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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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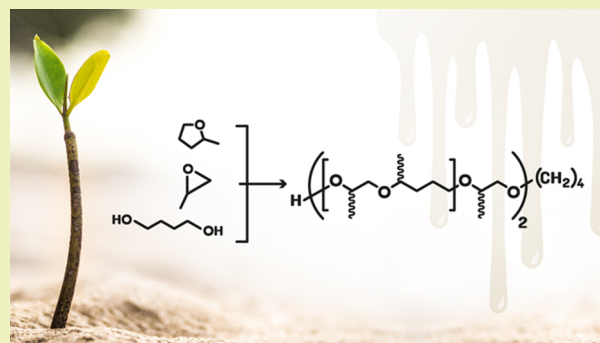
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Supporting Information

ABSTRACT: Commercial polyether polyols are usually obtained by the ring-opening polymerization of epoxides or tetrahydrofuran. 2-Methyl-tetrahydrofuran (2-MeTHF) could be an alternative bio-based building block for the synthesis of these polyols. Although 2-MeTHF cannot be polymerized, we did achieve the copolymerization of 2-MeTHF with propylene oxide (PO) using Lewis and Brønsted acids as catalysts and water or diols as initiators. 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 copolymer of 2-MeTHF and PO is produced when stoichiometric amounts of $\text{BF}_3 \cdot \text{OEt}_2$ are used. Here, the monomeric units in the chains alternate, but also cyclic or other nondiol products are formed that are detrimental to its further use in adhesives. Linear dihydroxyl-terminated polyether chains were formed when the heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 24\text{H}_2\text{O}$ was used as a catalyst and a diol as an initiator. The formation of cyclic products can be drastically reduced when the accumulation of propylene oxide during the reaction is avoided. ^1H 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 copolymer had increased tensile strength compared to polypropylene glycol in a two-component adhesive formulation.

KEYWORDS: 2-MeTHF, alternating, renewable, oligomer, adhesives



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, the use of renewable resources in their production can significantly reduce CO_2 emissions.^{1–6} Indeed, recently, bio-based polymeric materials have gained increased worldwide interest due to their wide range of applications.^{7–11} 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 an added value.³

Two important glue classes are the single- and two-component reactive adhesives.¹² 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^{13–16} and bio-based acrylic acid itself.^{17–22} In contrast, two-component adhesives require the

addition of a cross-linking agent, often containing thiols, isocyanates or, in recent research, the combination of a cyclic carbonate and a diamine.^{23–28} However, in most cases, these curable end groups need to be tethered to an oligomer, which is usually a polyester or a polyether polyol.²⁹ There is already a plethora of polyesters that can be made from platform chemicals in a manner that would allow the scale-up of these processes.^{30–38} In addition, polylactate is already commercially available. Polymerization typically occurs via the polycondensation of diols with diacids or the ring-opening polymerization (ROP) of appropriate lactones.^{32,39,40} For polyether polyols, the situation is quite different. Although innovative, alternative protocols, such as polycondensation employing acid–base pairs as catalysts^{41–43} or the reduction of polyesters,^{44–46} have

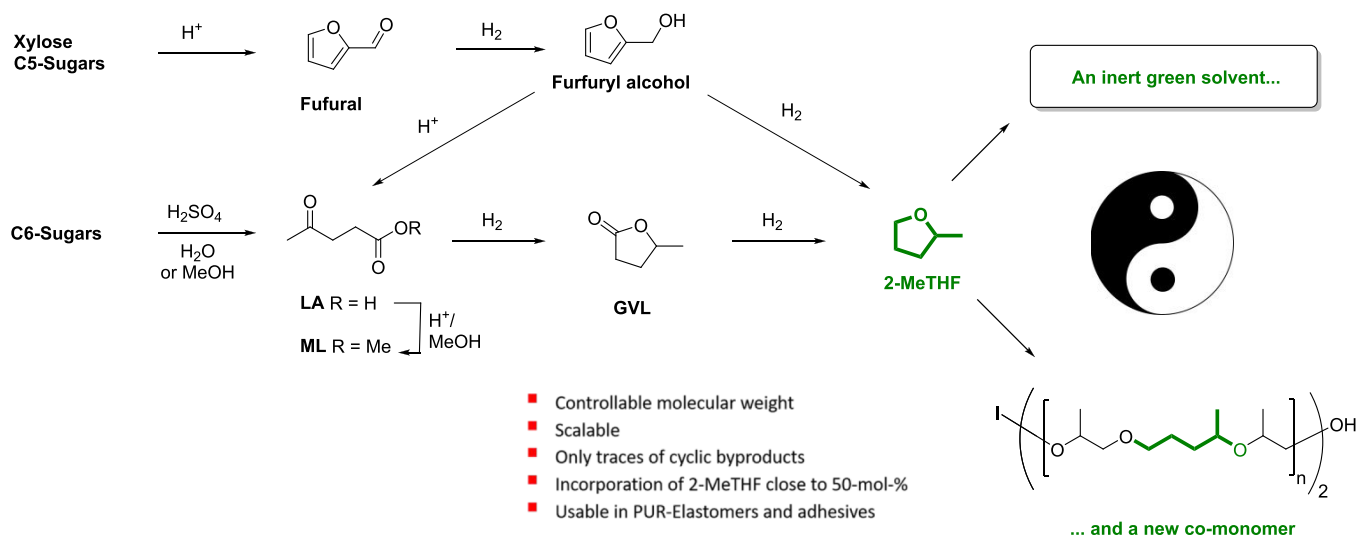
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Scheme 1. Bio-Based Origins of 2-MeTHF and Its Dual Use as a Solvent and as a Comonomer in Polyether Polyols (I = Initiator)



recently been developed for the synthesis of polyethers, their application in scalable processes is limited by harsh reaction conditions and/or the use of expensive catalysts or reductants. Hence, the commercial production of polyether polyols is still based on the ring-opening polymerization (ROP) of cyclic ethers. This is currently limited to epoxides, oxetanes, and tetrahydrofuran (THF).⁴⁷

