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Cheap and Fast: Oxalic Acid Initiated CO_2-based Polyols Synthesized by A Novel Preactivation Approach

Shunjie Liu,[a,b] Yusheng Qin,[b] Lijun Qiao,[b] Yuyang Miao,[b] Xianhong Wang,[b] Fosong Wang[b]

Oxalic acid, the cheapest dicarboxylic acid, was used as an effective starter to synthesize polyols from copolymerization of CO_2 and propylene oxide under zinc-cobalt double metal cyanide catalyst. Generally, long reaction time as 255 min was observed for complete PO conversion, due to the existence of free carboxylic acid group of oxalic acid. To overcome the disadvantage, we proposed a novel preactivation approach by formation of oxalic acid based oligo-ether-diol in advance, about 4.75 PO monomers were initiated at 80 °C, which was independent of time and oxalic acid amount, the diol was then acted as chain transfer agent for following copolymerization. The optimal condition showed that the reaction could be finished in 150 min, which was a remarkable shortening compared with that of 255 min. Notably, the resulting CO_2-based diol was stable up to 190 °C, indicating that oxalic acid may be applied as an effective starter for the copolymerization.

Introduction

Polyurethane (PU) is a class of polymer built up of carbamate linkages, which finds versatile applications as foams, adhesive, surface coatings, sealants, thermoplastic elastomer, and so on.[1, 2] PU is traditionally and most commonly formed by reacting isocyanate with polyols. However, with the precipitous slide of isocyanate price (< \$2000/ton since Mar. 30, 2015) in recent years, originally cheap polyols become the key factor to reduce PU cost. One promising route to reduce cost of the polyols is the introduction of extremely low-cost feedstock such as carbon dioxide (CO_2) into the backbone of polyether polyols, yielding oligo(carbonate-ether) polyols. Till now, it has been confirmed that low molecular weight oligo(carbonate-ether) polyols can afford high-quality polyurethane materials comparable with those from common polyether polyols.[3, 4]

As shown in Scheme 1, oligo(carbonate-ether) polyols can be synthesized from copolymerization of propylene oxide (PO) with CO_2 under zinc-cobalt double metal cyanide (Zn-Co-DMC) catalyst in the presence of proton-containing starter.[5-15] In Scheme 1, if the catalyst is fixed, in addition to copolymerization conditions, the starter is the most important variable to determine the feature of the resulting
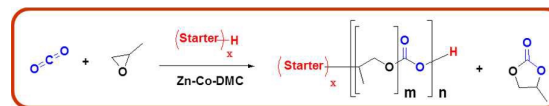
Scheme 1 Copolymerization of CO_2 with PO catalyzed by Zn-Co-DMC catalyst in the presence of starter.

oligo(carbonate-ether) polyols. Many efforts have been spent on developing suitable starters in last decades, among which oligo(carbonate-ether) polyols prepared using polypropylene glycol (PPG) as starter received considerable attention[16-20], nevertheless, the high reaction temperature resulted in polyols with low carbonate unit (CU) content. Generally, polyols with molecular weight (M_n) below 2000 g mol^{-1} and CU content over 40% are still difficult to prepare, though PPG is a cheap starter.[21, 22] Recently, we reported the tailor-made synthesis of oligo(carbonate-ether) diol using dicarboxylic acid as starter, where the M_n was controllable in the range 1200-3000 g mol^{-1}, while CU content was between 40% and 75%.[23] Moreover, the induction period of the copolymerization could be significantly reduced from 425 min to 20 min at similar reaction condition by simply replacing PPG with sebacic acid, suggesting significant influence of the starter on the copolymerization system. Many carboxylic acids starters were then used to further investigate the effect of acidic starter on the copolymerization.[24, 25] The initiation manner of different acidic starters is closely associated with their acidity (pk_{a1} value) in the initial copolymerization stage. For example, weak organic acid (pk_{a1}: 4.43~4.72) like sebacic acid only acts as the chain transfer agent directly participating in the copolymerization of CO_2 with PO, while relative strong organic acid ($1.87 < pk_{a1} < 4.2$) acts as the initiate-transfer agent which first initiates PO homopolymerization, then the *in-situ* formed

[a.] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China
[b.] Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China.
† Footnotes relating to the title and/or authors should appear here.
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polyols act as new chain transfer agent in the early stage of copolymerization.

