This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Controllable Synthesis of Narrow Polydispersity CO₂-Based Oligo(carbonate-ether) tetraol

Shunjie Liu, Yuyang Miao, Lijun Qiao, Yusheng Qin, Xianhong Wang, Xuesi Chen, Fosong Wang

CO₂-based oligo(carbonate-ether) tetraol was synthesized in a controlled manner by immortal copolymerization of carbon dioxide (CO₂) and propylene oxide (PO) in the presence of 1,2,4,5-benzenetetracarboxylic acid (btcH₄) catalyzed by zinc-cobalt double metal cyanide (Zn–Co–DMC) catalyst. The number average molecular weight (Mₙ) of the tetraol was in a good linear relationship with the molar ratio of PO and btcH₄ (PO/btcH₄), and hence can be precisely controlled. Besides, the rapid chain transfer in immortal copolymerization afforded tetraol with a narrow polydispersity index (PDI) of 1.08 at Mₙ of 1,400 g mol⁻¹. Notably, the weight fraction of byproduct propylene carbonate (Wpc) was reduced to as low as 4.0 wt%, which is the lowest Wpc ever reported for the synthesis of branched polyols. The structure of the oligo(carbonate-ether) tetraol was confirmed, providing a new evidence for the effect of the acidity (pkₐ value) of the chain transfer agent (CTA) on the initial catalytic mechanism. The acid only acts as the CTA directly participating in the copolymerization via the chain transfer reaction when its pkₐ value is higher than that of adipic acid (pkₐ = 4.43). However, when its pkₐ value is lower than that of succinic acid (pkₐ = 4.2), it acts as the initiate-transfer agent, which first initiates PO homopolymerization to oligo-ether polyol, then the in-situ formed polyol acts as a new CTA for the copolymerization.

1. Introduction

Chemical fixation of CO₂ is highly attractive not only from the viewpoint of CO₂ utilization, but also from the abatement of environmental pressure. A promising process of CO₂ utilization is the copolymerization of CO₂ and propylene oxide (PO) to prepare biodegradable polycarbonates pioneered by Inoue since 1969. Significant progress has been made to promote the process, owing to the fast developing catalyst systems, which have been summarized in the recent reviews. Though low-molecular-weight copolymers from CO₂ and PO have received less attention, their potential applications as polyols in the polyurethane industry may create a new era in CO₂ copolymer. Notably, high-quality polyurethane materials have been prepared with oligo(carbonate-ether) polyols using similar formulations as used for the current industrial standard polyether polyols. Salen Cobalt complex has been reported as very active and selective catalyst to make narrow polydispersity polyol, however, its specific selectivity in the formation of polar carbonate unit leads to polyols with a high viscosity, which is inconvenient to process with standard equipment used in the polyurethane industry. Unlike Salen Cobalt complex catalyst, double metal cyanide (DMC) catalysts are preferably used to prepare oligo(carbonate-ether) polyols, especially in industrial field. However, the reaction proceeds with relatively long induction period, and the resulting polyols suffer from low CO₂ incorporation and broad molecular weight distribution. To increase the carbonate unit (CU) content of the polyols, measures such as using crystalline multi-metal cyanide catalysts, adding CO₂-phobic compounds, or preactivation catalyst have been explored. Moreover, sterically hindered monofunctional agents were added, introducing suspending agents and continuously dosing hydrogen-functional starter substance methods to reduce the polydispersity index (PDI) of polyols, while the induction period can be shortened by activating DMC catalyst with sterically nonhindered phenols. Salen Cobalt may be used together with Zn-Co-DMC catalyst, but the obtained polyols still had relatively high Mₙ (5000 g mol⁻¹), broad PDI (4.1), and low CU (10%), which did not fit with either plastic or polyurethane productions. Therefore, the preparation of polyols with a suitable CU, low Mₙ, and narrow PDI is still a big challenge.

