

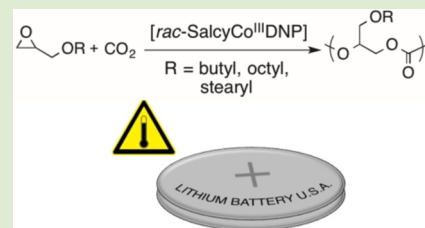
# Synthesis of Aliphatic Poly(ether 1,2-glycerol carbonate)s via Copolymerization of CO<sub>2</sub> with Glycidyl Ethers Using a Cobalt Salen Catalyst and Study of a Thermally Stable Solid Polymer Electrolyte

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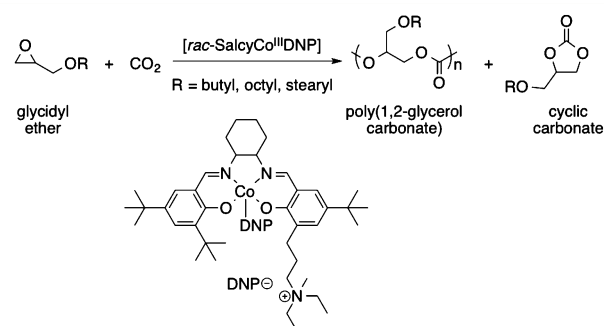
## Supporting Information

**ABSTRACT:** The synthesis and characterization of linear poly(ether 1,2-glycerol carbonate)s derivatized with pendant butyl, octyl, or stearyl tethers are reported. The polymers are obtained via the ring-opening copolymerization of butyl, octyl, or stearic glycidyl ethers with carbon dioxide using the  $[rac\text{-SalcyCo}^{\text{III}}\text{DNP}]$  catalyst bearing a quaternary ammonium salt. Synthesized polymers were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, FT-IR, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and rheometry. Polymers with controlled molecular weights in the range of 8970–31 900 g/mol were obtained with low polydispersities between 1.1 and 1.4. Thermal properties of the materials confirm amorphous structures of the polymers with butyl and octyl chains, with glass transition temperatures of –24 and –34 °C, respectively. The stearyl tether polymer exhibited a melting point of 55 °C. Additionally, the potential of poly(butyl ether 1,2-glycerol carbonate) as a thermally stable solid polymer electrolyte was investigated, and it exhibits temperature-dependent conductivity with values comparable to those of optimized PEO-based electrolytes.



Aliphatic polycarbonates are finding ever-increasing uses in the manufacturing, electronics, and medical industries because of their high thermal, tough mechanical, and scratch-resistant properties, as well as biodegradability.<sup>1–3</sup> This is in part a result of improved procedures to synthesize polycarbonates which provide finer control over the molecular weights and polydispersities using Zn, Co, and Cr metal complexes compared to the use of phosgene or metal salts.<sup>4–8</sup> From a chemical perspective, these metal-complex-catalyzed copolymerizations of epoxides with carbon dioxide (CO<sub>2</sub>) also address the need to utilize a natural and abundant C1 feedstock for synthesis and represent a conscious shift to a green approach to materials formation.<sup>9</sup>

Since the first report by Inoue in 1969, various alternating copolymerizations of CO<sub>2</sub> with epoxides are described in the literature.<sup>10</sup> Recently, the syntheses of polycarbonates, containing a glycerol-like unit in the backbone, are reported using Co or Zn catalysts and the corresponding glycidyl ethers and CO<sub>2</sub>.<sup>5,11–28</sup> Building on these results, our interest in poly(ether 1,2-glycerol carbonate)s stems from the need to expand the repertoire of aliphatic polycarbonates, investigate their structure–property relationships, and their possible application as thermally stable solid polymer electrolytes for downhole oil reservoir battery applications at high temperatures. Herein, we report: (1) the synthesis of aliphatic poly(ether 1,2-glycerol carbonate)s via copolymerization of glycidyl ethers carrying pendant butyl, octyl, or stearyl tethers, with CO<sub>2</sub> in the presence of a bifunctional  $[rac\text{-SalcyCo}^{\text{III}}\text{DNP}]$  catalyst (Figure 1), (2) the dependence of thermal properties and decomposition temperature on the side chain composition, and (3)



