

Multi-bond Network Hydrogels with Robust Mechanical and Self-healable Properties*

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Abstract Multi-bond network (MBN) which contains a single network with hierarchical cross-links is a suggested way to fabricate robust hydrogels. In order to reveal the roles of different cross-links with hierarchical bond energy in the MBN, here we fabricate poly(acrylic acid) physical hydrogels with dual bond network composed of ionic cross-links between carboxyl- Fe^{3+} interactions and hydrogen bonds, and compare these dually cross-linked hydrogels with singly and ternarily cross-linked hydrogels. Simple models are employed to predict the tensile property, and the results confirm that the multi-bond network with hierarchical distribution in the bond energy of cross-links endows hydrogel with effective energy-dissipating mechanism. Moreover, the dually cross-linked MBN gels exhibit excellent mechanical properties (tensile strength up to 500 kPa, elongation at break $\sim 2400\%$) and complete self-healing after being kept at 50 °C for 48 h. The factors on promoting self-healing are deeply explored and the dynamic multi-bonds are regarded to trigger the self-healing along with the mutual diffusion of long polymer chains and ferric ions.

Keywords Multi-bond network hydrogels; Poly(acrylic acid); Dual cross-linking; Mechanical properties; Self-healing

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1971-0>.

INTRODUCTION

Hydrogels are soft and wet materials, which are three-dimensional networks composed of water and cross-linked polymers. Owing to similarities to natural tissues and good biocompatibility, hydrogels have been widely explored as materials in drug delivery, cell encapsulation, tissue engineering, sensing, *etc*^[1–7]. However, several defects, such as weak and brittle properties, tedious synthetic process, time-consuming fabrication methods, and inability of self-healing, have limited the applications of hydrogels. Therefore, the development of highly tough and self-healable hydrogels which overcome the above-mentioned limitations is urgently needed, but remains challenging. The reasons of the weak properties of conventional hydrogels lie in the inhomogeneous network structure and the lack of efficient energy dissipating mechanism^[8–11]. Recently, several studies have made progress in the synthesis of strong and stretchable hydrogels, based on the strategy of designing a homogeneous gel network or introducing structural units for energy dissipation. Tetra-PEG gel^[12] and slide-ring gel^[13] are

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51633003 and 21474058), State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University (No. LK1404), Tsinghua University Scientific Research Project (No. 2014Z22069), and State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology (No. OIC-201601006).

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Invited paper for special issue of “Hydrogel”

Received April 9, 2017; Revised May 5, 2017; Accepted May 8, 2017

doi: 10.1007/s10118-017-1971-0

regarded as representatives of homogenous network gels. And the developments in energy dissipating mechanism have led to the generation of various tough hydrogels, including double-network hydrogels^[14], nanocomposite hydrogels^[15–19], hydrophobically associated hydrogels^[20] and macromolecular microsphere composite hydrogels^[21]. Generally, constructing double network is regarded as an effective energy-dissipating strategy, but still faces some limitations, such as time-consuming processes and unrecoverable sacrificial network. Therefore, utilizing dynamic crosslinking to replace the sacrificial covalent bonds can create a more efficient and recoverable energy dissipating system^[22].

In our recent research, we proposed the concept of multi-bond network (MBN) gels, *i.e.*, single network gels containing different bonds with hierarchical binding energy as permanent or dynamic cross-links. MBN structure can endow hydrogels with robust mechanical properties, owing to the synergy of different cross-links with hierarchical bond energy: stronger cross-links such as chemical cross-links afford and distribute the stress while weaker cross-links such as hydrogen bonds, ionic bonds or hydrophobic association dissipate the energy through break-recombination. The hierarchical distribution on binding energy of cross-links makes the hydrogels achieve successive energy dissipation. Based on this strategy, we recently reported a series of multi-bond network hydrogels (MBN gel) composed of a brush copolymer facilitated by silica nanoparticles^[18, 19, 23–26]. Supramolecular interactions between the polymer chains, including ionic interaction^[19], hydrogen bonds^[18, 23] and hydrophobic association^[24], act as the hierarchical dynamic cross-linking points, and polymer chains grafted silica nanoparticles serve as analogous cross-linking points. Tough poly(acrylic acid)/graphene oxide (PAA/GO) hydrogels and loosely chemical cross-linked PAA hydrogels enhanced by ionic interactions have also been reported^[27, 28].

Besides mechanical properties and self-healing ability, these hydrogels can repair themselves automatically after fracture or scratch, and have drawn a significant attention owing to the advantage to increase the lifetime of materials^[29]. Based on the twofold roles of dynamic crosslinks which may contribute to the effective energy dissipation and self-healing capability, some researchers have made breakthroughs in tough and self-healable hydrogels^[18–20, 24, 27, 28, 30–36]. However, improving the mechanical properties of hydrogels always needs a contrary variation in hydrogel composition or structure compared with accelerating the self-healing of hydrogels^[19, 35] and hence the fabrication of tough and fast self-healable hydrogels still remains challenge.

Herein, we report a facile and one-pot strategy for the fabrication of tough and self-healable poly(acrylic acid)-Fe³⁺ hydrogels with dynamic multi-bond network. And in order to understand the roles of cross-links with hierarchical bond energy and their synergy in mechanical properties, we use simulation models to estimate the tensile properties of the dually cross-linked MBN gels compared with singly and ternarily cross-linked hydrogels. Moreover, the influencing factors on mechanical properties are deeply explored exhibiting robust network structure of PAA-Fe³⁺ hydrogels and the tunable properties by modulation of the component concentrations. The hydrogels also show excellent self-healing properties, owing to the unique dually dynamic cross-linked MBN structure.

EXPERIMENTAL

Materials

Acrylic acid was purchased from Beijing Chemical Works and purified by distillation under reduced pressure before use. Ammonium persulfate (APS), Fe(NO₃)₃·9H₂O and *N,N'*-methylenebisacrylamide (Bis) were purchased from Beijing Chemical Reagent Co., Ltd. Triethoxyvinylsilane (VTES) was purchased from Alfa Aesar.

Characterization

Tensile test measurements

Tensile test was conducted on as-prepared and self-healed cylindrical PAA-Fe³⁺ sample (5 mm diameter) using a Shimadzu AGS-X at ambient temperature under the following conditions: cross-head speed = 100 mm·min⁻¹ and sample length between jaws = 15 mm.

Molecular weight

The PAA-Fe³⁺ gels were cut into small pieces and immersed into the solution with excess EDTA-2Na under stirring until the gels were completely dissolved and a transparent yellow solution was obtained. Then the solution was dialysed by dialysis membrane (molecular weight cut-off was 1×10^4) for one week and the water was changed every 12 h. The obtained achromatic solution was neutralized by the addition of sodium hydroxide solution ($0.5 \text{ mol}\cdot\text{L}^{-1}$) until the pH reached approximately 8. The concentrated solution was poured into excess alcohol to precipitate the sodium polyacrylate. The sodium polyacrylate was filtered and dried at 60°C under vacuum for 12 h, and then stored in a desiccator before use. The molecular weight of polymer was determined by viscometry. The sodium polyacrylate solid was dissolved in NaBr solution ($0.1 \text{ mol}\cdot\text{L}^{-1}$).

FTIR measurements

A Fourier transform infrared (FTIR) spectrometer Nicolet 6700 was used for the infrared analysis. Spectra were obtained by signal averaging 32 scans at the resolution of 4 cm^{-1} in the range of $4000\text{--}650 \text{ cm}^{-1}$.

UV-Vis measurements

The absorbance of $0.1 \text{ mol}\cdot\text{L}^{-1}$ Fe(NO₃)₃ solution, PAA solution (7.5 wt%) and PAA-Fe³⁺ hydrogel (Fe³⁺ concentration = 0.5 mol% of AA) was measured by a TU-1810 UV-Vis spectrophotometer at $\lambda = 400\text{--}600 \text{ nm}$.

