Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Supplementary Information

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

Tatsuya Saito,[a] Yusuke Aizawa,[a] Kenji Tajima,[b] Takuya Isono[b] and Toshifumi Satoh*[b]

[a] Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, 060-8628, Japan

[b] Division of Biotechnology and Macromolecular Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

,

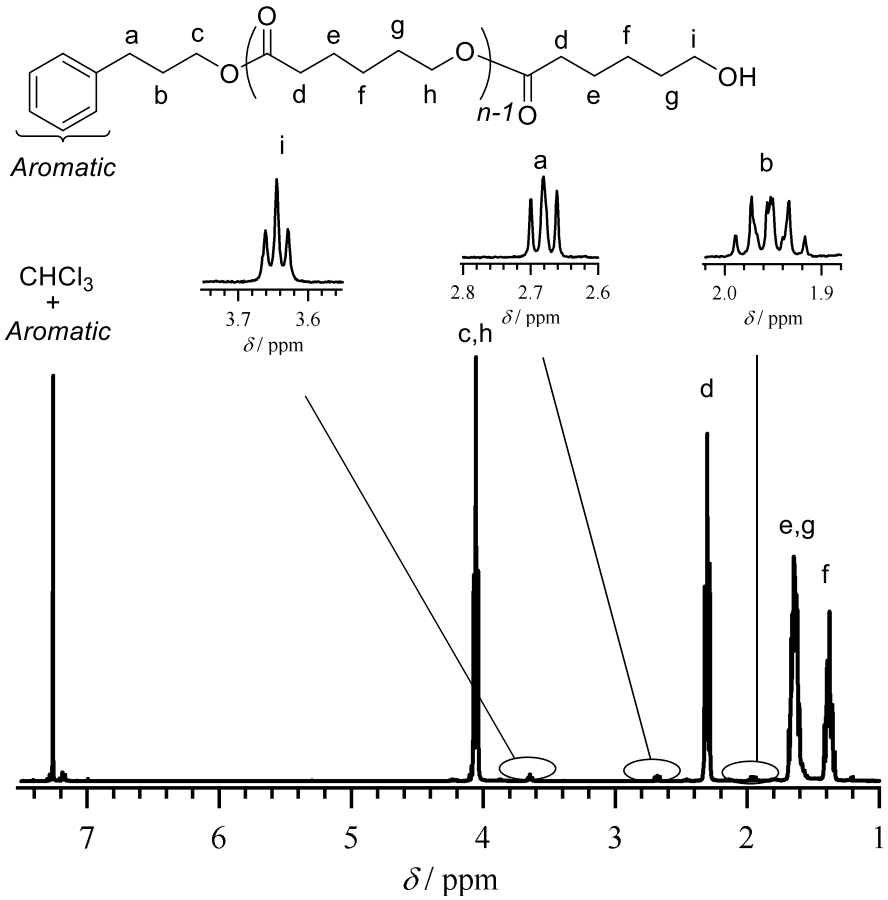


**Figure S1.** $^{1}$H NMR spectrum of PCL in $CDCl_3$ (run 1 in Table 1).

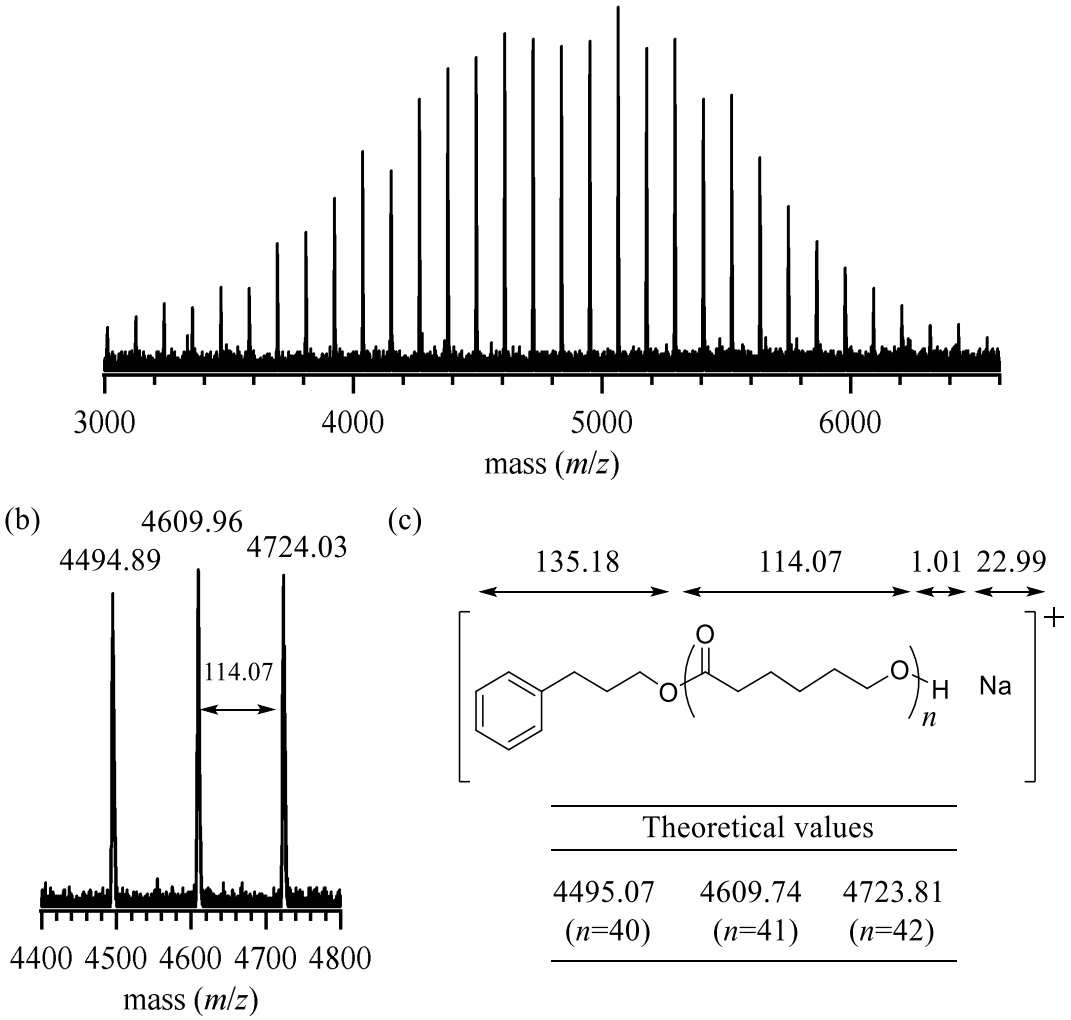


**Figure S2.** (a) MALDI-TOF MS spectrum of PCL (run 1 in Table 1), (b) expanded spectrum (ranging from 4,400 to 4,800), and (c) theoretical molar mass values.

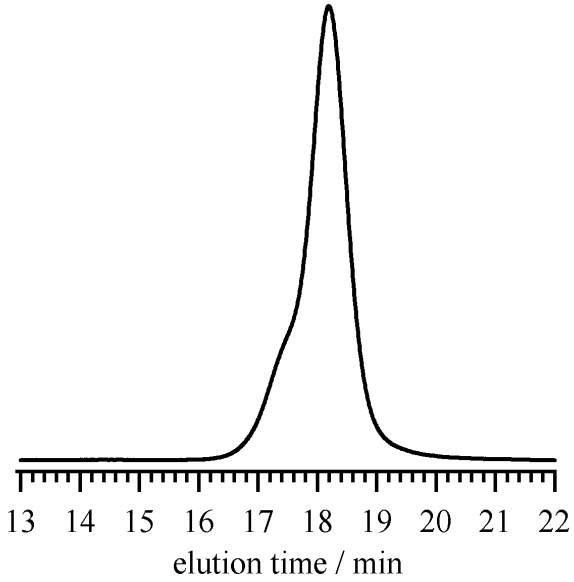


**Figure S3.** SEC trace of the obtained PCL initiated from $H_2O$ (eluent, $CHCl_3$; flow rate, 1.0 mL $min^{-1}$).

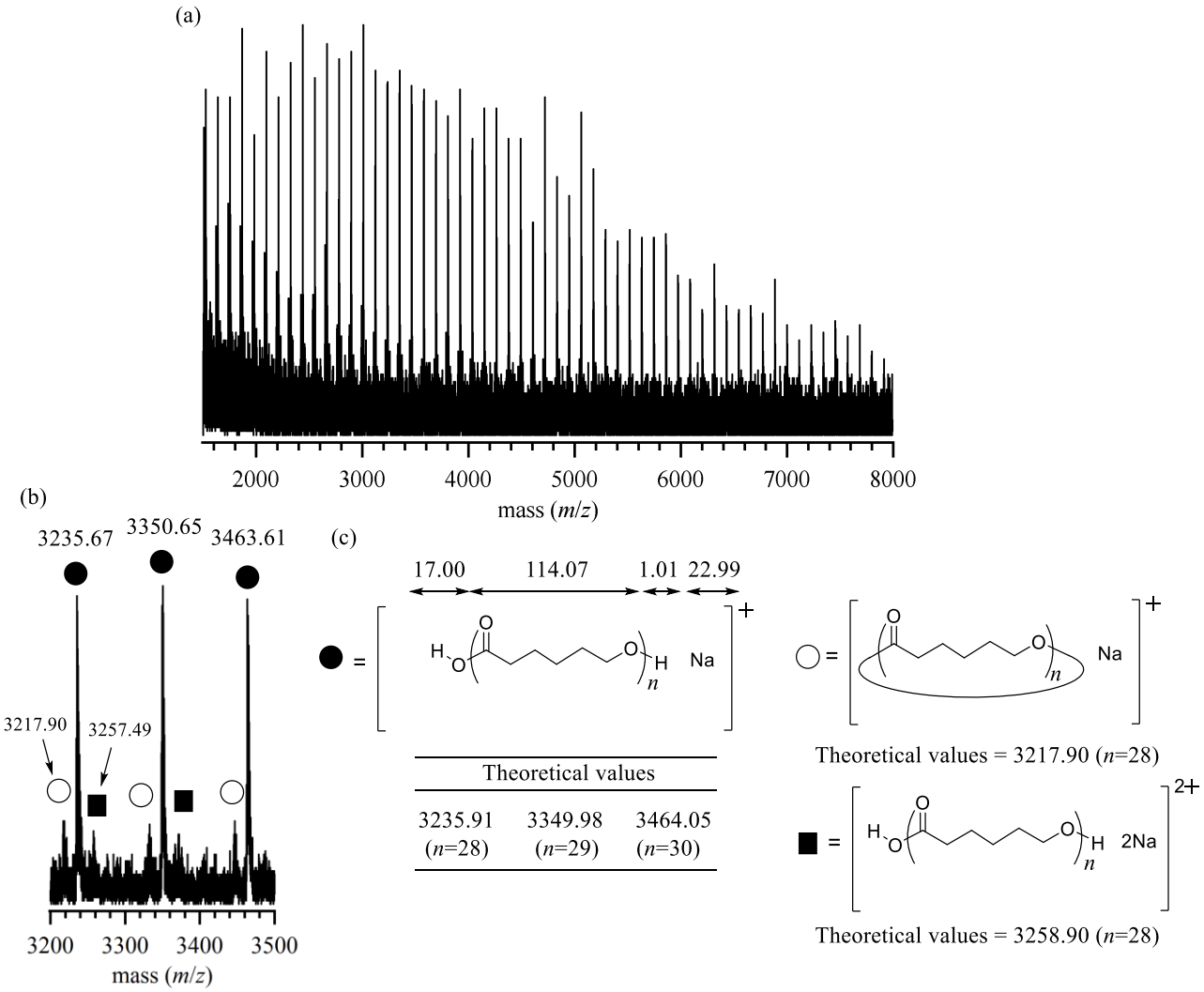


**Figure S4.** (a) MALDI-TOF MS spectrum of the PCL initiated from $H_2O$, (b) expanded spectrum (ranging from 3,200 to 3,500), and (c) theoretical molar mass values and expected structures.

