

Dual ionic cross-linked double network hydrogel with self-healing, conductive, and force sensitive properties

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ABSTRACT

Conventional chemically cross-linked double network hydrogels (DN hydrogels) are considered as one of the toughest soft materials. However, they lack self-healing properties due to their non-reversible covalent bonds. In this work, we propose a new design strategy to synthesize a dual ionic cross-linked polyethylene glycol (PEG)/poly(acrylamide-co-acrylic acid) (PAMAA) DN hydrogels, consisting of an ionic cross-linked linear chain extension of PEG and a PAMAA-Fe³⁺ as the first and second physical networks, respectively. Due to the reversible non-covalent bonds in both networks (Fe³⁺ coordination interactions and hydrogen bonds), the DN hydrogels can achieve high mechanical properties (σ_f of ~0.36 MPa and strain of ~1350%) and complete self-healing ability within 12 h. Moreover, due to the free ions diffusion in the water medium of the DN hydrogels, the as-prepared hydrogels also exhibited electrical conductivity and stretch sensitivity. Our results offer a new design strategy to improve the strength and self-healing ability of DN hydrogels by introducing a dual ionic cross-linking within the network, which we hope will provide an alternative focus for the design of tough and self-healing hydrogels with desirable properties.

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1. Introduction

Self-healing hydrogels, which are a class of functional polymers with high water content, stretchable ability and biocompatibility, have received growing interest due to their great potential applications in tissue engineering, drugs and genes delivery, as well as soft electronic devices [1–8]. As is well known, dynamic covalent and non-covalent interactions are two reversible features for the design of self-healing hydrogels. However, additional intervention (e.g., heat, pH or light) is usually required to trigger the corresponding healing process for the dynamic covalent interactive hydrogels. Comparatively, non-covalent interactions including hydrogen bonding [9], ionic bonds [10], metal coordination bonds [11,12], host-guest recognition [13], and hydrophobic interaction [14], have been the basic cross-linking forces to form non-covalent interactive hydrogels, which can repair cracks and re-form their network structures with initial functions. For example, Yang et al. fabricated a highly-stretchable self-healing poly(vinyl alcohol)

hybrid hydrogels based on metal–ligand interactions and hydrogen bonding [11] while Geng and co-authors reported a hydrophobic association-mediated physical hydrogels with high strength and healing ability [15].

Electrically-conductive hydrogels are specially promising for a diverse array of applications, such as human-motion devices and smart robots [16,17]. However till now, it remains a great challenge to fabricate integrated, self-healing hydrogels with excellent mechanical strength and electrical conductivity. For this purpose, efforts have been devoted to multifunctional self-healing hydrogels such as graphene oxide, carbon nanotubes, or metal nanoparticles enhanced electrical self-healing gels [18–20], even though those inorganic nanoparticles reduce the self-healing efficiency of the gels in most cases.

Recently, more attention has been paid to the fabrication of double network hydrogels (DN gels) [21,22] due to their high mechanical strength and toughness based on their unique contrasting network structures and efficient energy dissipation mechanism [23]. A tough and responsive ultrathin physical DN hydrogel films are reported by Tian et al., the obtained physical DN hydrogel films are transparent and show excellent mechanical performances with tensile breaking stress of 3–5 MPa [24]. Chen and co-workers designed fully physically linked Agar/hydrophobically associated

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polyacrylamide (HPAAm) DN gel with tough, fatigue resistant and self-healing properties with the fracture stress reaching 0.28 MPa, while the self-healing efficiency was lower than 40% [25]. Gong et al. prepared a high-strength and tough DN hydrogel composed of poly(acrylamide-co-acrylic acid) and poly(vinyl alcohol) by simple two-steps methods of copolymerization and freezing/thawing. However, the self-healing efficiency was only 37% [26]. In addition, more and more attention has been paid to using dynamic metal coordination bond to prepare self-healing gels [27,28]. Lin et al. fabricated a dual-crosslinked hydrogel with ultrahigh mechanical strength, toughness and good self-recovery, but the self-healing property was not mentioned [29]. Furthermore, Li and co-workers successfully prepared self-healing elastomer with high mechanical strength and self-healing efficiency (90%) by Fe^{3+} ions coordination [30]. Grindy et al. designed and synthesized a four arm PEG molecule containing coordination atoms, after which a self-healing polymer by the Zn^{2+} ions coordination was fabricated [31].

Nature has provided countless inspirations to develop synthetic materials. As is well-known, single-strand DNA was used as a template and control the growth of another single DNA chain based on the complementary base pairs, which eventually form a neat and orderly double-stranded DNA molecule [32,33]. Bio-inspired by the single-strand DNA template, a strategy that uses a linear macromolecule as a template to guide the polymerization of monomers and prepare high-performance hydrogels with relative neat structure and more cross-linking sites is proposed. In this work, we propose a strategy that uses a linear macromolecule as a template as well as the incorporation of metal ions coordination to guide the polymerization of monomers to prepare high-performances, self-healing DN hydrogels. Glycine (Gly) with abundant carboxylic groups incorporated into the PEG backbone (PEG-Gly, Scheme 1) was used as templates to form the first network by ferric ions coordination. Thereafter, acrylic acid (AA) was attached to the as-prepared templates by ferric ions coordination, followed by polymerization of AA and acrylamide (AM) which occurred around PEG-Gly templates to form the second network. Ultimately, an integrated, high-performance PEG/poly(-acrylamide-co-acrylic acid) (PEG/PAMAA) DN hydrogel was formed. These flexible and stretchable hydrogels with unique mechanical, self-healing and electrical properties can be used for various applications including electrical skins (E-skins), actuators and wearable electronics.

2. Materials and methods

2.1. Materials

Poly(ethylene glycol) (PEG_{2k} , $M_n = 2000$ g/mol) was purchased from Sigma-Aldrich Chemicals. Acrylic acid (AA, Reagent Grade, 99%), acrylamide (AM, GC, 99%) and ammonium persulphate (APS,

AR, 98%) were purchased from Sinopharm Chemical Reagent. Epoxy chloropropane and glycine were purchased from Aladdin Industrial Corporation (Shanghai, China). All reagents were used as received without further purification.

