


ORIGINAL ARTICLE

Synthesis of dihydroxy telechelic oligomers of β -butyrolactone catalyzed by titanium(IV)-alkoxides and their use as macrodiols in polyurethane chemistry

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Abstract

We report on a solvent-free approach for the synthesis of low molecular weight, α,ω -dihydroxy telechelic poly(β -butyrolactone). In the presence of Ti(IV) alkoxides, mixtures of β -butyrolactone and diols, like di- or triethylene glycol, were reacted in ratios between 4:1 and 10:1. The oligomerization proceeds at elevated temperatures (80–100°C). Different alkoxide substituents (R = Me, *i*Pr, *t*Bu) of the Ti(IV)(OR)₄ catalyst were investigated. The resulting oligomers were characterized by nuclear magnetic resonance (NMR), infra-red (IR), gel-permeation chromatography (GPC), titration, and matrix-assisted laser desorption-time-of-flight mass spectrometry (MALDI-ToF-MS) analysis. Aside from low molecular weight products, special effort was devoted to achieve high *O*-acyl cleavage selectivity and to circumvent the formation of unsaturated end-groups in order to form exclusively dihydroxy-telechelic oligomers. Optimized results in terms of selectivity and reaction rates were achieved at 100°C using catalyst loadings of 0.2 mol% with respect to the monomer. The molecular weights determined by GPC were in good accordance with the ratio of monomer to diol used, confirming successful oligomer formation. Polyurethanes prepared from crude macrodiols without any additional catalyst feature molecular weights up to 50,000 g/mol. The reported work serves as concept to utilize β -lactones for tailored polyol synthesis; the resulting products are suitable for polyurethane chemistry.

KEYWORDS

4-methyloxetan-2-one, oligodiols, polyester, polyurethane, β -butyrolactone

1 | INTRODUCTION

Polymers based on ring-opened β -lactones are used by bacteria and other microorganisms for energy storage.

They are also biodegradable and can be depolymerized in various natural environments.^{1–4} In combination with their material properties, these polymers also received significant attention in the fields of implant materials,

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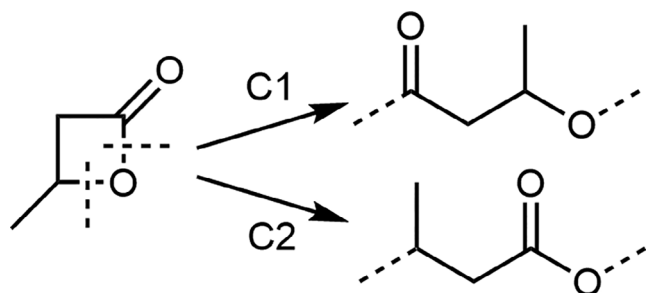
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drug delivery, and biodegradable polymers.^{5–7} Nonetheless, the balance act between suitable material characteristics and nonpersistence and/or biodegradability remains difficult.⁸

β -Lactones show special reactivity within the lactone family concerning the cleavage of bonds during ring opening polymerization (ROP). Whereas a nucleophilic attack at, for example, ϵ -caprolactone (ϵ -CL) selectively occurs at the carbonyl atom, leading to an acyl-oxygen cleavage (C1, Scheme 1), two competitive reaction pathways are observed for β -butyrolactone (BBL). In addition to the aforementioned acyl-oxygen cleavage, especially in anionic polymerization the alkyl-oxygen cleavage (C2, Scheme 1) predominates. While path C1 leads to an alkoxide (or hydroxyl) chain end-group, C2 results in a carboxylate (or carboxylic acid).^{6,9–11}

In terms of ROP, this results in a highly challenging situation because even if an alkoxide is formed in the initial step, there is again a certain probability in each subsequent ring opening step that either the alkoxide or the carboxylate forms. If, in contrast, a carboxylate is formed, further reactions proceed via *O*-alkyl (C2) cleavage. This renders the synthesis of oligomers or polymers via selective acyl-oxygen cleavage particularly demanding. In addition, elimination of the hydroxyl end-groups, leading to crotonate-type alkenes through elimination of H₂O (OH[−]) or by base-induced elimination of internal ester groups can reduce the number of terminal hydroxyl groups as well as the rearrangement of β -butyrolactone to crotonic acid, acting as additional initiator for *O*-alkyl cleavage.^{9–10,12–13}

