

Further Insights into the Catalytic Reduction of Aliphatic Polyesters to Polyethers

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The synthesis of medium- and short-chain aliphatic polyethers is industrially limited to the ring-opening polymerization of cyclic ethers with a high ring strain, such as oxiranes, oxetanes, or tetrahydrofuran. This structural limitation can be overcome by the gallium bromide catalyzed reduction of different polyesters into their corresponding polyethers. Herein, the scope of applicable polyesters is broadened, while the influence of the polyester structure on the reduction system is examined. The reactivity as well as side reactions, i.e., overreduction leading to chain cleavage, are shown to depend on the distance of the ester groups in the repeating unit of the polyester. Two different reducing agents, namely triethylsilane and 1,1,3,3-tetramethyldisiloxane, are studied and compared in terms of reactivity and work-up procedures, showing advantages and disadvantages depending on the reduced polyester properties. The reaction conditions are optimized and the reduction can be scaled-up to 60 g polyester. All products are thoroughly characterized.

pharmaceuticals,^[3] biomedical,^[4] and more. The physical properties of polyethers vary from liquids with low viscosity to soft waxes to thermoplastic materials, depending on the chemical building blocks, functionalities, and molecular weights.^[5] The main representatives are industrially synthesized by ring-opening polymerization (ROP) of epoxide monomers, such as ethylene oxide (EO), propylene oxide (PO), and less often butylene oxide (BO).^[6,7] These epoxides are readily available in industry from different oxidation methods of the respective alkenes.^[8] Nevertheless, also four- and five-membered cyclic ethers, such as tetramethylene oxide (TMO), can be polymerized via ROP.^[6,7] However, the structure of the achievable aliphatic polyethers obtained via ROP is limited to a small number of possible monomers, mainly due to the necessity of a high ring strain in the monomers.

1. Introduction

Aliphatic polyethers represent an important class of polymers that are commercially used for a broad variety of applications, such as polyurethane synthesis,^[1] surfactants,^[2]


Apart from ROP of cyclic ethers, polyethers can also be synthesized by a variety of different ways. In 1850, Williamson introduced the synthesis of ethers via nucleophilic substitution of an alkali alkoxide and an alkylating reagent, such as a haloalkane.^[9] Polyethers can be synthesized via acid-catalyzed polycondensation of glycols, which is reversible under strong acidic conditions.^[10] High molar mass poly(oxyalkylene)s with four to twelve methylene units were obtained by polyetherification at relatively low temperatures (130 °C) in Brønsted acid ionic liquids.^[11] Sardon et al. reported the self-condensation of diols in bulk, catalyzed by non-eutectic acid-base organocatalysts, such as methanesulfonic acid and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).^[12] Furthermore, polyethers were synthesized via acyclic diene metathesis (ADMET)^[13–15] of α,ω -diene ethers, or thiol-ene polymerization leading to poly(thio)ethers.^[16,17] The α,ω -diene ethers were synthesized via gallium bromide catalyzed reduction of the corresponding esters using 1,1,3,3-tetramethyldisiloxane (TMDS) as reducing agent.

The first reduction using silanes as reducing agents was described by Tsurugi et al.^[18–20] yielding ethers from the corresponding esters via reduction with trichlorosilane and γ -irradiation. First metal-catalyzed reductions of aliphatic, aromatic, linear, branched, and cyclic esters were performed in the presence of a manganese catalyst and PhSiH₃.^[21] Subsequently, several reports based on different metal catalysts, silanes, and substrates were published.^[22–27] The combination of a trivalent indium salt and hydrosilane enabled an efficient reaction

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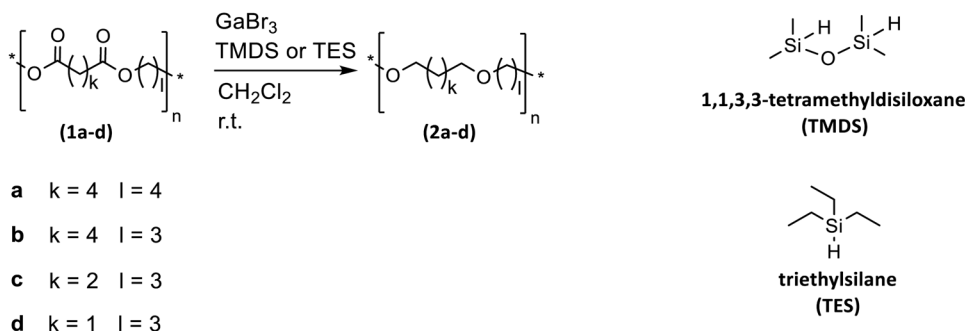
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DOI: 10.1002/macp.202200289



