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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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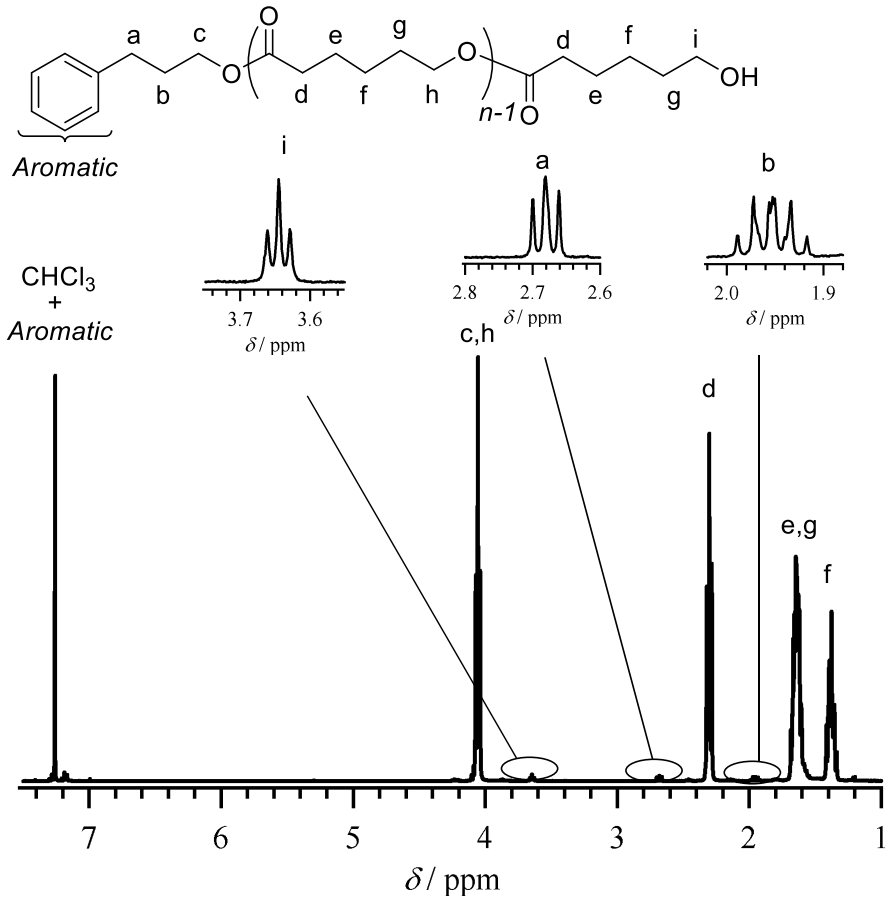

Figure S1. ^{1}H NMR spectrum of PCL in $CDCl_3$ (run 1 in Table 1).

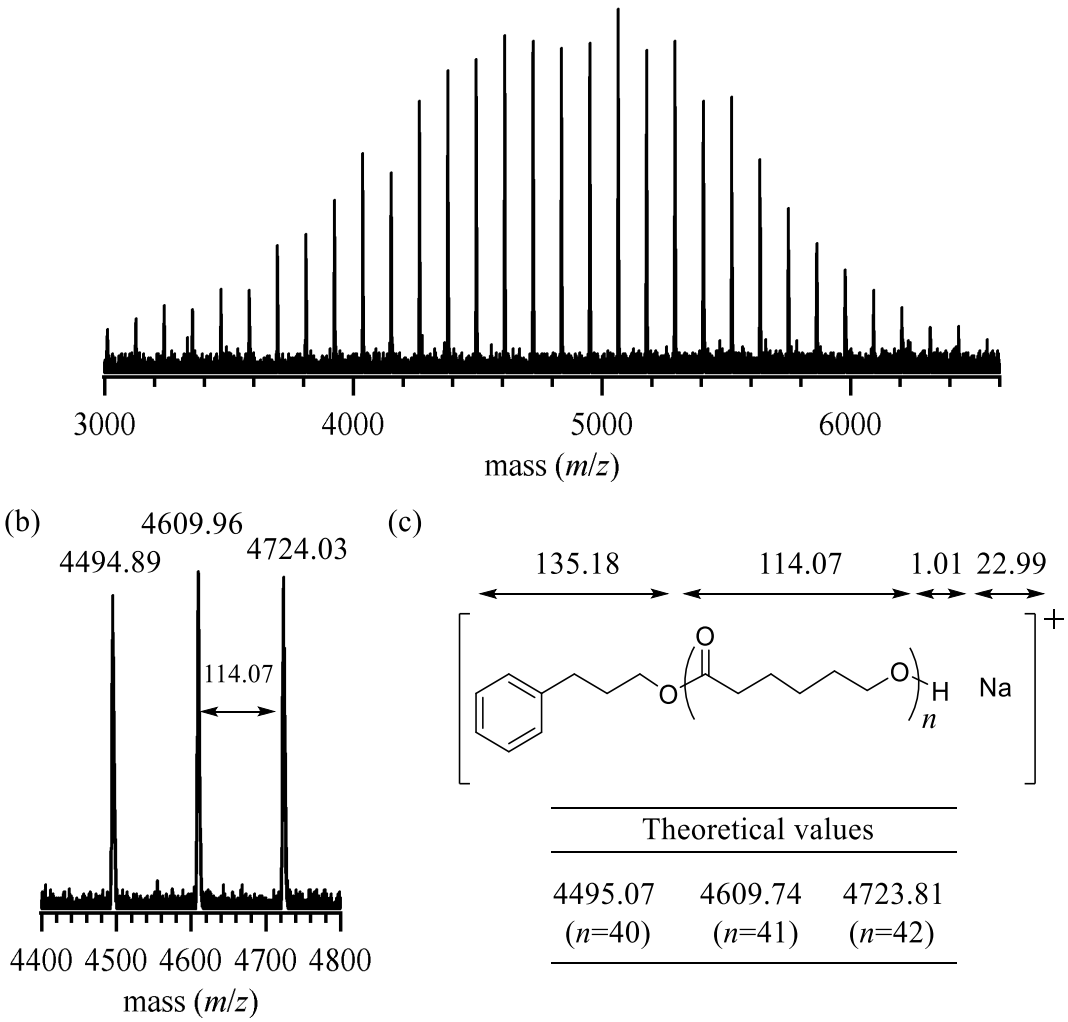

Figure S2. (a) MALDI-TOF MS spectrum of PCL (run 1 in Table 1), (b) expanded spectrum (ranging from 4,400 to 4,800), and (c) theoretical molar mass values.

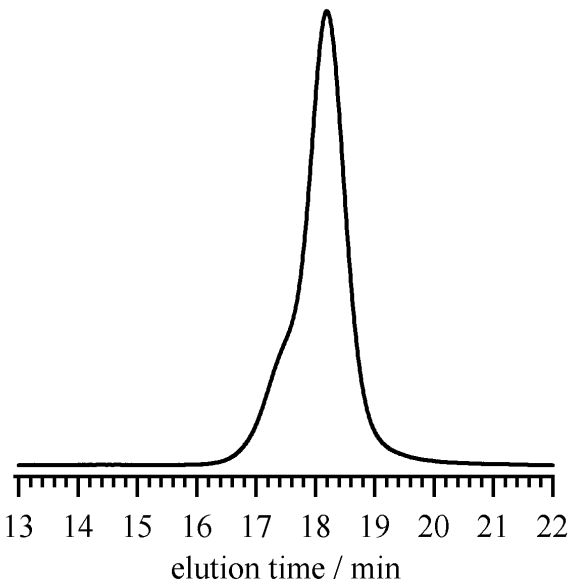

Figure S3. SEC trace of the obtained PCL initiated from H_2O (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

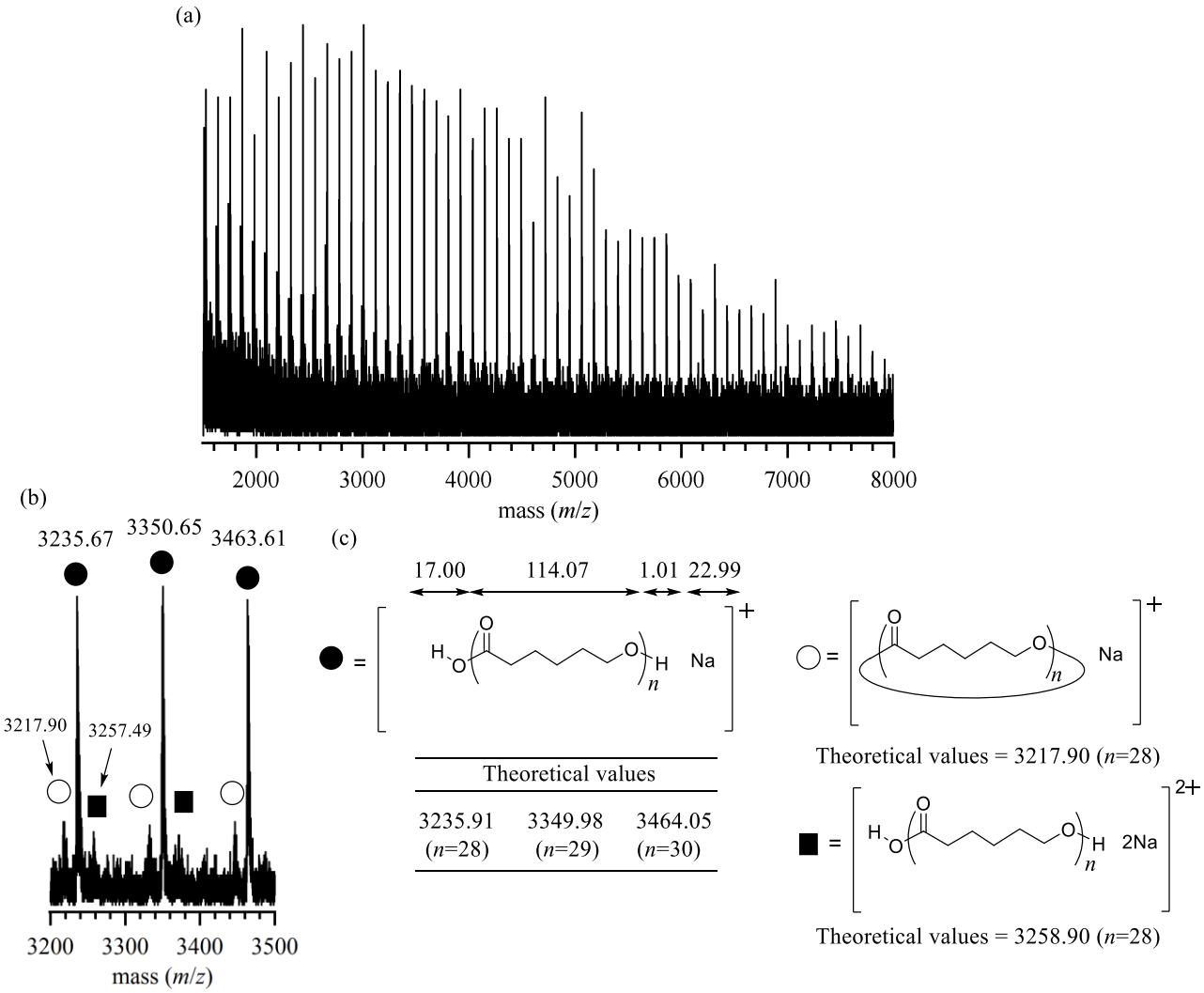

Figure S4. (a) MALDI-TOF MS spectrum of the PCL initiated from H_2O, (b) expanded spectrum (ranging from 3,200 to 3,500), and (c) theoretical molar mass values and expected structures.