Generally, much attention has been devoted to the polymerization of various lactones by organometallic compounds, including ϵ -CL and dilactide. Thus, complexes containing magnesium, aluminum, iron, zinc, yttrium, zirconium, tin, and hafnium have been applied.^{14–19} In terms of reaction control towards the ring opening mode of BBL, metal complexes turned out to be highly active and selective catalysts. Within this context, catalysts based on yttrium bis(phenolates) have been



SCHEME 1 Competitive reaction modes: *O*-acyl (C1) vs. *O*-alkyl cleavage (C2)

investigated.^{20–24} By NMR, the authors identified an insertion mechanism based on an *O*-acyl cleavage and generation of a hydroxyl group as one final end-group. At the same time, no crotonate or carboxylic acid formation was observed.

Titanium complexes play a pivotal role in the polymerization of lactones.^{25–32} Among the titanium alkoxides applied for the ROP of lactones, simple compounds like titanium tetramethoxide, titanium tetraisopropoxide, and titanium tetratertbutoxide so far played a subordinate role as catalysts due to their rather moderate activity.¹⁶ However, the polymerization of ϵ -CL and dilactide catalyzed by Ti(OiPr)₄ was successfully accomplished. By applying it to a racemic mixture of dilactide, molecular weights up to $M_n = 20$ kg/mol ($D_M = 2.1$) were achieved at 130°C within 15 h in bulk.²⁷ Also, air-stable titanium-organic frameworks were applied to synthesize dihydroxy telechelic poly(ϵ -CL) and poly(lactic acid).³³ The dihydroxy telechelic structure of the polymers was proved by MALDI-ToF, showing the incorporation of the diol.

Kricheldorf et al. reported on dialkyl tin(IV) diol compounds for the synthesis of telechelic macromolecules and macrocycles, respectively,^{34–37} using ϵ -CL, dilactide and BBL as monomers. The chain length followed the monomer to initiator ratio whereby high process control was achieved. Catalytic approaches forming telechelic dihydroxides, based on 1,4-butandiol or tetraethylene glycol, were found for ϵ -CL applying dialkyl Sn(II) compounds.³⁸

Trifluoromethanesulfonic acid was also applied to synthesize dihydroxy-terminated poly(BBL).³⁹ Likewise, block copolymers consisting of BBL and ϵ -CL were prepared by subsequent monomer addition showing the hydroxyl end-groups as addressable chain ends. Molecular weights of $M_n = 29$ kg/mol ($D_M = 1.33$) were found for a block copolymer of PCL-PBBL-PCL, whereby the central dihydroxy telechelic poly(BBL), which served as starter, displayed an M_n of 11 kg/mol ($D_M = 1.18$).

Zinc amino-oxalate complexes enabled the synthesis of cyclic and, in conjunction with aliphatic (di-)alcohols, linear (di-)hydroxy end-capped polymers from β -butyrolactone.⁴⁰ ¹H NMR signals in the olefinic region, indicating crotonate formation, were less pronounced for monols compared to diols.

Finally, dihydroxy-telechelic copolymers of ϵ -CL and BBL were synthesized, by applying Sn(II)alkyl catalysts and ethylene glycol or 1,4-butandiol, achieving molecular weights between 6600 and 8800 g/mol. The formed polymers allowed for a subsequent reaction with excess MDI (methylenediphenyl diisocyanate = bis(4-isocyanatophenyl) methane) applying a tin(IV) catalyst to yield polyurethanes with molecular weights between 20,000 and 24,000 g/mol.⁴¹

Polyurethanes synthesized from dihydroxy telechelic poly(BBL) were described before.^{42–44} Further, their properties (e.g., oil and water sorption) and morphology was investigated. However, the macrodiols were synthesized by anionic ROP and termination with 2-bromoethanol.

As outlined above, the properties of poly(BBL) as homopolymer are already interesting as such.⁵ In this report, a simple approach for the synthesis of oligomeric dihydroxy-telechelic poly(BBL) and its use as macromonomers is reported. Special attention was devoted to the selective formation of hydroxyl end-groups and to the precise adjustment of the molecular weight. These macromonomers can be further used in step growth polymerization to form polyesters, polycarbonates, and especially polyurethanes. In this context, the utilization of oligomeric polyester polyols for the production of rigid foams displays a highly interesting field of application.

