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Journal Name

ARTICLE

Rapid Formation of Highly Stretchable and Notch-insensitive Hydrogels

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Highly stretchable and notch-insensitive hydrogels was rapidly prepared by using redox initiators. The hydrogels had a large number of non-covalent crosslinking points, which come from hydrophobic side chains and metal ion coordination without any chemical crosslinking agents. The non-covalent crosslinking points in hydrogels were stochastic and dynamic, comparing to covalent crosslinking points. When the notched sample was stretched, the hydrophobic segments would contribute to elongation of hydrogels via molecular stretching. When the hydrogels had a notch, the new crosslinking points could be formed via metal ion coordination even some previous metal ion ligand bonds were destroyed. As a result, the sample notch was blunted, widened and merged into the edge gradually under the tensile stress. The hydrogels could be elongated up to 12 times its original length and show a notch-insensitive property. Moreover, the metal ion coordination interaction between the amide groups and Fe³⁺ was proved by flourier transform infrared spectroscopy (FTIR), the theological property and internal morphology of hydrogels were also measured with the different dosages of hydrophobic segments and metal ions. Spontaneously, it was envisioned that the non-covalent bonds would be possible to administer hydrogels with more unexpected properties.

Introduction

Hydrogels comprise a considerable amount of water and three-dimensional polymer networks as smart materials for biomedical applications in sensors,^{1,2} artificial muscles,³⁻⁵ drug delivery carriers,^{6,7} wound dressing,^{8,9} and model extracellular matrices.¹⁰ Moreover, other scientists focused on the applications of hydrogels from biomedicine to catalysis,¹¹ adsorption,^{12,13} electrochemistry,^{14,15} oil-water separation^{16,17} and so on. However, the poor mechanical property of hydrogels significantly limits the application range of hydrogels. For example, the pure polyacrylamide hydrogels with N,N'-methylenebisacrylamide as a chemical crosslinker exhibited a brittle fracture under the action of external forces. Therefore, many efforts have been focused on exploring new theories and improving the mechanical strength of hydrogels. These tough hydrogels include slide-ring hydrogels,^{18,19} double network hydrogels,^{20,21} organic-inorganic nano-composite

gels,^{22,23} macromolecular microsphere composite hydrogels,^{24,25} multi-armed hydrogels^{26,27} and hydrophobic association hydrogels.²⁸⁻³⁰ Although the mechanical strength of these hydrogels were significantly enhanced in compression or tensile tests, the hydrogels disrupted facily along the cracks and the strength decreases rapidly if there was a little notch or flaw in the bulk. As a result, the notch sensitivity of hydrogels obviously reduced their sustainability and reliability in the practical applications. Therefore, the notch-insensitive tough hydrogels had attracted great attention. Suo et al. reported an alginate-polyacrylamide hybrid hydrogels, which was formed by the combination of weak ionic effects and strong covalent crosslinking.³¹ Tong et al. reported a notch-insensitive nano-composite hydrogels, derived from the introduction of more hydrophilic acrylamide segments into clay-crosslinked copolymers.³² Moreover, Chen et al. reported a tough and notch-insensitive magnetic hydrogels which was dispersed alginate-coated Fe₃O₄ nanoparticles into the interpenetrating polymer networks of alginate and polyacrylamide.³³ These theories would greatly expand the application range of the hydrogels. However, the rapid formation of the notch-insensitive hydrophobic association hydrogels had been few reported.

Here, we reported the rapid formation of highly stretchable and notch-insensitive hydrogels by using redox initiation systems (Fe²⁺/K₂S₂O₈). The hydrogels was prepared by a free radical copolymerization of acrylamide (AAM) and hydrophobic vinyl groups. Sodium chloride and sodium dodecyl sulfate were added to increase the solubility of hydrophobic groups.²⁹ The crosslinking points of hydrogels were attributed to the

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combination effects of hydrophobic association and metal ion coordination. Moreover, the hydrogen bonds between amide groups in the hydrogels³⁴ and the entanglement of molecular chains were also conducive to crosslinking. These crosslinking points were dynamic, compared to the covalently crosslinking hydrogels. The hydrogels was formed immediately after adding ferrous chloride and exhibited the fantastic notch-insensitive and excellent mechanical property. Subsequently, the hydrogels was measured by the tensile test, rheological test, and scanning electron microscope (SEM) to investigate the influence on the mechanical property of the hydrogels with different concentrations of FeCl₂ and hydrophobic groups.

