Polymer Chemistry

Accepted Manuscript

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

One-pot Controllable Synthesis of Oligo(carbonate-ether) Triol by Zn-Co-DMC Catalyst: Special Role of Trimesic acid as Initiate-Transfer Agent

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

One-pot synthesis of oligo(carbonate-ether) triol was realized by copolymerization of CO_2 and propylene oxide (PO) using zinc-cobalt double metal cyanide (Zn-Co-DMC) catalyst in the presence of 1,3,5-Benzenetricarboxylic (Trimesic) Acid (TMA). The catalytic activity ranged from 0.3 to 1.0 kg/g DMC with various copolymerization conditions. The structure of the oligo(carbonate-ether) triol was clearly confirmed, providing sound evidence for the special role TMA played, i.e., it acted as initiate-transfer agent. At first stage TMA initiated PO homo-polymerization to afford oligo-ether triol via a core-first approach in the presence of Zn-Co-DMC, after all the TMA was consumed, the in-situ formed oligo-ether triol acted as new chain transfer agent to participate in the copolymerization forming carbonate-ether segments, and therefore the oligo(carbonate-ether) triol. Since every molecule of TMA participated in initiation and propagation steps, the molecular weight of the triol depended on the TMA amount rather than the Zn-Co-DMC amount. Subsequently, the number average molecular weight (M_n) of the oligo(carbonate-ether) triol could be well controlled from 1400 to 3800 g mol^{-1} with relatively narrow polydispersity index (PDI) (1.15-1.45), and its carbonate unit content (CU) could be adjusted between 20% and 54%.

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1. Introduction

Recently, conversion of CO_2 to chemicals or chemical materials has received much attention. One promising route is the alternating copolymerization of CO_2/epoxides to afford biodegradable polycarbonates,[1-~~6~~7] as first pioneered by Inoue in 1969.[~~7~~8,~~8~~9] Extensive work has been focused on this transformation, and a variety of promising catalysts have been developed to promote this copolymerization process during the past decades,[~~9~~10-~~15~~16] where the salen-cobalt complex catalysts have been developed as most active and selective catalysts.[~~16~~17-~~18~~19] However, compared to biodegradable polycarbonates, less attention has been paid for low molecular weight oligo(carbonate-ether) polyol, whereas they are potential large scale (in millions of ton) raw materials in modern polyurethane industry in the world,[~~19~~20] and the huge potential application of oligo(carbonate-ether) polyol may lead to breakthrough in CO_2 fixation into polymer materials.

In 2004, Hinz and coworkers prepared oligo(carbonate-ether) polyol with narrow PDI (< 1.4) from copolymerization of propylene oxide (PO) and CO_2 using double metal cyanide(DMC) as catalyst and polyetherol polyol as initiator in the presence of sterically hindered mono-functional chain transfer agent, but the carbonate unit content (CU) was below 15%.[~~20~~21] Late they employed crystalline multimetal cyanide compounds to react with polyol initiator, although the catalytic activity could reach 11 kg g^{-1} cat. at 110 °C~~°C~~,[~~21~~22] the final polyol still showed CU below 13.2%, even CO_2-philic compounds (fluorine-based compounds) was added into multimetal cyanide compound catalytic system, the CU of the resultant oligo(carbonate-ether) polyol did not excess 15%.[~~22~~23] In 2010 Mijolovic and coworkers reported a continuous feeding method, where the initiators were metered continuously into the reaction system, producing oligo(carbonate-ether) polyol with narrow polydispersity, however, the CU did not increase obviously (<20%).[~~23~~24] Haider and coworkers also used various non-crystalline DMC catalysts, but the oligo(carbonate-ether) polyol showed CU from 1% to 20%, and W_{pc} could be controlled less than 30wt%.[~~24~~25] Gürtler and coworkers used epoxides to pre-activate DMC catalyst, the CU of oligo(carbonate-ether) polyol reached 21.5%.[~~25~~26] Recently, sterically non-hindered phenols were added to the catalyst activation step, resulting in shorter induction time, however, CU of the triol still remained relatively low (< 20%).[~~26~~27] Despite extensive research on heterogeneous catalysts for oligo(carbonate-ether) polyol synthesis, reports on homogeneous catalysts were limited. Lee and coworkers reported that the star-shaped polypropylene carbonate (PPC) could be well synthesized with Salen-Co catalyst by feeding polybasic acids as chain transfer agent. Although Salen-Co catalyst showed excellent catalytic activity (turnover of frequency up to 9500 h^{-1}), the T_g (>40 °C~~°C~~) of the obtained PPC polyol was too high to act as the soft segment of polyurethane.[~~27~~28] Though the soft ether linkage was incorporated into the CO_2/PO copolymer chain by using dual catalyst composed of Salen–cobalt(III) complex and Zn-Co-DMC catalyst, the polyol showed M_n of 5000 g mol^{-1} with PDI of 4.1, its CU was only 10%, the moderate molecular weight and the broad PDI limited its applications in plastics or polyurethane industry.[~~28~~29] Thus, it is still a big challenge to prepare oligo(carbonate-ether) polyol with high CU, low M_n, and narrow PDI. In a recent work, Our group prepared oligo(carbonate-ether) diol with M_n of 3700 g mol^{-1} and CU of 62% using polypropylene glycols (PPGs) as chain transfer agent, but it was difficult to further decrease the M_n of the diol, because the more amount of hydroxyl groups (-OH) of PPGs could compete with PO to coordinate on the active center.[~~29~~30] More recently, we reported copolymerization of CO_2/PO with dicarboxylic acids as chain transfer agent, yielding oligo(carbonate-ether) diol with CU up to 75%, M_n lower than 2000 g mol^{-1}, and catalytic efficiency of 1.0 kg/g DMC.[~~30~~31] It was found that dicarboxylic acid could significantly reduce the induction period of the copolymerization due to its weaker coordination ability compared with PPG based polyol.

Although oligo(carbonate-ether) diol is important chemical intermediate which can be used in many fields, its linear structure makes it difficult to be applied in manufacturing crosslinking materials like hard or soft foam. It is natural to consider that oligo(carbonate-ether) triol may have the potential to meet this purpose. Based on our earlier work using dicarboxylic acid as chain transfer agent,[~~30~~31] here 1,3,5-Benzenetricarboxylic acid (TMA) was chosen as chain transfer agent to prepare the oligo(carbonate-ether) triol. Surprisingly, it was found that TMA played a special role in the copolymerization reaction, i.e., it not only acted as a chain transfer agent, but also a chain initiator, especially in the first stage, TMA was completely converted into oligo-ether triol via a core-first approach under DMC catalyst, no monohydric alcohol was detected, which was prerequisite for preparing triol. Then the *in-situ* formed oligo-ether triol acted as new chain transfer agent to participate in the copolymerization to produce oligo(carbonate-ether) triol. A mechanism for the copolymerization of CO_2 and PO in the presence of TMA under DMC catalyst was thus proposed.

2. Experimental section

2.1 Materials

$K_3[Co(CN)_6]$ was provided by Alfa Aesar and recrystallized in deionized water prior to use, $ZnCl_2$ and *tert*-butanol (*t*-BuOH) were analytical grade and used without further purification. Trimesic acid was purchased from Aladdin Reagent Database. Propylene oxide (PO) was refluxed over calcium hydride and then distilled under argon atmosphere. Carbon dioxide with purity over 99.99% was used as received.

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Preparation of DMC catalyst (Zn-Co-DMC): 20 ml of $K_3[Co(CN)_6]$ solution (0.2M) was added dropwise in 45 min into $ZnCl_2$ solution (11.42 g of $ZnCl_2$ in mixture solution of 60 ml deionized water and 30 ml *tert*-butanol) under vigorous stirring at 50 °C~~℃~~, the white suspension was centrifuged at 5000 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, centrifuged and dried under vacuum at 50 °C~~℃~~ to constant weight, which was denoted as Zn-Co-DMC.

2.2 Copolymerization

Copolymerization was carried out in a 500 ml autoclave equipped with mechanical stirring. Calculated amount of Zn-Co-DMC, PO (100 ml) and TMA were added into the pretreated reactor free of oxygen and water at ambient temperature, the autoclave was then put into a water bath at fixed temperature, and CO_2 was introduced to start the reaction. The autoclave was cooled down to room temperature to terminate the copolymerization, and the pressure was slowly released. The product was filtrated to remove the catalyst residual, and then the un-reacted PO monomer was collected at 40 °C~~℃~~ at reduced pressure, while the byproduct propylene carbonate (PC) was removed in vacuum at 80 °C~~℃~~ for 24h.

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, ^{13}C NMR and COSY NMR spectra were recorded at room temperature on Unity-400 NMR spectrometer using $CDCl_3$ as solvent. The M_n and PDI of the oligo(carbonate-ether) triol were measured by gel permeation chromatography (GPC) at 35 °C~~℃~~ with polystyrene as standard on Waters 410 GPC instrument 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) triol 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. The hydroxyl value (OHV) is defined as the equivalent amount of KOH corresponding to the hydroxyl groups in 1 g of copolymer, which was analyzed according to ASTM D4274D. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-7 instrument under a N_2 atmosphere. The samples were first heated from -50 °C~~℃~~ to 50 °C~~℃~~ at 10 °C~~℃~~ /min and then rapidly quenched to -50 °C~~℃~~, followed by the second heating process in the same way as the first. The glass transition temperature (T_g) was defined as the value of midpoint of transition in the second heating process.