2 | EXPERIMENTAL

All oligomerization and polymerization reactions were executed in an MBraun glovebox or by standard Schlenk techniques. Purification of the solvents and chemicals used is summarized in the supporting information (S1) along with the analytical methods.

Generally, for an *oligomerization* reaction, racemic BBL (0.25–4 g) was mixed with the appropriate amount of diol and the mixture was stirred or shaken until a clear homogeneous solution was obtained. This solution was added to the catalyst in a 4 or 10 ml-vial equipped with a magnetic stir bar, and the mixture was heated to the reaction temperature in a pre-heated aluminum block with drill holes, placed on a magnetic stirring heating plate. After the reaction was complete, the colorless, homogeneous mixture was cooled to room temperature.

Prior to work up, a small sample was withdrawn from the crude product and submitted to NMR analysis. The residual reaction mixture was brought outside the glovebox, diluted with THF (2–6 ml) and quenched with 5–10 drops of demineralized water under continuous stirring or shaking. After about 2 h a small amount of a colorless precipitate formed and was removed by filtration. Then, the solvent was removed at room temperature under reduced pressure to give the colorless, viscous product.

For *copolymerization* with MDI, the crude reaction mixture obtained after cooling to room temperature was reacted with a THF solution of MDI for 12 h using a 1:1 molar ratio of MDI and diol. As reaction proceeded, a rapid increase in viscosity was observed. After the indicated reaction time the solution was poured into pentane and a colorless solid precipitated. After centrifugation for 99 min at 4500 rpm the supernatant solution was discarded and the

residual substance was dried over night at 50°C in a vacuum oven to result in bright orange/brownish polymer.

3 | RESULTS AND DISCUSSION

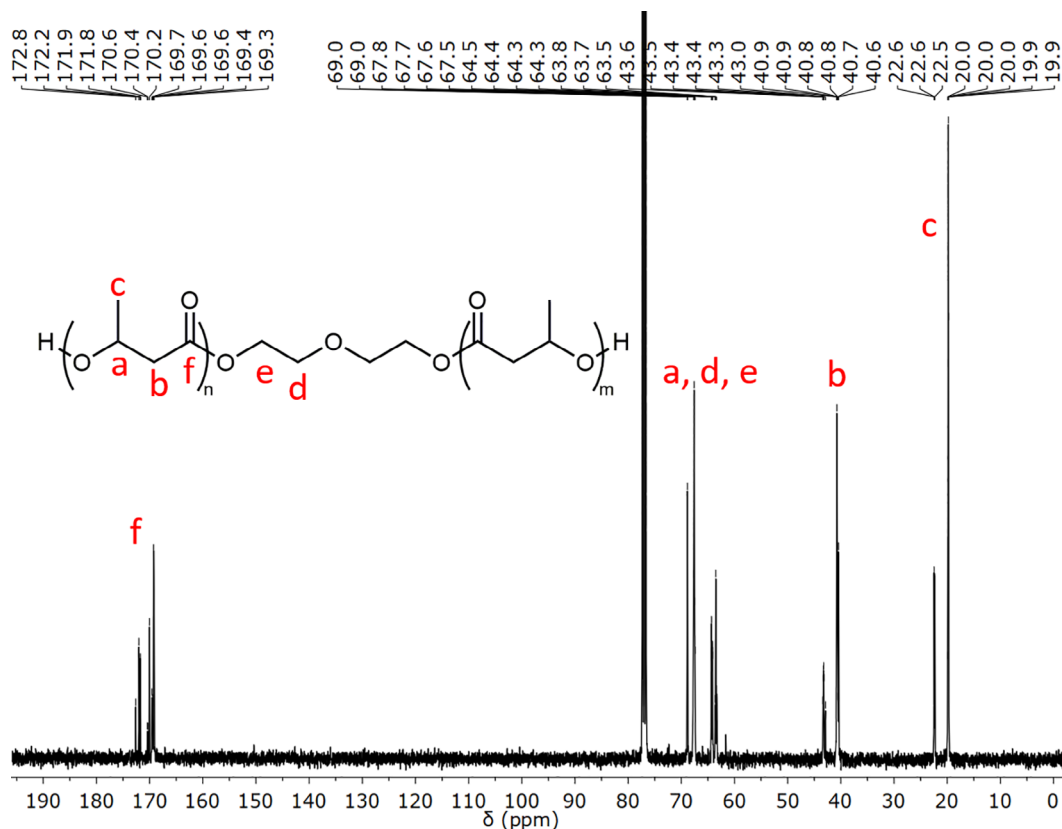
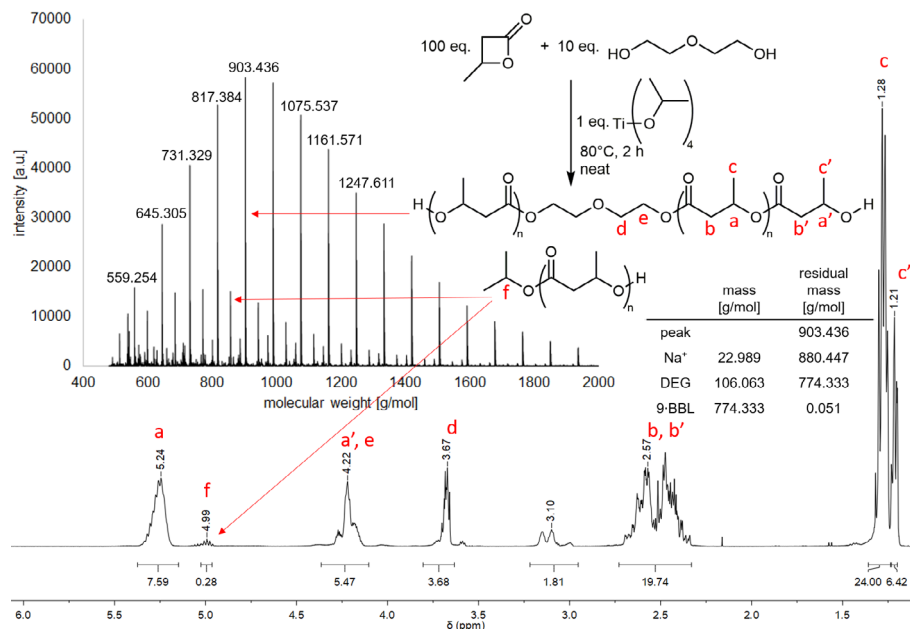
3.1 | Selective diol formation

