Chinese Journal of
POLYMER SCIENCE

RESEARCH ARTICLE

https://doi.org/10.1007/s10118-023-2947-x
Chinese J. Polym. Sci. **2023**, *41*, 1706–1713

Controlled Ring-opening (Co)Polymerization of Renewable Macrolactones by Al-based Catalysts with Different Sidearms

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Electronic Supplementary Information

Abstract It remains a challenging task to achieve ring-opening (co)polymerization (ROP) of macrolactones. Hence, we synthesized a series of **Al**-based catalysts and systemically investigated the effect of N-containing substituent on the sidearms on ROP of macrolactones. **Al3** possessing *N*-methyl group could effectively achieve controlled ROP of pentadecalactone (PDL) and macro(di)lactone ethylene brassylate (EB) in combination with BnOH, furnishing polyethylene-like PPDL and PEB with M_w up to 90.3 and 321 kg/mol, respectively. Random copolymerization of PDL and small-ring lactones *ε*-caprolactone (*ε*-CL) and *δ*-valerolactone (*δ*-VL) could prepare random copolyesters with tailored T_m in the range of 57–94 °C by controlling the ratios of PDL and *ε*-CL, *δ*-VL. More importantly, well-defined block copolyesters could be obtained by sequential adding PDL and *ε*-CL, *δ*-VL, which have been proved by GPC-MALLS, DSC and ^{13}C-NMR.

Keywords Ring-opening (co)polymerization; Macrolactones; Polyethylene-like polymers; Sidearm effect; Aluminum complex

Citation: Zhao, W. C.; Yuan, J.; He, J. H.; Zhang, Y. T. Controlled ring-opening (co)polymerization of renewable macrolactones by Al-based catalysts with different sidearms. *Chinese J. Polym. Sci.* **2023**, *41*, 1706–1713.

INTRODUCTION

Aliphatic polyesters, due to their environmentally friendly and renewable characteristics, are widely used in biomedical drug transportation and food packaging.[1–6] Ring-opening polymerization (ROP) is often used to synthesize polyesters on account of fast chain growth rate and controllable molecular weights.[7,8] The ROP of small and medium ring-sized cyclic esters, including *ε*-caprolactone (*ε*-CL), *δ*-valerolactone (*δ*-VL)[9–17] and lactide (LA),[18–23] *etc*., by diverse catalysts has been studied extensively. In contrast, it remains a challenge to achieve ROP of macrolactones, such as renewable pentadecalactone (PDL) and macro(di)lactone ethylene brassylate (EB). PPDL has aroused intensive attraction in recent years, of which the continuous methylene units with polyethylene-like crystalline structure endow with high heat resistance and excellent mechanic strength.[24–27] In view of these characters, they would be environmentally friendly alternatives for polyethylene (PE) to solve the "white pollution" problem.

Compared with small-ring lactones, more harsh polymerization conditions are needed to achieve ROP of PDL with decreased ring tension. Owing to low solubility and high T_m of PPDL, the ROP of PDL is generally performed at elevated temperatures to facilitate monomer diffusion and prevent polymer precipitation. Not satisfied is that more transesterification will occur at high temperature, making it difficult to obtain PPDL with high molecular weight and well-defined block copolymers of PDL. On the hand of homopolymerization of PDL, so far, most reports have been based on enzymatic catalysis.[28–32] Nevertheless, exorbitant price and moderate thermally stability of enzymes have limited their wide application. Various different types of catalysts have also been developed for the synthesis of PPDL, such as organic complexes,[33–37] metal-based systems.[38–41] However, results indicated that the majority exhibited relatively low catalytic reactivity and obtained moderate molecular weight polymers. For example, Duchateau *et al*. investigated ROP of macrolactones using salen-aluminum complexes, nevertheless, leading to very broad molecular weight distribution and showing poor control over homopolymerization.[41] The use of organic base *t*-BuP_2 with a primary alcohol as initiator would achieve living ROP of PDL, however, producing PPDL with merely M_n of 37.5 kg/mol.[34] Naumann and coworkers employed *N*-heterocyclic olefins (NHOs) cooperatively with several simple Lewis acids (such as $MgCl_2$ or LiCl) to homopolymerize PDL, low M_n of polyesters with 40 kg/mol would be obtained.[36] PPDL with higher molecular weights exhibited more superior mechanical strength and thermal stability, therefore, it is necessary to expand more catalyst systems to achieve this goal. On the other hand of copolymerization of PDL, to our knowledge, Li *et al*. utilized $Zn(C_6F_5)_2$/DBU Lewis

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Received December 14, 2022; Accepted January 5, 2023; Published online March 10, 2023

pair to prepare distinct diblock polyesters containing polyethylene segment with adding PDL followed by small-ring lactones, and no transesterification side reaction was observed.[37] Besides, only organic zinc and organic calcium complex could catalyze copolymerization of PDL, affording perfect block copolymers PPDL-*b*-PCL by sequential feeding.[38] Above all, we are committed to develop more efficient catalyst systems to achieve homopolymers with high molecular weights and sequence-controlled copolymers.

