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ORIGINAL CONTRIBUTION

Controlled ring-opening polymerization of cyclic esters with phosphoric acid as catalysts

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Abstract (*R*)-(−)-1,1′-Binaphthyl-2,2′-diyl hydrogen phosphate (BPA) has been demonstrated as an efficient organocatalyst for controlled ring-opening homopolymerization of ε-caprolactone (ε-CL) and copolymerization of ε-CL with glycolide and lactide. High molar mass PCL with narrow molar mass distribution has also been synthesized from the bulk ring-opening polymerization (ROP) of ε-CL with BPA as catalysts; the highest molar mass of PCL is 4.35×10^4 g/mol with polydispersity index of 1.20. The successful synthesis of high molar mass PCL is attributed to the bifunctional activation mechanism for the ROP of ε-CL catalyzed by BPA. More interestingly, ppm level of BPA is sufficient to catalyze controlled ROP of ε-CL.

Keywords Acid-catalyzed ring-opening polymerization · Polycaprolactone · Copolymerization · Copolyesters

Introduction

Polyesters are widely applied in drug delivery, tissue engineering, and medical devices and eco-friendly materials due to their biocompatibility and biodegradable property as well as good miscibility with other polymers [1–3]. Polyesters are often synthesized by ring-opening polymerization (ROP) of cyclic esters using a variety of catalysts including aluminum-based, tin-based, and rare earth metal-based catalysts [4–11]. The main drawback of conventional metal-based catalysts is the metal residue in resulting polymers, especially when the final polymers are to be used within medicinal or microelectronic devices. Pioneered by Hedrick and Waymouth, metal-free catalysts, so-called organocatalysts such as dialkylaminopyridine, phosphine, *N*-heterocyclic carbenes and thiourea/amine, have been reported as efficient catalysts for ROP of cyclic esters [12–17].

In another approach, various types of acids have been investigated for ROP of cyclic esters through activated monomer cationic polymerization [18–27]. Bourissou et al. have demonstrated that the activity of these acid catalysts does not simply correlate with their acidity and the strong Brønsted acid could deactivate the initiating/propagating alcohol [18]. Since the strong Brønsted acid may cause undesirable side reactions, it is of great interest to study the catalytic activity of weak acids for ROP of cyclic monomers.

ε-Caprolactone (ε-CL) is the mostly investigated cyclic monomer in the acid-catalyzed ROP. ROP of glycolide (GA) and lactide (LA) with acid catalyst receive little attention, despite their polymers; polyglycolic acid (PGA) and polylactic acid (PLA) have been widely used for biomedical applications such as sutures, tissue engineering, and orthopedic applications [28–32]. Among the numerous acidic compounds investigated, only trifluoromethanesulfonic acid and methyl trifluoromethanesulfonate have been proven to be efficient catalysts for ROP of lactide [27, 33–36].

Recently, phosphoric acids including diphenyl phosphate and BINOL phosphoric acid have been reported as organocatalysts for the ROP of ε-CL and δ-valerolactone via bifunctional mechanism [37–39]. We report herein, (*R*)-(−)-1,1′-Binaphthyl-2,2′-diyl hydrogenphosphate (BPA) can not only induce living ROP of ε-CL, but can also be used to prepare high molar mass poly(ε-caprolactone) (PCL) in bulk. We also find that parts per million (ppm) level of BPA is sufficient to catalyze controlled ROP of ε-CL. Successful copolymerization of glycolide with ε-CL has been proven in the presence of BPA. For the copolymerization of lactide with ε-CL, it shows faster incorporation of ε-CL into copolymer chains in contrast with lactide.

