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Supplementary Information

Organophosphate-Catalyzed Bulk Ring-Opening Polymerization as an Environmentally Benign Route Leading to Block Copolyesters, End-Functionalized Polyesters, and Polyester-Based Polyurethane

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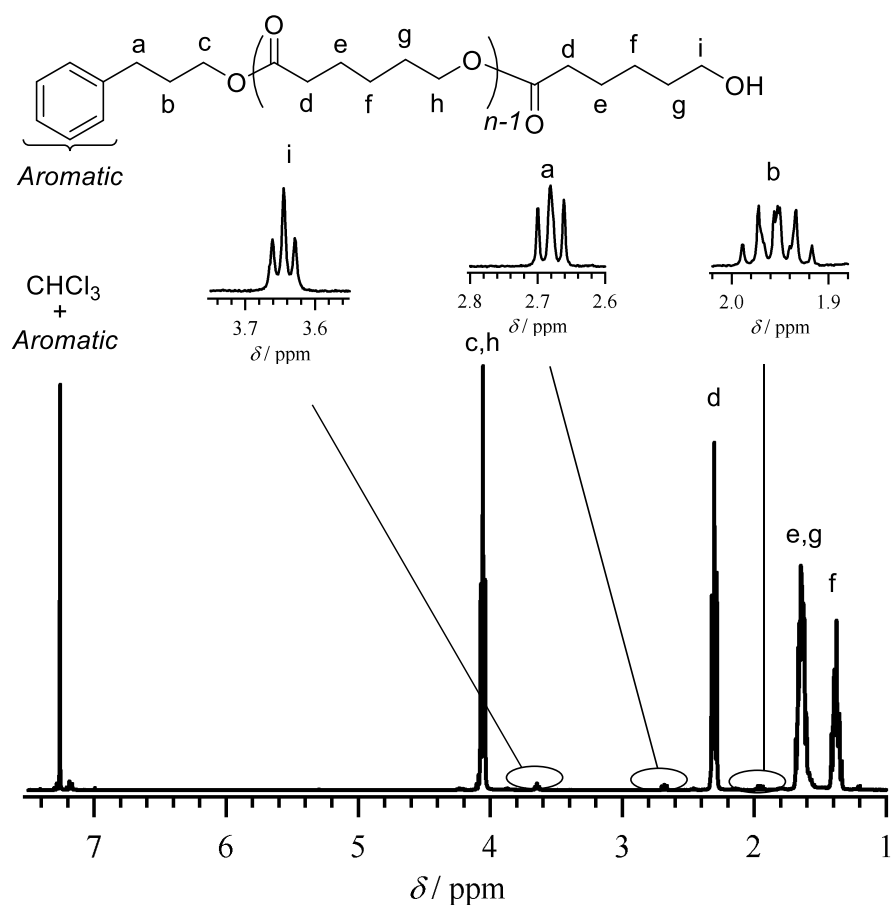


Figure S1. ^1H NMR spectrum of PCL in CDCl_3 (run 1 in Table 1).

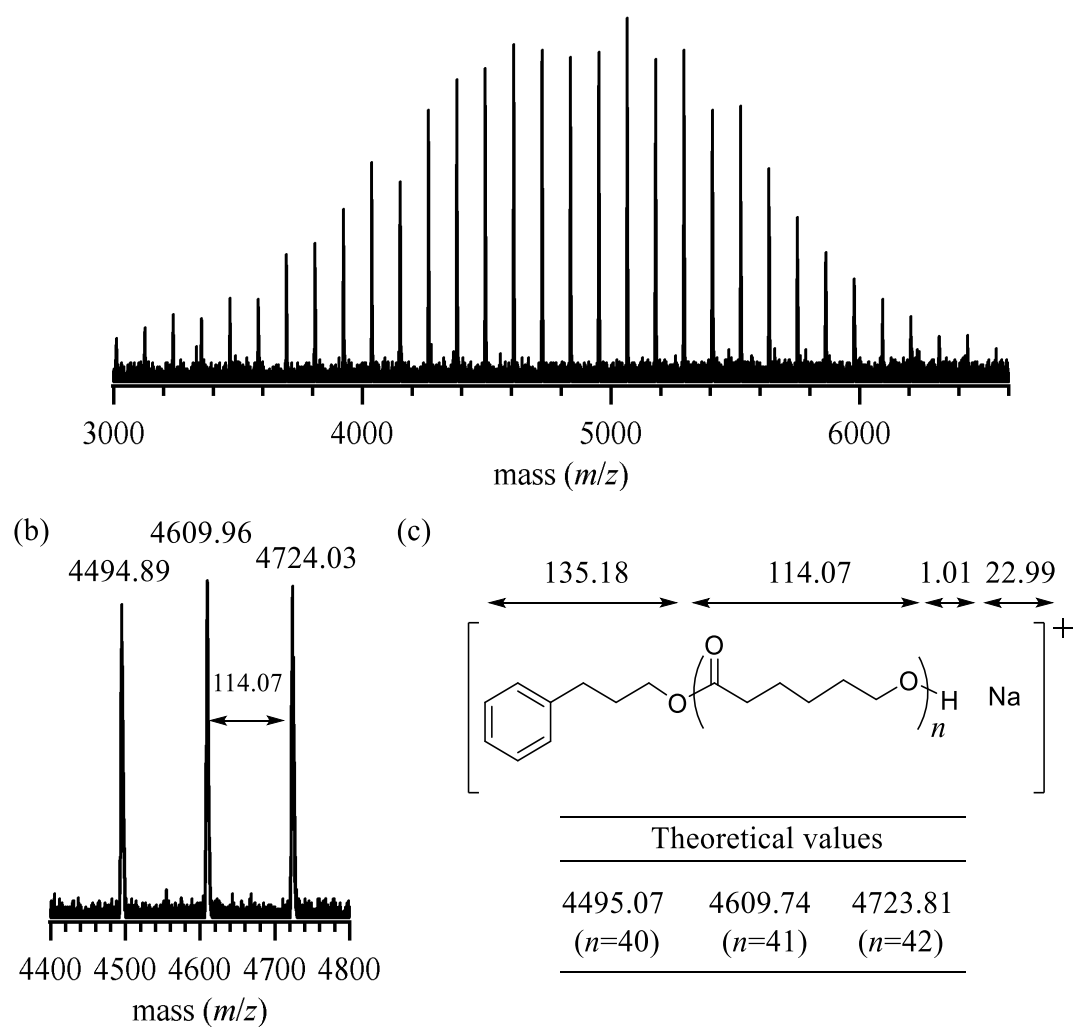


Figure S2. (a) MALDI-TOF MS spectrum of PCL (run 1 in Table 1), (b) expanded spectrum (ranging from 4,400 to 4,800), and (c) theoretical molar mass values.

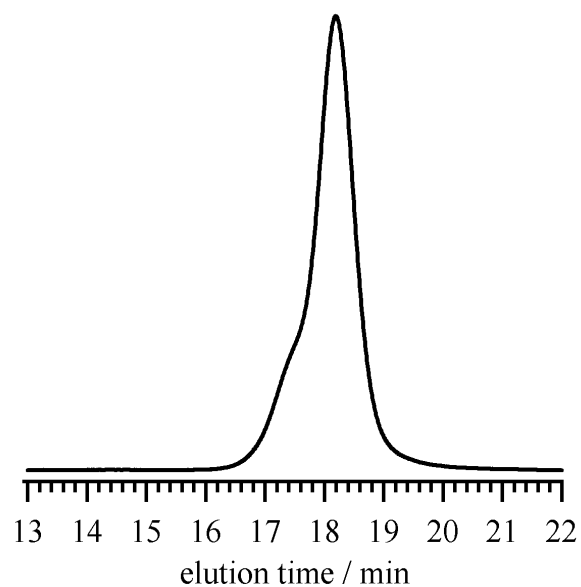


Figure S3. SEC trace of the obtained PCL initiated from H₂O (eluent, CHCl₃; flow rate, 1.0 mL min⁻¹).

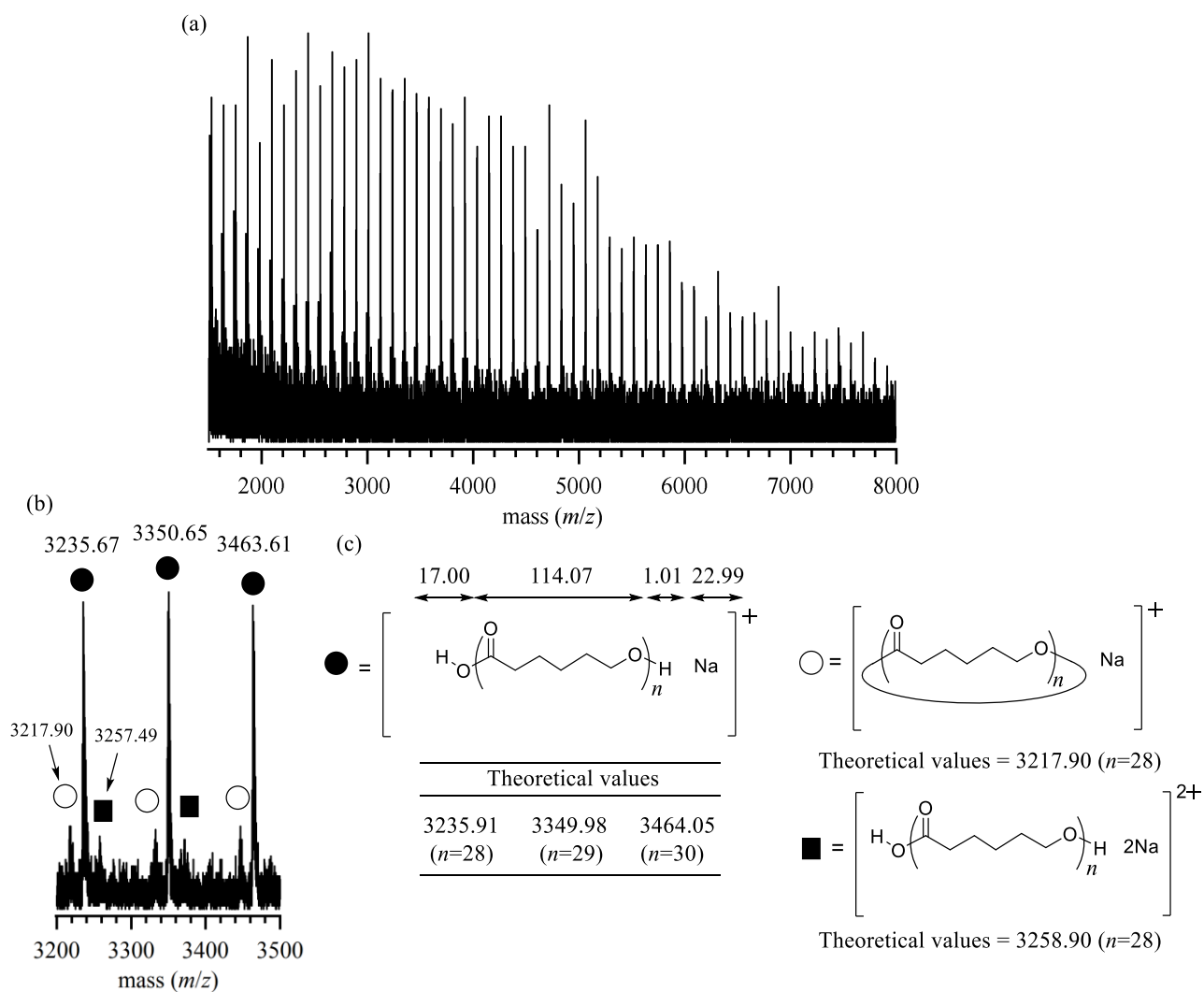


Figure S4. (a) MALDI-TOF MS spectrum of the PCL initiated from H₂O, (b) expanded spectrum (ranging from 3,200 to 3,500), and (c) theoretical molar mass values and expected structures.

