Synthesis of Polycarbonates and Poly(ether carbonate)s Directly from Carbon Dioxide and Diols Promoted by a Cs₂CO₃/CH₂Cl₂ System

Shi Bian, Cale Pagan, Anastasia A. Andrianova “Artemyeva”,* and Guodong Du*©

Department of Chemistry, University of North Dakota, 151 Cornell Street Stop 9024, Grand Forks, North Dakota 58202, United States

Supporting Information

ABSTRACT: Recently, polycarbonates have attracted considerable research interest because of their potential biodegradability and sustainability. Here, we present a direct route for the synthesis of polycarbonates and poly(ether carbonate)s from carbon dioxide (CO₂) and diols, promoted by Cs₂CO₃ and CH₂Cl₂ under 1 atm of CO₂. Quantitative conversion of diols and polymers with up to 11 kg/mol molecular weight could be obtained. While benzylic diols lead to predominantly carbonate linkage, aliphatic diols result in the incorporation of the methylene unit of CH₂Cl₂ that produces poly(ether carbonate)s. Both primary and secondary diols have been successfully incorporated into the polymer chain.

INTRODUCTION

Polymers are important materials widely used in modern society. Examples of synthetic polymers include commodity plastics, synthetic fabrics, rubbers, and so on.⁶ Polymer science has grown into a major research area in both industry and academia; however, the nearly exclusive utilization of petroleum-based feedstock for the synthesis of polymers will ultimately become an issue.⁴⁵ Therefore, development of effective processes for the manufacture of polymers from renewable resources has attracted significant attention. One prominent example is the production of polycarbonates from carbon dioxide (CO₂), which is considered an attractive renewable carbon source because of its low cost, nontoxicity, and availability in nature and from many industrial processes.⁷,⁸ Polycarbonates represent a class of polymers that is potentially biodegradable and biocompatible.⁹ Earlier studies have shown that aliphatic polycarbonates undergo slow hydrolytic degradation in vitro and accelerated enzymatic degradation in vivo.¹⁰ Some of the polycarbonates have been applied in the synthesis of engineering thermoplastics and resins and may be useful as coatings, adhesives, ceramic binders, and packaging materials.¹¹

Typical synthetic pathways for polycarbonates are summarized in Scheme 1. The classical method is the condensation of a diol with highly toxic phosgene (COCl₂) or its derivatives (route a), by which the conventional polycarbonate, poly(oxocarbonyloxy-1,4-phenylene isopropylidene-1,4-phenylene), is produced industrially.¹² The alternating copolymerization of CO₂ with oxepines/oxetanes (routes b and c), in the presence of catalysts/co-catalysts, has been widely studied.¹³,¹⁴ In particular, homogeneous single-site catalysts derived from Co, Cr, and Zn are among the most effective ones.¹⁵ Similarly, the catalytic ring-opening polymerization of cyclic carbonates is another promising approach for polycarbonates (route d).¹⁶ However, these routes (b−d) are restricted more or less by the epoxide/cyclic carbonate monomers that are available. In comparison, diols provide much greater flexibility because various structurally diverse diols are readily available for incorporation. Along this line, condensation/metathesis of diols with organic dicarbonates such as dimethyl and diphenyl carbonates has been recently developed (route e).¹⁷ However, dimethyl and diphenyl carbonates still need to be produced from phosgene or CO₂. Thus, a direct approach from CO₂ and diols for the synthesis of polycarbonates would be highly desirable, but this approach (route f) has been less explored.¹⁸

