Supplementary Information

Facile synthesis of eight-membered cyclic(ester-amide)s and their organocatalytic ring-opening polymerizations

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Preparation and characterization of M1–M6

Phthalic anhydride (PA, 1 equiv) was dissolved in DMF (1 M), and the solution was cooled to 0 °C in an ice bath. β-Amino alcohol (1 equiv) was added into the above solution dropwise, and the mixture was stirred at room temperature for 10 min. After DMF was removed by evaporation, the remaining residue was used directly in next step.

Monomer precursor solution (1 equiv) was dissolved in anhydrous THF to achieve a concentration of ~0.04 M. Then, BOP reagent (1.1 equiv) and Et_3N (1.5 equiv) were added into the solution. The reaction was stirred at room temperature for 2 h. After THF was removed by evaporation, the remaining residue was dissolved in ethyl acetate. The solution was washed successively with 10% citric acid solutions, saturated $NaHCO_3$ solution, saturated saline solution, and H_2O. The organic phase was collected, dried with anhydrous $MgSO_4$, and concentrated to remove the solvent under reduced pressure. The crude product was further purified by silica gel chromatography. The melting temperature (T_m) of these monomers was measured by DSC.

M1: The crude compound was purified by silica gel chromatography (EtOAc/PE = 1/1, v/v) and recrystallized from ethyl acetate to afford **M1** as a white solid. Yield: 56%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70-7.60 (m, 2H), 7.56-7.46 (m, 2H), 4.20-3.98 (m, 2H), 3.82-3.64 (m, 2H), 3.48-3.34 (m, 1H), 2.15-2.01 (m, 1H), 1.96-1.71 (m, 3H); ^{13}C NMR (101 MHz,

DMSO-d_6) δ 171.07, 167.34, 134.80, 131.89, 131.08, 129.71, 128.43, 127.77, 69.54, 56.80, 47.91, 32.55, 21.86；FT-MS (ESI, *m/z*): Calculated for $C_{13}H_{14}NO_3$ [(*M*+H)$^+$]: 232.0965, found: 232.0968. T_m = 129.5 °C.

M2: The crude compound was purified by silica gel chromatography (DCM/PE /EtOAc = 3/3/1, v/v/v) to afford **M2** as a white solid. Yield: 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.52 (m, 4H), 4.45-4.33 (m, 1H), 4.17-4.06 (m, 1H), 3.66 (m, *J* = 15.9, 9.5, 6.4 Hz, 1H), 3.30 (m, *J* = 15.4, 6.9, 3.4 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.52, 169.95, 135.77, 132.90, 130.28, 130.10, 129.54, 128.49, 64.67, 48.45, 34.76. FT-MS (ESI, *m/z*): Calculated for $C_{11}H_{12}NO_3$ [(*M*+H)$^+$]: 206.0815, found: 206.0811. T_m = 104.8 °C.

M3: The crude compound was purified by silica gel chromatography (MeOH/DCM = 10/1, v/v) to afford **M3** as a white solid. Yield: 22%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (m, 2H), 7.57-7.49 (m, 2H), 4.34 (m, 1H), 4.06 (m, 1H), 3.64 (m, *J* = 7.2, 4.0 Hz, 2H), 3.59-3.50 (m, 1H), 3.35 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.02, 169.82, 135.65, 132.52, 130.23, 130.10, 129.11, 128.12, 64.76, 46.00, 42.36, 13.16. FT-MS (ESI, *m/z*): Calculated for $C_{12}H_{14}NO_3$ [(*M*+H)$^+$]: 220.0974, found: 220.0968. T_m = 128.7 °C.

M4: The crude compound was purified by silica gel chromatography (DCM/EA = 10/1, v/v) to afford **M4** as a white solid. Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.49 (m, 4H), 4.34 (m, 1H), 4.06 (m, 1H), 3.68-3.47 (m, 3H), 3.34 (m, 1H), 1.65 (m, 2H), 1.48-1.36 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.04, 170.01, 135.83, 132.59, 130.17, 130.01, 129.18, 128.19, 64.79, 47.23, 46.35, 30.13, 20.15, 13.88. FT-MS (ESI, *m/z*): Calculated for $C_{14}H_{18}NO_3$ [(*M*+H)$^+$]: 248.1275, found: 248.1281. T_m = 56.0 °C.

M5: The crude compound was purified by silica gel chromatography (PE/EA = 1/1, v/v) and recrystallized from ethyl acetate to afford **M5** as a white solid. Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.53 (m, 4H), 7.39-7.31 (m, 5H), 5.06 (d, *J* = 14.7 Hz, 1H), 4.56 (d, *J* = 14.7 Hz, 1H), 4.12-3.95 (m, 2H), 3.47 (m, 1H), 3.27 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.54, 169.92, 136.33, 135.51, 132.78, 130.39, 130.06, 129.47, 128.90, 128.54, 128.02, 64.71, 50.15, 45.30. FT-MS (ESI, *m/z*): Calculated for $C_{17}H_{16}NO_3$ [(*M*+H)$^+$]: 282.1116, found: 282.1124. T_m = 93.4 °C.