Hydrogel Fabrication

The PAA-Fe³⁺ hydrogels were synthesized by *in situ* free-radical polymerization with the ferric ions as ionic crosslinkers. Typically, monomer acrylic acid (AA) (6 g) and ionic crosslinker Fe(NO₃)₃·9H₂O (0.50 mol% of AA) were dissolved in deionized water (24 g) and stirred for 5 h to obtain a transparent reddish brown solution. After degassing in vacuum for 15 min, the ammonium persulfate initiator (0.05 wt% of AA) was added and the solution was bubbled with nitrogen. The uniform suspension was then transferred into plastic syringes with 5 mm inner diameter or other required template, and then the polymerization was conducted at 30°C for 30 h under N₂ atmosphere. The chemically cross-linked hydrogels were prepared by the same procedure only using Bis (1.5 mol% relative to AA) instead of the Fe(NO₃)₃·9H₂O, and the amount of ammonium persulfate was 0.25 wt% of AA, and polymerization temperature was 45°C . Only hydrogen bonds singly cross-linked linear PAA (L-PAA) gels were prepared by the same procedure as the chemical cross-linked hydrogels without the addition of Bis. The ternarily cross-linked PAA-vinyl silica nanoparticles (VSNPs)-Fe³⁺ nanocomposite hydrogels were prepared referring to our previous paper^[19]. The fabrication process is similar as the fabrication process of PAA-Fe³⁺ hydrogels with the addition of a suspension of VSNPs (0.50 wt% of AA). VSNPs were prepared by the same procedure as our previous work^[18]. Typically, 3.8 g of triethoxyvinylsilane was mixed with 30 g of deionized water, and the mixture was magnetically stirred at room temperature for 12 h.

Self-healing Experiments

The cylindrical PAA-Fe³⁺ sample was cut by knife, and the self-healing was conducted by keeping the cut surface in contact mildly (without any healing agents) at different temperatures for different periods. In order to avoid water evaporation, the sample within plastic syringes was wrapped with polyethylene films and kept in a sealed polyethylene bag.

RESULTS AND DISCUSSION

Mechanical Properties of PAA-Fe³⁺ Hydrogels

The PAA-Fe³⁺ gels synthesized by *in situ* polymerization are cross-linked by ionic bonds between ferric ions and the carboxyl groups on the PAA chains, inter-polymer chain hydrogen bonds and polymer chain physical entanglements, which are all dynamic and reversible physical interactions (Fig. 1a). The formation of ionic bonds in the gel is confirmed by FTIR and UV-Vis spectra (Fig. S1 in supporting information, SI). The obtained ionic hydrogels are referred to as *F_n* gels, where *n* represents the concentration of ferric ions with respect to AA, e.g., hydrogels with 0.5 mol% ferric ions are referred to as F5 gels. Without stating otherwise, the water content of the PAA-Fe³⁺ gels is fixed as 80 wt%. Owing to the dynamic crosslinks in the hydrogel network structure, the

hydrogels are very tough and flexible, and can withstand the conformation of twisting (Fig. 1b), knotting (Fig. 1c) and stretching (Figs. 1d and 1e).

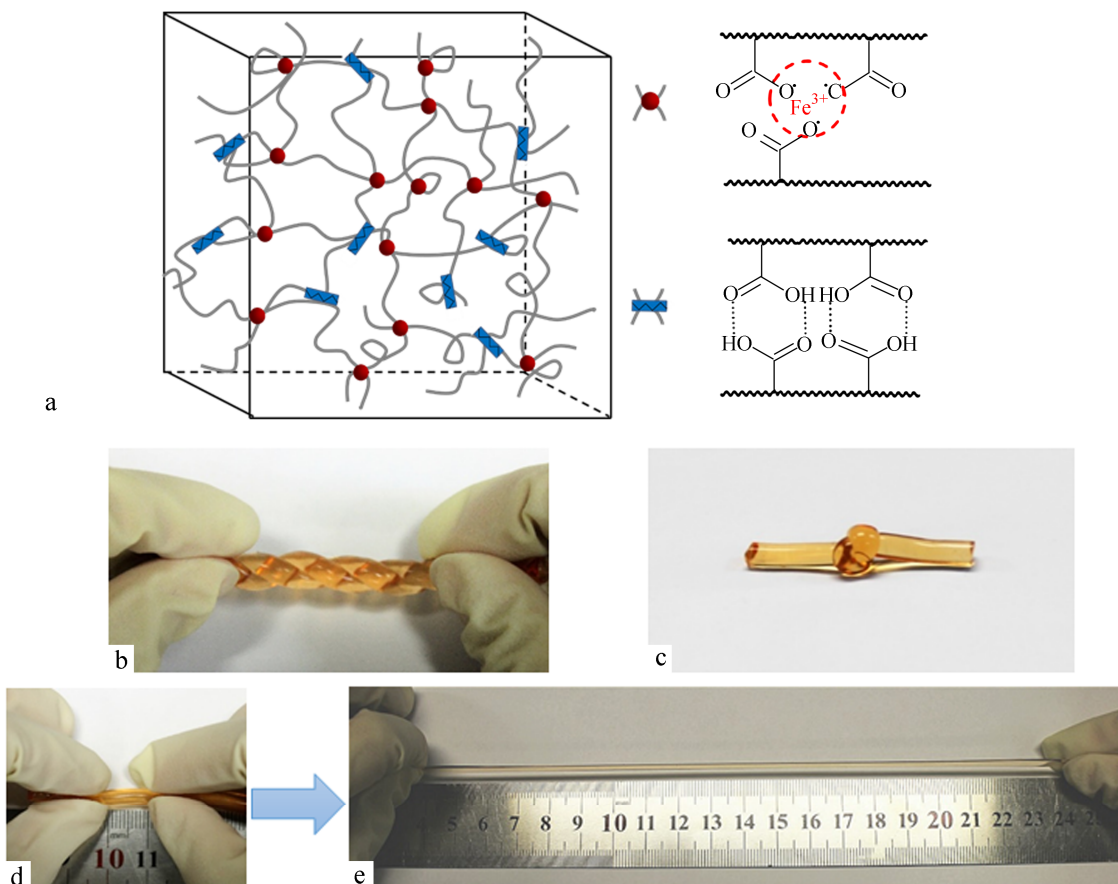


Fig. 1 (a) Illustration of the network structure of PAA-Fe³⁺ hydrogel and its physical crosslinks including hydrogen bonds and ionic interaction; The mechanical performance of PAA-Fe³⁺ hydrogels: (b) twisting, (c) knotting and (d, e) stretching (The online version is colorful.)

The quantification of mechanical properties is made *via* a series of tensile tests. PAA-Fe³⁺ hydrogels are demonstrated to have good mechanical properties (Figs. 2a and 2c, and Fig. S2 in SI). The tensile mechanical properties of PAA-Fe³⁺ hydrogels, including tensile strength, tensile modulus and fracture energy, show a remarkable improvement with increasing ferric ion concentration from 0 mol% to 0.5 mol%. When the ferric ion concentration increases from 0.1 mol% to 0.5 mol%, the tensile strength increases from 182 kPa to 504 kPa, while all the hydrogels show excellent flexibility with elongation at break of more than 2000%. The elongation at break decreases with the increase of ferric ion concentration owing to the increasing cross-linking points. Then a decline in mechanical properties has been observed when Fe³⁺ concentration is more than 0.5 mol%. The effects of ferric ions on strengthening the hydrogels mainly lie in two aspects. The increase of ferric ions results in the increase of crosslinking density of gels (Table 1). The crosslinking density is calculated by using the kinetic theory of rubber elasticity:

$$\tau = N^* RT(\alpha - \alpha^2) \quad (1)$$

where τ , α , R and T are tensile stress, extension ratio, gas constant and absolute temperature respectively. N^* is the effective crosslinking density. Here we assume $\alpha = 2$ (strain = 100%) and $T = 298.15$ K. N^* increases from

2.53 mol·m⁻³ to 4.88 mol·m⁻³ as the ferric ion concentration increases from 0.1 mol% to 1.0 mol%, underlying that increasing amount of crosslinks can afford the stress, and the increase of ferric ions contributes to the improvement of gel's energy dissipating efficiency through the break-recombination of ionic bonds. The chemically cross-linked hydrogels with equal crosslinking density as F5 hydrogel are fragile compared to PAA-Fe³⁺ hydrogels (Fig. S3 in SI). This phenomenon exhibits the significant energy-dissipating effects of ferric ions. However, when ferric ion concentration is higher than a certain value, the radical polymerization should be retarded and the molecular weight of polymer in hydrogels decreases^[19, 37–40], leading to the decline in mechanical properties of the PAA-Fe³⁺ hydrogels. The crosslinking density also decreases from 4.88 mol·m⁻³ to 4.05 mol·m⁻³ when the ferric ion concentration increases from 1.0 mol% to 1.25 mol%. According to Fig. S4 (in SI), the viscosity average molecular weights (M_η) of polymers in the F2, F5, F10 hydrogels determined by viscometry are 68.26×10^4 , 77.82×10^4 and 41.56×10^4 g·mol⁻¹. At a moderate content of ferric ions, the slight increase in M_η may be due to the acceleration of free-radical polymerization by ferric ions^[19, 38–40]. However, when there exists a large amount of ferric ions in the system, the radicals are likely to be transferred to the ferric ions, resulting in the facilitation on chain termination and the decrease of molecular weight^[19, 37, 40].

