Supplementary Information

Experimental Section

Materials

Methyl methacrylate (MMA) and 2,2'-azoisobutyronitrile (AIBN) were of analytical grade and were obtained from the Chengdu Reagent Factory. Ethylene glycol dimethacrylate (EGDMA) (Aldrich) was used as a crosslinker without further purification. MMA was distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from methanol solution. Poly(ethylene glycol) (PEG) purchased from local commercial company with weight-average molecular weights of 1000, 2000, 5000 was dried by heating at 70 °C for 7 h under a vacuum. The star PEG (SPEG) (three arms) were purchased from Polymer Source Inc. (Fig. S1), the weight-average molecular weights of arm chain were 1000, 2000, 5000. In this communication, we chose PMMA/SPEG 3×2000 (PEG arm chain $\boldsymbol{M}$w=2000, $\boldsymbol{T}_g$ =50 °C) network composites and PMMA-PEG2000 (PEG $\boldsymbol{M}$w=2000, $\boldsymbol{T}_g$ =55 °C) semi-IPNs as examples to demonstrate the star-shaped structural effect on mechanical and shape memory properities for the shape memory materials.

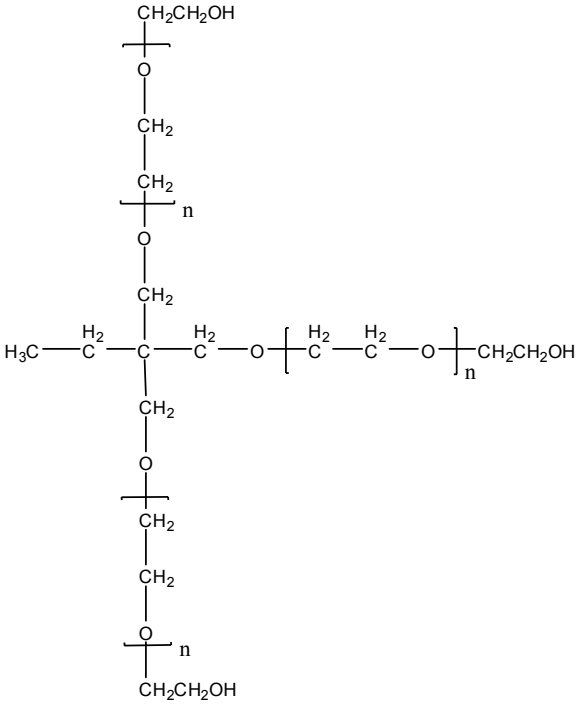


Fig. S1 Structure of three-arm star PEG.

Preparation

The PMMA/SPEG composites were prepared by radical polymerization and crosslinking of 55-65 wt% MMA in the presence of 0.5 wt% AIBN based on MMA weight as an initiator, 0.5 wt% EGDMA based on MMA weight as a cross-linker and 35-45 wt% star PEG. The PMMA-PEG semi-IPNs were preparaed by the same process in the presence of linear PEG. Nitrogen was bubbled through the reaction mixture for 15 min to remove any oxygen from the mixture, and the mixture was then injected into the space between two glass plates separated by polyethylene spacers (1 mm thick) or into a cylindrical glass tube with a diameter of 3 mm. Polymerization was carried out at 55 °C for 24h. All specimens were annealed and then dried under a vacuum at room temperature for 10 d to remove any unreacted monomer.

Measurements

1. Differential scanning calorimetry (DSC) measurements were performed on a TA instruments Q2000 with LNCS cooling accessory over the temperature range -50 °C—150 °C at a heating rate of 10 °C /min. Samples were heated until a temperature of 150 °C and cooled down to -50 °C at a speed of 10 °C /min to erase the thermal history.

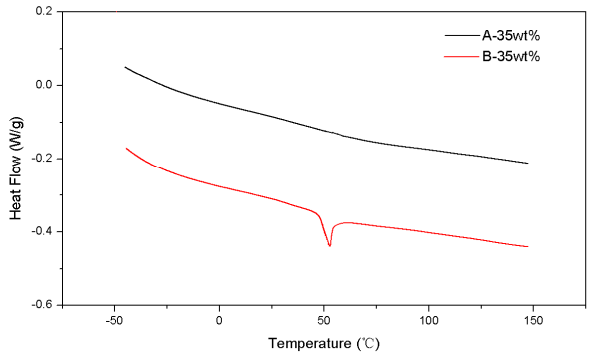
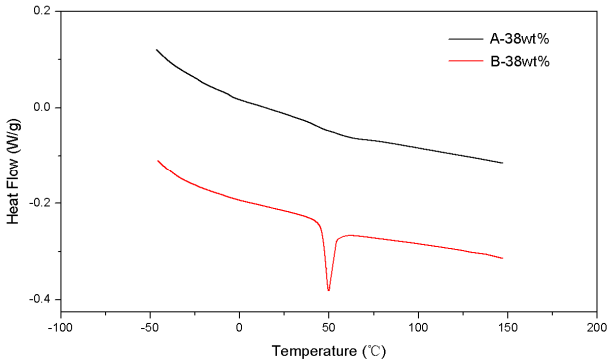
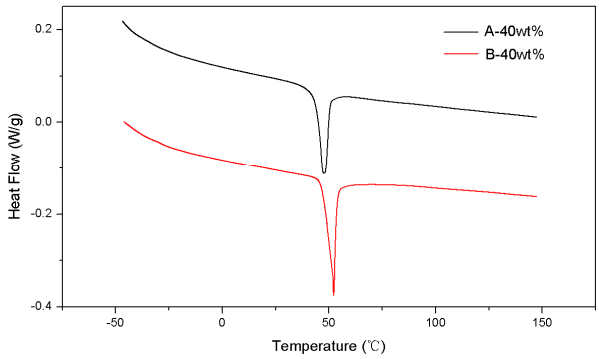


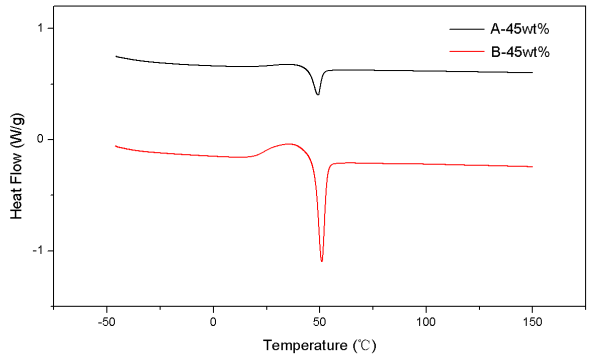
Fig. S2 (a) DSC thermograms of A-35wt% and B-35wt% samples, respectively;



(b) DSC thermograms of A-38wt% and B-38wt% samples, respectively;



(c) DSC thermograms of A-40wt% and B-40wt% samples, respectively;



(d) DSC thermograms of A-45wt% and B-45wt% samples, respectively.

2. Dynamic mechanical analysis (DMA) in tensile loading was carried out to determine the $\boldsymbol{T}_g$ of the networks on a TA Q800 DMA. Rectangular samples with dimensions of 1×5×25 mm^3 were cut and wrapped on thermal expansion during testing. The samples were thermally equilibrated at -50 °C for 3 minutes and then heated to 180 °C at a rate of 3 °C/min, as well as frequency of 1 Hz. $\boldsymbol{T}_g$ was defined at the peak of tan delta curves.

3. Mechanical and cyclic thermomechanical experiments were performed on a Tinius Olson H10K-T tensile machine with a 100N load cell with a strain rate of 5 mm/min. For the cyclic shape memory tests a thermochamber with temperature controller and connected to a liquid nitrogen Dewar is used. The sample was stretched to extensional strain of ε_1=60% and kept 5 min at 76 °C. With keeping this strain, the sample was cooled to room temperature (25 °C) with a cooling rate of 10 °C /min and kept 5 min. After unloading, the length of the sample was measured and fixed strain ε_2 was evaluated. The unloaded sample was heated to 76 °C again with a heating rate of 5 °C/min, and the length recovered to the original one was measured to evaluate recovering strain ε_3. A shape fixity rate (R_f) and a shape recovery ratio (R_r) were defined by the following equations.

$$R_f = \frac{\varepsilon_2}{\varepsilon_1} \times 100\%$$

$$R_r = \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1} \right) \times 100\%$$

4. Bending test which examined the shape memory effect as follows. A straight strip (60×12×2 mm) of the specimen was folded at 76 °C, then cooled to room temperature to maintain the deformation. The deformation sample was then heated again and the change of angle θ_f was recorded. The ratio of the recovery was defined as $\theta_f/180$.

Table S1 Summary of thermal-mechanical properties of A and B samples

Sample	T_g (°C)[a]	$\triangle H_m$ (J.g^{-1})[b]	E' 25 °C (M Pa)[c]	E' 76 °C (MPa)[d]	σ (MPa)[e]	ε (%)[f]	R_f (%)[g]	R_r (%)[h]	t_R (s)[i]
A-35wt%	77±0.1	NA[j]	527.7	8.2	11.7	243	69.8	87.3	163
A-40wt%	69±0.1	5.6	745.3	2.8	7.4	285	84.2	99.8	49
A-45wt%	67±0.1	7.2	1065.4	1.2	5.6	328	90.5	99.7	37
B-35wt%	79±0.1	1.6	1080.2	12.6	10.8	214	65.7	76.6	210
B-40wt%	74±0.1	9.6	705.2	3.4	5.3	212	92.1	96.4	97
B-45wt%	72±0.1	20.9	655.9	2.6	3.5	206	94.2	97.2	81

[a, c, d] Obtained from DMA results. [b] Determined by DSC. [e] Tensile strength measured on stress-strain test (25 °C). [f] Elongation at break measured on stress-strain test (25 °C). [g, h] Measured on cyclic thermomechanical experiment of the first cycle. [i] Measured by bending test. [j] Could not be measured for this sample.