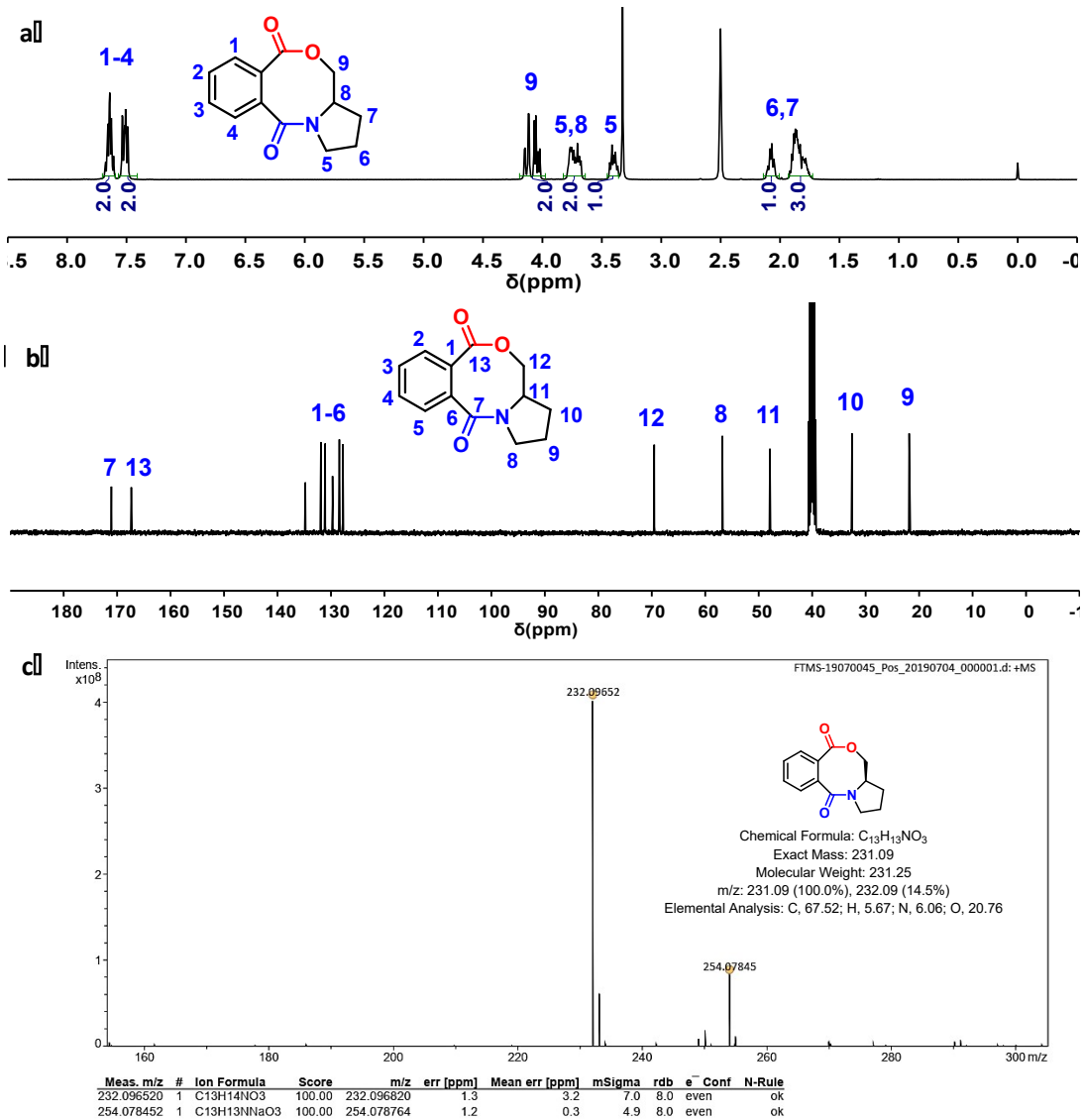

Fig. S1 (a) ^{1}H NMR, (b) ^{13}C NMR (DMSO-d_6), and (c) FT-MS spectra of **M1.**

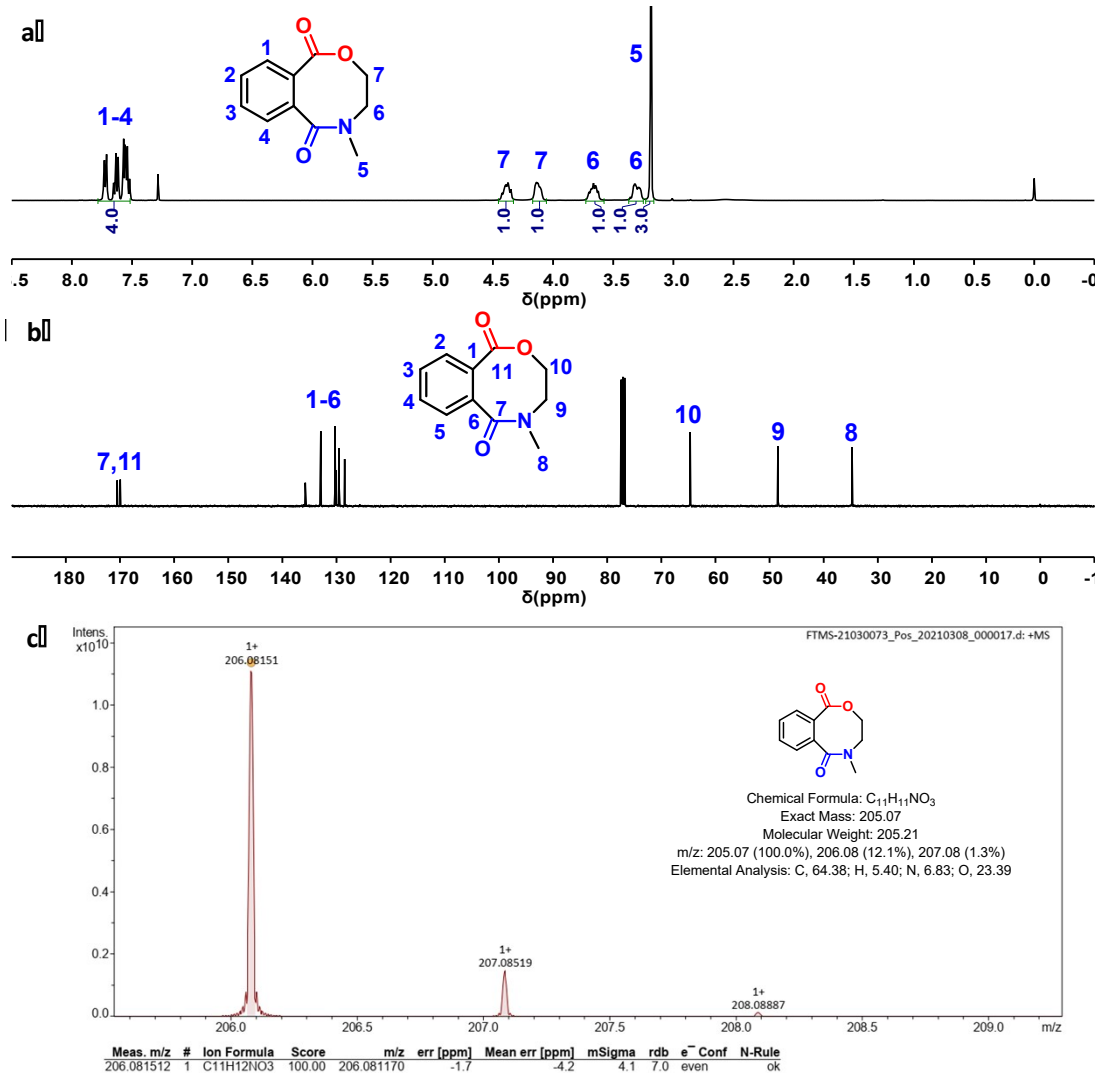

Fig. S2 (a) ^{1}H NMR, (b) ^{13}C NMR ($CDCl_3$), and (c) FT-MS spectra of **M2.**