In the context of CO₂ utilization, significant progress has been made for the direct synthesis of organic carbonate from CO₂ and alcohols, in part because CO₂ is used directly and...
water is the only byproduct. One typical approach involves the three-component coupling of CO$_2$, alcohols, and halides, in the presence of organic or inorganic base promoters. While asymmetric dialkyl carbonates are produced in general, symmetrical dicarbonates can be obtained by choosing the appropriate combination of alcohols and halides. For example, dimethyl carbonate has been synthesized from methanol and CO$_2$ mediated via inorganic bases and methyl iodide. In another approach, direct coupling of CO$_2$ and alcohols leads to the formation of symmetric dialkyl carbonates, again in the presence of a base promoter and an appropriate reagent that can serve as a leaving group. We are particularly drawn to the work of Saito and co-workers, in which various alcohols were converted to dialkyl carbonates using a combination of Cs$_2$CO$_3$ and dichloromethane (DCM). DCM plays an essential role in the transformation, yet it is not incorporated into the dialkyl carbonate products. Also of note is that the synthesis was achieved under 1 atm of CO$_2$. Prompted by these advances, we reason that a carbonate linkage would be generated when a diol is employed under similar conditions, thus leading to the formation of oligo- and polycarbonates. During the preparation of this manuscript, a Cs$_2$CO$_3$-promoted synthesis of polycarbonates from CO$_2$ diols, and dihalides was described. In the present study, we report our efforts that utilize Saito’s method toward various diols and CO$_2$ in the presence of Cs$_2$CO$_3$ and DCM, yielding polymers with polycarbonate and poly(ether carbonate) main chains.

## RESULTS AND DISCUSSION

In our study, 1,4-benzenedimethanol was first chosen as a representative diol that is unlikely to form cyclic carbonate on account of its rigid backbone structure. A combination of Cs$_2$CO$_3$/DCM in a solvent, N-methyl-2-pyrrolidone (NMP), was investigated as the reagents, as the system has been found to be effective in the synthesis of organic carbonates from CO$_2$ and alcohols. The reaction was initially carried out under optimized conditions for organic dicarbonates: 1 equiv of 1,4-benzenedimethanol with Cs$_2$CO$_3$/DCM. When a polar, aprotic, high-boiling solvent, dimethyl sulfoxide (DMSO), was used as an alternative solvent to NMP, a significant decrease in the diol conversion was observed under otherwise identical conditions (entry 5 vs 1). Concerning its role in the synthesis, Cs$_2$CO$_3$ was often considered as a strong base and could also be used to absorb a small amount of water. Therefore, Cs$_2$CO$_3$ was replaced by a strong organic base, 1,8-diazabicycloundec-7-ene (DBU), in combination with molecular sieves (entry 6). However, no conversion of the diol was observed in the reaction, which suggested that Cs$_2$CO$_3$ served as more than just a base or dehydrating agent in the reaction. In this context, it was noted that alkoxides conjugated with cesium ion can exhibit enhanced nucleophilicities that facilitate the attack on carbon dioxide.

The product obtained in the reaction (entry 1, Table 1) was isolated in decent yields (63.7%) via precipitation as an off-white solid and characterized via various spectroscopic techniques including $^1$H and $^{13}$C NMR, Fourier transform infrared (FT-IR), electrospray ionization mass spectrometry (ESI-MS), and gel permeation chromatography (GPC), which suggest the formation of a short-chain polycarbonate with alcohol end groups. According to a literature study, the carbonate linkage of the polymer results from the coupling of alcohols and CO$_2$, not from Cs$_2$CO$_3$. The $^1$H and $^{13}$C NMR spectra (Figures S1 and S2) are comparable with the reported data, in which the carbonyl carbon exhibits a characteristic peak at 156 ppm in the $^{13}$C NMR spectrum. The presence of the carbonyl group was also confirmed by the absorbance at 1740 cm$^{-1}$ in the FT-IR spectrum, similar to those in other polycarbonates. The ESI-time-of-flight (TOF) mass spectrum (Figure S22) features a main series of peaks at 164$n + 138 + 18$, which can be assigned to n(C$_9$H$_8$O$_3$) + 1,4-benzenedimethanol + NH$_4$+. The molecular weight ($M_w$) determined by GPC is 1700 g/mol, with $M_w/M_n = 1.2$. These observations support the assignment of a short-chain polycarbonate diol structure. The thermal property of the isolated product was studied with differential scanning calorimetry (DSC), and a melting transition at ∼188 °C was observed.

