J Polym Res (2012) 19:9878
DOI 10.1007/s10965-012-9878-5

ORIGINAL PAPER

Selective synthesis of oligo(carbonate-ether) diols from copolymerization of CO_2 and propylene oxide under zinc-cobalt double metal cyanide complex

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Received: 27 December 2011 / Accepted: 11 April 2012 / Published online: 25 April 2012

Abstract Colorless oligo(carbonate-ether) diols were selectively synthesized in high efficiency from copolymerization of CO_2 and propylene oxide (PO) using $Zn_3[Co(CN)_6]_2$-based double metal cyanide complex (DMC) as catalyst and different molecular weight polypropylene glycols (PPGs) as chain transfer agent. The catalytic activity was related to carbonate unit content and molecular weight of target oligo(carbonate-ether) diols, for oligo(carbonate-ether) diol with number average molecular weight of 6.4 kg/mol and carbonate unit content of 34.3 %, it reached 10.0 kg oligomer/g DMC catalyst during 10 h of copolymerization. Generally, the number average molecular weight of the oligo(carbonate-ether) diol was tunable between 1.8 kg/mol and 6.4 kg/mol, and the molecular weight distribution was controllable between 1.14 and 1.83. Moreover, the carbonate unit content in the oligo-diols can be adjusted between 15.3 % and 62.5 %, lower temperature and higher CO_2 pressure were favorable for higher carbonate content. Better selectivity of oligo(carbonate-ether)diol over propylene carbonate(PC) was realized, where the weight ratio of PC (W_{PC}) was controlled less than 8.0 wt%. We also found that the alkali metal ion residue may play an important role in PC formation, in some cases this effect may be more significant than backbiting process, removing the residual alkali metal ion should be meaningful in the future to further reduce the PC formation.

Keywords Carbon dioxide · Propylene oxide · Double metal cyanide complex catalyst · Oligo(carbonate-ether) diols

Introduction

Oligo(carbonate-ether) diols are low-molecular weight polyether carbonates telechelated by hydroxyl groups which are widely used as soft segments in polyurethane industry. Generally, they are prepared by the reaction of diols with phosgene or phosgene derivatives [1], ring-opening polymerization of six-membered cyclic carbonates [2], transesterification of dimethyl- or diethylcarbonate as well as alkylene carbonate with diols [3–8]. Copolymerization of CO_2 and propylene oxide(PO) to afford polycarbonate was first pioneered by Inoue in 1969 using $ZnEt_2/H_2O$ as catalyst [9, 10], this transformation has been studied extensively in the past four decades [11–22]. To date, many excellent reviews in different period contributed by Kuran [23], Darensbourg [24], Coates [25], Inoue [26], Williams [27] and Rieger [28] have made good description on this topic.

Although remarkable successes have been realized for copolymerization of CO_2 with PO to make high molecular weight polycarbonates, seldom reports are related to oligo-carbonate diols with improved carbonate unit content in high activity and high selectivity of oligo-diol against propylene carbonate(PC). Usually, active-hydrogen containing compounds are used as chain transfer agent to control the functionality and the molecular weight of the oligo-diols. However, most of the catalyst systems are sensitive to moisture and would be deactivated in the presence of active-hydrogen containing compound. Double metal cyanide complex (DMC) catalyst is a highly active catalyst for homopolymerization of PO, and it is more tolerant for active-hydrogen containing compounds, and oligoether

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diols with narrow molecular weight distribution can be produced in the presence of hydroxylic agent [29–31]. Thus, copolymerization of CO_2 and PO by DMC catalyst with suitable hydroxylic compound may be an effective method to prepare oligocarbonate diols. In fact, this process has been reported in several patents, the apparent efficiency did not exceed 2.0 kg oligomer/g DMC catalyst, the carbonate unit content was in the range of 10.0 % and 40.0 %, and the resulted oligo-diols usually contained PC over 20.0 wt % [32–34], therefore, the catalytic activity, carbonate unit content as well as selectivity still have great space to improve.

In the present work, the selective synthesis of oligo(carbonate-ether) diols was investigated by copolymerization of CO_2/PO using $Zn_3[Co(CN)_6]_2$-based DMC catalyst in the presence of polypropylene glycols (PPGs) as chain transfer agent. The catalytic activity changed with carbonate unit content and molecular weight of oligo(carbonate-ether) diols, it reached as high as 10.0 kg oligomer/g DMC catalyst. The carbonate unit content can be adjusted between 15.3 % and 62.5 %, and the weight ratio of PC (W_{PC}) was controlled less than 8.0 wt%.

Experimental section

Materials

$K_3[Co(CN)_6]$ (Alfa Aesar) was recrystallized in deionized water before use, $ZnCl_2$ and *tert*-butanol (*t*-BuOH) were analytical grade and used without further purification. Propylene oxide (PO) was refluxed over calcium hydride and then distilled under argon atmosphere. Carbon dioxide (>99.99 %) was used as received. Polypropylene glycols in different molecular weight were prepared using KOH as catalyst, which were treated with cationic exchange resin and then dehydrated under reduced pressure.

