One-pot terpolymerization of CO_2, cyclohexene oxide and maleic anhydride using a highly active heterogeneous double metal cyanide complex catalyst

Xue-Ke Sun [a], Xing-Hong Zhang [a,*], Shang Chen [b], Bin-Yang Du [a], Qi Wang [a], Zhi-Qiang Fan [a], Guo-Rong Qi [a]

[a] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China
[b] College of Chemistry and Chemical Engineering, Jishou University, Jishou, 416000, China

ARTICLE INFO

ABSTRACT

This paper describes a convenient one-pot terpolymerization of CO_2, cyclohexene oxide (CHO) and maleic anhydride (MAH) to afford a poly (ester-carbonate) with a low content of ether units (2.9–4.3 mol %) using a highly active Zn–Co(III) double metal cyanide complex (DMCC) catalyst. Terpolymerization was carried out in tetrahydrofuran (THF) at 75–90 °C and 1.0–4.0 MPa and no cyclic carbonate was observed in NMR spectra. The number-average molecular weight (M_n) of the terpolymer was up to 14.1 kg/mol with a narrow molecular weight distribution of 1.4–1.7. The apparent efficiency of the catalyst was up to 12.7 kg polymer/g Zn, representing the highest catalytic activity for terpolymerization of CO_2, epoxides and cyclic anhydrides to date. THF dramatically inhibited polyether formation in this terpolymerization owing to its nucleophilicity towards the Zn^{2+} center of Zn–Co (III) DMCC. This presents the first example of solvent-assisted selectivity for inhibiting ether units in CO_2 polymerization catalyzed by a heterogeneous system. Kinetic analyses of MAH/CHO/CO_2 terpolymerization (MAH/CHO 0.2) suggested that polyester production was slightly faster than polycarbonate production in the early stage. A mechanism for this terpolymerization catalyzed by Zn–Co (III) DMCC catalyst was proposed. Moreover, addition of small amounts of MAH (MAH/CHO molar ratio ≤0.2) during CO_2/CHO copolymerization can improve the thermal properties of the resultant terpolymers.

1. Introduction

Coupling of carbon dioxide (CO_2) and epoxides to afford biodegradable polycarbonates is an attractive pathway. Since pioneer work on alternating copolymerization of CO_2/propylene oxide (PO) using a $ZnEt_2$/H_2O catalyst by Inoue in 1969 [1], many studies have focused on finding new catalysts with improved activity and selectivity for alternating copolymerization of CO_2 and epoxides [2]. PO and cyclohexene oxide (CHO) have commonly been used to copolymerize with CO_2. Generally, a CO_2/PO copolymer has better biodegradability but is not suitable for direct utilization owing to its rather low thermal properties (e.g. T_g = 35–45 °C) [3]. CO_2/CHO copolymers have good thermal properties (e.g. T_g > 100 °C) [4] but are difficult to biodegrade owing to the presence of more hydrophobic bulky cyclohexane rings around the polymer chain. Copolymers with ester and carbonate units exhibit variable degradation rates and are useful for biodegradable materials [5], so a better choice might be to add a third monomer containing ester units (e.g. cyclic anhydride, cyclic ester) to CO_2/epoxide copolymerization to afford a poly(ester-carbonate).

To date, there are very few reports on terpolymerization involving CO_2, epoxides and a third monomer [6]. Introduction of a third monomer in CO_2/epoxide copolymerization might represent a challenge in terms of the catalyst. A poly(ethylene glycol)-supported bimetallic complex was used to catalyze terpolymerization of PO, CO_2 and maleic anhydride (MAH) at 60 °C and 3.5–4.0 MPa to afford a random terpolymer with production of more polyether [6a]. Another heterogeneous catalyst, zinc glutarate, initiated terpolymerization of CO_2, PO and ε-caprolactone at 60 °C and ∼2.8 MPa [6g]. However, the catalytic activity of both catalysts was rather low even for very long polymerization times (generally >20 h). A homogeneous zinc complex with aminoimidoacrylate ligands showed moderate activity for terpolymerization of CO_2, CHO and lactide at relatively high temperature (90 °C) and CO_2 pressure (4.0 MPa) [6d], but cyclic carbonates and polyether were clearly produced. The aforementioned terpolymers were all random polymers and

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exhibited better biodegradability than their counterpart CO_2/epoxides copolymers. Very recently, an elegant study by Coates et al. [6c] revealed that a homogeneous highly active β-diiminate zinc catalyst for CO_2/epoxide copolymerization could initiate terpolymerization of CO_2, CHO and diglycolic anhydride to afford a well-defined diblock copolymer in a convenient one-pot procedure under mild reaction conditions (50 °C and 6.8 atm). However, such homogeneous catalysts generally require a complex synthesis procedure and very strict conditions for polymerization. Taking reaction efficiency into account, a relatively high reaction temperature may be favorable for improving the catalytic activity for CO_2 polymerizations if side reactions, such as cyclic carbonate and polyether formation, can be minimized. To date, there have been no reports on CO_2 terpolymerizations with high activity and selectivity at relatively high temperature (>70 °C).