3. Results and discussion

3.1 Synthesis of oligo(carbonate-ether) triol

The influence of reaction condition on copolymerization of CO_2/PO was summarized in Table 1. To assure smooth initiation and copolymerization, calculated amount of Zn-Co-DMC catalyst was added, and all the reactions were terminated until the PO conversion was over 95%. Generally, the amount of Zn-Co-DMC increased slightly at larger amount of TMA or lower reaction temperature, or higher CO_2 pressure.[~~29~~30] Entries 1-5 in Table 1 showed the influence of TMA amount on the copolymerization, when the TMA amount increased, the CU and M_n of oligo(carbonate-ether) triol decreased, accompanied by the decrease of catalytic activity, while the PDI became narrower, in accordance with the copolymerization of CO_2/PO in the presence of PPGs,[~~29~~30] but differed from that of dicarboxylic acids, where the catalytic activity and CU did not change with different PO/sebacic acid (SA) ratio,[~~30~~31] indicating that the reaction process of TMA was somewhat like PPGs, rather than the analogous dicarboxylic acids. The CU of the triol could reach 43.3% at 80 °C~~°C~~ when 8 g TMA was used, which was much higher than the previous reports.[~~31~~32] However, the CU decreased gradually with the increase of TMA amount, suggesting that excess TMA might be unfavorable for higher CU of the triol. The apparent activity of the catalyst reached 1 kg polymer/g DMC at 8 g of TMA. The narrow PDI (< 1.45) indicated that there was no high molecular weight tail in the resulting products. The W_{pc} could be controlled in a relatively low range (8.9%~28.2%), while maintaining relatively high CU of the oligo(carbonate-ether) triol.

Table 1. Influence of the reaction condition on the copolymerization of CO_2/PO[a]

Entry	TMA (g)	DMC (mg)	Temp (°C~~°C~~)	P (MPa)	Time (h)	M_n[b] (g mol^{-1})	PDI[b]	CU[c] (%)	W_{pc}[c] (wt%)	M_n[c] (g mol^{-1})	M_n[d] (g mol^{-1})	OHV[e]	M_n[e] (g mol^{-1})	Activity[f] (kg g^{-1})
1	8	100	80	4	8	3800	1.45	43.3	8.9	2300	2400	71.1	2350	1.0
2	11	180	80	4	8	2600	1.33	35.7	16.9	1900	1800	90.1	1900	0.6
3	13	190	80	4	8	2200	1.26	35.3	19.3	1600	1500	96.6	1700	0.58
4	16	220	80	4	8	1800	1.18	32.7	21.3	1400	1200	111.8	1450	0.52
5	18	240	80	4	16	1400	1.15	25.8	28.2	1000	950	143.3	1350	0.46
6	13	240	70	4	13	2500	1.2	46.6	11.8	1900	1700	88.8	1900	0.47
7	13	360	60	4	28	2600	1.31	54.3	9.1	2000	1800	82.7	2000	0.33
8	13	240	70	2	8	2650	1.19	20.6	7.9	2000	1900	84.0	2000	0.43
9	13	240	70	3	9	2400	1.17	38.1	9.9	1800	1750	83.2	1800	0.45
10	13	240	70	5	20	2600	1.23	50	12.2	2000	1850	82.2	2000	0.47

[a] All copolymerization reactions were carried out in 100 ml PO. [b] Measured by GPC. [c] Calculated by ^{1}H NMR. [d] Calculated according to $M_n=W_{oligo}/n_{TMA}$, where W_{oligo} is the mass of the oligomer calculated according to W_{oligo}=[(1-wt%)*yield], and n_{TMA} is mole of TMA. [e] Determined by titration method. [f] Calculated by $W_{product}/W_{DMC}$.

Fig. 1 showed plots of M_n against TMA amount calculated by different method, the data set of the M_n (y) calculated by GPC (a), ^{1}H NMR (b), OHV (c), mass (d) methods fitted perfectly among each other, and all the correlation coefficients (R^2) were above 0.99. The molecular weight of the triol was consistent with the calculation based on the TMA amount rather than the Zn-Co-DMC amount, illustrating that every molecule of the initiator participated in initiation and propagation steps. Therefore, we could precisely control the M_n of the oligo(carbonate-ether) triol by simply altering the TMA amount. In Table 1, the absolute M_n calculated by ^{1}H NMR, mass, OHV methods agreed well among each other, however, discrepancy existed between GPC-measured M_n and absolute M_n, which was reasonable considering the limit of GPC analysis method for low molecular weight polymer (3000 g ~~/~~mol^{-1} or less).

The influence of temperature on CO_2/PO copolymerization can be summarized from entries 3, 6-7 in Table 1. The copolymerization can even proceed at a low temperature like 60 °C ~~°C~~ to afford oligo(carbonate-ether) triol with considerable productivity (0.33 kg polymer/g DMC), high selectivity (CU: 54.3% and W_{pc}: 9.1%) as well as low M_n (M_n: 2600 g/mol, entry 7 in Table 1). The CU of the triol increased with decreasing polymerization temperature, a clear decrease of W_{pc} with decreasing reaction temperature was observed (entries 3,6-7, Table 1), indicating that CU and W_{pc} could be well controlled by simply altering the reaction temperature. The catalytic activity increased from 0.33 to 0.58 kg polymer/g DMC when the temperature increased from 60 to 80 °C~~°C~~, however, the amount of catalyst increased while reaction time was prolonged to assure sufficient copolymerization at low temperature.