We envisioned the use of renewable 2-methyl-tetrahydrofuran (2-MeTHF) as a sustainable monomer to expand this scope (Scheme 1).⁴⁸ 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.^{48–57} LA is readily available by acid treatment of lignocellulosic biomass at elevated temperatures.^{50,58–71} Alternatively, 2-MeTHF can also be prepared by the hydrogenation of furfural.^{72–76} Furfural can be produced from the C5 sugars in lignocellulosic biomass^{77–79} and is available on a large scale from the conversion of agricultural waste streams such as corn cobs and sugarcane bagasse or as side streams from the paper industry.⁸⁰

Recently, 2-MeTHF has attracted increasing attention as a renewable fuel^{81–83} and as a renewable substitute for the fossil-based solvent THF.^{44,49,59–61} One of the main advantages of using 2-MeTHF as a solvent over THF is its resistance toward polymerization or ring opening.^{84–86} Although this property would seem to preclude the use of 2-MeTHF in homopolymerization reactions, co-oligomers with epoxides would seem to be accessible.⁸⁷ 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 five-membered cyclic ethers.⁸⁸ Extra substituents on the ring make these even more stable; therefore, it is even more challenging to polymerize. For example, only very few reports on the polymerization of 3-MeTHF exist in the literature.^{89,90} To the best of our knowledge, the homopolymerization of 2-MeTHF is unknown. Even the catalysts that are able to polymerize 3-MeTHF fail to polymerize 2-MeTHF, which suggests an even higher thermodynamic stability when the ring is substituted in the 2-position.⁸⁸ Similar observations have been made for the analogous lactone GVL.^{91,92}

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.⁹³ Cationic ring-opening polymerization (CROP), on the other hand, is less used due to the increased formation of these side products.^{93,94}

However, THF, which is regarded as the most reactive five-membered cyclic ether derivative, is only known to be polymerized via CROP.⁹⁵ CROP is difficult to control; therefore, oligomers typically in the range of 1000–2000 g mol⁻¹ are produced.⁹⁵ Only two short communications exist, which describe the copolymerization of 2-MeTHF with epoxides⁸⁷ and with 3,3-bis(chloromethyl)oxacyclobutane,⁹⁶ 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)^{93,97,98} were not investigated at that 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 byproducts.^{99,100} A triblock copolymer was also reported, which consisted of THF, 2-MeTHF, and ethylene oxide, where up to 40% of 2-MeTHF could be incorporated.¹⁰¹ Only 30% yield was achieved in this case, and the structure of the polymer was not described.

Here, we describe our work on the copolymerization 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.

MATERIALS AND METHODS

Reagents. 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 to use and dried over molecular sieves. Propylene oxide (PO) and boron trifluorodihydrate were purchased from Sigma-Aldrich and used as received.

General Procedure for the Initial Studies of Copolymerization of Epoxides and 2-MeTHF. An Example with 10 equiv 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) and cooled to 0 °C, and BF₃·Et₂O (0.88 mL, 7.13 mmol) was added dropwise. Then, the epoxide (7.15 mmol) was added dropwise over 3 min, and the resulting contents were stirred for 90 min. Then, an aqueous solution of NaOH (1.0 M, 20 mL) was added and the contents were stirred at room temperature for 30 min. Excess 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 × 20 mL) and brine (20 mL) and dried over MgSO₄, and toluene was removed under reduced pressure. The desired product was obtained as a colorless oil after the sample was left under high vacuum for 4 h.

General Polymerization Procedure. A dry three-necked round-bottomed flask equipped with a condenser and a magnetic stirrer was subjected to three vacuum-argon cycles. After this, the flask was charged with the desired amount of phosphotungstic acid, followed by the addition of 2-MeTHF (40 mL, 0.39 mol) and the desired amount of diol. Then, PO (0.5 mL min⁻¹, total 0.87 mol) and 2-MeTHF (1.0 mL min⁻¹, total 1.18 mol) were added via HPLC pumps to the reactor over 120 min. If necessary, the reactor was equipped with an ATR-IR probe. After this, the reaction was quenched by adding water and stirred for another hour. After this, 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 (2 × 100 mL). Evaporation of the volatiles in vacuo yielded the co-oligomers as colorless viscous liquids (17–72 mol % w.r.t. PO). The results are given in Table 2 and Table S2.

Formation of Polyurethane Films. Oligomer (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 w.r.t. to polyether polyol) was added and the mixture was stirred for 1 h. Subsequently, films with 1 mm thickness were cast and allowed to cure under ambient conditions for one week.

M_n Determination by ¹H NMR. Method I. The polymer (20 mg) dissolved in CDCl₃ (400 μL) was added to an NMR tube followed by the addition of 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.

Method II. The polymer (55 mg) was dried in vacuo for 30 min and dissolved in anhydrous DCM (5.5 mL). The resulting solution was cooled to 0 °C for 20 min 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 stirred for 1 h at 0 °C; then, the ice bath was removed and the resulting solution was stirred at RT overnight. After this, the volatiles were removed under reduced pressure and the resulting solids were left to dry in vacuo for 4 h. To the remaining red solid, C₆D₆ (0.6 mL) was added, and 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 and the molecular weight were calculated.

Stress–Strain Tests. Stress–strain tests were conducted using a Z010 test system from Zwick Roell equipped with a 500 N probe head. The 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 using 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 vibration¹ (810–840 cm⁻¹) was used. Calibration was achieved by step-wise adding defined amounts of PO to 2-MeTHF.