Scheme 1. Reduction of different short-chain polyesters to polyethers using different reducing agents.

applicable to a broad spectrum of functional groups for, e.g., the reduction of alcohols,^[28] aryl ketones^[29] and enones,^[30] the reductive aldol reaction^[31] and the deacetoxylation of propargylic acetates.^[32] Sakai and coworkers reported a detailed investigation of the influence of different indium salts, hydrosilanes, and solvents on the catalytic reduction of esters to their corresponding ethers.^[33] Biermann et al. applied the catalytic reduction of Sakai on long chain aliphatic unsaturated fatty acid esters, such as methyl oleate.^[34] Consecutively, the results were successfully transferred to high oleic sunflower oil and lactones.^[34,35] The authors reported an improved selectivity toward the desired ethers if GaBr₃ was used instead of InBr₃, because of the possible reduction of the ether to an alcohol. In a previous study of our group, the catalytic reduction was transferred to renewable polyesters synthesized via polycondensation of biobased monomers or ROP of lactones to obtain renewable medium- and long-chain aliphatic polyethers.^[36]

In this work, we broaden the scope of applicable polyesters and examine the gallium bromide catalyzed reduction of polyesters more in detail. Moreover, different reducing agents are compared regarding their reactivity and work-up procedures, while the reaction conditions are optimized for scale-up reactions on a multi-gram scale.

2. Results and Discussion

The gallium bromide catalyzed reduction of four different polyesters, obtained from short-chain dicarboxylic acids and diols, was investigated (**Scheme 1**). Noteworthy, polyesters obtained from short-chain dicarboxylic acids and diols showed the most significant degradation due to overreduction in a previous study and the polyesters investigated herein were not investigated before.^[36] The influence of the polyester structure and two different reducing agents, 1,1,3,3-tetramethyldisiloxane (TMDS) and triethylsilane (TES), on the described reaction system was examined (**Scheme 1**). Finally, the reaction conditions were adjusted for possible scale-up reactions.

The reduction of the respective polyester was followed by IR and ¹H-NMR spectroscopy and the obtained polyethers were fully characterized (IR, ¹H-, ¹³C-NMR, SEC-ESI). The analysis is exemplarily shown for polyether **2b**. The successful reduction of the ester groups was indicated in the proton NMR spectrum by the shift of the signal assigned to the CH₂ group adjacent to the carboxylic group with a chemical shift of 2.35 to 1.55 ppm

(**Figure 1**, signals 1 and 1'). Moreover, the chemical shift of the signal assigned to the CH₂ group adjacent to the ester oxygen (signal 3) was shifted from 4.15 to 3.45 ppm, while a new signal appeared at 3.35 ppm as a result of the reduction of the carbonyl group into a CH₂ group (signal 8'). The successful reduction was further evidenced by the vanishing C=O-vibration with a wavenumber of 1720 cm⁻¹, besides an increasing C–O–C-vibration at 1107 cm⁻¹ for the ether groups in the corresponding IR spectrum (**Figure 1**). Furthermore, representative masses of the desired polyether oligomers were found in the mass spectrum of the ESI coupled SEC, whereas the difference of *m/z* for the different oligomers corresponded the mass of the repeating unit of **2b** (**Figure 2**). Two different mass distributions were observed for polyether **2b**, having either two C4 end groups, or one C4 and one C6 end group. Finally, the high-resolution mass analysis of an exemplarily chosen **2b** octamer underlined the formation of the desired polyether, since the measured exact mass, as well as the isotopic pattern, were identical with the calculated ones (**Figure 2**). Polyethers **2b–d** were analyzed in the same way as shown in supporting information.

The influence of the polyester structure on the reduction process was investigated using 2.20 eq. of TMDS and 5 mol% GaBr₃ per repeating unit. Polyester **1a**, obtained from adipic acid (AA) and 1,4-butanediol (BD), was less reactive than polyester **1b**, which was synthesized from AA and 1,3-propanediol (PD), as quantitative conversion of **1b** was observed after 24 h, while only 70% of **1a** was converted after 48 h. The conversion was determined via proton NMR spectroscopy by comparing signals 1 and 1' as shown in **Figure 1**. Polyester **1c** showed a similar reactivity compared to **1b**. Thus, the difference between the C4 and C6 dicarboxylic acids had no significant influence on the reaction rate. The highest reactivity was observed for polyester **1d**, whereby almost quantitative conversion was obtained after four hours, as determined by IR spectroscopy. Consequently, the difference between C3 and C4 dicarboxylic acid influenced the reduction, which is in accordance with the previous observations of the C4 and C3 diol in polyester **1a** and **1b**.

