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Polyetheramine (PEA): a versatile platform to tailor the properties of hydrogels *via* H-bonding interactions†

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Hydrogels have promising applications in biomaterials and other fields. Here, to extend our previous work, we designed a novel class of PEA-_{P-A}-polyacrylamide (PAAm) hydrogels that contain two cooperative H-bonding interactions: PEO/amide groups and diol/carbonyl groups *via* a versatile platform (PEA). The strong H-bonding between PEA-_{P-A} and PAAm endows the PEA-_{P-A}-PAAm hydrogel with excellent performance (tensile strength is up to 1.15 MPa and elongation at break is up to 1277%). The reversible association and disassociation of the H-bonding impart the PEA-_{P-A}-PAAm hydrogels with pH response and reshaping ability. PEA-_{P-A}-20%-PAAm hydrogels can change the diameter from 4 cm to 2 cm, accompanied by their color change from transparent to white in a pH < 1 solution within 20 minutes. The sample of the PEA-_{P-A}-PAAm hydrogel also can be reshaped into a programmed shape by using the dynamic H-bonding. PEA-_{P-A}-PAAm hydrogels with excellent mechanical properties, fast pH response and reshaping ability could accelerate the practical applications of the hydrogels in many fields.

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Introduction

Hydrogels are being developed at a very fast pace because of their potential applications in biomaterials and other fields.^{1–8} In order to broaden the application field of hydrogels, many methods have been reported to improve the properties of hydrogels, such as double network (DN) hydrogels,^{9–13} nanocomposite (NC) hydrogels,^{14–19} slide ring (SR) hydrogels,^{20–22} poly(ethylene glycol) (PEG) hydrogels,^{23–25} macromolecular microsphere composite (MMC) hydrogels,²⁶ physical crosslinking hydrogels^{27–30} and others.^{31–33} Recently, we reported a novel class of PEA-PAAm hydrogel systems where PEA could be firstly used as a macromolecular co-initiator and crosslinking agent toward PAAm and the mechanical properties have a close relationship with the contents of PEA.³⁴ Furthermore, we introduce the benzophenone (BP) group into PEA *via* a new di-epoxy monomer to build PEA-PAAm hydrogels and this kind of hydrogel could be crosslinked like an elastomer and has a re-

shaping ability *via* photo-crosslinking.³⁵ Therefore, based on these two studies, it is found that PEA could not be only used as an initiator and crosslinking agent but also as a good matrix to attach new functional groups to endow the PEA-PAAm hydrogel with novel properties *via* flexible molecular design of PEA. In this paper, we focused on increasing the H-bonding interaction between PEA and PAAm *via* selecting different di-amine monomers to further improve the tough PEA-PAAm hydrogels.

It is generally known that H-bonding, especially cooperative H-bonding,^{36–38} plays an important role in the construction and stabilization of the secondary and tertiary structures in biosystems, such as DNA duplexes and proteins. Therefore, hydrogen bonding has also been applied in hydrogels to increase their mechanical properties.^{39,40} Recent work by Sheiko *et al.* on weak hydrogen bonding hydrogels has shown a high modulus of 28 MPa, a high rupture strength of 2 MPa and fast strain recovery.^{41,42} Meanwhile, Wang and co-workers reported a series of studies on tough hydrogels that were physically cross-linked by strong cooperative H-bonding.^{43–45} However, it is still a challenge to design hydrogels that combine high tensile strength (>1 MPa), high elongation at break (≈10×), and high elasticity (fast recovery ability under large deformation under ambient conditions).