In addition to the role as the chain transfer agent or chain initiate-transfer agent, the cost of the starter must be considered as well, because the starter usually accounts for 10-20 wt% in the resulting polyols, especially for polyols with low molecular weight, since the starter loading increases significantly with the decrease of the M_n of polyols. For example, sebacic acid has been confirmed as the effective starter, in that it can assure M_n and CU content control in addition to high productivity in short copolymerization time; however, the high price of sebacic acid may limit its industrial application. Oxalic acid is the cheapest saturated dicarboxylic acid[26], and its price is merely one sixth of that of sebacic acid. We are wondering whether oxalic acid can be used to prepare thermally stable oligo(carbonate-ether) diol. In a preliminary study, we found that the reaction time for complete PO conversion lasted as long as 255 min using oxalic acid as starter (the reaction time for sebacic acid was only 40 min at similar condition). The extension of reaction time will inevitably increase the cost of production. To accelerate the reaction, here we propose a novel preactivation approach based on understanding of the reaction mechanism, by homopolymerization of PO under oxalic acid, then the resulting oligo-ether-diol acts as chain transfer agent for the following copolymerization reaction, and the reaction time can be shortened to 150 min.

Results and discussion

Immortal polymerization discovered by Inoue in 1985[27] is an effective method to synthesize end-functional polymers with controllable M_n and narrow polydispersity index (PDI). The copolymerization of CO_2 with PO under Zn-Co-DMC catalyst in the presence of active proton containing starter is one of such immortal polymerization. However, when oxalic acid is used as the starter, the copolymerization reaction needs 255 min for complete PO conversion. According to our previous report[25], oxalic acid, pK_{a1} (1.25) < 4.2, should act as initiate-transfer agent in the early stage of the copolymerization. Since the starters usually affect the initial stage of copolymerization, clarification of the intermediates in this stage is vitally important to understand the long reaction time in oxalic acid system. Figure 1 shows the ESI-MS spectra of the reaction products at different reaction time, where the copolymerization was carried out at 80 °C and 4 MPa, using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO. After 4 min of reaction, four species were identified from Figure 1(a) (detailed information of each *m/z* species see the bottom of each picture).
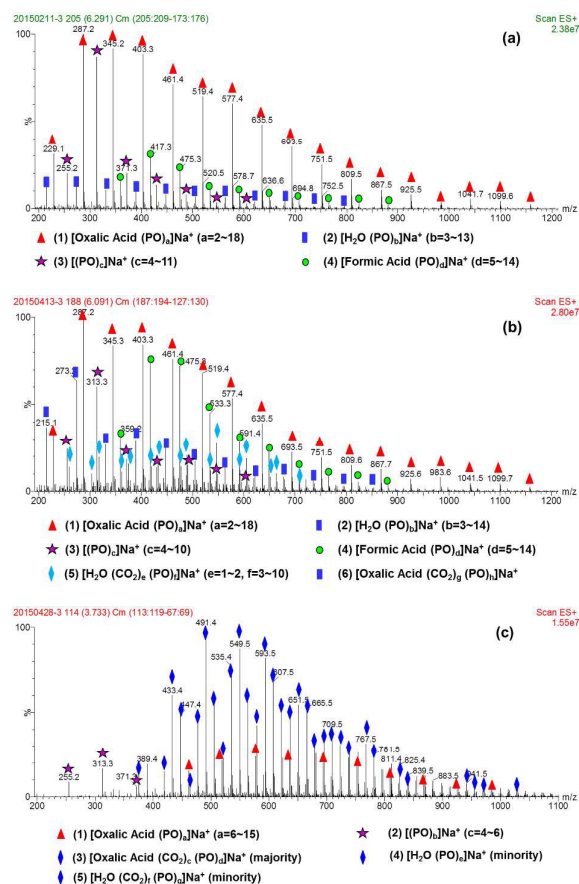
Figure 1. ESI-MS spectra of copolymerization products at different reaction time: (a) 4 min, (b) 30 min, (c) 180 min. The copolymerization reaction was carried out at 80 °C and 4 MPa using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