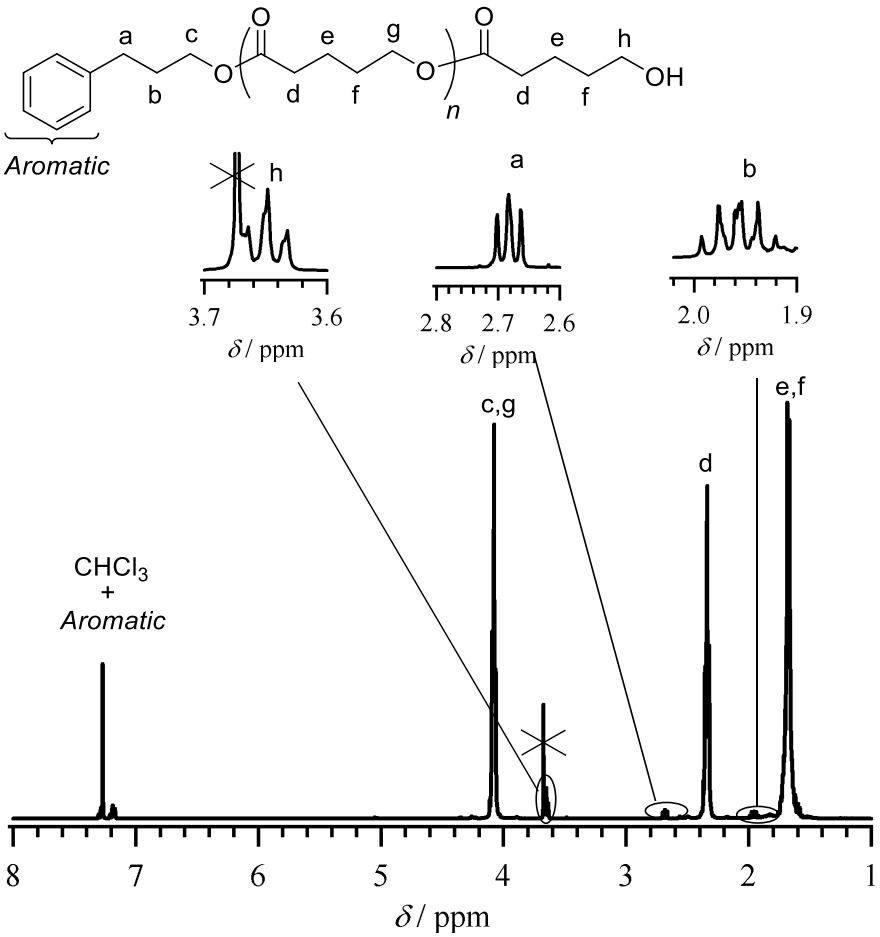


**Figure S5.** $^{1}$H NMR spectrum of PVL in $CDCl_3$ (run 13 in Table 2).

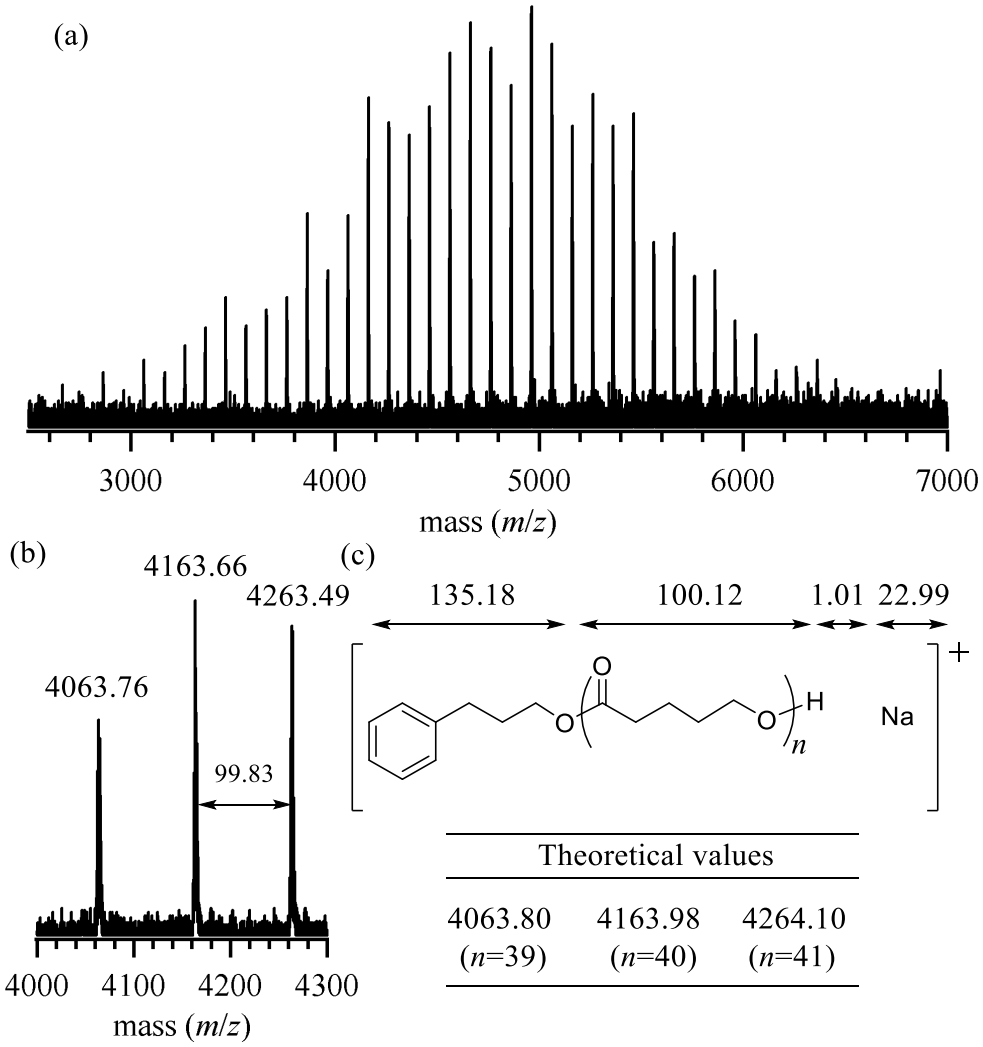


**Figure S6.** (a) MALDI-TOF MS spectrum of PVL (run 13 in Table 2), (b) expanded spectrum (ranging from 4,000 to 4,300), and (c) theoretical molar mass values.

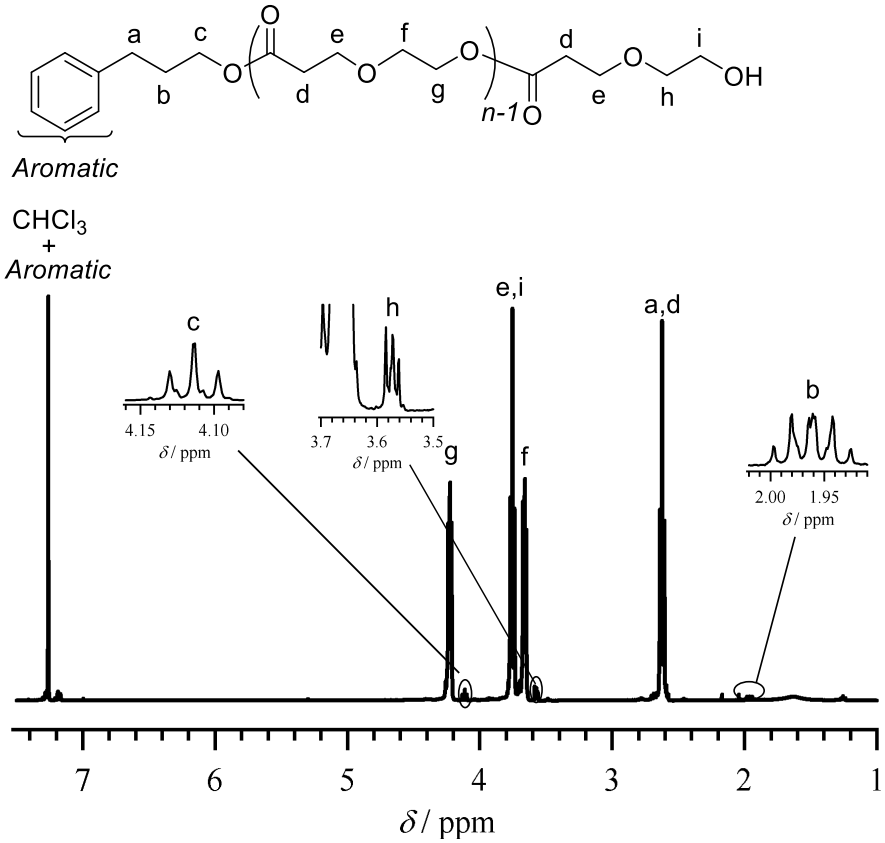


**Figure S7.** $^{1}$H NMR spectrum of PDXO in $CDCl_3$ (run 16 in Table 2).

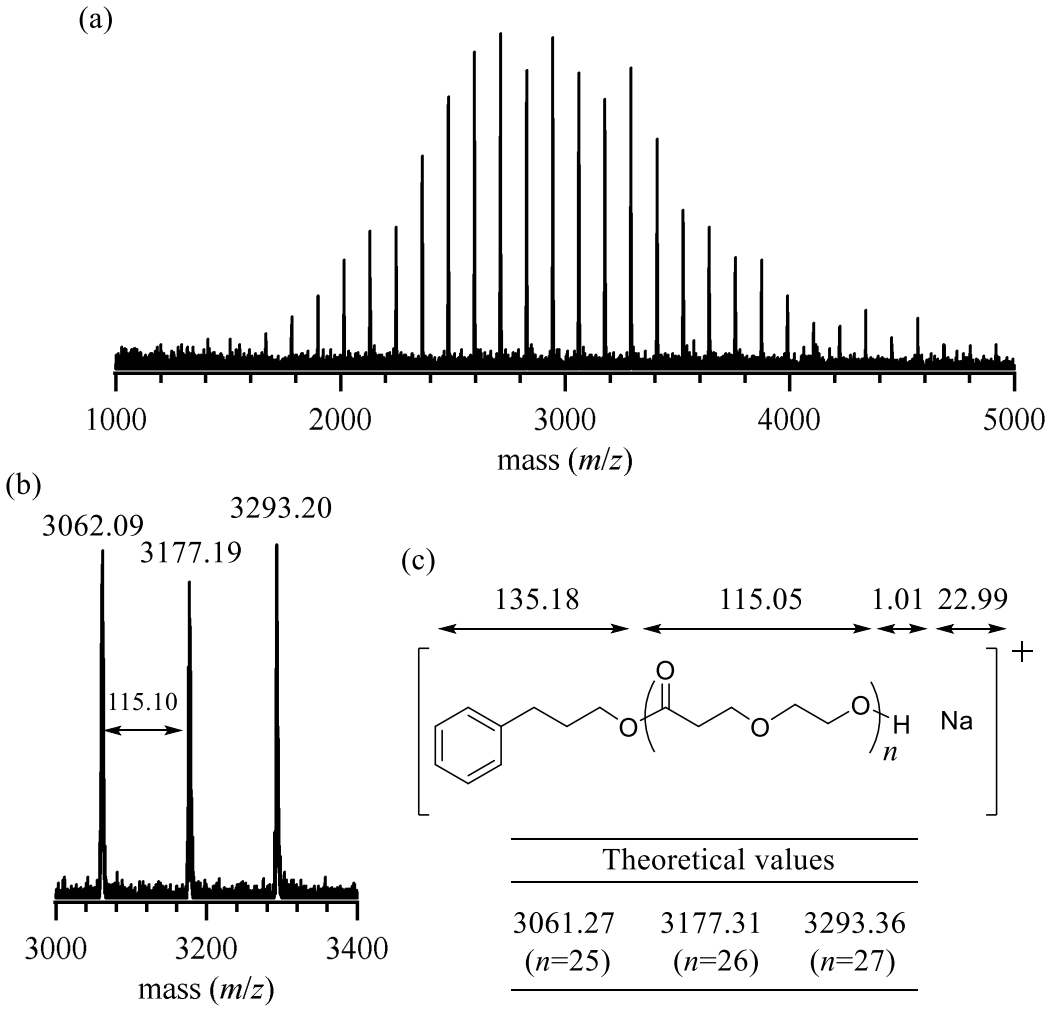


**Figure S8.** (a) MALDI-TOF MS spectrum of PDXO, (b) expanded spectrum (ranging from 3,000 to 3,400), and (c) theoretical molar mass values (run 16 in Table 2).