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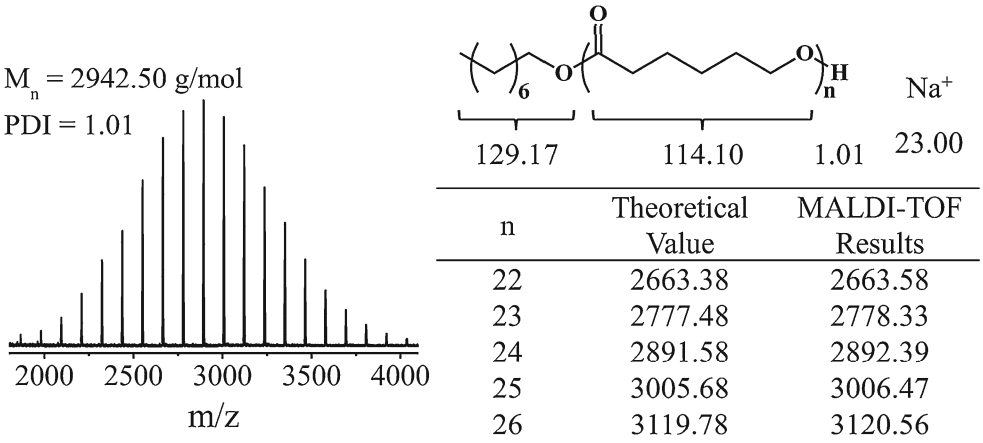


n	Theoretical Value	MALDI-TOF Results
22	2663.38	2663.58
23	2777.48	2778.33
24	2891.58	2892.39
25	3005.68	3006.47
26	3119.78	3120.56

Fig. 1 MALDI-TOF spectra of obtained PCL (Table 1, run 2). The theoretical value was calculated by the following equation: n×114.10+129.17+1.01+23.00

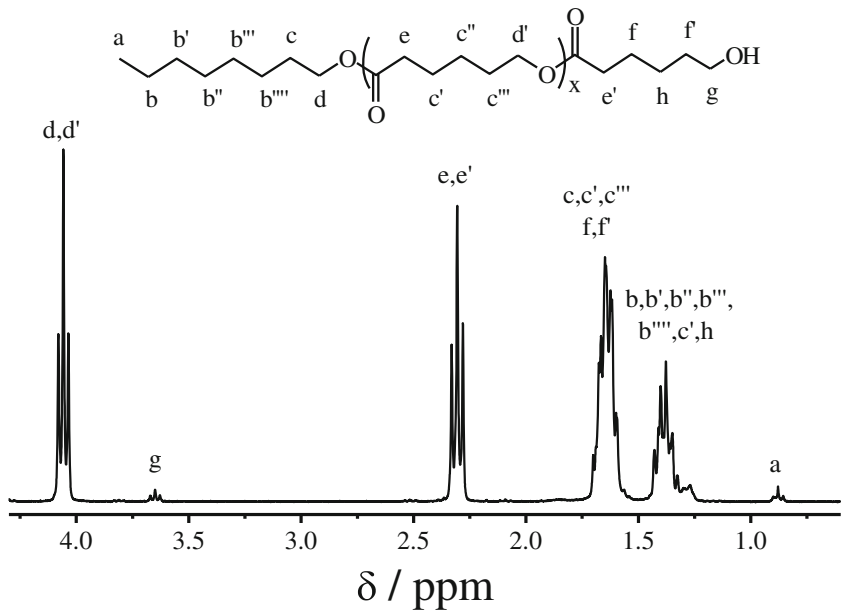


Fig. 2 ^{1}H NMR spectra of the obtained PCL (Table 1, run 2)

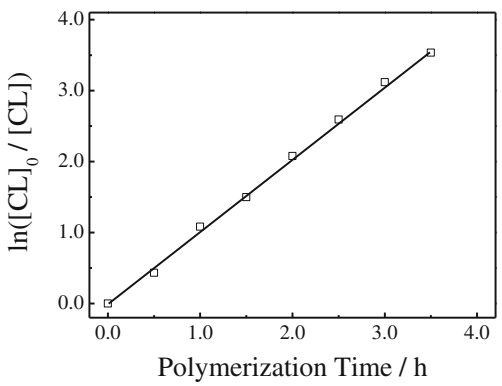


Fig. 3 Kinetic plots for the ROP of ε-CL (at 85 °C in toluene, $[CL]_0$= 0.9 M, $[CL]_0$/[Octanol]/[BPA]=40:1:0.5)

