# Supporting Information

## Mechanically Robust Hydrogel with Thermally Induced Plasticity and Shape Memory Effect

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**Materials:** n-Octadecyl acrylate (C18, Aldrich), Acrylamide (AAm, Sigma), N,N'-methylenebis(acrylamide) (MBA, Merck), sodium dodecyl sulfate (SDS, Sigma), NaCl (Merck), Iron(III) chloride hexahydrate ($FeCl_3$ $6H_2O$,Merck), and ammonium persulfate (APS, Sigma) were used as received. Acrylic acid (AAc Aldrich) was freed from its inhibitor by passing through an inhibitor removal column purchased from the Aldrich Chemical Co. All other chemicals and solvents are analytical grade.

**Preparation of the hydrogels:** Acrylamide, different mass ratios of n-Octadecyl acrylate (25%, 35%, 45%, mass ration of C18/AAm/AAc), and mass ratios of acrylic acid (10%, 15%, 20%, mass ration of C18/AAm/AAc) were added in the micellar solution from an 18% w/v SDS in 1.5M NaCl solution. The monomer concentration was fixed at 12w%. After stirring for 30min at 50℃ to obtain a transparent solution, stock solution of 1 wt% initiator APS (0.1mL) was added. The resulting solution was poured into a glass mold and placed at 65℃ for 12h. After polymerization, samples were immersed in a large excess of water at room temperature for by replacing water to extract SDS and residual monomers, till SDS in the external solution dropped below the detection limit of the methylene blue method(*Macromolecules, 2013, 46 (8), pp 3125–3131*). Then, samples were immersed in 50mM $FeCl_3$

solution for 24h to form the second network. At last, samples were rinsed in deionized water for 48h to remove superfluous $Fe^{3+}$ ions.

**Mechanical characterization:** Tensile and loading-unloading tests of the tough hydrogel were measured by an electrical universal material testing machine with a 500N load cell(EZTest, SHIMADZU), The samples were cut into long strips shape with length 40mm ,width 5 mm and thickness 1.6~2.0mm. the crosshead velocity was kept at 100 mm•min$^{-1}$ during the normal tensile tests. As for the loading-unloading test and the successive loading-unloading tests the crosshead velocity were both kept at 150 mm•min$^{-1}$. In addition, silicone oil was coated on the hydrogel surface during the successive loading-unloading tests. When the tests finished, the tested hydrogel was coated with a layer of silicone oil and encased by the plastic wrap to avoid water volatilizing. All the measurements were at room temperature. The nominal fracture tensile stress and nominal fracture tensile strain were determined by the rupture point of the stress-strain curve. The toughness was calculated from the area of stress-strain curves.

**Rheological measurements:** Dynamic viscoelasticity was measured using a rheometer (TA AR-G2, TA Instruments), fitted with a circulating environmental system for temperature control and using parallel plates of 40 mm diameter and a plate to plate distance of 1000 μm. To prevent water evaporation, the measuring system was surrounded with a solvent trap, and low-viscosity silicon oil was carefully added to the edges of the plate. Frequency sweep was performed at various temperatures within a linear range of viscoelasticity at a small strain (1%). The storage modulus (G’) and the loss modulus (G”) were measured as a function of angular frequency from 100 rad s$^{-1}$ to 0.01 rad s$^{-1}$.Temperature sweep was used to study thermal behaviour of the sample with a ramp in the range of 25–75℃ at a rate of increase of 5℃ min$^{-1}$, followed by a cooling process at a rate of 5℃ min$^{-1}$. The angular frequency was controlled at 6.28 rad s$^{-1}$.