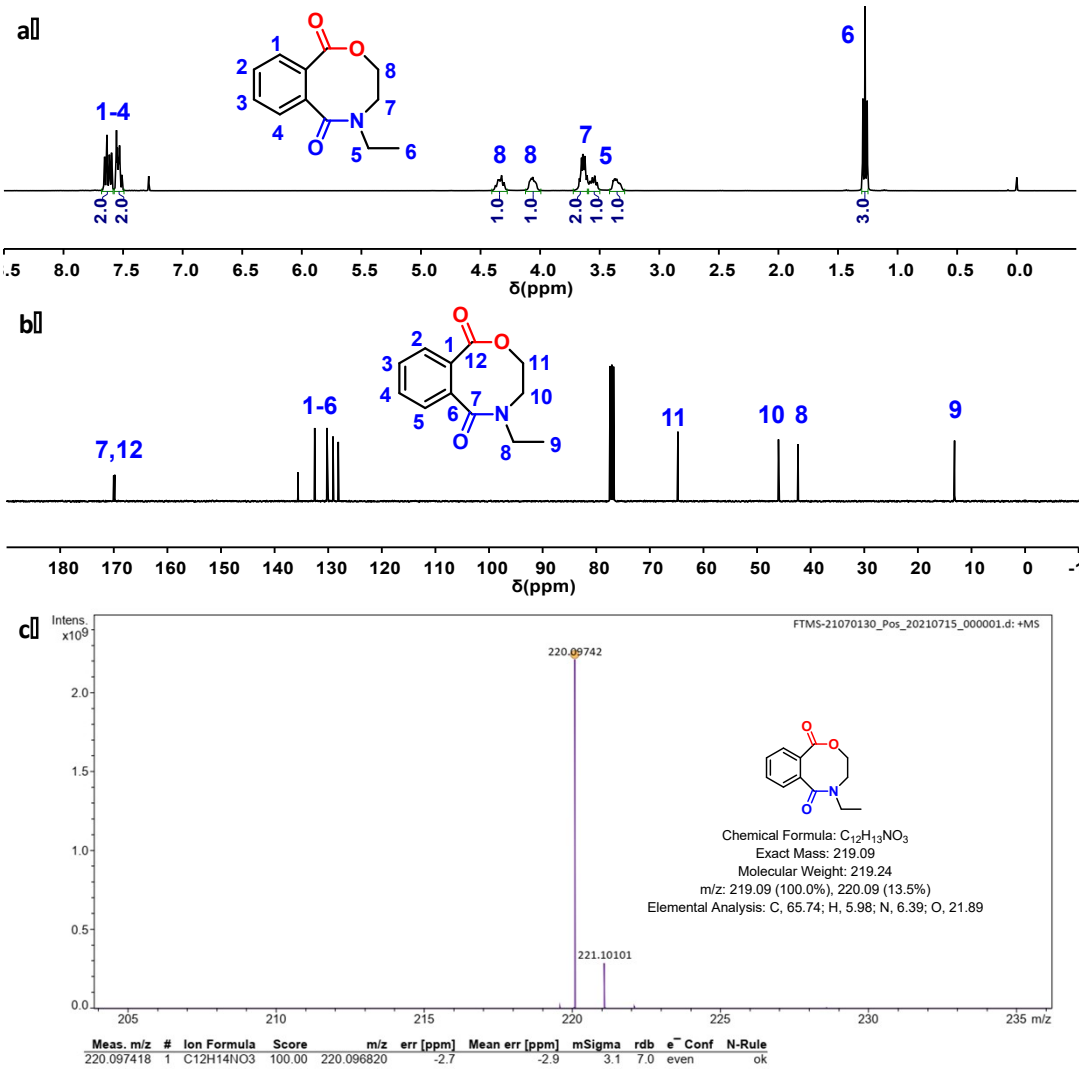

Fig. S3 (a) ^{1}H NMR, (b) ^{13}C NMR ($CDCl_3$), and (c) FT-MS spectra of **M3.**

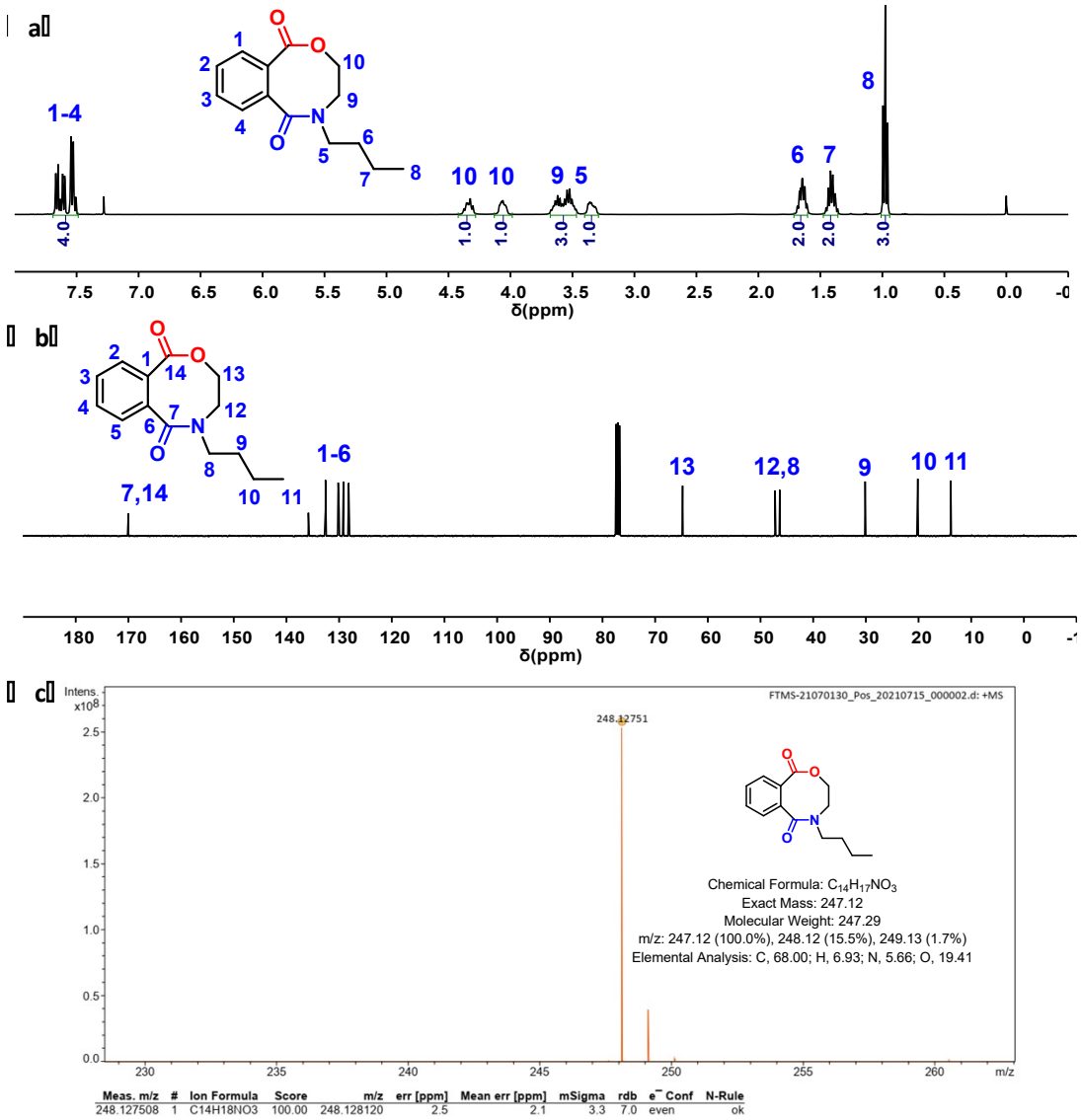

Fig. S4 (a) ^{1}H NMR, (b) ^{13}C NMR ($CDCl_3$), and (c) FT-MS spectra of **M4.**