Recently, our group synthesized dimethyl-aluminum complexes bearing with different sidearms for living ROP and copolymerization of small-ring lactones (*ε*-CL, *δ*-VL), producing well-controlled (co)polymers with predicted M_w and narrow molecular weight distributions.[16] For several **Al**-based catalysts, we observed significant transesterification occurred after monomer consumption at heated condition, indicating that they could activate and attack the ester group of polymer chains without ring tension in the absence of monomer. Inspired by these results, we speculated that it was of great potential for this strategy to achieve ROP of PDL and produce copolyesters with distinct structure.

In this work, we employed this **Al**-based catalyst system and explored the effect of different sidearms of **Al**-based complex on the ROP of PDL (Scheme 1). Satisfyingly, we successfully obtained polyethylene-like PPDL with absolute M_w up to 90.3 kg/mol. Moreover, **Al**/BnOH system could also efficiently catalyze the ROP of macro(di)lactone ethylene brassylate (EB), affording polyesters with 321 kg/mol at 100 °C. Random copolyesters with tailored T_m would be easily prepared by copolymerizing mixtures of PDL and small-ring lactones in one pot. In addition, well-defined diblock copolymers could be prepared by sequential adding PDL and *ε*-CL, *δ*-VL by strictly controlling polymerization time.

EXPERIMENTAL

Materials

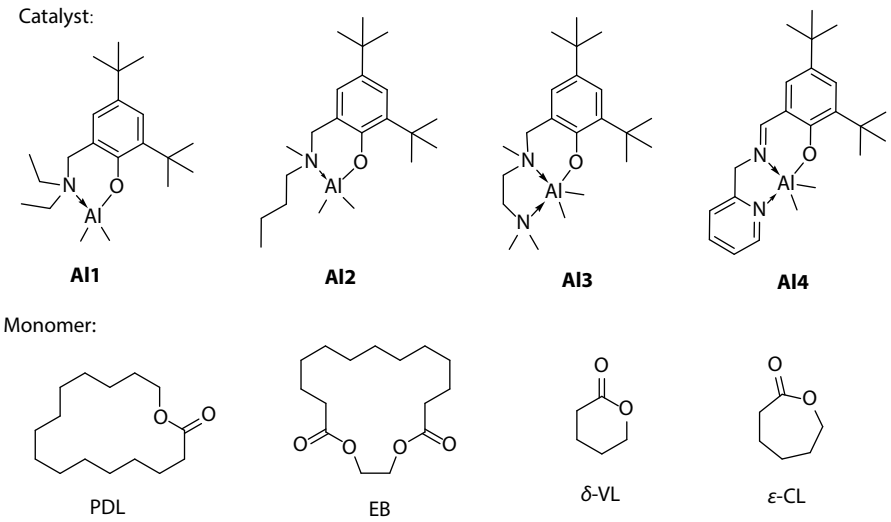
All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high-vacuum, or an argon-filled glovebox. The chemical reagents and solvents were all purchased from commercial sources (J&K, Sigma, Energy Chemical, Adamas-beta®). All chemicals were used as received unless otherwise specified as follows. Toluene was refluxed over a sodium/potassium alloy and hexane was refluxed over CaH_2, then followed by distillation under nitrogen atmosphere. Pentadecalactone (PDL) was dissolved in dry hexane, dried with CaH_2 before use. Ethylene brassylate (EB), *ε*-caprolactone (*ε*-CL) and *δ*-valerolactone (*δ*-VL) were dried over CaH_2 and then distilled under reduced pressure, and stored in a glovebox at −35 °C. The **Al1**–**Al4** complexes were synthesized according to our previous report[16] and literature procedures.[42–44]

Typical Procedures for ROP of PDL

In the glovebox filled with nitrogen, we firstly mixed **Al**-complex solution with an equal amount of BnOH in 2 mL of toluene in a 10 mL Schlenk tube and stirred vigorously for 2 min. Then 200 equiv. of PDL dissolving in a predetermined amount of toluene was added, while the initial monomer concentration kept 0.5 mol/L. The tube was taken outside and heated in an oil bath for the given time at 100 °C. After the measured time interval, a 0.1 mL of aliquot was taken from the reaction mixture *via* pipet in the glove box and quickly quenched into a 4 mL vial containing 0.6 mL of undried "wet" $CDCl_3$ stabilized by 250 ppm of BHT; the quenched aliquots were later analyzed by ^{1}H-NMR spectroscopy for monomer conversion. The reaction was quenched by hexane while hot and washed for several times, then dried in a vacuum oven at 50 °C for 24 h to a constant weight.

