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Renewable Polymers for Adhesives from Levulinic Acid and Polyester Upcycling

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Bernhard M. Stadler

Rostock, den 21.07.2020

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Kurzzusammenfassung

Der Großteil der Chemikalien die in unsrem tagtäglichem Leben eine Rolle spielen werden momentan aus Erdöl und anderen fossilen Rohstoffen hergestellt. Der Zeitpunkt, an dem diese Rohstoffe versiegen, ist immer wieder Gegenstand zahlreicher Debatten. Fakt ist, das durch die Natur ihrer Entstehung die Reservoirs endlich sind. Daneben wird durch die Nutzung dieser Rohstoffe eine nicht zu unterschätzende Menge CO_2 in die Biosphäre künstlich eingebracht was im beobachtbaren Klimawandel resultiert. Unter diesen Gesichtspunkten ist langfristig die schrittweise Substitution fossiler mit erneuerbaren Rohstoffen notwendig. Adhäsive repräsentieren hier einen interessanten Einstiegspunkt. Klebstoffe sind in fast allen Bereichen unseres modernen Lebens allgegenwärtig. Sie basieren in der Regel auf reaktiven Monomeren oder Oligomeren mit vernetzbaren Endgruppen. Ziel dieser Dissertation war es daher ausgehend von der bio-basierten Plattformchemikalie Lävulinsäure die Entwicklung neuartiger Poly- und Oligomere als potenzielle Bausteine für Adhäsive und Beschichtungen.

Im Rahmen der Arbeit konnte gezeigt werden das sich das Lävulinsäure Derivat β-Angelicalacton mittels atomeffizienter Diels-Alder Reaktionen in bicyclische Verbindungen überführen lässt. Diese wiederum sind hoch reaktive Monomer in Ringöffnungsmetathese Polymerisationen. Aus den resultierenden Polymeren lassen sich hochtransparente Filme herstellen und könnten durch ihre Polarität interessante Materialen für die Beschichtung von Oberflächen darstellen.

Aus 1,4-pentandiol, einer Diol-Komponente, die durch die Reduktion von Lävulinsäure erhalten werden kann, konnten neuartige hydroxylterminierte Polyesterpolyole durch Polykondensation mit bio-basierten Dicarbonäuren erhalten werden. Der niedrige Schmelzpunkt der kristallinen Materialen ermöglicht die Entwicklung von biobasierten Formgedächtnispolymeren mit sehr niedrigen Schalttemperaturen. Dies könnte als wärmeempfindliche Klebstoffe in der Verpackung von temperaturempfindlichen Gütern, wie Pharmazeutika Anwendung finden.

2-Methyltetrahydrofuran (2-MeTHF) ein weiteres Lävulinsäure Derivat das wegen seiner geringen Reaktivität als bio-basiertes Lösemittel diskutiert wird konnte mit Propylenoxid zu OH-terminierten Polyether umgesetzt werden. Hierbei wurden die Reaktionsbedingungen durch die Kombination eines Empirischen Models und *in-situ* IR Spektroskopie so optimiert das die Bildung zyklischer Oligomere nur in Spuren erfolgt. Weiterhin könnte gezeigt werden, dass der Einbau von 2-MeTHF in die wachsenden Polymerkette durch Alkylierung dieses mit PO erfolgt. Die Zusammensetzung der erhaltenen Polyetherpolyole wurde intensiv mittels Massenspektroskopie untersucht. Diese 2-MeTHF enthaltenen Polyole stellen somit in der Entwicklung von Klebstoffen eine interessante Alternative zu PPG und *poly*-THF dar.

Im letzten Teil der Arbeit wird auf die Problematik der immer größer werdenden Menge an Plastikabfall eingegangen. Ein Teil der Lösung könnte sogenanntes Upcycling zu höherwertigen Produkten sein. Für Polyester wurde ein Upcycling Konzept mittels Reduktion durch Wasserstoff zu Polyetherpolyolen für Adhäsive entwickelt. Dies gelingt mittels Rutheniums katalysierter Hydrogenierung in Gegenwart von Lewissäuren.

Abstract

The majority of the chemicals that play a role in our daily lives are currently made from petroleum and other fossil raw materials. The point at which these raw materials run dry is unclear. The fact is that the nature of their creation makes these reservoirs finite. In addition, the use of these raw materials artificially introduces a considerable amount of CO_2 into the biosphere. As CO_2 is potent greenhouse gas global warming is the consequence of its emission. From this point of view, the gradual substitution of fossil and renewable raw materials is necessary in the long term. Adhesives represent an interesting entry point here, since adhesives are omnipresent in almost all areas of our modern life. They are usually based on reactive monomers or oligomers with functional end groups. Based on the bio-based platform chemical levulinic acid, the aim of this dissertation was to develop novel poly- and oligomers as potential building blocks for adhesives. In addition, the smaller size and higher value-added nature of these products makes the transition from large scale production based on fossil raw materials production based on renewable raw materials easier.

In the course of the work it could be shown that the levulinic acid derivative β-angelica lactone can be converted into bicyclic compounds using atom-efficient Diels-Alder reactions. These in turn are highly reactive monomers in ring-opening metathesis polymerizations. Highly transparent films can be produced from the resulting polymers and due to their polarity, could represent interesting materials for coating surfaces.

From 1,4-pentanediol, which can be obtained by the reduction of levulinic acid, novel hydroxyl-terminated polyester polyols could be obtained by polycondensation with bio-based diacids. The low melting point of the crystalline materials enables the development of bio-based shape memory polymers with very low switching temperatures. This could be used as heat sensitive adhesives in the packaging of temperature sensitive goods such as pharmaceuticals.

2-methyltetrahydrofuran (2-MeTHF), another levulinic acid derivative that has been discussed as a bio-based solvent due to its low reactivity, could be co-polymerized with propylene oxide to an OH-terminated polyether. By optimizing the catalyst and the reaction conditions based on the input obtained from the combination of an empirical model and *in-situ* IR spectroscopy it was possible to suppress the formation of cyclic oligomers. Furthermore, it could be shown that 2-MeTHF is incorporated into the growing polymer chain by alkylating it with PO. The composition of the polyether polyols obtained was examined in detail by means of mass spectrometry. These 2-MeTHF polyols represent an interesting alternative to poly-propyleneglycol (PPG) and poly THF in the development of adhesives.

In the last part of the work, the problem of the ever-increasing amount of plastic waste is discussed, which is strongly related to the lack of economic recycling methods. Part of the solution could be so-called upcycling to higher value products. An upcycling concept was developed for polyesters by means of reduction to polyether polyols that can be used in adhesives. This was achieved using ruthenium-catalyzed hydrogenation in the presence of Lewis acids.

List of Abbreviations

1,4-PDO		1,4-Pentandiol
2-BuOH		2-Butanol
2-MeTHF		2-Methyltetrahydrofuran
ACEM		Activated chain end mechanism
AL		Angelica lactone
AMM		Activated monomer mechanism
Conv.	[%]	Conversion
CSTR		Continuous stirred tank reactor
$Đ$	[$M_w M_n^{-1}$]	Dispersity
ESI		Electro spray ionization
F_{break}	[N mm^{-2}]	Strength at break
F_{max}	[N mm^{-2}]	Ultimate strength
G	[kJ mol^{-1}]	Gibbs free enthalpy
GPC		Gel permeation chromatography
GVL		γ-Valerolactone
H	[kJ mol^{-1}]	Enthalpy
HMF		Hydroxymethylfurfural
LA		Levulinic acid
MEK		Methylethylketone
ML		Methy levulinate
M_n	[g mol^{-1}]	Number average molecular weight
MS		Mass spectroscopy
MTBE		Methyl tert-butyl ether
M_w	[g mol^{-1}]	Average molecular weight by weight
p	[bar]	Relative pressure
PO		Propylene oxide
Q	[cm^3 min^{-1}]	Volume flow
Ref.		Reference
ROP		Ring opening polymerization
S	[J K^{-1}]	Entropy
S/C		Substrate to catalyst ratio

Sel.	[%]	Selectivity
Sub.		Substrate
T	[°C]	Temperature
$T_{ceiling}$	[°C]	Ceiling temperature
T_g	[°C]	Glass transition temperature
THF		Tetrahydrofuran
T_m	[°C]	Melting temperature
w.r.t.		With respect to
Δ		Difference
ε_{break}	[%]	Elongation at break
ε_{max}	[%]	Maximum elongation
θ	[°]	Contact angle

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1 Introduction

The necessity to connect different materials together and consequently the usage of adhesives is almost as old as the onset of tool manufacturing.[1] These first glues merely consisted of tars obtained by the pyrolysis of birch wood[2] or the combination of bee's wax with ochre.[3] It was already possible to influence the properties of these prehistoric glues to some extent by adding various kinds of additives (eg. iron oxide for improved mechanical stability). The next development was the use of hydrolyzed collagen from animal's hide and bones, with the earliest reported use in the ancient city of Thebes in Egypt.[4] In the 16 century the first commercial animal glue production plant started operation in Holland. However, it was not until the early 1900s that synthetic adhesives were developed. Commonly regarded as the first type of these materials are the phenol formaldehyde resins which were prepared accidentally or intentionally by Baeyer and Baekeland.[5] The work of Baekeland additionally established these polymers as molding materials and glue for wood veneers. Over the last century the petrochemical industry enabled the large-scale production of a plethora of building blocks to produce a variety of adhesives.

In general, there are two basic characteristics of adhesives.[5, 6] First, they must be sufficiently fluid to rapidly cover the surface of the substrate. When the two substrates are brought together afterwards there needs to be a hardening or curing mechanism which dramatically increases viscosity or solidifies the adhesive, so that the two pieces are held together by their respective molecular interaction with the adhesive. These interactions can be covalent or hydrogen bonds, or ionic or Van der Waals forces.[7] The hardening can be achieved by cooling a molten thermoplastic polymer (hotmelt), evaporation of a solvent or by crosslinking.[5, 8] This allows to classify them in different categories (Table 1).

Table 1: Categories of adhesives

Adhesive category	Mechanism of curing	Examples
Solution/Dispersion	Evaporation of solvent	Polyurethanes
Hotmelt	Cooling and solidification of polymer melt	Polyesters, Polyamides
1-Component	External triggers: Heat, Moisture, (UV)-Light	Polysilanes, Acrylics, unsaturated polyesters, diisocyanate end capped polyols
2-Components	Mixing prepolymer and a hardening agent	Polyols + tri- and diisocyante, Epoxides + Amines
Pressure sensitive	Tackiness of adhesive surface	Polyacrylates, rubbers

Aside from hotmelts or pressure sensitive adhesives, other important classes are the single- and two- component reactive adhesives.[8] In single component adhesives functional groups are crosslinked by an exposure to an external trigger. For instance, acrylates can be used as single-component adhesives by curing them with UV-light. In contrast, two-component adhesives require the addition of a crosslinking agent, often containing thiols, isocyanates or, in recent research, the combination of a cyclic carbonate and a diamine.[9-14] In most cases these curable end-groups are tethered to an oligomer, which is usually a polyester or polyether polyol.[15] Polyols used in adhesives have much lower molecular weight (<10 kg mol^{-1}) than the polymers typically encountered in plastics,[15, 16] which ensures the aforementioned required fluidity in the pre-cured state. Currently, these oligomers are mainly produced by oxidative processes from petrochemical feedstocks. In view of the fact that adhesives are

used in almost every product there is a consideration to derive them and polymers in general from renewable feedstocks.[17-22] This is largely driven by the necessity to slow down the climate change and the increasing environmental public awareness. Ideally, they would be entirely made from bio-based resources which would not disturb the ecological carbon balance. However, currently 95% percent of chemical products originate from crude oil or natural gas. Novel technologies allow the access of previously unreachable reservoirs of fossil resources, but their depletion is inevitable. Renewable feedstocks should be gradually incorporated in the production of chemicals to solve this problem.

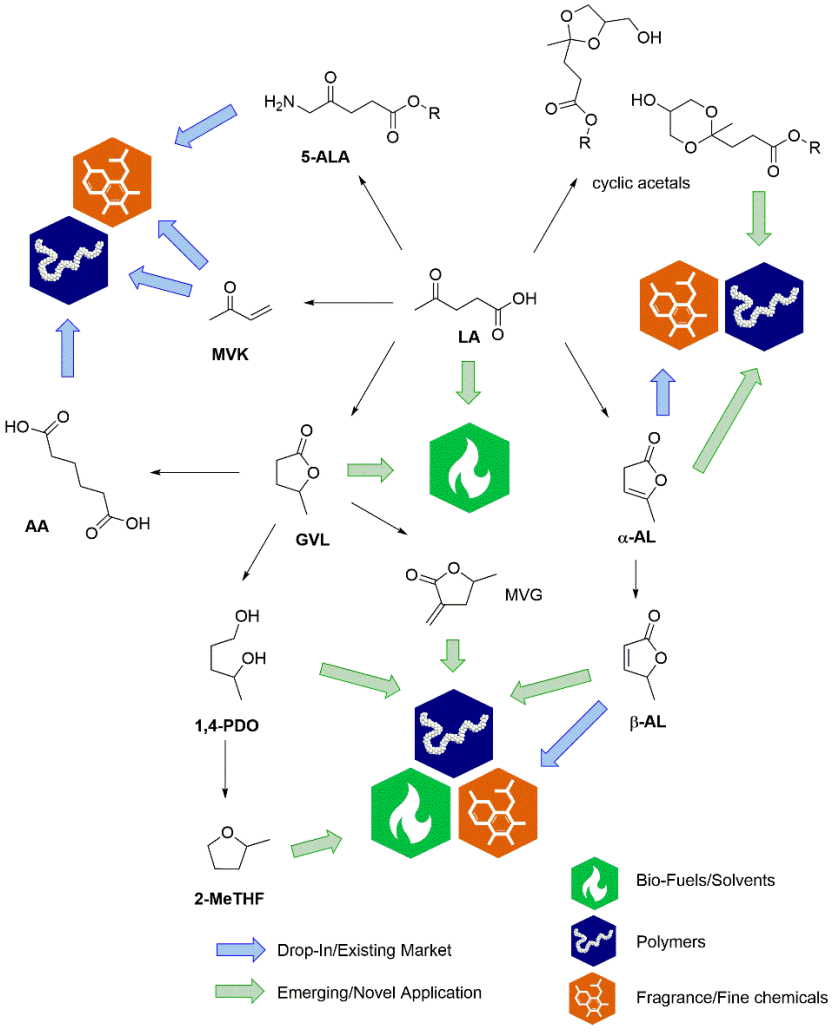


Figure 1: Levulinic acid as a platform chemical for the production of chemicals for existing or novel applications

This can be achieved by using so-called bio-based platform chemicals. The term platform chemical refers to a small molecule that can be produced in high yields from bio-based raw materials such as lignocellulose or sugars by fermentation or thermocatalytic reactions.[23, 24] Due to their origin from biomass these molecules contain a much higher number of oxygen atoms compared to petrochemical feedstocks. This can make the production of certain chemicals more efficient as less or no oxidation steps are needed.[25] One of the most important compounds here is levulinic acid (**LA**) since it can be readily convert to a huge diversity of chemicals. These are either drop-in chemicals for which there are already existing markets. For instance, the herbicide amino levulinic acid **(5-ALA),**[26] the monomer and building block methyl vinyl ketone (**MVK**)[27, 28] and the monomer adipic acid (**AA**)[29] can be obtained from bio-based LA. Another example is the application of levulinic acid derived products such as 2-methyl tetrahydrofuran (**2-MeTHF**),[30] levulinates[31] and γ-valerolactone (**GVL**)[32] as potential biofuels.

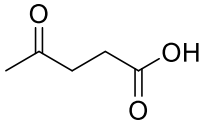
These drop-in compounds need to be able to compete on price with the petrochemical products. And since this will only be possible once they are produced on bulk scale (≥100 000 Ton/y) companies are very reluctant to invest these vast sums of money in their production. A starting point for including more and more renewable feedstocks in the chemical industry can be the introduction of so-called emerging products that can enable novel applications or have some other benefits beyond renewability that merit a higher price at lower volumes.[33] As mentioned earlier, polyesters and polyethers play a huge part in the adhesives world. Consequently, the derivates of levulinic acid could be a possible entry point for biomass to this market. They first part of this thesis therefore will deal with the synthesis and the integration of the LA derivate angelica lactone into polymers as well as that of the hydrogenation products 1,4-pentanediol (**1,4-PDO)** and 2-MeTHF.

In addition to global warming due to the usage of fossil resources, the rising standard of living of many people combined with the population increase leads to the production of an ever-increasing amount of plastic waste. This plastic waste can be seen as an alternative renewable resource.[34] The second part of the introduction will highlight the scope and the gravity of the problem and discuss several strategies for polymer recycling. In section 2 an approach to obtain polyether polyols for adhesives and polyurethanes from waste will be shown.

1.1 The Bio-based Platform Chemical Levulinic Acid

1.1.1 Synthesis and Applications of Levulinic acid (LA)

As previously mentioned levulinic acid (LA) (Figure 2) is one of the top 12 platform chemicals for the biorefinery concept according to the US Department of energy. The compound belongs to the class of γ-keto acids and is considered relatively safe to handle as no toxicity or mutagenic effects have been observed in mammals.[35, 36] The presence of a ketone and an acid function allows for the formation of a wide range of possible products.



Levulinic acid (LA)

CAS: 123-76-2

$C_5H_8O_3$

M: 116.12 g mol^{-1}

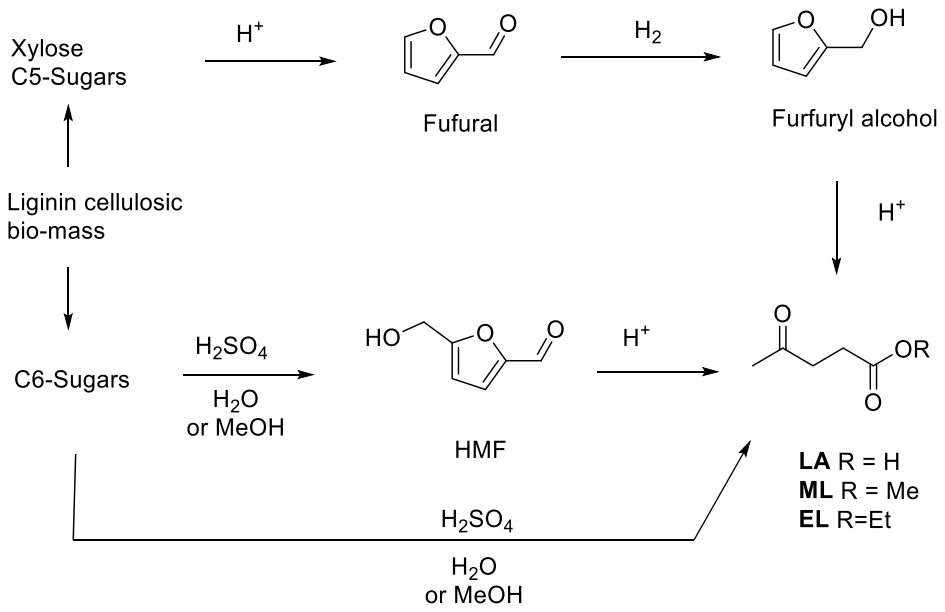
T_m=33-34°C

T_b=245°C

Figure 2: Levulinic (LA) acid and its properties. From left to right: A food grade sample of crystalline LA (99%), structural representation and selected properties

In 1840 levulinic acid (LA) was discovered by the Dutch chemist Gerardus J. Mulder when he was heating sugars in the presence of aqueous sulfuric acid.[37] In 1965 LA was for the first time reviewed in detail as raw material.[38] Furthermore, this early report already highlights the straightforward conversion of LA to alpha angelica lactone (α-AL) and γ-valerolactone (GVL) as solvents and building blocks. However, it was also pointed out that cellulose can be converted to LA, but the yield was only around 40%. Later it was discovered that LA can be obtained from non-edible lignocellulosic bio-mass mainly via three routes, that can be more or less interconnected depending on the feedstock used (Scheme 1).[39-41] One way is the hydrolysis of hemi cellulose to pentoses which in the presence of an

acid can be converted to furfural.[40] Commercial processes are conducted between 150°C-190°C and yield typically 50% of furfural based on the content of pentoses in the feed.[42] Under laboratory conditions yields of over 90% were achieved.[43] Currently, the market size of furfural is about 370 kt y^{-1} with the majority of this amount produced in China from corncob.[44]



Scheme 1: Routes to levulinc acid(esters) from lignocellulosic biomass

Table 2: Examples of the synthesis of LA, ML or EL using various substrates derived from lignocellulosic biomass

Entry	Substrate	Conditions	Catalyst	Yield [%]	Ref.
1	Furfuryl alcohol	125 °C, EtOH	ZSM-5	65 (EL)	[45]
2	Furfuryl alcohol	120 °C, 0.5 h ,THF/H_2O(4/1)	H-ZSM-5	73 (LA)	[46]
3	Furfuryl alcohol	120 °C, 2 h, H_2O	3 wt% $ArSO_3H$-Et-HNS[a]	83 (LA)	[47]
4	Furfuryl alcohol	130 °C, 2 h, MeOH	(0.6 mol%)[BMIM-HSO_4]Cl -H_2SO_4[b]	94 (ML)	[48]
5	Rice husk	60 °C, 56 bar, 70 min	4.5% (v/v) HCl	55 (LA)	[49]
6	Wheat straw	120°C, 2h -> 200°C, 0.5 h	1.2% w/w HCl	77 (LA)	[50]
7	Poplar sawdust	120°C, 2h -> 200°C, 0.5 h	1.2% w/w HCl	71 (LA)	[50]
8	Tobacco chops	120°C, 2h -> 200°C, 0.5 h	1.2% w/w HCl	83 (LA)	[50]
9	Cellulose	150 °C, 2 h, H_2O	1 M aq. H_2SO_4	54 (LA)	[51]
10	Fructose	140 °C, 8 h	6.7% Amberlyst 15	56 (LA)	[52]
11	Fructose	100 –120°C, 3h	H_2SO_4 (96-98%)	94 (LA)	[53]
12	Glucose	155 °C, 5 h	[BMIM-SO_3H]Cl-$NiSO_4$[c]	56 (LA)	[54]
13	5-HMF	170 °C, 5h	[C_3SO_3Hmim]HSO_4[d]	93 (LA)	[55]
14	5-HMF	98 °C, 3 h	1 M aq. H_2SO_4	94 (LA)	[56]

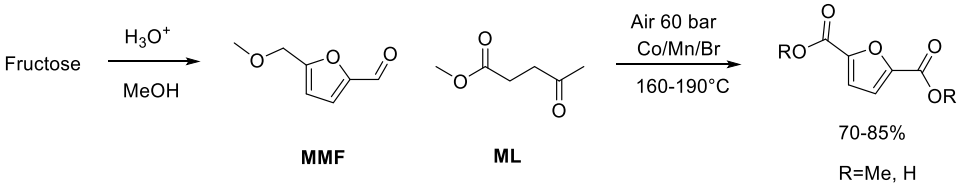
[a]Arene sulfonic acid organosilica nanospheres; [b]1-butyl-3-methylimidazolium hydrogen sulfate mixed with sulfuric acid; [c]1-(4-sulfonic acid)butyl-3-methylimidazolium chloride mixed with $NiSO_4$, [d]1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate; [e]yield of the product shown in brackets (LA=Levulinic acid, ML=Methyl levulinate, EL=Ethyl levulinate)

Alternatively, small amounts of furfural are available as a side stream from the paper industry. It can be extracted from the sulfite liquor, which is used to separate the lignin and hemicellusolic fraction from the cellulose.[57] About half of the produced furfural is then hydrogenated to furfuryl alcohol (FA).[44] The hydrogenation to FA is rather straightforward. The typical heterogeneous hydrogenation catalysts can be used, for example Cu-Cr or Ir-Re catalyst afford the product in high yields and selectivities (96-99%).[43] Furfuryl alcohol can then be dehydrated in the presence of acids to levulinic acid or its esters if an appropriate alcohol is used as solvent instead of water (Table 2, Entries 1-4). The typical side products in this reaction are humins (or furan resins) which are inevitably formed by the action of acid on furfuryl alcohol.[42] The deposition of these resins on heterogeneous acid catalysts such as H-ZSM may result in their inhibition.[46] Thus, more recent protocols use ionic liquids or polymeric Brønsted acids which increase the yield.[47, 48]

Alternatively, LA can be directly produced via acidic treatment of cellulose, fructose, glucose or directly from lignocellulosic biomass (Table 2, Entries 5-9). Especially the fact that LA can be directly made from bio-mass without any intermediate[50] helps to cement its pivotal role in the bio-refining concept. The company Bio-fine is very well known for the introduction of a scalable process to produce LA. It was demonstrated in two pilot plants. This process consists of the following steps[58]:

- At first the feedstock is ground and mixed with dilute sulfuric acid (1.5-3%)
- Hydrolysis - In this step conversion to levulinic acid, formic acid and biochar occurs
- Concentration of the product and separation of formic acid
- Separation of LA by crystallization which allows the mineral acid to be recycled.

Characteristic for this process is that the hydrolysis step is further subdivided into two stages.[59, 60] The first stage is typically run in a plug-flow reactor at 210-220 °C and 25 bar with a residence time of 12 seconds. The purpose of this stage is to convert to the bio-mass feed to soluble products (pentoses, hexoses and HMF).[50] The formation of levulinic acid mainly occurs in the second stage which is typically conducted in a CSTR. The temperature here is between 190 -200 °C and the residence time is about 20 minutes. Final yield of LA of the complete process is about 50%, which might be not as good as in the examples shown in Table 2. However, the process itself is rather robust, uses cheap catalysts and can tolerate a variety of different feedstocks. Furthermore, the produced formic acid can also be sold as profitable coupling product.[58] The first commercial-scale plant to use the Bio-fine process was set up in Caserta, Italy. The plant never produced any levulinic acid due to clogging of the first reactor.[51]



Scheme 2: Avantiums YXY-process for the production of furandicarboxylic acid(esters) in two steps from fructose

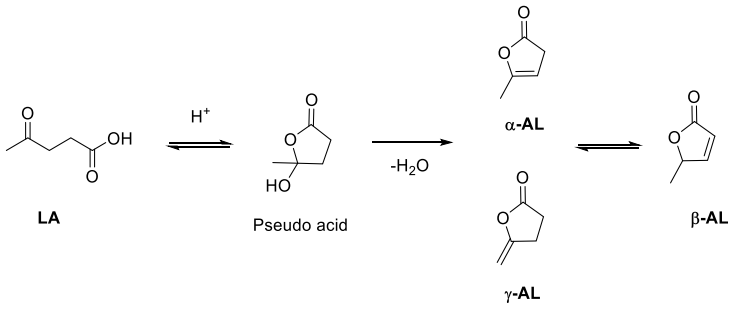
Another alternative source of levulinates are their formation as side products in the preparation of other bio-based chemicals. For example, Avantium has recently developed a process for the production of furandicarboxylic acid/ester from fructose (YXY-Process) via the methoxy ether derivate of HMF (5-methoxymethyl furfural, MMF) (Scheme 2).[27, 61] ML occurs here as the side product in the

first step – i.e. during acid catalyzed dehydration of fructose to MMF. Oxidation of MMF yields furandicarboxylic acid.[62]

GFBiochemicals recently announced that they intend to build a 30 kt plant for levulinic acid production, although it remains unclear which technology will be used.[63]

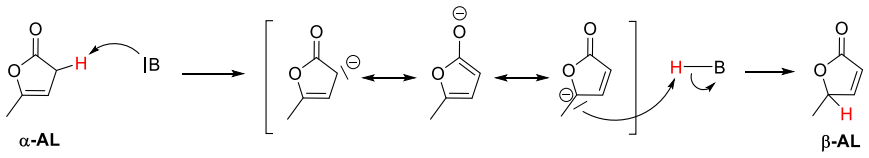
1.1.2 Conversion of LA to Angelica Lactones (AL) and their Polymerization

Angelica lactones were first described by Ludwig Wolf who observed their formation upon distillation of levulinic acid.[64] Owing to their coconut like odor these compounds are used in the flavor and fragrance industries. Angelica lactones can be obtained by reactive distillation of LA in the presence of an acidic catalyst as shown in Scheme 3. First LA reacts via an intramolecular ring closing reaction to a pseudo acid.[38] This is an unstable compound under the distillation conditions and quickly eliminates water to form α-angelica lactone (α-AL) and small quantities of the γ-isomer (<5%). Both isomers can further isomerize to β-AL.[28, 38, 65] In this way α-AL can be relatively easily obtained by distilling levulinic acid in the presence of phosphoric acid (1% w/w) at 160 °C and a pressure of 0.02 bar. The yield that can be obtained under these conditions is typically around 95%.[66]



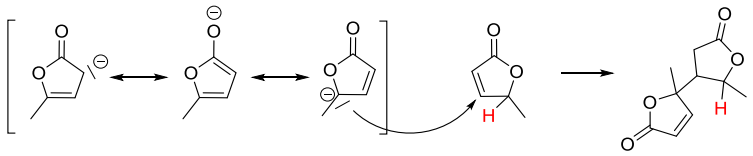
Scheme 3: Conversion of levulinic acid (LA) to angelica lactones

When α-AL is exposed to bases, it can be isomerized to β-AL which is very attractive reaction from an atom economic perspective. At first, deprotonation of the lactone in the α-position with respect to the ester moiety occurs. This leads to the formation of an intermediary 5-methylfuran-2-olate. Then reprotonation in the γ-position leads to the formation of β-AL. (Scheme 4). If sterically demanding and enantiopure bases are used, this isomerization can be done enantioselective.[67]



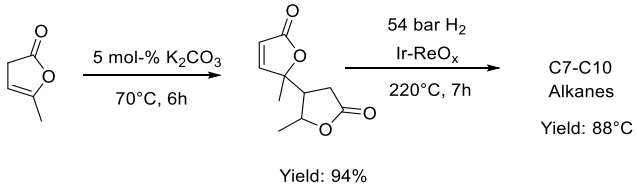
Scheme 4: Isomerization of α-AL to β-AL by proton transfer through a base (B)

However, the synthesis of β-AL in good yield and high purity is surprisingly challenging. At the moment, there is no synthesis protocol described in the literature that gives high yields of β-AL at high conversions of α-AL. The β-AL is isolated typically in yields of 40-60%.[67-69] First this might be the result of an equilibrium between the two isomers. Second the formed β-AL can react with unconverted α-AL to form a dimer via Michael-Addition (Scheme 5). In 2014 the group of Mascal showed that this reaction proceeds in nearly quantitative yield if potassium carbonate is used as the base.[70] Subsequently, they used this dimer to obtain jet-fuel type branched alkanes via its hydrodeoxygenation in the presence of heterogeneous iridium-rhenium oxide catalyst. About 70% of the obtained alkanes had 10 carbon atoms, and the rest contained between 7 and 9 (Scheme 6).



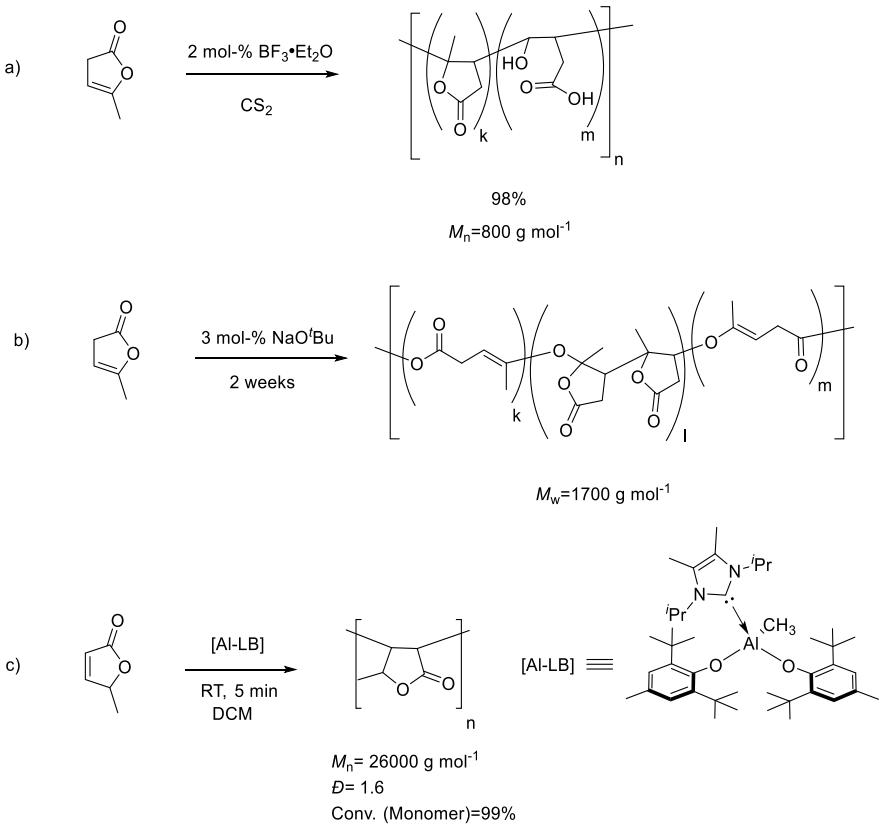
Scheme 5: Dimerization of the angelic lactone isomers via Michael-Addition

This indicates that decarboxylation is a significant pathway under the reaction conditions. Besides this there are also numerous examples were α-AL and β-AL are used in the synthesis of complex organic molecules like natural products. To describe this is beyond the scope of this thesis and the interested reader is referred to a recent review by Corrêa and co-workers.[71]



Scheme 6: Synthesis and conversion of the angelica lactone dimer to fuels

There is also some interest in using α-AL as a monomer for polymers since it has two functionalities – an ester and a vinyl ether group. Radical polymerization has not yet been described but cationic and anionic polymerizations are possible. Cationic polymerization of α-AL was first carried out using 2 mol-% $BF_3 \bullet Et_2O$ and yielded sticky yellow resins which consist on average of 10 monomer units connected by C-C bonds (Scheme 7a).[72]

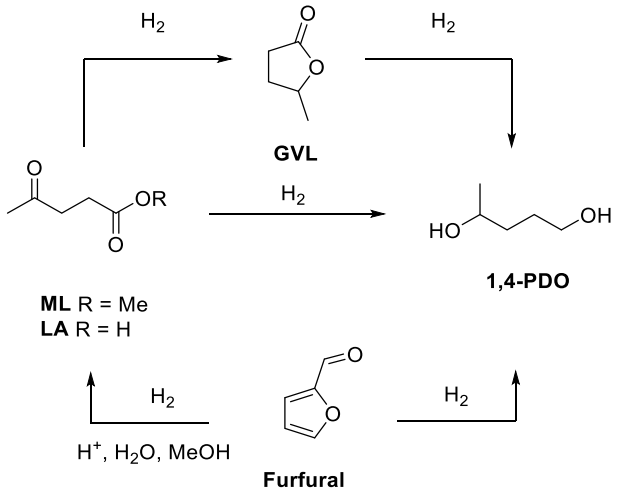


Scheme 7: Polymerization of the angelica lactones: a) Cationic polymerization of the α-AL, b) anionic polymerization of the α-AL and c) coordinative polymerization of β-AL using a Lewis-Pair as catalyst

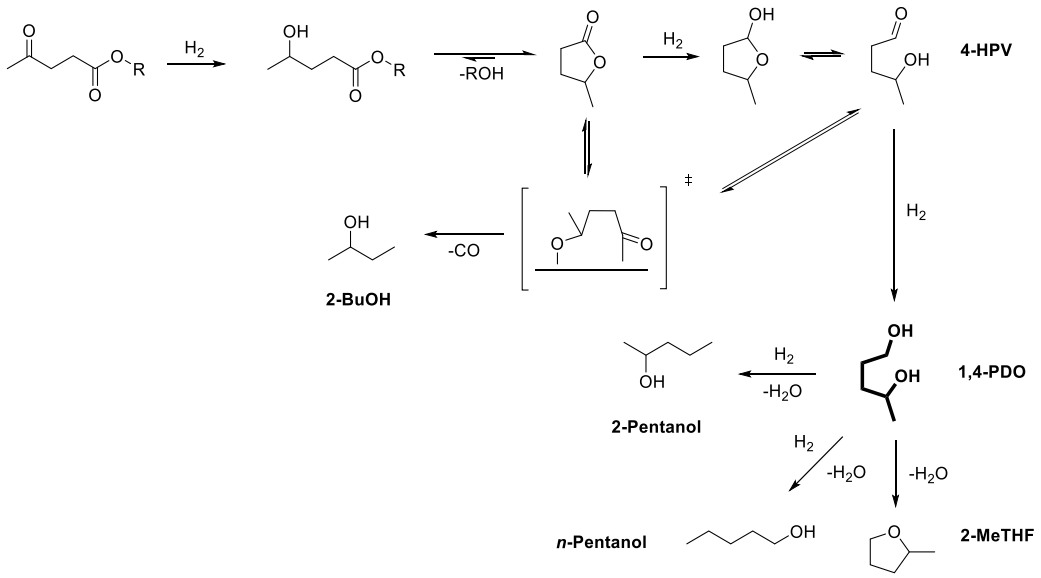
About 25% of the lactone moieties attached to the polymer's back-bone are hydrolyzed, presumably, during the aqueous work-up. While cationic polymerization proceeds almost exclusively via the vinyl ether moiety of α-AL,[72, 73] anionic polymerization also results in the partial ring opening of the lactone.[73] When NaO^{t}Bu is used as initiator, molecular weights of 1700 g mol^{-1} are achievable (Scheme 7b). This seems to be the maximum average molecular weight one can reach using this approach as the authors let the polymerization experiment run for 2 weeks.[73] Further analysis revealed that the polymer consists of around 68-80% of bonds formed by the ring-opening of the lactone. The rest (20-32%) consisted of chains connected via C-C bonds.[73 74] These C-C bonds might form in a similar fashion like in the in dimerization (Scheme 5). The β-isomer on the other hand was mainly used in several natural product syntheses. Surprisingly, no polymerization studies can be found in the literature on this molecule aside from the very recent work of the group of Hong, where the authors managed to polymerize β-AL via the C=C bond to acrylic macromolecules.[75] Using a Lewis-Pair adduct as catalyst they were able to convert β-AL to polymers with an average molecular weight of 26 kg mol^{-1} with a relatively low polydispersity of 1.6 and nearly quantitative conversion of the monomer (Scheme 7c). In addition, they also employed other initiators, but either no polymer formation was observed (AIBN, radical polymerization), or much lower molecular weights (ca. 5 kg mol^{-1}) were achieved ($B(C_6F_5)_3$). The Lewis-Pair they used is relatively active which allows the polymerization to be complete in around 5 minutes. On the downside this seems to make the catalyst rather sensitive to impurities or moisture as all the polymerizations were conducted inside a glove box.

1.1.3 Synthesis of 1,4-pentanediol (1,4-PDO)

The first interest in 1,4-PDO dates back to the era of World War II when it was investigated as a potential renewable precursor to 1,3-pentadienes as monomers for rubber production.[76] Here copper-chromium based heterogenous catalysts were used to obtain 1,4-PDO via the hydrogenation of levulinic acid (LA), its methyl ester or γ-valerolactone (GVL). However, the conditions were rather fierce as temperatures in the range of 190-300°C and hydrogen pressures of 100-260 bar were used resulting in a maximum yield of 72% from ethyl levulinate. Besides these routes based on GVL, LA and its esters, new catalytic approaches are also able to convert furfural to 1,4-PDO. Scheme 8 shows these routes. In the following section these different routes are described and discussed. Both heterogenous and homogenous catalysts can be used for the conversion of either levulinates or GVL. With heterogenous catalysts a complex reaction network has been identified,[77-80] which is shown in Scheme 9.



Scheme 8: Routes to 1,4-PDO from bio-based platform chemicals



Scheme 9: Observed reaction network in the hydrogenation of levulinates or GVL to 1,4-PDO

With all catalysts the ketone moiety of LA or its esters is hydrogenated first which yields hydroxyl valerates. The later ones are in in equilibrium with the lactone GVL. This equilibrium depends on the nature of the solvent, but the high thermodynamic stability of GVL[81] should always favor its formation in high concentration.[82, 83] Experimental work by the group of Palkovits[78] using Ru/C indicate that GVL can undergo decarbonylation to 2-butanol (2-BuOH) at temperatures over 160°C. When no solvent is present the yield of 2-BuOH can be as high as 36% when Ru/C is used as a catalyst at 190°C. Resasco and co-workers showed that this side reaction can be suppressed if a source of CO is added to the reaction mixture.[77] Although CO itself did not seem to have any effect, the addition of increasing amounts of methanol correlated which a reduced formation of 2-BuOH. Further DFT calculations indicate that the formation of 2-BuOH occurs via a metal acyl intermediate on the Ru surface, which is formed by the ring opening of GVL.[77, 84] Alternatively, GVL (formed in-situ or as a substrate) can be hydrogenated to the corresponding hemiacetal which is in equilibrium with 4-hydroxypentanal (4-HPV). 1,4-PDO is then formed by the reduction of the aldehyde functionality. However, 4-HPV can also form the aforementioned metal acylide and undergo decarbonylation to 2-BuOH.[78, 79] The product (1,4-PDO) can then undergo three different decomposition pathways. First dehydration can occur which leads to the formation of 2-MeTHF.[77-80] The other two pathways are hydrodeoxygenation reactions which result in the formation of 2-pentanol or n-pentanol depending on the position where the water loss occurs.[78, 79] Interestingly, 2-pentanol is formed in larger amounts than n-pentanol, which is surprising taking into consideration that primary alcohols are usually more difficult to hydrodeoxygenate than secondary ones.

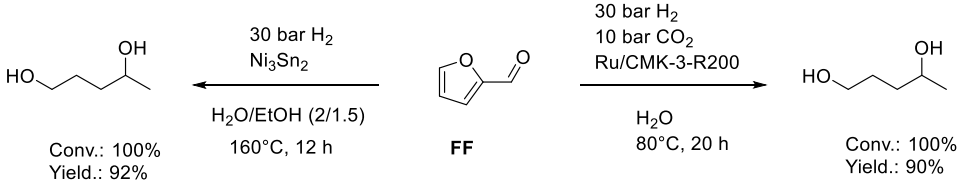
Consequently, the rather complicated reaction network and the potential value of 1,4-PDO as building block led to the development of sophisticated catalysts. Table 3 shows recent reports of highly selective hydrogenation of GVL, LA and EL to 1,4-PDO. The performance of the "working-horse" ruthenium on carbon (Ru/C) is shown for GVL and LA. Notably most of the catalysts for the hydrogenation of LA and its esters that exhibit high selectivities towards 1,4-PDO are bimetallic, with an exception of gold supported on titanium dioxide (Table 3, entry 8). Ruthenium in combination with molybdenum oxide on carbon can reach a selectivity of up to 97% at a conversion of >99% at temperature of only 70 °C (Table 3, entry 5).

Table 3: Heterogeneous catalysts for the synthesis of 1,4-PDO from GVL or levulinates

Entry	Catalyst	Sub.	T [°C]	p(H2) [bar]	S/C[a]	Conc. (Solvent) [mol l^{-1}]	Conv.[b] [%]	Sel.[b] [%]	Ref.
1	Ru/C	GVL	190	100	428	-	41	6	[78]
2	Ru/C	GVL	200	69	32	0.1 (Water)	29	9	[77]
3	Ru/C	LA	100	40	-[c]	Water	99	75	[79]
4	Re-Ru	LA	240	150	2290	Water	80	>99	[85]
5	Ru–MoO_x/C	LA	70	40	-[c]	Water	>99	97	[79]
6	Pt-$Mo_{0.25}$/ $Ca_5(PO_4)_3(OH)$	LA	200	30	50	Water	97	93	[86]
7	Cu/ZrO_2	GVL	200	30	10	0.5 (Ethanol)	100	>99	[87]
8	Au/TiO_2	LA	200	50	50	-	100	>99	[88]
9	Cu-$Al_{0.22}$-$Zn_{0.03}$	EL	160	60	1.02	0.1 (1,4-Dioxane)	100	98	[89]
10	Cu_2Co_1/Al_2O_3	EL	160	50	151	0.25 1,4-Dioxane	>99	93	[90]

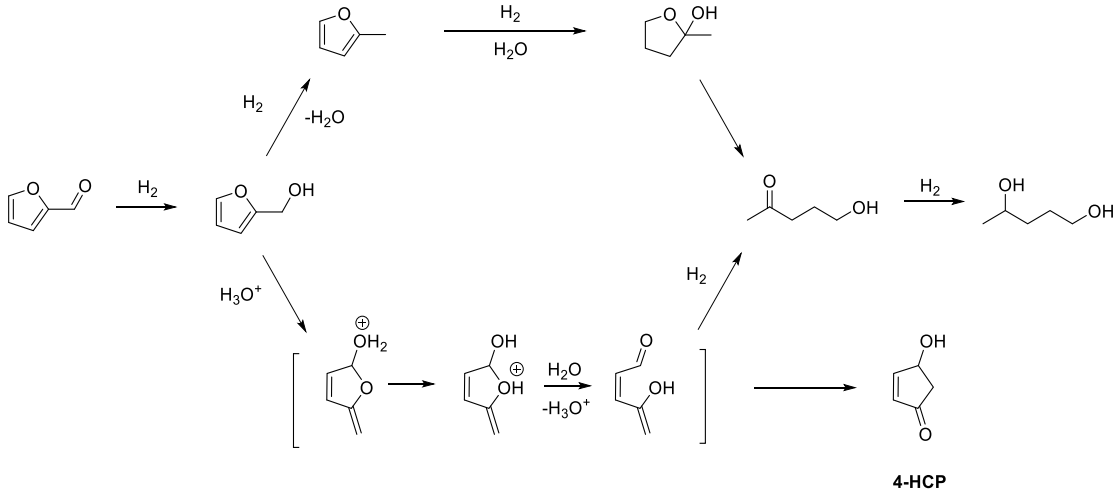
[a]S/C=Substrate/Catalyst[b] Conv. = Conversion, at which the selectivity to 1,4-PDO was the highest; Sel. = Selectivity; [c]Metal content of the catalyst was not stated by the authors

It is worthwhile to mention that the hydrogenation here is conducted in water which is a good solvent for LA. On top of that it is capable of suppressing the formation of 2-MeTHF, which occurs via dehydration of the desired product. Alternatively, platinum together with substoechiometric amounts of molybdenum (w.r.t. Pt) supported on hydroxyapatite also provides good selectivity[86] at comparable hydrogen pressures to Ru–MoOx/AC (40 vs. 50 bar) but requires the use of higher temperatures (200 vs. 70 °C) (Table 3, entries 5 & 6). In the attempt to use non-noble metal-based catalysts it was found by Fan and co-workers that copper supported on zirconium oxide can quantitatively hydrogenate GVL to 1,4-PDO at 200°C and 30 bar of H_2 gas in ethanol as solvent.[87] However, the substrate to catalyst ratio was rather low (Table 3, entry 7). Another promising copper-based catalyst are Raney type materials[89] that can be obtained by treating a Cu-Al-Zn alloy with a sodium hydroxide solution (Table 3, entry 9). Here the hydrogenation of ethyl levulinate to 1,4-PDO was possible with a selectivity of up to 98% at full conversion at 50 bar of hydrogen and an intermediate temperature of 160°C. On the downside a rather high amount of catalyst (Substrate vs. Copper) had to be employed. It was shown in this work that lowering the amount of catalyst had a negative impact on the selectivity. Another recent work by Wu *et al.* investigated the use of bimetallic copper-cobalt nanocomposites in the hydrogenation of EL.[90] They found that in order to obtain optimum selectivity Cu and Co must be deposited on Al_2O_3 in a 2:1 ratio. Physically mixing Cu and Co supported on Al_2O_3 only gave a selectivity of 29% as opposed to 93% with the bimetallic catalyst (Table 3, entry 10).



Scheme 10: Conditions used in the direct selective hydrogenation of furfural (FF) to 1,4-PDO

There is also some interest in the direct reduction of furfural to 1,4-PDO. The main products with most heterogenous catalysts are 1,5-PDO and 1,2-PDO and the selectivity towards 1,4-PDO is usually 23% at most at full furfural conversion.[40] Nevertheless, ruthenium supported on ordered mesoporous carbon (Ru/CMK-3-R200)[91] used by Liu *et al.* as well as a Ni-Sn alloy developed by Rodiansono *et al.* showed that with the right reaction conditions it is possible to obtain 1,4-PDO in high yields (see Scheme 10). Although achieved yields and conversions were similar with both catalytic systems the reaction sequences seem to be quite different (Scheme 11). In the presence of the Ni_3Sn_2 catalyst furfuryl alcohol (FA) undergoes hydrodeoxygenation to 2-methylfuran (**2-MF**). 2-MF is initially hydrogenated in the 4- and 5-position, followed by hydration (Scheme 11, *vide supra*). This hemiacetal intermediate can subsequently form 4-hydroxypentanone, that in turn is readily hydrogenated to 1,4-PDO. In contrast when the hydrogenation protocol using Ru/CMK-3-R200 in combination with CO_2, FA undergoes a Piancatelli rearrangement[92, 93] (Scheme 11, *vide infra*). In the absence of hydrogen this yields 4-hydroxycyclopentanone (4-HCP), as demonstrated by the authors. Under hydrogenation conditions however the enol intermediate is hydrogenated to 1,4-PDO in 90% yield.



Scheme 11: Proposed reaction pathways of hydrogenation of furfural catalyzed by different heterogenous catalysts. The top pathway takes place when Ni3Sn2 catalyst is used. The bottom pathway corresponds to Ru/CMK-3-R200 catalyzed hydrogenation of furfural.

