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Inspired by elastomers: fabrication of hydrogels with tunable properties and re-shaping ability *via* photo-crosslinking at a macromolecular level†

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Conventional hydrogels cross-linked by small molecular cross-linkers usually exhibit poor mechanical properties, limiting the application of hydrogels to a certain degree. Here, inspired by the fabrication technologies of elastomers, we firstly fabricate a macromolecular hydrogel pre-polymer (MHP) *via* thermal polymerization and then crosslink the MHP at a macromolecular level by UV irradiation. In this novel technology, polyetheramine (PEA) plays an important role in the fabrication of crosslinked hydrogels. In the thermal polymerization stage, N-CH₃ units in PEA acted as co-initiators and grafting agents to form an MHP. Under the UV irradiation, benzophenone (BP) moieties in PEA could be excited as photo-cross-linkers. More importantly, the tensile stress of PEA5%-PAAm hydrogel could be effectively tailored from 180 kPa to 500 kPa by controlling the crosslinking degree under different irradiation times. Through this important characteristic, we could also effectively build a hydrogel with a complex three dimensional (3D) geometry, which is not easily obtained by conventional polymerization methods.

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Introduction

Hydrogels, a kind of three-dimensional (3D) polymeric networks, can contain a large amount of water while maintaining their own shape.^{1–3} These materials have a very wide range of applications, such as drug delivery systems,^{4–8} scaffolds for tissue engineering,^{9–11} sensors and actuators,¹² *etc.* Conventional hydrogels crosslinked by small molecules (the most typical representative is *N,N*-methylenebisacrylamide (BIS)) usually exhibit poor properties, which seriously limit the scope of hydrogel applications.¹³ Regarding mechanical properties, hydrogels usually fall into two extremes.^{14,15} If the crosslinking degree of the hydrogel is very low, they tend to be soft and weak with low recovery. In contrast, highly cross-linked hydrogels are usually stiff and brittle due to low efficiency of load transfer. In order to improve the properties of hydrogels, the introduction of an effective energy dissipation mechanism and the preparation of a homogeneous

network structure in the hydrogel are two major methods,^{16,17} which spawned many strategies to enhance the mechanical properties of hydrogels. For instance, double network (DN) hydrogels,^{16,18–21} nanocomposite (NC) hydrogels,^{12,22–26} slide ring (SR) hydrogels,^{27–29} poly(ethylene glycol) (PEG) hydrogels,^{30–32} macromolecular microsphere composite (MMC) hydrogels,³³ *etc.* DN hydrogels are composed of two different networks; the rigid and brittle network plays the role of sacrificial bonds to effectively dissipate energy and the soft and supple network maintains the hydrogel's integrity when the deformation occurs.¹⁸ NC hydrogels were synthesized by using exfoliated nanoparticles (such as clays, carbon nanotubes, graphene, *etc.*) as crosslinking points to effectively improve the mechanical properties of the hydrogels. These two methods can be considered as the typical application of an energy dissipation mechanism in hydrogels. In addition, there are many other types of hydrogels based on physical crosslinks that are effective in dissipating energy, such as polyampholyte hydrogels,^{34,35} dipole–dipole and hydrogen bonding interaction reinforced (DHIR) hydrogels,³⁶ host–guest interaction hydrogels,³⁷ ion interaction hydrogels,^{17,38,39} and others.^{40–42} However, for DN hydrogels, the multi-step polymerization process is time-consuming and tedious. Additionally, due to the need for a swelling and diffusion process, the exact molar ratio of the DN hydrogel is not easy to determine. For NC hydrogels, aggregation of nanoparticles usually hinders the enhancement of properties,⁴³ and the introduction of nano-

