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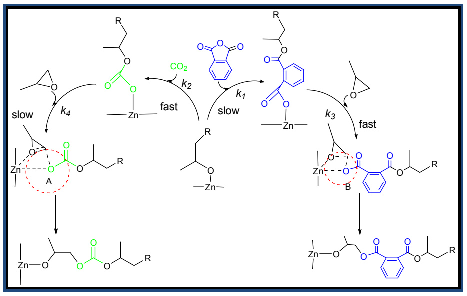
Monomer reactivity ratios of CO_2 and phthalic anhydride (PA) are evaluated and mechanism is discussed for ZnGA catalyzed PA/CO_2/PO terpolymerizations.



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ARTICLE TYPE

Mechanism Studies of Terpolymerization of Phthalic Anhydride, Propylene Epoxide, and Carbon Dioxide Catalyzed by ZnGA

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The terpolymerizations of carbon dioxide (CO_2), propylene oxide (PO) and phthalic anhydride (PA) using Zinc Glutarate (ZnGA) as catalyst were carried out in toluene solution. The monomer reactivity ratios of carbon dioxide and phthalic anhydride (r_{CO2}=5.94 and r_{PA}=0.21) were experimentally evaluated by Fineman–Ross methodology. The results indicate that the reactivity of CO_2 is much higher than that of PA, resulting in a random sequence structure of ester and carbonate units in the terpolymer. It is found that the introduction of small amount of the third monomer PA can significantly increase PO conversion and the molecular weight of the terpolymer. Terpolymers with very high number-average molecular weight (Mn) up to 221kg/mol can be obtained at the optimal reaction condition (PA/PO molar ratio:1/8, temperature:75℃, CO_2 pressure: 5MPa). This is the highest Mn reported to date for the terpolymerization of CO_2, epoxides and cyclic anhydrides, together with very high PO conversion of 72.5%. Moreover, the synthesized terpolymers exhibit a high Tg of about 41℃and higher thermal stabilities compared with the copolymer of PO and CO_2.

Introduction

The limited oil resources and growing environmental awareness have triggered in finding alternative carbon resources for the production of chemicals and polymers, and which should minimize the detrimental environmental effects when using oil resources. CO_2 is a main component of greenhouse gases that contributes to global warming, but it is also an inexpensive, virtually nontoxic, abundantly available carbon resource. Copolymerization of CO_2 and epoxides to produce biodegradable aliphatic polycarbonate is considered to be one of the most promising ways to chemical fixing CO_2 and has attracted intensive research interests since the pioneer work of Inoue.[1] In the past decades, a variety of catalysts, such as zinc carboxylates,[2, 4] rare-earth ternary catalyst,[5] β-diiminate zinc derivatives,[6, 7] metal salen derivatives [8-11] have been explored for effective copolymerization of CO_2 with various epoxides. The copolymerizations of propylene oxide (PO) or cyclohexene oxide (CHO) with CO_2 are the most intensively studied system, including the mechanism, the reaction conditions, and the properties of the corresponding copolymers.[12-14] Although tremendous progress has been made over the past decades in increasing polymer selectivity, suppressing ether linkages and controlling molecular weight, the comprehensive performances of the copolymers of CO_2 and single epoxide still can't meet the requirement of diverse applications. Therefore, further development of this green technology is needed to improve material performance as well as product type. Recently, researchers are putting their effort on introducing a third monomer into the copolymerization of CO_2 and PO or CHO, which was proved to be an effective way to tune the properties of the copolymers.[15-21]