Materials and methods

Materials

Acrylamide (99.0%), N,N'-methylenebisacrylamide (97%), sodium dodecyl sulfate (SDS, $\geq 97\%$), potassium persulfate (99.5%), ferrous chloride tetrahydrate ($\geq 97\%$), methyl methacrylate (99.0%), butyl methacrylate (99.5%), sodium chloride (99.5%), lauryl methacrylate (96%) were supplied by Aladdin (Shanghai, China). Hexadecyl methacrylate (95%) was supplied by Zhejiang Kangde New Materials Co., Ltd, China. Deionized water (18.2 Ω cm resistivity at 25 °C) was used in the experiment.

The hydrophobic association hydrogels without the metal ion coordination

The hydrophobically modified polyacrylamide hydrogels was prepared by dissolving NaCl (0.32 g), SDS (0.8 g) at room temperature in deionized water (10 mL) by constant stirring. After obtain the transparent solution. The hexadecyl methacrylate (0.3g) was added into the solution and stirred for 3 h to make the hydrophobic groups disperse completely. When the hydrophobic group was fully dissolved, the KPS (0.01 g) and AAm (2g) were added into the beaker and stirred completely. Then, the solution was kept at 70 °C for 3 h and the hydrophobic association polyacrylamide hydrogels was formed.

The highly stretchable and notch-insensitive hydrophobic association hydrogels

The highly stretchable and notch-insensitive hydrophobic association hydrogels was synthesized by free radical copolymerization. For describing the synthesis process clearly, we give the detail for the preparation of hydrogels with hexadecyl methacrylate (15 wt% in AAm) and FeCl₂ (15 wt% in AAm):

Firstly, NaCl (0.32 g), SDS (0.8 g) and deionized water (10 mL) were added into the beaker and stirred for 2 h at room temperature to obtain the transparent solution. After that, hexadecyl methacrylate (0.3g) was added into the solution and stirred for 3 h to make the hexadecyl methacrylate disperse completely. Then KPS (0.01 g) and AAm (2g) were added into

the beaker and stirred completely. Finally FeCl₂ (0.007 g) was added into the solution to obtain the hydrogels immediately. The resulting samples would be analysed in the following tests. In the following, all samples of the following components were fixed: NaCl (0.32 g), SDS (0.8 g), deionized water (10 mL), KPS (0.01 g).

Chemical structure by FTIR

Fourier transform infrared spectroscopy (FTIR) was used to identify the metal ion coordination interaction between the amide groups and Fe³⁺. The samples of PAAm hydrogels and PAAm-co-Fe³⁺ hydrogels (The PAAm-co-Fe³⁺ hydrogels was obtained by immersing PAAm hydrogels in saturated solution of ferric chloride for 4 hours) with a weight of 1.5 mg were ground and dispersed in potassium bromide (KBr), followed by compression to form the sheet. FTIR spectra were obtained in the wave number range from 400 cm⁻¹ to 4000 cm⁻¹.

Mechanical property

In order to explore the mechanical property of hydrogels, the tensile test of hydrogels was carried out by a mechanical tester (SHIMADZU, model AGS-X, 100N, Japan). According to ASTM D638, dumbbell-shaped tensile samples were fixed with two tensile clamps at each end and elongated at a tensile rate of 40 mm/min. The tensile strength of each sample was analysed at least three times. Moreover, the samples were cut to 50% its original width for the notch tensile test.

Rheological measurement

The frequency sweep measurement was used to investigate the viscoelastic property of hydrogels. All the samples were tested using a rheometer (AR 2000ex TA America) with a parallel plate geometry (25 mm diameter rotating top plate), and plate-to-plate distance was 3 mm. The storage modulus (G') and loss modulus (G'') were recorded over the frequency range of 0.1~100 rad/s at 25 °C.

