

# Ring-opening (Co)Polymerization of Macrolactones Catalyzed by a Simple Organoaluminum Complex of MeAl(BHT)<sub>2</sub>

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## Materials

Toluene was purified by purging with dry nitrogen, followed by passing through columns of activated alumina. Cyclododecan-1-one was donated by Wanhua Chemical Group Co., Ltd.  $\omega$ -Pentadecalactone (PDL, 98%) was purchased from Adamas and stirred with CaH<sub>2</sub> for 24 h, then distilled under reduced pressure. Benzyl alcohol (BnOH, 99%),  $\epsilon$ -caprolactone ( $\epsilon$ -CL, 99%), and  $\delta$ -valerolactone ( $\delta$ -VL, 99%) were purchased from Aladdin Co. and stirred with CaH<sub>2</sub> for 24 h, then distilled under reduced pressure, and stored over activated 4 Å molecular sieves in a glovebox. *L*-lactide (*L*-LA, 99%) was purchased from TCI and recrystallized twice from toluene. Diethylzinc (ZnEt<sub>2</sub>, 2 mol L<sup>-1</sup> in *n*-Hexane) and Stannous Octoate (Sn(Oct)<sub>2</sub>, 95%) was purchased from Adamas. Trimethylaluminum (AlMe<sub>3</sub>, 1.0 mol L<sup>-1</sup> in hexanes) and 2,6-di-tert-butyl-4-methylphenol (BHT-H, 99%) were purchased from J&K Chemical Co. All other chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted.

## Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer (400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR). Chemical shifts were reported in  $\delta$  (ppm), and the residual deuterated solvent peak was used as reference. The parameters used were as follows: 8.0% w/w polymer in CDCl<sub>3</sub>, temperature 25 °C, pulse width 90°, 18000 data points, relaxation delay 5.0 s, and the pulse program was zgig. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDITOF MS) analyses were conducted on a Bruker Microflex MALDITOF MS spectrometer equipped with a 337 nm nitrogen laser. The polymer was dissolved in chloroform; trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as the matrix and CF<sub>3</sub>COONa as the cationizing agent. The gel permeation chromatography (GPC) measurements were collected on a Wyatt OPTILAB rEX refractive index detector using chloroform as the eluent (flow rate: 1 mL/min, at 40 °C). The molecular weights (*M<sub>n</sub>*) and polydispersity (*D*) were calculated using polystyrene standards with narrow molecular weight distribution as references. The sample concentration used for GPC analysis was ca. 10 mg/mL. Differential scanning calorimetry (DSC) was performed using a TA differential scanning calorimeter DSC 25 that was calibrated using high purity indium at a heating rate of 10 °C/min. Melting points were determined from the second scan at a heating rate of 10 °C/min following a slow cooling rate of 10 °C/min to remove the influence of thermal history.

### **Procedures for the synthesis of DDL**

The DDL synthesis procedure of the DDL was in the previous article.<sup>1</sup> The synthesis of MeAl(BHT)<sub>2</sub> was described in the previous article.<sup>2</sup>

### **ROP of MLs by MeAl(BHT)<sub>2</sub>/BnOH**

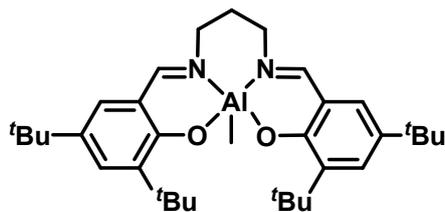
Polymerizations were performed in 25 mL flame-dried Schlenk tubes interfaced to the dual-manifold Schlenk line. The reactor was charged with a predetermined amount of MeAl(BHT)<sub>2</sub> (1 equiv.), BnOH (1 equiv.), MLs solution (in toluene, 100 equiv.), and solvent in the glovebox. The reactor was sealed, taken out of the glovebox, and immersed in the oil bath under the predetermined temperature. After a desired period of time, the polymerization was quenched by the addition of benzoic acid solution (10 mg/mL in chloroform). The quenched mixture was then precipitated with methanol, filtered, washed with methanol to remove unreacted monomer, and dried in a vacuum oven at 35 °C to a constant weight.

### **Preparation of PMLs-*b*-PLLA copolyesters by sequential addition process**

BnOH (1 equiv.), MeAl(BHT)<sub>2</sub> (1 equiv.), MLs solution (in toluene, 100 equiv.) and a predetermined amount of dry toluene were charged into a 25 mL flame-dried Schlenk tube. The reactor was sealed, taken out of the glovebox, and immersed in the oil bath at 130 °C. After heating and stirring for 4 h, and a hot solution of *L*-LA (100 equiv.) in toluene was added. The polymerization system was continued for another 2 h. The polymerization was quenched by the addition of benzoic acid solution (10 mg/mL in chloroform). The quenched mixture was then precipitated with methanol, filtered, washed with methanol to remove unreacted monomer, and dried in a vacuum oven at 35 °C to a constant weight.

### **Preparation of copolyesters of MLs and CL/VL by sequential addition process |**

BnOH (1 equiv.), MeAl(BHT)<sub>2</sub> (1 equiv.), MLs solution (in toluene, 100 equiv.) and a predetermined amount of dry toluene were charged into a 25 mL flame-dried Schlenk tube. The reactor was sealed, taken out of the glovebox, and immersed in the oil bath at 130 °C. After heating and stirring for 4 h, and a solution of CL/VL (100 equiv.) in toluene was added. The polymerization system was continued for another 1 h. The polymerization was quenched by the addition of benzoic acid solution (10 mg/mL in chloroform). The quenched mixture was then precipitated with methanol, filtered, washed with methanol to remove unreacted monomer, and dried in a vacuum oven at 35 °C to a constant weight.



**Scheme S1** The structures of MeAl[Salen] in this study.<sup>2</sup>

**Table S1** Results of ROPs of DDL<sup>a</sup>

Run	Time (h)	Conv. <sup>b</sup> (%)	$M_{n,theo}$ <sup>c</sup> (kDa)	$M_{n,GPC}$ <sup>d</sup> (kDa)	$\bar{D}$ <sup>d</sup>
1	0.5	38	7.6	12.4	2.04
2	2.0	59	11.8	16.7	2.39
3	3.0	70	14.0	23.2	1.76
4	4.0	75	15.0	24.7	2.00
5	6.0	82	16.3	29.2	1.84

<sup>a</sup> Conditions:  $[M]_0/[I]_0/[C]_0$  = monomer/initiator/catalyst = 100/1/1,  $[DDL]_0$  = bulk, T = 100 °C. <sup>b</sup> Determined by <sup>1</sup>H NMR. <sup>c</sup> The theoretical  $M_n$  was calculated based on:  $M_{n,theo} = ([M]_0/[I]_0) \times \text{Conv.}\% \times (\text{molecular weight of monomer}) + (\text{molecular weight of BnOH})$ . <sup>d</sup> Determined by GPC at 40 °C in chloroform relative to polystyrene standards.

**Table S2** Results of ROPs of PDL<sup>a</sup>

Run	Time (h)	Conv. <sup>b</sup> (%)	$M_{n,theo}$ <sup>c</sup> (kDa)	$M_{n,GPC}$ <sup>d</sup> (kDa)	$\bar{D}$ <sup>d</sup>
1	0.5	39	9.5	20.7	1.67
2	1.0	52	12.6	29.7	1.55
3	2.0	73	17.6	41.9	1.63
4	4.0	90	21.7	42.0	1.58
5	6.0	97	23.4	43.8	1.63

<sup>a</sup> Conditions:  $[M]_0/[I]_0/[C]_0$  = monomer/initiator/catalyst = 100/1/1,  $[PDL]_0$  = bulk, T = 100 °C. <sup>b</sup> Determined by <sup>1</sup>H NMR. <sup>c</sup> The theoretical  $M_n$  was calculated based on:  $M_{n,theo} = ([M]_0/[I]_0) \times \text{Conv.}\% \times (\text{molecular weight of monomer}) + (\text{molecular weight of BnOH})$ . <sup>d</sup> Determined by GPC at 40 °C in chloroform relative to polystyrene standards.

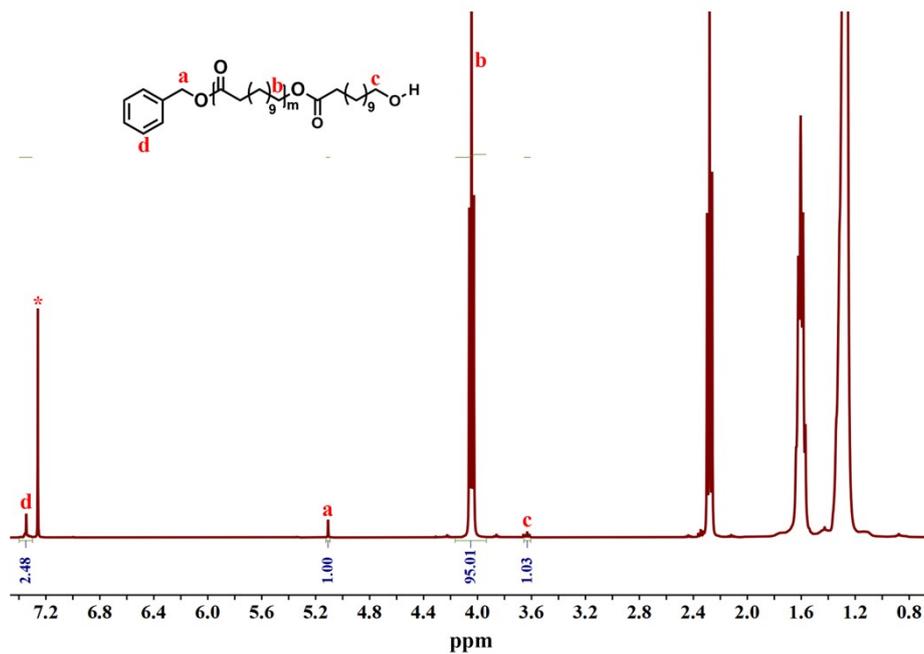


Fig. S1 <sup>1</sup>H NMR spectrum of PDDL obtained in Table 1, run 6.