Benzylic alcohols tend to behave quite differently from other aliphatic alcohols, so we chose a fully aliphatic diol, 1,4-cyclohexanediol, as the coupling partner with CO$_2$. The reaction was carried out using 4 equiv of Cs$_2$CO$_3$ and 6.2 equiv of DCM under 1 atm of CO$_2$ at 100 °C, and the conversion of 1,4-cyclohexanediol reached 100% within 12 h, as determined using $^1$H NMR spectroscopy. The product has been isolated as a light colored, soft material with 52.9% yield, and characterization via NMR and FT-IR spectroscopies revealed some remarkable features of the polymeric product. The most striking is the resonance at 5.35 ppm in the $^1$H NMR spectrum (Figure 1) that is assignable to the methylene (a) protons between two oxygen atoms, suggesting that both carbonate and ether linkages are present in the polymer backbone. The methylene group (c) connected to the other side of the carbonate group is represented by the peaks around 4.0 ppm, and the methylene group (f) connected to the opposite side of the cyclohexyl linkage was represented by the peaks around 3.5 ppm. The peaks between 1.0 and 2.0 ppm belong to the cyclohexane ring. The structure of the polymer was also corroborated by the $^{13}$C NMR spectrum (Figure 2), featuring a peak around 155 ppm, assignable to the carbonate carbon, and a peak around 92 ppm, assignable to the methylene (a) carbon. These assignments were supported by the 2D COSY and HSQC NMR spectra of the isolated products.

Table 1. Copolymerization of CO$_2$ and 1,4-Benzenedimethanol with Cs$_2$CO$_3$/DCM

| entry | Cs$_2$CO$_3$ (equiv) | DCM (equiv) | time (h) | conv. (%) |
|-------|---------------------|-------------|----------|-----------|
| 1     | 4                   | 6.2         | 12       | >99$^a$   |
| 2     | 2                   | 6.2         | 12       | 24.5      |
| 3     | 3                   | 3.1         | 12       | 26.8      |
| 4     | 2                   | 3.1         | 12       | 9.5       |
| 5$^b$ | 4                   | 6.2         | 12       | 30.2      |
| 6$^c$ | 0                   | 6.2         | 24       | 0         |
| 7     | 4                   | 0           | 24       | 0         |

$^a$Reactions were performed with 1 mmol 1,4-benzenedimethanol at 100 °C under 1 atm of CO$_2$ in 1 mL of NMP, unless noted otherwise. $^b$Determined using $^1$H NMR spectroscopy. $^c$The pure polymeric product was isolated from the mixture with 63.7% yield. The reaction was run in 1 mL of DMSO instead of NMP. The reaction was run with molecular sieves of 4 Å and DBU (4 equiv) without Cs$_2$CO$_3$. DOI: 10.1021/acsomega.6b00278

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Furthermore, the existence of the carbonyl group was confirmed by the absorbance at 1740 cm$^{-1}$ in the FT-IR spectrum.