The reaction conditions using TMDS as reducing agent were varied for polyesters **1a–d** in order to establish more suitable conditions for a possible scale-up reaction. First, the concentration was increased from 20 mg polyester mL⁻¹ in DCM to 50 mg mL⁻¹ using 5 mol% GaBr₃ and 2.20 eq. TMDS per repeating unit. After 2 h, almost quantitative conversion on a 500 mg scale for polyester **1b** was determined via IR spectroscopy, while 24 h were

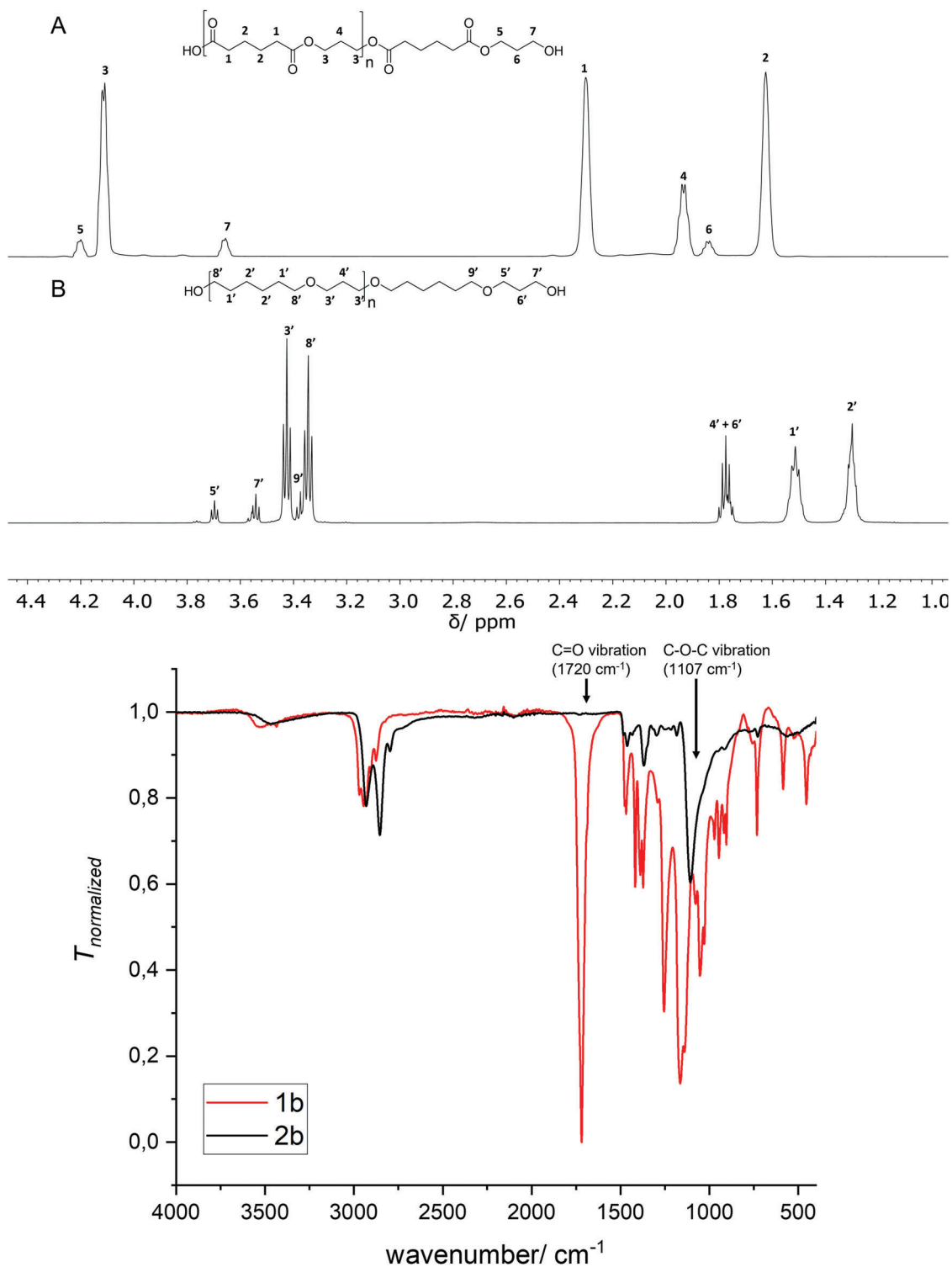


Figure 1. Top: $^1\text{H-NMR}$ analysis of A) polyester 1b and B) polyether 2b measured in CDCl_3 . Bottom: ATR-IR spectra recorded in transmission of polyester 1b (red) and polyether 2b (black). The integrals of polyether 2b are depicted in the supporting information.

