Supporting Information

Design of Triple Shape Memory Polymers with Stable yet Tunable Temporary Shapes by Introducing Photo-Responsive Units into a Crystalline Domain

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Table S1. Polymerization conditions\(a\) and characterization results of PBCL.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[BrCL]:[CL]:[DPP]:[Ini.]</th>
<th>Time (h)</th>
<th>BC(^b) (%)</th>
<th>CC(^c) (%)</th>
<th>MR(^d) (mol%)</th>
<th>(M_{n,NMR})^e (kDa)</th>
<th>(M_{n,GPC})^f (kDa)</th>
<th>(M_{w}/M_n)^f</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBCL1</td>
<td>3:90:2:1</td>
<td>18</td>
<td>97.1</td>
<td>98.3</td>
<td>3.0</td>
<td>10.7</td>
<td>12.8</td>
<td>1.30</td>
</tr>
<tr>
<td>PBCL2</td>
<td>10:100:2:1</td>
<td>16</td>
<td>66.9</td>
<td>97.7</td>
<td>6.0</td>
<td>12.5</td>
<td>14.8</td>
<td>1.23</td>
</tr>
</tbody>
</table>

\(a\) Polymerizations were carried out by using DPP as a catalyst and ethylene glycol as an initiator with monomer concentration of 1 M in toluene at room temperature. \(b\) BrCL
conversion calculated by $^1$H NMR of polymers before purification. $^c$ CL conversion calculated by $^1$H NMR of polymers before purification. $^d$ the molar ratio of BrCL units in the resulting copolymer calculated by $^1$H NMR of purified product. $^e$ $M_{n, \text{NMR}} = (\text{BrCL conversion} \times \text{ratio of BrCL to initiator} \times M_{\text{BrCL}} + \text{CL conversion} \times \text{ratio of CL to initiator} \times M_{\text{CL}} + M_{\text{Ini.}})/\text{initiation efficiency}$, where initiation efficiency was estimated to be 100%. $^f$ Determined by GPC in DMF with polystyrene standards as calibration.

Figure S1. FT-IR spectra of PNCL1 and PMCL1.
**Figure S2.** UV-Vis curves of reversible photo reactions of PLLA-PMCL2 in DMF solution when irradiation at 365 nm for 5 min and then at 254 nm for 90 min. (reversibility ratio = \((A_1 - A_2)/(A_0 - A_2)\))

**Figure S3.** Series of photographs showing a one-way shape memory programming procedure and shape recovery to demonstrate thermally-induced SME of PLLA-PMCL1.