Ti(OiPr)₄ allowed the oligomerization of BBL to form dihydroxy-telechelic oligomers in the presence of aliphatic dihydroxides at elevated temperatures. A mixture of BBL (100 eq.) and diethylene glycol (DEG, 10 eq.), catalyzed by Ti(OiPr)₄ (1 eq.), was oligomerized at 80°C within 2 h (Scheme 2). The crude proton NMR showed no remaining monomer (e.g., the tertiary hydrogen in BBL at 4.6–4.7 ppm). Thus, quantitative conversion was assumed. GPC analysis revealed a molecular weight of 900 g/mol ($\bar{M}_w = 1.3$; $M_{n, \text{theo}} = 967$ g/mol). Titration with NaOH indicated 23 μmol of free carboxylic acid per g_{oligomer} and further supports a predominantly dihydroxy-telechelic structure ($\geq 96\%$). NMR and MALDI-ToF analysis are displayed in Scheme 2. The major peaks in the MALDI-ToF spectra show the target molecules consisting of both, BBL and DEG. Besides, oligomer formation starting from only one side of DEG must be taken in account. In addition, a smaller amount of oligomeric BBL attached to the catalyst's *isopropoxide* group, which herein acts as a starter molecule, can be found in the MALDI-ToF-MS spectrum and was also confirmed by the signal for $\text{CH}(\text{CH}_3)_2$ at $\delta = 4.99$ ppm in the ¹H NMR spectrum. By comparison with literature data of methyl 3-hydroxybutanoate, the signals around $\delta = 3$ ppm can be assigned to the hydroxyl end-groups.^{45–46} Furthermore, the absence of any signals around $\delta = 5.8$ ppm indicates the absence of olefins formed as a result of hydroxyl end-group elimination.⁴⁷ ¹³C NMR analysis of the oligomer shows four signals, being the carbonyl carbons around $\delta = 170$ ppm, the O-bound sp^3 -carbons around $\delta = 65$ ppm, the CH_2 groups next to the carbonyl around $\delta = 42$ ppm and the CH_3 groups around $\delta = 21$ ppm (Scheme 3).