Fortunately, we have found that a heterogeneous Zn–Co (III) double metal cyanide complex (DMCC) catalyst, which is well known as an excellent catalyst for ring-opening polymerization (ROP) of epoxides and copolymerization of epoxides and CO_2 [7], exhibits very high catalytic activity for CO_2/CHO bulk copolymerization and surprising polymer/cyclic carbonate selectivity (without observation of cyclic carbonate [7c]) even at high temperature (80–110 °C) and high CO_2 pressure (3.0–6.0 MPa). However, small amounts of ether units (~10 mol%) are always produced in this copolymerization, which either deteriorates the thermal properties [3,7c] or causes inferior biodegradability of the products. Because MAH can react with epoxides via Zn–Co (III) DMCC to afford polyester with high efficiency [8], we investigated the effect of addition of this common and cheap cyclic anhydride to CO_2/CHO copolymerization. We initially expected inhibition of the production of ether units. Surprisingly, an inhibitory effect of tetrahydrofuran (THF) on polyether production was observed for this heterogeneous catalytic system for CO_2 polymerization. Here we report on this one-pot solution terpolymerization of CO_2/CHO/MAH catalyzed by Zn–Co (III) DMCC in THF (see Scheme 1), the structure and thermal properties of the resultant terpolymer, and the proposed catalytic mechanism.

2. Experimental

2.1. Materials

$K_3Co(CN)_6$ (Acros, 95%) was recrystallized from distilled water and dried in vacuum before use. CHO (Aldrich, 98%) was distilled over calcium hydride under nitrogen. MAH (analytical grade) was recrystallized from CH_2Cl_2 and dried overnight under vacuum and collected by sublimation under reduced pressure. THF, toluene and 1,4-dioxane were distilled over sodium under nitrogen. Carbon dioxide (>99.99%) was used as received. Zinc chloride, tert-butanol (t-BuOH), CH_2Cl_2 and methanol were all analytical grade and used without further purification.

2.2. Preparation of Zn–Co (III) DMCC catalyst

Zn–Co(III) DMCC was prepared according to the method previously reported [7]. An aqueous solution of $K_3Co(CN)_6$ (1.72 g in 20.0 mL of distilled water) was added dropwise to a $ZnCl_2$ solution (8.0 g in 10.0 mL of distilled water and 10.0 mL of t-BuOH) under

magnetic stirring at 75 °C. The resulting white suspension was pressure-filtered and isolated and resuspended in a mixed solution of distilled water and t-BuOH (1:1 v/v) under vigorous stirring and again isolated by pressure filtration. The process was repeated at least three times. Finally, the solid was resuspended in pure t-BuOH and isolated by pressure filtration. The resulting Zn–Co (III) DMCC catalyst was dried under vacuum at 60 °C for 6 h. Elemental analysis: C 24.87%; H 2.49%; N 18.59%; Zn 28.00%; Co 12.50%.

### 2.3. Terpolymerization of MAH, CHO and CO_2

A series of MAH/CHO/CO_2 terpolymerizations was performed in a 60-mL autoclave equipped with a magnetic stirrer and a pressure indicator. Desired amounts of catalyst, MAH, CHO and solvent (THF, toluene, 1,4-dioxane, or no solvent) were transferred into the autoclave, which was pre-dried. The autoclave was heated to the target temperature in a pre-heated oil bath and then filled with CO_2 to a set pressure and was kept stirring for a certain time. After the reaction, the autoclave was cooled and the pressure was vented. A small amount of sample was removed for ^{1}H NMR spectroscopy. The solvent was then removed by rotary evaporation and the crude product was dissolved in the minimum CH_2Cl_2 and poured into methanol to precipitate the polymer. The terpolymer was collected and dried under vacuum at 60 °C for 12 h. A terpolymerization with an MAH/CHO molar ratio of 0.2 was carried out at 75 °C with a low catalyst loading (~0.13 mg/mL) in a 500-mL autoclave (Buchi, ecoclave) equipped with a mechanical stirrer and a high-pressure sample-collecting device. Before reaction, the autoclave was dried under vacuum at 100 °C overnight and then cooled to 30 °C. A 7.8-mg sample of catalyst, 4.0 g of MAH, 20.0 mL of CHO and 40.0 mL of THF were transferred into the reactor under a dried N_2 atmosphere. The reactor was sealed and ~2.0 MPa CO_2 was introduced. The temperature was rapidly increased to 75 °C and the pressure was adjusted to 4.0 MPa. During the reaction, the crude terpolymer was sampled at each time point for ^{1}H NMR (to determine CHO conversion and chain composition) and GPC analyses (M_n and MWD).

### 2.4. Copolymerization of MAH/CHO

MAH/CHO copolymerization was performed in a 60-mL autoclave equipped with a magnetic stirrer and a pressure indicator. A 3.0-mg sample of Zn–Co(III) DMCC catalyst, 2.0 g of MAH, 2.0 mL of CHO and 4.0 mL THF were transferred into the autoclave, which was pre-dried. The autoclave was sealed and heated to 90 °C in a pre-heated oil bath and kept stirring for 5.0 h. After polymerization, the autoclave was cooled to room temperature. A small amount of sample was collected for ^{1}H NMR spectroscopy. The solvent was removed by rotary evaporation and the product was dissolved in the minimum CH_2Cl_2 and poured into methanol to precipitate the polymer. The MAH/CHO copolymer was collected and dried under vacuum at 60 °C to constant weight.