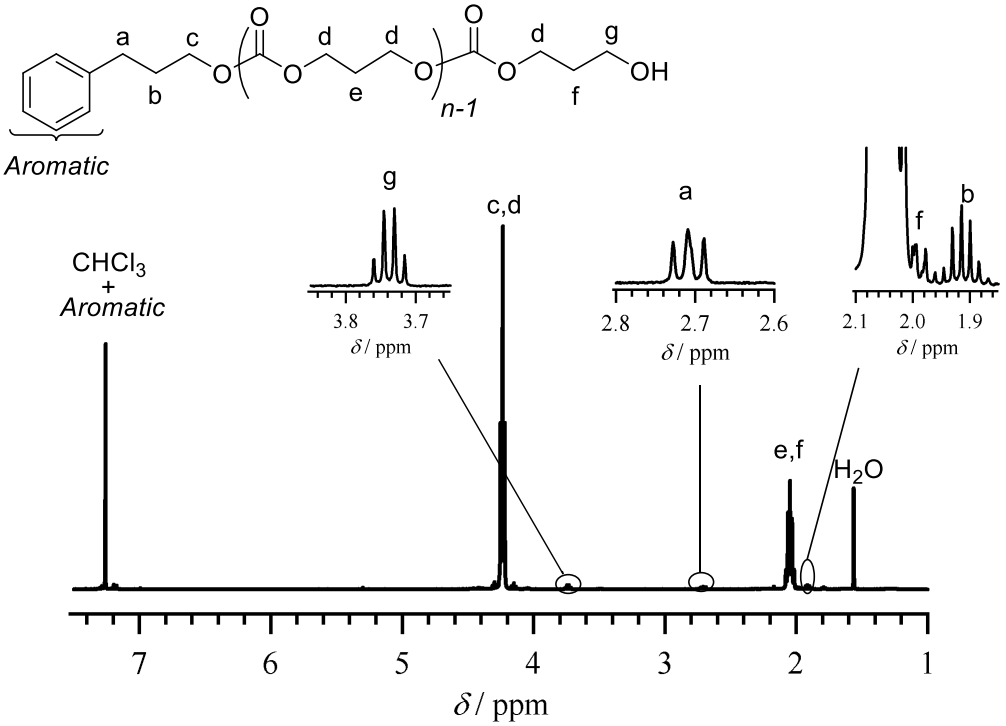


**Figure S9.** $^{1}$H NMR spectrum of PTMC in $CDCl_3$ (run 19 in Table 2).

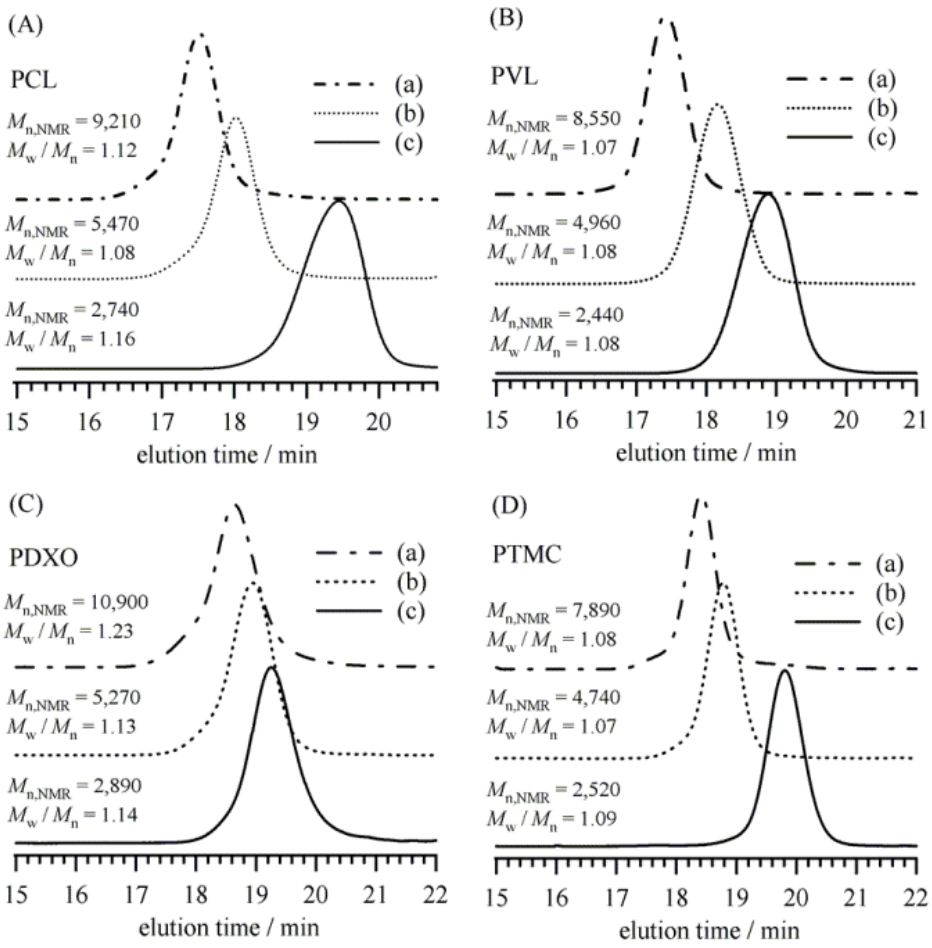


**Figure S10**. SEC traces of (A) the obtained PCLs, (B) PVLs, (C) PDXOs, and (D) PTMCs with the $[M]_0/[PPA]_0$ ratios of (a) 100/1, (b) 50/1, and (c) 25/1 (eluent, $CHCl_3$; flow rate, 1.0 mL $min^{-1}$).

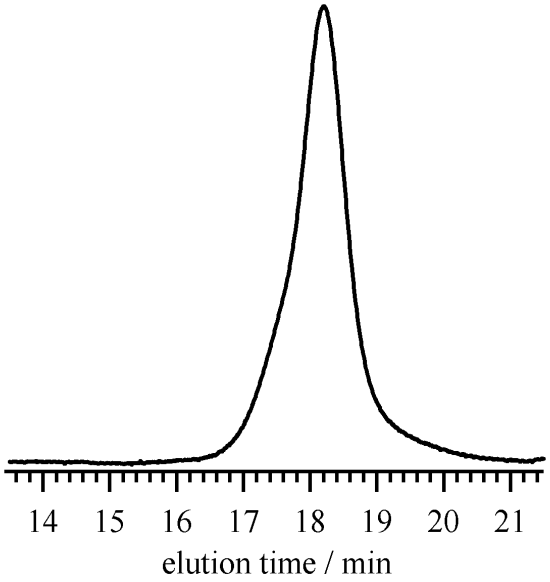


**Figure S11.** SEC trace of the PLLA obtained from run 21 in Table 2 (eluent, $CHCl_3$; flow rate, 1.0 mL $min^{-1}$).

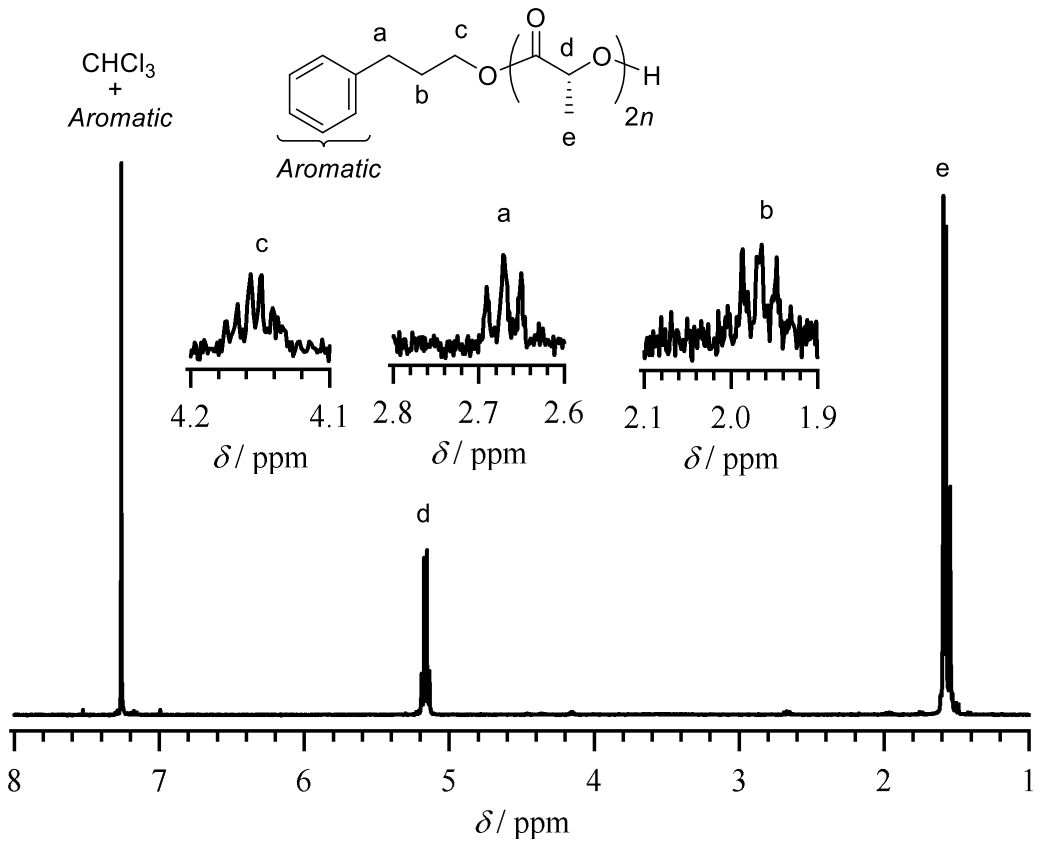


**Figure S12.** $^1H$ NMR spectrum of PLLA in $CDCl_3$ (run 21 in Table 2)

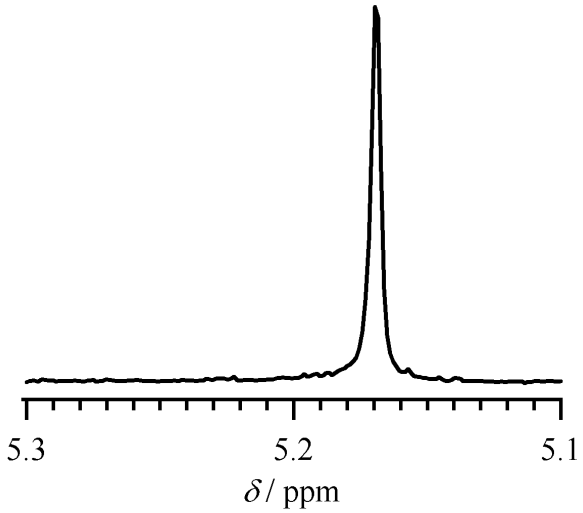


**Figure S13**. $^{1}$H NMR spectrum of PLLA methane resonances with selective decoupling of PLLA methyl resonances (run 21 in Table 2).