As a consequence of the oligomeric character and the different degrees of oligomerization on either side of the diol starter molecule, the individual carbon atoms of the repeat unit are represented by several slightly shifting signals caused by atacticity as a result of the non-stereospecific oligomerization.

However, the ¹³C NMR spectrum again showed no signals of olefins or carboxylic acids that could be formed in course of the reaction. Generally, a stringent suppression of any elimination of hydroxyl end-groups is necessary to avoid nonaddressable end-groups, which would prevent further growth. Hence, the temperature dependence of the elimination reaction was examined (Scheme 4).

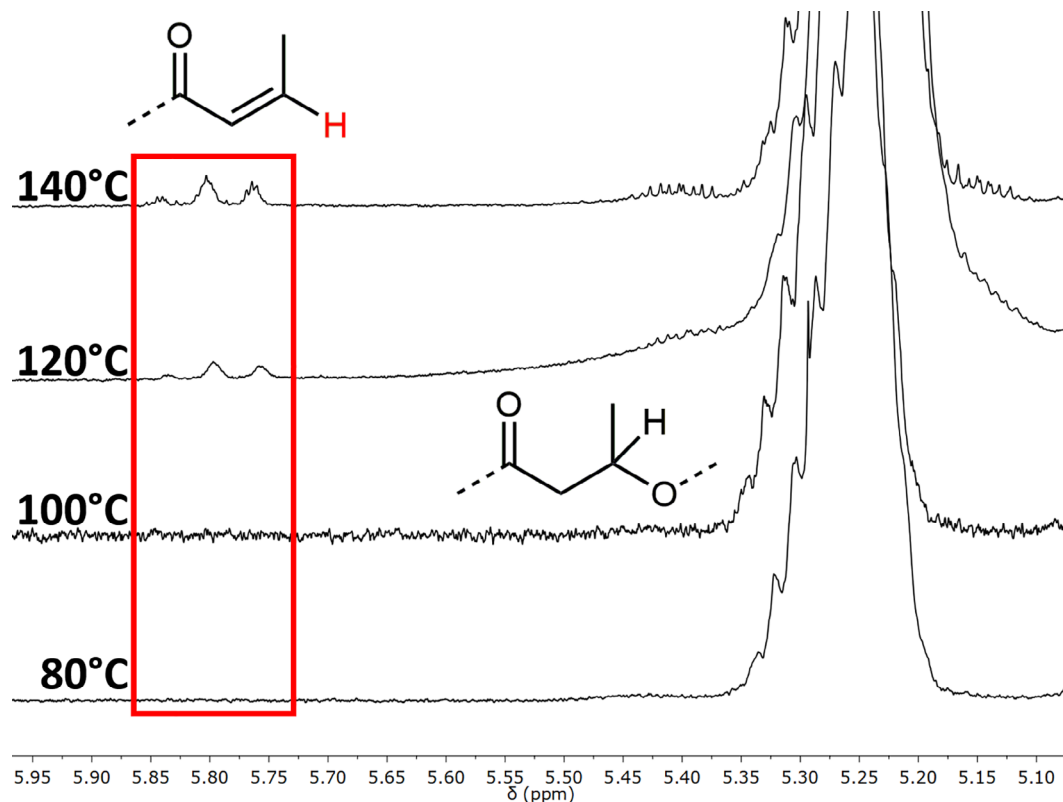
SCHEME 2 Crude ^1H NMR (CDCl₃) and MALDI-ToF-MS spectrum of the dihydroxy-telechelic oligomer formed from BBL and DEG showing an elimination-free (crotonate-free) product. A very minor amount of a monohydroxylic oligomer stems from initiation by the catalyst's isopropoxide group [Color figure can be viewed at wileyonlinelibrary.com]



SCHEME 3 ^{13}C NMR spectrum (CDCl₃) of the dihydroxy-telechelic oligo (BBL) based on DEG and the corresponding molecular structure [Color figure can be viewed at wileyonlinelibrary.com]

Reactions carried out up to 100°C showed no end-group elimination whereas oligomerization reactions carried out at 120°C and higher resulted in an increased content of olefinic end-groups. At 60°C, reactions proceeded slower (100:10:1 BBL:DEG:Ti(OiPr)₄ showed 91%

conversion after 5 h); at room temperature no reactivity was observed within 12 h reaction time. Chain-growth based on selective *O*-acyl cleavage was further supported by additional acid–base titration experiments of polymers prepared at different reaction temperature and time.