In addition, GVL and levulinates are also frequently included in studies using homogenous hydrogenation catalysts. Catalysts that achieve yields of more than 90% of 1,4-PDO are shown in Figure 3, and the reaction parameters are given in Table 4. Usually pressures of H_2 ranging from 30-100 bar and temperatures between 25-140°C are used. Most catalysts are sensitive towards acidic impurities and levulinic acid itself as they either need to be activated by a base or must contain an acid-labile ligand such as BH_4 or CH_2-Si$(Me)_3$. Exceptions to this are the ruthenium complexes bearing a triphos ligand (**C1**) (Table 4, entries 1-3). This makes them quite versatile and enables the hydrogenation of GVL, LA and ML. In all three cases the hydrogenation with this type of catalysts was conducted at 140°C which is substantially higher temperature than the one used with precatalysts which require an alkoxide as activator. For example, the PNNN complex (**C2**) introduced by Zhou and co-workers achieved a remarkable TON of 90000 in the hydrogenation of GVL at only 25°C (Table 4, entry 4). Notable examples for non-noble metal catalysts capable of converting GVL to 1,4-PDO are the iron (**C3**) and manganese (**C4**) catalysts (Table 4, entries 6 & 7) developed by the group of Beller and the cobalt complex (**C6**) prepared by Jones and co-workers. With the later a TON of 920 in 5 hours in absence of a solvent could be achieved.

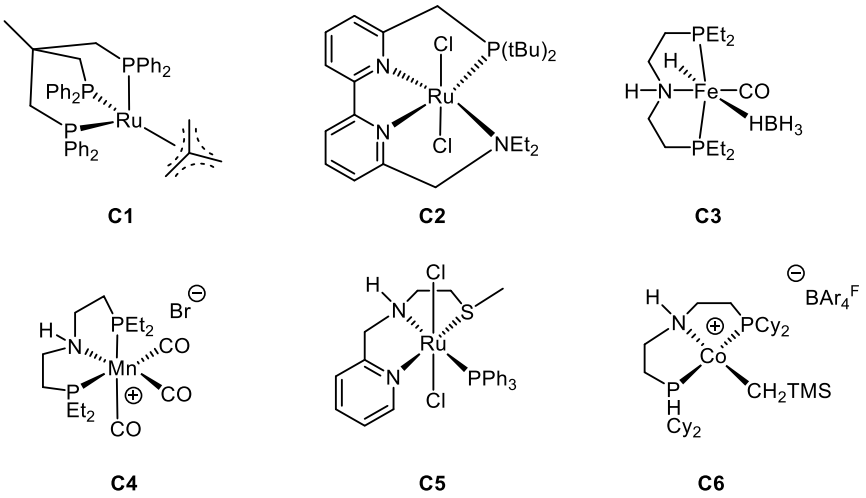


Figure 3: Precatalysts for the homogenous hydrogenation of LA, ML and GVL to 1,4-PDO with reported yields of over 90%

Table 4: Reaction parameters under which the complexes listed in Figure 3

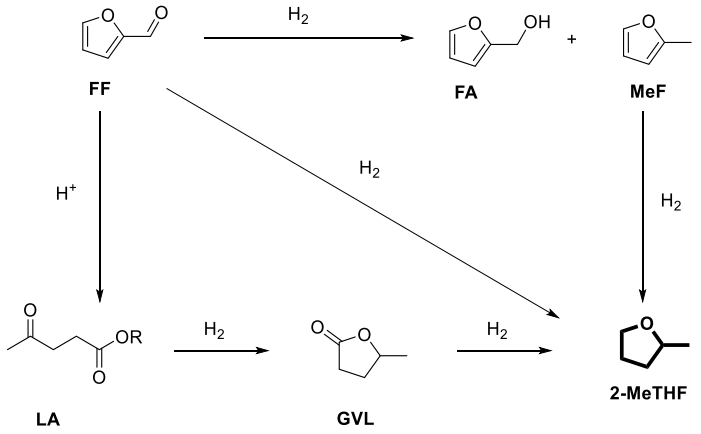
Entry	Complex	Substrate (S/C)	Additive	Solvent	$p(H_2)$ [bar]	T [°C]	t [h]	Yield [%]	Ref.
1	**C1**	GVL (100)	-	THF	75	140	16	99[a]	[94]
2	**C1**	ML (100)	-	THF	75	140	16	99[a]	[94]
3	**C1**	LA (50)	-	1,4-Dioxane	50	140	16	98[a]	[94]
4	**C2**	GVL (100000)	NaOMe (10 mol-%)	*i*PrOH	100	25	48	90	[95]
5	**C2**	ML (1000)	NaOMe (10 mol-%)	*i*PrOH	50	25	6	97	[95]
6	**C3**	GVL (50)	-	THF	30	100	18	98	[96]
7	**C4**	GVL (33)	KOtBu (10 mol-%)	1,4-Dioxane	30	110	24	95[a]	[97]
8	**C5**	GVL (2000)	KOtBu (2.5 mol-%)	-	60	80	2	91	[98]
9	**C6**	GVL (1000)	-	-	55	120	5	92	[99]

[a]*Determined by GC or NMR; others are isolated yields*

In summary, many reasonably selective heterogenous hydrogenation catalysts for the synthesis of 1,4-PDO from levulinic acid, its esters and GVL have been developed. In addition, the first reported results on the selective direct hydrogenation of furfural to 1,4-PDO are very promising for setting up a possible bulk production. On the other hand, many of these catalysts are not commercially available and require high loadings. Of course, these are no limitations when they are used in continuous processes, but it creates difficulties in the synthesis of 1,4-PDO in batch mode. The production of small batches of the diol is needed to initiate the polymer development. As shown in this section this gap can be bridged using one of the homogenous hydrogenation catalysts.

1.1.4 2-Methyltetrahydrofuran (2-MeTHF) – Synthesis, Application and potential Polymer Development

As discussed in the previous section, 2-MeTHF can be formed from 1,4-PDO via a simple dehydration reaction. For example, the diol can be readily converted to 2-MeTHF under distillation conditions in the presence of Nafion in 90% yield.[100] At the moment 2-MeTHF is made from 2-methylfuran (MeF) as a side product which forms during the production of FA from furfural (FF).[42] Logically if furfural, levulinates or GVL are hydrogenated under acidic conditions, 2-MeTHF should be the main product (Scheme 12). The acidity of levulinic acid might as well be enough for the dehydrative ring closure.



Scheme 12: Routes from bio-based platform chemicals to 2-MeTHF

For the hydrogenation of levulinic acid to 2-MeTHF bimetallic catalysts are beneficial (Table 5). Usually acidic supports like the zeolite H-β or a mixture of zirconia and aluminum oxides are used. A catalyst introduced by the group of Han gives the highest selectivity (99.8%) at full conversion so far (Table 5, entry 3). The catalyst consists of a ratio of copper to nickel of 1:1 supported on $AlZrO_x$. The interaction of both metals with each other on the support is responsible for the good selectivity. Mixing Ni and Cu separately supported on $AlZrO_x$ results only in poor selectivity (Table 5, entry 4). In contrast to LA, furfural (FF) can be converted to 2-MeTHF, albeit selective protocols are rare. An example is shown in the table below (entry 6). Here almost absolute selectivity was observed when palladium deposited on silica was used as the catalyst. The reaction was conducted in the gas phase at low pressure and therefore low furfural concentration. These conditions might be necessary to suppress oligo- or polymerization of FF, which is easily triggered by temperature and/or the presence of acids.[18, 101]

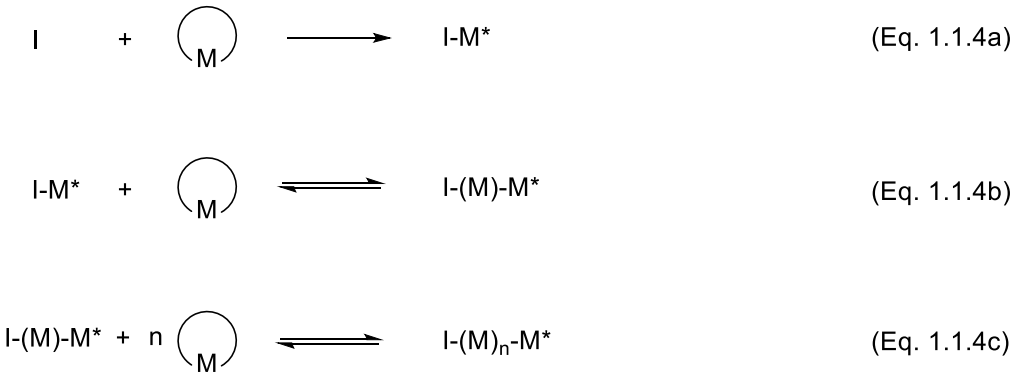
Table 5: Catalytic hydrogenation of LA and FF to 2-MeTHF

Entry	Catalyst	Sub.	T [°C]	p(H2) [bar]	S/C[a]	Conc. (Solvent) [mol l^{-1}]	Conv.[b] [%]	Sel.[b] [%]	Ref.
1	$Pt_{0.06}$-Mo/H-β	LA	130	50	50	0.3 (H_2O)	>99	86	[102]
2	$Ni_{0.1}$-Cu/SiO_2	LA	265	25	-	Gas phase	>99	85-92	[103]
3	$Cu_{0.5}$-Ni/$AlZrO_x$	LA	220	30	13	0.6 (2-Butanol)	100	99.8	[104]
4	Cu+Ni/$AlZrO_x$[c]	LA	220	30	13	0.6 (2-Butanol)	100	1.6	[104]
5	Pd/SiO_2	FF	170	1	-	Gas phase	89	99	[105]

[a]S/C=Substrate/Catalyst; [b]Conv. = Conversion, at which the selectivity to 1,4-PDO was the highest; Sel. = Selectivity; [c]Phyisical mixture of the two separate Cu and Ni catalysts.

Aside from the direct hydrogenation of FF which requires more development, the production of 2-MeTHF from LA seems feasible. As a result, 2-MeTHF currently attracts increasing attention as a renewable substitute for THF as the solvent, and as a renewable fuel.[30, 106, 107] The use as a solvent is particularly interesting from three points of view. Firstly, the higher boiling point (80°C vs. 66°C) and lower melting point (-136°C vs. -109°C for THF) of 2-MeTHF should be emphasized compared to THF.[42, 108] This allows its use in a much wider temperature range. Secondly, the immiscibility with water makes 2-MeTHF, while still having some polarity, a good solvent for biphasic reaction and extraction processes where it can replace the toxic solvent dichloromethane.[109] Lastly, 2-MeTHF is more stable towards strong acids and bases than THF which enable its more efficient use in the reactions which require strong Lewis acids, organic lithium compounds or lithium aluminum hydride.[109, 110]

The later point is also the most critical for polymer development based on 2-MeTHF. Being a cyclic ether devoid of other functionalities, ring opening polymerization (ROP) would be the only possible mode of (oligo-)polymerization of 2-MeTHF. ROP is a process which is largely governed by thermodynamics and can be described as follows: the reaction of a suitable initiator (I) with a cyclic monomer (M) leads to a linear adduct (I-M*, Eq. 1.1.4a) that itself is active enough to engage in ring-opening of another monomer (Eq. 1.1.4b) to generate a further species with active chain end. This active chain end thus can react with another monomer etc. which lead to the formation of an oligo- or polymer (Eq. 1.1.4c).[111, 112]



(Eq. 1.1.4a)

(Eq. 1.1.4b)

(Eq. 1.1.4c)

These chain growing reactions are always in equilibrium with the depolymerization. Generally, the direction of this equilibrium depends on the Gibbs free energy of ring opening polymerization (ΔG_{ROP}) which needs to be negative for the polymerization to occur. ΔG_{ROP} is derived from the ring-opening enthalpy (ΔH_{ROP}) and the entropy change (ΔS_{RoP}) during the polymerization. Both of these depend on the nature of the monomer.[81, 111-113] ΔH_{ROP} is the most negative for 3 and 4 membered cyclic molecules. In 5 membered it can be close to zero or even positive depending on the exact nature of substituents (attachment of *trans*-fused rings[114, 115] can be beneficial for reduction of ΔH_{ROP}). For rings consisting of 6-7 atoms ΔH_{ROP} increases again. Rings of greater sizes usually have very low values of $\Delta H_{ROP,}$ but the entropy of the polymer can be higher than that of the monomers. This enables polymerization. The temperature at which ΔG_{ROP}=0 is called the ceiling temperature ($T_{ceiling}$) (Eq. 1.1.4d).[112]

$$T_{ceiling} = \frac{\Delta H_{\mathrm{ROP}}}{\Delta S_{\mathrm{ROP}}} \qquad \text{(Eq. 1.1.4d)}$$

At this temperature, the polymerization and depolymerization are in equilibrium which translates to a maximum temperature at which a certain monomer can polymerize. In addition, the higher the difference of $T_{ceiling}$ to the temperature at which the ROP is conducted, the higher the possible monomer conversion. $T_{ceiling}$ therefore relates directly to the reactivity of a given monomer. Figure 4 shows the ceiling temperatures and relative reactivities of THF derivates.

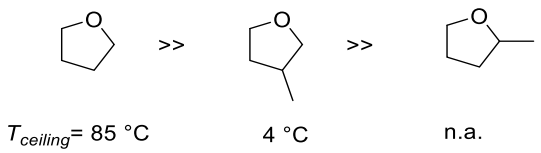


Figure 4: Ceiling temperature for THF and 3-MeTHF. For 2-MeTHF no ceiling temperature is known as the homo polymer has never been prepared

Unsubstituted THF has a ceiling temperature of 85 °C. It goes down to 4 °C if a methyl group is added in the 3- position. Thus, bellow 4°C 3-MeTHF can be homopolymerized. Highest 3-MeTHF conversion (40%) could be achieved at -22°C after 45 days in a study by Chang and Rhodes.[116] PF_3 and HSO_3Cl were used as catalysts. The polymer obtained had molecular weight of 1700 g mol^{-1} as measured by vapor phase osmometry. This could be later increased to about 5000-6000 g mol^{-1} if the conversion of 3-MeTHF is kept below 13% at 0°C and thus resulting in high excess monomer concentration.[117] For 2-MeTHF no homopolymer has so far been prepared. Hypothetically this can be due to of the following two reasons: firstly, the ceiling temperature for 2-MeTHF could lie below its melting point. Secondly, the molarity might not be even high enough in pure 2-MeTHF to shift the equilibrium towards polymerization (*c.f.* Eq. 1.1.4.). As a result, only the copolymerization of 2-MeTHF is possible. Only two studies conducted in the 1960s described copolymerization of 2-MeTHF, which employ rather reactive monomers such epichlorohydrine[83] or 3,3-bis(chloromethyl)oxacyclobutane.[118] Here it was shown that the maximum incorporation of 2-MeTHF is 50% and 30% respectively. However, neither molecular weights nor exact analyses on the structures of the products were provided. The chain compositions were only reported based on the chlorine content determined via titration.

1.2 Recycling of Polymers as a Renewable Feedstock

1.2.1 The Plastic Problem and Overview of Recycling Strategies

Polymers are involved in countless products ranging from high-tech materials used in areo-space industry, car parts, electronics to simple consumer goods such as clothing, sports gear, carpets, and various packing materials. Especially the use of plastics to create low-priced and single use products contributes a lot to their total yearly volume. Thus, in 2018 the annual global production of plastics reached around 360 million tons.[119] As a result, humanity currently produces a previously unmatched amount of plastic waste. This problem is further aggravated by the growing world's population and an increase of the living standard of most people.

Figure 5: Great pacific garbage Patch - Caroline Power

A lot of this waste is currently dumped in landfills or "mismanaged". The latter is a euphemism for the uncontrolled dumping of waste by organizations or individuals which results in pollution of the environment. This waste is transported by rivers and from there to the oceans,[120] where it forms "islands" that can reach three times the size of France (Figure 5).[121] In the worst case, plastics are directly dumped from ships to the waters.[122] Once the debris is in the water, it causes great harm to aquatic life and the micro plastic makes its way into various food chains – including the human food sources.[123] Estimation of the amount of plastic marine debris circulating in 2020 ranges from 50 to 150 million tons.[120] The risks for the global ecosystem as well as possible negative health effects for humans sparked by an increased public awareness led to various concepts for solving this problem. One of them is educating people about the single use plastics and making them to consider if there is a real need for the to use those (e.g. drinking straws, plastic cutlery, single use coffee cups). Another approach would be the usage of bio-degradable materials. They should most certainly be used in materials that have a high chance of ending up littering the environment like aforementioned single use plastics or in laundry products. However, for certain applications, biodegradability is still an unwanted property. In addition, while bio-degradable materials might not accumulate in the environment, their decomposition might still lead to the release of toxic additives or catalyst residues.

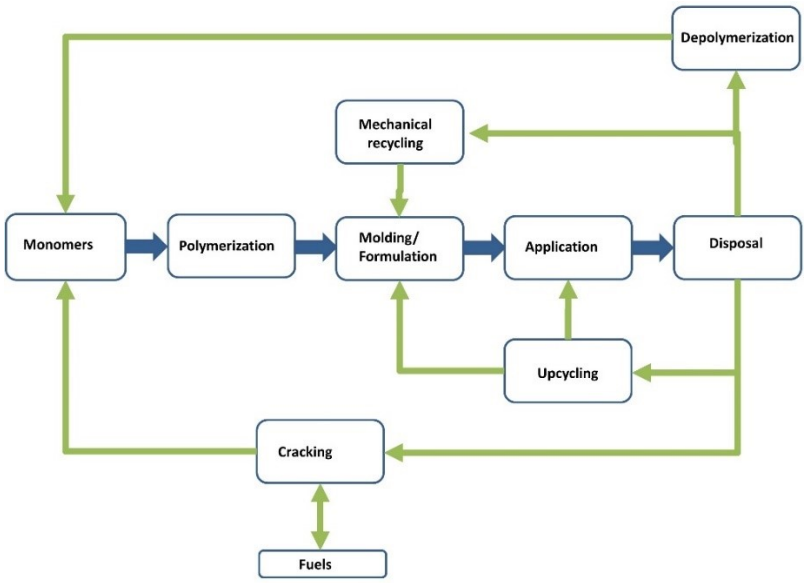


Figure 6: Possible pathways for recycling polymers and their entry points in the life cycle

Recycling of the polymeric materials is a very widely discussed topic with some already implemented solution. In general, four different strategies exist which depend on the polymer to be recycled and differ in the products obtained (Figure 6).[124] One straightforward strategy is the mechanical recycling in which the material is brought back by grinding or cutting to a form which can undergo another cycle of melting or molding to undergo another lifecycle. Alternatively, the material might be depolymerized using suitable catalysts and reaction conditions. The monomers thus can be regained separated and used to obtain new virgin type grade polymer. Analogous to that is the concept of feeding the polymer waste to cracker either to directly obtain the monomers or obtain small molecules that can be upgraded to fuels or monomers. An inherently different strategy is the so-called upcycling in which the waste is used as a resource to obtain more valuable products in an economical sense. The following section introduces and gives examples for each of the strategies.

1.2.2 Mechanical recycling

Mechanical recycling is already established on an industrial scale. In the European Union about 32% of the plastic consumer waste is recycled using this approach.[119] After selective collection and shredding the plastics can be given a new shape by injection molding, extrusion or heat pressing. In consequence the mechanical recycling is only possible with thermoplastic polymers such as PE, PP, PET and PVC.

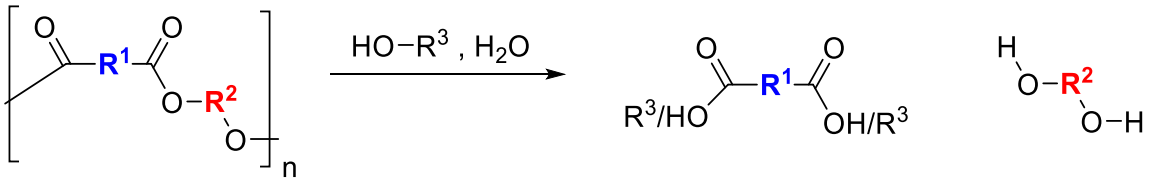
The main advantage here is that the energy and resource input of the polymerization is conserved. Another benefit is that, in principal, the existing process infrastructures can be used. On the downside, exposing the polymer again to high temperatures and friction may cause reduction in molecular weight which negatively affects mechanical properties of the recycled materials. This is caused by chain scissions that are triggered in the presence of water, trace amounts of acids, radicals and potential side products from additives decomposition.[124, 125] When additives are added to the polymer before the recycling step, this problem can be avoided. Typical additives for this are sterically hindered amines, which have been demonstrated to circumvent degradation in PE and PP reprocessing. [126] Another difficulty to overcome are the often-encountered heterogeneity of the feed. The solution here is to add so called compatibilizers prior processing, which increases the interaction between the immiscible polymers. Examples are ethylene-propylene diene rubber (EPDM) used for PP and PE.[127, 128] For PET

and PE copolymers of butadiene and styrene or poly methacrylates can be used as compatibilizers[129] as well as maleated poly styrene-ethylene-butylene-styrene.[128]

If necessary, or if no suitable additives are available, the polymer can be also recovered from waste by dissolution and reprecipitation. First the mixture of polymers is dissolved in an organic solvent. The desired polymer or mixture can then be recovered by adding its respective non-solvent.[130-133] It was demonstrated that using xylene, toluene, dichloromethane or benzyl alcohol as solvents and methanol or *n*-hexane as precipitating agents it is possible to separate a complicated blend of LDPE, HDPE, PP, PS, PVC and PET.[131] One other notable example is the VINYLOOP process developed by Solvay.[124, 130, 134-136] First the PVC is shredded followed by its transfer to a closed loop reactor in which the polymer is continually extracted from the waste mixture. For the selective extraction of PVC a mixture of methyl ethyl ketone, n-hexane and water is used as eluent (82/13/5 w/w). The obtained PVC has a relatively high purity and thus can easily be reshaped into new products. Successful runs on pilot scale eventually led to the operation of a large-scale plant in 2002 located in Ferrara, Italy which treated 10 kt y^{-1} of PVC waste.[137] Unfortunately, due to the nature of the process the recycled PVC contained phthalate based plasticizers originating from old PVC products. The use of these class of plasticizers in consumer products was banned in Europe via the REACH regulation in 2015. As a result, the plant was shut down in 2018.[138]

1.2.3 Depolymerization

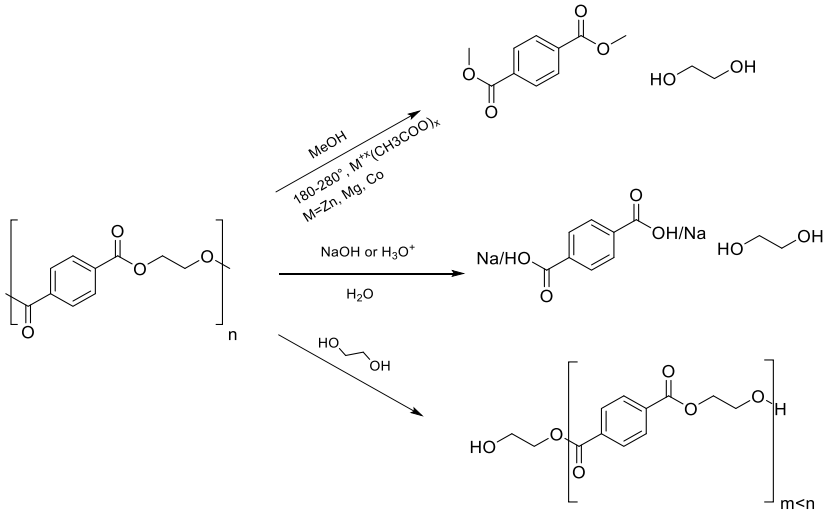
Alternatively, polyesters and polycarbonates can be depolymerized to their monomer by alcoholysis or hydrolysis (Scheme 13). Here the polymer is exposed to an excess of alcohol or water in the presence of suitable catalysts to obtain monomeric diols and the dicarboxylic acid derivatives. Since the structure of the monomers remains unchanged, it is possible to use these monomers in the same polymerization process.



Scheme 13: Depolymerization of a polyester by the solvolysis method

Organic bases, Lewis acids and alkoxides are generally used as catalysts.[139-143] Good examples of polymers in this category are polyethylene terephthalate (PET) and polylactide (PLA).[141, 142] It is noteworthy that depolymerization processes for PET were already developed almost in parallel to the onset of commercial production of the polymer in the 1950s.[139] The first commercial process that was developed is the so called methanolysis (Scheme 14), in which PET is treated with an excess of methanol at 180-280 °C and pressures of 20-40 bar in the presence of aryl sulfonic salts[139] or the acetates of zinc, magnesium and cobalt.[144] Yields of dimethyl terephthalate (DMT) of up to 90% are possible. Conveniently, the process conditions and even the catalysts are similar to the production process of PET via transesterification of DMT and ethylene glycol.[16] The methanolysis process was applied by Hoechst, DuPont and Eastman-Kodak.[145] The disadvantage of this approach nowadays is the decline of the price for virgin DMT[144] as well as the fact that in newly built PET plants the direct polycondensation between terephthalic acid (TPA) and ethylene glycol is the preferred method.[16]

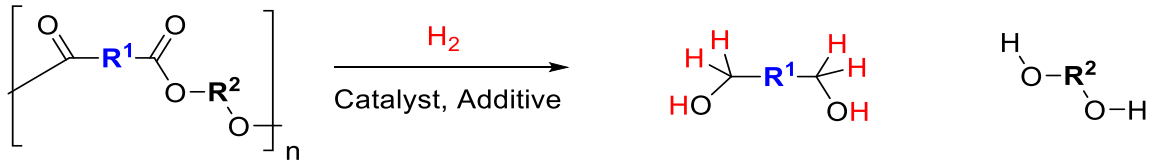
Nevertheless, Eastman Chemicals have announced in 2019 that they will build a plant for the depolymerization of PET from used soda bottles and food packaging by methanolysis.[146]



Scheme 14: Different solvolysis processes for the depolymerization of polyethylene terephthalate (PET)

PET can also be simply depolymerized via acid or base catalyzed hydrolysis.[139, 144, 145, 147, 148] This strategy is, however, the least favored one given the relatively huge amount of acids or bases involved and salts formed. The glycolysis of PET is an alternative pathway, where PET is transesterified with ethylene glycol (Scheme 14, bottom route).[145, 148-150] This produces short chain polyester polyols which can be used in adhesives or polyurethane applications.

An emerging alternative to the solvolysis method is the direct hydrogenation of the ester groups to alcohols which in contrast to the solvolysis processes will (at full conversion) yield a mixture of diols (Scheme 15). This approach is relatively new in the literature and mostly fueled by the development of metal organic complexes that can efficiently hydrogenate esters in the last 15 years.[151-153]



Scheme 15: Hydrogenation of polyesters to diols

The complexes that have been successful employed in the hydrogenative depolymerization of polyesters are based on tridentate pincer ligands with one exception (Figure 7). Many of them have already been proven to be applicable to a wide range of ester substrates such as the complex introduced by Milstein and co-workers (**C1**) in 2006,[154] as well as the PNP-ligated catalysts first introduced by Kuriyama *et al.* at Takasago.[155, 156] As described earlier (Section 1.2.3.) the complexes usually need basic additives or contain acid labile leaving groups to be converted into active forms. Figure 8 shows polyester and -carbonate substrates which are usually investigated in these hydrogenation reactions.[157-163] In one of the first examples Robertson and co-workers successfully employed complexes introduced by the Milstein's group (**C1** and **C4**) in the hydrogenation of various polyesters.

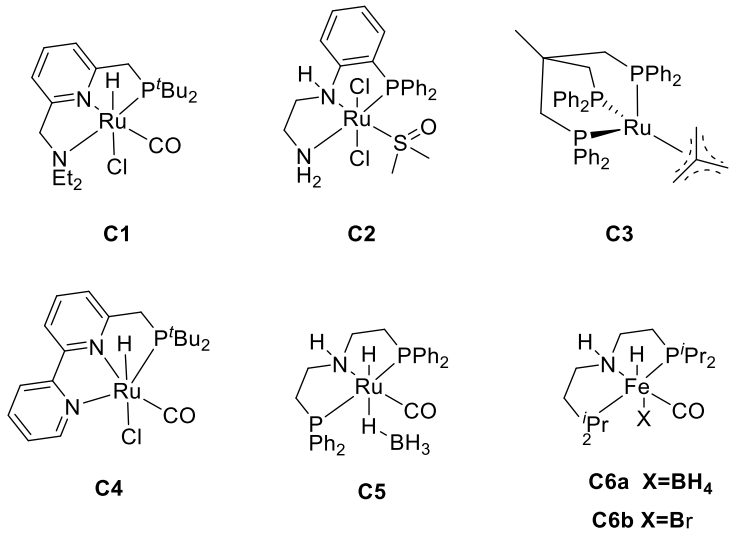


Figure 7: Precatalysts for the homogenous catalytic reduction of polyesters or polycarbonates

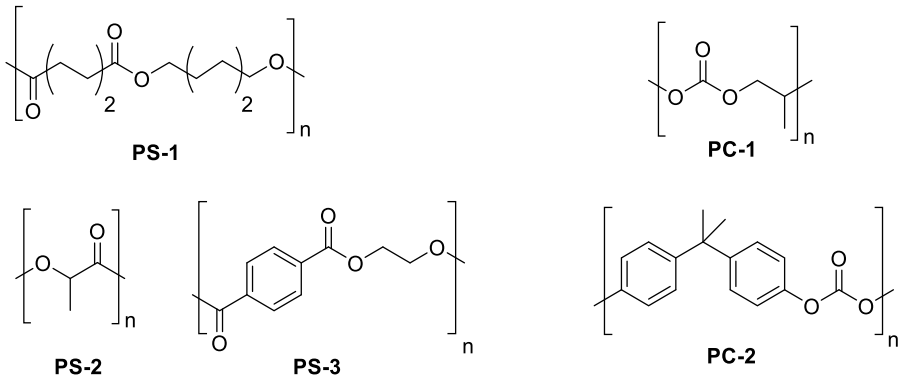
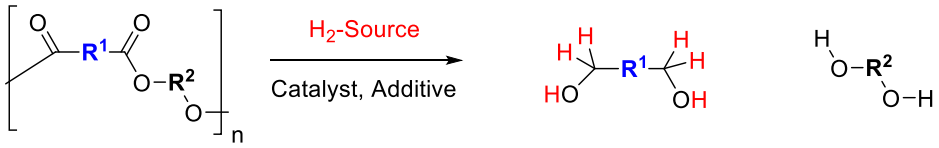


Figure 8: Common polyester and polycarbonate substrates used in the hydrogenolytic depolymerization

For PET (**PS-3**) and PLA (**PS-2**) full conversions to the alcohols (benzene dimethanol and propylene glycol respectively) was measured by NMR (Table 6, Entries 1-2). A mixture of anisole and THF was used as a solvent to hydrogenate the polymers at 120 °C and 54 bars of hydrogen. The polymers were obtained from a water bottle and drinking cup. Similar conditions were used by the group of Clarke who studied complex **C2** which differs from **C1** by the substituents on the phosphorous atom and replacement of the CO ligand by DMSO.[158] The authors used PET which they obtained from food trays as the substrate, from which benzene dimethanol was obtained in 73% (Table 6, Entry 3). These three catalysts have a common feature of the need to be activated by strong alkoxide bases in contrast to the triphos complex (**C3**) which requires strong acids. Employing this catalyst in combination with bistriflimide ($HN(Tf)_2$) Klankermayer and co-workers could reduce a range of polyester and -carbonates at slightly higher temperature (140°C) and significantly higher hydrogen pressure (90 bar).[159] The conversion of the polymers (obtained from a bottle, drinking cup and CD-ROM) was quantitative and the produced diols could be isolated in very good yields (Table 6, Entries 4-6). Enthaler and co-workers showed that Ru-MACHO-BH (**C5**) and Milstein's complex (**C1**) can also be used to hydrogenate polycarbonate **PC-2** (Table 6, Entry 7 & 8). In the recent work of de Vries and co-workers Fe-MACHO (**C6a**) was applied for the first time for the transfer hydrogenation of a commercial pre used polyester using ethanol as reductant.[161] The resulting diol could be isolated in 87% yield. The same complex in its bromide form (**C6b**) was used by Werner and co-workers to depolymerize polypropylene carbonate (**PC-1**) to propylene glycol and methanol.[162]

Table 6: Hydrogenation of polyesters and -carbonates



Entry	Cat.	Polymer[a] (S/C/A)	Additive	Solv.[b]	Red.[c]	T [°C]	t [h]	Yield(R^1) [%][d]	Yield(R^2) [%][d]	Ref.
1	**C1**	PS-2 50/1/1	KO^{t}Bu	Anisole /THF	H_2, 54 bar	120	48	>99	>99	[157]
2	**C4**	PS-3 50/1/1	KO^{t}Bu	Anisole /THF	H_2, 54 bar	120	48	>99	>99	[157]
3	**C2**	PS-3 50/1/20	KO^{t}Bu	Anisole /Tol	H_2, 50 bar	110	48	73	n.d.	[158]
4	**C3**	PS-3 100/1/1	$HN(Tf)_2$	1,4-Dx	H_2, 90 bar	140	16	>99(83)	n.d.	[159]
5	**C3**	PC-2 200/1/1	$HN(Tf)_2$	1,4-Dx	H_2, 90 bar	140	16	>99(73)	n.d.	[159]
6	**C3**	PC-2 200/1/1	$HN(Tf)_2$	1,4-Dx	H_2, 90 bar	140	16	>99(93)	n.d.	[159]
7	**C1**	PC-2 20/1/1	KO^{t}Bu	THF	H_2, 45 bar	140	24	99(91)	n.d.	[163]
8	**C5**	PC-2 200/1/-	-	1,4-Dx	H_2, 45 bar	140	24	99(97)	n.d.	[160]
9	**C6a**	PS-1 20/1/-	-	EtOH	EtOH 96. eq.	100	24	(87)	-	[161]
10	**C6b**	PC-1 20/1/1	KO^{t}Bu	THF/ *i*PrOH	iPrOH	140	24	65	43	[162]

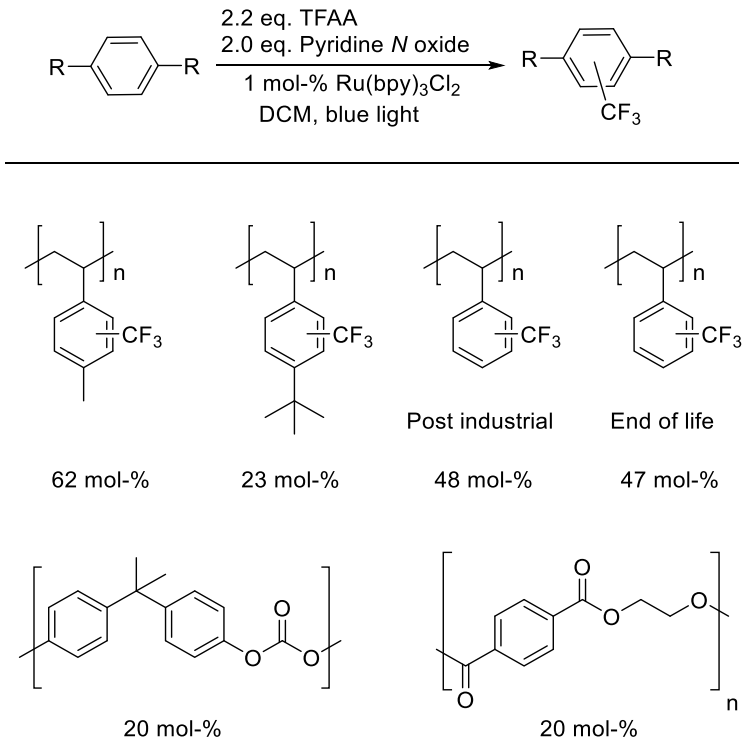
[a]Molar ratio of catalyst C and additive A with respect to the repetition unit of the polymer; [b]Solvents: Tol=Toluene, 1,4-Dx=1,4-Dioxane; [c]Reductant used; [d]Isolated yields in brackets

In this depolymerization approach the catalysts are employed at a relative high loading of 0.5-5 mol% per repetition unit. However, comparing the used catalysts, solely based on their catalyst loading, is difficult as the quality and purity of the polymer substrates used ranges from self-synthesized to end of life plastics that may contain fillers, additives and other impurities. As a result, it is not possible to estimate at the current state of literature if some type of catalyst is less active than others or is just more sensitive to poisoning by the potential impurities.

1.2.4 Chemical Polymer Upcycling

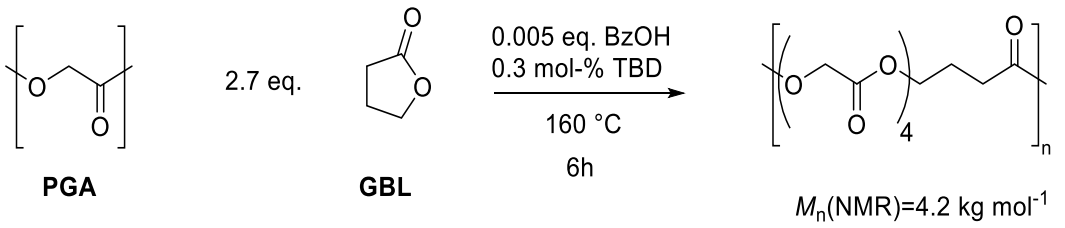
Mechanical recycling and depolymerization is always in competition with the use of virgin polymers or monomers. Thus, the degree to which they can be implemented always depends on the price difference. Chemical upcycling of polymer waste therefore might be an exit out of this dilemma. In this approach polymers are upgraded to access novel or special applications which could allow them to be sold a higher price. For instance, macromolecules that contain aromatic moieties in their repetition unit can be functionalized with CF_3 groups using trifluoracetic anhydride (**TFAA**) as triflate source (Scheme 16).[164] The reaction proceeds via trifluoromethyl radicals that are generated from TFFA by oxidation with pyridine-N-oxide mediated by blue light and $Ru(bpy)_3Cl_2$ as photocatalyst. For polystyrene about 48% of the phenyl groups could be trifluoromethylated. In the case of polycarbonate and PET this was significantly lower. The modified polystyrenes are significantly more hydrophobic

than the unfunctionalized polymer as evident by the measured of the contact angle with water (94 vs. 111°(fluorinated)). Which for example could enable their use in the water repellant clothing.



Scheme 16: Trifluoromethylation of aromatic polymers. The incoporation of CF_3 groups is given in mol%

To alter the thermophysical properties polyesters can be transesterified with a cyclic lactone. Such a reaction has been recently demonstrated by Hong, Falviene, Chen and co-workers.[165] Here poly(glycolic acid) (**PGA**) reacts with γ-butyrolactone (**GBL**) which also serves as the solvent. Organic base 1,5,7-triazabicyclo[4.4.0]dec-5-ene (**TBD**) as catalyst and benzyl alcohol (BzOH) as initiator afforded the highest GBL incorporation at reasonable reaction times (Scheme 17). As the ceiling temperature of pure poly GBL (-40°C) is far lower than the reaction temperature[166, 167] no adjacent GBL units are found in the polymer chain. On average the incorporation of GBL in the chains is about 20%. The obtained copolymer exhibits a much higher onset of decomposition (T_d= 290°C) than PGA (T_d= 254°C) under nitrogen atmosphere. If GBL is just copolymerized at lower temperature with glycolide (the monomer of PGA) this effect is not observed.

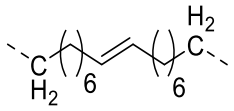
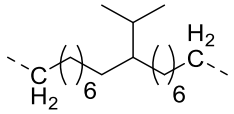
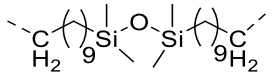


Scheme 17: Transesterification of PGA with GBL. Mol-% and equivalents (eq.) are based on the repeating unit of PGA

This is attributed to the formation of adjacent GBL units that create weak linkages. In the two previous examples the type of connectivity of the monomer units in the macromolecule does not change. A more drastic approach is to completely alter this connectivity and, thus, also the type of the

polymer. A good example for this approach is the hydrosylilation of polyesters as recently published(Table 7).[168] Here 1,1,3,3-tetramethyl disiloxane (TMDS) is used as a reductant in the presence of $GaBr_3$ as Lewis-Acid catalyst. The scope of the reaction included several aliphatic polyesters derived from polycondensation reactions (Table 7, entries 5-13) as well as polyesters obtained through the ROP of lactones (Table 7, entries 1-4). The degree of the reduction of the ester groups was in the range of 90-99% for all the examples. The reduction of the molecular weights is about 50-60% based on NMR in those cases where polyesters prepared via polycondensation reactions are used as substrates. This is quite different for the polylactones. Here the polymers are almost degraded in the cases where shorter aliphatic segments are used to the repetition units (Table 7, entries 1 & 2). If this segment is longer, the retained molecular weight increases. Since ester groups are converted to ether groups, this heavily alters the properties of the polymers. For instance, they have much lower melting points. New polyethers are accessible via this approach which are difficult to prepare by conventional routes.

Table 7: Reduction of polyesters to polyethers with 1,1,3,3-tetramethyl disiloxane

Entry	R	M_n(before)[a] [g mol^{-1}]	M_n(after)[a] [g mol^{-1}]	Yield [%]
	R1			
1	-CH(CH)$_3$-	26300	400	34
2	-CH$_2$CH(CH)$_3$-	197100	800	24
3	-(CH$_2$)$_5$-	8400	5650	85
4	-(CH$_2$)$_9$CH(CH$_3$)-	8100	8200	83
	R2			
5	-(CH$_2$)$_2$-	2200	1200	66
6	-(CH$_2$)$_4$-	3900	2600	83
7	-(CH$_2$)$_8$-	8800	3900	88
8	-(CH$_2$)$_{10}$-	8700	4000	90
10		9400	3100	50
12		13100	6500	93
13		8300	3500	42

[a]*Molecular weight as measured by NMR before and after the reduction*

2 Aim and Results of this Dissertation

2.1 Development of Polymers based on AL, 1,4-PDO and 2-MeTHF

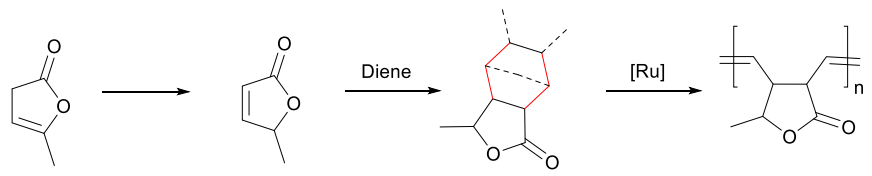
As described in 1.1.1, Levulinic acid (LA) is easily obtained by acidic treatment of lignocellulosic biomass. Aside from the usage of virgin wood it should be also possible to use wood waste. Alternatively, furfural is a possible source for LA with great potential. Furfural is already produced on scale of several hundred kt y^{-1} from corncob and in smaller amounts as side product in the paper industry. Aside from this the company Avantium is on the way to implement a process to produce the terephthalic acid substitute furandicarboxylic acid based on fructose. In this process a considerable amount of levulinic acid in the form of its methyl ester will be generated. From LA or its esters, the downstream products angelica lactone (AL), 1,4-PDO and 2-MeTHF can be obtained. These reactions are highly atom economic as they are hydrogenation and condensation reactions. Several homogenous and heterogenous catalysts to obtain these derivates in high yield and selectivitys are known.

On the contrary, not much literature exists on how to utilize these products directly in polymer applications, which is one of the biggest areas where chemicals are employed. The development of such applications is crucial for the establishment of the bio-based chemical industry. Additionally, using these products should have additionally benefits or at least novel features to compete with the traditional petrochemical products.

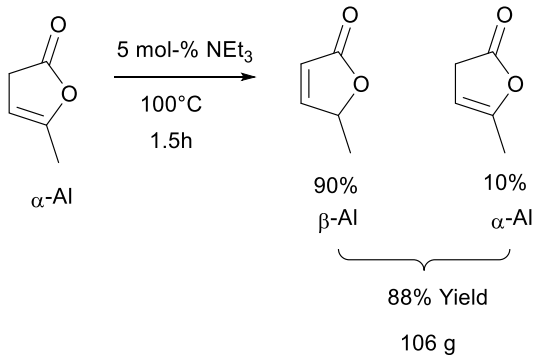
To demonstrate the competitiveness of this value chain is the goal of GreenSolRes a project funded by the Horizon 2020 research and innovation program of the European Union. The consortium consists of industrial partners (Henkel, BASF, Lenzing, Hybrid Catalysis, Vito, GFBiochemicals) and two academic partners (LIKAT, RWTH). While the other partners focus on the production and derivatization of levulinic acid as well as the relating regulatory affairs the goal of Henkel and us is to develop scalable procedures towards bio-based building blocks for adhesives based on levulinic acid and its derivates. This dissertation was conducted in the framework of this project and therefore aimed to develop scaleable routs to the aforementioned building blocks based on levulinic acid.

2.1.1 Diels-Alder Adducts of β-angelica lactone – Scalable Monomers

Section 1.1.2 describes two possible ways to obtain polymers from angelica lactone. First, α-Angelica lactone (α-AL) can be polymerized with strong bases or Lewis acids as initiators. The obtained materials are ill-defined oligomeric sticky resins. They lack the high molecular weight and high melting points, or glass transitions temperatures commonly found in thermoplastics.[16, 169] In addition, defined functional end-groups are absent which are usually encounter in the oligomers used for polyurethanes or 1 and 2 component adhesives. This makes them challenging to use in existing polymer applications. An alternative way can be the isomerization of α-AL to β-AL, the later can the polymerized to polyacrylates.



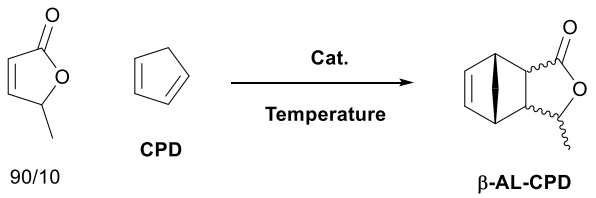
Scheme 18: Synthesis route to monomers for ROMP from β-AL and their polymerization via ROMP



Scheme 19: Isomerization of α-AL to a mixture of β-AL and α-AL in the absence of a solvent

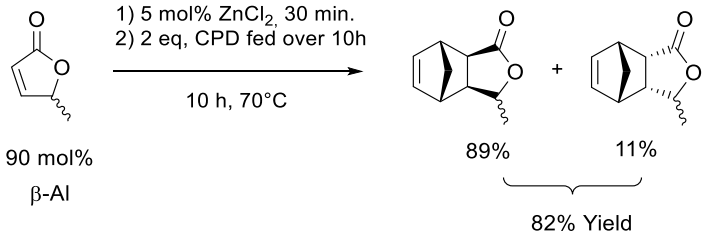
For the isomerization of the angelica lactone triethylamine is used typically as catalyst and toluene or dichloromethane as a solvent with reported isolated yields between 40-60%.[67-69] When we reproduced these experiments, it was noticed that when the reaction time is kept rather short (1.5 h) a mixture of 90:10 (β-AL / α-AL) could be obtained after distillation. In addition, no negative effect was observed when a solvent was absent. This made it relatively easy to conduct this reaction on 100g scale (Scheme 19). Next the solvent free Diels-Alder reaction of the mixture containing 90% β-AL with three equivalents cyclopentadiene (CPD) was investigated (Table 8). The use of aluminium triflate (Entries 1&2) resulted in the formation of black charred residue but no product could be observed. In contrast, when the reaction was carried out only with the two reactants, CPD and the angelica lactones, a yield of up to 40% could be observed at 100°C (Table 8, Entry 4). By adding zinc chloride as catalyst, it was possible to obtain the

Table 8: Optimization of the Diels-Alder reaction between the angelica lactone mixture and CPD



Entry	Catalyst	Eq. (CPD)	T [°C]	t [h]	Yield[a] [%]	Endo/Exo[a]
1	5 mol% $Al(OTf)_3$	3	RT	16	-	-
2	5 mol% $Al(OTf)_3$	3	100	2	-	-
3	-	3	80	0.5	19	91/9
4	-	3	100	0.5	40[b]	70/30
5	-	3	60	0.5	25	95/5
6	5 mol% $ZnCl_2$	3	80	0.5	40	84/16
7	5 mol% $ZnCl_2$	3	RT	16	63	89/11
8	5 mol% $ZnCl_2$	10	RT	16	90 (86)[b]	90/10

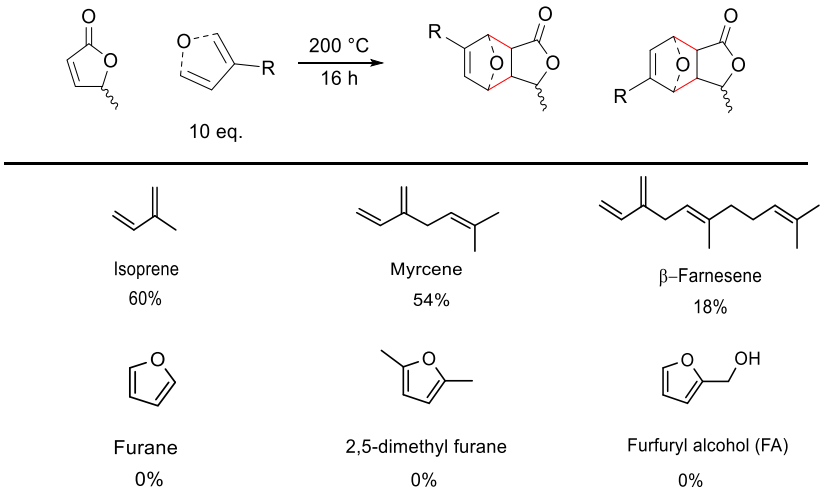
General conditions: Reactions were carried out in closed reaction tubes and heated with microwave irradiation.
[a]Determined by ^{1}HNMR spectroscopy; [b]Isolated by column chromatography



Scheme 20: Synthesis of the DA-adduct on a 50 g scale

target compound in 63% yield at room temperature after 16 hours. Since CPD dimerizes at room temperature with a half-life of 24h to dicyclopentadiene, the equivalents of CPD with respect to the angelica lactones were increased to 10 eq. which resulted in an isolated yield of 86%. The obtained product contained the two possible endo- and exo-isomers in a ratio of 90:10. The favored formation of the endo isomer is typical for 2+4 cycloadditions reactions with normal electron demand. In combination with the two possible orientations of the methyl group in the lactone moiety 4 diastereomers could be observed. However, a reaction that uses 10 equivalents of CPD is neither sustainable nor ideal for scaling up, it was decided to run the reaction in semi-batch mode on a 50g scale (Scheme 20). First anhydrous zinc chloride was dissolved in the angelica lactone mixture followed by the continuous dosing of 2 eq. of the CPD over 10 hours at 70°C. After this is was possible to remove the $ZnCl_2$ from reaction mixture by the addition of acetone which caused its precipitation. For further purification column chromatography was disregarded in view of the scale of the reaction. To judge the viability of a distillation of the product a DSC analysis of a sample isolated prior in the optimization step was carried out. This revealed that the retro Diels-Alder reaction to CPD and β-Al occurs at 136°C. Fortunately removal of the formed di- and trimers of CPD was possible by their precipitation with methanol. The mixture of the angelica lactone adducts could be isolated in an 82% yield. The generality of this approach was investigated by employing several other (bio-renewable) diene substrates (

Scheme 21). Unfortunately no product formation was observed when different Lewis acids ($ZnCl_2$, $AlCl_3$, Et_3Al, $In(OTf)_3$, $Yb(OTf_3)$ were employed as catalysts over a wide range of temperatures (60-130°C). On the other hand, product formation could be observed in the absence of a catalyst at high temperatures (200°C) and large diene excess (10 eq.) in case of the alkyl substituted dienes, isoprene, myrcene and β-farnesene. No 2+4 cycloaddition was observed in the case of furan and its derivates.