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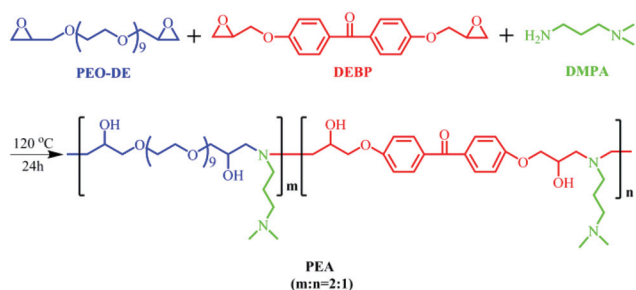
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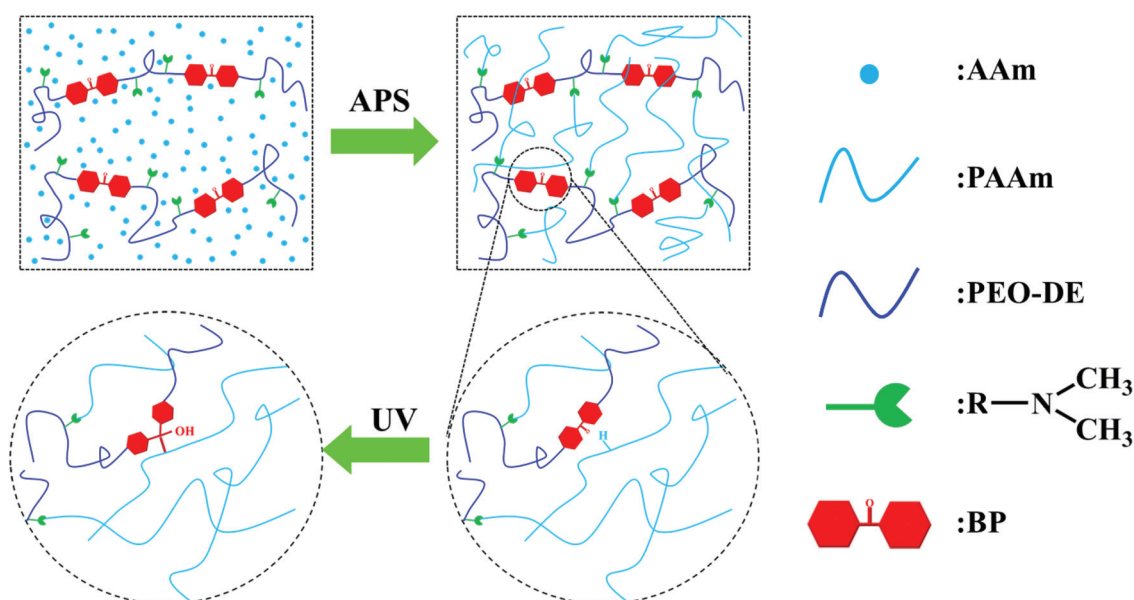
particles often leads to transparency problems. SR hydrogels (a hydrogel with sliding crosslinking points), MMC hydrogels (a hydrogel with macromolecular microsphere as both initiator and crosslinker) and PEG hydrogels (a hydrogel from tetrahedron-like macromonomers) exhibit high mechanical properties without fracture, which are attributed to their homogeneous network structures. Nevertheless, the applications of SR hydrogels, MMC hydrogels and PEG hydrogels are limited by finite components, insufficient functionalities and a complex synthetic process. In our previous study, we found that polyetheramine (PEA) containing N-CH₃ units can be used as both the co-initiator and cross-linker for the synthesis of PEA-PAAm hydrogels and just low content of PEA can significantly improve the mechanical properties of the hydrogel.⁴⁴ However, since the crosslinking point mainly comes from the coupling termination of a polyacrylamide free radical, only a low crosslinking degree could be obtained, which is detrimental to its application. Such a shortcoming would also push us to design new routes to increase the crosslinking degree. All in all, the preparation of hydrogels with high performance still

remains an extremely challenging task. In the meantime, we also noticed that the properties of hydrogels are very similar to elastomers with high elasticity and toughness. However, the fabrication of elastomers is quite different from hydrogels. For the fabrication of elastomers, usually a macromolecular pre-polymer was firstly synthesized, and then the network was built at the macromolecular scale with the presence of a cross-linking agent.⁴⁵ In this way, we could fabricate an elastomer with good mechanical properties. Therefore, whether the fabrication method of elastomers could be applied to the synthesis of hydrogels to improve its mechanical properties is considered.

Herein, inspired by the fabrication technologies of elastomers, we present a simple, novel, one-pot method for the synthesis of hydrogels that could realize the crosslinking reaction at a macromolecular level. We firstly polymerize a mixture of PEA and acrylamide (AAm) to prepare an active macromolecular hydrogel pre-polymer (MHP) and then place this sample under UV irradiation to perform the crosslinking reaction at a macromolecular level. Our design is dependent on the wide range of molecular design of PEA, where N-CH₃ units and benzophenone (BP) moieties could be easily incorporated into the structure of PEA and these two functional groups could play their important roles in the thermal polymerization and photo-crosslinking reaction (Schemes 1 and 2). N-CH₃ units could act as co-initiators and grafting sites for the growth of PAAm in the thermal polymerization to form the PEA-graft-PAAm MHP. BP could act as photo-cross-linkers in the subsequent photo-crosslinking reaction to realize the formation of crosslinked network at the macromolecular level. For hydrogels by photo-crosslinking, reaction conditions are mild and facile in the reaction process. In addition, adjusting the irradiation time and the exposure area can achieve the purpose



Scheme 1 The process for synthesis of PEA.



