

## Synthesis of poly(propylene-*co*-lactide carbonate) and hydrolysis of the terpolymer

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**Abstract** A new aliphatic polycarbonate, terpolymer of carbon dioxide, propylene oxide, and DL-lactide, was synthesized by using a polymer-supported bimetallic complex as a catalyst. The terpolymer prepared was characterized by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^1\text{H}$ - $^1\text{H}$  COSY, DSC, and WAXD measurements. The influence of molar ratio on the terpolymerization progress was investigated. The results showed that lactide unit was inserted into the backbone of  $\text{CO}_2$ -PO successfully. Because of the existence of the lactide ester unit, the terpolymers had stronger degradability than poly(propylene carbonate).

**Keywords** Carbon dioxide · Propylene oxide · DL-lactide · Aliphatic polycarbonate

### Introduction

Carbon dioxide is considered to be the major greenhouse gas responsible for global warming, which may be contributed to the climate change [1–4]. Hence how to capture and utilize  $\text{CO}_2$  effectively has attracted much attention [5, 6]. One possible utilization approach is to convert the abundant, cheap resources to polymer products [7]. Since the pioneering work of Inoue in 1969 [8], the synthesis of aliphatic polycarbonates from carbon dioxide and epoxides has been a long-standing interest as a potential way to carbon dioxide utilization [9, 10]. In the past decades, most of

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the researches have mainly focused on how to promote the efficiency of polymerization and activity of catalysts [11–17].

Recently, works on modification and application of polycarbonates have been hotspots. Researchers have obtained functional materials by altering or adding the third monomer unit to design new copolymers, which could be applied as electronic conducting polymers [18], biomimetic materials [19], and biomedical materials [20, 21]. As one family of biodegradable materials, polycarbonates have shown excellent biocompatibility, low toxicity, and appropriate biodegradability when used as drug carriers and implant materials [22, 23]. Some functional groups, such as alkyl, OH, NH<sub>2</sub>, COOH, and COOR, are used to regulate the hydrophilicity/hydrophobicity, permeability, and mechanical properties [24, 25]. In our work group, four kinds of terpolymers have been synthesized by terpolymerization, and they showed remarkable degradability than PPC [26–29]. Different from the previous work, to design a new kind of polycarbonate with more practical application, we chose the raw material DL-lactide (DL-LA) as the third monomer. As is known to all, polylactide (PLA), poly(glycolic acid) (PGA) and PLA/PGA copolymers are among the few biodegradable polymers with FDA approval for human clinical use. They have been widely used as drug delivery and tissue engineering scaffold. Though many studies [30, 31] suggest that these polymers are sufficiently biocompatible, yet some works [32, 33] suggest otherwise. And the accumulation of acidic degradation products may cause inflammatory response when the concentration reaches a high level. In this work, a new aliphatic polycarbonate was synthesized to modify the degradability of poly[(propylene oxide)-*co*-(carbon dioxide)] and overcome the disadvantages of PLA/PGA copolymers likewise. Though some work has been done to synthesize such a kind of aliphatic poly(alkylene carbonate–lactide) with good biodegradability [34], yet more details would be given about the structure of the copolymer and degradation process in this paper.

## Experimental

### Materials

DL-LA was purchased from Daigang biological science and technology Ltd. PO (Shanghai Chemical Reagents Co., A.R. grade) and toluene (Hengyang, Organic Chemical Reagents Plant, A.R. grade) was dehydrated by 0.4 nm molecular sieves prior to use. Carbon dioxide (purity more than 99.9%) was used as received. All other reagents and solvents were analytical grade and used without further purification.

### Instruments

FT-IR spectra were recorded on Nicolet AVATA360 FT-IR spectrometer. <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>1</sup>H–<sup>1</sup>H COSY spectra were recorded on a Varian Inova-400 spectrometer with CDCl<sub>3</sub> as solvent, and the molar fractions of CO<sub>2</sub>, PO, and LA

were calculated by integrating areas. The glass transition temperature ( $T_g$ ) of the copolymers was determined by differential scanning calorimetry (DSC) on a TA DSC-Q10 instrument. The temperature range was from  $-30$  °C to  $100$  °C and the heating rate was  $10$  °C/min in nitrogen atmosphere. The surface morphologies of copolymer films were taken by a scanning electron microscope (FEI Quanta-2000, Holand). Intrinsic viscosity  $[\eta]$  measurements were carried out in benzene at  $35 \pm 0.1$  °C using an Ubbelohde suspended level capillary viscometer. The molecular weight was calculated from the equation ( $[\eta] = 1.11 \times 10^{-4} [M_n]^{0.8}$  (dL/g)) [35]. The wide-angle X-ray diffraction (WXAD) measurement was performed at room temperature using a Rigaku D/max 2550 VB<sup>+</sup> 18 kW X-ray diffractometer to analyze the structure. Polydispersity index (PDI) was measured and calculated on a gel permeation chromatograph (Waters 1515, USA) with  $\text{CHCl}_3$  as mobile phase, and the PS with monodispersity was used as the standard sample. Elemental analysis was carried out on an Elementar Vario EL III instrument.