SCHEME 4 Stacked ¹H NMR spectra (5–6 ppm in CDCl₃) of oligomerization reactions of BBL and DEG catalyzed by Ti(OiPr)₄ at 80, 100, 120, and 140°C. After 2 h, a certain degree of elimination resulting in the formation of double bonds is detectable from 120°C on [Color figure can be viewed at wileyonlinelibrary.com]

Entry	BBL:DEG:Cat	T (°C)	t (h)	M _n (g/mol) (Đ _M) ^a	Acid value ^b (μmol/g)
1	100:10:1	80	2	900 (1.3)	23 (1.2)
2	100:10:1	90	2	1000 (1.4)	20 (1.1)
3	100:10:1	100	2	1000(1.6)	21 (1.2)
4 ^c	100:10:1	90	2	900 (1.5)	25 (1.4)
5	250:25:1	80	9	800 (1.4)	12 (0.6)
6	250:25:1	100	4	1000 (1.6)	37 (2.1)
7	100:25:1	80	2	300 (1.2)	n.d.
8	100:17:1	80	2	400 (1.3)	n.d.
9	500:50:1	100	13	1100 (1.4)	n.d.
10 ^d	500:50:1	100	13	1000 (1.6)	n.d.
11 ^e	500:50:1	100	13	1100 (1.4)	n.d.

TABLE 1 Molecular weights and acid values determined for oligomers synthesized at different temperatures, catalyst loadings, and monomer/diol ratios

^aDetermined by THF GPC; M_{n, theo}(BBL:DEG 100:10 or 250:25 or 500:50) = 967 g/mol, M_{n, theo}(BBL:DEG 100:25) = 450 g/mol; M_{n, theo}(BBL:DEG 100:17) = 622 g/mol.

^bDetermined by titration, μmol_{COOH}/g_{oligomer} (mg_{KOH}/g_{oligomer}).

^cTriethylene glycol was used instead of diethylene glycol.

^dTi(OMe)₄ instead of Ti(OiPr)₄ was used.

^eTi(OtBu)₄ was used instead of Ti(OiPr)₄.

^fcat = Ti(OiPr)₄.

The acid values of DEG-derived oligomers synthesized at 80, 90, and 100°C, respectively, as well as oligomers based on triethylene glycol (TEG, see Supporting information S1 for MALDI-ToF-MS) displayed similar

acid values in the range of 20–25 μmol_{COOH}/g_{oligomer} (Table 1, entry 1–4). Reduction of the catalyst loading slightly increased the acid values up to 37 μmol_{COOH}/g_{oligomer} while at 80°C and a prolonged reaction time a

