

## Electronic Supplementary Information

### High-Strain Shape Memory Polymers with Movable Cross-Links Constructed by Interlocked Slide-Ring Structure

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#### Experimental Section

##### Preparation of materials

###### Preparation of polyrotaxane (PR)

PR with low inclusion ratio value of  $\alpha$ -cyclodextrin ( $\alpha$ -CD) was synthesized using a method similar to that well documented in the literature.<sup>1,2</sup> In this case, polyethylene glycol (PEG) with a molecular weight of 20 000 was used as the axis of the PR, because larger molecular weight PEG could form sparse inclusion complexes with  $\alpha$ -CD. The structure of the product was characterized by <sup>1</sup>H NMR (Supporting Information, Figure S1, S2, and S3). The average number of  $\alpha$ -CDs per PEG chain was estimated by comparing the integral values of the corresponding signals in Figure S3, using the signals of C(1) H of  $\alpha$ -CD at 4.80 ppm and the methyl end groups of the end-capped PEG at 2.22 ppm. It indicates that 48  $\alpha$ -CD units are captured in the polymer chain, corresponding to a low inclusion ratio of 21%.

###### Preparation of modified polyrotaxane (MPR)

The PR was modified by 2-isocyanatoethyl methacrylate having both isocyanate and vinyl groups in its parent structure. It was synthesized according to the method similar to that of Ito et al.<sup>3</sup> The isocyanate group can form a stable carbamate bond with the hydroxyl group of the  $\alpha$ -CD of the PR to yield the cross-linker, which is referred to as modified polyrotaxane (MPR) in the article. The degree of substitution (DS) ( $0 \leq DS \leq 18$ ), that is, the average number of substituted hydroxyl groups per  $\alpha$ -CD unit of the MPR was found to be 2, which was

calculated using  $^1\text{H}$  NMR spectra (see Figure S4 in Supporting Information ). The structure of MPR was further evidenced by the FT-IR spectrum (Figure S5).

#### Preparation of topologically interlocked slide-ring materials

A certain amount of MA, MMA, MPR, and 2,2'-azobisisobutyronitrile (AIBN) were dissolved in anhydrous DMSO to obtain a homogeneous mixture. Next,  $\text{N}_2$  bubbling was passed through the mixture for 30 min to remove any oxygen, followed by sonication to remove excess  $\text{N}_2$  from the solution. The mixture was injected into the space between two glass plates separated by silicone rubber spacers (1 mm thick). The reaction was carried out at 60 °C for 24 h. The gels were thoroughly washed with DMSO, followed by ethanol for 1 week to remove DMSO. Then the sample was dried under a vacuum for 5 days to remove the solvent. Typical networks with chemical cross-linking and physical cross-linking were also prepared under identical conditions and were used as references against the slide-ring materials. Ethylene glycol dimethacrylate (EGDMA) was chosen as a cross-linker of chemically cross-linked network instead of modified CD and with the same molar weight of the cross-linker (Both EGDMA and modified CD contains two double bonds). There was no cross-linker in physically cross-linked network.

#### Characterization

$^1\text{H}$  NMR Characterization:  $^1\text{H}$  NMR spectra were recorded on a Bruker AV300 NMR spectrometer at 300 MHz at room temperature. Tetramethylsilane (TMS) was used as an internal standard for the analysis of chemical shifts.

FTIR Characterization: FTIR spectra were recorded using a ThermoFisher Nicolet 6700 FTIR spectrometer. All samples were scanned in the range of 400 – 4000  $\text{cm}^{-1}$ .

Dynamic Mechanical Analysis: Dynamic mechanical analysis (DMA) was carried out in tensile loading mode using a DMA Q800 (TA instruments). The samples were cut into rectangular slabs with dimensions of 30 × 5 × 1 mm and the tension film mode was used with an amplitude of 20  $\mu\text{m}$ , a frequency of 1 Hz. The samples were thermally equilibrated at 0 °C

for 5 minutes and then heated to 150 °C at a heating rate of 3 °C min<sup>-1</sup>. T<sub>g</sub> was defined at the peak of tanδ curves.