The effect of pressure on the copolymerization was listed in entries 6 and 8-10, Table 1. The productivity of Zn-Co-DMC

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catalyst was 0.43-0.47 kg polymer/g DMC, only slight variation was observed under different CO_2 pressure, while CU increased from 20.6% to 50%. High CO_2 pressure was effective for increasing CU, in addition, the cyclic propylene carbonate also increased with increasing pressure, indicating that high pressure may also be beneficial to backbiting of the propagating chains.[5] The molecular weight of triol did not change obviously for similar TMA amount at different pressure, again proved that the M_n of the triol was controlled by TMA amount.

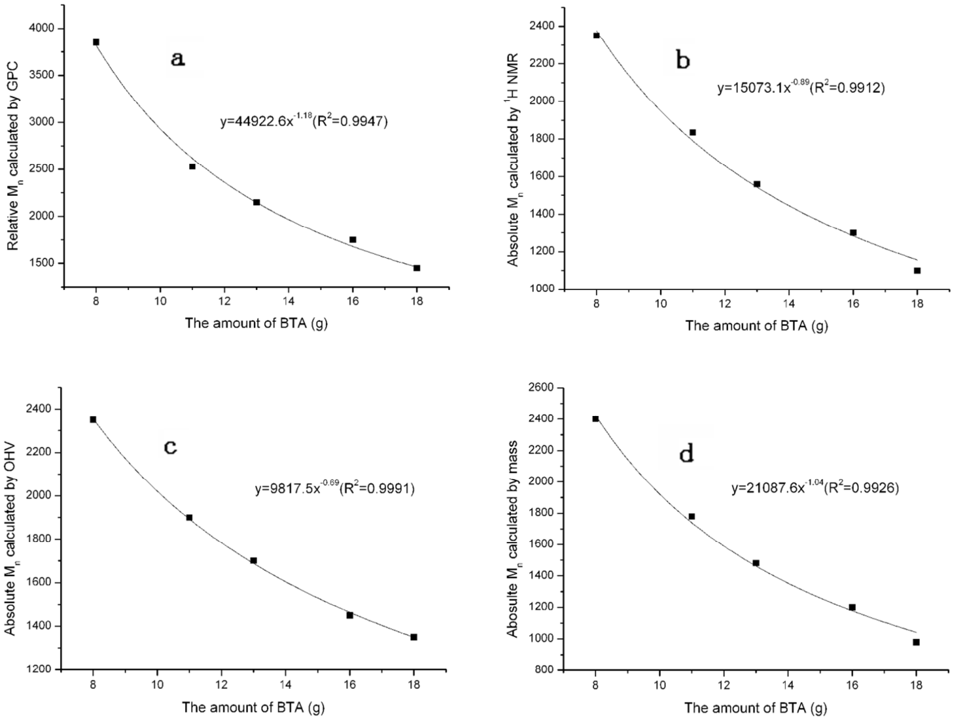

Fig. 1 Plots of M_n calculated by different methods against the TMA amount.

Table 2. Effect of reaction time on the copolymerization of CO_2/PO[a]

Entry	Time (min)	Conv[b] (%)	CU[b] (%)	Wpc[b] (wt%)	M_n[c] (g mol^{-1})	PDI[c]
1	150	21.1	0	0	600	1.02
2	180	23.7	4.4	1.7	670	1.03
3	240	31.7	5.2	3.7	700	1.05
4	260	43.7	33.5	9.0	1100	1.06
5	315	96.6	34.6	13.5	2600	1.11

[a] Copolymerization were carried out at 80 ºC~~□~~, 4 MPa with 100 ml PO, 11 g TMA, 180 mg DMC. [b] Calculated by ^1H NMR. [c] Measured by GPC.

In order to understand the chain propagation reaction, the apparent kinetics of CO_2/PO copolymerization was investigated. As listed in Table 2, the copolymerization was performed at 80ºC~~℃~~ and 4.0 MPa, the PO conversion, CU and W_{pc} were plotted against polymerization time as shown in Fig. 2. At first stage, the PO conversion, CU, M_n and W_{pc} all increased with the reaction time, while no CO_2/PO copolymer was collected till 150 min, even the PO conversion reached 21.1%, indicating that the resultant product was only PO homopolymer. However, a small amount of CO_2 was incorporated into copolymer when PO conversion reached 23.7% at 180 min, and the CU content increased rapidly to 34.6% at 240 min.

