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Controllable Synthesis of Narrow Polydispersity CO_2-Based Oligo(carbonate-ether) tetraol

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CO_2-based oligo(carbonate-ether) tetraol was synthesized in a controlled manner by immortal copolymerization of carbon dioxide (CO_2) and propylene oxide (PO) in the presence of 1,2,4,5-benzenetetracarboxylic acid ($btcH_4$) catalyzed by zinc–cobalt double metal cyanide (Zn–Co–DMC) catalyst. The number average molecular weight (M_n) of the tetraol was in a good linear relationship with the molar ratio of PO and $btcH_4$ (PO/$btcH_4$), 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 M_n of 1,400 g mol^{-1}. Notably, the weight fraction of byproduct propylene carbonate (W_{PC}) was reduced to as low as 4.0 wt%, which is the lowest W_{pc} 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 (pk_{a1} 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 pk_{a1} value is higher than that of adipic acid (pk_{a1} = 4.43). However, when its pk_{a1} value is lower than that of succinic acid (pk_{a1} = 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 CO_2 is highly attractive not only from the viewpoint of CO_2 utilization, but also from the abatement of environmental pressure. A promising process of CO_2 utilization is the copolymerization of CO_2 and propylene oxide (PO) to prepare biodegradable polycarbonates pioneered by Inoue since 1969.[1, 2] Significant progress has been made to promote the process, owing to the fast developing catalyst systems, which have been summarized in the recent reviews.[3–6] Though low-molecular-weight copolymers from CO_2 and PO have received less attention, their potential applications as polyols in the polyurethane industry may create a new era in CO_2 copolymer.[7–12] 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.[13] Salen Cobalt complex has been reported as very active and selective catalyst to make narrow polydispersity polyol;[14] however, its specific selectivity in the formation of polar carbonate unit leads to polyols with a high viscosity,[14] which is inconvenient to process with standard equipment used in the polyurethane industry.[13]

Unlike Salen Cobalt complex catalyst, double metal cyanide (DMC) catalysts are preferably used to prepare oligo(carbonate-ether) polyols, especially in industrial field.[8, 9, 11, 15–18] However, the reaction proceeds with relatively long induction period, and the resulting polyols suffer from low CO_2 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,[19] adding CO_2-philic compounds,[16] or preactivation catalyst[10] have been explored. Moreover, sterically hindered monofunctional agents were added,[15] introducing suspending agents and continuously dosing hydrogen-functional starter substance methods[17, 20, 21] to reduce the polydispersity index (PDI) of polyols, while the induction period can be shortened by activating DMC catalyst with sterically nonhindered phenols[18]. Salen Cobalt may be used together with Zn-Co-DMC catalyst, but the obtained polyols still had relatively high M_n (5000 g mol^{-1}), broad PDI (4.1), and low CU (10%), which did not fit with either plastic or polyurethane productions.[22] Therefore, the preparation of polyols with a suitable CU, low M_n, and narrow PDI is still a big challenge.

A CO_2-based oligo(carbonate-ether) diol (CU = 40–75%, M_n < 2000 g mol^{-1}) more suitable for polyurethane production was synthesized by replacing the starter with dicarboxylic acid in our group.[23, 24] The induction period of dicarboxylic acids was found to be shorter than that of the oligo-diol.[24] Based on this consideration, CO_2-based oligo(carbonate-ether) triol was synthesized using trimesic acid (TMA) as the chain transfer agent (CTA).[25] Interestingly, TMA played a special role, *i. e.*, it acted as the initiate-transfer agent in the copolymerization of CO_2 and PO.

Polyols with more than two hydroxyl groups are well known to afford widely used crosslinked polyurethane materials.[26] In this study, oligo(carbonate-ether) tetraol with a narrow PDI was synthesized in high productivity by the copolymerization of CO_2 and PO using a catalyst system comprised a Zn-Co-DMC component together with 1,2,4,5-benzenetetracarboxylic acid ($btcH_4$) as the CTA.

2. Experimental section

2.1 Materials

Sebacic acid, $btcH_4$, 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. $K_3[Co(CN)_6]$ was provided by Alfa Aesar and recrystallized in deionized water prior to use. $ZnCl_2$ 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.[27]

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 $btcH_4$ were added in the pretreated autocalve free of oxygen and water at ambient temperature, and the autoclave was then placed in a water bath at fixed temperature, followed by adding CO_2 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. CO_2 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 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.

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}. ^{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) 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 CH_2Cl_2 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 atuoflex 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) tetraol 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 CO_2-based oligo(carbonate-ether) tetraol

The extremely rapid chain transfer reaction by immortal polymerization successfully afforded oligo(carbonate-ether) tetraol. The effect of the reaction conditions on the copolymerization of CO_2/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/$btcH_4$ molar ratios. When the PO/$btcH_4$ molar ratio decreased from 37.4 to 16.7 (Entries 1–5), the PDI of the CO_2-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,[23] strongly proving the immortal polymerization mechanism[28]. At the same mole 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 $btcH_4$, 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 tetraol decreased from 32.7 to 25.6% when PO/$btcH_4$ ratio decreased from 37.4 to 16.7 (Entries 1–5), possibly because the increasing $btcH_4$ load might disfavor the CO_2 incorporation.

Table 1 Effect of reaction conditions on the copolymerization[a]

Entry	DMC (mg)	PO/btcH$_4$ (mol mol^{-1})	t (h)	P (MPa)	T (°C)	CU[b] (%)	W_{pc}[b] (wt%)	M_n[b] (g mol^{-1})	M_n[c] (g mol^{-1})	PDI[c]	Productivity[d] (kg g^{-1})
1	100	37.4	8	4	80	32.7	10.8	3050	3500	1.35	1.05
2	180	27.3	8	4	80	30.8	13.2	2300	2500	1.22	0.62
3	190	22.9	8	4	80	30.6	14.7	1900	2050	1.15	0.59
4	210	18.7	8	4	80	28.2	16.5	1600	1700	1.10	0.53
5	240	16.7	8	4	80	25.6	16.2	1400	1550	1.08	0.48
6	210	22.9	10	4	70	36.9	11.4	2000	2100	1.14	0.55
7	240	22.9	21	4	60	48.6	6.3	2050	2150	1.17	0.47
8	330	22.9	41	4	50	54.5	4.0	2000	2100	1.19	0.36
9	210	22.9	7	3	70	31.0	11.9	1900	2050	1.16	0.51
10	210	22.9	10	5	70	43.7	8.8	2000	2200	1.18	0.53
11	210	22.9	11	5.8	70	43.0	10.2	1800	2200	1.17	0.49
12[e]	220	18.7	8	4	80	32.7	21.3	1400	1800	1.18	0.52
13[f]	50	18.6	5	4	80	45.2	8.2	1500	2500	1.35	2.44

[a]All the copolymerization reactions were carried out using 100 mL PO, and the amount of btcH$_4$ used in Entries 1–5 was 9.7, 13.3, 15.8, 19.4, 21.7 g, respectively, entries 6–11, 15.8 g. [b]Calculated by ^{1}H NMR: CU = $(3A_{5.2} + A_{5.0} + A_{4.2} - 6A_{8.1} - 2A_{4.58})/(A_{5.2} + A_{5.0} + A_{4.2} + A_{3.5} - 2A_{4.58})$; $W_{pc} = 102A_{1.5}/[102(3A_{5.2} + A_{5.0} + A_{4.2} - 6A_{8.1} - 2A_{4.58} + A_{1.5}) + 58(A_{3.5} + 6A_{8.1} - 2A_{5.2})]$; $M_n = 68(3A_{5.2} + A_{5.0} + A_{4.2} - 6A_{8.1} - 2A_{4.58})/A_{8.1} + 116(A_{3.5} + 6A_{8.1} - 2A_{5.2})/3A_{8.1}+254$. [c]Measured by GPC. [d]Calculated by $W_{product}/W_{DMC}$. [e]TMA (16.0 g) acted as the CTA, data from reference 25. [f]sebacic acid (15.5 g) acted as CTA, data from reference 24.

The effect of temperature on the copolymerization is summarized 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 CO_2 at the same temperature.

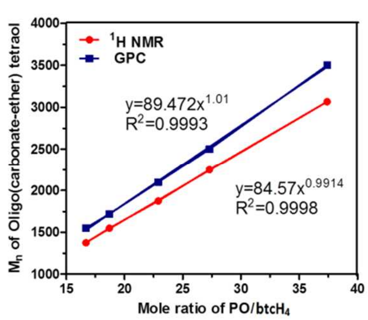


Fig. 1 Plot of M_n versus the mole ratio of PO and btcH$_4$.

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 M_n of the tetraol was exactly controlled by varying the PO/btcH$_4$ molar ratio, as the M_n measured by GPC or calculated by ^{1}H NMR fitted well with the PO/btcH$_4$ molar ratio (all the R^2 >0.999), but not the DMC catalyst amount. Therefore, tetraols with different M_ns 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 M_ns.[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 btcH$_4$ at a reaction time of 4 min (<10% PO conversion). Only one species, btcH$_4$ initiating polyether [btcH$_4$ (PO)$_x$] Na$^+$ ($4 \leqslant x \leqslant 11$), 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 CO_2 becoming feasible. Therefore, btcH$_4$ 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 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 $(PO)_x$]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 $(CO_2)_m$ $(PO)_n$]Na^+, was generated from the copolymerization of CO_2 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 CO_2. 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 CO_2/PO. We speculated that the different initiation pathways of acidic CTAs were possible because of their different pk_{a1} values, for example, the pk_{a1} values of $btcH_4$ and sebacic acid were 1.87 and 4.72, respectively.