On the basis of these analyses, the structure of the polymeric product from 1,4-cyclohexanedimethanol and CO$_2$ is characterized as poly(ether carbonate). The ratio of the integration of the set of peaks at 4.0 ppm (linked to carbonate) to the set of peaks at 3.5 ppm (linked to ether) was 1.07:1, and they were both close to the integration of the methylene peak at 5.3 ppm. These important observations suggest that about 93% of the repeating unit of the polymer consists of an ether−carbonate linkage. The rest was believed to be the pure carbonate linkage without incorporation of the OCH$_2$O ether moiety, which is consistent with the slightly larger integration of the set of peaks at 4.0 ppm. The ether−carbonate linkage was mostly alternating in nature, as suggested by an HMBC NMR experiment (Figure 3). The observed three sets of cross peaks clearly demonstrate the connection of C3−C1−C2−C4, which are interspersed with oxygen atoms. The ether−carbonate repeating unit of $\sim$200.1 Da was also detected in the ESI-MS spectrum (Figure 4), in agreement with the alternating nature of the structure. Minor incorporation of the methylene group of CH$_2$Cl$_2$ was observed in the reaction of CO$_2$ with alcohols for the synthesis of organic carbonates,$^{24,27}$ which is believed to result from the reaction between DCM and alkoxide CsOR or carboxylate CsO(C$\equiv$O)OR under the reaction conditions. It is worth mentioning that the formation of the alternating ether carbonate linkage is quite unique and has not been observed in other similar systems. In the polycondensation reaction of CO$_2$ with diols and $\alpha,\omega$-dihalides promoted by K$_2$CO$_3$,$^{18a}$ or Cs$_2$CO$_3$,$^{18f}$ the ether linkage was not
detected and both the diol and dihalide units were incorporated as carbonate linkages.

Another notable observation in the NMR spectra of the polymer is that the hydrogen and carbon signals associated with the 1,4-cyclohexanedicarboxylate moiety are represented by two separate sets of peaks. This is due to the cis- and trans-isomers of the 1,4-cyclohexanedicarboxylate because our starting material is a mixture of cis- and trans-1,4-cyclohexanedicarboxylate. The assignment was verified by synthesizing polymers from trans-1,4-cyclohexanedicarboxylate and comparing the respective NMR spectra (Figure S11).

Next, we investigated a variety of diols in direct copolymerization with CO2 under similar conditions (Table 2). For most of the diol substrates, high conversions and decent yields were achieved. The characterization data of the products, including the NMR and IR spectra, are compiled in the Supporting Information. As observed earlier, when another benzylic diol 1,3-benzenedicarboxylate was used (entry 4), the resulting polymer consisted of predominantly carbonate linkage (>95%) with no methylene incorporation; however, regular aliphatic diols afforded polymers with alternating polycarbonate/ether repeating units, as judged by the presence of a singlet around 5.3 ppm assignable to the methylene group in the 1H NMR. When 1,6-hexanediol, a linear aliphatic diol that is potentially bio-derived, was employed in the reaction, diol conversion up to 86% was achieved (Table 2, entry 5). The incorporated OCH2O unit is identified by the NMR signals at 5.29 ppm (1H) and 92.6 ppm (13C). However, the isolated yield (36.0%) of the reaction was somewhat low, probably due to the formation of short-chain oligomers that were not readily precipitated out of the mixture during the isolation. Nearly quantitative conversion was obtained when 1,4-cyclohexanedicarboxylate was employed as the starting diol, which indicated that secondary alcohols can be used in this synthesis (Table 2, entry 6). The corresponding poly(ether carbonate) was isolated in good yield (63.1%) with a moderate molecular weight (Mn = 5.1 kg/mol). However, when 1,4-hydroquinone, an aromatic diol, was used, only a small amount (∼8%) of low-molecular-weight polymeric material (Mn ∼800 g/mol) was isolated despite the high conversion of the starting diol (entry 7). Spectroscopic analysis of this isolated product showed the incorporation of the methylene unit (5.6 ppm in 1H NMR) and the absence of carbonate linkage (no peak at ∼1740 cm⁻¹ in FT-IR, see Figure S19), and the product is therefore characterized as an oligomeric -(OCH2O)n- . This is consistent with the literature report that the acetal PhOCH2OPh was the predominant product in the reaction of phenol and CO2 under the Cs₂CO₃/DCM conditions.23 Obviously, the reaction of phenoxide (ArO⁻Cs⁺) with DCM is preferred over the incorporation of CO2.
As the incorporation of the OCH2O unit was identified in the isolated products from all of the aliphatic diols, we thought it would be interesting to investigate the influence of the loading of DCM, from 1.6 to 12.3 equiv (vs 1,4-cyclohexanediol), on the outcome of the reactions. Initially, the loadings of DCM did not seem to affect the ether content, as the resulting products remained unchanged with an alternating ether−carbonate linkage, as indicated using 1H NMR spectroscopy. Then, the isolated yields of polymers (Table 3) increased with the loadings of DCM (from 1.6 to 9.3 equiv) and the highest yield (71%) was achieved with 9.3 equiv of DCM. Further increase in DCM seemed to be not helpful for the isolated yield. GPC analysis shows that most of the isolated polymers exhibit decent number average molecular weights (Mn) between 3800 and 7600 g/mol, with a broad polydispersity index from 1.8 to 2.5 (Table 3). We suspect that a considerable portion of the products are oligomers that are not readily isolated by the precipitation method. To support this notion, the methanol-soluble components during precipitation were collected and analyzed. The 1H NMR spectrum was very similar to that of the precipitated polymeric products, and GPC analysis showed a Mn of ∼700 g/mol. Furthermore, the combined yield of the methanol-soluble components and the precipitated polymers was >90%. In accordance with this notion, the yield of polymers could be improved by extending the reaction time (entry 2). With 6.2 equiv of DCM and 72 h of reaction, we were able to obtain a polymer with a Mn of 11 kg/mol in 75% isolated yield.