Scheme 2 Schematic models of the preparation process of PEA-PAAm hydrogels.

of controlling the reaction degree.⁴⁶ Therefore, many photo-cross-linkers such as benzophenone,^{47–49} cinnamoyl groups,⁴⁶ or phenyl azide⁵⁰ can be used to prepare hydrogels. Among these chromophores, BP is a photoactive group that has been widely studied owing to its good chemical stability, low cost, and high photochemical activity toward unreactive C–H bonds even in an aqueous environment.⁵¹ These two groups play their roles independently and do not affect each other in the thermal polymerization and photo-crosslinked reactions. All processes can be accomplished by the one-pot method which is simple and mild. Since the crosslinking degree of PEA-PAAm hydrogels induced by BP is closely related to irradiation time, we can control the irradiation time to prepare PEA-PAAm hydrogels with tunable properties. What's more, this type of hydrogel could be re-shaped into very complex and intricate three-dimensional (3D) geometries, which is not easily obtained by conventional polymerization methods.

Experimental

Materials

Poly(ethylene glycol)diglycidyl ether (PEO-DE, $M_n = 500$), and 3-(dimethylamino)-1-propylamine (DMPA, 98%) were purchased from Sigma-Aldrich. 4,4'-Dihydroxybenzophenone (DHBP), N,N,N',N' -tetramethylethylenediamine (TEMED, 99%), epichlorohydrin, K_2CO_3 , 2-butanone, acrylamine (AAm), N,N' -methylenebis(acrylamide) (BIS), ammonium persulfate (APS), propylene glycol monomethyl ether, and n -hexane were obtained from Sinopharm Chemical. All chemicals were used as received, and deionized water was used in all experiments.

Synthesis of 4,4-di(2,3-epoxypropyloxy)benzophenone (DEBP). 10.7 g (0.05 mol) DHBP, 46.3 g (0.5 mol) epichlorohydrin, and 27.6 g (0.2 mol) K_2CO_3 were added to 2-butanone (400 ml). The mixture was refluxed for 24 h in a N_2 atmosphere. Then, the reaction mixture was filtered to remove K_2CO_3 . After that, the filtrate was treated by rotary evaporation. Finally, the product was recrystallized in alcohol and dried in a vacuum oven. 1H NMR spectra of DHBP and DEBP are shown in Fig. S1.†

Synthesis of poly(ether amine) (PEA). 3.26 g (0.01 mol) DEBP, 10.0 g (0.02 mol) PEO-DE, and 3.06 g (0.03 mol) DMPA were dissolved in 20 mL propylene glycol monomethyl ether in a two-necked flask equipped with a reflux condenser and a nitrogen inlet tube. Under the protection of nitrogen, the mixture was heated to 120 °C for 24 h. Then the solution was dropped into 10-fold n -hexane. After removing the supernatant, the product was processed by reduced pressure distillation at 80 °C. The final product was collected and dried under vacuum at 40 °C overnight.

Synthesis of PEA-PAAm hydrogels. 10 g AAm and different amounts of PEA (50 mg, 100 mg, 300 mg and 500 mg) were dissolved in water for the fabrication of MHP containing 0.5, 1, 3 and 5 wt% PEA based on the weight of the AAm, respectively. The solution was bubbled with N_2 gas for 30 min to remove the dissolved oxygen. Then 0.01 g APS were added at room

temperature. (The water content is 70% in all hydrogels.) The system was deaerated under reduced pressure to remove the excess gas. Next, the solution was poured into a mold having two glass plates with a thickness of 2 mm separated by a silicone rubber spacer. Polymerization was carried out for 24 h at room temperature. The hydrogels were identified as being PEA n -PAAm hydrogels where n is the mass fraction of PEA against the AAm monomer. TEMED and TEMED–BIS hydrogels were also prepared according to the above method. All of the compositions of the reactants for the synthesis of the hydrogels are listed in Table S1.† The PEA n -PAAm MHP was exposed to 365 nm ultraviolet irradiation to make it crosslink. The hydrogels were identified as being PEA n -PAAm- m hydrogels where m is the UV irradiation time.

Preparation of model compounds

Due to PEA n -PAAm MHP being a solid-like object, it is not convenient to carry out the characterization of the NMR, UV-vis spectra and so on. The preparation method of the model compounds is the same as the synthesis of polyacrylamide hydrogels except for having 90 wt% water and a different dosage ratio of the reactants. After polymerization, the model compound is still liquid. The formulas of model compounds are shown in Table S2.†

Instruments and characterization methods

Mechanical tests of PEA-PAAm hydrogels. The tensile test was carried out with a commercial tensile tester (Instron 4465) with a 2000-N load cell, a crosshead speed of 100 mm min⁻¹, temperature of 25 °C, and an initial gauge length of 40 mm. The samples were formed in a glass mould with a thickness of 2 mm. Then, the PEA-PAAm hydrogels were tailored into standard dumbbell shaped samples to test the stress–strain curves. The modulus was calculated on the basis of the slope of the initial linear region of the stress–strain curve (strain between 10–30%). Samples of each formula were tested on at least three specimens. The instrument was also used to perform the compression test with a crosshead speed of 5 mm min⁻¹ (the cylinder-shaped hydrogels were 15 mm in diameter and 25 mm in height). Loading–unloading properties were tested with an electromechanical tester (Zwick, Germany) with a crosshead speed of 100 mm min⁻¹ at 25 °C (the cylindrical samples were 8.44 mm in diameter and 10 cm in length).