Morphology observation

The internal morphology of hydrogels was observed by Scanning Electron Microscope (SEM) (JSM 6510). The samples were first swollen for 12 h and freeze-dried in a freeze vacuum drier (FDU-2110, EYELA). Before measurement for SEM, all samples were sputtered with platinum. The magnification factor was 500 times

Results and Discussion

Design of highly stretchable and notch-insensitive hydrophobic association hydrogels

In this investigation, the redox initiation systems (Fe²⁺/K₂S₂O₈) were employed to initiate the polymerization for hydrogels. Comparing to the traditionally thermal initiation

systems, the redox initiation systems will release a large number of free radicals at low temperature immediately and enhance the formation velocity of hydrogels (Movie S1 in Support Information).³⁵ Moreover, with the increase of the concentration of FeCl_2 , the formation time of hydrogels decreased obviously. When the concentration of FeCl_2 in AAm was 0.55%, the formation time was only 8s at 25°C. In contrast, the formation time of hydrogels required several hours or even dozens of hours via other traditionally thermal initiation systems (Table 1).

Table 1. The formation time of hydrogels by redox initiation systems and other traditionally thermal initiation systems.

FeCl_2 (wt% in AAm)	Temperature (°C)	Forming time
0.25	25	19s
0.35	25	13s
0.45	25	10s
0.55	25	8s
---	25	24h ²⁸
---	50	12h ³⁰
---	65	6h ³⁶
---	70	3h ²⁵

The rapid formation hydrogels in the table contained water (10mL), NaCl (0.32g), SDS (0.8g), AAm (2g) and hexadecyl methacrylate (15 wt% in AAm).

During polymerization, the hydrophobic alkyl segments were also introduced into the side chains of PAAm, self-assembling into micelles as crosslinking points and the hydrophobic segments would contribute to elongation of hydrogels via molecular stretching.²⁸ Moreover, the Fe^{3+} ions, which were derived from KPS ($\text{K}_2\text{S}_2\text{O}_8$) and FeCl_2 as redox initiators, would be coordinated with the polyacrylamide (PAAm) as crosslinking points due to the complex effects between metal ions with unoccupied orbitals and amide groups with rich electrons. The hydrophobic association hydrogels exhibited notch-sensitive when the metal ions were removed from hydrogels (Figure 1A). Also, the hydrogels was not formed with only metal ions due to the weak effect of the metal ion coordination (Figure 1B). However, the hydrogels could be efficiently toughened owing to the effects of hydrophobic association and metal ion coordination. Moreover, the hydrogen bonds between amide in the hydrogels³⁴ and the entanglement of molecular chains were also conducive to crosslinking of hydrogels.

For demonstrating the metal ion coordination interaction between the amide groups and Fe^{3+} , the FTIR spectra of PAAm hydrogels and PAAm-co- Fe^{3+} hydrogels were measured and shown in Figure 2. The spectrum of PAAm-co- Fe^{3+} hydrogels exhibited a bending vibration peak 1571.03 cm^{-1} for N-H and a stretching vibration peak of 1640.41 cm^{-1} for C=O, comparing the spectrum of PAAm hydrogels. It indicates that the metal ion coordination interaction was occurred between amide groups and Fe^{3+} .

When the hydrogels with a notch was stretched in the tensile stress, the notch was gradually blunted, widened and merged into the edge. As a result, the notched hydrogels wasn't disrupted even it was stretched to the similar length as the original hydrogels, shown in Figure 3. The highly stretchable and notch-insensitive properties of hydrogels were attributed to the effects of hydrophobic association and metal

ion coordination. The non C-C covalently crosslinking PAAm hydrogels, different from C-C covalently crosslinking hydrogels, had the metal ion coordination and hydrophobic association as the temporary and dynamic crosslinking points. When the hydrogels was drawn in the tensile stress, the curly alkyl chains would slide and extend along with the deformation of micelles until the molecular chains disrupted. When the sample with a notch was stretched, the metal ions could form new crosslinking points with surrounding amide groups of polyacrylamide even some previous metal ion ligand bonds were destroyed. As a result, the hydrogels via effects of non C-C covalent bonds had highly stretchable and notch-insensitive properties. Even if there were several notches in the sample, the hydrogels still had a high tensile property.