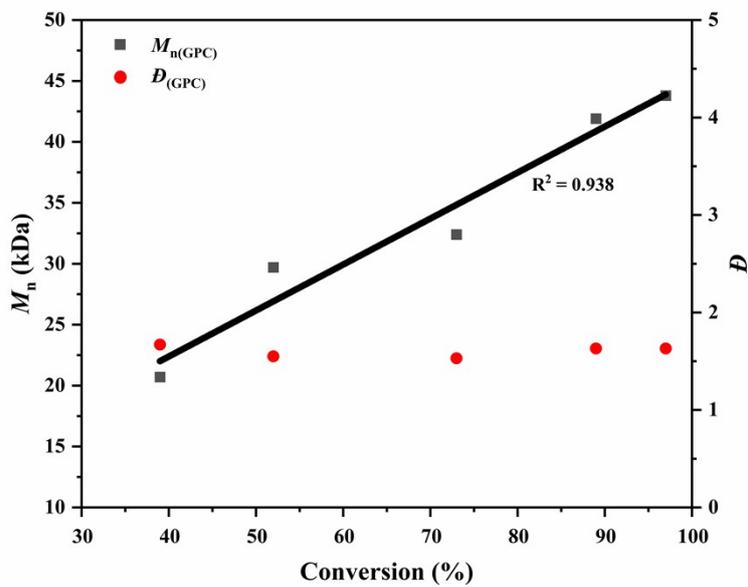


Fig. S2  $M_n$  and  $D$  of the resultant PDDL versus monomer conversion ( $[M]_0/[I]_0/[C]_0 = 100/1/1$ ,  $[M]_0 = \text{bulk}$ ,  $T = 100$  °C).

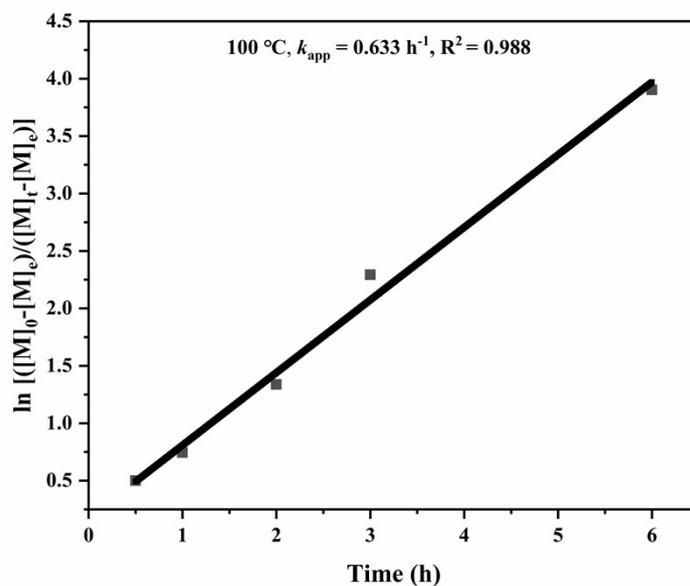


Fig. S3 Kinetic plots of  $\ln \frac{([M]_0 - [M]_e)}{([M]_t - [M]_e)}$  vs time ( $[M]_0/[I]_0/[C]_0 = 100/1/1$ ,  $[M]_0 = \text{bulk}$ ,  $T = 100 \text{ °C}$ ) of PDL.

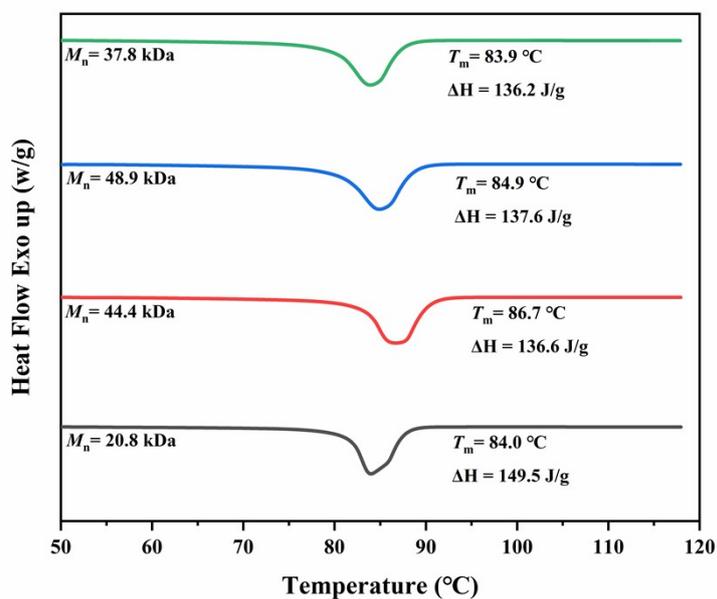


Fig. S4 DSC thermograms of the second heating run for different  $M_n$  of PDDL.

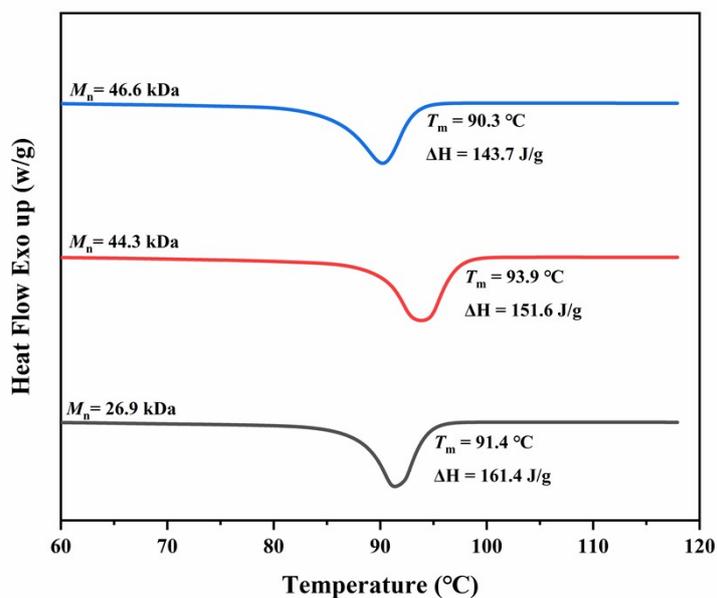


Fig. S5 DSC thermograms of the second heating run for different  $M_n$  of PPDL.

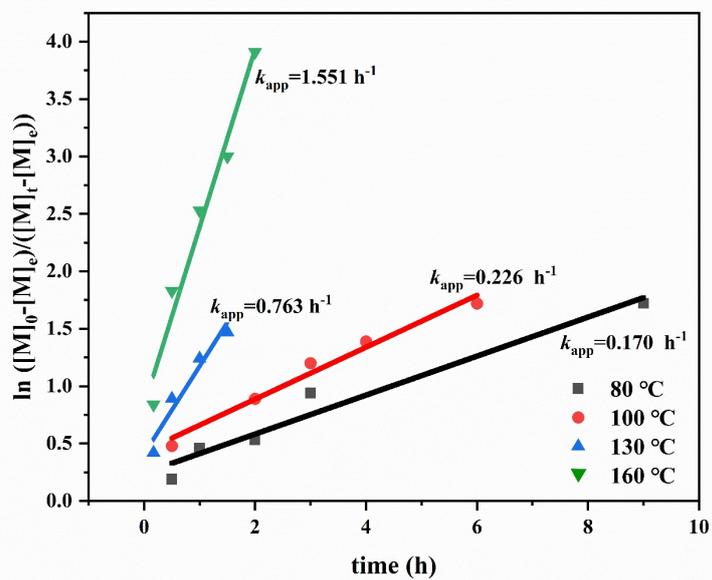


Fig. S6 The polymerization kinetics with different polymerization temperature ( $[DDL]_0 = \text{bulk}$ ).

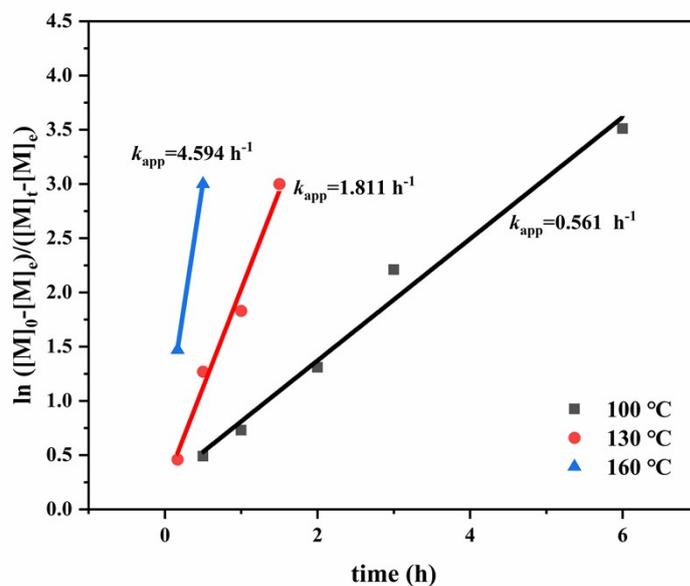


Fig. S7 The polymerization kinetics with different polymerization temperature ( $[\text{PDL}]_0 = \text{bulk}$ ).