Anhydrides are another kind of abundantly available monomers, which are used to synthesize biodegradable aliphatic polyesters.[22-24] Terpolymerization of CO_2, epoxides and anhydrides is an attractive way to afford biodegradable terpolymers with tailorable degradation rate as well as thermal and mechanical properties.[25] Zhang et al. reported one-pot terpolymerization of CO_2, CHO and maleic anhydride (MAH) to afford a random poly (ester-co-carbonate) using Zn-Co(III) double metal cyanide complex catalyst.[26] Whereas Coates and co-workers demonstrated the formation diblock poly(ester-b-carbonate)s upon terpolymerization of CO_2, CHO and diglycolic anhydride (DGA) using a β-diiminate zinc catalyst.[27] Terpolymerization of CO_2, CHO with various carboxylic acid anhydrites was also proved to be feasible by chromium tetraphenylprophyrinato catalyst or (Salen)CrCl catalyst.[28, 29] Despite of variety in catalysts, all the above reports demonstrated that the reactivity of anhydrides was higher than the reactivity of CO_2 from the fact that the ester: carbonate ratio was invariably higher than expected based on the initial ratio of anhydride and epoxide. We have studied the terpolymerization of CO_2, PO with MAH or phthalic anhydride (PA) using zinc glutarate (ZnGA) catalyst. ZnGA is not only an excellent catalyst for alternating copolymerization of CO_2 and epoxides, but also a highly active catalyst for these terpolymerizations.[30, 31] We observed that the molar ratio of ester to carbonate in the resultant terpolymer was lower than expected based on the feed ratio of anhydride and epoxide. Three possible reasons are supposed to explain the phenomenon. One is that the ZnGA catalyst favors CO_2 insertion over anhydride insertion. The second reason might be the lower solubility of the anhydride than CO_2 in PO during the bulk terpolymerization. The third explanation is that during the long time terpolymerization process, the anhydride concentration continuously decreasing while the concentration of CO_2 changes little by keeping CO_2 pressure constant. To further elucidate these suppositions, herein, the terpolymerization of CO_2, PO and PA using ZnGA catalyst in toluene solution (Scheme 1) is intensively reported.

Experimental Section

Materials

Carbon dioxide with a purity of 99.99% was used as obtained. propylene epoxide （PO） of 99.5% purity was refluxed over calcium hydride for 4 h. It was then distilled under dry nitrogen gas and stored over 4-Å molecular sieves prior to use. Phthalic anhydride (PA) was recrystallized from ethyl acetate. Zinc glutarate (ZnGA) was prepared according to previous work.[32] Solvents such as toluene, methanol, ethyl acetate, acetone, chloroform were of analytical reagent grade and used as received and without further treatment.

Terpolymerization of CO_2, PO, and PA

Terpolymerization of CO_2, PO, and PA was carried out in a 500 mL autoclave equipped with a mechanical stirrer using toluene as solvent. A typical terpolymerization process was as following: 1.0g dry catalyst and 12.76g PA were introduced into the autoclave as quickly as possible. The autoclave was then capped with its head, and the entire assembly was connected to the reaction system equipped with a vacuum line. The autoclave with catalyst and PA inside was further dried for 4h under vacuum at 80 ℃. Upon cooling down, 40g PO and 40g toluene were added to the autoclave. Subsequently the autoclave was purged with CO_2 and pressurized to 5.0 MPa. The terpolymerization was performed at 75 °C and a constant 5.0 MPa CO_2 pressure for 15h, and then the autoclave was cooled down followed by releasing the pressure. The very viscous resulting mixture was dissolved in chloroform. Then the Excess anhydride and catalyst was extracted from the product solution by pouring it into vigorously stirred methanol containing a small amount of hydrochloric acid (5%). The final PPCPA precipitates were filtered and dried in a vacuum oven at room temperature.

Scheme 1. Terpolymerization of PA,PO and CO_2 catalyzed by ZnGA .

Copolymerization of PA and PO

The procedure for copolymerization of PA and PO was similar to that for terpolymerization of PA, PO and CO_2, with the exception that the autoclave was purged with N_2 instead of CO_2 and was pressurized to 0.5 MPa.

Polymer Characterization

The molecular weight (Mn/Mw) and molecular weight distribution (MWD) were measured using a gel permeation chromatography (GPC) system (Waters 515 HPLC Pump, Waters 2414 detector) with a set of three columns (Waters Styragel 500 Å ,10,000 Å, and 100,000 Å). The GPC system was calibrated by a series of polystyrene standards with polydispersities of 1.02, which were supplied from Shodex Inc. Chloroform (HPLC grade) was used as eluent. The glass transition temperature (Tg) of the polymers determined by differential scanning calorimetry (DSC) measurements were carried out under nitrogen flow on a Netzsch calorimeter (Model 204) from -20 ℃ to 100 ℃ at a heating rate of 10 ℃/min. Tg of the samples was determined from the second run. Thermo gravimetric analysis (TGA) measurements were performed in a Perkin–Elmer TGS-2 under a protective nitrogen atmosphere. The temperature ranged from 50 to 500℃ with a heating rate of 10 ℃/min. All samples for thermal analyses were the purified samples.

