

## Poly(1,2-glycerol carbonate): A Fundamental Polymer Structure Synthesized from CO<sub>2</sub> and Glycidyl Ethers

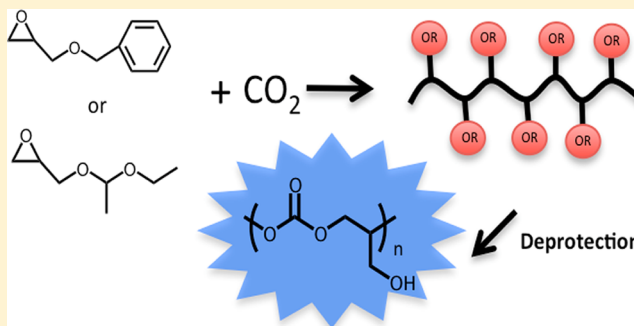
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### Supporting Information

**ABSTRACT:** The functional, aliphatic poly(1,2-glycerol carbonate) as a fundamental, simple polymer structure based on glycerol and CO<sub>2</sub> was prepared by combination of glycidyl ether monomers with carbon dioxide via two different approaches. The material was obtained by two-step procedures either via copolymerization of (i) ethoxy ethyl glycidyl ether (EEGE) or (ii) benzyl glycidyl ether (BGE) with CO<sub>2</sub>, followed by removal of the respective protecting groups via acidic cleavage for (i) and hydrogenation for (ii). The resulting protected polycarbonate structures and the targeted poly(1,2-glycerol carbonate) were investigated with <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy as well as 2D-NMR methods. Removal of both protecting groups was possible without significant backbone degradation; however, the hydrogenation route for (ii) turned out to be advantageous. All new poly(carbonate)s have been characterized with respect to their thermal behavior. Protected and deprotected poly(1,2-glycerol carbonate)s were obtained with molecular weights in the range of 5000–25 200 g/mol and a PDI from 1.24 to 2.33. The degradation kinetics of poly(1,2-glycerol carbonate) in DMF has also been studied, demonstrating rather rapid degradation within several days to oligomers and cyclic carbonates.



## ■ INTRODUCTION

Aliphatic poly(carbonate)s (PCs) represent a promising class of biodegradable polymers for a variety of applications.<sup>1–4</sup> Currently, there is an increasing interest in functional, aliphatic polycarbonates that can be prepared directly from carbon dioxide (CO<sub>2</sub>).<sup>5–11</sup> Functional groups that are distributed randomly at the polymer backbone could be employed to tailor the chemical properties of the materials, such as hydrophilicity/hydrophobicity, biocompatibility, and biodegradability. Ring-opening polymerization (ROP) of six-membered cyclic carbonates is the established pathway for the synthesis of functional aliphatic PCs.<sup>12–20</sup> For the synthesis of poly(trimethylene carbonate) (PTMC) and poly(dimethyl trimethylene carbonate) and their functional derivatives,<sup>21,22</sup> cyclic carbonates bearing different functional groups have been developed. A comprehensive overview of currently known cyclic carbonate monomers was recently given by Zhang and co-workers.<sup>2</sup>

An alternative method for the synthesis of aliphatic PCs is the copolymerization of epoxides and carbon dioxide (CO<sub>2</sub>). Since 1969, various catalysts have been developed for this reaction.<sup>23–25</sup> Mostly cobalt(III)–salen, phenoxide zinc, or  $\beta$ -diiminate–zinc complexes are used.<sup>26–31</sup> For example styrene oxide,<sup>32</sup> limonene oxide,<sup>33</sup> indene oxide,<sup>34</sup> and epichlorohydrin<sup>5</sup> have been copolymerized with CO<sub>2</sub>. However, the selective synthesis of polycarbonates from epoxides with electron-

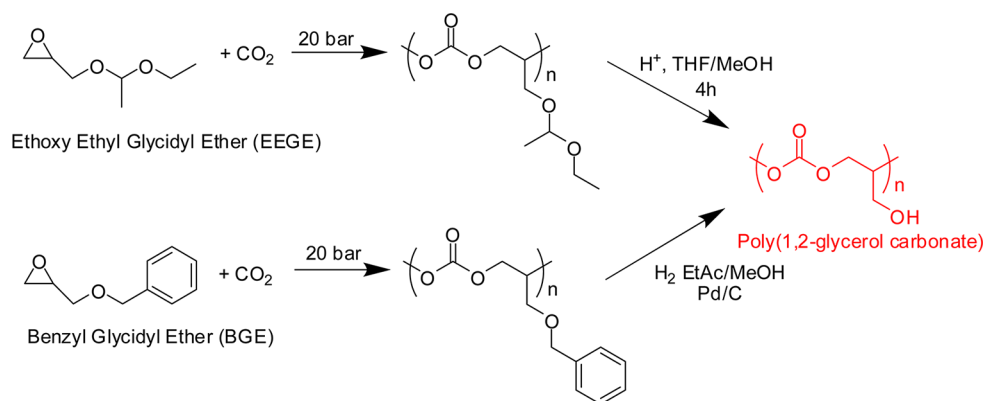
withdrawing groups still remains a challenge, and most often propylene oxide and cyclohexene oxide have been used.<sup>23–25,35</sup> To date, glycidyl ethers have rarely been employed, since copolymerization with carbon dioxide using common catalysts is not possible.