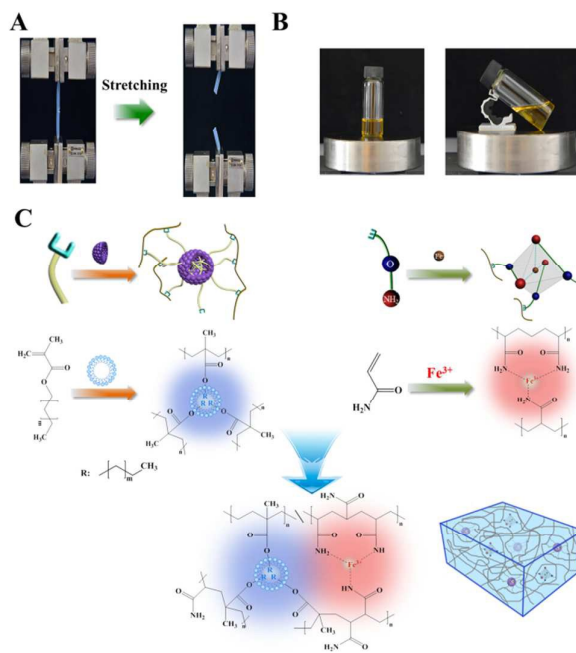


Figure 1. (A) the images for notch stretching of the hydrophobically modified PAAm hydrogels without the metal ion coordination (15 wt% hexadecyl groups in AAm); (B) the acrylamide solution with ferrous chloride (0.35 wt% FeCl_2 in AAm); (C) The schematic illustration of highly stretchable and notch-insensitive hydrophobic association hydrogels.

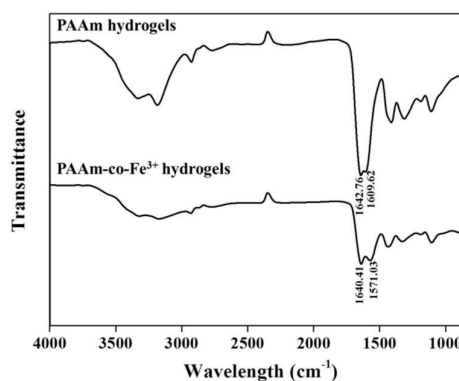


Figure 2. FTIR spectra of PAAm hydrogels and PAAm-co- Fe^{3+} hydrogels.

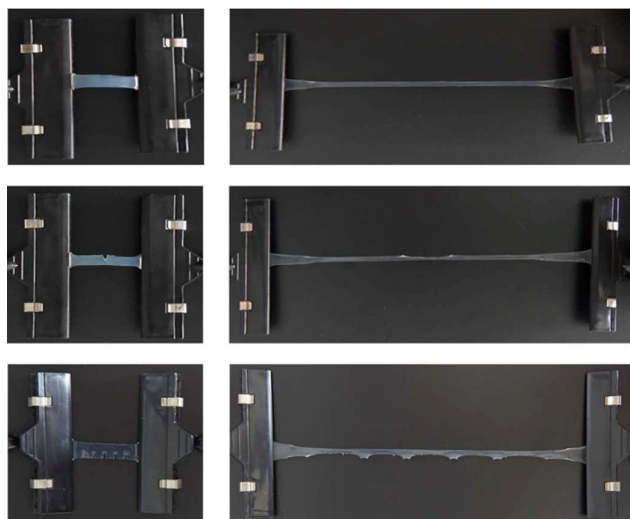


Figure 3. The images for notch stretching of PAAm hydrogels by the effects of hydrophobic association and metal ion coordination (0.35 wt% FeCl₂ in AAm, 15 wt% hexadecyl groups in AAm).

Effect of ferrous chloride (FeCl₂) on the properties of hydrogels

In this investigation, KPS and FeCl₂ was a couple of redox initiators. The Fe²⁺ would reduce the activation energy of KPS and release a large number of free radicals at room temperature, initiating monomers to form hydrogels immediately. Subsequently the transformed Fe³⁺, which came from Fe²⁺ of redox initiators, could coordinate with the PAAm as dynamic crosslinking points of hydrogels. Therefore, the properties of hydrogels were significantly influenced by different concentration of FeCl₂. It was found that when the concentration of FeCl₂ in acrylamide was lower than 0.25%, the hydrogels could not be formed due to the lower concentration of free radicals produced by the initiator. However, the hydrogels exhibited the maximum tensile strength when the concentration of FeCl₂ was appropriate 0.25%. With the concentration increase of Fe²⁺, the hydrogels exhibited the poor mechanical property in the stress-strain curves. When the concentration of FeCl₂ in AAm was 0.55%, the elongation was only 8 times and the sample disrupted after the tensile stress reached 26 KPa (Figure 4A), and the tensile stress of hydrogels with the notch exhibited the same trend (Figure 4B). But the notch insensitive property of hydrogels was enhanced with the concentration of FeCl₂ increasing (Figure 4C). The high concentration of Fe²⁺ ions produced the high concentration of free radicals immediately for the redox initiator in the reaction systems. The high concentration of free radicals would initiate the fast polymerization of AAm, subsequently, resulting in the short molecular chain for PAAm. The short PAAm segments would easily move and rearrange, and the high concentration of metal ions could enhanced the notch-insensitivity of hydrogels due to dynamic coordination effects. However, the short PAAm segments could not have the enough ability to curl over and entangle, inducing the toughness decrease of hydrogels.