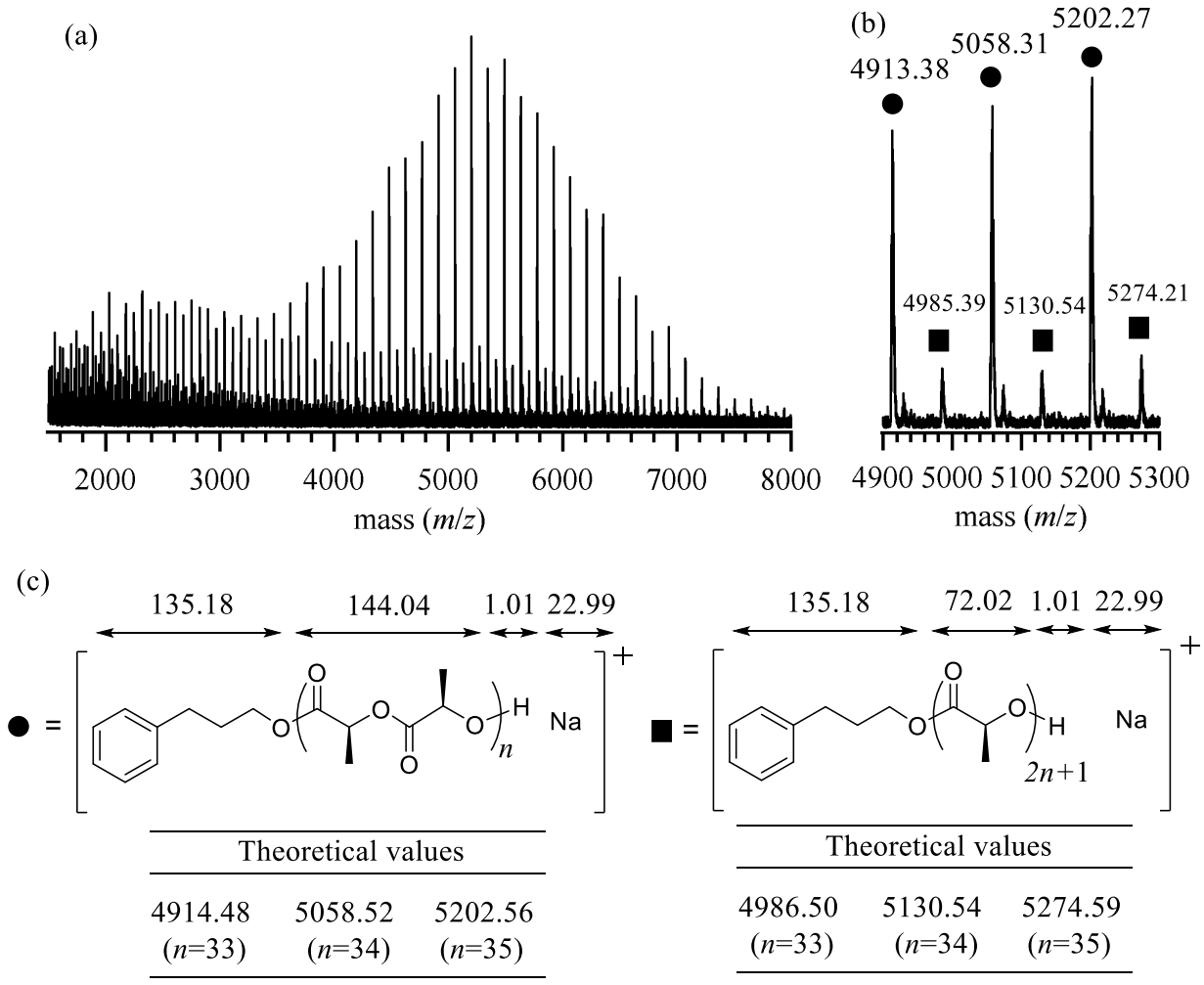


**Figure S14.** (a) MALDI-TOF MS spectrum of PLLA (run 21 in Table 2), (b) expanded spectrum (ranging from 4,900 to 5,300), and (c) theoretical molar mass values.

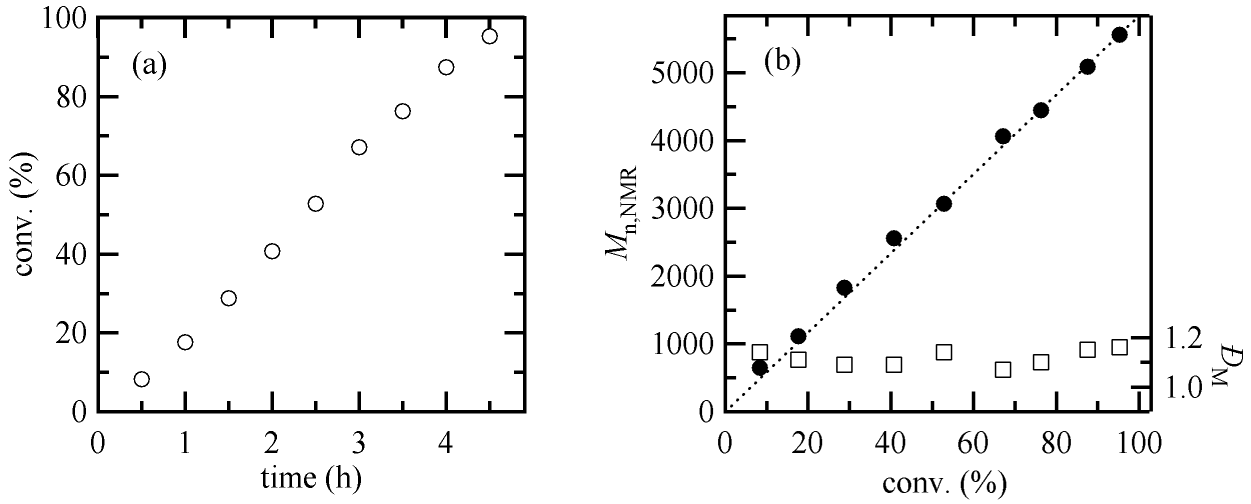


**Figure S15.** (a); Kinetic plots for the DPP-catalyzed bulk ROP of ε-CL with $[\varepsilon\text{-CL}]_0/[\text{PPA}]_0/[\text{DPP}]_0$ = 50/1/0.05, and (b); dependence of $M_{n,NMR}$ (●), $Đ_M$ (□) and $M_{n,th.}$ (dotted line) on monomer conversion (conv.).

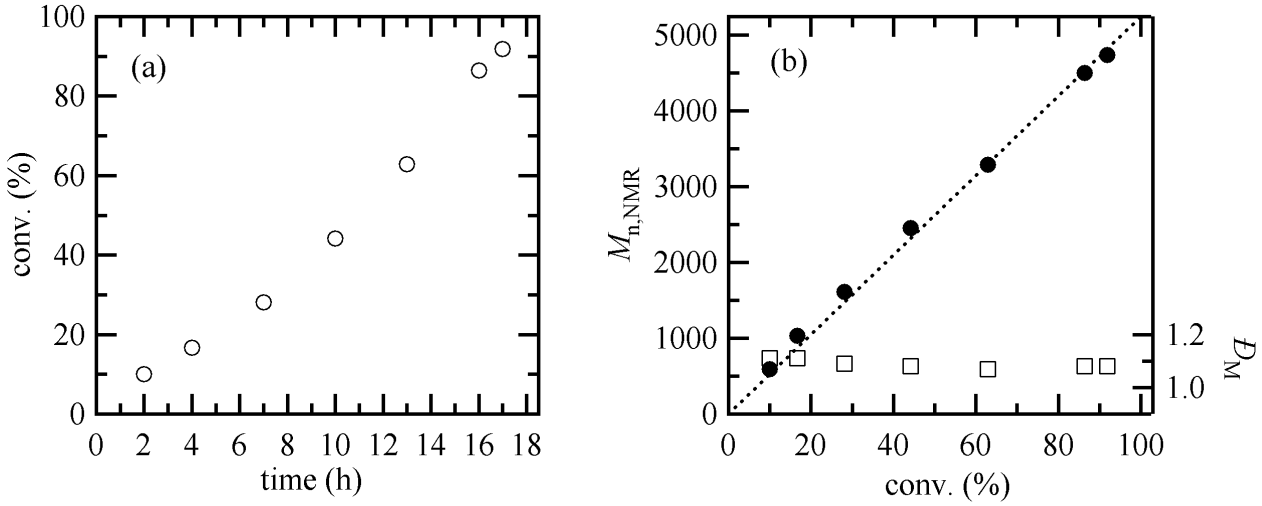


**Figure S16.** (a); Kinetic plots for the DPP-catalyzed bulk ROP of TMC with $[\text{TMC}]_0/[\text{PPA}]_0/[\text{DPP}]_0$ = 50/1/0.05, and (b); dependence of $M_{n,NMR}$ (●), $Đ_M$ (□) and $M_{n,th.}$ (dotted line) on monomer conversion (conv.).

**Table S1.** Block copolymerization of $\varepsilon$-CL, $\delta$-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 | $\varepsilon$-CL | 25/1 | 90min | 94.7 | 2,800 | 2,800 | 1.11 |
| | second | $\delta$-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 | $\delta$-VL | 25/1 | 20min | 78.4 | 4,500 | 4,800 | 1.13 |
| 33 | first | $\delta$-VL | 25/1 | 15min | 97.1 | 2,700 | 2,600 | 1.15 |
| | second | $\varepsilon$-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 | $\varepsilon$-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 $[M_1]_0/[PPA]_0 \times$ conv. $\times$ (M.W. of $M_1$) + (M.W. of PPA). [d] Determined by SEC measurement of the obtained polymer in $CHCl_3$. [e] Calculated from $[M_2]_0/[PPA]_0 \times$ conv. $\times$ (M.W. of $M_2$) + ($M_{n,NMR}$ of the polymer obtained from first polymerization).

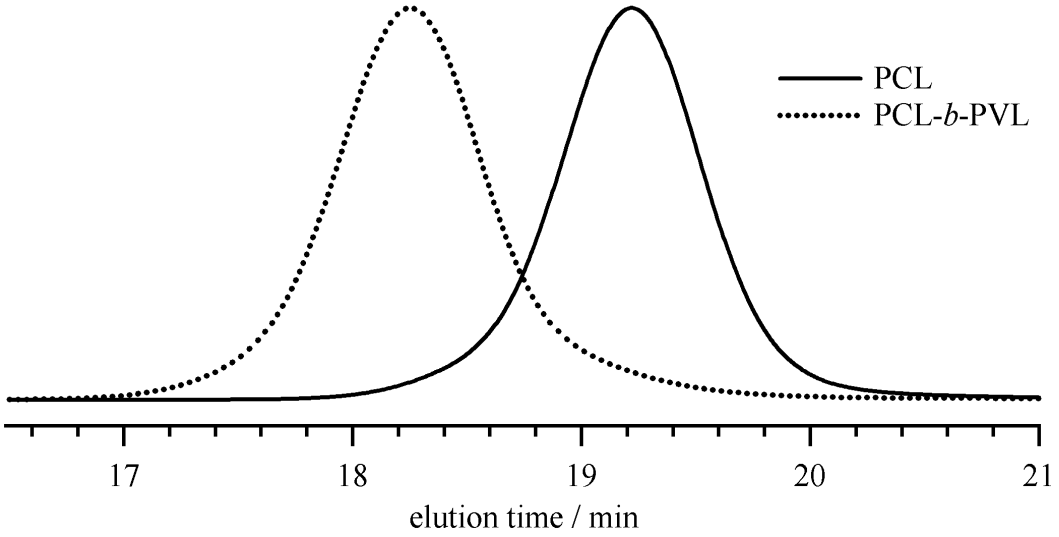


**Figure S17.** SEC traces of PCL obtained from the 1st polymerization and PCL-*b*-PVL (eluent, $CHCl_3$; flow rate, 1.0 mL $min^{-1}$).