**Shape Memory Characterization:** Quantitative assessment of the shape memory performance was carried out through cyclic thermomechanical experiment by the same DMA under a controlled force mode. Rectangular specimens with dimensions of 30 × 5 × 1 mm were used. The temperature for stress deformation studied was selected to be T<sub>g</sub> + 15 °C, respectively. The shape memory testing cycle was composed of four steps: (1) the deformation force was applied until the tensile strain reach 50% at T<sub>g</sub> + 15 °C; (2) with keeping this force, the sample was cooled to a fixity temperature (T<sub>g</sub> - 30 °C) with a cooling rate of 10 °C min<sup>-1</sup> and kept 5 min; (3) the force was unloaded and the temporary shape was fixed; (4) keeping 5 min, then the unloaded sample was heated to T<sub>g</sub> + 15 °C again with a heating rate of 5 °C min<sup>-1</sup> and kept isothermal for 20 min, the length recovered to the original one. The shape memory properties were quantified by shape fixity ratio (R<sub>f</sub>) and shape recovery ratio (R<sub>r</sub>) based on the Equation 1 and 2:<sup>4</sup>

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_l(N)} \quad (1)$$

$$R_r(N) = \frac{\varepsilon_l(N) - \varepsilon_p(N)}{\varepsilon_l(N) - \varepsilon_p(N-1)} \quad (2)$$

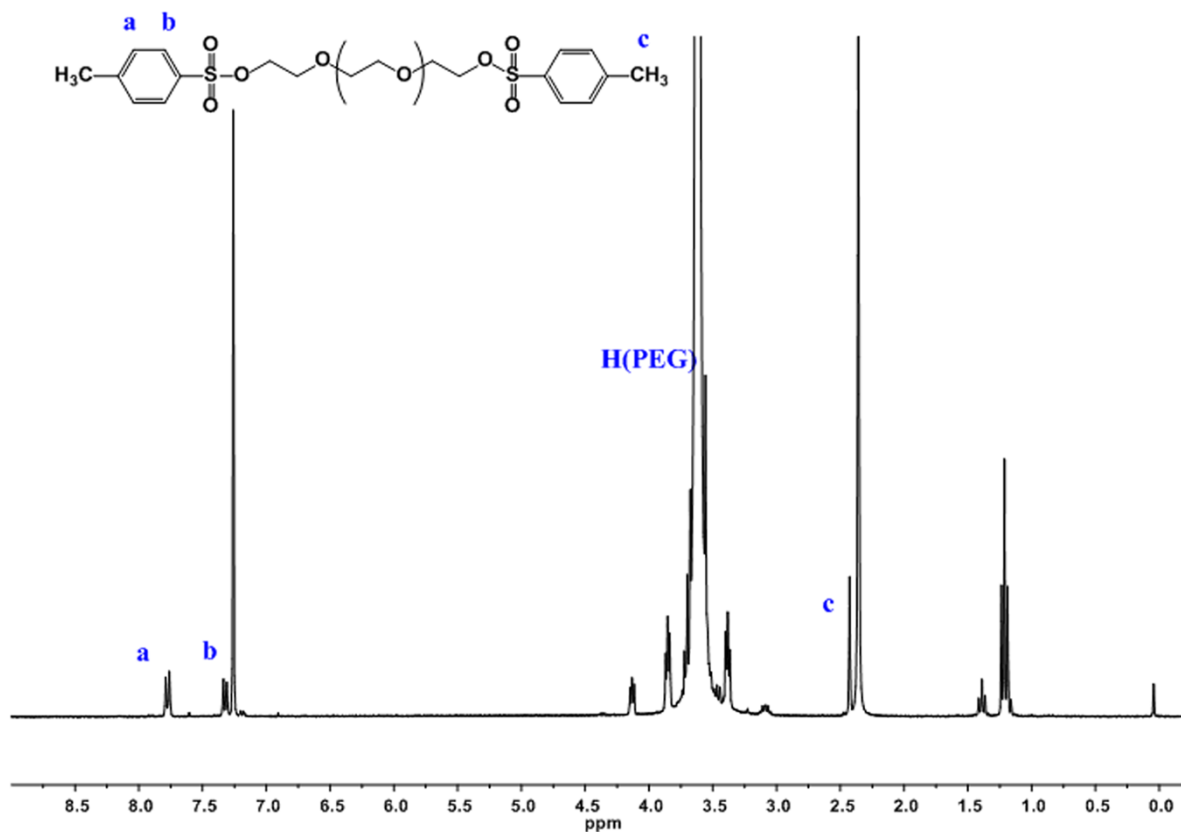
Here ε<sub>u</sub>(N), ε<sub>l</sub>(N) and ε<sub>p</sub>(N) represented the strain after unloading, the maximum strain at σ = σ<sub>m</sub> after cooling to T<sub>low</sub>, and the strain after recovery in the Nth cycle, respectively.