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With the excellent reactivity and selectivity achieved for the copolymerization of CO2 and diols promoted by the current Cs2CO3/DCM system, comparison can be made with the recent procedures reported. In the CeO2/2-cyanopyridine system, carbonate linkage is formed with >90% selectivity; however, the molecular weights of the obtained products are low (Mn about 0.5–1.7 kg/mol) and the procedure works poorly for secondary alcohols. In a more closely related Cs2CO3−dihalide system, higher molecular weights up to 43 kg/mol have been achieved. However, it requires high pressure of CO2 (10 bar, instead of 1 bar used in this study) and more significantly, the polymers obtained consist of mostly carbonate linkage incorporating both the diol and dihalide moieties, same as in the K2CO3-promoted reactions, but distinctly different from the results presented here. Similar polymers with mostly carbonate linkages incorporating both the diol and dihalide moieties have been obtained in our preliminary study of 1,4-cyclohexanediol with a high pressure of CO2 (40 bar), even though the molecular weights remained relatively low (Mn ~3.0 kg/mol). It thus appears that the pressure of CO2 plays a significant role in determining the polymer linkage and is likely responsible for the difference observed. The low molecular

### Table 2. Synthesis of Polycarbonates and Poly(ether carbonate)s from CO2 and Various Diols with Cs2CO3/DCM

| entry | Diol | Conv. (%) | Yield (%) | Mn (g/mol) | Mw/Mn | Tg (°C)<br> | Tm (°C)<br> |
|-------|------|-----------|-----------|------------|--------|-------------|-------------|
| 1     |      | >99       | 63.7      | 1.8        | 1.23   | n.o. (188)  |             |
| 2     |      | >99       | 52.9      | 5.0        | 1.84   | -1.4        |             |
| 3     |      | >99       | 53.6      | 5.1        | 1.77   | 1.0         |             |
| 4     |      | >99       | 57.2      | 3.4        | 1.22   | 4.6 (161)   |             |
| 5     |      | 85.8      | 36.0      | 6.6        | 1.41   | n.o.        |             |
| 6     |      | >99       | 63.1      | 5.1        | 1.62   | 30          |             |
| 7<sup>a</sup> | | 94.4     | 8.0       | 0.78      | 1.13   | n.d.        |             |

<sup>a</sup>Reactions were performed with 1 mmol diol at 100 °C under 1 atm of CO2 for 12 h. <sup>b</sup>Determined by 1H NMR spectroscopy. <sup>c</sup>Determined by GPC with polystyrene standard. <sup>d</sup>Determined by DSC from the second heating cycle. n.o.: not observed; n.d.: not determined. Values within parentheses refer to the melting transition (Tm). <sup>e</sup>Polyether was formed instead of polycarbonate.