2.5. Copolymerization of CHO/CO_2

The copolymerization of CO_2 and CHO was performed in a 60-mL autoclave equipped with a magnetic stirrer and a pressure indicator. A 3.0-mg sample of Zn–Co(III) DMCC catalyst, 4.0 mL of CHO and 4.0 mL of THF, 1,4-dioxane or no solvent were transferred into the
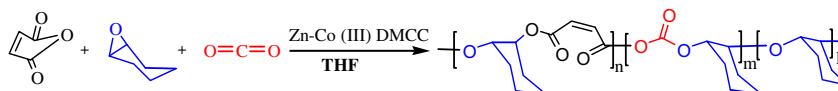
Scheme 1. MAH/CHO/CO_2 terpolymerization catalyzed by Zn–Co(III) DMCC in THF (containing only ~3 mol% ether units).
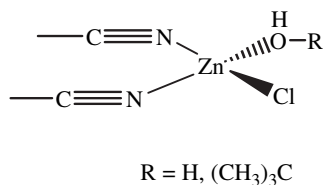
Scheme 2. Proposed ground-state structure of the active site of the Zn–Co(III) DMCC catalyst.

autoclave, which was pre-dried. The autoclave was heated to the target temperature in a pre-heated oil bath and then filled with CO_2 to 4.0 MPa and kept stirring for a set time. After copolymerization, the autoclave was cooled down and the pressure was slowly released. The crude product was dissolved in CH_2Cl_2 and precipitated from methanol. The CO_2/CHO copolymer was collected and dried in vacuum at 60 °C for 12 h.

2.6. Characterization

^{1}H and ^{13}C NMR spectra of the polymers were obtained on a Bruker Advance DMX 400-MHz spectrometer. Chemical shift values were referenced to TMS as internal standard at 0 ppm for ^{1}H NMR (400 MHz) and against $CDCl_3$ at 77.0 ppm for ^{13}C NMR (100 MHz). Elemental analysis was performed using an ICPAES instrument (Leeman Labs) and a Vario MACRO instrument (Elementar). The number-average molecular weight (M_n) and molecular weight distribution (MWD) were determined using a PL-GPC220 chromatograph (Polymer Laboratories, two PLgel 5 μm MIXED-C columns) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with THF at 1.0 mL/min at 40 °C. The sample concentration was 0.3 wt.% and the injection volume was 100 μL. Calibration was performed using monodisperse polystyrene standards covering the molecular weight range from 580 to 460,000 Da. The glass transition temperature (T_g) of the polymers was determined by differential scanning calorimetry (DSC) on a TA DSC-Q200 instrument. The samples were heated in two cycles from room temperature to 160 °C at a rate of 10 °C/min in a nitrogen atmosphere. T_g was determined from the second run. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 1 instrument under an N_2 atmosphere at a heating rate of 10 °C/min from room temperature to >500 °C. All samples for thermal analyses were the purified samples.
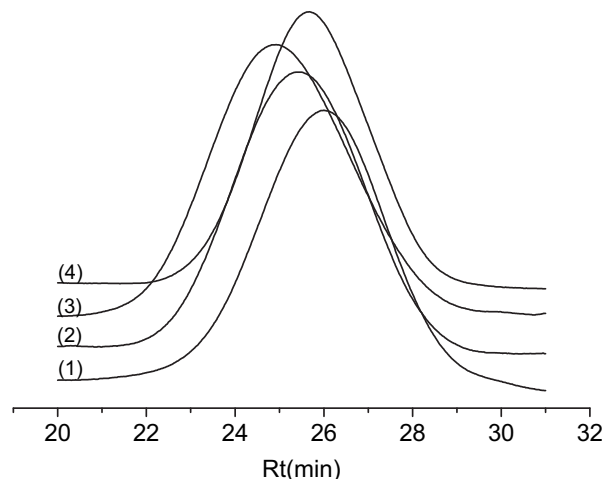

Fig. 1. GPC curves for the purified MAH/CHO/CO_2 terpolymers listed in Table 1. (1) entry 1 (MAH/CHO 0.1); (2) entry 2 (MAH/CHO 0.2); (3) entry 3 (MAH/CHO 0.4); and (4) entry 4 (MAH/CHO 0.6).

3. Results and discussion

DMCCs are heterogeneous catalysts with a non-stoichiometric character [7] and are highly efficient for ROP of epoxides [7a,d,8a,b,e,f], copolymerization of CO_2/epoxides [7c,8b–d,g], cyclic anhydrides/epoxides [9] and CS_2/epoxides [7e]. Zn–Co (III) DMCC has attracted interest in recent years because it is inexpensive, air- and moisture-stable. Traditionally, Zn–Co (III) DMCC has been prepared by precipitation reaction of excess $ZnCl_2$ and K_3 [Co (CN)$_6$] in water/t-BuOH solution. The use of excess $ZnCl_2$ and an appropriate amount of t-BuOH is indispensable for obtaining highly active Zn–Co(III) DMCC [7]. It was proposed that a zinc tetrahedral structure (Scheme 2) is the ground state of the active site of this catalyst [7c,e]. Presumably, the Cl^- in Zn–Co(III) DMCC serves as a good leaving group and can be easily substituted by attacking species so that the polymerization is initiated.

We have reported that Zn–Co(III) DMCC can catalyze CO_2/CHO bulk copolymerization with very high catalytic activity and ~100% polymer selectivity. However, the polycarbonate/polyether selectivity is not satisfactory. Since MAH can preferentially react with epoxides in the presence of Zn–Co(III) DMCC [9], we initially

Table 1
Terpolymerization of MAH/CHO/CO_2 catalyzed by Zn–Co(III) DMCC under various conditions.[a]