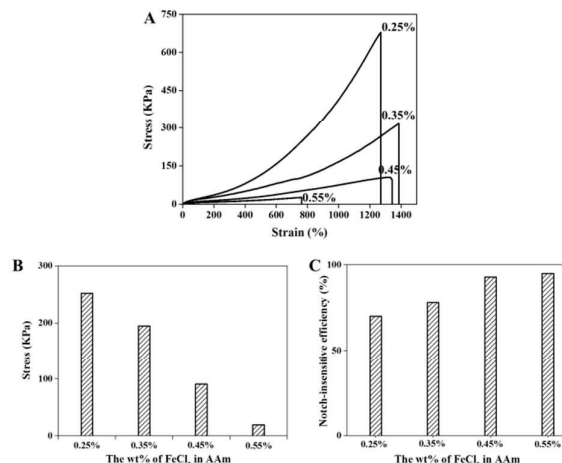


Figure 4. The mechanical property of hydrogels with different concentrations of FeCl₂ (the mass fraction is calculated by FeCl₂ / AAm × 100%): (A) the stress-strain curves of hydrogels without a notch; (B) the tensile stress of hydrogels with a notch. All samples had 15 wt% hexadecyl methacrylate groups in AAm; (C) the notch-insensitive property of hydrogels (the notch-insensitive property is the elongation of hydrogels with a notch / the elongation of hydrogels without a notch × 100%). All samples had 15 wt% hexadecyl methacrylate groups in AAm.

The viscoelasticity of hydrogels with different concentrations of FeCl₂ was shown in Figure 6. It was found that the hydrogels with higher concentration of FeCl₂ had lower storage modulus (G'), despite the loss modulus (G'') had little difference (Figure 5A). For the reaction systems with a low concentration of FeCl₂, the molecular weight of PAAm became high. That is, the longer molecular chains increased the entanglement between different chains as additional crosslinking, leading to a better elastic property of hydrogels and higher storage modulus (G'). Moreover, the loss factor (tanδ) of hydrogels exhibited a trend of decline with the increase of shear frequency (Figure 5B). It may be due to the movement rate of molecular chains couldn't keep up with the shear frequency increasing.

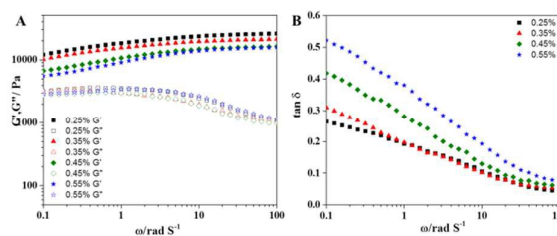


Figure 5. The rheological curves of hydrogels with different concentrations of FeCl₂ (the mass fraction was calculated by FeCl₂ / AAm × 100%): (A) storage moduli G' and loss moduli G''; (B) the loss factor (tan δ = G''/G'). All samples had 15 wt% hexadecyl methacrylate groups in AAm.