### Table 3. Copolymerization of CO2 and 1,4-Cyclohexanediol under Various Conditions

| entry | DCM (equiv) | Mn (g/mol)<br> | Mw/Mn | yield (%) | Tg (°C)<br> |
|-------|-------------|----------------|--------|------------|-------------|
| 1     | 1.6         | 4400           | 1.8    | 14         | n.d.        |
| 2<sup>c</sup> | 3.1         | 6400           | 2.2    | 43         | -1.1        |
| 3     | 6.2         | 5000           | 1.8    | 52         | -1.4        |
| 4     | 9.3         | 3800           | 2.2    | 71         | -25         |
| 5     | 12.4        | 7600           | 2.5    | 49         | -6.5        |
| 6<sup>e</sup> | 6.2         | 11100          | 2.7    | 75         | 7.0         |

<sup>a</sup>Reactions were performed with 1 mmol 1,4-cyclohexanediol and 4 mmol Cs2CO3 at 100 °C under 1 atm of CO2 in 1 mL of NMP for 12 h. <sup>b</sup>Determined by GPC. The reaction was performed for 24 h. <sup>c</sup>Determined by DSC from the second heating cycle. n.d.: not determined. <sup>e</sup>The reaction time was 72 h.
weights obtained so far in this study are generally insufficient to meet the requirement of industrial plastics and may indicate low CO₂ fixation. Efforts have been made to improve the chain length of the products, and polymers with Mᵣ up to 11 kg/mol were obtained by extending the reaction time (entry 6, Table 3).

On the basis of these results and the related studies in the literature, a possible, simplified pathway is proposed in Scheme 2. The nucleophilic attack on CO₂ by the alkoxide generated from deprotonation of diol by Cs₂CO₃ results in the formation of a carboxylate, which reacts with DCM to yield an intermediate A, again aided by Cs₂CO₃, although it is not entirely clear why so large an amount of Cs₂CO₃ is needed (see Table 1, entries 2 and 4). The preference of methylene incorporation into aliphatic diols over benzylic diols might stem from the difference in their acidity (pKa ~14.0 for benzylic diols and ~14.8–14.9 for aliphatic diols in this study). Whereas the attack at the carbonate position a by the less basic benzylic alkoxide leads to pure polycarbonate, the more basic aliphatic alkoxide seems to prefer to attack at the methylene position b, affording methylene-incorporated poly(ether carbonate).

Scheme 2. Possible Pathway for the Copolymerization of the Diols and CO₂

![Scheme 2](image)

**CONCLUSIONS**

In summary, a new procedure for the direct synthesis of polycarbonates and poly(ether carbonate)s from diols and CO₂ has been reported under 1 atm pressure of CO₂ using a combination of Cs₂CO₃ and CH₂Cl₂ as the reagent. Excellent conversions and isolated yields are achieved with various diols including benzylic and aliphatic alcohols. Both primary and secondary aliphatic diols have proven to be suitable substrates for the copolymerization. The isolated polymers have been fully investigated by IR, NMR, GPC, and ESI-MS, which confirmed the structure of the products. Notably, the polycarbonates from benzylic diols contain more than 90% of the carbonate linkage, whereas the polymers from aliphatic diols contain mainly the alternating carbonate/ether linkage. In addition, attempts at expanding the substrate scope and controlling the type of the linkage formed in the reaction are now underway in our laboratory.

**EXPERIMENTAL SECTION**

**Materials.** Organic compounds including all diols are commercially available and were purchased from Sigma-Aldrich. The diols were dried under vacuum overnight. DCM was dried over activated molecular sieves (4 Å) overnight. The predried Cs₂CO₃ and NMP were purchased from Sigma-Aldrich and used without further purification. All of the compounds were stored inside a glove box under a nitrogen atmosphere.