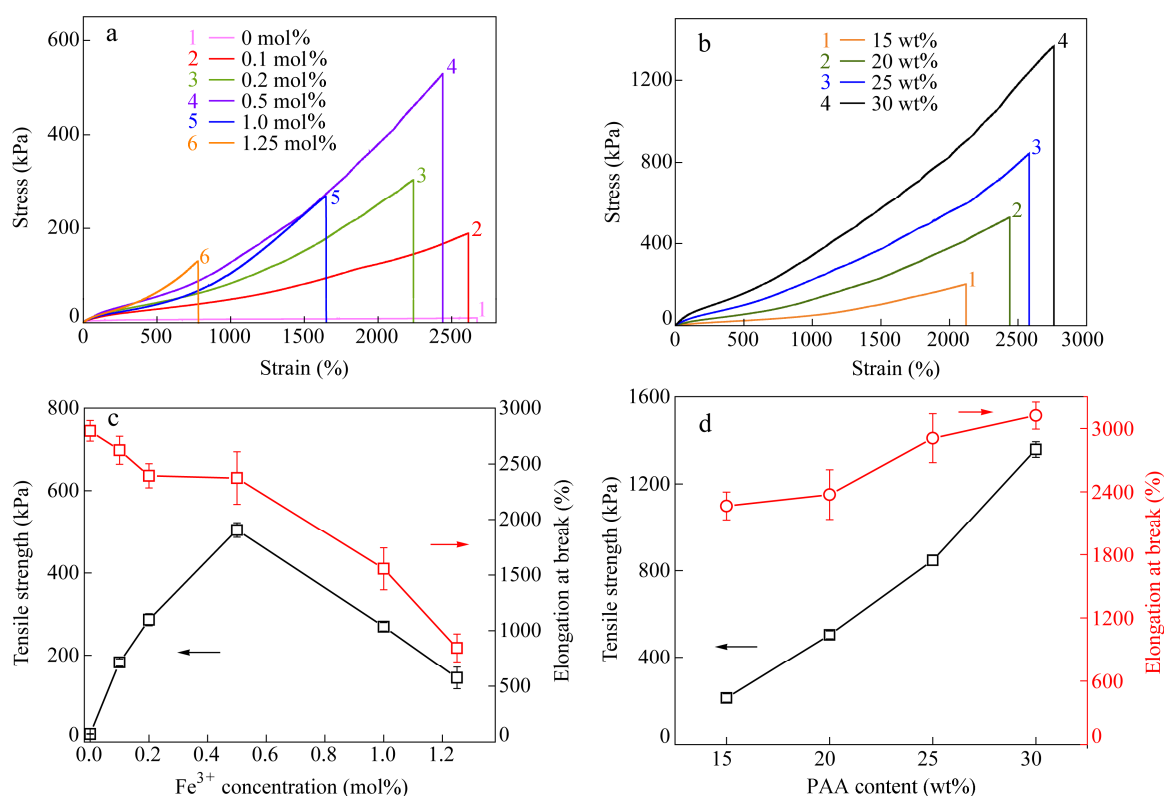


Fig. 2 Tensile stress-strain curves of hydrogels with (a) different Fe³⁺ concentrations (PAA content = 20 wt%) and (b) different PAA contents (Fe³⁺ concentration = 0.5 mol%); Tensile strength and elongation at break dependence on (c) different Fe³⁺ concentrations and (d) PAA contents

The effect of polymer content on the mechanical properties of the PAA-Fe³⁺ hydrogels is also significant as shown in Fig. 2(b). The tensile strength (Fig. 2d), elongation at break (Fig. 2d) and fracture energy (Fig. S2b in SI) of the hydrogels increase with increasing polymer content. Especially, for the hydrogel with polymer content of 30 wt%, the tensile strength and fracture energy are approximately 1.3 MPa and 14.9 MJ·m⁻³ respectively, indicating that the hydrogel has outstanding toughness and deformability. The enhancement in the mechanical properties of the hydrogel with higher polymer content results from the remarkable increase of crosslinking

density in the hydrogels (Table 1). With increasing polymer content, there is more polymer concentration in per unit cross-sectional area, leading to more effective stress dispersion. Meanwhile, along with increasing the polymer content, more polymer chains are likely to build effective dynamic physical crosslinks in the hydrogels. So the break-recombination of the dynamic bonds during deformation should also be quicker at high polymer content.

The general toughening mechanism of physical gels is attributed to dual even hierarchical physical crosslinks with wide distribution of bonding strength^[19, 41–43]. During deformation, the strong bonds and associations retain the original network configuration, while the weaker bonds and associations break and recombine to dissipate energy. There are ionic bonds between ferric ions and carboxyl groups as well as interchain hydrogen bonds between carboxyl groups in the PAA-Fe³⁺ gel network, both of which are considered to act as reversible sacrificial bonds to dissipate energy, while some of the stronger ionic bonds act as the quasi-permanent crosslinking points to afford the stress. The synergy of ionic bonds and hydrogen bonds endow PAA-Fe³⁺ gels with excellent mechanical properties.

Table 1 The effective cross-link density of hydrogels with different compositions

Fe ³⁺ concentration (mol%)	PAA content (wt%)	σ_a^a (kPa)	N^*^b (mol·m ⁻³)
0.50	15	9.30	2.14
0.50	20	18.03	4.16
0.50	25	36.79	8.48
0.50	30	56.27	12.97
0.10	20	10.98	2.53
0.20	20	14.28	3.29
1.00	20	21.18	4.88
1.25	20	17.57	4.05

^a Stress at 100% strain; ^b The effective crosslinking density

Network Structure of PAA-Fe³⁺ Hydrogels

In order to distinguish and understand the influence of the cross-links type on hydrogel network structure and properties, the mechanical properties of only hydrogen bonds singly cross-linked linear PAA (L-PAA) gels and the ternarily cross-linked PAA-vinyl silica nanoparticles (VSNPs)-Fe³⁺ nanocomposite physical hydrogels as controls are compared with those of the dually cross-linked PAA-Fe³⁺ hydrogels. The three kinds of hydrogels show remarkable difference in mechanical properties as shown in Fig. 3(a) as a result of different cross-links types. The strength of the L-PAA gel is only 9.8 kPa because that the gel is cross-linked only by weak hydrogen bonds with low energy-dissipating efficiency. Under deformation, the hydrogen bonds are easy to break and the linear PAA chains slide under stress. Further, it is obvious that the PAA-Fe³⁺ gel shows greatly improved mechanical performance compared with the L-PAA gel. The reason is that the two kinds of dynamic bonds in PAA-Fe³⁺ gel have hierarchical bond energy and exhibit synergistic effect on the strengthening of hydrogels. During deformation, the hydrogen bonds and a part of ionic bonds break to dissipate more energy, while some of the ionic bonds can sustain the stress to maintain the configuration of the gel network. As a result, the PAA-Fe³⁺ gel shows a remarkable improvement in tensile strength of 504 kPa. Moreover, in PAA-VSNPs-Fe³⁺ gel, the polymer chain grafted VSNPs act as analogous covalent cross-links and homogenize the stress distribution as transferring centers, while hydrogen bonds and ionic bonds break to dissipate much more energy^[19]. The synergy of the ternary crosslinking points in the single network endows PAA-VSNPs-Fe³⁺ gel with superior mechanical properties, and its tensile strength is increased up to 862 kPa. In order to distinguish the role of hierarchical bonds in MBN gels and understand their synergistic effects, simulation models are employed to estimate the tensile properties of these three kinds of MBN gels.