The microscopic morphology of hydrogels with different concentrations of FeCl₂ was exhibited in Figure 6. With the increase of FeCl₂ in hydrogels, the thickness of cavities wall

became thinner, suggesting the hydrogels was easier to stretch. As a result, the hydrogels with 0.55% FeCl₂ exhibited the poorest fracture elongation in the tensile test but had the best notch insensitive property. Besides, an interesting phenomenon was found that there were some fibers appearing on the surface of the cavities when the concentration of FeCl₂ was lower than 0.35% in the hydrogels. The fiber structure could significantly enhance the toughness of hydrogels.³⁷

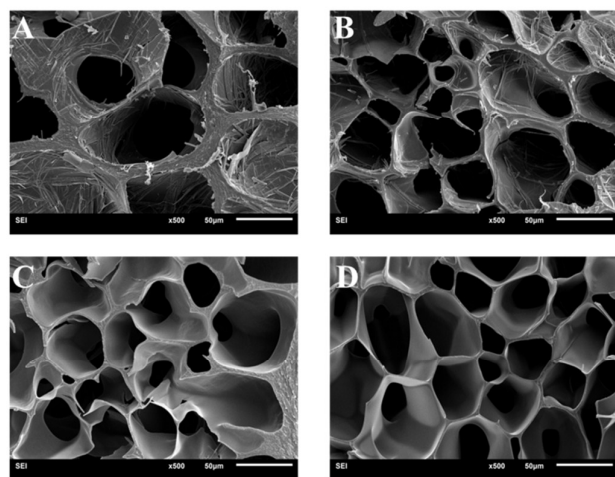


Figure 6. The SEM images of hydrogels with different concentrations of FeCl₂ (the mass fraction was calculated by FeCl₂ / AAm × 100%): (A) 0.25%; (B) 0.35%; (C) 0.45%; (D) 0.55%. All samples had 15 wt% hexadecyl methacrylate groups in AAm.

Effect of hydrophobic groups on the properties of hydrogels

Hydrophobic association interaction was acted as one of important toughening mechanisms for hydrogels. Okay had discussed that some factors could affect the mechanical property of hydrophobic association hydrogels, such as the concentrations of NaCl, SDS and hydrophobic groups, etc.²⁴ In our investigation, the different types and concentrations of alkyl segments were also considered to affect the mechanical property of PAAm hydrogels. Figure 7A was the stress-strain curves of hydrogels with different hydrophobic alkyl groups. When the length of the alkyl segments was shorter, the formed micelles were weaker as crosslinking points and more easily disrupted. For example, the PAAm with methyl side groups couldn't form hydrogels from the inserted images. With the increase of the length of alkyl side chains, PAAm with butyl groups could form hydrogels, but the mechanical strength was so weak that the sample couldn't be tested in the tensile test. Only when the length of alkyl groups was enough long that the hydrophobic segments could form stable micelles as crosslinking points, the hydrogels had an excellent mechanical strength in the tensile test. As can be seen, the hydrogels with hexadecyl groups exhibited the maximum elongation at break of 13 times their original length and the tensile strength of 320 kPa, larger than the hydrogels with lauryl groups. Although the longer length of the alkyl segments enhanced the mechanical property of hydrogels (Figure 7B), it

reduced the notch-insensitive property of hydrogels and the result was shown in Figure 7C. This may be the limited movement of molecular chains due to the close entanglement of hexadecyl groups, resulting in the PAAm main chains being rigid. As a result, the rearrangement property of molecular chains become poor and the hydrogels was easy to break when the sample had a gap. Figure 7D and 7E were the stress-strain curves of hydrogels with different concentration of hydrophobic groups. When the concentration of hydrophobic groups was 5% in the hydrogels, the elongation was only 9.5 times and the sample disrupted even less than 25 KPa. With the concentration of the hexadecyl groups increasing, however, the mechanical property of hydrogels was enhanced obviously. When the concentration of hexadecyl groups was 20%, the fracture strength could reach 400 KPa. When the concentration of hydrophobic groups was low, the hydrophobic groups in the micelles were entangled weakly and

