Supporting Information

Mechanically Strong and Stretchable PEG-based Supramolecular Hydrogel with Water-Responsive Shape-Memory Property

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1. Experimental

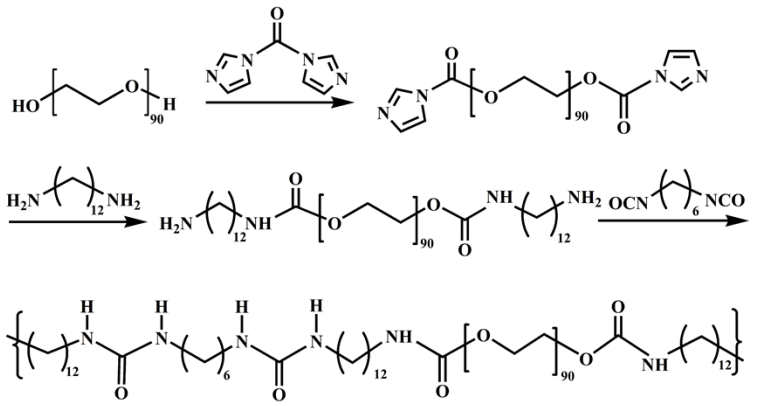
Synthesis and sample preparation: All reagents were purchased from commercial sources and used without further purification. N,N-Dimethylformamide (DMF) was dried by 4Å molecular sieves before use. The copolymer was synthesized according to procedure described in Scheme 1. The amino-terminated PEG was synthesized according to our previous reports.[1] The copolymer was achieved by a step-growth polymerization of amino-terminated PEG (M_n = 4000 g/mol, PEG4k) and hexamethylene diisocyanate (HDI). For example, 4.01 g (1.74 mmol) amino-terminated PEG4k was dissolved in 40 mL DMF. The solution was stirred under nitrogen at room temperature until the polymer was fully dissolved and the solution became clear. Then 1.74 mmol HDI was added dropwise into the solution, and the mixture was stirred for 1 h at room temperature before heating to 65 ºC. The mixed solution was further stirred for another 2 h at 65 ºC resulting in a clear viscous solution. The viscous solution was then cooled to room temperature and precipitated in 400 mL diethylether under vigorously magnetic stirring, yielding white cotton like polymer filament. The filament was collected and dried at 40 ºC under high vacuum. The bulk state polymer was first dissolved in methanol, and then the methanol solution was poured into Teflon molds, where the solvent evaporated to yield dry films. After fully swelling in a large amount of water, supramolecular hydrogel films were obtained.

The swelling ratio of the supramolecular hydrogel was determined in distilled water at room temperature. After removing the gel from the water and blotting off excess water with filter papers, the

hydrogel weight was recorded. The swelling ratio of the gel was then calculated by taking the ratio of the percentage of absorbed water to the original weight of the dry film:

Swelling ratio (%) = $100\times (m_w - m_d)/m_d$

where, m_w is the wet weight of the water swelling hydrogel film and m_d is the dry weight of the film.



Scheme S1. Synthesis procedure of the PEG-based copolymer.

2. Characterizations

^{1}H NMR spectra in $CDCl_3$ were recorded using a 400 MHz Inova NMR spectrometer. GPC in DMF was performed on a PL-GPC220 (Polytech Instrument) at 80 ºC using polystyrene as standard. Thermogravimetric analysis (TGA) was carried out on a Pyris 1 TGA instrument. Differential scanning calorimetry (DSC) measurement was performed on DSC 2010 (TA instrument) under a nitrogen atmosphere with heating and cooling rates of 10 °C/min. Samples were first heated at 20 ºC/min to 100 ºC and hold at 100 ºC for 5 min before further heating to 600 ºC under nitrogen atmosphere. Rheology measurements were performed on a HAAKE Rheometer (RS 6000) with a parallel plate accessory (20 mm in diameter). The existence and extent of the linear viscoelastic regime were determined by measuring the dynamic shear storage modulus (G') and loss modulus (G"), as a function of strain ($0.01<\gamma< 10$) at an angular frequency of 6.28 rad/s. All the measurements were carried out within the

linear viscoelastic range, where G' and G" are independent of strain. RPA 2000 rubber process analyzer was used for rheological temperature sweeps (3 ºC/min) with a frequency of 1 Hz and strain amplitude of 1%. Tensile-test was carried out on an INSTRON 5565 tensile test machine; the cross-head speed of the tensile measurements was 50 mm/min. Morphological studies of the cross-section of the freeze-dried hydrogel films were carried out on a Hitachi S-4700 scanning electron microscope (SEM). Samples for SEM were sputter-coated with a thin layer of Au/Pd prior to the observations to prevent samples-charging problems. Wide-angle X-ray experiments were carried out on a PANalytical X'Pert Pro MPD X-ray diffractometer with Cu Ka (1.540598 Å) radiation.

