography
TMDS	1,1,3,3-Tetramethyldisiloxane
TMHMDA	2,2-Dimethyl-4-methylhexamethylenediamine
TMSOTf	Trimethylsilyl trifluoromethanesulfonate
TON	Turnover number
triphos	1,1,1-Tris(diphenylphosphinomethyl)ethane
TsOH	*p*-Toluene sulfonic acid
UV	Ultraviolet
Y	Yield

7.2 List of publications

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