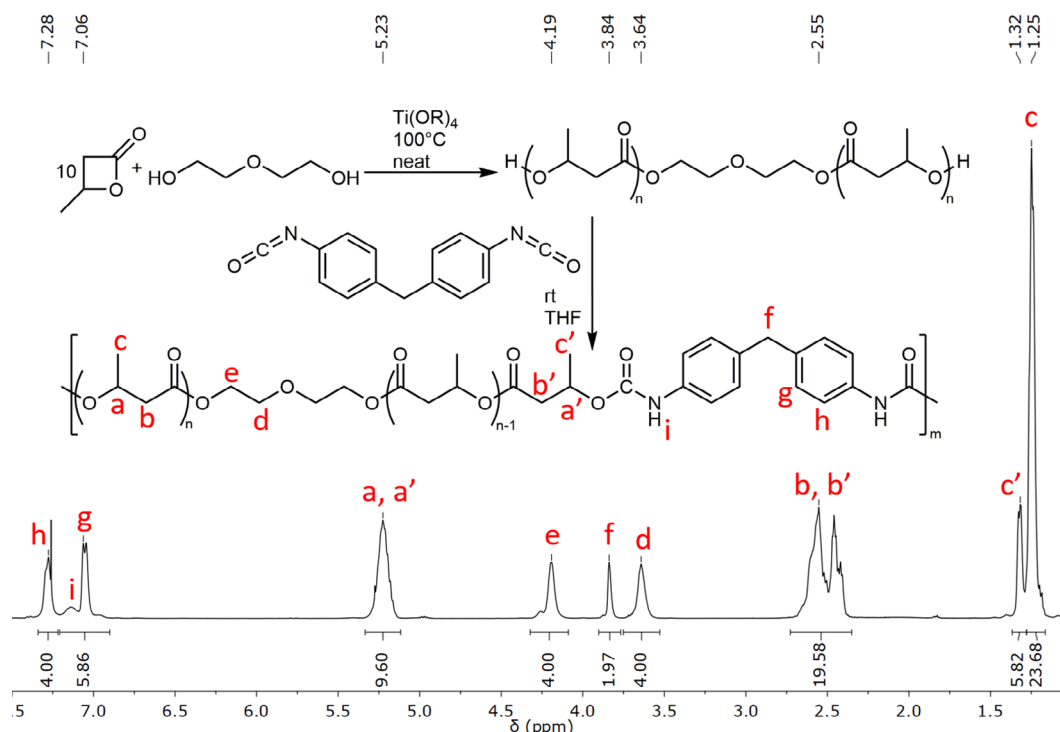
value of $12 \mu\text{mol}_{\text{COOH}}/\text{g}_{\text{oligomer}}$ was found (Table 1, entries 5–6). Notably, quantitative conversion of the monomer was observed for all reactions given in Table 1. In addition, comparison of entries 1 and 5, Table 1, show that the molecular weight of the final oligomer is not connected to the catalyst loading but instead to the ratio of monomer to diol. This is further supported by entries 7 and 8, Table 1, where the amount of starter was increased with the intention to decrease the average degree of polymerization to four and six, respectively. Accordingly, the measured values of 300 and 400 g/mol fit well the theoretical values of 450 and 622 g/mol. As shown in comparison with entries 9–11, Table 1, the molecular weight of the oligomers solely depends on the BBL:starter ratio but not on catalyst loading. As a consequence, the initiation by *isopropoxide* is diminished (see Supporting information S1). Note, such low catalyst loading results in a titanium loading of round 1 mg titanium per gram of oligomer.

3.2 | Polyurethane synthesis

Next, the dihydroxy telechelic oligomers were used in the synthesis of polyurethanes since good performance in a step-growth reaction is a measure for the quality of the telechelic oligomers. First, six different

oligomerization reactions were conducted at 100°C . For oligomerization, three different catalysts, that is, $\text{Ti}(\text{O}i\text{Pr})_4$, $\text{Ti}(\text{OMe})_4$ and $\text{Ti}(\text{O}t\text{Bu})_4$ where applied together with two different catalyst loadings (BBL:DEG:Ti(OR)₄ 100:10:1 and 500:50:1).

After the oligomerization reaction was completed the reaction mixtures were cooled to room temperature and a THF solution of MDI was added (Scheme 5). Note, no work up was carried out and no additional catalyst or initiator was added. An increase in the viscosity of the reaction solution was observed within 30 min, however, for the sake of completeness the reactions were stirred 12 h before precipitating the polymer into pentane. ^1H NMR analysis clearly showed the formation of a urethane-based polymer as indicated by the incorporated MDI signals (Scheme 5, signals f, g and h). Furthermore, the signals of the formed carbamate moiety become visible, which were broad but clearly detectable in between the aromatic peaks (signal i).^{48–49} The polymers structure was further confirmed by the carbamate and the aromatic signals using ^{13}C NMR and IR spectroscopy (sharp heteroatom-hydrogen vibration at 3346 cm^{-1} detectable (see Supporting information S1). Due to their atactic nature, the synthesized polyurethanes were found to be fully amorphous according to DSC analysis. In addition, no T_g values were found in the range from -70 to 200°C . The molecular weights of the resulting polyurethanes are given in



SCHEME 5 Synthesis of polyurethanes from dihydroxy telechelic BBL oligomers and MDI and a representative ^1H NMR spectrum of a resulting polymer [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Polyurethane synthesis from BBL oligomers