Typical Procedures for Random Copolymerization

In the glovebox filled with nitrogen, we firstly mixed **Al**-complex solution with an equal amount of BnOH in toluene and stirred vigorously for 2 min, and then 150 equiv. of *δ*-VL and 50 equiv. of PDL dissolving in a predetermined amount of toluene ($[M_{CL+PDL}]_0$=1.0 mol/L) was added at the same time. Then the tube was taken outside the glove box and heated at 100 °C. We quenched the reaction by adding excessive hexane and washed for several times, then dried under vacuum for 24 h to a constant weight.



Scheme 1 The structures of catalysts and monomers in this study.

https://doi.org/10.1007/s10118-023-2947-x

Typical Procedures for Block Copolymerization

In the glovebox filled with nitrogen, we firstly mixed **Al**-complex solution with an equal amount of BnOH in toluene and stirred vigorously for 2 min, and then 200 equiv. of PDL was added. A predetermined amount of toluene was further added to keep the initial concentration $[M]_0$=0.5 mol/L. The polymerization was conducted at 100 °C. After the complete conversion of PDL, we added 200 equiv. of *δ*-VL dissolving in toluene, then the polymerization of *δ*-VL was conducted at 100 °C. The mixtures were quenched adding excessive hexane, washed for several times and dried under vacuum for 24 h.

Polymer Characterization

Gel permeation chromatography (GPC) analyses were performed on a Waters 1515 instrument equipped with a guard column MIXED 7.5 × 50 mm PL column and two MIXED-C 7.5 × 300 mm columns and a differential refractive index detector using $CHCl_3$ (HPLC grade) as the eluent at 35 °C with a flow rate of 1 mL/min. The weight-average molar masses (M_w) and molecular weight distribution (MWD, M_w/M_n) of the polymer samples were determined by WYATT DAWAN 8+. The d*n*/d*c* value of PPDL was derived from 100% elution of the sample. Chromatograms were processed with Waters Breeze2 software. T_m of the polymer was measured with a differential scanning calorimeter (TA Q20). The polymer sample is equilibrated at −80 °C for 1 min, then heated from −80 °C to 120 °C at a heating rate of 10 °C/min, equilibrated at this temperature for 1 min, then cooled to −80 °C at a cooling rate of 10 °C/min, equilibrated at this temperature for 2 min, and then heated to 120 °C at 10 °C/min. The T_m value was obtained from the second heating curve.

RESULTS AND DISCUSSION

Homopolymerization of PDL

In early stage, our group has achieved living ROP of small-ring lactones (*ε*-CL, *δ*-VL) catalyzed by **Al**-based complex with benzyl alcohol (BnOH) as the initiator. Based on our previous study, these catalyst systems would convert block copolymers into random copolymers at 50 °C, suggesting that significant transesterification occurred at this temperature.[16] Hence, we firstly performed the polymerization of PDL at 50 °C.

As shown in Table 1, gratifyingly, results manifested that **Al**/BnOH catalyst systems showed high efficiency for ROP of PDL at 50 °C. With a 200:1:1 $[PDL]_0$:$[\mathbf{Al}]_0$:$[BnOH]_0$ ratio, 89% conversion of PDL was achieved by **Al1**/BnOH catalyst system within 51 h (Table 1, run 1), while 94% for **Al2**/BnOH (Table 1, run 2). Replacing **Al2** with **Al3** possessing one more *N*-methyl group, it approximately took 72 h to achieve 91% conversion of PDL (Table 1, run 4). All **Al1**–**Al3**/BnOH catalyst systems achieved similar monomer conversion, producing PPDL with M_w=39.6–44.3 kg/mol and $Đ$=1.45–1.53. Under the same polymerization temperature, initiation efficiency (*I**%) of **Al3**/BnOH was 143% (Table 1, run 4), while that of **Al1**–**Al2**/BnOH system was 157% and 156% (Table 1, runs 1 and 2). Whereas, switching to larger steric hinderance of sidearms with pyridine substituent lead to a dramatic decrease in the polymerization rate. Barely no polymerization activity has been observed at 50 °C catalyzed by **Al4**/BnOH. Even if the temperature increased to 100 °C, only 65% conversion of PDL could be converted in 120 h, furnishing polyesters with M_w=20.2 kg/mol, a narrow $Đ$ value of 1.26 and *I**%=195% (Table 1, run 15).

As can be seen from the above results, polymerization activity trend was observed for ROP of PDL by these **Al**/BnOH systems, following the order of **Al2** > **Al1**> **Al3** > **Al4**, consistent with that of small-ring lactones. Combined with our previous studies, all of these results strongly suggested that N-containing substituent on the sidearm of the **Al**-based catalysts had great impact on the reactivity of ROP of both small-ring lactones (*ε*-CL, *δ*-VL) and macrolactone PDL.[16] The order of Lewis acidity of **Al**-based complex was **Al4** > **Al3** > **Al1** > **Al2**, in contrast to the polymerization reactivity trend. During the polymerization, the minimum Lewis acidity made **Al2** more

Table 1 Selected polymerization results of PDL and EB by **Al**/BnOH catalyst system. [a]

Run	**Al**	Temp. (°C)	[M]/[**Al**]/[BnOH]	Time (h)	Conv. [b] (%)	M_n [c] (kg/mol)	M_w [c] (kg/mol)	$Đ$	*I** [d] (%)
1	**Al1**	50	200/1/1	51	89	27.3	39.6	1.45	157
2	**Al2**	50	200/1/1	51	94	28.8	44.1	1.53	156
3	**Al3**	50	100/1/1	50	99	17.3	25.9	1.51	137
4	**Al3**	50	200/1/1	72	91	30.5	44.3	1.45	143
5	**Al3**	50	400/1/1	96	82	41.9	62.0	1.48	187
6	**Al3**	50	800/1/1	204	40	39.4	54.0	1.37	195
7	**Al3**	50	400/1/1	24	45	50.5	72.1	1.43	86
8	**Al3**	50	400/1/2	24	52	28.6	40.2	1.41	87
9	**Al3**	70	200/1/1	24	94	25.7	36.3	1.41	173
10	**Al3**	70	400/1/1	24	89	36.7	43.3	1.41	231
11	**Al3**	100	100/1/1	9.7	95	14.9	22.5	1.51	153
12	**Al3**	100	200/1/1	9.7	93	23.1	33.1	1.43	196
13	**Al3**	100	400/1/1	9.7	91	41.9	61.6	1.46	208
14	**Al3**	100	800/1/1	18	89	63.8	90.3	1.42	268
15	**Al4**	100	200/1/1	120	65	16.0	20.2	1.26	195
16 [e]	**Al3**	100	100/1/1	16	93	84.7	178	2.10	30
17 [e]	**Al3**	100	200/1/1	29.5	82	159	321	2.02	28

[a] Conditions: carried out in toluene, $[\mathbf{Al}]_0$:$[BnOH]_0$=1:1, $[M]_0$=[monomer]=0.5 mol/L; [b] Monomer conversions measured by ^{1}H-NMR; [c] Absolute molecular weight (M_w) measured by GPC using a light scattering detector. Number average molecular weight (M_n) is calculated from $M_w/Đ$; [d] Initiation efficiency (*I**)% = M_n(calcd)/M_n(exptl) × 100, where M_n(calcd) = M_w(M) × ([M]/[I]) × (conversion) + M_w of chain-end groups; [e] EB was used as monomer.

https://doi.org/10.1007/s10118-023-2947-x

susceptible to cleave the Al-O(Bn) bond, following by nucleophilic attack of carbonyl carbon of the activated monomer by Bn-O group, which resulted in the fastest insertion.[16] These polymerization results corresponded to the mechanism we had explored earlier.

Comparing with the other catalysts, **Al3**/BnOH showed similar reactivity but the lowest *I**%, thus, inhibited the side transesterification reaction more effectively. Therefore, we would perform the ROP of PDL further by this system. With the increase of the $[PDL]_0$:$[BnOH]_0$ ratio from 100:1, 200:1 to 400:1, the M_w value of PPDL increased linearly from 25.9 kg/mol, 44.3 kg/mol to 62.0 kg/mol, while the $Đ$ value remained in a narrow range of 1.45–1.51 (Table 1, runs 3–5). The initiation efficiencies also increased from 137% to 187%, for which we speculated that viscosity of systems increased with higher M_w, trigging more serious transesterification. When the monomer ratio increased to 800:1, only 40% conversion of PDL could be obtained in 204 h, affording polyesters with M_w=54.0 kg/mol, $Đ$=1.37, and thus giving rise to *I**% of 195% (Table 1, run 6).

We further investigated the effect of reaction time on polymerization reactivity. Prolonging the polymerization time from 24 h to 96 h, the conversion of 200 equiv. of PDL enhanced from 45% to 82%, while M_w of polyesters decreased from 72.1 kg/mol to 62.0 kg/mol (Table 1, runs 5 versus 7). The reduced M_w might be account of the intramolecular transesterification.[39] In order to suppress the side reaction and obtain polyesters with high polymerization degree, we usually quenched the reaction in time in sacrifice of part conversions of monomers.

Besides the polymerization time, the amount of alcohol has also been proved to impact on ROP reactivity of macrolactones. The experimental M_w of polyester was inversely proportional to BnOH loading dosage. Increasing $[BnOH]_0$:$[\mathbf{Al3}]_0$ feed ratio from 1:1 to 1:2, M_w of PPDL reduced from 72.1 kg/mol to 40.2 kg/mol, while maintaining similar $Đ$ values and *I**% (Table 1, runs 7 versus 8), indicating BnOH acted as initiator (or chain transfer). Moreover, it appeared to accelerate monomer conversion growth, which is probably attributed to the reduced viscosity of reaction mixtures.[33]