The major species *(1)* was assigned to oxalic acid initiating polyether, showing dihydroxyl end-groups and a single unit of the incorporated starter. Species *(2)* with low relative abundance represented polyether diol prepared from the adventitious H_2O present in reaction system. Species *(3)* was a cyclic oligo-propylene oxide generated through a neutral loss of H_2O from $[H_2O(PO)_b]Na^+$ under ESI-MS test condition.[28] The species *(4)* was assigned to formic acid initiated polyether, which was observed with weak relative abundance. Considering the chemical unstable structure of oxalic acid,[26] we could reasonably assume that the formic acid based polyether was generated through decarboxylation from free carboxylic acid group present in oxalic acid initiated polyether under ESI-MS test. Thus, oxalic acid first initiated PO homopolymerization in the early stage of copolymerization, as evidenced by the exclusively formation of polyether.[25] A clear assignment of oxalic acid based polycarbonate-ether was not feasible due to its overlap with H_2O initiated polyether or polycarbonate-ether from the ESI MS spectrum. With extending reaction time, we observed an increasing H_2O initiated polyether or polycarbonate-ether signal, whereas the relative abundance of oxalic acid based
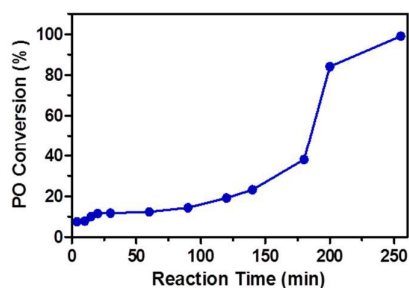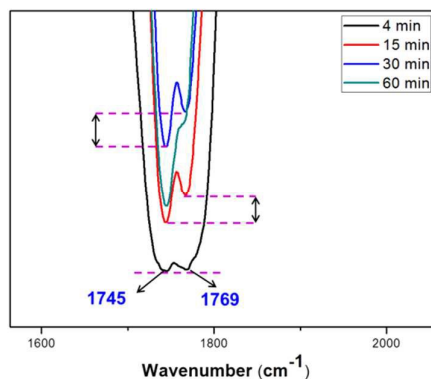
Figure 2. Plot of PO conversion versus time for the copolymerization of CO_2 and PO carried out at 80 °C and 4 MPa, using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

Figure 3. FTIR spectra in the C=O stretching region for the copolymerization products at different reaction time: (a) 4 min, (b) 15 min, (c) 30 min, (d) 60 min. The copolymerization was carried out at 80 °C and 4 MPa using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

polyether declined (Figure 1a-b, Figure S1-6). Since water content remained constant in the reaction system, implying that the above species possibly attributed to oxalic acid based oligo(carbonate-ether) diol. Notably, the relative abundance of species, [oxalic acid $(CO_2)_c$ $(PO)_d$]Na^+, increased significantly after 30 min and became dominant at 180 min (Figure 1c, mainly composed by oxalic acid based CO_2 and PO copolymer). Therefore, we could conclude that the induction period of oxalic acid for copolymerization was about 30 min, while that for adventitious H_2O was about 15 min (Figure S2), according to our previous definition.[24] Interestingly, the maximum number of PO homopolymerization initiated by oxalic acid and H_2O before 30 min was constant as 18 and 13, respectively, which was dependent on themselves rather than reaction time. Moreover, the thermal stability of the products increased with time, as evidenced by the disappearance of the species [Formic Acid$(PO)_d$]Na^+ at 180 min, in the ESI-MS spectrum (Figure 1c).

In order to understand the chain propagation reaction, the apparent kinetics of the CO_2/PO copolymerization in the presence of oxalic acid was investigated (Figure 2).

Plots of PO conversion versus reaction time exhibited sigmoid shape indicative of slow initiation reaction.[29] The PO conversion was only 20% at 120 min, and it increased to about 40% at 180 min, and rapidly increased to 85% at 200 min. The result suggested that the reaction time of PO conversion increased significantly corresponded to the time that the carboxylic acid group disappeared (180 min from Figure 1c). Therefore, the low PO conversion or long reaction time might result from the existence of free carboxylic acid group in the reaction system.