### Preparation of aliphatic polycarbonates

In this study, terpolymerization of  $\text{CO}_2$ , PO, and DL-LA was performed in a 500 mL titanium steel autoclave equipped with a magnetic stirrer using a polymer-supported bimetallic complex (PBM) as a catalyst as described previously [26, 27]. Briefly, required amount of the catalyst, PO, DL-LA were added into the autoclave in the absence of oxygen. According to our earlier work [27, 28], the optimal reaction conditions for polycarbonate synthesis such as reaction time and temperature are 24 h and  $70$  °C, respectively. Thus only the molar ratios of PO to DL-LA were investigated, which were 10:0, 10:1, 10:2, and 10:4 separately in this work. And the autoclave was then pressurized to 3.5 MPa by a  $\text{CO}_2$  cylinder at room temperature. The reaction mixture was stirred magnetically at  $70$  °C for 24 h. When the reaction was finished, the resulting viscous mixture was washed with  $\text{C}_2\text{H}_5\text{OH}$  containing 5% HCl at heating condition to dissolve residual DL-LA and terminate reaction. And the raw product was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered to remove catalyst. Finally, it was precipitated by being poured into vigorously stirred methanol. The methanol insoluble product was centrifuged, collected, and dried till a constant weight.

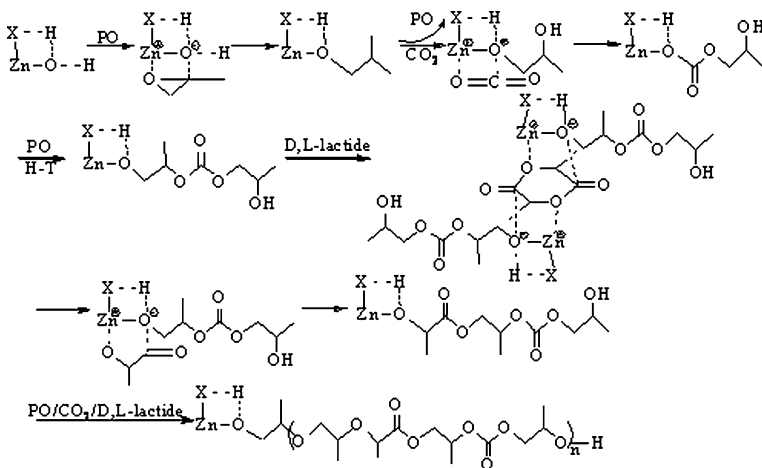
### Hydrolytic degradation of copolymers

The hydrolysis tests were performed to appraise the copolymers' degradability. The copolymers were dissolved in  $\text{CH}_2\text{Cl}_2$  to obtain 3 wt% solutions and formed thin films on polytetrafluoroethylene templates after the volatilization of the solvent. The thin films were dried under vacuum at  $35$  °C till constant weight. Then they were put in vials filled with pH 7.4 0.05 M Tris buffer and placed in a thermostat for various periods at  $37$  °C. The degradability of the copolymers was determined through total weight loss of the films over a certain time. The type of erosion was evaluated by changes in molecular weight.

## Results and discussion

### Expected mechanism of terpolymerization

PBM, in the form of  $P\text{-Zn}[\text{Fe}(\text{CN})_6]_a\text{Cl}_{2-3a}(\text{H}_2\text{O})_b$ , as a type of anionic coordination catalyst, has been known to be effective to produce aliphatic polycarbonates with nearly alternating structure [36]. The accepted mechanism of this reaction is anionic coordination–insertion mechanism, similar to the previously reported literature [37]. And the mechanism for the terpolymerization of  $\text{CO}_2$ , PO, and DL-LA is proposed as follows. As a type of double metal cyanide complex (DMC), zinc is the active metal center. Firstly, PO is activated by the coordination to the active sites of Zn(II) centers, and then is inserted into the Zn–O bond of catalyst, activating the zinc metal center. In the next step, PO,  $\text{CO}_2$ , and DL-LA will be the candidates to interact with the activated zinc metal center and are inserted into the growing chain. Ring-opened DL-LA could be equivalent to two units of lactic acid during the polymerization. Hence the copolymerization is considered to mainly proceed via the alternating repetition of additions of PO,  $\text{CO}_2$ , and DL-LA to the active terminal of the growing chain. On the other hand, reactions between epoxide could take place to form ether linkages, in addition to carbonate linkages in the block copolymer chain. However, neither homopolymerization nor copolymerization could take place for  $\text{CO}_2$  or DL-LA used PBM as the catalyst under the aforementioned reaction conditions. Thus only the competitive alternating copolymerization of PO with DL-LA, PO with  $\text{CO}_2$  and homopolymerization of PO need to be considered in the terpolymerization. As is known to all, there usually exist tail-to-tail (T–T), head-to-head (H–H) and head-to-tail (H–T) carbonate groups in the polycarbonates, and H–T unit is predominant [38]. To simplify the illustration, only the expected mechanism involved dominant insertion is illustrated in Scheme 1.