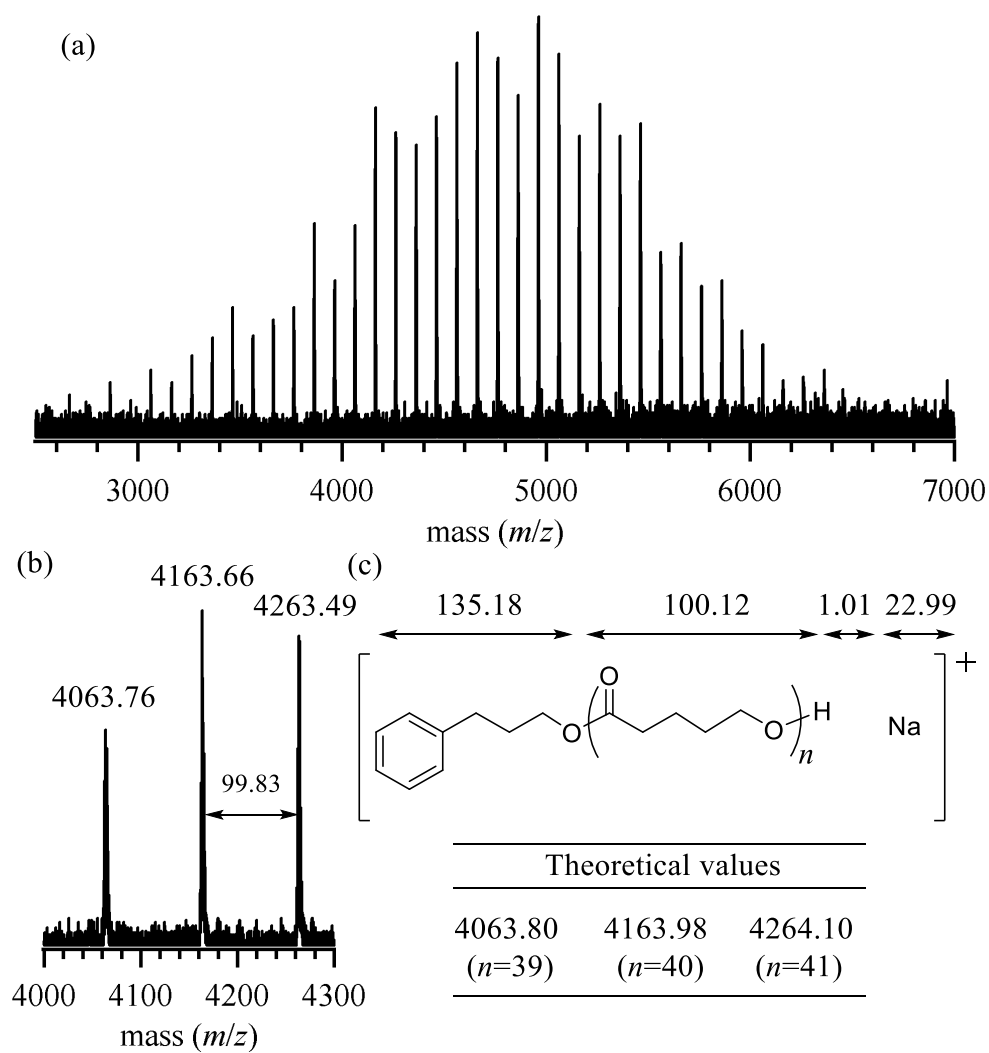


Figure S6. (a) MALDI-TOF MS spectrum of PVL (run 13 in Table 2), (b) expanded spectrum (ranging from 4,000 to 4,300), and (c) theoretical molar mass values.

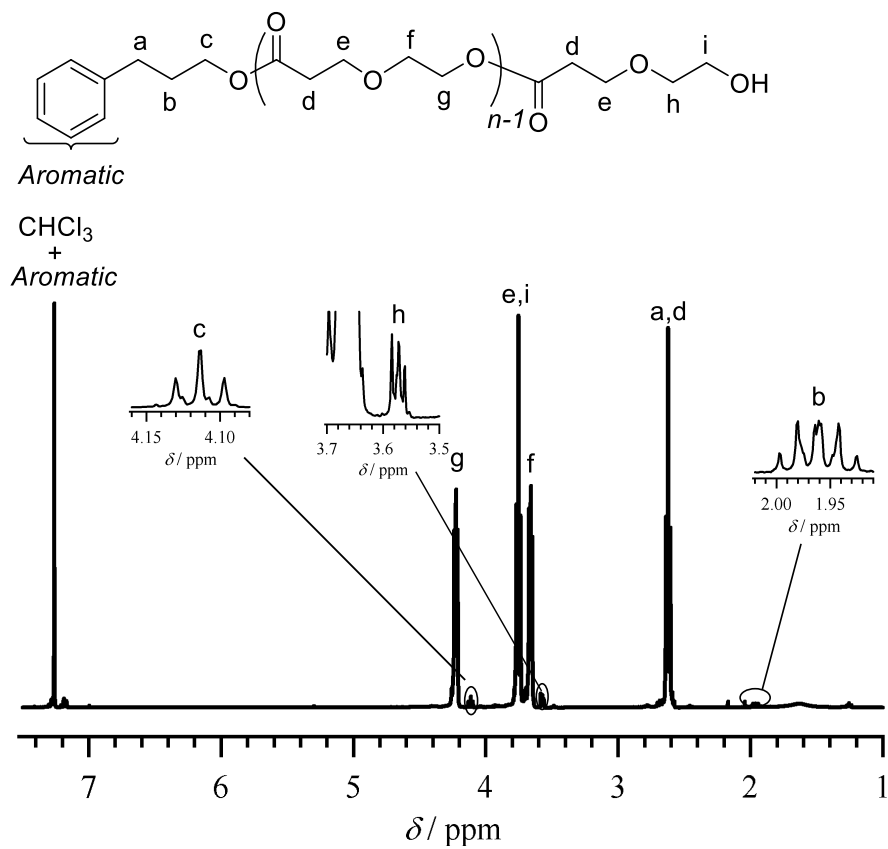


Figure S7. ¹H NMR spectrum of PDXO in CDCl₃ (run 16 in Table 2).

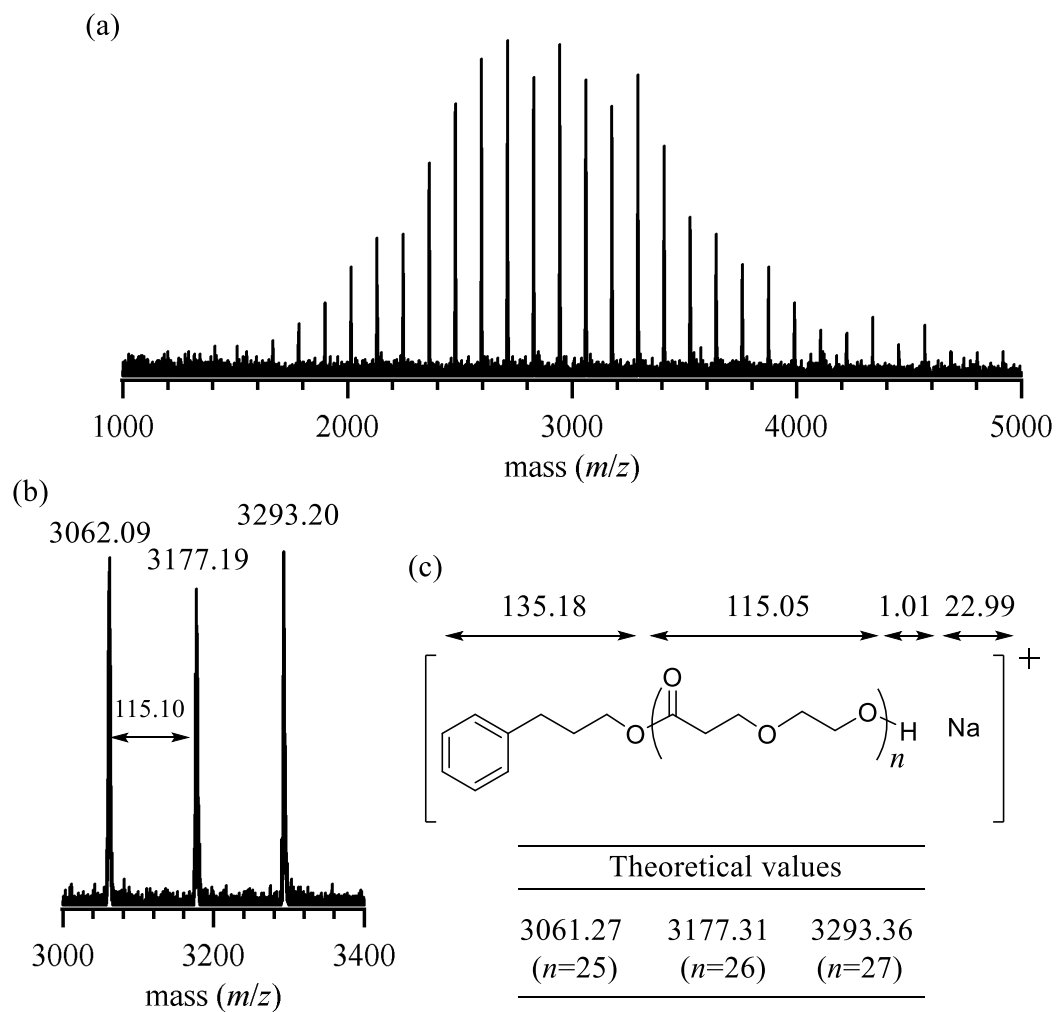


Figure S8. (a) MALDI-TOF MS spectrum of PDXO, (b) expanded spectrum (ranging from 3,000 to 3,400), and (c) theoretical molar mass values (run 16 in Table 2).

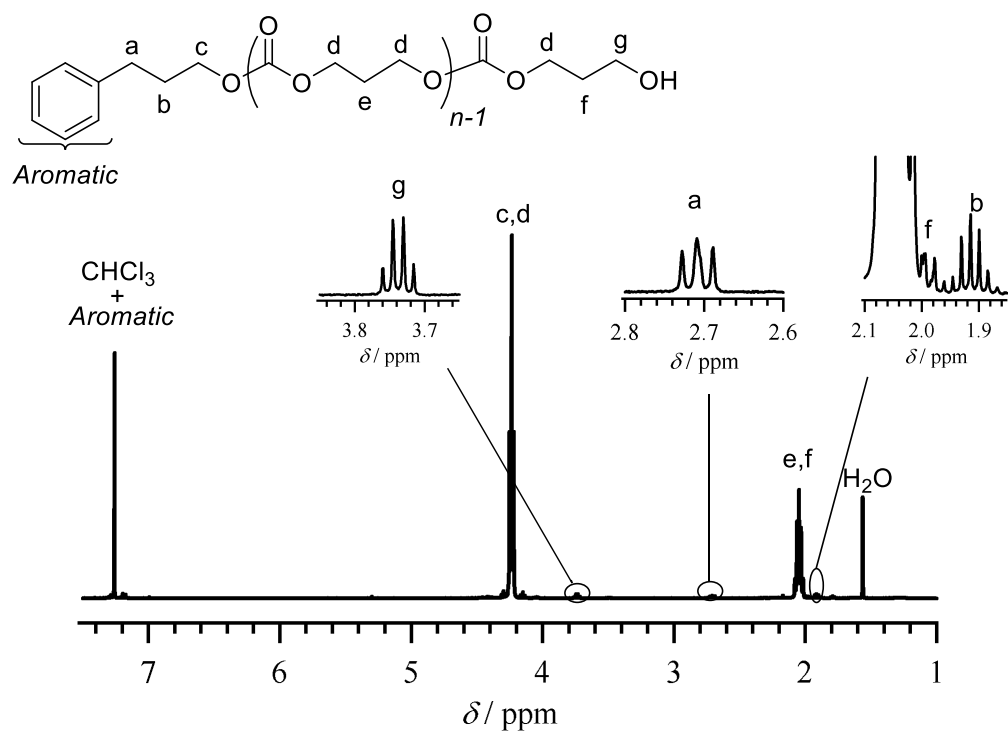


Figure S9. ^1H NMR spectrum of PTMC in CDCl_3 (run 19 in Table 2).

