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$_2$O (eluent, CHCl$_3$; flow rate, 1.0 mL min$^{-1}$).
Figure S4. (a) MALDI-TOF MS spectrum of the PCL initiated from H$_2$O, (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 $[M]/[PPA]$ 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, CHCl₃; flow rate, 1.0 mL min⁻¹).

Figure S12. ¹H NMR spectrum of PLLA in CDCl₃ (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 \( \varepsilon \)-CL with \([\varepsilon \text{-CL}]_0/[\text{PPA}]_0/[\text{DPP}]_0 = 50/1/0.05\), and (b); dependence of \( M_{n,\text{NMR}} \) (●), \( D_M \) (□) 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 \( M_{n,\text{NMR}} \) (●), \( D_M \) (□) 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 \(^a\)

<table>
<thead>
<tr>
<th>run</th>
<th>monomer (M)</th>
<th>[M](_0)/[PPA](_0)</th>
<th>time</th>
<th>conv. (%) (^b)</th>
<th>(M_{n,\text{th.}}) (^b)</th>
<th>(M_{n,\text{NMR}}) (^c)</th>
<th>(D_{M}) (^d)</th>
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<tr>
<td>31</td>
<td>first ε-CL</td>
<td>25/1</td>
<td>90min</td>
<td>94.7</td>
<td>2,800</td>
<td>2,800</td>
<td>1.11</td>
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<tr>
<td></td>
<td>second δ-VL</td>
<td>25/1</td>
<td>20min</td>
<td>78.6</td>
<td>4,800 (^e)</td>
<td>5,000</td>
<td>1.13</td>
</tr>
<tr>
<td>32</td>
<td>first TMC</td>
<td>25/1</td>
<td>560min</td>
<td>96.0</td>
<td>2,600</td>
<td>2,500</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>second δ-VL</td>
<td>25/1</td>
<td>20min</td>
<td>78.4</td>
<td>4,500</td>
<td>4,800</td>
<td>1.13</td>
</tr>
<tr>
<td>33</td>
<td>first δ-VL</td>
<td>25/1</td>
<td>15min</td>
<td>97.1</td>
<td>2,700</td>
<td>2,600</td>
<td>1.15</td>
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<tr>
<td></td>
<td>second ε-CL</td>
<td>25/1</td>
<td>125min</td>
<td>88.0</td>
<td>5,100 (^e)</td>
<td>5,200</td>
<td>1.15</td>
</tr>
<tr>
<td>34</td>
<td>first DXO</td>
<td>25/1</td>
<td>210min</td>
<td>97.2</td>
<td>3,000</td>
<td>3,100</td>
<td>1.20</td>
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<tr>
<td></td>
<td>second ε-CL</td>
<td>25/1</td>
<td>130min</td>
<td>90.1</td>
<td>5,500 (^e)</td>
<td>6,000</td>
<td>1.16</td>
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\(^a\) Polymerization conditions: atmosphere, Ar; temperature, 80 °C. \(^b\) Determined by \(^1\)H NMR spectrum of the obtained polymer in CDCl\(_3\). \(^c\) Calculated from \([M_1]_0/[PPA]_0 \times \text{conv.} \times (\text{M.W. of } M_1) + (\text{M.W. of PPA})\). \(^d\) Determined by SEC measurement of the obtained polymer in CHCl\(_3\). \(^e\) Calculated from \([M_2]_0/[PPA]_0 \times \text{conv.} \times (\text{M.W. of } M_2) + (M_{n,\text{NMR}} \text{ of the polymer obtained from first polymerization})\).
**Figure S17.** SEC traces of PCL obtained from the 1st polymerization and PCL-\(b\)-PVL (eluent, 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, 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-\textit{b}-PCL (eluent, CHCl$_3$; flow rate, 1.0 mL min$^{-1}$).

Figure S22. $^1$H NMR spectrum of PVL-\textit{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, CHCl₃; flow rate, 1.0 mL min⁻¹).
One-pot synthesis of PCL-\textit{b}-PVL.