It is universally acknowledged that the reaction temperature usually has remarkable influence on ROP of lactones, then we systemically investigated the polymerization behavior of PDL at different temperatures. With a fixed ratio of $[PDL]_0$: $[\mathbf{Al3}]_0$ = 200:1, 94% of PDL were converted to polyester in 24 h at 70 °C, producing PPDL with M_w=36.3 kg/mol and *I**%=173% (Table 1, run 9). When it rose to 100 °C, only 9.7 h was taken to achieve 93% conversion, affording polymers with M_w=33.1 kg/mol and *I**%=196% (Table 1, run 12). Increasing the temperature resulted in significant enhancement of polymerization rates (Table 1, runs 4 versus 9 versus 12). The same trend has also been revealed in other proportions. We envisioned that higher temperature would decrease the viscosity of the reaction system and facilitate monomer diffuse to active center, leading to more rapid conversion of PDL.[37] Moreover, the polymerization carried out at 70 and 100 °C showed higher *I**%, because a significant decrease of M_w of PPDL was observed at elevated temperature, indicative of more serious transesterification.

In consideration of above results, we subsequently investigated ROP of PDL at 100 °C. The polymerization catalyzed by **Al3**/BnOH system showed excellent polymerization efficiency and a controlled manner. With the increase of monomer ratio from 100, 200, 400 to 800, we could easily afford polyesters with M_w from 22.5 kg/mol, 33.1 kg/mol, 61.6 kg/mol to 90.3 kg/mol, thus achieving *I**% increase from 153%, 196%, 208% to 268%, while maintaining a moderate $Đ$ value range of 1.42–1.51 (Table 1, runs 11–14). And the GPC

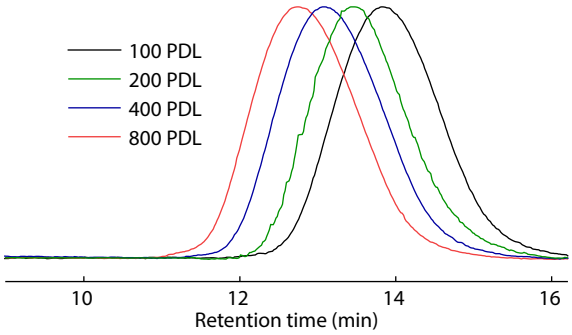


Fig. 1 GPC traces of PPDL samples with different $[PDL]_0/[\mathbf{Al3}]_0/[BnOH]_0$ ratios produced by **Al3**/BnOH catalyst system at 100 °C.

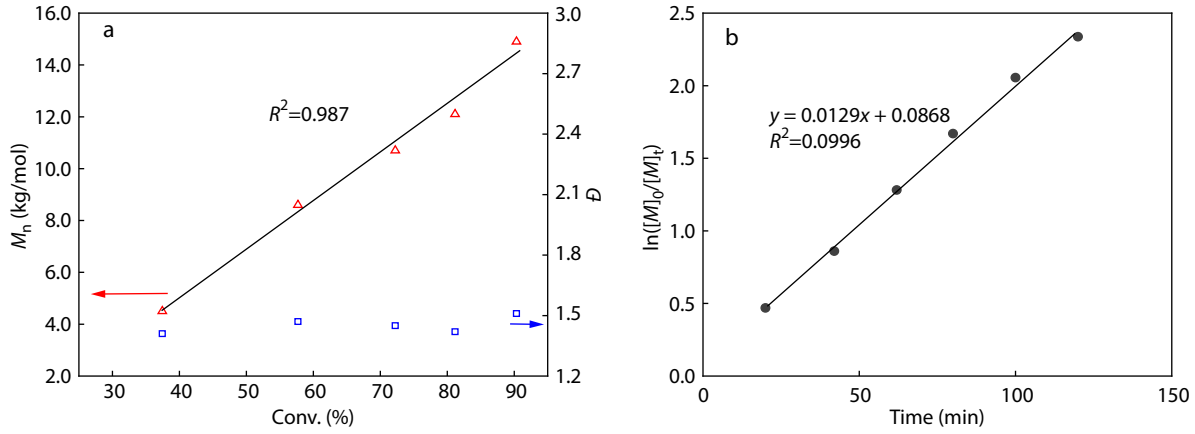


Fig. 2 (a) Plot of M_n and $Đ$ of the resultant PPDL verse conversion of monomer; (b) Kinetic plot of the ROP of PDL by **Al3**/BnOH in toluene at 100 °C with $[PDL]_0$ = 0.5 mol/L.

https://doi.org/10.1007/s10118-023-2947-x

traces of PPDL samples showed the gradual shift to the higher-molar-mass region with an increase of the monomer ratio from 100 to 800, while maintaining a narrow and unimodal molecular weight distribution (Fig. 1). With a fixed ratio of $[PDL]_0$:[**Al3**]$_0$:$[BnOH]_0$=100:1:1, M_n of the resultant PPDL and monomer conversion manifested positive linear correlation and MWD kept in a narrow range, indicating the polymerization proceeded in a controlled manner (Fig. 2a). Further kinetic analysis demonstrated that the $\ln([M]_0/[M]_t)$ increased almost linearly with time, approaching the first-order on PDL concentration (Fig. 2b), consisting with ROP of ε-CL.[16] Moreover, we also expanded monomer scope to renewable macro(di)lactone EB. It also exhibited high reactivity, polyesters with M_w up to 321 kg/mol could be obtained (Table 1, runs 16 and 17).