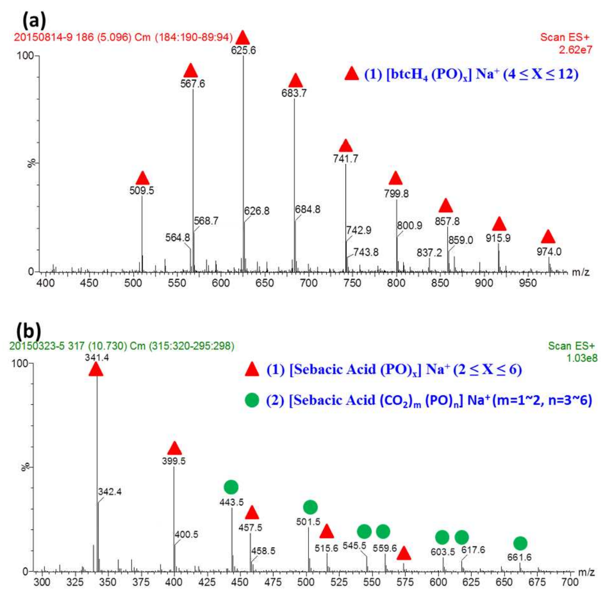


Fig. 2 ESI-MS spectra of the copolymerization product initiated by $btcH_4$ (a, 15 min, 0.45 g $btcH_4$) and sebacic acid (b, 0 min, 0.72 g). The copolymerization was carried out at 80 °C and 4 MPa using 20 mg Zn-Co-DMC catalyst and 10 mL PO.

To address this issue, several CTAs with different pk_{a1} values, such as adipic acid (pk_{a1} = 4.43), succinic acid (pk_{a1} = 4.2), and malonic acid (pk_{a1} = 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 (pk_{a1} = 4.43) system at a reaction time of 5 min, *(1)* [adipic acid $(PO)_x$] Na^+ and *(2)* [adipic acid $(CO_2)_m$ $(PO)_n$]Na^+ in Fig. S1, indicating that adipic acid directly participated in the copolymerization of CO_2 and PO in the initial stage. However, only one species, CTA initiating polyether, was identified with decreasing pk_{a1} value from 4.2 (succinic acid) to 2.82 (malonic acid) (Fig. S2-3). Therefore, we could reasonably assume that the initiation mechanism of acidic CTA in the early stage of copolymerization was tightly associated with their pk_{a1} values. When the pk_{a1} 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 pk_{a1} value of the acid is relatively low, *i. e.*, 1.87 ($btcH_4$), 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 $bctH_4$, the structure of the *in situ* formed $bctH_4$ 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 CH, CH_2, and CH_3 groups of the PO directly connected to $btcH_4$, respectively, in the β ring-opening mode ($PhCOOCHCH_3CH_2O$-). Likewise, the signals at 4.36, 4.16, and 1.23 ppm were attributed to CH_2, CH, and CH_3 groups of the PO directly connected to $btcH_4$, respectively, in the α ring-opening mode ($PhCOOCH_2CHCH_3O$-). The signals of PO indirectly connected to $btcH_4$ still appeared at ~3.5 ppm, because of the weaker electron-withdrawing inductive effects. Most importantly, the integration area met the equation of "$(A_{5.27} + A_{4.36} + A_{4.16} + A_{3.81\text{-}3.91})/A_{8.13} = 6$" (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 $btcH_4$ and PO. Notably, the proton transfer was regarded as a possible key step and promoter for the cationic chain initiation.[30] The four carboxylic groups of $btcH_4$ 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 $btcH_4$ 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 $btcH_4$ reacted with PO to form polyether. Moreover, there was no absorption peak corresponding to CO_2. Thus, the structure of the $btcH_4$-initiated oligo-ether-tetraol was clearly confirmed, as shown in the inset of Fig. 3b.

The results of the copolymerization using $btcH_4$ and $btcH_4$-based oligo-ether-tetraol as the CTA, respectively, are listed in Table 2. Control experiment clearly demonstrated that PO-reacted $btcH_4$ 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, $btcH_4$ acted as the chain initiate-transfer agent during the copolymerization. In the first stage, $btcH_4$ 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.

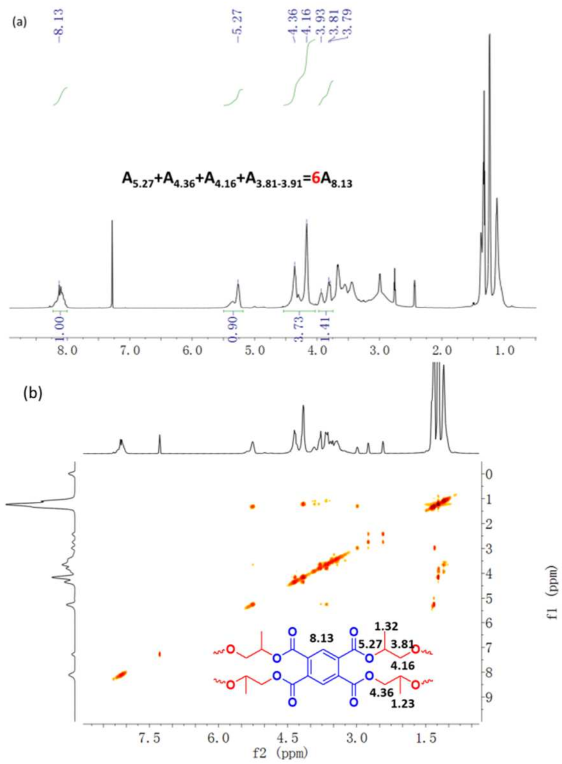


Fig. 3 [1]H NMR (a) and COSY NMR (b) spectra of oligo-ether tetraol (tetraol from Fig. 2a).

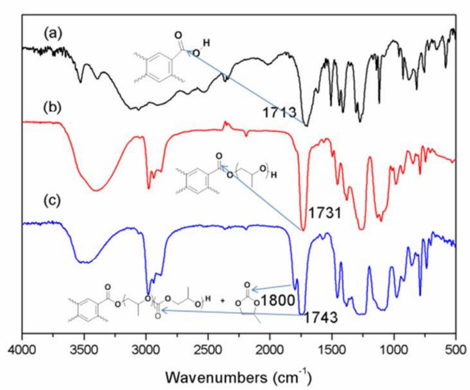


Fig. 4 The FTIR spectra of the products: (a) pure btcH$_4$; (b) oligo-ether-tetraol from Figure 2; (c) oligo(carbonate-ether) tetraol from Entry 8 Table 1.

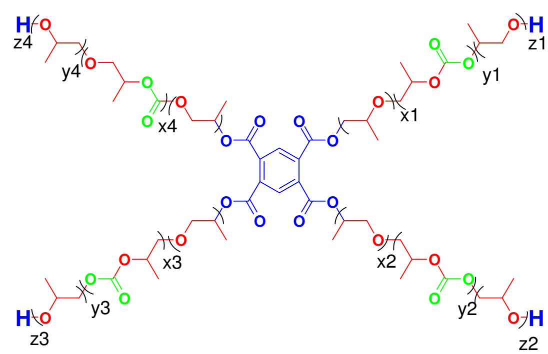
Table 2 Results of CO_2/PO copolymerization using btcH$_4$ and btcH$_4$-based oligo-ether-tetraol as the CTAs.[a]

Entry	DMC (mg)	PO (mL)	t (h)	P (MPa)	T (°C)	CU[b] (%)	W_{pc}[b] (wt%)	PDI[c]	M_n[c] (g mol^{-1})
1	10	10	8	4	80	33.2	10.5	1.32	3400
2	10	10	8	4	80	32.4	9.2	1.34	3500

[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 °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).



Scheme 1 The structure of the oligo(carbonate-ether) tetraol

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 copolymerization.

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Notes and References

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† 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

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Controllable Synthesis of Narrow Polydispersity CO_2-Based Oligo(carbonate-ether) tetraol

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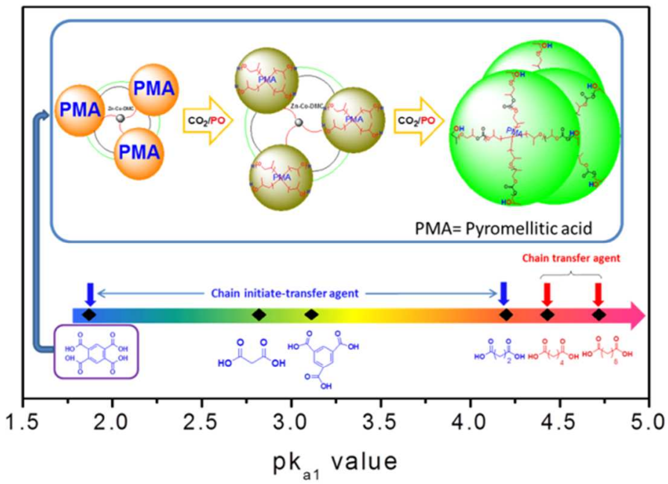

Controllable synthesis of narrow polydispersity oligo(carbonate-ether) tetraol provided the new relationship between acidity (pk_{a1} value) of chain transfer agent and catalytic mechanism in the initial stage.