^1H NMR spectra of the polymers were obtained on a Bruker DRX-400 NMR spectrometer using tetramethylsilane as an internal standard and D-chloroform ($CDCl_3$) as solvent. Typical ^1H NMR spectra of the PA/PO/CO_2 terpolymer, PA/PO copolymer and PO/CO_2 copolymer are shown in Fig.S1-S3 in ESI. The composition of copolymers was estimated according to the ^1H NMR spectra (see Eq.S1-S3 in ESI).

Measurement of CO_2 solubility

The solubility of the CO_2 in the reaction solution at 75℃ and 1MPa CO_2 pressure was measured as follows: firstly, an empty dry autoclave with volume of 110mL was weighed (W_1), then the autoclave was heated to 75 ℃ and purged with CO_2 and pressurized to 1.0 MPa and then was weighed again (W_2). After that, the CO_2 was released and 15 mL PO, 15 mL toluene and 4.0g PA (the mole ratio of PA to PO was 1:8) was added into the autoclave and sealed. The autoclave was then weighed to get the weight W_3. Subsequently the autoclave was heated to 75℃, and then was pressurized to 1.0 MPa via a CO_2 cylinder. After equilibrium, the autoclave was weighed again to get the weight W_4. The amount of CO_2 dissolved in the mixture of 15 mL PO, 15 mL toluene and 4.0g PA can be estimated by the following equation:

$$W_d=W_4-W_3-(W_2-W_1)\times V\div 110 \quad \text{(Eq.1)}$$

Where V is the volume of the mixture of 15 mL PO, 15mL toluene and 4.0g PA, and it is estimated to be 32.6 mL. By this method, the amount of CO_2 dissolved in the reaction solution at different CO_2 pressures was estimated.

Results and discussion

Firstly, the copolymerizations of PO with CO_2 or PA using ZnGA catalyst were performed at 75℃ in toluene solution for 15h. The results are given in Table **1** (entries 1-2). Evidently, ZnGA can effectively catalyze the copolymerization of PO with CO_2 in toluene solution with relatively high selectivity of polycarbonate over polyether. ZnGA can also catalyze the copolymerization of PO with PA in toluene solution, resulting in higher PO conversion as compared with the case of PO and CO_2 copolymerization. However, a poly(ester-co-ether) with relatively low molecular weight and 51% polyester linkage was obtained due to low selectivity of the reaction conditions employed. Since the molar feed ratio of PA and PO is 1:1, the very close percentage of polyester linkage and polyether linkage in the resulting copolymer indicates that the insertion reactivity of PO and PA into the zinc-alkoxide active chain end is almost same.

The as prepared poly(ester-co-ether) is proved to be a random one by ^{1}H NMR spectrum (Fig. **S2**). The clear resonance peak (δ5.25 ppm) appears adjacent to the peak for CH linked to the ester unit (δ5.45 ppm) can be attributed to the random inserted PA-PO-PO-PA structure in the ester rich linkage, and the obvious splitting of the NMR resonances of the ether unit indicates the existence of random inserted PO-PA-PO structure in the ether rich linkage.

Table 1 Effect of PA loading on ZnGA catalyzed terpolymerization of PA/PO/CO_2 [a]

Entry	PA/PO (mole ratio)	P_{CO_2} (MPa)	Mn[b] (kg/mol)	MWD[b] (Mw/Mn)	Composition (%)[c]			Yield[d] (g)	ηPO[e] (%)	ηPA[f] (%)
					PE	PC	PPO			
1	0:1	5	26.4	2.12	/	94.3	5.7	8.7	12.7	/
2	1:1	0	7.4	2.22	51.0	/	49.0	18.1	19.7	10.0
3	1:11	5	79.6	3.08	4.8	92.5	2.7	16.0	21.9	11.6
4	1:8	5	110.0	3.10	6.4	89.3	4.3	24.1	32.7	16.8
5	1:6	5	99.6	3.44	8.1	86.8	5.1	21.9	29.3	14.3
6	1:3	5	29.0	2.23	10.5	82.4	7.1	20.0	26.4	8.3

[a] Conditions: 1g ZnGA, 40g PO, 40 g toluene, 15h, 75℃, 5MPa CO_2.