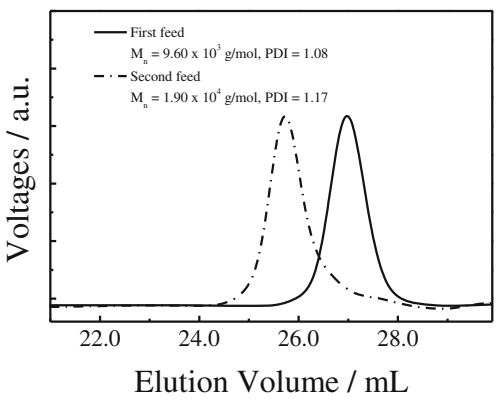


Fig. 4 SEC graphs of PCLs synthesized by sequential monomer addition at 85 °C in toluene (first feed:$[CL]_0$/[Octanol]/[BPA]= 60:1:0.5; second feed: 60 equiv. CL)

Table 1 Ring-opening polymerization of ε-CL catalyzed by BPA

Run	Initiator	$[CL]_0$/[Initiator]	Time/h	Conv (%)[b]	$M_{n,theo}\times10^3$ (g/mol) [c]	$M_{n,NMR}\times10^3$ (g/mol)[b]	$M_{n,GPC}\times10^3$ (g/mol)[d]	PDI [d]
1[a]	1-Octanol	10	3	99	1.13	1.13	2.60	1.12
2[a]	1-Octanol	30	3	90	3.07	3.08	4.90	1.10
3[a]	1-Octanol	50	4.5	99	5.60	5.80	6.60	1.20
4[a]	1-Octanol	70	6	98	7.80	8.01	10.1	1.11
5[a]	1-Octanol	80	9	99	9.00	9.60	11.0	1.18
6[a]	2-Propanol	40	12	99	4.51	4.60	5.60	1.14
7[a]	*tert*-Butyl alcohol	40	12	98	4.47	4.58	5.50	1.16
8[e]	1-Octanol	100	6	95	10.8	12.4	13.8	1.17
9[e]	1-Octanol	800	24	52	41.6	–	43.5	1.20

[a] Polymerization was carried out at 85 °C in toluene, [BPA]/[Octanol]=0.5, $[CL]_0$=0.9 M.

[b] Determined by ^{1}H NMR

[c] Calculated by the following equation: ([consumed CL]/[Octanol])×114

[d] Determined by SEC

[e] Polymerization was carried out in bulk at 85 °C, [BPA]/[Octanol]=0.5

Experimental

Materials ε-caprolactone (99 %, aladdin) was purified by distillation over CaH_2. Toluene (AR, aladdin) and 1-octanol (99.5 %, aladdin) were dried over sodium and distilled before use. (*R*)-(−)-1,1′-Binaphthyl-2,2′-diyl hydrogenphosphate (98 %, aladdin), triethylamine (AR, aladdin) and Amberlyst® A21(aladdin) were used as received. Glycolide (99.5 %) and DL-lactide (99.5 %) were purchased from Jinan Daigang Biomaterial Co., Ltd and purified by recrystallization in ethyl acetate.

ROP of ε-caprolactone All reactions were performed under an inert atmosphere of nitrogen, using standard Schlenk techniques. A general procedure for the polymerization is as follows: 0.75 mL ε-CL (6.75 mmol, 30 eq.) was dissolved in 7.5 mL toluene; the initiator, 1-octanol (35 μl, 0.223 mmol, 1 eq.), and the catalyst, (*R*)-(−)-1,1′-Binaphthyl-2,2′-diyl hydrogenphosphate (39.4 mg, 0.113 mmol, 0.5 eq.), were added. The reaction mixture was stirred at 85 °C for 3 h. The mixture was then treated with Amberlyst® A21 in order to eliminate the catalyst. The polymer was precipitated in hexane and dried under vacuum. Copolymerization of ε-CL with glycolide and lactide were carried out using a similar procedure.

Characterization The monomer conversions were determined by ^{1}H NMR measurements. The ^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker Avance 400 MHz spectrometers at 25 °C.

The number-average molar mass and polydispersity indices of the PCL samples were determined by a Waters 1515 size exclusion chromatography (SEC) equipped with a Waters 2414 refractive index detector. The columns used were of Styragel® HR 2, HR 4, and HR 6. Tetrahydrofuran (THF) was used as the eluent and the flow rate was set up at 1.0 mL/min. Calibrations were performed using polystyrene standards (1.30×10^3 g/mol−2.21×10^6 g/mol).

