Electronic Supplementary Information

A Versatile Approach to Achieve Quintuple-Shape Memory Effect by Semi-Interpenetrating Polymer Networks Containing Broadened Glass Transition and Crystalline Segments

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Experimental Section

Materials

Methyl methacrylate (MMA) and 2,2'-azobisisobutyronitrile (AIBN) were of analytical grade and obtained from the local Chengdu Reagent Factory. MMA was distilled under reduced pressure before use, and AIBN was recrystallized from methanol solution. Ethylene glycol dimethacrylate (EGDMA) and linear poly(ethylene glycol) (PEG) with $\overline{M}_n$ of 1000 were purchased from Sigma-Aldrich. EGDMA was used as received, and PEG was dried at 70 °C for 7 h under a vacuum before use.

Preparation

The PMMA/PEG semi-IPNs were prepared by free radical polymerization and crosslinking of 56.5~66.5 wt.-% MMA in the presence of 0.5 wt.-% AIBN, 3 wt.-%

EGDMA and 30~40 wt.-% PEG. PEG, EGDMA and AIBN were subsequently dissolved in MMA to obtain a homogeneous mixture, then nitrogen was bubbled through the mixture for 15 min to remove any oxygen, and the mixture was injected into the space between two glass plates separated by silicone rubber spacers (1 mm thick). The polymerization was carried out at 55 °C for 24 h. All specimens were annealed at 120 °C for 30 min to ensure complete polymerization and then dried under a vacuum at room temperature for 10 d to remove any unreacted monomer.

Characterization

DSC experiments were conducted on a DSC Q2000 (TA instruments). The samples were firstly heated from -50 °C to 150 °C, then cooled to -50 °C and again heated to 150 °C. All the experiments were performed with a heating/cooling rate of 10 °C·min^{-1}. T_m was determined from the melting peak temperature.

DMA experiments were carried out in tensile loading mode using a DMA Q800 (TA instruments). The samples were cut into rectangular slabs with dimensions of 15×4×1 mm and the tension film mode was used with an amplitude of 20 μm, a frequency of 1 Hz. The temperature was equilibrated at -50 °C for 3 min and then ramped to 150 °C at a heating rate of 3 °C·min^{-1}. T_g was determined from the tanδ curves.

The quantitative characterizations of multiple-SME were performed on the same DMA apparatus in a controlled force mode. The shape memory testing cycle was composed of two processes: (1) shape programming process, here the typical method was applied. The deformation force was applied to a target value at a T_d and kept constant during cooling to a fixity temperature (T_f), later the force was unloaded and the first shape was fixed. Then the rest shape fixity process can be done in the same manner. (2) shape recovering process, the multiple-step shape recovery was conducted in a staged heating fashion. The unloaded samples were heated to the respective T_r with a heating rate of 3 °C·min^{-1} and kept isothermal for 20 min at each

T_r. The details of these testing cycles were shown in the relevant figures of multiple-SME. The multiple-shape memory properties were quantified by the shape fixity rate (R_f) and shape recovery rate (R_r) defined as the following equations.[1]

$$R_f(X \to Y) = \frac{\varepsilon_y - \varepsilon_x}{\varepsilon_{y,load} - \varepsilon_x} \times 100\%$$

$$R_r(Y \to X) = \frac{\varepsilon_y - \varepsilon_{x,rec}}{\varepsilon_y - \varepsilon_x} \times 100\%$$

Here ε_x, $\varepsilon_{x,rec}$ and $\varepsilon_{y,load}$ represent the strain after cooling and unloading (the same for ε_y), the strain after recovery and the maximum strain before unloading, respectively. X and Y stand for two different shapes, respectively.