Preparation of DMC catalyst

20 ml of $K_3[Co(CN)_6]$ solution (0.2 M) was added dropwise into the $ZnCl_2$ solution (11.42 g in mixture solution of 60 ml deionized water and 30 ml *tert*-butanol) under vigorous stirring at 50 °C in 45 min, the white suspension was centrifugated at 5,000 rpm after 60 min. The isolated slurry was re-suspended with vigorous stirring in a solution of *tert*-butanol and deionized water (1:1,v/v) for 30 min. The process was repeated several times by gradually increasing the portion of *tert*-butanol against water. Finally, the solid was re-suspended in neat *tert*-butanol and stirred for 30 min, centrifugated and dried under vaccum at 50 °C to constant weight.

Copolymerization

Copolymerization was carried out in a 500 ml autoclave equipped with magnetic stirring. Calculated amount of DMC catalyst, PO and PPG were introduced into the reactor free of oxygen and water at ambient temperature, the autoclave was then put into a water bath at elevated temperature, and CO_2 was introduced to start the reaction. To terminate the copolymerization, the autoclave was cool down to room temperature and the pressure was slowly released. The product was filtrated to exclude the catalyst residual, and then dried under vacuum until constant weight at 40 °C.

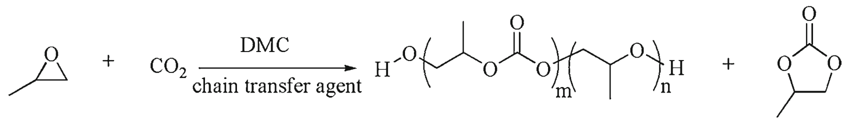
Measurements

FT-IR spectra were recorded by casting acetone solution of samples onto a disk of KBr with a Bruker TENSOR-27 spectrometer at a resolution of 4 cm^{-1}. ^1H-NMR and ^{13}C-NMR spectra were recorded at room temperature on Unity-400 NMR spectrometer using tetramethylsilane as the internal reference and $CDCl_3$ as solvent. The carbonate unit content in the copolymers and the weight ratio of PC content were calculated from ^1H-NMR according to literature [35]. The molecular weight and molecular weight distribution of the oligo(carbonate-ether) diols were determined by gel permeation chromatography (GPC) at 35 °C in polystyrene standard on Waters 410 GPC instrument with tetrahydrofuran as the eluent, where the flow rate was set at 1.0 ml/min. 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. Matrix 2,5-dihydroxybenzoic acid (DHBA) and oligo(carbonate-ether) diols sample were prepared in a solution of acetonitrile and water (1/2) with concentration of 20.0 mg/ml and 2.0 mg/ml, respectively. 1 ml of matrix and 1 ml of sample were thoroughly mixed together, 1 μl of this mixture solution was spotted on the target plate and allowed to dry. The hydroxyl value (OHV) is defined as the equivalent amount of KOH corresponding to the hydroxyl groups in 1 g of copolymer and was analyzed according to ASTM D4274D.

Results and discussion

Synthesis and characterization of oligo(carbonate-ether) diols

$Zn_3[Fe(CN)_6]_2$ and $Zn_3[Co(CN)_6]_2$-based DMC catalysts with three-dimensional structure were first discovered in the early 1960s at General Tire and Rubber Co., where Milgrom and coworkers found that these catalysts were mildly active toward homopolymerization of PO to give



Scheme 1 Copolymerization of CO_2/PO to oligo(carbonate-ether) diols by DMC catalyst

polypropylene oxide with lower level of unsaturation and narrower molecular weight distribution than those obtained by traditional catalyst like KOH [36]. Afterwards, $Zn_3[Co(CN)_6]_2$-based DMC catalyst with improved activity was prepared using excess $ZnCl_2$ toward $K_3[Co(CN)_6]$ in the presence of *tert*-butanol as complexing agent [37]. The excess $ZnCl_2$ and the complexing agents are indispensable for high activity, since the crystallinity of DMC is reduced [38]. The formed DMC catalyst is highly active for ring opening homopolymerization of epoxides and copolymerization of epoxides with CO_2 or cyclic anhydrides [29–31, 39–41]. In 2006, Coates et al. reported a new series of DMC catalyst of $Co[M(CN)_4]$ (M=Ni, Pd, Pt) with two-dimensional structure for compolymerization of CO_2/PO with a rapid initial reaction, and there was no cyclic propylene carbonate produced [42]. Unfortunately, the DMC catalyst is heterogeneous, the catalytic mechanism is still not clear, although Darensbourg prepared a series of homogeneous DMC catalyst for cyclohexene oxide/CO_2 copolymerization [43, 44]. According to Kim et al. [29], the zinc tetrahedral structure with both cationic and coordinative characters for polymerization was regarded as active center.