In the PAA-Fe³⁺ hydrogels, two kinds of dynamic interactions can contribute to the energy dissipation. Based on the earlier research of Creton^[44], the Upper Convected Maxwell (UCM) model, classically used in fluid mechanics to describe the flow of viscoelastic fluids, can describe the viscoelasticity and reversibility of the dynamic cross-linked network; the GENT strain hardening model for the elastic deformation of rubber network

is appropriate to describe the devotion to mechanical properties of strong chemical cross-links which act as the permanent crosslinking points in the hydrogel network. Due to the relative independence of different crosslinking points and the synergy of all kinds of crosslinking points in a single network, a parallel combination of the UCM elements describing different dynamic cross-links and the GENT element describing the permanent cross-link is used to describe the large-scale deformational behavior of the hydrogel. Therefore, a parallel combination of two UCM elements should be used to describe the integrated contribution to the mechanical properties of the hydrogen bonds and ionic bonds in the PAA-Fe³⁺ hydrogels (Fig. 4). Here the L-PAA hydrogels are only cross-linked by hydrogen bonds, while PAA-VSNPs-Fe³⁺ hydrogels contain hydrogen bonds, ionic cross-links and the silica nanoparticles which act as analogous covalent cross-links^[19]. So the tensile properties of L-PAA hydrogels and PAA-VSNPs-Fe³⁺ hydrogels can be fitted by single UCM model and UCM1 + UCM2 + GENT model, respectively, as shown in Fig. 4.

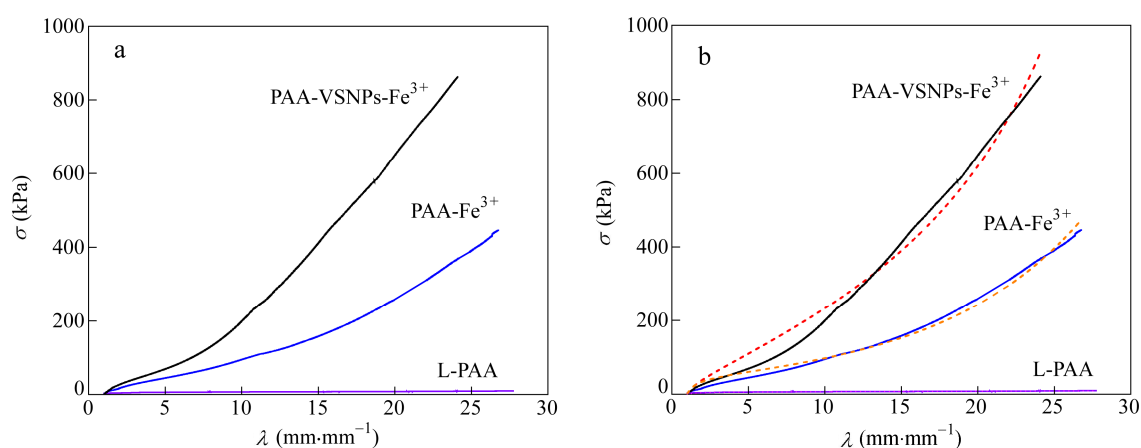


Fig. 3 (a) The tensile stress-strain curves and (b) the comparison of fitting curves (dotted) and experiment curves (solid) of L-PAA hydrogel, PAA-Fe³⁺ hydrogel and PAA-VSNPs-Fe³⁺ hydrogel

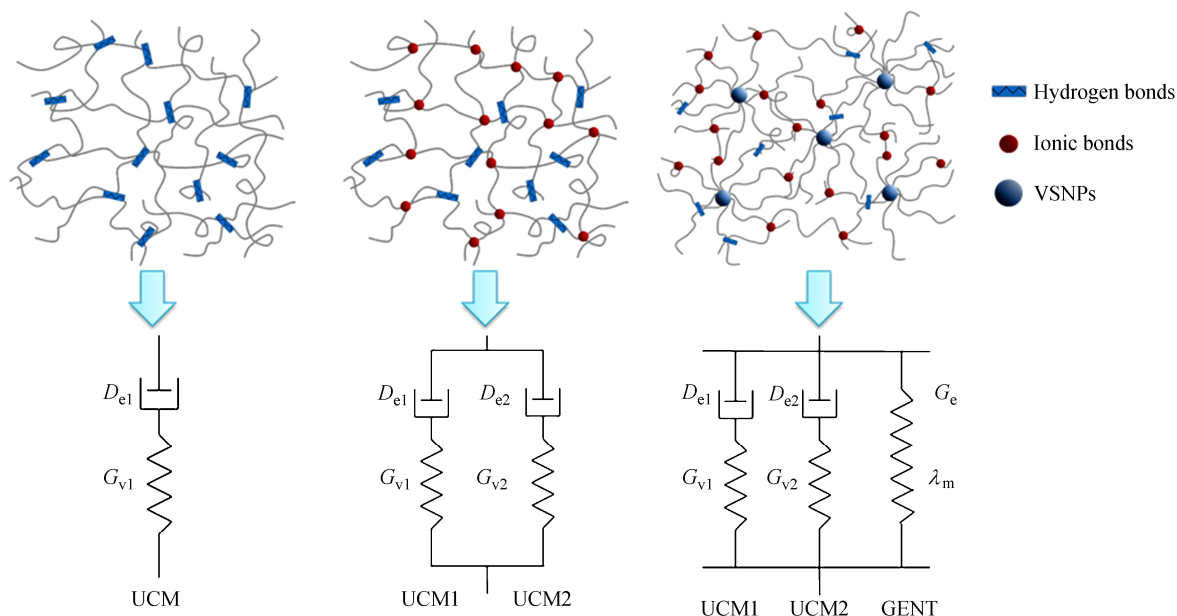


Fig. 4 Different kinds of hydrogel networks corresponding to different models

In the UCM1 + UCM2 model, the UCM1 element and UCM2 element are utilized to describe the contributions to the stress from hydrogen bonds $\sigma_{v1}(\lambda)$ and ionic bonds $\sigma_{v2}(\lambda)$ which act as energy-dissipation units. In the UCM1 + UCM2 + GENT model, the added GENT unit describes the contributions of the vinyl silica nanoparticles (VSNPs) as quasi-permanent crosslinking points. Here G_v and D_e are the initial modulus and the Deborah number of viscoelastic part. G_e is the small-strain shear modulus of GENT element and λ_m is maximum allowable value of the first strain invariant. The nominal stress σ can be calculated by the following equations.

$$\sigma(\lambda) = \sum_{i=1}^n \sigma_{vi}(\lambda), \quad n = 2 \quad (2)$$

where,

$$\sigma_{vi}(\lambda) = \frac{2G_{vi}D_{ei}}{1-2D_{ei}} \left(1 - \exp \left(-\frac{1-2D_{ei}}{D_{ei}} (\lambda-1) \right) \right) \lambda^{-1} + \frac{G_{vi}D_{ei}}{1+D_{ei}} \left(1 - \exp \left(-\frac{1+D_{ei}}{D_{ei}} (\lambda-1) \right) \right) \lambda^{-1} \quad (3)$$

In UCM1 + UCM2 + GENT model,

$$\sigma(\lambda) = \sum_{i=1}^n \sigma_{vi}(\lambda) + \sigma_e(\lambda), \quad n = 2 \quad (4)$$

where $\sigma_{vi}(\lambda)$ is the stress of UCM i unit as defined in Eq. (3), and $\sigma_e(\lambda)$ is defined in Eq. (5)

$$\sigma_e(\lambda) = \frac{G_e(\lambda^2 - \lambda^{-1})}{1 - \frac{\lambda^2 + 2\lambda^{-1} - 3}{\lambda_m^2 + 2\lambda_m^{-1} - 3}} \lambda^{-1} \quad (5)$$

Based on the models, fitting Eq. (2) or Eq. (4) to the tensile test data can allow us to determine the parameters in the equations. The fitting results show that the three different models can forecast the correct trends of stress with increasing strain of three different kinds of hydrogels with different combination of cross-links: cross-linked only by hydrogen bonds, cross-linked by ionic bonds and hydrogen bonds, or cross-linked by the above two dynamic interactions and quasi-permanent cross-links (Fig. 3b and Table 2).