**Scheme 1** The expected mechanism of  $\text{CO}_2\text{-PO-(DL-LA)}$  copolymerization. X = Cl

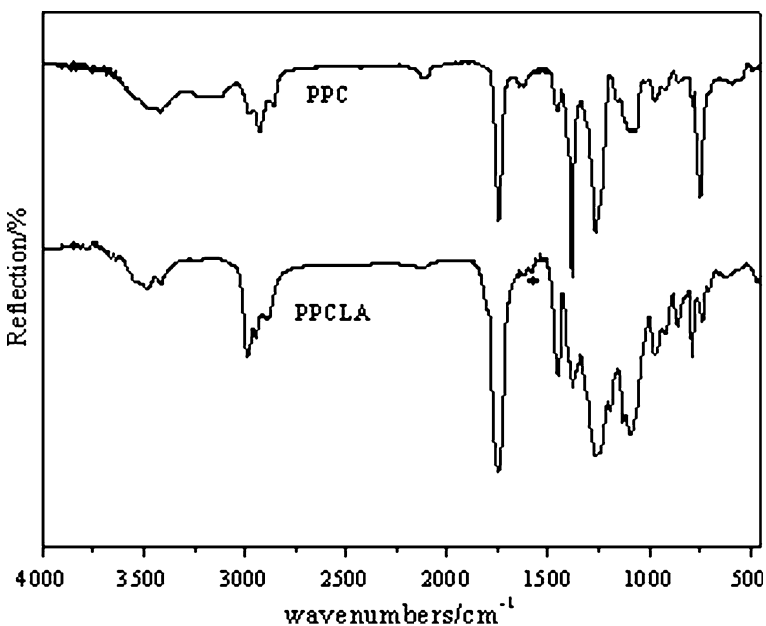
## Structural characterization of polymers

Poly[(propylene oxide)-*co*-(carbon dioxide)] (PPC) and poly[(propylene oxide)-*co*-(carbon dioxide)-*co*-(lactic acid)] (PPCLA2) ( $n_{\text{PO}}:n_{\text{DL-LA}} = 5:1$ ) were used as samples for the FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and  $^1\text{H}$ - $^1\text{H}$  COSY characterization.

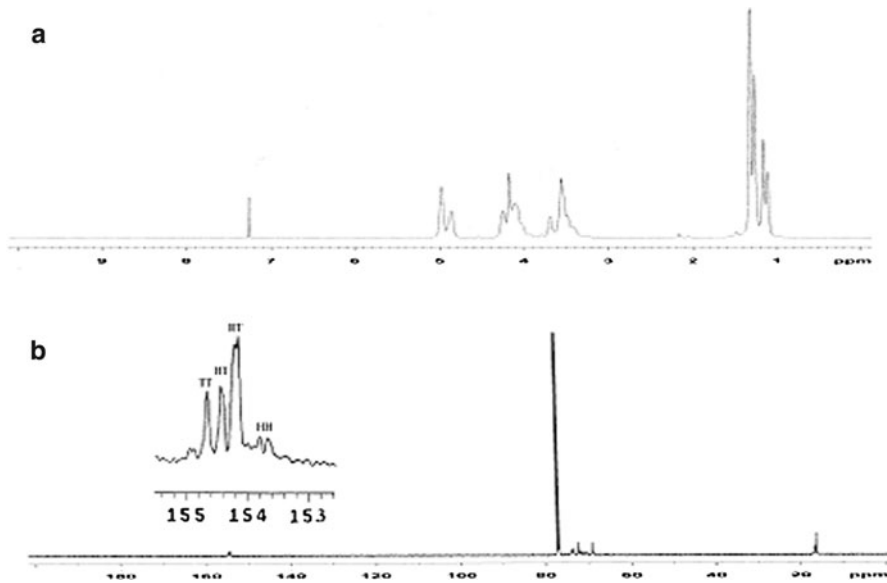
The FT-IR spectra of PPC and PPCLA2 are shown in Fig. 1. PPC and PPCLA2 had similar strong absorptions at  $1745\text{ cm}^{-1}$  (s, C=O),  $1263\text{ cm}^{-1}$  (s, C-O),  $789\text{ cm}^{-1}$ , and  $1074\text{ cm}^{-1}$  (s, C-O-C). Additionally, the asterisk-marked peak at  $1575\text{ cm}^{-1}$  was attributed to the asymmetric and symmetric stretching vibrations of  $-\text{CO}_2^{-1}$ , indicating the presence of carboxylate ions [39] in PPCLA.