\( \varepsilon \)-CL (0.570 mL, 5.00 mmol), PPA (27.2 \( \mu \)L, 200 \( \mu \)mol) and DPP (2.50 mg, 10.0 \( \mu \)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 \( ^1 \)H NMR measurement, then \( \varepsilon \)-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\(_2\)Cl\(_2\) solution into cold methanol/\( n \)-hexane (\( v/v = 9/1 \)) to give the PCL-\textit{b}-PVL (812 mg) as a white solid. Yield, 84.6%. \( M_{\text{a, NMR}} = 5,000; M_{\text{a, SEC}} = 8,700, D_M = 1.13. \)

\( ^1 \)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) (ppm) 1.37 (m, 2H \( \times \) \( n \), (-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( n \)), 1.57-1.75 (m, 2H \( \times \) \( n \), (-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( n \))), 2H \( \times \) \( n \), (-COCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( n \))), 2H \( \times \) \( m \), (-COCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 1.95 (m, 2H, ArCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 2.26-2.40 (m, 2H \( \times \) \( n \), (-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 2H \( \times \) \( n \), (-COCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \))), 2.69 (t, 2H, \textit{J} = 7.8 Hz, ArCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)) 3.65 (m, 2H,CH\(_3\)OH), 4.02-4.13 (m, 2H \( \times \) \( n \), (-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( n \))), 2H \( \times \) \( m \), (-OCH\(_2\)CH\(_2\)CH\(_2\)O-\( n \)), 2.72 (t, 2H, \textit{J} = 7.8 Hz, ArCH\(_2\)CH\(_2\)CH\(_2\)O-\( n \)), 3.65 (m, 2H, -CH\(_3\)OH), 4.08 (m, 2H \( \times \) \( m \), (-OCH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 4.13-4.30 (m, 2H \( \times \) \( n \), (-OCH\(_2\)CH\(_2\)CH\(_2\)O-\( n \))), 2H \( \times \) \( n \), (-OCH\(_2\)CH\(_2\)CH\(_2\)O-\( n \)), 7.16-7.32 (m, 5H, aromatic).

The syntheses of PTMC-\textit{b}-PVL, PVL-\textit{b}-PCL, and PDXO-\textit{b}-PCL were performed using similar process.

**PTMC-\textit{b}-PVL:** Yield, 88.0%. \( M_{\text{a, NMR}} = 4,800; M_{\text{a, SEC}} = 7,500, D_M = 1.13. \)

\( ^1 \)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) (ppm) 1.57-1.78 (m, 2H \( \times \) \( m \), (-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 2H \( \times \) \( m \), (-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \))), 1.96-2.12 (m, 2H \( \times \) \( n \), (-OCH\(_2\)CH\(_2\)CH\(_2\)O-\( m \))), 2H, ArCH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 2.34 (m, 2H \( \times \) \( m \), (-COCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \))), 2.72 (t, 2H, \textit{J} = 7.8 Hz, ArCH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 3.65 (m, 2H, -CH\(_3\)OH), 4.08 (m, 2H \( \times \) \( m \), (-OCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 4.13-4.30 (m, 2H \( \times \) \( n \), (-OCH\(_2\)CH\(_2\)CH\(_2\)O-\( n \))), 2H \( \times \) \( n \), (-OCH\(_2\)CH\(_2\)CH\(_2\)O-\( n \)), 2H, ArCH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 7.16-7.32 (m, 5H, aromatic).

**PVL-\textit{b}-PCL:** Yield, 74.1%. \( M_{\text{a, NMR}} = 5,200; M_{\text{a, SEC}} = 7,000, D_M = 1.15. \)

\( ^1 \)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) (ppm) 1.38 (m, 2H \( \times \) \( m \), (-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 1.58-1.75 (m, 2H \( \times \) \( n \), (-COCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \))), 2H \( \times \) \( n \), (-COCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( n \))), 2H \( \times \) \( m \), (-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 1.96 (m, 2H, ArCH\(_2\)CH\(_2\)O-\( m \)), 2.27-2.40 (m, 2H \( \times \) \( n \), (-COCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( n \))), 2H \( \times \) \( m \), (-COCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O-\( m \)), 2.69 (t, 2H, \textit{J} = 7.6 Hz, ArCH\(_2\)CH\(_2\)O-\( m \)), 7.16-7.32 (m, 5H, aromatic).
3.65 (t, 2H, J = 6.4 Hz, -CH₂OH), 4.02-4.12 (m, 2H × n, (-COCH₂CH₂CH₂O⁻)ₙ; 2H × (m-I), (-CH₂CH₂CH₂CH₂CH₂O⁻)ₘ₋₁; 2H, ArCH₂CH₂CH₂⁻), 4.20 (t, 2H × n, J = 4.8 Hz, (-COCH₂CH₂OCH₂CH₂⁻)ₙ), 7.15-7.31 (m, 5H, aromatic).