Using similar way as in the literatures, we prepared $Zn_3[Co(CN)_6]_2$-based DMC catalyst with simple formula of $Zn_3[Co(CN)_6]_2 \cdot 0.92ZnCl_2 \cdot 2.05$ *t*-BuOH·$1.93H_2O$. This DMC catalyst was used for copolymerization of CO_2 and PO without chain transfer agent, the catalytic activity reached as high as 60.6 kg polymer/g DMC catalyst, and the byproduct of PC was less than 1.0 wt%, although more than 50 % ether linkage existed in polymer chain [45]. This DMC catalyst showed high catalytic activity and high selectivity for copolymers over PC, therefore, it was used to prepare oligomers like oligo (carbonate-ether) diols from CO_2 and PO in the presence of chain transfer agent (Scheme 1).

Figure 1 was the FT-IR spectra of PPG-300 (b) and a typical oligomer with carbonate content of 58.4 % and number average molecular weight of 4.0 kg/mol (a). There were new peaks of 1,745 cm^{-1} and 1,247 cm^{-1} in a except peaks in b, which were assigned to stretching vibrations of C=O and C–O in oxycarbonyl group, respectively, indicating the incorporation of CO_2 into oligomer chain. Peaks at 1,801 cm^{-1} and 1,074 cm^{-1} indicated that the copolymerization was accompanied by side reactions like cycloaddition to form PC and successive insertion of PO to form ether linkages, respectively. The co-existence of ether linkages and carbonate linkages was a sign that the oligomer was a random copolymer other than a blend of oligo-propylene carbonate and oligo-propylene oxide. There was also obvious absorption peak at 3,480 cm^{-1} in a, which was ascribed to stretching vibration of hydroxyl end groups.

Figure 2 showed ^{1}H-NMR spectrum of a typical oligomer with carbonate content of 58.4 % and number average

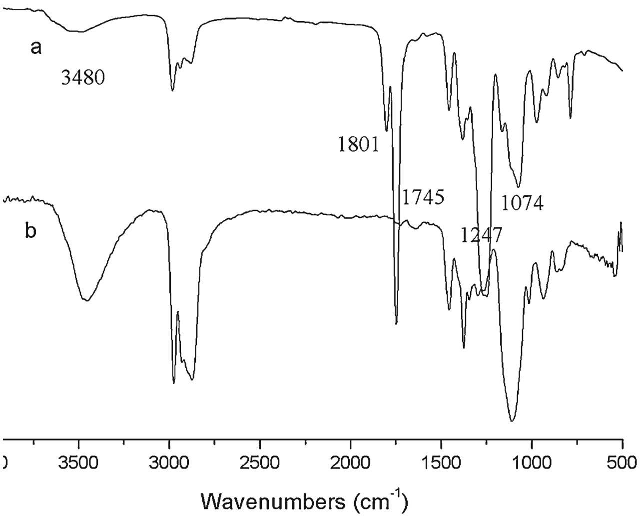


Fig. 1 FT-IR spectrum of olig(carbonate-ether) diol with carbonate content of 58.4 % (**a**) and PPG-300 (**b**)

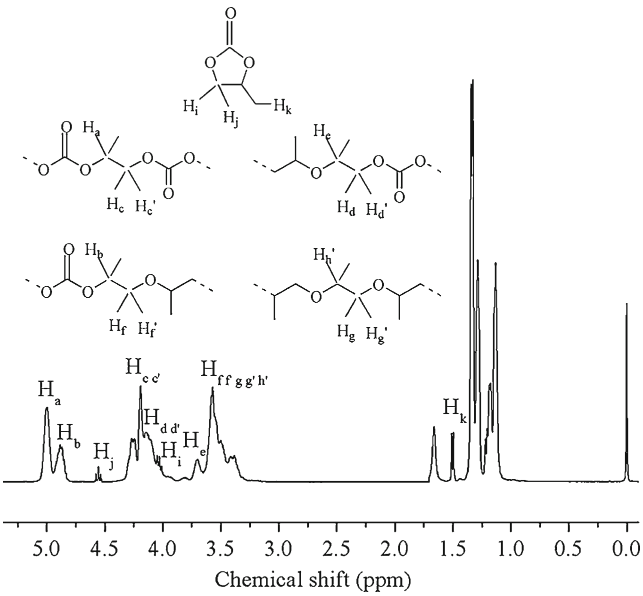


Fig. 2 ^{1}H-NMR spectrum of oligo(carbonate-ether) diol with carbonate content of 58.4 %

Table 1 Effect of molecular weight of PPGs on copolymerization of CO_2/PO[a]

Entry	PPG	PPG/DMC (g/mg)	M_n[b] (g/mol)	PDI[b]	CU[c] (%)	W_{PC}[c] (%)	OHV[f]	M_n[d] (g/mol)	Yield[e] (kg/g)
1	PPG-4	25/10	3300	1.49	24.9	7.9	33.5	3300	9.8
2	PPG-3	20/10	3300	1.44	27.1	4.7	35.8	3100	9.4
3	PPG-2	10/20	3000	1.26	29.6	2.9	36.3	3100	4.8