The weight-average molar mass was determined by a commercial LLS spectrometer (ALV/DLS/SLS-5022 F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW He-Ne laser (λ_0=632 nm, Uniphase) as the light source. *dn*/*dC* of PCL in THF is 0.072 mL/g, determined at 25 °C by using the BI DN/DC differential refractometer.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS spectra were recorded on the Bruker-autoflex III smartbeam. 2,5-Dihydroxybenzoic acid was used as the matrix and sodium iodide was used as the cationic agent. [37]

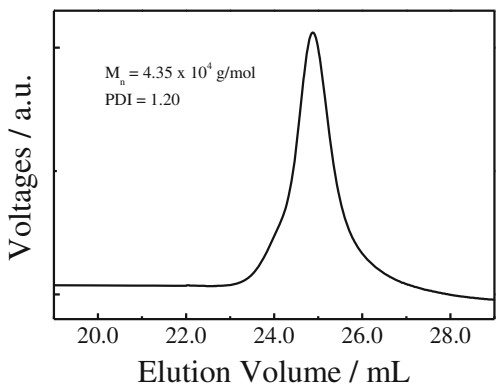


Fig. 5 SEC graph of PCL (Run 9 in Table 1)

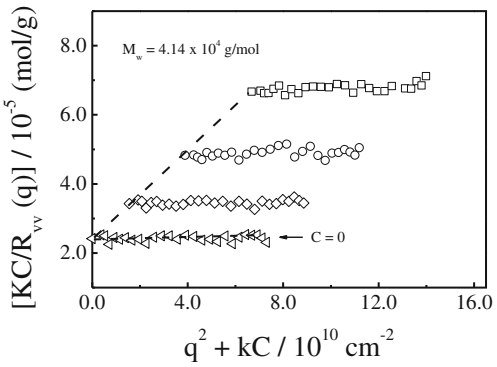


Fig. 6 Zimm plot of PCL (run 9 in Table 1) in THF, where the polymer concentration is in the range $(1.94–8.35)\times10^{-3}$ g/mL

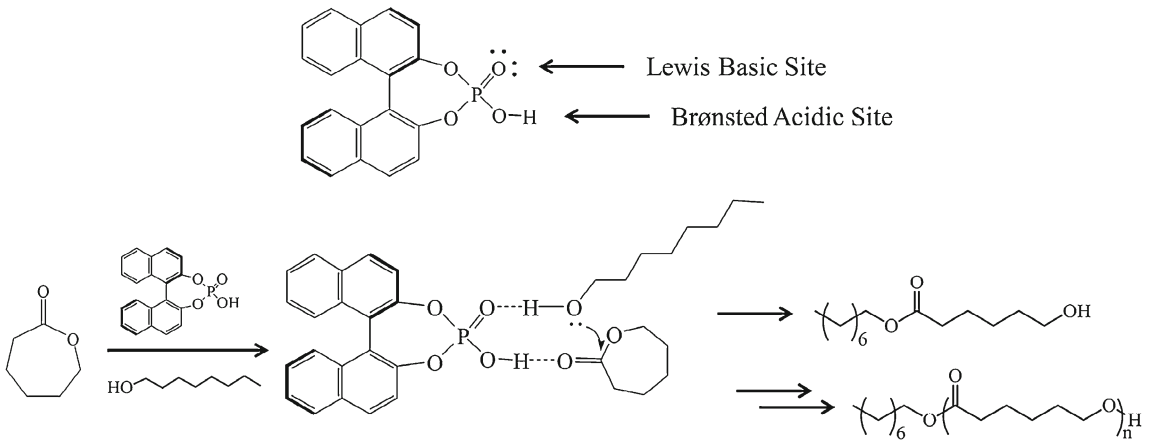
Differential scanning calorimetry (DSC) was conducted on a TA instrument Q2000 under a nitrogen flow of 50 mL/min. Samples were heated to 250 °C and kept for 10 min to remove thermal history and then cooled to −80 °C at a rate of 10 °C/min. Finally, they were reheated to 250 °C at the same rate.

Results and discussion

Figure 1 shows the MALDI-TOF MS spectra of the obtained PCL from ROP of ε-CL using BPA as catalyst and 1-octanol as initiator. The peaks agree well with the molar mass of PCL containing the 1-octanol residue and the hydroxyl chain end. The ^{1}H NMR spectrum of the obtained PCL shown in Fig. 2 also support this conclusion. The characteristic peak due to the methyl protons of 1-octanol is observed at 0.88 ppm. In addition, the peaks for PCL appear at 4.06, 2.31, 1.64, and 1.38 ppm, respectively, which are in agreement with those reported before. The peak due to the methylene protons adjacent to the ω-hydroxyl chain end is clearly observed at 3.65 ppm. All the facts indicate that the polymerization is initiated by 1-octanol and endcapped with hydroxyl group.