2.2. Synthesis of α, ω -epoxy-PEG_{2k} (DEP_{2k})

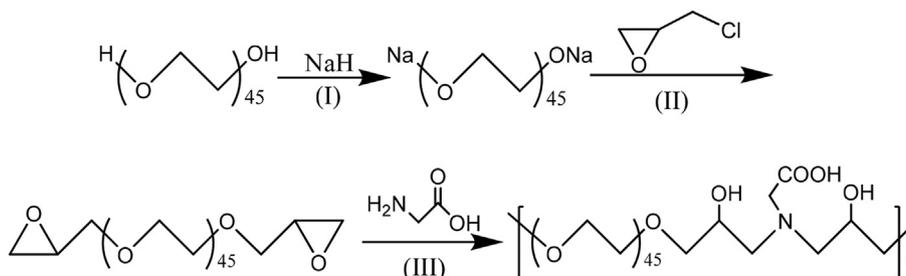
The synthesis of DEP_{2k} was carried out according to literature procedures with small modifications (Scheme 1) [34]. Briefly, 10 g (5 mmol) of PEG_{2k} and 50 mL of dry THF were added into a 100 mL three-neck flask. Then, the solution was heated to 40 °C to dissolve PEG_{2k}. After being cooled to room temperature, 0.44 g NaH (60%) was slowly added into the solution after which the reaction was allowed to proceed for 12 h under stirring at room temperature. Thereafter, 4 mL epoxy chloropropane was added into the reaction solution and stirred for further 24 h at room temperature. The reaction mixture was then passed through an alumina column to remove the NaH residue and salt by-product. The solution was further concentrated by rotary evaporation and precipitated in an excess amount of diethyl ether. After filtration and drying under vacuum overnight, about 9.3 g of white solid (DEP_{2k}) was obtained.

2.3. Synthesis of carboxylic-pendant linear PEG_{2k}-Gly

The synthesis of PEG_{2k}-Gly was carried out directly via amine-epoxy click polymerization (AECP) according to Saha [35]. In brief, 8.0 g DEP_{2k} (0.004 mol) was dissolved in 8 mL methanol in a round-bottom flask with constant stirring at room temperature for 1 h. Then, 0.3 g glycine (0.004 mol) was dissolved in 2 mL deionized water and added into the above solution with constant stirring for 5 days under room temperature. The resultant viscous liquid was precipitated in diethyl ether and washed with water immediately. The solid residue obtained after filtration was thereafter dried under reduced pressure overnight. The molecular weight of PEG_{2k}-Gly ($M_n \sim 8700$ g/mol) was tested by Gel Permeation Chromatography (GPC) and supplied in Fig. 1.

2.4. Preparation of self-healing PEG/PAMAA DN hydrogels

The PEG/PAMAA DN hydrogels were prepared by one-step method: PEG_{2k}-Gly (0.5 g) was dissolved in 6 mL deionized water under stirring. After complete dissolution, 0.5 mL Fe^{3+} ions solution (0.2 mol/L) was added into the solution under stirring for 30 min, followed by cross-linking of PEG_{2k}-Gly chains by Fe^{3+} ions coordination to form the first network. Thereafter, 1.25 g AA (~0.0174 mol) and 1.25 g AM (~0.0174 mol) were added into the above solution and stirred for another 30 min, in which part of AA monomers were coordinated with Fe^{3+} ions, followed by the addition of 0.5 mL initiator (APS, 0.04 g/mL). The final solution mixture was then transferred into a mold, after which it was covered with a piece of sealing film. The radical polymerization of AA and AM occurred at



Scheme 1. Schematic description of synthesis of DEP_{2k} and PEG_{2k}-Gly.

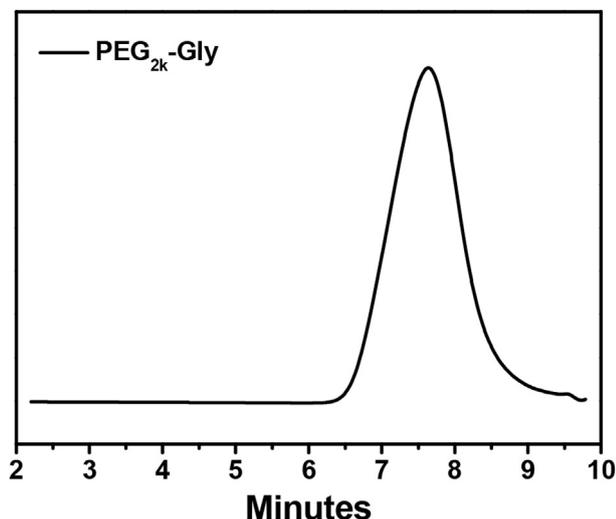


Fig. 1. GPC elution curve of PEG_{2k}-Gly.

room temperature for 12 h to form PAMAA chains and cross-linked by Fe³⁺ ions to form the second network, after which an integrated PEG/PAMAA DN hydrogel was finally formed. Different mass ratios of AA to AM, Fe³⁺ ions concentrations and PEG-Gly content were used to prepare a series of self-healing hydrogels, as shown in Table 1. The resulting hydrogels contain around 70 wt% water (similar to living cartilage, skin, and ligaments).

2.5. Characterization

Analytical gel permeation chromatography (GPC) experiments were performed on a Waters1515. All conductivity measurements were performed on 5 mm thick samples cut into 10 mm × 10 mm, using four-point probe measurements. All mechanical properties of the hydrogels were conducted on a WDW-05 electromechanical tester (Time Group Inc, China) at room temperature. Hydrogels with a thickness of 2 mm and cut into rectangle (50 mm in length and 5 mm in width) were used for the tensile stress test while the rate of extension was fixed at 60 mm/min. The samples were coated with a thin layer of silicone oil to prevent the evaporation of water and each sample test was repeated five times to ensure reproducibility.

2.6. Evaluation of self-healing efficiency

The original hydrogels were cut into halves using blades. One half of the hydrogels was dyed with Rhodamine B for visual discrimination purpose. Then, the separated hydrogel surfaces were re-contacted. The healing efficiency (*HE*) is defined as:

$$HE = \frac{\sigma_h}{\sigma_0} \times 100\% \quad (1)$$

Where σ_h is the tensile stress of self-healed hydrogel and σ_0 is the tensile strength of original hydrogel. The average values and errors were calculated from at least three independent samples for each specimen.