The fundamental poly(glycerol carbonate) structures that merely consist of glycerol and CO<sub>2</sub> as building units are highly intriguing. Both carbon dioxide and glycerol are readily available and inexpensive compounds, and the characteristics of fundamental polymer structures based on these two building units are promising with respect to potential application in various areas. There are two poly(glycerol carbonate) isomers: poly(1,2-glycerol carbonate) and poly(1,3-glycerol carbonate). The widely known poly(1,3-glycerol carbonate) is generally prepared by ROP of 5-benzoyl 1,3-dioxan-2-on (BTMC), followed by hydrogenation to remove the benzyl protecting group.<sup>36–38</sup> Unfortunately, the cyclic monomer has to be prepared in a three-step procedure. Poly(1,2-glycerol carbonate) would have to be prepared by ROP of the five-membered cyclic glycerol carbonate. However, the ROP of five-membered carbonates usually results in elimination of CO<sub>2</sub>, leading to the

**Received:** January 14, 2013

**Revised:** April 13, 2013

**Published:** April 29, 2013

**Scheme 1. Synthetic Strategies for the Preparation of the Elusive Poly(1,2-glycerol carbonate) via Copolymerization of CO<sub>2</sub> and EEGE or BGE and Subsequent Deprotection**

formation of a polycarbonate containing a significant fraction of ether groups in the polymer backbone.<sup>12</sup>

In this work we target the preparation of poly(1,2-glycerol carbonate) directly from carbon dioxide (CO<sub>2</sub>) and suitable glycidyl ethers with a subsequent deprotection step. It is known that glycidyl ethers can be polymerized with the simple zinc catalyst systems already developed by Inoue in 1969.<sup>39–41</sup> It was suggested that the epoxide/CO<sub>2</sub> copolymerization proceeds via alternating insertion of CO<sub>2</sub> and epoxide into the Zn–O bond.<sup>42,43</sup> However, in the past decades only scattered efforts have been made to copolymerize glycidyl ethers with CO<sub>2</sub>.<sup>9,44</sup> For instance, cross-linkable poly(propylene carbonate) was prepared by Tao et al.<sup>41</sup> and Listos and co-workers using allyl glycidyl ether as a comonomer.<sup>45</sup> Other epoxides such as phenyl glycidyl ether<sup>46</sup> or linear aliphatic glycidyl ethers and their copolymers with carbon dioxide have been explored as novel ion conducting materials.<sup>44</sup> Furthermore, in a recent work we described the copolymerization of stable, hydroxyl-functional polycarbonates with glycerol side chains using isopropylidene (glyceryl glycidyl ether) and carbon dioxide.<sup>11</sup>

Various epoxides suitable for the preparation of poly(1,2-glycerol carbonate) have been used by our group and others for the preparation of functional polyethers, including ethoxyethyl glycidyl ether (EEGE) and benzyl glycidyl ether (BGE).<sup>47,48</sup> After deprotection, EEGE and BGE release hydroxyl groups.

Using EEGE or BGE in a copolymerization reaction with carbon dioxide, poly(1,2-glycerol carbonate) is accessible (Scheme 1). The respective glycidyl ether monomers can be prepared in one-step procedures, starting from commercially available reagents. Polymerization with carbon dioxide leads to the hitherto unknown polycarbonate structures poly(ethoxyethyl glycidyl ether carbonate (P(EEGE C))) and poly(benzyl glycidyl ether carbonate) (P(BGE C)). From both polymers, the fundamental poly(1,2-glycerol carbonate) polymer structure can be obtained after deprotection. This polymer was mentioned by Inoue et al. in 1979; however, no further characterization was given.<sup>39</sup> To the best of our knowledge, poly(1,2-glycerol carbonate) has not been studied and characterized to date. In contrast to the other isomer poly(1,3-glycerol carbonate), which is a widely known biocompatible copolymer possessing secondary hydroxyl groups after deprotection,<sup>36,37</sup> poly(1,2-glycerol carbonate) contains primary hydroxyl groups. Recently, poly(1,3-glycerol carbonate) has gained considerable interest for biomedical applications; e.g., Grinstaff and co-workers studied the

conjugation of various hydrophobic biocompatible side chains to poly(glycerol-*co*-caprolactone) copolymers, aiming at prolonged and controlled release of a chemotherapeutic agent as well as other functionalized poly(glycerol-*co*-caprolactone) films.<sup>53–56</sup> Putnam and co-workers reported the synthesis of the random poly(carbonate ester)s derived from lactic acid and dihydroxyacetone by ring-opening polymerization.<sup>57,58</sup>

This current report describes both the novel poly(glycerol carbonate)s available from the combination of glycidyl ether chemistry with CO<sub>2</sub> as well as the synthesis and properties of poly(1,2-glycerol carbonate).