FTIR spectrum is powerful to detect carbonyl group in the sample. Figure 3 shows the FTIR spectra in C=O stretching region for the copolymerization products at different reaction time. For the reaction product at 4 min (oxalic acid initiated polyether), two nearly equivalent absorption peaks at 1745 cm^{-1} and 1769 cm^{-1} characterizing of stretching modes of C=O group were observed, suggesting almost complete reaction of the two carboxylic acid groups in oxalic acid, as proved by model compound diethyl oxalate.[30] The relative intensity of peaks at 1745 cm^{-1} to 1769 cm^{-1} increased with reaction time, due to the formation of CO_2 based copolymer ($v_{C=O}$ in carbonate segment was 1745 cm^{-1}), which matched the

induction period of H_2O and oxalic acid (15 and 30 min, respectively). For the reaction product at 60 min, the absorption peak at 1769 cm^{-1} weakened and appeared as a shoulder peak, which was suppressed by the incorporation of CO_2 in the copolymer. The increase of absorption intensity at 1745 cm^{-1} after 30 min further proved that species *(2)* in Figure 1b, S2-6 was assigned to oxalic acid initiated copolymer of CO_2 and PO.

As discussed above, the existence of free carboxylic acid group might result in low PO conversion or long reaction time. We are wondering whether the reaction time can be shortened by elimination of the free carboxylic acid group in the reaction system. Considering the relatively strong acidic character of oxalic acid (pk_{a1}=1.25, pk_{a2}=4.14), the two carboxylic acid
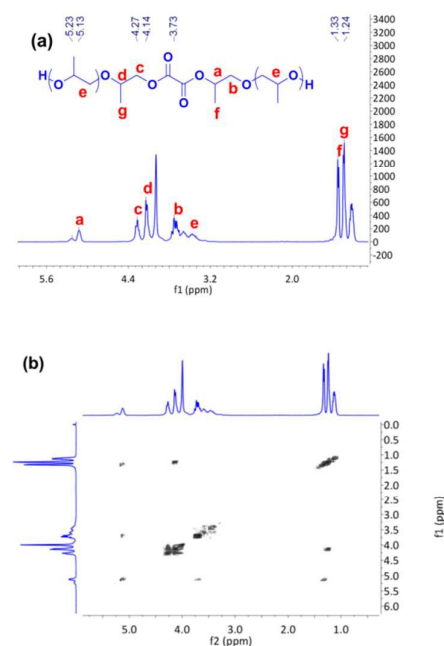
Figure 4. ^1H NMR (a) and COSY NMR (b) spectra of oligo-ether-diol (diol from Figure S7).

groups can be almost completely converted by reaction with PO. Therefore, a novel preactivation approach was proposed to reduce the copolymerization time. At first, oxalic acid was converted to oligo-ether-diol by reaction with PO, late DMC catalyst was added, and CO_2 was pressurized to initiate the copolymerization. ESI-MS spectrum was recorded to characterize the resulting oligo-ether-diol. No formic acid based polyether was detected from the pure product of oxalic acid and PO at 80 °C for short reaction time of 4 min (see ESI-MS spectrum of reaction product in Figure S7), indicating that the polyether was capped with two terminal hydroxyl groups. The microstructure of the oligo-ether-diol was further characterized by ^1H NMR and COSY NMR spectra. The absorption peaks were assigned and the possible structure of oligo-ether-diol is shown in the inset of Figure 4a. However, it should be noted that the absorption peak assigned to PO directly connected to oxalic acid overlapped with that of the carbonate group in oligo(carbonate-ether) diol, moreover, no characteristic protons present in the oxalic acid, which added difficulty for the precise calculation of CU content and W_{pc} of the final product.

The effect of the preactivation time on the copolymerization of CO_2/PO is summarized in Table 1. All polymerizations showed reduced copolymerization time than that of control experiment (255 min), and the copolymerization time decreased at first and then increased with extending preactivation time from 0 min to 120 min (Entries 1-7, 10). Notably, a minimum copolymerization time of 150 min was observed at the preactivation time of 15 min (Figure 5).