[a] All copolymerizations were carried out at 90 °C, 4.0 MPa with 83 g PO for 10 h; Molecular weight of PPG-4, PPG-3 and PPG-2 were 500 g/mol, 350 g/mol and 192 g/mol respectively

[b] Number average molecular weight(M_n) and polydispersity index(PDI) determined by GPC

[c] Carbonate unit content(CU) and weight ratio of PC in the product(W_{pc}) determined by ^{1}H-NMR

[d] Number average molecular weight calculated by hydroxyl value(OHV)

[e] Catalytic activity determined according to ($W_{product}$–W_{PPG}) / W_{DMC}, where Wproduct was the total amount of the product, W_{PPG} or W_{DMC} was the amount of PPG or DMC added during copolymerization

[f] Hydroxyl value, determined by titration method

molecular weight of 4.0 kg/mol, according to the fully assignment of polycarbonate with high ether content catalyzed with $Co[Ni(CN)]_4$ by Coates [42], the signals at 5.0 ppm and 4.0–4.3 ppm were assigned to CH and CH_2 groups in carbonate segments in polymer chain, respectively, while the signals at 3.2–3.8 ppm were assigned to both CH and CH_2 groups in ether segments. Therefore, the existence of carbonate and ether linkages in oligo-diol chain was further confirmed. There existed small peaks at 4.89 ppm, 4.58 ppm, 4.04 ppm and 1.50 ppm, which were assigned to characteristic peaks of PC. According to the integrating area of these signals, the molar fraction of carbonate unit content in oligomer and weight fraction of PC can be calculated by Eqs. 1 and 2 [35], the results were listed in Tables 1, 2 and 3. Figure 3 was the ^{13}C-NMR spectrum of this sample, the existence of 153.98 ppm, 68.71–72.12 ppm confirmed the incorporation of CO_2 into the polymer chain, and the peaks at 73.34 ppm and 75.03 ppm verified the co-existence of ether linkages, the peaks at 65.0 ppm was the evidence of carbon bonded with hydroxyl end groups which was also confirmed by FT-IR characterization.

$$CU = \frac{(A_{5.0} + A_{4.2} - 2A_{4.58})}{(A_{5.0} + A_{4.2} - 2A_{4.58}) + A_{3.5}} \qquad (1)$$

$$W_{PC} = \frac{102A_{1.5}}{58A_{1.14} + 102(A_{1.33} + A_{1.5})} \qquad (2)$$

where CU was carbonate unit content in the oligomer, W_{pc} was weight fraction of PC in the as-polymerized product, and A_x was the integrated area of corresponding peak x.

Figure 4 was the MALDI-TOF/MS spectrum of a typical oligomer with carbonate unit content of 30 % and number average molecular weight of 2.0 kg/mol, four species, (1) $[HO(PO\text{-}CO_2)_2(PO)_nH]Na^+$, (2) $[HO(PO\text{-}CO_2)_2(PO)_nH]K^+$, (3) $[HO(PO\text{-}CO_2)_3(PO)_nH]Na^+$ and (4) $[HO(PO\text{-}CO_2)_4(PO)_nH]Na^+$, were observed, indicating that the oligomer ended with both sides by hydroxyl groups. However,

Table 2 Effect of amount of PPG-3 on copolymerization of CO_2 and propylene oxide[a]

Entry	PPG-3 (g)	M_n[b] (g/mol)	PDI[b]	CU[c] (%)	W_{PC}[c] (%)	OHV[f]	M_n[d] (g/mol)	Yield[e] (kg/g)
1	10.0	6400	1.83	34.3	3.8	18.2	6100	10.0
2	15.0	4100	1.54	32.7	4.3	28.1	4000	9.8
3	20.0	3300	1.44	27.1	4.7	35.8	3100	9.4
4	25.0	3100	1.39	22.3	6.6	35.1	3200	8.1
5	27.0	1900	1.14	15.3	6.9	65.0	1700	3.8
6	30.0	–	–	–	–	–	–	Trace

[a] See the explanations of all symbols in Table 1, all copolymerizations were carried out at 90 °C, 4.0 MPa, 10.0 mg DMC with 83 g PO for 10 h

[b] Determined by GPC

[c] Determined by ^{1}HNMR

[d] Calculated by OHV

[e] Determined according to ($W_{product}$–W_{PPG})/W_{DMC}

[f] Determined by titration method

Table 3 Effect of reaction conditions on copolymerization of CO_2/PO[a]