3. Results and discussion

3.1. Preparation of the PEG-PAMAA DN hydrogel

Carboxylic groups functional and chain-extended PEG_{2k}-Gly were used to fabricate the first network as well as serving as linear macromolecule template. PEG_{2k}-Gly chains were cross-linked by Fe³⁺ ions coordination to form the first network, with part of acrylic acid (AA) monomers being attached to the PEG_{2k}-Gly templates (PEG-AA) by Fe³⁺ ions coordination (Scheme 2b). Thereafter, PEG-AA conjugations with free AA and AM monomers were subsequently polymerized to form the second network (PAMAA-Fe³⁺), which eventually formed an integrated PEG-PAMAA DN hydrogel (Scheme 2c). In fact, there are three types of coordination involved in the whole hydrogel fabrication process, namely: (i) coordination between Fe³⁺ ions, AA monomers and PEG_{2k}-Gly, (ii) coordination between Fe³⁺ ions and AA monomers, and (iii) coordination between Fe³⁺ ions and PEG_{2k}-Gly. In this DN, double reversible cross-linked and abundant cross-linking sites were formed between the PEG and PAA chains. This neat structure and synergy of metal coordination bonds and hydrogen bonds (Scheme 2d) endowed the PEG-PAMAA DN hydrogel with excellent mechanical strength and self-healing properties.

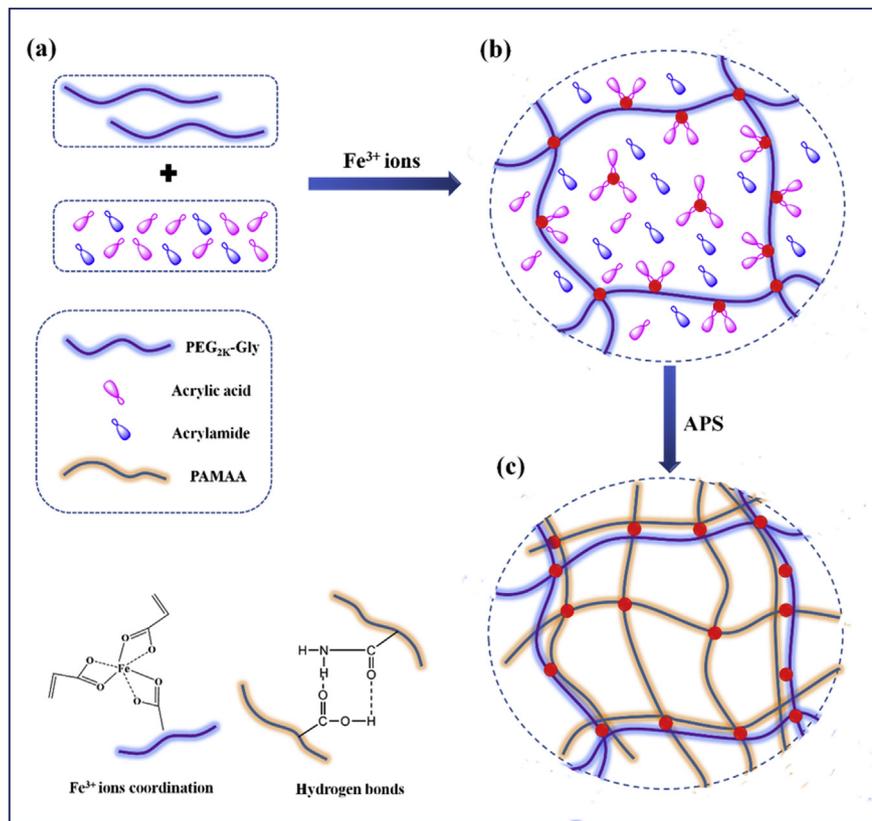
UV-Vis absorption test was performed to confirm the attachment of AA monomers to PEG_{2k}-Gly templates. As shown in Fig. 2, the Fe³⁺ ions, AA, and PEG-Gly aqueous solutions showed no UV absorption spectra. A weak absorption at 405 nm appeared after AA was mixed with Fe³⁺ ions, which demonstrated that the Fe³⁺ ion coordinated with AA. Also, the UV-Vis absorption spectrum of the mixture of Fe³⁺ ions and PEG_{2k}-Gly aqueous solution is different from that of individual aqueous solution of Fe³⁺ ions and PEG_{2k}-Gly, suggesting that a coordination complex was formed after the reaction between Fe³⁺ ions and PEG_{2k}-Gly. Furthermore, UV-Vis absorption spectra for mixture of AA, Fe³⁺ ions and PEG_{2k}-Gly aqueous solution was also performed. This UV-Vis absorption spectrum is different from the previously-mentioned solutions, which indicated that the AA monomers was attached to PEG_{2k}-Gly chains by Fe³⁺ ions coordination.

3.2. Mechanical properties of the PEG-PAMAA DN hydrogel

Taking advantage of the fully physically cross-linked DN

Table 1
Hydrogels with various compositions.

Samples	PEG _{2k} -Gly (g)	AA (g)	AM (g)	Fe ³⁺ ions (mmol)	APS (g)	Water content (%)
Gel-1	0.25	1.25	1.25	0.10	0.05	70
Gel-2	0.50	1.25	1.25	0.10	0.05	70
Gel-3	1.00	1.25	1.25	0.10	0.05	70
Gel-4	0.50	1.25	1.25	0	0.05	70
Gel-5	0.50	1.25	1.25	0.025	0.05	70
Gel-6	0.50	1.25	1.25	0.05	0.05	70
Gel-7	0.50	1.25	1.25	0.20	0.05	70
Gel-8	0.50	1.25	1.25	0.40	0.05	70
Gel-9	0.50	1.66	0.83	0.10	0.05	70
Gel-10	0.50	0.83	1.66	0.10	0.05	70



Scheme 2. Schematic description for the preparation of self-healing PEG/PAMAA DN hydrogel: (a) PEG_{2k}-Gly macromolecule templates mixed with AA and AM monomers, (b) AA monomers were attached onto the PEG_{2k}-Gly templates by Fe³⁺ ions coordination, (c) Integrated PEG/PAMAA hydrogel was formed by free radical polymerization, and (d) the binding mode of the polymer chains of PEG and PAA in hydrogel network.