## EXPERIMENTAL SECTION

**Instrumentation.** <sup>1</sup>H NMR spectra (300 and 400 MHz) and <sup>13</sup>C NMR spectra (75.5 MHz) were recorded using a Bruker AC300 or a Bruker AMX400 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in DMF (containing 0.25 g/L of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column (10<sup>6</sup>/10<sup>5</sup>/10<sup>4</sup> g mol<sup>−1</sup>), a UV detector (275 nm), and a RI detector. Calibration was carried out using poly(ethylene oxide) standards provided by Polymer Standards Service. DSC measurements were performed using a PerkinElmer DSC 8500 with a PerkinElmer CLN2 in the temperature range from −100 to 150 °C at heating rates of 10 K min<sup>−1</sup> under nitrogen.

**Reagents.** Benzyl glycidyl ether, epichlorohydrin (99%), and sodium hydroxide as well as dimethyl sulfoxide (puriss, over molecular sieve), tetrahydrofuran (puriss, over molecular sieve), and toluene (puriss, over molecular sieve) were purchased from Aldrich. Pyrogallol was recrystallized from benzene/EtOH. Deuterated chloroform-*d*<sub>1</sub> and DMSO-*d*<sub>6</sub> were purchased from Deutero GmbH. Carbon dioxide (99.995%) was purchased from Westfalen AG and used as received. All other solvents and reagents were purchased from Acros Organics. The synthesis of ethoxy ethyl glycidyl ether (EEGE) is described elsewhere.<sup>47,50</sup>

**Preparation of the Zn Catalyst.** The catalyst was prepared under argon immediately before use following the procedure described previously.<sup>49</sup> A solution of pyrogallol (0.47 g, 4 mmol) in 10 mL of 1,4-dioxane was slowly added to a stirred solution of ZnEt<sub>2</sub> (2 mmol in 35 cm<sup>3</sup> of dioxane) at room temperature. After the addition was complete, stirring was continued until the evolution of ethane stopped.

**Polymerization.** The copolymerization was carried out in dioxane in the presence of a catalytic system based on ZnEt<sub>2</sub> and pyrogallol at a molar ratio of 2:1. The above-described catalyst solution (2 mmol) and 50 mmol of epoxide were placed into a stainless steel autoclave filled with argon. CO<sub>2</sub> was then introduced at a pressure of ~20 bar. The reaction was carried out at room temperature for 72 h. The reaction was stopped by decompression of the autoclave. The resulting solution was diluted with CHCl<sub>3</sub>, washed with 10% HCl and twice

with water, dried with  $\text{MgSO}_4$ , precipitated in cold methanol, and dried in vacuum. Yields of the crude products were ca. 60% for P(EEGE-C) and >80% P(BGE-C). The purified polymers are white, soft solids that are soluble in acetone as well as chlorinated and aromatic solvents and insoluble in water, lower alcohols, and diethyl ether.

**Deprotection of Poly(EEGE carbonate).** The acetal protecting groups were removed by the addition of 10 wt % acidic ion exchange to a 20% solution of the polymer in MeOH/THF, stirring at room temperature for a period of 3 h. The ion-exchange resin was subsequently removed by centrifugation, and the reaction solution was concentrated in vacuum and then dried in vacuum overnight. Yields: 90–100%.

**Deprotection of Poly(BGE carbonate).** Poly(benzyl glycidyl ether carbonate) was dissolved in a 1:1 mixture of ethyl acetate and methanol, and palladium on activated charcoal (10%) was added. The reaction vessel was flushed with hydrogen (40 bar), and the reaction was allowed to stir for 24 h at 40 °C. The solution was filtered and concentrated, and the product was dried in vacuum. Poly(1,2-glycerol carbonate) was obtained as a soft, clear solid in 90% yield.

## RESULTS AND DISCUSSION

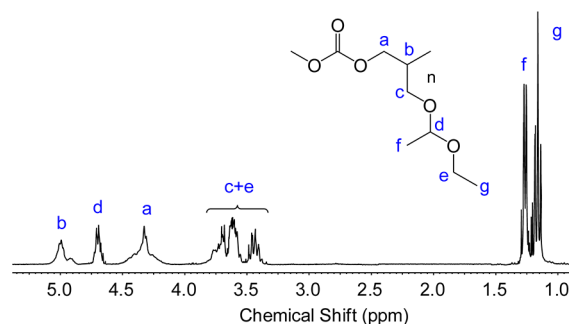
The synthesis of the zinc catalyst is based on the reaction of diethylzinc with pyrogallol in 1,4-dioxane. The ratio of 2:1 guarantees fast and complete conversion under ethane evolution. When the addition of pyrogallol to the diethylzinc solution was complete, stirring was continued until no more ethane was formed. The concentration of the catalyst can be calculated from the volume of ethane formed.

Moderate to medium molecular-weight polycarbonates with hydroxyl groups were obtained by combination of glycidyl ether chemistry and copolymerization of epoxides with  $\text{CO}_2$ . The synthesis was accomplished in a straightforward two-step procedure using protected glycidyl ethers as epoxide monomers. Two routes for the deprotection were investigated (Scheme 1).