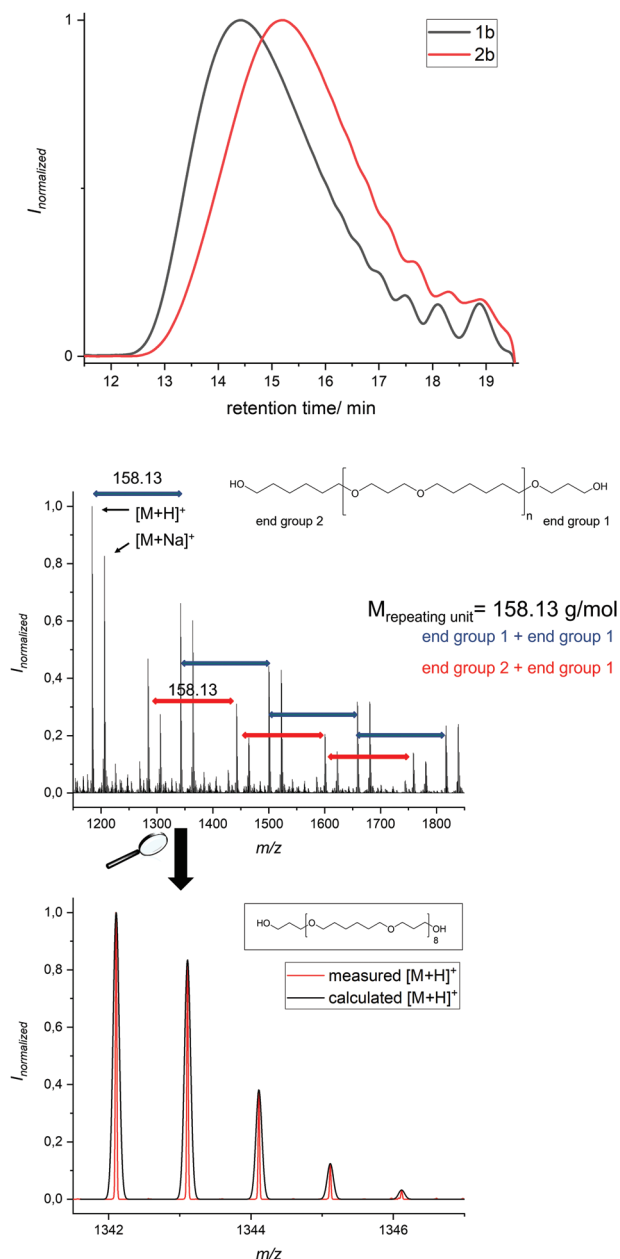


Figure 2. SEC-ESI measurement of polyester **1b** (black) and polyether **2b** (red) with corresponding ESI spectra of polyether **2b** at a retention time of 16.5 min and high-resolution MS data for an exemplary chosen oligomer.

necessary in 20 mg mL^{-1} for the same results. When the catalyst loading was decreased to 1 mol%, even after five days of reaction time, only 85% of polyester **1b** was converted, as determined via proton NMR spectroscopy. Hence, a higher catalyst loading seemed to be necessary, whereby an almost quantitative conversion of **1b** was obtained for 2 mol% after 6 h. A possible reason for this strong difference in reactivity is the hydrolysis of the gallium bromide, leading to a higher relative amount of catalyst deactivation if only 1 mol% catalyst is used.

The reaction conditions of 2.20 eq. TMSD and 2 mol% GaBr₃ per repeating unit as well as $50 \text{ mg polyester mL}^{-1}$ in DCM

Table 1. Scale-up reactions of polyester **1a–d** with TMSD.