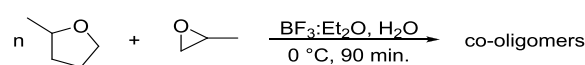
Sample Preparation for ESI-MS Measurements. Prior to the measurements, a polyether sample (500 mg) was heated in a 2 mL vial to 80 °C and kept under vacuum (0.2 × 10⁻³ bar) while being stirred for 2 h to ensure the removal of water. After this, the vial was repressurized with an argon atmosphere and 2.2 equiv phenylisocyanate with respect to the M_n value (as measured by NMR or titration) was added via a syringe. Subsequently, the contents were stirred for 3 h. After this, vacuum was applied for 30 min to remove most of the remaining excess phenyl isocyanate. The vial was repressurized and allowed to cool to room temperature. The next day a ¹H NMR spectrum acquired to ensure the full functionalization of the sample. The success of the derivatization was confirmed by the fact that the integral of the terminal CH₂–O and CH–O did not change with respect to the –CH₃ groups in the oligomer chain. Representative spectra are shown in the Supporting Information (Figures S9 and S10). In the next step, a solution of the derivatized oligomer in methanol (1 mg mL⁻¹) was prepared. To 1 mL of this solution distilled triethyl amine (100 μL) was added. The solution was then immediately transferred to a gold-coated ESI-MS-capillary and subsequently measured. The corresponding spectra are shown in the Supporting Information. Figure S11 shows the overview spectra of the measured oligomer. Figures S14–S17 show different sections of the full spectra.

RESULTS AND DISCUSSION

Copolymerization of 2-MeTHF and PO. Our initial studies were focused on the copolymerization of 2-MeTHF and propylene oxide, since routes via bio-based propylene toward PO exist and have great potential.^{21,102,103} For application in adhesives, the polyether polyols should have a molecular weight between 1000 and 4000 Da. The polymerizations, initiated by stoichiometric amounts of BF₃·OEt₂, were performed in water, taking care to maintain 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 copolymer. 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 the further incorporation of 2-MeTHF into the oligomers.

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. To understand the connectivity between the monomeric units in the oligomers, LC–MS–MS spectra were recorded. An example of the 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; 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 Supporting Information (Figures S4 and S5).

Since these results looked promising, we decided to scale up this procedure to 300 g 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

Table 1. Copolymerization of 2-MeTHF with Propylene Oxide^a


entry ^a	MeTHF [equiv] ^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

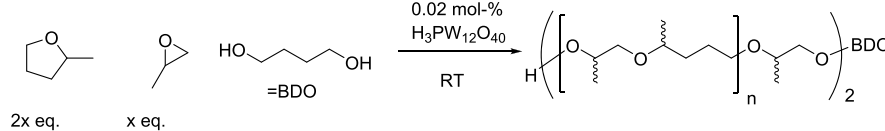
^aGeneral conditions: 2-MeTHF (n equiv w.r.t. PO), 7.15 mmol of PO, 7.15 mmol of $\text{BF}_3\cdot\text{Et}_2\text{O}$, and 7.15 mmol of H_2O . ^bDetermined by ^1H NMR after conversion of the $-\text{OH}$ end groups to $-\text{OSiMe}_3$ groups. ^cDetermined by ^1H NMR. ^dIsolated yield. ^e5 mol % of $\text{BF}_3\cdot\text{Et}_2\text{O}$ w.r.t. PO (2.57 mol); PO was added at 0.4 equiv h^{-1} in the absence of water.

dosed to the reaction and $\text{BF}_3\cdot\text{OEt}_2$ was used in a catalytic amount (Table 1, Entry 6). These modifications resulted in a significantly higher M_n without seemingly affecting the amount of 2-MeTHF incorporation.

Unfortunately, the obtained polyol was not able to cure and form solid polyurethane (PU) films when mixed with 4,4'-methylenediphenyl diisocyanate (4,4'-MDI) (See Usage of the Novel Polyether Polyol for the Preparation of Elastic Polyurethanes, Table 3, and Figure 8a). This is commonly caused by nonhydroxyl-functionalized impurities that act as a solvent for the polyurethane.

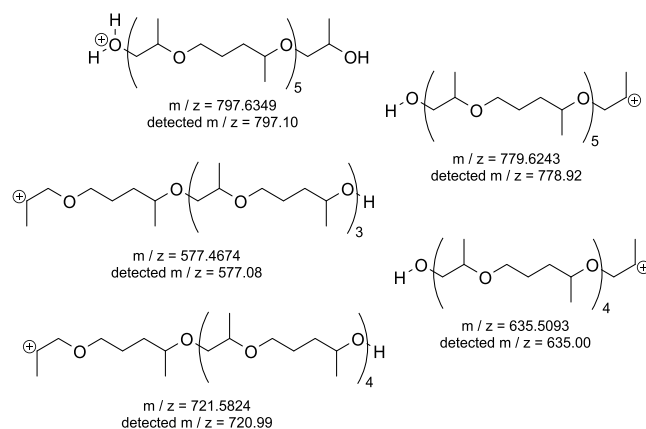
After derivatization of the end groups with trimethylsilyl chloride, it was also possible to identify ethoxylated propylene glycol, an ethoxylated trimer, and other low-molecular-weight products that could be cyclic products by GC-MS (Supporting Information, Figure S10). The presence of these impurities would be very detrimental to their use in adhesives; 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 $\text{BF}_3\cdot\text{H}_2\text{O}$. Unfortunately, when this catalyst was used (Supporting Information, Figure 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.

Table 2. PO/2-MeTHF Copolymerization Catalyzed by HPA with Diols as Initiators^a


entry	I^b	PO [equiv] ^c	$M_n(\text{th})^d$ [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 ^h	BDO	20	1446	90	0(45)	<1

^aGeneral conditions: 0.02 mol % $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ w.r.t. PO in 50 mL (490 mmol) 2-MeTHF and initiator (21 mmol) followed by the addition of 2-MeTHF and PO. Flows (Q): $Q(\text{PO}) = 0.5 \text{ cm}^3 \text{ min}^{-1}$; $Q(2\text{-MeTHF}) = 1.0 \text{ cm}^3 \text{ min}^{-1}$ Workup: filtration through silica. ^bBDO = 1,4-butanediol; PDO = 1,4-pentanediol; BDM = 1,4-benzenedimethanol. ^cEquivalents of BDO w.r.t. initiator. ^dCalculated using eqs 1–3 assuming full PO conversion. ^eMeasured with ^1H NMR (see the Supporting Information). ^fContent of 2-MeTHF in the oligomer, predicted value in brackets. ^gIsolated yields based on PO. ^hAnhydrous $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was used as the catalyst; no oligomers were formed.

**Figure 1.** Detected fragments from an MS-MS spectrum of the MH^+ peak with $m/z = 797.10$ in the range between 797.10 and 577.