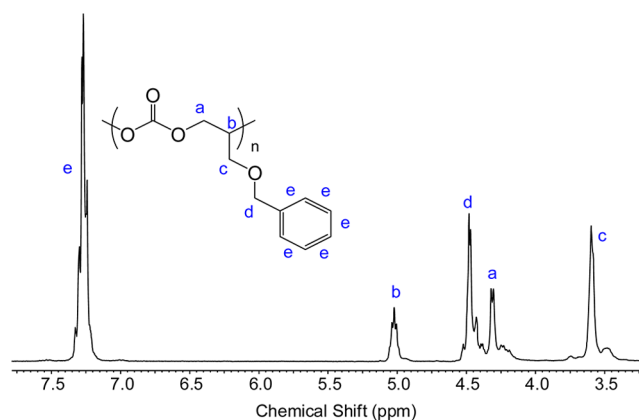
Starting from commercially available benzyl glycidyl ether (BGE), poly(benzyl glycidyl ether carbonate) (P(BGE-C)) was prepared in good yields (>80%). Neither polyether linkages nor cyclic carbonates were detected by  $^1\text{H}$  NMR spectroscopy. Ethoxy ethyl glycidyl ether was prepared as described in the literature.<sup>47,50</sup> Both copolymer syntheses were carried out at room temperature in a high-pressure autoclave (20 bar carbon dioxide pressure) for 72 h using a diethylzinc/pyrogallol catalyst system. Copolymerization with carbon dioxide led to poly(ethoxy ethyl ether carbonate) (P(EEGE-C) copolymers without ether linkages in the backbone. Increasing the temperature led to an increasing amount of a cyclic carbonate side product.<sup>51</sup> The resulting NMR spectra for both copolymers are shown in Figures 1 and 2.

After a certain period of reaction time the pressure was reduced to atmosphere to terminate the reaction. The purification process was followed as reported in the Experimental Section. The resulting samples were clear rubber-like and colorless amorphous solids. The structure of the copolymers obtained is shown in Scheme 1.

All synthesized polycarbonates were characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy. Molecular weights and polydispersities were determined using size exclusion chromatography (SEC, cf. Table 1). Most SEC results of the protected copolymers show a monomodal molecular weight distribution in the molecular weight range of 16 400–25 200 g/mol with a moderate PDI between 1.39 and 1.80. Some of the copolymers exhibited bimodal distributions, which is a typical phenomenon in the copolymerization of  $\text{CO}_2$  and epoxides when using



**Figure 1.**  $^1\text{H}$  NMR spectrum of poly(ethoxyethyl glycidyl ether carbonate).



**Figure 2.**  $^1\text{H}$  NMR spectrum of the poly(benzyl glycidyl ether carbonate) copolymer.

**Table 1. Overview of the Characterization Data for All Copolymer Samples Prepared<sup>a</sup>**

no.	sample	% carbonate linkages <sup>b</sup>	$M_n$ g/mol (SEC) <sup>c</sup>	PDI (SEC)	$T_g$ °C (DSC)
1	P(EEGE-C)	>99	17 000	1.46	−18.0
2	P(EEGE-C)	>99	16 400	1.39	−17.3
3	P(BGE-C)	>99	21 100	1.24	−22.0
4	P(BGE-C)	>99	25 200	1.80	−21.6
5	P(G-C) <sup>d</sup>	>99	5 370	2.33	−4.0
6	P(G-C) <sup>e</sup>	>99	17 800	1.67	−3.9

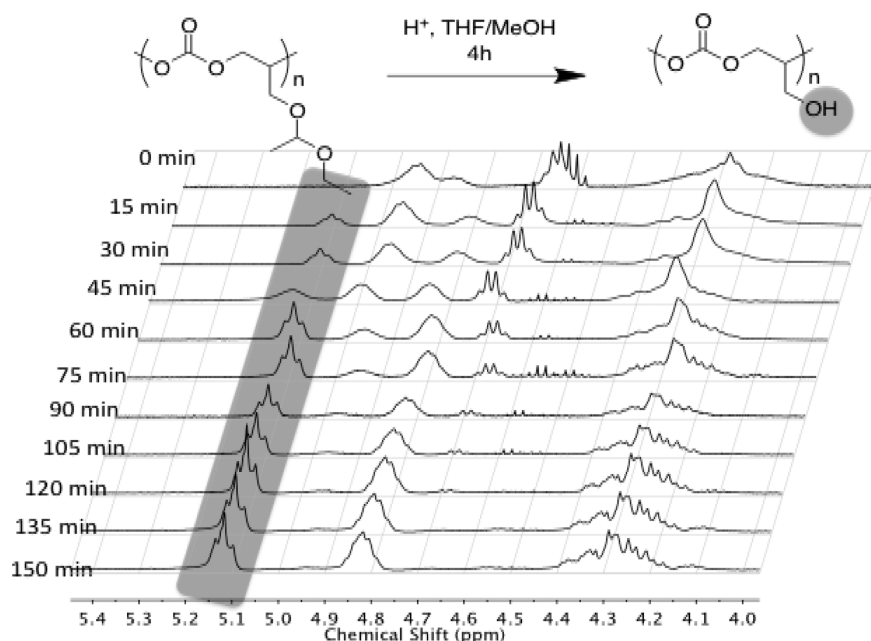
<sup>a</sup>Polymerization conditions: catalyst/epoxide 1:25; reaction time 72 h;  $\text{CO}_2$  pressure 20 bar. <sup>b</sup>Determined by  $^1\text{H}$  NMR spectroscopy.