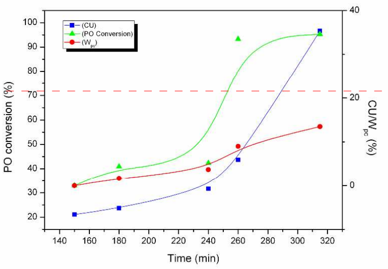

Fig. 2 Plots of PO conversion, CU and W_{pc} against reaction time at 80 ℃~~℃~~, 4 MPa with 180 mg DMC, 11g TMA, the data corresponded to entries 1-5, respectively, in Table 2.

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Based on above observation, we deduced that TMA was a novel chain initiation-transfer agent having two functions: at first TMA was an initiator to homopolymerize PO producing polyether triol, then the *in-situ* produced triol participated in the chain transfer reaction of the CO_2/PO copolymerization. Therefore, as revealed in entries 1-5, Table 1, the increase of TMA amount resulted in more PO being incorporated into backbone of the triol, combined with the decrease in molecular weight, and less chance for CO_2 to distribute along the copolymer chain, it was for this reason that CU of the triol decreased with increasing TMA amount. We defined the time till CO_2 participation in the copolymerization as copolymerization induction period, which was about 150 min at this polymerization condition. The induction period of TMA was longer than SA,[~~30~~31] since TMA initiated PO homopolymerization to oligo-ether triol at first, the strong coordination ability of thus produced triol might hinder the approach of PO to the active center of DMC catalyst. The rapid transfer reaction resulted in polyether triol with low molecular weight (<700) and narrow PDI (~1) before 240 min. As depicted in Fig. 2, W_{pc} increased continuously through the reaction process, but it increased slowly before 220 min, suggesting that low CU restrained the backbiting of the growing chains. The ^{1}H NMR spectra of the products from Table 2 at different reaction times can be seen in Fig. S1. It should be noted that proton signals at 8.8 ppm split at low PO conversion, then converted to a single symmetrical peak at high PO conversion, which would be investigated in the context.

3.2 Structure characterization of oligo(carbonate-ether) triol

The IR spectra of copolymer (sample from Entry 7, Table 1) indicated that CO_2 was incorporated into the backbone of the triol and the triol was ended with hydroxyl groups (Supporting Information Fig. S2).

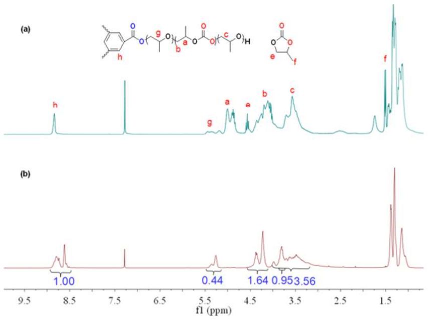


Fig. 3 ^{1}H NMR spectra of (a) oligo(carbonate-ether) triol (Entry 7, Table 1), (b) oligo-ether triol (Entry 1, Table 2).

Fig. 3a showed the ^{1}H NMR spectrum of oligo(carbonate-ether) triol (sample from Entry 7, Table 1), the signals at 4.8-5.0 ppm and 3.9-4.3 ppm were assigned to CH and CH_2 groups in carbonate segment, and those at 3.3-3.8 ppm were assigned to the CH and CH_2 groups in the ether linkage,[~~32~~33] while the single symmetrical peak at 8.84 ppm was ascribed to the aromatic protons of TMA, indicating that three aromatic protons were magnetically equivalent and the three carboxyl groups were all converted into ester groups.[~~33~~34] There were new proton signal at 5.2-5.4 ppm, which might be attributed to CH of PO directly connected to the TMA, it shifted toward low field compared with that of PPC (the chemical shift of CH directly connected to the carbonate group was in the range of 4.8-5.0 ppm), mainly due to the stronger electron withdrawing effect of TMA than carbonate group. Coincidentally, as could be seen from Fig. 2, the reaction products during the induction period were merely oligo-ether triol initiated by TMA without the incorporation of CO_2. To make it more clear, the structure of oligo-ether triol was analyzed in the context.

The ^{1}H NMR and ESI-MS, COSY NMR spectra of the oligo-ether triol (sample of Entry 1, Table 2) were depicted in Fig. 3b, S3, 4, respectively. In Fig. 3b, there existed proton signals at 5.2-5.4 ppm, which was in accordance with the result in Fig. 3a. In addition, the existence of proton signals at 3.3-3.7 ppm confirmed that the product contained polyether structure. The most important information came from the split signals around 8.8 ppm, indicating the existence of different chain length of polyether, due to the different pKa value of carboxyl group of TMA. New proton signals appeared at 4.2-4.3 ppm and 3.8 ppm might be assigned to the rest protons of the PO directly connected to TMA, however, these proton signals overlapped with those assigned to CH_2 groups in carbonate segment and CH, CH_2 groups in ether segment, respectively, which made the structure analysis more complicated. ESI-MS spectrum in Fig. S3 confirmed that the formation of -OH terminated oligo-ether triol, and each oligo-ether triol contained only one TMA molecule. Futhermore, there was no oligo-ether diol existed from the ESI-MS spectrum, indicating that the water content could be ignored in the reaction system.[~~34~~35]