Entry	Polyester	X_n polyester (NMR)	Conversion (NMR) [%]	T	X_n polyether (NMR) ¹	Yield [%]
1	1a	5.1	>99	9 d	2.5	22
2	1a	5.1	>98	7 d	3.3	42
3	1b	10.5	>99	18 h	10.0	72
4	1b	10.5	>99	18 h	10.0	54
5	1c	13.3	>99	4 d	6.3	97
6	1d	13.3	>99	18 h	1.6	51

Conditions: 40.0 g polyester, 50 mg mL^{-1} , 2 mol% GaBr₃, 2.20 eq. TMSD; ¹After work-up

were then applied on a 40 g scale for polyesters **1a–d** as summarized in **Table 1**. For polyester **1a**, after 64 h, neither full conversion nor any further increase of the conversion was observed and hence, 0.1 mol% additional catalyst was added. The reaction was stopped after seven and nine days, respectively, then showing > 99% conversion of the ester groups (Table 1, Entries 1+2). For polyester **1b**, quantitative conversion was obtained after 18 h, while 96% polyester **1c** was converted after this reaction time (Table 1, Entries 3+4). Therefore, the reaction was further stirred over a weekend to achieve full conversion (Table 1, Entry 5). In general, quantitative conversion was aimed for and thus, these long reaction times were necessary on a laboratory scale. The scale-up reaction of polyester **1d** showed full conversion after 18 h (Table 1, Entry 6). For polyethers **2a** and **2c**, a triplet with a typical chemical shift of a methyl group at 0.9 ppm was observed in the proton NMR spectrum. This indicates a possible overreduction of the ether to the corresponding alcohol and an alkyl end group, which is a known side reaction of this system.^[36] For polyether **2b**, no triplet was observed, indicating no overreduction for this structure under the applied reaction conditions, while polyether **2d** showed a high amount of methyl groups per repeating unit, according to the proton NMR. This observation is further strengthened by the degree of polymerization, which was determined via ¹H-NMR spectroscopy after work-up as summarized in Table 1. Moreover, the SEC traces after work-up further underlined the strong degradation accompanied by the overreduction for polyethers **2d** and **2a** according to **Figure 3**. Thus, the reduction of the ether to an alcohol, accompanied by a cleavage of the polymer backbone, depended on the polymer structure. Hereby, no clear tendency for the different polyester monomers were observed, but the limits of this reduction seem to be reached for polyester **1d**, which was synthesized from malonic acid and 1,3-propanediol.

The major challenge of this reaction system was the separation of the polyethers from the byproduct, poly(dimethylsiloxane) PDMS, since the obtained polyethers were highly viscous liquids due to their low molecular weights and hence, precipitation was not possible. Therefore, the polyethers were dissolved in a mixture of methanol and water to then extract PDMS with petroleum ether. However, Table 1 clearly shows that this work-up procedure suffers from reproducibility besides overall poor yields for polyester **1a**. A reason for this is the rather good solubility of the polyether **2a** in petroleum ether and the resulting poor phase separation. In general, moderate yields for polyethers **2b** and **2d**