Inspired by the cooperative H-bonding, we firstly attached the diol group (H-bonding donor) to the chain of PEA-_{P-A} to increase the H-bonding interaction between PEA and PAAm,

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and the diol structure could function as a bridging molecule to connect PAAm chains by forming multiple intermolecular H-bonding with PAAm chains.⁴⁴ In this way, two kinds of H-bonding pairs were introduced into the PEA-PAAm hydrogel system, including the original H-bonding pair from the PEO (H-bonding acceptor, PEA)/amide group (H-bonding donor, PAAm) and an additional new H-bonding pair from the diol group (H-bonding donor, PEA)/carbonyl groups (H-bonding acceptor, PAAm).^{38,46} Therefore, these two H-bonding pairs could be effectively combined together to provide an effective energy-dissipating route toward hydrogels *via* their easy breaking and re-forming, so the mechanical properties of PEA-PAAm hydrogels were greatly improved. Furthermore, since the H-bonding interaction between PEA and PAAm could be increased under acidic conditions (pH < 7) and decreased in an alkaline environment (pH > 7), the PEA-PAAm hydrogel could exhibit good pH response and re-shaping behaviors upon the external stimulus. All in all, high-performance PEA-PAAm hydrogels with pH-response and re-shaping behaviors can be prepared *via* a very simple and feasible method.

Experimental

Materials

Poly(ethylene glycol) diglycidyl ether (PEO-DE, $M_n = 500$) and 3-(dimethylamino)-1-propylamine (DMPA) were obtained from Sigma-Aldrich. 3-Amino-1,2-propanediol, 1-propanamine, acrylamine (AAM), *N,N*-dimethylacrylamide (DMAA), *N,N'*-methylenebis (acrylamide) (BIS), ammonium persulfate (APS), propylene glycol monomethyl ether, and *n*-hexane were purchased from Sinopharm Chemical.

Synthesis of poly(ether amine) (PEA)

PEA was synthesized according to previous reports.^{34,35} 0.02 mol (10 g) PEO-DE and 0.02 mol (1.82 g) 3-amino-1, 2-propanediol were dissolved in 20 mL of propylene glycol monomethyl ether. Under the protection of nitrogen and vigorous stirring, the mixture was refluxed for 24 h at 120 °C. Then, the product was precipitated in *n*-hexane and treated by rotary evaporation at 60 °C. Finally, the product was dried in a vacuum oven overnight. All PEA was synthesized by the same method. PEA was denoted as PEA_{M-N}, where M and N represent the initials of the di-epoxy and di-amine monomer, respectively.

Synthesis of PEA-PAAm hydrogels

The formulae of PEA-PAAm hydrogels are shown in Table S1.† Firstly, all components except for the initiator (APS) were dissolved in deionized water. The solution was stirred and bubbled with nitrogen for 20 min. Then, a specific amount of APS was added at room temperature, and the mixture was immediately degassed for 1 min by using a vacuum pump. Finally, the pre-gel solution was transferred to the mold and polymerized for 24 hours at room temperature. The hydrogels were identified as being PEA-*m*-PAAm hydrogels where *m* is the content of PEA.

Preparation of model compounds

In order to compare the grafting efficiency of N-CH₃ and N-CH₂-, we prepare a series of model compounds. The compositions of model compounds are recorded in Table S2.† The preparation process of model compounds is the same as the preparation of PEA-PAAm hydrogels.

Mechanical tests of PEA-PAAm hydrogels

The tensile tests were performed on a commercial tensile tester (Instron 4465) at a crosshead speed of 100 mm min⁻¹. At least three dumbbell-shaped specimens were used to obtain the stress-strain curves. The linear region at the beginning of the stress-strain curve (10%–30%) was used to calculate the modulus. The loading-unloading properties were analysed on an electromechanical tester (Zwick, Germany) with a crosshead speed of 100 mm min⁻¹. The cylindrical sample with a diameter of 8 mm was used in the loading-unloading test.

Rheological property measurements

Rheological properties were conducted by using a rotational rheometer (MARS 3, Thermo Hakke Corporation). The temperature sweep was conducted in the range of 20–90 °C at a fixed strain of 0.5% and a fixed frequency of 1 Hz.

Swelling test of hydrogels

The swelling ratio (*Q*) of the hydrogels is defined as:

$$Q = (m_s - m_d)/m_d$$

where m_s is the swollen weight and m_d is the dry weight of each sample.