Entry	T (°C)	P (MPa)	DMC (mg)	t (h)	M_n[b] (g/mol)	PDI[b]	CU[c] (%)	W_{PC}[c] (%)	OHV[f]	M_n[d] (g/mol)	Yield[e] (kg/g)
1	90	4.0	10.0	10	3300	1.44	27.1	4.7	35.8	3100	9.4
2	80	4.0	20.0	10	3800	1.30	33.8	4.1	28.2	4000	5.1
3	70	4.0	35.0	12	3300	1.32	39.4	6.2	36.1	3100	2.9
4	60	4.0	80.0	24	4200	1.37	50.5	4.8	29.8	3800	1.3
5	50	4.0	200.0	28	3800	1.61	54.8	2.2	28.7	3900	0.57
6	50	5.0	230.0	50	4000	1.67	58.4	2.8	29.6	3800	0.50
7	50	6.0	300.0	50	3700	1.75	62.5	2.5	28.0	4000	0.40
8	50	5.0	230.0	32	1800	1.26	38.6	1.8	55.2	2000	0.16
9	50	5.0	230.0	38	2800	1.35	51.0	2.2	37.0	3000	0.28
10	50	5.0	230.0	45	3500	1.52	55.8	2.5	30.3	3700	0.39

[a] See the explanations of all symbols in Table 1, all copolymerizations were carried out with 83 g PO and 20.0 g PPG-3

[b] Determined by GPC

[c] Determined by ^{1}H-NMR

[d] Calculated by OHV(mg KOH/g)

[e] Determined according to $(W_{product}-W_{PPG})/W_{DMC}$

[f] Determined by titration method

the main interval between peaks in Fig. 4 was 58 in accordance with the molecular weight of PO, which may be the reason that there were much more ether unit than carbonate unit in oligomer chain for this sample. Thus we investigated a olig(carbonate-ether) diol with 55 % carbonate unit content and molecular weight of 3.5 kg/mol by MALDI-TOF/MS, the result was shown in Fig. 5. Seven species also terminated with both side by hydroxyl group were observed, and the obvious intervals between peaks was 102 in consistent with the molecular weight of carbonate repeat unit except intervals of 58. To our surprise, we found one species (★) with 100 % alternative structure, which may be ascribed to the chain transfer reaction to water, which meant that the method preparing oligcarbonate diols in this paper was really attractive. Titration analysis also confirmed that the oligomer was capped with hydroxyl group at two ends.

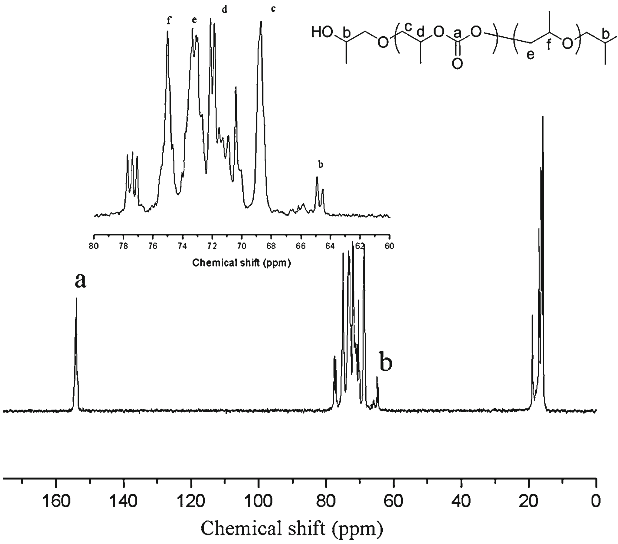


Fig. 3 ^{13}C-NMR spectrum of oligo(carbonate-ether) diol with carbonate content of 58.4 %

Table 1 listed the influence of molecular weight of chain transfer agents (PPGs) on copolymerization of CO_2/PO, generally, the molecular weights were obtained from GPC profiles of the samples, for comparison, the molecular weight from hydroxyl value (OHV) were also listed in the table, which were in good accordance. By controlling the mole ratio of PPGs to PO to DMC (I/M/DMC), oligo(carbonate-ether) diols with similar number average molecular weights (3.0–3.3 kg/mol) were prepared. However, when the molecular weight of PPG decreased, the catalytic activity decreased accompanied by the increase of induction period, which may be attributed to the competing coordination with Zn center between –OH in PPG and PO. It is well known that three-membered ring ethers are poorer donors than other cyclic ethers and open chain ethers [46], while –OH is a stronger base than PO in cationic ring opening polymerization, and the coordination ability of –OH may increase with decreasing of the molecular weight of PPG [47]. Therefore, it can be deduced that decrease of the molecular weight of PPG or increase of I/DMC may be unfavorable for PO coordination to Zn center (also see data in Table 2). However, the carbonate unit content increased when the lower molecular weight of PPG was used, therefore, there may be a balance using PPG as chain transfer agent with proper molecular weight.