Scheme 21: Screening of different dienes in the Diels-Alder reaction with β-AL; Reaction conditions: β-Angelica lactone (1.0 mmol), N_2 (30 bar), 200°C

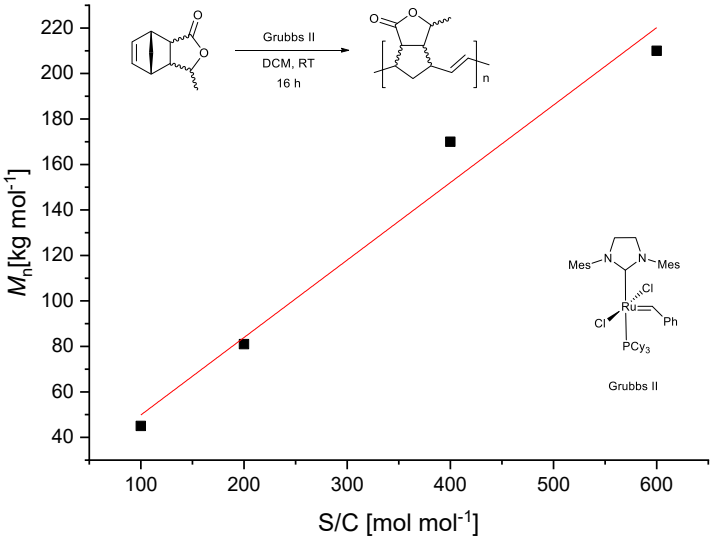


Figure 9: Polymerization of the cyclopentadiene angelica lactone adduct using Grubbs II

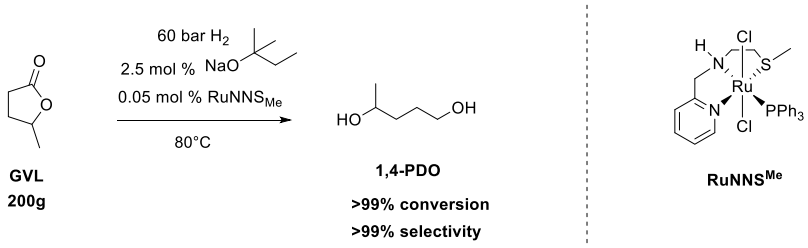
Subsequently their polymerization via ROMP with the Grubbs second generation catalyst was investigated. The adducts based on the bio-based dienes were not polymerizable, probably to the absence of sufficient ring strain. In the case of the cyclopentadiene adduct a linear relationship between catalyst ratio and the molecular weight was observed when DCM was used as a solvent (Figure 9). Other solvents (MTBE, 2-MeTHF, MEK and ethyl acetate) can be used as well but in this case lower molecular weights were observed. This is the result of the polymer precipitating out in these solvents once a certain chain length is reached in contrast to DCM. The obtained polymers resemble polynorbornene (poly-NB) in their transmittance of UV and VIS-radiation. No melting point (T_m) or glass transition temperature (T_g) was observed and therefore might be higher than the decomposition temperature of 378°C. Polynorbornene obtained by ROMP typically has a T_g of about 35°C.[170] The presence of the lactone moiety makes poly-β-AL-CPD more hydrophilic compared to poly-NB, as evident by contact angle measurements (θ(poly-β-AL-CPD)=75.7±1.9°; θ(Poly-NB)=83.9±2.3°). In summary it was demonstrated that a monomer for ROMP can be produced in a scalable manner from the renewable chemical α-angelica lactone. The high transparency of the polymer allows the use in coatings or waveguides. In addition, their higher polarity could increase the compatibility with other polymers or certain additives.

The published article concerning this work is included in section 5.1

2.1.2 Polyesters Polyols based on 1,4-pentanediol

Producing polyesters from bio-based diols and diacids is an attractive prospect as these polymers usually can be made via industrial well-established polycondensation reactions which allows the use of existing process concepts and plant infrastructure. In addition, the size of the market is very large. Thus, the research area of renewable polyesters is a very vivid field.[169, 171-179] One potential bio-based diol is 1,4-pentanediol (1,4-PDO). Its synthesis from levulinic acid derivates and furfural has received a lot of attention (Section 1.1.3).

Despite the development of many effective catalytic methods for obtaining 1,4-PDO the literature on its intended use in polyesters is limited to one study of the thermal behavior of 2,5-furan-dicarboxylic acid, succinic acid and adipic acid polyesters by van den Broek and co-workers.[180] Nothing is known so far about their applicability in polyurethanes or adhesives. One reason for this might be that 1,4-PDO is only commercial available at the moment in very small quantities at a relatively high price (22-73€ g^{-1}).[181, 182] To study mechanical properties of derived polyurethanes, however 20-50g are needed per experiment. Hence, it was decided to prepare the diol by hydrogenation of GVL. For this, we applied a catalyst that we developed earlier, which is able to achieve one of the highest published TONs in the hydrogenation of GVL to 1,4-PDO (Section 1.1.3). Additionally, the pre-catalyst complex is air-stable and is based on a cheap ligand that can be synthesized in a straightforward two step procedure in high yields.[98] This hydrogenation procedure was then successfully upscaled to 2 the mol scale (Scheme 22). For this, only minor changes in the original hydrogenation procedure had to be made. The base KO*t*Bu was replaced with sodium pentanoate this made handling outside of the glove box easier as a solution of this alkoxide in toluene can be prepared. Although one can also prepare solutions of KO*t*Bu in THF or *tert*-butanol we found that these compounds seem to inhibit the catalyst. Using only 0.05 mol% of catalyst, GVL was fully converted after 16h at 80 °C and 60 bar H_2 to 1,4-PDO. Further it was found that in the product isolation process the removal of the catalyst via absorption through silica at this scale was no longer practical due to the high viscosity of the product. The direct distillation of the product out of the reactor however proved to be possible if the catalyst is beforehand deactivated by the addition of benzoic acid.



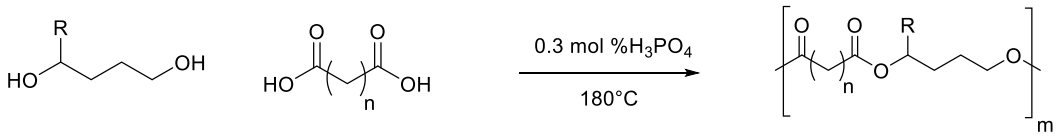
Scheme 22: Hydrogenation of GVL to 1,4-PDO for the use in polyester synthesis

Next it was aimed to prepare a series of polyester polyols preferable with renewable diacids on an average scale of 100g. A hydroxyl number (OH-N) of 30 mg KOH g^{-1} was targeted. This corresponds to an average molecular weight M_n of 3450 g mol^{-1} which is in the proper range for the application in adhesives.[183] This Mn value represents a compromise between viscosity, mechanical properties and reaction time (production cost of the polyester). The diacids that we decided to use (Carbon numbers in brackets) were succinic acid (**C4**), sebacic acid (**C10**), azelaic acid (**C9**) - these are currently available from renewable raw materials-[20, 184, 185] as well as adipic acid (**C6**), dodecanedioic acid (**C12**), which can be produced from bio-based feedstocks[186-195] and tetradecanedioic acid (**C14**) which is available from

fermentation of glucose.[196] The polycondensation reactions were conducted in a two-step approach consisting of an autocatalytic pre-condensation step at ambient pressure, followed by further condensation in vacuum in the presence of phosphoric acid as catalyst.

At first, reactions were carried out at 220°C; this temperature is commonly used for polyester synthesis in industry.[16] Unfortunately, at this temperature and under the acidic conditions most of the 1,4-PDO was observed to convert to 2-MeTHF. At 180°C the polyester polyols can be obtained in nearly quantitative yield with low residual acid contents. In most cases the measured OH-N of the polyester polyols was close to the target. This is an indication for the absence of significant side reactions, as these would greatly change the stoichiometries and hence greatly affect the obtainable molecular weights (Table 9).

Table 9: Polycondensation of 1,4-BDO and 1,4-PDO with various diacids



R=Me 1,4-PDO
R=H 1,4-BDO

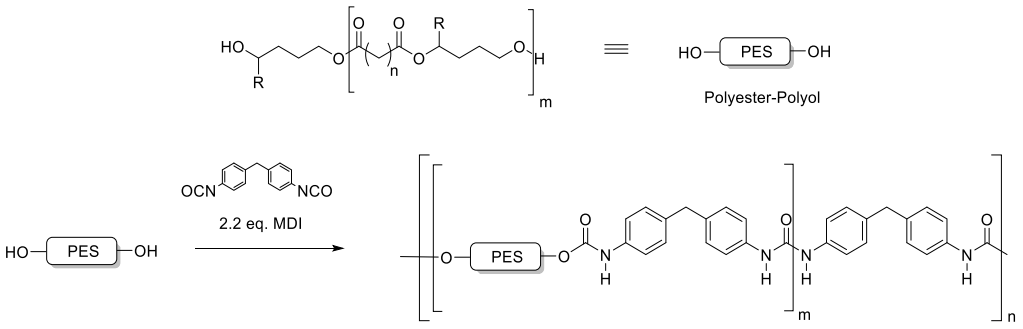
n=2; Succinic acid
n=4; Adipic acid
n=7; Azelaic acid

n=8; Sebacic acid
n=10; Dodecandioic acid
n=12; Tetradecanedioic acid

Entry	n	R	OH-N[b] [mg g^{-1}]	A-N[b] [mg g^{-1}]	M_n(Calc.)[c] [kg mol^{-1}]	M_n(OH)[b] [kg mol^{-1}]	M_n(GPC)[d] [kg mol^{-1}]	$Đ$[d]	X(COOH)[b] [%]
1	2	Me	30	10	3.7	3.7	3.6	2.4	98
2	2	H	30	2	3.7	3.7	1.7	2.4	99.5
3	4	Me	30	3	3.7	3.7	4.2	2.4	99.0
4	4	H	42	1	3.7	2.7	3.8	2.2	99.2
5	7	Me	39	4	3.7	2.9	3.8	2.5	99.0
6	7	H	46	4	3.7	2.4	4.0	2.2	99.0
7	8	Me	26	4	3.7	4.3	4.8	3.0	99.5
8	8	H	33	1	3.7	3.4	5.5	2.4	99.8
9	10	Me	29	2	3.7	3.9	4.6	2.8	99.7
10	10	H	33	2	3.7	3.4	5.0	2.7	99.7
11	12	Me	12	3	-	9.4	5.3	4.4	99.7

[a]Polycondensation procedure: 480 mmol 1,4-PDO, 0.85-0.89 eq. of diacid; 0.3 mol% H_3PO_4 (0.85 w/w in H_2O); [b]Determined by titration with KOH_{aq} (0.5 mol l^{-1}); X(COOH) conversion of carboxylic acid groups; [c]Targeted molecular weight; [d]Measured by GPC

As expected, most of the chain ends consisted of secondary alcohols (66% vs. 33% primary). For comparative reasons analogous polyester polyols with the linear diol 1,4-butane diol (1,4-BDO) were made. With enough of the materials in hands the polyols were chain extended with an excess of 4,4'-methylene diphenyldiisocyanate (MDI). This resulted in an isocyanate terminated prepolymer that further was subjected to moisture curing finally resulting in solid polyurethane (PUR) films. This curing mechanism is typical for one component adhesives and proceeds by exposing the prepolymer to ambient humidity. The absorbed water then converts some of the NCO groups to primary amines that immediately from urea linkages. From these solid films, samples were taken and analyzed by DSC



Scheme 23: Synthesis of polyurethane (PUR) films based on the synthesized polyester-polyols

alongside the polyester-polyols (Figure 10). As expected, the 1,4-PDO derived polyester-poylols were amorphous in contrast to their crystalline 1,4-BDO counterparts. The T_g decreased with increasing chain length (-32°C to -63°C). Nearly identical T_g values were observed in the corresponding PURs. Surprisingly, in the case of the C12 diacid and 1,4-PDO derived polyester polyol a melting point at -15°C was observed. The corresponding PUR had a T_m of about -22°C.

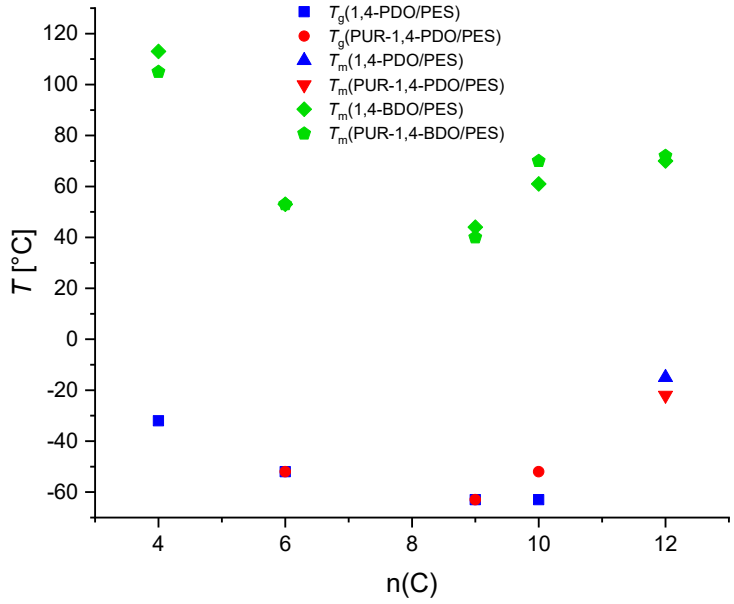


Figure 10: Glass Transition temperatures (T_g) and melting points (T_m) of 1,4-PDO polyester-polyols (1,4-PDO/PES) and the corresponding polyurethanes (PUR-1,4-PDO/PES) vice versa for their linear 1,4-BDO analogues. The values are plotted against the chain length of the dicarboxylic acid building block n(C)

Next samples were punched out of the films and subjected to tensile testing to determine the elongation at break (ε_{break}) and the breaking stress (F_{break}) (Figure 11). Due to their high crystallinity the films obtained from the polyester polyol containing the linear 1,4-BDO required a higher stress to rupture than the 1,4-PDO analogous. This effect was observed until the C9 diacid after which it decreased to lower values. The ε_{break} were over-all higher for the 1,4-PDO derived materials except for the C6 diacids base polyurethanes. In general, the films obtained from the linear 1,4-BDO polyesters were ductile materials as demonstrated by their stress-strain diagrams and the films obtained from the branched 1,4-PDO behaved more like elastomers. Here elongation of the specimens completely reversed when no rupture occurred. This is interesting in combination with the previous mentioned

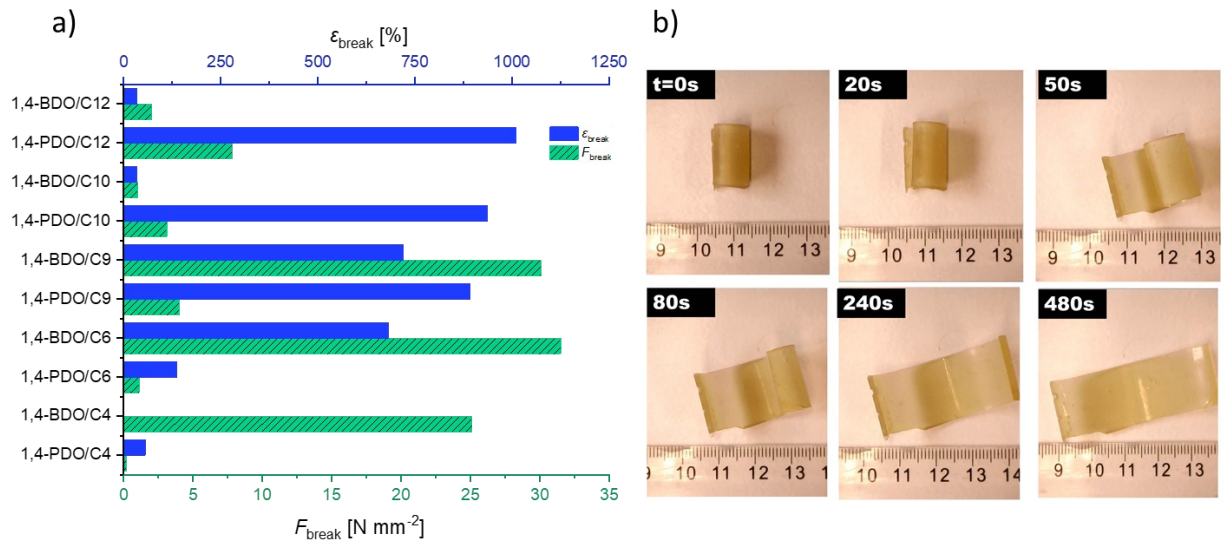


Figure 11: a) Measured values for the elongation at break (ε_{break}) and the breaking stress (F_{break}) of the different films. The values represent an average of three experiments. The test specimen were SF3A-bones with the dimensions 1 x 6 x 35 mm according to DIN 53504. Speed of sample elongation was 50 mm min-1. b) Unfolding of a film of PUR 1,4-PDO/C12 at RT. Prior the sample was fixated in the shape of a coil by cooling it to -30°C.

existence of a melting point (-23°C) in the case of the 1,4-PDO/C12 derived material. The elastomeric nature and the presence of a melting point should result in shape memory properties. Below T_m the polyester segments should crystalize and allow to fixate the polymer in a certain shape. If the specimen is then warmed above T_m the crystalline segments "should" melt and the strain should be released, and the film return to its shape prior fixation. This was possible to observe in the case of the PUR derive from 1,4-PDO/C12 (Figure 11b).

In summary, five polyester polyols have been successfully prepared from 1,4-PDO and different dicarboxylic acids. The polyester containing azelaic acid (C9), sebacic acid (C10) and dodecandioic acid (C12) have been synthesized for the first time. The comparison of this polyesters with their 1,4-BDO analogues showed that 1,4-PDO should not be treated as a simple bio-based substituted but instead could be a value adding building block for the design of formulations in coatings, sealants, adhesives and elastomers. For instance, a great benefit of the polyester polyols based on 1,4-PDO is their liquid state at room temperature. This eliminates the step of pre-melting the material before crosslinking in a two-component adhesive system which may enable faster production cycles in the manufacturing of certain goods (eq. car parts, shoes). Additionally, the observed low temperature shape memory effect might find use in smart materials. One such an application could be in an adhesive for a label for temperature sensitize goods such as certain drugs. Disruption of the cooling chain then would lead to the loss or irreversible change of the label or QR code.

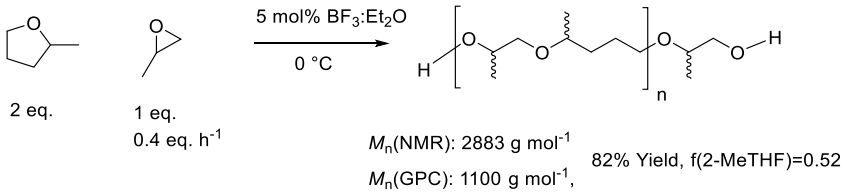
The published article concerning this work is included in section 5.2.

2.1.3 2-MeTHF as Monomer in the Synthesis of Renewable Polyether-polyols

Although polyester polyols play a large role in the production of polyurethanes, polyether-polyols are used more widely.[197 15] Whether a polyester or a polyether polyol is used depends on which properties one wants to achieve in a product formulation. In general, it can be said that polyesters tend to have higher melting points whereas polyethers are more resistant to microbiological or hydrolytic degradation. [197] While polyesters are in principal accessible by the polycondensation of virtually any

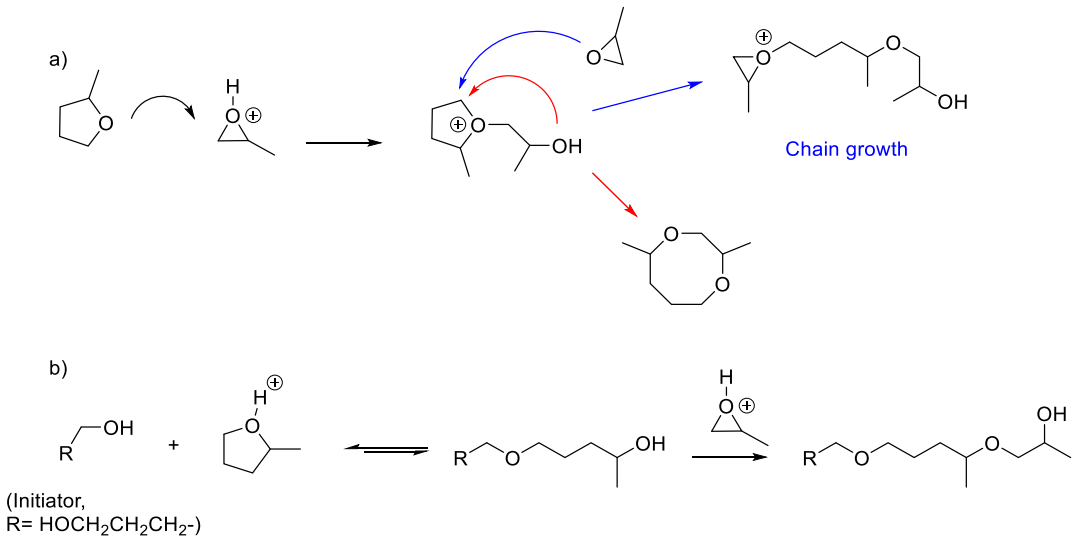
diol and diacid on industrial scale the situation for polyethers is different. The method of choice for polymerization here is usually ROP. Although innovative, alternative protocols for the synthesis of polyethers, such as reduction of polyesters[168, 198, 199] or the polycondensation of aliphatic diols employing acid-base pairs as catalysts have recently been developed,[200, 201] their application is currently limited by harsh reaction conditions and/or use of expensive catalysts or silanes as reductants. As such, the commercial production of polyethers relies almost completely on the (co)-polymerization of strained cyclic ethers such as epoxides, oxetanes and tetrahydrofuran (THF).[202, 203] The use of bio-based cyclic ethers thus could increase the bio-based content and potentially add novel properties.

2-MeTHF is such a potentially bio-based cyclic ether for which many efficient synthesis processes exist from furfural or levulinic acid derivatives (Section 1.1.4). Unfortunately, the additional methyl group decreases its ring-strain tremendously in comparison to THF. The This makes its efficient use as a monomer rather difficult. As mentioned before there are only two published reports on the copolymerization of 2-MeTHF from the 1960s using $BF_3 \bullet Et_2O$ as catalyst. However, the topology (open chains or cyclic structures) and molecular weights were not determined, probably due to analytic limitations. We successfully reproduced this reaction followed by optimization to reduce the excess of 2-MeTHF and to increase the molecular weight. If the PO is dosed slowly to a solution of $BF_3 \bullet Et_2O$ a co-polymer containing 52% of 2-MeTHF could be obtained (Scheme 24). The M_n calculated based on the end-groups was 2883 g mol^{-1}. While these numbers at first seem not so bad, GPC analysis showed that the situation is more complex. The Mn obtained by GPC was only 1100 g mol^{-1}. While it is not possible to compare these two values exact one to one this big discrepancy is an indication for the presence of non-hydroxyl terminated side-products. Additional evidence for this is the relatively high *Đ* of 4.8.



Scheme 24: Co-polymerization of PO in the absence of water

Further analysis by MS revealed that these side products are 4 membered cyclics consisting of equimolar ratios of PO and 2-MeTHF as well as 5 membered cyclics containing PO and 2-MeTHF in a ratio of 3:2. Additionally, GC-MS showed the presence of short ethoxylated chains as well as ethoxylated propylene glycol (Section 6.1). The presence of these impurities made curing with 4,4'-MDI impossible. From investigations on the cationic homopolymerization of PO and THF it is known that the chain growth can proceed via a tertiary oxonium ion located at the chain end.[203, 204] This path is usually referred to as the active chain end mechanism (ACEM). Besides propagation also intramolecular reactions ("back biting") with the active chain end are possible resulting in the formation of cyclic oligomers (Scheme 25a). Alternatively, if there is a high concentration of hydroxyl groups containing initiators (I) present during the cationic ROP of cyclic ethers, the activated monomers are initially attacked by I. This leads to the formation of a new hydroxyl group which in turn can attack another monomer and so on. (Scheme 25b). Next several BF_3 adducts were screened in combination with different amounts of water as initiator. Unfortunately, in all the cases, high values for *Đ* were still found, and even bimodal MW distributions were observed.



Scheme 25: a) Proposed ACEM b) proposed AMM for the copolymerization of PO and 2-MeTHF

The switch to Brønsted acids as catalysts, in particular phosphotungstic acid hydrate (PTA, $H_3PW_{12}O_{40}{\cdot}24H_2O$) in combination with 1,4-Butandiol (1,4-BDO) as initiator resulted in values for *Đ* around 2.0. As the exact quantification of the side products is rather difficult, an empirical approach was used to further lower the amount of side products and thus improve the quality of the obtained polyol. In theory, if no side reactions are occurring and the polymerization proceeds strictly via AMM, the obtained molecular weight should on the one hand depend directly on the degree of polymerization (*DP*). (Eq. 2.1.3a) and on the other hand on the amount of 2-MeTHF incorporated. If 2-MeTHF is not homopolymerizable it should not be possible to have two 2-MeTHF molecules in a row and the total content of 2-MeTHF units in a linear chain should be one less than PO (Eq. 2.1.3b). These two equations can then be combined (Eq. 2.1.3c) which in turn with the respective molecular weights of the components gives the theoretical molecular weight of ideal linear chains for a given PO to initiator ratio. Comparison with the experimental weight should then allow a first judgment of the quality of the polyol.

$$DP = \frac{X n_{\mathrm{PO}}}{z_{\mathrm{I}}\, n_{\mathrm{I}}} \qquad \text{(Eq. 2.1.3a)}$$

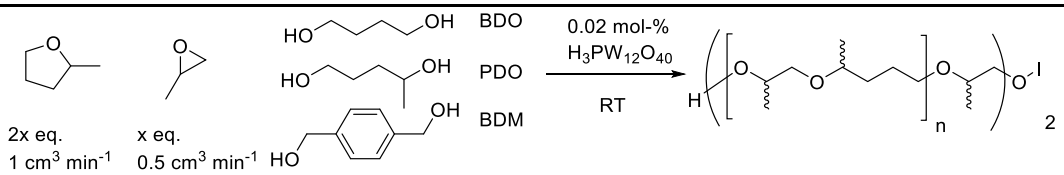
$$\mathrm{f}_{2\mathrm{MeTHF}} = \frac{\frac{n_{\mathrm{PO}}}{z_{\mathrm{I}} n_{\mathrm{I}}} - 1}{\frac{n_{\mathrm{PO}}}{z_{\mathrm{I}} n_{\mathrm{I}}}} \qquad \text{(Eq. 2.1.3b)}$$

$$Mn = \frac{X n_{\mathrm{PO}}}{z_{\mathrm{I}} n_I} \left(M_{\mathrm{PO}} + f_{2\mathrm{MeTHF}} M_{2\mathrm{MeTHF}}\right) + M_I \qquad \text{(Eq. 2.1.3c)}$$

(Eq. 2.1.3): DP = Degree of polymerization, X_{PO} = Conversion of PO, z_I = Functionality of the initiator, n_I = amount in moles, n_{PO} = amount of PO in moles, M = molecular weights

To avoid potential changes in the 2-MeTHF incorporation due to its consumption it was co-fed at twice the rate of PO. When 40 eq. of PO w.r.t. to 1,4-BDO were used the molecular weight was lower than the predicted one and again a high difference between the values measured with GPC and NMR was found (Δ=1222 g mol-1) as well as a high dispersity (*Đ*=3.6) (Table 10, Entry 1). Fortunately, if 20 eq. of PO are used this difference drops to only 168 g mol^{-1} and a *Đ* of 2.0 was observed (Table 10, Entry 2). Changing the initiator diol did not change the dispersity very much, however when it contains a secondary alcohol functionality, a slightly higher molecular weight than calculated was observed

Table 10: Selected results of the copolymerization of 2-MeTHF and PO using PTA as catalyst



Entry	I[b]	PO [eq][c]	M_n(th)[d] [g mol^{-1}]	M_n(NMR)[e] [g mol^{-1}]	M_n(GPC)[f] [g mol^{-1}]	$Đ$[f] [-]	2-MeTHF[g] [%]	Y[h] [%]
1	BDO	40	2888	2222	900	3.6	39(48)	75
2	BDO	20	1446	1368	1200	2.0	43(45)	69
3	PDO	20	1460	1720	1300	2.1	37(45)	92
4	BDM	20	1494	1325	1000	1.9	35(45)	77
5[i]	BDO	20	1446	90	-	-	0(45)	<1

[a]General conditions: 0.02 mol-% $H_3PW_{12}O_{40}·24H_2O$ w.r.t. PO in 50 cm^3 (490 mmol) 2-MeTHF and initator (21 mmol) followed by addition of 2-MeTHF and PO (30-60 cm^3). Flows (Q): Q(PO)=0.5 cm^3 min^{-1}; Q(2-MeTHF)=1.0 cm^3.min^{-1} Workup: filtration through silica. [b]BDO=1,4-butanediol; PDO=1,4-pentanediol; BDM=1,4-benzenedimethanol. [c]Equivalents of BDO w.r.t. initiator. [d]Calculated using Equations 2.1.3 assuming full PO conversion. [e]Measured with ^{1}H-NMR; [f]Measured by GPC [g]Content of 2-MeTHF in the oligomer, predicted value in brackets; [h]Isolated yields based on PO. [i]Anhydrous $H_3PW_{12}O_{40}$ was used as catalyst; no oligomers were formed.

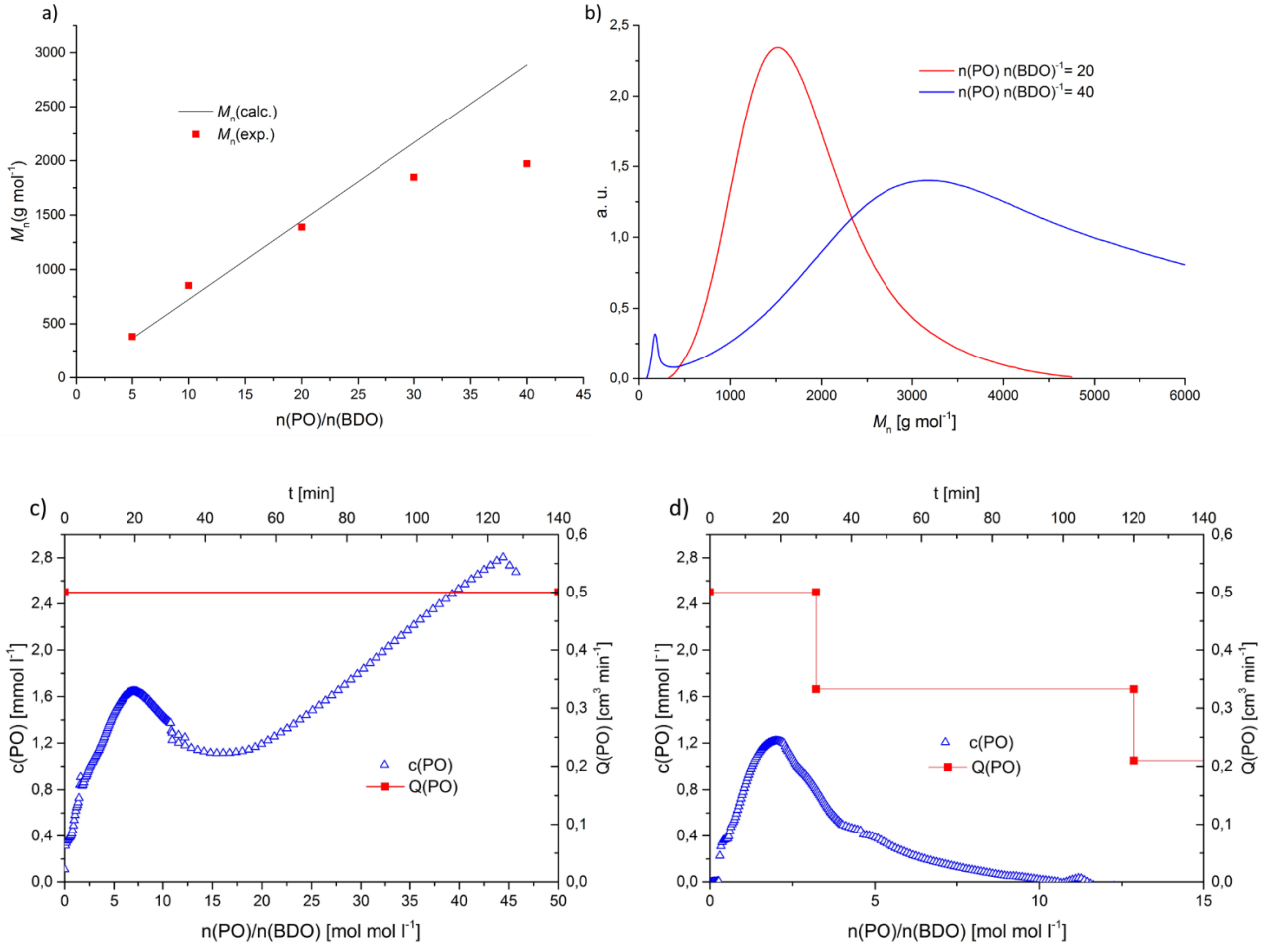


Figure 12: a) Comparison of measured M_n values with calculated values (Eq. 2.1.3c) as function of equivalents of PO dosed b) GPC of product samples at different PO to 1,4-BDO ratios. c) Concentration c(PO) of propylene oxide in the reaction mixture versus the amount of the dosed PO at a constant addition rate Q(PO). d) c(PO) vs. amount of dosed PO with declining addition rate. The concentration was measured in each case using in-situ ATR-IR spectroscopy.

(Table 10, Entry 3). The lower nucleophilicity of the secondary OH, might be the cause of this behavior. 1,4-Benzenedimethanol (BDM) which has again two primary alcohol groups behaved in this respect more like 1,4-BDO. In addition to the effect observed with PDO, the molecular weights were slightly lower than those expected in theory. Since the catalyst PTA contains 24 molecules of H_2O bound as crystal water, it seems plausible that these can act as an additional initiator. Interestingly, when the crystal water was removed from the PTA according to a literature procedure it lost its ability to catalyze the copolymerization ((Table 10, Entry 5). From the experiments in Table 10 it can further be concluded that there is certain limit to the chain length were the concentration of the polyether end groups becomes too low slowing down the polymerization via AMM and as a result new chains are initiated according to ACEM, eventually resulting in the formation of cyclic side products.

To further get insight in the dependence of the observed molecular weight on the amount of dosed propylene oxide, the molecular weight as well as the PO concentration in the reaction mixture was monitored (Figure 12a-c). It was observed that the M_n determined by ^{1}H-NMR is close to the predicted one until about 25 eq. of PO are dosed after which the increase declines.

After the dosage of about 30 eq. there seems to be no further increase in M_n. When GPC traces of samples obtained at 20 eq. PO and 40 eq. (Figure 12a) are compared a much broader distribution and low molecular side products are formed after the addition of 40 eq.. ESI-MS analysis revealed that the side products are cyclics that consist of 2-MeTHF and PO in the ratios of 2:2 and 2:3 (Section 5.3). Monitoring of the PO concentration in the reaction mixture shows that in the beginning there is first a rise in PO concentration after which the PO is then reacting faster than its fed (Figure 12c). When about 20 eq. are dosed, however, accumulation of PO is observed. Since cyclical by-products are also reduced if no more than 20 eq. are dosed, it is therefore obvious that their formation is caused by the accumulation of the PO. Aiming to address this issue the dosing rate of PO was adjusted to the reaction rate to avoid a buildup of its concentration (Figure 12d), which led to the formation of only traces of cyclics.

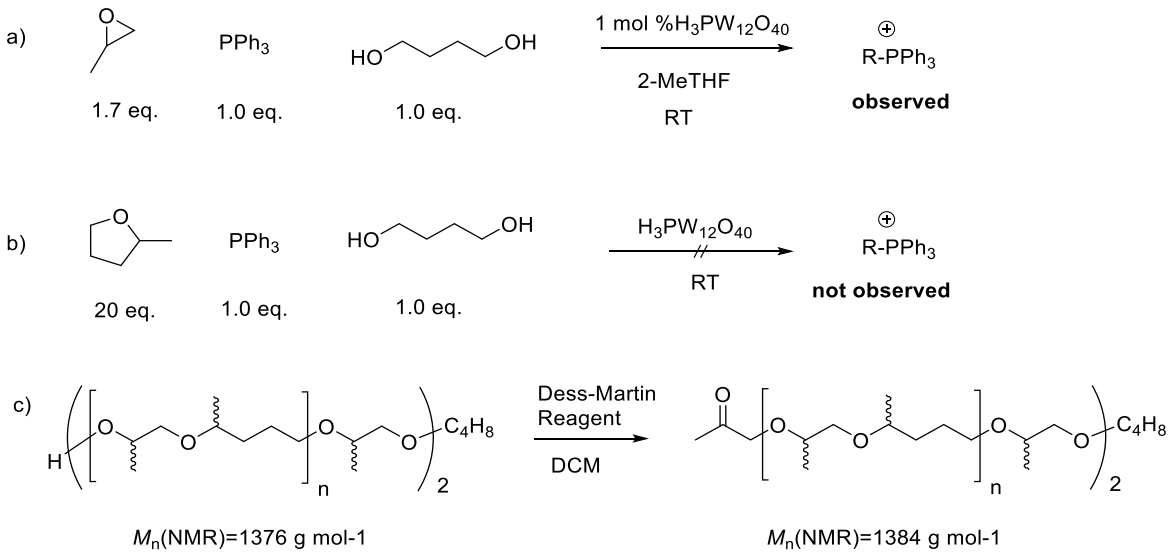
Table 11: Polyether polyols obtained and the mechanical properties of their corresponding PUR films

Entry	Catalyst [mol-%]	Initiator [mol-%]	2-MeTHF[a] [mol-%]	M_n(NMR)[a] [g mol]	M_n(GPC)[b] [g mol]	$Đ$[b]	ε_{max}[c] [%]	F_{max}[c] [N mm^2]
1	BF_3.Et_2O (5)	-	52	2883	1100	4.8	n.a.	n.a.
2	BF_3•2 H_2O (1)	H_2O (5.0)	52(45)	1081	500	3.1	60	0.8
3[d]	$H_3PW_{12}O_{40}$•24 H_2O (0.02)	1,4-BDO (5.0)	43(45)	1278	1200	2.0	600	3.0
4[e]	$H_3PW_{12}O_{40}$•24 H_2O (0.02)	1,4-BDO (5.0)	43(43)	1288	1100	1.9	1100	3.2

[a]Measured with ^{1}H-NMR after derivatization of the oligomer with trifluoroacetic anhydride. GPC measurement of the oligomer. [c]DIN 53504-SF3A-bones from 4,4'-MDI crosslinked films ε_{max}: Maximum elongation; F_{max}: Ultimate strength. [d]Constant dosing rate of PO and 2-MeTHF (Figure 12c); [e]Dynamic dosing rate (Figure 12d).

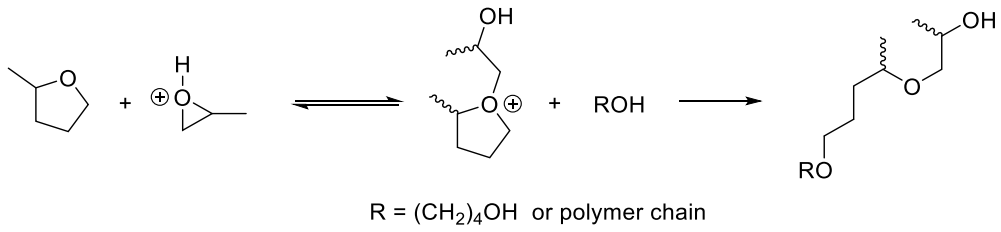
The usability of these materials was further investigated by the formation of PUR films using 4,4'-MDI as the diisocyanate (Table 11). The ultimate strength as well as the maximum elongation increased with declining values for $Đ$ and the difference between M_n values measured by GPC and ^{1}H-NMR. The highest values were obtained when PTA was used as catalyst. Almost twice the elongation was possible when the accumulation of PO was avoided. The buildup of PO at the beginning of the reaction however could not be eliminated. To investigate this phenomenon a series of control experiments were

conducted. First, we conducted ion-trapping experiments based on the methodology developed by Penczek and co-workers.[205, 206] This showed that PO and mixtures of it with 2-MeTHF led to the formation of oxonium ions that could react with triphenylphosphine (Scheme 26a). No phosphonium ions were observed when PO was absent (Scheme 26b). By oxidation of the end groups of the polymer it was possible to show that there were no terminal 2-MeTHF units (Scheme 26c) as they would have led to characteristic signal in the ^{1}H-NMR (Section 6.1). Based on the observations that 2-MeTHF does not undergo ring-opening in the absence of PO under the conditions of the copolymerization and with the observed composition of the chain ends a mechanism for the incorporation of 2-MeTHF in the growing polymer chain can be proposed (Scheme 27). The key step seems to be the alkylation of 2-MeTHF by activated ("protonated") PO to for a tertiary oxonium ion. Examples in the literature of ring-opening of 2-MeTHF to linear monomeric molecules by acylating reagents[119, 120] support this. This also explains the initial build up of the PO concentration. PO is significantly less basic than 2-MeTHF (ΔpKa=2),[207-209] therefore some PO must be dosed to shift the equilibrium towards the formation of protonated PO.



Scheme 26: Control experiments a) Ion-trapping with both PO and 2-METHF b) 2-MeTHF alone c) Oxidation of the polymer end groups to investigate their structure by NMR

It could be shown that 2-MeTHF, despite being very unreactive, can be co-polymerized with propylene oxide to hydroxy terminated polyols. However, care must be taken in choosing the right catalyst, conditions and reaction control. Otherwise cyclic side products are easily formed. Based on *in situ* IR monitoring and control experiments it was shown that the incorporation of 2-MeTHF proceeds via alkylation and accumulation of PO in the reactor leads to the formation of cyclic side products.



Scheme 27: Proposed mechanism for the incorporation of 2-MeTHF in the growing polymer chain

This accumulation happens also at the beginning of the reaction and is an unavoidable side effect of the mechanism, however at the beginning of the polymerization the concentration of hydroxyl groups is high enough to suppress the formation of active chain ends and therefore backbiting. The obtained polyols are in combination with diisocyanates such as 4,4'-MDI suitable for the formation of elastic PURs or adhesives. With $H_3PW_{12}O_{40} \bullet 24\ H_2O$ a catalyst can be used that is readily available since it is already used in many industrial processes.[210] It was possible to simply remove the catalyst by filtration through a plug of silica. The excess of 2-MeTHF can be distilled off from the polymer and re-used. In summary, the presented results show that 2-MeTHF represents a valid bio-based building block to produce polyether polyols for adhesives.

The submitted article concerning this work is included in 5.3.

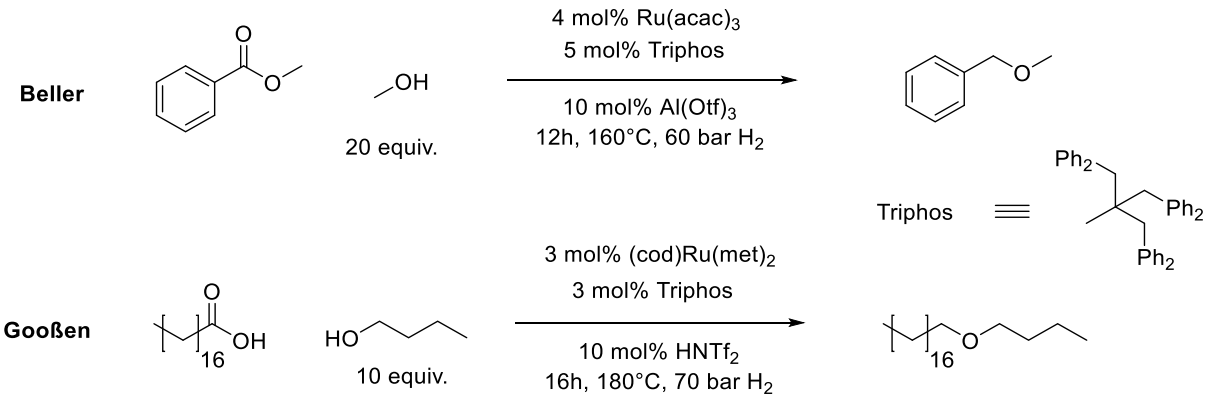
2.2 Plastic Waste as a Resource

Whereas the previous sections described how to obtain polymers from biomass, this section will focus on how existing plastic waste can be utilized to obtain polyols. As described earlier, the most investigated recycling concepts are mechanical reprocessing and depolymerization (Section 1.2). There are many examples that were even implemented on industrial scale. Despite this, only 8% of the global amount of plastic is recycled.[211] This is largely due to economic reasons. In the case of mechanical recycling extra energy and resources need to be used to reprocess to obtain a product that often has inferior properties due to degradation or cannot be used in food contact applications due to an unknown content of potential toxic compounds. Depolymerization on the other hand usually results in materials that yields virgin grade polymers. However, this approach is still preluded by cumbersome collection and separation processes. As a result, it is very difficult for these monomers to be cost-efficient with their virgin counterparts made from petrochemical feedstocks, at least at the moment.

A possible solution to this dilemma could be the chemical upcycling of plastic waste to higher valuable products. Although, it is clear that this strategy cannot be applied to recycle all the circulating waste, it would serve as an additional means to reduce waste and to promote the idea of recycling. On top of this, the upcycling of existing polymers could lead to novel materials with exciting new properties.

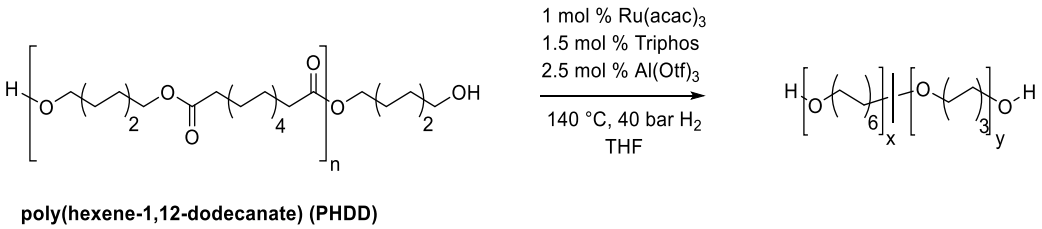
2.2.1 Conversion of Polyesters to Polyether Polyols

As mentioned in the previous section, the types of polyether polyols available for the adhesive or polyurethane developer, are traditionally limited to oligomers derived from epoxides or tetrahydrofuran. We surmised that the reduction of polyester to polyether polyols might be an alternative way to obtain these compounds. In contrast to the previous work of Meier (Section 1.2.4) we aimed to use hydrogen as a reductant instead of silanes. Hydrogen is a cheaper, more atom economic and avoids the formation of organo silicon compounds as by-products. When we searched the literature for suitable homogenous catalysts promising for the direct reduction of carboxylic acid ester to ethers only two reports on this transformation were found, one from the group of Beller[212] and one from Gooßen[213] (Scheme 28). In both protocols a ruthenium precursor in combination with a triphos ligand and a Lewis or Brønsted acid is used. Combinations of ruthenium[214, 215] or cobalt[216] with a triphos ligand and bipyridine complexes[217, 218] of iridium and rhodium are one of the few exceptions of homogeneous catalysts capable of hydrogenating carboxylic acids and esters under acidic conditions.