**High Strain Shape Memory Characterization:** As the characterization could not be performed at large deformation by DMA, due to the stroke length limit on the DMA Q800, the shape memory test at large deformation was performed on a tensile machine equipped with a temperature controller. The sample was stretched to extensional strain of ε<sub>1</sub> = 800% with a strain rate of 5 mm min<sup>-1</sup> and kept 5 min at T<sub>g</sub> + 15 °C. With keeping this strain, the sample was cooled to T<sub>g</sub> - 30 °C with a cooling rate of 10 °C min<sup>-1</sup> and kept 5 min. After unloading, the length of the sample was measured and fixed strain ε<sub>2</sub> was evaluated. The unloaded sample was heated to T<sub>g</sub> + 15 °C again with a heating rate of 5 °C min<sup>-1</sup>, and the

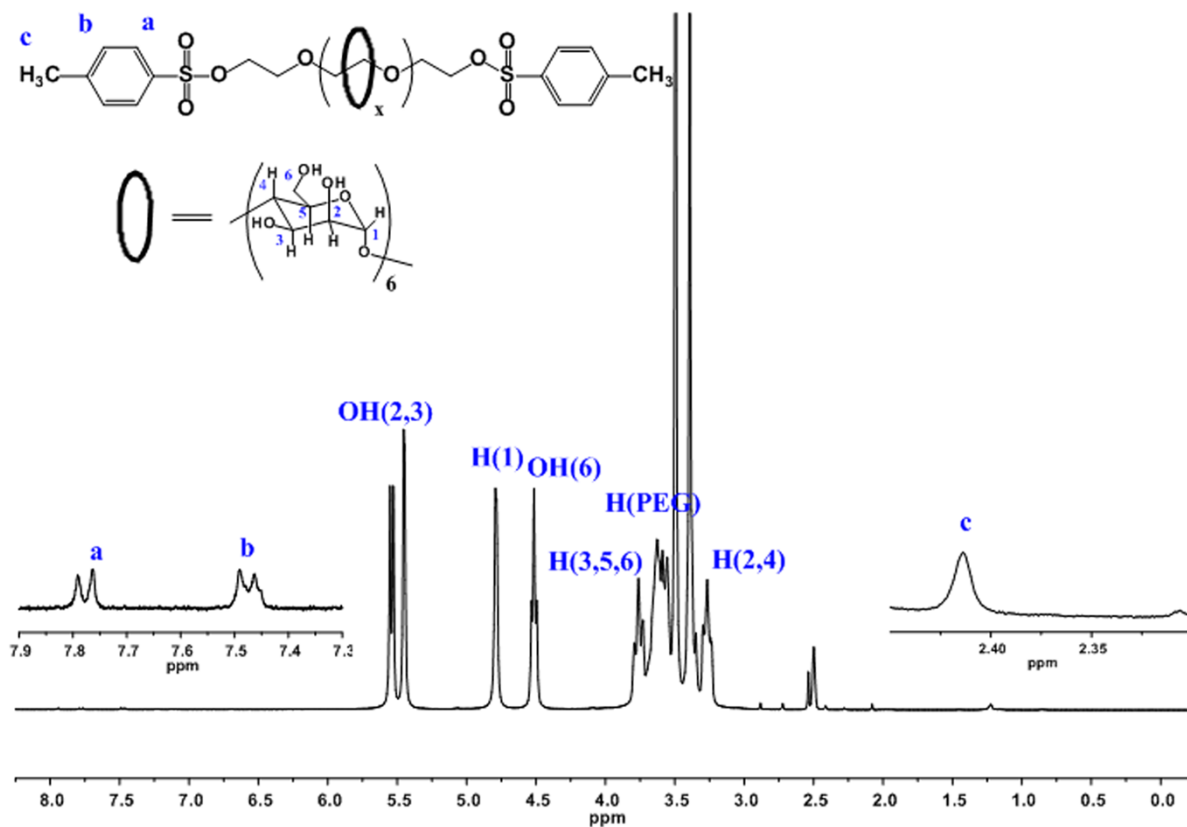
length recovered to the original one was measured to evaluate recovering strain  $\varepsilon_3$ . A shape fixity ratio ( $R_f$ ) and a shape recovery ratio ( $R_r$ ) were defined by the Equation 3 and 4.