A CO₂-based oligo(carbonate-ether) diol (CU = 40–75%, Mₙ < 2000 g mol⁻¹) more suitable for polyurethane production was synthesized by replacing the starter with dicarboxylic acid in our group. The induction period of dicarboxylic acids was found to be shorter than that of the oligo-diol. Based on this consideration, CO₂-based oligo(carbonate-ether) triol was synthesized using trimesic acid (TMA) as the chain transfer agent (CTA). Interestingly, TMA played a special role, i.e., it acted as the initiate-transfer agent in the copolymerization of CO₂ and PO. Polyols with more than two hydroxyl groups are well known to afford widely used crosslinked polyurethane materials. In this study, oligo(carbonate-ether) tetraol with a narrow PDI was synthesized in high productivity by the copolymerization of CO₂ and PO using a catalyst system comprised a Zn-Co-DMC component together with 1,2,4,5-benzenetetracarboxylic acid (btcH₄) as the CTA.
2. Experimental section

2.1 Materials

Sebacic acid, btcH₄, adipic acid, succinic acid, and malonic acid were purchased from Aladdin Industrial Inc. and dried for 48 h in vacuum at 50 °C prior to use. K₃[Co(CN)₆] was provided by Alfa Aesar and recrystallized in deionized water prior to use. ZnCl₂ and tert-butanol (t-BuOH) were of analytical grade and used without further purification. PO was refluxed over calcium hydride and then distilled under argon atmosphere. Carbon dioxide with purity >99.99% was used as received. Zn–Co–DMC catalyst was prepared according to the previous report.

2.2 Copolymerization

Copolymerization was carried out in a professional 500 mL autoclave equipped with a mechanical stirring and water-cooling and recycling equipment to function under 20 MPa pressure. Calculated amounts of Zn–Co–DMC, PO (100 mL), and btcH₄ were added in the pretreated autoclave free of oxygen and water at ambient temperature, and the autoclave was then placed in a water bath at fixed temperature, followed by adding CO₂ to start the reaction. The autoclave was cooled down to room temperature to terminate the copolymerization when the pressure drop stopped, and the pressure was slowly released. Other copolymerization process was carried out as follows: in a glove box free of oxygen and water, calculated DMC catalyst, carboxylic acids, and PO were added to a 50 mL professional stainless-steel autoclave (10 MPa) under magnetic stirring. CO₂ was pressurized into this mixture, and the reaction was carried out at the determined condition. After the copolymerization, the autoclave was cooled to room temperature, and the CO₂ pressure was released by opening the outlet valve. A small aliquot of the copolymerization mixture was taken out for ¹H NMR spectroscopy.

Caution: The polymerization of PO is highly exothermic. Because of the possibility of runaway reactions, the reactor needs to be equipped with an appropriate pressure release system and operated in an explosion-proof safety box.

2.3 Measurements

Fourier transform infrared spectra were recorded by casting acetone solution of the collected product onto a disk of KBr by a Bruker TENSOR-27 spectrometer with 30 scans per experiment at a resolution of 4 cm⁻¹. ¹H NMR, ¹³C NMR and COSY NMR spectra were recorded at room temperature on Unity-500 NMR spectrometer using CDCl₃ as solvent. The Mn and PDI of the oligo(carbonate-ether) tetraol were measured by gel permeation chromatography (GPC) at 35 °C using polystyrene standard on Waters 410 GPC instrument (tandem double columns: WAT044222, 7.8×300 mm, molecular weight range 500-30000 g mol⁻¹; WAT044234, 7.8×300 mm, molecular weight range 100-5000 g mol⁻¹, RID detector) with CH₂Cl₂ as eluent, where the flow rate was set at 1.0 ml/min. ESI-MS analyses were performed on Waters Quattro Premier XE mass spectrometer, using methanol/water (4:1) as solvent. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a Bruker autoflex III mass spectrometer in linear, positive ion mode. The matrix was 2,5-dihydroxybenzoic acid (DHBA), and solvent was acetonitrile/water (1/2). For sample preparation, at first two solutions were prepared, one was DHBA solution with concentration of 20.0 mg/ml, the other was oligo(carbonate-ether) tetroal solution with concentration of 2.0 mg/ml, then 1 ml of matrix solution and 1 ml of sample solution were thoroughly mixed together, 1µl of this mixture solution was spotted on the target plate and allowed to dry for next MALDI-TOF-MS test.