As can be seen from Table 1, if high catalytic activity and high carbonate unit content were the targets, PPG-3 may be suitable chain transfer agent. Table 2 listed the amount of

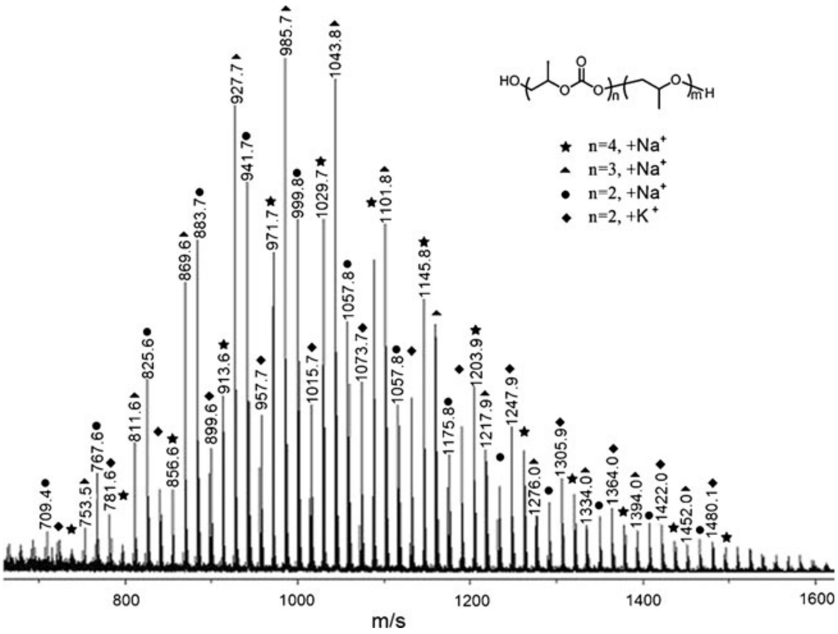


Fig. 4 MALDI-TOF/MS spectrum of the poly(carbonate-ether) diol with 30 % carbonate unit content and the number average molecular weight of 2.0 kg/mol

PPG-3 on copolymerization of CO_2/PO, when the amount of PPG-3 increased, the induction period increased while the catalytic activity decreased, accompanied by the decrease of molecular weight of oligo(carbonate-ether) diols, and the polydisersity indexes became narrower, which was in accordance with the homopolymerization of PO [48]. The presence of PPG competed with PO to complex with Zn and thus the induction period increased. As shown in Scheme 2, PPG coordinated to Zn center and freed one of the Cl to form precursor of active center S, and then the free Cl opened the coordinated propylene oxide to form active center S*(a, b). Because coordination of PO is the rate-determining step, when the coordinative ability of chain transfer agent was too strong, such as diethylamine and urea [31], the coordination of PO was suppressed totally for the decrease of the acidity of the Zn center, which is also the reason that the induction period existed. After the formation of the active center, PO/CO_2 inserted randomly into the active Zn–O bond to form the propagating chain. Meanwhile, the amount of PPG was 10^3 over that of Zn center, there must be a fast chain transfer reaction between PPG and propagating chain to form a new propagating chain and a hydroxyl terminated dormant chain, which assured that all PPG participated chain propagation, and the hydroxyl terminated dormant chain may reversibly participated the chain transfer reaction. When the chain transfer reaction rate was faster than that of chain propagation, the molecular weight of the final copolymer decreased and the polydispersity index became narrower with the increase of the amount of PPG. In another words, copolymerization of CO_2/PO under DMC catalyst in the presence of chain transfer agent possessed some characteristics of immortal polymerization [49]. The catalytic activity decreased strongly when the amount of PPG-3 used was over 25.0 g, which may be attributed to the too long induction period and thus the conversion of PO decreased sharply when the copolymerization was carried out at such high I/DMC. Another encouraging point was that the increase of carbonate unit content in the oligo(carbonate-ether) diol with the decrease of the amount of PPG. It should be noted here, though the weight ratio of PC increased with increasing of PPG amount, but it didn't exceed 8.0 wt% which was much lower than earlier reports [50].

The influence of reaction conditions on copolymerization of CO_2/PO were listed in Table 3. Calculated amount of DMC were added to assure smooth initialization and copolymerization, the reaction was terminated until the conversion of PO was over 90 % (Entry 1–7). Generally, the amount of DMC increased slightly at lower reaction temperature or higher CO_2 pressure. The molecular weight of oligo(carbonate-ether) diols did not change obviously for similar I/M ratio, indicating that the molecular weight of oligo(carbonate-ether) diols was controlled by I/M ratio. As listed in entry 1–5, when the reaction temperature decreased from 90 °C to 50 °C at 4.0 MPa, the carbonate unit content of oligo(carbonate-ether) diol increased from 27.1 % to 54.8 %, and the catalytic activity decreased from 9.40 kg oligomer/g DMC to 0.59 kg oligomer/g DMC. As listed in entry 5–7, when the reaction pressure increased from 4.0 MPa to 6.0 MPa at 50 °C, the carbonate unit content of oligo(carbonate-ether) diol increased from 54.8 % to 62.5 %, while the activity decreased slightly. When the reaction time was prolonged, the molecular weight, carbonate unit content and activity increased (see entry 6, 8–10). It should be noted again, that the weight ratio of PC in product did not exceed 8.0 wt% in all reactions.

