## **Properties of Triple Shape Memory Composites Prepared via Polymerization-Induced Phase Separation**

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## **Supplementary Information**



**Figure S1**. POM images under crossed polarizers exhibited by: (A) PPG-EP/PCL and (B) PEO-EP/PCL. The scale bar represents 50 µm.



**Figure S2**. POM images under crossed polarizers exhibited by: (A) PPG-EP/PCL and (B) PEO-EP/PCL. The scale bar represents 200 µm.



**Figure S3.** POM images under crossed polarizers at room temperature exhibited by: (A) PPG-EP, (B) PEO-EP, and (C) PCL. The scale bar represents 200 µm.



**Figure S4**. DMA loss tangent (tan  $\delta$ ) trace of (I) PPG-EP/PCL and (II) PEO-EP/PCL in log scale demonstrating all three transition temperatures. Red lines show the transition temperatures of each composite.



**Figure S5.** DSC thermograms of 1<sup>st</sup> cooling (dashed line) and 2<sup>nd</sup> heating (solid line) for: (I) PPG-EP, (II) PPG-EP/10%-PCL, (III) PEO/EP, (IV) PEO-EP/10%-PCL, and (V) PCL. Heating rate of 10 °C/min was used for cooling and heating of both samples. It is noted that the heat flow magnitude of the DSC thermogram for PCL was reduced by half for scaling purposes.



**Figure S6.** (a) Tensile storage modulus (E') and (b) loss tangent (tan  $\delta$ ) trace of PEO-EP/PCL with different PCL content in comparison with neat epoxy PEO-EP, measured by DMA. (i) PEO-EP and (ii) PEO-EP/10%PCL.



**Figure S7.** The triple-shape memory cycle of PEO-EP/PCL with (a) 0% and (b) 10% PCL content using one-step fixing. The beginning of the cycles are marked by the asterisk. Samples were loaded to a tensile strain of 20%, cooled to -10 °C and unloaded (fixing), followed by continuous heating to 75 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery.