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Renewable polyethers via GaBr₃ catalyzed reduction of polyesters

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Abstract: Herein, we demonstrate a novel approach for the synthesis of middle and long chain aliphatic polyethers **2** by applying the GaBr₃-catalyzed reduction with TMDS as reducing agent to polyesters **1**. Thus, various linear and branched aliphatic polyesters **1** were prepared and systematically investigated for this reduction strategy, demonstrating the applicability and versatility of this new polyether synthesis protocol. Middle and long methylene chain polyethers were obtained from the respective polyesters without or with minor chain degradation, whereas short chain polyesters, such as poly-L-lactide **1i** and poly[(*R*)-3-hydroxybutanoate] **1j**, showed major chain degradation. In this way, yet unavailable and uncommon polyethers were obtained and studied.

Aliphatic polyethers, such as poly(ethylene oxide), poly(propylene oxide) and poly(tetramethylene oxide), constitute a well-established and industrially important class of polymers being produced by very efficient ring-opening polymerization of the respective cyclic ethers.[1] Procedures for the synthesis of other polyethers, for instance the acid catalysed polycondensation of glycols[2] or polycondensation of glycols and dihalides,[3] are severely limited in terms of the achievable molecular weight. On the other hand, some polyethers bearing longer aliphatic segments have been synthesized by ADMET polymerizations of α,ω-diene ethers.[4] However, the synthesis of the α,ω-diene ethers was not straightforward.[4d, 4e] Most recently, we reported on a general protocol for the high-yielding reduction of aliphatic esters to the respective ethers using GaBr₃ as catalyst and tetramethyldisiloxane (TMDS) as reducing agent.[5] This protocol could be applied successfully also to the reduction of α,ω-diene esters giving easy access to the respective α,ω-diene ethers.[6] Triglycerides could be reduced as well to give the respective glyceryl trialkyl ethers.[7] Further methods were recently reviewed[8] and the most relevant reductions of esters to ethers with silanes involve lewis acids catalysts based on indium,[9] iron[10] or ruthenium.[11]

A novel, powerful and generally applicable method for the synthesis of middle and long chain aliphatic polyethers would be of high interest and is demonstrated herein by the successful and up to now unknown reduction of polyesters, being available in a

great variety of chain lengths of the diacid and the diol. Herein, we thus report on the application of the GaBr₃/TMDS system to predominantly renewable polyesters **1a-l** as a new route for the synthesis of polyethers **2a-l** (Scheme 1). Polyesters **1a-h** were prepared from the respective dimethyl esters and their corresponding diols, polyesters **1i** and **1k** from L-lactide and ε-caprolactone by ring-opening polymerization and **1l** from methyl 10-hydroxyundecanoate. Poly[(*R*)-3-hydroxybutanoate] **1j** is produced by *cupriavidus necator* bacteria and was obtained commercially. The respective polymerizations of diol and dimethyl ester were carried out without solvent at elevated temperatures and reduced pressure using either titanium isopropoxide (Ti(OⁱPr)₄) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst. Ring-opening polymerizations of L-lactide **1i** and ε caprolactone **1j** were carried out in CH₂Cl₂ with pyrene butanol as initiator and TBD as catalyst. Since polyester **1e** is insoluble in most common solvents at room temperature, polyesters **1f-h** were synthesized representing soluble variants with a long distance in between the ester groups. Thus, polyesters with 4 to 22 methylene groups (as well as heteroatom linkages in the case of **1h**) between the ester moieties were obtained. The structure of these polyesters was confirmed by ¹H-NMR and IR-spectroscopy. GPC analysis showed number average molecular weights up to 31,700 g mol⁻¹ (Table 1).
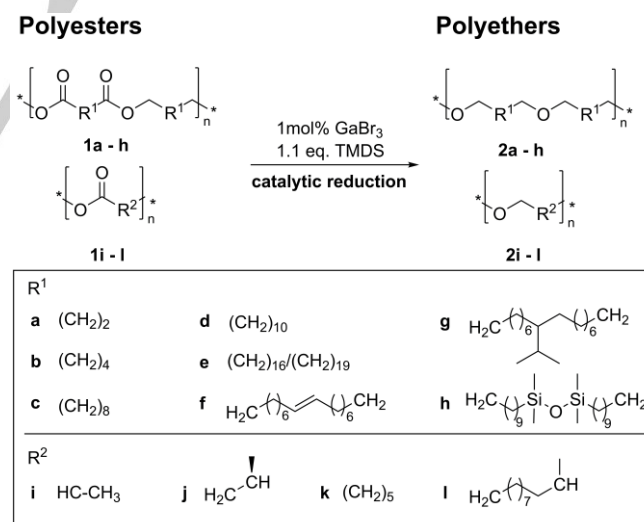
Scheme 1. Catalytic reduction of renewable polyesters **1a-h** (obtained from the respective dimethyl esters and diols), **1i** and **1k** (obtained by ring-opening polymerization of L-lactide and ε-caprolactone, respectively), **1j** (natural origin) and **1l** (obtained from methyl 10-hydroxyundecanoate) to polyethers **2a-l**.