Results and discussion

PEA preparation and H-bonding formation mechanism

Here, we used poly(ethylene glycol) diglycidyl ether (P) as the di-epoxy monomer and selected three kinds of diamine monomers, including 3-(dimethylamino)-1-propylamine (D), 3-amino-1,2-propanediol (A), and 1-propanamine (P). Based on these di-epoxy and diamine monomers, several kinds of PEA (Table 1) were prepared to tailor the H-bonding interaction between PEA and PAAm. There are two different types of PEA-PAAm hydrogels based on the H-bonding interaction. One is the PEA_{P-A}-PAAm hydrogel which has two cooperative H-bonding couples: (i) the PEO chain segment as the H-bond acceptor and the amide group as the H-bond donor, (ii) carbonyl groups on AAm as the H-bond acceptor and the diol group on PEA_{P-A} as the H-bond donor. As shown in Fig. 1a, there are two cooperative H-bonding couples in the PEA_{P-A}-PAAm hydrogel. In the case of a small deformation, stretching results in the dissociation of smaller/weaker H-clusters. When the deformation increases further, larger/stronger H-clusters also dissociated. Meanwhile, the presence of chemical crosslinking (supported by *N,N'*-methylenebis (acrylamide) (BIS)) ensures the full recovery after unloading and mechanical properties. It should be noted that there are also other inter- or intra-molecular

Table 1 The PEA structure and monomer used in different types of hydrogels, and the transparency of the hydrogel

Sample	PEA ^a structure	Monomer	Hydrogel transparency ^b
PEA _{P-A} -PDMAA hydrogel			Transparent
PEA _{P-D} -PAAm hydrogel			Transparent
PEA _{P-P} -PAAm hydrogel			Non-transparent
PEA _{P-A} -PAAm hydrogel			Non-transparent

^a PEA_{M-N}, M and N represent the initials of the di-epoxy and diamine monomer, respectively. ^b Hydrogel transparency is shown in Fig. S1.

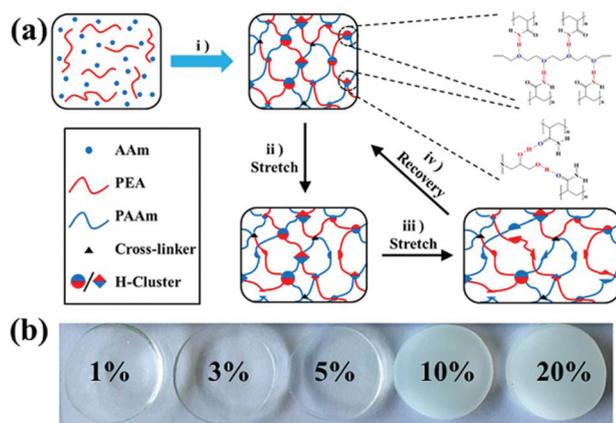


Fig. 1 (a) Structure of the PEA_{P-A}-PAAm hydrogel. Schematic illustration of the hydrogel by the persistent covalent network and reversible H-cluster network with a proposed mechanism of the stretching and recovery processes: (i) polymerization of AAm initiated by APS at room temperature; (ii) stretching results in the dissociation of smaller/weaker H-clusters; (iii) further stretching results in the dissociation of larger/stronger H-clusters; (iv) complete recovery after unloading. (b) Photographs of the polymerization products of the PEA_{P-A}-PAAm hydrogel with different PEA_{P-A} concentrations.

H-bonding interactions, *e.g.* H-bonding between diol groups and that between diol and PEO, as well as those between PAAm chains. Another is in the PEA_{P-P}-PAAm hydrogel and PEA_{P-D}-PAAm hydrogel which have only the PEO chain segment as the H-bond acceptor and the amide group as the H-bond donor. Therefore, PEA_{P-A}-PAAm would be expected to possess the highest mechanical properties due to its two kinds of H-bonding interactions. In order to support our proposal, we firstly prove the importance of the H-bonding pair PEO/amide for hydrogels. We replaced acrylamine (AAm) with