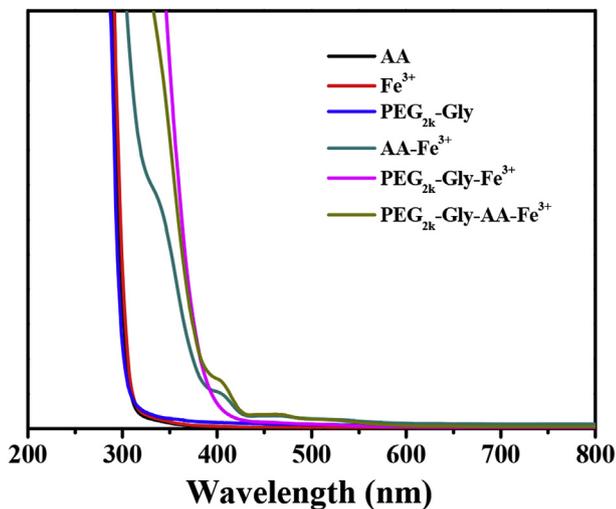


Fig. 2. UV-vis absorbance of Fe³⁺ ions, AA, PEG_{2k}-Gly, mixture of PEG_{2k}-Gly-Fe³⁺, AA-Fe³⁺, and PEG_{2k}-Gly-AA-Fe³⁺ aqueous solutions.

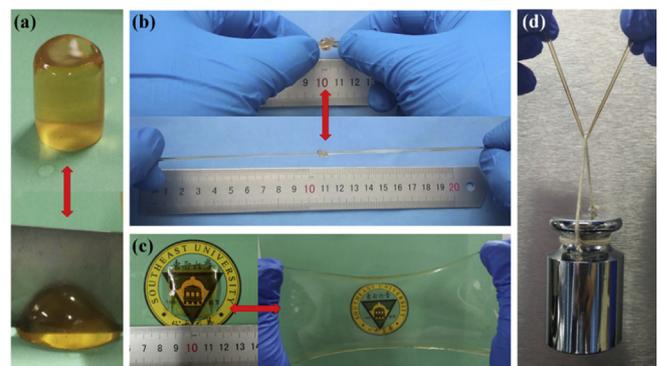


Fig. 3. Photographs demonstrating the excellent mechanical behavior of the PEG/PAMAA DN hydrogels: (a) Using a sharp blade on PEG/PAMAA DN hydrogel, (b) Highly stretched even with a knot, (c) stretch to different directions to form a thin and transparent film, and (d) Sustain a hanging load of 500 g.

architecture and the synergistic effect of Fe³⁺ ions coordination and hydrogen bonds, the PEG/PAMAA DN hydrogel exhibited excellent mechanical properties. As shown in Fig. 3a, the PEG/PAMAA DN hydrogel exhibited cutting-resistance and high toughness, as the hydrogel recovered its original shape without any damage under a sharp blade compression. In addition, the PEG/PAMAA DN hydrogel can be knotted and stretched with high elongation ((Fig. 3b and Movie S1). The rectangle hydrogel film can also be stretched to

different directions to form a thin and transparent film (Fig. 3c). Furthermore, the hydrogel with a thickness of 2 mm and width of 5 mm can sustain a load of 500 g (Fig. 3d). The highly stretchable capability and toughness were mainly attributed to the double network structure and Fe³⁺ ions coordination, which thereby act as reversible sacrificial bonds and cracks to dissipate energy [30].

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.polymer.2018.01.046>.

To investigate the mechanical properties of the PEG/PAMAA DN hydrogel, a series of PEG/PAMAA DN hydrogels were prepared (Table 1). First, the influence of the PEG_{2k}-Gly template contents on

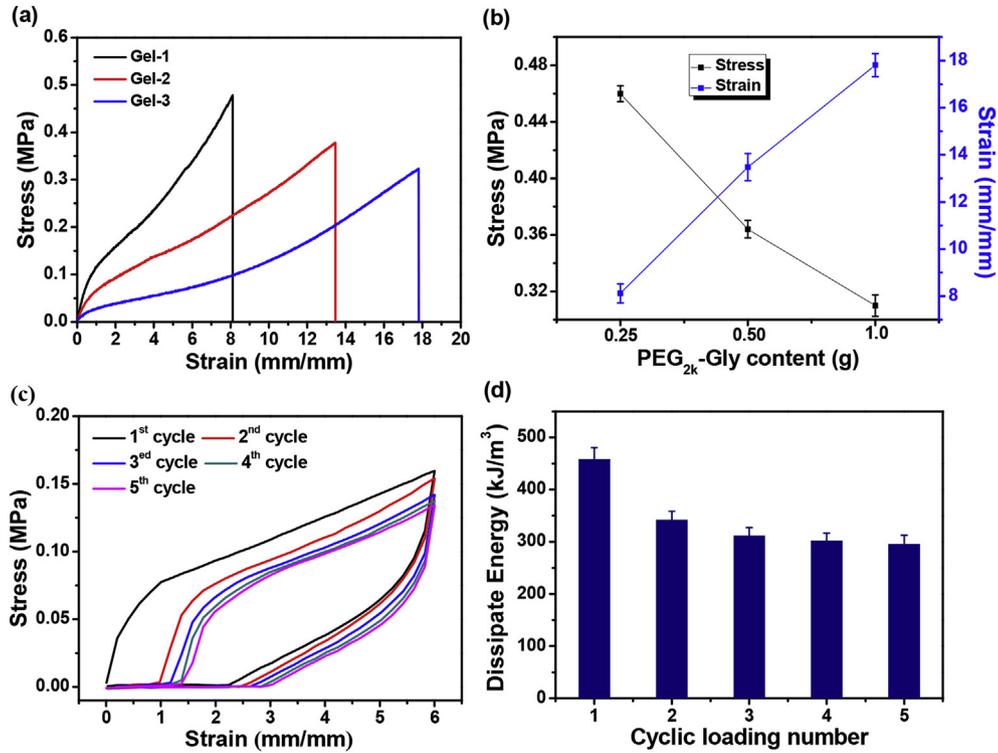


Fig. 4. Mechanical properties of PEG/PAMAA DN hydrogel. (a) Typical stress-strain curves of PEG_{2k}-PAA hydrogels prepared with different PEG_{2k}-Gly contents, (b) Fracture stress and strain values, (c) Five successive loading–unloading cycles of the as-prepared Gel-2, and (d) Dissipated energy of Gel-2 calculated from the area of their hysteresis loops.