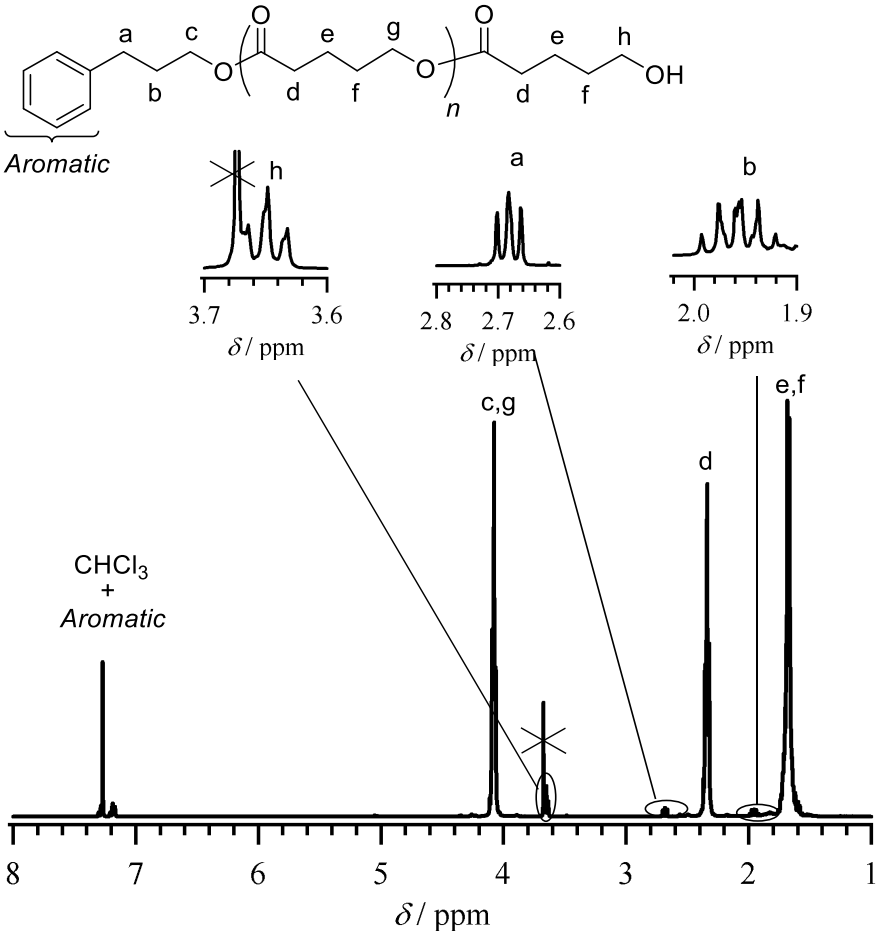

Figure S5. ^{1}H NMR spectrum of PVL in $CDCl_3$ (run 13 in Table 2).

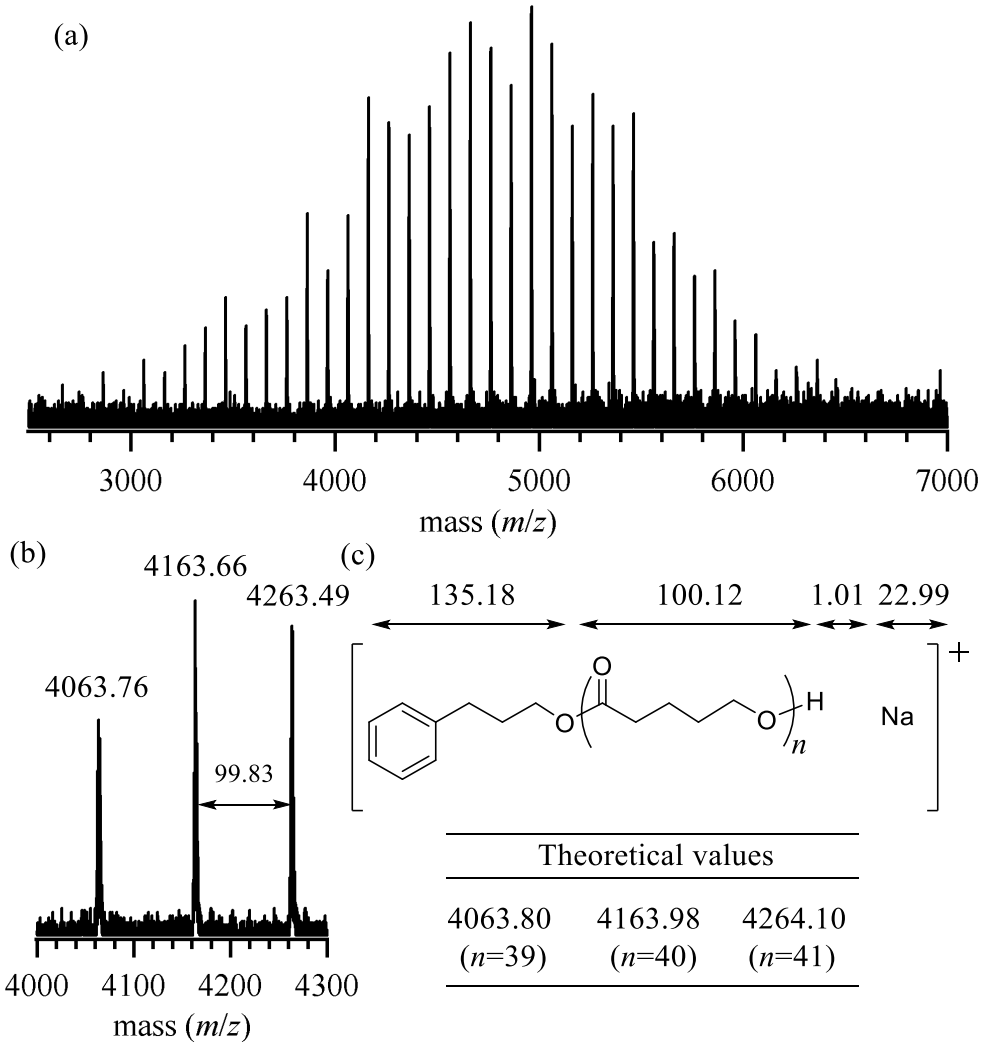

Figure S6. (a) MALDI-TOF MS spectrum of PVL (run 13 in Table 2), (b) expanded spectrum (ranging from 4,000 to 4,300), and (c) theoretical molar mass values.

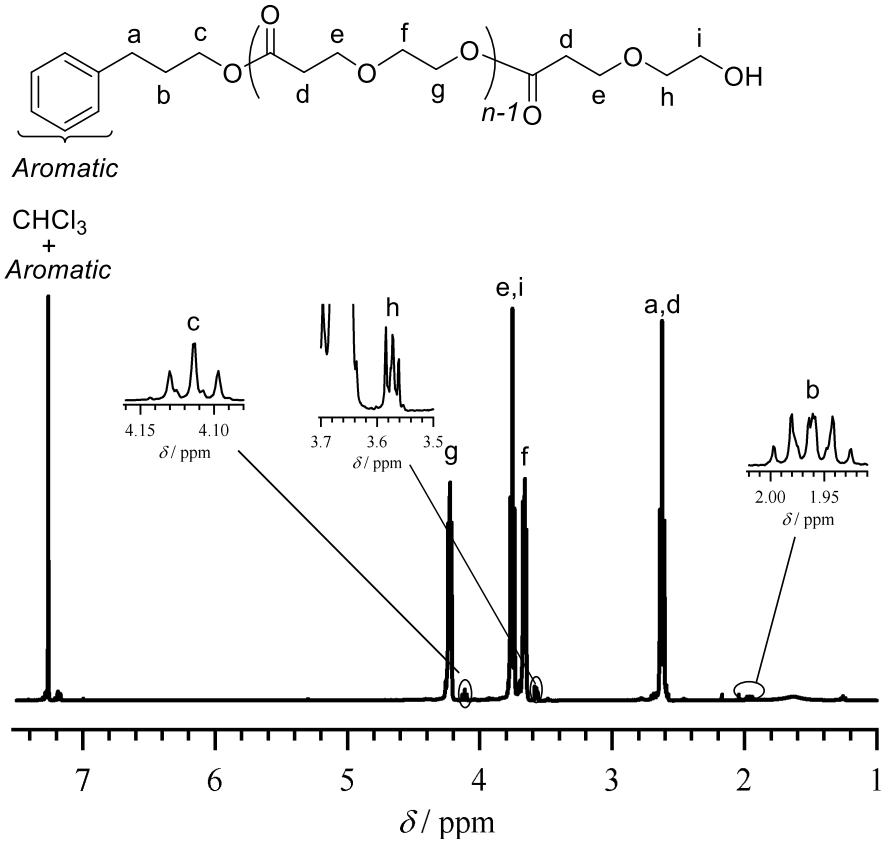

Figure S7. ^{1}H NMR spectrum of PDXO in $CDCl_3$ (run 16 in Table 2).

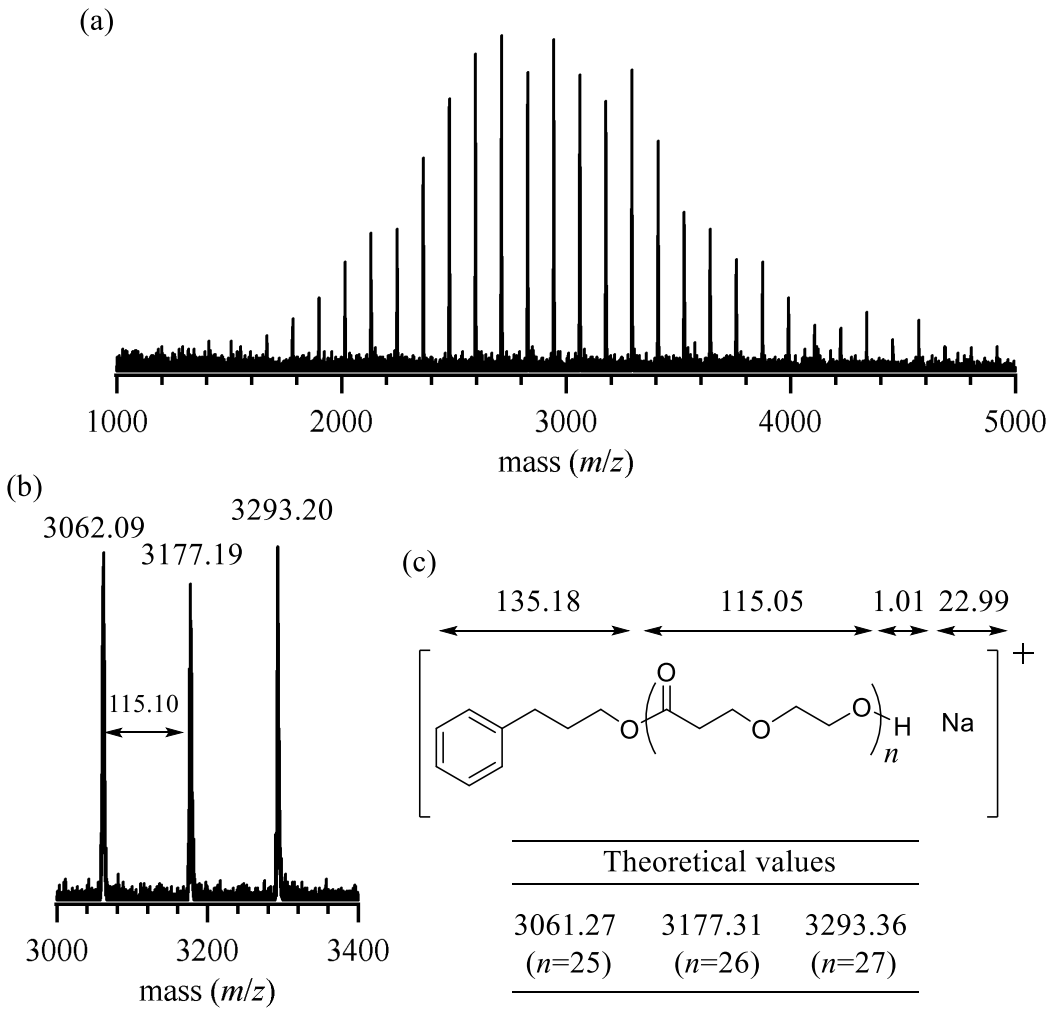

Figure S8. (a) MALDI-TOF MS spectrum of PDXO, (b) expanded spectrum (ranging from 3,000 to 3,400), and (c) theoretical molar mass values (run 16 in Table 2).