Table 2 Comparison of deduced results of different kinds of gel networks

Gel type	Model	G_{v1}	G_{v2}	D_{e1}	D_{e2}	G_e	λ_m	G_{v1}/G_{v2}	G_v/G_e	R^2
PAA-Fe ³⁺	UCM1 + UCM2	1.316	26.135	0.536	0.536	—	—	0.050	—	0.992
PAA-VSNPs-Fe ³⁺	UCM1 + UCM2 + GENT	1.301	7.670	0.564	0.564	16.496	34.111	0.170	0.544	0.989
L-PAA	UCM	3.367	—	0.506	—	—	—	—	—	0.982

It is obvious that good curve fittings can be obtained, and the values of the parameters picked up from the fitting curves are exhibited in Table 2. The network of the L-PAA gel is constructed *via* hydrogen bonds and chain entanglements, so the L-PAA gels show the biggest G_{v1} . As for PAA-Fe³⁺ hydrogels, the addition of ferric ions leads to the formation of strong carboxyl-Fe³⁺ ionic bonds. Through the process of break-recombination, the ionic bonds dissipate a lot of energy, and some amount of ionic cross-links act as the quasi-permanent cross-links to distribute stress, so the PAA-Fe³⁺ hydrogels show the biggest G_{v2} , and the contribution to the modulus from the hydrogen bonds is less than that from ionic bonds. With the addition of VSNPs, free radical grafting polymerization initiated at the vinyl groups on the surface of VSNPs results in the formation of nanobrush gelators. When the physical cross-links, *i.e.* ionic interactions, have been established, the VSNPs will act as multivalent covalent cross-linking points, called analogous crosslinking points^[18, 19, 23, 24]. The increase of analogous crosslinking points leads to the increase of quasi-permanent crosslinking points. As a result, the contribution to modulus of analogy cross-links G_e is larger than the summation of the physical cross-links?

contribution to modulus G_v . And VSNPs take the role of distributing stress, leading to the decrease of the contribution to modulus of ionic bonds, and VSNPs also hinder the movement of polymer chains, resulting in less ionic cross-links compared with PAA-Fe³⁺ hydrogels. As a result, PAA-VSNPs-Fe³⁺ hydrogels exhibit smaller G_{v2} . The fitting results show that different combination of various types of cross-links endows hydrogels with different network structures as well as multiple mechanically strengthening mechanism. All in all, multi-bond network system containing reversible bonds with hierarchical bond energy helps to build an effective energy-dissipation mechanism and enhance the toughness of hydrogels.

In the PAA-Fe³⁺ hydrogels, the varying number of ionic bonds has a deep influence on the number of crosslinking points. The tensile curves of the hydrogels with different ferric ion concentrations are fitted by the UCM1 + UCM2 model, and a series of parameters and their change regularity depending on the variation in ferric ion concentration come out and are shown in Fig. 5 and Table 3. Utilizing the UCM1 + UCM2 model, the fitting results of the hydrogels with different ferric ion concentration $c_{\text{Fe}^{3+}}$ are much close to experimental data. With increasing $c_{\text{Fe}^{3+}}$, the contribution to the modulus of hydrogen bonds shows a little decrease owing to the formation of the competitive ionic bonds. G_{v2} shows a remarkable increase with increasing $c_{\text{Fe}^{3+}}$, but decrease when $c_{\text{Fe}^{3+}}$ is 1 mol%. We assume that the decrease in molecular weight degrades the formation of ionic crosslinking points. As a result, the contribution to modulus of ionic cross-links decreases and the G_{v1}/G_{v2} increases.

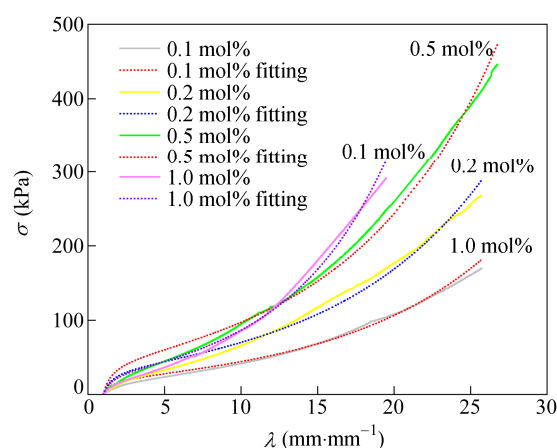


Fig. 5 Curve fitting results of PAA-Fe³⁺ hydrogels with different Fe³⁺ concentrations compared with test data

Table 3 The curve fitting results of PAA-Fe³⁺ hydrogels with different ferric ion concentrations

$c_{\text{Fe}^{3+}}$ (mol%)	G_{v1}	G_{v2}	D_{v1}	D_{v2}	G_{v1}/G_{v2}	R^2
0.1	1.279	11.606	0.535	0.535	0.110	0.995
0.2	1.200	19.149	0.535	0.535	0.063	0.988
0.5	1.316	26.135	0.536	0.536	0.050	0.992
1.0	0.903	17.153	0.552	0.552	0.053	0.992

Self-healing of PAA-Fe³⁺ Hydrogels

Supramolecular interactions can not only improve the mechanical properties of hydrogels but also endow hydrogels with self-healing ability. As shown in Fig. 6, a cut off disc-like PAA-Fe³⁺ hydrogel is exhibited (Fig. 6a) and it can be completely self-healed automatically at 50 °C after 2 h without any visible healed interface (Fig. 6b). At ambient temperature, after the hydrogel was healed for 2 h, it is observed that the gel is strong enough to sustain stretching (Figs. 6c and 6d). This phenomenon exhibits the rapid self-healing rate of PAA-Fe³⁺ hydrogel. Without adding any healing agents, by simply keeping two cut off samples of the hydrogels in contact with each other at the cut off surfaces for a period of time, the hydrogels can realize self-healing to a

certain extent. To investigate the self-healing properties quantitatively, tensile tests are performed to measure the mechanical properties of healed cylindrical gel samples in comparison to the as-prepared gels, and the self-healing efficiency (η_σ or η_ε) is defined by the ratio of tensile strength (σ_h) or elongation at break (ε_h) of the healed gels to that of as-prepared gels (σ_p or ε_p). As shown in Figs. 7(a) and 7(b), the healing efficiency is influenced by healing time and temperature. At a certain temperature, with the increase of healing time, the long polymer chains and ferric ions diffuse across the interface and form new ionic interaction between ferric ions and polymer chains in the contacted surfaces of the cut off cylindrical gel samples, leading to the recombination of the gel network in the interface. As a result, the healing efficiency increases along with lapsing time. Representatively, at 25 °C after healing for 48 h, the η_σ of PAA-Fe³⁺ gels reaches 87%. Moreover, the rising temperature promotes the self-healing of hydrogels, because the mutual diffusion of PAA chains and Fe³⁺ ions is accelerated by higher temperature. It is worth noting that complete self-healing (100% recovery of tensile strength) is achieved by maintaining for 48 h at 50 °C. Even at 4 °C, hydrogels can realize self-healing ability but the rate of self-healing is lower remarkably.

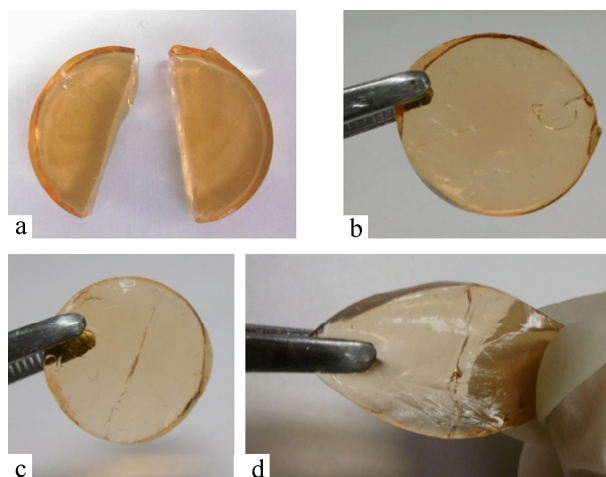


Fig. 6 Self-healing of PAA-Fe³⁺ hydrogels: (a) round shaped F5 gel cut into two part, (b) F5 gel self-healing at 50 °C for 2 h, (c) F5 gel self-healing at 25 °C for 2 h with visible healed interface and (d) the gel sustaining stretching (The online version is colorful.)