<sup>c</sup>Determined by SEC calibrated with a polystyrene standard in DMF at 40 °C. <sup>d</sup>Obtained from P(EEGE-C). <sup>e</sup>Obtained from P(BGE-C).

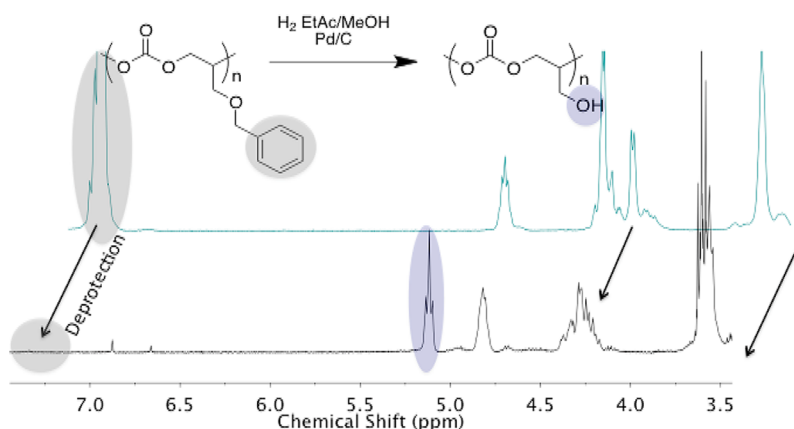
binary catalyst systems. This effect is caused by two reactive catalyst species and possible initiation by traces of water.

The alternating structure of the product was confirmed by IR and  $^1\text{H}$  NMR spectroscopy. All polymers show a strong IR absorption at around  $1750\text{ cm}^{-1}$ , which can be assigned to the  $\text{C}=\text{O}$  group of the linear carbonate, confirming the incorporation of carbon dioxide into the polymer as a carbonate structure. The characteristic vibration band of cyclic carbonate side products can usually be found at around  $1800\text{ cm}^{-1}$  and cannot be seen in the IR spectra (Figure S8).

In Figure 1, an exemplary  $^1\text{H}$  NMR spectrum of P(EEGE-C) in  $\text{CDCl}_3$  is shown (sample 1). In addition to the polycarbonate backbone signal ( $\delta = 5.00\text{ ppm}$ , signal b and  $\delta = 4.30\text{ ppm}$ , signal a), the resonances for the side group ( $\delta = 3.3\text{--}3.8\text{ ppm}$ , signal c) and the acetal protecting (signals d–f) group can be



**Figure 3.** Time-resolved 300 MHz  $^1\text{H}$  NMR spectra for the acidic deprotection of poly(ethoxyethyl glycidyl ether carbonate).



**Figure 4.**  $^1\text{H}$  NMR spectra for the acidic deprotection of poly(benzyl glycidyl ether carbonate). Middle spectrum: incomplete deprotection.

found. The glycidyl ether methylene signal (signal c) splits up, which is clearly observable in 2D NMR spectroscopy (Figures S3–S6).

No epoxide homopolymer that would be manifested by ether linkages can be detected in the  $^1\text{H}$  NMR spectra. Such structures would result in additional signals between 3 and 4 ppm. This supports the strictly alternating placement of ethoxyethyl glycidyl ether or benzyl glycidyl ether and  $\text{CO}_2$ . For signal b a small shoulder can be seen. Since the work-up was carried out under acidic conditions (cf. Experimental Section), some acetal protecting groups might be already cleaved; however, this effect was not observed for all samples. The structure of poly(benzyl glycidyl ether carbonate) was also confirmed by  $^1\text{H}$  NMR spectroscopy. The polycarbonate backbone peaks, signals a and b, can be found at  $\delta = 4.28$  and 5.05 ppm; the benzyl proton signal appears at  $\delta = 7.30$  ppm (signal e). Signal d ( $\delta = 4.50$  ppm) and signal c ( $\delta = 3.6$  ppm) can be assigned to the four side-chain methylene protons.

All assignments were confirmed by 2D NMR spectroscopy (Figure S5).  $^{13}\text{C}$  NMR measurements for both polymers show

a signal at around  $\delta = 154$  ppm of the carbonyl group ( $\text{C}=\text{O}$ ) in the main chain.

The thermal properties of poly(ethoxyethyl ether carbonate) and poly(benzyl glycidyl ether carbonate) have not been studied to date. They were examined by differential scanning calorimetry (DSC). No melting point was observed for any of the copolymers, confirming their amorphous character. The results are summarized in Table 1. The glass-transition temperature ( $T_g$ ) of P(EEGE-C) and P(BGE-C) is  $-17.3$  and  $-21.6$   $^\circ\text{C}$ , respectively. Compared to benzyl-protected poly(1,3-glycerol carbonate) having a glass transition temperature of  $0$   $^\circ\text{C}$ , which was described by Liu et al., the  $T_g$  is lower in our case.<sup>38</sup> Both P(EEGE-C) and P(BGE-C) are colorless, rubber-like solids, which are soluble in toluene, benzene, chloroform, DMF, and DMSO.