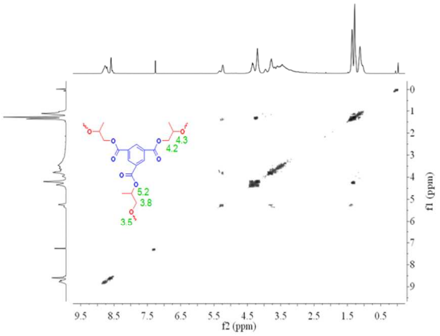
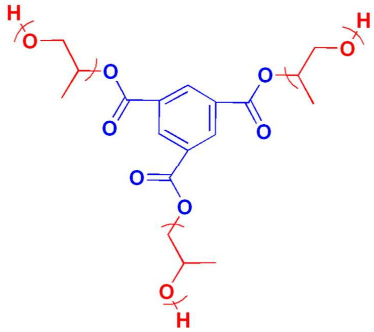


Fig. 4 COSY NMR spectra of oligo-ether triol (Entry 1, Table 2).

In order to further confirm the microstructure and the proton assignment of the oligo-ether triol, COSY NMR spectra were recorded. Two-dimensional COSY allowed us to determine the connectivity of a molecule by determining which protons were spin-spin coupled. There were two ring opening modes of PO under TMA attack: α and β (see Scheme S1). From a detailed analysis of the COSY NMR spectra, the ^{1}H NMR peaks were assigned as noted in the inset of Fig. 4. Proton signals at 5.2 ppm coupled with both signals at 3.8 ppm and at 1.37 ppm as a cross-correlation peak, indicating that the structure was β ring opening ($PhCOOCHCH_3CH_2O$-), signals at 5.2 ppm, 3.8 ppm, 1.37 ppm were assigned to CH, CH_2 and CH_3 of PO directly connected to

TMA, respectively. In the same way, signals at 4.2 ppm, 4.3 ppm, 1.28 ppm were assigned to CH, CH_2 and CH_3 of PO directly connected to TMA by α ring opening mode, respectively. Since the electron-withdrawing inductive effects of aromatic ring in TMA could be ignored when the distance between two groups was longer than 3 C-C bonds, the proton signals of the PO indirectly connected to the TMA were still around 3.5 ppm. From Fig. 3b, integrated area ratio of CH and CH_2 of PO directly connected to TMA on its aromatic proton met the equation of $(A_{5.2}+A_{4.2\sim4.3}+A_{3.78})/A_{8.8}=3$, again confirmed that the oligo-ether triol was capped with three terminal hydroxyl groups. As a summary, the accurate structure of oligo-ether triol was shown in Scheme 1.



Scheme 1 Structure of oligo-ether triol.

Considering that the two different ring opening modes of PO had almost same probability (the integrated area of α/β was 1.64/1.39 from Fig. 3b), the DMC catalyzed reaction between TMA and PO might contain some characteristics of cationic polymerization during induction period.[~~35~~36] The integrated area ratio of the CH and CH_2 in ether segment to the aromatic proton of TMA met the equation of $[(A_{5.2}+A_{4.2\sim4.3}+A_{3.78}+A_{3.5})/3A_{8.8}=2]$ in Fig. 3b, and the highest peak in Fig. S3 corresponded to 6 POs, both indicating that the average chain length of the oligo-ether triol was only 2 POs unit. Thus, it was further demonstrated that the splitting of the signals at 8.8 ppm at low PO conversion resulted from the different chain length of each carboxyl of TMA.

The precise characterization of oligo-ether triol facilitated our understanding of the structure of final oligo(carbonate-ether) triol. The rapid chain transfer reaction led to the incorporation of oligo-ether triol into the polymer chain, which was verified by ^{13}C NMR (Fig. S4) and GPC/DSC spectra (Fig. S5), respectively. The presence of characteristic absorption peaks of TMA (164.1, 134.5, 131.1 ppm) and secondary hydroxyl group (65-67 ppm)[~~36~~37, ~~37~~38] further confirmed the formation of oligo(carbonate-ether) triol (see Fig. S4)]. As revealed in Fig. S5, there were only one single symmetrical peak in GPC curve and one T_g (-13.3 °C~~°C~~) in DSC curve, respectively, again proved that the oligo(carbonate-ether) triol was homogeneous product, not the blend of polyether and polycarbonate.[~~38~~39, ~~39~~40]