Copolymerization of PDL with ε-CL or δ-VL Catalyzed by Al/BnOH

When PDL was copolymerized with small-ring lactones in one pot, due to the enormous reactivity difference between PDL and small-ring lactones (ε-CL, δ-VL) in combination with the similarity of the chain-end structure after insertion of monomers, it tended to form random or block copolymers.[38] However, our results indicated that random copolyesters were obtained during the copolymerization of mixtures of lactones. We fixed the total ratio of comonomers at 200 equiv., but varying the feeding ratio of PDL to small-ring monomers from 0.25, 0.50 to 0.75, and successfully synthesized a series of

Table 2 Random copolymerization of PDL with ε-CL or δ-VL catalyzed by **Al3**/BnOH. [a]

Run	Monomer ratio	Conv. (%)	M_n [b] (kg/mol)	M_w [b] (kg/mol)	$Đ$	PC(V)L:PPDL	T_m (°C)
1	50PDL+150CL	CL100, PDL54	12.4	54.0	4.37	85/15	63.4
2	100PDL+100CL	CL100, PDL90	23.6	42.2	1.79	53/47	74.5
3	150PDL+50CL	CL100, PDL100	34.8	68.2	1.96	25/75	84.4
4	50PDL+150VL	VL63, PDL91	8.1	29.9	3.72	68/32	67.2
5	100PDL+100VL	VL66, PDL95	27.0	51.6	1.91	41/59	78.8
6	150PDL+50VL	VL70, PDL97	32.7	62.8	1.92	19/81	85.9

[a] Conditions: Carried out in toluene at 100 °C for 12 h, [**Al3**]$_0$:$[BnOH]_0$=1:1, both monomers were added at the same time, $[M_{CL+PDL}]_0$=1 mol/L; [b] Absolute molecular weight (M_w) measured by GPC using a light scattering detector. Number average molecular weight (M_n) is calculated from $M_w/Đ$.