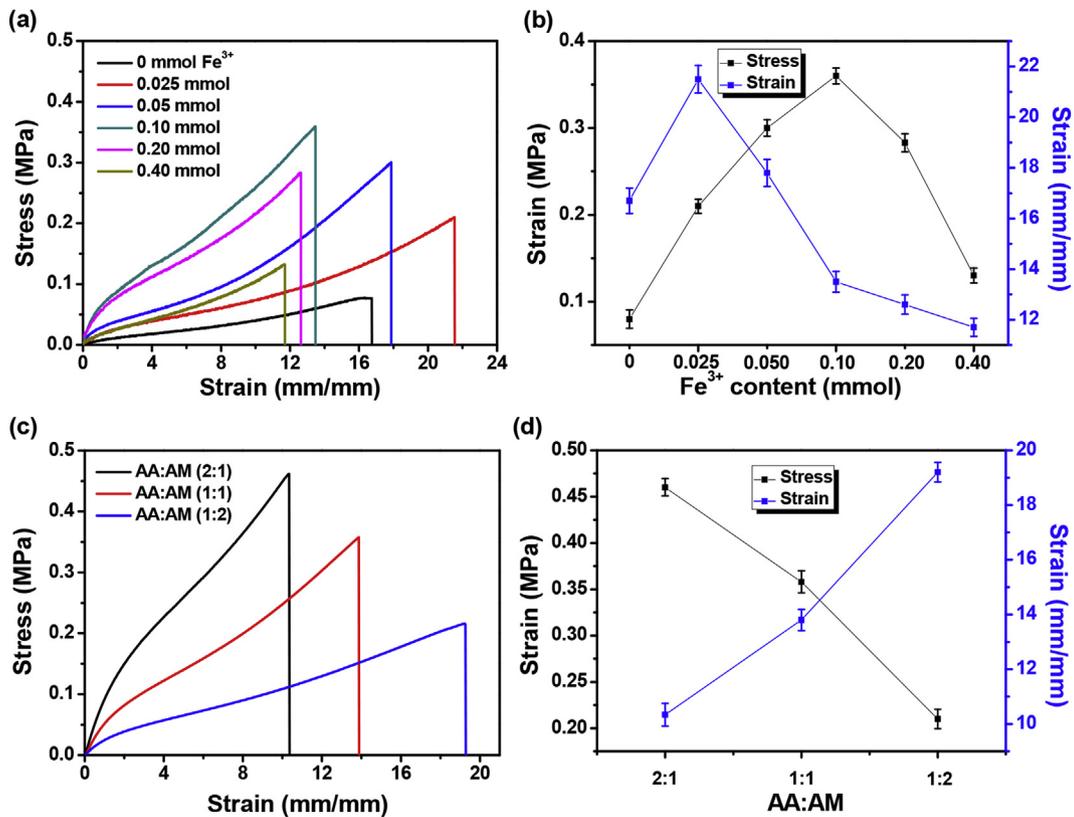


Fig. 5. The influence of Fe³⁺ ions contents and ratios of AA to AM on mechanical properties of PEG/PAMAA DN hydrogels: (a) Typical stress-strain curves of PEG/PAMAA DN hydrogels prepared with different Fe³⁺ ions contents, (b) Stress and strain values, (c) Typical stress-strain curves of PEG/PAMAA DN hydrogels prepared with different mass ratio of AA to AM, (d) Stress and strain values.

the mechanical properties of the DN hydrogels is systematically studied. The DN hydrogels with different PEG_{2k}-Gly contents were prepared in which the Fe³⁺ ions content was fixed at 0.1 mmol and the ratio of AA to AM fixed at 1:1. Fig. 4a displays the stress-strain curves of DN hydrogels with different PEG_{2k}-Gly contents. It can be seen that all the DN hydrogels show excellent mechanical properties, with the fracture stress of Gel-1 with 0.25 g PEG_{2k}-Gly content reaching 0.46 MPa with a fracture strain of 810 ± 40%. With an increase in PEG_{2k}-Gly content, the fracture stress of Gel-2 with 0.5 g PEG_{2k}-Gly content reaches 0.36 MPa with a fracture strain of 1350 ± 50%. However, further increase in the PEG_{2k}-Gly contents resulted in a decrease in the stress while the strain increases. This can be attributed to the presence of hydrophilic PEG chains which served as plasticizer [36,37], in addition to promoting the mobility of the whole hydrogels, thereby giving it a higher strain and lower stress.

Considering that the network in DN hydrogels were dynamic

metal ions coordination and hydrogen bonds, loading-unloading tests were further carried out at the strain of 600% to evaluate the self-recovery of DN hydrogel (Gel-2) at room temperature (Fig. 4c). A pronounced hysteresis was observed, which indicates an energy dissipation from the bond breakage. Due to the successive stretching and release, the tensional stresses of the after stretch were lower than those of the previous cycle. In addition, a quantified datum for the energy dissipation of DN gel is demonstrated in Fig. 4d. It clearly shows that the as-prepared Gel-2 can dissipate energy as much as 458 ± 25 kJ/m³ at the strain 600%. After five cycles, the dissipated energy reduced to 295 kJ/m³ (65% recovery). In total, after five successive stretching loading-unloading cycles, the tensile strength and hysteresis loop recovered effectively, indicating the good self-recoverability of the as-prepared PEG-PAA hydrogels.

Subsequently, the PEG/PAMAA DN hydrogels with different Fe³⁺ ions contents were prepared, in which the PEG-Gly content was