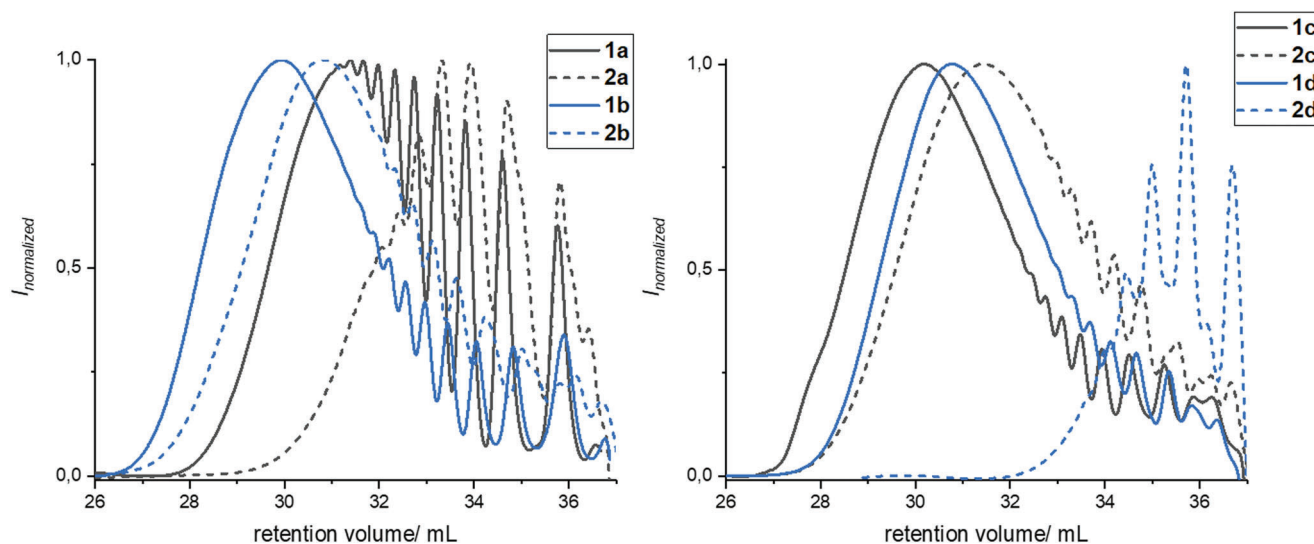


Figure 3. SEC traces of polyesters 1a–d and polyethers 2a–d according to Table 1 after work-up, measured in THF.

besides almost quantitative yields for polyether **2c** were obtained by this procedure. Within this context, it has to be mentioned that the analysis after the work-up procedure has to be treated with some caution, since the polyethers were fractionated during purification, except of polyether **2c** (Table 1).

Thus, a different reducing agent, triethylsilane (TES), was investigated to address the problems during the work-up procedure, since TES dimerizes to hexaethyldisiloxane (HEDS) instead of polymerizing to PDMS. Therefore, the byproduct could be removed through distillation at 130 °C under reduced pressure, leading to higher yields and better reproducibility. Under these conditions, also polyethers with lower molecular weights were removed during the distillation. On a 500 mg scale, HEDS and unreacted TES were quantitatively removed, while for larger scale reactions some siloxane remained in the final polyether after the distillation.

The influence of TES instead of TMDS on the gallium bromide catalyzed reduction of polyester **1a–d** thus had to be studied. For all polyesters **1a–d**, the reaction rate for TES was lower compared to TMDS. For instance, after 4 h full conversion was obtained for polyester **1a** with TMDS, while only 90% of **1a** was converted for TES under the same reaction conditions, determined via ¹H-NMR spectroscopy. Polyester **1b** showed full conversion already after one hour on a 500 mg scale under these reaction conditions, as determined by proton NMR spectroscopy. For the TES approach, 97% of polyester **1b** was converted after 24 h for the same reaction conditions. Polyester **1c** showed the same trend in reactivity. For polyester **1d**, a lower concentration and catalyst loading was applied due to the high reaction rate. Hereby, **1d** was fully converted after 4 h with TMDS, while almost full conversion was observed for TES after 66 h for the same reaction conditions. However, still strong degradation of polyether **2d** was detected in the proton NMR spectrum and thus, polyether **1d** was not suitable for this reaction system either. Polyester **1c** showed the same trend in reactivity, while similar X_n for both reducing agents were determined via ¹H-NMR spectroscopy. Since for polyester **1c** no significant decrease in the side reaction for TES was observed and quantitative yields were obtained by the

Table 2. Scale-up reactions of polyester **1a** with TES.

Entry	Scale [g]	t [d]	X_n polyester 1a (NMR)	Conversion (NMR) [%]	X_n (NMR)	mol% ¹ HEDS (NMR)
1	50	4	5.1	>99	3.8	14
2	60	5	5.1	>99	3.5	19

Conditions: 2 mol% GaBr₃, 125 mg mL⁻¹, 4.40 eq. TES; ¹ per polyether repeating unit

scale-up with, TES was not further investigated as reducing agent for polyester **1c**. For polyester **1b**, no degradation besides moderate yields for the scale-up with TMDS were observed, while the reaction rate was significantly higher compared to TES. Therefore, the reaction conditions for TES were further optimized in terms of possible scale-up reactions only for polyester **1a**.

Thus, the concentration of **1a** was increased from 50 up to 125 mg mL⁻¹, showing a steady increase of the reaction rate, while full conversion was obtained after 4.5 h instead of 19 h. Moreover, the obtained SEC traces after work-up were both similar, indicating little to no degradation. This observation was strengthened through similar X_n observed by ¹H-NMR spectroscopy. The catalyst loading was decreased to 0.5 mol% showing only 50% conversion of polyester **1a** after 96 h. Thus, again 2 mol% were necessary, whereby almost full conversion was observed after 96 h, determined via proton NMR spectroscopy. Subsequently, scale-up reactions of 50 and 60 g polyester **1a** were successfully conducted, showing full conversion of the ester groups after four and five days, respectively, determined via proton NMR spectroscopy (Table 2). However, as already mentioned above, the removal of the byproduct was difficult in larger scales (Table 2). This problem could be solved on lab scale by several distillations on smaller scales and re-combination afterward. The X_n indicated a small amount of side reactions leading to degradation of the polymeric backbone, while the SEC traces showed a slight shift toward lower retention times, implying a higher observed molecular weight (Figure 4). Since the molar mass of the repeating unit decreases during this reaction, a possible explanation is

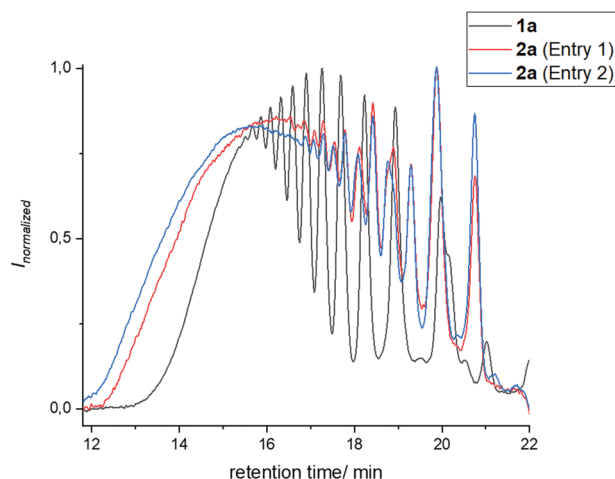


Figure 4. SEC traces of the scale up reactions of polyester **1a** with TES according to Table 2, measured in THF.

the increase of the hydrodynamic radius of the polyether compared to the polyester precursor in THF. This assumption is in accordance with the results obtained described in previous work.^[36]

3. Conclusion

In conclusion, all polyesters **1a–d** were successfully reduced to their corresponding polyethers **2a–d** using two different reducing agents, TES and TMDS, catalyzed by GaBr₃. A scale-up reaction of up to 40 and 60 g polyester was conducted for TMDS and TES, respectively, and all polyethers were fully analyzed via NMR-, IR-, and SEC-ESI analysis. We observed that the lower the distance between the ester groups in the repeating unit of the polyesters, the higher the reactivity for the gallium bromide catalyzed reduction. Polyester **1c** showed a similar reactivity compared to **1b**, indicating that the difference between the C4 and C6 dicarboxylic acids had however no further influence on the reaction. In general, TES showed a lower reactivity compared to TMDS, while no clear influence on the side reaction was observed for both reagents. Especially for polyethers with low molecular weights, for which a precipitation was not feasible, TES was a promising alternative reducing agent due to the possible removal by distillation, leading to almost quantitative yields. Further understanding of this reaction system thus revealed advantages and disadvantages of different polyester structures and reducing agents as well as the boundaries of this reduction protocol.

4. Experimental Section

Materials: Polyester **1a–d** were obtained from BASF SE. All other reagents and solvents were used as received without further purification: 1,1,3,3-tetramethyldisiloxane (97%, Sigma–Aldrich), chloroform-d (99.8 atom% D, Eurisotop), dichloromethane anhydrous (>99.8%, Sigma–Aldrich), gallium(III) bromide (99.999%, Sigma–Aldrich), hydrochloric acid (37%, VWR), methanol (>99.8%, VWR), petroleum ether (>90% Sigma–Aldrich), triethylsilane (99%, Sigma–Aldrich).

General Procedure for the Reduction of Polyester 1a–d with TMDS: The respective polyester was placed, under inert conditions, in a Schlenk-Flask and dissolved in dry DCM. Afterward, GaBr₃ was added and the mixture was stirred at room temperature. Then, 1,1,3,3-tetramethyldisiloxane

(TMDS) was added dropwise within one hour via syringe pump and stirred at room temperature. After full conversion, the crude product was washed with diluted hydrochloric acid (5%) and water, dried over Na₂SO₄, and concentrated under reduced pressure. The crude mixture was dissolved in a mixture of methanol and water (ratio 10:1) and extracted with petroleum ether (5×) to remove polysiloxane. The methanolic layer was concentrated in vacuo, the residue was again dissolved in a mixture of methanol and water (ratio 10:1, 25% v/v as before) and extracted again with petroleum ether (5×, 25% v/v as before). The methanolic layer was dried over Na₂SO₄ and after filtration the solvent was removed in vacuo.

General Procedure for the Reduction of Aliphatic Polyester with TES: The respective polyester was placed, under inert conditions, in a Schlenk-Flask and dissolved in dry DCM. Afterward, GaBr₃ was added and the mixture was stirred at room temperature. Then, triethylsilane (TES) was added dropwise within one hour via syringe pump and stirred at room temperature. After full conversion, the crude product was washed with diluted hydrochloric acid (5%) and water, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was distilled under reduced pressure (1 mbar) at 130 °C.