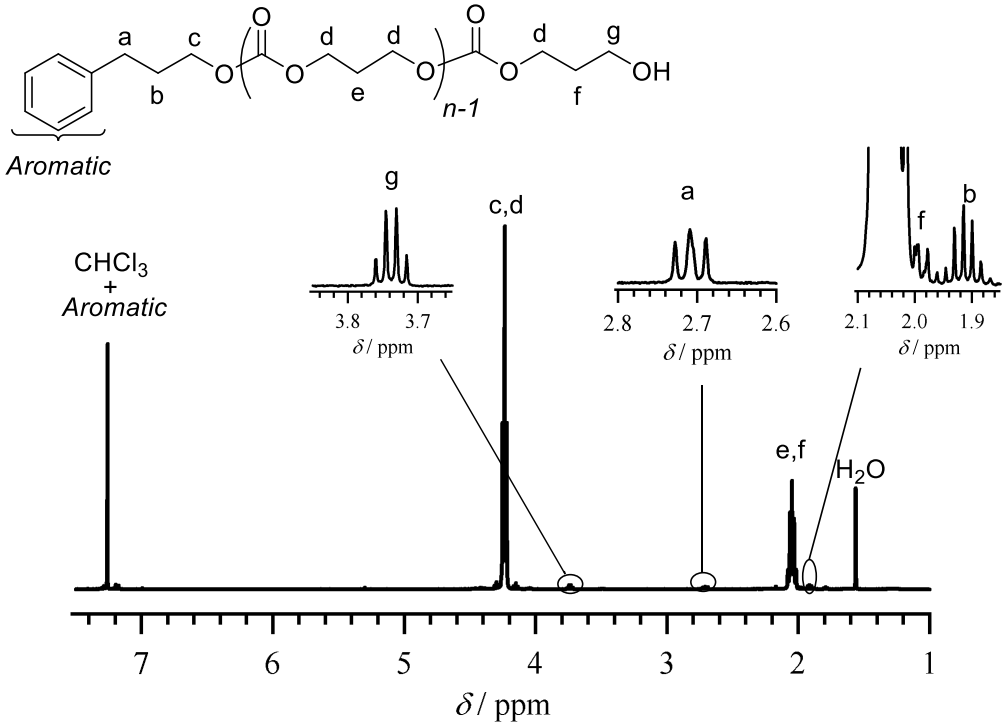

Figure S9. ^{1}H NMR spectrum of PTMC in $CDCl_3$ (run 19 in Table 2).

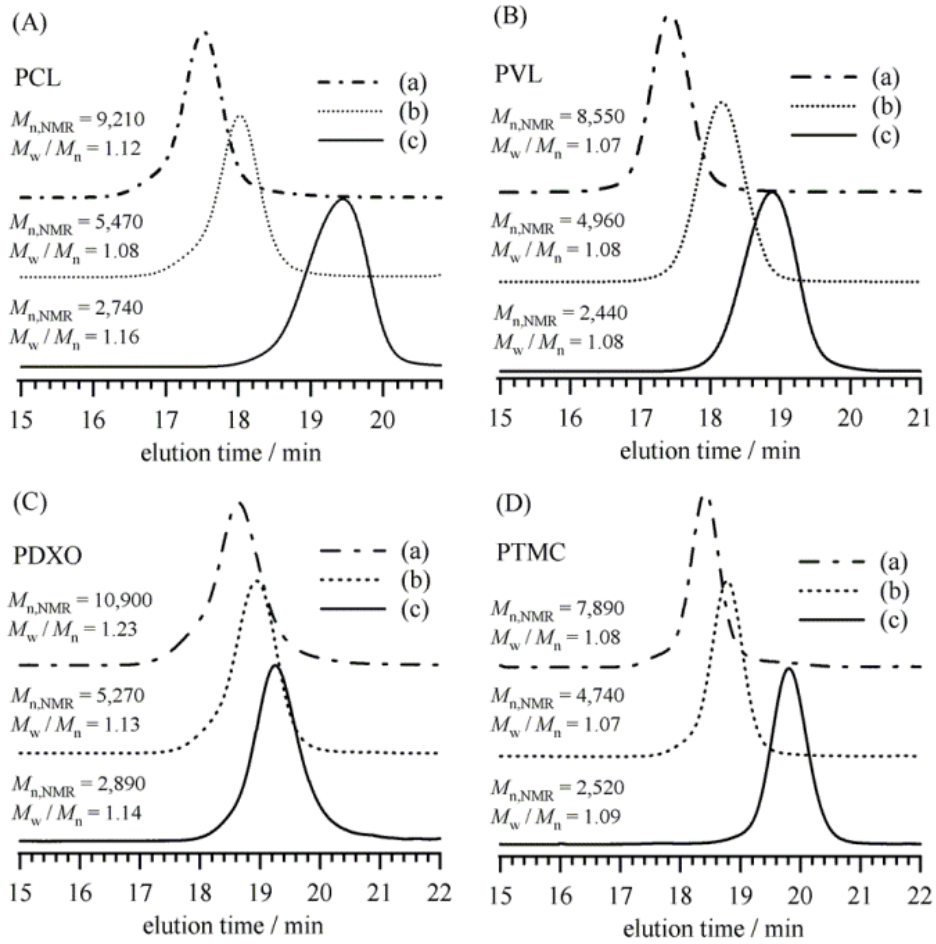

Figure S10. SEC traces of (A) the obtained PCLs, (B) PVLs, (C) PDXOs, and (D) PTMCs with the $[M]_0/[PPA]_0$ ratios of (a) 100/1, (b) 50/1, and (c) 25/1 (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

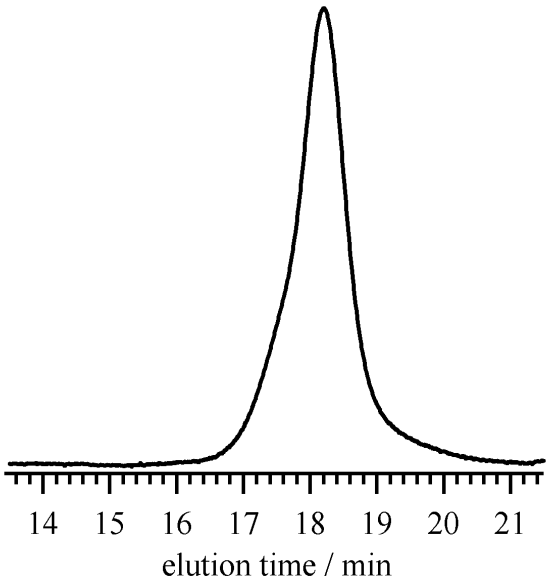

Figure S11. SEC trace of the PLLA obtained from run 21 in Table 2 (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

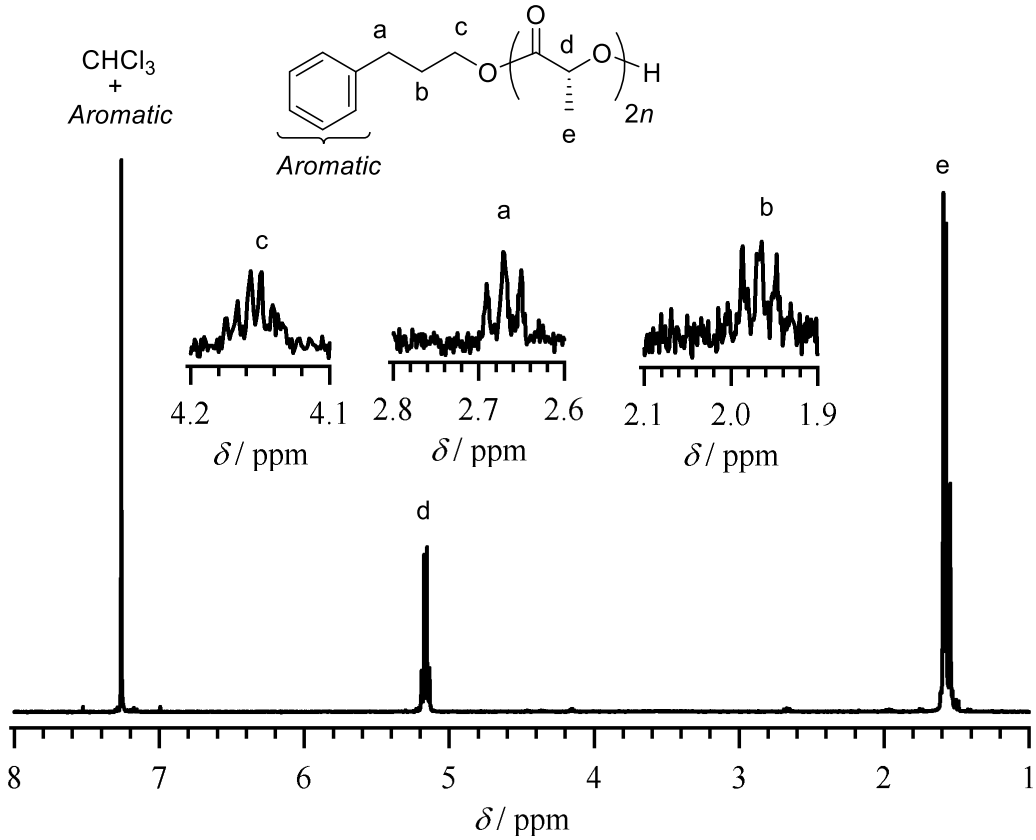

Figure S12. ^1H NMR spectrum of PLLA in $CDCl_3$ (run 21 in Table 2)

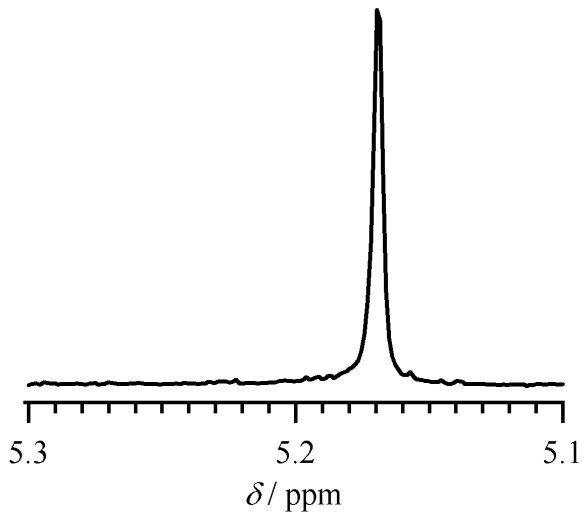

Figure S13. ^{1}H NMR spectrum of PLLA methane resonances with selective decoupling of PLLA methyl resonances (run 21 in Table 2).

