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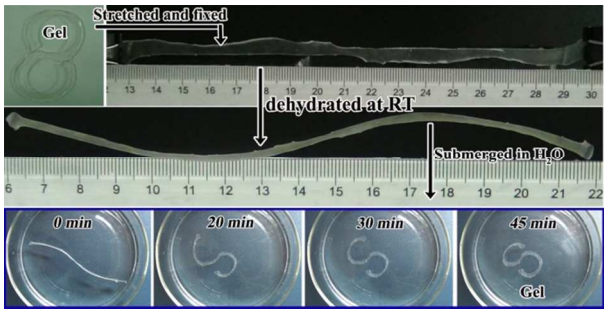
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Stretchable and elastic supramolecular hydrogel with water-responsive shape-memory behavior which can be realized under mild and green conditions was developed.

COMMUNICATION

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

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Strong and highly stretchable supramolecular hydrogel with shear modulus of 200 kPa, elongation at break of 770% at 4 MPa stress and water-responsive shape-memory property is developed. The whole shape-memory procedure including shape deformation, fixing and recovery can be realized under mild and green conditions, i.e. in air and water.

Supramolecular hydrogels are water insoluble but high water containing three-dimensional networks cross-linked by non-covalent interactions, such as hydrogen-bond, hydrophobic interaction, π - π stacking, metal-ligand, electro-static interaction and so on.^{1,2} Due to many of their unique properties such as flexible, high water content, small molecule and large molecule diffusion are very similar to natural tissues, this kind of weak and reversible non-covalent interaction based soft material has tremendously extended our view on new matters with great capacity for processability, recycling, self-healing, stimuli-response etc., and are opening up the prospect of many new applications including subsequently release cargo, actuators and sensors, biomedical device, tissue engineering and regenerative medicine research fields as synthetic biomaterials.³⁻¹⁰ However, due to the inherent weak character of the non-covalent interactions, most reported supramolecular hydrogels are often weak and brittle, just like jelly or past. It is these disadvantages that severely limit their many potential uses as biomaterials.

At the same time, shape-memory polymers (SMPs) are an emerging class of active polymers. They have the capability of changing their shapes from temporary shape to permanent shape upon exposed to an appropriate external stimulus, including heating, light, electricity, magnetic field, solvent and

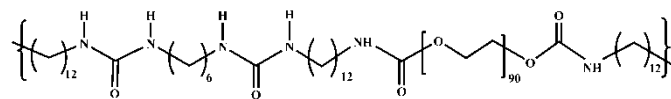
water.¹¹⁻¹³ SMPs have enabled diverse possible biomedical applications such as vascular stents, clot removal micro-actuator, dialysis needles, soft tissue reconstruction, drug carrier and release systems and so on.¹⁴⁻¹⁸ However, only very limited SMPs can really be used in living biological systems, because the external stimulus may damage surrounding tissues and cells,¹⁹⁻²¹ or the activity of the loaded drugs. Additionally, to get the temporary shape, almost all the reported SMPs have to be deformed at high temperature (above the T_g or T_m of the used polymers), which may also cause the above mentioned undesirable effects. Thus, water, the friendliest and most abundant solvent in nature, triggered SMPs may be the most ideal candidate as smart biological materials.

Based on the above mentioned backgrounds, in this report, we describe a novel mechanically strong and stretchable linear multi-block poly(ethylene glycol) (PEG) based supramolecular hydrogel with water-responsive shape-memory property. Here, both the shape deformation (from permanent shape to temporary shape) and shape recovery (from temporary shape to original permanent shape) processes can be realized at room temperature thanks to the elastic character of the obtained hydrogel and the hydrophilic and semi-crystallization behaviour of PEG. Additionally, taking advantages of the dynamic and reversible cross-linking character of the present material, easy processability including solution casting, electro spinning and compression moulding methods can be used for its various possible applications.

It is well known that hydrogen bonds and hydrophobic force play a dominant role in the formation of large biological systems. However, hydrogen-bond, a common driving force for

aggregation in hydrogelator, lose their strength in water unless many are cooperatively combined and protected from solvents, thus hydrophobic forces become most important in aqueous environments.^{1,22,23} Recently, Lafleur and Muley reported that hydrophobic interaction and hydrogen bond can mutually reinforce each other in some biological systems.²⁴ Herein, we attempt to use the cooperative enhancement effect between hydrogen-bond and hydrophobic interaction to construct strong and stretchable supramolecular hydrogel.