Rheological property measurements

Rheological properties were determined by using a TA ARES-G2 rheometer using parallel plates of diameter 20 mm at 25 °C. The gap between the two parallel plates was set at 1.8 mm. The frequency sweep was conducted over the frequency range of 0.05–100 rad s⁻¹ at a fixed strain of 0.5%.

Equilibrium swelling ratio of hydrogels

The equilibrium swelling ratio (Q) of the hydrogels was gauged at room temperature using a weighing method. The hydrogel was first fully swollen in DI water. Then, we take out the hydrogel from water, gently beat the surface with filter paper and

immediately weigh it on an electronic balance. Afterwards, the hydrogels are fully dried in a vacuum oven at 70 °C. The Q 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.

Scanning electron microscope (SEM) analysis

The microstructure of the PEA-PAAm hydrogel before and after UV irradiation was measured by using a Field Emission Scanning Electron Microscope (Nova NanoSEM 450, FEI Company, USA) at an accelerated electron energy of 10 kV. Swollen hydrogels were rapidly frozen in liquid nitrogen for 10 min and dried for two days in a vacuum freeze dryer.

Nuclear magnetic resonance (NMR)

All NMR experiments are carried out in a Varian MERCURYplus 400 spectrometer (400 MHz, Inc., USA). DHBP and DEBP were dissolved in DMSO- d_6 , PEA was dissolved in $CDCl_3$. For model compounds, they were firstly precipitated in methanol, then the supernatant liquid was entirely dried at 60 °C and dissolved in $CDCl_3$.

UV-vis absorption spectra

UV-vis absorption spectra of model compounds were recorded on a Shimadzu UV-2550 spectrophotometer. Firstly, 0.15 ml model compounds under different UV irradiation times were diluted in 30 ml DI H_2O and then 4 ml solution were used to measure the UV-vis absorption spectra.

Results and discussion

Synthesis and characterization of PEA

The PEA was synthesized by PEO-DE and DEBP as a difunctional epoxy monomer and DMPA as a diamine at 120 °C for 24 h (Scheme 1). The synthesized product was characterized by 1H NMR (Fig. 1a). As shown in Fig. 1a, the peak (a) at 2.25 ppm is attributed to the signal related to the hydrogen of the N- CH_3 , the peak (b) at 3.66 ppm is assigned to the proton of the two methylenes of PEO-DE, and the peaks (c) and (d) at

7.00 ppm and 7.75 ppm belong to the hydrogen of the benzene ring from BP. The integral area ratio of peaks a, b and c is about 18 : 72 : 4, which is consistent with the molar ratio of the raw reactants. Therefore, we can confirm that PEA has been successfully synthesized and BP and N- CH_3 moieties, two important functional groups, have been incorporated into the PEA chain. More importantly, good water solubility of this kind of PEA is important for them to be used as a co-initiator and crosslinking agent in the fabrication of hydrogels.

Fabrication of PEA-PAAm hydrogels

We firstly synthesize PEA-graft-PAAm MHP by thermal polymerization. In this stage, N- CH_3 in PEA can form a redox initiation system with peroxydisulfate (APS) to form two kinds of radicals: N- $CH_2\cdot$ and $HO_3SO\cdot$ during the thermal polymerization.^{52,53} In order to support this proposal, we design a kind of model reaction (Table S2†) involving AAm, PEA and two different amounts of APS (0.5, 1 wt%) and NMR measurements were conducted to monitor the content of N- CH_3 in the PEA before and after the model reaction. As shown in Fig. 1a, the intensity (or the integral area) of peak (a) that is related to N- CH_3 sharply decreased on increasing the dosage of APS. This strongly suggests that the N- CH_3 /APS can interact to form a redox initiation system and AAm can graft from N- CH_3 . In this way, PEA-graft-PAAm MHPs (denoted as PEA n -PAAm-0 min hydrogel) were prepared in this stage. After the thermal polymerization, the MHPs containing the BP group were exposed to UV light (365 nm, 5 mW cm^{-2}). Under UV irradiation, the BP groups in the PEA were excited, and induced to abstract hydrogens from the adjacent alkyl chain of the hydrogels, which resulted in the generation of ketyl and aliphatic radicals.^{47,54–56} Radical recombination could yield cross-links in PEA-PAAm hydrogels.^{47–49} We also monitor the content of BP in model compounds (Table S2†) which has a similar structure to the PEA-PAAm hydrogel by UV-vis spectra before and after UV exposure. As depicted in Fig. 1b, with increasing irradiation time up to 240 min, the $n-\pi^*$ absorption peak of BP at 290 nm decays greatly but still exists, which indicates that more and more BP groups were involved in the cross-linking reaction within 240 min. In the meantime, the color of both model compounds and prepared PEA-PAAm hydrogels becomes yellow (Fig. S2†). All these phenomena indicate that the PEA n -PAAm-0 min hydrogel could be crosslinked at the macromolecular level *via* photo-crosslinking reaction and the conversion of BP photo-crosslinkers is a monotonically increasing function of UV irradiation time. Therefore, we could control the crosslinking degree of the hydrogel by selecting different UV irradiation times. Through this method, the properties of the PEA-PAAm hydrogel could be easily tailored.