[b] Determined by gel permeation chromatography (GPC), calibrated by polystyrene standards.

[c] PE=polyester, PC= polycarbonate. PPO=polyether. The compositions were estimated according to the ^{1}H NMR spectra by Eq.S1-S3(see ESI).

[d] Weight of the polymer obtained.

[e] Conversion of PO, calculated from the weight of the polymer obtained and the composition of the polymer.

[f] Conversion of PA, calculated from the weight of the polymer obtained and the composition of the polymer.

A series of one-pot terpolymerizations of PA, PO and CO_2 with various PA/PO molar ratios (entries 3-6, Table **1**) were then performed at 75℃, 5MPa CO_2 in toluene for 15h. It is apparent that the contents of polyester in the resulting terpolymers increase with increasing PA amount. By comparing the molar ratios of ester unit to carbonate unit in terpolymers with PA/PO molar feed ratios, we find that ester/carbonate molar ratios are much lower than expected. This phenomenon was also observed in the bulk polymerization of PA, CO_2 and PO in previous work.[31] Since the solubility of PA in toluene is pretty high at 75℃, the lower ester/carbonate molar ratios in the resulting terpolymers is not resulted from the low solubility of PA in reaction system. It needs to elucidate whether ZnGA catalyst favors CO_2 insertion over PA insertion in the terpolymerization.

To quantitatively compare the reactivity of PA and CO_2, we carefully measured the solubility of CO_2 in the mixture solution of PO, toluene and PA (mass ratio of PO/toluene equals to 1, molar ratio of PA/PO equals to 1/8) under different CO_2 pressures at 75℃. The terpolymerization was then conducted under these pressures in a period of 2h. The experiment results are shown in Table 2. If ignoring the formation of the ether linkages, the terpolymerization is considered as a copolymerization of the PO-PA and PO-CO_2 units as shown in Scheme 2. Therefore, the reactivity ratio of PA and CO_2 can be defined as $r_{PA}=r_1= k_{11}/k_{12}$ and $r_{CO2}=r_2= k_{22}/k_{21}$, respectively. From PA/$CO_2$ feed ratios and PE/PC ratios in resulting polymers, the reactivity ratios of PA and CO_2 at 75℃ were evaluated by Fineman-Ross method (Eq.2).[33]

The data for PA/CO_2 mole ratios in feed (F) and PE/PC ratios in polymers (f) fit Fineman-Ross plot well (R^2 =0.982, Figure **1**), and the monomer reactivity ratios r_{PA} (k_{11}/k_{12}) and r_{CO2} (k_{22}/k_{21}) obtained from the intercept and slop are 0.21 and 5.94, respectively. It is obvious from the results that the reactivity of CO_2 is much higher than that of PA. It is interesting that other catalysts, such as Zn-Co(III) double metal cyanide complex catalyst, β-diiminate zinc catalyst, chromium tetraphenylprophyrinato catalyst and (Salen)CrCl catalysts were reported to favor anhydride insertion over CO_2 insertion.[26-29] ZnGA catalyst used in this work is the only exception reported so far.

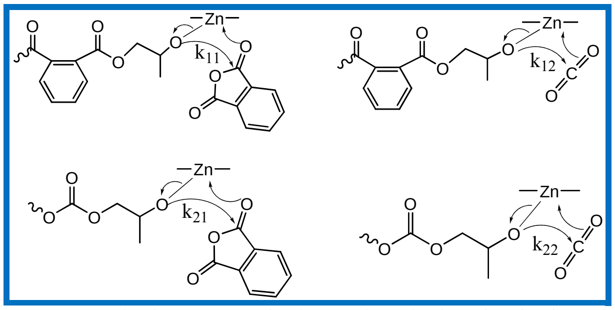
Table **2** Monomer reactivity ratio evaluation in terpolymerization [a].

Entry	P_{CO_2} (MPa)	M_{CO2} in feed (mol)	M_{PA} in feed (mol)	ηPO (%)	F[b]	f [c]
1	0.5	0.044	0.086	3.50	1.96	0.35
2	1.5	0.060	0.086	3.67	1.44	0.27
3	2.0	0.081	0.086	3.82	1.07	0.18
4	2.5	0.116	0.086	3.89	0.74	0.13

[a] Terpolymerization conditions: 1g ZnGA, 40g PO, 40 g toluene, PA/PO feed molar ratio =1/8, 2h, 75℃.