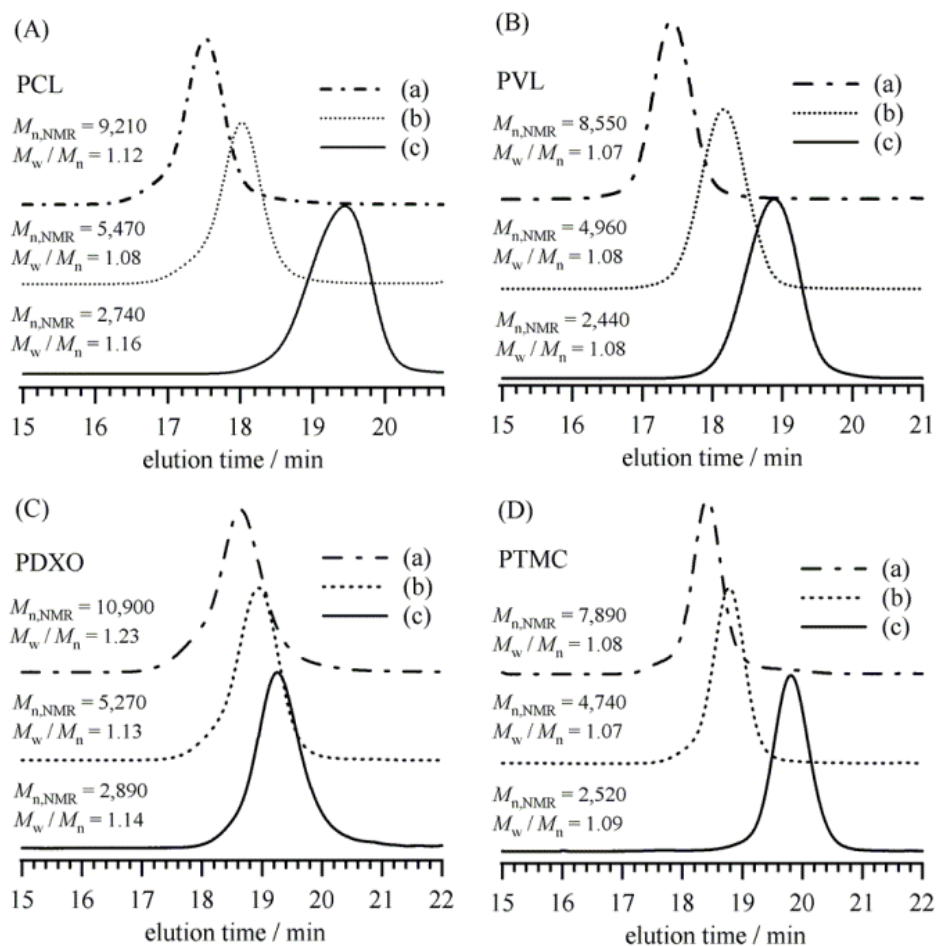


Figure S10. SEC traces of (A) the obtained PCLs, (B) PVLs, (C) PDXOs, and (D) PTMCs with the $[M]_0/[PPA]_0$ ratios of (a) 100/1, (b) 50/1, and (c) 25/1 (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

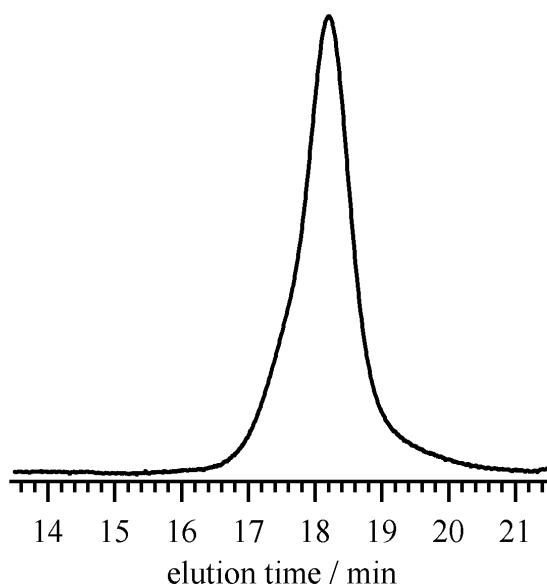


Figure S11. SEC trace of the PLLA obtained from run 21 in Table 2 (eluent, CHCl_3 ; flow rate, 1.0 mL min^{-1}).

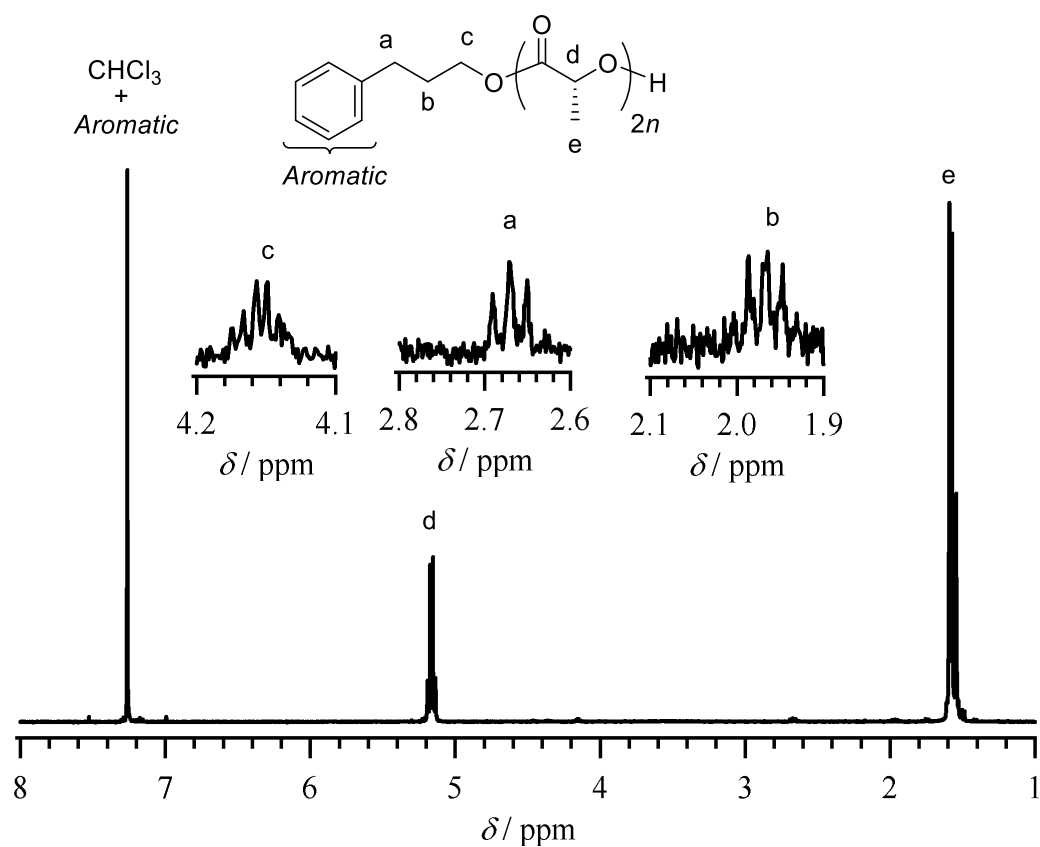


Figure S12. ^1H NMR spectrum of PLLA in CDCl_3 (run 21 in Table 2)

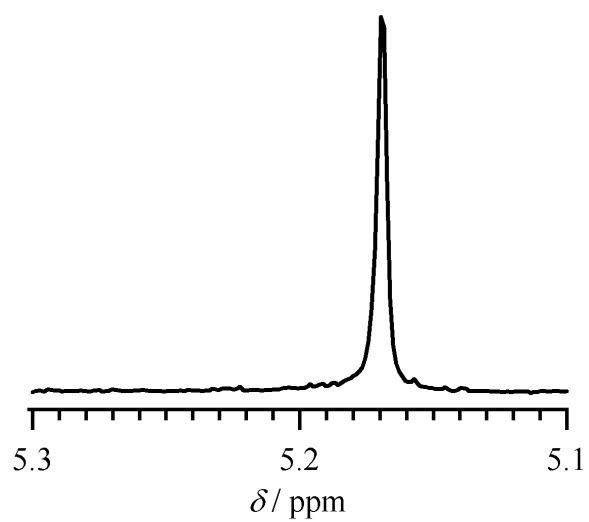


Figure S13. ^1H NMR spectrum of PLLA methylene resonances with selective decoupling of PLLA methyl resonances (run 21 in Table 2).