Characterization of the crosslinked structure for the PEA-PAAm hydrogel

After polymerization, we immersed the synthesized hydrogels in 5 mol L^{-1} urea solution, a well-known hydrogen-bond-breaking reagent,^{40,57,58} to characterize its covalent crosslinked

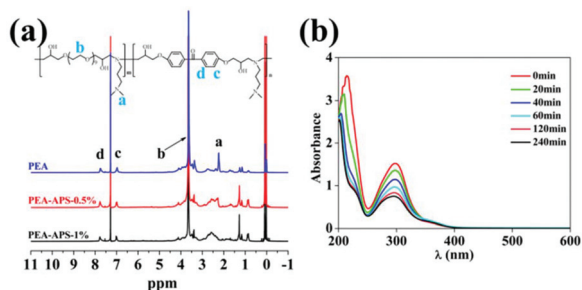


Fig. 1 (a) 1H NMR spectra of PEA, PEA-APS-0.5% and PEA-APS-1% in $CDCl_3$. (b) UV-vis spectra of the model compound.

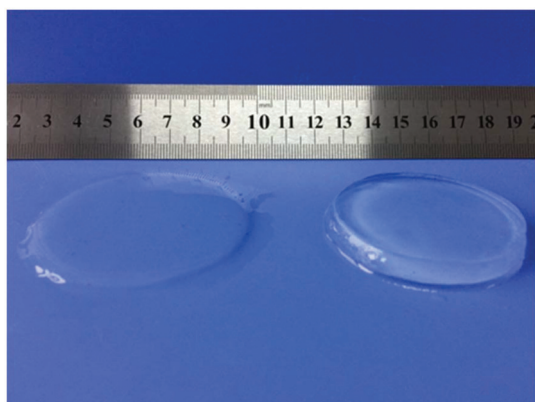


Fig. 2 Photographs of PEA5%-PAAm-0 min (left) and PEA5%-PAAm-120 min (right) hydrogels dissolved in the urea solution after one month.

structure. Fig. 2 shows the representative image of the solvent resistance of a hydrogel with 5 wt% PEA before and after photo-crosslinking reaction. It is found that PEA n -PAAm-0 min hydrogels with different contents of PEA (0.5–5 wt%) do not completely dissolve, but they cannot maintain their own shape in the urea solution after one month (Fig. 2, left). This phenomenon indicated that PEA n -PAAm-0 min hydrogels have a very low crosslinked degree, which originates from the coupling termination of free radicals of PAAm. After the second photo-cross-linked reaction, hydrogels show a quite different stability in the urea solution. The PEA n -PAAm-120 min hydrogel shows great improvement in solvent resistance in the urea solution (Fig. 2, right). It is evident that BP in PEA under UV light can indeed be excited to make the hydrogel covalent crosslinking. As the PEA content is increased from 0.5 wt% to 5 wt%, the shape stability of PEA n -PAAm-120 min hydrogel was also greatly improved in the urea solution. Such behavior could be interpreted as – the increasing content of BP could

lead to an increased crosslinking degree, which finally facilitates the hydrogel maintaining its shape in the urea solution.