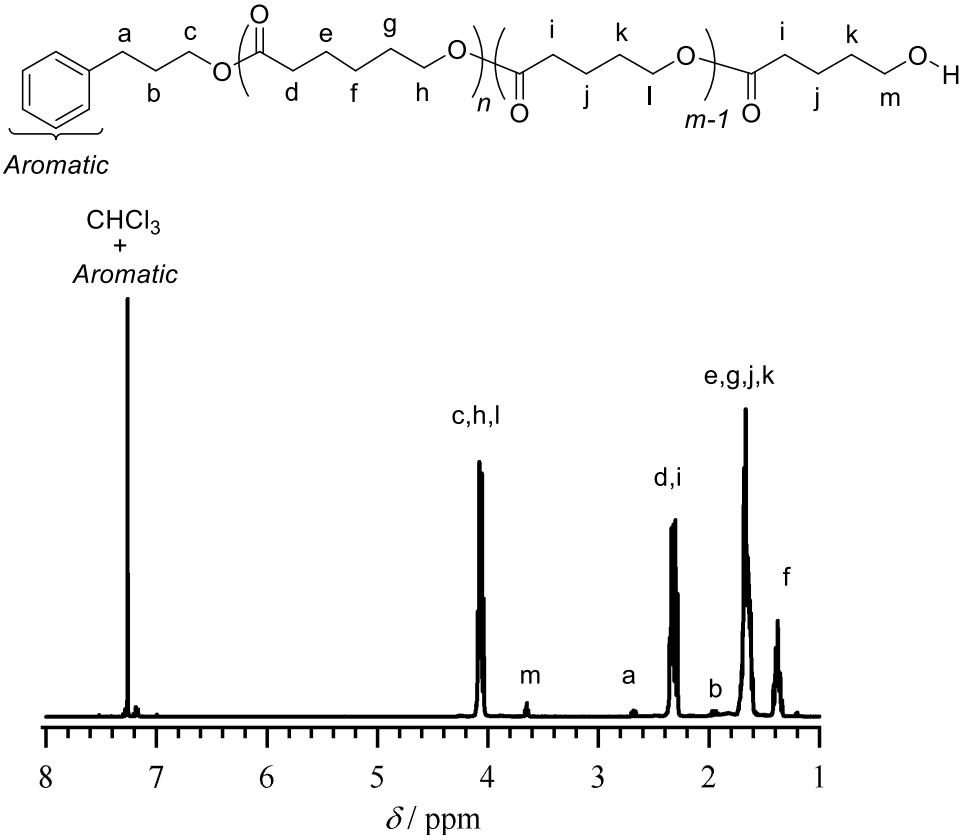


**Figure S18.** $^1H$ NMR spectrum of PCL-*b*-PVL in $CDCl_3$ (run 31 in Table S1).

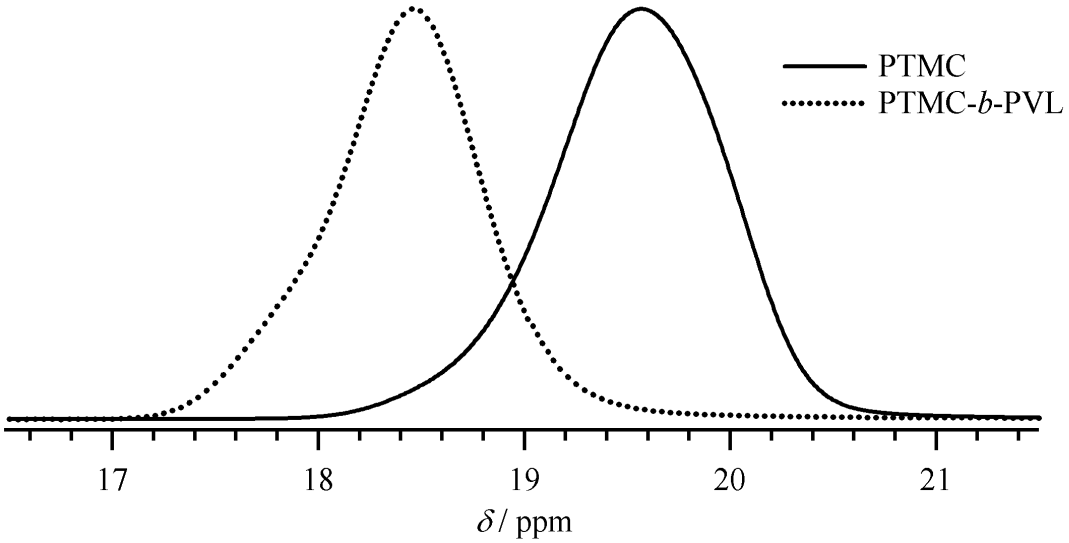


**Figure S19.** SEC traces of PTMC obtained from the 1st polymerization and PTMC-*b*-PVL (eluent, $CHCl_3$; flow rate, 1.0 mL $min^{-1}$).

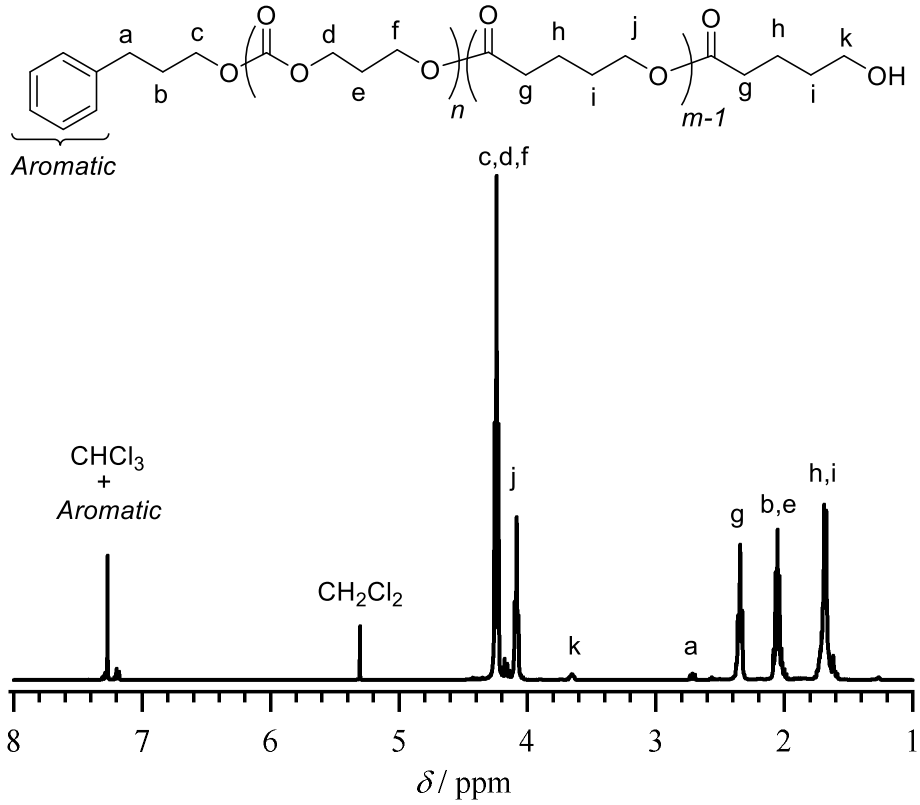


**Figure S20.** $^1H$ NMR spectrum of PTMC-*b*-PVL in $CDCl_3$ (run 32 in Table S1).

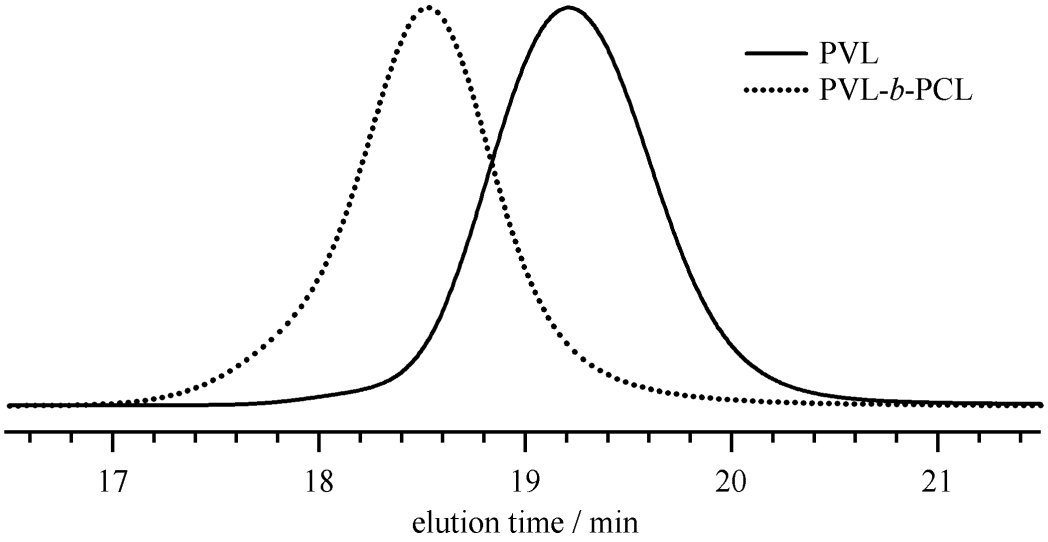


**Figure S21.** SEC traces of PVL obtained from the 1st polymerization and PVL-*b*-PCL (eluent, $CHCl_3$; flow rate, 1.0 mL $min^{-1}$).