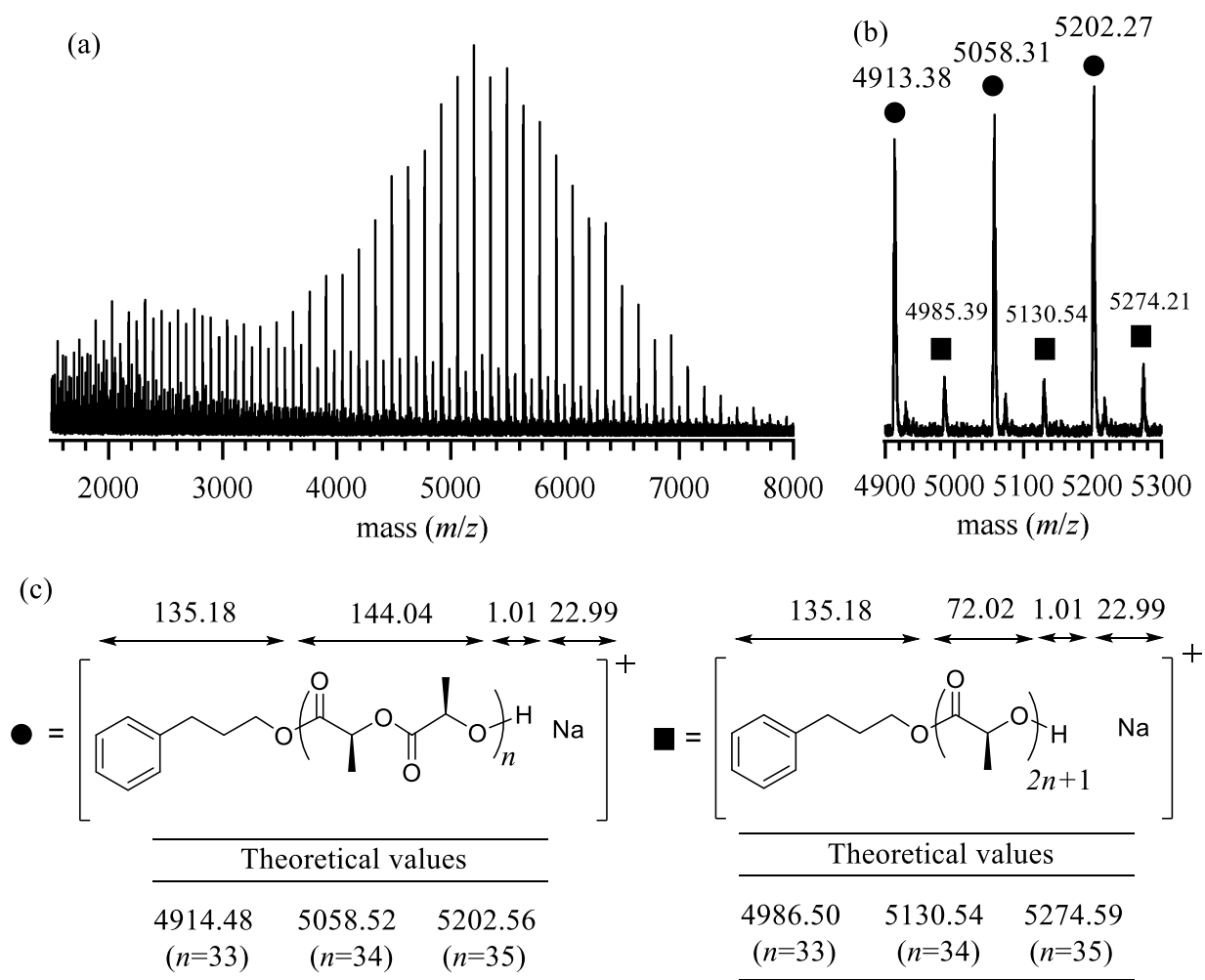


Figure S14. (a) MALDI-TOF MS spectrum of PLLA (run 21 in Table 2), (b) expanded spectrum (ranging from 4,900 to 5,300), and (c) theoretical molar mass values.

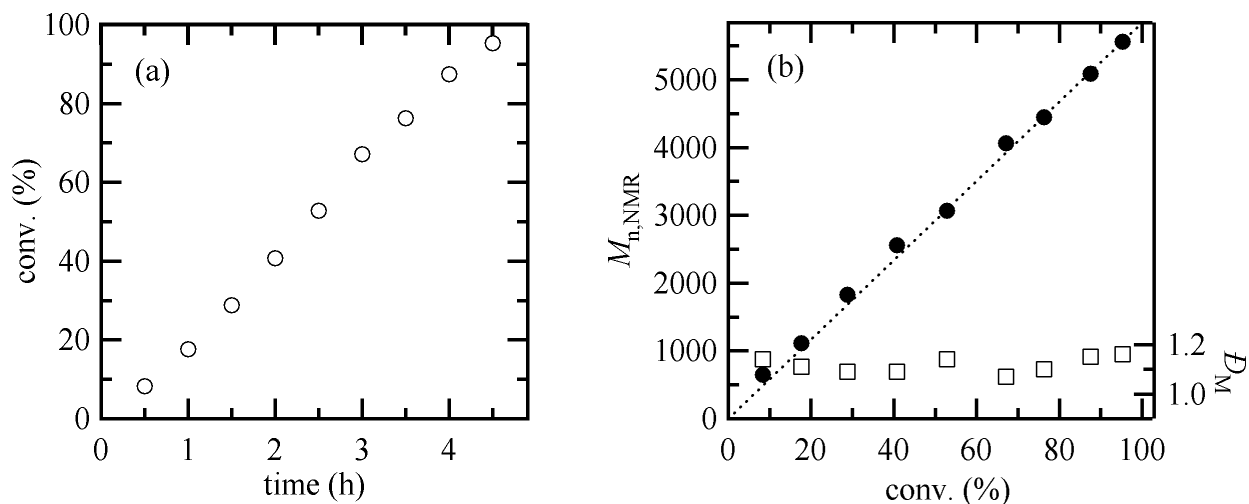


Figure S15. (a); Kinetic plots for the DPP-catalyzed bulk ROP of ϵ -CL with $[\epsilon\text{-CL}]_0/[\text{PPA}]_0/[\text{DPP}]_0 = 50/1/0.05$, and (b); dependence of $M_{n,\text{NMR}}$ (●), $\bar{D}_M$ (□) and $M_{n,\text{th.}}$ (dotted line) on monomer conversion (conv.).

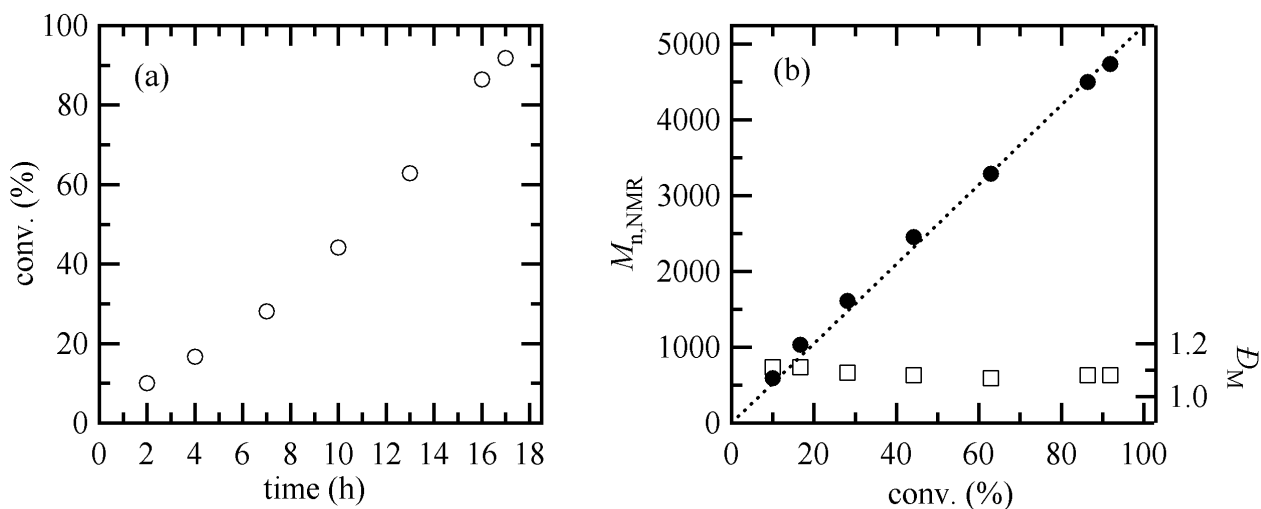


Figure S16. (a); Kinetic plots for the DPP-catalyzed bulk ROP of TMC with $[\text{TMC}]_0/[\text{PPA}]_0/[\text{DPP}]_0 = 50/1/0.05$, and (b); dependence of $M_{n,\text{NMR}}$ (●), $\bar{D}_M$ (□) and $M_{n,\text{th.}}$ (dotted line) on monomer conversion (conv.).

Table S1. Block copolymerization of ε -CL, δ -VL, DXO, and TMC catalyzed by DPP in the bulk ^a

run		monomer (M)	$[M]_0/[PPA]_0$	time	conv. (%) ^b	$M_{n,th.}$ ^b	$M_{n,NMR}$ ^c	$\bar{D}_M$ ^d
31	first	ε -CL	25/1	90min	94.7	2,800	2,800	1.11
	second	δ -VL	25/1	20min	78.6	4,800 ^e	5,000	1.13
32	first	TMC	25/1	560min	96.0	2,600	2,500	1.17
	second	δ -VL	25/1	20min	78.4	4,500	4,800	1.13
33	first	δ -VL	25/1	15min	97.1	2,700	2,600	1.15
	second	ε -CL	25/1	125min	88.0	5,100 ^e	5,200	1.15
34	first	DXO	25/1	210min	97.2	3,000	3,100	1.20
	second	ε -CL	25/1	130min	90.1	5,500 ^e	6,000	1.16

^a Polymerization conditions: atmosphere, Ar; temperature, 80 °C. ^b Determined by ¹H NMR spectrum of the obtained polymer in CDCl₃. ^c Calculated from $[M_1]_0/[PPA]_0 \times \text{conv.} \times (\text{M.W. of } M_1) + (\text{M.W. of PPA})$. ^d Determined by SEC measurement of the obtained polymer in CHCl₃. ^e Calculated from $[M_2]_0/[PPA]_0 \times \text{conv.} \times (\text{M.W. of } M_2) + (M_{n,NMR} \text{ of the polymer obtained from first polymerization})$.

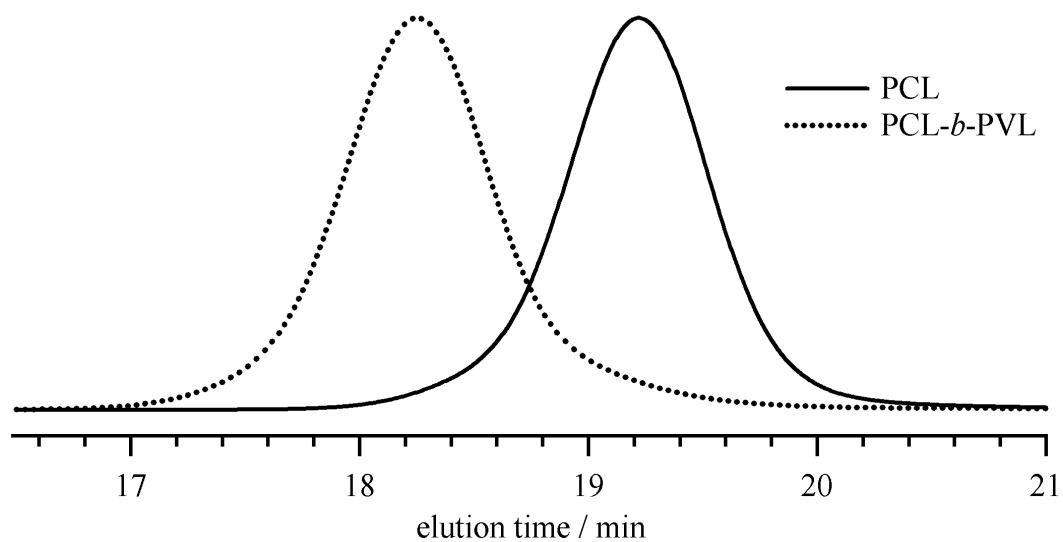


Figure S17. SEC traces of PCL obtained from the 1st polymerization and PCL-*b*-PVL (eluent, CHCl₃; flow rate, 1.0 mL min⁻¹).