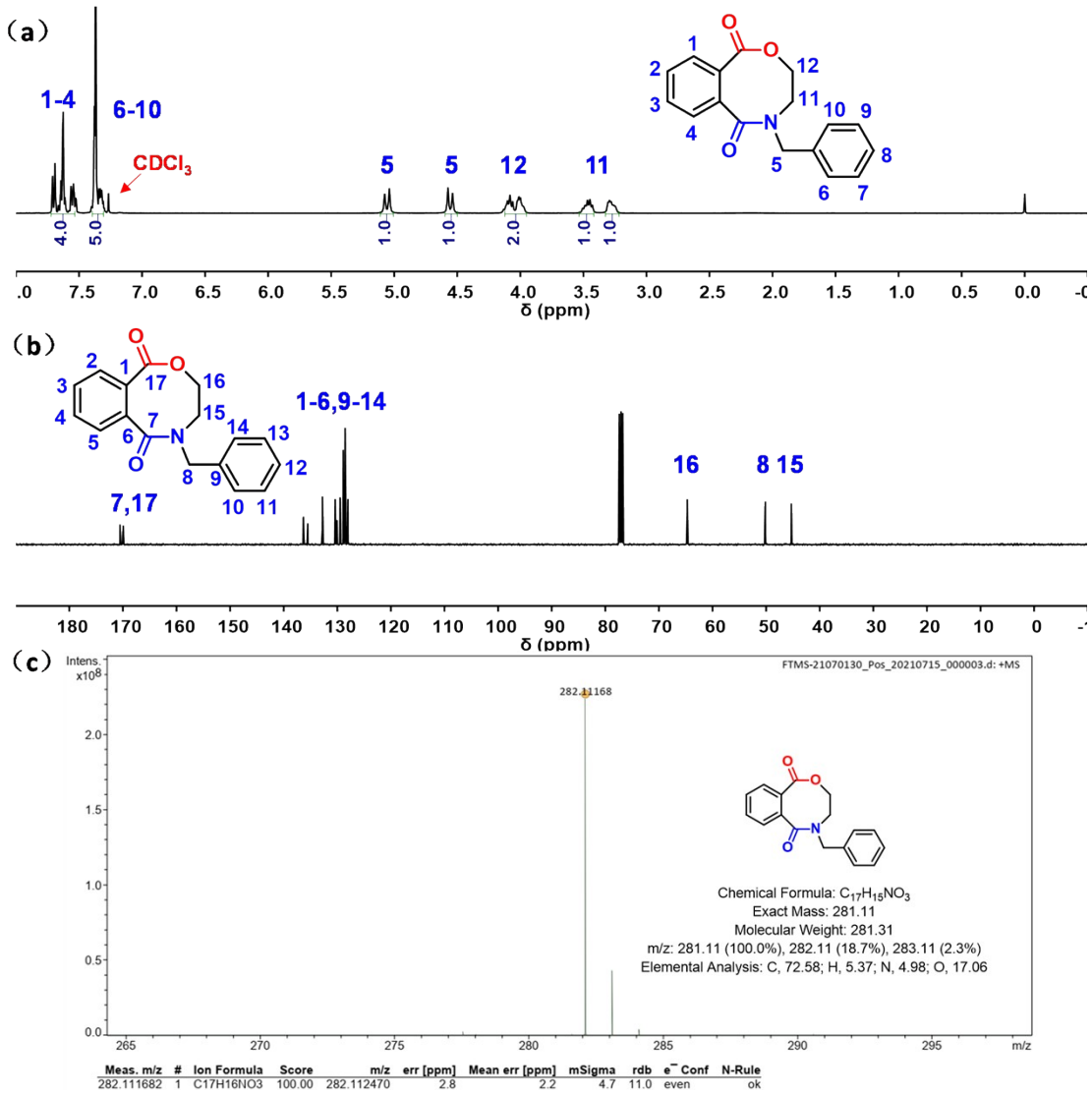

Fig. S5 (a) ^{1}H NMR, (b) ^{13}C NMR ($CDCl_3$), and (c) FT-MS spectra of **M5.**

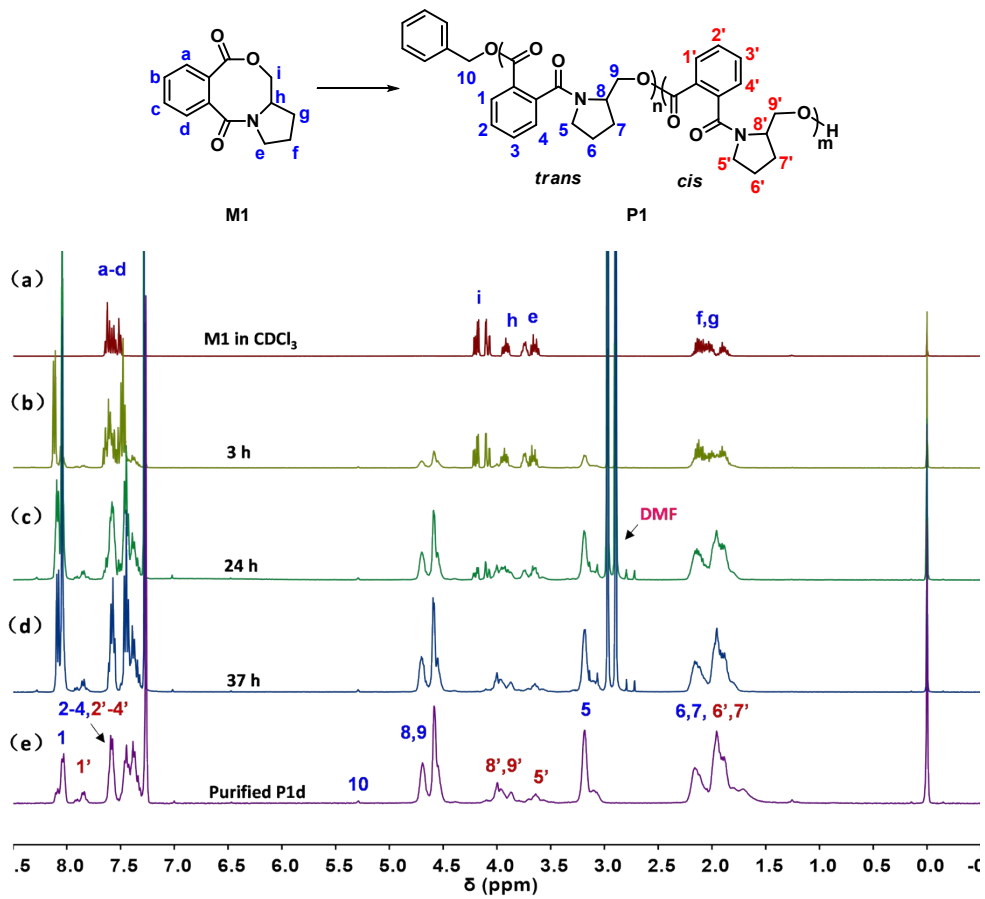

Fig. S6 Time-dependent ^{1}H NMR spectra of the samples taken out from the ROP mixture of **M1** (Table 1, for the preparation of **P1d**). Monomer conversion was determined by comparing the intensity of the peaks i (4.03-4.26 ppm) and that of the peaks 8 + 9 (4.43-4.81 ppm) and 1' (7.78-7.95 ppm). Conv.(%) = (1-I_i/(I_i + 2I_{8+9}/3 + 2$I_{1'}$)) x 100%. Degree of polymerization (DP) was calculated by comparing the peak intensities of three groups of protons: 1 + 1' (7.78-8.15 ppm), and 10 (5.27-5.31 ppm).

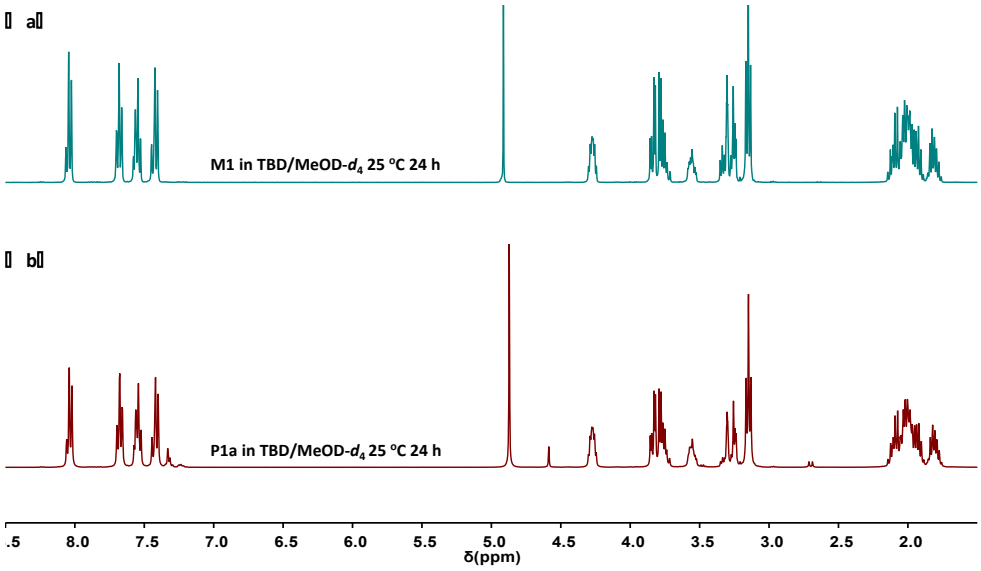

Fig. S7 ^{1}H NMR spectra of the alcoholysis products of (a) **M1** and (b) **P1a** in MeOD-d_4.