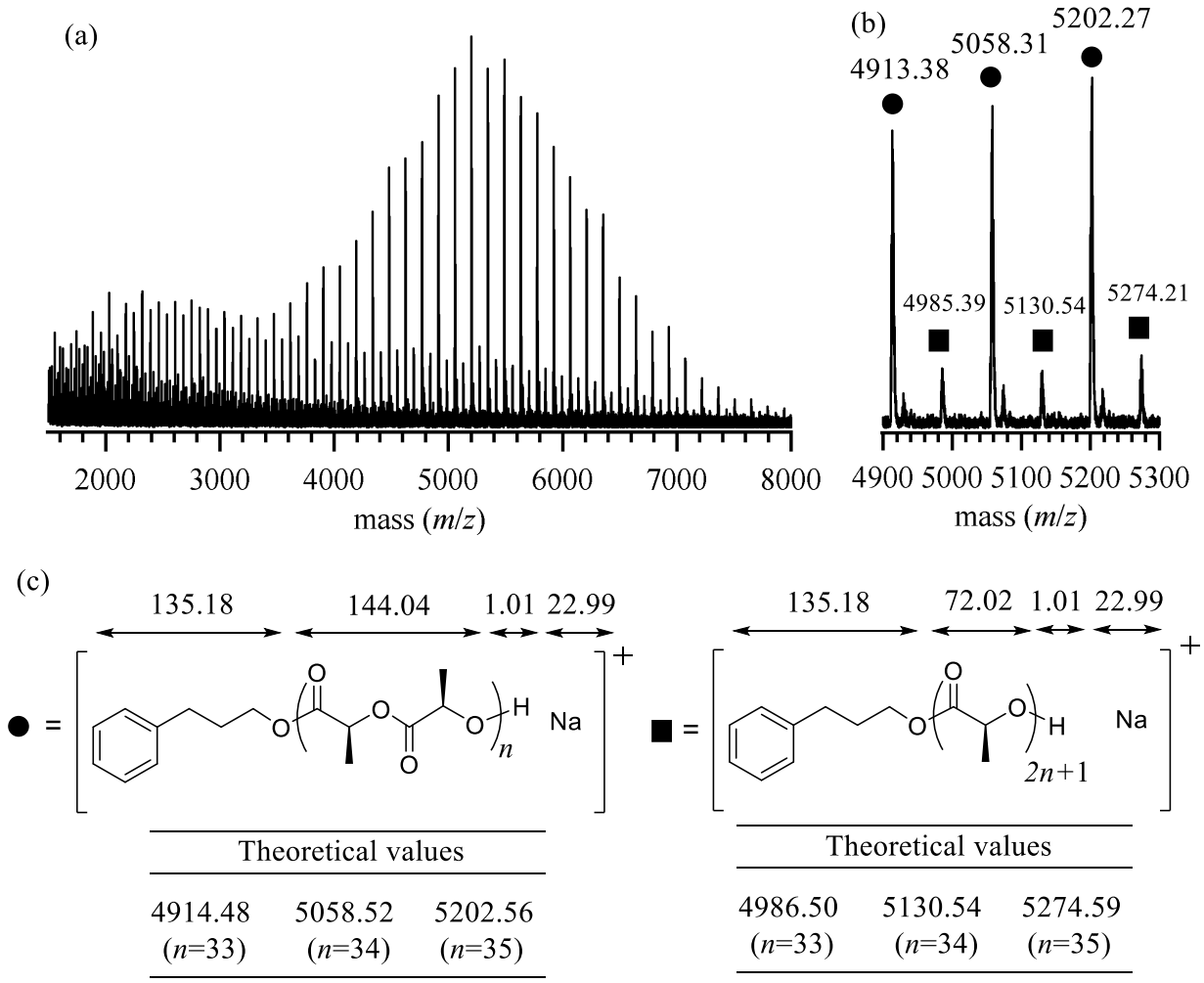

Figure S14. (a) MALDI-TOF MS spectrum of PLLA (run 21 in Table 2), (b) expanded spectrum (ranging from 4,900 to 5,300), and (c) theoretical molar mass values.

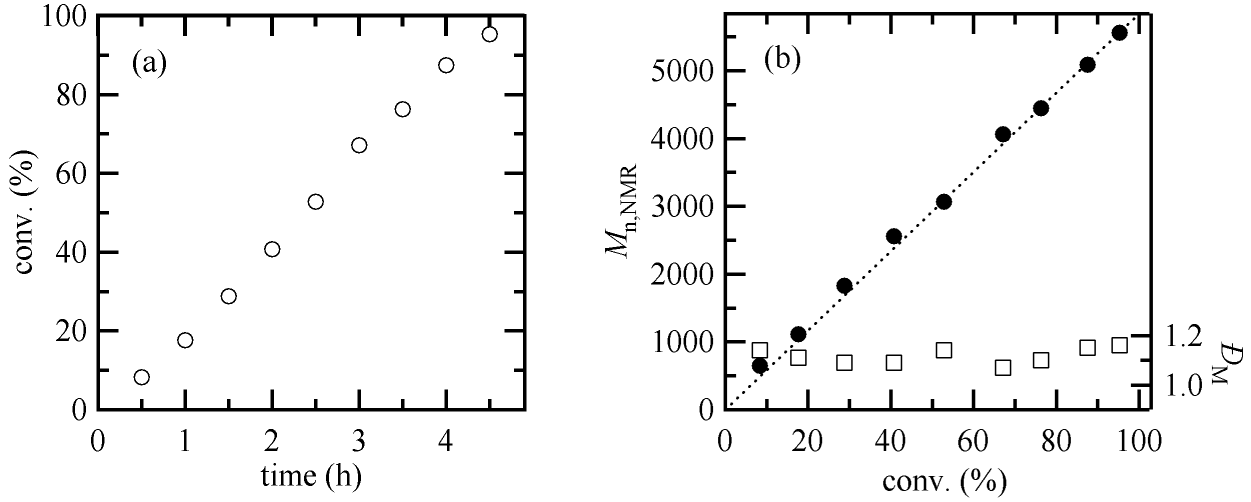

Figure S15. (a); Kinetic plots for the DPP-catalyzed bulk ROP of ε-CL with $[\varepsilon\text{-CL}]_0/[\text{PPA}]_0/[\text{DPP}]_0$ = 50/1/0.05, and (b); dependence of $M_{n,NMR}$ (●), $Đ_M$ (□) and $M_{n,th.}$ (dotted line) on monomer conversion (conv.).

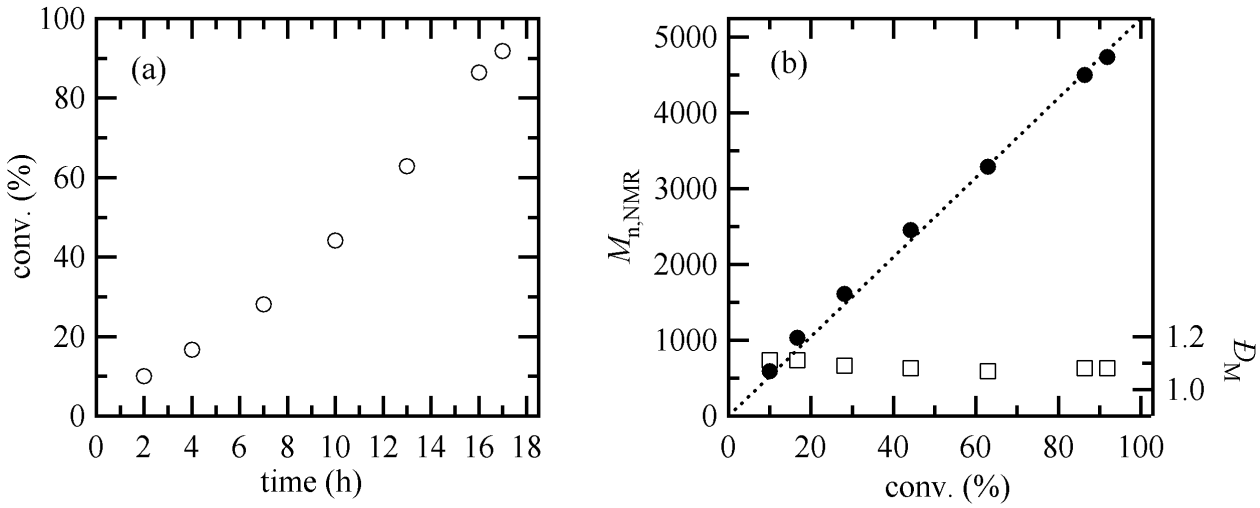

Figure S16. (a); Kinetic plots for the DPP-catalyzed bulk ROP of TMC with $[\text{TMC}]_0/[\text{PPA}]_0/[\text{DPP}]_0$ = 50/1/0.05, and (b); dependence of $M_{n,NMR}$ (●), $Đ_M$ (□) and $M_{n,th.}$ (dotted line) on monomer conversion (conv.).

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]	$Đ_M$ [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 ^{1}H NMR spectrum of the obtained polymer in $CDCl_3$. [c] Calculated from $[M_1]_0/[PPA]_0$ × conv. × (M.W. of M_1) + (M.W. of PPA). [d] Determined by SEC measurement of the obtained polymer in $CHCl_3$. [e] Calculated from $[M_2]_0/[PPA]_0$ × conv. × (M.W. of M_2) + ($M_{n,NMR}$ of the polymer obtained from first polymerization).

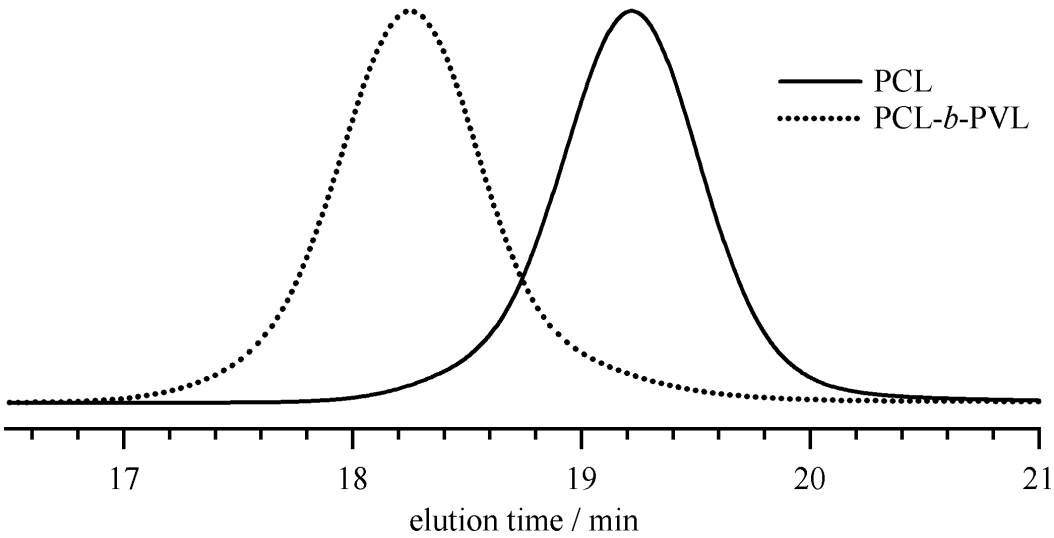

Figure S17. SEC traces of PCL obtained from the 1st polymerization and PCL-*b*-PVL (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

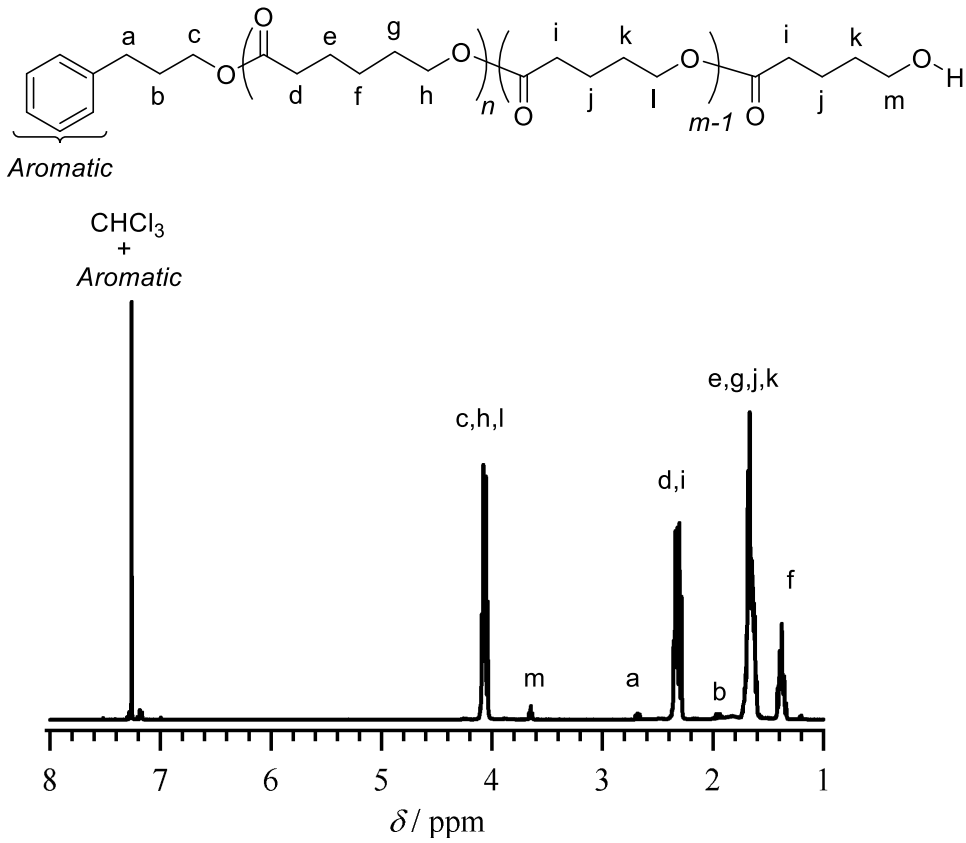

Figure S18. ^{1}H NMR spectrum of PCL-*b*-PVL in $CDCl_3$ (run 31 in Table S1).