3. Results and discussion

3.1 Preparation of CO₂-based oligo(carbonate-ether) tetraol

The extremely rapid chain transfer reaction by immortal polymerization successfully afforded oligo(carbonate-ether) tetroal. The effect of the reaction conditions on the copolymerization of CO₂/PO is summarized in Table 1. Calculated amount of Zn–Co–DMC catalyst was added to afford smooth initiation and copolymerization. As listed in Table 1, in the studied copolymerization conditions, the catalytic productivity was in the range 0.48–1.05 kg/g DMC with various PO/btcH₄ molar ratios. When the PO/btcH₄ molar ratio decreased from 37.4 to 16.7 (Entries 1–5), the PDI of the CO₂-based tetraol dropped from 1.35 to 1.08. To the best of our knowledge, the PDI of 1.08 was the narrowest ever reported for the heterogeneous copolymerization systems, strongly proving the immortal polymerization mechanism. At the same molar ratio of PO/CTA as 18.7 (Entries 4, 12, 13), the PDIs of the polyols were 1.10, 1.18, and 1.35, respectively, increasing in the order of btcH₄, TMA, and sebacic acid. This indicates that the PDIs of the polyols were closely associated with the amount of the carboxyl groups existed in the reaction system. Therefore, CTA with the maximum number of carboxyl groups might have the narrowest PDI at comparable molecular weight, assuming that Zn–Co–DMC catalyst could withstand the interference of the acidic CTA. The CU of the tetroal decreased from 32.7 to 25.6% when PO/btcH₄ ratio decreased from 37.4 to 16.7 (Entries 1–5), possibly because the increasing btcH₄ load might disfavor the CO₂ incorporation.
Table 1 Effect of reaction conditions on the copolymerization

<table>
<thead>
<tr>
<th>Entry</th>
<th>DMC (mg)</th>
<th>PO/btcH₄ (mol mol⁻¹)</th>
<th>t (h)</th>
<th>P (MPa)</th>
<th>T (°C)</th>
<th>CUb (%)</th>
<th>Wₐ,c (wt%)</th>
<th>Mₐ,b (g mol⁻¹)</th>
<th>Mₐ,c (g mol⁻¹)</th>
<th>PDF</th>
<th>Productivityd (kg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>37.4</td>
<td>8</td>
<td>4</td>
<td>80</td>
<td>32.7</td>
<td>10.8</td>
<td>3050</td>
<td>3500</td>
<td>1.35</td>
<td>1.05</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>27.3</td>
<td>8</td>
<td>4</td>
<td>80</td>
<td>30.8</td>
<td>13.2</td>
<td>2300</td>
<td>2500</td>
<td>1.22</td>
<td>0.62</td>
</tr>
<tr>
<td>3</td>
<td>190</td>
<td>22.9</td>
<td>8</td>
<td>4</td>
<td>80</td>
<td>30.6</td>
<td>14.7</td>
<td>1900</td>
<td>2050</td>
<td>1.15</td>
<td>0.59</td>
</tr>
<tr>
<td>4</td>
<td>210</td>
<td>18.7</td>
<td>8</td>
<td>4</td>
<td>80</td>
<td>28.2</td>
<td>16.5</td>
<td>1600</td>
<td>1700</td>
<td>1.10</td>
<td>0.53</td>
</tr>
<tr>
<td>5</td>
<td>240</td>
<td>16.7</td>
<td>8</td>
<td>4</td>
<td>80</td>
<td>25.6</td>
<td>16.2</td>
<td>1400</td>
<td>1550</td>
<td>1.08</td>
<td>0.48</td>
</tr>
<tr>
<td>6</td>
<td>210</td>
<td>22.9</td>
<td>10</td>
<td>4</td>
<td>70</td>
<td>36.9</td>
<td>11.4</td>
<td>2000</td>
<td>2100</td>
<td>1.14</td>
<td>0.55</td>
</tr>
<tr>
<td>7</td>
<td>240</td>
<td>22.9</td>
<td>21</td>
<td>4</td>
<td>60</td>
<td>48.6</td>
<td>6.3</td>
<td>2050</td>
<td>2150</td>
<td>1.17</td>
<td>0.47</td>
</tr>
<tr>
<td>8</td>
<td>330</td>
<td>22.9</td>
<td>21</td>
<td>4</td>
<td>50</td>
<td>54.5</td>
<td>4.0</td>
<td>2000</td>
<td>2100</td>
<td>1.19</td>
<td>0.36</td>
</tr>
<tr>
<td>9</td>
<td>210</td>
<td>22.9</td>
<td>7</td>
<td>3</td>
<td>70</td>
<td>31.0</td>
<td>11.9</td>
<td>1900</td>
<td>2050</td>
<td>1.16</td>
<td>0.51</td>
</tr>
<tr>
<td>10</td>
<td>210</td>
<td>22.9</td>
<td>10</td>
<td>5</td>
<td>70</td>
<td>43.7</td>
<td>8.8</td>
<td>2000</td>
<td>2200</td>
<td>1.18</td>
<td>0.53</td>
</tr>
<tr>
<td>11</td>
<td>210</td>
<td>22.9</td>
<td>11</td>
<td>5.8</td>
<td>70</td>
<td>43.0</td>
<td>10.2</td>
<td>1800</td>
<td>2200</td>
<td>1.17</td>
<td>0.49</td>
</tr>
<tr>
<td>12</td>
<td>220</td>
<td>18.7</td>
<td>8</td>
<td>4</td>
<td>80</td>
<td>32.7</td>
<td>21.3</td>
<td>1400</td>
<td>1800</td>
<td>1.18</td>
<td>0.52</td>
</tr>
<tr>
<td>13</td>
<td>50</td>
<td>18.6</td>
<td>5</td>
<td>4</td>
<td>80</td>
<td>45.2</td>
<td>8.2</td>
<td>1500</td>
<td>2500</td>
<td>1.35</td>
<td>2.44</td>
</tr>
</tbody>
</table>