**Figure 1.** Reaction of glycidyl ether and CO<sub>2</sub> to yield poly(ether 1,2-glycerol carbonate) and cyclic carbonate (DNP = 2,4-dinitrophenoxy).

the conductivity of poly(butyl ether 1,2-glycerol carbonate) films doped with lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) as a function of temperature, with performance at 100 and 120 °C.

By tailoring the length of the tether chain on the polymer backbone, we can alter the physicochemical properties of the polymers with the goal to identify a polymer with a low glass transition temperature,  $T_g$ , and high thermal stability. Poly(butyl ether 1,2-glycerol carbonate) was first synthesized via ring-opening copolymerization of butyl glycidyl ether with CO<sub>2</sub> (220 psi) using the bifunctional  $[rac\text{-SalcyCo}^{\text{III}}\text{DNP}]$  catalyst

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**Table 1. Optimization of Reaction Parameters for Copolymerization of CO<sub>2</sub> and Butyl Glycidyl Ether<sup>a</sup>**

| entry          | catalyst loading | temp (°C) | TOF (h <sup>-1</sup> ) | selectivity <sup>b</sup> (%) | T <sub>g</sub> (°C) | T <sub>decomp</sub> <sup>5/50</sup> (°C) | M <sub>n</sub> <sup>d</sup> (kg/mol) | PDI (M <sub>w</sub> /M <sub>n</sub> ) |
|----------------|------------------|-----------|------------------------|------------------------------|---------------------|--|--------------------------------------|---------------------------------------|
| 1              | 2000:1           | 25        | 65                     | 99                           | -22                 | 222/253                                  | 19.3                                 | 1.3                                   |
| 2              | 2000:1           | 40        | 119                    | 98                           | -24                 | 219/269                                  | 20.9                                 | 1.3                                   |
| 3              | 2000:1           | 60        | 183                    | 91                           | -25                 | 210/261                                  | 23.8                                 | 1.2                                   |
| 4 <sup>e</sup> | 2000:1           | 40        | 57                     | 98                           | ND                  | ND                                       | ND                                   | ND                                    |
| 5              | 4000:1           | 40        | 105                    | 99                           | -22                 | 215/259                                  | 19.3                                 | 1.1                                   |
| 6              | 10000:1          | 40        | ND                     | ND                           | ND                  | ND                                       | ND                                   | ND                                    |
| 7 <sup>f</sup> | 2000:1           | 40        | 150                    | 97                           | -23                 | 216/272                                  | ND                                   | ND                                    |
| 8 <sup>g</sup> | 2000:1           | 40        | 70                     | 95                           | -38                 | 217/273                                  | 29.3                                 | 1.2                                   |

<sup>a</sup>All reactions were performed in neat butyl glycidyl ether in a 15 mL autoclave under 220 psi of CO<sub>2</sub> pressure to 40–60% conversion (2–3 runs). ND = Not Determined. TOF = ([product]/[product + monomer])·catalyst loading·h<sup>-1</sup> determined by <sup>1</sup>H NMR. <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>The temperature at 5 and 50% weight loss, respectively, on the TGA curve of the copolymers. <sup>d</sup>Determined by GPC analysis using polystyrene as standards. All resultant polycarbonates showed bimodal distribution. <sup>e</sup>Reaction was run in 1 mL of toluene. <sup>f</sup>Reaction was run under 440 psi of CO<sub>2</sub> pressure. <sup>g</sup>Reaction was run to >93% conversion as determined by <sup>1</sup>H NMR.