Scheme 28: Reductive etherifications developed by Beller and Gooßen

Notably, in both protocols an alcohol is added in excess. While the paper of Beller does not comment on this, the work of Gooßen shows that this prevents the dimerization of the intermediate alcohols. Hence the question arose if it is possible to directly obtain polyethers from polyester by further developing this method.



Scheme 29: Hydrogenation of PHDD to random co-polyethers

For further investigation we choose poly(hexen-1,12-dodecanate) as model substrate (Scheme 29). An initial screening identified 1,4-dioxane and THF as most promising solvents. A higher selectivity was observed in the case of THF. Next, we checked the effect of the Lewis acid on the reductive etherification of PHDD (Figure 13). Here an increase of the selectivity towards the formation of ether bonds with growing charge density of the Lewis acids was observed. Aluminum, tin and gallium triflates gave selectivities between 90-99%. Lanthanoids except for yitterbium and indium did not give any selectivity. An interesting observation was made in the case of hafnium(IV) triflate here the selectivity increased to 130%. The reason might be that it is capable to open the THF even at this rather high temperature. A similar observation has been made by Marks and co-workers in their study of the hydrogenolysis of cyclic ethers.[219]

After this the ratio of ligand and aluminum triflate to the ruthenium precursor as well as the catalyst loading were investigated (Section 5.4). This revealed that the optimum ratio of triphos ligand to $Ru(acac)_3$ was about 1.5. To achieve optimum selectivity (92% at 91% conv.), it was necessary to increase the amount to use 2.5 eq. of $Al(OTf)_3$ w.r.t. Ru. Higher loadings of the Lewis acid did not increase the selectivity but decreased the achievable conversion. In addition, a substantial breakdown in molecular weight was observed with increasing conversion. This indicates that the reaction proceeds via a tandem hydrogenation-etherification (Scheme 30a). Gooßen and co-workers made similar observations.[213]

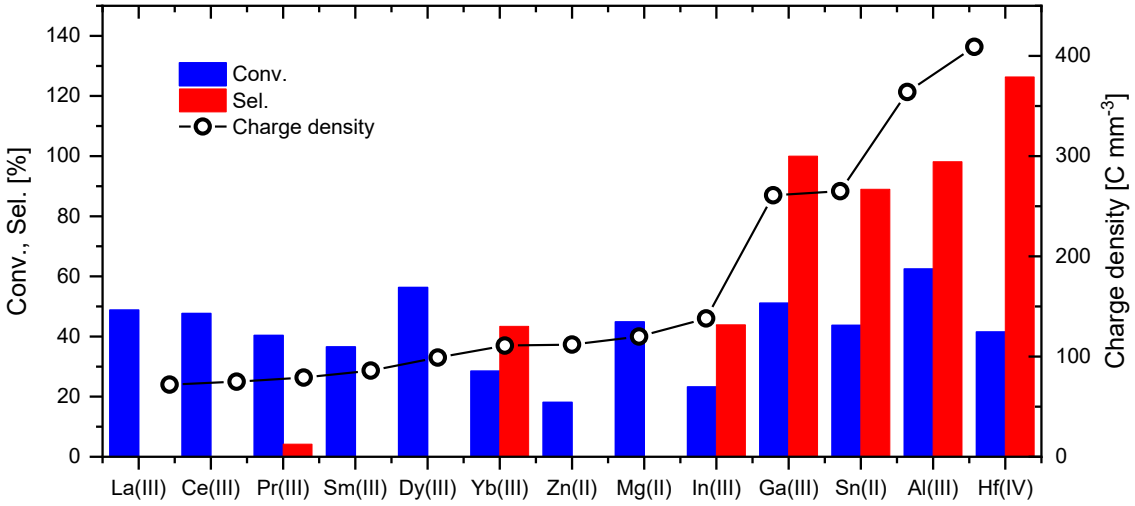
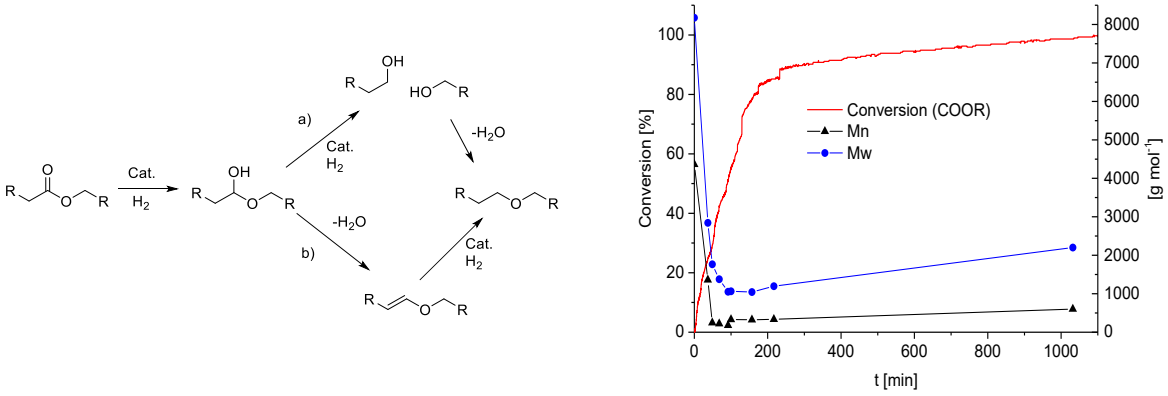


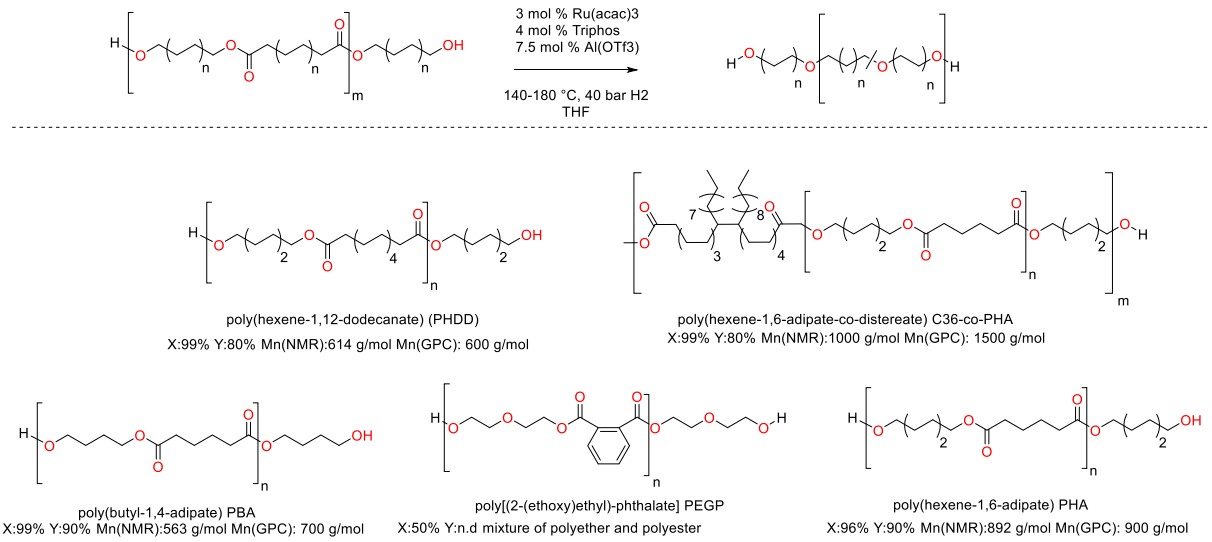
Figure 13: Effect of different metal triflates on the conversion and selectivity of the reductive etherification of PHDD compared to their corresponding estimated charge densities. Reaction conditions: PHDD (200 mg, 1.28 mmol COOR groups), 1 mol% $Ru(acac)_3$, 1.5 mol% Triphos, 2.5 mol% Lewis acid in 2 cm^3 THF. T = 140 °C, 40 bar H_2, t = 16 h. Charge density was derived from the respective ion-radii of the corresponding cations.[220]



Scheme 30: Different mechanistic proposals (left). Right: Figure 14: Conversion calculated from the hydrogen uptake and molecular weight in the hydrogenation of PHDD over time. Conditions: 3.0 g of polymer in 30 ml of THF, 3 mol % $Ru(acac)_3$, 4.5 mol-% Triphos, 7.5 mol% $Al(OTf)_3$, T= 140 °C; $p(H_2)$ = 60 bar (right).

On the contrary, a mechanism in which etherification occurs via the acid catalyzed elimination of water from the hemiacetal intermediate (Scheme 30b), was proposed by Beller and co-workers.[212] To gain more insight, the conversion and the molecular weight was monitored over time (Figure 14). This showed that after 200 minutes 80% of the ester linkages are hydrogenated. In the same time, the molecular weight almost reaches the value of the monomers. Then, over the next 14 hours the molecular weight slowly increases. This leads to the conclusion that in our case tandem hydrogenation-etherification occurs. For further exploration of the generality of the reaction, we subjected a range of industrial grade polyesters to the hydrogenation. Notably no purification, except drying under reduced pressure was necessary. The scope was easily extended to other aliphatic polyesters (Scheme 31). Poly[(2-(ethoxy)ethyl)-phthalate] (PEGP) in contrast was not fully reduced and yielded a complicated mixture of polyesters and polyethers.

Polyethylene terephthalate (PET) was also subjected to the procedure but no conversion of the ester groups occurred. The most likely reason for the absence of reactivity is the insolubility of this polymer under the reaction conditions.



Scheme 31: Scope and limitation of the reduction of polyesters to polyether polyols. X refers to the conversion of carboxylic acid ester groups. Y to the yield of ether groups in the product oligomer.

In all cases the molecular weight of the obtained polyethers was reduced but it is still in the range of 400-2000 g mol^{-1} as other common polyols in polyurethane based adhesives. The applicability of the obtained polyether polyols was further verified by adding 1.1 eq. of 2,4-toluene diisocyanate to the polyether derived from poly(hexene-1,6-adipate) (PHA,) followed by moisture curing at ambient conditions. This yielded a polyurethane film with a leather like haptic. DSC measurements showed that poly[oxy(hexane-1,6-diyl)] obtained by the reduction of PHA retained its crystallinity. However, the melting range was reduced from 45°C-50°C (PHD) to 14-17°C (the hydrogenated product). This could be an advantage to the widely used poly-THF polyether that melts at 28°C and usually requires heated distribution pipes and storage tanks.

3 Summary

To enable the entry of bio-based chemicals to the market high margin low volume products need to be found which justify the investment in pilot or demonstration type plants as a first step towards the production of these bio-based intermediates. Once the process has been derisked in this way and a growing market is established, it will be easier to find a company willing to invest in a large scale plant that will allow the reduction of the price to such an extent that it can also compete in the high volume low margin segment. One very good example for this is the aforementioned project GreenSolRes in which we seek to develop alternative building blocks for glues and coatings together with the company Henkel. Henkel aims to increase the content of bio-based chemicals (preferable if there is an added advantage beyond renewability) in their product portfolio.

As presented in this thesis, AL can be easily and straight forward converted to a bicyclic monomer. Although the synthesis consisted of 3 steps from levulinic acid, all the steps can be conducted in the

absence of a solvent and no chromatographic separations are necessary. The synthesis of about 50g of this monomer was successfully demonstrated. This molecule is very reactive in a ROMP reaction and yields polymers that are more polar than polynorbornene due to the lactone moiety present in the backbone, while still retaining the optical clarity of the regular polynorbornenes.

The diol 1,4-PDO should not be merely treated as a substitute for the currently used 1,4-BDO as its use offers the possibility to obtain polyester polyols with much lower melting points. For the usage in adhesive formulations this considered to be an advantage as no pre-melting of the polyol is required. Further it is possible by the choice of the diacid to obtain amorphous or crystalline polyester polyols. The derived polyurethanes exhibit in elastomeric behavior at room temperature compared to the ductile and brittle 1,4-BDO analogues. Additionally, the low melting point of the crystalline 1,4-PDO derived polyester polyols leads to interesting low temperature shape memory effects in the resultant polyurethane. An effect that could be exploited in the design of adhesives for smart labels. Currently the development of suitable formulations containing this diol are taking place at Henkel, which could be a promising entry path for this bio-based building blocks to the global adhesive market.

In the case of 2-MeTHF it was possible to obtain polyester polyols via copolymerization with PO. The main challenge in this copolymerization is the formation of cyclic side products. Their formation could be successfully suppressed by careful control of the reaction conditions, choice of initiator and un-revealing the reaction mechanism. The applicability of the obtained polyether polyols was demonstrated by converting them into the corresponding polyurethanes. The usage of inexpensive phosphotungstic acid makes the scalability of these oligomers feasible. Additionally, its novel structure adds to the toolbox of the adhesive and sealant developers. As a result, these oligomers are at the moment further evaluated by our collaborator Henkel.

The use of plastic is currently associated with a high level of waste generation. Although many recycling processes have already been established, these conventional processes are still in competition with polymers made from fossil raw materials. This thesis showed that polyesters can be hydrogenated with a combination of ruthenium, triphos ligand and Lewis acids to polyether polyols. The polyether polyols obtained are OH terminated and their molecular weight makes them suitable for the use in polyurethanes and adhesives. This makes it possible to obtain polyether polyols, which can otherwise only be produced from petrochemical feedstocks with great difficulty.

In conclusion, three different polymers have been prepared from the levulinic acid derivates angelica lactone (AL), 1,4-pentanediol (1,4-PDO) and 2-mehtyltetrahydrofuran (2-MeTHF). They could be made without the use of expensive reagents and catalysts. This demonstrates the promising role of levulinic acid as a bio-based platform chemical. Besides that, it was shown that hydrogenation reactions can be a promising way of upcycling of polymer waste to materials of potential higher value.

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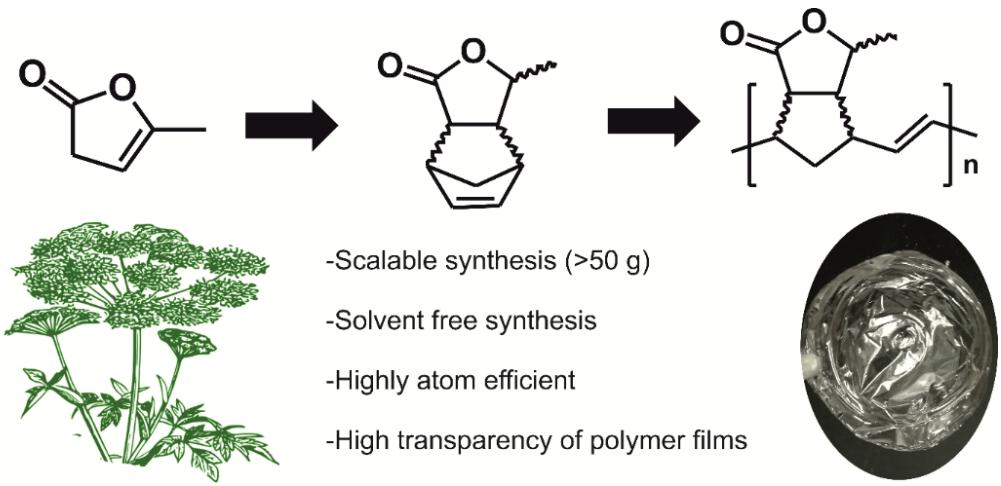
5 Selected Publications

5.1 Scalable synthesis and polymerization of α-angelica lactone derived monomer



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Scalable synthesis and polymerisation of a β-angelica lactone derived monomer†

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Bio-based levulinic acid is easily ring-closed to α-angelica lactone (α-AL). α-AL can be isomerized to the conjugated β-AL under the influence of base, but since this is an equilibrium mixture it is very hard to devise a scalable process that would give pure β-AL. This problem was circumvented by distilling the equilibrium mixture to obtain a 90 : 10 mixture of β- and α-AL in 88% yield. This mixture was used for Diels–Alder reactions on 3 terpenes and on cyclopentadiene in up to 100 g scale. The latter DA adduct was subjected to a ROMP reaction catalysed by the Grubbs II catalyst. The resulting polymer has some similarities to poly-norbornene but is more polar. The polymer can be processed into films with very good transparency.

Introduction

The debate about when fossil fuels will run out has been ongoing for many years. Technological advancements have made the exploitation of an increasing number of reservoirs profitable. However, there is a consensus that all the natural reservoirs may eventually become depleted, and thus a gradual switch to renewable feedstocks will be necessary. And although it will be impossible to fulfil the total global demand for fuel and energy with biomass-based analogues, there is more than enough biomass available on a yearly basis to serve as the raw material for all of the chemicals we need.[1]

Platform chemicals are small molecules that can be produced in good yields from bio-based raw materials such as lignocellulose or sugars by fermentation or by using thermocatalytic reactions.[2,3] Further (preferably catalytic) conversions of these chemicals allows the synthesis of fine chemicals,[4–8] monomers,[8–13] and fuels.[14,15] Especially renewable polymers[16–18] and adhesives[19] based on them, often have novel properties which are considered an advantage beyond renewability. One very prominent example of a bio-based platform chemical is levulinic acid (LA) which can be efficiently obtained by the acid-catalysed decomposition of the C-6 sugars in lignocellulose.[2,20–23] LA itself can be converted into a wide range of useful compounds.[24] The most studied and used ones are aminolevulinic acid (herbicide), 2-methyl tetrahydrofuran (solvent and fuel),[25,26] γ-valerolactone[27] (solvent), ester derivatives (plasticisers, fragrances and fuels),[28–30] and the nylon intermediates adipic acid and caprolactam.[31–37] LA can be converted into methyl vinyl ketone (monomer, vitamin A precursor) under oxidative conditions,[38] or *via* decarbonylation of the intermediate angelica lactone.[39,40]

There are three isomers of angelica lactone (α-AL, β-AL, and γ-AL) which are shown in Scheme 1a. α-AL is conveniently obtained by reactive distillation of LA in high yields with water being the sole side product.[41–43] This makes α-AL an interesting bio-based building block, which has been used as a monomer in UV-light induced, cationic and ring-opening polymerisations.[44] The UV-light induced and cationic polymerisations tend to afford only sticky colourful oligomers.[45,46] The product obtained by anionic ring-opening polymerisation has a higher molecular weight but consists of a mixture of C–C and ester connected monomer units.[47] Such an irregular structure would make it rather challenging to use these polymers in applications where an exact control of the polymer structure is necessary. For instance, the oligomers that are typically used in the production of thermoplastic polyurethanes require well-defined end groups.[48] Higher molecular weight polyesters on the other hand are typically used in extrusion and spinning processes[49] for which high crystallinity and melting points are desirable traits, something poly α-AL may not provide due to the high stereo- and regio-irregularity. Other studies which were initiated by Mascal and co-workers focused on the utilisation of α-AL as a precursor for jet-fuels. Here α-AL is converted in the presence of K_2CO_3 to its di- and trimers, which can then be hydrodeoxygenated to the branched alkanes typically used in gasoline (Scheme 1b).[50,51] The dimerisation step caught our attention as this reaction is known to occur *via* the β-isomer which we deem to be an interesting building block. β-AL itself has been dimerised to jet-fuels precursor and, for

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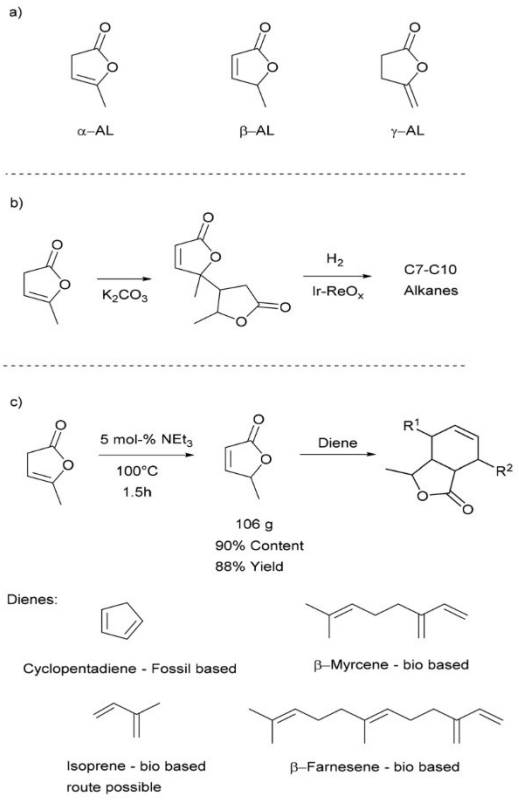


Scheme 1 a) Different isomers of angelica lactone. (b) The pioneering work of Mascal and co-workers regarding the conversion of Al to fuels. (c) Our approach to upgrade α-AL to functional monomers for ROMP.

the first time, polymerized to acrylic-type polymers by the group of Hong.[52]

We have explored the synthesis of bio-based monomers *via* Diels–Alder reactions (Scheme 1c) to obtain lactone functionalised derivatives. Diels–Alder reactions for the preparation of bio-based monomers recently received much attention[53–56] as they are very atom-efficient and usually can be conducted in the absence of a solvent. Such functionalised norbornenes can then be used for example as monomer for adhesives,[57] shape memory materials[58] and polymer based electrolytes in batteries.[59] Adducts containing the angelica lactone moiety have been prepared using this approach, but thus far the β-AL that was used in these reactions was not made from α-AL, likely due to the necessity to have pure β-AL.[60–62]

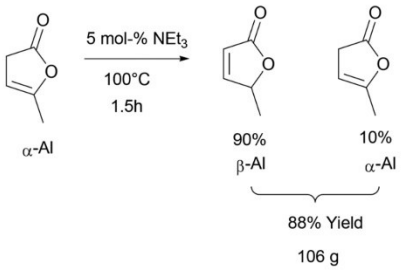
We wanted to use these Diels–Alder adducts in ring-opening metathesis reactions (ROMP) to obtain bio-based norbornene polymers. They can be easily functionalised as it is known that the γ-valerolactone moiety readily undergoes reactions with primary amines.[63]

Results and discussion

α-AL and β-AL are in equilibrium with each other in the presence of base but also undergo dimerisation under the reaction conditions necessary for isomerisation, a fact that makes the highly selective synthesis of pure β-AL from α-AL at high conversion a very challenging reaction that has not been achieved up to this date. Usually yields between 40–60% of β-AL can be achieved.[64–66] This and the fact that in the existing protocols product separation needs to be carried out by column chromatography negatively affects the sustainability and scalability. Additionally, the formation of various azeotropes (see ESI†) of the isomers under vacuum distillation conditions results in a further yield penalty.

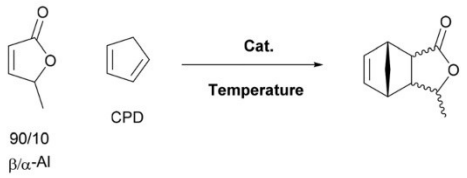
However, as shown in Scheme 2, we found that it is possible to obtain a high content of β-AL in the product fraction (90 mol%), if the reaction time is kept rather short and no solvent is used. The usage of triethylamine allows its easy separation during vacuum distillation preventing further dimerisation. The mixture of the two angelica lactones was thus obtained in 88% yield after distillation on a 100 g scale. A small forerun was obtained, containing mostly α-AL, which can be reused. The only side products that remain are the di- and trimers which might be interesting raw materials for fuels.[50,67]

Next the solvent free Diels–Alder reaction of the AL-mixture containing 90% β-AL with cyclopentadiene (CPD) was investigated in the presence and absence of a catalyst (Table 1).



Scheme 2 Synthesis of a mixture enriched with β-AL.

Table 1 Screening of the reaction conditions for the DA-reaction between β-AL and CPD



Entry	Catalyst	Eq. (CPD)	T [°C]	t [h]	Yield[a] [%]	*Endo/exo*[a]
1	5 mol% $Al(OTf)_3$	3	RT	16	—	—
2	5 mol% $Al(OTf)_3$	3	100	2	—	—
3	—	3	80	0.5	19	91/9
4	—	3	100	0.5	40[b]	70/30
5	—	3	60	0.5	25	95/5
6	5 mol% $ZnCl_2$	3	80	0.5	40	84/16
7	5 mol% $ZnCl_2$	3	RT	16	63	89/11
8	5 mol% $ZnCl_2$	10	RT	16	90 (86)[b]	90/10

General conditions: Reactions were carried out in closed reaction tubes and heated with microwave irradiation. [a] Determined by ^{1}HNMR spectroscopy. [b] Isolated by column chromatography.

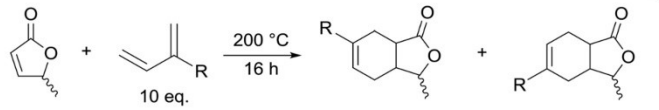
When aluminium triflate was used as the catalyst (entries 1 + 2) the contents were converted to a black charred residue and no desired product formation was observed. When no catalyst was used it was possible to obtain the product in 19 to 25% at 80 °C to 90 °C respectively (Table 1, entries 3 and 5). At a higher temperature (100 °C) it was possible to isolate 40% of the DA-adduct. A similar yield was obtained at 80 °C in 30 minutes when anhydrous zinc chloride was used as catalyst. Increasing the reaction time from 30 minutes to 16 hours only led to a yield of 63%. As it was apparent that the low yields are caused by the competing di- and trimerisation of the CPD with itself, the equivalents of CPD with respect to β-AL were increased up to 10. This resulted in 90% yield of the desired product. Since a process that uses 10 eq. of CPD is not very efficient and sustainable, we decided to perform the reaction under semi-batch conditions on a 50 g scale (see Scheme 3). After dissolving zinc chloride in the β-AL enriched mixture 2 equivalents of CPD were slowly added over 10 hours. The $ZnCl_2$ could be easily separated by adding acetone and any formed di- or trimers of CPD could be precipitated by simple dissolution of the product mixture in methanol. No column chromatography was necessary to obtain the product as a mixture of isomers in 82% yield. This is very fortunate as purification by distillation of the adduct is not an option since the retro-Diels–Alder reaction to β-AL commences at 136 °C (see ESI† for a DSC/TGA). Aiming for a higher renewable atom content, dienes other than cyclopentadiene have also been investigated. Use of furans was not successful under both catalysed and thermal conditions, due to rapid formation of humines (see ESI†). On the other hand, use of isoprene and terpenes (β-myrcene and farnesene) were more promising (Table 2). Upon reaction with β-AL at high temperature, full conversion was achieved. The diene oligomers formed as by-product were removed by a simple filtration through a short silica path, affording the Diels–Alder products in yields of up to 60%.

The ring-opening metathesis polymerisation (ROMP) of the DA adducts was next investigated.[68–70] Grubbs' 2nd generation catalyst was chosen for this (Fig. 1). Dichloromethane (DCM) is the solvent of choice for this reaction, since the polymeric products normally dissolve in it, thus allowing the formation of higher molecular weight polymers. The fully bio-based adducts shown in Table 2 were not polymerizable under these conditions, probably due to the absence of the ring strain that is present in the norbornene-type structure. On the other hand, the polymerization of the Cp/β-AL adduct was successful. Interestingly, at the initial monomer concentration of 1 mol l^{-1} after the addition of the initiator (0.5 mol% w.r.t. Cp/β-AL) the reaction mixture formed a gel within one minute indicating a great reactivity of this monomer in ROMP reactions (see Scheme 4). To further fine tune the polymerisation conditions different solvents, commonly considered as "greener" or safer choices, beside DCM were investigated at a lower catalyst loading. These solvents and their influence on the ROMP of the CP adduct are shown in Table 3. 2-Methyltetrahydrofuran was chosen due to its similar polarity to DCM but lower toxicity[71] and potential renewability. Ethyl acetate (EtOAc) was included as it is one of the safest solvents regarding flammability and toxicity,[72,73] which is also applicable for methyl isobutyl ketone (MIBK). Although not a "green" compound in general we also included *tert*-butyl methyl ether (MTBE) since it remains still a common solvent in industry and does not form peroxides.

Notably, in all solvents expect DCM a white precipitate appeared after a few minutes of reaction time. In all the attempts the DA adduct did polymerise, yielding white gummy materials after precipitation with cold methanol.

As expected, the polymer obtained in DCM had a substantially higher molecular weight than the one predicted assum-

Table 2 Screening of dienes in the Diels–Alder reaction with β-AL



Entry	Diene	Yield[a] [%]
1	Isoprene (R = Me)	60
2	Myrcene (R =)	54
3	β-Farnesene (R =)	18

General conditions: reactions were carried out in 4 ml vials equipped with a septum and magnetic stirring bar placed into a stainless steel 300 ml autoclave pressurised with 20 bar of nitrogen. [a] Isolated yield.

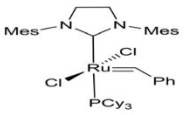
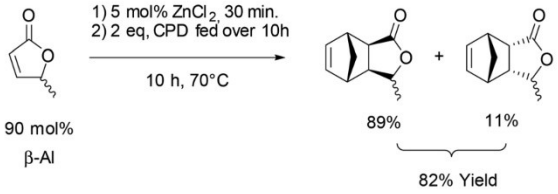
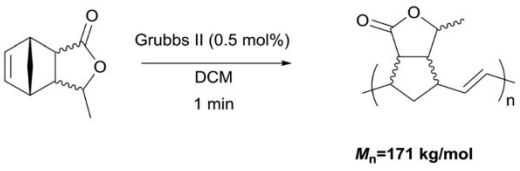


Fig. 1 Grubbs II metathesis catalyst.

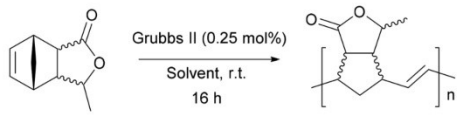


Scheme 3 Synthesis of the DA-adduct with CPD on 50 g scale.



Scheme 4 Initial ROMP experiment with Cp/β-AL.

Table 3 Influence of different solvents in the ROMP of Cp/β-AL



Entry	Solvent	Yield[a] [%]	M_n[b] [kg mol^{-1}]	M_w[b] [kg mol^{-1}]	$Đ$[b]
—	Calc.	—	65.6	—	—
1	DCM	78	122	264	2.17
2	2-MeTHF	69	80.6	154	1.91
3	EtOAc	61	64.1	118	1.85
4	MIBK	52	70.9	1.46	2.06
5	MTBE	70	67.8	138	2.04

[a] Isolated yield. [b] Determined by GPC (DMF/LiBr).

ing a living polymerization (Table 3, entry 1). When using 2-MeTHF the obtained molecular weight was reduced to 80.6 kg mol^{-1}. Ethyl acetate (EtOAc) and MTBE on the other hand afforded molecular weights of 64.1 kg mol^{-1} and 67.8 kg mol^{-1} respectively which are relatively close to the theoretical molecular weight of 65.6 kg mol^{-1}. These findings indicate that the very safe and potentially renewable solvent EtOAc does not lead to catalyst deactivation/inhibition compared to DCM.

Aiming to assess the relation between substrate to catalyst ratio and molecular weight of the polymer, different catalyst loadings were investigated. A substantial linearity in the range between 100 : 1 and 600 : 1 (mol of substrate per mol of catalyst) was achieved, showing that the final molecular weight can be controlled by varying the amount of catalyst (Fig. 2).

The obtained polymers tend to decompose at about 378 °C in a nitrogen atmosphere. No melting points were detected in the DSC analysis (as expected) confirming the amorphous nature of the polymer. In addition, a glass transition could also not be observed, which is an indication that the T_g occurs at or above the decomposition temperature (Fig. S8 and S9†). In contrast, poly-norbornene has a T_g at 35 °C. It is not easy to account for the huge difference in T_g between the two polymers. The high T_g of our polymer can possible be explained by the stereoregular nature. For steric reasons, the polymer has to be *all trans*.

Contact angle measurement revealed that the presence of the lactone moiety in poly-Cp/β-AL is increasing the hydrophilicity compared to poly-norbornene (θ(Cp/β-AL) = 75.7 ± 1.9°; θ(Cp/poly-norbornene) = 83.9 ± 2.3°).

As shown in Fig. 2 the polymer obtained *via* the ROMP of Cp/β-AL can be cast into clear transparent films. Comparison with poly-norbornene (prepared with the same catalyst in DCM) shows there is no negative effect of the lactone group on transparency (Fig. 3). Therefore it might be possible to find similar applications in optical wave guides,[74] transparent coatings[75] or other applications where high transparency in a large range of wavelengths is necessary.[76]

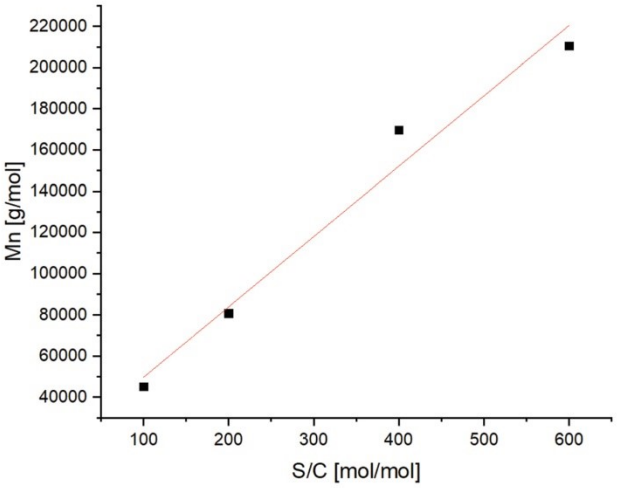


Fig. 2 Obtained M_n values *via* ROMP of Cp/β-AL performed at different substrate to catalyst ratios (S/C).

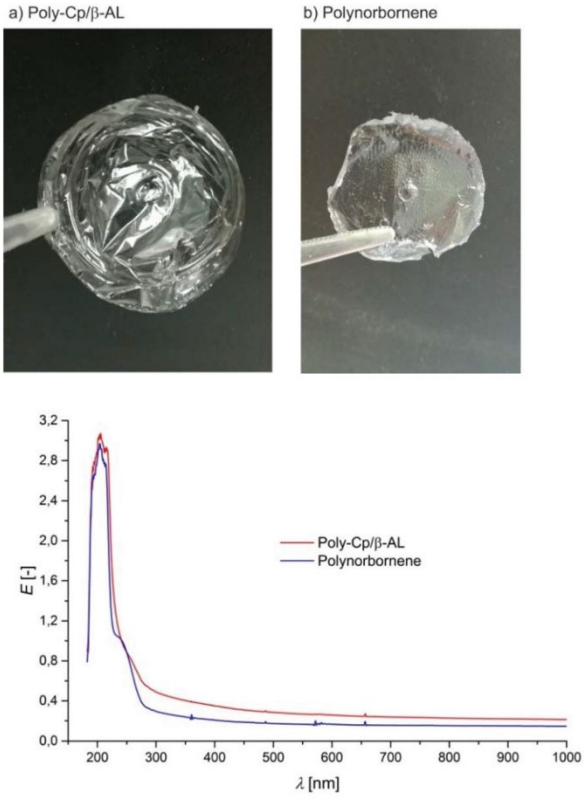


Fig. 3 Films obtained from (a) poly-Cp/β-AL and (b) polynorbornene obtained by solution castings. Below: absorbance spectra of these films in the range from 150–1000 nm. E = extinction.

Conclusions

It is still challenging to obtain pure β-AL from renewable α-AL in a scalable and sustainable procedure. In this work we show that a 90 : 10 mixture of the two can be prepared in a scalable

procedure. This mixture is rich enough in β-AL to be used efficiently as dienophile in Diels–Alder reactions with cyclopentadiene, isoprene, myrcene and β-farnesene. The adduct obtained with cyclopentadiene can be efficiently polymerized in a ROMP reaction catalysed by the Grubbs II catalyst, either in DCM or alternatively using the renewable solvents 2-MeTHF or ethyl acetate. A linear relationship between M_n and the amount of catalyst is observed between a monomer to catalyst ratio of 100 to 600, thus allowing control of the molecular weight. The resulting polymers can be processed into films that have high transparency over a wide range of wavelengths. Compared with poly-norbornene the lactone moiety increases (surface) hydrophilicity, which could give rise to various benefits; for instance, higher miscibility with polar additives or better interaction with certain (wet) surfaces in coating applications. The lactone moiety does not only increase the bio-based carbon content of the materials, but it also enables further derivatization which gives easy access to a plethora of different polymers.

Experimental section

Preparation of a mixture of angelica lactones with 90 mol% content of the β-isomer

α-Angelica lactone (98%, 120 g, 1.2 mol) was added to a 250 ml two neck flask equipped with a condenser and a magnetic stirrer followed by the addition of triethyl amine (5 mol%, 8.5 ml). The mixture was heated to 100 °C under an argon atmosphere and monitored by ^{1}H-NMR. After 1.5 hours a ratio of β/α-angelica lactone of 90–95/10–5 was reached and the condenser exchanged with a distillation head. Subsequent vacuum distillation at 6×10^{-2} mbar yielded two fractions: 38–42 °C containing mainly the α-isomer (this fraction can be reused for the next isomerisation run) and a fraction at 45–50 °C containing a mixture of angelica lactones with 90 mol% content of the β-isomer (106 g, 88% of theory).

^{1}H NMR (400 MHz, CD_2Cl_2, signals of β-isomer are reported) δ 7.46 (dd, J = 5.7, 1.5 Hz, 1H), 6.04 (dd, J = 5.7, 2.0 Hz, 1H), 5.11 (qt, J = 6.9, 2.0, 1.5 Hz, 1H), 1.41 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 173.3, 158.0, 121.3, 80.0, 19.0.

Diels–Alder reaction between β-angelica lactone and cyclopentadiene

In a dry and argon purged 10 ml reaction tube the angelica lactone mixture (β-AL = 90%, 10 mmol, 900 μl) and the desired catalyst were mixed. Freshly prepared CPD (3.0–10 eq. 2.5–8.3 ml) was added, the tube was sealed and heated with a microwave oven to the desired reaction temperature where it is kept for the indicated time. The 2 diastereomers of the product were separated by flash column chromatography (heptane/ethyl acetate 8 : 2), affording the *endo* and *exo* isomers (each of them is a racemic mixture of 2 stereoisomers) adduct as colourless oils (*endo*: 949 mg, 5.9 mmol, 30%; *exo*: 119 mg, 0.7 mmol, 7%; *endo*/*exo* 89/11).

Exo: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.21–6.04 (m, 2H), 4.17 (qd, J = 6.4, 3.2 Hz, 1H), 3.24–3.03 (m, 1H), 2.82 (dtq, J = 3.1, 1.5, 0.8 Hz, 1H), 2.59 (dt, J = 8.3, 1.3 Hz, 1H), 2.08–1.97 (m, 1H), 1.50–1.35 (m, 7H), 1.30 (d, J = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 177.4, 136.4, 134.9, 78.9, 51.6, 48.5, 48.2, 46.0, 45.6, 22.8.

Endo: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.22–6.09 (m, 2H), 3.95 (qd, J = 6.5, 3.1 Hz, 1H), 3.26–2.97 (m, 3H), 2.67–2.54 (m, 1H), 1.57–1.46 (m, 1H), 1.39–1.29 (m, 1H), 1.25 (d, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 137.6, 137.5, 80.7, 50.0, 48.9, 47.6, 46.3, 43.1, 23.2.

Semi continuous synthesis of the β-angelica lactone CPD adduct

A 500 mL 2-neck round bottom flask was filled with dicyclopentadiene (100 mL) and iron(0) powder and equipped with a distillation setup. Cyclopentadiene was obtained by thermal cracking of its corresponding dimer at 180 °C and then condensed into a dropping funnel. 2 equivalents (84 mL, 67 g, 1.0 mol) were dropped over 10 hours into a 1 liter 3-necks round bottom flask containing the angelica lactone mixture (β-AL = 90%; 50 g, 0.5 mol) and zinc(II) chloride (3.5 g, 0.03 mol, 0.05 eq.) while heating up to 70 °C. Once the addition was complete, the reaction was stirred for another 10 hours and monitored by GC. After cooling down to room temperature, acetone (80–150 ml) was added to precipitate the Lewis acid catalyst. The remaining cyclopentadiene and α-angelica lactone were removed by vacuum distillation (50 °C/0.06 mbar) and the remaining cyclopentadiene dimers were precipitated by addition of ice-cold methanol (100 ml) followed by filtration. Solvent removal afforded the product as an orange liquid (69 g, 0.4 mol, 82% yield, *endo* : *exo* 89/11).

Ring-opening metathesis polymerization of the Cp/βAL adduct

To a stirred solution of Grubbs II catalyst (4.7 mg, 0.006 mmol, 0.25 mol%) in the desired solvent (Table 3) the Cp/βAL adduct (0.2 mL, 2.2 mmol, 1 eq.) was added under argon atmosphere. The reaction was stirred overnight. In few minutes after the addition, all the solutions turned opalescent and a whiteish precipitate appeared, except for the reaction in DCM. The reaction mixtures were then concentrated *in vacuo* and washed several times with methanol (using DCM to re-dissolve the polymer). All the reaction afforded a whiteish, gummy solid. A small portion of each sample was dissolved in a DMF/LiBr solution and analyzed by GPC. ^{1}H-NMR spectra were recorded in $CDCl_3$.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84–5.12 (m, 2H, –C*H*=), 4.53–4.09 (m, 1H, O–C*H*–CH_3), 3.33–2.38 (m, 4H, ring junction- and allylic-C*H*-), 1.89 (m, 2H, bridged-CH_2-), 1.62–0.92 (m, 3H, CH_3).

Film formation procedure

Films were obtained by casting a saturated solution of the polymer in DCM into a Teflon mold (depth 1 mm), letting the solvent evaporate over 4 hours.

Conflicts of interest

The authors declare no conflict of interest.

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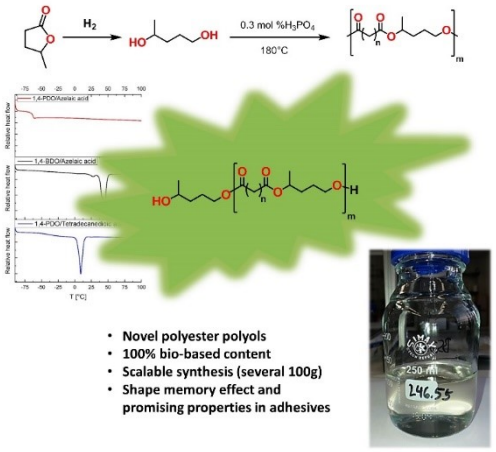
5.2 Properties of Novel Polyesters Made from Renewable 1,4-Pentanediol



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Properties of Novel Polyesters Made from Renewable 1,4-Pentanediol

Bernhard M. Stadler,[a] Adrian Brandt,*[b] Alexander Kux,[b] Horst Beck,[b] and Johannes G. de Vries*[a]

Novel polyester polyols were prepared in high yields from biobased 1,4-pentanediol catalyzed by non-toxic phosphoric acid without using a solvent. These oligomers are terminated with hydroxyl groups and have low residual acid content, making them suitable for use in adhesives by polyurethane formation. The thermal behavior of the polyols was studied by differential scanning calorimetry, and tensile testing was performed on the derived polyurethanes. The results were compared with those of polyurethanes obtained with fossil-based 1,4-butanediol polyester polyols. Surprisingly, it was found that a crystalline polyester was obtained when aliphatic long-chain diacids ($>C_{12}$) were used as the diacid building block. The low melting point of the C_{12} diacid-based material allows the development of biobased shape-memory polymers with very low switching temperatures ($<0\,^{\circ}C$), an effect that has not yet been reported for a material based on a simple binary polyester. This might find application as thermosensitive adhesives in the packaging of temperature-sensitive goods such as pharmaceuticals. Furthermore, these results indicate that, although 1,4-pentanediol cannot be regarded as a direct substitute for 1,4-butanediol, its novel structure expands the toolbox of the adhesives, coatings, or sealants formulators.

Introduction

Petrochemicals are still the main raw material for plastics. However, oil reserves are limited, and their continued use leads to increased CO_2 emissions, resulting in climate change. Thus, it is clear that we need to switch to the use of biobased building blocks for the production of polymers. It is predicted that the global market for bioplastics will grow by approximately 20% until 2022.[1] Polyesters are an attractive target market for this switch because they are industrially produced by well-established polycondensation reactions, which allow the use of the existing reactor infrastructure when renewable diols and diacids are used. This has resulted in the development of numerous (partially) biobased polyesters, which in addition show novel promising properties for several applications,[2] in particular for adhesives.[3]

Polyesters are materials that are produced on an overall scale of over one million tons per annum because they are used in everyday consumer goods (e.g., clothes, bottles), as soft segment in thermoplastic polyurethanes (TPUs) (e.g., medical devices), and in industrially used coatings and adhesives (mostly in the automotive industry). Whereas polyesters used in spinning and molding processes have molecular weights (M_n) of several 10 kg mol^{-1}, the materials used in TPUs and adhesives have a M_n that is typically substantially lower than 10 kg mol^{-1} to ensure processability, which requires lower viscosity and reasonable reaction times with crosslinking- and chain-extension agents.[4]

These oligo esters are basically building blocks the structural variation of which allows finetuning of the properties of the final products. The oligomer chains are usually OH-terminated and hence referred to as polyester polyols. In addition, the preparation of monomers, necessary for the production of polyester polyols, can be performed more atom-efficiently from biobased platform chemicals because they already contain oxygen atoms.[5] For instance, succinic acid obtained by fermentation can be selectively hydrogenated to 1,4-butanediol (1,4-BDO), a common building block in polyester polyols for polyurethanes. One common application of 1,4-BDO is as monomer in the synthesis of polyester polyols, which are then further utilized in polyurethanes or adhesives. The isocyanate component that is needed can also be obtained from renewables, for instance from renewable fatty acids as recently demonstrated by Mecking and co-workers.[6]

Furthermore, isocyanate-free crosslinking- and chain-extension protocols have been developed by using either the combination of cyclic carbonates with diamines[7] or a thiol–ene re-

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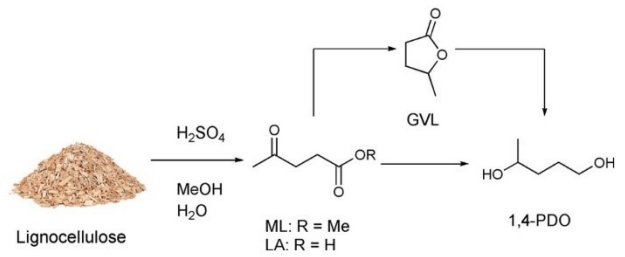
action between mercaptans and alkene containing oligomers, for example, based on limonene.[8] Other important platform chemicals for biobased polymers are levulinic acid (LA)[9] and its esters, which are accessible by treatment of lignocellulose with dilute acid at approximately 200 °C.[10] As shown in Scheme 1, hydrogenation of LA can either yield γ-valerolactone



Scheme 1. Route from lignocellulose to 1,4-PDO.

(GVL) or 1,4-pentanediol (1,4-PDO) depending on the conditions.[11] Although GVL cannot be polymerized—with the exception of its copolymerization with very reactive lactones[12]—it is commonly used as a green solvent[13] because of its low reactivity and relatively high polarity compared with other esters. The diol 1,4-PDO, in contrast, can be regarded as a useful building block for polyester synthesis.[14] Consequently, various heterogeneous[11,15] and homogeneous[16] catalysts have been used for the hydrogenation of levulinates or GVL to 1,4-PDO.

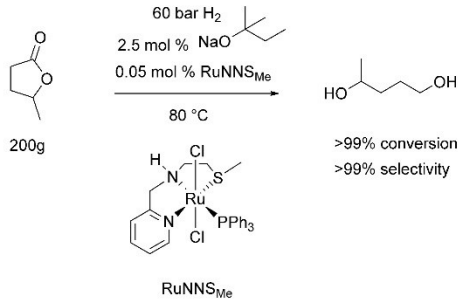
However, to the best of our knowledge, there is no literature concerning the properties and applicability of 1,4-PDO polyesters apart from a study of the thermal behavior of 2,5-furan-dicarboxylic acid, succinic acid, and adipic acid polyesters.[17] However, this work does not provide insights into the mechanical performance of these compounds. This is rather surprising in view of the relevance of 1,4-PDO as biobased building block. In addition, the extra methyl group in 1,4-PDO is expected to impart unusual properties that cannot be found in conventional polyesters based on 1,4-BDO, such as lower viscosity and lower crystallinity. This effect has to some extent been observed in polyesters derived from the biobased diol 2,5-hexanediol.[17,18] Unfortunately, the two secondary alcohol groups makes this diol less reactive than 1,4-PDO in standard polycondensation procedures. This led us to develop a scalable protocol for the synthesis of biobased 1,4-PDO polyester polyols terminated with hydroxyl groups. For economic and ecological reasons, the oligomerizations were performed without the use of solvent. In addition, we decided against the usage of the traditional metal catalysts (e.g., alkoxides/carboxylates of Ti, Sb, or Sn) because in a viable technological process the catalyst is usually not removed from the oligomer, which could lead to unwanted side effects in products derived from the oligomer. Examples for disadvantageous side effects are toxicity of leaching metal residues (Sb/Sn)[19] and formation of yellow impurities (Sn).[20] In the synthesis of polyester polyols the molecular weight is usually controlled through the stoichiometry of the reactants. Because transesterification reactions are also promoted by metal catalysts, it makes them more suitable to synthesize high-molecular-weight polyesters, whereas control of the molecular weight in the synthesis of lower-molecular-weight oligomers is more challenging.