$$R_f = \frac{\varepsilon_2}{\varepsilon_1} \quad (3)$$

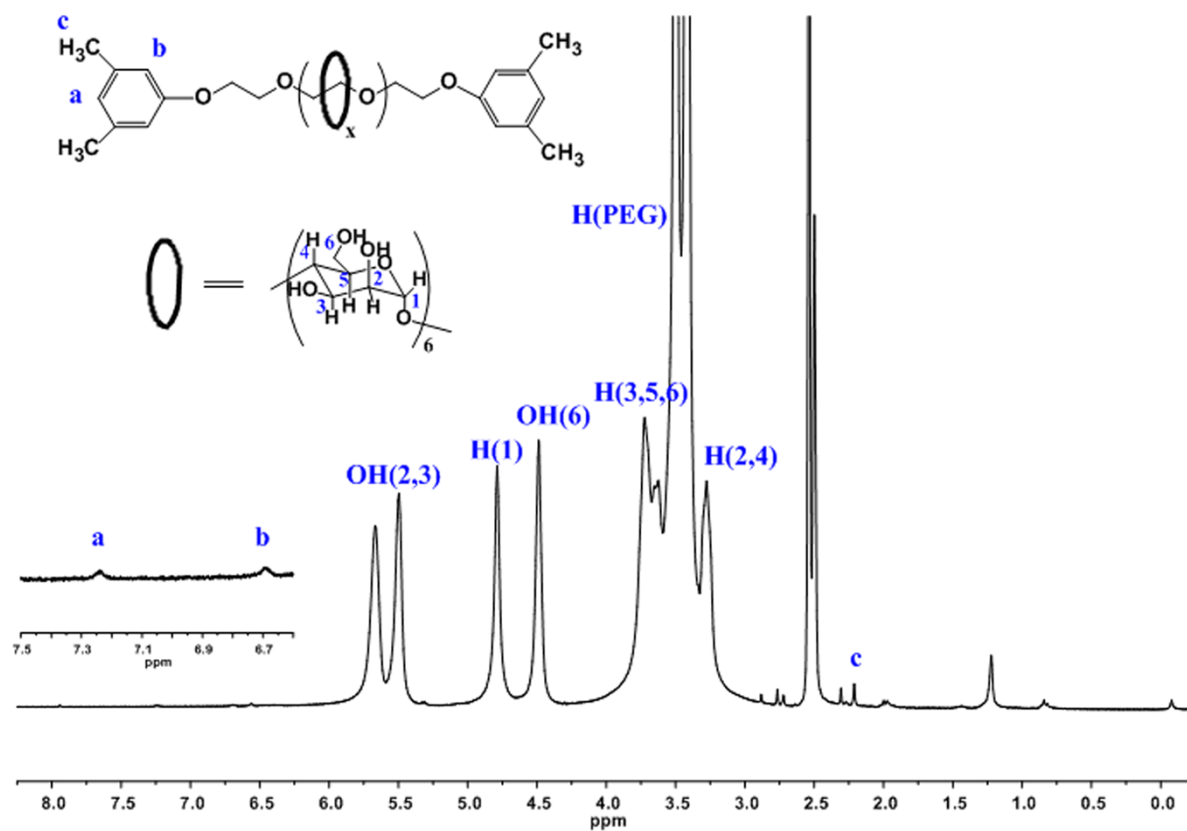
$$R_r = \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1} \quad (4)$$