Mechanical properties of PEA-PAAm hydrogels

Fig. 3a shows the tensile stress–strain curves of hydrogels with varied contents of PEA after thermal polymerization. It is found that increasing the PEA content could result in a lower tensile strength from 600 kPa to 180 kPa, which indicates that increasing the PEA content could soften our hydrogel (Fig. S3a†).⁴⁴ After the PEA-PAAm hydrogels with different contents of PEA were cured under irradiation of 365 nm UV-light for 120 min, both of them show a tendency towards rupture stress and modulus increasing as well as the elongation at break decreasing (Table S3†). In particular, the fracture stress of PEA5%-PAAm-120 min hydrogel is nearly two times higher than PEA5%-PAAm-0 min hydrogels, increasing from 180 kPa to 500 kPa after UV irradiation, which is closely related to the increased crosslinking density under UV irradiation. It is worth noting that the mechanical performance of PEA-PAAm hydrogels without UV irradiation is better than conventional TEMED and TEMED-BIS hydrogels. In our experiments, the lowest fracture stress in PEA5%-PAAm-0 min hydrogels can still reach 180 kPa, while the fracture stress of TEMED hydrogels only is about 35 kPa (Fig. S3b†). Although the elongation at break of the TEMED hydrogel is very long, this kind of hydrogel is a kind of plastic material and its resilience is very poor. When 0.5 wt% BIS (crosslinking agent) is added in the system, the elongation at break of the TEMED–BIS hydrogels is only 160%. That is to say, PEA-PAAm hydrogels can commendably balance the relationship between breaking stress and elongation at break. For the small molecular crosslinking agent, crosslinking sites tend to be distributed randomly. For the PEA, however, N–CH₃ and BP groups are anchored in a PEA chain, the free radicals will initiate from the PEA and the crosslinking reaction will occur from the PEA. Therefore, the

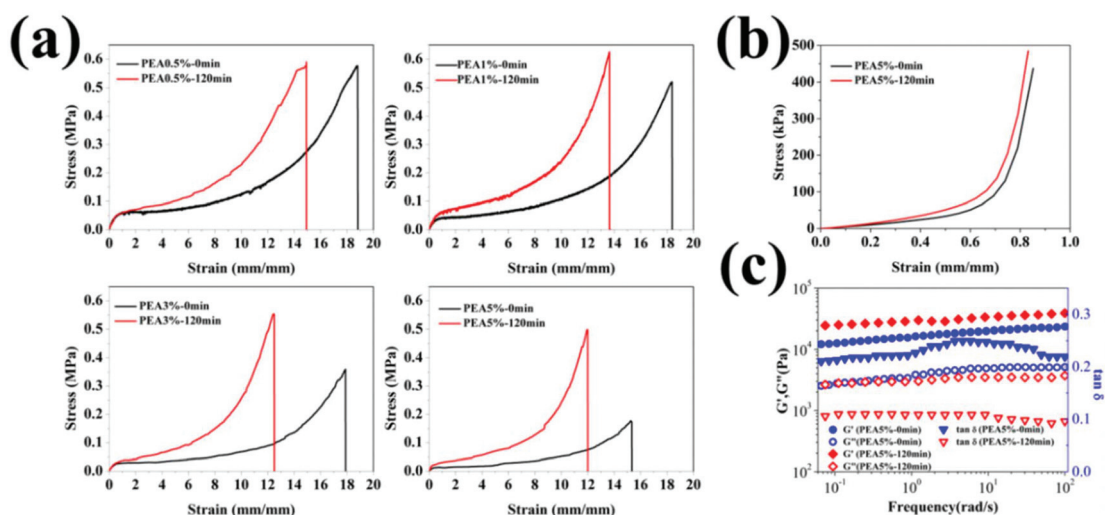


Fig. 3 (a) Tensile stress–strain curves of PEA-PAAm hydrogels with different contents of PEA before and after UV irradiation 120 min, (b) compressive stress–strain curves and (c) dynamic rheology of PEA5%-PAAm hydrogels before and after ultraviolet radiation 120 min.

homogeneous degree for the hydrogel network was improved with the presence of PEA in the hydrogels. At the same time, because one end of the polyacrylamide chain is connected to the PEA, the number of dangling ends of polyacrylamide chains is effectively reduced and the integrity of network structure is improved. These two points are the basis for the good properties of PEA-PAAm hydrogels. Fig. 3b illustrates the compressive stress–strain curves of PEA5%-PAAm-0 min and PEA5%-PAAm-120 min hydrogels. Similar to the extension tests described above, PEA5%-PAAm-120 min hydrogels show an increased compressive strength and modulus after UV light irradiation, because of the enhanced stiffness originating from the generation of cross-linked networks.

Dynamic rheology measurements were carried out at variable frequencies and fixed strain to analyse the dynamic mechanics of UV irradiated samples and unirradiated samples, providing the elastic modulus (G') and viscous modulus (G''); the former (G') stands for the ability to store deformation energy that can be recovered when removing the load,⁵⁹ and the latter (G'') represents viscous behaviors.⁶⁰ In Fig. 3c, whether it is PEA5%-PAAm-0 min hydrogels or PEA5%-PAAm-120 min hydrogels, the elastic modulus is larger than the viscous modulus at overall frequencies, suggesting that the prepared hydrogels display a predominantly elastic-like response. In addition, G' is hardly dependent on frequency. Based on the above two points, we can verify that the PEA-PAAm hydrogel is indeed a gel instead of a viscoelastic polymer solution.^{61,62} Compared with the PEA5%-PAAm-0 min hydrogel, the PEA5%-

PAAm-120 min hydrogel's G' increases and G'' decreases, which demonstrates that the elastic performance of the PEA5%-PAAm-120 min hydrogel improves due to the formation of a chemical crosslinking point under UV-light.