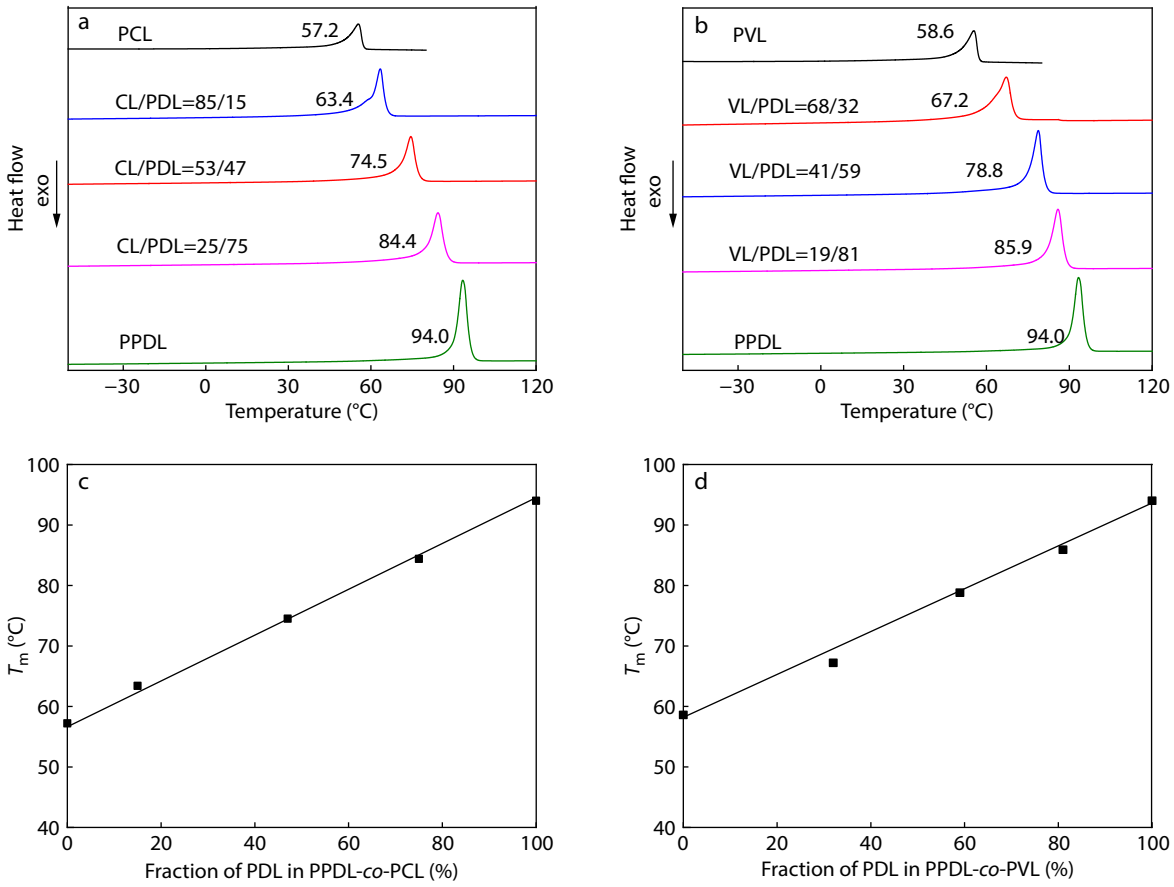


Fig. 3 DSC curves of (a) PCL, PPDL and PPDL-*co*-PCL; (b) PVL, PPDL and PPDL-*co*-PVL. The relationship between T_m and fraction of PDL in (c) PPDL-*co*-PCL; (d) PPDL-*co*-PVL.

https://doi.org/10.1007/s10118-023-2947-x

random copolymers PPDL-*co*-PCL (CL/PDL=85/15, 53/47 and 25/75) (Table 2, Figs. S1–S6 in the electronic supplementary information, ESI). The T_m of the resultant copolyesters shows an increasing trend from 63.4 °C, 74.5 °C to 84.4 °C (Table 2, runs 1–3 and Fig. 3a). Further analysis revealed that these copolymers displayed cocrystallinity that T_m linearly positively correlated with the fraction of PDL (Fig. 3c). Previous studies demonstrated that PVL and PCL could undergo cocrystallization, so we surmised PVL and PPDL could also go through the same process.[45–47] According to the same procedure, a series of random copolymers PPDL-*co*-PVL (VL/PDL=68/32, 41/59 and 19/81) were prepared (Table 2, Figs. S7–12 in ESI). Satisfyingly, we observed that T_m of PPDL-*co*-PVL was also linearly dependent on the composition of comonomers. Therefore, according to this scheme, it would provide a new strategy to prepare copolyesters with tailored T_m within the range of 57–94 °C simply by copolymerizing PDL with small-ring lactones in one pot.

The transesterification side reaction including inter- and intramolecular transesterification always led to random copolymers with broad dispersity at elevated temperature, hence, restricted the application of the copolymers obtained from ROP of lactones. Previously, during the copolymerization of ε-CL and δ-VL catalyzed by **Al**/BnOH catalyst system, we found that the catalyst preferentially activated the monomer in the case of incomplete conversion of the monomer, while transesterification reaction occurred only after monomer was completely consumed. Therefore, we expected to apply this strategy to afford well-defined block copolymers by strictly controlling the polymerization time.

By sequential addition of PDL followed by ε-CL or δ-VL, we have successfully obtained binary block polymers PPDL-*b*-PCL and PPDL-*b*-PVL (Table 3, runs 1 and 2). Fixing $[PDL]_0$:[**Al3**]$_0$:$[BnOH]_0$=200:1:1, M_w of polyesters shifted from 33.1 kg/mol to 63.1 kg/mol after copolymerization with ε-CL, while the polymer dispersity kept a low value of 1.31 as evidenced by GPC-MALLS test (Fig. 4a, blue line). In the DSC test, we observed two melting peaks of resulting copolymer, respectively corresponding to the T_m=87 °C of PPDL segment and the T_m=54 °C of PCL segment (Fig. 4b, black line). Moreover, ^{13}C-NMR analysis of block polymer further confirmed the exact structure (Fig. 4c), indicating the formation of well-defined block copolymer PPDL-*b*-PCL. Furthermore, changing the comonomer to δ-VL, block copolymer PPDL-*b*-PVL could be also prepared by sequential monomer addition, as evidenced by GPC-MALLS (Fig. 4a, red line), DSC test (Fig. 4b, red line) and ^{13}C-NMR analysis (Fig. 4d), showing the versatility of our catalyst system.

Table 3 Block copolymerization of PDL with ε-CL or δ-VL catalyzed by **Al3**/BnOH.[a]

Run	**Al**	M1/M2	M_n [b] (kg/mol)	M_w [b] (kg/mol)	$Đ$
1	**Al3**	200PDL/200CL	48.4	63.1	1.31
2	**Al3**	200PDL/200VL	40.3	53.4	1.32

[a] Conditions: Homopolymerization of PDL was firstly conducted at 100 °C, then copolymerized with ε-CL or δ-VL at 100 °C, [**Al3**]$_0$:$[BnOH]_0$=1:1, $[M]_0$ = $[monomer]_0$ = 0.5 mol/L; [b] Absolute molecular weight (M_w) measured by GPC using a light scattering detector. Number average molecular weight (M_n) is calculated from $M_w/Đ$.