Entry	solvent	MAH (g)	CHO (g)	MAH/CHO (mol ratio)	M_n[b] (kg/mol)	MWD[b]	Composition (%) [c]			η_{CHO}[d] (%)	Efficiency [e] (kg/g Zn)
							PE	PC	PCHO		
1	THF	0.4	4.0	0.1	7.0	1.5	8.2	87.5	4.3	94	6.9
2	THF	0.8	4.0	0.2	8.8	1.5	22.5	73.7	3.8	92	7.1
3	THF	1.6	4.0	0.4	10.0	1.6	41.1	55.8	3.1	> 99	8.0
4	THF	2.4	4.0	0.6	8.0	1.4	61.8	35.3	2.9	> 99	8.5
5	none	0.4	4.0	0.1	7.3	1.9	14.2	77.0	8.8	90	6.4
6	toluene	0.8	4.0	0.2	/	/			/	< 1	/
7[f]	THF	2.0	2.0	1.0	5.3	1.6	93.2	0	6.8	> 99	4.7
8	THF	0	4.0	0	5.1	1.8	0	97.0	3.0	> 99	7.0
9[g]	1,4-dioxane	0	4.0	0	6.1	2.0	0	96.0	4.0	> 99	7.0
10	none	0	4.0	0	11.9	2.3	0	88.3	11.7	71	5.3

[a] One-pot polymerization: 3.0 mg of Zn–Co (III) DMCC catalyst, 4.0 mL solvent, 4.0 MPa CO_2, 5.0 h, 90 °C, magnetic stirring.
[b] M_n and MWD were determined by GPC using purified polymers and polystyrene standards for calibration.
[c] Molar fraction of three types of unit in the terpolymer: PE(polyester)% = $A_{4.85–4.90}$/($A_{4.85–4.90}$ + $A_{4.65}$ + $A_{3.2–3.6}$), PC(polycarbonate)% = $A_{4.65}$/($A_{4.85–4.90}$ + $A_{4.65}$ + $A_{3.2–3.6}$), PCHO(polyether)% = $A_{3.2–3.6}$/($A_{4.85–4.90}$ + $A_{4.65}$ + $A_{3.2–3.6}$) according to the ^{1}H NMR spectra.
[d] Total CHO conversion according to ^{1}H NMR spectra of the crude polymers.
[e] Apparent efficiency of the catalyst, total grams of products per gram of zinc, calculated based on elemental analysis.
[f] CHO/MAH copolymerization, no CO_2 involved.
[g] At 100 °C; note that very small product amounts were obtained at 90 °C for this copolymerization.

expected that MAH addition to CO_2/CHO copolymerization could either inhibit the production of ether units or lead to a random poly (ester-carbonate). Thus, a series of one-pot terpolymerizations of MAH, CHO and CO_2 with various MAH/CHO molar ratios (entries 1–4, Table 1) was performed using a Zn–Co(III) DMCC catalyst. THF was used as the solvent to avoid the diffusion effect in the later stages of the polymerization.

For the terpolymerizations in Table 1(except entry 6), the total CHO conversion was ≥90% (see Table 1), and ≥90% MAH was consumed within 5.0 h at 90 °C according to the ^{1}H NMR spectrum of the crude terpolymer. The apparent efficiency of the catalyst was high and up to 8.5 kg polymer/g Zn for an MAH/CHO molar ratio of 0.6. M_n of the terpolymers (entries 1–3, Table 1) increased from 7.0 to 10.0 kg/mol when the MAH/CHO ratio increased from 0.1 to 0.4, but retained a single elution peak (Fig. 1) and the same MWD level (1.4–1.6) as for entries 7 and 8 (1.6–1.8). This suggests that the product was not a simple mixture of polyester and polycarbonate. However, M_n decreased to 8.0 kg/mol when the MAH/CHO molar ratio increased to 0.6 (entry 4). It is likely that some diacid impurities arising from anhydride hydrolysis in the system [6c] have a remarkable influence on M_n when greater amounts of MAH are added.

^{1}H and ^{13}C NMR spectra of the terpolymer (entry 3 in Table 1), polycarbonate (entry 10 in Table 1) and polyester (entry 7 in Table 1) are shown in Fig. 2. In comparison with the ^{1}H NMR spectrum of polyester (curve 1, Fig. 2A), a clear shoulder (δ 4.85 ppm) adjacent to the peak for CH linked to the ester unit (δ 4.90 ppm) is evident in the ^{1}H NMR spectrum of the terpolymer (curve 3, Fig. 2A). The ^{13}C NMR spectrum of the terpolymer also has a shoulder at 164.3 ppm beside the peak for the C = O group of the ester unit (164.7 ppm, curve 3, Fig. 2B). Such shoulders can be attributed to the MAH–CHO–CO_2 structure resulting from random insertion of CO_2 into polyester segments [6c]. Since ether units in the polyester chain did not result in observable splitting of the CH structure adjacent to ester units (curve 1, Fig. 2A,B), it is probable that only the formation of an MAH–CHO–CO_2 structure could cause such splitting of the NMR resonances. Such random insertion suggests one type of propagating chain in this terpolymerization. Furthermore, ^{1}H NMR results for the crude product showed that the polyester and polycarbonate contents in the terpolymer were roughly consistent with the molar feed ratio of MAH and CHO.

