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.

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

[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] $M_{n,\ NMR}$ = (BrCL conversion × ratio of BrCL to initiator × M_{BrCL} + CL conversion × ratio of CL to initiator × M_{CL} +$M_{Ini.}$)/initiation efficiency, where initiation efficiency was estimated to be 100%. [f] Determined by GPC in DMF with polystyrene standards as calibration.

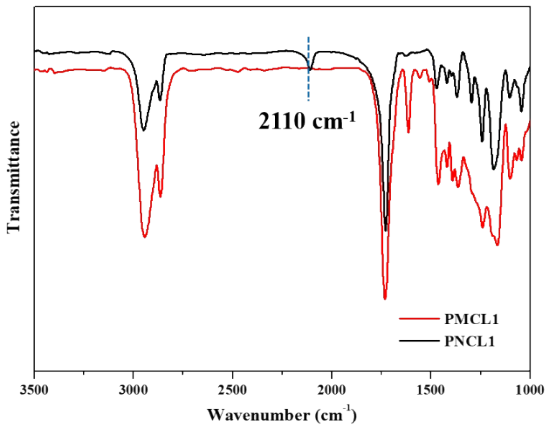

Figure S1. FT-IR spectra of PNCL1 and PMCL1.

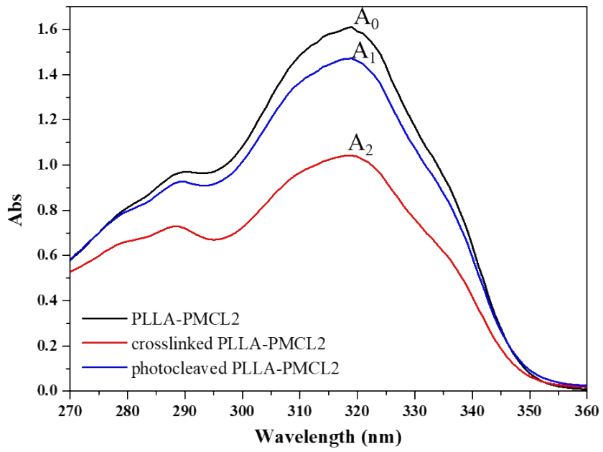

Figure S2. UV-Vis curves of reversible photo reactions of PLLA-PMCL2 in DMF solution when irradiation at 365 nm for 5 min and then at 254 nm for 90 min. (reversibility ratio = $(A_1 - A_2)/(A_0 - A_2)$)

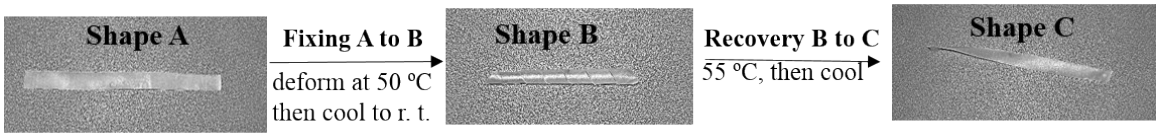

Figure S3. Series of photographs showing a one-way shape memory programming procedure and shape recovery to demonstrate thermally-induced SME of PLLA-PMCL1.