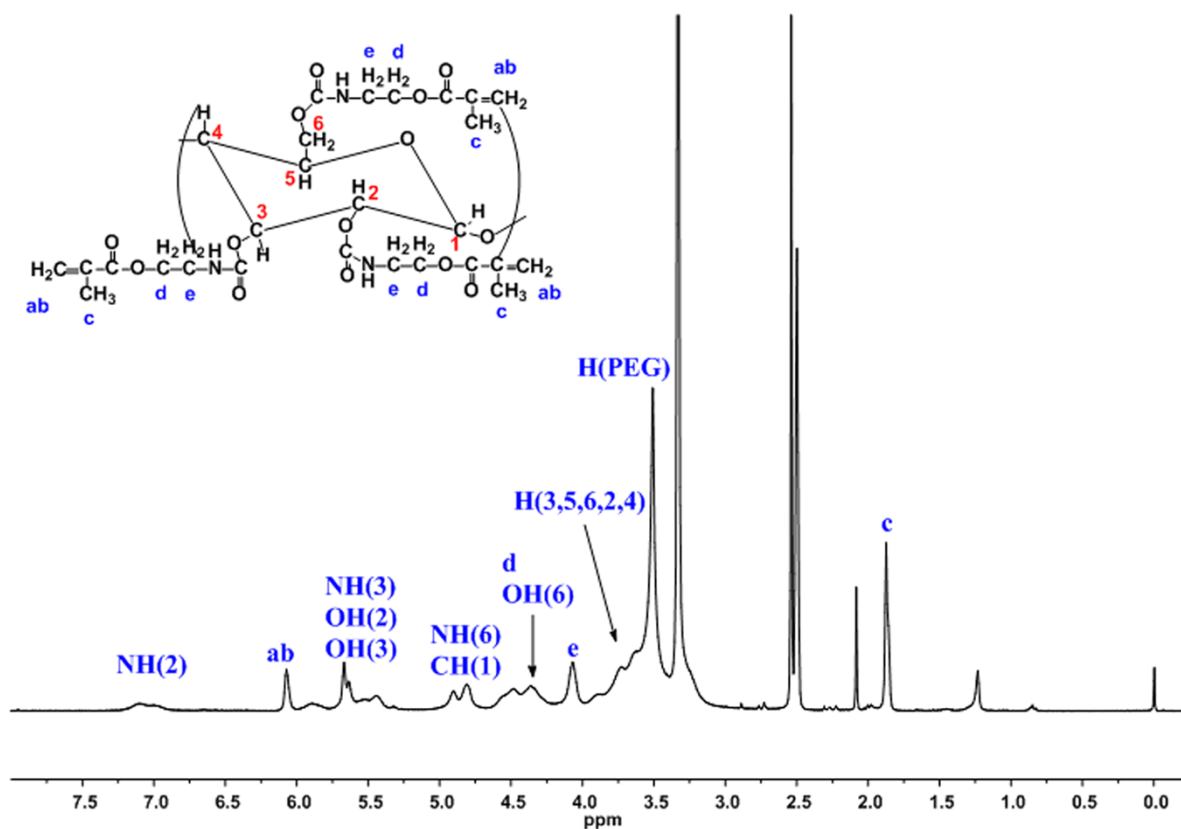
**Figure S1.**  $^1\text{H}$  NMR spectra of bis-tosyl-terminated PEG in  $\text{CDCl}_3$ .



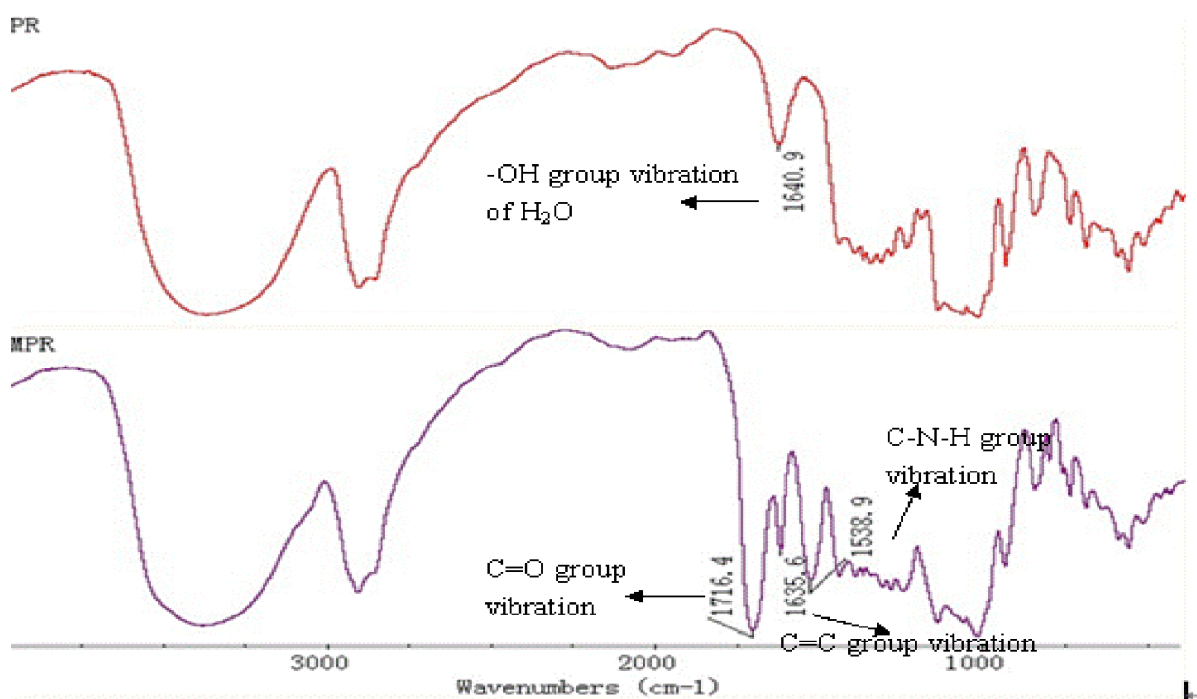
**Figure S2.**  $^1\text{H}$  NMR spectra of pseudo-PR in  $\text{DMSO-d}_6$  with TMS as an internal standard.