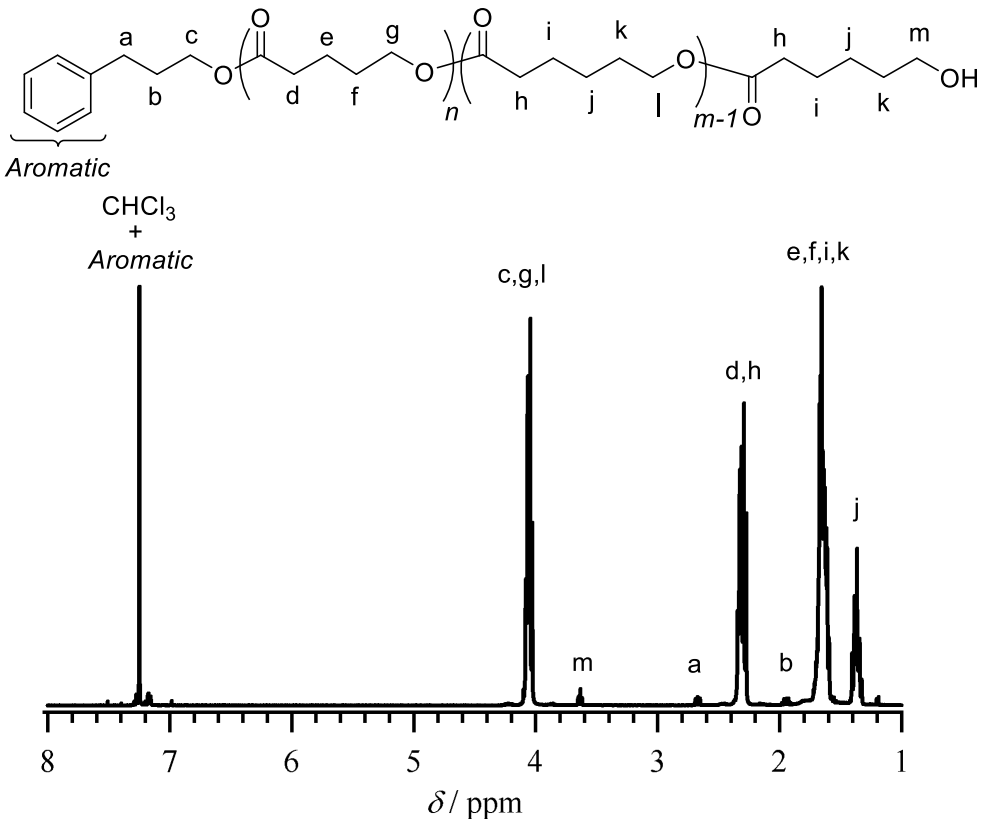


**Figure S22.** $^1H$ NMR spectrum of PVL-*b*-PCL in $CDCl_3$ (run 33 in Table S1).

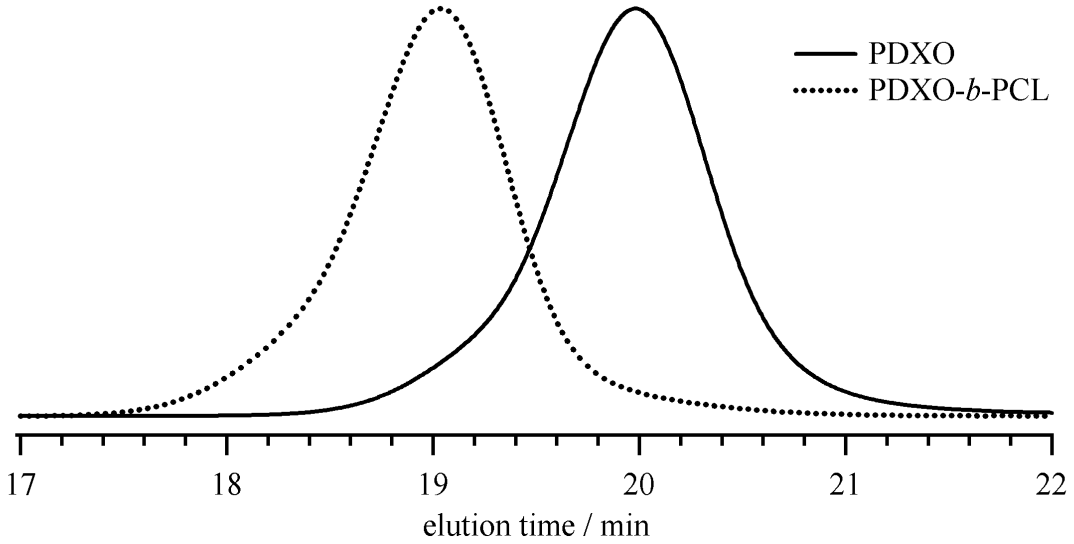


**Figure S23.** SEC traces of PDXO obtained from the 1st polymerization and PDXO-*b*-PCL (eluent, $CHCl_3$; flow rate, 1.0 mL $min^{-1}$).