All the copolymerization reactions were carried out using 100 mL PO, and the amount of btcH₄ used in Entries 1–5 was 9.7, 13.3, 15.8, 19.4, 21.7 g, respectively. Entries 6–11. The CU content of the tetraol increased from 31 to 43% with increasing pressure from 3 to 5.8 MPa, whereas the PC content slightly changed. Therefore, the CU content of the tetraol could be slightly regulated by changing the pressure of CO₂ at the same temperature.

The effect of temperature on the copolymerization is also shown in Entries 3, 6–8, Table 1. The CU content of the tetraol increased from 30 to 54% by simply decreasing the reaction temperature from 80 to 50 °C, and the propylene carbonate (PC) content decreased from 14.7 to 4%, accompanied by a slight decrease in the catalytic productivity (0.59 to 0.36 kg g⁻¹), though the catalyst amount should be increased to assure sufficient copolymerization. To the best of our knowledge, it is the lowest PC content (4%) for branched oligo(carbonate-ether) polyols synthesis.²⁵ Consequently, changing reaction temperature was a simple way to substantially alter the CU and PC contents of the products. The effect of pressure on the copolymerization is also shown in Entries 6, 9–11. The CU content of the tetraol increased from 31 to 43% with increasing pressure from 3 to 5.8 MPa, whereas the PC content slightly changed. Therefore, the CU content of the tetraol could be slightly regulated by changing the pressure of CO₂ at the same temperature.

The accurate control of the molecular weight of the polyols is one of the most necessary requirements in the polyurethane industry. As shown in Fig. 1, the Mₙ of the tetraol was exactly controlled by varying the PO/btcH₄ molar ratio, as the Mₙ measured by GPC or calculated by ¹H NMR fitted well with the PO/btcH₄ molar ratio (all the R² >0.999), but not the DMC catalyst amount. Therefore, tetaols with different MₙS can be designed to meet various needs of polyurethane.