The composition of hydrogels is also a significant influencing factor on the self-healing of PAA-Fe³⁺ gels. The dependence of η_σ and η_ε (hydrogels are healed at 50 °C for 18 h) on ferric ion concentration and polymer content is illustrated in Figs. 7(c) and 7(d). The self-healing efficiency of PAA-Fe³⁺ hydrogels is improved with increasing ferric ions, but when the ferric ions exceed 1 mol%, the self-healing efficiency is weakened. When the ferric ion concentration increases from 0.1 mol% to 1 mol%, the self-healing efficiency of hydrogels is improved from 52% to 100% at the same self-healing conditions (time and temperature). The acceleration effect of ferric ion concentration on the self-healing ability of gels lies in the following two aspects. Firstly, the diffusion of ferric ions is an important part of self-healing progress and will be enhanced by increasing the ferric ion concentration. In addition, the polymer chains at the two cut off surfaces diffusing into each other may have more probability to interact with ferric ions at high ferric ion concentration. As a result, the mechanical properties of interface are improved. However, excessive ferric ions may restrict the movement of long polymer chains. And the molecular weight of PAA decreases when ferric ion concentration is over 1.0 mol%, and the shorter PAA chains cannot diffuse deeper at the interface. Polymer content also affects the self-healing ability of hydrogels remarkably. Since the increase of polymer content means the decrease of water content and the increase of crosslinking density, the motion of polymer chains is hindered. Therefore, the healing efficiency decreases rapidly with increasing polymer content at the same healing conditions (Fig. 7d).

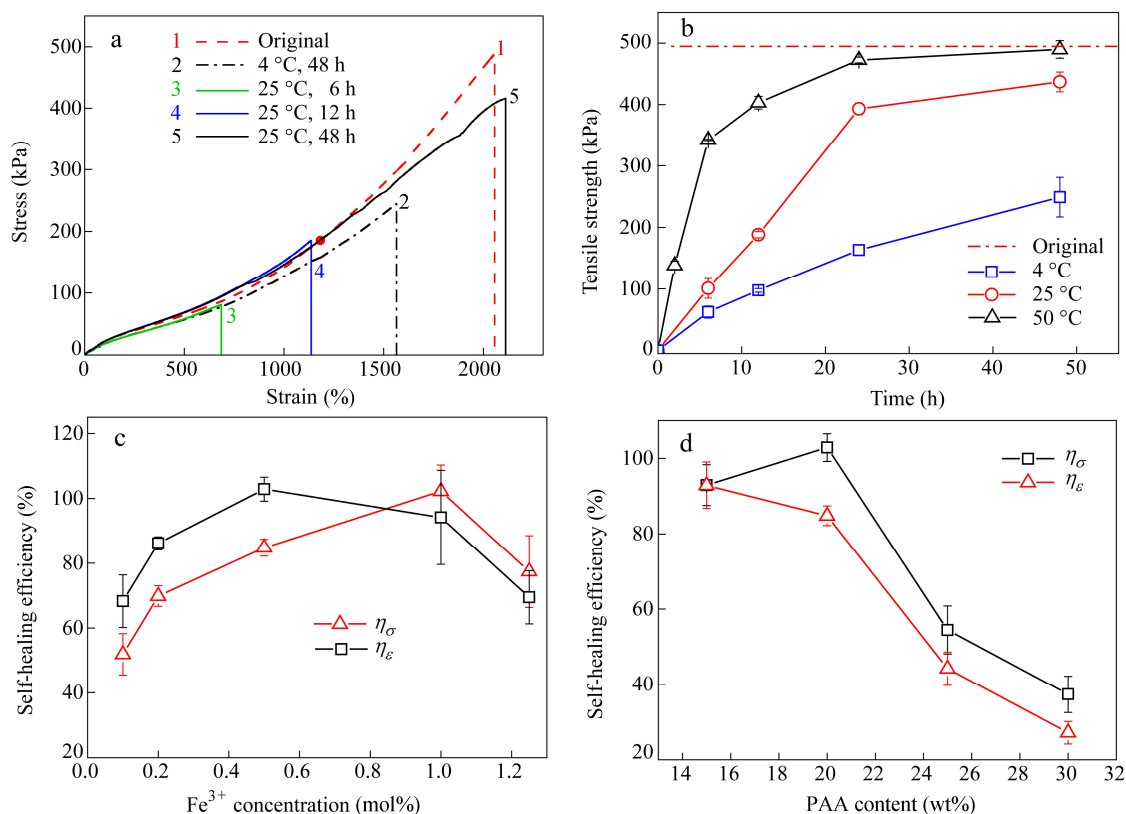


Fig. 7 Effects of self-healing condition (time and temperature) and hydrogel composition on the self-healing of PAA-Fe³⁺ hydrogels: (a) stress-strain curves of original and self-healed F5 hydrogels from once-separated gels healed at 25 °C for 6, 12 and 48 h or 4 °C for 48 h and (b) effects of time and temperature on the tensile strength of self-healed PAA-Fe³⁺ hydrogels; Effects of hydrogel composition on the self-healing of PAA-Fe³⁺ hydrogels: (c) the Fe³⁺ concentrations and (d) PAA contents

The self-healing capability of PAA-Fe³⁺ hydrogels can be attributed to the unique dually cross-linked dynamic MBN structure. The characteristics of self-healing are summarized as follows. (1) The linear polymers are cross-linked only by the dynamic physical interactions including ionic bonds and hydrogen bonds, which leads to lesser block in the movement of polymer chains compared to the chemical cross-linked hydrogels, even some physical cross-linked nanocomposite hydrogels. For example, the self-healing capability of the PAA-Fe³⁺ hydrogels is better than that of ternarily cross-linked PAA-VSNPs-Fe³⁺ nanocomposite physical hydrogels, which is reported earlier by our group^[19]. The VSNPs as analogous covalent cross-linking points are successful transfers of force and delay crack propagation. However, the VSNPs also lead to the sacrifice in the moving ability of polymer chains. The increasing VSNPs content leads to the enhancement of mechanical properties but the decrease in self-healing rate. This phenomenon has also been observed in GO composite gels and nanocomposite gels^[27, 33, 35]. However, for the PAA-Fe³⁺ hydrogels, when the ferric ion concentration is less than 1 mol%, the self-healing rate and mechanical strength increase with increasing ferric ion concentration. (2) Besides the mutual diffusion of long polymer chains which exists necessarily in the self-healing of abundant hydrogels with supramolecular interactions, there is another important physical process in the self-healing of the ionic hydrogels—the diffusion of ferric ions. Because of the carboxyl-Fe³⁺ ionic interaction, the diffusion of ferric ions may have a complex effect on the diffusion of polymer chains, and as a result, self-healing will be accelerated when the diffusion of ferric ions is enhanced.

In order to prove acceleration of ferric ion diffusion, two cylindrical samples of hydrogels with different ferric ion concentrations (0.2 mol% and 0.5 mol%) and the same polymer content (20 wt%) are put together at

the cut off surfaces and healed at 50 °C. The healed hydrogels obtained by this way are referred to as hetero-Fe³⁺ concentration hydrogels. As shown in Fig. 8, after healing for 12 h, the hydrogels can be knotted (Fig. 8b) and stretched to approximately 2000% strain (Fig. 8c), and the diffusion of ferric ions from high-concentration cylindrical sample to low-concentration cylindrical sample could be clearly observed from the magnification of the interface (Fig. 8c). The time-dependent self-healing properties of the hetero-Fe³⁺ concentration hydrogels have been discussed compared with the corresponding homo-Fe³⁺ concentration hydrogels with the same ferric ion concentration as one cylindrical sample of the hetero-Fe³⁺ concentration hydrogels. Figure S5 (in SI) shows the stress-strain curves of F2F5 (hetero-Fe³⁺ concentration hydrogels composed of F2 and F5 gel samples), F2F2 and F5F5 (homo-Fe³⁺ concentration hydrogels) hydrogels self-healed under the same conditions (50 °C, 24 h). As shown in Fig. S5 (in SI), the stress-strain curve of F2F5 hydrogels also has inversive S-shape which is the same as those of F2F2 and F5F5 gels, indicating the synergetic deformation of the hydrogel network. Because of the lower modulus of F2 cylindrical sample in the hetero-Fe³⁺ concentration hydrogels, F2 cylindrical sample exhibits larger deformation than F5 cylindrical sample, and hydrogels will break at F2 cylindrical sample after self-healing for enough time, indicating the stronger mechanical properties of the interface compared to F2 cylindrical sample. After healing for more than 18 h, the F2F5 hydrogels break in the F2 rod and reach the tensile strength of as-prepared F2 gels. Figure 8(d) displays the tensile strength σ_t -healing time t curves of the healed F2F5, F2F2 and F5F5 hydrogels. All the curves rise to approach the maximum, and for the homo-Fe³⁺ concentration hydrogels the maximum is the tensile strength of as-prepared hydrogels, whereas, for hetero-Fe³⁺