Table 1. The Effect of preactivation time on the copolymerization[a]

| Entry	Time-1[b] (min)	$\bar{N}_{PO}$[c]	Time-2[d] (min)	CU[e] (%)	W_{pc}[e] (%)	M_n[f] (g mol^{-1})	PDI[f]
1	0	3.56	240	40.8	7.2	5000	1.33
2	5	4.0	195	39.4	6.9	4800	1.29
3	15	4.69	150	41.4	7.6	4800	1.28
4	30	4.78	160	41.2	7.3	4800	1.28
5	60	4.83	180	39.9	6.7	4800	1.29
6	90	4.74	215	42.2	6.0	4900	1.29
7	120	4.81	225	42.4	6.5	4900	1.28
8[g]	15	4.73	190	45.8	6.4	7400	1.34
9[h]	15	4.72	200	38.7	7.3	3500	1.26
10[i]	-	-	255	37.8	7.6	5200	1.30

[a] The preactivation reaction between oxalic acid (0.32 g) and PO (10 ml) was carried out at 80 °C for different time, then 20 mg Zn-Co-DMC was added and the reaction system was pressured to 4 MPa to initiate copolymerization. [b] Time-1 referred to the preactivation time. [c] $\bar{N}_{PO}$ was average PO number calculated by ^1H NMR, $\bar{N}_{PO}=(A_{3.5}-2A_{5.12})/(3A_{5.12}+A_{4.14-4.27})$ + 2. [d] Time-2 was the time needed for complete PO conversion after preactivation. [e] Calculated by ^1H NMR spectrum, CU=$(A_{5.0}+A_{4.2}-2.73A_{5.2}-2A_{4.58})/(A_{5.0}+A_{4.2}-2.73A_{5.2}-2A_{4.58}+A_{3.5}+3.73A_{5.2})$, $W_{pc}=102A_{5.2}/[102(A_{5.0}+A_{4.2}-2.73A_{5.2}-2A_{4.58}+A_{1.5})+58(A_{3.5}+3.73A_{5.2})]$, see Figure S8. [f] Measured by GPC. [g] 0.2 g oxalic acid and 15 mg DMC were used, other conditions were the same as in Note [a]. [h] 0.4 g oxalic acid and 25 mg DMC were used, other conditions were the same as in Note [a]. [i] Control experiment, without pre-activation process.
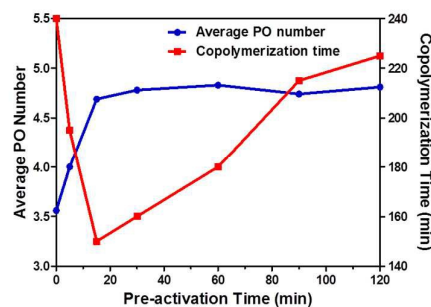
Figure 5. Typical plot of average PO number and copolymerization time versus time for the copolymerization of CO_2 and PO carried out at 80 °C and 4 MPa, using 0.32 g oxalic acid, 20 mg DMC and 10 ml PO.

The total reaction time (165 min) was still significantly shorter than 255 min, suggesting the feasibility of preactivation approach, which was vitally important in industrial production. Moreover, the similar results (CU, W_{pc}, M_n, PDI of the diol) of the preactivation experiment and control experiment showed that the oxalic acid initiated oligoether diol participated in the copolymerization rather than as a blend existed in the final diol. The average PO number ($\bar{N}_{PO}$) of the preactivation product was an important parameter to observe the initiation character of oxalic acid. As shown in Figure 5, $\bar{N}_{PO}$ of the preactivation product increased dramatically to 3.56 at 5 min preheating (corresponding to 0 min in Figure 5), the $\bar{N}_{PO}$ maintained constant as 4.75 PO after 15 min. The slight change of $\bar{N}_{PO}$ was in good agreement with the variation in PO conversion before 120 min (Figure 2). Moreover, different oxalic acid loading displayed neglectable effect on $\bar{N}_{PO}$ (Entires 4, 8-9). Generally, about 4.75 PO monomers were initiated by oxalic acid in the early stage of homopolymerization, which was independent of time and starter loading. It was for this reason that drop in molecular weight resulted in the decrease of CU content in the final oligo(carbonate-ether) diol.