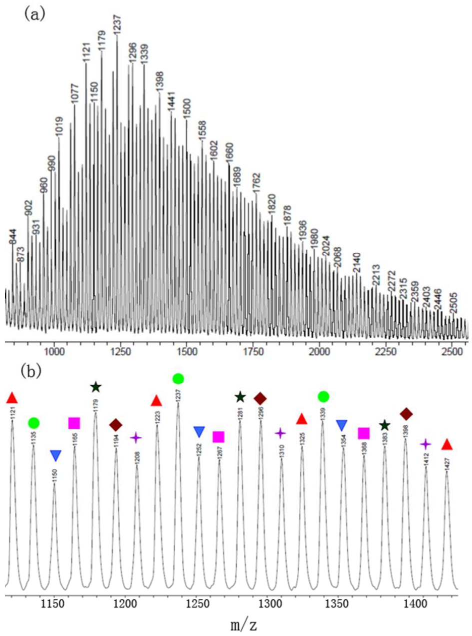


Fig. 5 MALDI-TOF-MS spectra of oligo(carbonate-ether) triol (Entry 7, Table 1), (a) full spectrum, (b) mass from 1100 to 1450 g mol^{-1}.

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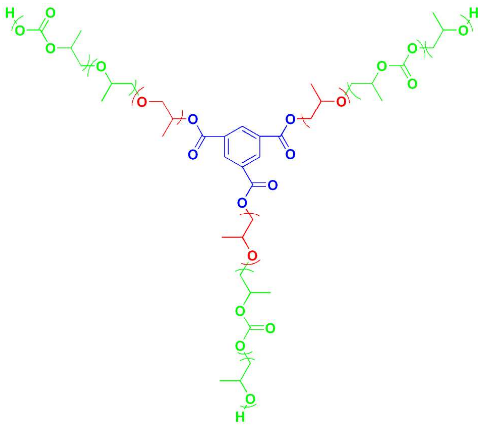
The MALDI-TOF-MS spectra of oligo(carbonate-ether) triol (Entry 7, Table 1) were shown in Fig. 5, seven species were observed: (1) $[TMA(PO\text{-}CO_2)_n(PO)_2]Na^+$(■), (2) $[TMA(PO\text{-}CO_2)_n(PO)_3]Na^+$(▲), (3) $[TMA(PO\text{-}CO_2)_n(PO)_4]Na^+$(★), (4) $[TMA(PO\text{-}CO_2)_n(PO)_5]Na^+$(●), (5) $[TMA(PO\text{-}CO_2)_n(PO)_6]Na^+$(◆), (6) $[TMA(PO\text{-}CO_2)_n(PO)_7]Na^+$(▼), (7) $[TMA (PO\text{-}CO_2)_n(PO)_8]Na^+$(✦), indicating that the oligomer was ended in three sides by hydroxyl groups. The obvious intervals between various peaks were 102 and 58, which was in consistent with the molecular weight of carbonate unit and PO unit, respectively. Titration analysis from Table 1 also confirmed that the oligomer was capped with hydroxyl group at three ends. Thus, the oligo(carbonate-ether) triol was successfully synthesized by immortal copolymerization of CO_2/PO in the presence of TMA under Zn-Co-DMC catalyst.



Scheme 2 The structure of oligo(carbonate-ether) triol.

The structure of oligo(carbonate-ether) triol was shown in Scheme 2, where the three ester groups of TMA were connected with ether linkage of PO by core-first approach, then the carbonate-ether linkage of CO_2/PO grew from the core, it seemed to produce a diblock of oligo[ether-b-(carbonate-ether)] triol.

For the copolymerization of CO_2/PO in the presence of TMA, the accurate carbonate unit content (CU) in the copolymer, the weight fraction of propylene carbonate (W_{pc}) and the number average molecular weight (M_n) of the oligo(carbonate-ether) triol were calculated as follows:

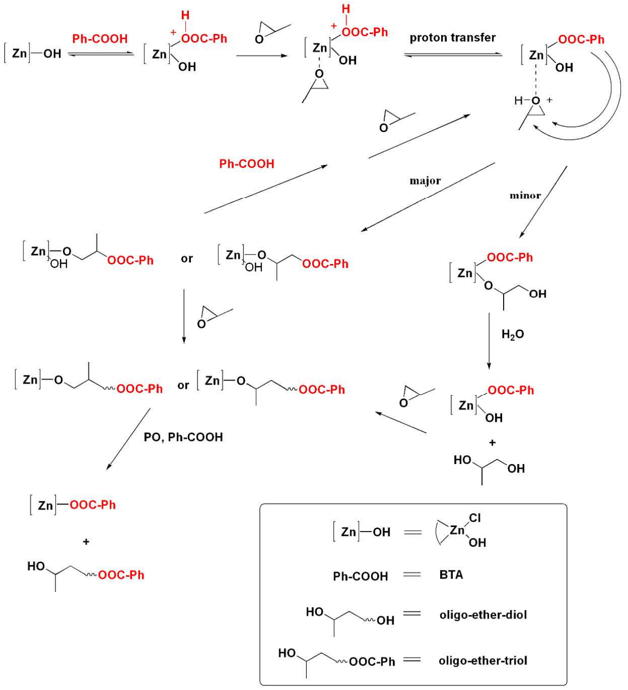
$$CU = (A_{5.0}+A_{4.2}+3A_{5.2}-2A_{4.58}-3A_{8.8})/(A_{5.0}+A_{4.2}+A_{5.2}+A_{3.5}-2A_{4.58}) \quad . \tag{1}$$