Control of PC formation

Copolymerization of CO_2/PO by DMC catalyst usually produces high molecular weight copolymers with Wpc less than 1.0 wt% in the absent of PPG [45]. However, W_{pc} increased several times when the copolymerizaions were conducted in the presence of PPG, sometimes the value may even be over 30 wt% [32, 33]. In most cases, PC are thought to be generated by the backbiting of a metal-alkoxide on the adjacent carbonate linkage in the growing polymer chain (Scheme 3) [51]. According to the backbiting mechanism, PC can only form when polypropylene carbonate chain end consists of adjacent CO_2 and PO units. That means PC formation would be stopped if the backbiting process encountered more than one adjacent PO units. Copolymers from CO_2 and PO by DMC catalyst usually bear carbonate unit content less than 70 %, in other words, there are much successive PO units in polymer chain, the backbiting process may be suppressed. This can be demonstrated by the results in Table 3, the PC content didn't change obviously as the reaction time increased. Thus, backbiting reaction may not be the leading path to the

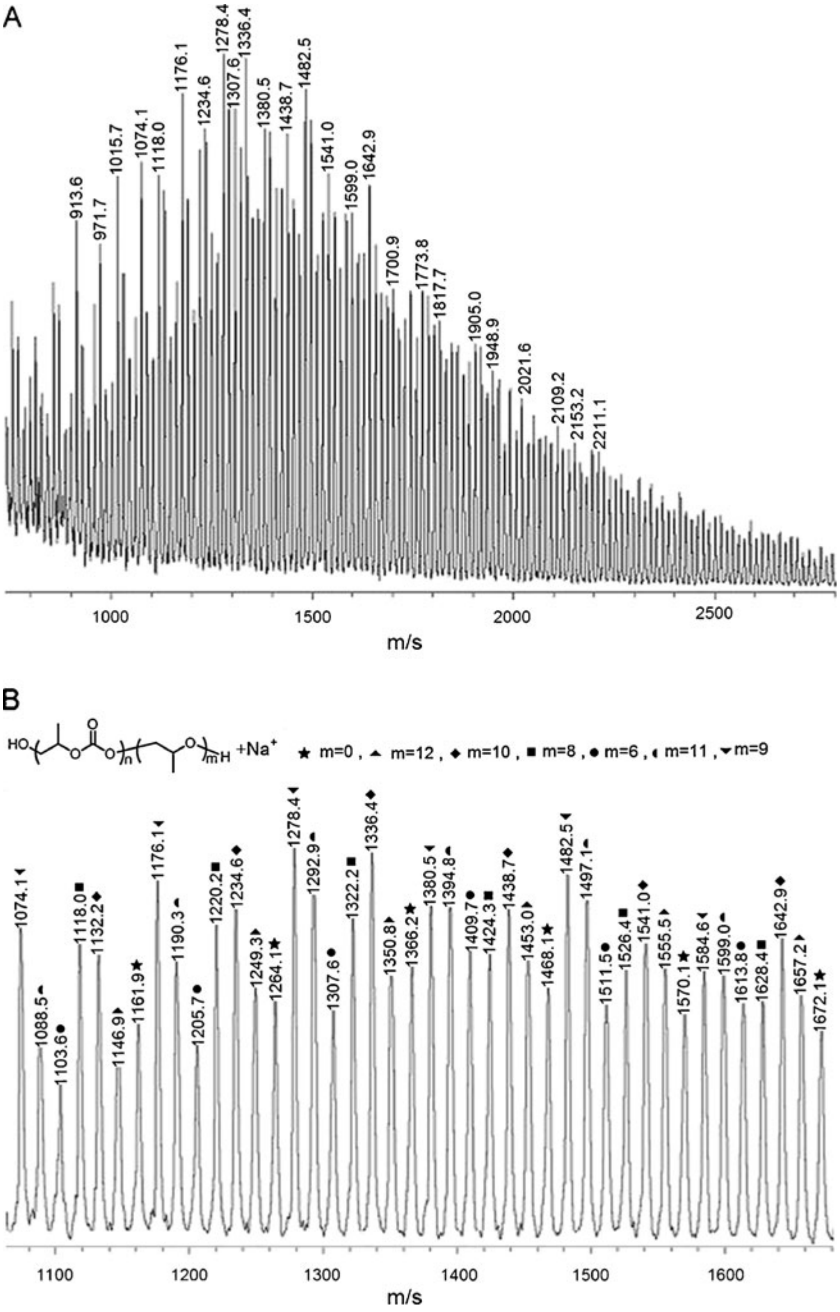
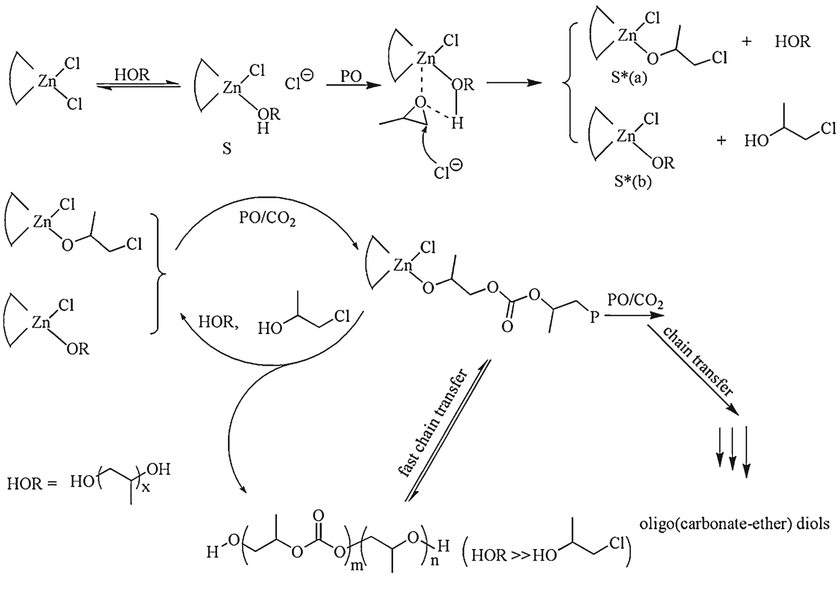