**Table 2. Copolymerization of CO<sub>2</sub> and Butyl, Octyl, and Stearyl Glycidyl Ethers<sup>a</sup>**

| entry          | tether length (C <sub>n</sub> ) | time (h) | TOF (h <sup>-1</sup> ) | selectivity <sup>b</sup> (%) | T <sub>g</sub> (°C) | T <sub>decomp</sub> <sup>5/50</sup> (°C) | M <sub>n</sub> <sup>d</sup> (kg/mol) | PDI (M <sub>w</sub> /M <sub>n</sub> ) |
|----------------|---------------------------------|----------|------------------------|------------------------------|---------------------|--|--------------------------------------|---------------------------------------|
| 1              | butyl (4)                       | 8        | 119                    | 98                           | -24                 | 219/269                                  | 20.9 <sup>e</sup>                    | 1.3                                   |
| 2              | octyl (8)                       | 24       | 41                     | 93                           | -34                 | 206/273                                  | 31.9                                 | 1.4                                   |
| 3 <sup>f</sup> | stearyl (18)                    | 24       | 26                     | 94                           | 55 <sup>g</sup>     | 199/249                                  | 8.97                                 | 1.3                                   |

<sup>a</sup>All reactions were performed in neat glycidyl ethers in a 15 mL autoclave under 220 psi of CO<sub>2</sub> pressure at 40 °C and 2000:1 catalyst loading to 40–60% conversion. TOF = ([product]/[product + monomer])·catalyst loading·h<sup>-1</sup> determined by <sup>1</sup>H NMR. <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>The temperature at 5 and 50% weight loss, respectively, on the TGA curve of the copolymers (Figures S13–15, Supporting Information). <sup>d</sup>Determined by GPC analysis using polystyrene as standards. <sup>e</sup>Resultant polycarbonates showed bimodal distribution. <sup>f</sup>Reaction was run in 0.5 mL of toluene. <sup>g</sup>Melting point was observed instead of T<sub>g</sub>.

with DNP (2,4-dinitrophenoxy) as an axial ligand and quaternary ammonium salt on the ligand framework (Table 1). This catalyst has been reported to be stable and active under elevated temperatures and diluted conditions.<sup>25,29,30</sup> During the optimization studies, we obtained polymers with low polydispersities (PDIs) in the range of 1.1–1.3 and bimodal distributions of molecular weights in the range of 19 300–29 300 g/mol, containing >99% carbonate linkage with >90% selectivity for the polymer over cyclic carbonate (Table 1). In order to obtain significant quantities of the polymer, the polymerizations were stopped upon reaching 40–60% conversion. It is known that at higher conversion cyclic carbonate is formed via depolymerization.<sup>5</sup> At a monomer-to-catalyst ratio of 2000:1, increasing the temperature from 25 to 60 °C resulted in an increase in catalyst turnover frequency (TOF) from 65 to 183 h<sup>-1</sup>, with slightly compromised selectivity of 91% (Table 1, entry 3).<sup>14,31,32</sup> This is attributed to a lower viscosity of the reaction mixture at higher temperatures and, therefore, an increased robustness of the catalyst. Additionally, to determine the effect of the viscosity of the reaction mixture, the reaction was run in 1 mL of toluene at a 2000:1 catalyst loading which resulted in a decrease in TOF from 119 to 57 h<sup>-1</sup> (Table 1, entries 2 and 4). Contrary to our expectations, decreasing catalyst loading to 4000:1 resulted in a slight decrease in catalyst activity as compared to the conditions with a higher catalyst concentration (Table 1, entries 2 and 5). At catalyst loading of 10000:1, no reaction took place (Table 1, entry 6).

Subsequently, we carried out copolymerizations at higher CO<sub>2</sub> pressures of 440 psi. There was a small change in reactivity as the catalyst activity increased from 119 to 150 h<sup>-1</sup> with a slight drop of selectivity from 98 to 97% (Table 1, entries 2 and 7). Running the reaction for prolonged time resulted in nearly complete conversion of the monomer (>93%) with TOF of 70 h<sup>-1</sup> and high selectivity of 95% (Table 1, entry 8).