[b] Molar ratio of PA and CO_2 in feed.

[c] Molar ratio of PE and PC in copolymer, determined by ^{1}H NMR spectroscopy of the polymer.



Scheme 2. Kinetic parameters for the terpolymerization of PA/PO/CO_2

$$\frac{(f-1)}{F} = -r_2\frac{f}{F^2} + r_1 \qquad \text{(Eq.2)}$$

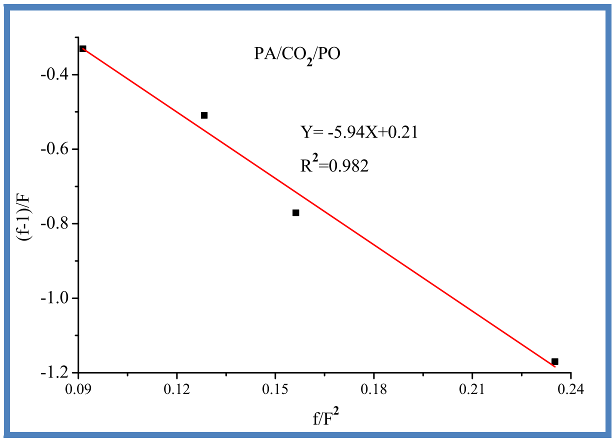
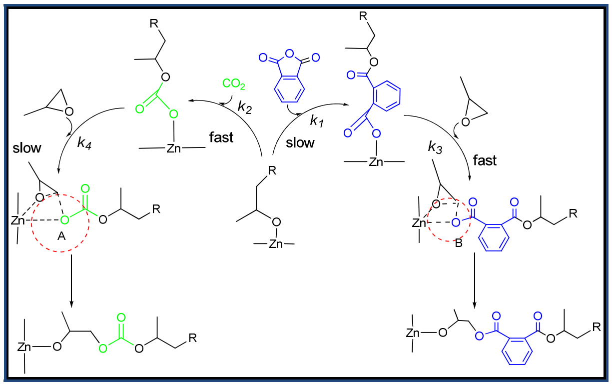


Fig 1. Fineman-Ross plot of PA/ PO /CO_2 terpolymerization reaction.

According to Fineman–Ross plot and reactivity ratio conception, a carbonate polymer end group has a much greater propensity for CO_2 insertion over PA insertion. Therefore, the alternate insertion of CO_2 and PO into polymer chain dominates the chain propagation. PA can randomly insert into the polycarbonate chain to form $(CO_2\text{-PO})_n$ -PA-PO-$(CO_2\text{-PO})_m$ linkages. This is consistent with the result of a large polycarbonate peak (δ5.0 ppm) companied with an adjacent small shoulder peak (δ5.1 ppm) in ^{1}H NMR (Fig.S1) of terpolymers. Certainly, it cannot exclude the random insertion of two successive ester unit (PA-PO-PA-PO linkages) in polycarbonate chain since $r_{PA} \neq 0$. The peak at δ5.4 ppm in ^{1}H NMR (Fig.S1) of the terpolymer indicates the existence of aforementioned linkage.



Scheme 3. Mechanism for terpolymerization of PA, PO and CO_2.

Comparing the results between terpolymerization and PO/CO_2 copolymerization (Table **1**, entries 1, 3-6), it should be noted that the introduction of the third monomer PA results in a significant increasing of yield and molecular weight of the polymer. The yield of polymer increases from 8.7g to 24.1g and the Mn of polymer increases from 26.4kg/mol to 110.0 kg/mol when PA/PO molar ratio increases from 0:1 to 1:8. However, Mn and yield of polymer decrease with further increasing PA molar fraction in the feed. The introduction of PA has two opposite effects on the reaction rate as shown in Scheme **3**. On one hand, since the reactivity of CO_2 is higher than that of PA ($k_2 > k_1$), excess PA competes with CO_2 to coordinate with ZnGA, therefore decreasing the reaction rate. On the other hand, the activity of a zinc benzoate chain end reacting with an epoxide is higher than that of a zinc carbonate chain end reacting with an epoxide. As indicated in Scheme **3**, complex B coordinates with a relatively stronger electron-withdrawing group of phthalic benzoyl, while complex A connects with a relatively weaker electron-withdrawing group of carbonyl. The polarity of Zn-O bond in complex B is stronger than that of Zn-O bond in complex A, leading to its more active in reacting with epoxide ($k_3 > k_4$).[34] In this sense, the more PA in the feed, the more zinc benzoate chain end formed at propagating chain. Consequently, faster reaction rate is expected. Due to the opposite effect on the reaction rate, there should exist an optimal PA molar fraction in the feed to reach the highest reaction rate and molecular weight of terpolymer. This value has been experimentally proved to be PA /PO=1:8. Moreover, the molecular weight of terpolymer decreases with increasing the amount of anhydride, which has also been disclosed by Sun et.al for the terpolymerization of CO_2, CHO and maleic anhydride using double metal cyanide complex catalyst. They proposed that some diacid impurities in anhydride act as chain transfer agent and thus obviously decreases Mn.[26] Similarly, this might be another reason for the significant decrease in Mn when PA/PO molar ratio in the feed increases up to 1/3.