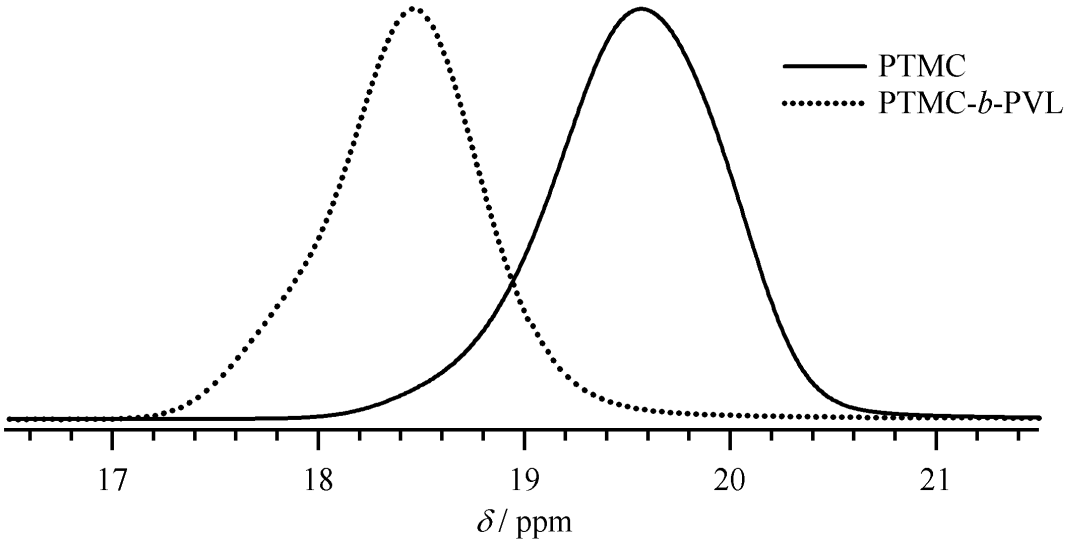

Figure S19. SEC traces of PTMC obtained from the 1st polymerization and PTMC-*b*-PVL (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

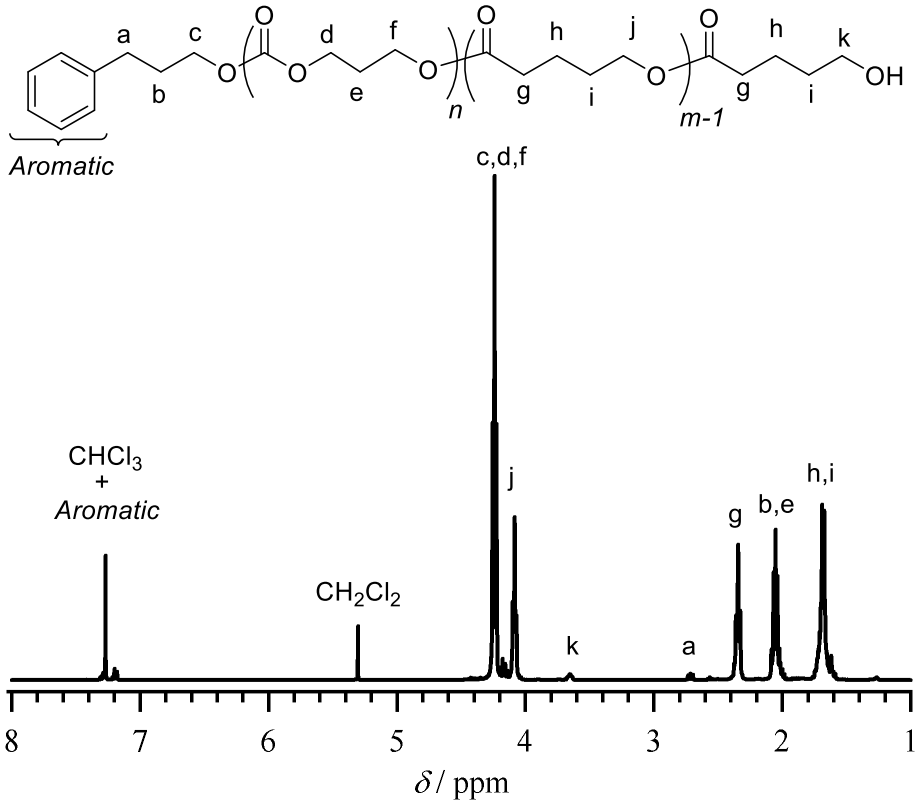

Figure S20. ^{1}H NMR spectrum of PTMC-*b*-PVL in $CDCl_3$ (run 32 in Table S1).

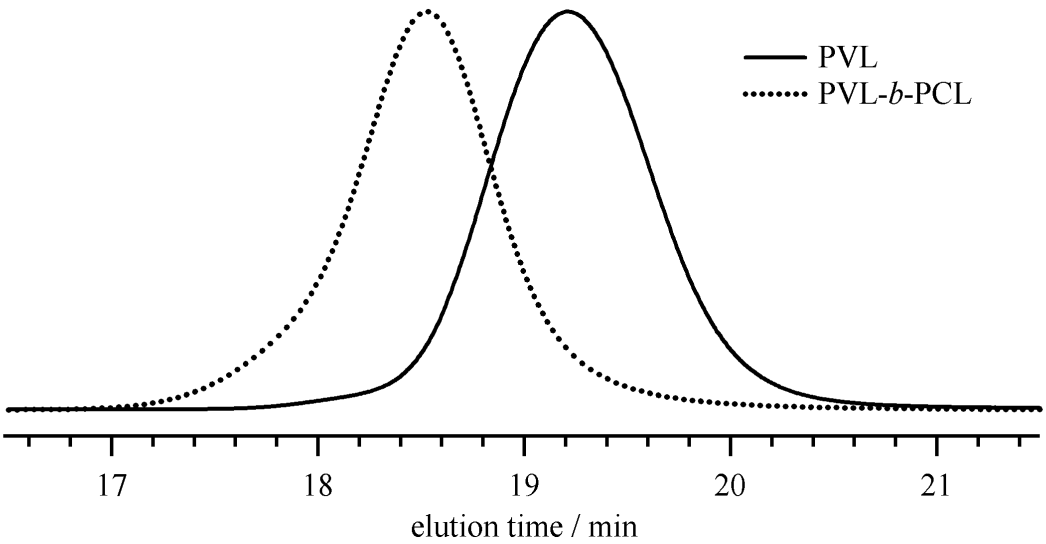

Figure S21. SEC traces of PVL obtained from the 1st polymerization and PVL-*b*-PCL (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

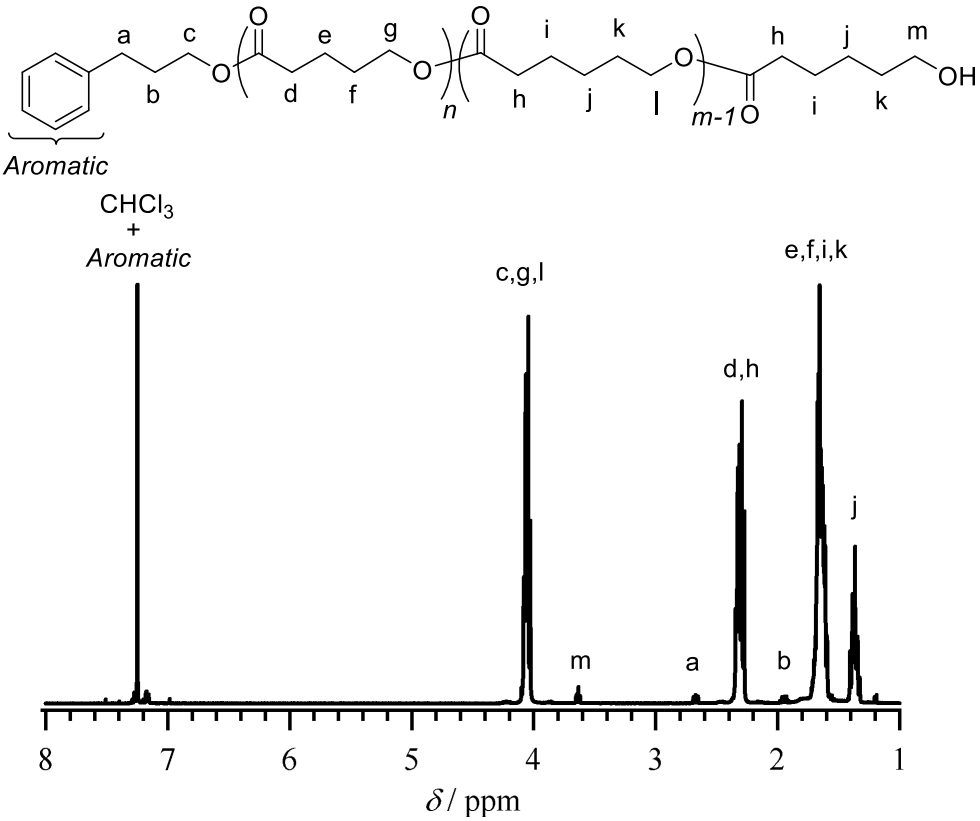

Figure S22. ^{1}H NMR spectrum of PVL-*b*-PCL in $CDCl_3$ (run 33 in Table S1).