**Deprotection.** Acidic removal of the ethoxyethyl protecting group yielded linear poly(1,2-glycerol carbonate). Deprotection of the P(EEGE-C) polymer obviously is not trivial, since acidic deprotection can not only cleave the acetal protection group but also may affect the polycarbonate backbone, when the conditions are too harsh. However, acetal cleavage in our



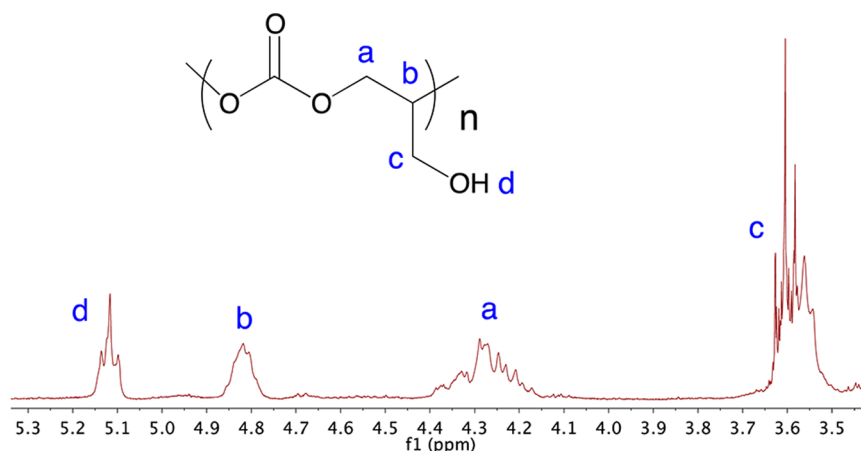


Figure 5.  $^1\text{H}$  NMR spectrum of poly(1,2-glycerol carbonate).

experience is usually faster than carbonate degradation. In order to study the kinetics of the deprotection, the reaction was monitored by  $^1\text{H}$  NMR spectroscopy. The reaction was carried out in a THF/methanol mixture, using acidic ion-exchange resin (Dowex 50WX8), and samples were taken in increasing intervals from 5 to 30 min for 4 h. The results of the study of deprotection kinetics are shown in Figure 3.

In Figure 3, the spectral region from  $\delta = 5.4$  to 4.0 ppm is shown. Deprotection was monitored by comparison of the intensity of the decreasing methylene signal of the glycidyl ether and the integration of the increasing hydroxyl group proton signal. The deprotection was complete after 3.5 h. Prolonged reaction times led to polymer degradation. Moreover, after extended periods cross-linking occurred, when using hydrochloric acid as a proton source for the deprotection, and the resulting copolymer became insoluble in both organic and aqueous solvents. In summary, precisely defined conditions are required to obtain soluble, fully deprotected poly(1,2-glycerol carbonate).

Deprotection of the benzyl groups of poly(benzyl glycidyl ether carbonate) by hydrogenation using Pd/C as a catalyst is also shown in Scheme 1 (vide supra). The reaction was not successful when using THF, DMF or 1,4-dioxane as solvents, even if the temperature was raised to 60  $^\circ\text{C}$ . However, removal of the benzyl groups could be carried out using an ethyl acetate (EtOAc) methanol mixture 1:1 as a solvent at 40  $^\circ\text{C}$  for 24 h and at a pressure of 40 bar. At room temperature the reaction remained incomplete. When running the deprotection reaction for more than 24 h, degradation of the polymer backbone commenced. The  $^1\text{H}$  NMR spectrum of the deprotected sample of poly(1,2-glycerol carbonate) obtained in  $\text{DMSO}-d_6$  demonstrates complete disappearance of the benzyl proton signals ( $\delta = 7.1$  ppm) (Figure 4).

**Poly(1,2-glycerol carbonate).** Both synthesis and deprotection strategies lead to the same product, the poly(1,2-glycerol carbonate), which can be seen in Figure 5, however, with different molecular weights. In both cases full removal of the protecting groups was achieved. Size exclusion chromatography measurements and detailed NMR studies of the resulting poly(1,2-glycerol carbonate) evidence that no (or very little) chain degradation occurred. The backbone signals are found at  $\delta = 4.85$  and 4.25 ppm, whereas the side group methylene signal and the hydroxyl group signals are observed at  $\delta = 3.55$  and 5.12 ppm. No cyclic carbonate degradation products were found in NMR as well as in IR spectra, and no cyclic carbonate

signal typical for degradation can be found.  $^{13}\text{C}$  NMR spectroscopy also confirmed the structure of poly(1,2-glycerol carbonate), as can be seen in Figure 6. Signal a in Figure 6 at