At around  $1800$  and  $1180\text{ cm}^{-1}$ , no peaks were found in the FT-IR spectra, suggesting that no cyclic carbonate was formed in the product [40].

The  $^1\text{H}$  NMR spectra of PPC are shown in Fig. 2a. The  $^1\text{H}$  NMR spectra confirmed the existence of carbonate link:  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ), 1.3 [d,  $\text{CH}_3(\text{a})$ ], 5.0 [m,  $\text{CH}(\text{CO}_3)(\text{c})$ ], 4.2 [m,  $\text{CH}_2(\text{CO}_3)(\text{b})$ ]. And the peaks located at 4.2 ppm also included the protons between both ether and carbonate linkages [41]. The signals at 3.5 ppm [3H,  $\text{CH}-\text{CH}_2(\text{b}', \text{c}'')$ ] and 1.2 ppm [3H,  $\text{CH}_3(\text{a}'')$ ] were assigned to the hydrogens in the ether linkage of propylene oxide. Further, no signals at 4.77–4.88, 4.55–4.49, and 4.01–3.96 ppm were observed, confirming the absence of cyclic product in copolymerization [42, 43]. The characteristic proton chemical shifts of carbonate link and ether link of propylene oxide were also observed in the  $^1\text{H}$  NMR spectra of PPCLA in Fig. 3. Additionally, in Fig. 3a, proton chemical shifts at around 5.15 ppm [ $\text{CH}(\text{CO}_2)(\text{c}')$ ] and 1.46–1.48 ppm [3H,  $\text{CH}_3(\text{CH})(\text{a}')$ ] indicated



**Fig. 1** FT-IR spectra of PPC and PPCLA2



**Fig. 2**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of PPC

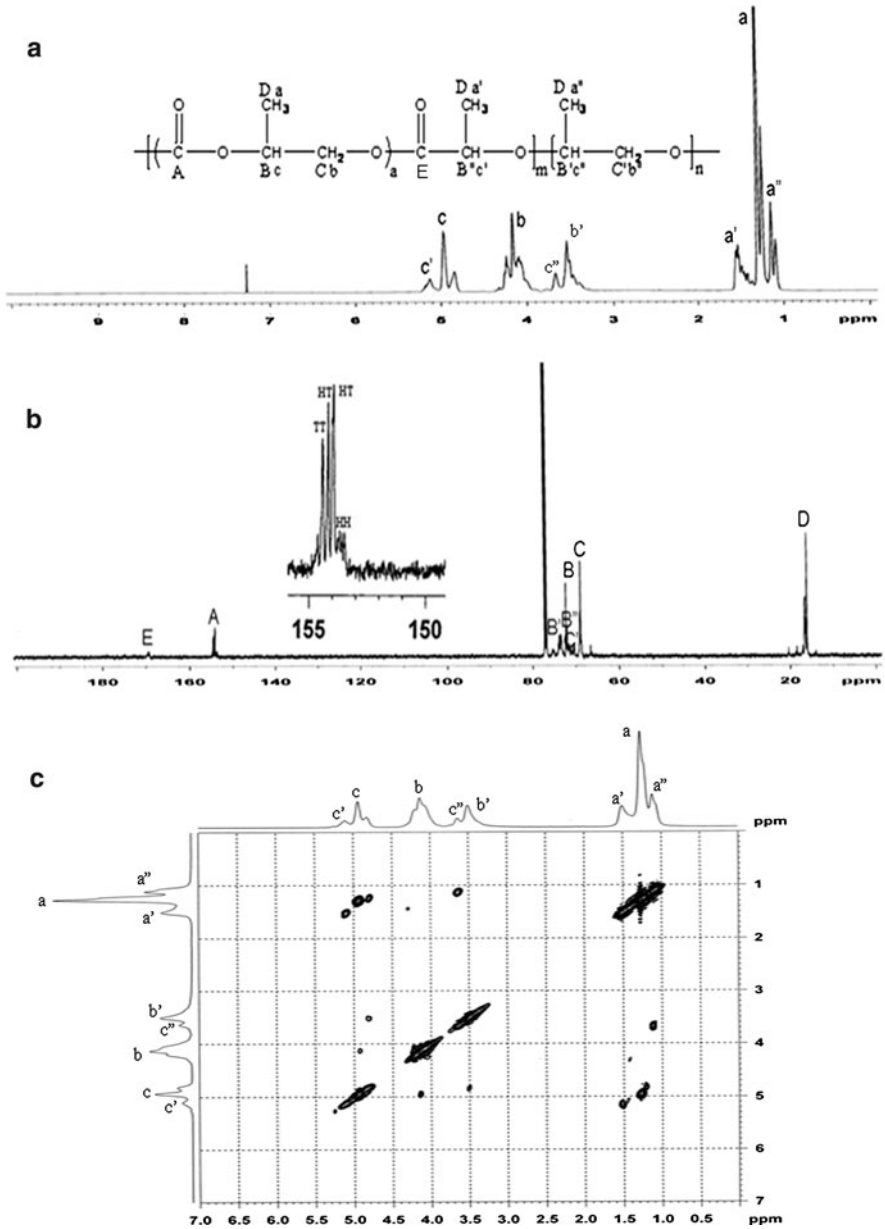
the content of the LA unit was inserted into the backbone of  $\text{CO}_2\text{-PO}$  [44]. And no peaks shown at around 5.2 ppm also confirmed no homopolymerization of lactide took place in the copolymerization [44]. Furthermore, as shown in  $^1\text{H}\text{-}^1\text{H}$  COSY spectrum in Fig. 3c, the coupling between protons  $\text{H}_a$  and  $\text{H}_c$  can be seen as a cross peak at  $\delta$  1.3 ppm/5.0 ppm whilst the coupling between protons  $\text{H}_{a'}$  and  $\text{H}_{c'}$  appear at  $\delta$  1.2 ppm/5.15 ppm. Additionally, the cross-correlation peak centered at 1.2 ppm/3.5 ppm corresponds to the coupling between the protons  $\text{H}_{a''}$  and  $\text{H}_{c''}$ . Thus, the COSY spectrum, which highlights the three bond coupling of  $^1\text{H}$  protons, confirmed the suggested structure of PPCLA shown in Fig. 3.