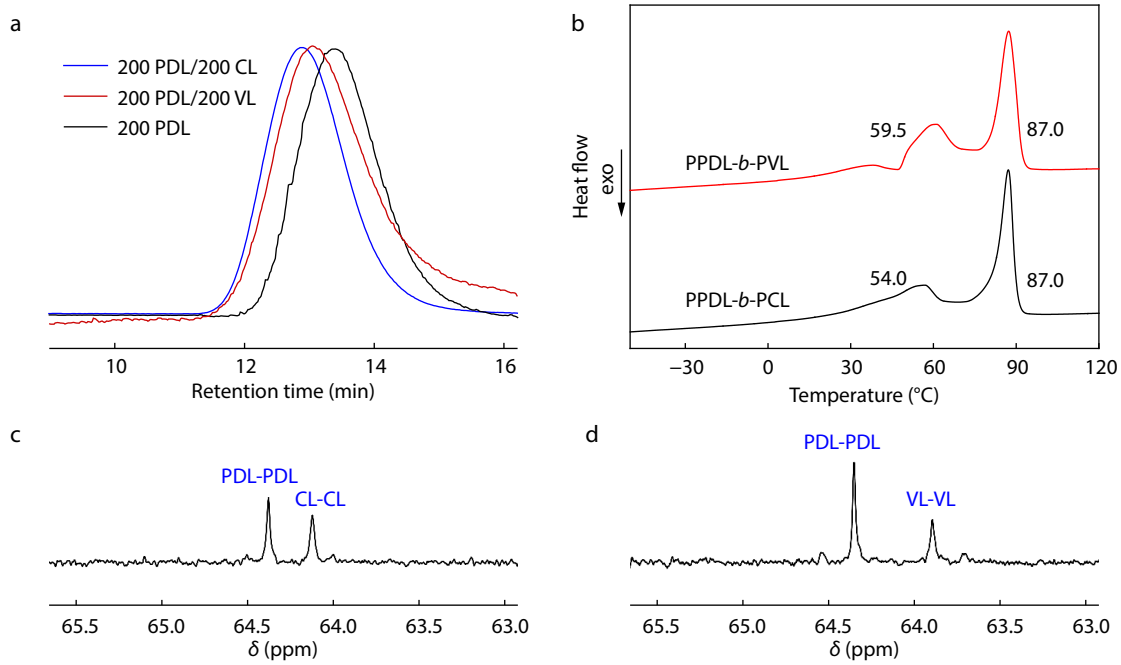


Fig. 4 (a) GPC traces for homopolymer PPDL (black), diblock copolymer PPDL-*b*-PVL (red) and PPDL-*b*-PCL (blue) produced by **Al3**/BnOH system at 100 °C; (b) DSC curves of PPDL-*b*-PCL (black) and PPDL-*b*-PVL (red); (c) ^{13}C-NMR spectra of block copolymer PPDL-*b*-PCL of run 1 in Table 3; (d) ^{13}C-NMR spectra of block copolymer PPDL-*b*-PVL of run 2 in Table 3.

https://doi.org/10.1007/s10118-023-2947-x

CONCLUSIONS

In conclusion, we synthesized a series of **Al**-based complexes and explored the effect of different substituents of ligands on the ROP of PDL and copolymerization of PDL with small-ring sized lactones. Results indicated that the order of Lewis acidity of ligand is just opposite to the polymerization reactivity trend: **Al2** > **Al1** > **Al3** > **Al4**, while **Al3**/BnOH inhibited the side transesterification reaction more effectively among these catalyst systems. The $\ln([M]_0/[M]_t)$ increased linearly with time, approaching the first-order reaction kinetic on monomer concentration. Further investigation on reaction time, temperature and initiator ratio demonstrated that these conditions exerted a marked influence on the resultant PPDL. Polymerization of macro-lactone PDL could produce polyethylene-like polyester with M_w high up to 90.3 kg/mol. Moreover, this strategy could also be applicable for ROP of macro(di)lactone ethylene brassylate, affording polyester with M_w up to 321 kg/mol. Finally, when PDL was copolymerized with small-ring lactones *ε*-CL and *δ*-VL, random copolymers would be obtained. Due to the cocrystallization, we could customize a series of polyesters with T_m in the range of 57–94 °C by regulating the proportion of PDL and *ε*-CL, *δ*-VL. Importantly, well-defined diblock copolymers PPDL-*b*-PCL and PPDL-*b*-PVL could be prepared by strictly controlling polymerization conditions. The formation of block structure has been evidenced by GPC-MALLS, DSC and ^{13}C-NMR analysis. These results show the versatility of our **Al**-based catalyst system, and also provide inspiration for the design of catalyst for ROP of macrolactones.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-023-2947-x.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 22225104, 22071077, 21871107 and 21975102) and China Postdoctoral Science Foundation (Nos. 2022TQ0115 and 2022M711297).

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https://doi.org/10.1007/s10118-023-2947-x