Entry	BBL ^a	DEG ^a	Catalyst	MDI ^a	T ₁ /T ₂ ^b (°C)	t ₁ /t ₂ ^b (h)	Yield ^c (%)	M _n ^d (g/mol)	Đ _M ^d	DP ^e
1	100	10	Ti(OiPr) ₄	10	100/rt	2/12	79	8000	1.6	13
2	500	50	Ti(OiPr) ₄	50	100/rt	13/12	90	20,000	1.7	33
3	100	10	Ti(OMe) ₄	10	100/rt	2/12	76	12,000	2.2	20
4 ^b	500	50	Ti(OMe) ₄	50	100/rt	13/12	83	20,000	1.8	33
5	100	10	Ti(OtBu) ₄	10	100/rt	2/12	82	29,000	1.4	48
6	500	50	Ti(OtBu) ₄	50	100/rt	13/12	89	53,000	1.5	87

^aEquivalents with respect to Ti.

^bT₁/t₁ temperature and time for the oligomerization, T₂/t₂ temperature and time for polyurethane synthesis. rt = room temperature.

^cOf the polyurethanes after workup, determined gravimetrically.

^dBy GPC in CHCl₃.

^eDegree of polymerization estimated from GPC.

Table 2. Degrees of polymerization (DP) were calculated based on a molecular weight of the repeat unit of 1217 g/mol (10·BBL + 1·DEG + 1·MDI). A comparison of the molecular weights of the polyurethanes in entries 1 and 2, Table 2, reveals a higher molecular weight for the latter. This is attributed to the lower catalyst loading used for the oligomerization in entry 2 relative to entry 1. Thus, a ratio of 100:10:1 (BBL:DEG:Ti(OR)₄, 1 mol% relative to BBL) was used in entry 1, while a ratio of 500:50:1 (0.2 mol%) was used in entry 2. Quantitative consumption of the lactones was observed in both cases. Based on the findings outlined above, a lower catalyst loading is expected to go along with a lower degree of initiation by the monofunctional alkoxide ligand of the Ti(OiPr)₄ catalyst. Similar behavior was observed for entries 3–6, Table 2. Higher catalyst loadings applied in the oligomerization reactions in entries 3 and 5 lead to lower molecular weights of the polyurethane than the comparable reactions in entry 4 and 6, where lower catalyst loadings lead to higher molecular weights of the polyurethanes. Simultaneously, the different alkoxide ligands of the applied Ti(IV) catalysts were found to influence molecular weights. While only marginal differences in the molecular weights of the resulting polyurethanes were observed for Ti(OiPr)₄ (Table 2, entries 1 and 2) and Ti(OMe)₄ (Table 2, entries 3 and 4), the use of Ti(OtBu)₄ (Table 2, entries 5 and 6) resulted in significantly higher molecular weights of the polyurethanes. This is attributed to a significantly reduced initiation rate of the *tert*butoxide group compared to the less sterically crowded alkoxide derivatives, resulting in lower amounts of α-alkoxide-ω-hydroxy oligomers. Clearly, both, the catalyst loading and the nature of the alkoxide finally affect the integrity of the two hydroxy end-groups that determine the OH-functionality of the product and thus the ability of uninterrupted chain growth in polyurethane formation (compare Supporting information S1, hydroxyl fidelity).

4 | CONCLUSIONS

The solvent-free synthesis of low molecular weight, dihydroxy-telechelic oligoesters from β-butyrolactone has been demonstrated. Diols like diethylene glycol were applied as starter molecules. Reactions proceeded at elevated temperatures and were catalyzed by Ti(IV) alkoxides. Structure and molecular weights were analyzed by NMR and IR spectroscopy, GPC and MALDI-ToF-MS. Molecular weights were adjusted by the ratio of diol to lactone. The end-groups were quantified by acid–base titration; diols were used in polyurethane synthesis, which served as additional probe for the integrity of the end-groups. Depending on the catalyst, molecular weights of the polyurethanes up to 50,000 g/mol were found. The most satisfying results in terms of end-group selectivity were achieved by applying low Ti(OtBu)₄ loadings, offering future possibilities in polyurethane, polyester and polycarbonate production, based on dihydroxy-telechelic poly(BBL).

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