In this paper we describe the preparation of polyester polyols from 1,4-PDO catalyzed by acid and compare their properties with the traditional 1,4-BDO-based analogues in films obtained by chain extension with 4,4′methylenediphenylisocyanate.

Results and Discussion

For mechanical characterization of polymers by tensile testing, amounts in the order of 100 g of polyesters and therefore of 1,4-PDO are necessary. However, 1,4-PDO is not commercially available in large quantities, so we decided to prepare the diol by hydrogenation of GVL.

Although there are existing heterogeneous catalysts that give good selectivities in this transformation, they often require high loadings and are not commercially available. Although this is of course no limitation when setting up a continuous process on reasonable scale, it is inconvenient for producing quantities for polymer development in batch mode. Thus, we decided to use a homogeneous ruthenium catalyst developed earlier in our group, which can be synthesized by a straightforward two-step protocol in high yield.[16c] The complex is air-stable and has already achieved one of the highest turnover numbers (TONs) reported so far in the solvent-free hydrogenation of GVL to 1,4-PDO (see Scheme 2). Fortunately,



Scheme 2. Hydrogenation of GVL to 1,4-PDO.

we were able to scale this procedure up to a 200 g scale. Using only 0.05 mol% of catalyst, GVL was fully converted after 16 h at 80 °C and 60 bar H_2 with >99% selectivity to 1,4-PDO. With sufficient quantities of 1,4-PDO in hand we embarked on the solvent-free synthesis on an average scale of 100 g of different polyester polyol oligomers with a target hydroxyl number (OH-N) of 30 $mg_{KOH}\,g^{-1}$, corresponding to an average molecular weight of $M_n = 3450\ g\,mol^{-1}$. This molecular weight is in the right range for application in adhesives.[4] In general, the molecular weight represents a compromise between viscosity, mechanical properties, reaction time (production cost of the polyester), and other performance parameters. The diacids used were succinic acid (C_4), sebacic acid (C_{10}), and azelaic acid (C_9), which are currently produced from renewable raw materi-

als,[21] as well as adipic acid (C_6) and dodecanedioic acid (C_{12}), for which processes from renewable feedstocks have been developed,[22] and tetradecanedioic acid (C_{14}), which is available from fermentation of glucose.[23] The polycondensation was conducted in a sequential approach consisting of a precondensation step at ambient pressure, followed by further condensation in vacuum in the presence of phosphoric acid as catalyst (Figure 1). Initially, 220 °C was used as reaction temperature, which is commonly used for polyester synthesis. However, at this temperature and under the acidic conditions most of the 1,4-PDO was converted to 2-methyl-teytrahydrofuran (2-MeTHF). Secondary reactions occurring during polyester synthesis are well documented.[24]

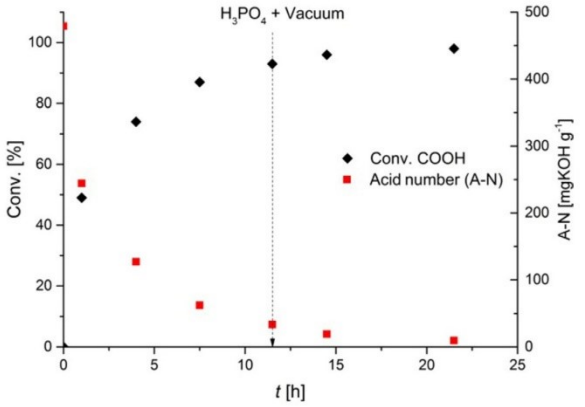
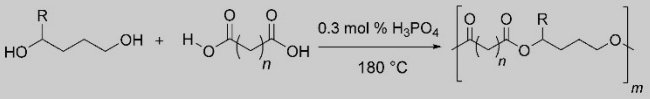


Figure 1. Acid number and derived conversion in the polycondensation reaction of succinic acid and 1,4-PDO; the dashed arrow marks the time and conversion of addition of 0.3 mol% H_3PO_4 and switching from ambient pressure to vacuum (0.1–0.8 mbar).

Typically, they occur at elevated temperatures and can change the stoichiometry of the reaction and cause a limitation of the molecular mass. Common side reactions are ether formation, ring-closure of the diol (e.g., 1,4-PDO to 2-MeTHF), alkene formation, and formation of cyclic structures. These side reactions are an important issue that needs to be addressed when scaling up these polycondensations. At a reaction temperature of 180 °C, using only 0.3 mol% of H_3PO_4 as catalyst, the polyester polyols were obtained in 98–99.5% isolated yields; only trace amount of the side products 2-MeTHF, 5-hydroxypentan-2-one, GVL, and 1,4-PDO were found in the aqueous distillate, and small amounts of cyclic oligomers in the low-molecular-weight fraction could be observed (see S5, S6 in the Supporting Information). However, molecular weights close to the target could be reached. ^{1}H NMR spectra of these products verified the absence of impairing alkene groups, which could be formed from the dehydration of the secondary alcohol chain ends. As expected, the majority of chain ends consisted of secondary alcohols (secondary/primary: 67:33). Figure 1 shows the conversion of carboxylic acid groups versus time for the exemplary case of succinic acid. For comparative reasons polyesters with 1,4-BDO were prepared in a similar way. Table 1 gives an overview of the prepared polyesters and their molecular weight as well as the residual acid content expressed as acid number (A-N) [$mg_{KOH}\,g^{-1}$]. The thermal properties of the polyesters were thoroughly investigated by differential scanning calorimetry (DSC, see Figure 2). This showed that the polyesters obtained from 1,4-PDO and one of the C_4–C_{10} diacids were amorphous as expected, in contrast to their 1,4-BDO analogues.

Amorphous chain segments and side groups are usually important in polyurethane formulations to increase flexibility and strain recovery as well as viscosity. Furthermore, it was recently shown by Hillmyer and co-workers that amorphous chain segments in polyester-based elastomers can increase the hydrolyzability and thus the enzymatic degradability, which may reduce bioaccumulation.[25] We assume the amorphous character is caused by the random orientation of the extra methyl groups in the atactic polymer, which prevents crystallization (see the Supporting Information for the individual DSC traces). This may be further increased by the high degree of regio-ir-

Table 1. Poperties of the polyesters prepared with 1,4-BDO and 1,4-PDO.[a]



Entry	n	R	OH-N[b] [mg g^{-1}]	A-N[b] [mg g^{-1}]	M_n(calcd)[c] [kg mol^{-1}]	M_n(OH)[b] [kg mol^{-1}]	M_n(GPC)[d] [kg mol^{-1}]	$Đ$[d]	X(COOH)[b] [%]	T_g[e] [°C]	T_m[e] [°C]
1	2	Me	30	10	3.7	3.7	3.6	2.4	98	−32	n.d.
2	2	H	30	2	3.7	3.7	1.7	2.4	99.5	n.d.	113
3	4	Me	30	3	3.7	3.7	4.2	2.4	99.0	−52	n.d.
4	4	H	42	1	3.7	2.7	3.8	2.2	99.2	n.d.	53
5	7	Me	39	4	3.7	2.9	3.8	2.5	99.0	−63	n.d.
6	7	H	46	4	3.7	2.4	4.0	2.2	99.0	n.d.	44
7	8	Me	26	4	3.7	4.3	4.8	3.0	99.5	−63	n.d.
8	8	H	33	1	3.7	3.4	5.5	2.4	99.8	n.d.	61
9	10	Me	29	2	3.7	3.9	4.6	2.8	99.7	n.d.	−15/9
10	10	H	33	2	3.7	3.4	5.0	2.7	99.7	n.d.	70
11	12	Me	12	3	–	9.4	5.3	4.4	99.7	n.d.	9

[a] Polycondensation procedure: 480 mmol 1,4-PDO, diacid (0.85–0.89 equiv.), H_3PO_4 (0.3 mol%, 0.85 *w/w* in H_2O). [b] Determined by titration with KOH_{aq} (0.5 mol L^{-1}); OH-N analogous to DIN 53240-1. [c] Targeted molecular weight. [d] Measured by GPC. [e] Measured by DSC; n.d. = not possible to determine.

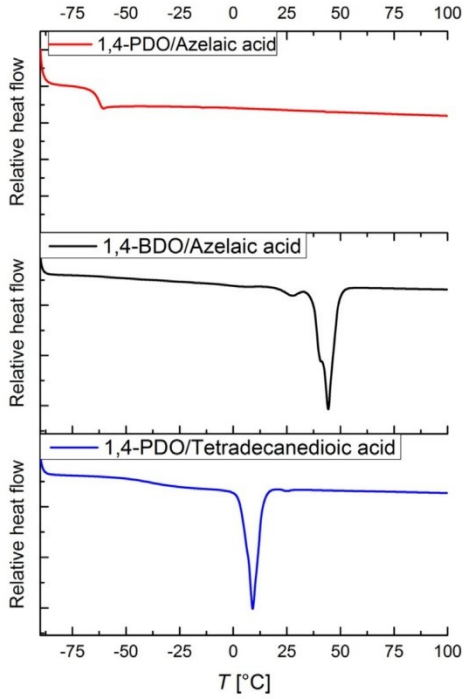


Figure 2. Influence of the diacid building block on the thermal behavior: comparison of the heating curves of 1,4-PDO/azelaic acid, 1,4-BDO/azelaic acid, and 1,4-PDO/tetradecanoic acid polyester polyols. Exothermic heat flow increases along the *y* axis.

regularity caused by the possible head–head, tail–tail, and tail–head orientation of the diol with respect to the dicarboxylic acid. This is generally observed in polyesters obtained from a racemic monomer mixture. Examples of this are the polycondensation product of racemic lactic acid,[26] polymers obtained from substituted lactones,[25] and the combination of methyl succinate with branched diols.[27]

Furthermore, it was observed that the glass transition temperature T_g ranged from −32 to −64 °C and decreased with the increasing number of carbons in the dicarboxylic acid block. An analogous trend was observed with the melting points of the crystalline 1,4- BDO polyester polyols (Table 1), which were solid below −15 and 8 °C respectively. The reason for this behavior might be that the crystallization tendency of long aliphatic chains ($>C_{10}$) with an even carbon number now dominates over the disorder caused by the methyl groups. In addition, a higher degree of flexibility of the longer chains prompts crystallization. A similar effect has been observed for the polyesters of isosorbide with aliphatic diacids.[28]

Interestingly, the polyester polyol derived from 1,4-PDO and dodecanedioic acid showed a second melting point at 8 °C, which might indicate that it consists of two different crystal phases. All polyesters were prepared in the same molecular-weight range with low acid numbers that are suitable for curing experiments with diisocyanates (Table 1). In these chain-extension experiments, the polyesters were end-capped with 4,4′diphenylmethane diisocyanate (4,4′-MDI) at 80 °C and casted in polytetrafluoroethylene (PTFE) molds, after which they were transferred to climate chambers with controlled temperature and air humidity (23 °C, 50% relative humidity). The isocyanate-terminated polymers react with moisture, forming urea linkages resulting in the typical polyurethane networks (PUR).[29] Next, samples were punched out and subjected to tensile testing. The films obtained from the linear 1,4-BDO polyesters were brittle and fibrous materials as demonstrated by their stress–strain curves, which is attributed to their high degree of crystallinity. However, the films obtained from the branched 1,4-PDO behaved more like elastomers with tensile strengths and elongations increasing with the length of the carbon chain in the diacid.

Table 2 and Figure 3 summarize these results. The thermal transitions observed by DSC analysis of the PUR changed only very slightly (max. 8–9 °C) compared with the polyesters, and in PURs based on the amorphous polyols no crystallization phenomena were observed. The exception to this is the film obtained from the 1,4-PDO/C_{12} diacid-derived polyol (Table 2, entry 9). Instead of two peaks, a single peak was observed at −22 °C that could be attributed to the melting of the crystalline chain segments. This observation suggests the possibility to switch the shape of the PUR by changing the temperature. This shape-memory effect is usually observed in polymers that are crosslinked but still contain chains or domains that can undergo either phase transitions (melting or crystallization)[30] or reversible photochemical dimerization reactions between chains.[31]

Table 2. Thermal properties and tensile testing of the corresponding 4,4′-MDI films.

Entry	*n*	R	Film	ε_{break} [%][a]	F_{break} [N mm^{-2}][a]	T_g[b] [°C]	T_m[b] [°C]
1	2	Me	A	55	0.2	–	–
2	2	H	B	n.d.[c]	25.1	n.d.	105
3	4	Me	C	136	1.1	−52	n.d.
4	4	H	D	681	31.5	n.d.	53
5	7	Me	E	892	4	−63	n.d.
6	7	H	F	720	30.1	n.d.	40
7	8	Me	G	936	3.1	−53	n.d.
8	8	H	H	33	1	n.d.	70
9	10	Me	I	1010	7.8	n.d.	−22
10	10	H	J	33	2	n.d.	72

[a] DIN 53504-SF3A-bones from 4,4′-MDI chain extended films; ε_{break}: elongation at break; F_{break}: stress at break; [b] measured by DSC of the films; [c] could not be determined owing to the brittleness of the film.

Here we have the unusual situation that the phase transition would be feasible at low temperatures. Consequently, this material would be of use as a low-temperature shape-memory polymer. This prediction was borne out in praxis when film I (Table 2, entry 9) was fixated in a spiral shape, cooled to −30 °C, and subsequently allowed to warm to room temperature. It was indeed observed that the morphology of the film changed over time and temperature. The timeline of this change is shown in Figure 4, and a full video can be found in the Supporting Information. Because the currently known low-temperature shape-memory polymers have switching points between 30 and 75 °C and are tailored for the use in medical

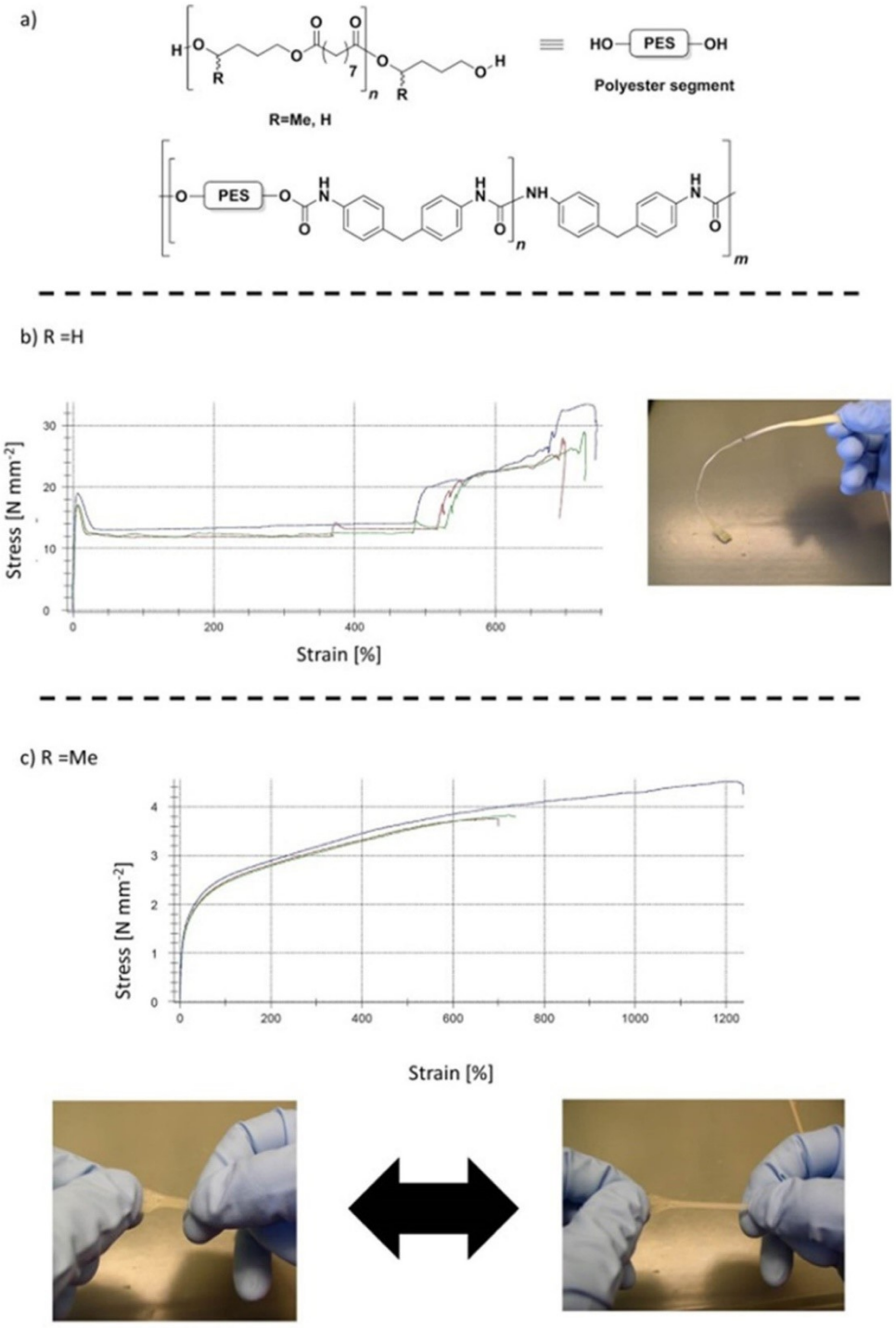


Figure 3. Differences between films obtained from the polyester polyols consisting of the C_9 diacid and 1,4-BDO respective 1,4-PDO. a) General structure of the polyurethanes; b) stress–strain curve of film E (Table 2, entry 5) and visual representation of the ductile behavior; c) stress–strain curve of film F (Table 2, entry 6) and visual demonstration of the elastic behavior of the specimen.

applications,[32] this finding opens the way to novel smart materials that may be used in low-temperature applications. One possibility would be its application as adhesive for smart labels for packaging of temperature-sensitive drugs. Exposure to undesired high temperatures would induce the loss or an irreversible change of the label or a QR-Code.

Conclusions

We have shown that we can prepare fully renewable polyesters based on 1,4-pentanediol (1,4-PDO), obtained from bio-based γ-valerolactone in excellent yields by homogeneous hydrogenation, and a series of diacids that can already be obtained from renewable resources or for which renewable

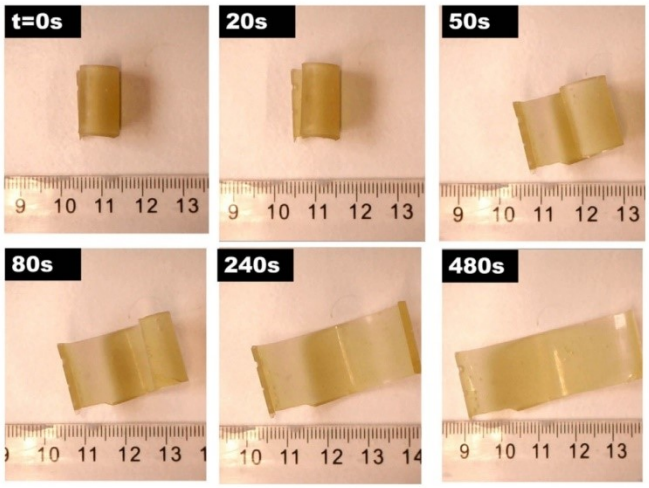


Figure 4. Deconvolution of a sample (film I) to its original form at room temperature. Prior, the specimen was formed to a coil and cooled in a freezer to −30 °C before transfer to ambient conditions.

routes have been developed. Yields are very high, and only traces of side products are formed. For the application in adhesives, diisocyanates need to be used, which are currently not made from renewable resources, although credible routes from renewables have been developed.[33]

Differential scanning calorimetry (DSC) experiments as well as the tensile testing of polyurethane films of the 1,4-PDO polyester polyols made with 4,4-MDI clearly demonstrate that 1,4-PDO cannot be regarded as a substitute for 1,4-butanediol (1,4-BDO). Instead, it can be used to obtain elastomeric/rubbery materials in contrast to the crystalline polyesters obtained with BDO.

The interesting feature of the polyester polyols based on 1,4-PDO and long-chain diacids is the combination of their crystallinity and melting point below room temperature. This phenomenon can be used to design shape-memory polymers with switching points far below and near room temperature. Beyond this aspect, these polyester polyols can be expected to have several use scenarios in the CASE (coatings, adhesives, sealants, and elastomers) market because they possess relatively low viscosity and are liquid at ambient conditions. These findings demonstrate that 1,4-PDO is a valuable biorenewable compound that can broaden the toolbox for polyurethane adhesives and coatings. Its use not only allows increasing the bio content but also results in promising performance features.

Experimental Section

Polycondensation of 1,4-PDO and various diacids

To obtain the necessary ratio of diol to diacid the following version of Carothers equation was used:

$$M_n = \left(M_A + M_B - 2M_{H_2O}\right)\left(1 + \frac{n_B}{n_A}\right)/1 + \frac{n_B}{n_A} - 2X_A\frac{n_B}{n_A}$$

The indices A and B represent the diacid and the diol, X is the conversion, M the molecular weights of the components, M_n the number average weight of the polymer, and n the number of moles. M_n is further connected with the hydroxyl number (OH-N) via the following equation:

$$\text{OH-N} = \frac{zM_{KOH}10^3}{M_n}$$

in which z is the number of hydroxy groups per polyol molecule. The OH-N corresponds to the amount of KOH needed to neutralize the amount of acid equivalent to the esterification of terminal OH groups with acetic acid anhydride. The OH-N in this work was determined by titration in an analogous procedure to DIN 53240-1. For determining the conversion of carboxylic acid groups, polyester (100–300 mg) was dissolved in a THF–ethanol mixture (30 mL, 3.1, *v/v*) followed by addition of a grain of phenolphthalein and subsequent titration with aqueous KOH (0.5 mol L^{-1}) by using a microliter syringe.

General polycondensation procedure

The ratio of diol and diacid for the desired target OH-Number was calculated by using the above-mentioned equations. Typically, an OH-N of 30 mg g^{-1} was targeted. The reaction setup consisted of a two-neck flask equipped with a magnetic stirrer, a Vigreux column, and a distillation setup. The calculated amounts of components were weighed into the flask, and the whole setup was subjected to three vacuum/argon cycles and left under an argon atmosphere at ambient pressure. After that, the reaction mixture was heated to 150 °C. When all solid components were dissolved/molten, the stirrer was started, and the mixture was subsequently heated to 180 °C. When conversion of 80–85% of the acid groups was reached (14–20 h), H_3PO_4 was added (0.3 mol%, 0.85 *w/w* in H_2O). After that, vacuum was applied (0.2–1 mbar). When the conversion of the carboxylic acid groups had slowed down, (e.g., $X > 98\%$, 40–48 h) corresponding to an acid value below 5 (if possible), the reaction mixture was placed under an argon atmosphere and allowed to cool. Typically, no further purification of the obtained polyester was necessary.

Poly(2-methyl-butylene-succinate)

1,4-Pentanediol (50 g, 480 mmol) and succinic acid (50.78 g, 430 mmol) were reacted, giving poly(2-methyl-butylene-succinate) as clear, viscous, slightly yellowish liquid. X(COOH) = 98%; OH-N: 30 mg g^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.87 (h, J = 6.2 Hz, 1H), 4.02 (t, J = 5.9 Hz, 2H), 2.58–2.50 (m, 4H), 1.65–1.47 (m, 4H), 1.16 ppm (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.31, 171.87, 70.82, 64.39, 32.27, 29.39, 29.07, 24.61, 19.93 ppm; GPC: M_n = 3600 g mol^{-1}, $Đ$ = 2.4.

Poly(2-methyl-butylene-adipate)

1,4-Pentanediol (50 g, 480 mmol) and adipic acid (61.40 g, 420 mmol) were reacted, giving poly(2-methyl-butylene-adipate) as clear, viscous, slightly yellowish liquid. X(COOH) = 99%; OH-N: 32 mg g^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.86 (h, J = 6.2 Hz, 1H), 4.06–3.95 (m, 2H), 3.76 (q, J = 6.2 Hz, 0.09H, C*H*OH), 3.58 (t, J = 6.2 Hz, 0.04H, CH_2OH), 2.35–2.19 (m, 4H), 1.66–1.43 (m, 9H), 1.15 ppm (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.30, 172.89, 77.36, 70.32, 64.05, 34.19, 33.84, 32.35, 24.71, 24.44, 24.36, 19.99 ppm; GPC: M_n = 5800 g mol^{-1}, $Đ$ = 2.4.

Poly(2-methyl-butylene-azelate)

1,4-Pentanediol (50 g, 480 mmol) and azelaic acid (77.46 g, 411 mmol) were reacted, giving poly(2-methyl-butylene-azelate) as clear, viscous liquid. X(COOH) = 99.5 %; OH-N: 39 mg g^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.91 (q, J = 6.0 Hz, 1 H), 4.06 (dt, J = 11.8, 6.5 Hz, 2 H), 3.81 (q, J = 6.2 Hz, 0.09 H), 3.63 (t, J = 5.7 Hz, 0.05 H), 2.26 (q, J = 7.8 Hz, 4 H), 1.59 (ddd, J = 12.3, 8.2, 5.4 Hz, 7 H), 1.30 (s, 5 H), 1.20 ppm (d, J = 5.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.79, 173.72, 173.43, 173.32, 70.12, 63.92, 34.55, 34.19, 32.36, 28.93, 28.92, 28.89, 28.85, 24.92, 24.84, 24.71, 19.99 ppm; GPC: M_n = 4200 g mol^{-1}, $Đ$ = 2.4.

Poly(2-methyl-butylene-sebacate)

1,4-Pentanediol (50 g, 480 mmol) and sebacic acid (82.7 g, 409 mmol) were reacted, giving poly(2-methyl-butylene-sebacata) as clear, viscous liquid. X(COOH) = 99.5 %; OH-N: 26 mg g^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.91 (p, J = 6.0 Hz, 1 H), 4.06 (dt, J = 11.8, 6.5 Hz, 2 H), 3.81 (q, J = 6.2 Hz, 0.09 H), 3.63 (t, J = 5.7 Hz, 0.05 H), 2.26 (q, J = 7.8 Hz, 4 H), 1.59 (ddd, J = 12.3, 8.2, 5.4 Hz, 7 H), 1.30 (s, 5 H), 1.20 ppm (d, J = 5.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.79, 173.72, 173.43, 173.32, 70.12, 63.92, 34.55, 34.19, 32.36, 28.93, 28.92, 28.89, 28.85, 24.92, 24.84, 24.71, 19.99 ppm; GPC: M_n = 5700 g mol^{-1}, $Đ$ = 3.0.

Poly(2-methyl-butylene-dodecanedioate)

1,4-Pentanediol (50 g, 480 mmol) and dodecanedioic acid (92.91 g, 404 mmol) were reacted, giving poly(2-methyl-butylene-dodecandioate) as clear, viscous liquid. X(COOH) = 99.7 %; OH-N: 29 mg g^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.91 (h, J = 6.0 Hz, 1 H), 4.06 (dt, J = 11.8, 6.5 Hz, 2 H), 3.81 (q, J = 6.2 Hz, 0.09 H), 3.63 (t, J = 5.7 Hz, 0.05 H), 2.26 (q, J = 7.8 Hz, 4 H), 1.59 (ddd, J = 12.3, 8.2, 5.4 Hz, 7 H), 1.30 (s, 5 H), 1.20 ppm (d, J = 5.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.79, 173.72, 173.43, 173.32, 70.12, 63.92, 34.55, 34.19, 32.36, 28.93, 28.92, 28.89, 28.85, 24.92, 24.84, 24.71, 19.99 ppm; GPC: M_n = 4600 g mol^{-1}, $Đ$ = 2.8.

Poly(2-methyl-butylene-tetradecanedioate)

1,4-Pentanediol (46.4 g, 446 mmol) and tetradecanedioic acid (100 g, 387 mmol) were reacted, giving poly(2-methyl-butylene-tetradecanedioate) as clear, viscous liquid X(COOH) = 99.7 %, OH-N: 18 mg g^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.91 (h, J = 6.0 Hz, 1 H), 4.06 (t, J = 11.8, 6.5 Hz, 2 H), 3.81 (m, J = 6.2 Hz, 0.09 H), 3.6 (t, J = 5.7 Hz, 0.05 H), 2.3 (q, J = 7.8 Hz, 4 H), 1.5–1.8 (m, 8 H), 1.30 (m, 16 H), 1.20 ppm (d, J = 5.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.2, 173.8, 70.5, 64.3, 35.9, 35.0, 34.7, 34.7, 32.8, 30.0, 29.8, 29.8, 29.7, 29.5, 29.5, 25.4, 25.1, 24.0, 20.4 ppm; GPC: M_n = 5300 g mol^{-1}, $Đ$ = 4.4.

Chain-extension reactions with 4,4′-MDI

Polyester (25 g) was heated to 80 °C and kept at this temperature under vacuum (< 0.001 mbar) for 1.5 h. After this, 4,4′-MDI (2.2 equiv. with regard to polyester) was added, and the mixture was stirred for 1 h. Subsequently, films with 1 mm thickness were casted and stored at ambient conditions for one week.

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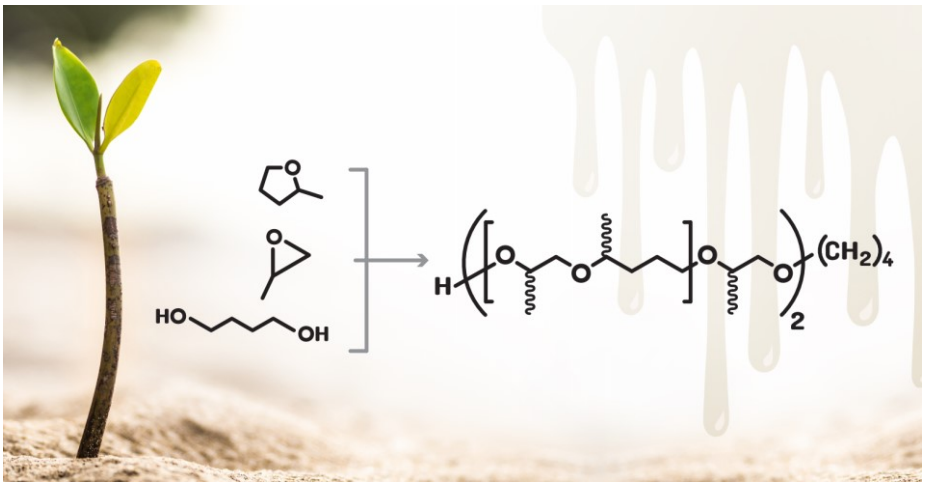
5.3 *Co-oligomers of renewable and "inert" 2-MeTHF and propylene oxide for use in bio-based adhesives*



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Co-oligomers of renewable and "inert" 2-MeTHF and propylene oxide for use in bio-based adhesives

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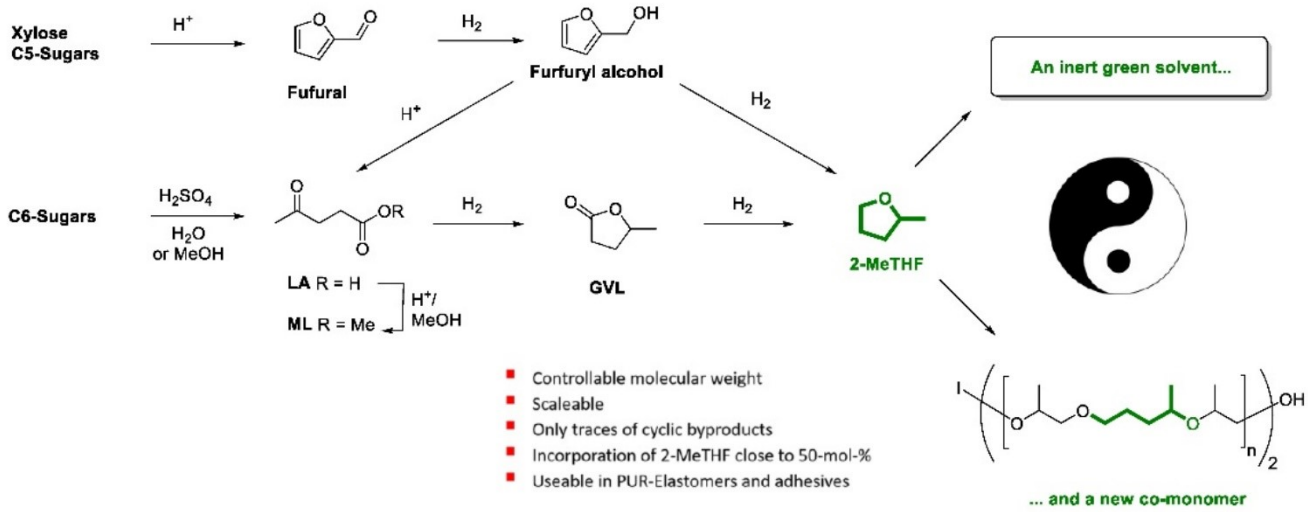
ABSTRACT: Although 2-methyl-tetrahydrofuran (2-MeTHF) cannot be polymerized, we did achieve co-polymerization of 2-MeTHF with propylene oxide (PO) using Lewis and Brønsted acids. The resulting polyether polyols have a molecular weight range which allows their use as components for adhesives. The molar content of 2-MeTHF in the oligomers can be up to 48%. A 1 : 1 co-polymer of 2-MeTHF and PO is produced when stoichiometric amounts of $BF_3.OEt_2$ are used. Here, the monomeric units in the chains alternate, but also cyclics or other non-diol products are formed that are detrimental to its further use in adhesives. Linear dihydroxyl terminated polyether chains were formed when the heteropolyacid $H_3PW_{12}O_{40}\cdot 24H_2O$ was used as catalyst and a diol as initiator. The formation of cyclic products can be drastically reduced when the accumulation of propylene oxide during the reaction is avoided. ^{1}H NMR experiments indicate that the step of 2-MeTHF incorporation is the alkylation of 2-MeTHF by protonated PO. It was shown that the 2-MeTHF/PO co-polymer had increased tensile strength compared to PPG in a two-component adhesive formulation.

1. Introduction

Although we may not always be aware of their presence, adhesives are ubiquitous in nearly every aspect of our modern lives. They are used in the automotive, aerospace and construction industries, in simple consumer goods such as shoes and furniture as well as in medical applications (e.g. band aid). Hence, using renewable resources in their production can significantly reduce CO_2-emissions.[1-8] And indeed, there currently is an increased world-wide interest in bio-based polymeric materials for all kinds of applications.[9-13] As an added bonus, the novel structures that are the result of the use of bio-based platform chemicals and derivatives may lead to adhesives exhibiting novel properties with added value.[4]

Two important glue classes are the single- and two-component reactive adhesives.[14] Single component adhesives contain a functional group that can undergo cross-linking when exposed to an external trigger. For example, acrylates can be used as single-component adhesives, which can be cured with UV-light. Examples of renewable monomers suitable for this type are itaconic acid,[15-18] and bio-based acrylic acid itself.[19-24] In contrast, two-component adhesives require the addition of a crosslinking agent, often containing thiols, isocyanates or, in recent research, the combination of a cyclic carbonate and a diamine.[25-30] However, in most cases these curable end-groups need to be tethered to an oligomer, which is usually a polyester or polyether polyol.[31] There already is a plethora of polyesters that can be made from platform chemicals in a manner that would allow scale-up of these processes.[32-40] In addition, poly-lactate is already commercially available. Polymerization typically takes place via polycondensation of diols with diacids or ring-opening polymerization (ROP) of appropriate lactones.[34, 41, 42] For polyether polyols, the situation looks quite different. Although innovative, alternative protocols for the synthesis of polyethers, such as polycondensation employing acid-base pairs as catalysts[43-45] or the reduction of polyesters [46-48] have recently been developed, their application in scalable processes is limited by harsh reaction conditions and/or use of expensive catalysts or reductants. Hence, the commercial production of polyether polyols is still based on ring-opening polymerization (ROP) of cyclic ethers. This is currently limited to epoxides, oxetanes and tetrahydrofuran (THF).[49] We envisaged the use of renewable 2-methyl-tetrahydrofuran (2-MeTHF) as a sustainable monomer to expand that scope (Scheme 1).[50]



Scheme 1. Bio-based origins of 2-MeTHF and its dual use as solvent and as co-monomer in polyether polyols (I – initiator)

2-MeTHF can be obtained in high yields and selectivity via the hydrogenation of the platform chemical levulinic acid (LA) or its esters, or from its hydrogenation product γ-valerolactone (GVL) (as shown in Scheme 1) using heterogeneous or homogeneous hydrogenation catalysts under acidic conditions.[50-62] LA is readily available by acidic treatment of lignocellulosic biomass at elevated temperatures.[54, 63-76] Alternatively, 2-MeTHF can also be prepared by hydrogenation of furfural.[77-81] Furfural can be produced from the C5 sugars in lignocellulosic biomass,[82-84] and is available on large scale from the conversion of agricultural waste streams such as corn cobs and sugarcane bagasse, or as side stream from the paper industry.[85]

2-MeTHF currently attracts increasing attention as a renewable fuel [86-88] and as a renewable substitute for the fossil-based solvent THF.[44,50 59-61] One of the main advantages of 2-MeTHF as a solvent over THF is its resistance towards polymerization or ring opening. [89-91] And although this property would seem to preclude the use of 2-MeTHF in homo-polymerization reactions, co-oligomers with epoxides would seem to be accessible.[92] These could be very interesting new materials as we would expect them to impart favorable properties to the adhesives they will be used in. The extra methyl group in every unit in the chain would lead to more amorphous oligomers than poly-THF. Since they are not crystalline, they do not need to be stored at elevated temperatures or heated before application. In addition, the viscosity will be lower, which speeds up handling. These new materials would broaden the toolbox of the adhesives developer. However, to the best of our knowledge no attempts have been made to develop 2-MeTHF based polyether polyols for use in adhesives. This is likely due to the great thermodynamic stability of 5-membered cyclic ethers.[93] Extra substituents on the ring make these even more stable, and therefore even more challenging to polymerize. For example, only very few reports exist in the literature on the polymerization of 3-MeTHF.[94, 95] To the best of our knowledge, the homo-polymerization of 2-MeTHF is unknown. Even the catalysts which are able to polymerize 3-MeTHF fail with 2-MeTHF, which suggests an even higher thermodynamic stability when the ring is substituted in the 2-position.[93] Similar observations have been made for the analogous lactone GVL.[96, 97]

Cationic, anionic and coordinative ROP can be used with epoxides and oxetanes. The last two options are often preferred since the formation of side products such as cyclic oligomers and alkene terminated chains tends to be rather low.[98] Cationic ring-opening polymerization (CROP) on the other hand is less used due to the increased formation of these side products. [99, 98]

However, THF, which is regarded as the most reactive 5-membered cyclic ether derivative, is only known to be polymerized via CROP.[100] CROP is difficult to control and therefore typically oligomers in the range of 1000-2000 g mol^{-1} are produced.[100] Only two short communications exist which describe the co-polymerization of 2-MeTHF with epoxides[92] and with 3,3-bis(chloromethyl)oxacyclo-butane[101] only highlighting its low reactivity, without investigating the structure or potential application. The occurrence and the nature of side reactions (e.g. backbiting due to low hydroxyl-content, dehydration and chain-transfers due to long reaction times)[98, 102, 103] were not investigated at the time. These side-products would preclude the use of these polymers in adhesives due to their plasticizing effect. With today's knowledge we have to assume that the materials most likely contained a significant amount of cyclic by-products. [104, 105] A tri-block co-polymer was also reported which consisted of THF, 2-MeTHF and ethylene oxide, where up to 40% of 2-MeTHF could be incorporated.[106] Only 30% yield was achieved there, and the structure of the polymer was not described.

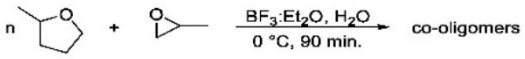
Here, we describe our work on the co-polymerization of propylene oxide (PO) and 2-MeTHF leading to the highly selective formation of hydroxyl terminated oligomers with a low content of cyclic oligomers. In addition, the mechanical properties of the polyurethane films formed from the obtained poly-[(2-methyltetrahydrofuran)-*co*-(propyleneglycol)] have been investigated and were compared to poly-THF and PPG.

2. Results and discussions

2.1. Co-polymerization of 2-MeTHF and PO

Our initial studies concentrated on the co-polymerization of 2-MeTHF and propylene oxide, since routes via bio-based propylene towards PO exist and have great potential.[23, 107, 108] For application in adhesives, the polyether polyols should have a molecular weight between 1000-4000 D. The polymerizations, initated by stoechiometric amounts of $BF_3.OEt_2$, were performed in water, taking care to keep the temperature around 0 °C by slow addition of the epoxide. The results are shown in Table 1. It appears that when the ratio of 2-MeTHF to the epoxide is 5 : 1 or higher, the formed polymers contain the same number of units of the two monomers, suggestive of the formation of a largely alternating co-polymer. When entries 1 and 2 are compared, it is clear that increasing the starting ratio of 2-MeTHF : PO above 10 : 1 does not lead to further incorporation of 2-MeTHF into the oligomers.

Table 1. Co-polymerization of 2-MeTHF with propylene oxide [a]



Entry[a]	MeTHF [eq][a]	M_n[b] [g mol^{-1}]	MeTHF/PO[c] ratio	Y[d] [%]
1	20	1003	53 : 47	81
2	10	980	52 : 48	64
3	5	853	47 : 53	50
4	2	795	43 : 57	37
5	1	850	32 : 68	33
6[e]	2	2880	52 : 48	82

[a]General conditions: 2-MeTHF (n eq. w.r.t. PO), 7.15 mmol of PO, 7.15 mmol of $BF_3{\cdot}Et_2O$ and 7.15 mmol of H_2O. [b]Determined by ^{1}H NMR after conversion of the –OH end groups to -OSiMe$_3$ groups. [c]Determined by ^{1}H NMR. [d]Isolated yield. [e]5 mol% of $BF_3{\cdot}Et_2O$ w.r.t. PO (2.57 mol); PO was added at 0.4 eq. h^{-1} in the absence ofwater

2.2 Structures of the oligomers and side products

Oligomers shown in Table 1, entries 1, 2 and 4 were extensively studied by MS and LC-MS-MS. High resolution MS was used to detect the desired compounds. In order to understand the connectivity between the monomeric units in the oligomers, LC-MS-MS spectra were recorded. An example of observed fragments of one of the polymer chains (the product from Table 1 entry 1) is shown in Figure 1. The MS-MS peaks typically have lower accuracy, and thus, the error range is +/- 0.6-0.7 units. As can be seen, the numbers of monomers in any fragment is always either the same, or +/- 1 of one unit relative to the other one. Further details on the MS and MS-MS studies are shown in the SI (S4-S5).

Since these results looked promising we decided to scale up this procedure to 300g scale with the aim to study the mechanical properties of the polyols in polyurethane films. For better control of the temperature and the rate the PO was dosed to the reaction and $BF_3.OEt_2$ was used in a catalytic amount (Table1, Entry 6). These modifications resulted in a significantly higher M_n without seemingly affecting the amount

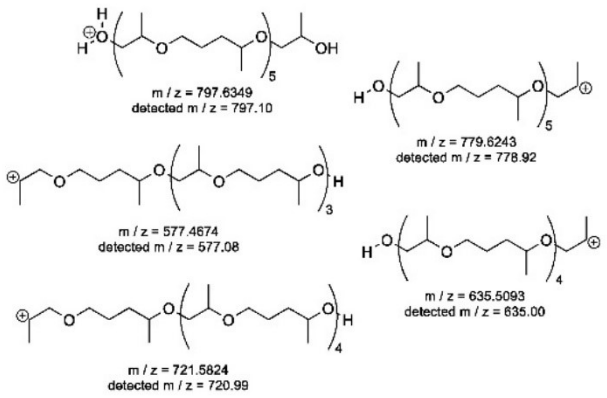


Figure 1. The detected fragments from an MS-MS spectrum of the MH$^+$ peak with *m/z* = 797.10 in the range between 797.10 and 577of 2-MeTHF incorporation. Unfortunately, the obtained polyoyl was not able to cure and form solid polyurethane (PU) films when mixed with 4,4'-methylenediphenyl diisocyanate (4,4'-MDI) (See Section 2.5, Table 3 and Fig. 8a). This is commonly caused by non-hydroxyl functionalized impurities that act as solvent for the forming PU.

After derivatization of the end groups with trimethylsilyl chloride it was also possible to identify ethoxylated propylene glycol an ethoxylated trimer and other low molecular weight products that could be cyclics by GC-MS (SI, S10). The presence of these impurities would be very detrimental for their use in adhesives and thus, further in-depth analysis was warranted.

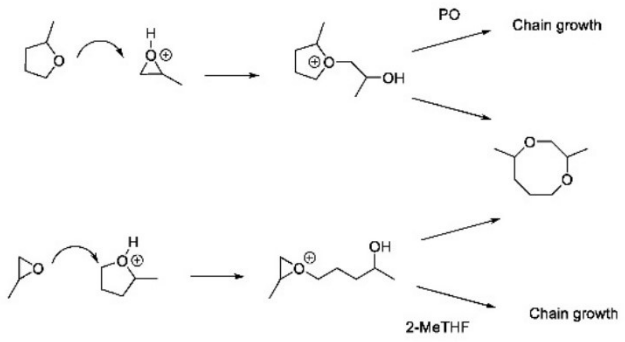
An obvious remedy for the ethoxylation, caused by the presence of Et_2O in the catalyst, would be the use of $BF_3{\cdot}H_2O$. Unfortunately, when this catalyst was used (SI, S7) the molecular weight distributions were rather broad (D and the M_n values measured by NMR and GPC differed by about 1700 g/mol.

These findings confirm that the polymers obtained with the boron based lewis acids as catalyst contain relatively large amounts of non-diol products. In addition to the ethoxylated polymers, a second detrimental impurity could be caused by formation of cyclic oligomers. Initial MS analysis of the polyether polyols of Table 1 did indeed find a number of low molecular weight compounds with a molecular weight that showed the loss of a molecule of water from the oligomer. Unfortunately, the quantification of these cyclic oligomers is not trivial as linear molecules and cyclics exhibit very similar shifts in ^{1}II- and ^{13}C NMR spectra. In the MS, the cyclic structures are indistinguishable from linear structures that tend to form cations by loss of a secondary hydroxy group. Furthermore, co-elution of both molecules is expected to occur in GPC measurements. Nevertheless, experiments described in section 2.3 (see Scheme 4 and Figure 3) confirmed that these were indeed cyclics; they consist of PO and 2-MeTHF in the ratio of 2:2 as well as 3:2.

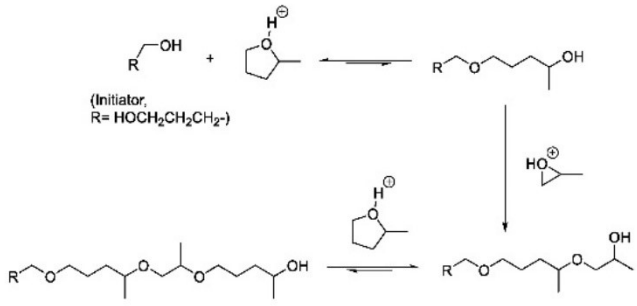
2.3 Further fine tuning of the polymerization

For further optimization of the reaction conditions toward oligomers with low cyclic content an empirical approach can be used. It is known through investigations[103, 109-111] by the group of Penzcek, that the cationic homo- polymerization of epoxides can proceed via a so-called activated chain end mechanism (ACEM) and/or via an activated monomer mechanism (AMM).[73, 79-81] In the activated chain end mechanism, the chain

ends are oxonium ions which can react easily with another monomer. This chain growth competes with an intramolecular reaction of the ether oxygens in the chain leading to cyclic molecules. Scheme 2 shows a proposed unwanted ACEM for the copolymerization of PO and 2-MeTHF in the presence of a Brønsted acid. Here, in the first step an oxonium ion of either 2-MeTHF or PO undergoes a nucleophilic attack by



Scheme 2. Possible reaction mechanism based on ACEM leading to cyclic side products



Scheme 3. Proposed AMM which should lead to linear hydroxyl terminated chains

the respective co-monomer which leads to ring-opening. The resulting fragment contains both a hydroxyl group and an alkyl oxonium ion – the so-called active chain end. This intermediate can then react with another co-monomer leading to the growth of the polymer chain. On the other hand, a backbiting of the oligomer chain is also possible by reaction of the terminal oxonium ion with the hydroxyl group or the ether oxygens along the chain which results in the cyclized oligomer.