As seen from Table 1, polyether production could be inhibited to a certain extent when MAH was introduced into the CO_2/CHO

Table 2
Effect of reaction time on Zn–Co(III) DMCC-catalyzed terpolymerization of MAH/CHO/CO_2.[a]

Entry	Time (min)	M_n[b] (kg/mol)	MWD[b]	Composition (%)[c]			η_{CHO} (%)	Efficiency (kg/g Zn)
				PE	PC	PCHO		
1	45[d]	/	/		/		< 1	/
2	75	5.5	2.0	50.9	36.9	12.2	27.7	4.1
3	105	8.5	1.8	45.8	39.5	14.7	45.5	6.5
4	120	11.7	1.5	44.5	44.2	11.3	49.5	7.2
5	205	12.0	1.7	37.8	57.8	4.4	60.7	9.0
6	290	13.3	1.6	32.3	64.2	3.5	72.9	10.6
7	530	14.1	1.7	28.0	68.7	3.3	88.5	12.7

[a] Polymerization conditions: 7.8 mg of Zn–Co(III) DMCC catalyst, 20.0 mL of CHO, 40.0 mL of THF, 4.0 g of MAH, 4.0 MPa and 75 °C, catalyst concentration ~0.13 mg/mL, mechanical stirring.
[b] Determined by GPC for the crude product.
[c] Calculated as the integral area in ^{1}H NMR spectra of the crude polymers.
[d] Initiation time; only very small amounts of polymer detected, similar to the induction period previously reported [7a,8b,e,f].

copolymerization system (cf. entries 1–4, entries 5, 10). However, it is surprising that ether units in the terpolymer were further dramatically inhibited when terpolymerization was carried out with THF as the solvent (cf. entries 1 and 5, Table 1). Control experiments for CO_2/CHO copolymerization catalyzed by Zn–Co (III) DMCC in THF and 1,4-dioxane (entries 8 and 9, Table 1) revealed that the resultant polycarbonate had only 3.0 and 4.0 mol% ether units, respectively. These results strongly support the notion that THF is a key factor in inhibiting polyether production in CO_2/CHO/MAH terpolymerization and CO_2/CHO copolymerization. Presumably, THF can coordinate with the Zn^{2+} center of Zn–Co (III) DMCC owing to its nucleophilic character and thus significantly affect the CHO/catalyst equilibrium, leading to inhibition of consecutive insertion of CHO on the Zn^{2+} center [10]. Such an inhibitory effect of THF and 1,4-dioxane on the production of ether units was also observed in CO_2/CHO copolymerization catalyzed by a homogeneous rare-earth metal bis(alkyl) complex [11]. Here we present the first example of solvent-assisted selectivity for inhibiting ether units in CO_2 polymerization catalyzed by a heterogeneous system.

A relatively slow polymerization rate is favorable for observing the chain propagation mechanism. Thus, terpolymerization with an MAH/CHO molar ratio of 0.2 was carried out at 75 °C with a low catalyst loading (~0.13 mg/mL) in an autoclave with a high-
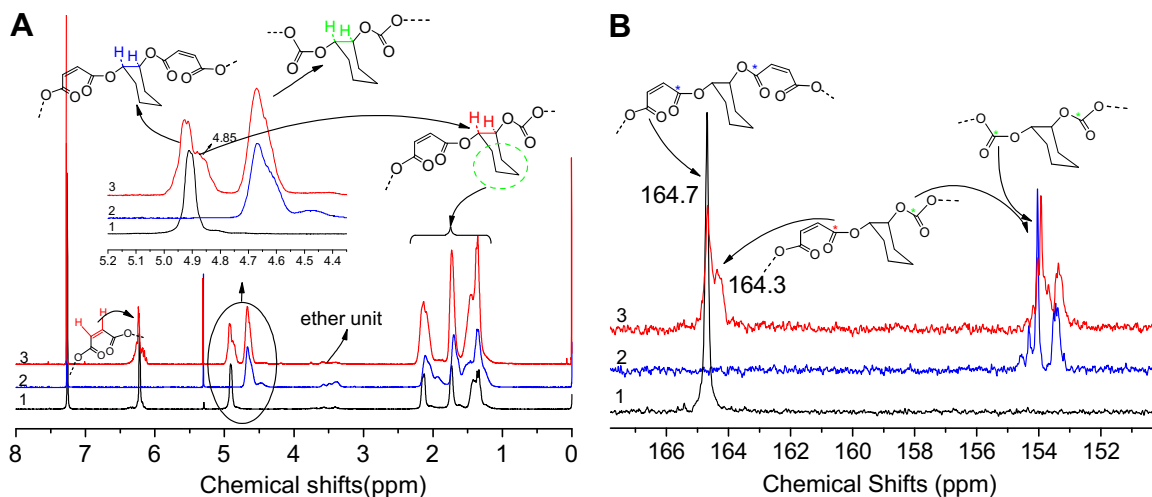

Fig. 2. (A) ^{1}H and (B) ^{13}C NMR spectra of (1) purified MAH/CHO copolymer (entry 7, Table 1), (2) purified CHO/CO_2 copolymer (entry 10, Table 1) and (3) purified MAH/CHO/CO_2 (MAH/CHO 0.4, entry 3, Table 1) terpolymer.
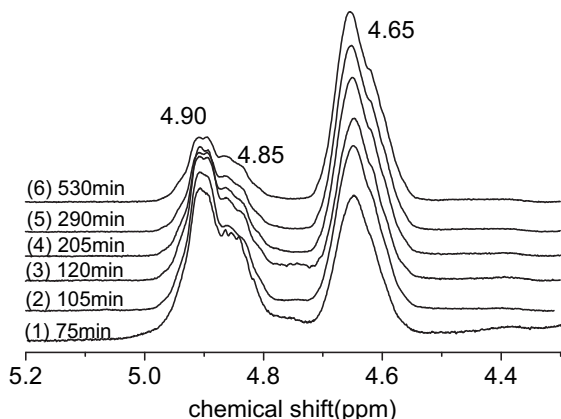
Fig. 3. ^{1}H NMR spectra of the crude MAH/CHO/CO_2 terpolymer (MAH/CHO 0.2) sampled at different polymerization times. Reaction conditions: 75 °C, 4.0 MPa in THF.