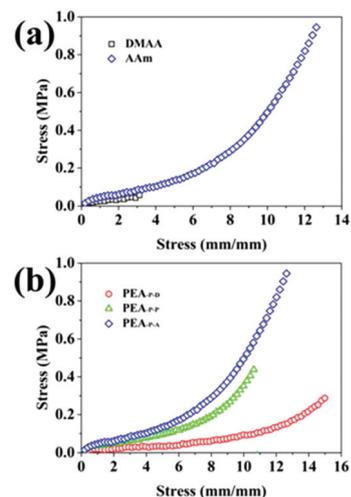


Fig. 2 (a) Tensile stress–strain curves of PEA_{P-A}-10% hydrogels with different monomers, (b) tensile stress–strain curves of PEA-10%-PAAm hydrogels with different PEA structures.

N,N-dimethylacrylamide (DMAA) to prepare the PEA-PDMAA hydrogel. As a result, the tensile strength of the PEA_{P-A}-10%-PDMAA hydrogel only is 60 kPa with 316% elongation at breaking (Fig. 2a). However, the rupture strength of the PEA_{P-A}-10%-PAAm hydrogel is 976 kPa and elongation at breaking is 1275%. This comparison shows that AAm plays an irreplaceable role in the formation of dense H-bonding clusters toward PEO to prepare high-performance hydrogels in our PEA-PAAm hydrogel system. Furthermore, in order to prove the function of the H-bonding couple diol/carbonyl groups in building a tough hydrogel, we also prepare PEA_{P-P}-10%-PAAm and PEA_{P-D}-10%-PAAm hydrogels without having the diol group. It is found that the mechanical properties of the PEA_{P-P}-10%-PAAm hydrogel (tensile strength 466 kPa, elongation at break 1079%) and PEA_{P-D}-10%-PAAm (tensile strength 306 kPa, elongation at break 1499%) are also inferior to the PEA_{P-A}-10%-PAAm hydrogel (Fig. 2b). This indicates that H-bonding between the diol group and PAAm could function as an important bridge linkage to connect different PAAm chains and PEA to increase its mechanical properties.⁴⁴ On intensive comparison of these three hydrogels (Table 1), we found that N-CH₂- seems much more efficient at making the hydrogel stronger than N-CH₃. It is generally known that N-CH₃ and APS can make up a much more effective redox initiation system than N-CH₂-.^{47,48} In order to demonstrate the different roles of N-CH₃ and N-CH₂- in hydrogels, we designed a set of model compounds (Table S2[†]). When the same volume (3 ml) model compound was dropped into methanol after polymerization, PEA_{P-P}-PAAm and PEA_{P-A}-PAAm model compounds immediately produced a large amount of precipitation while the PEA_{P-D}-PAAm model compound remained a homogeneous solution (Fig. 3b). This indicates that there is a large number of homopolymers of PAAm in PEA_{P-P}-PAAm and PEA_{P-A}-PAAm model compounds (methanol is a precipitating agent for PAAm). However, for PEA_{P-D}, homogeneous solution indicated that PAAm was grafted onto

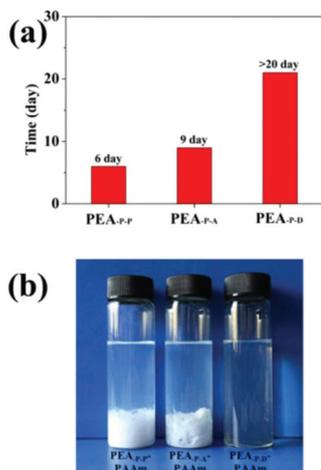


Fig. 3 (a) The time for complete dissolution of the PEA_{p-p}-5%-PAAm hydrogel, PEA_{p-A}-5%-PAAm hydrogel and PEA_{p-D}-5%-PAAm hydrogel without BIS in 5 mol L⁻¹ urea solution, (b) comparison of the precipitation of model compounds (PEA_{p-p}-PAAm, PEA_{p-A}-PAAm and PEA_{p-D}-PAAm) in methanol.