These findings confirm that the polymers obtained with the boron-based Lewis acids as catalysts contain relatively large amounts of nondiol products. In addition to the ethoxylated polymers, a second detrimental impurity could be caused by the formation of cyclic oligomers. Initial MS analysis of the polyether polyols in 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 ^1H and ^{13}C NMR spectra. In the MS, the cyclic structures are indistinguishable from linear structures that tend to form cations by the loss of a secondary hydroxy group. Furthermore, coelution of both molecules is expected to occur in GPC measurements. Nevertheless, experiments described in Further Fine Tuning of the Polymerization (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.

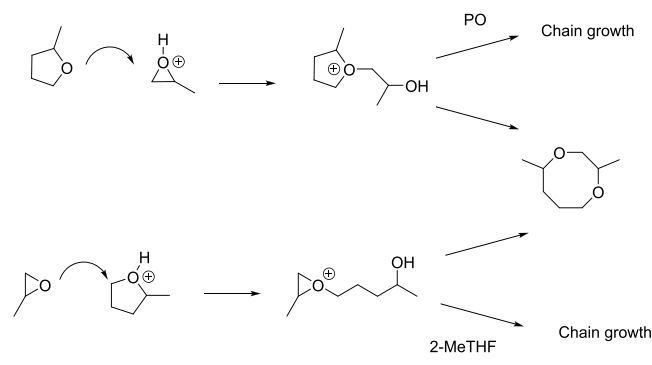
Further Fine Tuning of the Polymerization. For further optimization of the reaction conditions toward oligomers with a low cyclics content, an empirical approach can be used. It is known through investigations^{98,104–106} by the group of Penzcek that the cationic homopolymerization of epoxides can proceed via a so-called activated chain end mechanism (ACEM) and/or via an activated monomer mechanism

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 ^d [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	BF ₃ ·Et ₂ O (5)		52	2883	1100	4.8	A	n.a.	n.a.
2	BF ₃ ·2H ₂ O (1)	H ₂ O (5.0)	52(45)	1081	500	3.1	B	60	0.8
3 ^d	H ₃ PW ₁₂ O ₄₀ ·24H ₂ O (0.02)	1,4-BDO (5.0)	43(45)	1278	1200	2.0	C	600	3.0
4 ^e	H ₃ PW ₁₂ O ₄₀ ·24H ₂ O (0.02)	1,4-BDO (5.0)	43(43)	1288	1100	1.9	D	1100	3.2

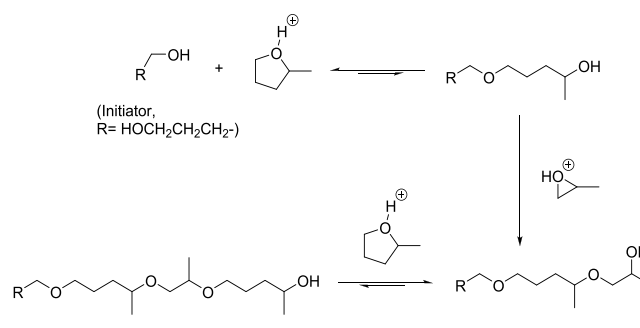
^aMeasured by ¹H NMR after derivatization of the oligomer with trifluoroacetic anhydride. GPC measurement of the oligomer. ^bĐ: polydispersity. ^cDIN S3504-SF3A-bones from 4,4'-MDI cross-linked films; ε_{max}: maximum elongation; F_{max}: ultimate strength. ^dConstant dosing rate of PO and 2-MeTHF (Figure 2b). ^eDynamic dosing rate as shown in Figure 5.

(AMM).^{72,78–80} In the activated chain end mechanism, the chain ends are oxonium ions that 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

Scheme 2. Possible Reaction Mechanism Based on ACEM, Leading to Cyclic Side Products

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 the respective comonomer, 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 comonomer, leading to the growth of the polymer chain. On the other hand, a backbiting of the oligomer chain is also possible by the 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 backbiting mechanism. Scheme 3 contains a proposed AMM for the copolymerization of 2-MeTHF and PO. The mechanism is based on the fact that homopolymerization of 2-MeTHF has never been reported and is probably impossible. Henceforth, we propose that in the case of the Brønsted acid-initiated 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

Scheme 3. Proposed AMM Which Should Lead to Linear Hydroxyl-Terminated Chains

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 (eq 1). However, it also means that when linear hydroxyl-terminated chains are desired, a 1:1 molar ratio of 2-MeTHF to PO can only be achieved at infinite chain lengths. To describe this, eq 2 can be used, which represents the fraction of 2-MeTHF units per PO unit at a given DP, assuming full PO conversion. Taking eqs 1 and 2 into account, the molecular weight (M_n) with respect to the initiator/PO ratio can be predicted via eq 3, which also takes the molecular weight of the initiator I into account.

$$DP = \frac{Xn_{PO}}{z_1n_1} \quad (1)$$

$$f_{2MeTHF} = \frac{\frac{n_{PO}}{z_1n_1} - 1}{\frac{n_{PO}}{z_1n_1}} \quad (2)$$

$$M_n = \frac{Xn_{PO}}{z_1n_1} (M_{PO} + f_{2MeTHF}M_{2MeTHF}) + M_I \quad (3)$$

where DP = degree of polymerization, X_{PO} = conversion of PO, z₁ = functionality of the initiator, n₁ = amount in moles, n_{PO} = amount of PO in moles, and M = molecular weights.

Schemes 2 and 3 suggest that the concentration of hydroxyl groups should play a crucial role in determining 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 phosphotungstic acid (HPA), a heteropoly acid that is used with good results in the cationic homopolymerization of THF.¹⁰⁷ In our case, this catalyst also appeared to be promising (see Supporting Information, Figure S1) for an initial screening). It was expected that if the selectivity of the linear polymer is high, the molecular weight calculated from eq 3 should match the observed M_n values 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 a catalyst. Comparing entries 1 and 2 in Table 2, it is easy to see that at 20 equiv of PO (w.r.t. BDO), the molecular weight obtained is close to the predicted. When more PO is dosed (40 equiv), the measured M_n deviates significantly downward, suggesting the formation of cyclic side products.