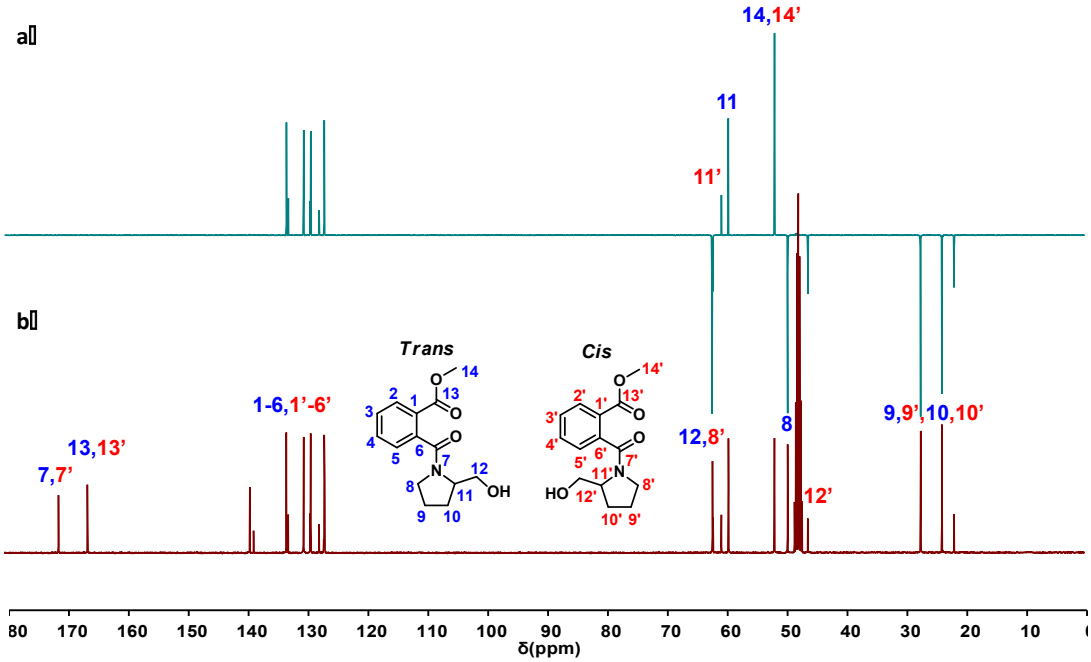

Fig. S8 (a) DEPT 135 ^{13}C NMR spectrum and (b) ^{13}C NMR spectrum of **D1** in MeOD-d_4.

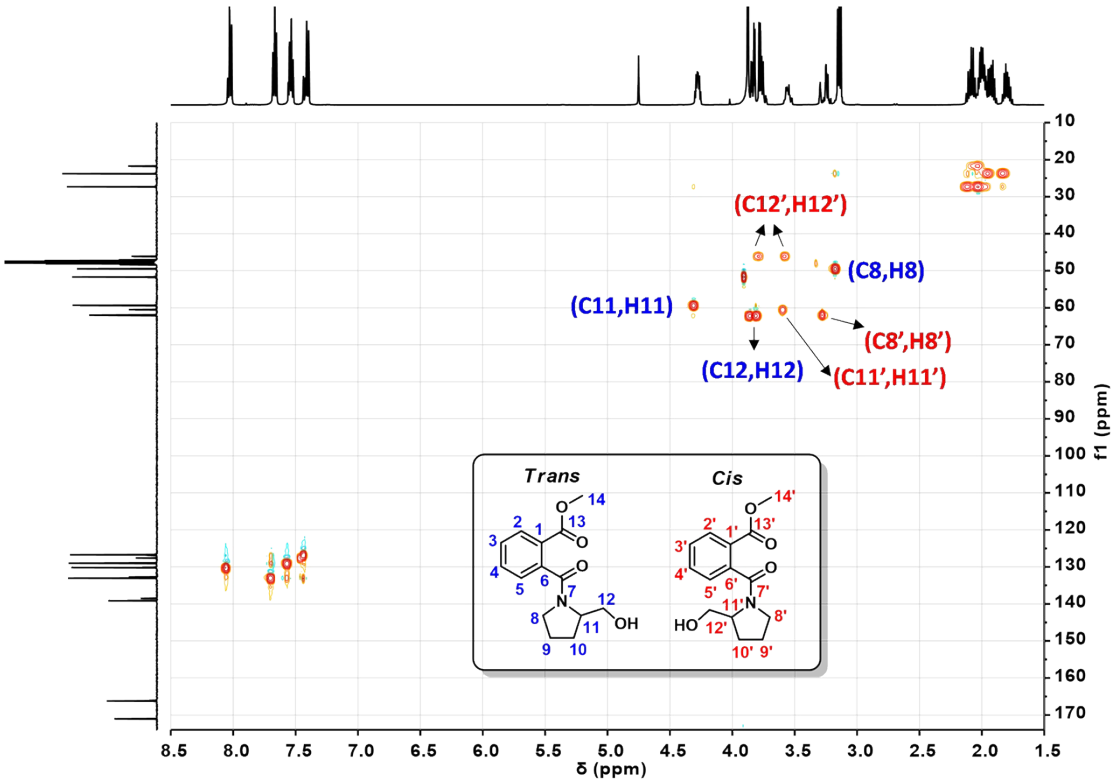

Fig. S9 ^{1}H-^{13}C HSQC NMR spectrum of the degradation product **D1** in MeOD-d_4.