The  $^{13}\text{C}$  NMR spectra of PPC and PPCLA are shown in Figs. 2b and 3b, respectively. The main signals for PPC were as follows ( $\delta$ ,  $\text{CDCl}_3$ ): 154–155 ( $\text{CO}_3$ ), 72.4 ( $\text{CH-O}$ ), 70.4 ( $\text{CH}_2$ ), 16.2–16.8 ( $\text{CH}_3$ ), and 77.3 ( $\text{CDCl}_3$ ). The signals for PPCLA were assigned as follows ( $\delta$ ,  $\text{CDCl}_3$ ): 153.5–155 [ $\text{CO}_3(\text{A})$ ], 72.3 [ $\text{CH-O}(\text{B})$ ], 68.9 [ $\text{CH}_2(\text{C})$ ], 16.0–16.6 [ $\text{CH}_3(\text{D})$ ], 169.2 [ $\text{CO}_2(\text{E})$ ], 73.4 [ $\text{CH-O}(\text{B}')$ ], 70.3 [ $\text{CH}_2(\text{C}')$ ], and 71.1 [ $\text{CH}(\text{CO}_2)(\text{B}'')$ ].

The signals located at 154.7, 154.2, 154.4, and 153.6–153.9 ppm were found in  $^{13}\text{C}$  NMR spectra. According to the literatures reported previously [45–47], the corresponding carbonate groups were T–T (154.7), H–T (154.2 and 154.4), and H–H (153.6–153.9), respectively. Thus the carbonate carbon signals of PPC and PPCLA reveal that H–T junctions are predominant in both carbonate linkages.

The FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra, and  $^1\text{H}\text{-}^1\text{H}$  COSY spectrum confirmed that DL-LA was ring-opened and inserted into the backbone of  $\text{CO}_2\text{-PO}$  as LA units successfully.

According to the integration of the  $^1\text{H}$  NMR spectra of the copolymers, the calculation results of composition of copolymer were present in Table 1.