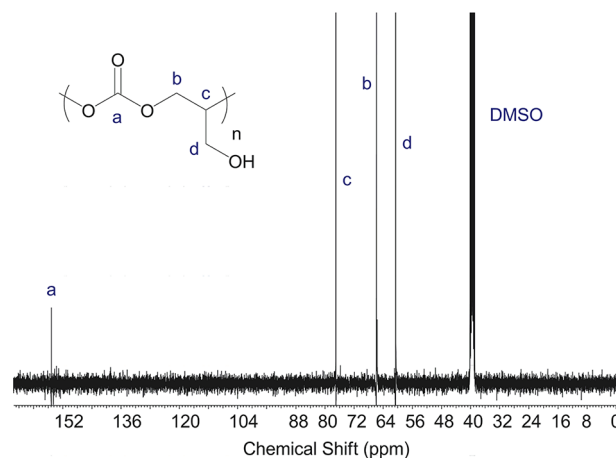
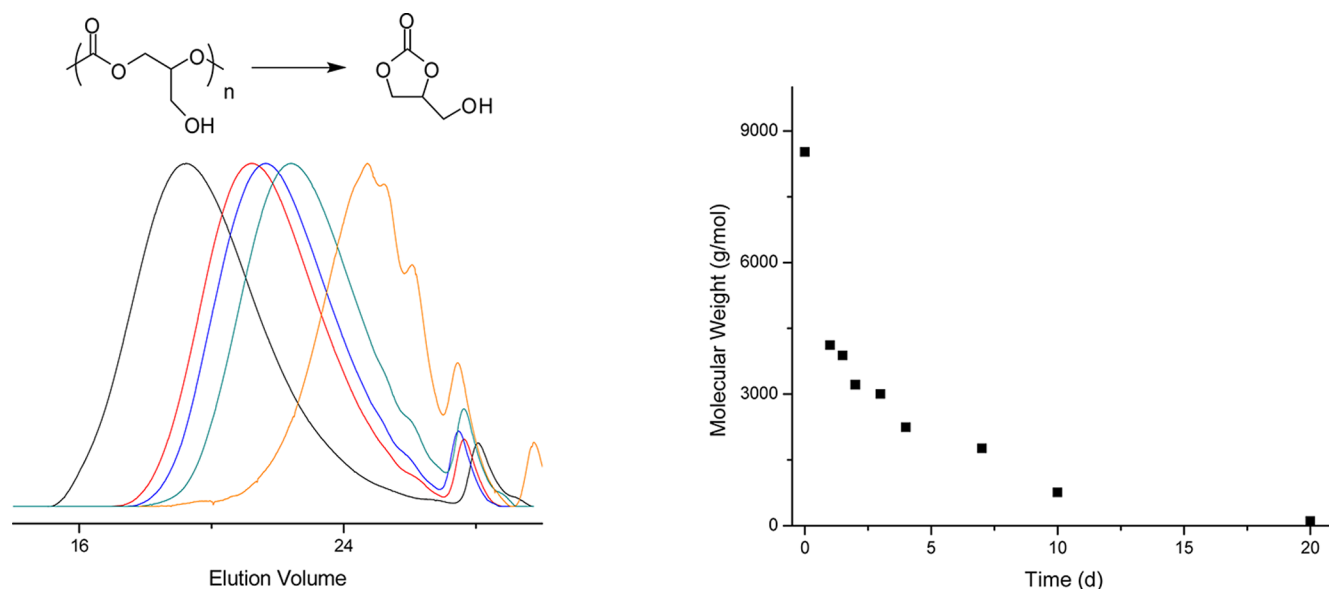


Figure 6.  $^{13}\text{C}$  NMR spectrum of poly(1,2-glycerol carbonate).

around  $\delta = 154$  ppm can be assigned to the carbonyl group ( $\text{C}=\text{O}$ ) in the main chain, and it is obvious that all signals of the protection groups have disappeared (compare Figures S5 and S8).

Figure 5 shows the expected, simple  $^1\text{H}$  NMR spectrum for the fundamental poly(1,2-glycerol carbonate). For the polymer obtained from the P(BGE-C) copolymer, SEC analysis results reveals that the deprotection reaction did not result in a remarkable decrease in molecular weight or significantly broader molecular weight distributions. In contrast, the poly(1,2-glycerol carbonate) copolymers obtained from P-(EEGE-C) showed slightly lower molecular weights than the precursor, maybe due to a low extent of degradation of the polymer backbone. However, all poly(1,2-glycerol carbonate) samples obtained possessed unimodal distributions with moderate PDIs (Figure 7).

**Properties of Poly(1,2-glycerol carbonate) and Degradation Studies.** The resulting colorless, rubber-like poly(1,2-glycerol carbonate) was insoluble in toluene, benzene, and chloroform but soluble in DMF and DMSO. In methanol and water swelling of the material was observed. The isomer structure, poly(1,3-glycerol carbonate), on the other hand, is



**Figure 7.** (a, left) SEC results for the degradation of poly(1,2-glycerol carbonate) in DMF. (b, right) The resulting molecular weights plotted versus time.

also soluble in DMF and DMSO and partially soluble in  $\text{CH}_3\text{OH}$ , but its solubility in  $\text{CHCl}_3$  and ether is poor.<sup>38</sup>

Compared to the protected copolymers, the glass-transition temperature of the poly(1,2-glycerol carbonate) is observed at  $-4^\circ\text{C}$  and therefore higher than that of the protected copolymers, which we ascribe to the interaction of the hydroxyl groups.