the PEA_{p-D} *via* the N-CH₃ of PEA_{p-D} to improve its solubility in methanol. In order to support the fact that N-CH₃ can act as an anchor to graft the PAAm onto PEA, we further immersed the PEA_{p-p}-5%-PAAm hydrogel, PEA_{p-A}-5%-PAAm hydrogel and PEA_{p-D}-5%-PAAm hydrogel without *N,N'*-methylenebis (acrylamide) (BIS) in 5 mol L⁻¹ urea solutions. The PEA_{p-p}-5%-PAAm hydrogel and PEA_{p-A}-5%-PAAm hydrogel were completely soluble in urea solutions at day 6 and day 9, respectively, due to the absence of the covalent crosslinking point. In contrast, the PEA_{p-D}-5%-PAAm hydrogel does not completely dissolve even after 20 days. The different solubility shows that the PEA_{p-D}-5%-PAAm hydrogel has a low crosslinking degree and this crosslinked structure could come from the coupling termination of the PAAm free radical grafted from PEA_{p-D}. Therefore, the steric hindrance of the grafted PAAm would hinder the formation of dense cooperative H-bonding, which finally embodied the negative effects on the strength of the hydrogel.⁴⁴ It needs to be emphasized that N-CH₂- could activate APS to initiate AAm polymerization at room temperature, although N-CH₂- could not form a large number of grafted products like N-CH₃. In Fig. S2,[†] the PEA_{p-A}-10%-PAAm hydrogel and PEA_{p-D}-10%-PAAm hydrogel can gel at room temperature within 2 hours. However, single APS cannot initiate the polymerization of AAm within 12 hours. Thus, based on the above analyses, we found that the combination of PEO, diol group and N-CH₂- contributed to the high strength of PEA_{p-A}-PAAm hydrogels.

Mechanical properties of the PEA_{p-A}-PAAm hydrogel

The mechanical properties of the PEA_{p-A}-PAAm hydrogels were further investigated in detail. Fig. 4a shows the tensile stress-strain curves of PEA_{p-A}-PAAm hydrogels at different contents of PEA_{p-A} and the specific data of elongation at break, tensile strength and tensile modulus are summarized in Fig. 4b-d,

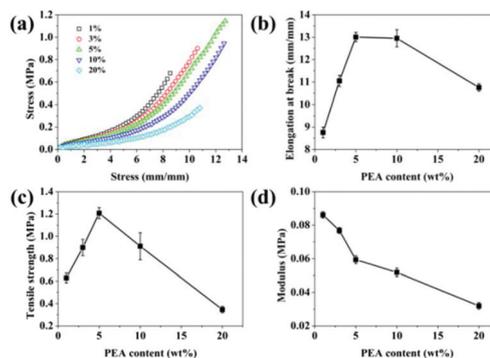


Fig. 4 (a) Tensile stress-strain curves of PEA_{p-A}-PAAm hydrogels with different contents of PEA_{p-A}, (b) elongation at break, (c) tensile strength, and (d) tensile modulus of PEA_{p-A}-PAAm hydrogels at different contents of PEA_{p-A}.

respectively. It is found that the tensile strength and elongation at break obviously increased with increasing PEA_{p-A} content until 5% and then decreased. The PEA_{p-A}-5%-PAAm hydrogels possess 1.15 MPa tensile strength and 1277% elongation at break. The strong H-bonding between PEA_{p-A} and PAAm endows the PEA_{p-A}-5%-PAAm hydrogels with high tensile strengths and elongations. Further increasing content of PEA could make the hydrogel much softer. For example, the strength of PEA_{p-A}-20%-PAAm hydrogels only is 367 kPa with 1080% elongation at break. Such phenomena could also be closely related to one factor that PEA_{p-A} is a honey-like liquid polymer with low strength. At the low content of PEA_{p-A} below 5%, H-bonding between PEA and PAAm could contribute much more to the increasing strength. However, this reinforcement effect *via* increasing H-bonding densities was gradually counteracted by further increasing this soft liquid polymer (PEA). Therefore, the tensile strength and elongation decrease above 5% content.