Characterization of the tunable properties of PEA5%-PAAm hydrogels under different irradiation times

Since the crosslinking degree induced by BP is closely related to irradiation time, it is necessary to establish the relationship between the properties and the irradiation time for the PEA-PAAm hydrogel. Considering the fact that the PEA5%-PAAm hydrogels show the best performance on shape stability in urea solution and the greatest reinforcement after UV irradiation, we focused on investigating the properties of PEA5%-PAAm hydrogel during the process of photo-crosslinking. We firstly performed tensile tests on the hydrogels with different irradiation times. The tensile strength was gradually increased from 180 kPa to 500 kPa and the modulus was also increased from 42 kPa to 76 kPa with an increase of UV irradiation time to 120 min (Fig. 4a and b). On further increasing irradiation time up to 240 min, the tensile strength did not show an obvious increase (Fig. 4a). Meanwhile the elongation at break gradually descends but still stays at about 1200% (Fig. 4b). Therefore, 120 min could be considered as the best irradiation time for the PEA5%-PAAm hydrogel. We further selected 6 hydrogels with different irradiation times to measure their recoverability. Fig. 4c shows the typical loading–unloading curves at 500% strains of PEA5%-PAAm hydrogels

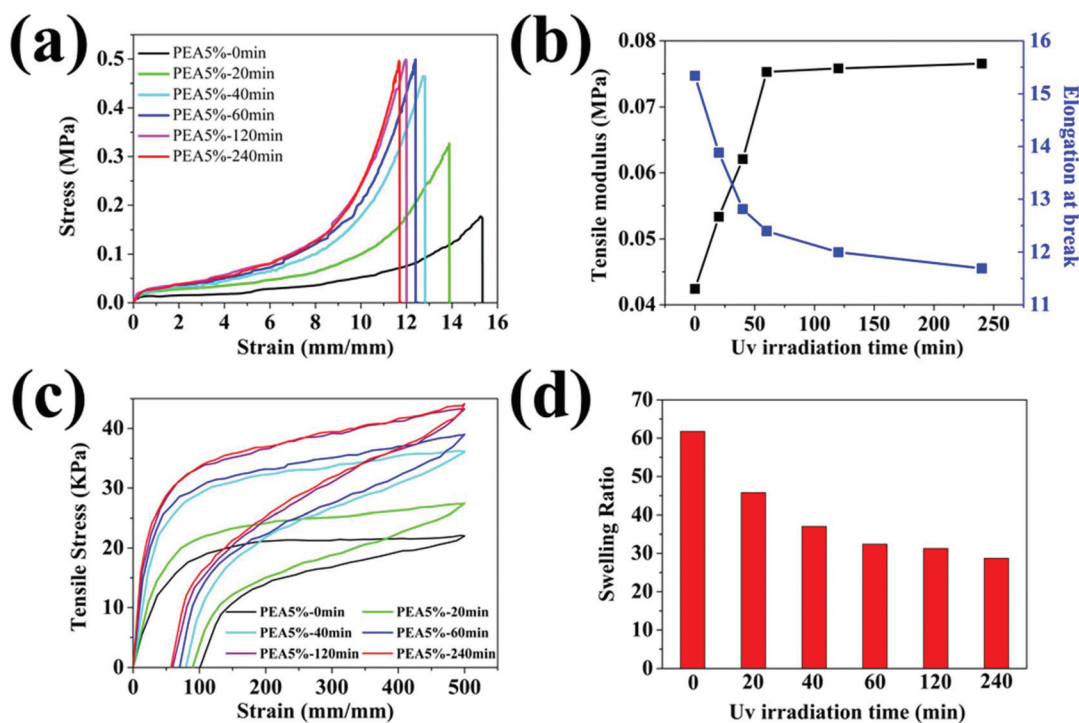


Fig. 4 (a) Tensile stress–strain curves, (b) tensile modulus and elongation at break, (c) loading–unloading curves and (d) equilibrium swelling ratio of PEA5%-PAAm hydrogels under different UV irradiation times.