The second type of cationic polymerization mechanism (AMM) typically requires the addition of a nucleophilic initiator. Primary alcohols (diols) are commonly used for this purpose. This initiator (I) reacts with an activated monomer via ring-opening, producing a hydroxyl chain end that can further react with another activated monomer leading only to the desired hydroxyl functionalized chain ends. In this mechanism, the ether atoms in the chain cannot compete with the more nucleophilic alcohol (diol), precluding the back-biting mechanism. Scheme 3 contains a proposed AMM for the co-polymerization of 2-MeTHF and PO. The mechanism is based on the fact that homo polymerization of 2-MeTHF has never been reported and is probably impossible. Henceforth, we propose that in the case of the Brønsted acid initated cationic copolymerization of 2-MeTHF with PO an equilibrium between 2-MeTHF and its ring-opened form exists. This intermediate can only react with PO (and not with 2-MeTHF) in a productive manner, and is thus removed from the equilibrium, as ring opening of PO is irreversible. The formed hydroxyl group can then start the cycle again and polymerization commences. The preference for reaction with the protonated Me-THF in the next step can be explained by the very large excess of 2-MeTHF over PO. This also explains the observed alternation of the 2-MeTHF and PO units. Nevertheless, the build-in of two consecutive PO molecules remains possible and is also observed. As is evident by the above scheme, in the ideal case, the chain-length (degree of polymerization (DP)) depends on the conversion (X) and the ratio of PO to the initiator as well as the functionality z of the latter (Equation 1). However, it also means that when we want to obtain linear hydroxyl terminated chains a 1:1 molar ratio of 2-MeTHF to PO can only be reached at infinite chain lengths. To describe this, we use Equation 2 which represents the fraction of 2-MeTHF units per PO unit at a given DP assuming full PO conversion. Taking equations 1 and 2 into account we can predict the molecular weight (M_n) with respect to initiator/PO ratio via Equation 3 that also takes the molecular weight of the initiator I into account.

Equation 1: $$DP = \frac{X n_{PO}}{z_I n_I}$$

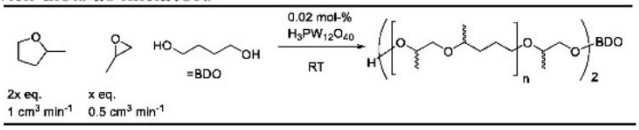
Equation 2: $$f_{2MeTHF} = \frac{\frac{n_{PO}}{z_I n_I} - 1}{\frac{n_{PO}}{z_I n_I}}$$

Equation 3: $$Mn = \frac{X n_{PO}}{z_I n_I} (M_{PO} + f_{2MeTHF} M_{2MeTHF}) + M_I$$

DP = Degree of polymerization, X_{PO} = Conversion of PO, z_I = Functionality of the initiator, n_I = amount in moles, n_{Po} = amount of PO in moles, M = molecular weights

Schemes 2 and 3 suggest that the concentration of hydroxyl groups should have a crucial influence on which of the two mechanisms prevails. Since the AMM requires a relatively strongly acidic catalyst with a poor nucleophilicity of its anion, it was decided to change the catalyst to phospho-tungstic acid (HPA), a heteropoly acid that is used with good results in the cationic homo polymerization of THF.[112] In our case this catalyst also appeared to be promising (see SI, S1) for an initial screening). It was expected that if the selectivity for the linear polymer is high, the molecular weight calculated from Eq.3. should match the observed M_n if all of the dosed PO is immediately converted and built into the growing polymer chain. Table 2 shows some selected results obtained with phosphotungstic acid ($H_3PW_{12}O_{40} \cdot 24H_2O$, HPA) as catalyst. Comparing entries 1 and 2 in Table 2, it is easy to see that at 20 eq. of PO (w.r.t. BDO), the molecular weight obtained is close to the predicted. When more PO is dosed (40 eq.), the measured M_n deviates significantly downwards, Suggesting formation of cyclic side products.

Table 2. PO/2-MeTHF copolymerization catalyzed by HPA with diols as initiators[a]



Entry	I[b]	PO [eq][c]	M_n(th)[d] [g mol^{-1}]	M_n[e] [g mol^{-1}]	2-MeTHF[f] [%]	Y[g] [%]
1	BDO	40	2888	2222	39(48)	75
2	BDO	20	1446	1368	43(45)	69
3	PDO	20	1460	1720	37(45)	92
4	BDM	20	1494	1325	35(45)	77
5[f]	BDO	20	1446	90	0(45)	<1

[a]General conditions: 0.02 mol-% $H_3PW_{12}O_{40}\cdot 24H_2O$ w.r.t. PO in 50ml (490 mmol) 2-MeTHF and initator (21 mmol) followed by addition of 2-MeTHF and PO. Flows (Q): Q(PO)=0.5 cm3 min-1; Q(2-MeTHF)=1.0 cm^3.min^{-1} Workup: filtration through silica. [b]BDO=1,4-butanediol; PDO=1,4-pentanediol; BDM=1,4-benzenedimethanol. [c]Equivalents of BDO w.r.t. initiator. [d]Calculated using eq. 1-3 assuming full PO conversion. [e]Measured with ^{1}H-NMR (see ESI); [f]Content of 2-MeTHF in the oligomer, predicted value in brackets; [g]Isolated yields based on PO. [f]Anhydrous $H_3PW_{12}O_{40}$ was used as catalyst; no oligomers were formed.

Next, we tested different diols as initiators (Entries 3 and 4). The result obtained with 1,4-pentanediol (PDO) is particular interesting as a higher molecular weight than predicted could be obtained. The secondary alcohol group in this diol which should be less nucleophilic, might be the cause of this behavior. 1,4-Benzenedimethanol which has again two primary alcohol groups behaves like BDO. However, the incorporation of 2-MeTHF was slightly higher when BDO was used. Next we wanted to investigate if the added PO is immediately incorporated into the chain during the addition over the entire course of the reaction. An experiment, using BDO as initiator was performed with the same dosing rate as in Table 2. Samples were taken and the M_n determined via ^{1}H-NMR spectroscopy (Figure 2a). In addition, the PO concentration was monitored via in-situ IR spectroscopy (Figure 2b). Here we could observe that the M_n is in correspondence with the predicted molecular weight, calculated according to Eq. 3, during the addition of up to 20 equivalents of PO. Monitoring the amount of PO in the reaction mixture during the addition of PO revealed that there is an induction period at the beginning of the reaction in which the concentration rises until 7.5 equivalents of PO have been added. The next equivalents of PO (7.5-20) are consumed faster than they are fed into the reactor. After this, we observe a continuous increase of the concentration of PO. It is known from the literature on cationic homo polymerization of PO that accumulation and high concentrations can lead to unwanted side products such as cyclic oligomers.[113] The presence of low molecular weight products is also evident upon comparison of the GPC traces of the products at 20 and 40 eq. PO (Figure 2c). The molecular weight distribution resulting from the 40 eq. experiment is bimodal, showing the presence of small molecules or oligomers in the lower molecular weight fraction.

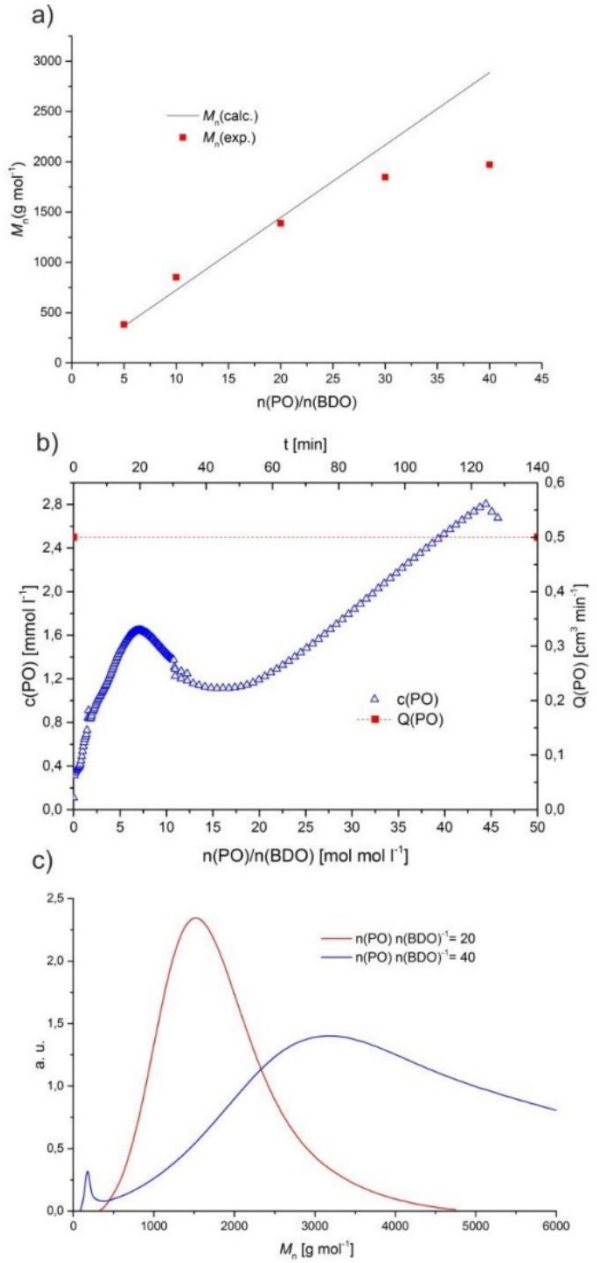
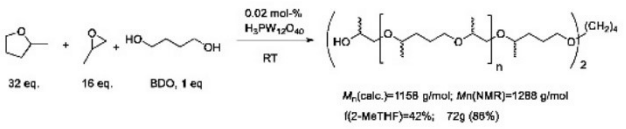


Figure 2. a) Comparison of measured M_n values with calculated values (Eq. 3) as function of equivalents of PO dosed b) Concentration c(PO) of propylene oxide in the reaction mixture as function of the amount dosed and flow Q(PO) of PO. The concentration was measured with in-situ ATR-IR spectroscopy. c) GPC of product samples at different PO to initiator ratios

To minimize the effect of the crystal water on the reaction, anhydrous $H_3PW_{12}O_{40}$ was prepared, but, surprisingly, this material was not able to catalyze the copolymerization (Table 2, entry 5). Samples of the oligomers obtained under the conditions of the entries 1 and 2 in Table 2 were used to elucidate the nature of these side products. To distinguish between linear hydroxyl terminated chains, oligomers with dehydrated chain ends and cyclics, phenyl isocyanate was added to convert the hydroxy groups into carbamates, and the

samples kept at 80°C for 4 hours. After the derivatization was complete, as validated by NMR spectroscopy, ESI-MS measurements were carried out using a method published by van den Brink and co-workers They reported the use of triethylamine which suppresses the fragmentation of the molecular ions.[109] Figure 3a shows the measured spectra of the 2-MeTHF/PO copolymer obtained with 40 eq. of PO vs. initiator. It was possible to identify two cyclic oligomers as the major side products. Having a 2-MeTHF/PO ratio of 2:2 respective 2:3, the composition of these cyclics provides further evidence that for thermodynamic reasons no two 2-MeTHF units can be adjacent to each other. The MS spectra of the polyol that was obtained from the reaction with PO/I = 20 shows, in contrast with the former, only propylene glycol and its dimer as low molecular weight side products and no cyclics (Figure 3b). Having now identified the accumulation of PO as cause for the formation of the cyclic oligomers, we adjusted the rate of the PO addition (Scheme 4, Figure 4). This resulted in a polymer whose low molecular weight fraction contained only traces of cyclics and short chains besides trace amounts of propylene glycol (Figure 3c). No larger cyclic oligomers could be found (see SI S10 for the full spectra and assignment data). Interestingly, besides the expected 1,4-butanediol initiated chains we could also find some chains which were initiated by water. Although according to ^{1}H NMR spectroscopy the overall degree of incorporation of 2-MeTHF in the oligomer is 42 mol%, analysis by ESI-MS of the individual chains shows that the individual incorporation varies between 20 and 48 mol% (Figures 5 and 6). It did not have a noticeable influence on the chain composition whether a chain was initiated by 1,4- BDO or by the crystal water of the heteropoly acid catalyst



Scheme 4. Result of the co-polymerization under the dosing conditions as shown in Figure 5

2.4. Mechanistic investigations

When the experimental molecular weights and the theoretical molecular weights are compared to each other, it seems that the polymerization follows an activated monomer mechanism (AAM) up to the addition of 20 equivalents of PO w.r.t. to the initiator diol. However, monitoring of the PO concentration during the polymerization revealed that there is always a build-up in PO concentration at the beginning of the reaction (Figure 4). Propylene oxide is significantly less basic than 2-MeTHF. This was proven by DFT calculations using the M05-2X functional which give a difference in pK_a of 9 for the respective protonated species in the gas phase (SI, S22). This functional was identified earlier by Truhlar and co-workers as a reasonable method to calculate the energies of protonated epoxides.[114] IR spectroscopy experiments support the order of basicity and a ΔpK_a of 2 is found.[115-117]The reason for the difference is probably that the DFT calculations were carried out in the gas phase for simplifications.. The lag time, that is implicit in the PO concentration increase at the beginning of the reaction, probably points to the fact that, due to the unfavorable pK_a of the epoxide compared to 2-MeTHF, it takes a while

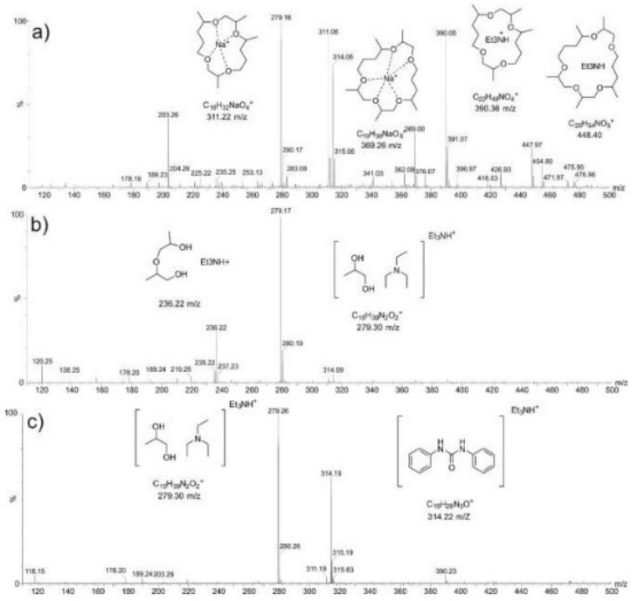


Figure 3. Comparison of the ESI-MS spectra of the low molecular weight fraction (100-500 m/z) of 2-MeTHF/PO co-oligomers after derivatization with phenyl isocyanate. a) Table 2, entry 1; b) Table 2, entry 2; c) obtained with the non-constant addition rate of PO as shown in Figure 4

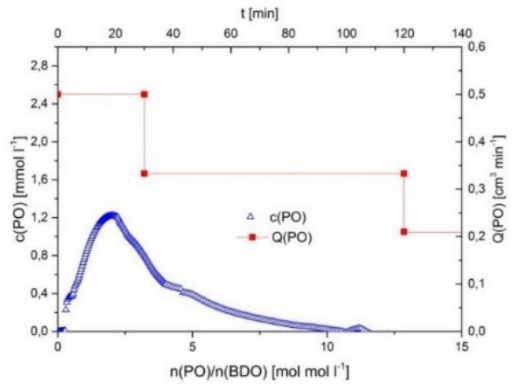


Figure 4. Effect of a non-constant PO addition rate Q on the PO concentration during the reaction.

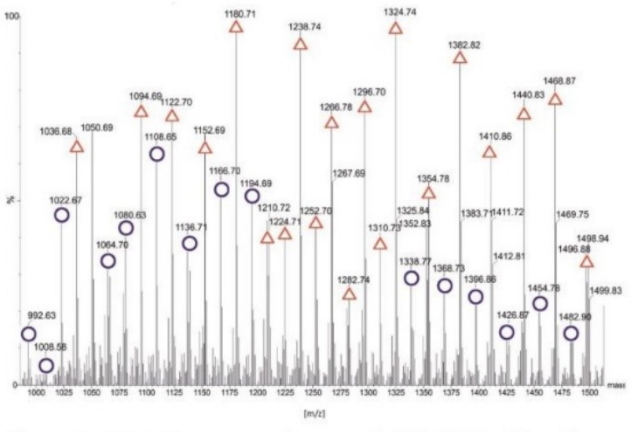


Figure 5. ESI-MS spectrum (Range m/z 900-1600) of the oligomer obtained under the condition of scheme 3; Blue dots: H_2O initiated chains; Red triangles: 1,4-BDO initiated chains

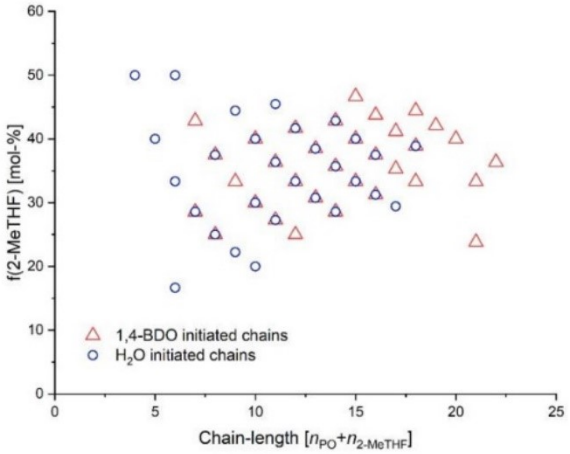
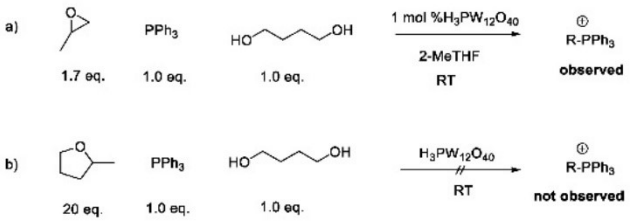


Figure 6. Incorporation of 2-MeTHF vs. chain-length n(PO+2-MeTHF) as determined with ESI-MS

before a sufficiently high concentration of protonated epoxide has formed to allow the onset of the polymerization. To further investigate this, two control experiments were performed. These are based on the methodology developed by Penczek and co-workers.[118, 119]



Scheme 5. Control experiments to elucidate the propagation mechanism

By adding phosphines to the cationic polymerization, it is possible to verify that the cationic polymerization proceeds via oxonium ions as active chain end (ACEM), in which case phosphonium salts are formed that are easily detectable in ^{31}P-NMR spectroscopy.

When PO and 2-MeTHF were reacted in the presence of triphenylphosphine (Scheme 5a), the formation of phosphonium salts was observed. When no PO was present, no additional signals appeared in the ^{31}P-NMR spectra. To verify that these signals belong indeed to the adduct of the co-polymer, the reaction was repeated without 2-MeTHF which yielded only one signal characteristic for the phosphonium ion. This indicates that 2-MeTHF cannot be ring-opened in the absence of PO under the reaction conditions. To further verify this result and our claim that due to thermodynamic constraints a terminal 2-MeTHF unit is not possible we tried to establish that the polymer chains are indeed terminated with C3 on both sides. To establish this, we took a sample of the polymer, prepared according to Table S3 (Entry 3) and submitted this to oxidation with the Dess-Martin periodinane.

The resulting polymer was analyzed by ^{1}H NMR, which clearly shows a set of singlets at δ 2-2.2, which can be assigned to the terminal CH_3CO- and a set of singlets between δ 3,8-4.1, which can be assigned to -$OC\underline{H}_2COCH_3$ (Figure 7). The fact that multiple peaks are found is related to the presence of diastereomers as well as chains of different length. Note that in

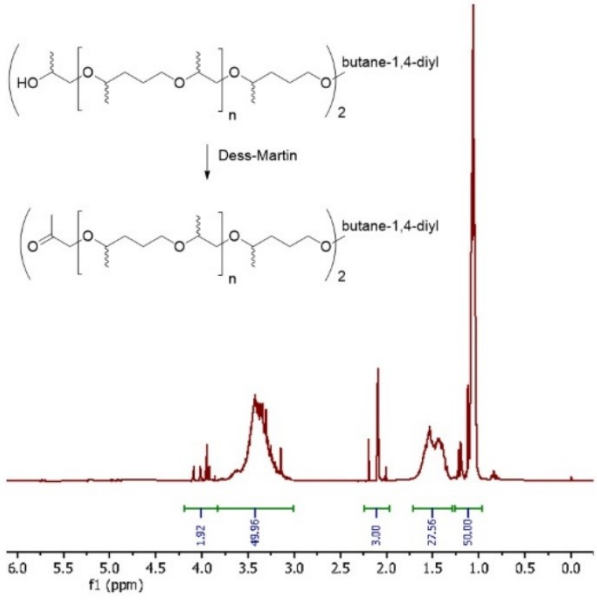
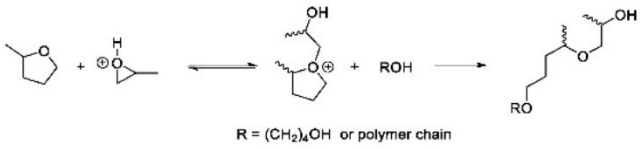


Figure 7. ^{1}H NMR of the oxidized polymer

the case of a terminal C5 unit triplets would be expected between δ 2.0-2.5 for the -CH_2CO- unit. This experiment confirms that the polymer is terminated at both ends with a C3 unit.

Based on these observations it seems that the key step of incorporation of 2-MeTHF in the co-polymerization of PO and 2-MeTHF is the alkylation of 2-MeTHF by activated ("protonated") PO, as shown in Scheme 6. This is further supported by examples from the literature regarding the ring-opening of 2-MeTHF to linear monomeric molecules by acylating reagents.[120, 121]



Scheme 6. Proposed 2-MeTHF incorporation mechanism

It explains why there needs to be a sufficient build-up of PO, or rather protonated PO, before the reaction can start. The alternative mechanism from Scheme 3, in which protonated 2-MeTHF reacts with butanediol resulting in an equilibrium which is largely on the ring-closed side, but which can be "fixated" by reaction with protonated epoxide, cannot be excluded entirely, but seems less likely in view of the fact that the combination of 2-MeTHF, BDO and PPh_3 did not lead to the formation of phosphonium salts under the influence of the catalyst, which suggests that the mere addition of acid is not enough to create a carbocation from 2-MeTHF.

2.5. Usage of the novel polyether polyol for the preparation of elastic polyurethanes

To demonstrate the applicability of the obtained polyether polyols for polyurethane based adhesives, polyols were end capped with 4,4'-MDI and subjected to moisture curing. During

the curing procedure the isocyanate terminated oligomers react with ambient humidity, resulting in the formation of amine groups that can react with the remaining isocyanate groups forming the typical polyurethane networks. Figure 8 shows these films, while Table 3 gives an overview of their properties.

This type of curing was not possible on polyether polyols obtained with $BF_3{\cdot}Et_2O$ and a brittle material was obtained(Figure 8a). When water was used as initiator the curing of the resulting oligomers was possible. However, the elongation of this film (Figure 8b) was only 60% and the ultimate strength measured was about 0.8 N mm^{-2}. In contrast, using the polyether polyol obtained with a combination of $H_3PW_{12}O_{40}.24H_2O$ as catalyst and 1,4-BDO as initiator, the maximum elongation of the derived polyurethane increased to 600 % and the ultimate strength was about 3.0 N.mm^{-2} (Table 3, entry 3; Figure 8c). Using the addition protocol shown in Figure 4, it was further possible to increase these values significantly (Table 3, entry 4, Figure 8d).

The tensile strength of this film was then compared with the one obtained from commercial polypropylene glycol (PPG) which can be a component of an adhesive formulation (Table 4). [122, 123] When the properties of the co-polyether from 2-MeTHF and PO is compared with PPG it is evident that the incorporation of 2-MeTH improves the tensile strength of the resulting polyurethanes.

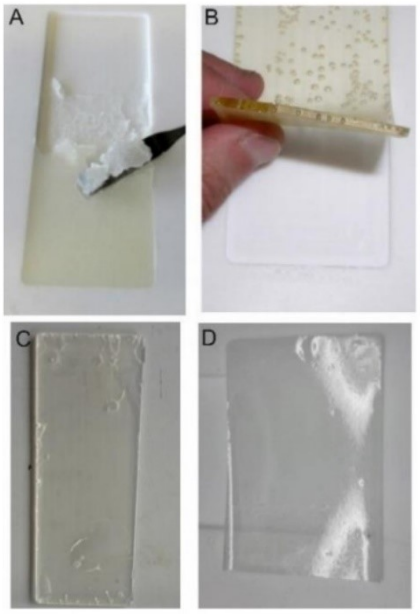


Figure 8. Films (A-D) from the different 2-MeTHF/PO co-polyether polyols obtained under different conditions shown in Table 3

Table 3: Selected samples of 2MeTHF/PO co-oligomers prepared under different conditions and mechanical properties of the films obtained by curing with 4,4'MDI

Entry	Catalyst [mol-%]	Initiator [mol-%]	2-MeTHF[a] [mol-%]	M_n(NMR)[a] [g mol]	M_n(GPC)[b] [g mol]	$Đ$[b]	Film	ε_{max}[c] [%]	F_{max}[c] [N mm^2]
1	BF3.Et2O (5)	-	52	2883	1100	4.8	A	n.a.	n.a.
2	$BF_3.2H_2O$ (1)	H_2O (5.0)	52(45)	1081	500	3.1	B	60	0.8
3[d]	$H_3PW_{12}O_{40}$.24H2O (0.02)	1,4-BDO (5.0)	43(45)	1278	1200	2.0	C	600	3.0
4[e]	$H_3PW_{12}O_{40}$.24H2O (0.02)	1,4-BDO (5.0)	43(43)	1288	1100	1.9	D	1100	3.2

[a]Measured with ^{1}H-NMR after derivatization of the oligomer with trifluoroacetic anhydride. GPC measurement of the oligomer. [c]DIN 53504-SF3A-bones from 4,4'-MDI crosslinked films ε_{max}: Maximum elongation; F_{max}: Ultimate strength. [d]Constant dosing rate of PO and 2-MeTHF (Figure 2b); [e]Dynamic dosing rate as shown in Figure 5

Table 4: Comparison of the initial strength

	2-MeTHF/PO (43/57)	PPG[a]
ε [%][b]	F [N mm^{-2}][c]	F [N mm^{-2}][c]
50	2.18(0.04)	1.54(0.07)
100	2.49(0.04)	1.87(0.08)
200	2.81(0.05)	2.30(0.10)
300	3.00(0.05)	2.75(0.10)

[a]Industrial PPG sample Mn=1700 g mol^{-1} [b]Elongation; [c]Force at different elongations, standard deviation (N=3) in brackets

3. Conclusions

We have shown that it is possible to obtain co-polymers of propylene oxide with the renewable platform chemical 2-MeTHF. The oligomers are exclusively hydroxy terminated and thus useful for the preparation of polyurethanes and adhesives based on them. The molecular weight range is suitable for their application in adhesives and can be varied within certain limits to suit the needs. *In-situ* IR experiments revealed accumulation of PO in semi-batch mode at the beginning of the reaction. This and NMR experiments suggest that the propagation step is best described by an alkylation of 2-MeTHF by protonated PO. This activated species can react with a hydroxy group from BDO or the growing polymer chain. Using a heteropolyacid as catalyst and a diol as initiator it was possible to obtain oligomers that contain only trace amounts of cyclics through controlled PO addition. These oligomers form elastic solid films upon crosslinking with 4,4-MDI. Notably, no further purification is

necessary other than removing the catalyst (phosphotungstic acid) via filtration through silica and evaporation of the volatiles. In summary, the presented results show that 2-methyl tetrahydrofuran represents a valid bio-based building block for the production of polyethers for adhesives.

ASSOCIATED CONTENT

Supporting information is available free of charge via the internet at http://pubs.acs.org.".

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

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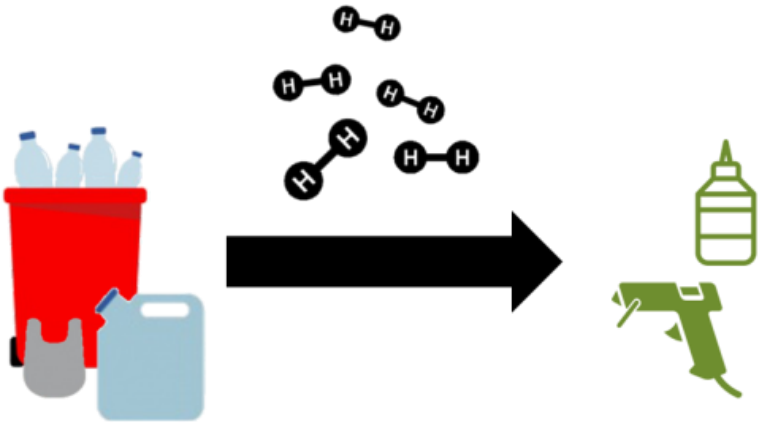
5.4 Hydrogenation of Polyesters to Polyether Polyols



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Hydrogenation of Polyesters to Polyether Polyols

Bernhard M. Stadler, Sandra Hinze, Sergey Tin, and Johannes G. de Vries*[a]

The amount of plastic waste is continuously increasing. Besides conventional recycling, one solution to deal with this problem could be to use this waste as a resource for novel materials. In this study, polyesters are hydrogenated to give polyether polyols by using in situ-generated Ru-Triphos catalysts in combination with Lewis acids. The choice of Lewis acid and its concentration relative to the ruthenium catalyst are found to determine the selectivity of the reaction. Monitoring of the molecular weight during the reaction confirms a sequential mechanism in which the diols that are formed by hydrogenation are etherified to the polyethers. To probe the applicability of this tandem hydrogenation etherification approach, a range of polyester substrates is investigated. The oligoether products that form in these reactions have the chain lengths that are appropriate for application in the adhesives and coatings industries. This strategy makes polyether polyols accessible that are otherwise difficult to obtain from conventional fossil-based feedstocks.

Introduction

The world-wide production volume of polymers is predicted to rise in the future as these materials are used in the manufacturing of an increasing number of consumer goods.[1] As a result, there will be an increase in plastic waste. To counteract the pollution of the environment, as well as to conserve natural resources, several strategies have been proposed and developed for the recycling of polymeric materials.[2] Depolymerization and mechanical recycling are among the most applied ones (Figure 1). In the first approach, some polymers can be converted back into their monomers by heating,[3] hydrogenation,[4] or hydrolysis.[5] At the moment, this strategy is questionable from an economic point of view, given the low prices of conventional monomer feedstocks. In contrast, mechanical recycling is starting to be implemented on an industrial scale for PVC-based products.[6] However, there are disadvantages associated with this approach. The molecular weight will drop owing to chain scissions by thermal stress during extrusion or reaction with impurities may lead to inferior mechanical properties. The chemical conversion of one polymer into another could be a viable alternative recycling method. In addition, it could establish new routes to novel materials.

Herein we report on a tandem hydrogenation–acid-catalyzed etherification strategy to synthesize oligoethers in suitable molecular weight ranges for use in adhesives from polyesters.

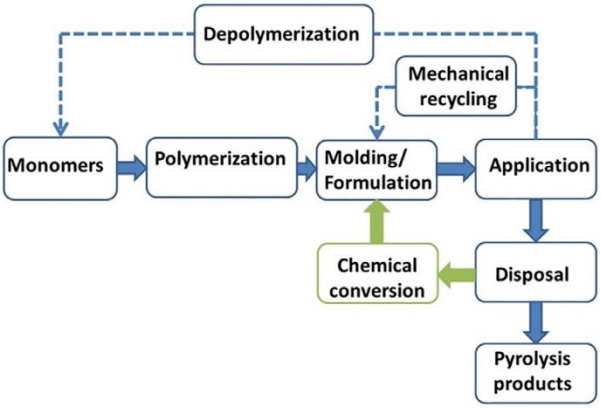

Figure 1. Possible polymer life cycles.

Whereas in recent years many highly active and selective homogeneous catalysts for ester hydrogenation have been reported, most of these catalysts require base for their activation.[7] Alternatively, they must contain an acid-labile ligand, such as BH_4^- or $-CH_2Si(Me)_3$,[8] which also makes them useless for hydrogenation under acidic conditions. To date, the only homogeneous hydrogenation catalysts known to tolerate acidic conditions are bipyridine complexes of rhodium or iridium[9] and combinations of ruthenium[10] or cobalt[11] with a Triphos ligand. In particular the Triphos-based metal complexes have achieved much attention, owing to their broad applicability in reactions including the reduction of esters[12] and of CO_2,[13] hydrogenation of lactams to cyclic amines,[14] hydrogenolysis of polyesters to diols[4c] and direct reductive etherification of carboxylic acid esters to ethers (Scheme 1).[15] This versatility and their stability towards acids and high temperatures resulted in our decision to investigate this system for the chemical recycling of polyesters to polyether oligomers.

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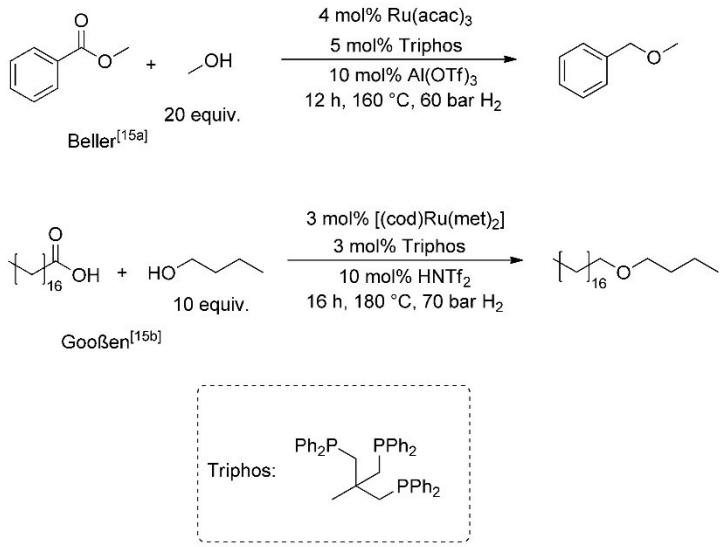


Scheme 1. Previous work on reductive etherification using hydrogen as reductant (met = 2-methylallyl).

Results and Discussion

To achieve realistic conditions, industrial grade poly(hexene 1,12-dodecanate) (PHDD; Figure 2) was used as a model substrate. Initially, a solvent screening was conducted (Table 1). Toluene and cyclohexene were chosen as apolar solvents. Protic solvents were excluded as they would react with the potential intermediates. Diethyl ether, tetrahydrofuran (THF), and 1,4-dioxane were employed as polar aprotic solvents. Although not a green solvent, chloroform was included in the screening as it is known to positively affect selectivity and rate in reductive etherification via hydrosilylation.[16]

In all solvents, conversion of the ester groups of the polymer was observed. However only in 1,4-dioxane and THF a significant formation of ether bonds was observed. In THF the selectivity was twice as high as in dioxane at nearly the same conversion. Based on this, THF was chosen as the solvent for further experiments. The effect of the different metal triflates as Lewis acid co-catalysts was also studied (Figure 3). All of the investigated metal triflates were found to facilitate the hydrogenation of the ester moieties.

The role of the Lewis acid is twofold: It provides protons from the reaction with water impurities, which are thought to be crucial for the activation of the catalytic system.[15a] In addition, the Lewis acid is needed to catalyze the etherification reaction (Scheme 2, pathway I; see also the Supporting Information, Table S4). The selectivity for ether bond formation seems to correlate with the charge density, which can be estimated from the charge number and the respective ionic radii.[17] In addition, there seems to be a certain threshold below which no etherification is possible. The highest selectivities were obtained with Ga^{III}, Sn^{II}, and Al^{III} triflates. Curiously, addition of Hf^{IV} triflate results in a selectivity for ether formation of over 100%. This finding can be rationalized by the capability of Hf^{IV} triflate to open the THF ring at higher temperatures, which, in combination with the reducing conditions, results in the formation of *n*-butyl ethers alongside *n*-alkanes, as reported by Marks and co-workers.[18]

To exclude the possibility that THF ring-opening by aluminum triflate is the reason behind the observed high selectivi-

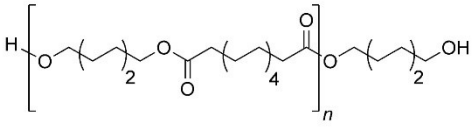


Figure 2. Structure of poly(hexene-1,12-dodecanate) (PHDD).

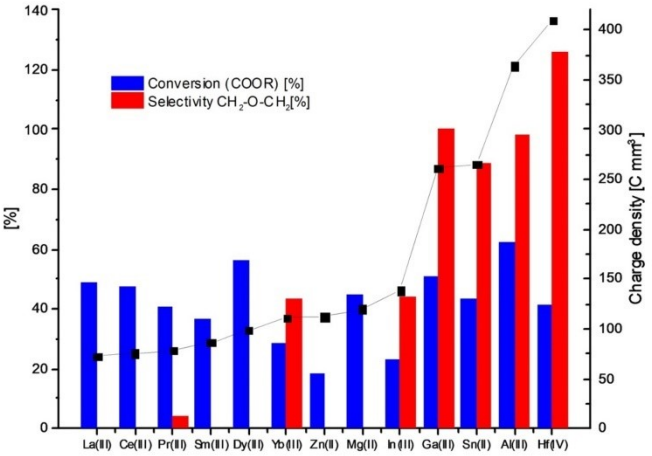
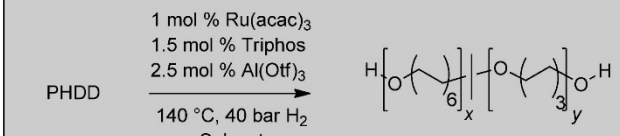


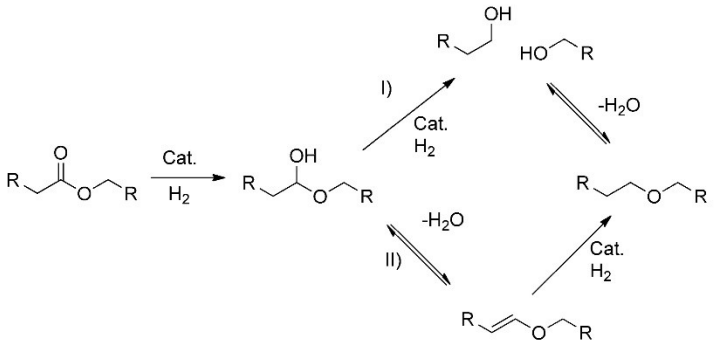
Figure 3. Effect of different metal triflates on the conversion and selectivity of the reductive etherification of PHDD compared to their corresponding estimated charge densities. Reaction conditions: PHDD (200 mg, 1.28 mmol COOR groups), $Ru(acac)_3$ (1 mol%), Triphos (1.5 mol%), Lewis acid (2.5 mol%), THF (2 mL), $T = 140\,^{\circ}C$, 40 bar H_2, $t = 16$ h.

Table 1. Solvent screening for the reduction of PHDD to the polyether.[a]



Entry	Solvent	Conv.[b,c] [%]	Yield[b,d] [%]	Sel.[b] [%]
1	Et_2O	33	0	0
2	THF	44	37	84
3	cyclohexane	40	2	4
4	$CHCl_3$	24	2	9
5	1,4-dioxane	38	17	46
6	toluene	17	0	0

[a] Conditions: PHDD (200 mg, 1.28 mmol COOR groups), $Ru(acac)_3$ (5 mg, 13 µmol, 1 mol%), Triphos ligand (12 mg, 20 µmol, 1.5 mol%), $Al(OTf)_3$ (15 mg, 33 µmol, 2.5 mol%), solvent (2 mL), 140 °C, 24 h. [b] Calculated from NMR spectra. [c] Conversion of COOR. [d] Yield of R–CH_2OCH_2–R groups.



Scheme 2. Possible reaction pathways for the formation of oligoethers from polyesters.

ties, we performed a control experiment. Heating THF together with $Al(OTf)_3$ to 140 °C for 24 h did not yield any oligomer of THF or other ethers (see the Supporting Information for details). Having identified a selective system with $Al(OTf)_3$, we further attempted to increase the conversion by varying the aluminum triflate/ruthenium ratios. Interestingly, at higher ruthenium loadings (1 mol%), increasing the $Al(OTf)_3$ content led to lower conversions (Table 2, entries 2 and 5), whereas at lower ruthenium loadings a large excess of $Al(OTf)_3$ is beneficial and increased the conversion (Table 2, entries 3 and 4). When a 1:1 ratio of $Ru(acac)_3$ and $Al(OTf)_3$ was used, no ether linkages were formed, although full conversion occurred. The reaction rather seemed to yield only the free diols, since no oligomers were detected by gel permeation chromatography (GPC; Table 2, entry 8). This indicates that a certain Lewis acid concentration is necessary to facilitate etherification of the free alcohol groups formed by the hydrogenation.

Thus, the reaction proceeds according to a tandem hydrogenation–etherification mechanism (Scheme 2, pathway I), consistent with the observations reported by Gooßen and co-workers (Scheme 1).[15b] However, a mechanism whereby etherification occurs through acid-catalyzed elimination of water from the hemiacetal intermediate (Scheme 2, pathway II) was also deemed plausible by Beller and co-workers.[15a]

To further verify which hypothesis is correct for this reaction, we monitored the molecular weight of the resulting polyester/polyether mixture during the course of the reaction. At the start of the reaction, a steep drop in the molecular weight of the substrate was detected (Figure 4), in line with the formation of the mixture of diols. Over the course of the reaction, the formed alcohols were slowly etherified to give

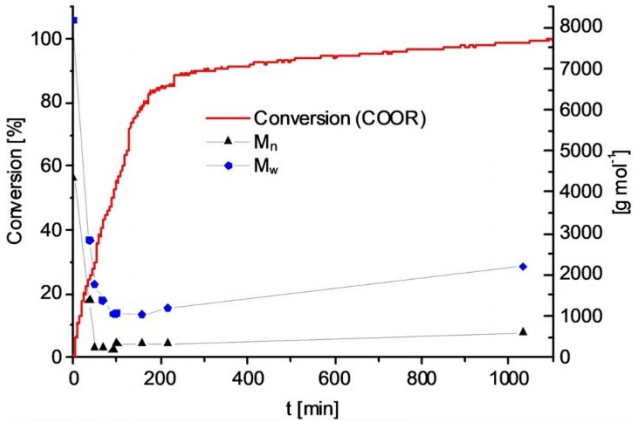
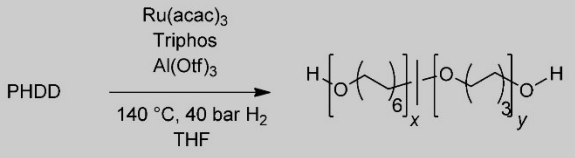


Figure 4. Molecular weight over time in the hydrogenation of PHDD. Conditions: Polymer (3.0 g), THF (30 mL), $Ru(acac)_3$ (3 mol%), Triphos (4.5 mol%), $Al(OTf)_3$ (7.5 mol%), $T = 140$ °C, 60 bar H_2.

Table 2. Effect of different Al/Ru-ratios.[a]



Entry	Al/Ru	Ru[b] [mol%]	Conv. [%][c]	Sel. [%]	M_w[d] [g mol^{-1}]	M_n[d] [g mol^{-1}]
1	2.5	3	91	92	1200	600
2	2.5	1	62	98	2200	800
3	10	0.25	33	73	2250	1500
4	20	0.125	62	100	2400	1400
5	15	1	28	41	2100	1300
6	7.5	1	49	100	2400	1400
7	2.5	1	58	100	2700	1600
8	1	1	>99	0	n.d.[e]	n.d.[e]

[a] Conditions: PHDD (200 mg, 1.28 mmol COOR), $Ru(acac)_3$ (5 mg, 13 µmol, 1 mol%), Triphos ligand (12 mg, 20 µmol, 1.5 mol%), $Al(OTf)_3$ (15 mg, 33 µmol, 2.5 mol%), solvent (2 mL), 140 °C, 24 h. [b] w.r.t. amount of COOR groups in the polyester. [c] Calculated from NMR spectra. [d] Determined by GPC. [e] No oligomers were detected inside the calibration range of the GPC method

polyether oligomers. The polycondensation of diols with Brønsted or Lewis acids is a known method to obtain polyethers that cannot be obtained by ring-opening polymerization of cyclic ethers.[19] Additional proof was obtained in a control experiment in which 1,12-dodecanediol was treated with $Al(OTf)_3$ at 140 °C. After 16 h, complete conversion was achieved and oligomers were obtained with a M_w of 1850–2000, as indicated by GPC analysis (see the Supporting Information for details).

As expected, switching the setup from simple vials to a mechanically stirred autoclave resulted in the reduction of all ester groups in a reasonable period of time. To get more insight into the generality of this approach, we subjected several other polyesters (Figure 5) to the reaction conditions.

Table 3 shows a comparison of the polyether molecular weights compared to the molecular weights of the starting polyesters. From the results obtained, it is clear that the catalytic protocol also works for other commercially available polyesters. The polyether polyols were obtained with molecular weights suitable for application in adhesives. It was not possible to obtain products with higher molecular weights, owing to the presence of water, which forms in the etherification reaction and cannot be removed, leading to an equilibrium with relatively low-M_w oligoethers. We tried adding drying agents to

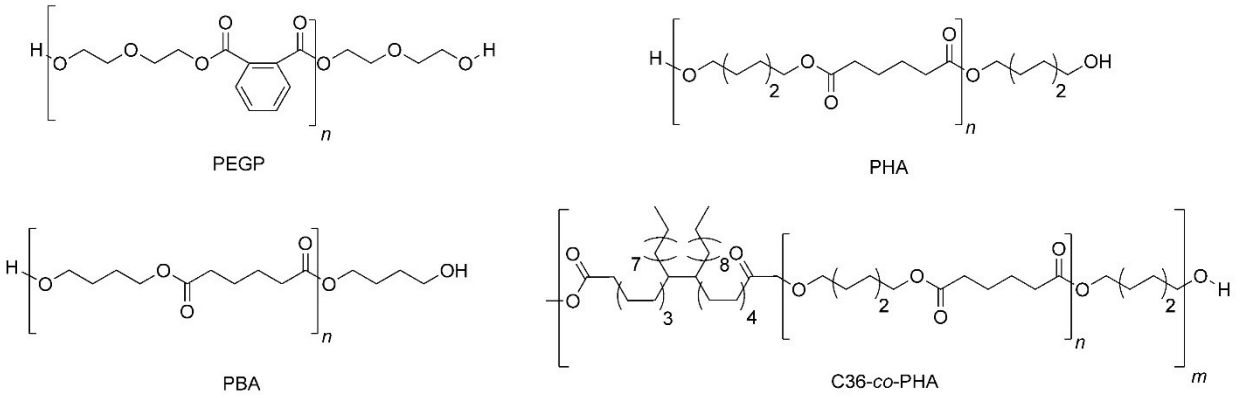


Figure 5. Other polyesters subjected to the hydrogenation procedure. PEGP = poly[(2-(ethoxy)ethyl)phthalate]; PHA = poly(hexyl-1,6-adipate); PBA = poly(butyl-1,4-adipate); C36-*co*-PHA = poly(hexene-1,6-adipate-co-distearate).

Table 3. Results of the hydrogenation/re-etherification of the polyesters shown in Figure 5.[a]

Entry	Polyester	M_n(GPC)[b] [g mol^{-1}]	M_w(GPC)[b] [g mol^{-1}]	M_n(GPC)[c] [g mol^{-1}]	M_w(GPC)[c] [g mol^{-1}]	M_n(NMR)[c,d] [g mol^{-1}]	Conv.[e] [%]	Yield[f] [%]
1	PHDD	4200	13000	600	2000	614	>99	80
2[g]	PHA	3000	13000	900	2100	892	96	90
3	PEGP	3200	13000	n.d.	n.d.	n.d.	49[i]	n.a.
4[h]	PBA	4200	11000	700	1100	563	>99	>99
5	C36-co-PHA	2400	4000	1500	2800	1000	>99	80
6[j]	PHA + 1,4-BDM	–	–	1100	2000	1238	>99	89

[a] Conditions (unless otherwise stated): Polymer (3.0 g), $Ru(acac)_3$ (3 mol%), Triphos (4.5 mol%), $Al(OTf)_3$ (7.5 mol%), THF (30 mL), 40 bar H_2 at RT, 140 °C, 24 h. [b] Determined by GPC with THF as eluent, before hydrogenation of the polyester sample. [c] Measured after hydrogenation. [d] Calculated from NMR spectra by end group analysis. [e] Conversion of COOR groups as analyzed by NMR spectroscopy. [f] Calculated w.r.t. the theoretical conversion of all ester groups into ether groups. [g] T = 180 °C; [h] $Ru(acac)_3$ (2 mol%), Triphos (3 mol%), $Al(OTf)_3$ (5 mol%). [i] Determined from hydrogen consumption. [j] 1,4-benzene dimethanol (22 mol%) was added; yield based only on the ether groups obtained by the conversion of original ether groups.

the hydrogenation reactions, but these did not have the desired effect.

Notably, industrial grade polyesters were used without purification, except drying under vacuum. Poly[(2-(ethoxy)-ethyl)phthalate] (PEGP), in contrast, was not fully reduced and yielded a complicated mixture of polyesters and polyethers (Table 3, entry 3). Polyethylene terephthalate (PET) was also subjected to the procedure but no conversion of the ester groups occurred. The most likely reason for the absence of reactivity is the insolubility of this polymer under the reaction conditions. However, a polyester polyol based on a dimer of a fatty acid could be easily reduced to a branched polyether structure (Table 3, entry 5). Integration of the peaks in the aliphatic region of the ^{1}H NMR spectra clearly shows the absence of THF incorporation in all obtained polyether polyols. To provide further evidence for the stepwise mechanism, we performed an experiment in which an exogenous diol was added, which, according to the mechanism, should be inserted into the polyether chain. Thus, 1,4-benzene dimethanol (1,4-BDM) was added as co-substrate to the hydrogenation reaction of PHA (Table 3, entry 6). 1,4-BDM is a suitable probe for this since there should be no ^{1}H NMR signal overlap between its free diol or ether form with the formed aliphatic polyether. PHA was chosen as polyester substrate to further simplify the NMR analysis of the product. Analysis of the ^{1}H NMR spectrum revealed that 8–10% of the added diol was incorporated in the oligomer, which had a slightly increased molecular weight of 1238 g mol^{-1} compared to the other products in Table 3. Further verification was provided by converting the free hydroxy groups into the corresponding trifluoroacetates, which did not result in any significant change with respect to the chemical shift of the signal assigned to the benzylic protons of the 1,4-BDM ether fragment. This signal consisted of two peaks indicating the presence of bonds of the 1,4-BDM to each other as well as to the 1,6-hexandiol fragments (Figure 6). Thus, if different diols are present in the reaction mixture they are, as expected, randomly incorporated in the oligomer chain.