As shown in Scheme. 1, the present supramolecular hydrogel is based on a linear PEG (molecular weight = 4000 g/mol) copolymer with many urea unites, which are shielded in a hydrophobic dodecyl ($C_{12}H_{24}$) spacer, in the main chain (detailed synthesis procedure and characterizations including 1H NMR, GPC, TGA and DSC as shown in Scheme. S1 and Fig. S1-S4 can be found in ESI). Here, the hydrophobic spacer was expected to protect the urea moieties from hydrophilic environment and thus to enhance the hydrogen-bond interactions between the urea linkages to give a strong and stretchable supramolecular hydrogel.^{25,26}



Scheme. 1 Chemical structure of the linear PEG-based copolymer.

The equilibrium water swelling ratio of the resultant supramolecular hydrogel is about 285% (Fig. 1a), i.e. the equilibrium water content is about 74 wt %, which is very close to many of human soft tissues, such as skin, cartilage and muscle (~70 wt %). Fig. 1b shows the scanning electron microscope (SEM) image of the cross-section morphology of the freeze-dried fully water swelling supramolecular hydrogel film. Different from the classic hydrogels, the microstructure of the present supramolecular hydrogel is a three-dimensional network with only limited porous structure composed of close-gained thick walls of the copolymer. Thus this thick wall porous structure was expected to be expressed by remarkable mechanical stability and may have profound influence on the mechanical properties.²⁷

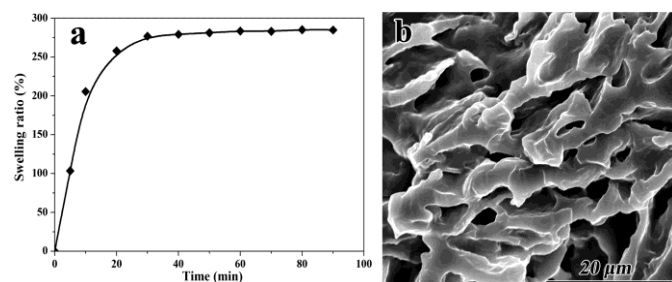


Fig. 1 (a) Time dependent water swelling ratio curve and (b) SEM micrograph showing the cross section of the freeze-dried hydro-gel film.

Fig. 2a shows the plots of storage (G') and loss (G'') modulus as a function of frequency (ω) at a fixed strain, $\gamma = 1\%$, at room temperature. The sample has a single plateau region in its

dynamic moduli. The G' value has a substantial elastic response and is always higher than the G'' over the entire range of frequency. The typical G' value is about 200 kPa, which is much higher than that of many other reported PEG based supramolecular hydrogels (from hundreds to tens of thousands Pa).^{25,26,28,29} At the same time, contrary to most other supramolecular hydrogels that generally show temperature-responsive reversible gel-to-sol transition behaviour. The present supramolecular hydrogel showed high thermal stability by no obvious decrease of the modulus up to temperatures as high as 90 °C, and the G' value is always higher than that of G'' over the entire experimental temperature range (Fig. 2b).

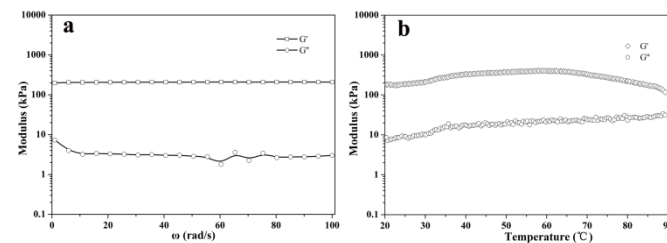


Fig. 2 Frequency dependent (a, at room temperature) and temperature dependent (b) oscillatory rheology measurements of the hydrogel film.

To further investigate the ductility of the present supramolecular hydrogel, tensile test was also conducted. From Fig. 3a one can see that the elongation at break of the present supramolecular hydrogel is about 770%, and the strength at break is 4 MPa, which is higher than many reported classic hydrogels and comparable to previously reported famous high mechanical strength hydrogels, including sliding hydrogel (< 20 kPa),³⁰ double-network hydrogel (< 3.8 MPa),³¹ tetra-PEG hydrogel (< 200 kPa),³² hydrogen-bond and covalent bond cross-linked hydrogel (< 1.8 MPa),³³ and inorganic clay cross-linked nanocomposite hydrogel (< 1 MPa).³⁴ Fig. 3b-c (details can be found in movie S1 in ESI) further indicate the present supramolecular hydrogel's excellent mechanical properties. As shown in Fig. 3b and movie S2 in ESI, the hydrogel film can even withstand 200 g load without breaking, and immediately recovery to its original shape after unloading. At the same time, as shown in movie S3 in ESI, the fully water swelling hydrogel ball fell freely to the bottom of the beaker and then rebounded, behaved just like a Ping-Pong. These indicate that our supramolecular hydrogel also has an excellent elastic property. Of special note, previously, Sijbesma and co-workers reported injectable and self-healing supramolecular hydrogels from PEG-bisurea segmented copolymers with similar chemical structures to ours.²⁹ But the molecular weight of PEG and the hydrophobic spacer they used were 8000 or 20000 g/mol and decyl ($C_{10}H_{20}$) group, respectively. While, what we used here are PEG with molecular weight of 4000 g/mol and dodecyl ($C_{12}H_{24}$) group, respectively. Thus, the shorter hydrophilic PEG chains and the longer hydrophobic spacer should be responsible for the much better mechanical properties of our supramolecular hydrogel, and this is also in accordance with previous reports.^{25,26} This is because hydrogen