$$W_{pc} = 102A_{1.5}/[102(A_{5.0}+A_{4.2}+3A_{5.2}+A_{1.5}-3A_{8.8}-2A_{4.58})+58(A_{3.5}+3A_{8.8}-2A_{5.2})] \tag{2}$$

$$M_n = 102[(A_{5.0}+A_{4.2}+3A_{5.2}-3*A_{8.8}-2A_{4.58})/A_{8.8}]+58[(A_{3.5}+3A_{8.8}-2A_{5.2})/A_{8.8}]+210 \tag{3}$$

Noted that the proton signals of PO directly connected to TMA (δ= 4.2-4.3, 3.8 ppm) overlapped with those assigned to CH_2 groups in carbonate segments and CH, CH_2 groups in ether segments, respectively. Thus, these peak areas were subtracted in the equation. Because the peak area at 4.2-4.3 and 3.8 ppm were equal to $3A_{8.8}$-$A_{5.2}$, and $A_{3.8}$=$2A_{5.2}$, according to the accurate structure of polyether triol. Additionally, the peaks at 8.8 ppm and 5.2 ppm could be integrated distinctly. So the peak area of $3A_{8.8}$-$3A_{5.2}$ and $2A_{5.2}$ replaced the overlapped peak area of PO at 4.2-4.3 and 3.8 ppm, respectively. Besides, the peaks of cyclic propylene carbonate (4.89 and 4.04 ppm) overlapped with the peaks of the copolymer, these peak areas also should be subtracted in the equation.[~~40~~41]

3.3 Plausible mechanism of TMA as initiate-transfer agent



Scheme 3 Plausible mechanism of TMA as initiate and transfer agent in the initial stage of copolymerization catalyzed by DMC.

Although Zn-Co-DMC catalyst shows high catalytic activity for CO_2/PO copolymerization, the mechanism and the structure of the active sites of the catalyst still remained obscure.[~~41~~42] Currently, the plausible mechanism of TMA as initiate-transfer agent in CO_2/PO copolymerization catalyzed by DMC can be proposed. Because of the strong acidity of TMA (pK_{a1}=3.12) and exclusively formation of PO homopolymer during the induction period, a possible coordinative cationic polymerization mechanism is proposed. As shown in Scheme 3, at the initiation stage, TMA firstly coordinated with the Zn-Co-DMC catalyst to form the new active center (TMA-coordinated DMC) (Fig. S6), in case of PO explosive reaction on exposure to excessive catalyst,[~~42~~43] which verified starter coordination first mechanism speculated by Kim et al.[~~43~~44] Subsequent coordinated PO was protonated by the proton transfer of the neighboring coordinated TMA. PO ring opening at both sides with the same probability (the integrated area of α/β was about 1.64/1.39 as could be seen from Fig. 3b) proved the existence of oxygen onium ion, so the proton transfer was regarded as the possible key step and promoter for chain initiation during induction period.[~~34~~35] Then the coordinated TMA catalyzed the PO homopolymerization to afford the TMA-based oligo-ether triol. Notably, no CO_2 was incorporated into the backbone of the oligo-ether triol during the induction period, this may be another evidence that the reaction of TMA/PO proceeded by a coordinative cationic mechanism at the initial stage of polymerization,[~~44~~45] since the incorporation of CO_2 traditionally proceeded by a anionic one.[~~45~~46] The IR spectra analysis of Zn-Co-DMC during the induction period and the verification of copolymerization induction period were shown and explained in Fig. S7, and Table S1, respectively. Finally, TMA-based oligo-ether triol acted as new chain transfer agent to participate in the copolymerization of CO_2/PO to form oligo(carbonate-ether) triol.

4. Conclusions

Controllable synthesis of oligo-(carbonate-ether) triol was realized by Zn-Co-DMC catalyst with TMA as a initiate and transfer agent. The M_n of the triol was in the range of 1400-3800 g mol^{-1}, and PDI was below 1.45, the CU could be tunable in the range of 20%-54%. The molecular weight of the triol could be precisely controlled by TMA amount, and the structure of the triol was clearly confirmed. The role of TMA was of key importance, it acted as a chain initiate-transfer agent, which first coordinated to the active center of DMC, the newly formed TMA-based active species initiated PO homopolymerization to afford oligo-ether triol by a coordinative cationic mechanism, then the *in-situ* produced oligo-ether triol acted as transfer agent to participate in the copolymerization of CO_2/PO to form carbonate-ether segments via a coordinative anionic mechanism, leading to formation of oligo(carbonate-ether) triol.

Acknowledgements

The authors thank financial support from the National Natural Science Foundation of China (Grant No. 51321062, 51273197 and 21134002).

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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