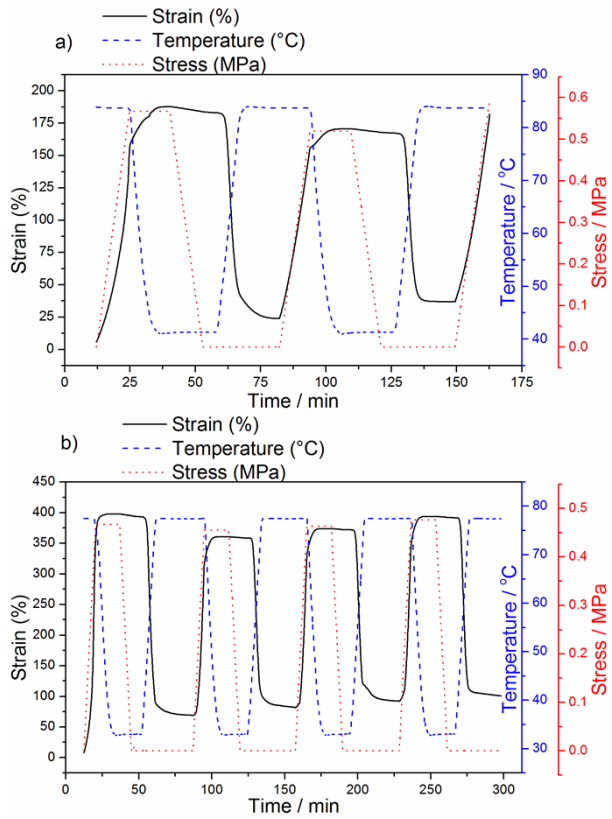
**Figure S3.**  $^1\text{H}$  NMR spectra of PR in  $\text{DMSO-d}_6$  with TMS as an internal standard.



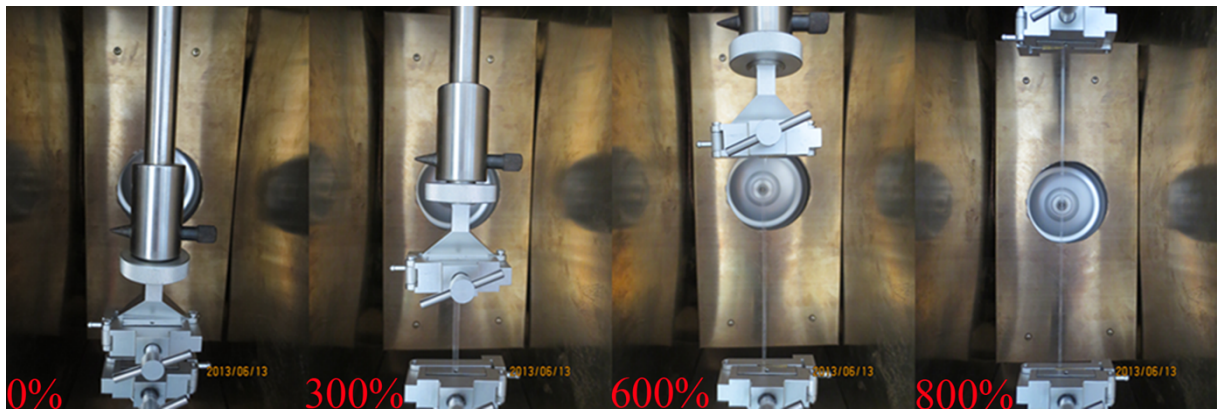
**Figure S4.**  $^1\text{H}$  NMR spectra of MPR in  $\text{DMSO-d}_6$  with TMS as an internal standard.