bonds will lose their strength in water or hydrophilic environment, and thus hydrophobic interactions play important role in the design of organic hydrogelators.^{1,23}

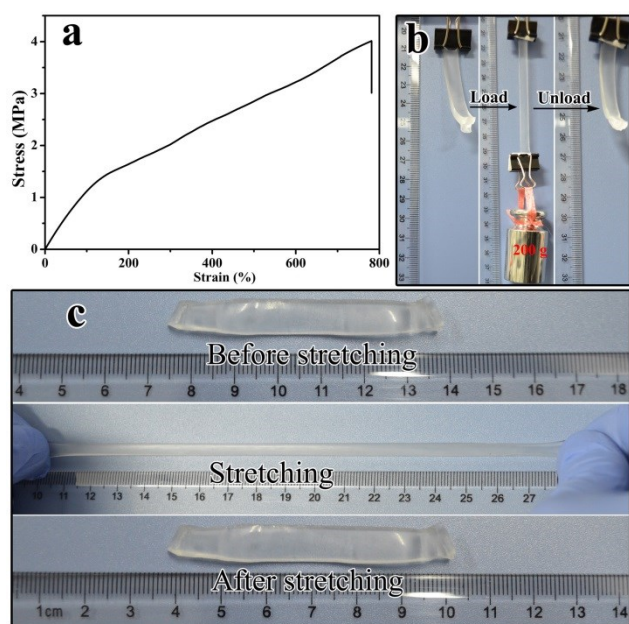


Fig. 3 Tensile test strain-stress curve (a) and digital images (b and c) of the hydrogel films.

On the other hand, crystallization has been widely used in the thermo-responsive shape-memory polymer research field to fix the temporary shape. But there are only limited reports on the water-responsive shape-memory materials using the crystallization transition behavior.^{20,35} Here, wide-angle X-ray (Fig. 4) and DSC (Fig. S4 in ESI) experiments clearly show that the PEG chains form crystalline phase in the dry hydrogel film. While, in the fully water swelling hydrogel film case, no crystalline peaks can be observed due to dissolution of the PEG chains.

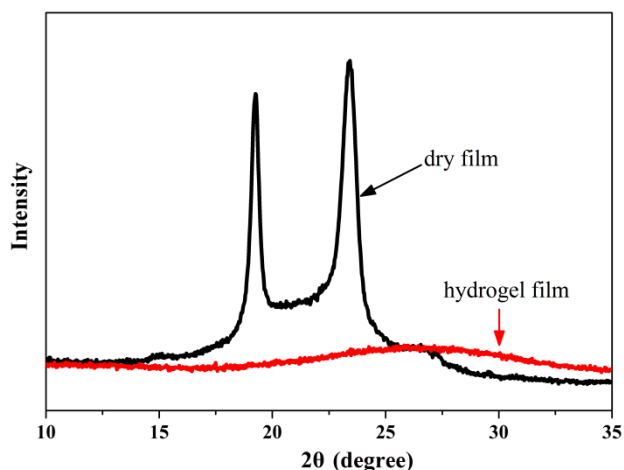


Fig. 4 Wide-angle XRD curves of the dry and hydrogel film.

Thus, taking advantages of the elastic character of the obtained supramolecular hydrogel and the dehydration-hydration

induced crystallization-dissolution transition of PEG chains, both the shape deformation and shape recovery processes were expected to be realized at room temperature in air and water. So that many previously mentioned undesirable effects of shape-memory polymers can be avoided,¹⁹⁻²¹ and may greatly benefit its further use as biomaterials.