pressure sample-collecting device for product sampling at various time points for ^{1}H NMR and GPC characterization. No polymer was detected at 45 min. Small amounts of terpolymer with M_n of 5.5 kg/mol was detected at 75 min (Table 2). This may mean that this terpolymerization in THF has a long initiation time. This phenomenon was also observed for Zn–Co (III) DMCC-catalyzed CO_2/CHO copolymerization [7c] and is very similar to the induction period for ROP of epoxides [7a, 8b,e,f] catalyzed by this catalyst. After this point, the terpolymer M_n and the apparent efficiency of the catalyst increased with the polymerization time and reached 14.1 kg/mol and 12.7 kg polymer/g Zn, respectively, at 530 min (Table 2). To the best of our knowledge, such apparent efficiency may be the highest catalytic activity reported for terpolymerization of epoxides, CO_2 and cyclic anhydrides so far. Furthermore, no cyclic carbonates were detected in ^{1}H NMR spectra.

Fig. 3 shows ^{1}H NMR spectra for different polymerization times. The polyester, polycarbonate and polyether contents in the terpolymer were calculated on the basis of ^{1}H NMR results (Table 2). In the early stages of the polymerization, the polyester peak (δ 4.90 ppm) and polycarbonate peak (δ 4.65 ppm) emerged separately and the peak area was bigger for polyester than for polycarbonate (curve 1 in Fig. 3). The clear emergence of a shoulder at 4.85 ppm indicates that CO_2 insertion into the polymer chain was comparably competitive in this stage. ^{1}H NMR results show that the relative

Scheme 3. Proposed mechanism for the terpolymerization of CO_2, CHO and MAH using Zn–Co(III) DMCC catalyst.

content of polyester and polyether decreased with increasing reaction time, whereas the polycarbonate content increased with the reaction time (Table 2). Further investigation of this reaction was carried out by plotting the conversion of CHO to polyester, polycarbonate and total terpolymer as a function of the reaction time (Fig. 4). The CHO → polyester conversion rate was slightly faster than that for CHO → polycarbonate before 105 min, after which the CO_2 insertion reaction was dominant. It is found that 95% MAH was consumed at 120 min. As a result, a random poly (ester-carbonate) was generated first and then a polycarbonate block with tapering structure, since MAH was consumed in advance under low MAH loadings. It seems to produce a diblock of poly [(ester-carbonate)-*b*-carbonate]. However, the experimental results of relative low M_n and broad MWD of the resultant terpolymer were against the production of pure diblock, for that the possible initiation or chain transfer reaction [7b–c] involved the adventurous water in the system would produce small amounts of CHO/CO_2 copolymer.

Owing to the heterogeneous character of Zn–Co(III) DMCC catalysts, the mechanism of catalysis for polymerization is still very poorly understood to date. Here we propose a mechanism for CO_2/CHO/MAH terpolymerization catalyzed by Zn–Co (III) DMCC catalyst (Scheme 3).

First, it is reasonable that terpolymerization is initiated when CHO coordinates to the Zn site of the catalyst, leading to ring
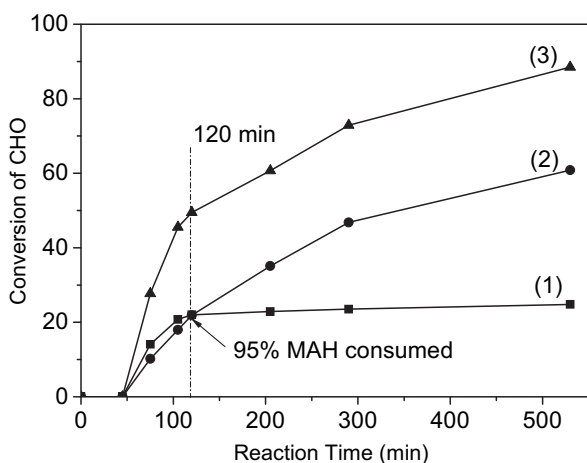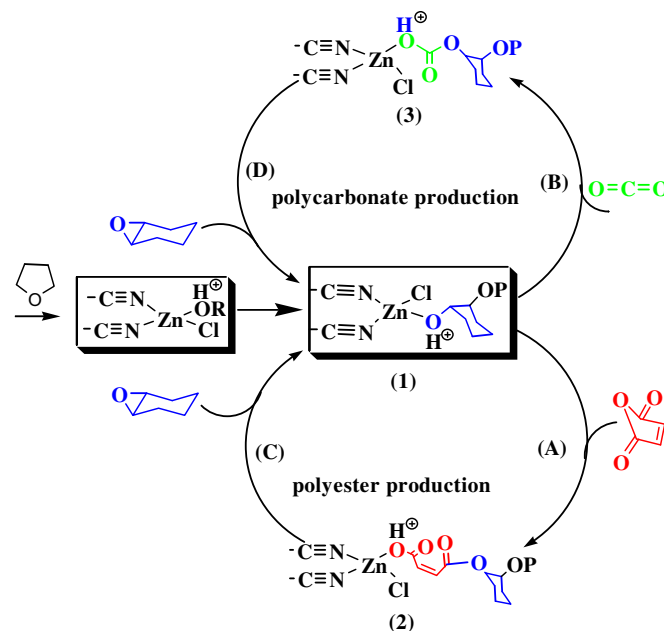

Fig. 4. CHO conversion to polyester (curve 1), polycarbonate (curve 2) and terpolymer (curve 3) as a function of reaction time. Data points correspond to entries 1–7, respectively, in Table 2.