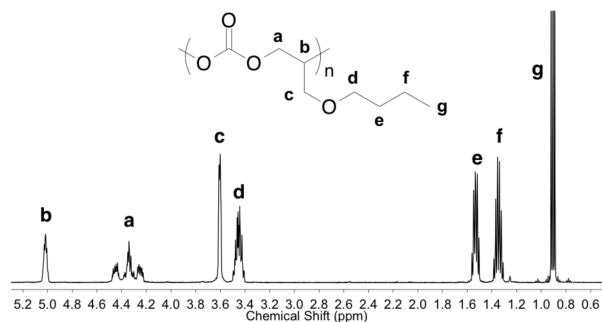
Under the optimized reaction conditions (220 psi, 40 °C, 2000:1 catalyst loading), epoxides with longer alkyl chains (octyl and stearic) were copolymerized with CO<sub>2</sub> using the bifunctional catalyst (Table 2). Poly(octyl ether 1,2-glycerol carbonate) was synthesized with TOF of 41 h<sup>-1</sup> and selectivity of 93%, while poly(stearyl 1,2-glycerol carbonate) was synthesized with TOF of 26 h<sup>-1</sup> and selectivity of 94% (Table 2, entries 2 and 3). Completely alternating copolymers were obtained with only small quantities of cyclic carbonates, albeit with decreased catalytic activities.<sup>33</sup>

The catalyst, along with cyclic carbonate side product and unreacted monomer, can be efficiently removed from the synthesized polymer solution after copolymerization by precipitation in cold methanol and centrifugation (three cycles total). After purification, the cyclic carbonate side product was not observed in either <sup>1</sup>H NMR or FT-IR spectra (Figures S1–3 or S7–9, Supporting Information). All three polymers are soluble in DCM, THF, toluene, and chloroform but not in alcohols or water.

The molecular weights, determined by gel permeation chromatography (GPC), were lower than the theoretical values for all synthesized polymers (174 000 g/mol for poly(butyl ether 1,2-glycerol carbonate), 230 000 g/mol for poly(octyl ether 1,2-glycerol carbonate), and 370 000 g/mol for poly(stearyl ether 1,2-glycerol carbonate)). This may be due to the presence of adventitious water in the system that caused a rapid and reversible chain transfer.<sup>12,15,34,35</sup> For example, poly(butyl ether 1,2-glycerol carbonate) exhibited a narrow polydispersity index of 1.3 with a molecular weight of 20 900 g/mol (Table 2, entry 1). This result is an improvement over the previous report by Tominaga describing a zinc glutaric acid-catalyzed polymerization method, which afforded a polymer with a polydispersity index of 2.3 and a TOF of less than one.<sup>36</sup> Similar to poly(butyl ether 1,2-glycerol carbonate), the polycarbonates with octyl and stearyl side chain tethers

possessed narrow PDIs of 1.4 and 1.3 and molecular weights of 31 900 and 8970 g/mol, respectively (Table 2, entries 2 and 3).

As shown in the  $^1\text{H}$  NMR spectrum (Figure 2) of the synthesized poly(butyl ether 1,2-glycerol carbonate), the signals



**Figure 2.** Representative  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of poly(butyl ether 1,2-glycerol carbonate).

at 5.0 and 4.4 ppm correspond to the resonances of the methane CH (b) and methylene  $\text{CH}_2$  (a) of the carbonate moiety, respectively. The relationship of 1.0:2.1:2.0 of the CH (b),  $\text{CH}_2$  (a), and  $\text{CH}_2$  (c, glycidyl tether) confirms the alternating nature of the copolymer (for integration, see Figure S1, Supporting Information). The same integration ratios were observed in the  $^1\text{H}$  NMR spectra of the octyl and stearyl chain-containing copolymers (see S1).