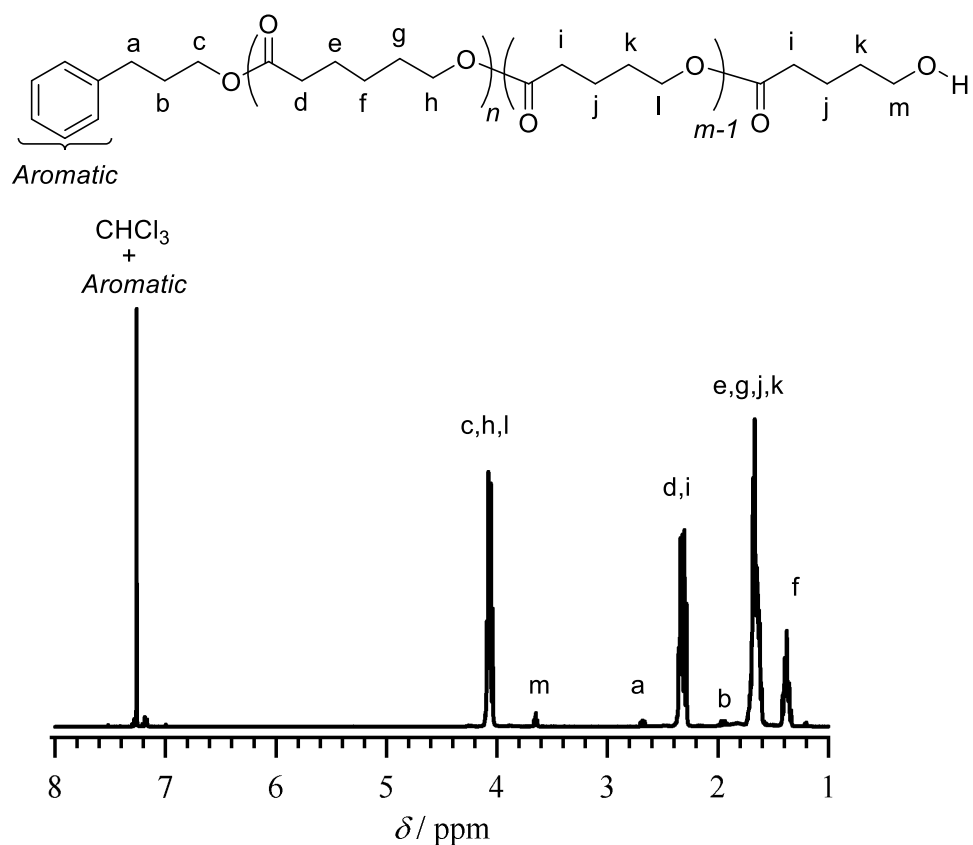


Figure S18. ¹H NMR spectrum of PCL-*b*-PVL in CDCl₃ (run 31 in Table S1).

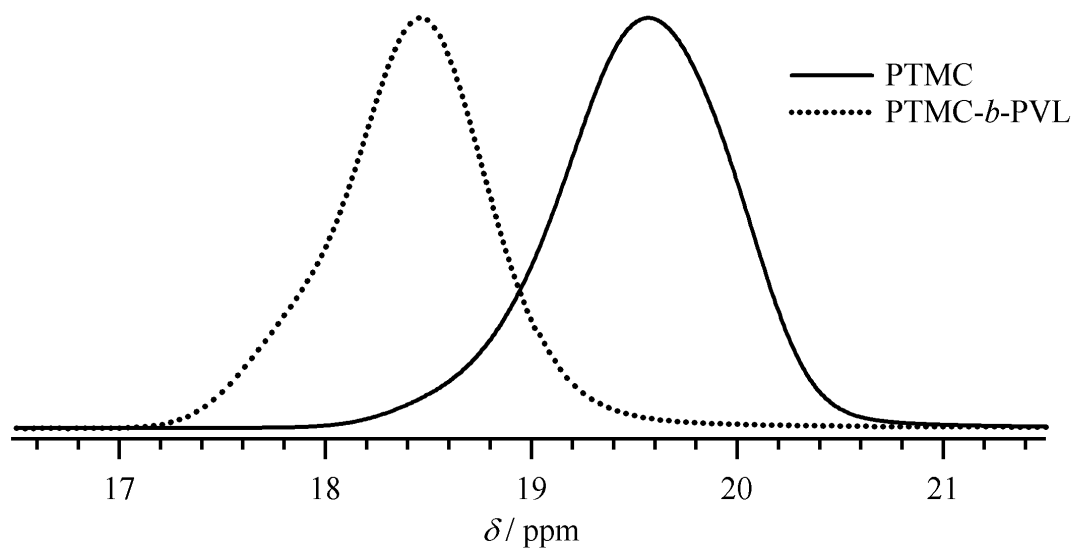


Figure S19. SEC traces of PTMC obtained from the 1st polymerization and PTMC-*b*-PVL (eluent, CHCl₃; flow rate, 1.0 mL min⁻¹).

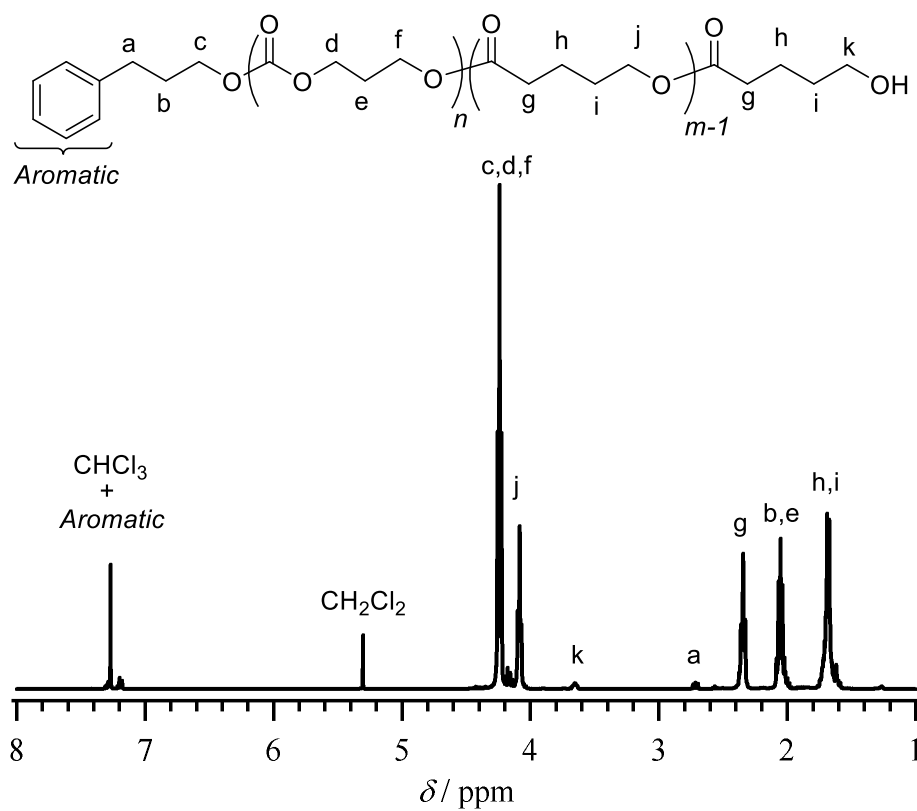


Figure S20. ¹H NMR spectrum of PTMC-*b*-PVL in CDCl₃ (run 32 in Table S1).

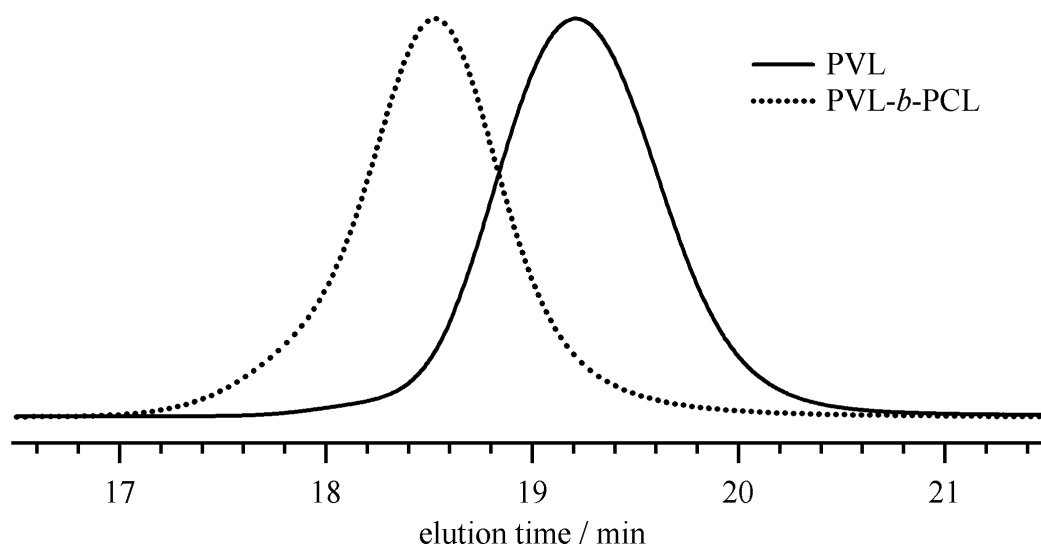


Figure S21. SEC traces of PVL obtained from the 1st polymerization and PVL-*b*-PCL (eluent, CHCl₃; flow rate, 1.0 mL min⁻¹).

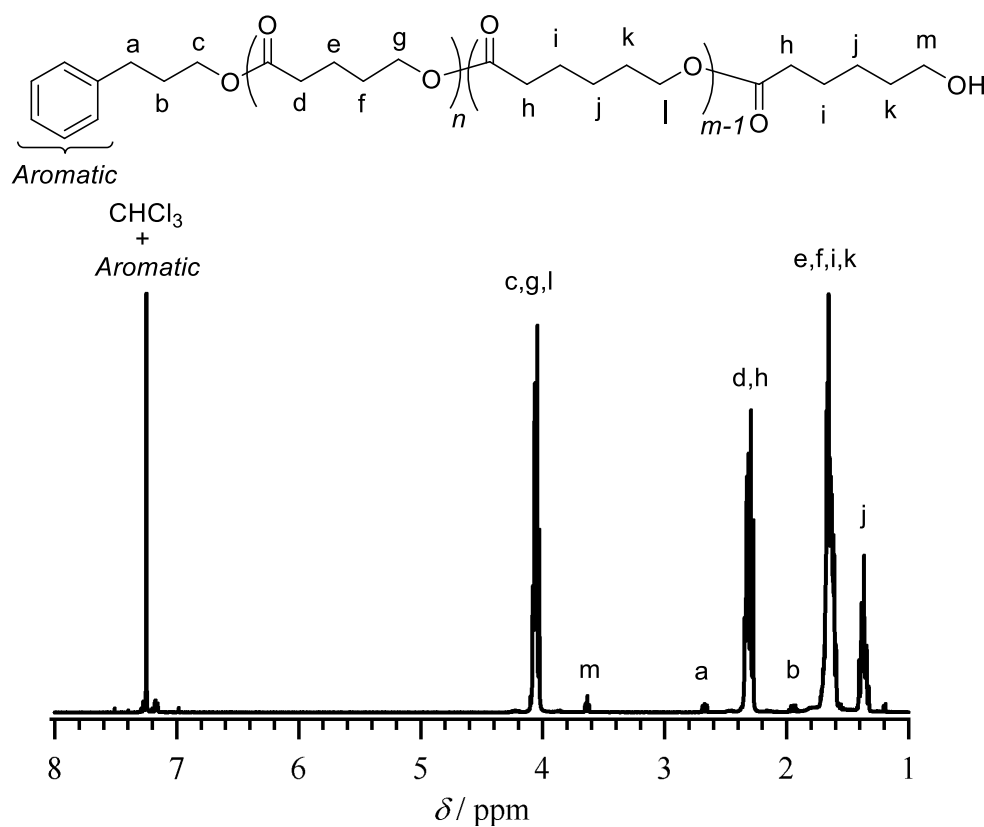


Figure S22. ¹H NMR spectrum of PVL-*b*-PCL in CDCl₃ (run 33 in Table S1).