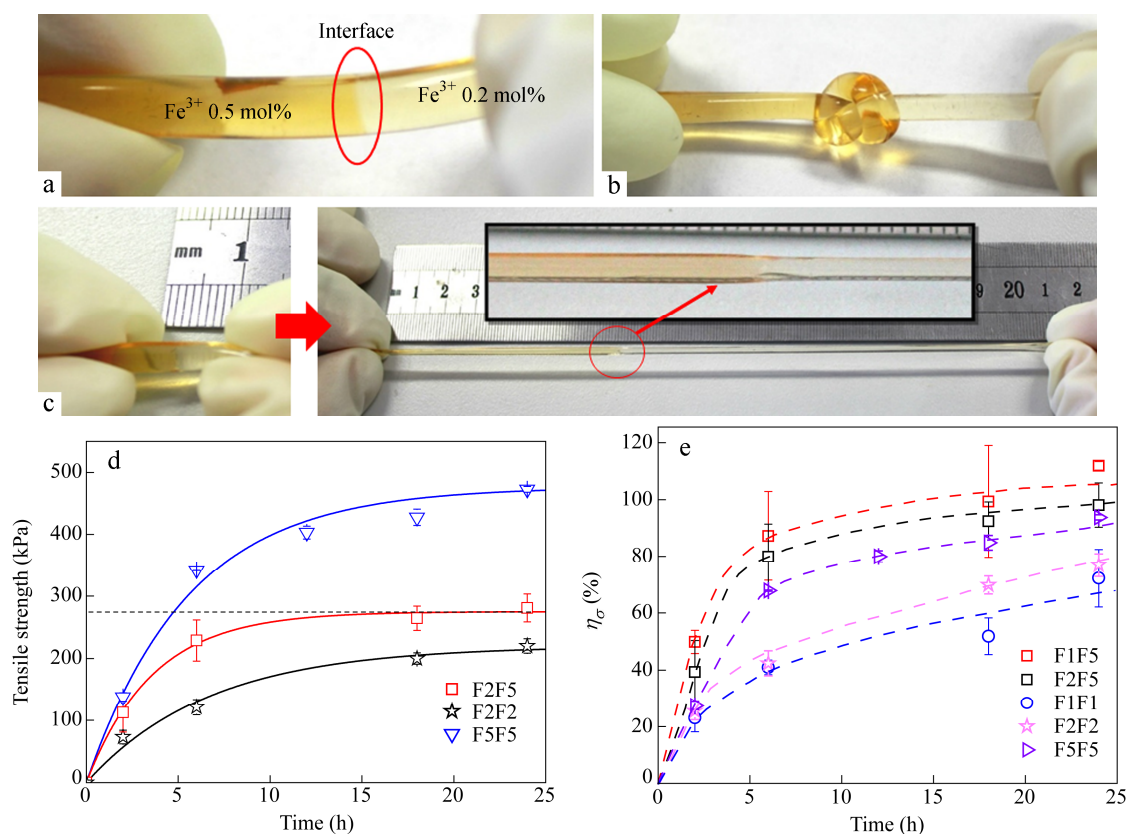


Fig. 8 Self-healing of the hetero-Fe³⁺ concentration hydrogels: (a) the photographs of F2F5 hetero-Fe³⁺ concentration hydrogels composed of F2 and F5 gels, where cut off surfaces are brought into contact at 50 °C for 18 h; (b, c) the mechanical properties of the hetero-Fe³⁺ concentration hydrogels for (b) knotting and (c) stretching to approximately 20 times of F2F5 gels (The magnifying picture was the interface of F2F5 gel); (d) the tensile strength of F2F5, F2F2 and F5F5 (homo- Fe³⁺ concentration hydrogels) hydrogels as a function of healing time at 50 °C; (e) the self-healing efficiency (η_σ) of F1F5, F2F5, F1F1, F2F2 and F5F5 hydrogels depending on healing time (The online version is colorful.)

concentration hydrogels the maximum is approximately the tensile strength of as-prepared hydrogels with the lower ferric ion concentration. Noticeably, the F2F5 needs less time to reach the supreme σ_h , indicating that the self-healing rate of the hetero- Fe^{3+} concentration hydrogels is higher than that of the homo- Fe^{3+} concentration hydrogels (Fig. 8d). Both the hetero- Fe^{3+} concentration hydrogels and the homo- Fe^{3+} concentration hydrogels could reach the equilibrium supreme σ_h after self-healing for a period of time. Thus it will be reasonable to compare the self-healing efficiency (η_σ) of hydrogels which is the ratio of tensile strength of healed hydrogels to the supreme σ_h . As shown in Fig. 8(e), the initial slope of the self-healing efficiency η_σ versus time curve of F1F5 (hetero- Fe^{3+} concentration hydrogels composed of F1 and F5 gel samples) is the highest among the hydrogels, and the slope of F2F5 ranks the second. The time to realize complete self-healing of F1F5 gels is less than that of F2F5 gels owing to the bigger ion concentration gradient. The hetero- Fe^{3+} concentration hydrogels can achieve higher self-healing efficiency than the homo- Fe^{3+} concentration hydrogels under the same healing conditions, and self-healing will be accelerated by ion concentration gradients. This phenomenon demonstrates that the acceleration in diffusion of ferric ions may promote the mutual diffusion of long polymer chains and the self-healing of hydrogels.

Thus, the self-healing mechanism of the hetero- Fe^{3+} concentration hydrogels can be proposed as shown in Fig. 9. Hetero- Fe^{3+} concentration hydrogels are composed of two cylindrical samples with different Fe^{3+} concentrations. As the time lapses, the Fe^{3+} concentration gradients at the contact cut off surfaces of the hetero- Fe^{3+} concentration hydrogels lead to the acceleration of ferric ions diffusion from the higher Fe^{3+} concentration gel sample to lower Fe^{3+} concentration gel sample. Along with mutual diffusion of the polymer chains and ferric ions, reformed cross-linking points around the interface appear. And the interface contains more ionic cross-links compared with cylindrical sample with lower Fe^{3+} concentration and shows stronger mechanical strength. The self-healing mechanism of the hetero- Fe^{3+} concentration hydrogels reveals the promising effects of ion concentration gradients which can accelerate the self-healing and improve the mechanical properties of interface.

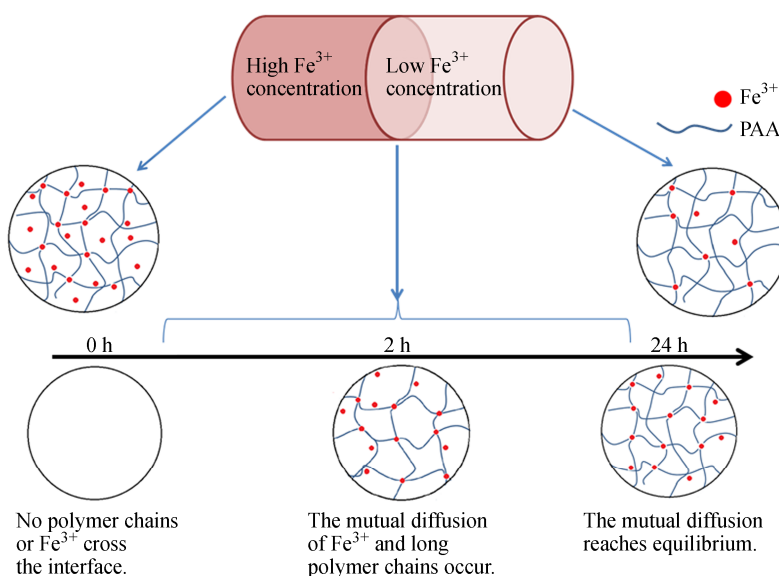


Fig. 9 Self-healing mechanism of the hetero- Fe^{3+} concentration hydrogels

CONCLUSIONS

In summary, the tough and completely self-healable physical MBN gels by *in situ* polymerization of acrylic acid with ferric ions as ionic cross-linkers are successfully synthesized by a facile one-pot method. The dynamic dually cross-linked hydrogels have tensile strength of ~ 500 kPa, elongation at break of $\sim 2400\%$ and can completely self-heal by simple contact of the cut off surfaces at 50°C . To compare the dually cross-linked

hydrogel with singly and ternarily cross-linked hydrogels, the roles of different cross-links with hierarchical bond energy in the MBN are revealed. The tensile data of these three kinds of hydrogels fitted by parallel models demonstrate that the strengthening mechanism of MBN hydrogels could be attributed to the different roles of cross-links and their synergy, that is, the hierarchical dynamic cross-links with different bond energy can successively break to gradually dissipate energy from the weaker bonds and then recombine to form homogenized network, while the strong cross-links such as analogy cross-links can homogenize the stress as transferring center. The dynamic ionic interaction can play the vital role in self-healing mechanism of the gels, and the ferric ion concentration gradients at the contacted cut off surfaces in the hetero-Fe³⁺ concentration gel system can accelerate the self-healing rate of the gels. We anticipate that the combination of excellent mechanical properties, self-healing abilities and the facile synthetic strategy can contribute to the potential applications of PAA-Fe³⁺ hydrogels in biomedical and engineering fields, and the MBN strategy can contribute to the innovation of tough and robust hydrogels.