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While we already demonstrated the successful reduction of esters to ethers on small organic molecules,[5, 7] a transfer of this reaction to polymers is highly demanding: For instance, even a

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Table 1. Complete overview of polyesters **1a-l** and polyethers **2a-l**. Molecular weights, percentage of reduced ester groups and yields of the reduction.

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

[a] determined by GPC in THF calibrated with PMMA; [b] determined by GPC in HFIP calibrated with PMMA; [c] percentage of ester groups reduced determined by NMR spectroscopy; [d] percentage of ester groups reduced determined by IR spectroscopy, normalized to CH stretching vibration at 2930 cm⁻¹; [e] yield after precipitation; [f] no data, because of insolubility in THF, HFIP or CHCl₃; [g] not determined due to superimposition of vibrations; [h] DP (degree of polymerization): M_n/M_0, for polyesters M_0 is the average molecular weight of the diacid and diol component; [i] glass transition; [j] due to overlap of -COO-CH_3 and -CH_2-OH end groups estimated with the assumption of a 1:1 ratio of methyl ester end group and OH end group; [k] estimated by normalization -OCH₃ and -CH₂-OH end groups; [l] estimated by normalization to pyrene butanol end group; [m] estimated by normalization to -CH-OH end group; [n] estimated by normalization to -COO-CH_3 end group; [o] estimated by normalization to -CH_2-OH and/or pyrene butanol end group; [p] all vibrations are changing significantly before and after reduction: conversion cannot be determined; [q] not determined due to overlap of -OCH₃ end group and -CH-O-CH₂ ether signal.

slight amount of the reduction of an ester group to an alcohol instead of an ether, a side reaction, that has been observed,[5, 7] would lead to a significant degradation of the polymer chain. In order to avoid this side reaction as far as possible, the reaction conditions were optimised and applicable for most of the polyesters: 2 mmol of the polyester were dissolved in CH₂Cl₂ and 1-2 mol % of GaBr₃ (based on one ester group) added and 4.4 mmol of TMDS (1.1 eq. per ester unit) served as reductant. The mixture was stirred at room temperature overnight. To remove the formed polysiloxane, typically, the polyethers were purified by simple precipitation in hexane or petroleum ether achieving yields between 83% and 92% for polyethers **2b**–**e**, **2g**, **2k** and **2l**. For polyethers **2a**, **2f, 2h, 2i** and **2j** lower yield of 66%, 50%,42%, 34% and 74% were achieved, respectively, which might be attributed to a higher solubility of the polyethers and thus more difficult precipitation, but possibly also to some degradation (**2i**, **2j**). As confirmed by ¹H NMR-spectroscopy, a quantitative reduction of the ester groups (>99%) was achieved for **2a-d** and **2f-l** (see Table 1 and NMR-spectra for products **2a-l** in supporting information). IR spectroscopy confirms this quantitative reduction. Polyester **1e** – at room temperature insoluble – was reacted at 60°C in toluene. A conversion of ~90% of the ester groups could be achieved according to IR spectroscopy. Table 1 gives a comprehensive overview of the molecular weights of the different polyesters and the respective polyethers. The reduction of the polyesters resulted in many cases in an increased dispersity,