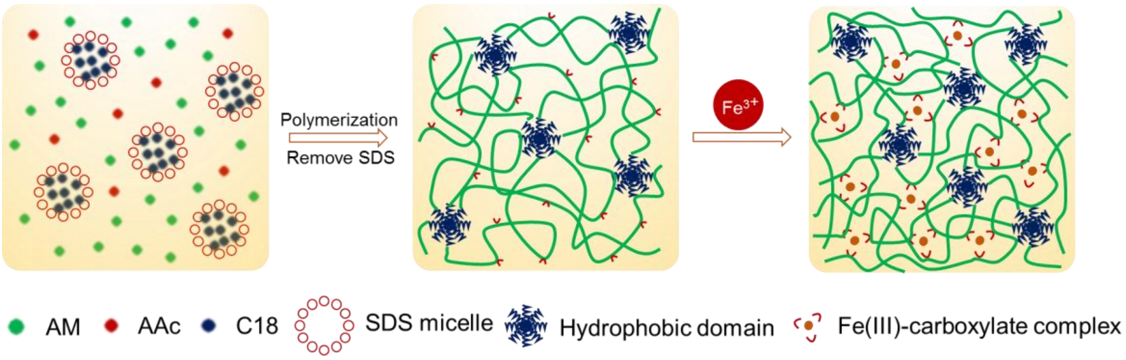

**Figure S1.** Schematic illustration of preparation of the dual physically crosslinked hydrogel.

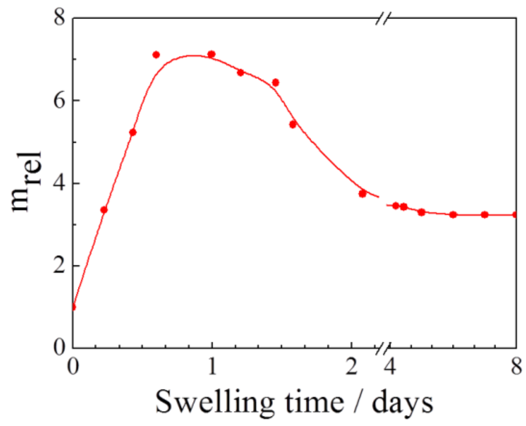

**Figure S2.** Relative weight swelling ratio $m_{rel}$ of the physical gel plotted against the swelling time in water.

| Samples | $hm_{25}p_{10}$ | $hm_{35}p_{10}$ | $hm_{45}p_{10}$ | $hm_{35}p_{5}$ | $hm_{35}p_{15}$ |
|---|---|---|---|---|---|
| EWC(%) | 98.28 | 96.98 | 95.13 | 96.80 | 97.18 |
| Samples | $HM_{25}P_{10}$ | $HM_{35}P_{10}$ | $HM_{45}P_{10}$ | $HM_{35}P_{5}$ | $HM_{35}P_{15}$ |
| EWC(%) | 72.67 | 72.50 | 70.32 | 79.70 | 65.45 |

**Table S1.** Equilibrium water contents (EWCs) of hydrogels with different contents of C18 and AAc.

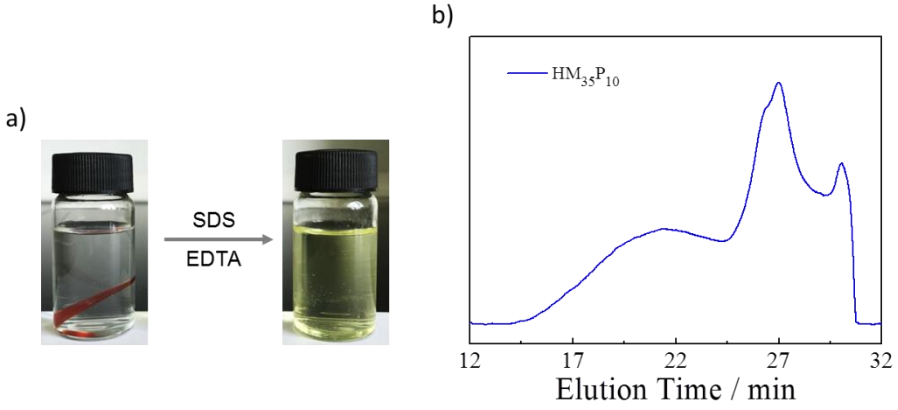

**Figure S3**. a)A HM$_{35}$P$_{10}$ hydrogel, stable in water for a month, was treated with a 15w% SDS and 5w% EDTA aqueous solution at 65℃. Upon stirring, the sample dissolved. b) GPC trace of the polymer in DMF. The molecular weight was 6.9×105 with $M_w/M_n$=1.8.