The living nature of the ROP of ε-CL catalyzed by BPA has been confirmed by the linearity of kinetic plot and chain extension experiments, as shown in Figs. 3 and 4, respectively. Figure 3 shows the time dependence of $\ln([CL]_0/[CL])$ for ROP of ε-CL, where $[CL]_0$ and [CL] are the initial concentration of ε-CL and the concentration at a certain time, respectively. A distinct first-order relationship between $\ln([CL]_0/[CL])$ and polymerization time is observed, which indicates that the monomer consumption rate is constant during the polymerization. The linearity of the kinetic plot is typically used as a criterion of polymerization livingness. In addition, the obtained polymer is monodispersed, and the polydispersity index is 1.10. The chain extension experiments also support the living nature of the BPA catalyzed ROP of ε-CL. Figure 4 shows the SEC graphs of the PCLs synthesized by sequential monomer addition. After confirming the quantitative monomer conversion of the first feed of ε-CL, the second feed of ε-CL is added into the reaction mixture to restart the polymerization. The SEC curve shifts to a higher molar mass region and remains a monodisperse distribution.

We also carry out the ROP of ε-CL with varying the initial ratio of ε-CL to 1-octanol from 10 to 80 in toluene, as shown in Table 1. The number-average molar mass of PCLs estimated from ^{1}H NMR linearly increase with increasing the initial ratio of ε-CL to 1-octanol, whose values fairly agree with the molar mass calculated from the initial ratios and the monomer



Scheme 1 Ring-opening polymerization of ε-CL using BINOL phosphoric acid as catalysts

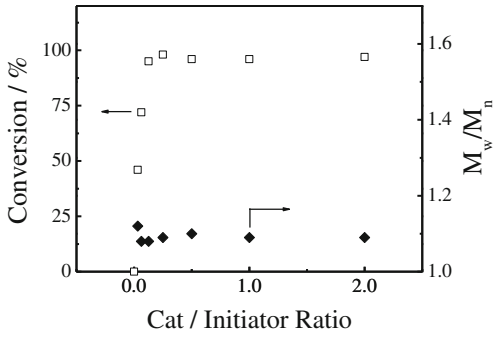


Fig. 7 Influence of catalyst to initiator molar ratios on the monomer conversion □ for the ROP of ε-CL and polydispersity indices △ of the obtained PCLs (at 85 °C in toluene for 3 h, $[CL]_0$/[Octanol]/[BPA]= 40:1:0.5, $[CL]_0$=0.9 M)

conversions. The apparent number-average molar mass of PCLs determined by SEC also show this upward trend. In other words, the molar mass of the designed PCL can be well controlled by varying the initial ratio of the monomer to initiator, while the obtained polymers have narrow molar mass distribution, and their polydispersity indices are 1.09–1.20. In addition, both secondary and tertiary alcohol, such as 2-propanol and *tert*-butyl alcohol, can also initiate controlled ROP of ε-CL catalyzed by BPA.

In bulk, the ROP of ε-CL catalyzed by BPA is also well controlled. For the run 9 in Table 1, where the initial molar ratio of ε-CL to 1-octanol was 800, the polymerization is carried out in bulk with BPA at 85 °C. The polymerization was stopped when the reaction mixtures formed gels at 52 % monomer conversion. The number-average molar mass was 4.35×10^4 g/mol and the polydispersity index was 1.20 characterized by SEC. The SEC graph and zimm plot in static laser light scattering is shown in Figs. 5 and 6, respectively.

Regarding to the slow polymerization rate of ε-CL, high molar mass PCL needs prolonged polymerization time, which in turn induces significantly increasing contribution of side reactions, such as inter- or intramolecular transesterification [24, 25, 40]. It is worth noting that PCL chain ends have high tendency to transesterification reaction [40]. Synthesis of PCL with a molar mass higher than 1.5×10^4 g/mol as well as with narrow molar mass distribution is still a challenge [13, 24]. From the zimm plot, the weight-average molar mass of PCL synthesized in bulk was 4.14×10^4 g/mol. To the best of our knowledge, this is the highest molar mass of PCL synthesized through the ROP of ε-CL catalyzed by organocatalysts.