The influence of reaction time on the terpolymerization was further investigated at a fixing PA/PO feed ratio of 1/8. As shown in Table **3**, the PE contents of the terpolymer decrease slightly with increasing reaction time. It is owing to that the anhydride concentration continuously decreases during the polymerization process while the concentration of CO_2 is relatively stable due to its constant pressure. We can also see from Table **3** that the PO conversions and molecular weights of resulting terpolymers increase significantly with increasing reaction time. The highest PO conversion of 72.5% PO to poly(ester-co-carbonate) was achieved together with very high molecular weight of 221kg/mol. This is the highest molecular weight reported for the terpolymerization of CO_2, epoxides and cyclic anhydrides to date. Compared to the copolymerization of CO_2 and PO under same conditions, only 55.3% PO conversion and a poly(propylene carbonate) (PPC) with Mn of 68kg/mol can be obtained.

Table 3 Effect of reaction time on terpolymerization of PA/PO/CO_2.[a]

Entry	PA/ PO (mol ratio)	Time (h)	Mn[b] (kg/ mol)	MWD[b] (Mw/ Mn)	Composition[c] (%) PE	PC	PPO	Yield[d] (g)	ηPO[e] (%)	ηPA[f] (%)
1	1:8	5	72.1	3.7	8.2	87.6	4.2	7.9	10.5	6.9
2	1:8	10	74.8	2.8	6.6	89.2	4.2	18.0	24.4	12.9
3	1:8	15	110.0	3.1	6.4	89.3	4.3	24.1	32.7	16.8
4	1:8	25	172.5	3.9	5.8	90.9	3.3	32.2	43.8	20.4
5	1:8	40	221.0	2.8	5.6	89.3	5.1	52.8	72.5	32.6
6	0:1	40	68.0	2.0	0	95.2	4.8	38.1	55.3	/
7[g]	1:8	40	220.0	2.8	6.7	88.0	5.3	52.0	70.7	38.1

[a] Conditions: 1g ZnGA, 40g PO, 40 g toluene, 75℃, 5MPa CO_2.

[b] Determined by gel permeation chromatography (GPC), calibrated by polystyrene standards.

[c] PE=polyester, PC= polycarbonate. PPO=polyester. The compositions were estimated according to the ^{1}H NMR spectra by Eq.S1-S3(see ESI).

[d] Weight of the polymer obtained.

[e] Total PO conversion calculated from the weight of the polymer obtained and the composition of the polymer.

[f] Conversion of PA, calculated from the weight of the polymer obtained and the composition of the polymer.

[g] Polymerization was conducted under 2.5MPa CO_2 pressure

Due to the incorporation of aromatic phthalic groups, the synthesized terpolymers exhibit better thermal properties compared with the copolymer of CO_2 and PO (PPC). The glass transition temperature (Tg) of the terpolymer (Table **3** entery 5) is higher than 40℃, which is 6℃ higher than that of PPC (Table **3** entery6) (Fig2). The 5% weight loss temperature ($T_{5\%}$) and the temperature of maximum decomposition temperature (T_{max}) are 258℃ and 300℃ (Fig. **3**) respectively, which is 14℃ and 33℃ higher than that of PPC.