**Fig. 3** <sup>1</sup>H NMR (a), <sup>13</sup>C NMR (b), and <sup>1</sup>H-<sup>1</sup>H COSY (c) spectra of PPCLA

As shown in Table 1, the molar fractions of LA units increased as the DL-LA amount in feed went on increasing. However, when the amount of DL-LA fed was low, the transformation efficiency was not high. As the PO:DL-LA ratio reached 10:4,  $f_{LA}$  had a maximum value of 9.35%. On the other hand, the  $f_{CO_2}$  went a sharp

**Table 1** Influence of PO:DL-LA molar ratio on composition of the copolymers

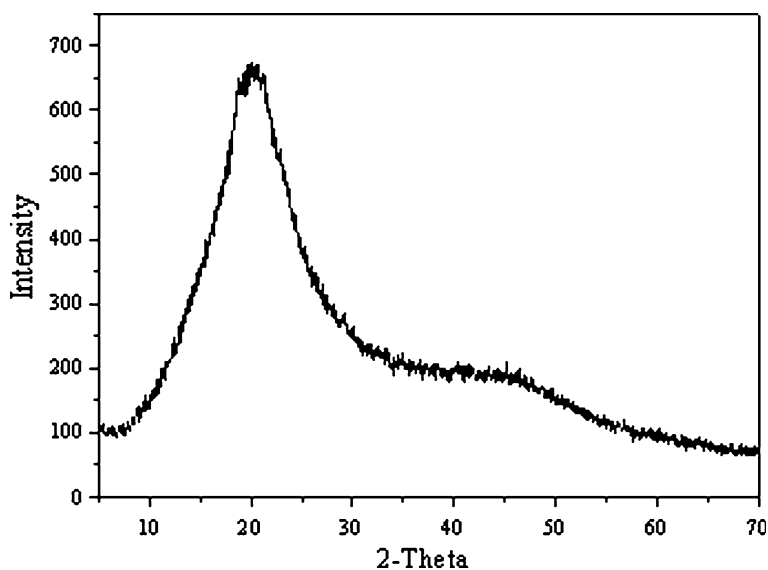
Copolymer	PO:DL-LA (molar ratio)	Composition <sup>a</sup> (molar fraction in %)			Elemental analysis (%)			
		$f_{\text{CO}_2}$	$f_{\text{PO}}$	$f_{\text{LA}}$	C	H	O	
PPC	10:0	39.2	60.8	0	Calcd	50.64	6.95	42.41
					Found	49.94	6.98	43.08
PPCLA1	10:1	42.73	56.25	1.02	Calcd	48.25	6.44	45.31
					Found	47.74	6.23	46.03
PPCLA2	10:2	42.10	54.26	3.64	Calcd	49.77	6.54	43.79
					Found	49.15	6.42	44.43
PPCLA3	10:4	33.93	57.72	9.35	Calcd	50.15	6.96	42.89
					Found	49.95	6.54	43.51

Reaction conditions:  $T = 70\text{ }^\circ\text{C}$ ;  $t = 24\text{ h}$

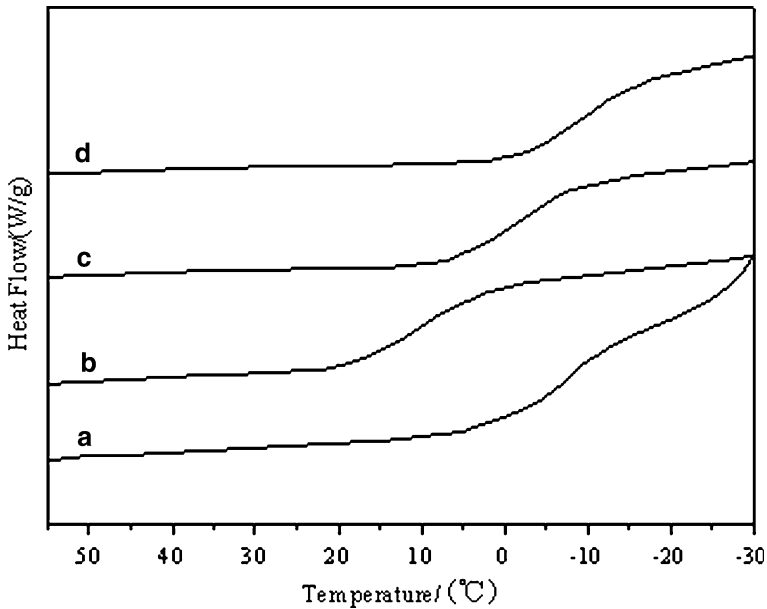
<sup>a</sup> The molar fractions of  $\text{CO}_2$ , PO, and DL-LA calculated by integrating areas of  $^1\text{H}$  NMR spectra of PPC and PPCLA

decrease to 33.93% in PPCLA3, while the molar fractions of  $\text{CO}_2$  in PPC was up to 39.2%. Additionally, LA and  $\text{CO}_2$  could not copolymerize under the reaction conditions. Thus, when more LA units were inserted into the backbone,  $\text{CO}_2$  would be hampered, which resulted in the decrease of  $f_{\text{CO}_2}$ . And the results in Table 1 showed that the calculated data of elemental contents were close to the found data.