**PDXO-b-PCL:** Yield, 5.5%. Mₐ,NMR = 6,000; Mₐ,SEC = 5,200, Dₐ = 1.16. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 1.38 (m, 2H × m, (-CH₂CH₂CH₂CH₂CH₂⁻)ₘ); 1.58-1.71 (m, 2H × m, (-CH₂CH₂CH₂O⁻)ₘ; 2H × m, (-COCH₂CH₂CH₂⁻)ₘ), 1.97 (m, 2H × m, ArCH₂CH₂⁻), 2.28 (m, 2H × m, (-COCH₂CH₂CH₂⁻)ₘ), 2.56-2.72 (m, 2H × n, (-COCH₂CH₂O⁻)ₙ; 2H, ArCH₂CH₂⁻), 3.62-3.71 (m, 2H × n, (-COCH₂CH₂OCH₂⁻)ₙ), 4.01-4.11 (m, 2H × (m-I), (-CH₂CH₂CH₂O⁻)ₘ₋₁; 2H, ArCH₂CH₂CH₂⁻), 4.20 (t, 2H × n, J = 4.8 Hz, (-COCH₂CH₂OCH₂CH₂⁻)ₙ), 7.13-7.29 (m, 5H, aromatic).

**Syntheses of functional PCLs with various initiators.**

**N₃-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 N₃-PCL (740 mg) as a white solid. Yield, 69.9%. Mₐ,NMR = 5,500; Mₐ,SEC = 12,700, Dₐ = 1.11. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 1.31-1.41 (m, 2H × n, (-CH₂CH₂CH₂CH₂CH₂⁻)ₙ; 4H, N₃CH₂CH₂CH₂CH₂⁻), 1.55-1.69 (m, 2H × n, (-CH₂CH₂CH₂O⁻)ₙ; 2H × n, (-COCH₂CH₂CH₂⁻)ₙ; 4H, N₃CH₂CH₂CH₂CH₂⁻), 2.31 (t, 2H × n, J = 7.6 Hz, (-COCH₂CH₂⁻)ₙ), 3.28 (t, 2H, J = 7.0 Hz, N₃CH₂⁻), 3.63 (m, 2H, -CH₂CH₂OH), 4.01-4.09 (m, 2H × (n-I), (-CH₂CH₂O⁻)ₙ₋₁; 2H, N₃CH₂CH₂CH₂CH₂CH₂⁻).

**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%. Mₐ,NMR = 5,500; Mₐ,SEC = 13,400, Dₐ = 1.15. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 1.36 (m, 2H × n, (-CH₂CH₂CH₂CH₂CH₂⁻)ₙ), 1.58-1.71 (m, 2H × n, (-CH₂CH₂CH₂O⁻)ₙ; 2H × n, (-COCH₂CH₂CH₂⁻)ₙ), 2.29 (t, 2H × n, J = 8.2 Hz, (-COCH₂CH₂⁻)ₙ), 3.64 (m, 2H, -CH₂CH₂OH), 3.79 (t, 2H, J = 5.4 Hz, -NCH₂⁻), 4.06 (t, 2H × (n-I), J = 6.6 Hz, (-CH₂CH₂O⁻)ₙ₋₁), 4.23 (t, 2H, J = 5.2 Hz, -NCH₂CH₂⁻), 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%. $M_{n,NMR} = 5,100$; $M_{n,SEC} = 11,400$, $D_M = 1.13$. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 1.36 (m, 2H × n, -(CH$_2$CH$_2$CH$_2$CH$_2$-)$_{n/2}$ × 2). 1.58-1.71 (m, 2H × n, -(CH$_2$CH$_2$CH$_2$O-)$_{n/2}$ × 2; 2H × n, -(COCH$_2$CH$_2$CH$_2$-)$_{n/2}$ × 2), 1.97 (m, 2H, -OCH$_2$CH$_2$CH$_2$O-), 2.29 (t, 2H × n, $J = 8.2$ Hz, -(COCH$_2$CH$_2$-)$_{n/2}$ × 2), 3.63 (t, 2H × 2, $J = 6.4$ Hz, -CH$_2$CH$_2$OH) 4.06 (t, 2H × (n-1), $J = 6.6$ Hz, -(CH$_2$CH$_2$O-)$_{(n-1)/2}$ × 2). 4.15 (t, 4H, $J = 6.2$ Hz, -OCH$_2$CH$_2$CH$_2$O-).

**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%. $M_{n,NMR} = 5,200$; $M_{n,SEC} = 11,500$, $D_M = 1.07$. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 0.89 (t, 3H, $J = 7.4$ Hz, CH$_3$CH$_2$), 1.36 (m, 2H × n, -(CH$_2$CH$_2$CH$_2$CH$_2$-)$_{n/3}$ × 3), 1.55-1.72 (m, 2H, CH$_3$CH$_2$-; 2H × (n-1), -(CH$_2$CH$_2$CH$_2$O-)$_{n/3}$ × 3; 2H × n, -(COCH$_2$CH$_2$CH$_2$-)$_{n/3}$ × 3), 2.31 (m, 2H × n, -(OCOCH$_2$CH$_2$CH$_2$-)$_{n/3}$ × 3), 3.65 (m, 6H, -CH$_2$CH$_2$OH × 3), 4.01 (s, 6H, C(CH$_2$O-)$_3$), 4.06 (t, 2H × (n-1), $J = 6.6$ Hz, -(CH$_2$CH$_2$O-)$_{(n-1)/3}$ × 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%. $M_{n,NMR} = 10,600$; $M_{n,SEC} = 16,900$, $D_M = 1.07$. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 1.37 (m, 2H × n, -(CH$_2$CH$_2$CH$_2$CH$_2$-)$_{n/4}$ × 4), 1.54-1.73 (m, 2H × n, -(CH$_2$CH$_2$CH$_2$O-)$_{n/4}$ × 4; 2H × n, -(COCH$_2$CH$_2$CH$_2$-)$_{n/4}$ × 4), 2.32 (m, 2H × n, -(OCOCH$_2$CH$_2$-)$_{n/4}$ × 4), 3.65 (t, 8H, $J = 6.6$ Hz, -CH$_2$CH$_2$OH × 4) 4.06 (t, 2H × (n-1), $J = 6.6$ Hz, -(CH$_2$CH$_2$O-)$_{(n-1)/4}$ × 4), 4.11 (s, 8H, C(CH$_2$CO-)$_4$).
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%. $M_{n,NMR} = 4,500$; $M_{n,SEC} = 5,600$, $D_M = 1.09$. $^1$H NMR (CDCl$_3$, 400MHz): δ (ppm) 1.42 (m, 4H, N$_3$CH$_2$CH$_2$CH$_2$CH$_2$-), 1.92 (m, 2H, N$_3$CH$_2$CH$_2$CH$_2$CH$_2$H$_2$-), 2.01-2.11 (m, 2H, N$_3$CH$_2$CH$_2$H$_2$-; 2H × (n-1)), 3.28 (t, 2H, $J = 7.0$ Hz, N$_3$CH$_2$H$_2$-), 3.74 (m, 2H, -CH$_2$OH), 4.21-4.27 (m, 2H, N$_3$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$-; 4H × (n-1), (-OCH$_2$CH$_2$H$_2$O-)$_{n-1}$; 2H, -CH$_2$CH$_2$CH$_2$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%. $M_{n,NMR} = 4,700$; $M_{n,SEC} = 6,400$, $D_M = 1.13$. $^1$H NMR (CDCl$_3$, 400MHz): δ (ppm) 1.92 (m, 2H, -CH$_2$CH$_2$OH), 2.00-2.13 (m, 2H × (n-1), (-OCH$_2$CH$_2$H$_2$-)$_{n-1}$), 3.74 (m, 2H, -CH$_2$OH), 3.85 (t, 2H, $J = 5.4$ Hz -NCH$_2$CH$_2$-), 4.21-4.29 (m, 2H, -NCH$_2$CH$_2$-; 4H × n-1, (-OCH$_2$CH$_2$H$_2$O-)$_{n-1}$; 2H, -CH$_2$CH$_2$CH$_2$OH), 6.74 (s, 2H, -COCHCHCO-).