which can be explained by some degradation as mentioned above and thus an increasing quantity of lower molecular weight species. A typical example for this behaviour is polycaprolactone **1k.1**, which was polymerized in a controlled fashion and shows a broadening of the dispersity from 1.13 to 1.79 after reduction. To investigate the influence of the molecular weight on the reduction, polycaprolactones with different molecular weights ranging from 4,400 to 15,400 g mol⁻¹ were reduced (see supporting information, Table S1). Polyethers **2k.1-4** have a lower average molecular weight than that of the parent polyester, which can be expected as, even though the reduction shows remarkable selectivity, a slight amount of side reaction to the alcohol (and thus chain cleavage) remains. As it can be expected, this effect is more pronounced for higher molecular weights. For some of the other polyethers, (see i.e. shifted SEC-trace of **2b** in Figure 2 or broad SEC-trace of **2c** in the supporting information), SEC seems to reveal higher molecular weights than that of the parent polyester. Due to the mechanistically highly unlikely formation of higher molecular weights (i.e. chain-chain coupling), a change in hydrodynamic volume due to the decreased solubility of the polyether in comparison to the polyester seems more reasonable to explain these results. Further confirmation for a solvent/solubility effect is the observed increase in molecular weight for **2b** compared to **1b** when measured in THF (Figure 2, **1b**: M_n = 6,300 g mol⁻¹, Đ = 1.67, **2b**: M_n = 7.300 g mol⁻¹, Đ = 1.71), in contrast to a constant molecular weight when measured

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in HFIP (see Table 1, **1b**: M_n = 7,500, $Đ$ = 1.62, **2b**: M_n = 7.600 g mol^{-1}, $Đ$ = 1.67). The ^{1}H-NMR and IR spectra of polyester **1c** before and after reduction to polyether **2c** are exemplarily shown in Figure 1. Full conversion can be observed in the ^{1}H NMR spectrum, as the integrals for the characteristic triplets for CH$_2$-groups **c** (2.28 ppm) and **d** (4.04 ppm) of the polyester decreased (>99%) after reduction and a new triplet corresponding to the CH$_2$ group **c'** of the polyether appears at 3.38 ppm. Moreover, a slight shift can be observed for multiplet **b** to **b'** from 1.51 – 1.69 to 1.45 – 1.67 ppm, while signals **a** and **a'** for the remaining CH$_2$-groups can be assigned at 1.14 – 1.41 ppm. The triplet at 3.64 ppm can be assigned to the -CH_2-OH end group and at 3.66 ppm a singlet can be assigned to the methyl ester group for the polyester, which changes after reduction to a methoxy signal at 3.35 ppm. Average molecular weight determination by end group analysis is difficult due to partly overlapping signals, but the spectra reveal polyethers with two hydroxy end groups or a hydroxyl, possibly silylated, and a methoxy end group. The data also shows that most polyesters chains are cleaved on average one time. In general, the average molecular weight determined by GPC analysis was significantly higher than the estimated molecular weights by NMR end group analysis. At 0.07 ppm, a singlet can be assigned to remaining <0.5 wt% silyl species in the polymer (Figure 1). In the corresponding IR-spectrum, the signal intensity of the carbonyl vibration of the ester at a wavenumber of 1733 cm^{-1} is reduced (>99%) after the reduction, confirming the conversion determined by ^{1}H NMR. Additionally, at a wavenumber of 1112 cm^{-1}, a signal belonging to the ether vibration can be observed after reduction. SEC analysis coupled with ESI-mass spectrometry (shown in Figure 2 on the example of **1b** and **2b**) further confirms the success of the reductions. Oligomers with 5-7 repeating units and different end groups could be assigned to the structure of polyester **1b** and oligomers with 11-17 repeating units to polyether **2b** in the same mass range of m/z 1200 – 1800. The example of a polyether with 13 repeating units and OH as well as OMe end-groups is shown in Figure 2 in high resolution. The theoretical mass [M+Na]$^+$ = 1356.17003 together with the calculated isotope pattern both fit to the measured mass of m/z [M+Na]$^+$ = 1356.17010 and the observed isotope pattern, clearly confirming the assigned structures. Polyethers **2a-h** were in general less soluble in common organic solvents than the respective polyesters. An example of this observation is polyether **2g**, which in contrast to polyester **1g** does not dissolve in THF. To investigate the influence of the end groups on the reduction, a low molecular weight version of polyester **1c** was prepared using an excess of diol (1.26 eq) to ensure only OH-end groups (see supporting information, polyester **1c.1**). Moreover, the OH-end groups were acetylated using acetyl chloride ensuring OAc-end groups (see supporting information, polyester **1c.2**). In both cases, the polyester could be reduced quantitatively to polyethers **2c.1** and **2c.2** as confirmed by IR- and NMR-spectroscopy (supporting information, Figure S1) without significant molecular weight loss (supporting information, Figure S2), thus indicating that OH-end groups do not significantly influence the here presented reduction procedure. In order to investigate if the mechanism of the reduction occurs predominantly statistical or block-wise, partially reduced **2a-c** (4-8% reduced groups, using 0.1 eq. TMDS) were cleaved and