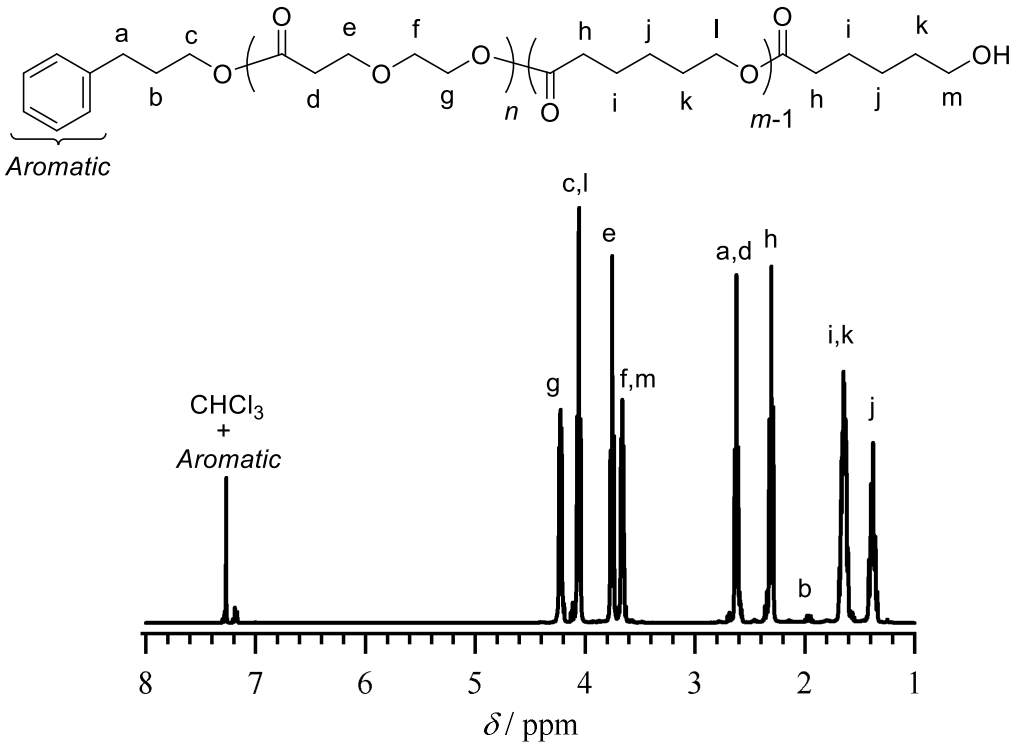


**Figure S24.** $^1H$ NMR spectrum of PDXO-*b*-PCL in $CDCl_3$ (run 34 in Table S1).

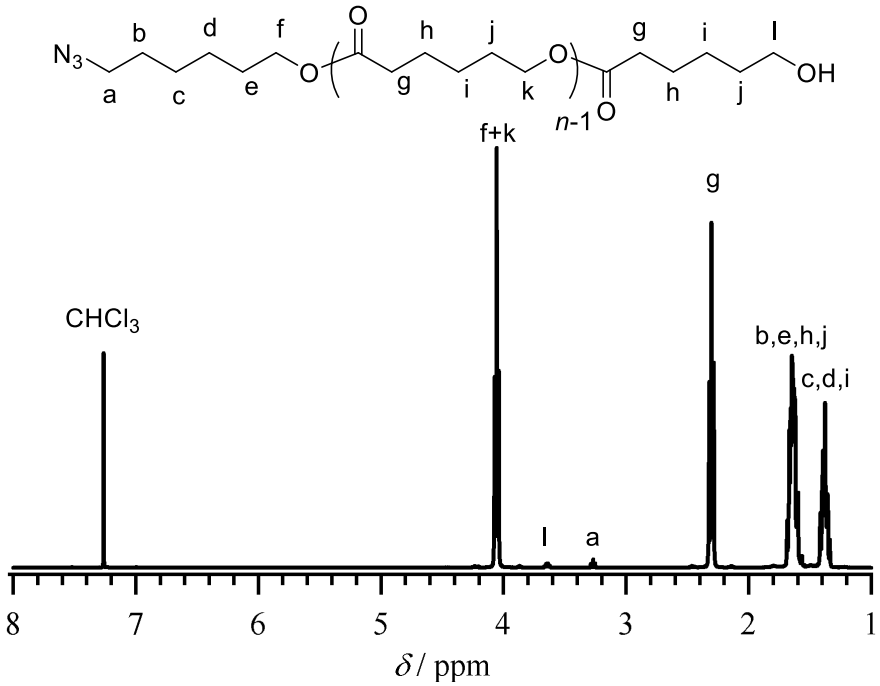


**Figure S25.** $^{1}$H NMR spectrum of $N_3$-PCL in $CDCl_3$ (run 22 in Table 3).

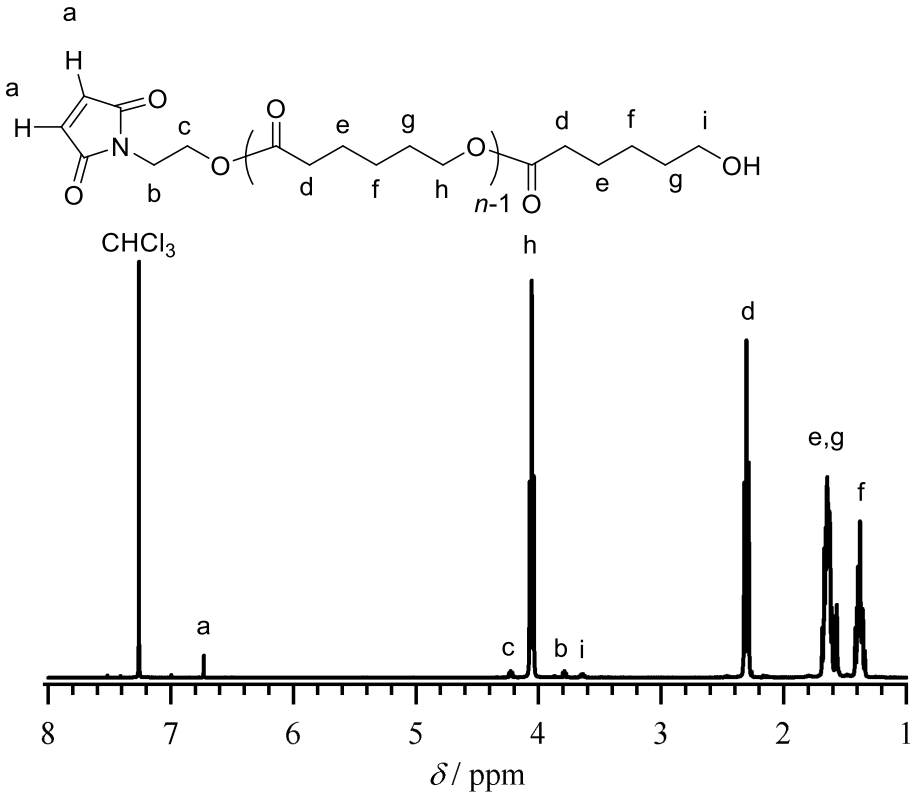


**Figure S26.** $^{1}$H NMR spectrum of MI-PCL in $CDCl_3$ (run 23 in Table 3).

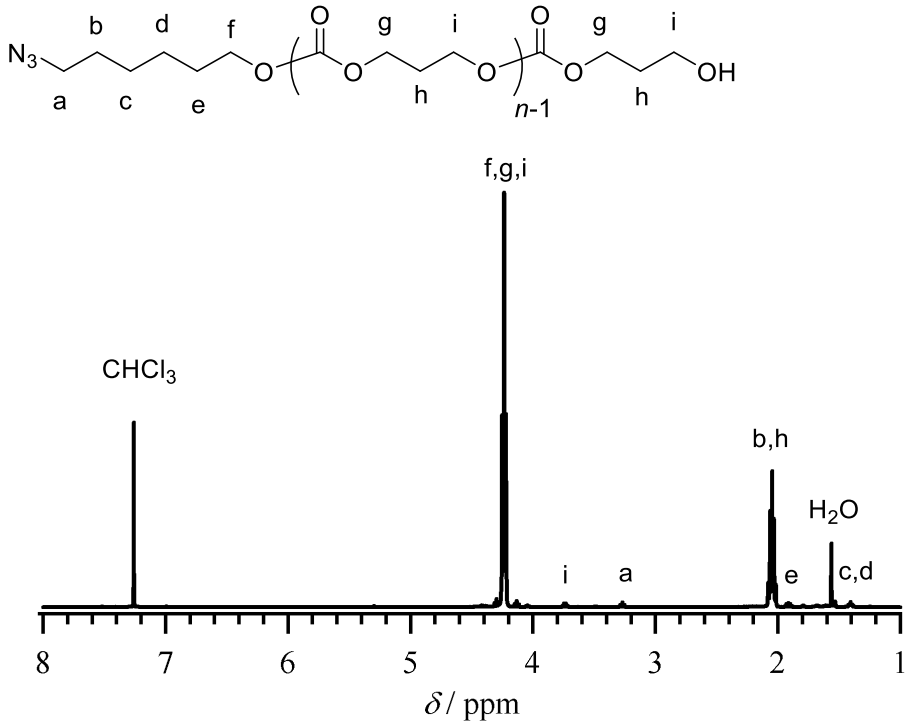


**Figure S27.** $^{1}$H NMR spectrum of $N_3$-PTMC in $CDCl_3$ (run 24 in Table 3).

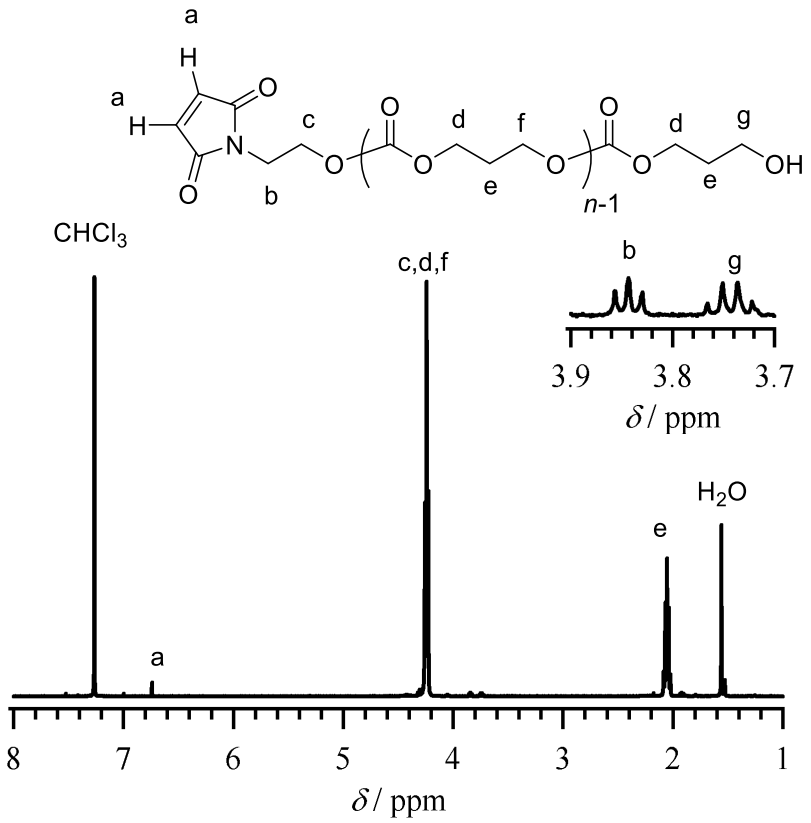


**Figure S28.** $^{1}$H NMR spectrum of MI-PTMC in $CDCl_3$ (run 25 in Table 3).

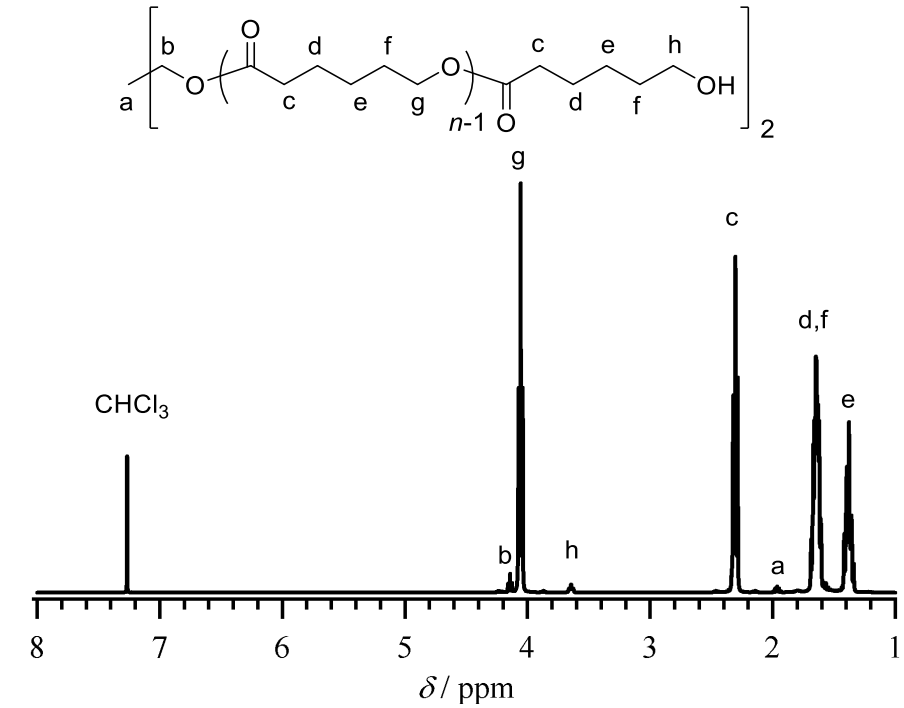


**Figure 29.** $^{1}$H NMR spectrum of PCL-diol in $CDCl_3$ (run 26 in Table 3).

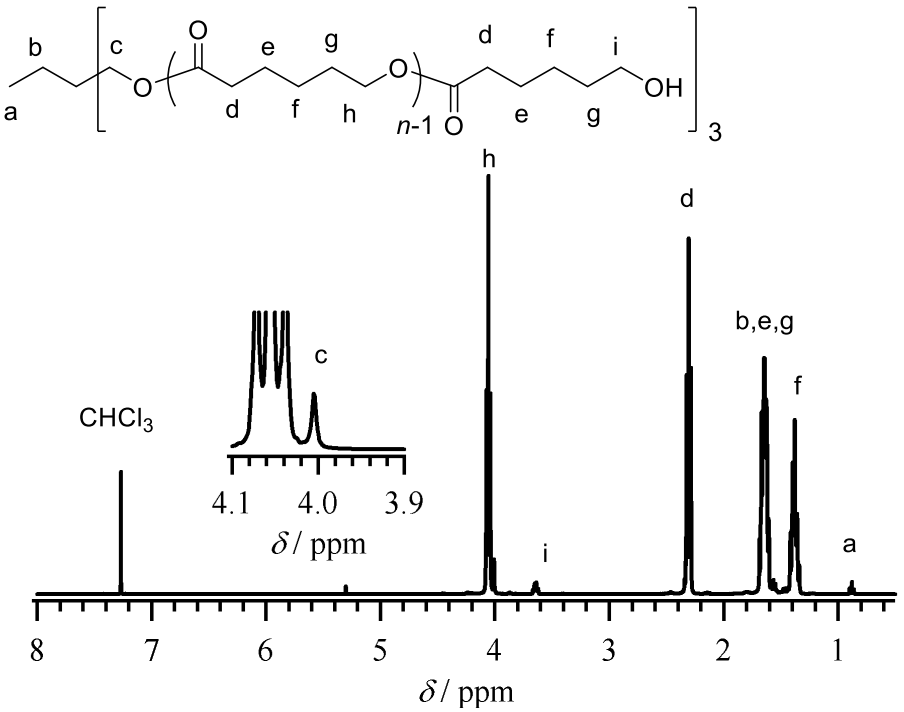


**Figure S30.** $^{1}$H NMR spectrum of PCL-triol in $CDCl_3$ (run 27 in Table 3).

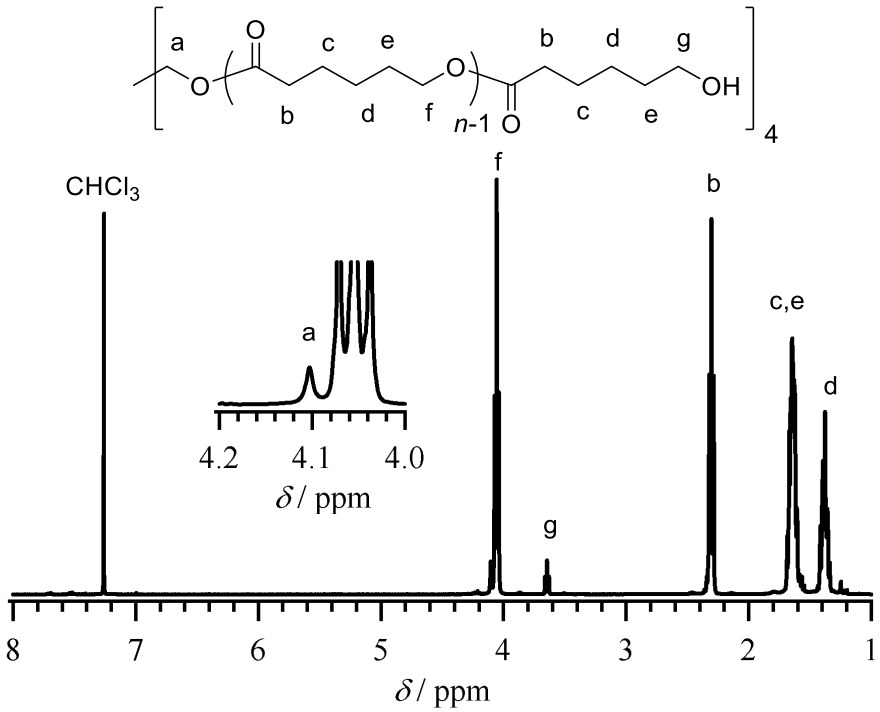


**Figure S31.** $^{1}$H NMR spectrum of PCL-tetraol in $CDCl_3$ (run 28 in Table 3).

.

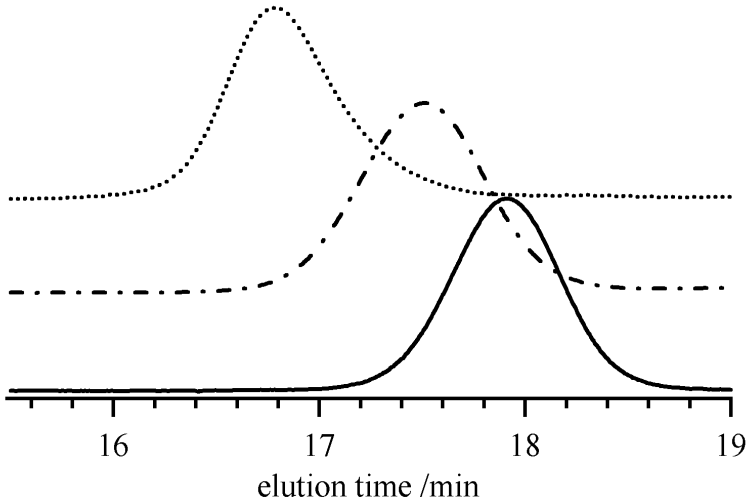


**Figure S32.** SEC traces of the obtained polymer in $CHCl_3$ (solid line, run 28; chained line, run 29; dotted line, run 30).