Table S3 Copolymerization of PDL with *L*-LA catalyzed by  $\text{MeAl}(\text{BHT})_2$ <sup>a</sup>

Run	$[\text{PDL}]_0/[\text{L-LA}]_0/[\text{I}]_0/[\text{C}]_0$	Time (min)	$C_{\text{DDL}}$ <sup>b</sup> (%)	$C_{\text{L-LA}}$ <sup>b</sup> (%)	$M_{n,\text{theo}}$ (kDa)	$M_{n,\text{GPC}}$ <sup>c</sup> (kDa)	$D$ <sup>c</sup>
1	0/100/1/1	30	-	73	10.6	21.6	1.04
2 <sup>d</sup>	10/100/1/1 (PDL+ <i>L</i> -LA)	30+60	89	87	14.8	28.7	1.30
3 <sup>d</sup>	50/100/1/1 (PDL+ <i>L</i> -LA)	60+90	95	73	22.0	36.1	2.10
4 <sup>d</sup>	100/100/1/1 (PDL+ <i>L</i> -LA)	180+120	96	77	34.2	62.7	2.12

<sup>a</sup> Conditions:  $[\text{M}]_0 = [\text{PDL}]_0 + [\text{L-LA}]_0 = 3.0 \text{ mol L}^{-1}$ , the solvent was toluene,  $T = 130 \text{ }^\circ\text{C}$ . <sup>b</sup> Determined by  $^1\text{H NMR}$ .

<sup>c</sup> Determined by GPC at  $40 \text{ }^\circ\text{C}$  in chloroform relative to polystyrene standards. <sup>d</sup> Sequential addition of PDL and *L*-LA.

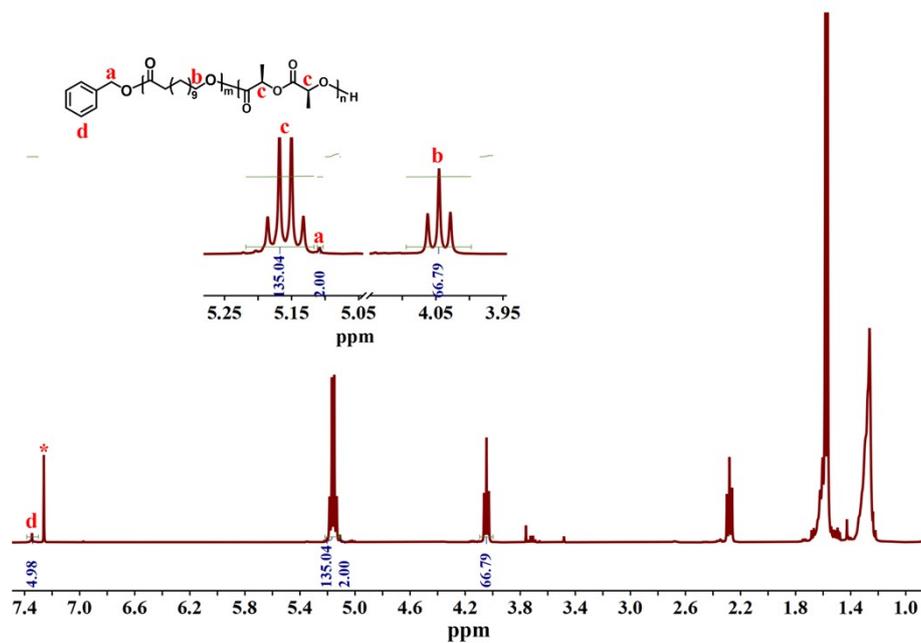


Fig. S8  $^1\text{H}$  NMR spectrum of PDDL-*b*-PLLA copolyester obtained in Table 2, run 4.

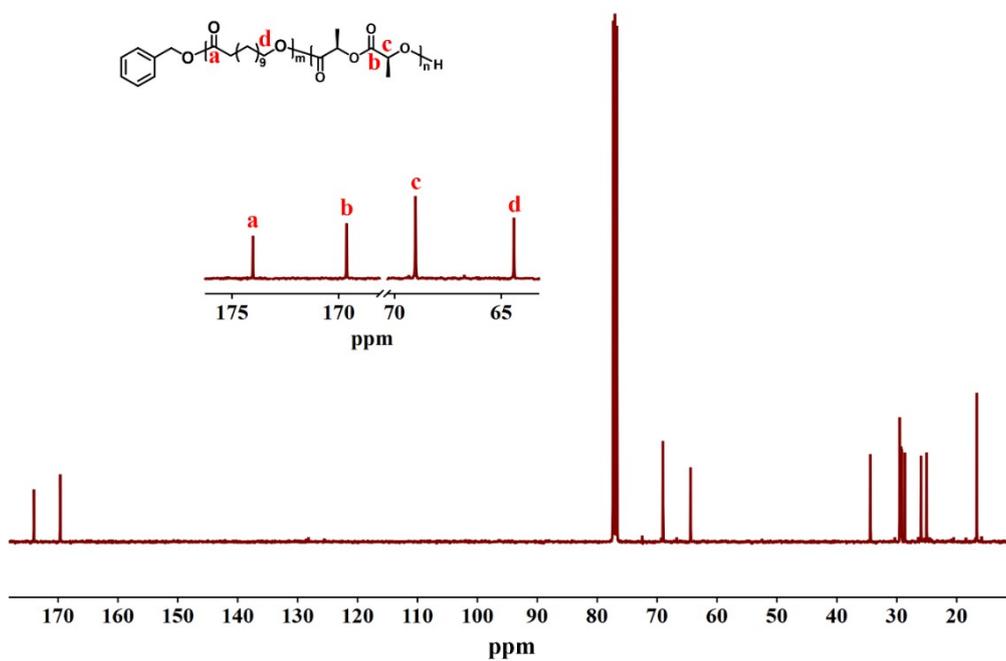
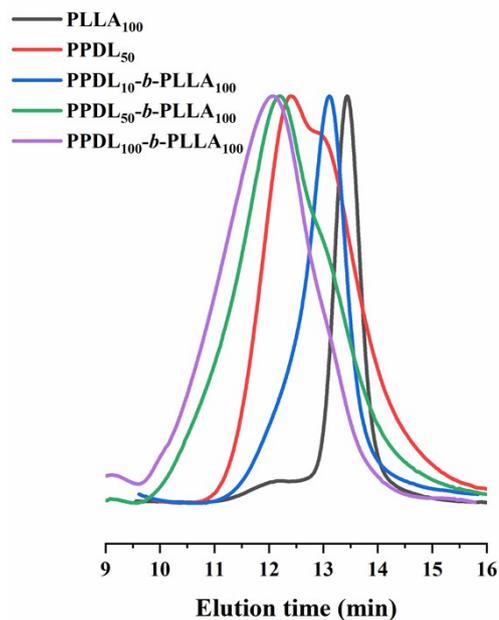
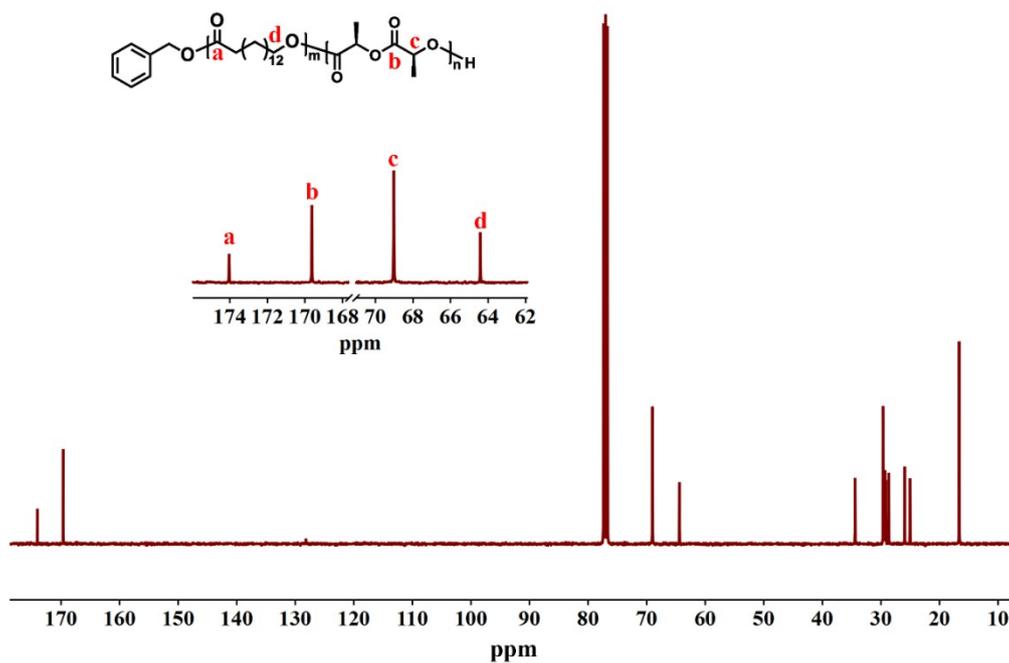


Fig. S9  $^{13}\text{C}$  NMR spectrum of PDDL-*b*-PLLA copolyester obtained in Table 2, run 5.