3.2 The initiation manner of various CTAs under DMC catalyst.

The insolubility of the DMC catalyst in most solvents makes many difficulties in the spectroscopic analyses on the interaction of DMC and CTA. Moreover, during the late stage of copolymerization, CTA was incorporated into the polyols. Therefore, it is important to understand the initiation mechanism of different CTAs in the early stage of copolymerization. ESI-MS is a soft ionization method and can keep weak bonds in a compound; therefore, it is suitable for characterizing the products with low Mₘₘₜ.²⁹ To simplify the discussion, the amount of DMC catalyst and the mole number of the carboxyl groups in each CTA were kept constant. Fig. 2a shows the ESI-MS spectrum of the product initiated by btcH₄ when reacted at a reaction time of 4 min (<10% PO conversion). Only one species, btcH₄ initiating polyether [btcH₄ (PO)ₓ] Na⁺ (4 ≤ x ≤ 11), was identified in Fig. 2a. The increasing molecular weight of polyether homolog indicates that the acid groups always reacted first with the epoxide before the reaction of the newly formed hydroxyl end group with CO₂ becoming feasible. Therefore, btcH₄ acted as the initiate-transfer agent in the initial stage of copolymerization, corresponding to that of the TMA.²⁵ The ESI-MS spectrum of the product initiated.

Fig. 1 Plot of Mₙ versus the mole ratio of PO and btcH₄.
by sebacic acid at a reaction time of 0 min is shown in Fig. 2(b). Unexpectedly, two types of species were observed and are listed in the inset of Fig. 2(b). The major species (1), [sebacic acid (PO)₄]Na⁺, was assigned to polyether initiated by sebacic acid, showing dihydroxyl end groups and a single unit of the incorporated starter. Species (2), [sebacic acid (CO₂)₄(PO)₄]Na⁺, was generated from the copolymerization of CO₂ and PO initiated by sebacic acid by Zn–Co-DMC catalyst. Notably, the acid groups always reacted first with the epoxide before the reaction with CO₂. Meanwhile, sebacic acid initiated homopolymer and copolymer appeared simultaneously even at a short reaction time of 0 min, indicating that sebacic acid only acted as the CTA and directly participated in the copolymerization of CO₂/PO. We speculated that the different initiation pathways of acidic CTAs were possible because of their different pkₐ values, for example, the pkₐ values of btcH₄ and sebacic acid were 1.87 and 4.72, respectively.

Two species were identified for adipic acid (pkₐ = 4.43), succinic acid (pkₐ = 4.2), and malonic acid (pkₐ = 2.82) were used to study their initiation mechanisms in the early stage of copolymerization by the ESI-MS technique. Two species were identified for adipic acid (pkₐ = 4.43) system at a reaction time of 5 min, (1) [adipic acid (PO)₄] Na⁺ and (2) [adipic acid (CO₂)₄(PO)₄]Na⁺ in Fig. S1, indicating that adipic acid directly participated in the copolymerization of CO₂ and PO in the initial stage. However, only one species, CTA initiating polyether, was identified with decreasing pkₐ value from 4.2 (succinic acid) to 2.82 (malonic acid) (Fig. S2-S3). Therefore, we could reasonably assume that the initiation mechanism of acidic CTA in the early stage of copolymerization was tightly associated with their pkₐ values. When the pkₐ value of the acid is relatively high, i.e., 4.43 (adipic acid) or 4.72 (sebacic acid), the acid acts only as the CTA, whereas when the pkₐ value of the acid is relatively low, i.e., 1.87 (btcH₄), 2.82 (malonic acid), 3.12 (trimesic acid), or even 4.2 (succinic acid), the acid acts as the initiate-transfer agent in the initial stage of copolymerization.