Reference

1. T. Xie, *Nature*, 2010, **464**, 267-270.

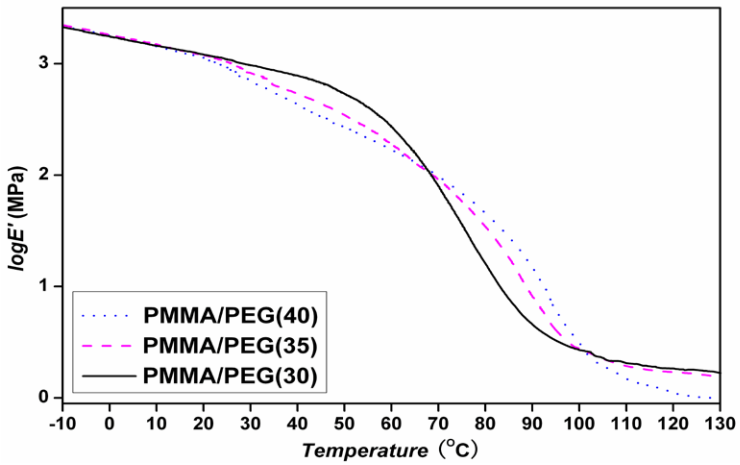
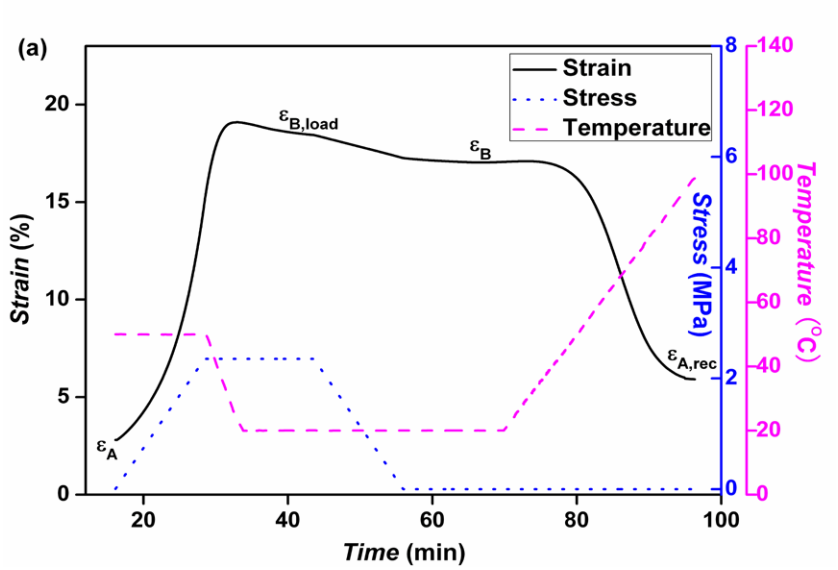
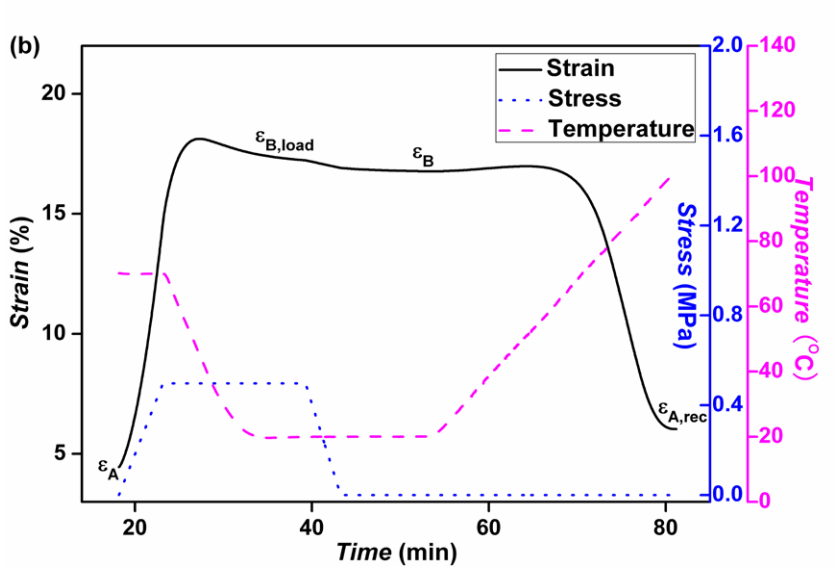


Fig. S1 The storage modulus (E') of dynamic mechanical analysis for PMMA/PEG semi-IPNs.