afterwards transesterified with methanol and TBD. Investigation of the obtained fragments by SEC-ESI MS analysis
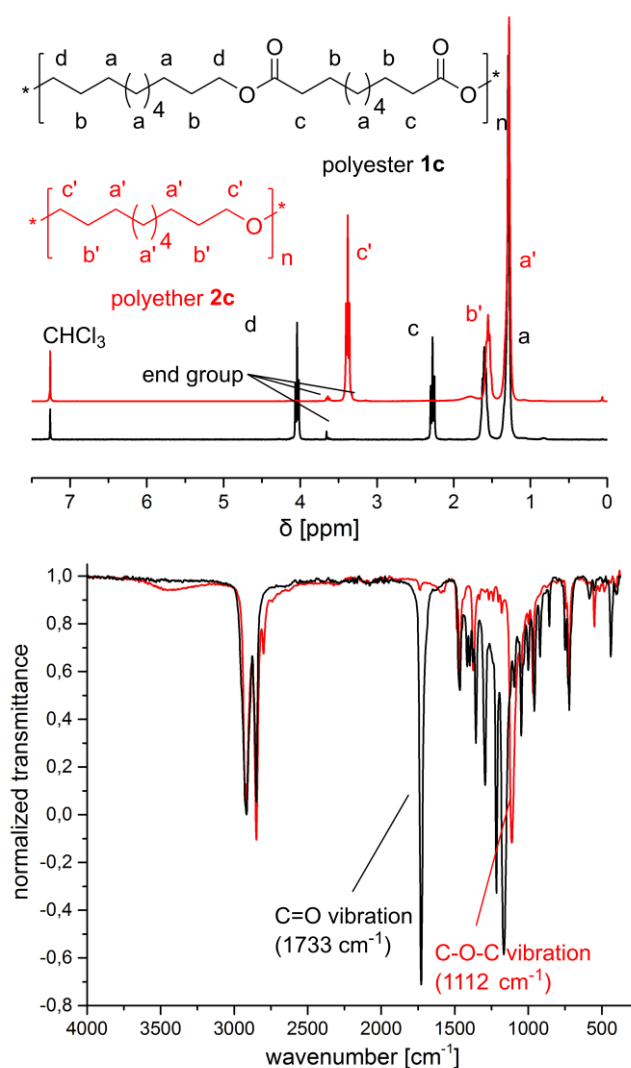

Figure 1. ^{1}H-NMR spectrum (top) and IR spectrum (bottom) of polyester **1c** (black) and the respective polyether **2c** (red).

(see supporting information, Schemes S2-S4, Figures S5-S7, Tables S3-S5) revealed a statistical mechanism as no higher molecular weight polyether fragments could be identified, which would suggest a reduction starting from the end-groups. For the reduction of (L)-polylactide **1i** instead of 1 mol% catalyst GaBr$_3$ and 1.1 eq. reducing agent TMDS per ester group, 5 mol% GaBr$_3$ and 5 eq. TMDS were required for full conversion of the ester groups. Interestingly, polypropylene glycol **2i** might still have a defined stereochemistry as the reduction does not involve the stereocenter. However, due to the cleavage reaction and very low molecular weight, the ^{13}C-NMR spectrum of **2i** shows several peaks of different oligomers and isotacticity cannot be proven at this stage (see supporting information, Figure S8). In contrast, poly(oxy-1-methyl-propylene) **2j** is a stereo- and regiochemically

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defined oligoether with sharp peaks at chemical shift of 72.4 (-OCHCH$_3$), 65.1 (-OCH$_2$), 37.3 (-OCH$_2$CH$_2$-), 19.8 (-CH$_3$) in good agreement with literature (see supporting information, Figure S9).[12] In the typical synthesis of **2j** by cationic polymerization of
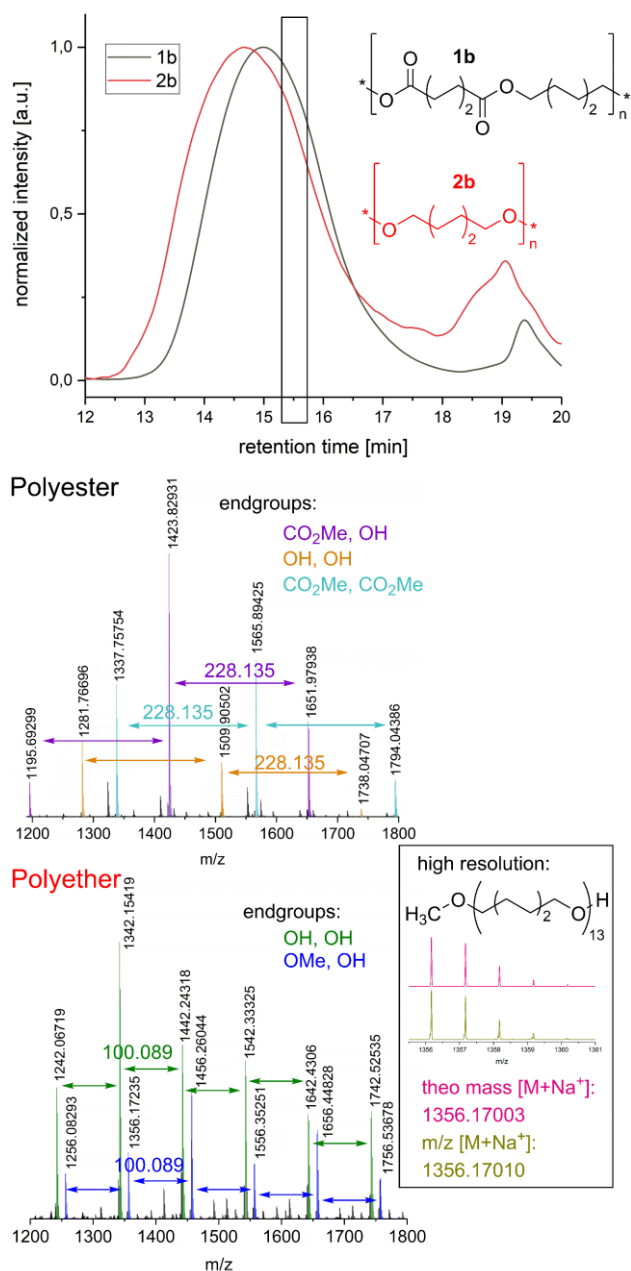

Figure 2. SEC-ESI MS analysis of polyester **1b** (black) and polyether **2b** (red). The mass spectrum was obtained at a retention time interval of 15.3 - 15.8 min (indicated by a black box in the chromatogram).