**General Methods.** NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer (1H and 13C). GPC analysis was performed on a Varian Prostar, using a Plgel 5 μm Mixed-D column, a Prostar 355 RI detector, and tetrahydrofuran as the eluent at a flow rate of 1 mL/min (20 °C). Polystyrene standards were used for calibration. The HR-MS (ESI-TOF) was performed on a high-resolution time of flight G1969A instrumentation (Agilent) using 2.5 mM ammonium acetate as an ionizing agent. The DSC data were collected on a PerkinElmer Pyris DSC using 10.0 °C/min heating rate with 20 mL/min nitrogen flow. The FT-IR spectrum was recorded on a PerkinElmer Spectrum 400 FT-IR spectrophotometer.

**Typical Procedure for Polymerization.** A 100 mL Schlenk flask was dried by heating under vacuum and then transferred into a dry nitrogen glove box, where it was loaded with 1 mmol of a diol, 4 mmol of Cs₂CO₃, 6.2 mmol of DCM, and 1 mL of NMP. The flask was then taken out of the glove box, the reaction mixture was frozen using liquid N₂, and the N₂ atmosphere was replaced by dry CO₂ with three evacuation–refill cycles. The reaction mixture was heated at 100 °C for 12 h with stirring. The conversion was checked by 1H NMR of the crude mixture. The isolation procedure of the polymeric products depended on the substrates. For benzylic diols, the reaction mixture was first treated with water (10 mL), and the insoluble solid was collected by filtration or centrifugation and washed with methanol (2 mL) thrice. For aliphatic diols, the reaction mixture was filtered and washed with DCM (5 mL) thrice. The filtrate was collected and concentrated to ~1 mL under vacuum. Methanol (5 mL) was then added, and the precipitate formed was collected by centrifugation and washed further with methanol (1 mL × 3). Finally, the solid product was dried under vacuum to a constant weight to determine the yield.

**Polycarbonate from 1,4-Benzenedimethanol.** Yield: 63.7%, 1H NMR (CDCl₃, 298 K): δ 7.38 (s, ArH), 5.17 (s, ArCH₂OCOO), 4.71 (d, ArCH₂OH, J = 7.0). 13C NMR (CDCl₃, 298 K): δ 155.19 (C=O), 128.84, 127.35, 69.74 (ArCH₂OCOO), 66.22 (ArCH₂OH).

**Polycarbonate from 1,3-Benzenedimethanol.** Yield: 57.2%, 1H NMR (CDCl₃, 298 K): δ 7.38 (m, ArH, 11H), 5.15 (s, ArCH₂OCOO, 10H), 4.72 (s, ArCH₂OH, 1H). 13C NMR (CDCl₃, 298 K): δ 155.22 (C=O), 135.77, 129.15, 128.77, 128.33, 69.68 (ArCH₂OCOO), 69.15 (ArCH₂OH).

**Poly(ether carbonate) from 1,4-Cyclohexanedi- methanol.** Yield: 52.9%, 1H NMR (CDCl₃, 298 K): δ 5.31 (s, OCH₂O, 1H), 4.10 (d, J = 5.0, COOCH₂CH₂, 1H), 4.00 (s, COOCH₂CH₂, 6.0H), 3.58 (d, J = 5.0, OCH₂CH₂, 0.8H), 3.50 (s, OCH₂CH₂, 0.7H), 1.93 (s, CH₂CH₂CH₂, 1.84 (d, J = 10, CH₂CH₂CH₂, 1.5H), 1.67 (s, CH₂CH₂CH₂, 0.5H), 1.43 (s, CH₂CH₂CH₂, 2H), 1.01 (m, CH₂CH₂CH₂, 1H). 13C NMR (CDCl₃, 298 K): δ 154.93 (C=O), 92.72 (OCH₂O), 76.32 (OCH₂CH₂), 73.94 (OCH₂CH₂), 73.19 (OCH₂CH₂), 70.93 (OCH₂CH₂), 38.15 (CH₂CH₂CH₂), 37.37 (CH₂CH₂CH₂), 35.48 (CH₂CH₂CH₂), 34.66 (CH₂CH₂CH₂), 29.20 (CH₂CH₂CH₂), 25.42 (CH₂CH₂CH₂).