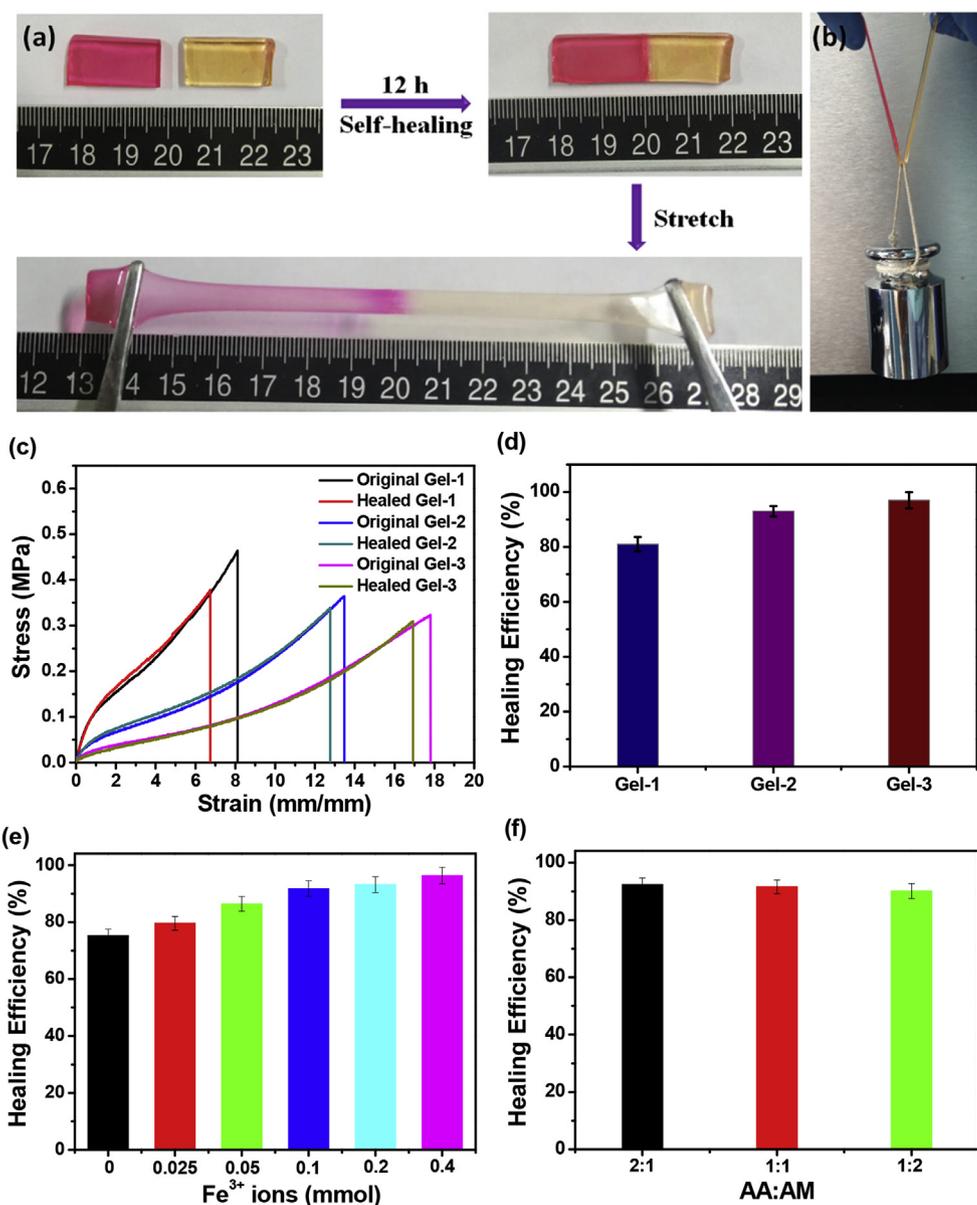


Fig. 6. (a) Photographs demonstrating the excellent healing ability of the PEG/PAMAA DN hydrogel, (b) Sustain a hanging load of 500 g (healed Gel-2), (c) Typical stress-strain curves of PEG-PAA hydrogels prepared with different PEG_{2k}-Gly contents before and after healed for 12 h, (d) Healing efficiency values for Gel-1, Gel-2, and Gel-3, and (e-f) Influence of different Fe³⁺ ions contents and ratio of AA to AM on the self-healing efficiency.

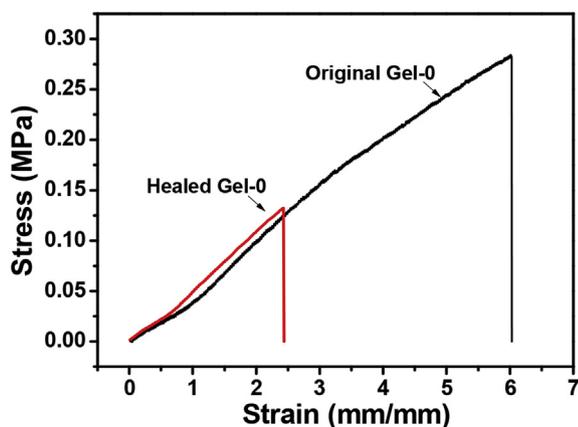


Fig. 7. Typical stress-strain curves of PAA hydrogel (without PEG_{2k}-Gly) before and after being healed for 12 h.

fixed at 0.5 g. The typical stress-strain curves were displayed in Fig. 5a, where it can be seen that the introduction of Fe³⁺ ions into the DN hydrogels improved the mechanical properties, while on the other hand, the DN hydrogel (Gel-4) without Fe³⁺ cross-linking showed lower mechanical properties, with a stress of 0.05 MPa and strain of ~10.2%. With respect to Gel-2, the stress was improved by more than 10 times with a corresponding 50% improvement in strain when the Fe³⁺ ions content was 0.05 mol%. The dynamic Fe³⁺ ions coordination bonds allow the hydrogel to break and re-form during stretching, leading to the unfolding and sliding of the polymer chains which impacts the high stretchability [18]. However, with further increase of Fe³⁺ ions content, the PEG/PAMAA DN hydrogels (Gel-8) exhibited degraded stress and strain. This is mainly ascribed to the negative influence of Fe³⁺ ions on the free radical polymerization as well as initiating the polymerization [38–40]. This is confirmation that higher concentration of Fe³⁺ ions results in less compact coordinate complexes with small stability constant due to the decrease in pH [41].

Furthermore, we studied the influence of the ratio of AA to AM on the mechanical properties. Fig. 5c displays the stress-strain curves of Gel-2, Gel-9 and Gel-10 at the mass ratio of 1:1, 2:1 and 1:2. It can be seen that Gel-9 exhibited higher mechanical strength due to the more cross-linked sites which were formed. With the AA content decreasing, the tensile stress of the DN hydrogels was also decreasing, with Gel-10 showing a lower fracture stress (~0.19 MPa)

and a higher strain. From the previous discussion, it can be concluded that PEG_{2k}-Gly content, Fe³⁺ ions content, and the mass ratio of AA to AM significantly influence the mechanical properties of the PEG/PAMAA DN hydrogel.