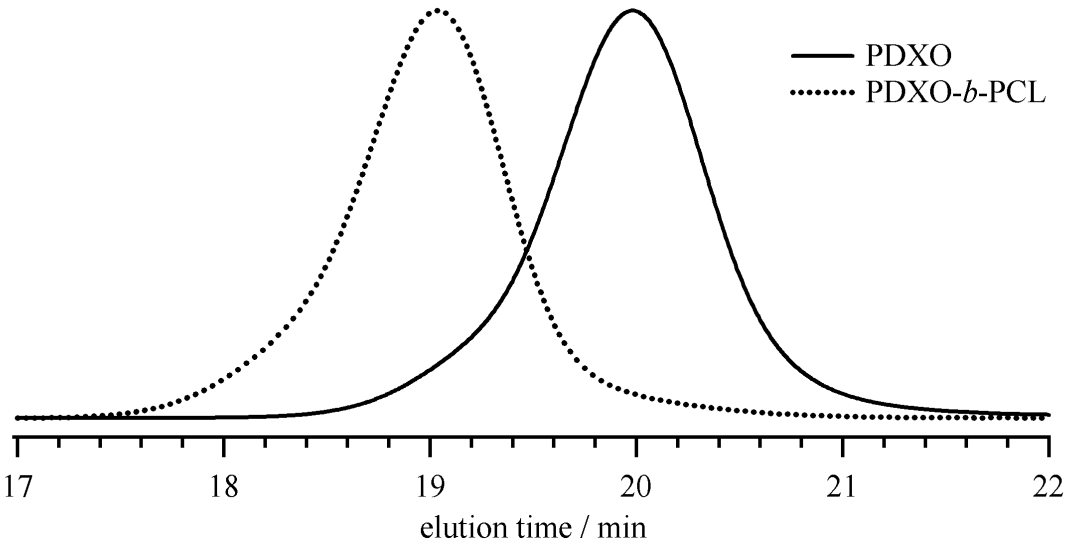

Figure S23. SEC traces of PDXO obtained from the 1st polymerization and PDXO-*b*-PCL (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

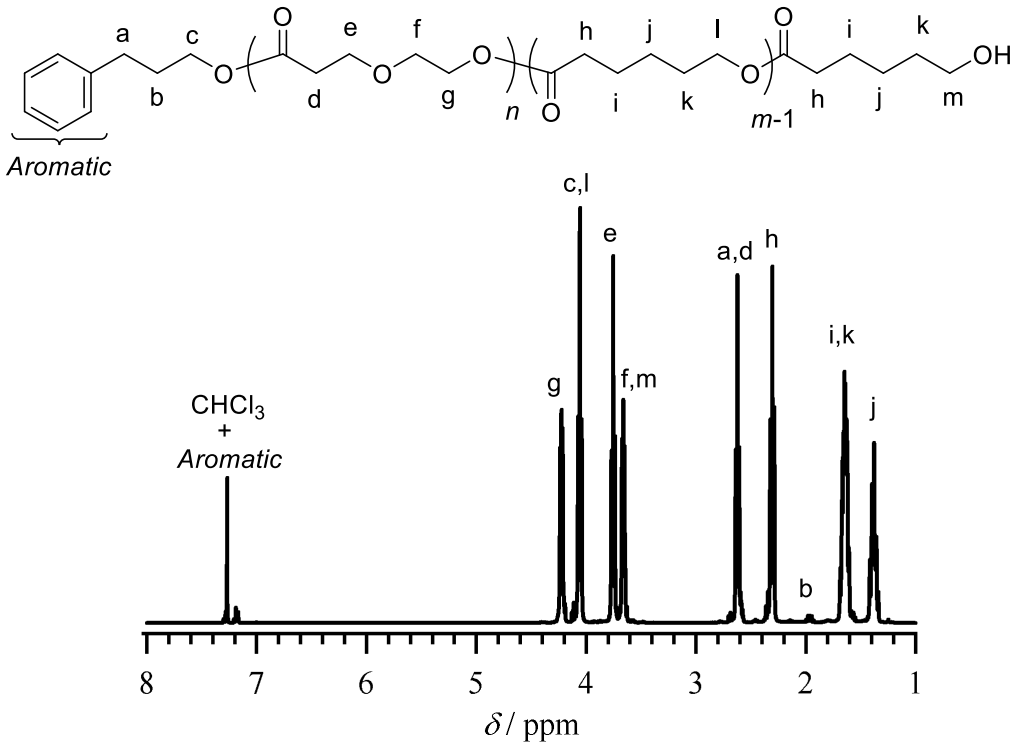

Figure S24. ^{1}H NMR spectrum of PDXO-*b*-PCL in $CDCl_3$ (run 34 in Table S1).

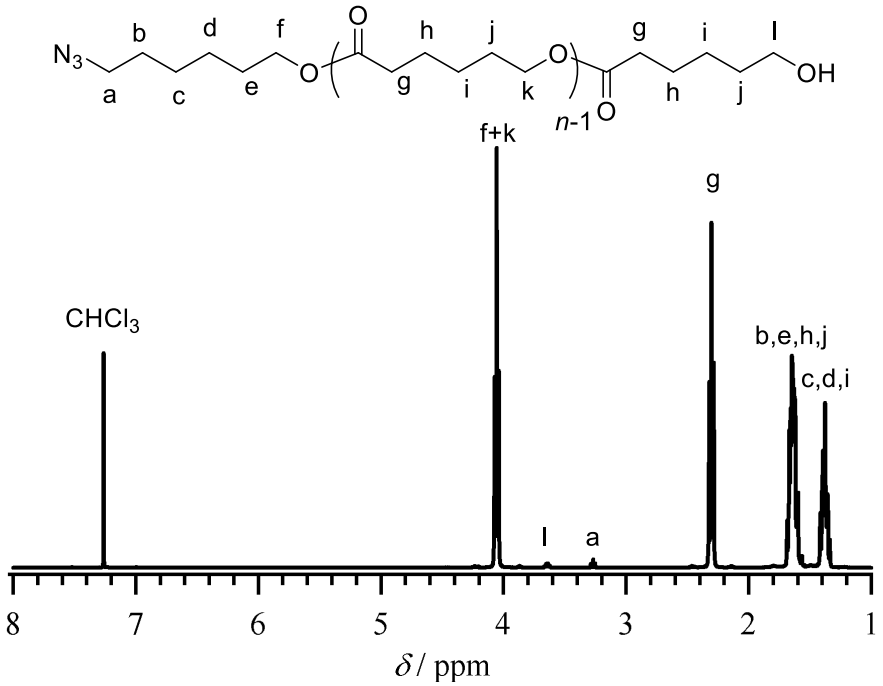

Figure S25. ^{1}H NMR spectrum of N_3-PCL in $CDCl_3$ (run 22 in Table 3).

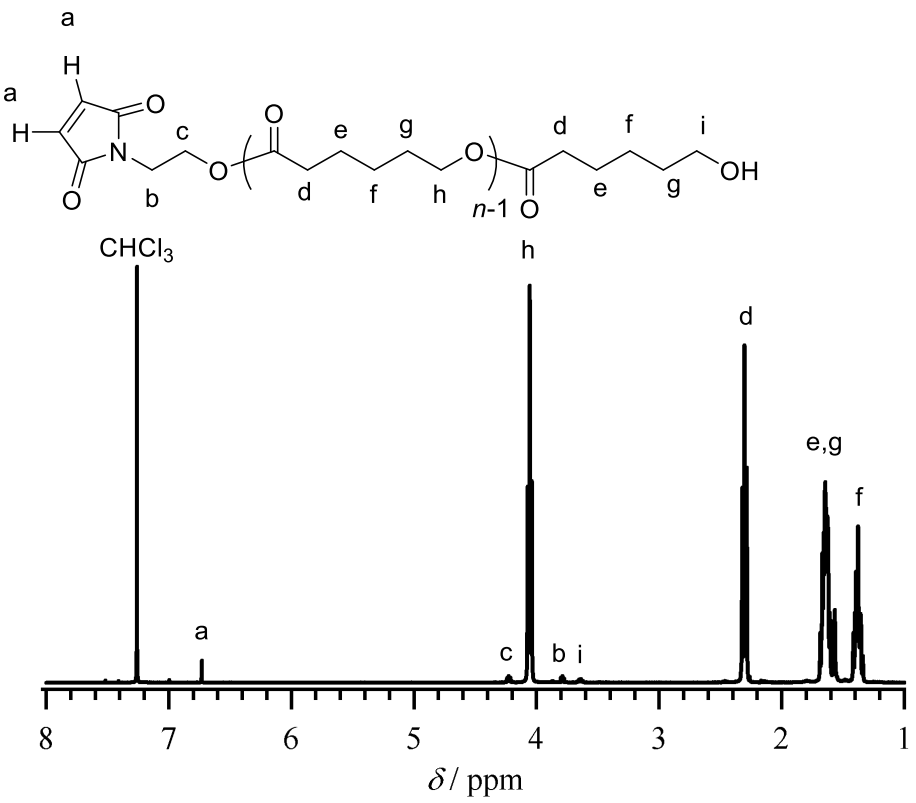

Figure S26. ^{1}H NMR spectrum of MI-PCL in $CDCl_3$ (run 23 in Table 3).

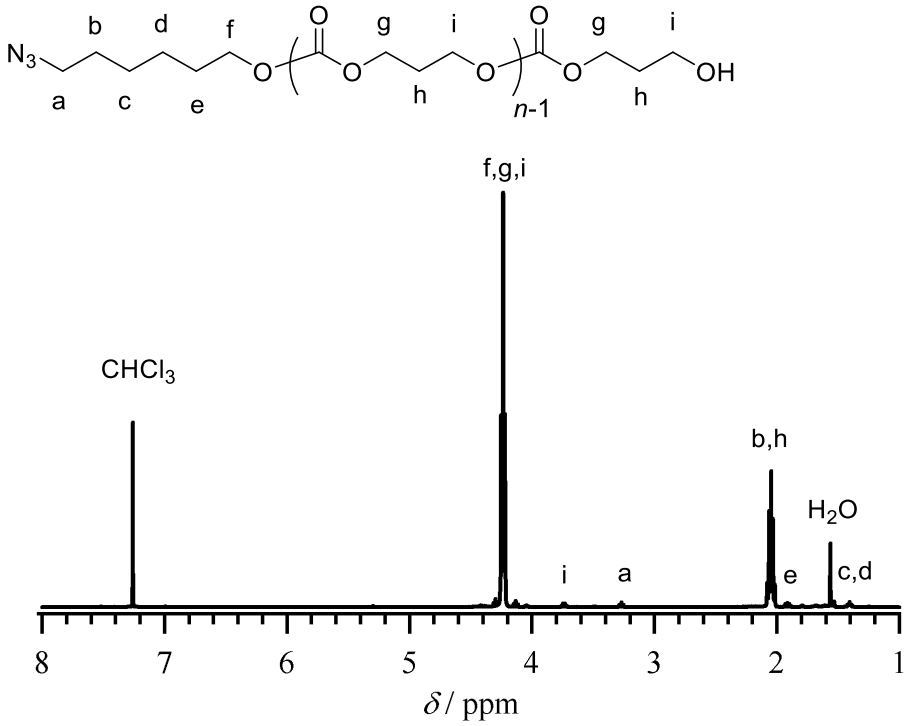

Figure S27. ^{1}H NMR spectrum of N_3-PTMC in $CDCl_3$ (run 24 in Table 3).

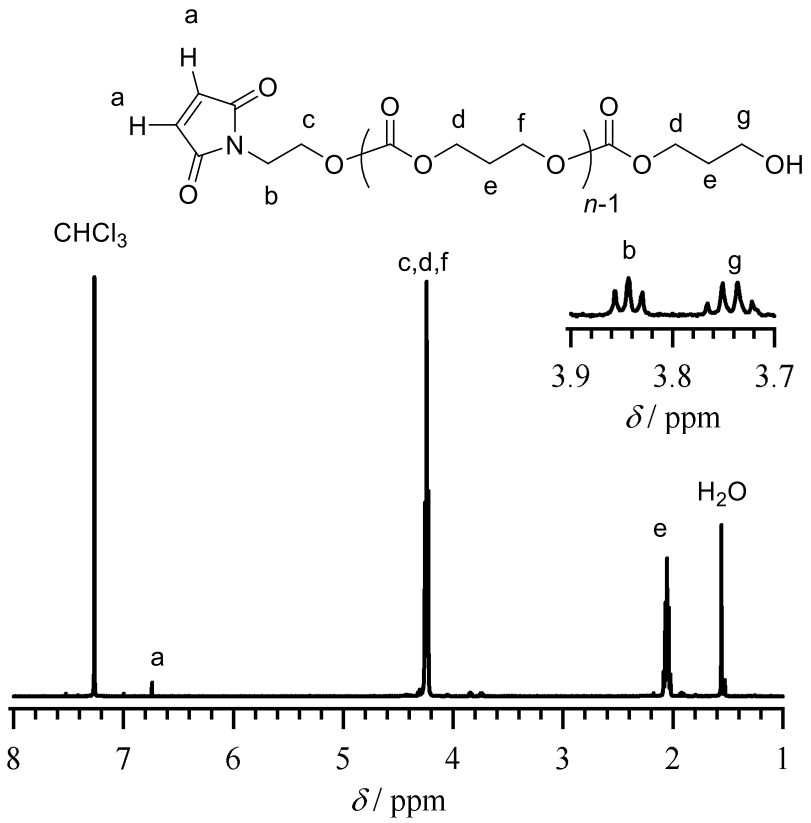

Figure S28. ^{1}H NMR spectrum of MI-PTMC in $CDCl_3$ (run 25 in Table 3).