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, acts 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 an initiator, was performed with the same dosing rate, as mentioned in Table 2. Samples were taken and the M_n was determined via 1H 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 value is in correspondence with the predicted molecular weight, calculated according to eq 3, during the addition of up to 20 equiv 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 increases until 7.5 equiv 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, a continuous increase of the concentration of PO is observed. It is known from the literature on cationic homopolymerization of PO that accumulation and high concentrations can lead to unwanted side products such as cyclic oligomers.¹⁰⁸ The presence of low-molecular-weight products is also evident upon comparison of the GPC traces of the products at 20 and 40 equiv PO (Figure 2c). The molecular weight distribution resulting from the 40 equiv experiment is bimodal, showing the presence of small molecules or oligomers in the lower molecular weight fraction.

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 mentioned in 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 and oligomers with dehydrated chain ends and cyclics, phenyl isocyanate was added to convert the hydroxy groups into carbamates, and the samples were kept at 80 °C for 4 h. After the derivatization was complete, as validated by NMR

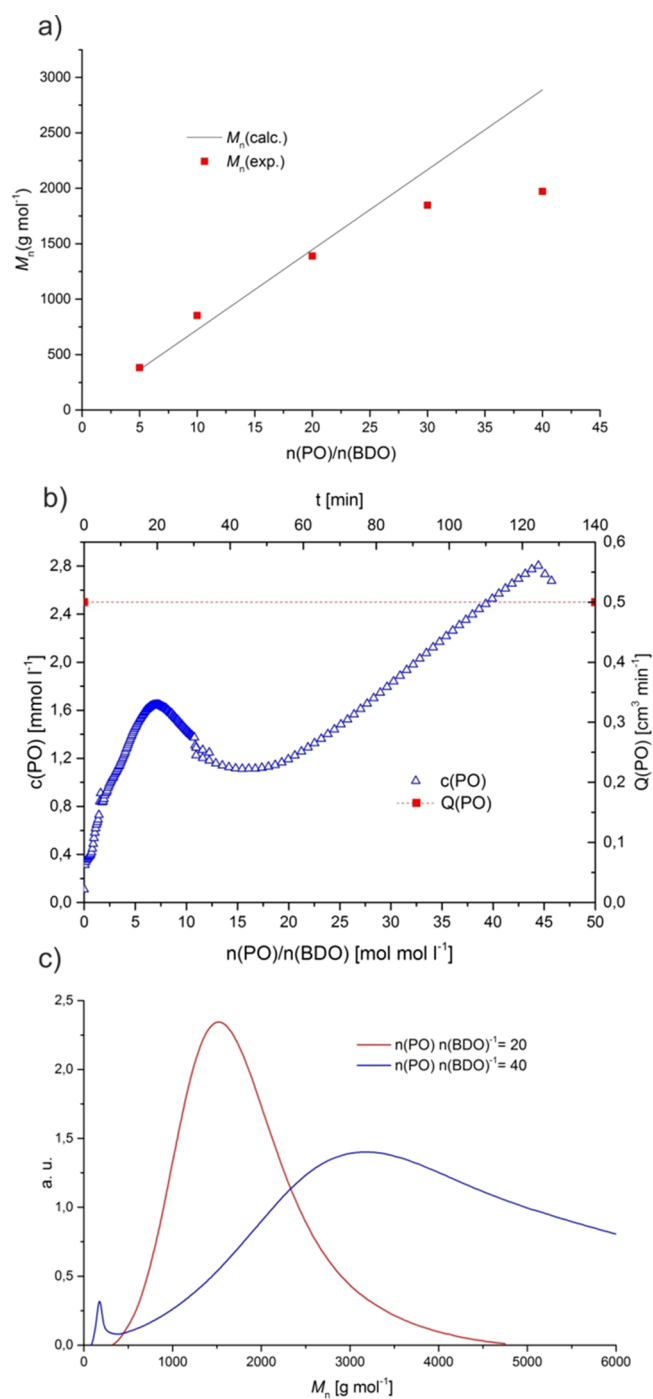


Figure 2. (a) Comparison of the measured M_n values with calculated values (eq 3) as function of equivalents of PO dosed, (b) concentration $c(PO)$ of propylene oxide in the reaction mixture as function of the amount dosed and flow $Q(PO)$ of PO. The concentration was measured by in situ ATR-IR spectroscopy.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

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.¹⁰⁸ Figure 3a shows the measured spectra of the 2-MeTHF/PO copolymer obtained with 40 equiv of PO versus initiator. It was possible to identify two cyclic oligomers as the major side products. These cyclic compounds have a 2-MeTHF/PO ratio of 2:2 or 2:3, which