The WXAD spectra in Fig. 4 suggested the terpolymer was amorphous. And the DSC curves in Fig. 5 revealed only a  $T_g$  and no crystalline melting point, indicating that no PLA or crystalline blocked LA in the products.

**Fig. 4** The wide-angle X-ray diffraction spectra





**Fig. 5** DSC curves of polymers prepared from different PO:DL-LA molar ratio (*a* PPC; *b* PPCLA1; *c* PPCLA2; *d* PPCLA3)

#### Influence of PO:DL-LA molar ratio

Table 2 shows the influence of PO:DL-LA molar ratio on the properties of the terpolymers. The  $M_v$  and  $T_g$  are all related to the structure and components of the copolymers. As the amount of DL-LA increased, the  $M_v$  decreased and PDI got higher. It was considered that at the beginning excess third monomers produced by DL-LA would surround the active center, which may hinder the chain propagation reaction. Thus some molecules with relatively low polymerization degree (DP) would be produced at the early reaction stage, which resulted in the increase of PDI with more contents of DL-LA fed. And the  $T_g$  of copolymer would get higher with

**Table 2** Influence of PO:DL-LA molar ratio on terpolymerization

Copolymer	PO:DL-LA (molar ratio)	Yield <sup>a</sup> (g/g of cata.)	TOF <sup>b</sup> (h <sup>-1</sup> )	$M_v$ ( $\times 10^4$ )	$T_g^c$ (°C)	$M_w/M_n$ ( $\times 10^4$ )	PDI
PPC	10:0	16.3	18.0	2.65	-4.3	3.95/1.66	2.38
PPCLA1	10:1	22.2	23.2	2.45	8.4	3.90/1.43	2.72
PPCLA2	10:2	25.2	26.1	2.40	-3.0	2.80/0.90	3.12
PPCLA3c	10:4	16.5	18.8	0.95	-3.08.4	1.40/0.31	4.59

Reaction conditions:  $T = 70$  °C;  $t = 24$  h; 0.3 mol PO; 1 g catalyst

<sup>a</sup> Yield defined as the mass of copolymer produced per gram PBM in 24 h

<sup>b</sup> TOF: Mole of PO converted to polymer per mole Zn per hour

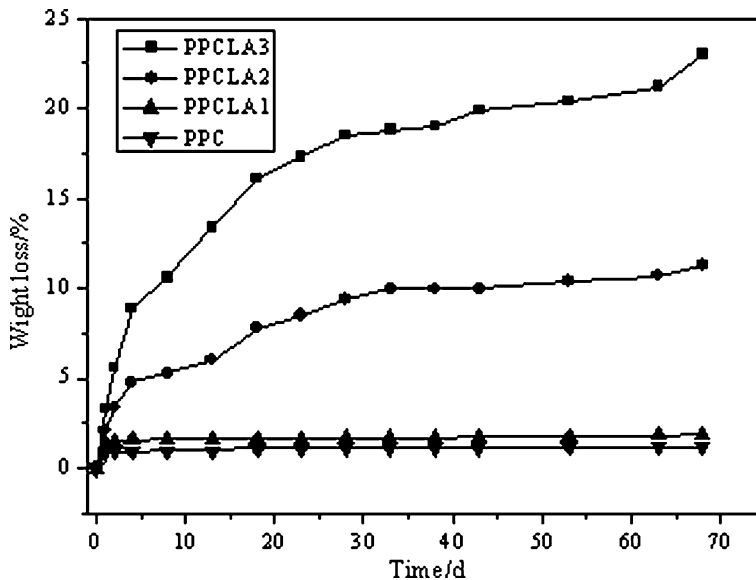
<sup>c</sup> Insoluble copolymer in methanol for DSC tests

low molar ratio of LA units inserted into the backbone of PPC. However, as DL-LA molar ratio got higher, the  $T_g$  of the terpolymers decreased. It may ascribe to more free chain terminals as a result of some molecules with low DP. In addition, the yield and TOF reached highest when the molar ratio of PO:DL-LA was 10:2.