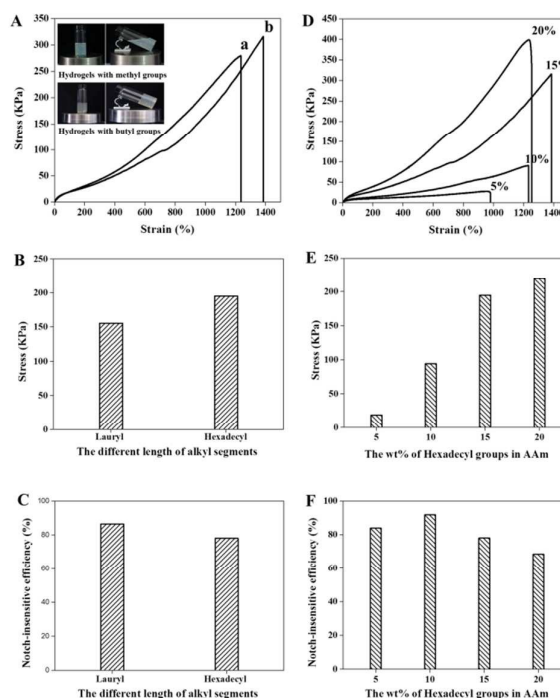


Figure 7. (A) The stress-strain curves of hydrogels with different hydrophobic alkyl groups (without the notch), a) lauryl groups and b) hexadecyl groups (the inserted images were PAAm with methyl groups and hexadecyl groups, respectively) (The hydrophobic group was 15 wt% in AAm); (B) the tensile stress of hydrogels with different hydrophobic alkyl groups (have the notch); (C) the notch-insensitive property of hydrogels with different hydrophobic alkyl groups (the notch-insensitive property is the elongation of hydrogels with a notch / the elongation of hydrogels without a notch × 100%); (D) The stress-strain curves of hydrogels with different concentrations of hexadecyl groups (without the notch) (the mass fraction was calculated by hexadecyl methacrylate / AAm × 100%); (E) the tensile stress of hydrogels with different concentrations of hexadecyl groups (have the notch); (F) the notch-insensitive property of hydrogels with different concentrations of hexadecyl groups. All samples had the 0.35 wt% FeCl₂ in AAm.

easily disconnected under the tensile condition. With the increase of hydrophobic groups, the molecular entanglement was more closely in the micelles and it means that the accumulated molecules need more external force to separate at the same elongation condition. Also, the notch-insensitive property of hydrogels with different concentration of hydrophobic groups was shown in Figure 7F. It showed that the notch-insensitive property of hydrogels was decreased due to the close entanglement of hexadecyl groups with the concentration of hexadecyl groups increasing. Moreover, the sample with 10% hydrophobic groups exhibited the better notch-insensitive property of hydrogels than 5% may be because the low concentration of hexadecyl groups could not provide the effective crosslinking in hydrogels.

The viscoelastic behavior of hydrogels with lauryl and hexadecyl groups, the different concentration of hexadecyl groups as side chains were also investigated and shown in Figure 8. Although the tensile property of the hydrogels with hexadecyl groups was better than that with lauryl groups, the loss modulus (G'') of hydrogels with lauryl groups was lower than that of hydrogels with hexadecyl groups at a low shear frequency and higher at a shear frequency over 40 rad S^{-1} (Figure 8A) and the loss factor ($\tan\delta$) exhibited a similar trend in Figure 8B. It may be due to the length of lauryl groups shorter than that of hexadecyl groups, and the lauryl hydrogels had less frictional resistance at a shear frequency lower than 40 rad S^{-1} , leading to lower loss modulus (G'') and loss factor ($\tan\delta$). For the viscoelastic property of hydrogels with lauryl groups, the curve of loss modulus (G'') firstly decreased and then increased, indicating that the accumulated lauryl groups in the micelles may be disentangled partially at the shear

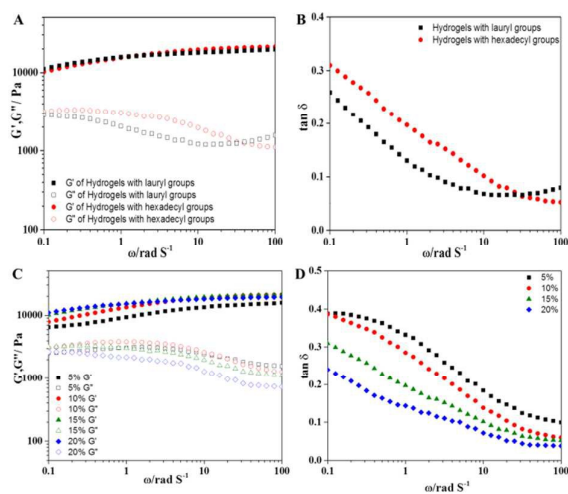


Figure 8. (A) storage moduli G' and loss moduli G'' of hydrogels with different hydrophobic alkyl groups; (B) the loss factor ($\tan\delta = G''/G'$) of hydrogels with different hydrophobic alkyl groups. The hydrophobic group of (A) and (B) was 15 wt% in AAm; (C) the storage moduli G' and loss moduli G'' of hydrogels with different concentrations of hydrophobic groups (the mass fraction was calculated by hexadecyl methacrylate / AAm $\times 100\%$); (D) the loss factor ($\tan\delta = G''/G'$) of hydrogels with different concentrations of hydrophobic groups. All samples had 0.35 wt% FeCl_2 in acrylamide.