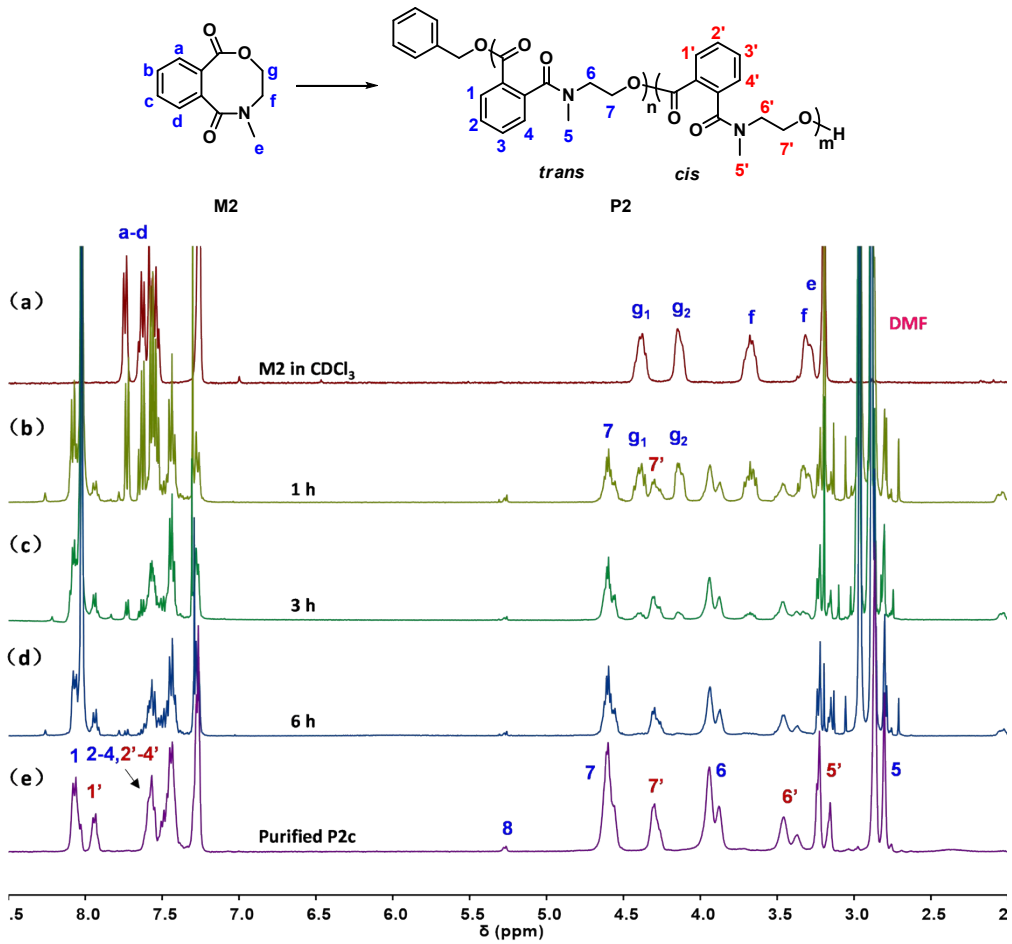

Fig. S10 Time-dependent ^{1}H NMR spectra of the samples taken out from the ROP mixture of **M2** (Table 2, for the preparation of **P2c**). Monomer conversion was determined by comparing the intensity of peaks g_1 +g_2 (4.30-4.47 ppm, 4.07-4.22 ppm) and that of the peaks 7 + 7' (4.48-4.72 ppm, 4.20-4.40 ppm), Conv.(%) = $I_{7+7'}/(I_{g1+g2} + I_{7+7'})$ x 100%. Degree of polymerization was calculated by comparing the peak intensities of three groups of protons: 1 + 1' (7.86-8.15 ppm), and 8 (5.25-5.31 ppm).

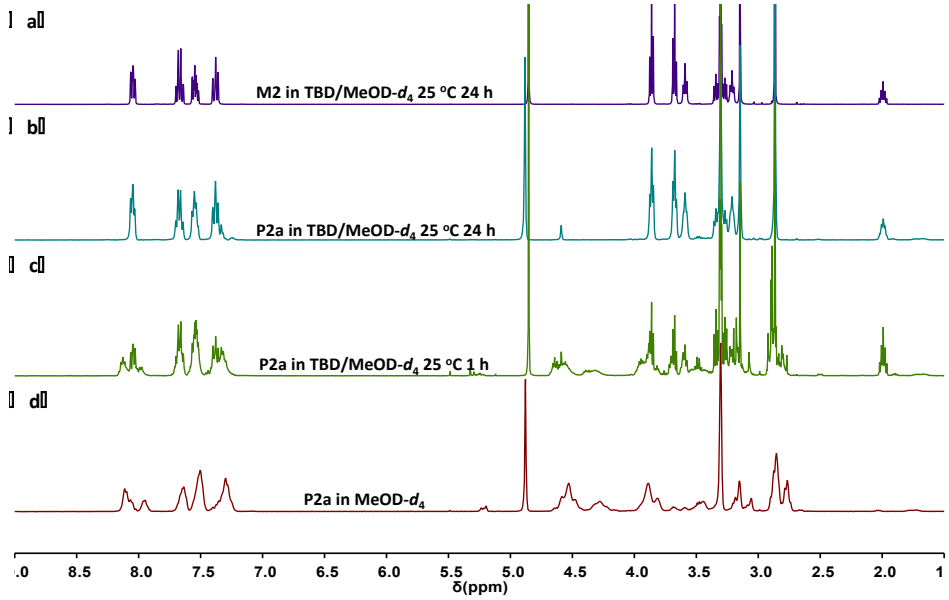

Fig. S11 ^{1}H NMR spectra of the alcoholysis products of (a) **M2** and (b-d) **P2a** in MeOD-d_4.

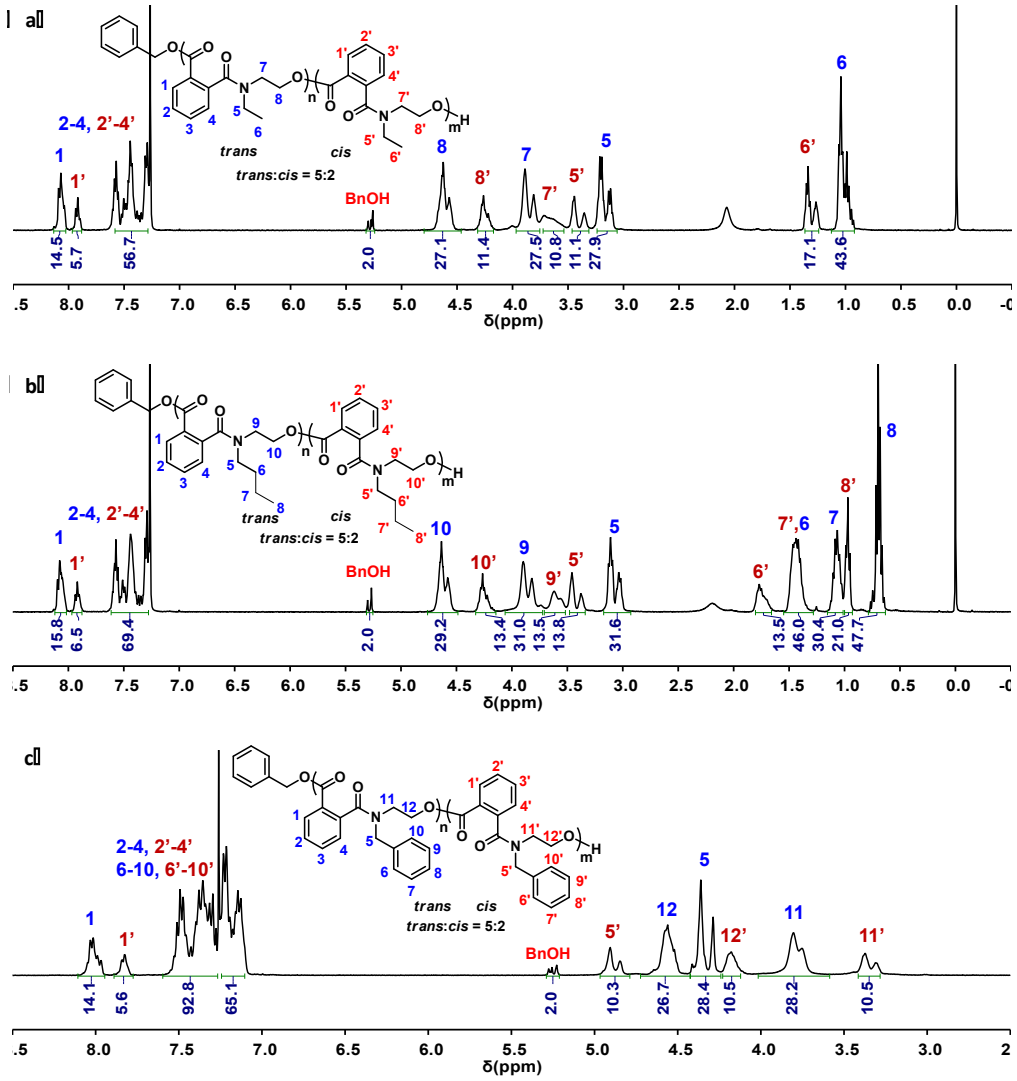

Fig. S12 ^{1}H NMR spectra of (a) **P3a**, (b) **P4a** and (c) **P5a**. The *trans* to *cis* ratio was calculated based on the intensity of peaks 1 and 1'.