**Poly(ether carbonate) from 1,3-Cyclohexanedi- methanol (trans).** Yield: 53.6%, 1H NMR (CDCl₃, 298 K): δ 5.28 (s, OCH₂O, 1H), 4.00 (d, J = 5.0, COOCH₂CH₂, 1H), 3.50 (d, J = 5.0, OCH₂CH₂, 1H), 1.85 (m, CH₂CH₂CH₂, CH₂CH₂CH₂, 2H), 1.68 (s, CH₂CH₂CH₂, 1H), 1.04 (m, CH₂CH₂CH₂, 2H). 13C NMR (CDCl₃, 298 K): δ 154.95 (C=O), 92.77 (OCH₂O), 76.32 (OCH₂CH₂), 73.94 (OCH₂CH₂), 73.19 (OCH₂CH₂), 70.93 (OCH₂CH₂), 38.15 (CH₂CH₂CH₂), 37.37 (CH₂CH₂CH₂), 35.48 (CH₂CH₂CH₂), 34.66 (CH₂CH₂CH₂), 29.20 (CH₂CH₂CH₂), 25.42 (CH₂CH₂CH₂).
Poly(ether carbonate) from 1,4-Cyclohexanediol (trans). Yield: 63.1%. 1H NMR (CDCl₃, 298 K): δ 5.34 (s, OCH₂O, 1H), 4.74 (s, br, COOCH₂CH₂O, 0.5H), 3.77 (s, br, CH₂OCH₂CH₂O, 0.5H), 1.93 (s, CH₂CH₂OCH₂, 1H), 1.81 (s, CHCH₂CH₂, 2H), 1.70 (s, CH₂CH₂CH₂CH₂, 1H). 13C NMR (CDCl₃, 298 K): δ 154.25 (C=O), 90.61 (OCH₂O), 75.06 (OCH(OCH₂)₃), 74.12 (OCH₂CH₂), 28.18 (CH₂CH₂CH₂CH₂), 27.35 (CH₂CH₂CH₂).

Poly(ether carbonate) from 1,6-Hexanediol. Yield: 36.0%. 1H NMR (CDCl₃, 298 K): δ 5.29 (s, OCH₂O, 1H), 4.17 (m, COOCH₂CH₂, 1H), 3.67 (m, CH₂OCH₂CH₂, 1H), 1.71 (s, CH₂CH₂CH₂, 1H), 1.62 (s, CH₂OCH₂CH₂, 1H), 1.43 (s, CH₂CH₂CH₂, 2H). 13C NMR (CDCl₃, 298 K): δ 154.90 (C=O), 92.55 (OCH₂O), 70.81 (OCH₂CH₂), 68.26 (OCH₂CH₂), 29.64 (CH₂CH₂CH₂), 28.79 (CH₂CH₂CH₂), 25.92 (CH₂CH₂CH₂).

Polyether from Hydroquinone. Yield: 8.0%. 1H NMR (CDCl₃, 298 K): δ 7.01 (m, ArH, 4H), 5.60 (s, OCH₂O, 2H). 13C NMR (CDCl₃, 298 K): δ 152.51 (ArO), 118.00 (Ar-C), 92.51 (OCH₂O).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00278.

Experimental details and characterization data (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: guodong.du@und.edu. Tel: +1-701-777-2241. Fax: +1-701-777-2331.

ORCID

Anastasia A. Andrianova “Artemyeva”: 0000-0002-7034-7574
Guodong Du: 0000-0002-3833-233X

Notes

The authors declare no competing financial interest.

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