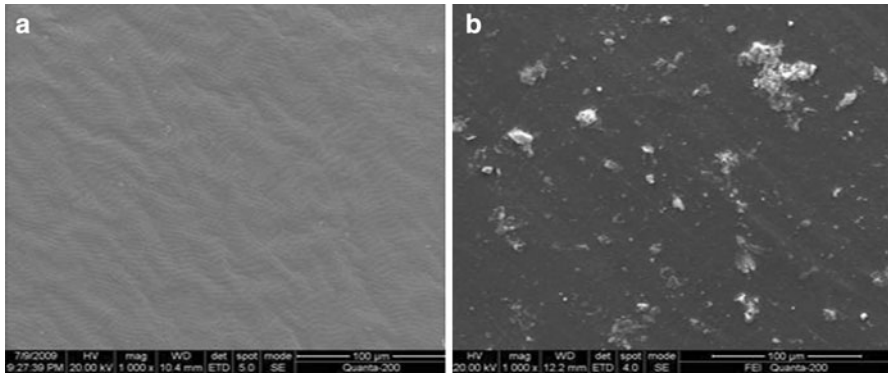
### Hydrolytic degradation

The degradability of the terpolymers was determined in order to evaluate the influence of LA units inserted into the backbone. Physical erosion was ignored to simplify the analysis during the degradation of copolymers. In this work, hydrolytic degradation was caused by the reaction of water with ester bonds [48]. Figure 6 revealed that when the LA units in the backbone of PPC was low (1.02%), the degradability of the terpolymer showed little change and only 2% mass was lost after nearly 10 weeks. However, the degradability was modified a lot as LA units inserted increased. The PPCLA3 had the best degradability, and as high as 23% mass loss was reached during the early 10 weeks. The mechanism of the hydrolytic degradation may be proposed undergoing three stages. Firstly, water diffused and penetrated into the matrix of polymer, which resulted in the copolymer swelling. Then, the ester bond cleavage was caused by the reaction with water. Finally, oligomers and monomers were released from the matrix, which was shown as the form of mass loss.

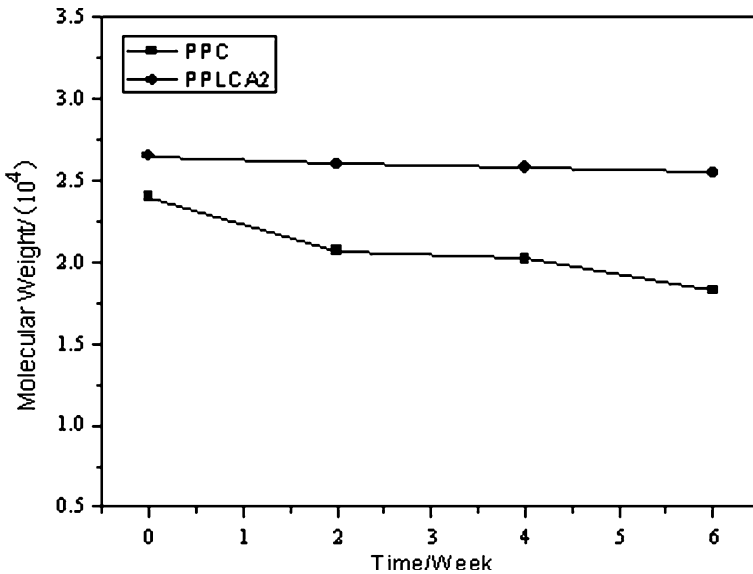
As shown in Fig. 7, the surface of PPCLA was smooth before degradation, and after degradation for 10 weeks, the surface got roughed and some micron-sized erosion spots appeared. Meanwhile, Fig. 8 revealed that no apparent molecular weight decreased during degradation, indicating that the erosion mainly occurred on the surface of PPCLA.



**Fig. 6** Influence of PO:DL-LA ratio on the degradability of PPCLA



**Fig. 7** SEM micrographs of PPCLA films: **a** before degradation; **b** after degradation in Tris buffer for 10 weeks (pH = 7.4)



**Fig. 8** Molecular weight variation of PPC and PPCLA2 during the degradation

**Conclusion**

PPCLA was synthesized from CO<sub>2</sub>, PO, and DL-LA successfully using a polymer supported bimetallic complex as a catalyst. As an amorphous terpolymer, the *M<sub>v</sub>* decreased with LA units inserted into the backbone of PPC. The *T<sub>g</sub>* of the terpolymer was 8.4 °C with low LA contents introduced, which showed 12.7 °C higher than that of PPC. However, as more DL-LA monomers were added, the *T<sub>g</sub>* got a decrease, and only −8.4 °C was observed when molar ratio of PO and DL-LA was 10:4. The PPCLA showed better degradability. The weight loss of PPCLA3 was

nearly 23% after degradation in Tris buffer (pH = 7.4) for 10 weeks. On the other hand, PPC revealed only a tiny weight loss. These results indicate that the new terpolymer PPCLA could be considered to be a promising controlled drug delivery. The copolymer with DL-LA as the third monomer would not only help to eliminate the disadvantages of PLA/PGA, also greatly modify the degradability of PPC.

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