Nuclear Magnetic Resonance Spectroscopy (NMR): ¹H-NMR and ¹³C-NMR spectra were recorded on Bruker Avance DRX (500 MHz for ¹H- and 126 MHz for ¹³C-NMR) or Bruker Ascend 400 (400 MHz for ¹H- and 101 MHz for ¹³C-NMR) spectrometer at ambient temperature. The chemical shifts for ¹H-NMR and ¹³C-NMR spectra were reported in ppm relative to the solvent signal DMSO-d₅ (¹H-NMR: 2.50 ppm; ¹³C-NMR: 39.52 ppm) or CHCl₃ (¹H-NMR: 7.26 ppm; ¹³C-NMR: 77.16 ppm). Data for ¹H-NMR were reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, b = broad) and assignment. Furthermore, correlated spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond correlation (HMBC) were carried out to determine the structures.

Size Exclusion Chromatography (SEC): For SEC, two different systems were used:

A PSS SECcurity² GPC system based on Agilent infinity 1260 II hardware. The system was equipped with a refractive index detector SECcurity² RI, a column oven “(Bio)SECcurity² column compartment TCC6500”, a “standard SECcurity²” autosampler, isocratic pump “SECcurity² isocratic pump”. THF (flow rate 1 mL min⁻¹) at 30 °C was used as mobile phase. The analysis was performed using the following column system: Two columns PSS SDV analytical (3 μm, 300 × 8.0 mm², 1000 Å) with a PSS SDV analytical precolumn (3 μm, 50 × 8.0 mm²). For the calibration, narrow linear poly(methyl methacrylate) standards (Polymer Standards Service, PSS, Germany) ranging from 102 to 62200 Da were used.

Size exclusion chromatography (SEC) was performed on an Agilent 1200 system, comprising an auto-sampler, a PLgel 5 μm bead-size guard column (50 × 7.5 mm²), one PLgel 5 μm Mixed-E column (300 × 7.5 mm²), three PLgel 5 μm Mixed C columns (300 × 7.5 mm²) and a differential refractive index detector as well as a UV detector using THF as eluent at 35 °C with a flow rate of 1 mL min⁻¹. The SEC system was calibrated using linear poly(styrene) standards ranging from 370 to 6 × 10⁶ g mol⁻¹ or poly(methyl methacrylate) standards ranging from 800 to 2.2 × 10⁶ g mol⁻¹. All SEC calculations were carried out relative to poly(methyl methacrylate) calibration.

Infrared Spectroscopy (IR): Infrared spectra were recorded using a Bruker Alpha-p instrument with ATR technology in a range of ν = 400–4000 cm⁻¹ with 12 scans per measurement at room temperature.

Size Exclusion Chromatography–Electrospray Ionization Mass Spectrometry (SEC–ESI): Size exclusion chromatography-electrospray ionization mass spectrometry (SEC-ESI MS) spectra were recorded on an LTQ Orbitrap XL Q Exactive mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the m/z range 74–1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 4.6 kV, a dimensionless sheath gas of 8, and a dimensionless auxiliary gas flow rate of 2 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0 V, respectively. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD),

autosampler (WPS 3000TSL), and a thermostated column department (TCC 3000SD). Separation was performed on two mixed bed size exclusion chromatography columns (Polymer Laboratories, Mesopore 250 × 4.6 mm², particle diameter 3 μm) with precolumn (Mesopore 50 × 4.6 mm²) operating at 30 °C. THF at a flow rate of 0.30 mL min⁻¹ was used as eluent. The mass spectrometer was coupled to the column in parallel to (a UV-Detector (VWD 3400 RS), and) a RI detector (RefractoMax520, ERC, Japan) in a setup described earlier.^[37] 0.27 mL min⁻¹ of the eluent were directed through the RI-detector and 30 μL min⁻¹ infused into the electrospray source after postcolumn addition of a 100 μM solution of sodium iodide in methanol at 20 μL min⁻¹ by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 50 μL aliquot of a polymer solution with a concentration of 2 mg mL⁻¹ was injected onto the HPLC system.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank BASF SE for financial support.
Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

gallium(III)bromide, polyesters, polyethers, reduction, scale-up, tetramethylsiloxane, triethylsilane

Received: August 8, 2022

Revised: August 31, 2022

Published online:

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