3.3. Self-healing properties of the PEG-PAMAA DN hydrogel

The healing properties of the PEG/PAMAA DN hydrogel was further evaluated. As shown in Fig. 6a, the rectangular PEG/PAMAA DN hydrogel (Gel-2) was cut into two, with one piece dyed using rhodamine B, after which the cut surfaces were kept in contact at room temperature for 12 h. The healed hydrogel possesses high extensibility and can be stretched to a large deformation without breaking (about 15 times), indicating the excellent self-healing efficiency of the PEG-PAA hydrogel. Moreover, the healed Gel-2 can be sustained with a hanging load of 500 g without any damage (Fig. 6b). The results indicated the mobility of the polymer chains and the new reconstruction of the metal ions coordination bonds. Notably, other samples also displayed high self-healing capability.

The self-healing properties of PEG-PAA hydrogels were further evaluated using the tensile test protocol which consists of measuring the tensile stress of a healed sample at break, in addition to normalization with respect to the initial hydrogel before fracture to yield the self-healing efficiency. The tensile stress-strain curves of the original and healed hydrogels are plotted in Fig. 6c. It can be seen that the tensile stress-strain curve of healed samples is similar to the original samples, which indicated that those hydrogels exhibited excellent self-healing properties. The healing efficiency of the Gel-2 reached 91.8% after being healed for 12 h, while Gel-1 and Gel-3 also exhibited high self-healing efficiency, attaining 80.4% and 97.1% respectively. Furthermore, the influence of the Fe³⁺ ions content as well as the ratio of AA to AM on the self-healing efficiency of the DN hydrogels was investigated. As shown in Fig. 6e and f, self-healing efficiency increases with increasing Fe³⁺ ions content, while the ratio of AA to AM exhibited a slight effect on the self-healing efficiency. To confirm the role of PEG_{2k}-Gly, a control sample (Gel-0, without PEG_{2k}-Gly) was prepared. However, the control sample (Gel-0) has a self-healing efficiency of 45% (Fig. 7), which is much lower than the as-prepared DN hydrogel with PEG_{2k}-Gly. In recent years, several kinds of self-healing DN hydrogels including agar/hydrophobically associated polyacrylamide (HPAAm) DN gels [25], graphene oxide/poly(acryloyl-6-aminocaproic acid) dual network hydrogel [2], and poly(vinyl alcohol)-poly(ethylene glycol) DN hydrogel, just to mention a few,

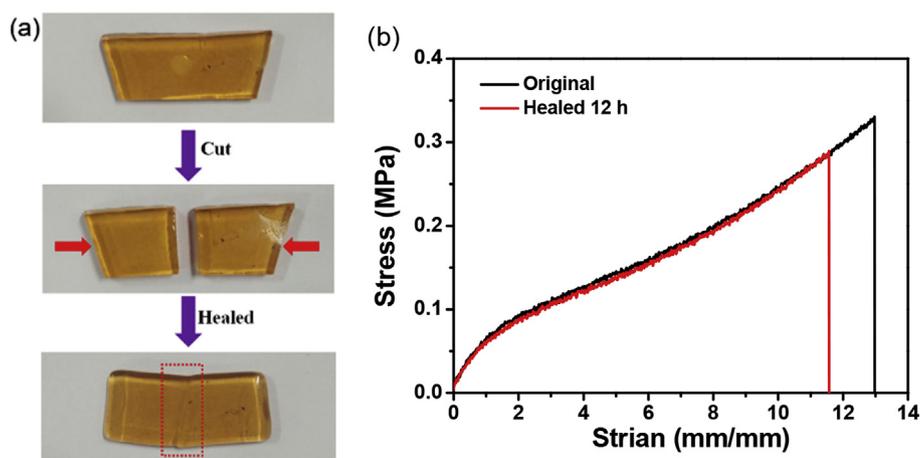


Fig. 8. (a) Photographs demonstrating the uncut surfaces of the DN hydrogel (Gel-2) can be healed with high efficiency, and (b) Stress-strain curves of Gel-2 before and after healing with uncut surfaces contact.

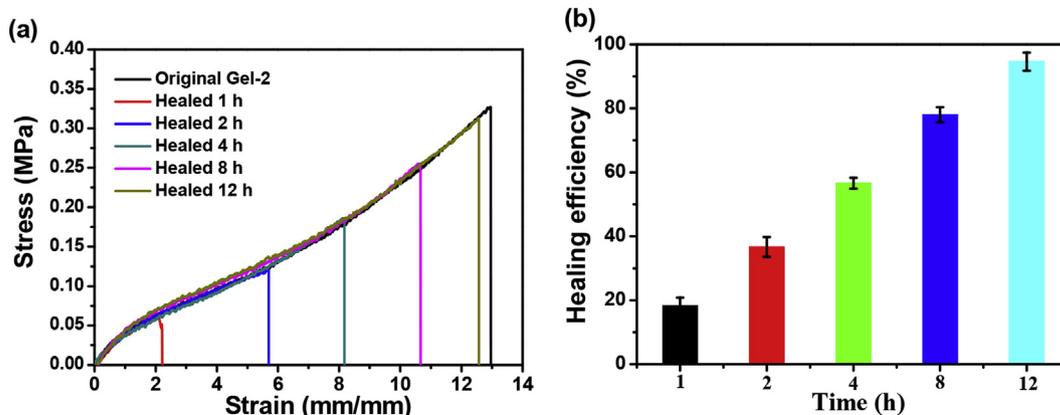


Fig. 9. Self-healing of the PEG/PAMAA DN hydrogel (Gel-2): (a) Typical stress-strain curves of the original and self-healed hydrogels with different healing times, and (b) Healing efficiency values for Gel-2 with different healing times.

have been reported [42]. Compared to the afore-mentioned DN hydrogels, PEG/PAMAA DN hydrogel exhibited comparable mechanical properties and higher self-healing efficiency.

In addition, when two uncut surfaces were brought together (Fig. 8a), they could also self-heal with high efficiency. Fig. 8b displays the stress-strain curves of Gel-2 before and after healed with uncut surfaces healing. The healing efficiency reaches 85%, which indicated the mobility of the polymer chains and the new reconstruction of the reversible bonds in the whole matrix of hydrogel.