Bifunctional activation mechanism for the ROP of ε-CL catalyzed by BPA has been confirmed by the Density Functional Theory calculations, as shown in scheme 1 [38]. Double hydrogen bonding interactions occur between BPA, monomer, and hydroxyl chain end. This activation mode significantly depresses inter- or intramolecular transesterification since the steric barrier between polymeric hydroxyl chain ends and ester bond among polymer chains. This is the possible reason for the successful synthesis of high molar mass PCL with BPA.

In addition, we investigate the influence of the amount of catalyst used on the kinetics of the polymerization by varying the ratio of catalyst to initiator, as shown in Fig. 7. The initial molar concentration ratio of ε-CL to 1-octanol is fixed at 40 for all polymerization. Without the addition of catalyst, there is no polymer obtained after heating the solution at 85 °C for 3 h. On the other hand, the monomer conversion increases sharply from 0 to around 100 % in the presence of BPA. Even when the ratio of catalyst to 1-octanol is 6.25/100, the monomer conversion approaches as high as 72 % under the same polymerization condition. Most interestingly, there is only 255 ppm BPA in the polymerization mixtures when the ratio of BPA to 1-octanol is 3.20 %. In bulk polymerization, the catalyst amount can be even lower. As in the run 9 in Table 1, there is only 190 ppm BPA in the polymerization mixtures when the ratio of catalyst to 1-octanol is 50/100. This behavior makes BPA particularly attractive, since the polymerization can be conducted even with ppm levels of catalysts. In addition, the amount of BPA used does not affect the molar mass distribution of PCL, and the polydispersity indices are around 1.10.

Table 2 Ring-opening copolymerization of ε-CL with glycolide (GA) and lactide (LA)[a]

Run	Monomer	$[M]_0/[CL]_0$	$[CL]_0$/[Octanol]	Time/h	[M]/[CL][b]	$M_{n,NMR}\times10^3$ (g/mol)[b]	$M_{n,GPC}\times10^3$ (g/mol)[c]	PDI [c]
1	GA	0.5	56	38	0.42	7.21	5.90	1.22
2	GA	0.2	56	38	0.17	7.38	6.50	1.28
3	LA	0.5	56	39	0.08	3.95	5.70	1.29

[a] Polymerization was carried out at 85 °C, [BPA]/[Octanol]=0.5

[b] Determined by ^{1}H NMR

[c] Determined by SEC

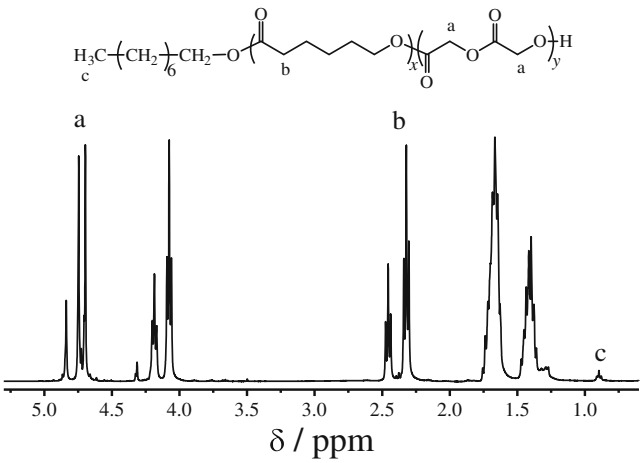


Fig. 8 ^{1}H NMR spectra of PCL-*co*-PGA copolymer (Run 1 in Table 2)

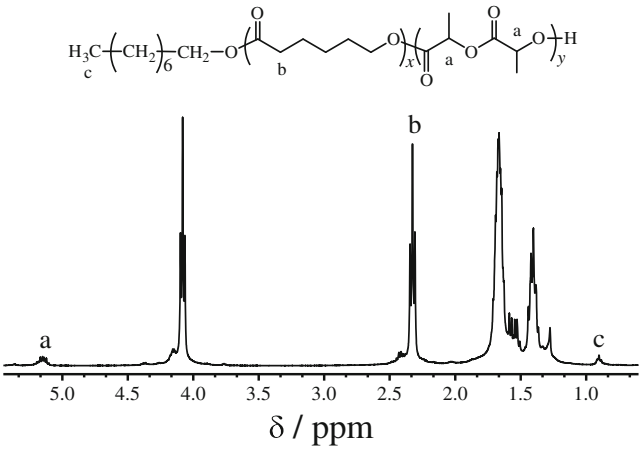


Fig. 10 ^{1}H NMR spectra of PCL-*co*-PLA copolymer (Run 3 in Table 2)