To understand the chain initiation-transfer reaction of btcH₄, the structure of the in situ formed btcH₄ initiating polyether was first characterized. From the cross-correlation peak in the COSY NMR (Fig. 3b), the proton signals at 5.27, 3.81, and 1.32 ppm were attributed to CH₂, CH₃, and CH₂ groups of the PO directly connected to btcH₄, respectively, in the β ring-opening mode (PhCOOCHCH₃CH₂O⁻). Likewise, the signals at 4.36, 4.16, and 1.23 ppm were attributed to CH₃, CH₂, and CH₃ groups of the PO directly connected to btcH₄, respectively, in the α ring-opening mode (PhCOOC₃H₃CH₂O⁻). The signals of PO indirectly connected to btcH₄ still appeared at ~3.5 ppm, because of the weaker electron-withdrawing inductive effects. Most importantly, the integration area met the equation of “[(A₅₋₂₇ + A₄₋₁₆ + A₃₋₁₋₉₋₁)]/A₁₃ = 6” (Fig. 3a), indicating that oligo-ether-polyol was capped by four hydroxyl groups. Moreover, the nearly same probability of the two ring-opening methods (the integrated area of α/β was 2.31/3.73 from Fig. 5a) proved the cationic characteristic of the reaction between btcH₄ and PO. Notably, the proton transfer was regarded as a possible key step and promoter for the cationic chain initiation. The four carboxylic groups of btcH₄ participated in the PO initiation under rapid chain transfer reaction, narrowing the PDIs of the products. The normal distribution in the ESI-MS spectrum also showed the formation of -OH terminated oligo-ether-tetraol and the incorporation of one btcH₄ molecule into one oligomer chain (Fig. 2a). Besides, the PO units in the oligomer were >₄, again proving that all the four carboxyl groups participated in the homopolymerization of PO. Fig. 4 shows the FTIR spectra of the corresponding products. The peaks at 1713 cm⁻¹ (carboxylic acid group) shifted to 1731 cm⁻¹ (carboxyl ester group), indicating that btcH₄ reacted with PO to form polyether. Moreover, there was no absorption peak corresponding to CO₂. Thus, the structure of the btcH₄-initiated oligo-ether-tetraol was clearly confirmed, as shown in the inset of Fig. 3b.

The results of the copolymerization using btcH₄ and btcH₄-based oligo-ether-tetraol as the CTA, respectively, are listed in Table 2. Control experiment clearly demonstrated that PO-reacted btcH₄ indeed acted as the CTA, because the performance of the resulting oligo(carbonate-ether) tetraol was almost same to that of the tetraol prepared by the conventional method. Therefore, btcH₄ acted as the chain initiate-transfer agent during the copolymerization. In the first stage, btcH₄ initiated PO homopolymerization to afford oligo-ether-tetraol in the presence of DMC catalyst, and the in situ formed tetraol then acted as the CTA to participate in the copolymerization.
Fig. 3 $^1$H NMR (a) and COSY NMR (b) spectra of oligo-ether tetraol (tetraol from Fig. 2a).

Table 2 Results of CO$_2$/PO copolymerization using btcH$_4$ and btcH$_4$-based oligo-ether-tetraol as the CTAs.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>DMC (mg)</th>
<th>PO (mL)</th>
<th>t (h)</th>
<th>P (MPa)</th>
<th>T ($^\circ$C)</th>
<th>CU$^b$ (%)</th>
<th>W$_{pc}^b$ (wt%)</th>
<th>PDI</th>
<th>$M_n^c$ (g mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>4</td>
<td>80</td>
<td>33.2</td>
<td>10.5</td>
<td>1.32</td>
<td>3400</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>4</td>
<td>80</td>
<td>32.4</td>
<td>9.2</td>
<td>1.34</td>
<td>3500</td>
</tr>
</tbody>
</table>

$^a$0.97 g btcH$_4$ was added as CTA for the copolymerization in Entry 1. However, as for Entry 2, btcH$_4$ (0.97 g)-based oligo-ether-tetraol acted as CTA in the copolymerization. The tetraol was prepared as the process in Fig. 2a, except that 0.97 g btcH$_4$ and 10 mg DMC were used. After 15 min of copolymerization, the autoclave was cooled to room temperature. The resulting low-viscosity slurry was centrifuged (12,000 rpm) to separate DMC catalyst. A colorless transparent liquid (btcH$_4$-based oligo-ether-tetraol) was obtained after evaporating excess PO, and the resulting btcH$_4$-based oligo-ether-tetraol was dried for 48 h in vacuum at 50 $^\circ$C prior to be used as the CTA.