As shown in Fig. 5, the permanent “8” shape transparent hydrogel film (Fig. 5a) was first stretched into a straight strip and the strip was then fixed by two clamps (Fig. 5b). After being dehydrated at room temperature in air overnight, an opaque straight temporary shape (Fig. 5c) with almost 100% fixed ratio was obtained due to the crystallization of PEG chains, which fixed the temporary shape. This temporary shape can be kept at room temperature for several months without any shape changing. While, when it was immersed in room temperature water, it can recovery to its original water swelling “8” shape transparent hydrogel within 45 min (Fig. 5d) due to the dissolution of the PEG chains. It is noteworthy that lots of air bubbles aggregated on the surface of the hydrogel film during the water swelling process, thus it looked a little bit opaque (Fig. 5d). Besides, the supramolecular hydrogel also has thermo-responsive shape-memory property. As shown in Fig. S5 in ESI, the stretching and dehydration induced strip temporary shape can recovery to its dehydrated saw tooth shape within 50 seconds (movie S4 in ESI) upon submerging in silicon oil at 60 °C (above the T_m of the PEG segment, ~50 °C, Fig. S4 in ESI). After further swelling in water at room temperature, original saw tooth shape hydrogel was obtained. Note again, here the temporary shape can also be obtained by heating and stretching at 60 °C, followed by cooling to room temperature. And the shape recovery speed for both the water- and thermo-responsive shape recovery processes are greatly dependent on the size/dimension of the sample, the smaller/thinner the faster, which can be adjusted according to different applications. Besides, even faster shape-recovery speed can be realized by the combination of water- and thermo-responsiveness, i.e. immersing in hot water.

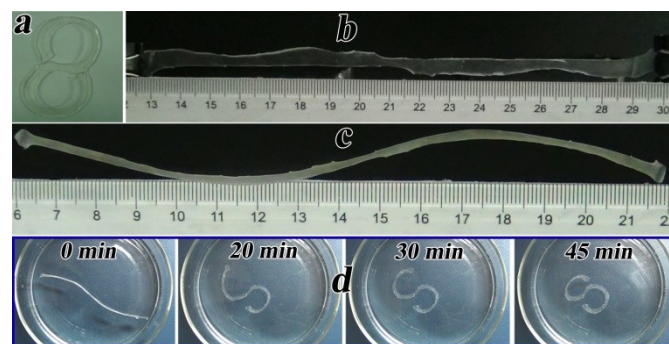


Fig. 5 Photo images showing the water-responsive shape-memory behavior at room temperature. (a) permanent “8” shape hydrogel film, (b) stretched and fixed hydrogel film at room temperature, (c) temporary straight dry hydrogel film after being dehydrated in air at room temperature and (d) water-responsive shape recovery process at room temperature in water.

In addition to the above mentioned good mechanical and shape-memory properties, another advantage of the present material is

its easy processability due to the non-covalent nature. As shown in Fig. S6a in ESI, although the linear copolymer is not soluble in water, it can be dissolved in many organic solvents, including methanol (Fig. S6b in ESI), ethanol, chloroform, dimethylformamide (DMF) etc. Thus films can be easily prepared by solution casting method, and nano-fibres can also be obtained by wet-spinning. For example, as shown in Fig. 6, electro-spun nano-fibres were also obtained by electro-spinning technique from its methanol solution (Fig. S6b in ESI).

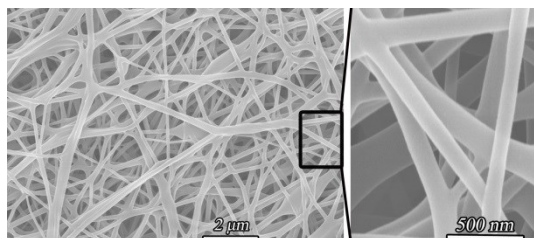


Fig. 6 SEM images of the electro-spun nano-fibres from methanol solution of the copolymer.

Conclusions

In summary, we described a novel type of transparent supramolecular hydrogel with excellent mechanical properties using the cooperative enhancement effect between hydrogen bond and hydrophobic interaction via rational molecular design. The superior mechanical properties of the present supramolecular are suggested to be due to: 1) the hydrophobic dodecyl spacers protect the urea groups from water and the hydrophilic PEG chains and thus increase the strength of the hydrogen-bond due to stabilizing its geometry, and conversely the strong hydrogen-bonds hold the hydrophobic spacers closer and more firmly against the hydrophobic pocket wall; 2) the chain-extension effect can greatly improve the mechanical properties of the hydrogen-bond based supramolecular materials.³⁶ The excellent stretchable property of the present supramolecular hydrogel and the dehydration-hydration induced crystallization-dissolution transition of PEG chains provide it with water-responsive shape-memory property. Besides, in contrast to the chemically cross-linked materials, the non-covalent nature promotes its easy processability, and thus could be made into different forms by various manufacturing methods. This study opens a new, simple and mild avenue to the formation of mechanically strong, stretchable, elastic and transparent supramolecular hydrogels with water-responsive shape-memory behaviour, which can be conducted in air and water at room temperature and will greatly benefit its potential use as an ideal biomaterial.

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Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details and characterizations results, including ¹H NMR, GPC, TGA, DSC, Fig. S1-S7 and movie S1-S4. See DOI: 10.1039/c000000x/

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