3. Supplementary Figures:

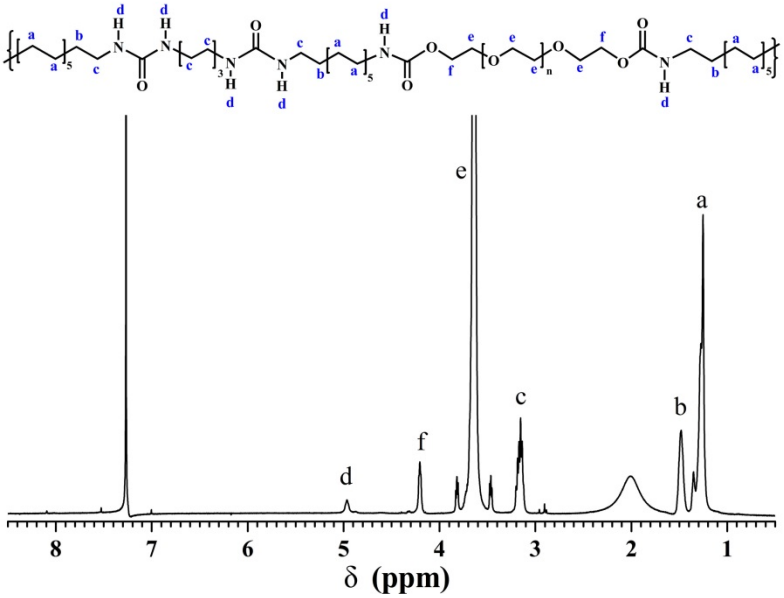


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) of the PEG-based copolymer.

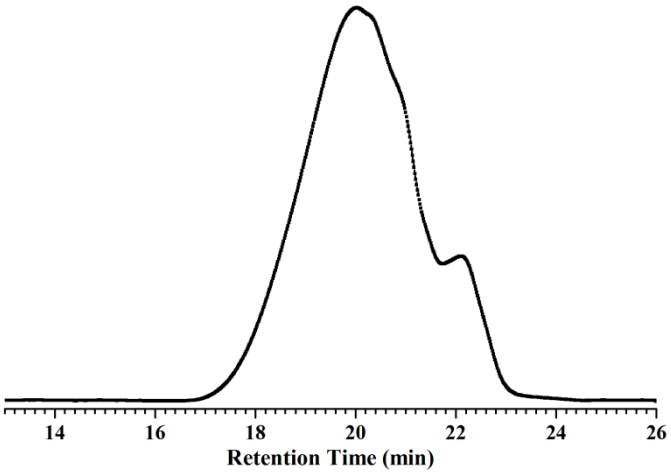


Fig. S2 GPC curve of the PEG-based copolymer.

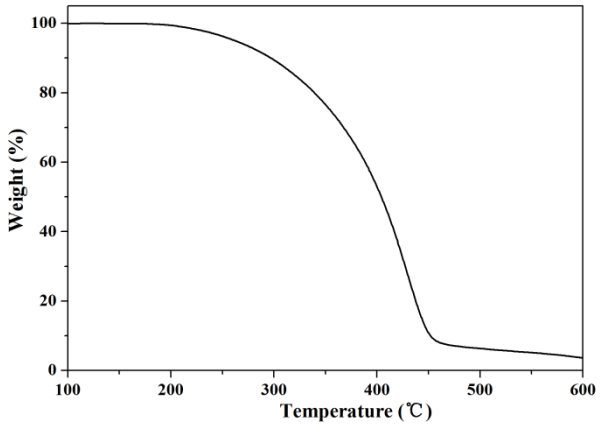


Fig. S3 TGA curve of the PEG-based copolymer.

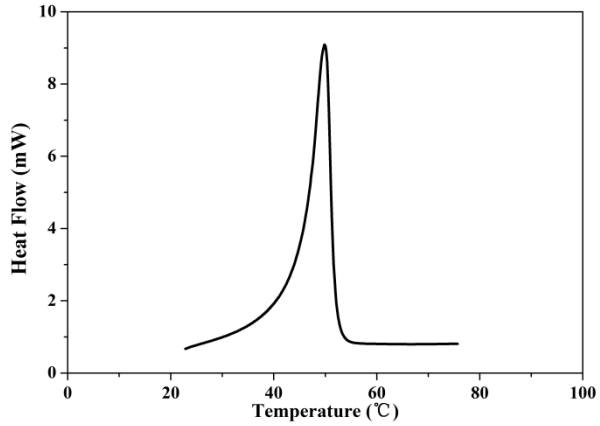


Fig. S4 DSC curve of the PEG-based copolymer.

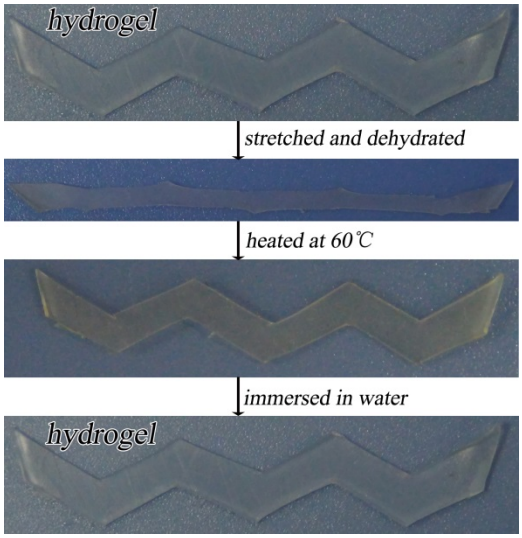


Fig. S5 Thermo-responsive shape-memory behavior of the supramolecular hydrogel.

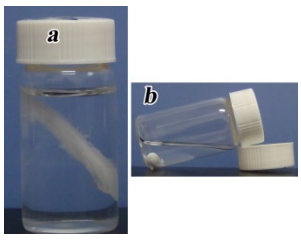


Fig. S6 Photo images of the copolymer after being immersed in water for two months (a) and its methanol solution (b).

Fig. S7 The white cotton like polymer filaments.

References

1. M. Guo, X. Cao, E. W. Meijer, Patricia Y. W. Dankers, *Macromol. Biosci.,* 2013, **13**, 77-83.