In addition to its high strength, the PEA_{p-A}-PAAm hydrogel also shows very good elasticity. The recovery of hydrogels is characterized by loading-unloading tests. In Fig. 5a, the residual deformation of all hydrogels is less than 35% at 300% strains, regardless of the content of PEA_{p-A}. Meanwhile, we test PEA_{p-A}-10%-PAAm hydrogels by cycling tensile tests at different strains (Fig. 5b). Even in the case of large strain (500%), the residual deformation of the PEA_{p-A}-10%-PAAm hydrogel is only 54%. The hydrogel's elasticity is based on its H-bonding which is easy breaking and re-forming. At the same time, the PEA_{p-A}-10%-PAAm hydrogel has good fatigue resistance. As shown in Fig. S3,[†] after three consecutive loading-unloading cycles, the residual deformation remains almost constant. In general, hydrogels with good elasticity and fatigue-resistance can be fabricated in the presence of PEA_{p-A}.

pH response induced shape memory behavior and reshaping ability

As discussed above, the PEA_{p-A}-PAAm hydrogel is a typical dual network structure: persistent network (sponsored by the

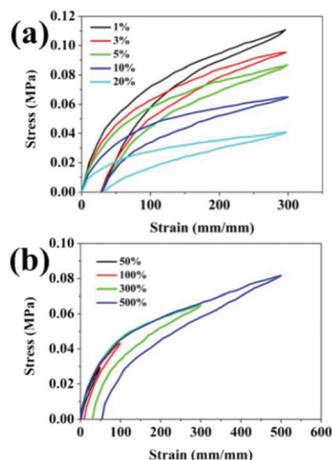


Fig. 5 (a) Loading–unloading curves of PEA_{P-A}-PAAm hydrogels with different contents of PEA_{P-A} at 300% strain, and (b) loading–unloading curves of PEA_{P-A}-10%-PAAm hydrogels at different strain values.

covalent crosslinking point *via* BIS) and reversible network (supported by H-bonding between PEA and PAAm). When we soak the PEA_{P-A}-PAAm hydrogel in water and sodium hydroxide solution (which are typical hydrogen bond breaking agents),^{45,49} the volume of the PEA_{P-A}-PAAm hydrogel in alkali is obviously larger than the volume in water and the PEA_{P-A}-PAAm hydrogels became transparent and mechanically weak because of the damage of the H-bonding network (Fig. 6a). Furthermore, we could also observe that increasing the content of PEA_{P-A} could make the hydrogel gradually transfer from transparent (below 5%) to opaque (above 10%) (Fig. 1b), which is closely related to the increasing amount of cooperative H-bonding. It is interesting that the transparency of the PEA_{P-A}-10%-PAAm hydrogel increased when heating it up: the higher the temperature, the greater the transparency (Fig. 6c). For example, the transparency of PEA_{P-A}-10%-PAAm hydrogels

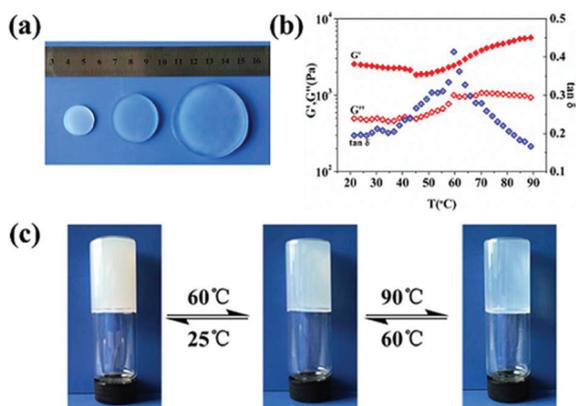


Fig. 6 (a) Photographs of PEA_{P-A}-10%-PAAm hydrogels before (left) and after dissolving in deionized water (middle) and sodium hydroxide solution (right) after one month, (b) dynamic rheology of PEA_{P-A}-10%-PAAm hydrogels under variable temperature conditions, (c) photographs of PEA_{P-A}-10%-PAAm hydrogels at different temperatures.