Table 3
Effect of pressure and anhydride type on MAH/CHO/CO_2 terpolymerization.[a]

Entry	P_{CO_2} (MPa)	M_n (kg/mol)	MWD	Composition (%)			η_{CHO} (%)	Efficiency (kg/g Zn)
				PE	PC	PCHO		
1	4.0	8.8	1.5	22.5	73.7	3.8	92	7.1
2	2.0	6.4	1.5	21.7	74.6	3.7	97	7.4
3	1.0	6.8	1.8	25.3	69.5	5.2	80	6.2
4[b]	4.0	3.7	1.9	8.2	89.0	2.8	83	5.9

[a] Polymerization conditions: 3.0 mg of Zn–Co(III) DMCC catalyst, 1.2 g of cyclic anhydride, 4.0 g of CHO, 4.0 mL of THF, 5.0 h, 90 °C. Molecular weight and composition of the resultant terpolymers were from GPC and NMR characterizations (for crude products) respectively.
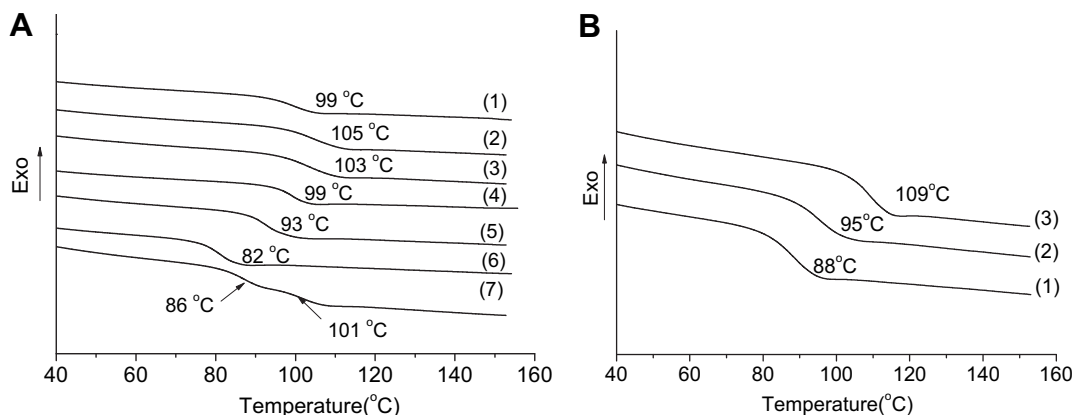[b] 0.8 g of succinic anhydride, 10.0 h.

Fig. 5. (A) DSC curves of (1) polycarbonate (entry 10, Table 1), (2–5) terpolymers with MAH/CHO molar ratios of 0.1, 0.2, 0.4 and 0.6 (entries 1–4, Table 1), (6) polyester (entry 7, Table 1), (7) polycarbonate (entry 10, Table 1)/polyester (entry 7, Table 1) mixture (weight ratio 1). (B) DSC curves of terpolymer at (1) 120, (2) 205 and (3) 530 min in Table 2. Heating rate 10 °C/min under an N_2 atmosphere.

opening and the formation of a zinc alkoxide intermediate (**1**) (Scheme 3) for which the ether unit is mainly generated in the early polymerization stages. This is supported by the observation that the relative polyether content in the terpolymer gradually decreased with increasing reaction time. Moreover, monomer coordination to the catalyst may be inhibited by a coordinating solvent such as THF, thus leading to a longer initiation time, as clearly observed in the initiation stage (entry 1 in Table 2).

Second, after generation of the zinc alkoxide intermediate (**1**), two paths for chain propagation are possible. One is polyester production (steps **A** and **C**, Scheme 3). MAH inserted into intermediate **1** to generate a zinc carboxylate intermediate (**2**), followed by insertion of CHO to regenerate a new zinc alkoxide intermediate and thus completing one full polyester formation cycle. The other is polycarbonate production, in which a zinc carbonate intermediate (**3**) is generated by CO_2 insertion (step **B**) and insertion of CHO then yields a new zinc alkoxide intermediate (step **D**). If polyester production is much faster than polycarbonate production or vice versa, a diblock copolymer of poly(ester-*b*-carbonate) will be produced. This may require a special catalyst and a very unique anhydride monomer, as reported by Coates [6c]. However, for Zn–Co(III) DMCC-catalyzed CO_2/CHO/MAH terpolymerization, polyester production and polycarbonate production compete in the early stages of the polymerization and the rate of the former was slightly faster than that of the latter, as observed from plots of CHO conversion to polyester and polycarbonate as a function of reaction time up to 105 min (Fig. 4). As a result, a random poly (ester-

carbonate) could be produced, however, the ester unit and carbonate unit of the resultant terpolymer was not evenly distributed along the chain.

The effect of CO_2 pressure was explored. Terpolymerization proceeded very well at relatively low CO_2 pressure (entries 2 and 3 in Table 3). Polyester, polycarbonate and polyether units in the terpolymer produced at 4.0 MPa (entry 1 in Table 3) were almost the same as those at 2.0 MPa. The polymer yield at 1.0 MPa was also high (up to 6.2 kg polymer/g Zn). Unfortunately, too low a CO_2 pressure (1.0 MPa) resulted in slight ether unit enrichment in the terpolymer (5.2 mol%).

The Zn–Co(III) DMCC catalyst exhibited strong selectivity towards the cyclic anhydride used. Phthalic anhydride, glutaric anhydride, succinic anhydride, nadic anhydride and diglycolic anhydride were tested, but only succinic anhydride, which is structurally similar to MAH, could polymerize with CHO and CO_2 (entry 4, Table 3) at relatively low CHO conversion (83%) even after 10 h. The resulting terpolymer had a relatively low M_n of 3.7 kg/mol and a wide MWD of 1.9. Presumably, succinic anhydride is not easy to open owing to its relatively low ring strain in comparison to MAH, which explains the relatively low activity and M_n.