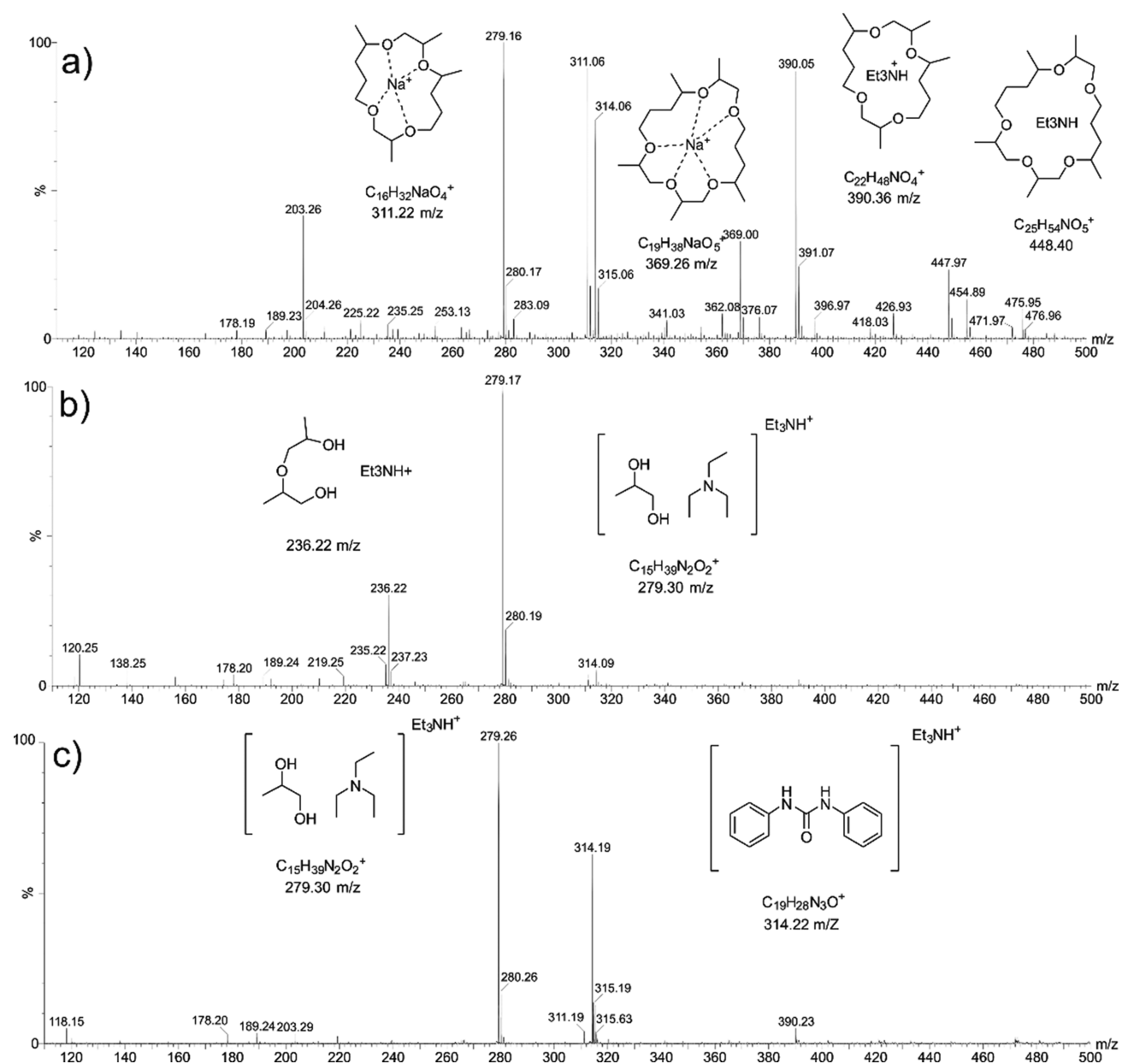
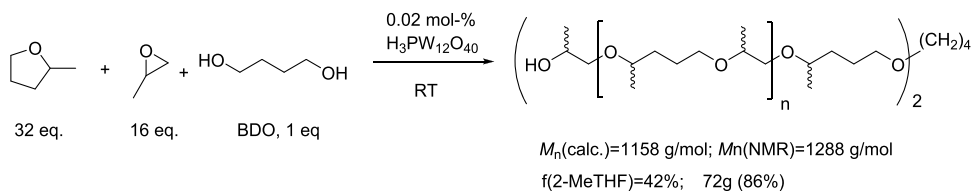


Figure 3. Comparison of the ESI-MS spectra of the low-molecular-weight fraction (100–500 m/z) of 2-MeTHF/PO co-oligomers after derivatization with phenyl isocyanate. (a) Table 2, entry 1; (b) Table 2, entry 2; and (c) obtained with the nonconstant addition rate of PO, as shown in Figure 4

Scheme 4. Result of the Copolymerization under the Dosing Conditions as Shown in Figure 5



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 the cause for the

formation of the cyclic oligomers, the rate of the PO addition was adjusted (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 Supporting Information Figure S10 for the full spectra and assignment data). Interestingly, besides the expected 1,4-

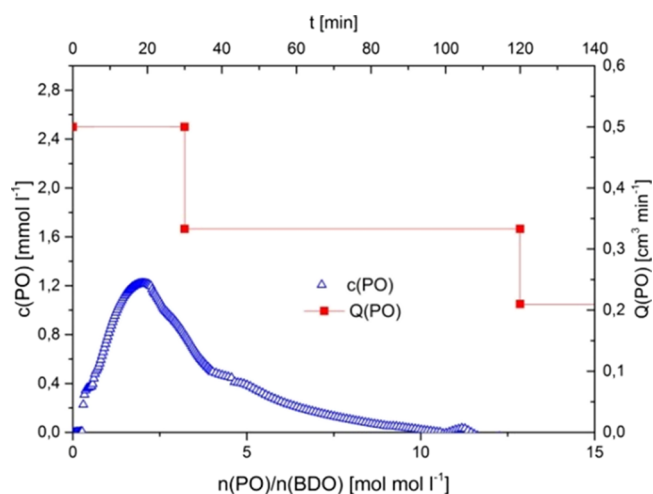


Figure 4. Effect of a nonconstant PO addition rate Q on the PO concentration during the reaction.

butanediol initiated chains, we could also find some chains which were initiated by water. Although according to ^1H 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 notable influence on the chain composition whether a chain was initiated by 1,4-BDO or by the crystal water of the heteropoly acid catalyst

Mechanistic Investigations. When the experimental molecular weights and the theoretical molecular weights are compared with each other, it seems that the polymerization follows an activated monomer mechanism (AAM) up to the addition of 20 equiv of PO w.r.t. to the initiator diol. However, monitoring of the PO concentration during the polymerization