at 90 °C is improved compared with that at 60 °C. In turn, the PEA_{P-A}-10%-PAAm hydrogel can restore to its original state as the temperature is cooled down to room temperature. This is consistent with the truth that H-bonding is reversible and can be damaged by thermal treatment.⁴⁴ The dynamic mechanical properties of the PEA_{P-A}-10%-PAAm hydrogel were measured under variable temperature conditions to further investigate its H-bonding interaction. In Fig. 6b, G' is greater than G'' in all temperature range, indicating the elastic nature of the PEA_{P-A}-10%-PAAm hydrogel.^{50,51} The loss factor ($\tan \delta$) increased with the increase of temperature until 60 °C then decreased, which is related to the simultaneous breakage and formation of H-bonding. In the lower temperature stage (<50 °C), H-bonding is very stable (that is, the formation rate of H-bonding is larger than the breakage rate). As the temperature rises further (50–70 °C), the breakage rate of H-bonding is increased to be comparable to the formation rate of H-bonding. The dynamic breakage/re-formation behaviors make the internal friction force increase as reflected in the increase of $\tan \delta$. When the temperature is above 70 °C, the damage rate of H-bonding is far greater than the formation rate which makes the loss factor decrease. This analysis of dynamic H-bonding is in agreement with the dynamic rheology test results shown in Fig. 6b.

Since H-bonding between PEA_{P-A} and PAAm is also closely related to pH, it is necessary to observe the pH response of PEA_{P-A}-PAAm hydrogels. In pH > 13 solution, the hydrogel is swollen and becomes transparent and soft due to the breaking of H-bonding. When the hydrogel is placed in an acid solution, the hydrogel becomes opaque and the volume obviously shrinks because of the reformation of the H-bonding. It is also found that the increase of PEA_{P-A} content could speed up the response rate of PEA_{P-A}-PAAm hydrogels. In Fig. S4,† both the size and color of PEA_{P-A}-20%-PAAm hydrogels exhibit the fastest transformation. As shown in Fig. 7 and Fig. S5,† PEA_{P-A}-20%-PAAm hydrogels, which were immersed in 1 mol L⁻¹ sodium hydroxide solution for 24 hours in advance, showed a very fast response rate in pH < 1 hydrochloric acid water solution. After ten seconds, the surface of the hydrogel has begun to turn white. One minute later, the hydrogel surface has all turned white and the volume has begun to shrink. After 20 minutes, the diameter of the sample was changed from 4 cm to 2 cm, and the sample diameter remained almost unchanged for an extended time to 24 hours. In turn, when the above hydrogel (soaked in pH < 1 hydrochloric acid solution for 24 hours) is immersed in 1 mol L⁻¹ sodium hydroxide solution, the PEA_{P-A}-20%-PAAm hydrogel gradually became transparent and the diameter restored from 2 cm to 4 cm in 24 hours. The equilibrium swelling ratio of the PEA_{P-A}-20%-PAAm hydrogels is 1.27 in pH < 1 solutions and 32.50 in pH > 13 solutions (Fig. S5†). Importantly, the above cycle can be repeated several times (>10). Therefore, the PEA_{P-A}-20%-PAAm hydrogel shows good shape memory behavior between acid and alkaline conditions. Furthermore, the damage and re-formation of H-bonding endow the PEA-PAAm hydrogel with reshaping ability. As shown in Fig. 8, the