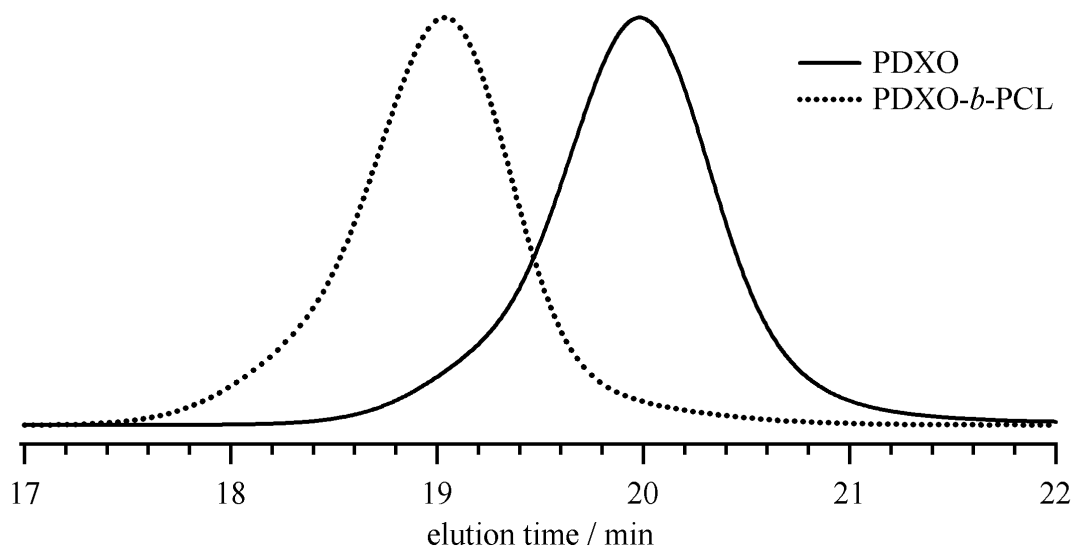


Figure S23. SEC traces of PDXO obtained from the 1st polymerization and PDXO-*b*-PCL (eluent, CHCl₃; flow rate, 1.0 mL min⁻¹).

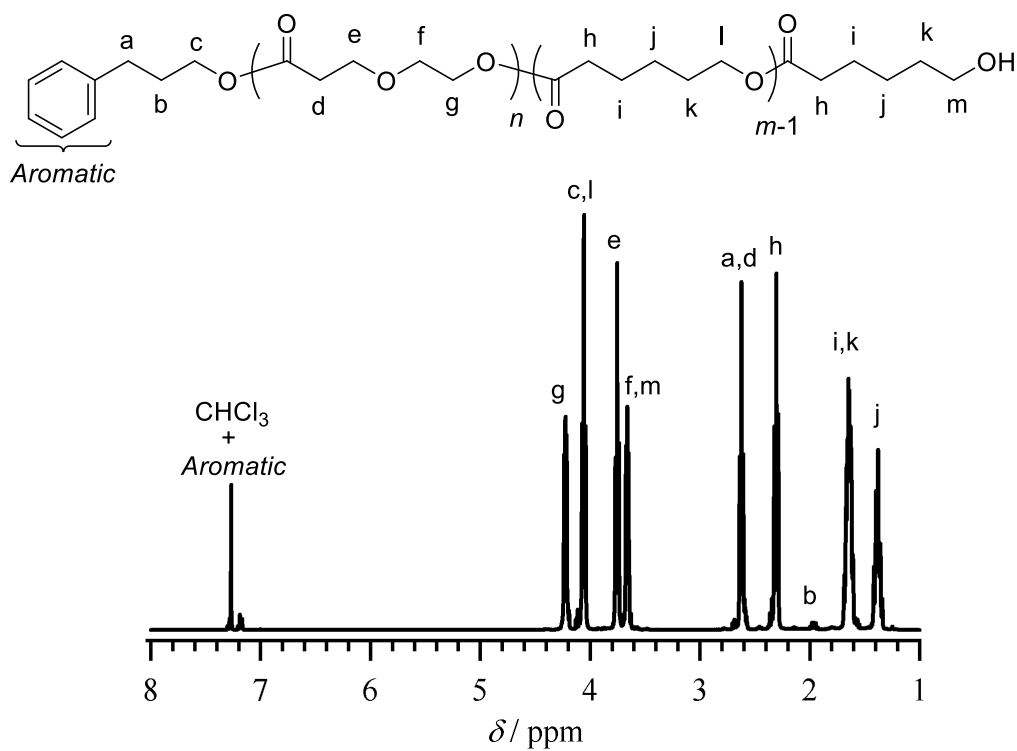


Figure S24. ¹H NMR spectrum of PDXO-*b*-PCL in CDCl₃ (run 34 in Table S1).

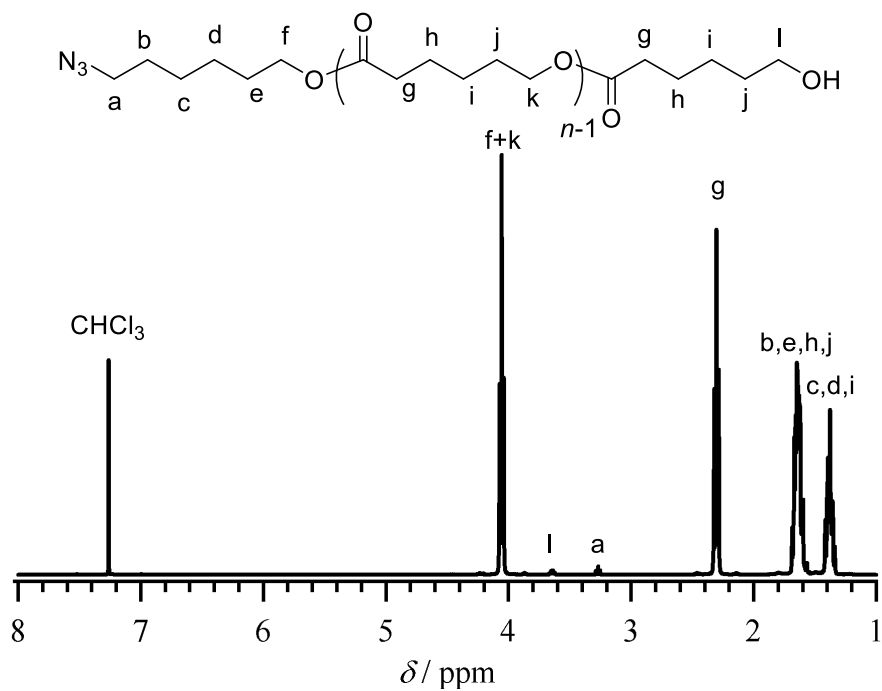


Figure S25. ¹H NMR spectrum of N₃-PCL in CDCl₃ (run 22 in Table 3).

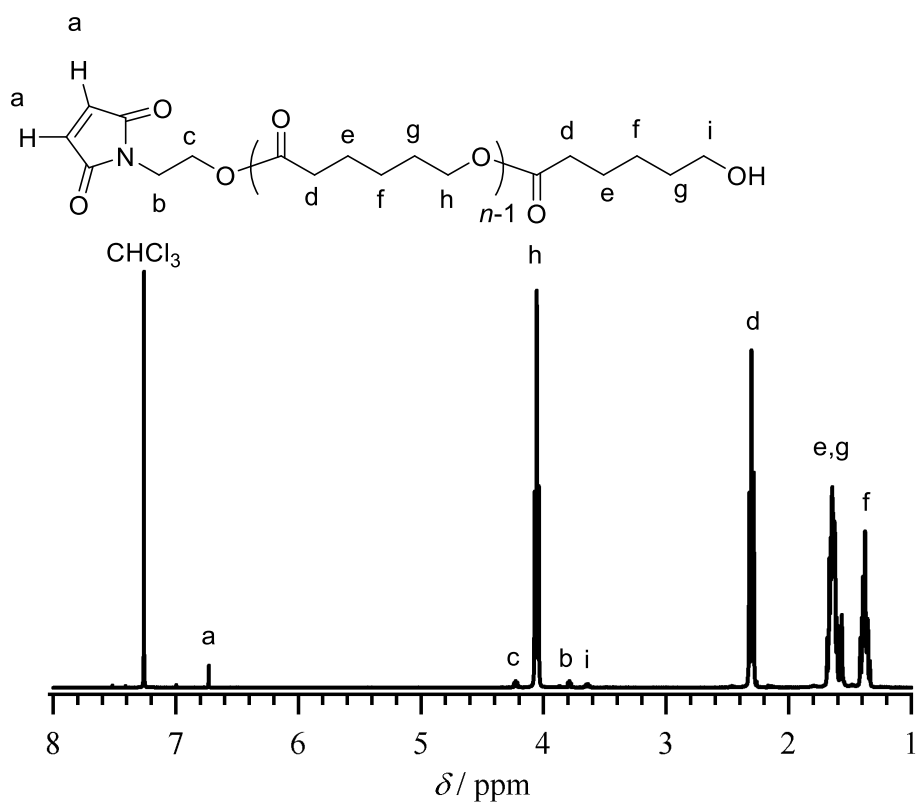
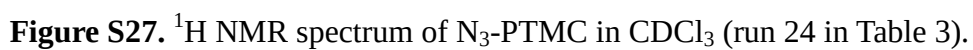


Figure S26. ¹H NMR spectrum of MI-PCL in CDCl₃ (run 23 in Table 3).



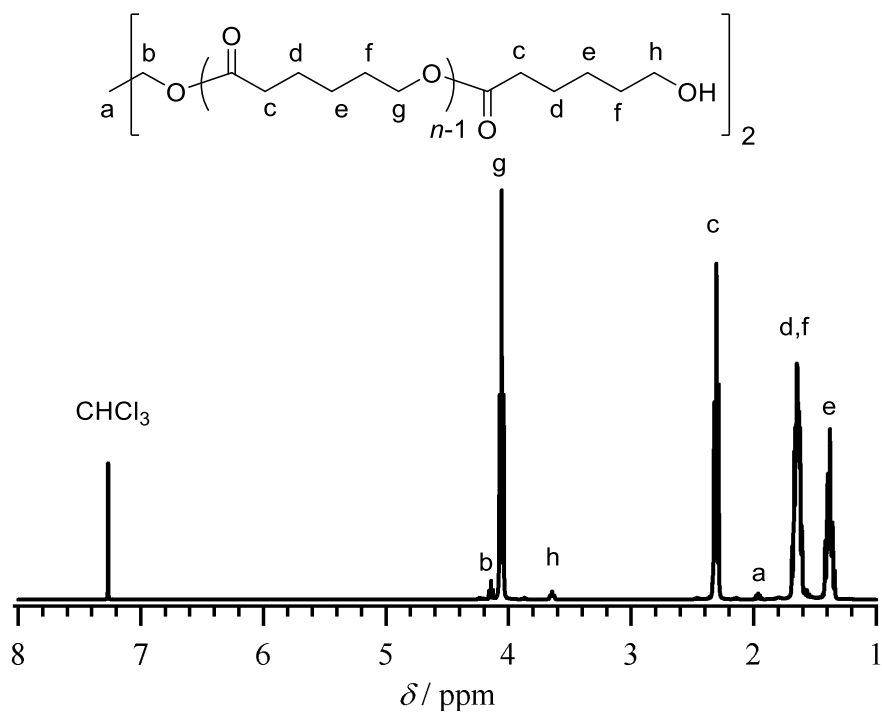


Figure 29. ¹H NMR spectrum of PCL-diol in CDCl₃ (run 26 in Table 3).