The molecular weight of these polyether polyols obtained from end-group analysis is in agreement with the GPC-derived M_n value. This is a strong indication that the content of cyclic oligomers is low. The reduced molecular weight of the obtained polyethers is still in the range of 400–2000 g mol^{-1}, as for other common polyols in polyurethane-based adhesives.[20] Their usefulness was further verified by adding 1.1 equivalents of 2,4-toluene diisocyanate to the polyether obtained in entry 2 of Table 3, followed by moisture curing under ambient conditions. This procedure yielded a polyurethane film with a leather like haptic. Figure S2 shows this film which is flexible

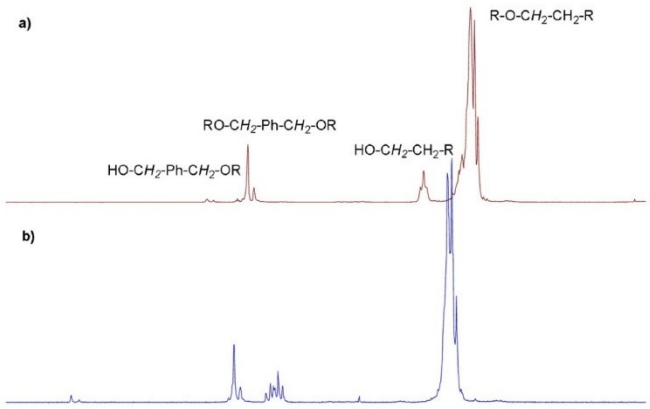


Figure 6. ^{1}H NMR spectra (3.0–5.7 ppm) of the oligoether described in Table 3, entry 6: a) before and b) after the addition of excess trifluoroacetic acid anhydride.

but still tightly engulfs a PTFE stirring bar. DSC measurements showed that poly[oxy(hexane-1,6-diyl)] obtained by the reduction of poly(hexene-1,6-adipate) retained its crystallinity. However the melting range was reduced from 45–50 °C (PHA) to 14–17 °C (the hydrogenated product). This can be seen as an advantage of the widely used poly-THF polyether that melts at 28 °C, which usually requires heated distribution pipes and storage tanks.

Conclusions

In conclusion, we have shown that a catalyst combination consisting of $Ru(acac)_3$, Triphos and $Al(OTf)_3$ can perform the hydrogenolysis of polyesters to polyethers. It was also possible to replace aluminum triflate with gallium or tin triflate. Control experiments supported a tandem hydrogenation etherification pathway. The reaction worked well with linear aliphatic polyesters. The polyether products could be converted into polyurethanes, opening up the possibility of adding novel polyols to the polyurethane chemist's toolbox. In addition, it provides an alternative to established hydrolysis and hydrogenolysis approaches for the recycling of polyesters. Although the molecular weight is reduced compared to the starting polyesters, the MW range is right for use in polyurethane-based adhesives.

Experimental Section

Hydrogenation and re-etherification of polyesters (Table 3)

PHDD (3 g; n(COOR) = 20 mmol) was added to a 100 mL Hastelloy autoclave equipped with a mechanical stirrer, followed by $Ru(acac)_3$ (240 mg, 3 mol%), Triphos (581 mg, 5 mol%), and $Al(OTf)_3$ (735 mg, 7.5 mol%). The reactor was then subjected to three vacuum–argon cycles. Next, THF (30 mL) was added to the reactor while having the latter under a flow of argon. Then the reactor was sealed, purged two times with N_2 (10 bar), pressurized with H_2 (40 bar), and heated to 140 °C. The temperature was controlled by a thermocouple inside the reactor. During the next 16 h, the pressure was recorded by a digital pressure read-out. After approximately 120 min, extra pressure of H_2 was added again to keep the pressure at 40–50 bar. Samples (100 μL) were taken according to the observed speed of pressure drop; these were filtered over silica, diluted with THF (ca. 1000 μL) and analyzed by GPC. Table S2 contains the GPC results of the reaction of PHDD at 140 °C. Figures S1 and S2 show the pressure, temperature, and calculated conversion over the course of the reaction. The polyether products were isolated by removing the solvent under reduced pressure followed by dissolution in toluene and filtration through silica to remove the residual catalyst and Lewis acid.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: hydrogenation · polymers · ruthenium · sustainable chemistry · waste prevention

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5.5 Declaration of the Contributions to the Individual Publications

A. Dell'Acqua, B. M. Stadler, S. Kirchhecker, S. Tin, J. G. de Vries, *Green Chem.* **2020**, in press

"*Scalable synthesis and polymerization of a β-angelica lactone derived monomer*"

The concept of the project was developed by me. The screening for the optimum conditions of the Diels-Alder reaction between cyclopentadiene and β-angelica lactone was carried out by me. Based on these parameters I designed the scale up experiment. The proof of concept for the polymerization of the adduct was done by me. I wrote about half of the manuscript and contributed to further editing. My own contribution to this work is about 40%.

B. M. Stadler, A. Brandt, A. Kux, H. Beck, J. G. de Vries, *ChemSusChem* **2020***, 13*, 556-563.

„*Properties of Novel Polyesters Made from Renewable 1,4-Pentanediol*"

The protocol for the synthesis of 1,4-PDO was developed by me and all the 1,4-PDO polyester polyols expect the product with the C14-Diacid were synthesized by me. Additionally, I synthesized the majority of the 1,4-BDO based polyester polyols. Further, I analyzed the experimental data, wrote the first draft of the manuscript and contributed to further editing. My own contribution to this work is about 75%

B. M. Stadler, S. Tin, A. Kux, R. Grauke, C. Koy, T. D. Tiemersma-Wegman, S. Hinze, H. Beck, M. O. Glocker, A. Brandt, J. G. de Vries, A*CS Sustain. Chem. Eng.* manuscript under revision

"Co-oligomers of renewable and "inert" 2-MeTHF and propylene oxide for use in bio-based adhesives"

I conducted a part of the experiments using boron-based Lewis acids as catalysts. I designed and carried out the experiments using tungstic phosphoric acid as catalyst and analyzed the corresponding NMR, in-situ IR and GPC data. The majority of the ESI-MS data was interpreted by me. I derived the equations for the optimization of the polymerization. Control experiments were conducted and analyzed by me. I wrote the first draft of the manuscript and contributed to further editing. My own contribution to this work is about 70%.

B. M. Stadler, S. Hinze, S. Tin, J. G. de Vries, *ChemSusChem* **2019**, *12*, 4082-4087

"Hydrogenation of Polyesters to Polyether Polyols"

The design of the experiments and all the laboratory work was carried out by me. All the data was analyzed and mostly interpreted by me. I wrote the first draft of the manuscript and contributed to further editing. My own contribution is about 85%.

6 Appendices

6.1 Supporting Information: Co-oligomers of renewable and "inert" 2-MeTHF and propylene oxide for the use in bio-based adhesives

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Supporting Information

A) General remarks

A.1) Reagents and solvents

2-Methyltetrahydrofuran (2-MeTHF), fluoroboric acid, and phosphotungstic acid hydrate were purchased from *abcr* GmbH. Boron trifluoride diethyl etherate was purchased from Acros. 2-Methyltetrahydrofuran was distilled prior use and dried over molecular sieves. Propylene oxide (PO) and boron trifluoro dihydrate were purchased from *Sigma Aldrich* and used as received.

A.2) NMR-Spectroscopy

^{1}H-NMR and ^{13}C-NMR spectra were recorded at ambient temperature on 300 MHz spectrometers (Avance 300 respectively Fourier 300) or a 400 MHz spectrometer (Avance 400) from Bruker. The chemical shifts δ are given in ppm and referenced to the residual proton signal of the particular solvent.

A.3) GPC, LC-MS-MS, stress-strain tests and In-Situ ATR-IR measurements:

Gel permeation chromatography (GPC): Gel permeation chromatograms were measured with a *1260 Infinity GPC/SEC System* from *Agilent Technologies*. The setup consisted of a *SECcurity Isocratic Pump*, SECcurity 2-Canal-Inline-Degaser*, SECcurity GPC-Column thermostat TCC6000, SECcurity Fraction Collector* and *SECcurity Differential Refractometer detector.* The measurements were performed at a constant temperature of 50 °C using three columns with a polyester co-polymer network as the stationary phase (PSS GRAM 30 Å, 10 µm particle size, 8.0 × 50 mm; PSS GRAM 30 Å, 10 µm particle size, 8.0 × 300 mm; PSS GRAM 1000 Å particle size, 8.0 × 300 mm). As the mobile phase a DMF lithium bromide solution (1.5 g·L^{-1}) with a flow rate of 1 mL min^{-1} was applied. Polystyrene standards from *ReadyCal* (PSS-pskitr1l-10, M_p = 370–2520000 g mol^{-1}) were used for calibration purposes.

Stress-strain tests: Stress-strain testing was conducted using a *Z010* test system from *Zwick-Roell* equipped with a 500 N probe head. Speed of sample (DIN 53504-SF3A-bones) elongation was 50 mm min^{-1}.

In-Situ ATR-IR measurements

ATR-IR spectra were recorded between 3000 – 620 cm^{-1} by a ReactIR 15 spectrometer equipped with a fiber optical diamond probe (Metler Toledo). For the quantification of PO, the integral of the signal of the characteristic ring deformation vibration[1] (810-840 cm^{-1}) was used. Calibration was achieved by adding increasing defined amounts of PO to 2-MeTHF.

B) Polymerization and characterization of the oligomers with NMR

B.1) Procedures of polymerization

I) General procedure for initial studies of co-polymerization of epoxides and 2-MeTHF (Table 1). An example with 10 eq. of 2-MeTHF: An oven-dried flask was charged with 2-MeTHF (7.3 mL, 72.0 mmol) and water (0.13 mL, 7.21 mmol), cooled to 0 °C and $BF_3{\cdot}Et_2O$ (0.88 mL, 7.13 mmol) was added dropwise. Then the epoxide (7.15 mmol) was added dropwise over 3 minutes and the resulting contents were left to stir for 90 minutes. After this time, an aqueous solution of NaOH (1.0 M, 20 mL) was added and the contents were left to stir at room temperature for 30 minutes. The excess of 2-MeTHF was

removed under reduced pressure and the resulting aqueous phase was extracted with toluene (25 mL). The organic layer was washed with water (3 x 20 mL), brine (20 mL), dried over $MgSO_4$ and toluene was removed under reduced pressure. The desired product was obtained as colorless oil after the sample was left under high vacuum for 4 hours.

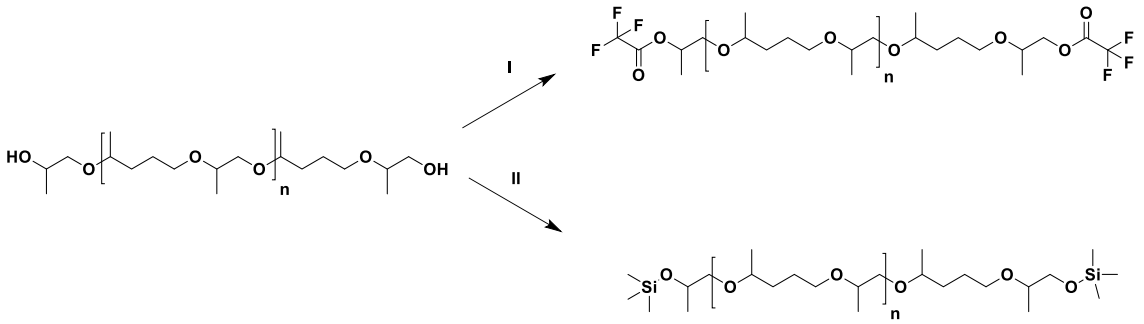
II) General procedure of polymerizations procedure described in Table S1: A dry 2-neck-round-bottom flask equipped with a condenser and magnetic stirrer is subjected to three vacuum-argon cycles. After that, the flask is charged with the desired amount of 2-MeTHF and the desired amount of water is added (0-10 mol% w.r.t. PO) followed by 1 mol% (w.r.t. PO) of the boron catalyst. The mixture is subsequently stirred for 20 minutes, followed by addition of the desired amount of PO over 1 hour via an HPLC-pump. When the addition was complete, 2-MeTHF (10 mL) was fed through the pump to remove residues of PO. After that the reaction was quenched by adding an aqueous solution of sodium hydroxide (c(NaOH)=1.0 mol l^{-1}) and stirred for another hour. After this time the reaction mixture was poured into a separation funnel, diluted with toluene to double the volume and washed with water (3 x 20 mL). The organic layer was separated. Evaporation of the volatiles *in vacuo* yielded the co-oligomers as colorless viscous liquids (17-72% w.r.t. PO). Results are given in TableS1.

Example: Reacting 2-MeTHF (44 mL, 425 mmol) with PO (6.0 mL, 85 mmol) in the presence of $BF_3 \bullet 2H_2O$ (54 µl, 4.25 mmol, 1 mol-% w.r.t. PO) at RT according to the standard procedure yielded poly-[(2-methyltetrahydrofurane)-*co*-(propyleneglycol)] (6.3 g, 50%). Ratio of 2-MeTHF : PO is 52:48; M_n(NMR)=1081 g mol^{-1}; hydroxyl number: 95 mg KOH g^{-1}

III) General procedure of polymerizations procedure described in Table S3: A dry 3-neck-round-bottom flask equipped with a condenser and magnetic stirrer is subjected to three vacuum-argon cycles. After that, the flask is charged with and the desired amount of tungstic phosphoric acid, followed by the addition of 2-MeTHF (40 ml, 0.39 mol) and the desired amount of diol. After PO (0.5 ml min^{-1}, total 0.87 mol) and 2-MeTHF (1.0 ml min^{-1}, total 1.18 mol) was fed via HPLC pumps to the reactor over 120 min. If necessary, the reactor was equipped with an ATR-IR probe. After that the reaction was quenched by adding water and stirred for another hour. After that the reaction mixture was adjusted to pH=7 by adding sodium carbonate. To remove the catalyst and salts the reaction mixture was filtered through a pad of silica which was washed with toluene (2x100 ml). Evaporation of the volatiles *in vacuo* yielded the co-oligomers as colorless viscous liquids (17-72 mol% w.r.t. PO). Results are given in Table 3 and Table S2 of the manuscript.

B.2) M_n determination by ^{1}H-NMR

The number average molecular weight of the oligomers (M_n) was determined by the corresponding ^{1}H-NMR spectrum after derivatization of the hydroxyl end groups with trifluoroacetic anhydride (TFA) (I, Scheme 1) or with chlorotrimethylsilane (TMS-Cl) (II, Scheme 1)



Scheme S32: Derivatization reactions of the oligomers

Method I: The polymer (20 mg) is added to an NMR tube dissolved in $CDCl_3$ (400 µL) followed by addition an excess of trifluoroacetic anhydride (200 µL). Subsequently the spectrum was recorded and the molecular weight and the monomer ratio were calculated based on the ratio of the high field shifted protons next to the trifluoroacetate moiety. Note: This method can only be used in cases were the polymer does not contain acid sensitive groups; otherwise method II should be used. Figure S1 contains an exemplary spectrum.

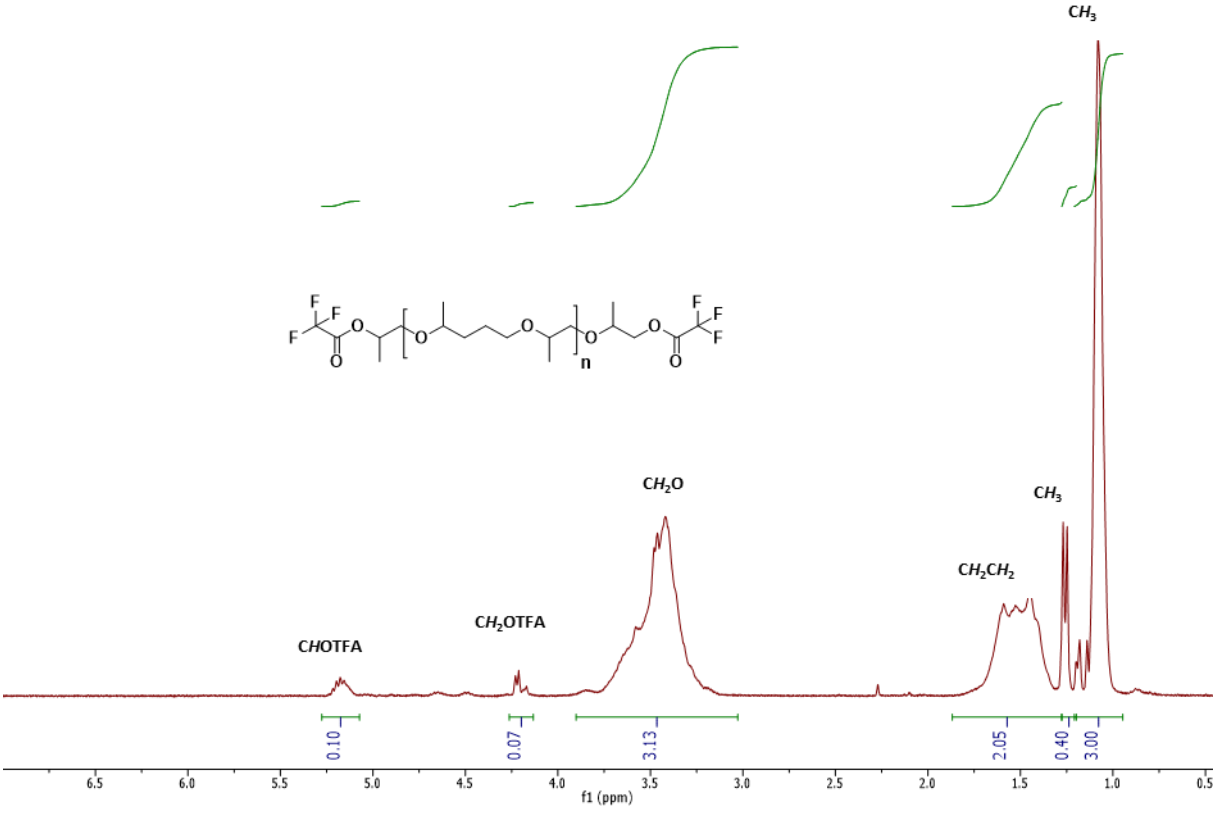


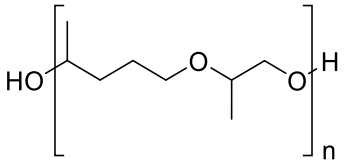
Figure S 1: ^{1}H-NMR spectrum of poly-[(2-methyltetrahydrofuran)-alt-(propyleneglycol)] derivatized with TFA; M_n=1081 g mol^{-1}.

Method II: The polymer (55 mg) was dried in vacuo for 30 minutes and dissolved in anhydrous DCM (5.5 mL). The resulting solution was cooled to 0 °C for 20 minutes and dry triethylamine (1.0 mL, 7.17 mmol) was added followed by the dropwise addition of TMS-Cl (0.5 mL, 3.94 mmol). The reaction solution was left to stir for 1 hour at 0 °C, then the ice-bath was removed and the resulting solution was left to stir at RT overnight. After this time, the volatiles were removed under reduced pressure and the resulting solids were left to dry *in vacuo* for 4 hours. To the remaining red solid C_6D_6 (0.6 mL) was added, the benzene solution was filtered into an NMR tube and the spectrum was recorded. From the resulting spectrum, the ratio of the monomers in the polymer, as well as the molecular weight, were calculated.

B.3) MS analysis of the reaction products obtained with stoichiometric BF_3

The results of LC-MS-MS studies are shown in the paper for poly-[(2-methyltetrahydrofuran)-*alt*-(propyleneglycol)] obtained with by the copolymerization of 2-MeTHF and PO in the presence of stoichometric amounts of $BF_3 \bullet Et_2O$ (Table 1 in the manuscript, entry 1). The LCMS of some selected peaks are shown below.

LC-MS and some selected MS-MS fragmentation spectra of poly-[(2-methyltetrahydrofuran)-*alt*-(propyleneglycol)]



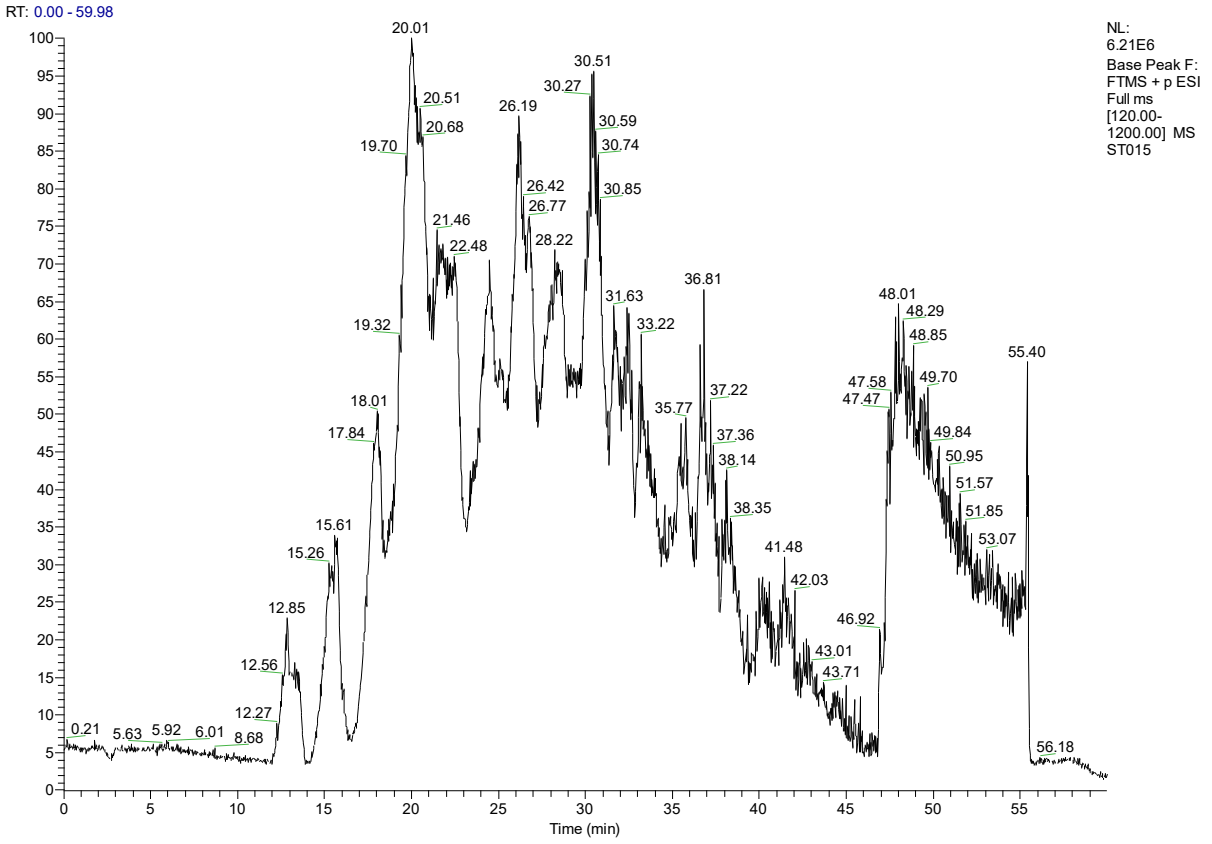


Figure S 2: LC of the copolymer obtained with stoichiometric amounts of $BF_3 \bullet Et_2O$. Repetition unit above

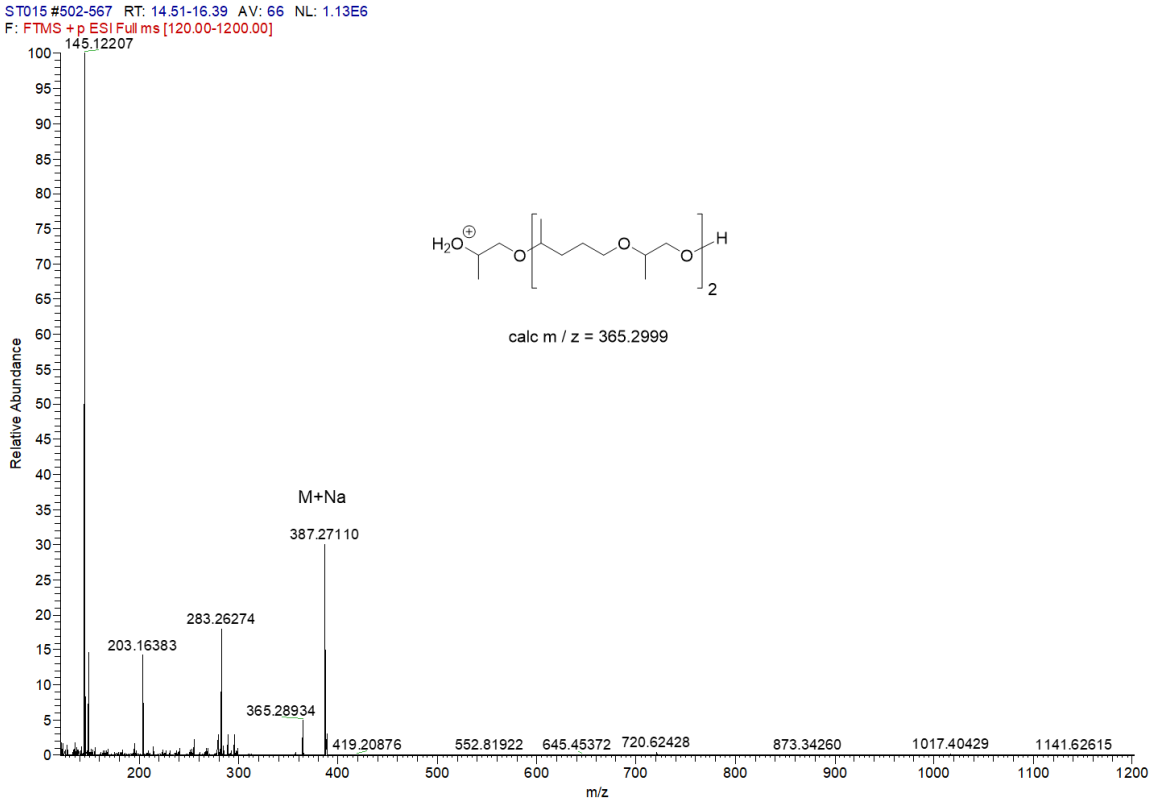


Figure S 3: ESI-MS of the singal at 15 min

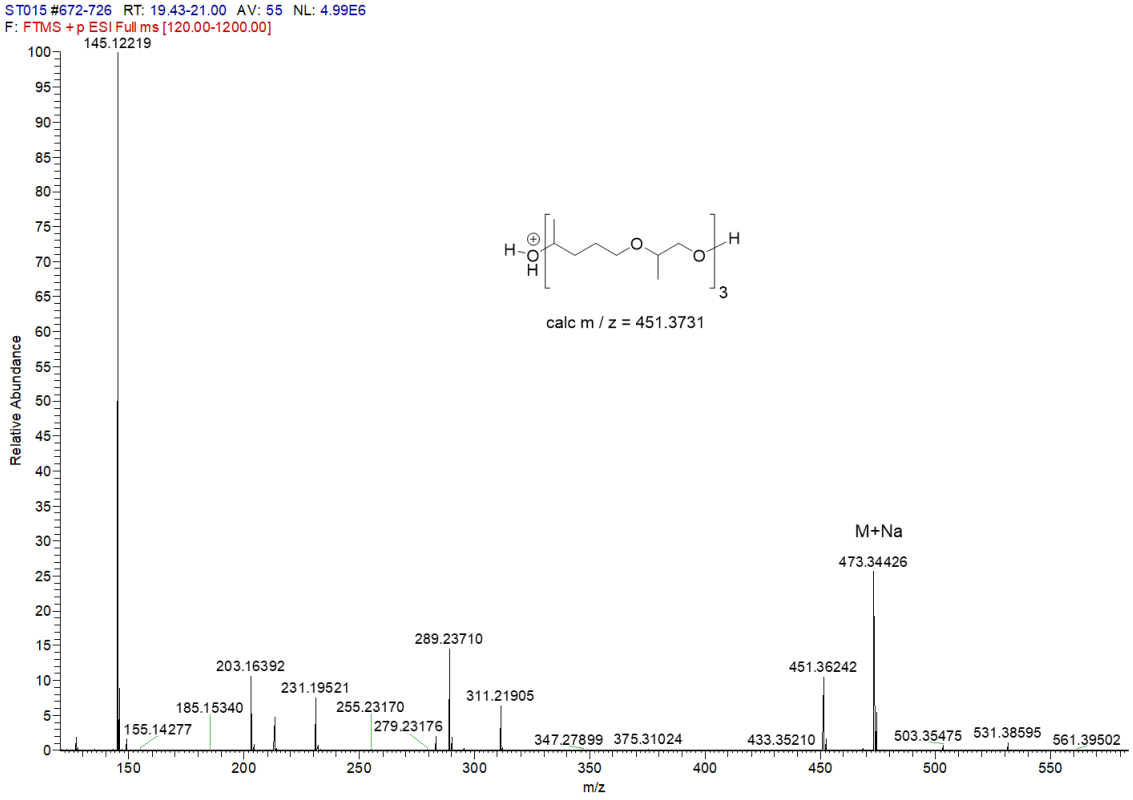


Figure S 4: ESI-MS of the singal at 20 min

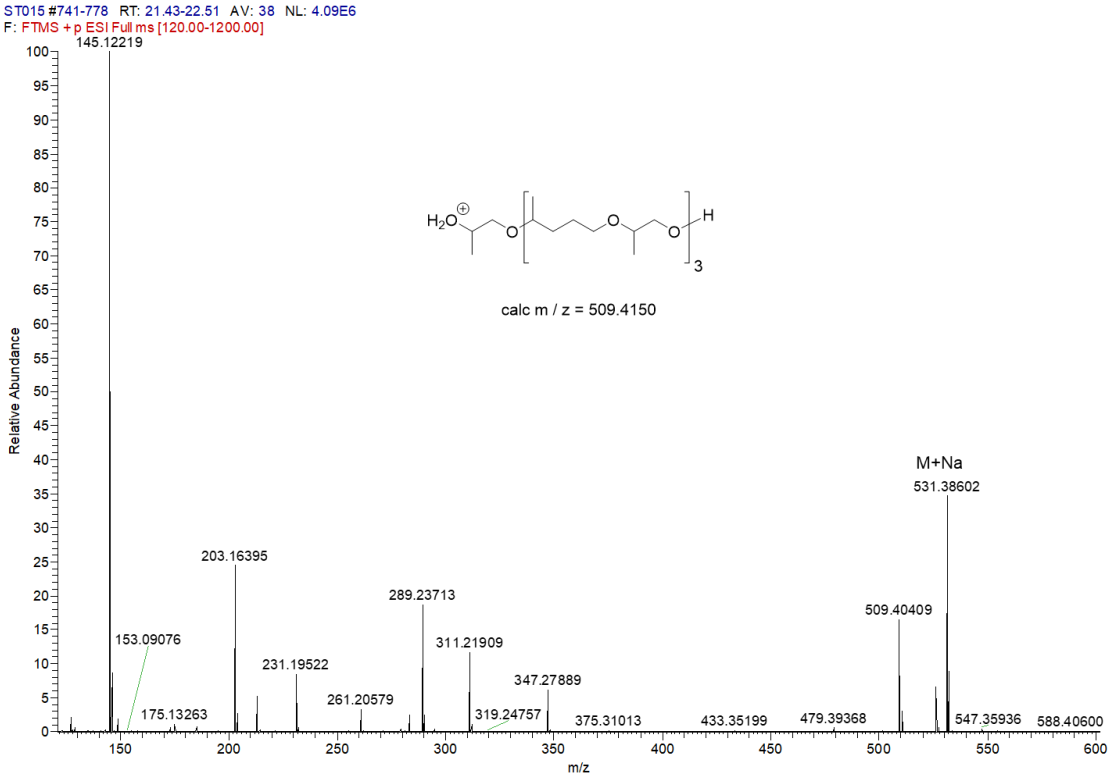


Figure S 5: ESI-MS of the singal at 21-22.5 min

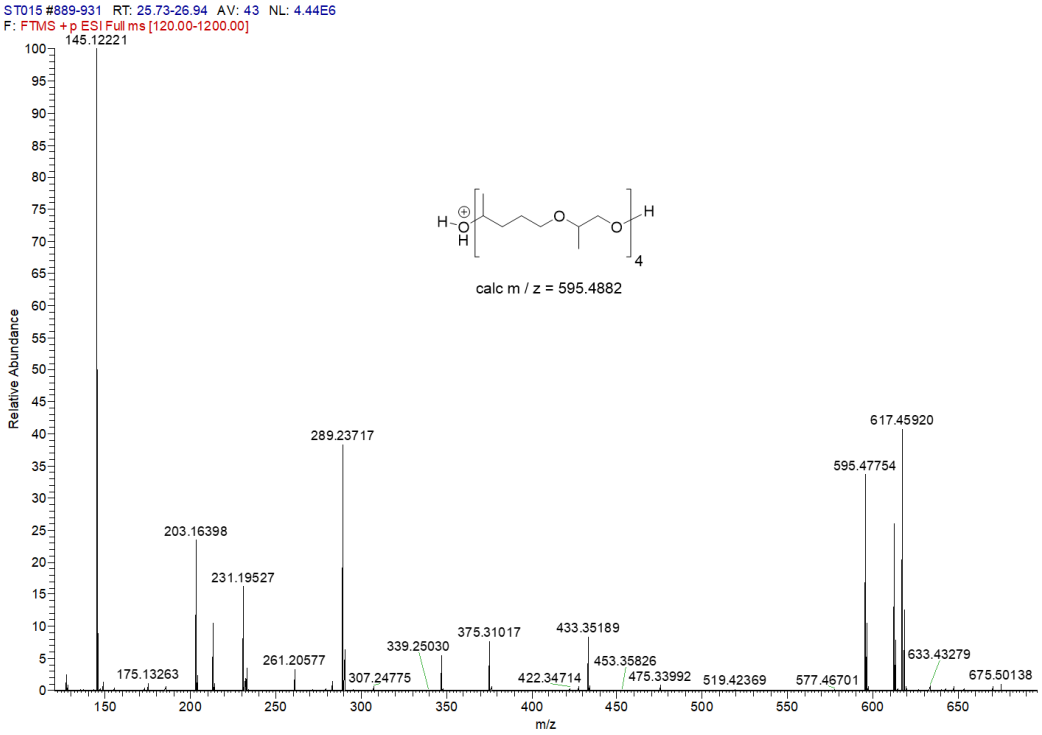


Figure S 6: ESI-MS of the singal at 25.73-26.94 min

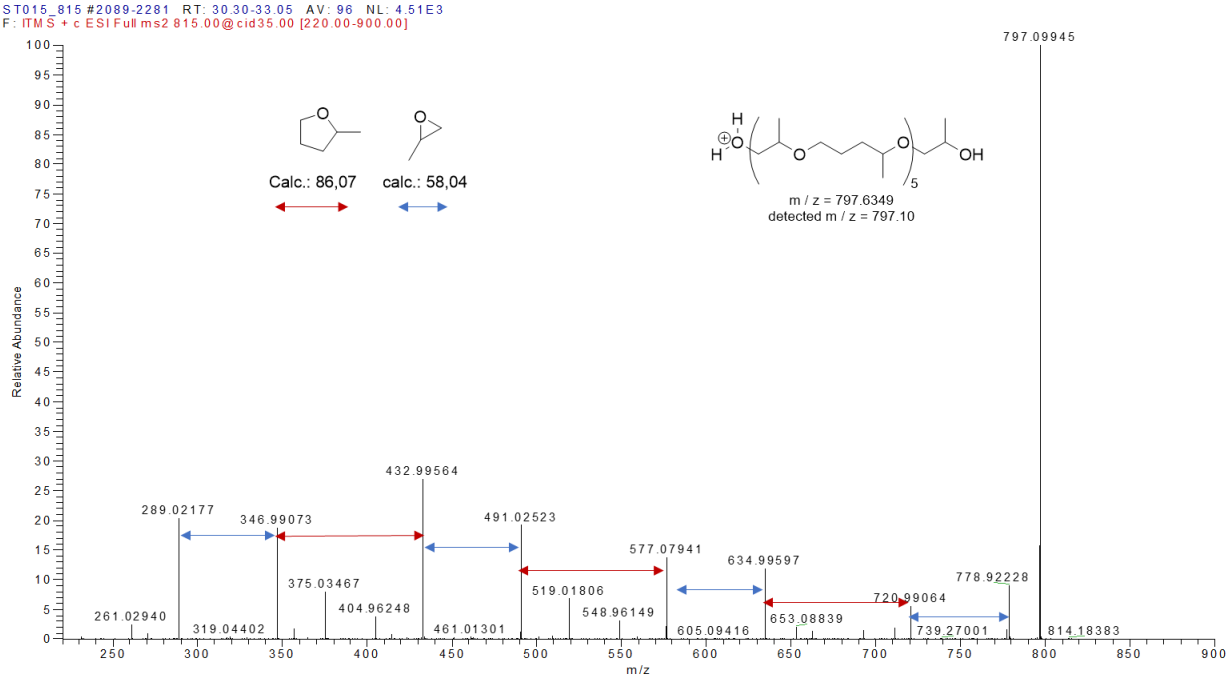
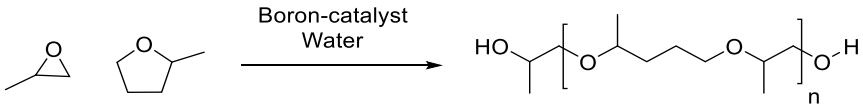


Figure S7: : ESI-MS of the singal at 32 min

B.4) Initial screenings of the catalytic copolymerization and MS analysis of impairing side products

Table S 1: Effect of different boron catalysts and different amount of water on the polymerization



#	Cat.	MeTHF [eq][a]	Cat. [mol %][a]	H_2O [mol %][a]	M_n(NMR)[b] [g mol^{-1}]	M_n(GPC)[c][g mol^{-1}]	*Đ*	MeTHF/ Oligomer[a] [%]	Y[%][d]
1[e]	BF_3•Et_2O	2	5	0	2883	1100	4.8	52	82
2[e]	BF_3•Et_2O	5	5	0	744	500	2.5	52	43
3[e]	BF_3•Et_2O	5	5	2.5	1262	500	2.6	49	64
4[e]	BF_3•Et_2O	5	5	5	1685	500	3.6	49	34
5[e]	BF_3•Et_2O	5	5	10	741	500	3.8	49	17
6[f]	BF_3•Et_2O	5	0.1	5	n.a	n.a	n.a	n.a	0
7[f]	BF_3•Et_2O	5	1	5	n.a	n.a	n.a	n.a	0
8[g]	BF_3•Et_2O	2	1	5	1793	700	6.3	40	72
9[g]	BF_3•$2H_2O$	2	1	5	1734	500	4.6	34	60
10[g]	BF_3•$2H_2O$	5	1	5	1081	500	3.1	52	50
11[g]	HBF_4[h]	5	1	4.75	1316	1000	1.5	48	51
12[g]	HBF_4[h]	2	1	4.75	903	800	2.2	44	65

General remarks: PO was added at 0.1 ml/min (0.25 eq. h^{-1}). After PO addition was finished reactions were stirred for 1 hour. [a]w.r.t. propylene oxide (PO). [b]Determined by ^{1}H-NMR after derivatization with trifluoro acetic acid anhydride (TFA). [c]Determined by GPC via calibration against polystyrene with DMF as eluent. [d]Isolated yield. [e]Addition of water, catalyst and PO at 0°C. Quenching at RT. PO addition 0.4 eq. h^{-1}; [f]Water and catalyst stirred for 1 hour at RT, PO was added at 0°C; [g]Everything added at RT. [h]50 % w/w in water

Table S1 shows a screening of different boron based acidic catalysts. The reactions were carried out according to procedure II) described in section B.1. When the results are evaluated with the polydispersity the Brønsted acid HBF_4 performed best. However, the resulting PUR films had only poor elongation values (See section 2.4 in the manuscript). This is an evidence for the presence of cyclic side products or chains containing "blocked" OH-Groups. These side products are ethoxylated propylene glycol and ethoxylated oligomers (from BF_3*Et_2O) and 3 or 4 membered cylcics as found via GC-MS analysis see figures below.

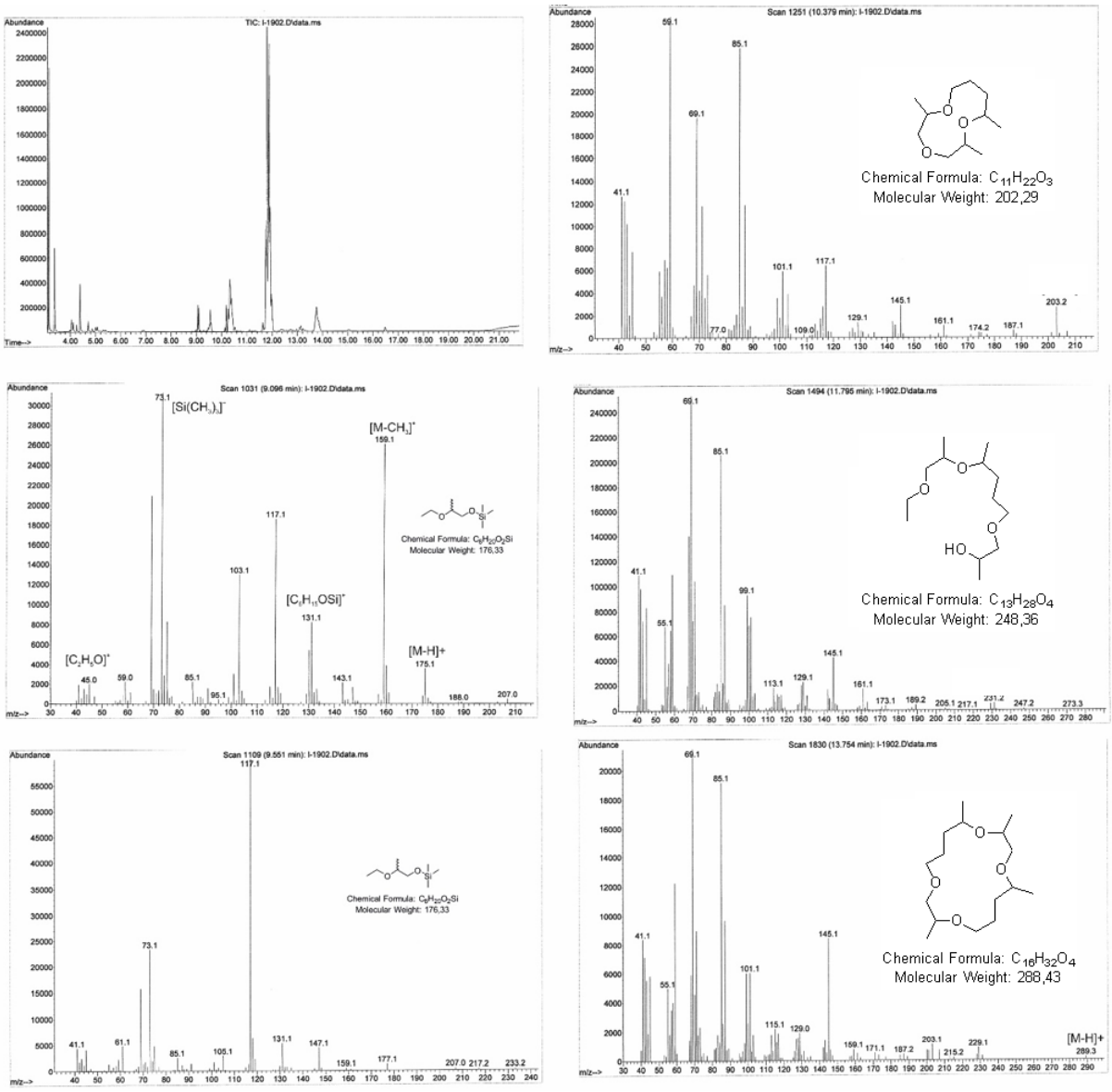


Figure S 8: GC-MS analysis of the sample of Table S1, entry 1 after derivatization with trimethylchlorosilane.

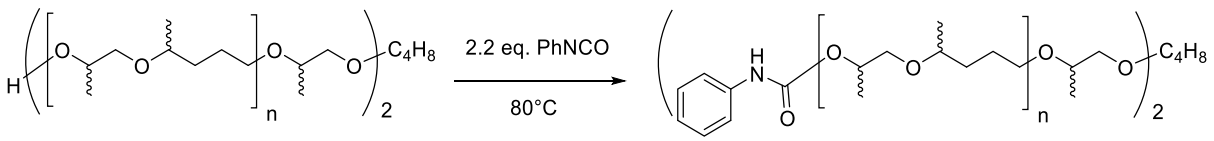
Hence to further improve our oligomerization process the stronger Brønsted acid $H_3PW_{12}O_{40}*_{24}H_2O$ was investigated as catalyst. The results are shown in Table S2.

Table S2. Testing of $H_3PW_{12}O_{40}*_{24}H_2O$ under different conditions

#	I[a]	PO [eq][b]	Cat [mol%][c]	*M*n(calc.)[d] [g mol^{-1}]	Mn(NMR)[e] [g mol^{-1}]	Mn(GPC)[f] [g mol^{-1}]	PDI[f]	OH(Trit.)[g] [mg g^{-1}]	Mn (Trit.)[g] [g mol^{-1}]	MeTHF[e] [%]	Y [%]
1	BDO	20	0.33	1446	1201	1155	1.4	98	1145	43(45)	52
2	BDO	40	0.33	2888	1309	1469	1.6	99	1133	40(48)	60
3	BDO	40	0.02	2888	2225	871	3.5	nd	nd	44(48)	52
4[h,i]	BDO	40	0.02	2888	1924	908	2.8	nd	nd	48(48)	72
5[i]	BDO	40	0.02	2888	2222	874	3.6	62	1810	39(48)	75
6[i]	BDO	20	0.02	1446	1278	1158	2.0	74	1516	43(45)	69
7[i]	PDO	20	0.02	1460	1720	1311	2.1	64	1753	37(45)	92
8[i]	BDM	20	0.02	1494	1325	1012	1.9	94	1194	35(45)	77
9[k]	BDO	16	0.02	1302	1288	1500	1.4	80	1408	43(43)	
10[l]	BDO	20	0.02	1446	90	n.d.	n.d.	n.d.	n.d.	0(45)	n. d.

General conditions: Oligomerization reactions were carried out at RT; PO and 2-MeTHF were fed to a solution of initiator and catalyst in 2-MeTHF (50 mL) via HPLC pumps for 120 min. Flows (Q): Q(PO)=0.5 cm^3 min^{-1}; Q(2-MeTHF)=1.0 cm^3 min^{-1}. [a]Initiator; BDO=1,4-butanediol, PDO=1,4-pentanediol, BDM=1,4-benzenedimethanol. [b]W.r.t. initiator. [c]W.r.t. PO. [d]Predicted M_n. [e]Determined with ^{1}H-NMR after derivatization with triflouroacetic anhydride. [g]Determined by GPC. [g]Determined by titration analogous to DIN 53240. [h]At 50°C in a sealed stainless steel autoclave. [i]No aqueous workup. [k]Flow rate of PO according to Figure 5 in the manuscript. [l]Anhydrous $H_3PW_{12}O_{40}$ was used

B.5) ESI-MS characterization of the sample obtained in Figure 12d



M_n(calc.)=1158 g/mol; *M*n(NMR)=1288 g/mol

f(2-MeTHF)=42%;

Scheme S2: Derivatization reactions of the oligomers with phenylisocyanate

Prior to the measurments a polyether sample from Table S2, Entry 10 (500 mg) was heated in a 2 mL vial to 80°C and kept under vaccum ($0.2*10^{-3}$ bar) while being stirred for 2 hours to ensure removal of water. After this, the vial was repressurized with an argon atmosphere and 2.2 eq. phenylisocyanate with respect to the M_n value (as measured by NMR or titration) was added via syringe. Subsequently the contents were left to stirr for 3 hours. After this time, vacuum was applied for 30 min to get rid of most of the excess of phenyl isocyanate left. The vial was repressurized and allowed to cool to room temperature. The next day ^{1}H NMR spectrum was acquired to ensure the full functionalization of the sample. Figure S 9 shows the ^{1}H-NMR spectrum prior to the phenyl isocyanate derivatisation and Figure S 10 after. The success of the derivatisation was judged by the fact that the integral of the terminal CH_2-O and C*H*-O did not change with respect to the -CH_3 groups in the oligomer chain.