**Fig. S10** GPC curves of PLLA (Table S3, run 1), PPDL (Table 1, run 17) and block copolyesters (Table S3, runs 2-4).



**Fig. S11** <sup>13</sup>C NMR spectrum of PPDL-*b*-PLLA copolyester obtained in Table 2, run 6.

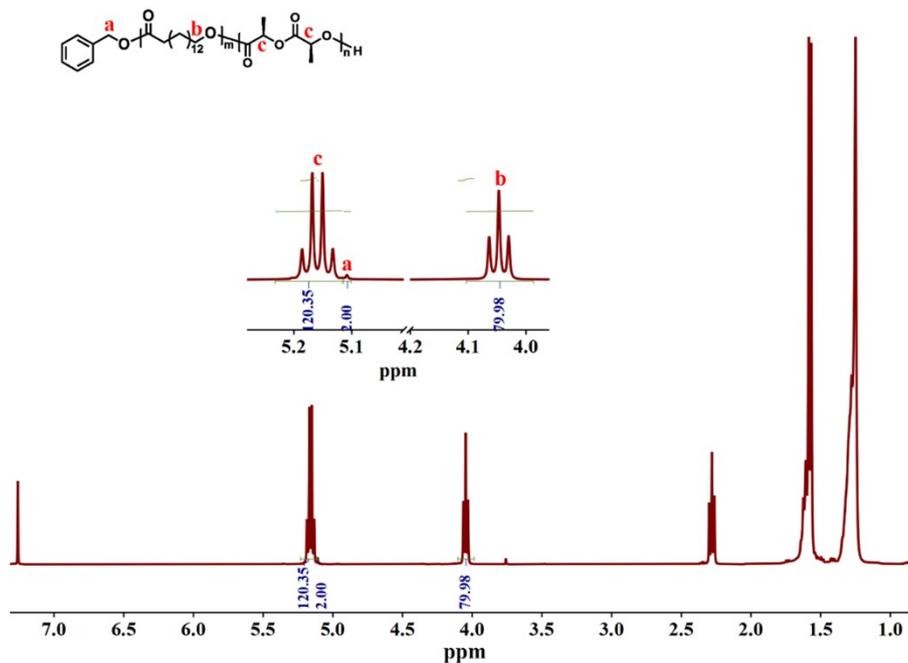


Fig. S12  $^1\text{H}$  NMR spectrum of PPDL-*b*-PLLA copolyester obtained in Table 2, run 6.

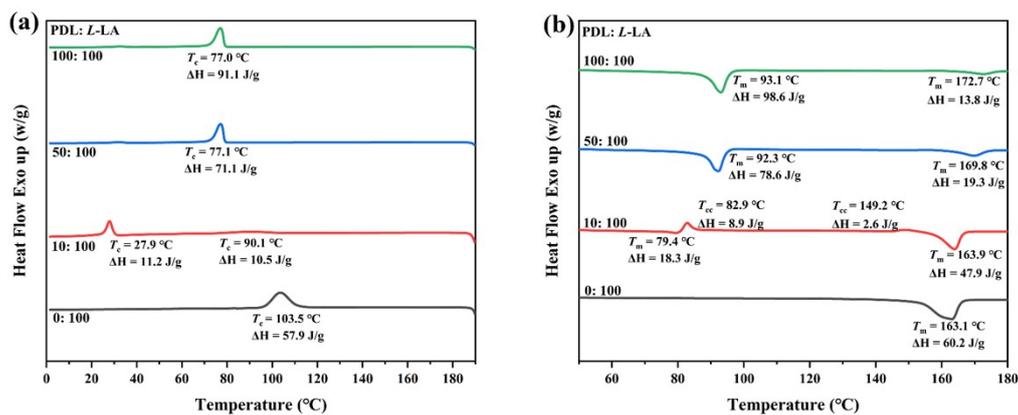
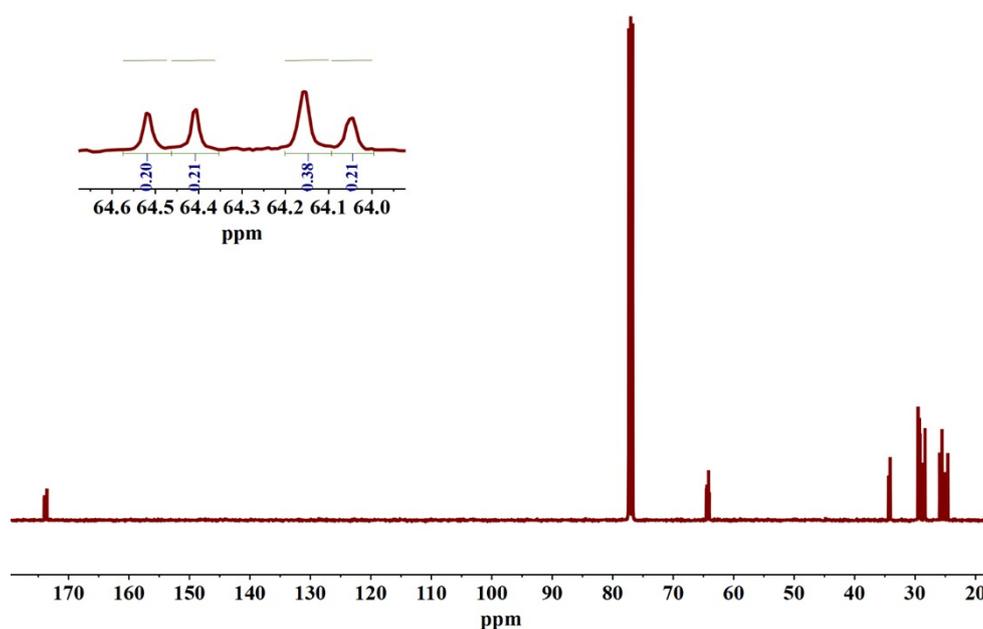


Fig. S13 DSC thermograms of (a) the first cooling run and (b) the second heating run for different  $[\text{PDL}]_0/[\text{L-LA}]_0$ :  $[\text{PDL}]_0: [\text{L-LA}]_0 = 100: 100$  (Table S3, run 4);  $[\text{PDL}]_0: [\text{L-LA}]_0 = 50: 100$  (Table S3, run 3);  $[\text{PDL}]_0: [\text{L-LA}]_0 = 10: 100$  (Table S3, run 2); neat PLLA (Table S3, run 1).

**Table S4** Copolymerization of DDL or PDL with CL catalyzed by MeAl(BHT)<sub>2</sub><sup>a</sup>

Run	[ML] <sub>0</sub> /[CL] <sub>0</sub> /[I] <sub>0</sub> /[C] <sub>0</sub>	Time (min)	Conv. <sup>b</sup> (%)	M <sub>n,theo</sub> (kDa)	M <sub>n,GPC</sub> <sup>c</sup> (kDa)	D <sup>c</sup>
1 <sup>d</sup>	10/100/1/1/1 (CL + DDL)	10+30	96	3.0	28.8	1.51
2 <sup>d</sup>	50/100/1/1/1 (CL + DDL)	10+120	97	20.8	29.1	1.55
3 <sup>d</sup>	100/100/1/1/1 (CL + DDL)	10+240	81	25.4	57.0	1.78
4 <sup>d</sup>	10/100/1/1/1 (DDL + CL)	30+10	98	13.2	30.6	3.3
5 <sup>d</sup>	50/100/1/1/1 (DDL + CL)	120+30	96	20.6	32.1	2.09
6 <sup>e</sup>	0/100/1/1	30	96	11.0	26.7	1.51
7 <sup>e</sup>	10/100/1/1/1 (one-pot)	60	93	12.9	23.1	1.71
8 <sup>e</sup>	50/100/1/1/1 (one-pot)	180	89	20.9	29.4	1.71
9 <sup>e</sup>	100/100/1/1/1 (one-pot)	360	88	31.3	53.8	1.50
10 <sup>f</sup>	10/100/1/1/1 (CL + PDL)	30+60	88	12.3	20.8	1.78
11 <sup>f</sup>	50/100/1/1/1 (CL + PDL)	30+180	84	19.8	29.6	1.72
12 <sup>f</sup>	100/100/1/1/1 (CL + PDL)	30+360	83	29.5	46.9	1.64
13 <sup>f</sup>	10/100/1/1/1 (PDL + CL)	60+30	96	13.4	23.0	1.81
14 <sup>f</sup>	50/100/1/1/1 (PDL + CL)	180+120	98	23.0	28.2	1.98
15 <sup>d, g</sup>	100/100/1/1/1 (DDL + CL)	240+60	98	30.7	29.7	1.73
16 <sup>d, h</sup>	100/100/1/1/1 (DDL + CL)	240+60	97	30.4	35.7	2.34

<sup>a</sup> Conditions: [M]<sub>0</sub> = [ML]<sub>0</sub> + [CL]<sub>0</sub>, the solvent was toluene. <sup>b</sup> Total conversion of ML and CL determined by <sup>1</sup>H NMR. <sup>c</sup> Determined by GPC at 40 °C in chloroform relative to polystyrene standards. <sup>d</sup> Sequential addition of DDL and CL, [M]<sub>0</sub> = 4.4 mol L<sup>-1</sup>; T = 130 °C. <sup>e</sup> The ML was PDL, one-pot addition of PDL and CL, [M]<sub>0</sub> = 2.0 mol L<sup>-1</sup>; T = 100 °C. <sup>f</sup> The ML was PDL, sequential addition of PDL and CL, [M]<sub>0</sub> = 2.0 mol L<sup>-1</sup>; T = 100 °C. <sup>g</sup> The catalyst was MeAl[salen]. <sup>h</sup> The catalyst was ZnEt<sub>2</sub>.