with UV irradiation for 0 min, 20 min, 40 min, 60 min, 120 min and 240 min, respectively. It is found that the residual deformation ratio was 100% for the PEA5%-PAAm-0 min hydrogel and the residual deformation ratio is progressively decreased from the initial 100% to 55% as the irradiation time is increased from 0 to 240 min. Therefore, the recoverability of the PEA5%-PAAm hydrogels was greatly improved *via* prolonging the irradiation time. Next, we put PEA5%-PAAm hydrogels with different ultraviolet times in DI water to measure the equilibrium swelling ratio (Q). Generally speaking, the swelling ratio is inversely proportional to the degree of crosslinking; the higher the crosslinked degree, the lower the swelling ratio, and *vice versa*.^{63,64} As might have been expected, the swelling ratio decreased from 62 to 29 (Fig. 4d). Fig. 5 presents the typical morphology images of the freeze-dried PEA5%-PAAm hydrogels before and after UV irradiation. In PEA5%-PAAm hydrogels, the size of the porous structure decreased from 35 μm to 27 μm after 120 min UV irradiation and the thickness of pore wall increased clearly (Fig. 5b and d). This is consistent with the increase in the degree of crosslinking after UV irradiation. From what has been discussed above, controlling the irradiation time could effectively tailor the properties of PEA-PAAm hydrogels.

Re-shaping of PEA-PAAm hydrogels

It is usually difficult to fabricate hydrogels with very complex and intricate geometries, which are highly desirable in some specific applications. Since our method for fabrication of hydrogels could effectively tailor their properties *via* controlling their crosslinking degree under different irradiation times at the macromolecular level, we could also effectively use this characteristic to build a hydrogel with a complex three dimensional (3D) geometry *via* the photo-crosslinking reaction. As shown in Fig. 6, rectangular hydrogels (8 cm in length, 1 cm in

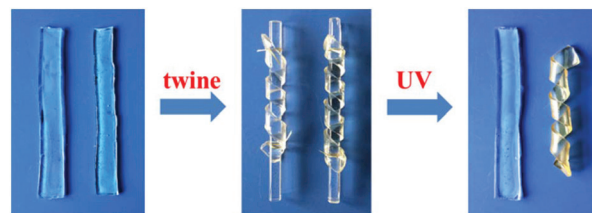


Fig. 6 The re-shaping photographs of TEMED-BIS (left) and PEA5%-PAAm (right) hydrogels.

width and 2 mm in thickness) were spirally twined on a glass rod. In order to prevent water loss, the hydrogels were immersed in *n*-hexane and simultaneously irradiated to make the hydrogels crosslink. Two hours later, we removed the hydrogels from the glass rod, and the TEMED-BIS hydrogel was immediately restored to its original rectangular shape due to lack of the crosslinking reaction. However, the PEA-PAAm hydrogel can maintain its spiral shape. Even one month later, the shape of the spiral remains unchanged. This indicates that the PEA-PAAm hydrogel can indeed be re-shaped into a complex structure without using a sophisticated mould and high-cost processes, which opens a new avenue for practical application of hydrogels.

Conclusions

In summary, we synthesized a kind of polyetheramine (PEA) containing N-CH₃ units as co-initiators and grafting agents as well as benzophenone (BP) moieties as photo-cross-linkers. We firstly polymerize the mixture of PEA and AAm to prepare the active MHP and then put this sample under UV irradiation to perform the crosslinking reaction at the macromolecular level. In this approach, the PEA-PAAm hydrogel can create a more homogeneous distribution of cross-linking points in the polymer network, which ensures their excellent mechanical properties. Because of the response of BP to UV light, the degree of crosslinking of PEA-PAAm hydrogels can be tuned by controlling the UV irradiation time so as to achieve the tunable properties of PEA-PAAm hydrogels. Furthermore, we can utilize these characteristic properties to build a hydrogel with complex three dimensional (3D) geometries *via* the photo-crosslinking reaction.

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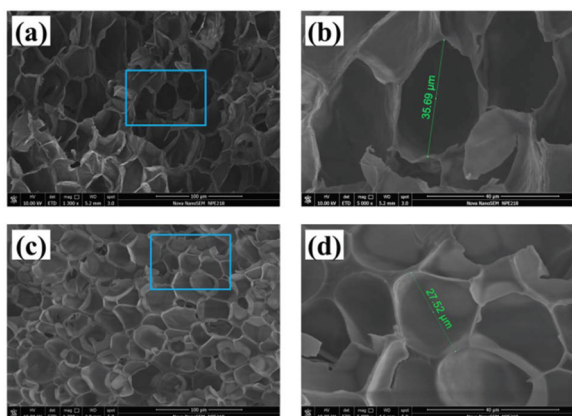


Fig. 5 Morphology and structure of PEA5%-PAAm hydrogels. (a) Scanning electron microscope (SEM) image of PEA5%-PAAm-0 min hydrogel. Scale bar, 100 μm . (b) Zoomed SEM image of the box region in (a). Scale bar, 40 μm . (c) SEM image of PEA5%-PAAm-120 min hydrogel. Scale bar, 100 μm . (d) Zoomed SEM image of the box region in (c). Scale bar, 40 μm .

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