As discussed above, it is difficult to calculate the CU content and W_{pc} of the final oligo(carbonate-ether) diol, due to the overlapping of absorption peak of PO directly connected to oxalic acid (δ = 4.1-4.2, 3.7 ppm) with that of the carbonate group in oligo(carbonate-ether) diol, therefore, these peak areas should be subtracted in the calculation to obtain accurate data. Fortunately, though there were no characteristic protons in oxalic acid molecule, the molar ratio of α, β ring opening method was constant as 2.73/3 in directly attached PO (Figure S9), and the peaks at 5.2 ppm could be integrated distinctly. Therefore, the peak area at 4.1-4.2 and 3.7 ppm were equal to $2.73A_{5.2}$ and $2A_{5.2}$, respectively, which coincidently solved the problem of precisely calculating the CU, $\bar{N}_{PO}$ and W_{pc} of the final product. It should be noted that the peaks of the cyclic propylene carbonate (4.89 and 4.04 ppm) also overlapped with the peaks of the copolymer, all these peak areas should be considered in the calculation. Based on above analysis, CU, $\bar{N}_{PO}$ and W_{pc} of the final product can be calculated according to the equations 1-3:
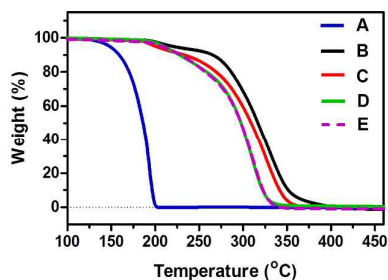
Figure 6. Thermogravimetric Analyzer (TGA) curves of (A) anhydrous oxalic acid；(B) sebacic acid based oligo(carbonate-ether) diol (M_n=5200, CU=46%, PDI=1.25); oxalic acid based oligo(carbonate-ether) diol (C) (M_n=5200, CU=42%, PDI=1.3); (D) (M_n=3500, CU=34%, PDI=1.25); (E) (M_n=1200, CU=15%, PDI=1.22).

$$CU=(A_{5.0}+A_{4.2}-2.73A_{5.2}-2A_{4.58})/(A_{5.0}+A_{4.2}-2.73A_{5.2}-2A_{4.58}+A_{3.5}+3.73A_{5.2}) \quad (1)$$

$$\bar{N}_{PO}=(A_{3.5}-2A_{5.12})/(3A_{5.12}+A_{4.14-4.27}) + 2 \quad (2)$$

$$W_{pc}=102A_{1.5}/[102(A_{5.0}+A_{4.2}-2.73A_{5.2}-2A_{4.58}+A_{1.5})+58(A_{3.5}+3.73A_{5.2})] \quad (3)$$

In order to further demonstrate that the shortening of copolymerization time was due to the formation of polyether diol. After preactivation for 15 min, the copolymerization stopped even at the beginning (only preheating for 5min). The absorption peak characteristics of carbonate unit in the ^{1}H NMR appeared, proving the incorporation of CO_2 (Figure S10). Therefore, the oxalic acid based polyether diol did act as chain transfer agent at once during the copolymerization. We could reasonably conclude that the complete conversion of oxalic acid or the disappearance of carboxylic acid group in the initial stage was the key of shortening reaction time.

In another consideration, oxalic acid is sensitive to heat, therefore question like thermal instability arose in oxalic acid based diol due to the existence of two neighboring carboxylic acid groups. It was encouraging to find that almost the same starting gravimetric temperature (~190 °C) of oxalic acid-based and sebacic acid-based oligo(carbonate-ether) diol (M_n=5200 g mol^{-1}) was observed from TGA (Figure 6), which was higher than that of anhydrous oxalic acid (125 °C, part of which might be caused by sublimation), suggesting the formation of the highly stable oxalic acid based oligo(carbonate-ether) diol. Moreover, as shown in Figure 6, even though the M_n of the oxalic acid diol changed from 5200 g mol^{-1} to 1200 g mol^{-1}, the starting gravimetric temperature remained constant, further proved the thermally stability of the resulting oligo(carbonate-ether) diol.