**Fig. S14** Quantitative <sup>13</sup>C NMR spectrum of PDDL-*ran*-PCL copolyester obtained in Table 3, run 4.

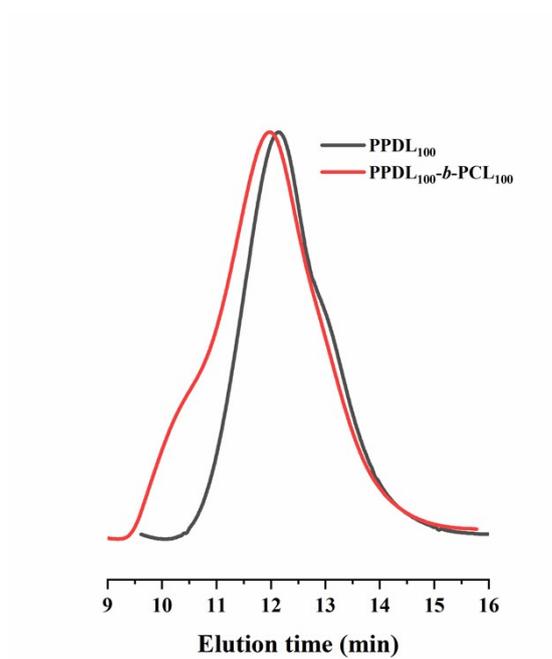


Fig. S15 GPC curves of PPDL (Table 1, run 15) and copolyesters (Table 3, run 6).

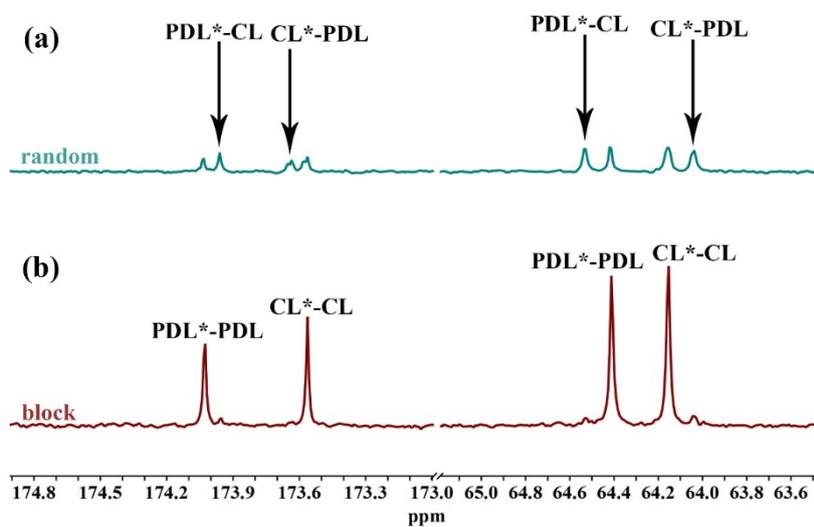
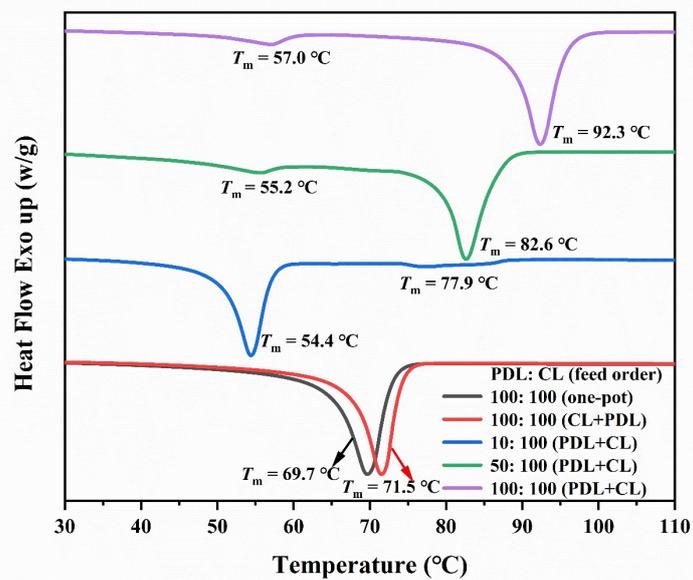
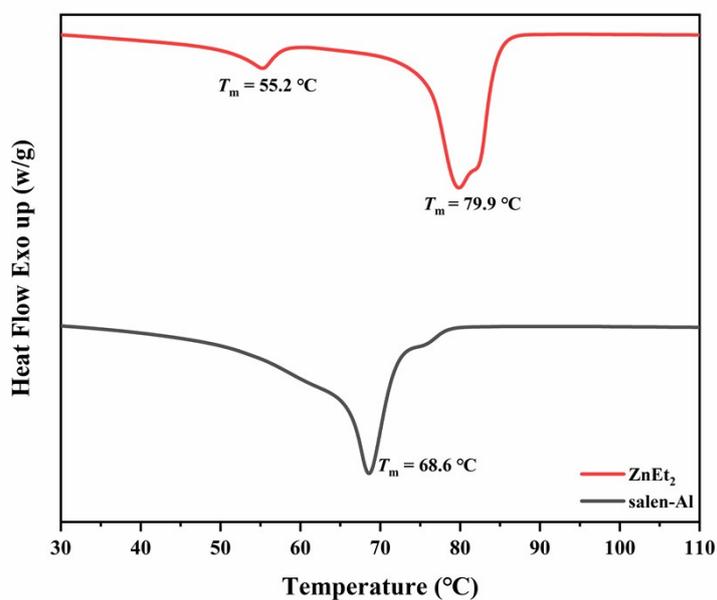


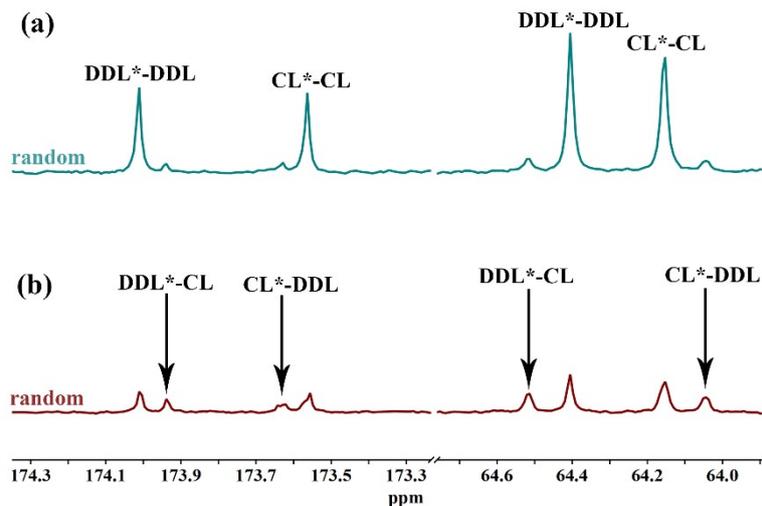
Fig. S16  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  of (a) the random copolyester PPDL-*ran*-PCL (Table S4, run 12) and (b) the block copolyester PPDL-*b*-PCL (Table 3, run 6).



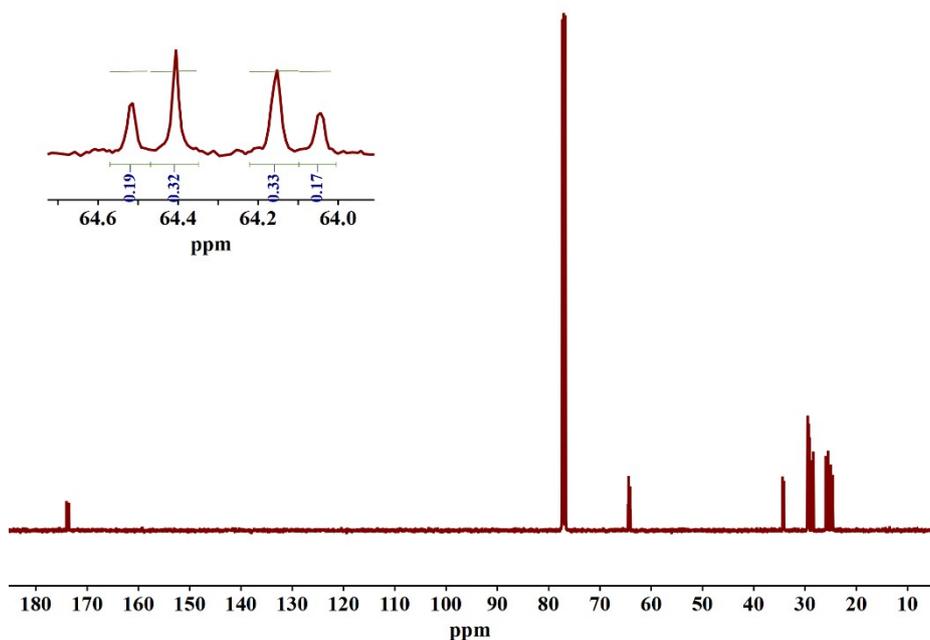
**Fig. S17** DSC thermograms of the second heating run for copolyester of PDL/CL: PPDL-*ran*-PCL (black spectrum, Table S4, run 9); PPDL-*ran*-PCL (red spectrum, Table S4, run 12); PPDL-*ran*-PCL (blue spectrum, Table S4, run 13); PPDL-*ran*-PCL (green spectrum, Table S4, run 14); PPDL-*b*-PCL (purple spectrum, Table 3, run 6).



**Fig. S18** DSC thermograms of the second heating run for copolyester of DDL/CL: PDDL-*ran*-PCL (black spectrum, Table S4, run 15); PDDL-*ran*-PCL (red spectrum, Table S4, run 16).



**Fig. S19**  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  of (a) the random copolyester PDDL-*ran*-PCL (Table S4, run 16) and (b) the random copolyester PDDL-*ran*-PCL (Table S4, run 15).



**Fig. S20** Quantitative  $^{13}\text{C}$  NMR spectrum of PDDL-*ran*-PCL copolyester obtained in Table S4, run 15.

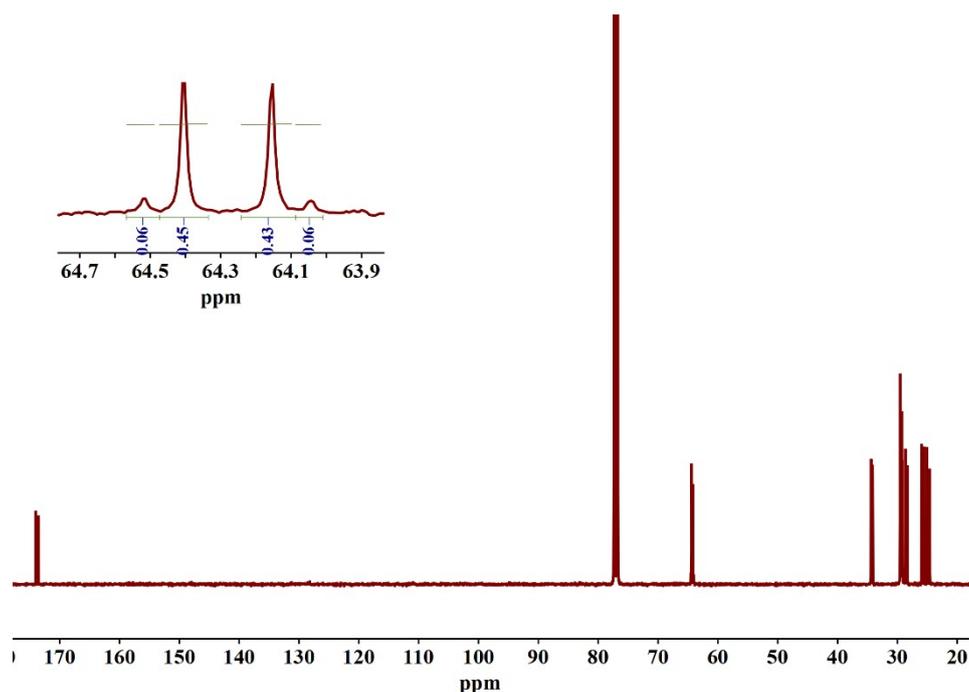


Fig. S21 Quantitative  $^{13}\text{C}$  NMR spectrum of PDDL-*ran*-PCL copolyester obtained in Table S4, run 16.

Table S5 Copolymerization of DDL or PDL with VL catalyzed by  $\text{MeAl}(\text{BHT})_2$ <sup>a</sup>

Run	$[\text{ML}]_0/[\text{VL}]_0/[\text{I}]_0/[\text{C}]_0$	Time (min)	Conv. <sup>b</sup> (%)	$M_{n,\text{theo}}$ (kDa)	$M_{n,\text{GPC}}^c$ (kDa)	$\bar{D}^c$
1 <sup>d</sup>	10/100/1/1/1 (VL + DDL)	10+30	97	11.6	28.2	1.33
2 <sup>d</sup>	50/100/1/1/1 (VL + DDL)	10+120	95	19.0	27.8	1.50
3 <sup>d</sup>	100/100/1/1/1 (VL + DDL)	10+240	81	24.2	34.8	1.63
4 <sup>d</sup>	10/100/1/1/1 (DDL + VL)	30+10	92	11.1	20.1	2.32
5 <sup>d</sup>	50/100/1/1/1 (DDL + VL)	120+30	89	17.8	32.6	1.60
6 <sup>e</sup>	0/100/1/1	30	90	9.1	29.4	1.26
7 <sup>e</sup>	10/100/1/1/1 (one-pot)	60	97	12.1	27.1	1.38
8 <sup>e</sup>	50/100/1/1/1 (one-pot)	180	84	18.6	31.5	1.45
9 <sup>e</sup>	100/100/1/1/1 (one-pot)	360	85	29.0	48.6	1.56
10 <sup>f</sup>	10/100/1/1/1 (VL + PDL)	30+60	85	10.6	34.6	1.28
11 <sup>f</sup>	50/100/1/1/1 (VL + PDL)	30+180	77	17.0	37.3	1.51
12 <sup>f</sup>	100/100/1/1/1 (VL + PDL)	30+360	79	27.0	50.2	1.51
13 <sup>f</sup>	10/100/1/1/1 (PDL + VL)	60+30	95	11.9	22.7	1.61
14 <sup>f</sup>	50/100/1/1/1 (PDL + VL)	180+120	84	18.6	39.5	2.05

<sup>a</sup> Conditions:  $[\text{M}]_0 = [\text{ML}]_0 + [\text{VL}]_0$ , the solvent was toluene. <sup>b</sup> Total conversion of ML and VL determined by  $^1\text{H}$  NMR. <sup>c</sup> Determined by GPC at 40 °C in chloroform relative to polystyrene standards. <sup>d</sup> Sequential addition of DDL and VL,  $[\text{M}]_0 = 4.4 \text{ mol L}^{-1}$ ;  $T = 130 \text{ }^\circ\text{C}$ . <sup>e</sup> The ML was PDL, one-pot addition of PDL and VL,  $[\text{M}]_0 = 2.0 \text{ mol L}^{-1}$ ;  $T = 100 \text{ }^\circ\text{C}$ . <sup>f</sup> The ML was PDL, sequential addition of PDL and VL,  $[\text{M}]_0 = 2.0 \text{ mol L}^{-1}$ ;  $T = 100 \text{ }^\circ\text{C}$ .

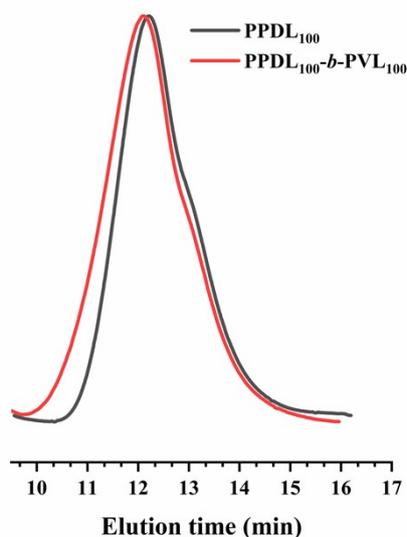


Fig. S22 GPC curves of PPDL ( $[M]_0 = 2.0 \text{ mol L}^{-1}$ ;  $T = 100 \text{ }^\circ\text{C}$ ,  $M_n = 42.8 \text{ kDa}$ ,  $D = 1.57$ ) and copolyesters PPDL-*b*-PVL (Table 4, run 6).

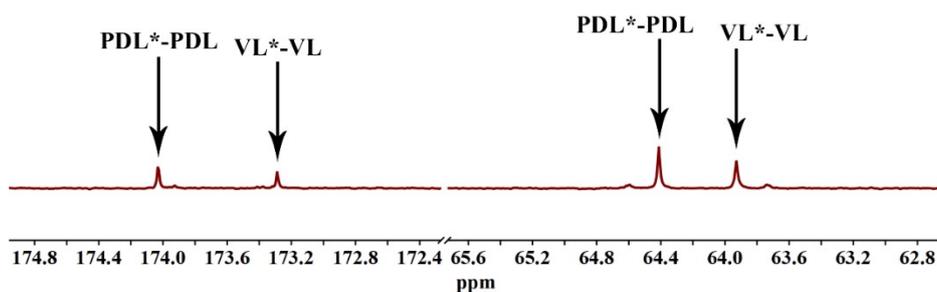


Fig. S23  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  of the block copolyester PPDL-*b*-PVL (Table 4, run 6).