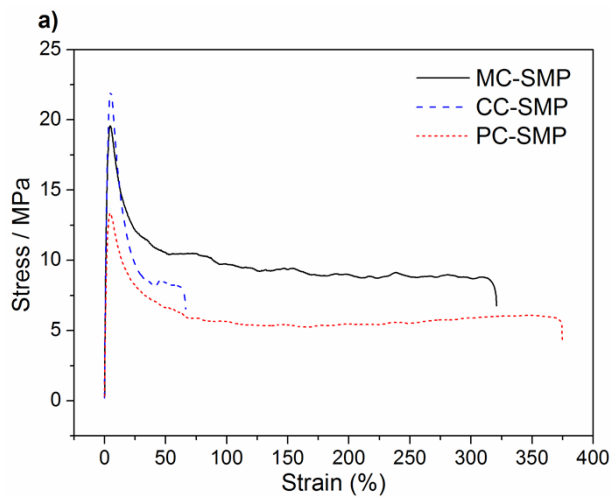
**Figure S5.** FTIR spectra of PR and MPR.

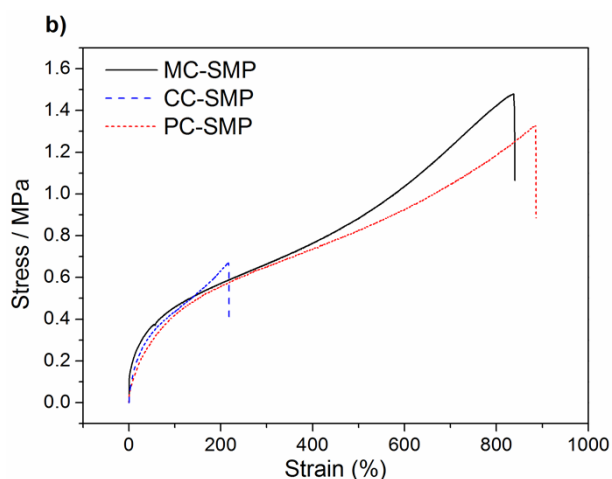


**Figure S6.** Shape-memory cycles of a) CC-SMP and b) PC-SMP under a stress-controlled deformation condition.



**Figure S7.** Photographs of MC-SMP at 800% deformation strain.





**Figure S8.** The stress-strain curves of MC-SMP, CC-SMP and PC-SMP at different temperature: (a) 25 °C (below  $T_g$ ), (b)  $T_g+15$  °C.

**Table S1.** Composition of the samples

Sample	MA [mol]	MMA [mol]	AIBN [mol%]	cross-linker [mol%]
MC-SMP	1	1	0.5	1 ( $\alpha$ -CD)
CC-SMP	1	1	0.5	1 (EGDMA)
PC-SMP	1	1	0.5	0

**Table S2.** Summary of shape memory properties of MC-SMP, CC-SMP and PC-SMP at 50% deformation strain

Sample	$T_g$ [°C]	$R_f$ [%]	$R_r$ [%]
MC-SMP	65.7	99.0	99.7
CC-SMP	68.8	99.2	95.2
PC-SMP	62.4	99.4	89.6

**Table S3.** Summary of shape memory properties of MC-SMP and PC-SMP at 800% deformation strain

Sample	$R_f$ [%]	$R_r$ [%]
MC-SMP	94.4	92.5
PC-SMP	93.2	68.9

- 1 T. J. Zhao and H. W. Beckham, *Macromolecules*, 2003, **36**, 9859-9865.
- 2 G. Fleury, C. Brochon, G. Schlatter, G. Bonnet, A. Lappb and G. Hadziioannou, *Soft Matter*, 2005, **1**, 378-385.
- 3 A. B. Imran, T. Seki, K. Ito and Y. Takeoka, *Macromolecules*, 2010, **43**, 1975-1980.
- 4 W. Wagermaier, K. Kratz, M. Heuchel and A. Lendlein, *Adv. Polym. Sci.*, 2010, **226**, 97-145.