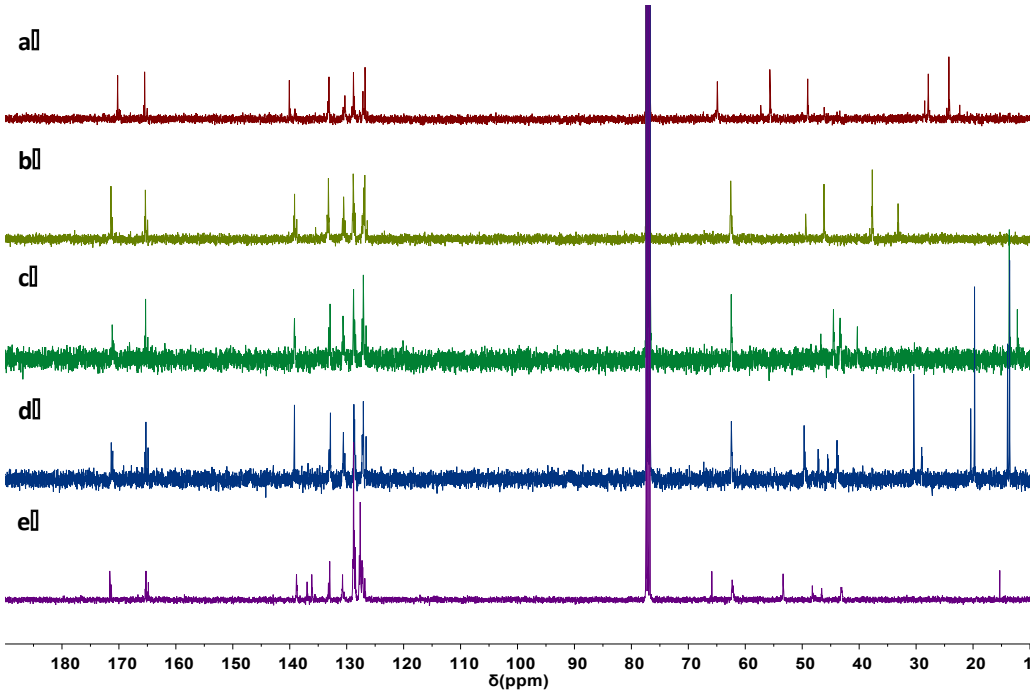

Fig. S13 ^{13}C NMR spectra of (a) **P1a**, (b) **P2a**, (c) **P3a**, (d) **P4a** and (e) **P5a**.

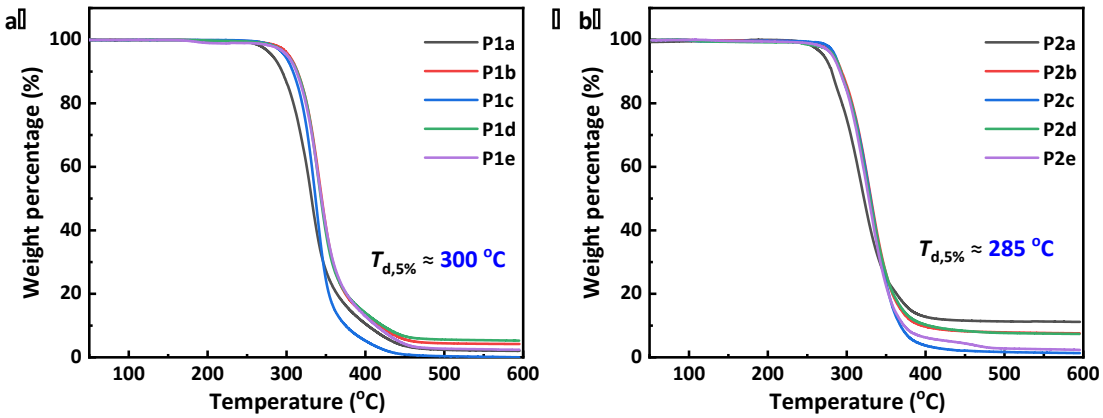

Fig. S14 TGA thermograms of (a) **P1** and (b) **P2** with different molar masses.

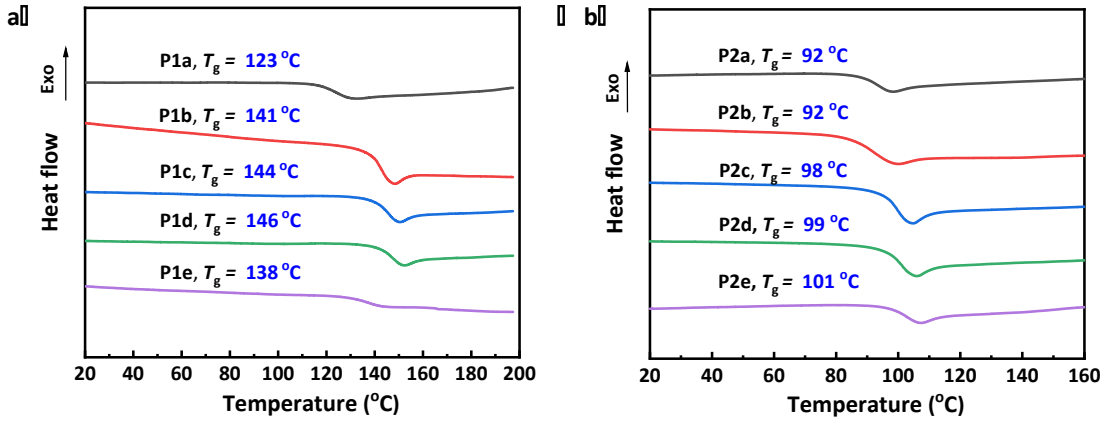

Fig. S15 DSC thermograms of (a) **P1** and (b) **P2** with different molar masses.