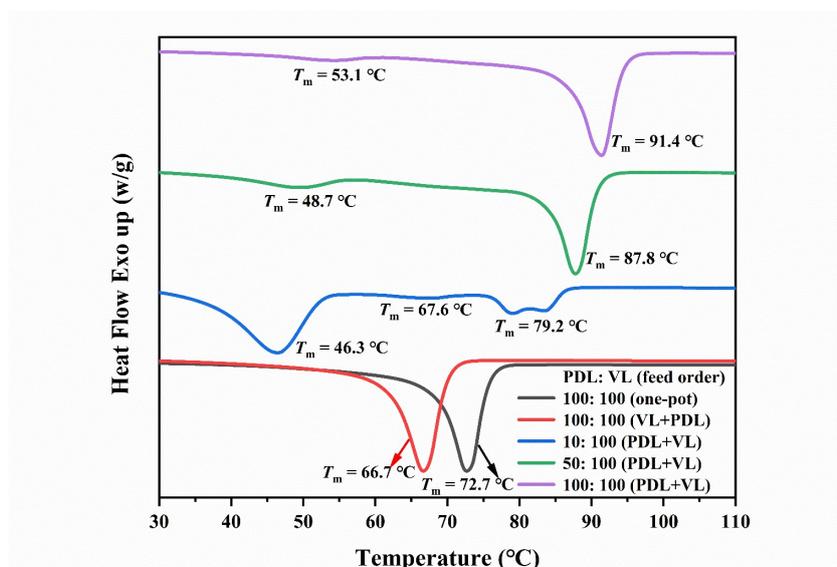
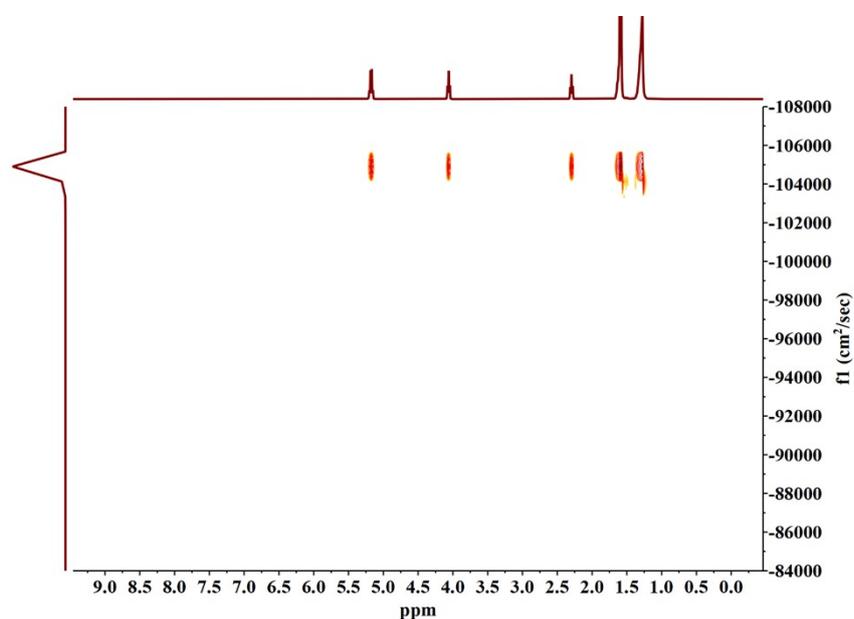


Fig. S24 DSC thermograms of the second heating run for copolyester of PDL/VL: PPDL-*ran*-PVL (black spectrum, Table S5, run 9); PPDL-*ran*-PVL (red spectrum, Table S5, run 12); PPDL-*ran*-PVL (blue spectrum, Table S5, run 13); PPDL-*ran*-PVL (green spectrum, Table S5, run 14); PPDL-*b*-PVL (purple spectrum, Table 4, run 6).

**Table S6** Copolymerization of MLs/SLs catalyzed by MeAl(BHT)<sub>2</sub><sup>a</sup>

Run	MLs/SLs/I/C	Copolyester composition MLs/SLs (mol%) <sup>f</sup>	Diads <sup>g</sup>			
			ML*ML	ML*SL	SL*ML	SL*SL
1 <sup>b</sup>	100/100/1/1 (one-pot DDL/CL)	41/59	0.21	0.20	0.21	0.38
2 <sup>b</sup>	100/100/1/1 (DDL + CL)	44/56	0.48	-	-	0.52
3 <sup>c</sup>	100/100/1/1 (CL + PDL)	44/56	0.23	0.23	0.25	0.30
4 <sup>c</sup>	100/100/1/1 (PDL + CL)	56/44	0.50	-	-	0.50
5 <sup>d</sup>	100/100/1/1 (VL + DDL)	43/57	0.24	0.22	0.24	0.30
6 <sup>d</sup>	100/100/1/1 (DDL + VL)	57/43	0.63	-	-	0.37
7 <sup>e</sup>	50/100/1/1 (PDL + VL)	38/62	0.31	0.08	0.09	0.52
8 <sup>e</sup>	100/100/1/1 (PDL + VL)	54/46	0.58	-	-	0.42

<sup>a</sup> Conditions: MLs/SLs/I/C = macrolactones/small-ring lactones/initiator/MeAl(BHT)<sub>2</sub>. <sup>b</sup> Sequential addition of DDL and CL, [M]<sub>0</sub> = 4.4 mol L<sup>-1</sup>; T = 130 °C. <sup>c</sup> The ML was PDL, sequential addition of PDL and CL, [M]<sub>0</sub> = 2.0 mol L<sup>-1</sup>; T = 100 °C. <sup>d</sup> Sequential addition of DDL and VL, [M]<sub>0</sub> = 4.4 mol L<sup>-1</sup>; T = 130 °C. <sup>e</sup> The ML was PDL, sequential addition of PDL and VL, [M]<sub>0</sub> = 2.0 mol L<sup>-1</sup>; T = 100 °C. <sup>f</sup> Determined by <sup>1</sup>H NMR of the resulting polymers. <sup>g</sup> Determined by quantitative <sup>13</sup>C NMR of the resulting polymers.

**Fig. S25** Typical DOSY NMR spectrum of a PDDL-*b*-PLLA diblock copolymer in CDCl<sub>3</sub> (Table 2, run 4).

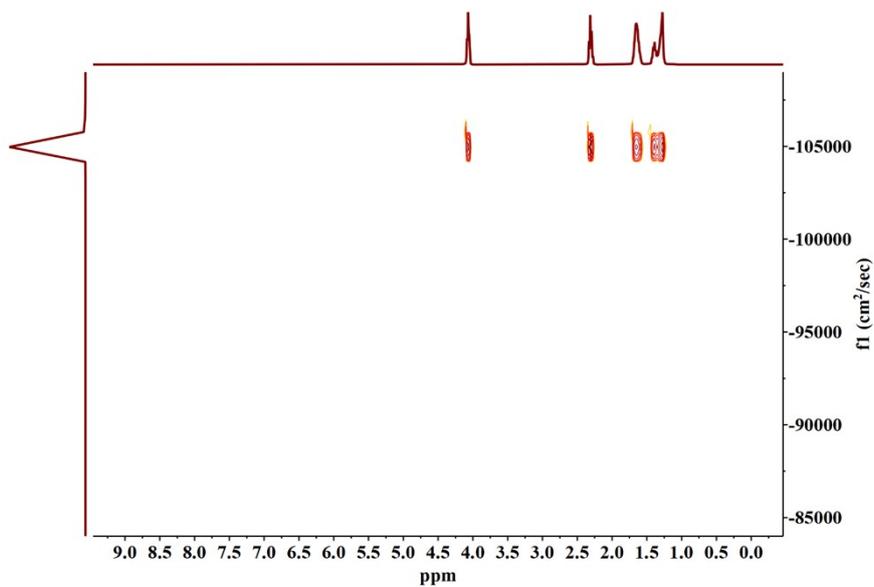


Fig. S26 Typical DOSY NMR spectrum of a PDDL-*b*-PCL diblock copolymer in CDCl<sub>3</sub> (Table 3, run 5).

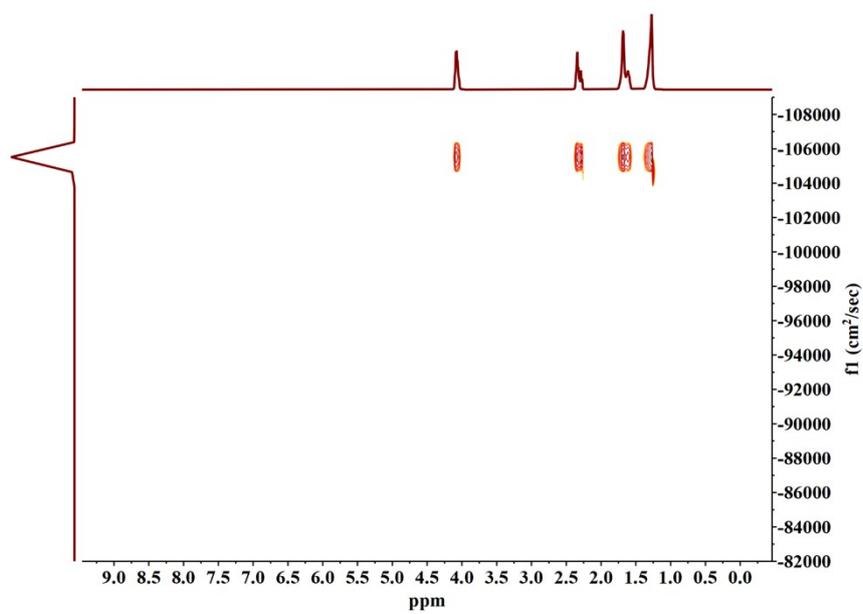


Fig. S27 Typical DOSY NMR spectrum of a PDDL-*b*-PVL diblock copolymer in CDCl<sub>3</sub> (Table 4, run 5).