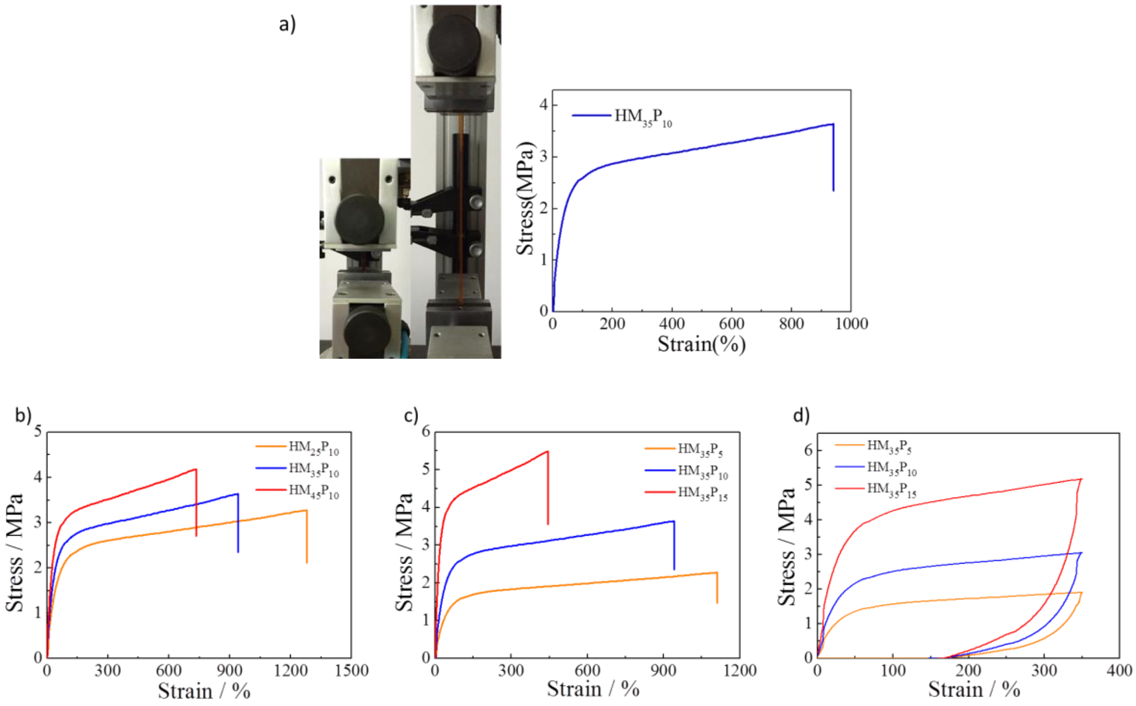

**Figure S4.** a)Tensile test and tensile-stress curve of the HM$_{35}$P$_{10}$ hydrogel. b) Tensile-stress curves of hydrogels with different concentrations of C18. c) Tensile-stress curves of hydrogels with different concentrations of AAc. d) Loading-unloading tests of hydrogels with different concentrations of AAc under 350% strain.

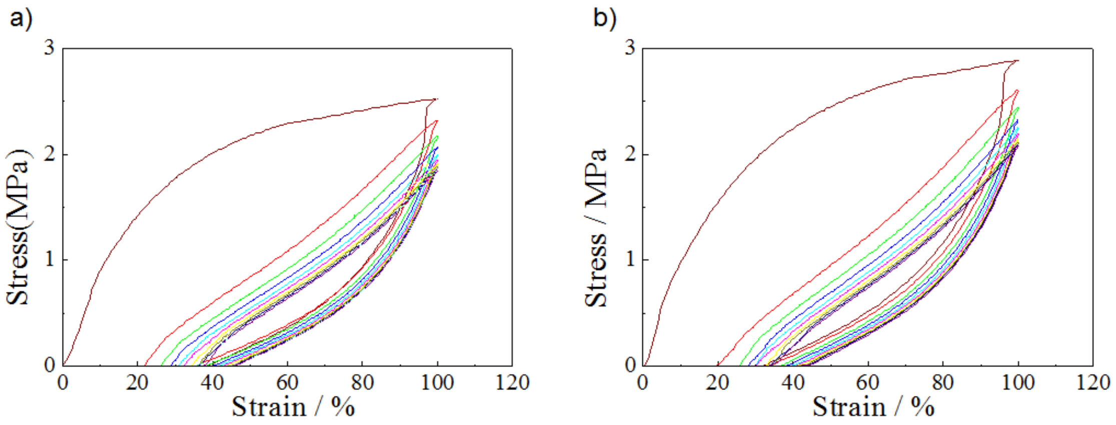

**Figure S5.** a) Ten successive loading-unloading cycles of the as prepared sample; and b) recovered sample (21h at RT).

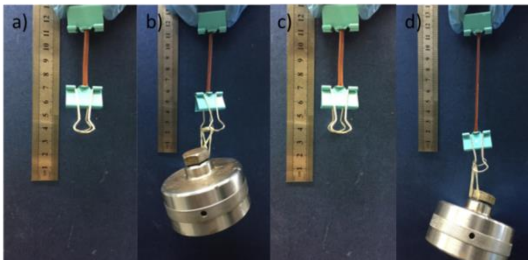

**Figure S6.** a) At room temperature, the sample is at no-load state; and b) after immediately applied a fixed stress; c) after stored in water at 75℃ for 3 minutes, at no-load state; and d) after immediately applied the same stress.