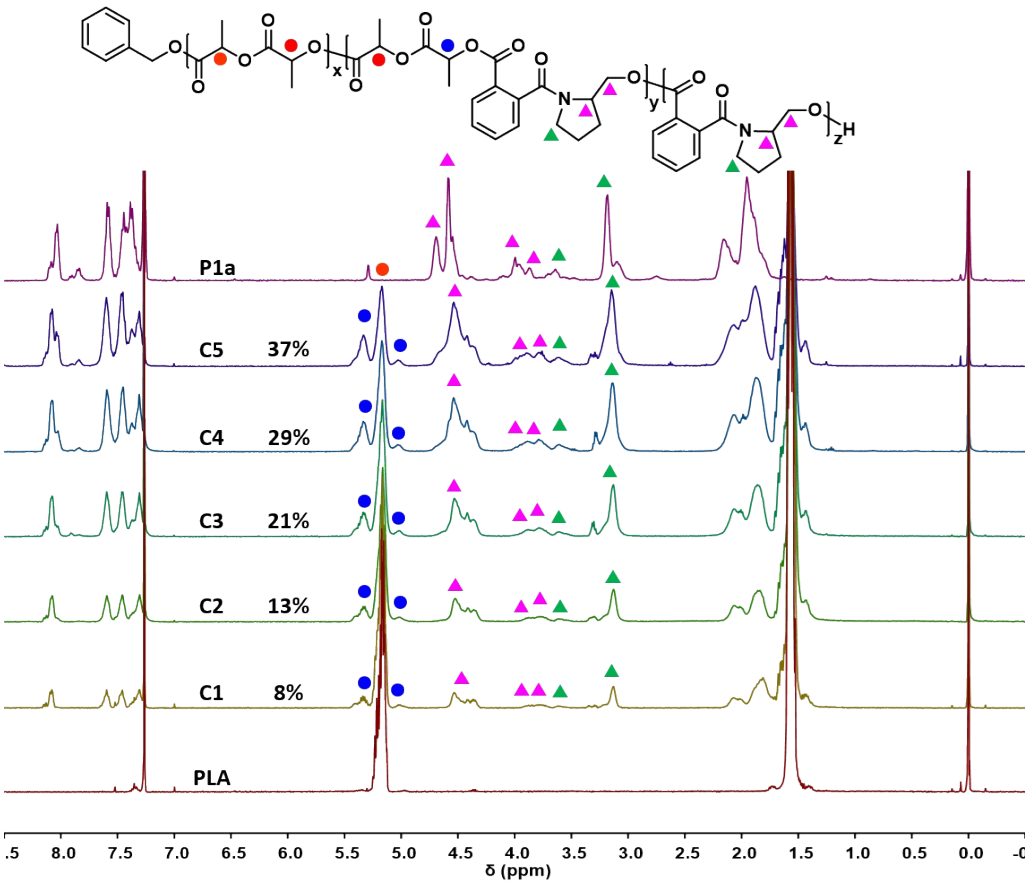

Fig. S16 ^{1}H NMR spectra of **P1a**, PLA, and copolymers **C1-C5**. Refer to Table 4 for the ROP conditions. The fraction of hetero-sequence of **M1**-LA diads was calculated by comparing the intensity of peaks **M1**-LA (blue dots) and that of the peak LA-LA (red dot).

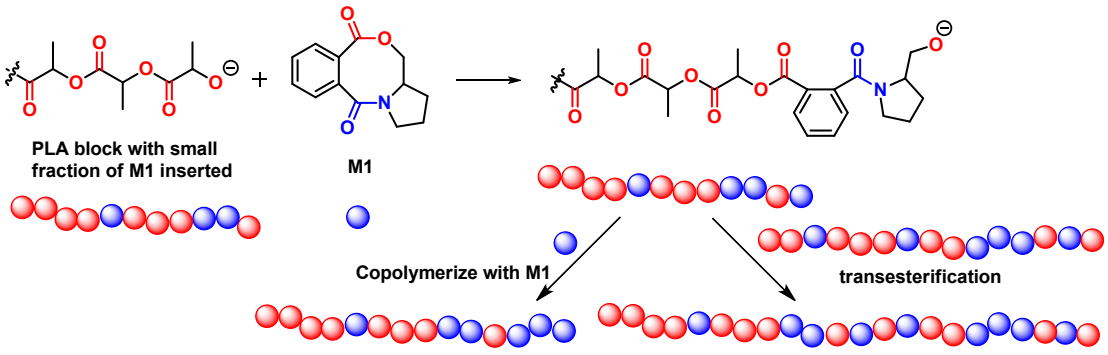

Fig. S17 Plausible copolymerization diagram of **M1** and LA.

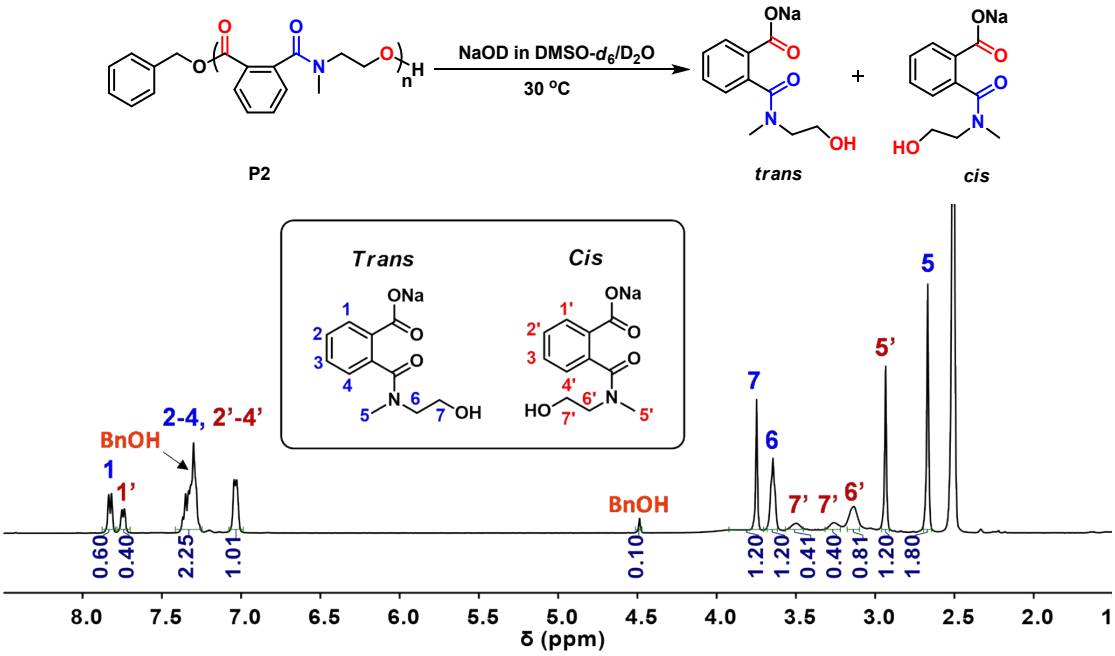

Fig. S18 ^{1}H NMR spectrum of the hydrolytic degradation product of **P2a** in D_2O/DMSO-d_6.

Table S1 TBD-catalyzed ROP of **M2**

Entry[a]	$[M]_0/[TBD]/[I]_0$	Time (h)	Conv.[b] (%)	Yield[c] (%)	$M_{n,calcd}$[d] (kDa)	$M_{n,SEC}$[e] (kDa)	$Đ$[e]
1	20:1:1	5 min	> 99	87	4.2	3.1	1.70
2	40:1:1	5 min	> 99	90	8.3	4.9	1.69
3	80:1:2	4	> 99	86	16.5	8.6	1.53
4	120:1:2	6	> 99	79	24.7	9.9	1.44
5	200:1:2	7	90	71	37.0	12.3	1.36

[a]All reactions were conducted in DMF ($[\mathbf{M2}]_0$ = 2.5 M) with BnOH as the initiator and TBD as the catalyst at 30 °C. [b] Determined by ^{1}H NMR. [c]Isolated yield. [d]$M_{n,calcd}$ = ($[\mathbf{M2}]_0/[BnOH]_0$) × conv. × (molar mass of **M2**) + (molar mass of BnOH). [e]Determined by SEC using DMF (containing 0.1 M LiBr) as eluent and calibrated with PMMA standards.