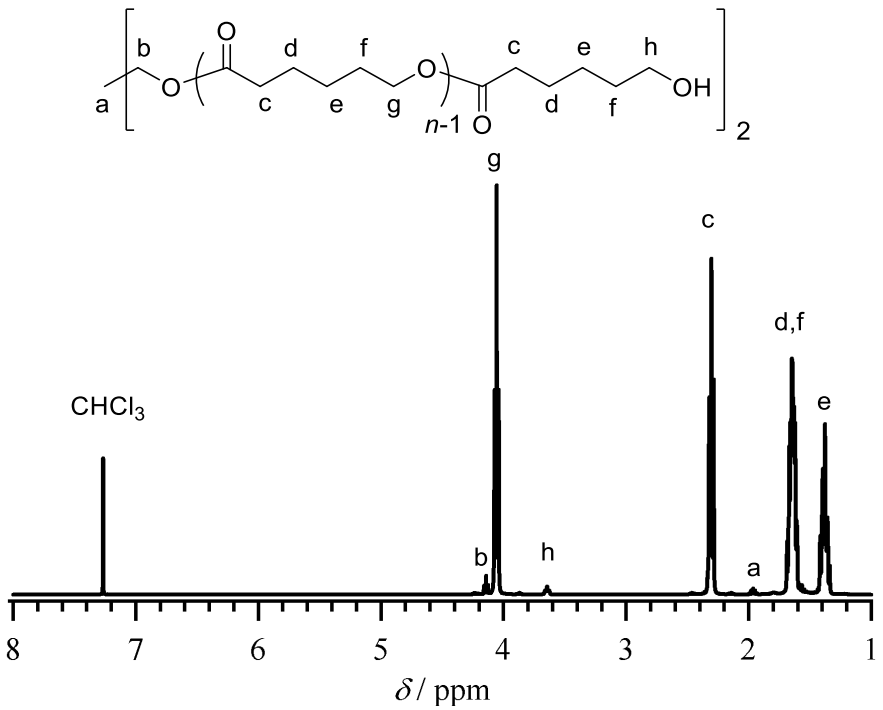

Figure 29. ^{1}H NMR spectrum of PCL-diol in $CDCl_3$ (run 26 in Table 3).

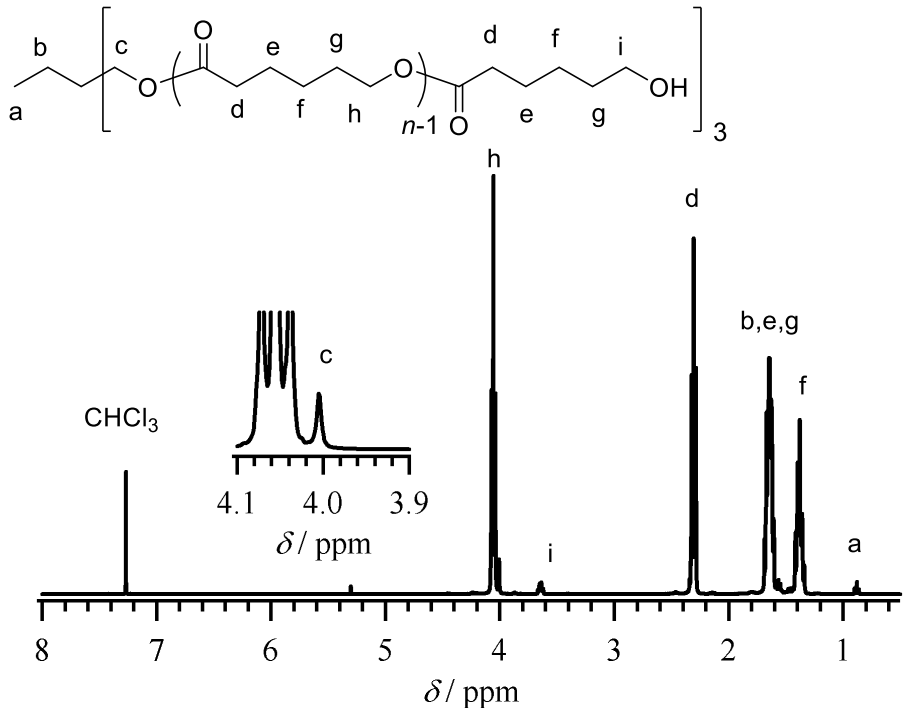

Figure S30. ^{1}H NMR spectrum of PCL-triol in $CDCl_3$ (run 27 in Table 3).

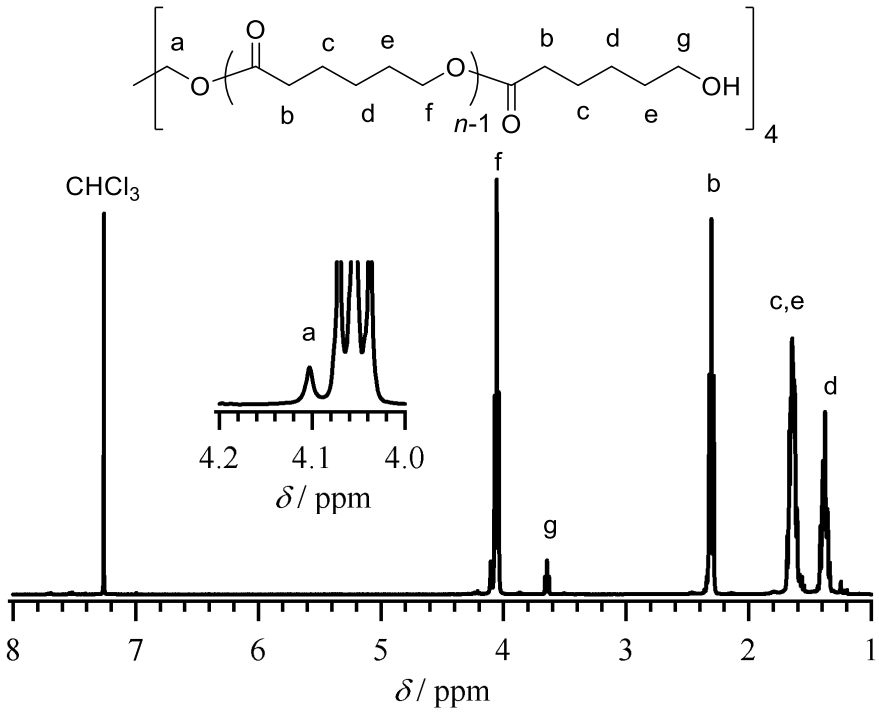

Figure S31. ^{1}H NMR spectrum of PCL-tetraol in $CDCl_3$ (run 28 in Table 3).

.

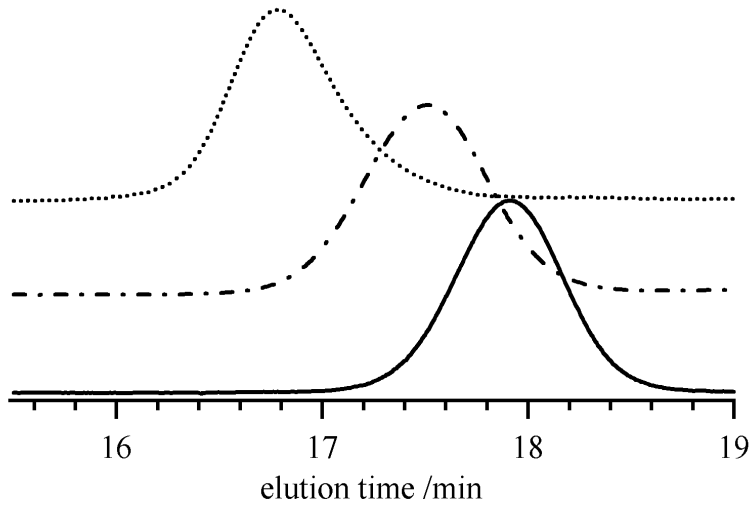

Figure S32. SEC traces of the obtained polymer in $CHCl_3$ (solid line, run 28; chained line, run 29; dotted line, run 30).

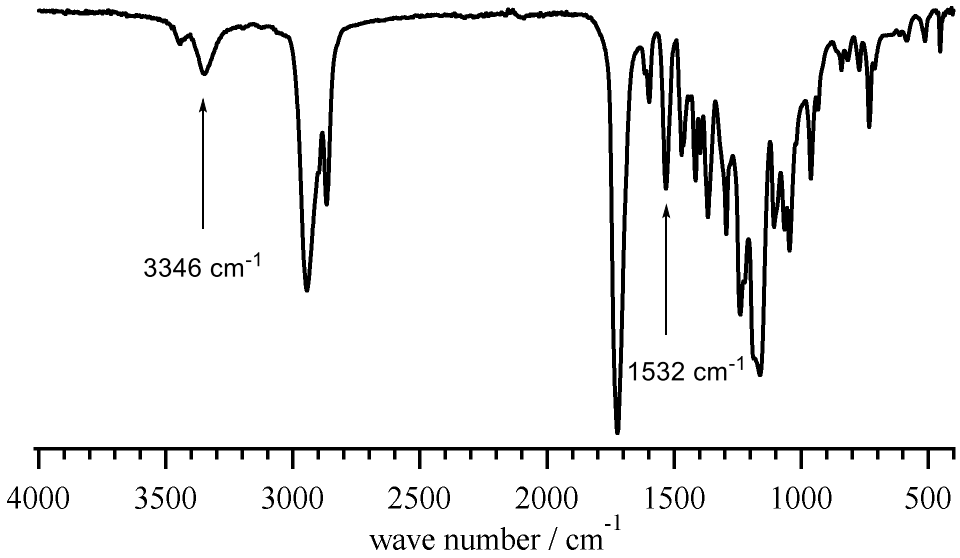

Figure S33. FT-IR spectrum of the obtained PCL-based polyurethane in the presence of DPP.

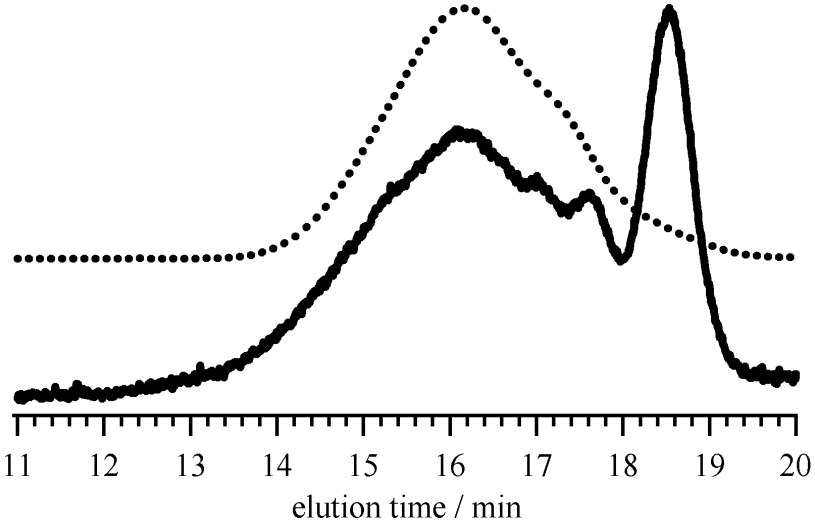

Figure S34. SEC traces of the obtained PCL-based polyurethane in the presence of DPP; dotted line and in the absence of DPP; solid line (eluent, $CHCl_3$; flow rate, 1.0 mL min^{-1}).