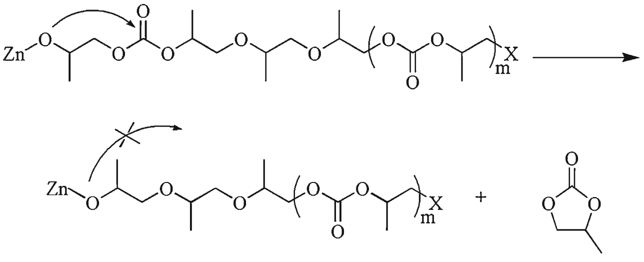
Fig. 5 MALDI-TOF/MS spectrum of oligo(carbonate-ether) diol with 55 % carbonate unit content and molecular weight of 3.5 kg/mol, (**a**) full spectrum, (**b**) mass from 1000 to 1700



Scheme 2 Possible immortal copolymerization due to fast chain transfer reaction

formation of PC in copolymerization of CO_2/PO under DMC catalyst.

We observed that W_{pc} didn't change significantly when the amount of DMC increased, while it increased with increasing of PPG amount (see Table 2). There was 9.8 ppm Na^+ in PPG, so the amount of Na^+ increased with increasing amount of PPG. Table 4 listed the effect of concentration of Na^+ on W_{pc} and catalytic activity while keeping the amount of PPG constant, W_{pc} increased from 4.7 wt% to 10.3 wt% when Na^+ concentration increased from 9.8 ppm to 20 ppm, while the catalytic activity decreased from 9.4 kg oligomer/g DMC to 7.8 kg oligomer/g DMC, thus alkali metal ions residual was detrimental to copolymerization of PO/CO_2 under DMC catalyst. There are reports that alkali metal halides and DMC/ammonium salt system were catalysts for the cycoaddition of CO_2 and PO to give PC [52, 53], therefore, the alkali metal ion residue may play an important role in PC formation, in some cases this effect may be more significant than backbiting process, removing the residual alkali metal ion should be meaningful in the future to further reduce the PC formation.



Scheme 3 Proposed backbiting degradation of PPC to PC

Conclusion

Oligo(carbonate-ether) diols were prepared by copolymerization of CO_2 and PO under $Zn_3[Co(CN)_6]_2$-based DMC in the presence of PPG. The copolymerization of CO_2/PO by DMC in the presence of PPG had some feature of immortal polymerization. The catalytic activity was related to carbonate unit content and molecular weight of the target oligo (carbonate-ether)diols, for oligo(carbonate-ether)diol with M_n of 6.4 kg/mol and CU of 34.3 %, it reached 10.0 kg oligomer/g DMC catalyst during 10 h of copolymerization. The M_n of the oligo(carbonate-ether) diol was tunable between 1.8 kg/mol and 6.4 kg/mol, and the PDI was controllable between 1.14 and 1.83, while the carbonate unit content in the oligo-diols can be adjusted between 15.3 % and 62.5 %. Generally, the W_{PC} was controlled less than 8.0 wt%, removing the residual alkali metal ion should be meaningful in the future to further reduce the PC formation.

Table 4 Effect of concentration of Na^+ on PC content[a]

Entry	Na^+(ppm)[b]	W_{PC}(%)[c]	Yield (kg/g)[d]
1	9.8	4.7	9.4
2	14.9	8.4	8.6
3	20.0	10.3	7.8

[a] See the explanations of corresponding symbols in Table 1, copolymerizations were carried out at 90 °C, 4.0 MPa, 83 g PO, 10.0 mg DMC for 10 h, PPG used was 20.0 g

[b] Concentration of Na^+ in PPG

[c] Determined by ^{1}H-NMR

[d] Determined according to $(W_{product}-W_{PPG})/W_{DMC}$

Acknowledgments Financial support from Natural Science Foundation of China (Gr. No. 51021003 and 21134002) is greatly appreciated.

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