Ring-opening homopolymerization of glycolide catalyzed by BPA resulted with little white polymer due to the poor solubility of polyglycolide in toluene. Copolymerization of glycolide with ε-CL at different molar ratios has been shown in Table 2. Figure 8 shows the ^{1}H NMR spectrum of PCL-*co*-PGA obtained using 1-octanol as initiator and BPA as catalyst. Peaks at (a) 4.6–4.9 ppm and (b) 2.2–2.5 ppm are assigned to methylene groups in PGA and methylene groups adjacent to carbonyl group in PCL, respectively [41]. The molar ratio of glycolide unit to ε-CL in resulting polymer is fairly agree with the feed ratios of glycolide and ε-CL as shown in Table 2. These results clearly demonstrate that BPA is an efficient organocatalyst for the copolymerization of glycolide and ε-CL.

Figure 9 shows the DSC curves for PCL homopolymer and PCL-*co*-PGA copolymers. The melting peak of PCL homopolymer is around 50 °C; with regard to PCL-*co*-PGA copolymers, the melting endotherm-specific peaks of PCL shift to lower temperature. When the GA content increase to around 30 % (Run 1 in Table 2), the melting peak of PCL is no longer observed. These results indicate that CL and GA repeating units are randomly distributed along the polymer chain [42].

In contrast to glycolide, there is no polymer obtained for the ring-opening homopolymerization of lactide catalyzed by BPA. We also run the copolymerization of lactide with ε-CL in toluene with BPA as catalysts. Figure 10 shows ^{1}H NMR spectrum of PCL-*co*-PLA. Characteristic peaks of ε-CL and LA repeating units are shown in 4.1 ppm and 5.1–5.2 ppm [27]. While the molar ratio of LA to ε-CL in resulting copolymer chain 0.08 is much lower than the feeding ratio 0.5. These results show faster incorporation of ε-CL unit into copolymer chains in contrast with LA. The melting peak of PCL in PCL-*co*-PLA copolymer, shown in Fig. 9, also shift to lower temperature with the incorporation of LA unit in polymer chain.

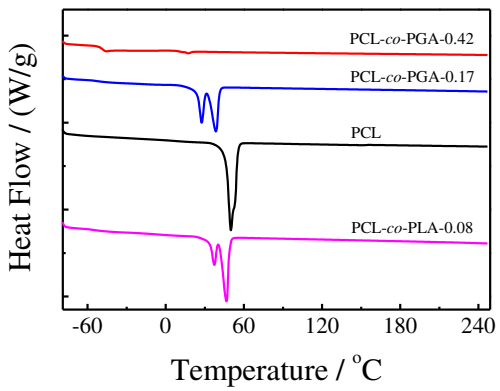


Fig. 9 DSC curves for the PCL homopolymer, PCL-*co*-PGA copolymers, and PCL-*co*-PLA copolymers at a heating rate of 10 °C/min. (The *number* after the copolymers indicate the molar ratio of GA or LA to ε-CL)

Conclusions

(*R*)-(−)-1,1′-Binaphthyl-2,2′-diyl hydrogenphosphate can induce reproducible controlled/living ROP of ε-CL in the presence of alcohol initiator either in solution or in bulk. Besides ε-CL, BPA can catalyze the copolymerization of GA and LA with ε-CL. High molar mass PCLs with narrow molar mass distribution have been successfully synthesized with BPA in bulk. Bifunctional activation mechanism, which excludes the side reactions, is the possible reason for the successful synthesis of the high molar mass PCL with BPA. We also find ppm level of BPA is sufficient to catalyze the ROP of ε-CL. With those properties, BPA is potentially useful for the preparation of polyesters with high

molar mass and narrow molar mass distribution, especially in medicinal and microelectronic fields.

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