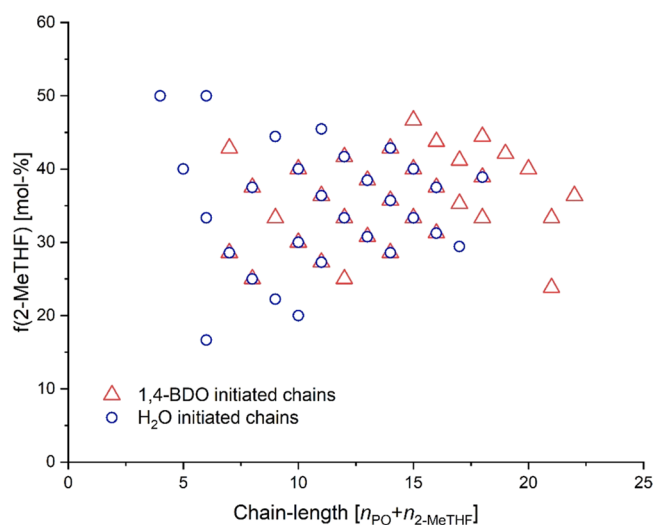


Figure 6. Incorporation of 2-MeTHF vs chain length $n(\text{PO} + 2\text{-MeTHF})$, as determined by ESI-MS

revealed that there is always a build-up in the 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 gives a difference in pK_a of 9 for the respective protonated species in the gas phase (Supporting Information, Figure S22). This functional was identified earlier by Truhlar and co-workers as a reasonable method to calculate the energies of protonated epoxides.¹⁰⁹ IR spectroscopy experiments support the order of basicity and a ΔpK_a value of 2 is observed.^{110–112} The reason for the difference is probably that the DFT calculations were carried out in the gas phase for simplification.

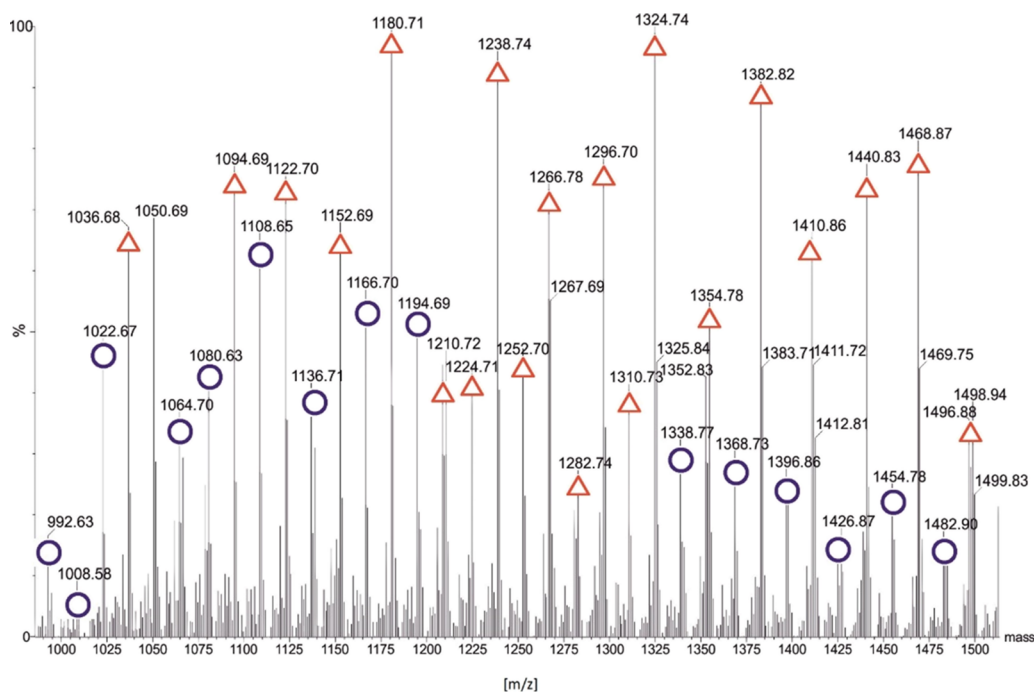


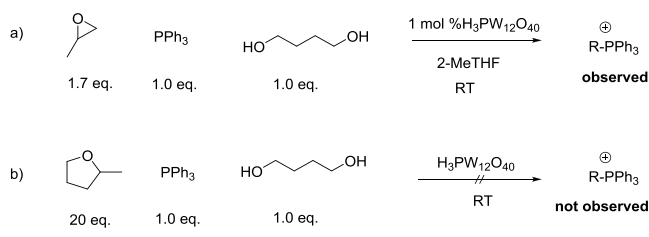
Figure 5. ESI-MS spectrum (range m/z 900–1600) of the oligomer obtained under the conditions mentioned in scheme 3; blue dots: H_2O -initiated chains; red triangles: 1,4-BDO-initiated chains

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 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.^{113,114}

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, which 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 phospho-

Scheme 5. Control Experiments To Elucidate the Propagation Mechanism



nium 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 copolymer, the reaction was repeated without 2-MeTHF, which yielded only one signal characteristic of 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, a sample of the polymer, prepared according to Table S3 (entry 3), was taken and oxidized with the Dess–Martin periodinane.

The resulting polymer was analyzed by ^1H 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 and 4.1, which can be assigned to $-\text{OCH}_2\text{COCH}_3$ (Figure 7). The fact that multiple peaks are found is related to the presence of diastereomers as well as chains of different lengths. Note that in the case of a terminal C5 unit, a triplet would be expected between δ 2.0 and 2.5 for the $-\text{CH}_2\text{CO}$ – 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 copolymerization 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.^{115,116}

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

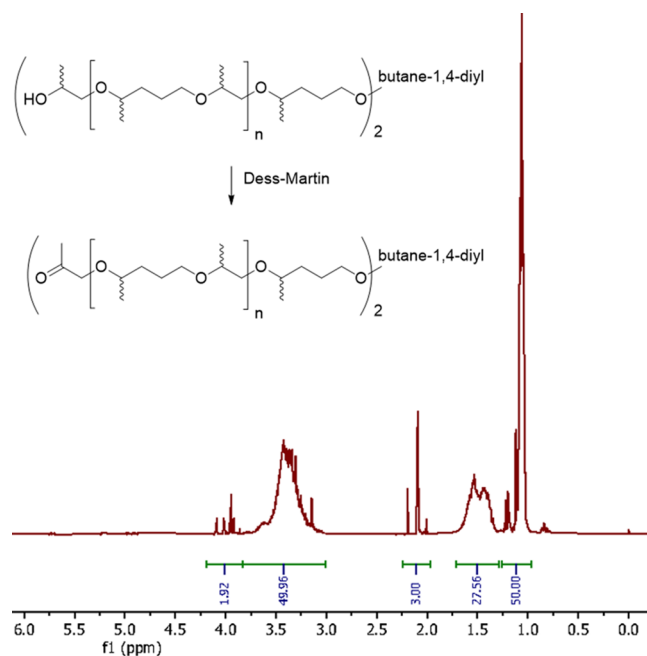
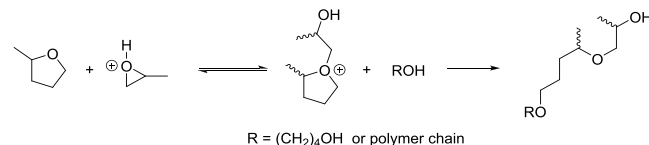


Figure 7. ^1H NMR of the oligomer after oxidation with Dess–Martin periodinane. The signals at 4.0 ppm are indicative of the $-\text{OCH}_2\text{COCH}_3$ groups.