$^b$Calculated by $^1$H NMR.

$^c$Measured by GPC.

3.3 Structural characterization of oligo(carbonate-ether) tetraol

The precise characterization of the oligo-ether-tetraol facilitated our understanding of the structure of the final oligo(carbonate-ether) tetraol. The rapid chain transfer reaction assured that the in situ formed oligo-ether-tetraol continuously participated in chain growth reaction. The IR (Fig. 4c), $^1$H NMR and $^{13}$C NMR (Fig. S4) spectra indicated that CO$_2$ was incorporated into the backbone of the oligo(carbonate-ether) tetraol, and the tetraol was terminated with hydroxyl groups. Besides, the signals at 69.1 and 66.2 ppm were attributed to the carbon of primary and secondary terminal hydroxyls, respectively (Fig. S4b). Moreover, the high ratio of the two carbons ($A_{66.2}/A_{69.1} = 1/0.13$) indicates that the oligo(carbonate-ether) tetraol was mainly capped by the secondary hydroxyl group. From the MALDI-TOF-MS spectrum, seven species were observed as shown in the inset in Fig. S5b, indicating that every oligomer contained one btcH$_4$ molecule, and the oligomers were terminated on the four sides by hydroxyl groups. As a consequence, the structure of the oligo(carbonate-ether) tetraol was clearly identified (Scheme 1).

4. Conclusions

A CO$_2$-based oligo(carbonate-ether) tetraol was successfully prepared by the copolymerization of CO$_2$/PO in the presence of btcH$_4$ using Zn-Co-DMC as the catalyst. The $M_n$ of the tetraol was controlled in the range 1500–3500 g mol$^{-1}$ (by the GPC method), and its CU content was tunable in the range 25–55%, while its PDI was quite low (even could be 1.08), the PC content could be controlled less than 4%, which was the lowest W$_{pc}$ ever reported for the polyols from heterogeneous catalyst system. The structures of both the oligo-ether-tetraol and oligo(carbonate-ether) tetraol were completely characterized. The copolymerization mechanism during the induction period was closely associated with the acidity (pk$_{a1}$ value) of the CTA, and weak organic acid (pk$_{a1}$: ~4.43–4.72) only acted as the CTA, while strong organic acid (pk$_{a1}$: ~1.87–4.2) not only acted as the CTA, but also as the chain initiator during the initial stage of the
copolymers.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Grant No. 51321062 and 21134002) for financial support.

Notes and References

*Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People’s Republic of China.

University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China.

*Corresponding author: Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People’s Republic of China.

Fax: +86 0431 85262252; Tel: +86 0431 85262252.

**Corresponding author at: Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People’s Republic of China.

Fax: +86 0431 85689095; Tel: +86 0431 85262250.

E-mail addresses: ysqin@ciac.ac.cn, xhwang@ciac.ac.cn

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Controllable Synthesis of Narrow Polydispersity CO₂-Based Oligo(carbonate-ether) tetraol

Shunjie Liu\textsuperscript{a,b}, Yuyang Miao\textsuperscript{a}, Lijun Qiao\textsuperscript{a}, Yusheng Qin\textsuperscript{a,\*, Xianhong Wang\textsuperscript{a,**}, Xuesi Chen\textsuperscript{a}, Fosong Wang\textsuperscript{a}

\textsuperscript{a}Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People’s Republic of China.

\textsuperscript{b}University of Chinese Academy of Sciences, Beijing 100039, People’s Republic of China

\*Corresponding author at: Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People’s Republic of China.

Fax: +86 0431 85262252; Tel: +86 0431 85262252.

**Corresponding author at: Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People’s Republic of China.

Fax: +86 0431 85689095; Tel: +86 0431 85262250.

E-mail addresses: ysqin@ciac.ac.cn, xhwang@ciac.ac.cn

Controllable synthesis of narrow polydispersity oligo(carbonate-ether) tetraol provided the new relationship between acidity ($p_{ka_1}$ value) of chain transfer agent and catalytic mechanism in the initial stage.