The glass transition temperature (T_g) the resultant terpolymers were measured by DSC. As observed in Fig. 5 T_g for the polycarbonate with 11.7 mol% ether unit was 99 °C (curve 1), which is clearly higher than the 82 °C for polyester, which contains more flexible ester linkages and 6.8 mol% ether units. All the terpolymers in Fig. 5A (curves 2–5, terpolymers with MAH/CHO molar ratios of
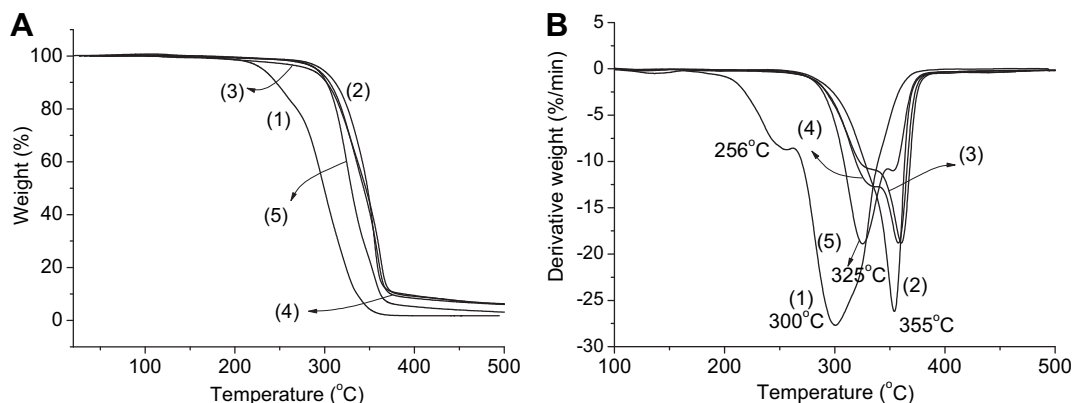

Fig. 6. (A) TGA and (B) derivative TGA curves of: (1) polycarbonate (entry 10, Table 1); (2) polyester (entry 7, Table 1); (3–5) terpolymer at 120, 205 and 530 min in Table 2. Heating rate 10 °C/min under an N_2 atmosphere.

0.1, 0.2, 0.4 and 0.6 (entries 1−4, Table 1)) had a single T_g. Moreover, a blend of the copolymers for entries 7 and 10 in Table 1 at a weight ratio of 1 (dissolved in THF and then dried) showed two clear T_g peaks at 86 °C (polyester) and 101 °C (polycarbonate) (curve 7 in Fig. 5A), which also confirms that the terpolymers were not a blend of polyester and polycarbonate. We also observed that the terpolymers collected at 120, 205 and 530 min (entries 4, 5 and 7 in Table 2) exhibited a single T_g transition at 88, 95 and 109 °C, respectively (curve 1−3 in Fig. 5B). This is mainly attributed to the increase of carbonate unit and molecular weight of the terpolymer.

Fig. 6 shows TGA curves and the corresponding derivative curves for polycarbonate (entry 10, Table 1), polyester (entry 7, Table 1) and three terpolymers collected at 120, 205 and 530 min (Table 2). It is clear that the initial decomposition temperature ($T_{d,5 \text{ wt.%}}$, Fig. 6A) and the temperature for the maximum decomposition rate (T_p, Fig. 6B) were higher for polyester and these terpolymers than for polycarbonate. These terpolymers had nearly the same $T_{d, 5 \text{ wt.%}}$, although their molecular weights are clearly different. Moreover, the terpolymers collected at 120, 205 and 530 min showed two clearly differentiable degradation stages (325 °C and 355 °C) and the relative intensity of T_p for decomposition of polycarbonate increased with the reaction time. The first T_p of the terpolymer collected at 530 min is 325 °C, which is slightly higher than that of the reported T_p of the full alternating polycarbonate [12]. This is attributed to the incorporation of ester units into the polycarbonate.

Furthermore, since T_g (≥103 °C) and $T_{d, 5wt\%}$ (≥273 °C) were higher for entries 1 and 2 in Table 1 and entry 7 in Table 2 than for polycarbonate, we conclude that addition of small amounts of MAH during CO_2/CHO copolymerization can improve the thermal properties of the resultant terpolymers.

4. Conclusions

We have demonstrated a convenient and highly efficient one-pot synthesis method for terpolymerization of CO_2, CHO and MAH using a heterogeneous Zn−Co (III) DMCC as catalyst. The polymer/cyclic carbonate selectivity and poly(ester-carbonate)/polyether selectivity were very good at a relatively high reaction temperature (75−90 °C) and CO_2 pressure (4.0 MPa), which may be superior to the reported catalysts to date. THF dramatically inhibited the formation of ether units in Zn−Co(III) DMCC-catalyzed MAH/CHO/CO_2 terpolymerization and CHO/CO_2 copolymerization. M_n of the terpolymer was up to 14.1 kg/mol with a narrow molecular weight distribution of 1.4−1.7. The apparent efficiency of the catalyst was up to 12.7 kg polymer/g Zn. Terpolymerization kinetic analyses suggests that polyester production was faster than polycarbonate production in the early stage. Addition of small amounts of MAH (MAH/CHO ≤ 0.2) during CO_2/CHO copolymerization can improve the thermal properties of the resultant terpolymers.

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