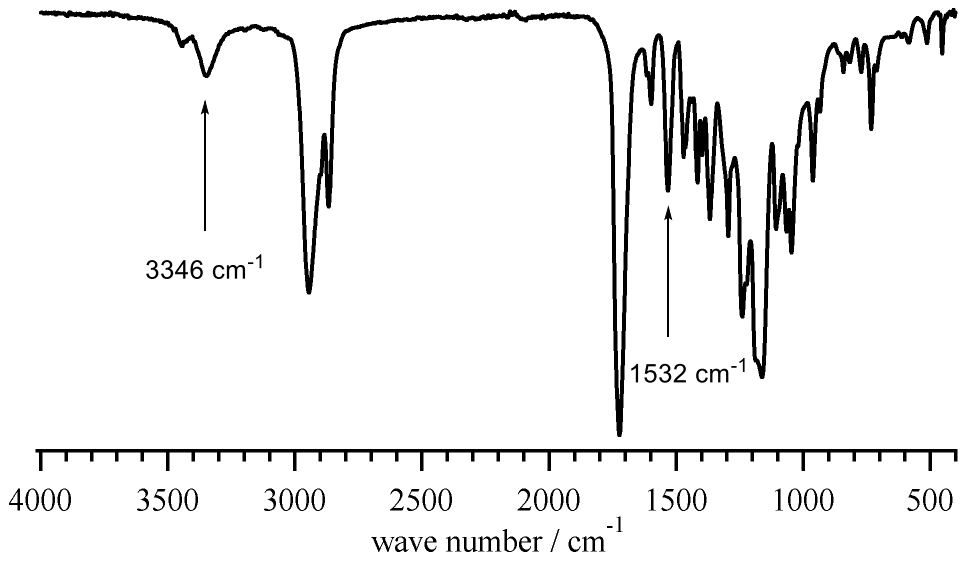


**Figure S33.** FT-IR spectrum of the obtained PCL-based polyurethane in the presence of DPP.

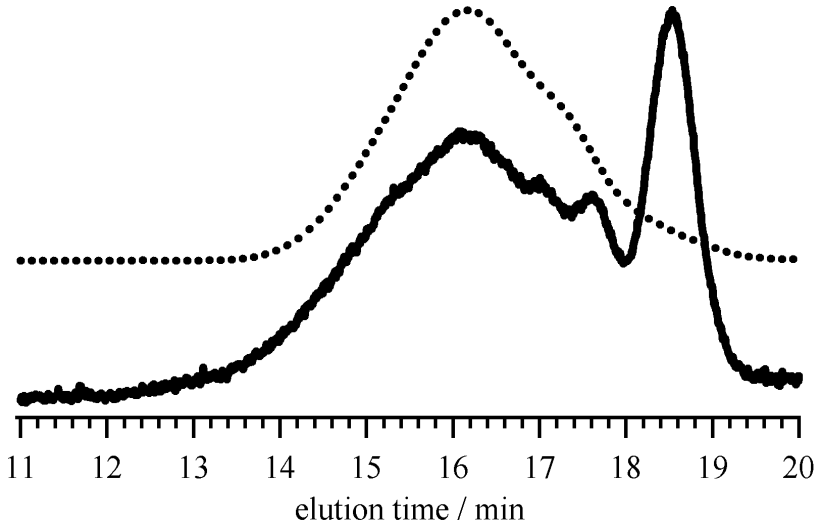


**Figure S34**. SEC traces of the obtained PCL-based polyurethane in the presence of DPP; dotted line and in the absence of DPP; solid line (eluent, $CHCl_3$; flow rate, 1.0 mL $min^{-1}$).

**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, Ar$CH_2CH_2CH_2$-), 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, Ar$CH_2$-) 3.65 (m, 2H,$CH_2$OH), 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, Ar$CH_2CH_2CH_2$-), 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, Ar$CH_2CH_2$-), 2.34 (m, 2H × *m*, (-$COCH_2CH_2CH_2CH_2$-)$_m$), 2,72 (t, 2H, *J* = 7.8 Hz, Ar$CH_2$-), 3.65 (m, 2H, -$CH_2$OH), 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, Ar$CH_2CH_2CH_2$-), 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, Ar$CH_2CH_2$-), 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, Ar$CH_2$-),

3.65 (t, 2H, *J* = 6.4 Hz, -C*H*$_2$OH), 4.02-4.12 (m, 2H × *n*, (-COCH$_2$CH$_2$CH$_2$C*H*$_2$O-)$_n$; 2H × (*m-1*), (-CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$O-)$_{m-1}$; 2H, ArCH$_2$CH$_2$C*H*$_2$-), 4.20 (t, 2H × *n*, *J* = 4.8 Hz, (-COCH$_2$CH$_2$OCH$_2$C*H*$_2$-)$_n$), 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$_2$C*H*$_2$CH$_2$CH$_2$-)$_m$), 1.58-1.71 (m, 2H × *m*, (-CH$_2$C*H*$_2$CH$_2$O-)$_m$; 2H × *m*, (-COCH$_2$C*H*$_2$CH$_2$-)$_m$), 1.97 (m, 2H × *m*, ArCH$_2$C*H*$_2$-), 2.28 (m, 2H × *m*, (-COC*H*$_2$CH$_2$CH$_2$-)$_m$), 2.56-2.72 (m, 2H × *n*, (-COC*H*$_2$CH$_2$O-)$_n$; 2H, ArC*H*$_2$CH$_2$-), 3.62-3.71 (m, 2H × *n*, (-COCH$_2$CH$_2$OC*H*$_2$-)$_n$; 2H, -C*H*$_2$OH), 3.74 (m, 2H × *n*, (-COCH$_2$*CH*$_2$O-)$_n$), 4.01-4.11 (m, 2H × (*m-1*), (-CH$_2$CH$_2$C*H*$_2$O-)$_{m-1}$; 2H, ArCH$_2$CH$_2$C*H*$_2$-), 4.20 (t, 2H × *n*, *J* = 4.8 Hz, (-COCH$_2$CH$_2$OCH$_2$C*H*$_2$-)$_n$), 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$_2$C*H*$_2$CH$_2$CH$_2$-)$_n$; 4H, N$_3$CH$_2$CH$_2$C*H*$_2$C*H*$_2$- ), 1.55-1.69 (m, 2H × *n*, (-CH$_2$C*H*$_2$CH$_2$O-)$_n$; 2H × *n*, (-COCH$_2$C*H*$_2$CH$_2$-)$_n$; 4H, N$_3$CH$_2$C*H*$_2$CH$_2$CH$_2$C*H*$_2$-), 2.31 (t, 2H × *n*, *J* = 7.6 Hz, (-COC*H*$_2$CH$_2$-)$_n$), 3.28 (t, 2H, *J* = 7.0 Hz, N$_3$C*H*$_2$-), 3.63 (m, 2H, -CH$_2$C*H*$_2$OH), 4.01-4.09 (m, 2H × (*n-1*), (-CH$_2$C*H*$_2$O-)$_{n-1}$; 2H, N$_3$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$-).

**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$_2$C*H*$_2$CH$_2$CH$_2$-)$_n$), 1.58-1.71 (m, 2H × *n*, (-CH$_2$C*H*$_2$CH$_2$O-)$_n$; 2H × *n*, (-COCH$_2$C*H*$_2$CH$_2$-)$_n$), 2.29 (t, 2H × *n*, *J* = 8.2 Hz, (-COC*H*$_2$CH$_2$-)$_n$), 3.64 (m, 2H, -CH$_2$C*H*$_2$OH), 3.79 (t, 2H, *J* = 5.4 Hz, -NC*H*$_2$-), 4.06 (t, 2H × (*n-1*), *J* = 6.6 Hz, (-CH$_2$C*H*$_2$O-)$_{n-1}$), 4.23 (t, 2H, *J* = 5.2 Hz, -NCH$_2$C*H*$_2$-), 6,74 (s, 2H, -COC*H*C*H*CO-).

**PCL-diol**: Procedure A was used for the ROP of $\varepsilon$-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): $\delta$ (ppm) 1.36 (m, 2H × *n*, (-$CH_2CH_2C\mathit{H}_2CH_2CH_2$-)$_{n/2}$ × 2), 1.58-1.71 (m, 2H × *n*, (-$CH_2C\mathit{H}_2CH_2O$-)$_{n/2}$ × 2; 2H × *n*, (-$COCH_2C\mathit{H}_2CH_2$-)$_{n/2}$ × 2), 1.97 (m, 2H, -$OCH_2C\mathit{H}_2CH_2O$-), 2.29 (t, 2H × *n*, *J* = 8.2 Hz, (-$COC\mathit{H}_2CH_2$-)$_{n/2}$ × 2), 3.63 (t, 2H × 2, *J* = 6.4 Hz, -$CH_2C\mathit{H}_2OH$) 4.06 (t, 2H × (*n-1*), *J* = 6.6 Hz, (-$CH_2C\mathit{H}_2O$-)$_{(n-1)/2}$ × 2), 4.15 (t, 4H, *J* = 6.2 Hz, -$OC\mathit{H}_2CH_2C\mathit{H}_2O$-).

**PCL-triol**: Procedure A was used for the ROP of $\varepsilon$-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): $\delta$ (ppm) 0.89 (t, 3H, *J* = 7.4 Hz, $C\mathit{H}_3CH_2$), 1.36 (m, 2H × *n*, (-$CH_2CH_2C\mathit{H}_2CH_2CH_2$-)$_{n/3}$ × 3), 1.55-1.72 (m, 2H, $CH_3C\mathit{H}_2$-; 2H × (*n-1*), (-$CH_2C\mathit{H}_2CH_2O$-)$_{n/3}$ × 3; 2H × *n*, (-$COCH_2C\mathit{H}_2CH_2$-)$_{n/3}$ × 3), 2.31 (m, 2H × *n*, (-$OCOC\mathit{H}_2CH_2$-)$_{n/3}$ × 3), 3.65 (m, 6H, -$CH_2C\mathit{H}_2OH$ × 3), 4.01 (s, 6H, $C(C\mathit{H}_2O$-)$_3$), 4.06 (t, 2H × (*n-1*), *J* = 6.6 Hz, (-$CH_2C\mathit{H}_2O$-)$_{(n-1)/3}$ × 3).

**PCL-tetraol**: Procedure A was used for the ROP of $\varepsilon$-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): $\delta$ (ppm) 1.37 (m, 2H × *n*, (-$CH_2CH_2C\mathit{H}_2CH_2CH_2$-)$_{n/4}$ × 4), 1.54-1.73 (m, 2H × *n*, (-$CH_2C\mathit{H}_2CH_2O$-)$_{n/4}$ × 4; 2H × *n*, (-$COCH_2C\mathit{H}_2CH_2$-)$_{n/4}$ × 4), 2.32 (m, 2H × *n*, (-$OCOC\mathit{H}_2CH_2$-)$_{n/4}$ × 4), 3.65 (t, 8H, *J* = 6.6 Hz, -$CH_2C\mathit{H}_2OH$ × 4) 4.06 (t, 2H × (*n-1*), *J* = 6.6 Hz, (-$CH_2C\mathit{H}_2O$-)$_{(n-1)/4}$ × 4), 4.11 (s, 8H,$C(C\mathit{H}_2CO$-)$_4$).

**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): $\delta$ (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, -$CH_2$OH), 4.21-4.27 (m, 2H, $N_3CH_2CH_2CH_2CH_2CH_2CH_2$-; 4H × (*n-1*), (-$OCH_2CH_2CH_2O$-)$_{n-1}$; 2H, -$CH_2CH_2CH_2$OH).

**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): $\delta$ (ppm) 1.92 (m, 2H, -$CH_2CH_2$OH), 2.00-2.13 (m, 2H × (*n-1*), (-$OCH_2CH_2$-)$_{n-1}$), 3.74 (m, 2H, -$CH_2$OH), 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, -$CH_2CH_2CH_2$OH), 6,74 (s, 2H, -COCHCHCO-).