Scheme 6. Proposed 2-MeTHF Incorporation Mechanism



“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 sufficient to create a carbocation from 2-MeTHF.

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 $\text{BF}_3\cdot\text{Et}_2\text{O}$ and a brittle material was obtained (Figure 8a). When water was used as an 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 $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ 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).

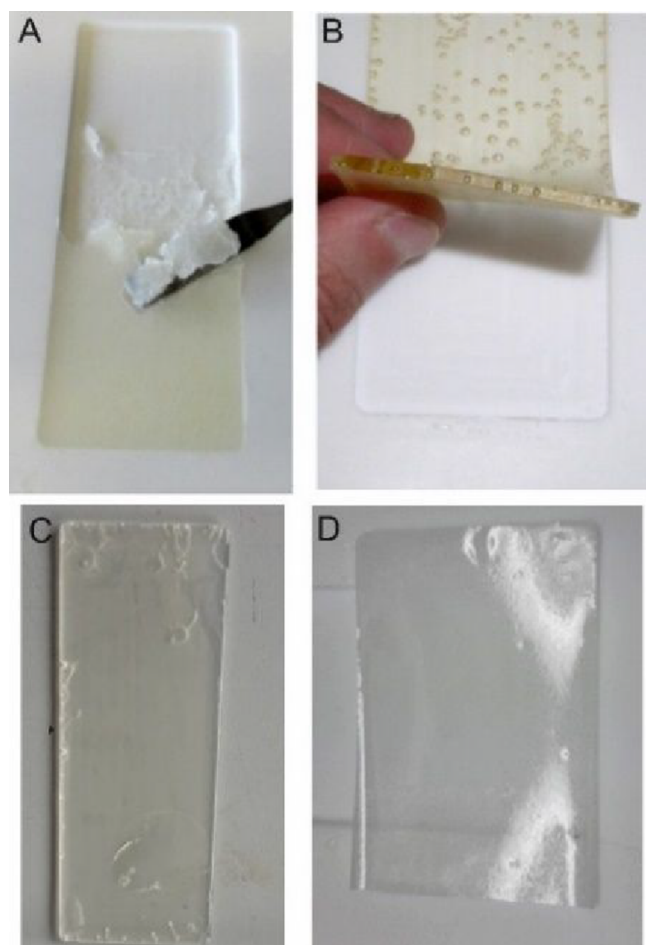


Figure 8. Films (A–D) from the different 2-MeTHF/PO copolyether polyols obtained under different conditions shown in Table 3

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).^{117,118} When the properties of the copolyether from 2-

Table 4. Comparison of Initial Strength versus Elongation for Polyurethanes Derived from 2-MeTHF/PO and PPG

ϵ [%] ^b	2-MeTHF/PO (43/57)		PPG ^a
	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)

^aIndustrial PPG sample $M_n = 1700$ g mol⁻¹. ^bElongation. ^cForce at different elongations, standard deviation ($N = 3$) in brackets.

MeTHF and PO is compared with PPG, it is evident that the incorporation of 2-MeTHF improves the tensile strength of the resulting polyurethanes.

DSC analysis showed that the glass transition temperature (T_g) of the polyurethanes prepared with the 2-MeTHF/PO co-oligomer is about 14 °C lower when compared with a poly-THF-derived polyurethane (Table 5, entries 1 and 4) but 10 °C higher than if only PPG was used (Table 5, entry 3). This suggests that the flexibility of the PO/2-MeTHF polyether chain is in between PPG and pTHF and slightly lower than the

Table 5. Glass Transition Temperatures of Polyurethanes Synthesized with 4,4-MDI and Different Polyether Polyols

entry	polyetherpolyol ^a	T_g [°C] ^b
1	2-MeTHF/PO (52/48)	-56
2	THF/PO (58/42) ^c	-50,23
3	PPG	-66
4	pTHF	-42

^aMolar ratio of copolymers in brackets. ^b T_g : glass transition temperature. ^cCured with BDO, taken from ref 119.

reported values for the copolymer of PO and THF (Table 5, entry 2).

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 that PO accumulates in the early stages of the reaction. This and NMR experiments suggest that the propagation step is best described as 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 a catalyst and a diol as an 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 cross-linking with 4,4-MDI. Tensile testing of the polyurethanes showed superior strength at elongations from 50 to 300% when compared with a PPG-based polyurethane. Additionally, when the polyether based on PO and 2-MeTHF is used, a lower T_g value compared to pTHF can be observed, which might be an advantage in formulations for applications at low temperatures where brittleness caused by a high T_g might be an issue.

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 is a valid bio-based building block for the production of polyethers for adhesives.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c04450>.

NMR spectra; ESI-MS spectra; experimental details; and procedures of DFT calculations (PDF)

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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.

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Notes

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ABBREVIATIONS

ACEM, activated chain end mechanism; AMM, activated monomer mechanism; ATR-IR, attenuated total reflection infrared; BDO, 1,4-butanediol; CROP, cationic ring-opening polymerization; DFT, density functional theory; ESI, electrospray ionization; GVL, gamma-valerolactone; HPA, heteropolyacid; LA, levulinic acid; M_n , number average molecular weight; PO, propylene oxide; PPG, poly-propylene glycol; ROP, ring-opening polymerization; SI, supporting information; T_g , glass transition temperature; THF, tetrahydrofuran

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