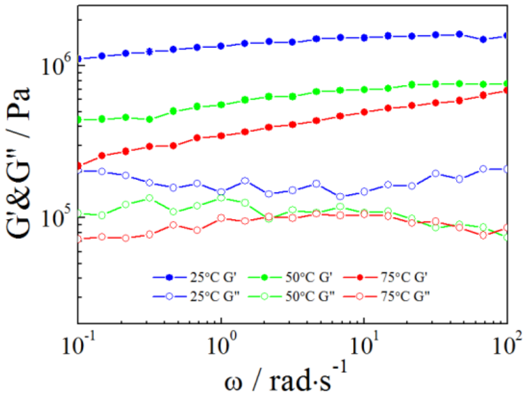

**Figure S7.** Frequency sweep of $HM_{35}P_{10}$ at different temperatures (25, 50, 75℃) in terms of G’.

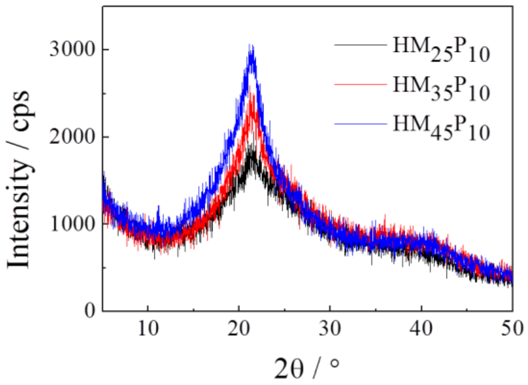

**Figure S8.** The XRD patterns of hydrogels with varied contents of C18.

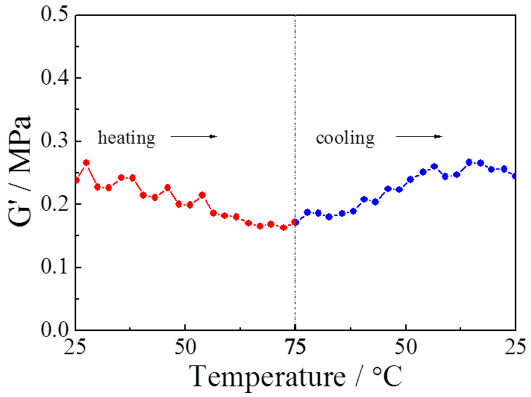

**Figure S9.** Temperature sweep in terms of G' of hydrogels with 0.1 mol% MBA instead of hydrophobic domains (conc($Fe^{3+}$)=50mM).

**Figure S10.** After immersion in vitamin C (ascorbic acid) solution, the second crosslinked network structure was erased; then transferred into $Fe^{3+}$ solution under external stress, the previous hydrogel was reprocessed into a new geometrical shape.

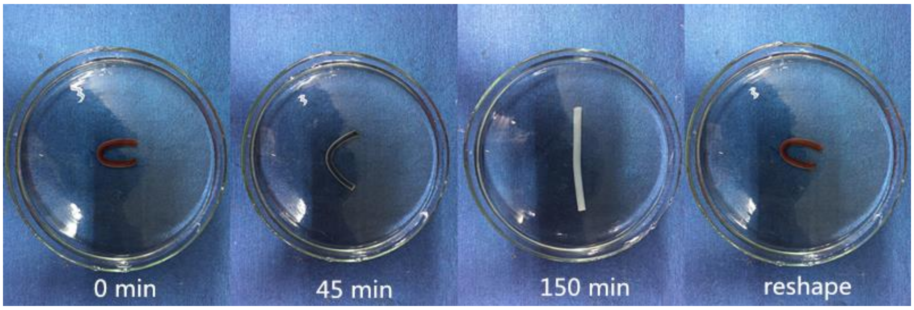

**Figure S11.** The shape fixity ratio ($R_f$) and shape recovery ratio ($R_r$) were defined by the follwing equation: $R_f = \theta_t/\theta_i \times 100\%$, $R_r = (\theta_i - \theta_f)/\theta_i \times 100\%$. Where $\theta_i$ is the given angle, $\theta_t$ is the temporarily fixed angel and $\theta_f$ is the final angle.