REFERENCES

- 1 Vermonden, T., Censi, R. and Hennink, W.E., *Chem. Rev.*, 2012, 112(5): 2853
- 2 Collier, J.H., *Soft Matter*, 2008, 4(12): 2310
- 3 Dankers, P.Y.W., Harmsen, M.C., Brouwer, L.A., van Luyn, M.J.A. and Meijer, E.W., *Nat. Mater.*, 2005, 4(7): 568
- 4 Lee, K.Y. and Mooney, D.J., *Chem. Rev.*, 2001, 101(7): 1869
- 5 Buenger, D., Topuz, F. and Groll, J., *Prog. Polym. Sci.*, 2012, 37(12): 1678
- 6 Liang, D., Agarwal, A.K., Beebe, D.J. and Hongrui, J., *Nature*, 2006, 442(7102): 551
- 7 Erdodi, G. and Kennedy, J.P., *Prog. Polym. Sci.*, 2006, 31(1): 1
- 8 Sakai, T., Matsunaga, T., Yamamoto, Y., Ito, C., Yoshida, R., Suzuki, S., Sasaki, N., Shibayama, M. and Chung, U., *Macromolecules*, 2008, 41(14): 5379
- 9 Okumura, Y. and Ito, K., *Adv. Mater.*, 2001, 13(7): 485
- 10 Naghash, H.J. and Okay, O., *J. Appl. Polym. Sci.*, 1996, 60(7): 971
- 11 Gong, J.P., *Soft Matter*, 2010, 6(12): 2583
- 12 Malkoch, M., Vestberg, R., Gupta, N., Mespouille, L., Dubois, P., Mason, A.F., Hedrick, J.L., Liao, Q., Frank, C.W., Kingsbury, K. and Hawker, C.J., *Chem. Commun.*, 2006(26): 2774
- 13 Ito, K., *Polym. J.*, 2007, 39(6): 489
- 14 Gong, J.P., Katsuyama, Y., Kurokawa, T. and Osada, Y., *Adv. Mater.*, 2003, 15(14): 1155
- 15 Haraguchi, K., Takehisa, T. and Fan, S., *Macromolecules*, 2002, 35(27): 10162
- 16 Yang, J., Wang, X.P. and Xie, X.M., *Soft Matter*, 2012, 8(4): 1058
- 17 Liu, J.Q., Chen, C.F., He, C.C., Zhao, J., Yang, X.J. and Wang, H.L., *ACS Nano*, 2012, 6(9): 8194
- 18 Shi, F.K., Wang, X.P., Guo, R.H., Zhong, M. and Xie, X.M., *J. Mater. Chem. B*, 2015, 3(7): 1187
- 19 Zhong, M., Liu, X.Y., Shi, F.K., Zhang, L.Q., Wang, X.P., Cheetham, A.G., Cui, H.G. and Xie, X.M., *Soft Matter*, 2015, 11(21): 4235
- 20 Tuncaboylu, D.C., Argun, A., Sahin, M., Sari, M. and Okay, O., *Polymer*, 2012, 53(24): 5513
- 21 Huang, T., Xu, H.G., Jiao, K.X., Zhu, L.P., Brown, H.R. and Wang, H.L., *Adv. Mater.*, 2007, 19(12): 1622
- 22 Sun, J., Zhao, X., Illeperuma, W.R.K., Chaudhuri, O., Oh, K.H., Mooney, D.J., Vlassak, J.J. and Suo, Z., *Nature*, 2012, 489(7414): 133
- 23 Zhong, M., Shi, F.K., Liu, Y.T., Liu, X.Y. and Xie, X.M., *Chinese Chem. Lett.*, 2016, 27(3): 312
- 24 Shi, F.K., Zhong, M., Zhang, L.Q., Liu, X.Y. and Xie, X.M., *J. Mater. Chem. B*, 2016, 4(37): 6221
- 25 Zhang, L.Q., Chen, L.W., Zhong, M., Shi, F.K., Liu, X.Y. and Xie, X.M., *Chinese J. Polym. Sci.*, 2016, 34(10): 1261
- 26 Shi, F.K., Zhong, M., Zhang, L.Q., Liu, X.Y. and Xie, X.M., *Acta Polymerica Sinica (in Chinese)*, 2017, (3): 491
- 27 Zhong, M., Liu, Y.T. and Xie, X.M., *J. Mater. Chem. B*, 2015, 3(19): 4001
- 28 Zhong, M., Liu, Y.T., Liu, X.Y., Shi, F.K., Zhang, L.Q., Zhu, M. and Xie, X.M., *Soft Matter*, 2016, 12(24): 5420

- 29 Taylor, D.L. and Panhuis, M.I.H., *Adv. Mater.*, 2016, 28(41): 9060
- 30 Phadke, A., Zhang, C., Arman, B., Hsu, C., Mashelkar, R.A., Lele, A.K., Tauber, M.J., Arya, G. and Varghese, S., *Proc. Natl. Acad. Sci.*, 2012, 109 (12): 4383
- 31 Dai, X.Y., Zhang, Y.Y., Gao, L.N., Bai, T., Wang, W., Cui, Y.L. and Liu, W.G., *Adv. Mater.*, 2015, 27(23): 3566
- 32 Tuncaboylu, D.C., Sahin, M., Argun, A., Oppermann, W. and Okay, O., *Macromolecules*, 2012, 45(4): 1991
- 33 Haraguchi, K., Uyama, K. and Tanimoto, H., *Macromol. Rapid Commun.*, 2011, 32(16): 1253
- 34 Gao, G.R., Du, G.L., Sun, Y.N. and Fu, J., *ACS Appl. Mater. Interfaces*, 2015, 7(8): 5029
- 35 Liu, J.Q., Song, G.S., He, C.C. and Wang, H.L., *Macromol. Rapid Commun.*, 2013, 34(12): 1002
- 36 Zhang, H.J., Xia, H.S. and Zhao, Y., *ACS Macro Lett.*, 2012, 1(11): 1233
- 37 Bera, P. and Saha, S.K., *Polymer*, 1998, 39(6): 1461
- 38 Yoshizawa, S., Takehara, Z., Ogumi, Z. and Nagai, C., *J. Appl. Electrochem.*, 1976, 6(2): 147
- 39 Wei, Z., He, J., Liang, T., Oh, H., Athas, J., Tong, Z., Wang, C. and Nie, Z., *Polym. Chem.*, 2013, 4(17): 4601
- 40 Hernandez, S., Papp, J.K. and Bhattacharyya, D., *Ind. Eng. Chem. Res.*, 2014, 53(3): 1130
- 41 Zheng, S.Y., Ding, H., Qian, J., Yin, J., Wu, Z.L., Song, Y. and Zheng, Q., *Macromolecules*, 2016, 49(24): 9637
- 42 Zhao, X.H., *Soft Matter*, 2014, 10(5): 672
- 43 Sun, T.L., Kurokawa, T., Kuroda, S., Ihsan, A.B., Akasaki, T., Sato, K., Haque, M.A., Nakajima, T. and Gong, J.P., *Nat. Mater.*, 2013, 12(10): 932
- 44 Deplace, F., Rabjohns, M.A., Yamaguchi, T., Foster, A.B., Carelli, C., Lei, C., Ouzineb, K., Keddie, J.L., Lovell, P.A. and Creton, C., *Soft Matter*, 2009, 5(7): 1440