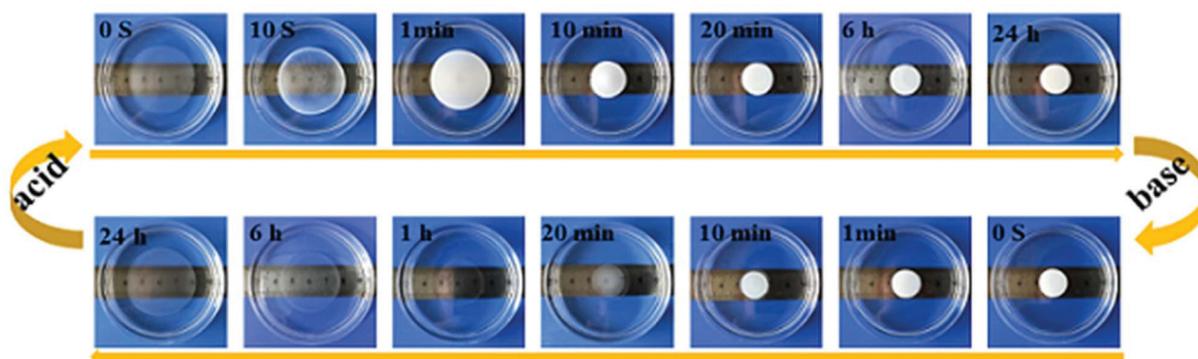


Fig. 7 The size and color change of PEA_{P-A}-20%-PAAm hydrogels at different times in hydrochloric acid and sodium hydroxide aqueous solution.

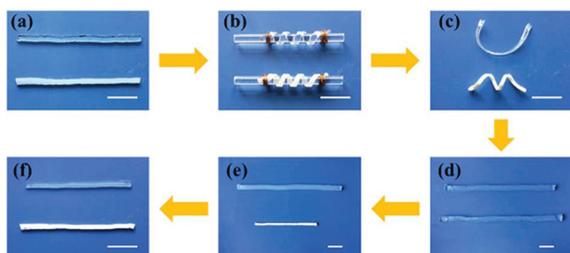


Fig. 8 Reshaping process of the PAAm hydrogel (up) and PEA_{P-A}-20%-PAAm hydrogel (down). (a) The original as-prepared hydrogel strips, (b) hydrogels were twisted into a helix for 6 hours at 80 °C in pH < 1 water, then the shape was fixed by cooling them to 5 °C for 12 hours, (c) the deformed hydrogel strips, (d) the hydrogel shape after being immersed in pH > 13 water for 24 hours, (e) the hydrogel shape after being immersed in pH < 1 water for 20 minutes, (f) the hydrogel sample with recovered shape after being immersed in pH < 1 water for 24 hours (scale bar: 2 cm).

PEA_{P-A}-20%-PAAm hydrogel sample with an original straight strip was twisted into a helix for 6 hours at 80 °C in pH < 1 water, and then the shape was fixed at 5 °C for 12 hours (Fig. 8c). In contrast, the PAAm hydrogel did not possess the ability to reshape due to the absence of cooperative H-bonding in the PAAm hydrogel. It is worth noting that the fixed shape of the PEA-PAAm hydrogel can recover its initial shape upon two subsequent soaking procedures. After firstly putting the deformed hydrogel in pH > 13 water for 24 hours, we could obtain the sample with a bigger size. When the deformed sample was subsequently immersed in pH < 1 water, the shape of the PEA_{P-A}-20%-PAAm hydrogel almost recovered to its original size in 20 min. Therefore, PEA-PAAm hydrogels can be reshaped into a programmed shape and its initial shape can be restored based on tailoring its H-bonding interaction between PEA and PAAm at different pH values.

Conclusions

In summary, we have designed a kind of PEA_{P-A}-PAAm hydrogel composed of two H-bonding couples (PEO/amide groups

and diol/carbonyl groups) to achieve a great combination of high strength (1.15 MPa), high elongation at break (1277%) and good elasticity through a facile method. The cooperative H-bonding between PEA_{P-A} and PAAm endows PEA_{P-A}-PAAm hydrogels with excellent mechanical properties. Meanwhile, fast pH response based on H-bonding provides PEA_{P-A}-PAAm hydrogels with shape memory behavior at different pH values and good reshaping ability. We believe that PEA_{P-A}-PAAm hydrogels with excellent mechanical properties, pH response and reshaping ability could facilitate the practical applications of hydrogels in many fields.

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