2-methyloxacyclobutane, a mixture of head-to-head, tail-to-tail, and head-to-tail additions is obtained.[11a] Although the molecular weights of the here obtained **2i** (M$_n$ = 300 g mol^{-1}) and **2j** (M$_n$ = 800 g mol^{-1}) are rather low, they might still be used as a polyols for the synthesis of polyurethanes. The more pronounced

degradation for polyethers **2i** and **2j** might be related to the close distance in between the ester groups. As comparison, the GaBr$_3$ catalyzed reduction of triglycerides, having respective neighbouring oxygen atoms, showed about 7% reduction per ester unit to the alcohol,[7] which is in agreement to the reduction of **1i** and **1j**. An influence of the methyl group in α-position to the ester functionality can be excluded, as the reduction of **1l** to **2l** did not result in excessive cleavage. The result of the GPC analysis of polypropylene oxide **2i** was confirmed by mass spectrometry (ESI-MS) showing the main peak at m/z=315.2354 (C$_{15}$H$_{32}$LiO$_6$) corresponding to five monomer-units. Since some of the prepared polyesters and all polyethers (except **2a**, which can be obtained by ring opening polymerization of THF) are novel or in case of **2b** and **2c** known as oligomers,[2b] their thermal properties were studied in order to establish their basic material properties. The comparison of the melting points of the different polyesters and polyethers shows interesting results (Table 1). A direct comparison of polyesters and the thereof derived reduced polyethers reveals lower melting points for the polyethers. This difference increases with a smaller distance in between the ester/ether groups. This is an expected, yet interesting to confirm observation for this set of AA-BB type polyesters with even numbers of carbon atoms and the thereof derived polyethers. For polyesters **1f-l** and polyethers **2f-l**, the interpretation of the change in thermal behavior is not as straightforward. A slight increase in melting point can be observed for polyester **1f** and **1h** (64.6 °C and -5.1 °C) to polyether **2f** and **2h** (67.7 °C and 0.6 °C). The isopropylated polyester **1g** and polyether and **2g** show a glass transition at -66.8 °C and -66.3 °C due to their bulky side-chains that also prevent crystallization and thus increase solubility. Polyester **1l** and polyether **2l** show a glass transition at -58,0 °C and -69,0 °C. Comparing the melting point of polyether **2a** (35.8 °C) with its commercial counterpart polyTHF (31.3 °C) of similar molecular weight reveals good agreement.

In conclusion, we could demonstrate that polyesters can be reduced to polyethers applying GaBr$_3$ as catalyst and TMDS as reducing agent and thereby introduce a novel polyether synthesis method. Thus, various novel polyethers as well as poly(tetramethylene oxide) and poly(propylene oxide) oligomers were obtained from renewable resources. Ester groups were quantitatively reduced, as proven by NMR and IR spectroscopy and mass spectrometry, while degradation of the polymer chain could be kept to a minimum for polyethers with four or more methylene groups between functional groups. End group modification could prove that a moderate amount of hydroxy end groups does not have a significant influence on the reduction. Mechanistic studies revealed that the reduction occurs at random positions in the polymer chain. Finally, a comparison of the thermal properties of the different polyesters and polyethers revealed interesting structure property relationships.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

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Polyester, you shall be reduced: A direct conversion of polyesters to polyethers is enabled by homogeneous catalysis with gallium bromide as catalyst and tetramethyldisiloxane as reducing agent. Mild reaction conditions ensure minimal degradation of the polymer chain and give full conversion of the ester groups as proven by NMR- and IR spectroscopy as well as SEC-ESI MS analysis.
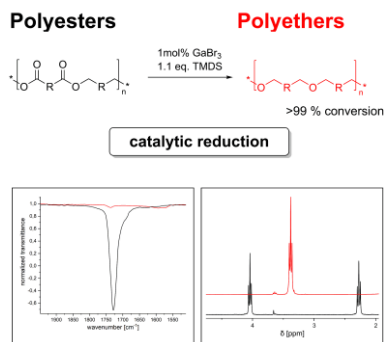
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