Experimental

Materials

Anhydrous oxalic acid was purchased from Alfa Aesar and dried for 48 h in vacuum at 50 °C prior to use. $K_3[Co(CN)_6]$ was also provided by Alfa Aesar and recrystallized in deionized water prior to use, $ZnCl_2$ and tert-butanol (t-BuOH) were analytical grade and used without further purification. PO was refluxed over calcium hydride and then distilled under argon atmosphere. Carbon dioxide with purity over 99.99% was used as received.

Zn-Co-DMC catalyst was prepared according to the previous report.[6]

Copolymerization

One-pot copolymerization: in a glove box free of oxygen and water, calculated DMC catalyst, acidic starter and PO were added to a 50 ml professional stainless-steel autoclave with a magnetic stirring. CO_2 was pressurized to this mixture and the reaction was carried out at determined condition. After copolymerization, the autoclave was cooled to room temperature, and the CO_2 pressure was released by opening the outlet valve. A small aliquot of the copolymerization mixture was taken out for ^{1}H NMR spectroscopy.

Pre-activation approach: in a glove box free of oxygen and water, calculated acidic starter and PO were added to a 50 ml professional stainless-steel autoclave with a magnetic stirring. The reaction was carried out at determined condition. After pre-activation, the autoclave was cooled to room temperature, a small aliquot of the reaction mixture was taken out for ^{1}H NMR spectroscopy. Then calculated DMC catalyst was added to the autoclave and CO_2 was pressurized to this mixture and stabilized for 5 min. After copolymerization, the autoclave was cooled to room temperature, and the CO_2 pressure was released by opening the outlet valve. A small aliquot of the copolymerization mixture was taken out for ^{1}H 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.

Measurements

Fourier transform infrared (FTIR) 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}. ^{1}H NMR, ^{13}C NMR and COSY NMR spectra were recorded at room temperature on Unity-500 NMR spectrometer using $CDCl_3$ as solvent. The M_n and PDI of the oligo(carbonate-ether) diol 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 CH_2Cl_2 as eluent, where the flow rate was set at 1.0 ml/min. Electrospray ionization mass spectrometry (ESI-MS) analyses were performed on Waters Quattro Premier XE mass spectrometer, using methanol/water (4:1) as solvent. Thermogravimetric analyzer (TGA) test was carried out on a Perkin-Elmer Pyris 1 TGA thermal analyser from 40 °C to 500 °C under nitrogen protection at a heating rate of 10 °C min^{-1}.

Conclusions

Oxalic acid initiated thermally stable oligo(carbonate-ether) diol was cheaply and fast synthesized by the immortal copolymerization of CO_2 and PO using Zn-Co-DMC catalyst via a novel preactivation approach. The existence of carboxylic acid group of oxalic acid resulted in the prolongation the copolymerization time. By using preactivation approach, the reaction time could be significantly reduced from 255 min to 150 min, and the resulting oligo(carbonate-ether) diol showed almost the same structure to that prepared by one-pot method. The studies revealed that about 4.75 PO monomers were initiated during preactivation, accounting for the CU content dropped with decreasing M_n. The studies also highlighted that the oligo-ether-diol formed by preactivation approach almost immediately participated in the copolymerization of CO_2 and PO and therefore shortened the reaction time. Thus, such preactivation approach may be an interesting means to shorten the reaction time of polyols in the strong acidic starter system.

Acknowledgements

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Cheap and Fast: Oxalic Acid Initiated CO$_2$-based Polyols Synthesized by A Novel Preactivation Approach

Shunjie Liu,[a,b] Yusheng Qin,[b] Lijun Qiao,[b] Yuyang Miao,[b] Xianhong Wang,[b] Fosong Wang[b]
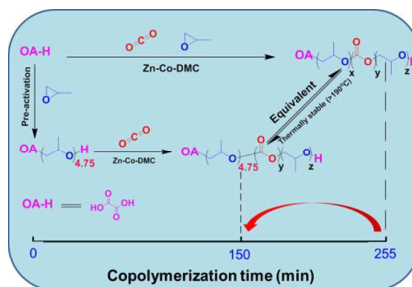
Preactivation: an interesting means to shorten the copolymerization time of the CO$_2$-based polyols synthesized by strong acidic but cheap oxalic acid.