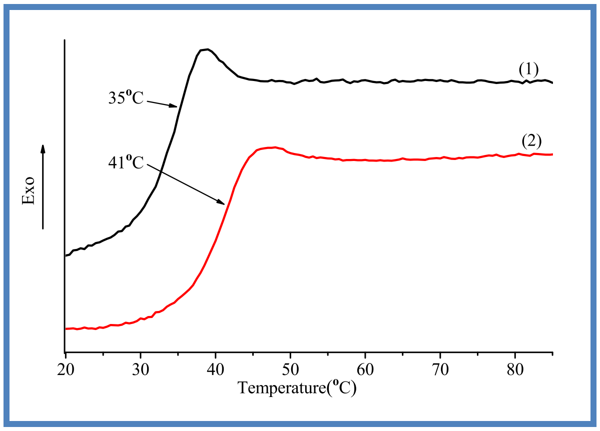


Fig. 2. DSC curves of (1) PPC (entry 6, Table **3**), (2) terpolymer (entry 5, Table **3**).

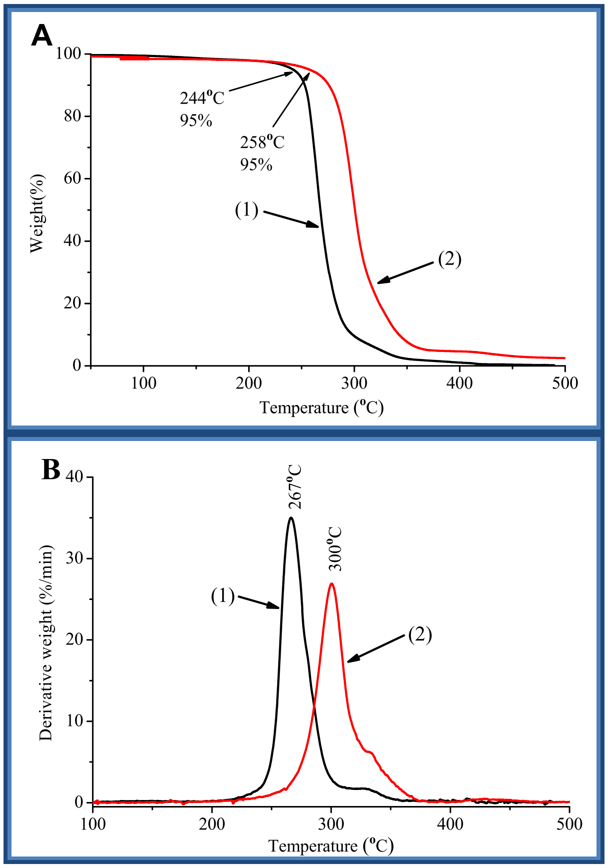


Fig. 3. TG (A) and DTG (B) curves of (1)PPC (entry 6, Table **3**) (2) terpolymer (entry 5, Table **3**).

It is well known that the homopolymerization of PO generally takes place during the copolymerization of PO and CO_2 at relatively higher temperature and lower CO_2 pressure, thus resulting in higher polyether (PE) content. We have carried out the copolymerization of PO and CO_2 in toluene at 75℃ and 2.5MPa CO_2 pressure for 40h, leading to a polycarbonate with Mn of 61.9 kg/mol and 16% PE moieties. However, it is very interesting that the terpolymerization at 2.5MPa CO_2 pressure (Table **3** entry 7) gave a terpolymer with relatively lower polyether content. Presumably, the competitive coordination of PA and PO with Zn^{2+} center inhibits the consecutive insertion of PO.

Conclusions

For the terpolymerizations of carbon dioxide (CO_2), propylene oxide (PO) and phthalic anhydride (PA) using Zinc Glutarate (ZnGA) as catalyst, the monomer reactivity ratios of CO_2 and PA can be evaluated using Fineman–Ross plot method. The results reveal that the reactivity of CO_2 is much higher than that of PA in the terpolymerization of PA/PO/CO_2 catalyzed in toluene at 75℃. The introduction of PA monomer exhibits two opposite effects on the terpolymerization rate. The optimal PA/PO molar ratio of about 1/8 in feed results in the fastest reaction rate and highest molecular weight of resulting polymer. Furthermore, the incorporation of small amount of PA is found to enhance the thermal properties of the polymers and inhibit the formation of polyether under relatively lower CO_2 pressures.

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Notes and references

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