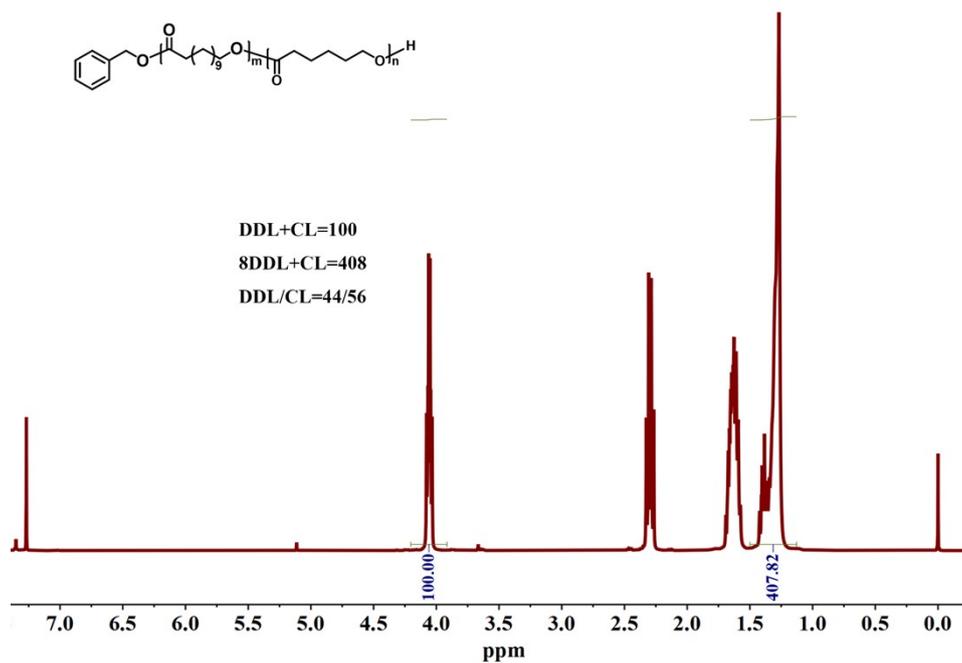


Fig. S28  $^1\text{H}$  NMR spectrum of PDDL-*b*-PCL copolyester obtained in Table 3, run 5 (Table S6, run 2).

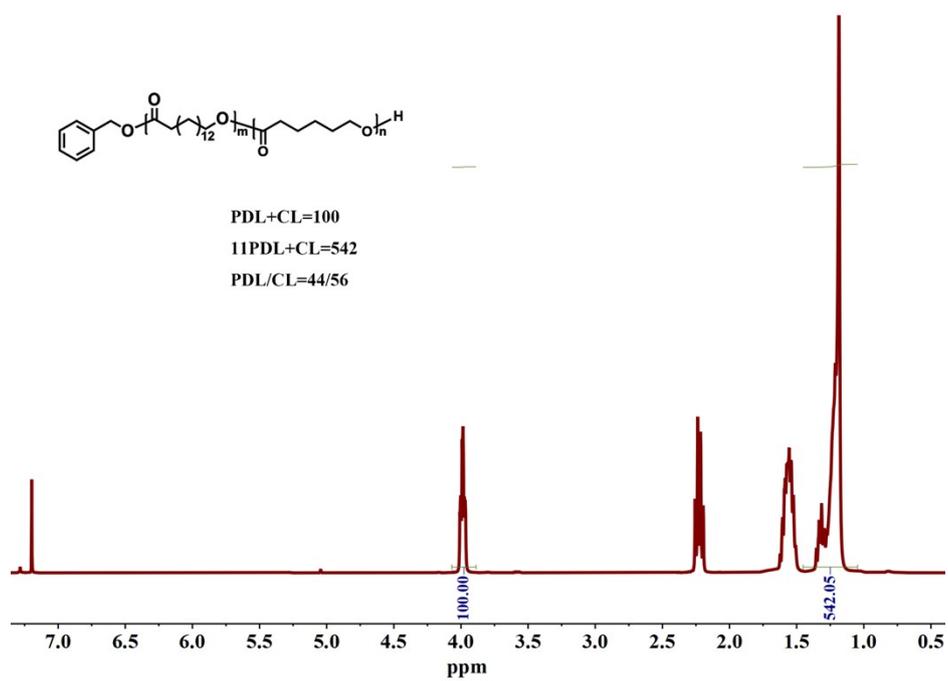


Fig. S29  $^1\text{H}$  NMR spectrum of PPDL-*b*-PCL copolyester obtained in Table S4, run 12 (Table S6, run 3).

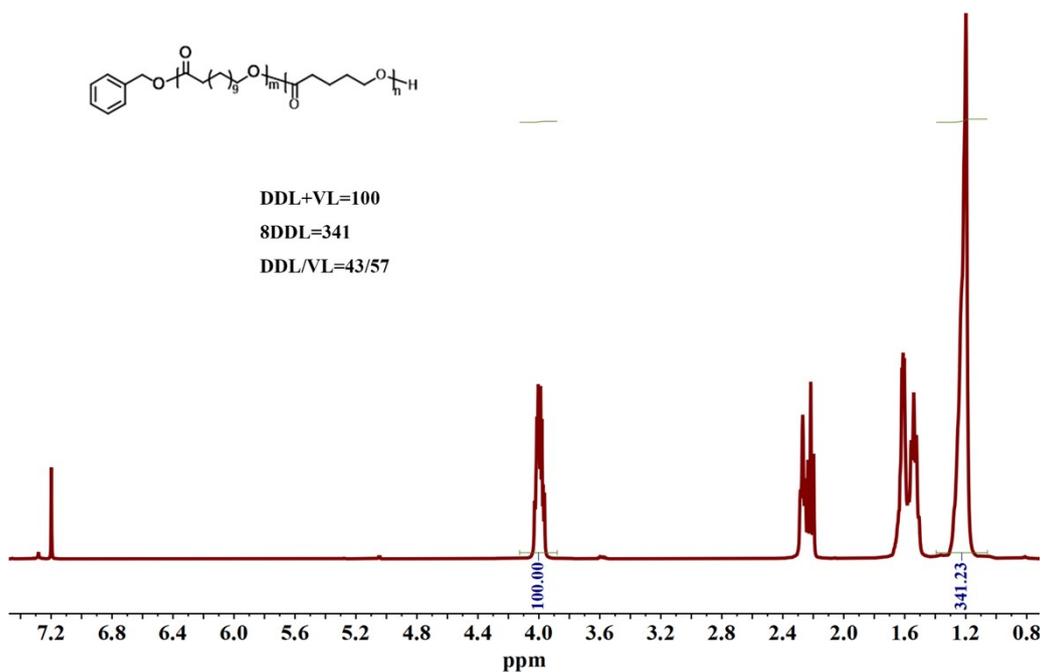


Fig. S30  $^1\text{H}$  NMR spectrum of PDDL-*b*-PVL copolyester obtained in Table S5, run 3 (Table S6, run 5).

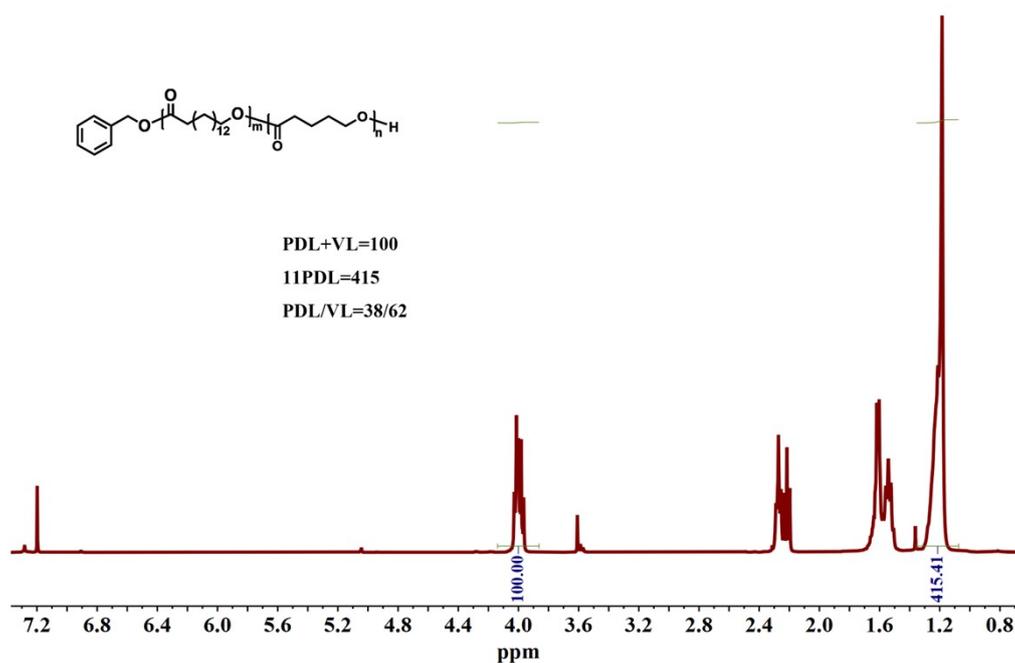


Fig. S31  $^1\text{H}$  NMR spectrum of PPDL-*b*-PVL copolyester obtained in Table S5, run 14 (Table S6, run 7).

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