One of the central properties of poly(glycerol carbonate)s is their hydrolytic degradability. The degradation behavior of poly(1,2-glycerol carbonate) in solution was investigated at neutral pH in bulk, DMF, and THF. Size exclusion chromatography measurements were performed in DMF and THF for several days, and the decrease in molecular weight was followed. The results can be seen in Figure 7 and Figure S14.

During degradation the more thermodynamically stable cyclic 1,2-glycerol carbonate with a molecular weight of 118.09 g/mol is formed. The decrease in molecular weight can clearly be seen in the SEC traces (Figure 7a). For the degradation in DMF after 20 days only oligomers are left in the solution (Figure 7). Degradation in THF was even faster; i.e., after 2 weeks only the cyclic five-membered glycerol carbonate was observed (cf. Figure S14). To investigate the degradation in bulk, a poly(1,2-glycerol carbonate) sample was stored at  $-28^\circ\text{C}$ , i.e., below the glass transition for several weeks. After 8 weeks a significant amount of cyclic carbonate was formed also in this case (Figure S15). Compared to other poly(carbonate)s used in biomedical application such as poly(trimethylene carbonate), the degradation rate of poly(1,2-glycerol carbonate) is much faster, whereas the related poly(1,2-propylene carbonate), which can be prepared from carbon dioxide and propylene oxide, completely suppresses enzymatic attack and is also stable in solution.<sup>59,60</sup>

Degradation took also place in the solid state in moist atmosphere, as indicated by the appearance of an infrared absorption at about  $1800\text{ cm}^{-1}$  at the expense of that at  $1750\text{ cm}^{-1}$ , belonging to the carbonyl stretching vibration of the five-membered cyclic glycerol carbonate produced. The rapid degradation of poly(1,2-glycerol carbonate) compared to poly(propylene carbonate) (PPC) or also poly(1,3-glycerol

carbonate) is due to an intramolecular attack of the pendant hydroxyl groups of poly(1,2-glycerol carbonate) at the carbonate linkage and subsequent formation of the thermodynamically stable 5-membered cyclic glycerol carbonate (Figure 7).

Water absorption is a simple way to evaluate the hydrophilicity of polymers, and it is defined as the weight percentage of water in wet polymer. It was measured after the polymer had been immersed in distilled water to equilibrium at room temperature.<sup>52</sup> The water absorbance of poly(1,2-glycerol carbonate) compared to the protected analogues is considerably higher, confirming that the presence of hydroxyl groups at the polymer chains result in an enhancement of chain hydrophilicity. The same results were also found for poly(1,3-glycerol carbonate).

## CONCLUSIONS

Two routes for the synthesis of the hitherto elusive, fundamental polymer structure poly(1,2-glycerol carbonate) have been developed. Since the building units glycerol and carbon dioxide represent readily available waste products, the behavior of this basic polymer structure is interesting. On the one hand, a vast amount of almost pure carbon dioxide is formed as a byproduct in many processes for energy production, and glycerol is obtained as a side product in the production of bioethanol. Reacting ethoxyethyl glycidyl ether and benzyl glycidyl ether in a copolymerization with carbon dioxide using a simple zinc catalyst system, protected poly(1,2-glycerol carbonate)s were obtained.  $^1\text{H}$  NMR spectra as well as  $^{13}\text{C}$  NMR and IR spectroscopy confirmed the structure of the resulting polymers. The protecting groups could be cleaved in both cases, either by acidic treatment or by hydrogenation, respectively. However, hydrogenation turned out to be the more effective way, since no reduction of molecular weights was observed in this case. For poly(ethoxy ethyl glycidyl ether carbonate) the protection groups had to be removed under acidic conditions, which leads to a certain degradation of the polymer backbone and lowered molecular weight after deprotection, since the carbonate bonds are also acid labile.

Thus, the synthesis of poly(1,2-glycerol carbonate) using a benzyl glycidyl ether/CO<sub>2</sub> copolymerization represents the preferred route.

Furthermore, thermal properties and degradation behavior of all new polycarbonates have been studied. DSC results show that all synthesized polymers are amorphous materials with glass transitions below 0 °C. Preliminary examination in solution as well as in bulk revealed that poly(1,2 glycerol carbonate) is a hydrophilic, degradable material showing considerably faster degradation kinetics than the known poly(1,3-glycerol carbonate).

In summary, the combination of CO<sub>2</sub> and glycidyl ether chemistry offers an innovative route for the synthesis of poly(1,2-glycerol carbonate), a hitherto elusive polymer, which consists only of carbon dioxide and glycerol, two prominent nontoxic side products in chemical industry.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Additional data, SEC elugrams, and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

J.G. is grateful for a fellowship through the Excellence Initiative (DFG/GSC 266) in the context of the graduate school of excellence "MAINZ" (Materials Science in Mainz). J.G. also thanks the Fond der Chemischen Industrie (FCI) for a fellowship. Furthermore, we thank Pascal Guckes and Tobias Fiedler for technical assistance.

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