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

ε-CL (0.570 mL, 5.00 mmol), PPA (27.2 μL, 200 μmol) and DPP (2.50 mg, 10.0 μmol) 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 ^{1}H 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%. $M_{n,NMR}$ = 5,000; $M_{n,SEC}$ = 8,700, $Đ_M$ = 1.13. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.37 (m, 2H × *n*, $(-CH_2CH_2CH_2CH_2CH_2O-)_n$), 1.57-1.75 (m, 2H × *n*, $(-CH_2CH_2CH_2CH_2CH_2O-)_n$; 2H × *n*, $(-CH_2CH_2CH_2CH_2CH_2O-)_n$; 2H × *m*, $(-COCH_2CH_2CH_2CH_2O-)_m$; 2H × *m*, $(-COCH_2CH_2CH_2CH_2O-)_m$), 1.95 (m, 2H, $ArCH_2CH_2CH_2-$), 2.26-2.40 (m, 2H × *n*, $(-CH_2CH_2CH_2CH_2CH_2O-)_n$; 2H × *m*, $(-COCH_2CH_2CH_2CH_2O-)_m$), 2.69 (t, 2H, *J* = 7.8 Hz, $ArCH_2-$) 3.65 (m, 2H,CH_2OH), 4.02-4.13 (m, 2H × *n*, $(-CH_2CH_2CH_2CH_2CH_2O-)_n$; 2H × (*m-1*), $(-COCH_2CH_2CH_2CH_2O-)_{m-1}$, 2H, $ArCH_2CH_2CH_2-$), 7.16-7.32 (m, 5H, aromatic).

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

PTMC-*b*-PVL: Yield, 88.0%. $M_{n,NMR}$ = 4,800; $M_{n,SEC}$ = 7,500, $Đ_M$ = 1.13. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.57-1.78 (m, 2H × *m*, $(-CH_2CH_2CH_2CH_2-)_m$; 2H × *m*, $(-CH_2CH_2CH_2CH_2-)_m$), 1.96-2.12 (m, 2H × *n*, $(-OCH_2CH_2CH_2O-)_n$; 2H, $ArCH_2CH_2-$), 2.34 (m, 2H × *m*, $(-COCH_2CH_2CH_2CH_2-)_m$), 2,72 (t, 2H, *J* = 7.8 Hz, $ArCH_2-$), 3.65 (m, 2H, $-CH_2OH$), 4.08 (m, 2H × (*m-1*), $(-COCH_2CH_2CH_2CH_2O-)_{m-1}$), 4.13-4.30 (m, 2H × *n*, $(-OCH_2CH_2CH_2O-)_n$; 2H × *n*, $(-OCH_2CH_2CH_2O-)_n$; 2H, $ArCH_2CH_2CH_2-$), 7.16-7.32 (m, 5H, aromatic).

PVL-*b*-PCL: Yield, 74.1%. $M_{n,NMR}$ = 5,200; $M_{n,SEC}$ = 7,000, $Đ_M$ = 1.15. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.38 (m, 2H × *m*, $(-CH_2CH_2CH_2CH_2CH_2-)_m$), 1.58-1.75 (m, 2H × *n*, $(-COCH_2CH_2CH_2CH_2O-)_n$; 2H × *n*, $(-COCH_2CH_2CH_2CH_2O-)_n$; 2H × *m*, $(-CH_2CH_2CH_2CH_2CH_2O-)_m$; 2H × *m*, $(-CH_2CH_2CH_2CH_2CH_2O-)_m$), 1.96 (m, 2H, $ArCH_2CH_2-$), 2.27-2.40 (m, 2H × *n*, $(-COCH_2CH_2CH_2CH_2O-)_n$; 2H × *m*, $(-COCH_2CH_2CH_2CH_2CH_2-)_m$), 2.69 (t, 2H, *J* = 7.6 Hz, $ArCH_2-$),

3.65 (t, 2H, J = 6.4 Hz, -CH_2OH), 4.02-4.12 (m, 2H × n, (-COCH$_2$CH$_2$CH$_2$CH_2O-)$_n$; 2H × (m-1), (-CH$_2$CH$_2$CH$_2$CH$_2$CH_2O-)$_{m-1}$; 2H, ArCH$_2$CH$_2$CH_2-), 4.20 (t, 2H × n, J = 4.8 Hz, (-COCH$_2$CH$_2$OCH$_2$CH_2-)$_n$), 7.15-7.31 (m, 5H, aromatic).

PDXO-*b*-PCL: Yield, 5.5%. $M_{n,NMR}$ = 6,000; $M_{n,SEC}$ = 5,200, $Đ_M$ = 1.16. ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 1.38 (m, 2H × m, (-CH$_2$CH$_2$CH_2CH$_2$CH$_2$-)$_m$), 1.58-1.71 (m, 2H × m, (-CH$_2$CH_2CH$_2$O-)$_m$; 2H × m, (-COCH$_2$CH_2CH$_2$-)$_m$), 1.97 (m, 2H × m, ArCH$_2$CH_2-), 2.28 (m, 2H × m, (-COCH_2CH$_2$CH$_2$-)$_m$), 2.56-2.72 (m, 2H × n, (-COCH_2CH$_2$O-)$_n$; 2H, ArCH_2CH$_2$-), 3.62-3.71 (m, 2H × n, (-COCH$_2$CH$_2$OCH_2-)$_n$; 2H, -CH_2OH), 3.74 (m, 2H × n, (-COCH$_2$$CH_2$O-)$_n$), 4.01-4.11 (m, 2H × ($m$-$1$), (-CH$_2CH_2CH_2$O-)$_{m-1}$; 2H, ArCH$_2CH_2CH_2$-), 4.20 (t, 2H × n, J = 4.8 Hz, (-COCH$_2$CH$_2$OCH$_2$CH_2-)$_n$), 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%. $M_{n,NMR}$ = 5,500 ; $M_{n,SEC}$ = 12,700, $Đ_M$ = 1.11. ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 1.31-1.41 (m, 2H × n, (-CH$_2$CH$_2$CH_2CH$_2$CH$_2$-)$_n$; 4H, N$_3$CH$_2$CH$_2$CH_2CH_2-), 1.55-1.69 (m, 2H × n, (-CH$_2$CH_2CH$_2$O-)$_n$; 2H × n, (-COCH$_2$CH_2CH$_2$-)$_n$; 4H, N$_3$CH$_2$CH_2CH$_2$CH$_2$CH_2-), 2.31 (t, 2H × n, J = 7.6 Hz, (-COCH_2CH$_2$-)$_n$), 3.28 (t, 2H, J = 7.0 Hz, N$_3$CH_2-), 3.63 (m, 2H, -CH$_2$CH_2OH), 4.01-4.09 (m, 2H × (n-1), (-CH$_2$CH_2O-)$_{n-1}$; 2H, N$_3$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$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%. $M_{n,NMR}$ = 5,500; $M_{n,SEC}$ = 13,400, $Đ_M$ = 1.15. ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 1.36 (m, 2H × n, (-CH$_2$CH$_2$CH_2CH$_2$CH$_2$-)$_n$), 1.58-1.71 (m, 2H × n, (-CH$_2$CH_2CH$_2$O-)$_n$; 2H × n, (-COCH$_2$CH_2CH$_2$-)$_n$), 2.29 (t, 2H × n, J = 8.2 Hz, (-COCH_2CH$_2$-)$_n$), 3.64 (m, 2H, -CH$_2$CH_2OH), 3.79 (t, 2H, J = 5.4 Hz, -NCH_2-), 4.06 (t, 2H × (n-1), J = 6.6 Hz, (-CH$_2$CH_2O-)$_{n-1}$), 4.23 (t, 2H, J = 5.2 Hz, -NCH$_2$CH_2-), 6,74 (s, 2H, -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 (14.3μL, 200 μmol) and DPP (2.50 mg, 10.0 μmol) 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, $Đ_M$ = 1.13. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.36 (m, 2H × *n*, $(-CH_2CH_2CH_2CH_2CH_2-)_{n/2}$ × 2), 1.58-1.71 (m, 2H × *n*, $(-CH_2CH_2CH_2O-)_{n/2}$ × 2; 2H × *n*, $(-COCH_2CH_2CH_2-)_{n/2}$ × 2), 1.97 (m, 2H, $-OCH_2CH_2CH_2O-$), 2.29 (t, 2H × *n*, *J* = 8.2 Hz, $(-COCH_2CH_2-)_{n/2}$ × 2), 3.63 (t, 2H × 2, *J* = 6.4 Hz, $-CH_2CH_2OH$) 4.06 (t, 2H × (*n-1*), *J* = 6.6 Hz, $(-CH_2CH_2O-)_{(n-1)/2}$ × 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 μmol) and DPP (2.50 mg, 10.0 μmol) 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, $Đ_M$ = 1.07. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 0.89 (t, 3H, *J* = 7.4 Hz, CH_3CH_2), 1.36 (m, 2H × *n*, $(-CH_2CH_2CH_2CH_2CH_2-)_{n/3}$ × 3), 1.55-1.72 (m, 2H, CH_3CH_2-; 2H × (*n-1*), $(-CH_2CH_2CH_2O-)_{n/3}$ × 3; 2H × *n*, $(-COCH_2CH_2CH_2-)_{n/3}$ × 3), 2.31 (m, 2H × *n*, $(-OCOCH_2CH_2-)_{n/3}$ × 3), 3.65 (m, 6H, $-CH_2CH_2OH$ × 3), 4.01 (s, 6H, $C(CH_2O-)_3$), 4.06 (t, 2H × (*n-1*), *J* = 6.6 Hz, $(-CH_2CH_2O-)_{(n-1)/3}$ × 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 μmol) and DPP (2.50 mg, 10.0 μmol) 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, $Đ_M$ = 1.07. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.37 (m, 2H × *n*, $(-CH_2CH_2CH_2CH_2CH_2-)_{n/4}$ × 4), 1.54-1.73 (m, 2H × *n*, $(-CH_2CH_2CH_2O-)_{n/4}$ × 4; 2H × *n*, $(-COCH_2CH_2CH_2-)_{n/4}$ × 4), 2.32 (m, 2H × *n*, $(-OCOCH_2CH_2-)_{n/4}$ × 4), 3.65 (t, 8H, *J* = 6.6 Hz, $-CH_2CH_2OH$ × 4) 4.06 (t, 2H × (*n-1*), *J* = 6.6 Hz, $(-CH_2CH_2O-)_{(n-1)/4}$ × 4), 4.11 (s, 8H,$C(CH_2CO-)_4$).

Syntheses of functional PTMCs with various initiators.

N_3-PTMC: Procedure A was used for the ROP of TMC (510 mg, 5.00 mmol) in the presence of AHA (14.3 mg, 100 μmol) and DPP (1.2 mg, 0.50 μmol) for 19 h to give N_3-PTMC (379 mg) as a colorless waxy solid. Yield, 84.1%. $M_{n,NMR}$ = 4,500; $M_{n,SEC}$ = 5,600, $Đ_M$ = 1.09. ^{1}H NMR ($CDCl_3$, 400MHz): δ (ppm) 1.42 (m, 4H, $N_3CH_2CH_2CH_2CH_2$-), 1.92 (m, 2H, $N_3CH_2CH_2CH_2CH_2CH_2$-), 2.01-2.11 (m, 2H, $N_3CH_2CH_2$-; 2H × (*n-1*), $(-OCH_2CH_2-)_{n-1}$), 3.28 (t, 2H, *J* = 7.0 Hz, N_3CH_2-), 3.74 (m, 2H, $-CH_2OH$), 4.21-4.27 (m, 2H, $N_3CH_2CH_2CH_2CH_2CH_2CH_2$-; 4H × (*n-1*), $(-OCH_2CH_2CH_2O-)_{n-1}$; 2H, $-CH_2CH_2CH_2OH$).

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 μmol) and DPP (1.2 mg, 0.50 μmol) 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, $Đ_M$ = 1.13. ^{1}H NMR ($CDCl_3$, 400MHz): δ (ppm) 1.92 (m, 2H, $-CH_2CH_2OH$), 2.00-2.13 (m, 2H × (*n-1*), $(-OCH_2CH_2-)_{n-1}$), 3.74 (m, 2H, $-CH_2OH$), 3.85 (t, 2H, *J* = 5.4 Hz $-NCH_2CH_2$-), 4.21-4.29 (m, 2H, $-NCH_2CH_2$-; 4H × *n-1*, $(-OCH_2CH_2CH_2O-)_{n-1}$; 2H, $-CH_2CH_2CH_2OH$), 6,74 (s, 2H, -COC*H*C*H*CO-).