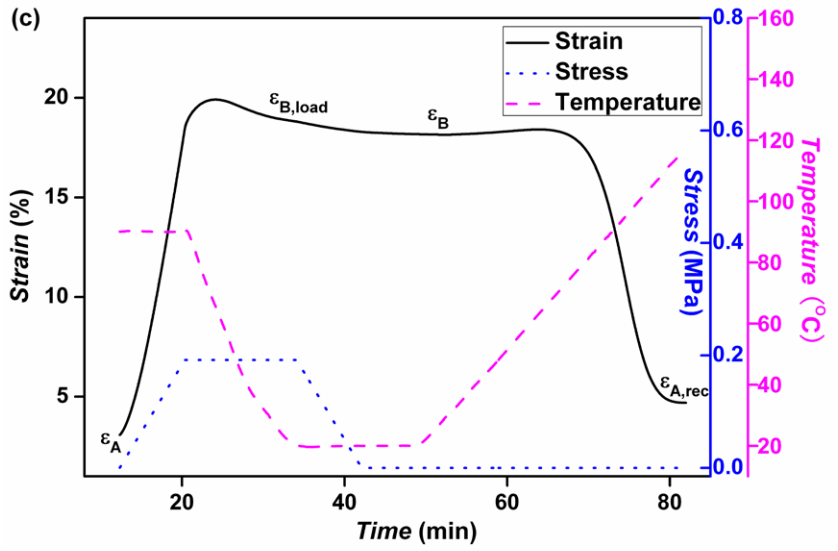


Fig. **S2** Dual-shape memory properties of PMMA/PEG(35). The sample was initially deformed at different temperatures: (a) 50 °C, (b) 70 °C and (c) 90 °C. Then it was cooled down to 20 °C to maintain the deformation. Finally, the unloaded sample was heated to the target temperature in a continuous heating fashion (heating rate: 3 °C·min^{-1}). (a) R_f(A→B): 91%, R_r(B→A): 78.1%. (b) R_f(A→B): 96.4%, R_r(B→A): 87%. (c) R_f(A→B): 95.9%, R_r(B→A): 89.2%.

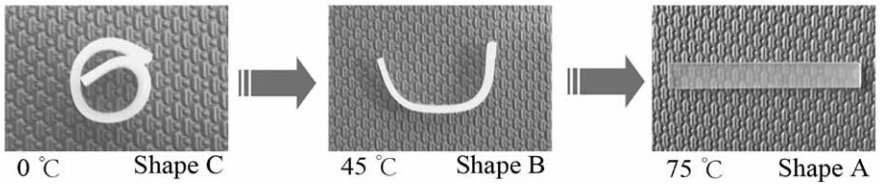


Fig. **S3** The photograph series demonstrating the triple-SME of PMMA/PEG(35). The shape B was the first temporary shape, shape C was the second temporary shape and shape A was the permanent shape.

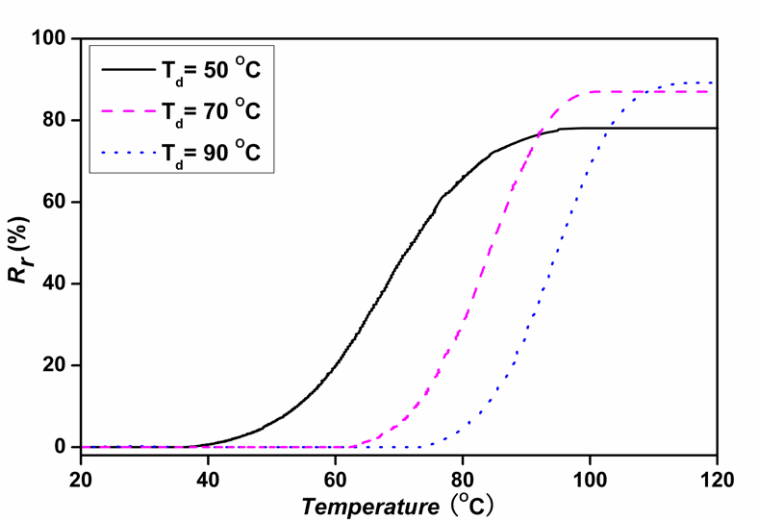


Fig. **S4** Dual-shape recovery rate (R_r) in a continuous heating fashion for PMMA/PEG(35) that have been deformed at different T_d: 50 °C, 70 °C and 90 °C.

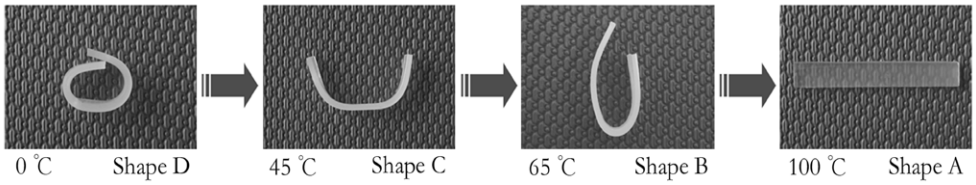


Fig. **S5** The series of photographs showing the quadruple-SME of PMMA/PEG(35). The shape B was the first temporary shape, shape C was the second temporary shape, shape D was the third temporary shape and shape A was the permanent shape.