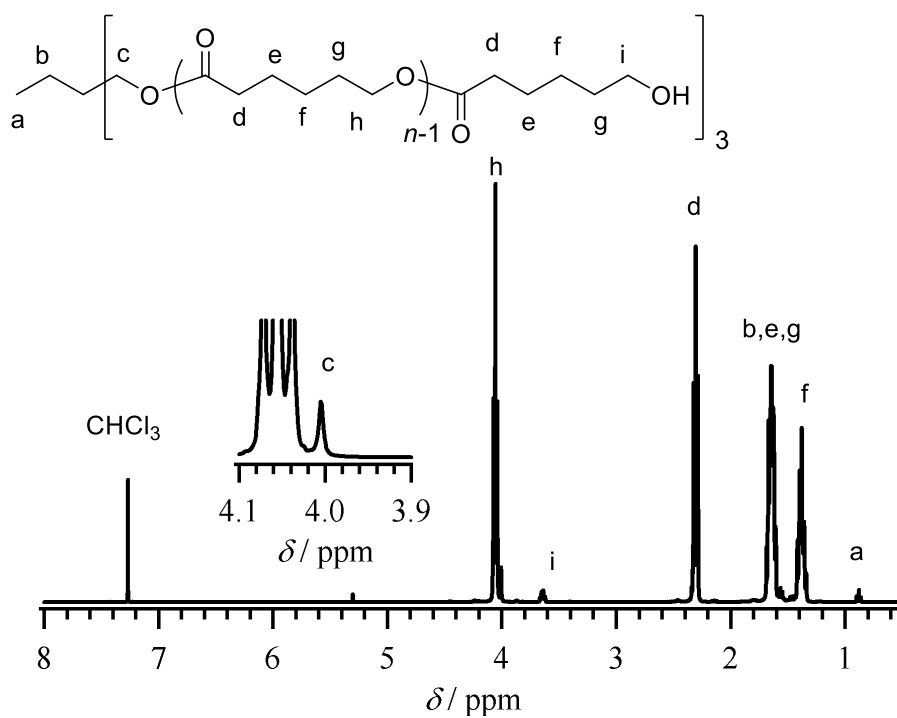


Figure S30. ¹H NMR spectrum of PCL-triol in CDCl₃ (run 27 in Table 3).

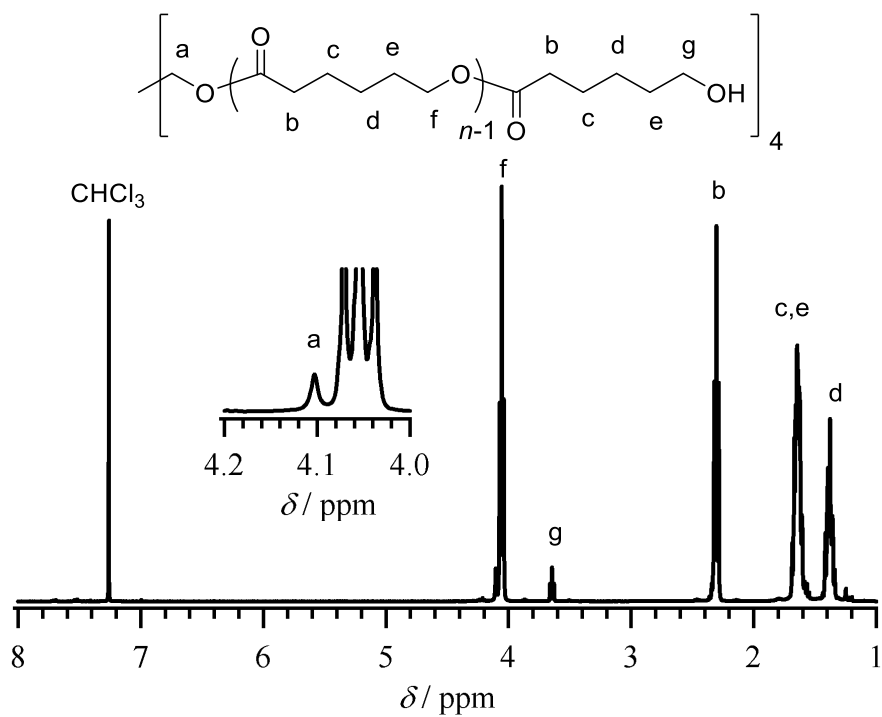


Figure S31. ^1H NMR spectrum of PCL-tetraol in CDCl_3 (run 28 in Table 3).

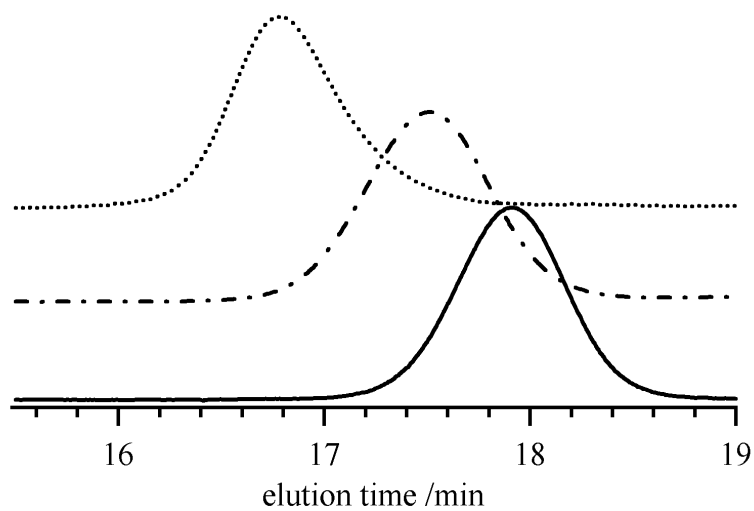


Figure S32. SEC traces of the obtained polymer in CHCl_3 (solid line, run 28; chained line, run 29; dotted line, run 30).

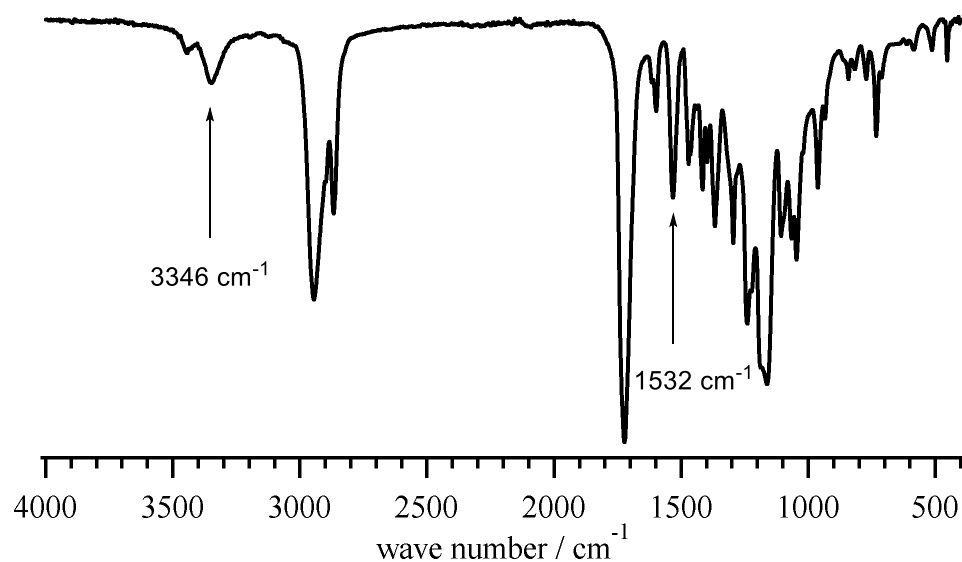


Figure S33. FT-IR spectrum of the obtained PCL-based polyurethane in the presence of DPP.

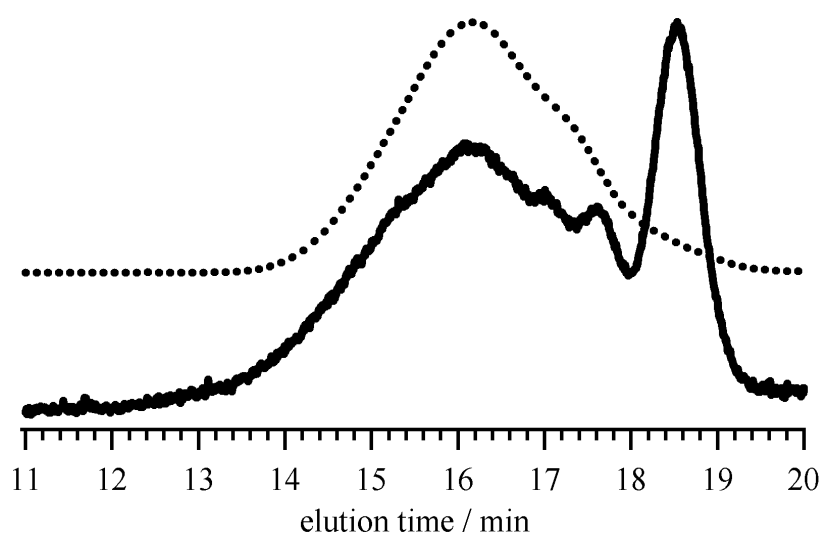


Figure S34. SEC traces of the obtained PCL-based polyurethane in the presence of DPP; dotted line and in the absence of DPP; solid line (eluent, CHCl_3 ; flow rate, 1.0 mL min^{-1}).

One-pot synthesis of PCL-*b*-PVL.

ϵ -CL (0.570 mL, 5.00 mmol), PPA (27.2 μ L, 200 μ mol) and DPP (2.50 mg, 10.0 μ mol) were placed in a reaction vessel, which was sealed under an argon atmosphere. The reaction mixture was stirred at 80 °C in an oil bath. After 90 min, we obtained a portion of the reaction mixture for SEC measurement and ^1H NMR measurement, then δ -VL (0.453 mL, 5.00 mmol) was added to the reaction mixture. The polymerization was quenched by adding Amberlyst® A21. The reaction mixture was purified by reprecipitation from CH_2Cl_2 solution into cold methanol/*n*-hexane (v/v = 9/1) to give the PCL-*b*-PVL (812 mg) as a white solid. Yield, 84.6%. $M_{n,\text{NMR}} = 5,000$; $M_{n,\text{SEC}} = 8,700$, $D_M = 1.13$. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 1.37 (m, $2\text{H} \times n$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$), 1.57-1.75 (m, $2\text{H} \times n$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times n$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times m$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_m$; $2\text{H} \times m$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_m$), 1.95 (m, 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2-$), 2.26-2.40 (m, $2\text{H} \times n$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times m$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_m$), 2.69 (t, 2H, $J = 7.8$ Hz, ArCH_2-), 3.65 (m, 2H, CH_2OH), 4.02-4.13 (m, $2\text{H} \times n$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times (m-1)$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_{m-1}$, 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2-$), 7.16-7.32 (m, 5H, aromatic).

The syntheses of PTMC-*b*-PVL, PVL-*b*-PCL, and PDXO-*b*-PCL were performed using similar process.

PTMC-*b*-PVL: Yield, 88.0%. $M_{n,\text{NMR}} = 4,800$; $M_{n,\text{SEC}} = 7,500$, $D_M = 1.13$. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 1.57-1.78 (m, $2\text{H} \times m$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-)_m$; $2\text{H} \times m$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-)_m$), 1.96-2.12 (m, $2\text{H} \times n$, $(-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; 2H, $\text{ArCH}_2\text{CH}_2-$), 2.34 (m, $2\text{H} \times m$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-)_m$), 2.72 (t, 2H, $J = 7.8$ Hz, ArCH_2-), 3.65 (m, 2H, CH_2OH), 4.08 (m, $2\text{H} \times (m-1)$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_{m-1}$), 4.13-4.30 (m, $2\text{H} \times n$, $(-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times n$, $(-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2-$), 7.16-7.32 (m, 5H, aromatic).

PVL-*b*-PCL: Yield, 74.1%. $M_{n,\text{NMR}} = 5,200$; $M_{n,\text{SEC}} = 7,000$, $D_M = 1.15$. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 1.38 (m, $2\text{H} \times m$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-)_m$), 1.58-1.75 (m, $2\text{H} \times n$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times n$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times m$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_m$; $2\text{H} \times m$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_m$), 1.96 (m, 2H, $\text{ArCH}_2\text{CH}_2-$), 2.27-2.40 (m, $2\text{H} \times n$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times m$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-)_m$), 2.69 (t, 2H, $J = 7.6$ Hz, ArCH_2-),

3.65 (t, 2H, $J = 6.4$ Hz, $-\text{CH}_2\text{OH}$), 4.02-4.12 (m, $2\text{H} \times n$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times (m-1)$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_{m-1}$; 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2-$), 4.20 (t, $2\text{H} \times n$, $J = 4.8$ Hz, $(-\text{COCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-)_{n-1}$), 7.15-7.31 (m, 5H, aromatic).

PDXO-*b*-PCL: Yield, 5.5%. $M_{n,\text{NMR}} = 6,000$; $M_{n,\text{SEC}} = 5,200$, $\bar{D}_M = 1.16$. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 1.38 (m, $2\text{H} \times m$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-)_{m-1}$), 1.58-1.71 (m, $2\text{H} \times m$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_m$; $2\text{H} \times m$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2-)_{m-1}$), 1.97 (m, $2\text{H} \times m$, $\text{ArCH}_2\text{CH}_2-$), 2.28 (m, $2\text{H} \times m$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2-)_{m-1}$), 2.56-2.72 (m, $2\text{H} \times n$, $(-\text{COCH}_2\text{CH}_2\text{O}-)_n$; 2H, $\text{ArCH}_2\text{CH}_2-$), 3.62-3.71 (m, $2\text{H} \times n$, $(-\text{COCH}_2\text{CH}_2\text{OCH}_2-)_{n-1}$; 2H, $-\text{CH}_2\text{OH}$), 3.74 (m, $2\text{H} \times n$, $(-\text{COCH}_2\text{CH}_2\text{O}-)_n$), 4.01-4.11 (m, $2\text{H} \times (m-1)$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_{m-1}$; 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2-$), 4.20 (t, $2\text{H} \times n$, $J = 4.8$ Hz, $(-\text{COCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-)_{n-1}$), 7.13-7.29 (m, 5H, aromatic).

Syntheses of functional PCLs with various initiators.

N_3 -PCL: Procedure A was used for the ROP of ϵ -CL (1.120 mL, 10.0 mmol) in the presence of AHA (28.6 mg, 200 μmol) and DPP (2.50 mg, 10.0 μmol) for 420 min to give N_3 -PCL (740 mg) as a white solid. Yield, 69.9%. $M_{n,\text{NMR}} = 5,500$; $M_{n,\text{SEC}} = 12,700$, $\bar{D}_M = 1.11$. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 1.31-1.41 (m, $2\text{H} \times n$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-)_{n-1}$; 4H, $\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.55-1.69 (m, $2\text{H} \times n$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times n$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2-)_{n-1}$; 4H, $\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 2.31 (t, $2\text{H} \times n$, $J = 7.6$ Hz, $(-\text{COCH}_2\text{CH}_2-)_{n-1}$), 3.28 (t, 2H, $J = 7.0$ Hz, N_3CH_2-), 3.63 (m, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$), 4.01-4.09 (m, $2\text{H} \times (n-1)$, $(-\text{CH}_2\text{CH}_2\text{O}-)_{n-1}$; 2H, $\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$).

MI-PCL: Procedure A was used for the ROP of ϵ -CL (1.120 mL, 10.0 mmol) in the presence of HEMI (28.2 mg, 200 μmol) and DPP (2.50 mg, 10.0 μmol) for 450 min to give MI-PCL (779 mg) as a white solid. Yield, 73.2%. $M_{n,\text{NMR}} = 5,500$; $M_{n,\text{SEC}} = 13,400$, $\bar{D}_M = 1.15$. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 1.36 (m, $2\text{H} \times n$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-)_{n-1}$), 1.58-1.71 (m, $2\text{H} \times n$, $(-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-)_n$; $2\text{H} \times n$, $(-\text{COCH}_2\text{CH}_2\text{CH}_2-)_{n-1}$), 2.29 (t, $2\text{H} \times n$, $J = 8.2$ Hz, $(-\text{COCH}_2\text{CH}_2-)_{n-1}$), 3.64 (m, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$), 3.79 (t, 2H, $J = 5.4$ Hz, $-\text{NCH}_2-$), 4.06 (t, $2\text{H} \times (n-1)$, $J = 6.6$ Hz, $(-\text{CH}_2\text{CH}_2\text{O}-)_{n-1}$), 4.23 (t, 2H, $J = 5.2$ Hz, $-\text{NCH}_2\text{CH}_2-$), 6.74 (s, 2H, $-\text{COCHCHCO}-$).

PCL-diol: Procedure A was used for the ROP of ϵ -CL (1.120 mL, 10.0 mmol) in the presence of 1,3-propanediol (14.3 μ L, 200 μ mol) and DPP (2.50 mg, 10.0 μ mol) for 180 min to give PCL-diol (776 mg) as a white solid. Yield, 75.5%. $M_{n,NMR} = 5,100$; $M_{n,SEC} = 11,400$, $D_M = 1.13$. 1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.36 (m, $2H \times n$, $(-CH_2CH_2CH_2CH_2CH_2-)_n \times 2$), 1.58-1.71 (m, $2H \times n$, $(-CH_2CH_2CH_2O-)_n \times 2$; $2H \times n$, $(-COCH_2CH_2CH_2-)_n \times 2$), 1.97 (m, $2H$, $-OCH_2CH_2CH_2O-$), 2.29 (t, $2H \times n$, $J = 8.2$ Hz, $(-COCH_2CH_2-)_n \times 2$), 3.63 (t, $2H \times 2$, $J = 6.4$ Hz, $-CH_2CH_2OH$) 4.06 (t, $2H \times (n-1)$, $J = 6.6$ Hz, $(-CH_2CH_2O-)_n \times 2$), 4.15 (t, $4H$, $J = 6.2$ Hz, $-OCH_2CH_2CH_2O-$).

PCL-triol: Procedure A was used for the ROP of ϵ -CL (1.120 mL, 10.0 mmol) in the presence of trimethylolpropane (26.8 mg, 200 μ mol) and DPP (2.50 mg, 10.0 μ mol) for 150 min to give PCL-triol (666 mg) as a white solid. Yield, 66.1%. $M_{n,NMR} = 5,200$; $M_{n,SEC} = 11,500$, $D_M = 1.07$. 1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 0.89 (t, $3H$, $J = 7.4$ Hz, CH_3CH_2), 1.36 (m, $2H \times n$, $(-CH_2CH_2CH_2CH_2CH_2-)_n \times 3$), 1.55-1.72 (m, $2H$, CH_3CH_2 ; $2H \times (n-1)$, $(-CH_2CH_2CH_2O-)_n \times 3$; $2H \times n$, $(-COCH_2CH_2CH_2-)_n \times 3$), 2.31 (m, $2H \times n$, $(-OCOCH_2CH_2-)_n \times 3$), 3.65 (m, $6H$, $-CH_2CH_2OH \times 3$), 4.01 (s, $6H$, $C(CH_2O)_3$), 4.06 (t, $2H \times (n-1)$, $J = 6.6$ Hz, $(-CH_2CH_2O-)_n \times 3$).

PCL-tetraol: Procedure A was used for the ROP of ϵ -CL (2.240 mL, 20.0 mmol) in the presence of pentaerythritol (27.2 mg, 200 μ mol) and DPP (2.50 mg, 10.0 μ mol) for 430 min to give PCL-tetraol (1.07 g) as a white solid. Yield, 48.2%. $M_{n,NMR} = 10,600$; $M_{n,SEC} = 16,900$, $D_M = 1.07$. 1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.37 (m, $2H \times n$, $(-CH_2CH_2CH_2CH_2CH_2-)_n \times 4$), 1.54-1.73 (m, $2H \times n$, $(-CH_2CH_2CH_2O-)_n \times 4$; $2H \times n$, $(-COCH_2CH_2CH_2-)_n \times 4$), 2.32 (m, $2H \times n$, $(-OCOCH_2CH_2-)_n \times 4$), 3.65 (t, $8H$, $J = 6.6$ Hz, $-CH_2CH_2OH \times 4$) 4.06 (t, $2H \times (n-1)$, $J = 6.6$ Hz, $(-CH_2CH_2O-)_n \times 4$), 4.11 (s, $8H$, $C(CH_2CO-)_4$).

Syntheses of functional PTMCs with various initiators.

N₃-PTMC: Procedure A was used for the ROP of TMC (510 mg, 5.00 mmol) in the presence of AHA (14.3 mg, 100 μ mol) and DPP (1.2 mg, 0.50 μ mol) for 19 h to give N₃-PTMC (379 mg) as a colorless waxy solid. Yield, 84.1%. $M_{n,NMR} = 4,500$; $M_{n,SEC} = 5,600$, $D_M = 1.09$. 1H NMR (CDCl₃, 400MHz): δ (ppm) 1.42 (m, 4H, N₃CH₂CH₂CH₂CH₂-), 1.92 (m, 2H, N₃CH₂CH₂CH₂CH₂CH₂-), 2.01-2.11 (m, 2H, N₃CH₂CH₂-; 2H $\times$ (n-1), (-OCH₂CH₂-)_{n-1}), 3.28 (t, 2H, $J = 7.0$ Hz, N₃CH₂-), 3.74 (m, 2H, -CH₂OH), 4.21-4.27 (m, 2H, N₃CH₂CH₂CH₂CH₂CH₂CH₂-; 4H $\times$ (n-1), (-OCH₂CH₂CH₂O-)_{n-1}; 2H, -CH₂CH₂CH₂OH).

MI-PTMC: Procedure A was used for the ROP of TMC (510 mg, 5.00 mmol) in the presence of HEMI (14.1 mg, 100 μ mol) and DPP (1.2 mg, 0.50 μ mol) for 19 h to give MI-PTMC (429 mg) as a colorless waxy solid. Yield, 89.7%. $M_{n,NMR} = 4,700$; $M_{n,SEC} = 6,400$, $D_M = 1.13$. 1H NMR (CDCl₃, 400MHz): δ (ppm) 1.92 (m, 2H, -CH₂CH₂OH), 2.00-2.13 (m, 2H $\times$ (n-1), (-OCH₂CH₂-)_{n-1}), 3.74 (m, 2H, -CH₂OH), 3.85 (t, 2H, $J = 5.4$ Hz -NCH₂CH₂-), 4.21-4.29 (m, 2H, -NCH₂CH₂-; 4H $\times$ n-1, (-OCH₂CH₂CH₂O-)_{n-1}; 2H, -CH₂CH₂CH₂OH), 6.74 (s, 2H, -COCHCHCO-).