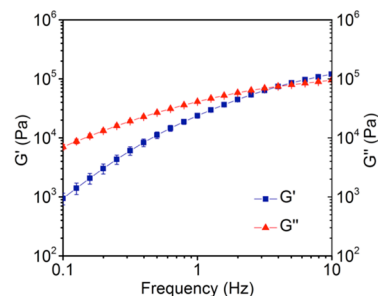
The incorporation of  $\text{CO}_2$  and corresponding glycidyl ethers was also verified with  $^{13}\text{C}$  NMR, as the linear carbonate resonance at  $\delta = 154$  ppm was observed for all three polymers (Figures S4–6, Supporting Information). Additionally, no polyether signals were detected in the corresponding  $^{13}\text{C}$  NMR spectra of the polymers confirming the carbonate backbone in the polymer.

The presence of  $\text{CO}_2$  in the polymer backbone was also observed by FT-IR spectroscopy (Figure S7–9, Supporting Information). All polymers exhibited a strong stretch at approximately  $1750\text{ cm}^{-1}$ , which was assigned to the  $\text{C}=\text{O}$  group in the linear carbonate chain. In all obtained FT-IR spectra, no vibration bands were observed at frequencies of about  $1800\text{ cm}^{-1}$  corresponding to the cyclic carbonate side product.

The thermal properties of poly(butyl ether 1,2-glycerol carbonate), poly(octyl ether 1,2-glycerol carbonate), and poly(stearyl ether 1,2-glycerol carbonate) were determined by differential scanning calorimetry (DSC). The amorphous character of the butyl and octyl tether-containing polymers was confirmed as no melting point was observed for these polymers but a  $T_g$  of  $-24$  and  $-34$   $^\circ\text{C}$ , respectively (Figures S10 and S11, Supporting Information). This exemplifies the dependence of  $T_g$  on the flexibility of the polymer chains: more sterically demanding and, hence, flexible chains permit internal mobility and reorientational motions, lowering the  $T_g$ . However, in the case of the stearic tether-containing polymer, a melting point at  $55$   $^\circ\text{C}$  was observed, indicating a semicrystalline structure (Figure S12, Supporting Information). This is attributed to the presence of hydrophobic interactions between the longer alkyl chains in the poly(stearyl ether 1,2-glycerol carbonate) polymer.

The butyl and octyl chain-containing polymers are honey-like materials, and the stearic chain-containing polymer is a solid. The viscoelastic properties of the poly(butyl ether 1,2-glycerol

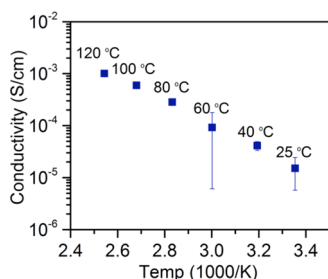
carbonate) were investigated using rheological measurements as they possess the highest  $T_g$  of the two polymers. First, the stress sweep test was performed at a frequency of 1 Hz to establish the range of linear viscoelasticity (Figure S16, Supporting Information). Then, the frequency sweep at 2% strain was determined (Figure 3). At frequencies below 4 Hz



**Figure 3.** Frequency sweep at 2% strain of poly(butyl ether 1,2-glycerol carbonate). Data are expressed as mean  $\pm$  standard deviation ( $n = 3$ ).

(gel point), the  $G''$  was greater than the  $G'$  signifying the liquid-like characteristic of the material, and at higher frequencies, the  $G'$  was greater than the  $G''$  affording a more elastic material. In the case of poly(stearyl ether 1,2-glycerol carbonate), we were unable to obtain conclusive rheological data due to the polymer's brittle nature as tested at a wide range of temperatures.