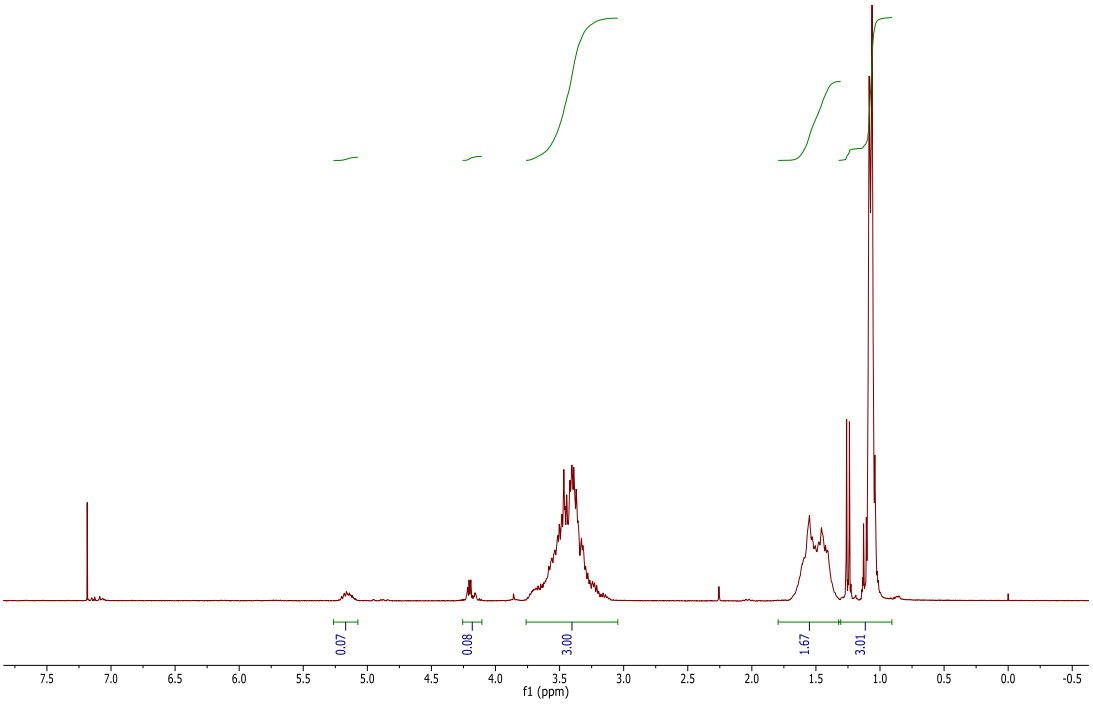


Figure S 9: ^{1}H-NMR of poly-2-MeTHF-PO copolymer. End groups are marked with trifluoracetic acid esters.

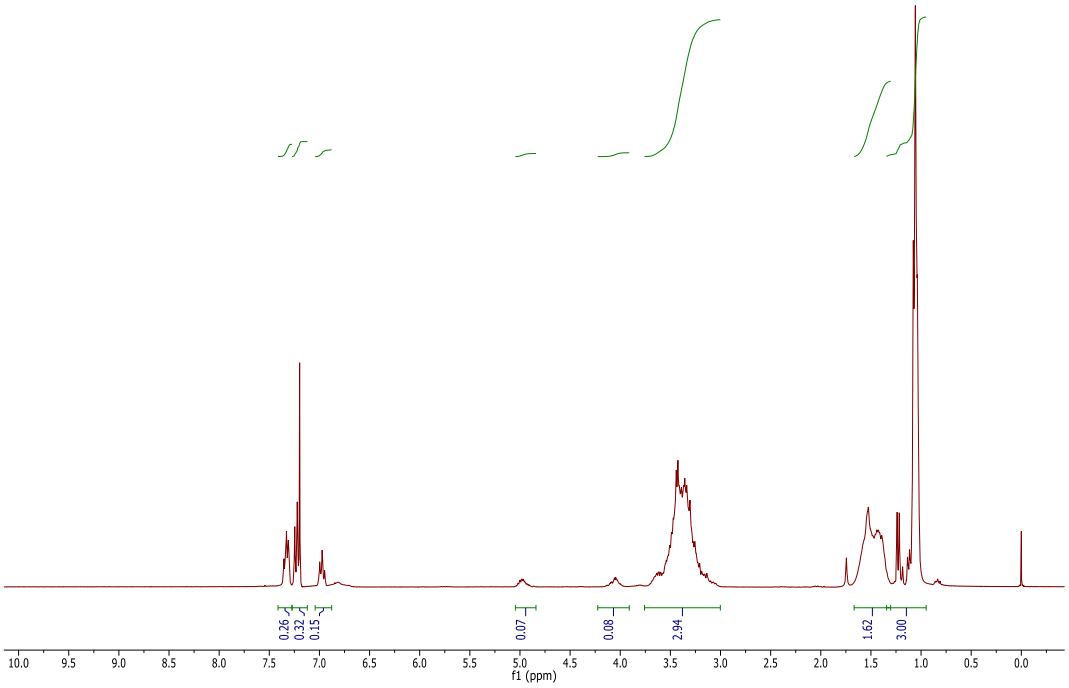


Figure S 10: The same sample as in Figure S8 but derivatized with phenyl isocyanate

In the next step a solution of the derivatized oligomer in methanol (1 mg mL^{-1}) was prepared. To this solution (1 mL) of distilled triethylamine (100 µL) was added. The solution was then immeditaly transferred to a gold coated ESI-MS-capillary and subsequently measured. Figure S 11 shows the overview spectra of the measured oligomer. Figures S14, S15, S16 and S17 contain different sections of the full spectra.

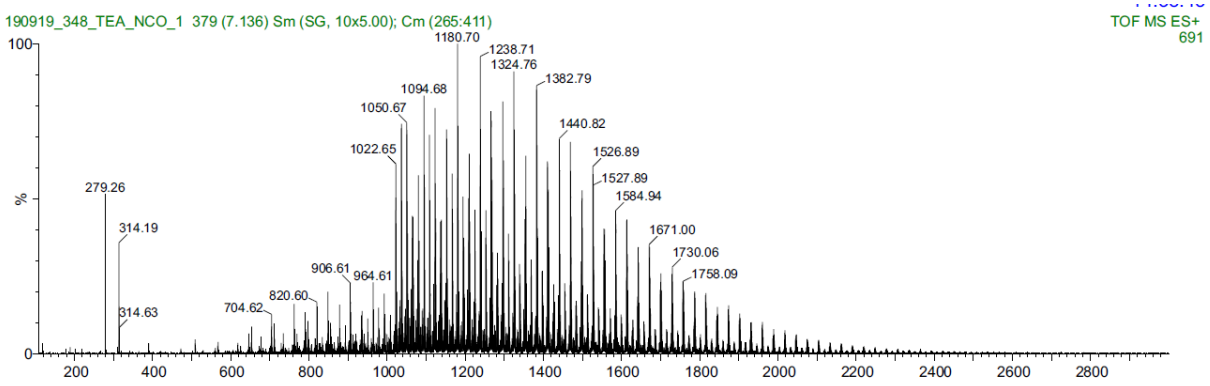


Figure S 11: Full ESI-MS spectra. Table S2, Entry 10, Manuscript:

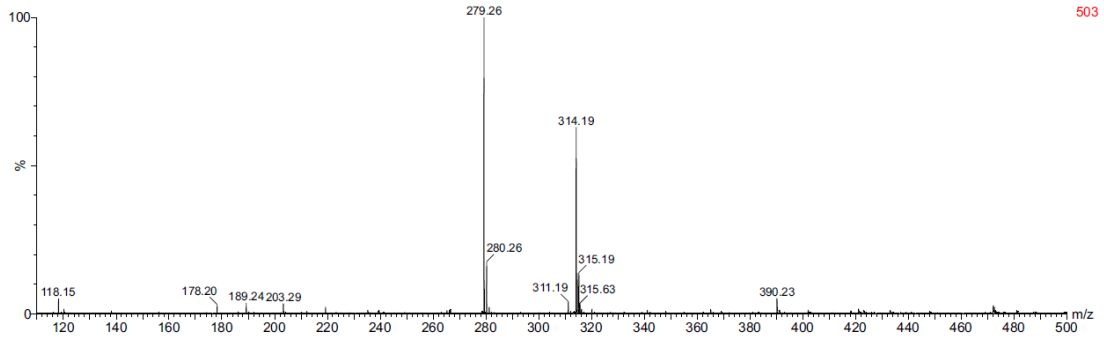


Figure S 12: Section from 100 to 500 m/z of spectrum shown in Figure S 11.

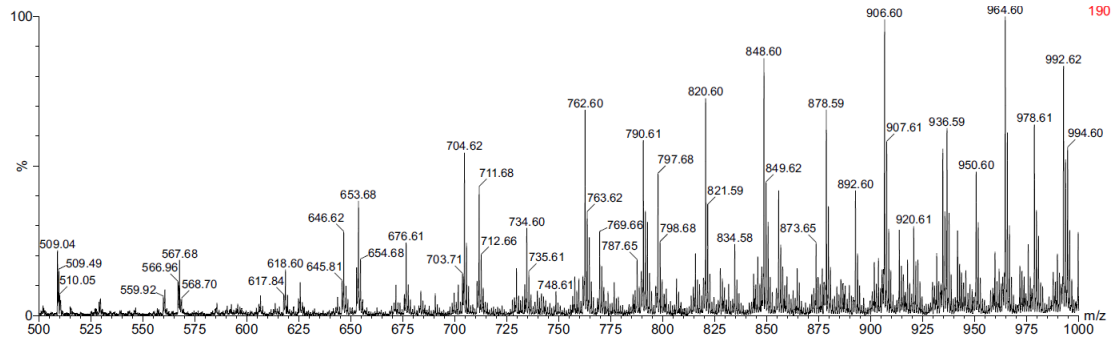


Figure S 13: Section from 500-1000 m/z of spectrum shown in Figure S 11.

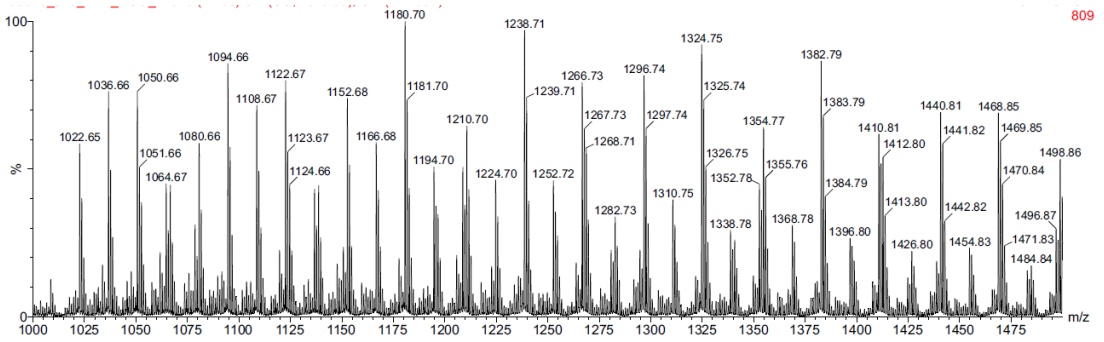


Figure S 14: Section from 1000-1500 m/z of spectrum shown in Figure S 11.

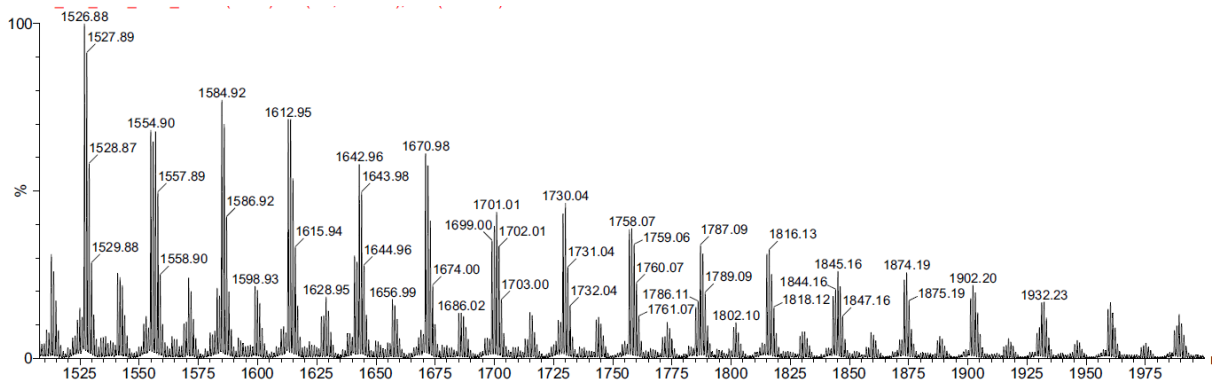


Figure S 15: Section from 1500 – 2000 m/z of spectrum shown in Figure S 11.

1,4-BDO initiated chains

Table S3 contains the measured signals which could be assigned to linear hydroxyl terminated chains, which are now end capped with phenyl isocyanate and contain one molecule of 1,4-butane diol (1,4-BDO). The molecular weight *M* of these chains was calculated using the following equation:

$$M = n_{\mathrm{PO}} M_{\mathrm{PO}} + n_{\mathrm{MeTHF}} M_{\mathrm{MeTHF}} + M_{1,4-\mathrm{BDO}} + 2M_{\mathrm{PhNCO}} + M_{\mathrm{HNEt_3}}$$

where n = number of molecules in the chain. Indices: PO = propylene oxide, MeTHF = 2-methyltetrahydrofurane, PhNCO = phenyl isocyanate, $HNEt_3$ = triethylammonium cation; *M* = the corresponding exact molecular weights.

Table S3: Calculated and measured masses of 1,4-BDO initiated chains

n(PO)	n(MeTHF)	M(Calculated) [m/z]	M(Measured) [m/z]	Δ [m/z]
5	2	892.62	892.60	0.02
4	3	920.65	920.61	0.04
6	2	950.66	950.56	0.10
5	3	978.69	978.61	0.08
6	3	1036.73	1036.66	0.07
7	3	1094.78	1094.66	0.12
6	4	1122.81	1122.67	0.14
8	3	1152.82	1152.68	0.14
7	4	1180.85	1180.7	0.15
9	3	1210.86	1210.7	0.16
8	4	1238.89	1238.71	0.18
7	5	1266.92	1266.73	0.19
9	4	1296.93	1296.74	0.19
8	5	1324.97	1324.75	0.22
10	4	1354.98	1354.77	0.21
9	5	1383.01	1382.79	0.22
8	6	1411.04	1410.81	0.23
8	6	1411.04	1410.81	0.23
10	5	1441.05	1440.81	0.24
9	6	1469.08	1468.86	0.22
8	7	1497.11	1496.87	0.24
11	5	1499.09	1498.86	0.23
10	6	1527.12	1526.89	0.23
9	7	1555.15	1554.9	0.25
11	6	1585.16	1584.92	0.24
10	7	1613.20	1612.95	0.25

12	6	1643.21	1642.96	0.25
11	7	1671.24	1670.98	0.26
10	8	1699.27	1701.01	-1.74
11	8	1757.31	1758.07	-0.76
11	8	1757.31	1758.07	-0.76
16	5	1789.30	1787.09	2.21
12	8	1815.35	1815.13	0.22
14	7	1845.36	1845.16	0.20
14	8	1931.44	1931.23	0.21

Water initiated chains

Table contains the measured signals which could be assigned to linear hydroxyl terminated chains, which are now end capped with phenyl isocyanate and contain one molecule of water. The theoretical molecular weight *M* of these chains was calculated using the following equation:

$$M = n_{\mathrm{PO}} M_{\mathrm{PO}} + n_{\mathrm{MeTHF}} M_{\mathrm{MeTHF}} + M_{\mathrm{H2O}} + 2M_{\mathrm{PhNCO}} + M_{\mathrm{HNEt_3}}$$

where n = number of molecules in the chain. Indices: PO = propylene oxide, MeTHF = 2-methyltetrahydrofurane, PhNCO = phenyl isocyanate, $HNEt_3$ = triethylammonium cation; *M* = the corresponding exact molecular weights.

Table S4: Calculated and measured masses of water-initiated chains

n(PO)	n(MeTHF)	M(Calculated) [m/z]	M(Measured) [m/z]	Δ [m/z]
2	2	646.45	646.34	0.11
3	2	704.49	704.36	0.13
5	1	734.50	734.38	0.12
4	2	762.53	762.40	0.13
3	3	790.56	790.43	0.13
5	2	820.57	820.45	0.12
6	2	878.61	878.50	0.11
5	3	906.64	906.53	0.11
7	2	936.65	936.54	0.11
5	4	992.72	992.60	0.12
8	2	994.70	994.59	0.11
7	3	1022.73	1022.65	0.08
6	4	1050.76	1050.66	0.10
8	3	1080.77	1080.66	0.11
7	4	1108.80	1108.67	0.13
6	5	1136.83	1136.67	0.16

8	4	1166.84	1166.68	0.16
7	5	1194.88	1194.70	0.18
9	4	1224.89	1224.70	0.19
8	5	1252.92	1252.70	0.22
10	4	1282.93	1282.73	0.20
9	5	1310.96	1310.75	0.21
8	6	1338.99	1338.78	0.21
10	5	1369.00	1368.78	0.22
11	7	1599.19	1598.93	0.26
9	6	1397.03	1396.80	0.23
11	5	1427.04	1426.80	0.24
10	6	1455.07	1454.83	0.24
12	5	1485.09	1484.84	0.25
12	6	1571.16	1570.99	0.17
12	7	1657.23	1656.99	0.24
13	6	1629.20	1628.95	0.25
13	7	1715.27	1714.91	0.36

B.6) Triphenylphosphine trapping experiment

These experiments were based on the method published by Penczek et. al[2,3]

A) An oven dried 10 mL Schlenk tube equipped with a magnetic stirrer was charged with phosphotungstic acid hydrate (225 mg, 0.08 mmol). After that 1,4-BDO (220 µl, 2.4 mmol) was added followed by the addition of a solution of triphenylphosphine (629 mg, 2.4 mmol) in dry 2-MeTHF (5.0 mL). During stirring propylene oxide (300 µl, 4 mmol) was added via a syringe. The contents were left to stir for 60 minutes. After this time, a sample was taken, diluted with CD_2Cl_2 and measured by ^{31}P-NMR spectroscopy. This revealed the presence of several signals at δ_P = 23 ppm which can be attributed to the presence of phosphonium salts. Further triphenylphosphine oxide could be identified (δ=26.5 ppm) and residues of tungstic phosphoric acid (δ=-15.4 ppm) (Figure S15)

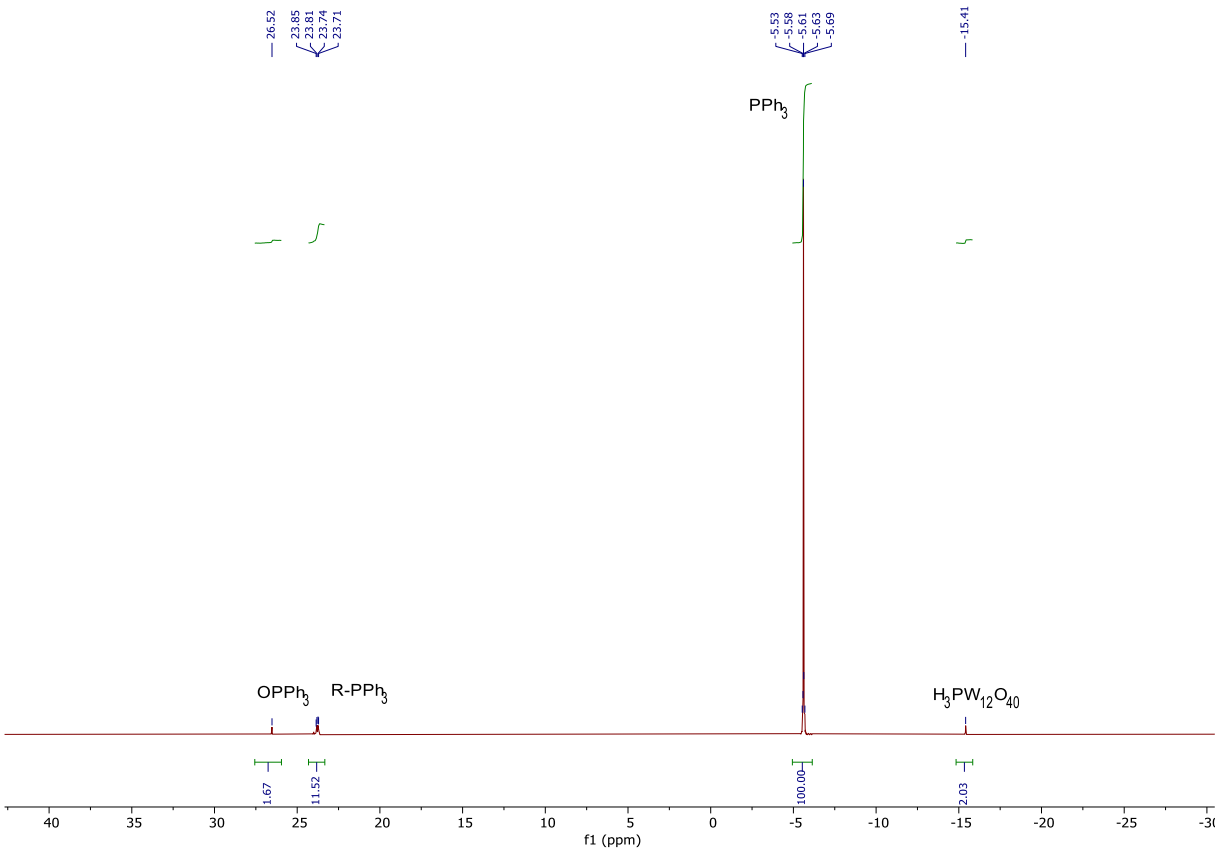


Figure S15: ^{31}P NMR spectrum of the reaction mixture obtained according to method A.

B) Same procedure as method A, but without the addition of propylene oxide. Only triphenylphosphine could be identified in the ^{31}P-NMR spectra

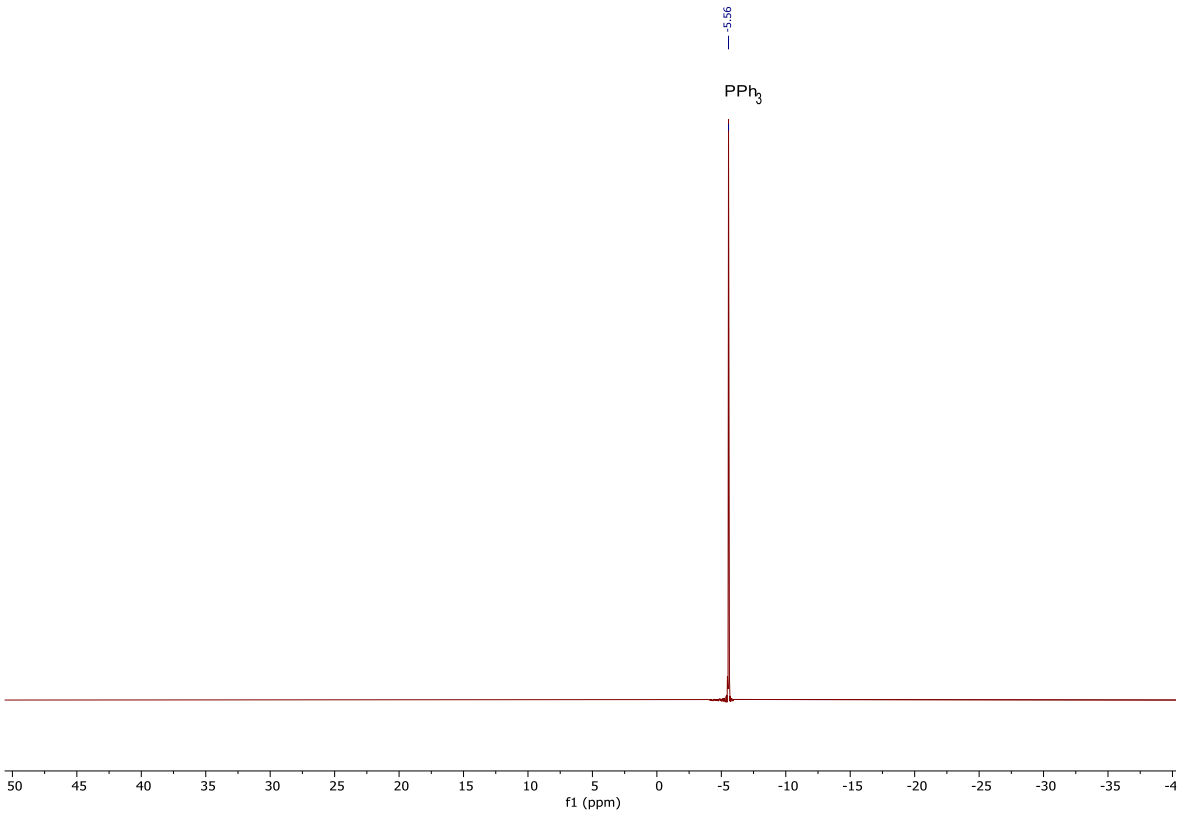


Figure S16: ^{31}P-NMR spectrum of the reaction mixture obtained according to method B.

C) Same procedure as method A, but 2-MeTHF was replaced with dichloro methane. Besides triphenyl phosphine one singlet at 23.4 ppm corresponding to a quaternary phosphonium salt could be observed. Figure S17

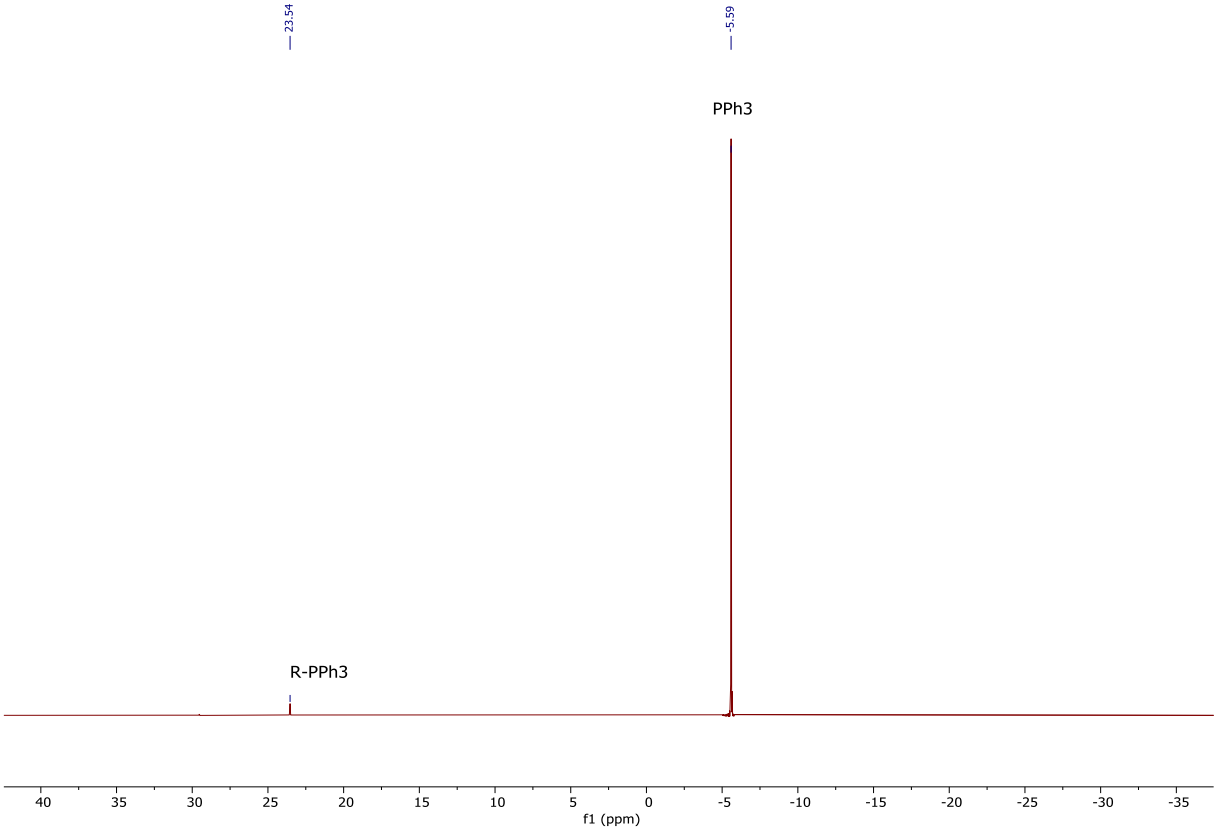


Figure S17: ^{31}P-NMR spectrum of the reaction mixture obtained according to method C.

B.7) Oxidation of the oligomer end groups

The oligomer of 2-MeTHF/PO obtained with the procedure III (Page 92) (M_n(NMR)= 1376 g mol^{-1}) was used. The oxidation of the terminal hydroxyl groups was carried out analogous to a previous published procedure.[4] First Dess-Martin-Reagent (600 mg, 1.42 mmol) was weighed in a 25 mL Schlenk tube equipped with a magentical stirrer inside a glove box. Afterwards the tube was brought outside of the glove box and kept under an argon atmosphere. Afterwards inhibitor free DCM (10 mL) was added, followed by the addition of a solution oligomer (980 mg, 0.71 mmol) in DCM (6 mL). The contents were then stirred at room-temperature for approximately 18 hours. Workup was achieved by first washing the cloudy reaction mixture with a solution of $Na_2S_2O_5$ (1.3 g, 7 mmol) in saturated $NaHCO_3$ solution (30 mL). The aqueous layer was extracted with MTBE (3x30 mL). The organic extracts were washed with water (2x20 mL) and brine (10 mL). Drying over anhydrous $MgSO_4$ and removal of the volatiles yielded the oxidized oligomer (883 mg, M_n(NMR)=1384 g mol^{-1}, 0.63 mmol, 88 %).

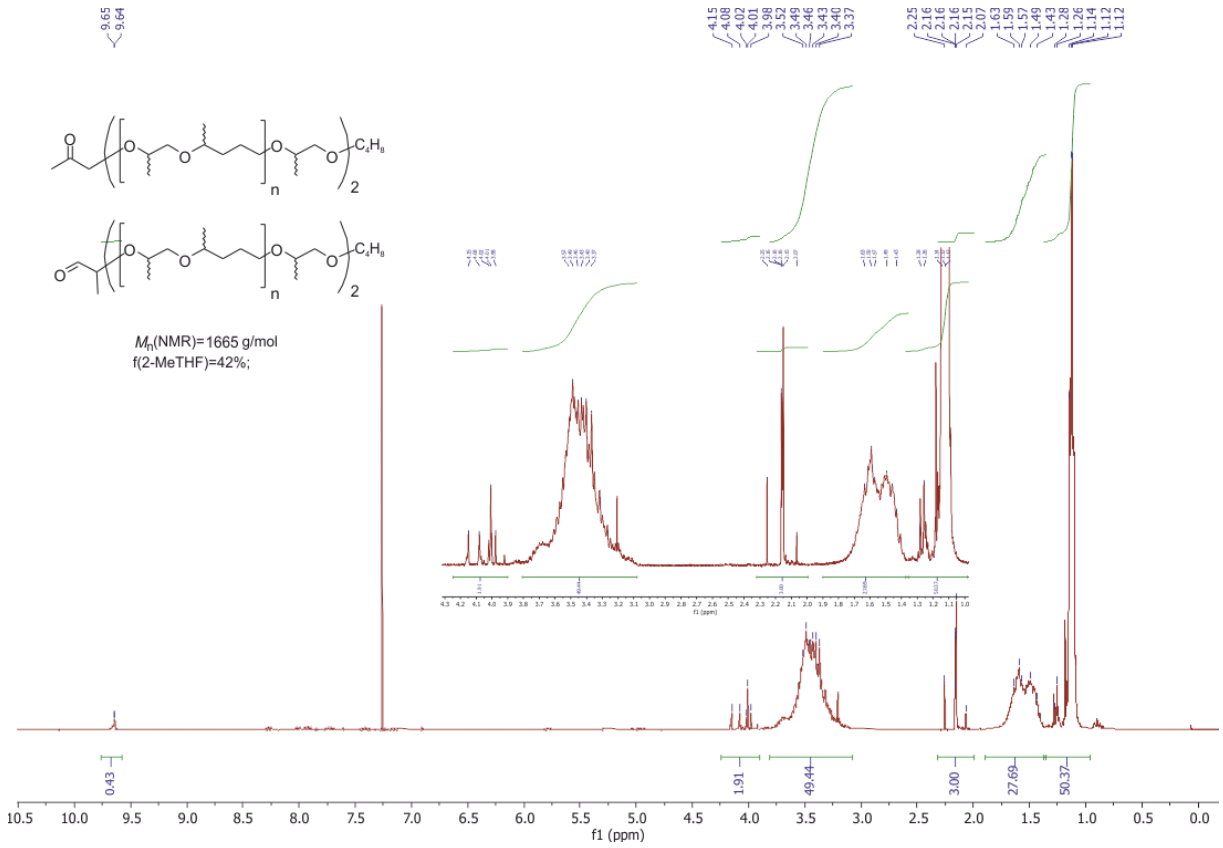


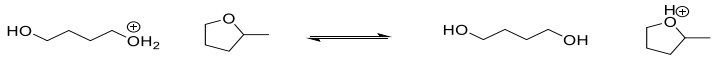
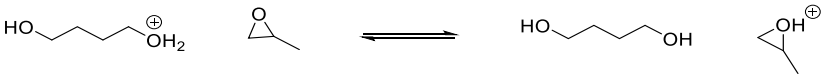
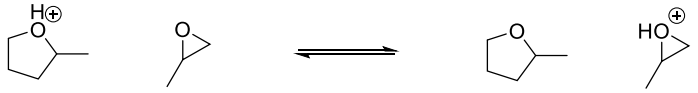
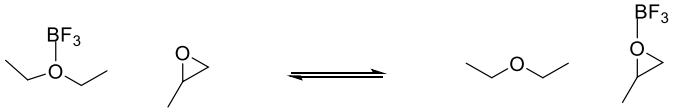
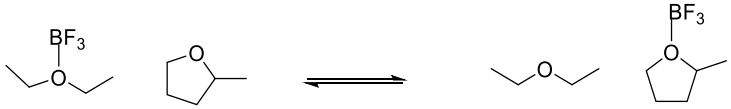
Figure S18: ^{1}H-NMR spectrum of the oligomer after reaction with Dess-Martin reagent. Signals between 4.25 and 4.0 ppm and the singlets between 2.3 and 2.1 ppm indicate termination with propylene glycol moieties. Absences of multiplets between 2.9 and 2.4 ppm indicate no 2-MeTHF derived chain ends.

As evident from the ^{1}H-NMR spectra (Figure S18) the hydroxyl groups have been converted to the corresponding aldehydes or ketone. The signals at 4.25 – 4.0 ppm are typical for the methylene groups of alkoxy aceteones.[5] Between 2.3 and 2.1 singlets can be observed that based on their integral correspond to the methyl groups of these ketones. This suggest that the oligomer is terminated with propylene glycol units. Multiplets between 2.9 and 2.4 ppm would be indicative for a *n*-propyl ethyl ketone moiety[6-8] but are absent.

B.8) Estimation of basicity of the different species

All DFT calculation were conducted using the Gaussian 09 package[9] employing the M05-2X functional and the 6-311++G(d,p) basis set. This approach has been verified to be a reliable method for the geometry optimization of protonated cyclic ethers.[10] The difference in the free energies of the different equilibria in gas phase can be found in Table S5.

Table S5: Changes in free in energy in relevant equilibria in the reaction mixture.

Entry	Equilibrium	ΔG_{298}[kcal mol^{-1}]
1		-15.2
2		-3.6
3		+11.6
4		+1.5
5		-4.2

The optimized geometries (XYZ, cartesian coordinates) and the obtained free energies can be found below:

2-MeTHF

C	-1.3595300000	-0.8324650000	-0.1816460000
O	0.0162690000	-1.1350470000	0.0705920000
C	0.7342940000	0.0598270000	0.4018840000
C	-1.5302180000	0.6640520000	0.0951600000
C	-0.1187810000	1.1905830000	-0.1616790000
C	2.1338350000	-0.0376470000	-0.1632040000
H	-1.9853340000	-1.4546300000	0.4576610000
H	-1.5781370000	-1.0706960000	-1.2245300000
H	0.7784270000	0.1478020000	1.4940640000
H	-1.8060800000	0.8305000000	1.1371660000

H	-2.2885860000	1.1196780000	-0.5383280000
H	0.0835970000	2.1472470000	0.3168240000
H	0.0677810000	1.2856560000	-1.2340470000
H	2.6470410000	-0.9069810000	0.2448080000
H	2.7073650000	0.8560860000	0.0860830000
H	2.0861720000	-0.1403900000	-1.2475190000

Sum of electronic and thermal Free Energies= -271,686

2-MeTHF+H

O	0.0318540000	-1.1197720000	-0.0229150000
C	1.4763600000	-0.7486650000	0.2357520000
C	-0.8024530000	0.1290900000	-0.4075250000
C	1.5154240000	0.7202150000	-0.1341650000
C	0.0928040000	1.2103440000	0.1520550000
C	-2.1694710000	-0.0336550000	0.1875550000
H	-0.1023610000	-1.8946130000	-0.5866790000
H	2.0875800000	-1.4049000000	-0.3747520000
H	1.6158800000	-0.9448150000	1.2926800000
H	-0.8006210000	0.1252300000	-1.4961780000
H	1.7604370000	0.8451860000	-1.1881400000
H	2.2614480000	1.2445260000	0.4578840000
H	-0.0825050000	1.3203780000	1.2229860000
H	-0.1186840000	2.1604730000	-0.3340620000
H	-2.6970220000	-0.8896230000	-0.2295600000
H	-2.7451720000	0.8612930000	-0.0530700000
H	-2.1097970000	-0.1289360000	1.2701790000

Sum of electronic and thermal Free Energies= - 272,004571

1,4-BDO

C	-1.8643900000	0.5062320000	0.0000000000
C	-0.6504540000	-0.3985700000	0.0000010000
C	0.6504540000	0.3985700000	0.0000010000
H	-0.7022250000	-1.0444880000	-0.8793250000
H	-0.7022250000	-1.0444870000	0.8793280000
C	1.8643900000	-0.5062320000	0.0000000000
H	0.7022260000	1.0444870000	0.8793270000
H	0.7022250000	1.0444880000	-0.8793250000
O	3.0236160000	0.3210610000	0.0000000000
H	1.8494520000	-1.1464470000	-0.8876050000
H	1.8494520000	-1.1464490000	0.8876030000
H	3.8047650000	-0.2326280000	-0.0000040000
O	-3.0236160000	-0.3210610000	0.0000000000
H	-1.8494520000	1.1464470000	-0.8876050000
H	-1.8494530000	1.1464480000	0.8876040000
H	-3.8047650000	0.2326270000	-0.0000040000

Sum of electronic and thermal Free Energies= -308,816236

1,4-BDO-H+

C	1.7136670000	-0.5789240000	0.0068350000
C	0.5821240000	0.4019140000	-0.0236320000
C	-0.7316290000	-0.3921390000	0.0124290000
H	0.6356540000	1.0037090000	-0.9317980000

H	0.6282460000	1.0643200000	0.8453320000
C	-1.9401420000	0.5299250000	-0.0322170000
H	-0.7947560000	-0.9900710000	0.9229860000
H	-0.7910180000	-1.0726790000	-0.8382470000
O	-3.0653360000	-0.3178720000	0.0355230000
H	-1.9320720000	1.1108250000	-0.9595070000
H	-1.9123450000	1.2230860000	0.8147140000
H	-3.8729390000	0.1947990000	-0.0289810000
O	3.0395180000	0.2358930000	-0.0583540000
H	1.7872150000	-1.1957200000	-0.8822480000
H	1.7816750000	-1.1589770000	0.9220540000
H	3.8626620000	-0.2789300000	-0.0148840000
H	3.0701000000	0.9908180000	0.5527370000

Sum of electronic and thermal Free Energies= -309,110284

PO

C	0.1507190000	-0.0456790000	0.4934220000
O	-0.8189600000	-0.7807220000	-0.2509260000
C	-1.0354260000	0.6154530000	-0.0554060000
H	-1.8661760000	0.8634130000	0.5932690000
H	-0.9291490000	1.2214130000	-0.9476180000
C	1.4992720000	0.1018080000	-0.1478830000
H	0.1450900000	-0.2800750000	1.5527640000
H	1.3835600000	0.3354320000	-1.2054210000
H	2.0657690000	-0.8248700000	-0.0584320000
H	2.0651950000	0.9009640000	0.3320480000

Sum of electronic and thermal Free Energies= -193,072106

PO+H

C	0.2262030000	0.0728240000	0.5070050000
O	-0.8616430000	-0.7389590000	-0.2571560000
C	-0.9235670000	0.7533640000	-0.0811760000
H	-1.7480020000	1.0676500000	0.5430980000
H	-0.8237810000	1.2259620000	-1.0474330000
C	1.5491630000	0.0040940000	-0.1588490000
H	0.1675180000	-0.1587410000	1.5633060000
H	1.4603780000	0.1431360000	-1.2342110000
H	2.0442650000	-0.9393290000	0.0596490000
H	2.1597640000	0.8120950000	0.2514800000
H	-1.4777960000	-1.2207970000	0.3194800000

Sum of electronic and thermal Free Energies= -193,371864

$BF3Et_2O$

C	2.3713190000	0.6765180000	0.4829950000
C	1.5386600000	0.6355810000	-0.7796580000
O	0.1201100000	0.4392310000	-0.4967710000
C	-0.5161160000	1.5740940000	0.1670370000
C	-2.0118180000	1.5227920000	-0.0334230000
B	-0.3332770000	-1.0599120000	0.0481810000
F	-0.4657470000	-0.8869950000	1.4042620000
F	-1.5021940000	-1.3204660000	-0.6001760000
F	0.7130360000	-1.8637640000	-0.3130160000
H	3.4237610000	0.7384730000	0.2062510000

H	2.1333530000	1.5418020000	1.0998060000
H	2.2169250000	-0.2316500000	1.0619570000
H	1.8121310000	-0.1994030000	-1.4132950000
H	1.5992590000	1.5601200000	-1.3512910000
H	-0.2483260000	1.5359040000	1.2202310000
H	-0.0848210000	2.4606250000	-0.2950080000
H	-2.4425930000	2.4327980000	0.3846020000
H	-2.2552340000	1.4687220000	-1.0926020000
H	-2.4470770000	0.6654340000	0.4712830000

Sum of electronic and thermal Free Energies= -558,240018

Et_2O

C	-2.3835445426	-0.3972911007	0.0000068668
C	-1.1798907524	0.5238777599	0.0000207292
O	-0.0000000749	-0.2760762714	0.0000102386
C	1.1798906429	0.5238777005	0.0000216227
C	2.3835443868	-0.3972912206	0.0000084116
H	-3.3143356890	0.1767578588	0.0000136838
H	-2.3701805700	-1.0491925064	-0.8797388752
H	-2.3701824859	-1.0492164701	0.8797348768
H	-1.1967237764	1.1585203912	0.8928336564
H	-1.1967225856	1.1585455555	-0.8927743324
H	1.1967231033	1.1585456394	-0.8927733259
H	1.1967231034	1.1585201869	0.8928346629
H	3.3143355620	0.1767576921	0.0000160558
H	2.3701816523	-1.0492168205	0.8797362405
H	2.3701810263	-1.0491923945	-0.8797375115

Sum of electronic and thermal Free Energies= -233,575743

2MeTHF+BF3

B	-1.4675920000	0.0116030000	-0.0976250000
F	-2.2199320000	-0.5824020000	0.8737700000
F	-1.3766670000	-0.7285830000	-1.2588150000
F	-1.7127850000	1.3400070000	-0.3117860000
O	0.0417360000	-0.0121270000	0.5007400000
C	1.0315250000	0.7691970000	-0.2875760000
C	2.2538040000	-0.1383100000	-0.3264910000
C	1.6592860000	-1.5439490000	-0.2470570000
C	0.5558950000	-1.3577100000	0.7760440000
C	1.2275330000	2.1075270000	0.3786390000
H	0.5901390000	0.8733710000	-1.2770690000
H	2.8352070000	0.0316710000	-1.2299290000
H	2.8894680000	0.0597280000	0.5389330000
H	2.3790120000	-2.2975550000	0.0646990000
H	1.2275150000	-1.8331510000	-1.2043600000
H	-0.2793920000	-2.0434880000	0.6876940000
H	0.9278110000	-1.3440190000	1.7979920000
H	0.2926410000	2.6613860000	0.3995450000
H	1.9674700000	2.6798950000	-0.1822640000
H	1.5903980000	1.9694270000	1.3970840000

Sum of electronic and thermal Free Energies= -596.357335

PO+BF3

B	-1.0730010000	-0.1372090000	0.0190790000
F	-2.0975330000	0.6774910000	-0.3246030000
F	-0.9982390000	-1.3285700000	-0.6356700000
F	-0.8295370000	-0.2141550000	1.3690500000
O	0.2586400000	0.6876870000	-0.5896530000
C	1.1844600000	1.4056060000	0.2672760000
C	1.6421250000	0.2196270000	-0.4641570000
C	1.8818010000	-1.0987580000	0.2030860000
H	1.4000890000	2.3966910000	-0.1023450000
H	0.9519630000	1.2993000000	1.3171770000
H	2.1580760000	0.3892410000	-1.3995680000
H	2.9485020000	-1.1802230000	0.4143910000
H	1.5906450000	-1.9135060000	-0.4559840000
H	1.3240720000	-1.1786940000	1.1319360000

Sum of electronic and thermal Free Energies= -517,733932

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6.2 Curriculum Vitae

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Date of Birth: 06.07.1989

Education

Since 01/2017	**Ph.D Studies – Dr. rer. nat.** **Leibniz Institute for Catalysis, Department: "Catalysis with renewable resources"** Studies on the conversion of bio-based platform chemicals to reactive monomers via homogenous catalysis (e.g. hydrogenation) as well as their polymerization and subsequent applicability for adhesive technologies as part of the EU Horizon 2020 project GreeSolRes funded by Bio-Based Industries Joint Undertaking in collaboration with Henkel AG & Co. KGaA Supervisor: Johannes G. de Vries
02/2015-01/2017	**Studies on Applied Chemistry – Master of Science** **Technische Hochschule Nuremberg - Georg Simon Ohm** **Specialization:** Catalysis and Organic Synthesis **Project Work:** Synthesis of novel Thiophen-2,2'-bipyridil copolymers as ligands for iron based photo catalysts **Additional Courses:** Advanced Polymer chemistry, drug development **Master Thesis: "**Ru-Catalysts for the hydrogenation of α,β-unsaturated esters to allylic alcohols" At Leibniz Institute for Catalysis, Rostock, Germany in the group of Prof. Dr. Johannes G. de Vries
10/2011 – 02/2015	**Studies on Applied Chemistry – Bachelor of Science** **Technische Hochschule Nuremberg - Georg Simon Ohm** **Focus Subjects:** Organic and inorganic chemistry, synthesis and structure determination **Additional Courses:** Physical chemistry, technical chemistry, particle technology, thermos analytics and rheology **Bachelor thesis**: „Photo Induced Oxidative Cleavage of Carbon-Boron-Bonds"

At Fudan University, Shanghai, P.R. China in the group of "Organic Photochemistry" of Prof. Dr. Hao Guo

09/2008 - 07/2011 **Vocational education as Chemical Laboratory Assistant at Nabaltec AG, Schwandorf**

09/2006 - 07/2008 **Fachoberschule Amberg – Qualification for higher education**

Professional Experience

03/2014-02/2016 **Tutor - Technische Hochschule Nürnberg**

Supervising exercises accompanying the lectures „Advanced Synthetic Chemistry" und „Basics of Organic Chemistry"

03/2013 - 07/2013 **Industrial-Praxis Semester at 3M Deutschland GmbH, Seefeld bei München**

Development of novel end group modified polyether-pre-polymers for the application in dental impression materials

08/2012-09/2012 **Working Student – Department of Environment and Wastewater of the City of Nuremberg.**

Analytics of environmental samples and industrial waste waters

02/2012-03/2012
08/2011-09/2011 **Working Student – Nabaltec AG**

Preparation and Characterization of new PP, PE, and PU-Formulations using novel mineral flame retardants

Volunteer Work

09/2013-08/2014 Member of the student's association of the Faculty of Applied Chemistry at TH Nuremberg

Scholarships & Awards

09/2014-02/2015 DAAD Scholarship „PROMOS" for the stay in the PR. China

06.10.2011 Award of the IHK-Regensburg for outstanding performance in the examination as chemical laboratory assistant

Publications

(5) Dell'Acqua, A.; Stadler, B. M.; Kirchhecker, S.; Tin, S.; de Vries, J. G., Scalable synthesis and polymerisation of a β-angelica lactone derived monomer. *Green Chem.* **2020**.

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Conference contributions

(6) Oral presentation "Catalytic reduction of esters and polyesters"
Webinar: Untying the Knots to Developing a Circular Economy From Waste Plastics
24th Annual Green Chemistry & Engineering Conference, Virtual 2020

(5) Poster "Angelica lactones. From flavoring agents to monomers for plastics"
24th Annual Green Chemistry & Engineering Conference, Virtual 2020

(4) Poster "Adhesives. Back to the Roots!"
24th Annual Green Chemistry & Engineering Conference, Virtual 2020

(3) Poster "Hydrogenation of polyesters as resource for novel polyethers"
51th Jahrestreffen Deutscher Katalytiker, Weimar, 2017

(2) Oral presentation "Hydrogenation of polyesters as resource for novel polyethers"
21th International Symposium on Homogeneous Catalysis, Amsterdam, 2018

(1) Poster "Ruthenium catalysts for the selective hydrogenation of α,β-unsaturated esters to allylic alcohols"
50th Jahrestreffen Deutscher Katalytiker, Weimar, 2017