Fig. 9 displays the typical stress-strain curves for the Gel-2 after self-healing at different times. It is obvious that the tensile strength increases with increasing healing time, with about 58% of the

original strength recovered after 4 h. After 8 h, the degree of recovery attained ~80% and 93% at 12 h. The results of the healing time t dependence of the hydrogel indicated that the mobility of the PEG and PAMAA chains and the formation of the new Fe^{3+} ions coordination is time dependent.

A great deal of researches has revealed high mechanical properties and self-healing ability of the as-prepared PEG/PAMAA DN hydrogel based on the macromolecular templates inducing and metal ions coordination. Under the inducing and guiding of the macromolecular templates, perfect combination between polymer chains and high binding sites was obtained. Moreover, the presence of the $\text{PEG}_{2k}\text{-Gly}$ templates promotes the mobility of the polymer

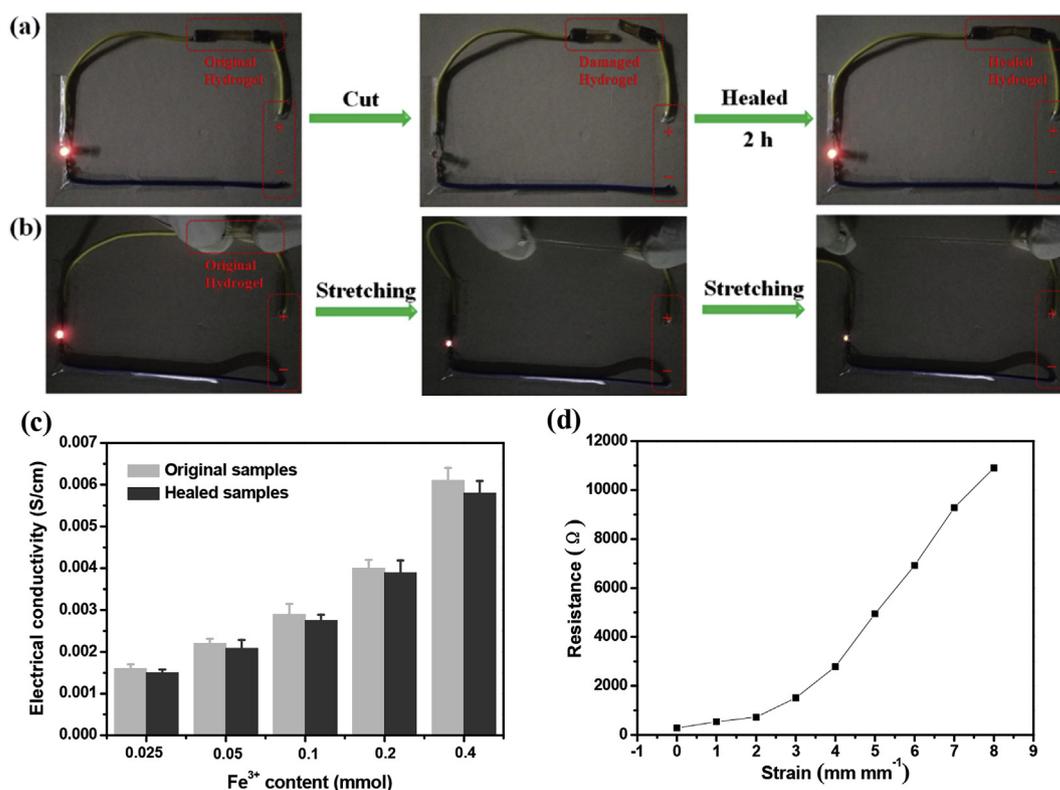


Fig. 10. (a) Photographs demonstrating the electrical conductivity of the PEG/PAMAA DN hydrogel, (b) Photographs demonstrating the luminance variations of a LED with the increase in strain, (c) Volume electrical conductivity of the self-healing PEG/PAMAA DN hydrogel from four-point probe measurements and (d) The dependence of resistance of Gel-2 on applied tensile stress.

chains. Furthermore, based on the mobility of the polymer chains and the synergistic effect of metal ions coordination and hydrogen bonds, the as-prepared hydrogels exhibited excellent mechanical properties and full self-healing ability.

3.4. Conductive and force sensitive properties of the PEG-PAMAA DN hydrogel

Interestingly, it was discovered that the DN hydrogels exhibited favorable conductivity. As shown in Fig. 10, a battery-powered circuit was constructed to demonstrate the conductivity of the PEG/PAMAA DN hydrogels. The LED showed high brightness (Fig. 10a), which demonstrated the conductivity of Gel-2. However, open circuit occurred when the hydrogel was severed, but the LED recovered its brightness after reconnection. This demonstrated the excellent repeatable restoration of electrical performance of the DN hydrogels. Fig. 10c shows the electrical conductivity of the self-healing hydrogels with different Fe^{3+} ions contents, with the electrical conductivity of the original Gel-2 reaching 0.003 S/cm. A 2 h contact resulted in a nearly full restoration of the electrical properties, with electrical conductivity reaching 0.0029 S/cm. Other samples also exhibited electrical conductivity properties, with values ranging from 0.0016 to 0.0062 S/cm. The conductivity of the hydrogels was mainly attributed to the free ions diffusion (Fe^{3+} and Cl^- ions) in the network with high water content. Furthermore, the resistance of the Gel-2 increased from 0.34 Ω to 10.85 k Ω with an increase in the tensile strain from 0 to 800% (Fig. 10d), while the LED gradually darkened with increasing tensile strain (Fig. 10b and Movie S2). The results indicated the force sensitivity of the self-healing DN hydrogels. Due to the mechanical strength, electrical conductivity and tensile sensitivity, these functional self-healing hydrogels have a potentially applications in E-skins or smart devices.

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.polymer.2018.01.046>.

4. Conclusion

In summary, a novel strategy that uses a linear macromolecule as template and Fe^{3+} ions cross-linking to prepare high-performance self-healing PEG/PAMAA DN hydrogel is proposed. Due to the perfect combination between PEG and PAMAA chains, high cross-linked density and synergistic effect of the coordination bonds and hydrogen bonds, the as-prepared PEG/PAMAA DN hydrogel exhibited high mechanical strength, stretchable, and full self-healing properties, in addition to exhibiting electrical conductivity and tensile sensitivity. We envision that this strategy can be employed to prepare other functional polymers. Moreover, the self-healing, mechanically tough and conductive DN hydrogels could have potential applications in artificial skins, stretchable electronics and assisted health technologies.

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