With regards to the development of the next generation batteries that operate at high temperatures, solid polymer electrolytes (SPEs) have attracted considerable attention due to their nonflammability, thermal stability, and nonvolatility.<sup>37–39</sup> Examples of extensively studied polymers include poly(ethylene oxide) (PEO), PEO derivatives, polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), and poly(vinylidene fluoride) (PVDF).<sup>40–42</sup> Recently, polycarbonates have been the focus for this application as these polymers contain a large fraction of oxygen to promote salt dissociation, have low glass transition temperatures (indicating increased segment mobility and ion transport), and have high thermal decomposition temperatures.<sup>36,43–49</sup> Within the polycarbonate class of polymers, those based on a glycerol repeat unit are of particular interest due to (1) their resemblance to the molecular structure of low molecular weight linear and cyclic carbonates (such as ethylene carbonate and dimethyl carbonate) used as traditional liquid electrolytes and (2) having a higher oxygen to carbon ratio than pure aliphatic polycarbonates. Thus, based on the above characteristics and its facile and controlled synthesis, we selected poly(butyl ether 1,2-glycerol carbonate) for evaluation as an SPE. The conductivity of poly(butyl ether 1,2-glycerol carbonate) was measured by electrochemical impedance spectroscopy over a range of temperatures from 25 to 120  $^\circ\text{C}$ . The polymer was mixed with LiTFSI at a  $[\text{Li}^+]:[\text{O}]$  ratio of 1:10. LiTFSI was used as the lithium salt dopant due to the salt's good thermal stability and high mobility. As shown in the plot of the ionic conductivity versus temperature (Figure 4), Vogel–Tammann–Fulcher (VTF) behavior was observed, indicating that the polycarbonate electrolyte was amorphous within the tested temperature range (also see Figure S17, Supporting Information).<sup>50</sup> This result was in agreement with the thermal data, which showed the absence of a melting point or glass transition in this temperature range. Low conductivity



**Figure 4.** Conductivity measurement of poly(butyl ether 1,2-glycerol carbonate) as a dependence of temperature by electrochemical impedance spectroscopy ( $n = 3$ ).

( $10^{-5}$  S/cm) was observed at 25 °C. At temperatures above 100 °C, the conductivity significantly increased by approximately 2 orders of magnitude and reached  $10^{-3}$  S/cm at 120 °C. This result is consistent with increased polymer chain mobility and, thus, enhanced Li salt mobility and conductivity. These values are comparable to those of well-optimized PEO-based electrolytes and higher than the existing polycarbonate-based systems.

In summary, we describe the facile and efficient synthesis of aliphatic polycarbonates using the bifunctional [*rac*-Salcy-Co<sup>III</sup>DNP] catalyst. Specifically, poly(ether 1,2-glycerol carbonate)s possessing pendant butyl, octyl, and stearyl tethers are prepared with molecular weights between 8970 and 31 900 g/mol with low polydispersities (1.1–1.4). Additionally, the thermal properties of the resultant poly(ether 1,2-glycerol carbonate)s are dependent on the alkyl tether chain length. The butyl and octyl ether analogues possess  $T_g$  below  $-20$  °C, while the stearyl-containing polymer exhibits a melting point of 55 °C. Poly(butyl ether 1,2-glycerol carbonate) is the most thermally stable of all three polymers, followed by poly(octyl ether 1,2-glycerol carbonate) and poly(stearyl ether 1,2-glycerol carbonate). At room temperature, poly(butyl ether 1,2-glycerol carbonate) is a viscoelastic material, while at elevated temperatures, the material flows. Finally, we evaluated poly(butyl ether 1,2-glycerol carbonate) containing 65 wt % LiTFSI as a potential SPE for applications between 100 and 125 °C. This thermally stable polymer exhibits high conductivity ( $\sim 10^{-3}$  S/cm) at elevated temperatures. As we are cognizant of the need to design biodegradable materials that enable environmentally friendly disposal routes, poly(butyl ether 1,2-glycerol carbonate) also satisfies this requirement. Continued efforts into the synthesis of novel polycarbonates via various catalysts, substrates, or postpolymerization modification strategies will furnish previously unreported materials as well as application-specific opportunities.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and characterization data. 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

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