frequency of over 16 rad S^{-1} . As a result, the lauryl chains could move more flexibly and the loss modulus (G'') became higher. The viscoelastic results of hydrogels with different concentrations of hexadecyl groups revealed that the hydrogels had the higher storage modulus (G') and lower loss modulus (G'') (Figure 8C and 8D) when the hydrophobic groups tangled more closely with each other in micelles. It may be due to the more rigid of polyacrylamide main chains lead to the hysteresis weakened, resulting in the decrease of internal friction when the molecules moved.

To observe the internal morphology, the scanning electron microscope (SEM) was utilized to measure fracture surface of hydrogels. As can be seen from Figure 9, the SEM images showed the morphology of hydrogels with different concentrations of hexadecyl groups from 5% to 20%. With the increase of hydrophobic segments in the hydrogels, the thickness of cavity walls became thicker. To deserve to be mentioned, the fibers were also observed on the surface of the cavities when the concentration of hexadecyl groups was higher than 15%.

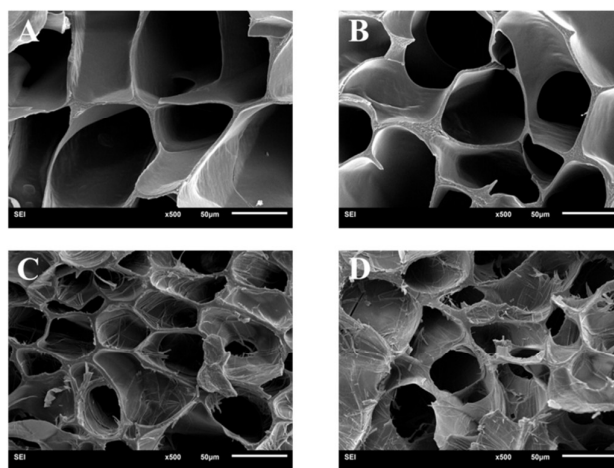


Figure 9. The SEM images of hydrogels with different concentrations of hydrophobic groups (the mass fraction is calculated by hexadecyl methacrylate / AAm $\times 100\%$): (A) 5%; (B) 10%; (C) 15%; (D) 20%. All samples had 0.35 wt% FeCl_2 in AAm.

Conclusions

In a conclusion, we successfully realized the rapid formation of hydrophobic association hydrogels by using the redox initiation systems. It was found that the crosslinking points of hydrogels, which were derived from hydrophobic association and metal ion coordination, were stochastic and dynamic. As a result, the hydrogels could be elongated up to 12 times its original length and show a notch-insensitive property. The test results indicate that when the crosslinking points of hydrogels was rigid or the molecular chain of hydrogels was longer, the mechanical property and elasticity of hydrogels were better. Moreover, we found that the structure of fiber-attached cavities would significantly enhance the mechanical property of hydrogels. It was envisioned that more interaction, including

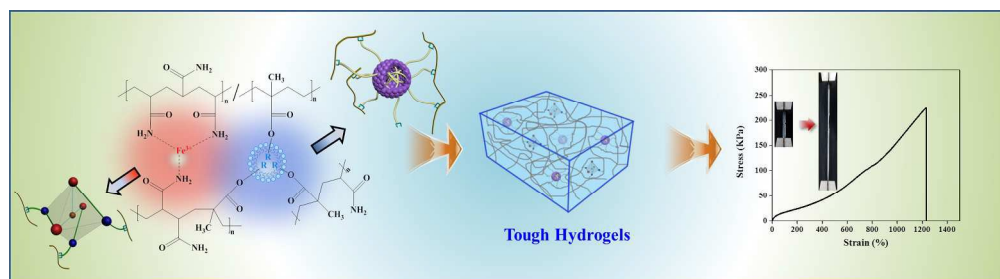
hydrogen bonds, coulomb force, electrostatic effect and so on, would be possible to administer hydrogels with more unexpected surprises (self-healing, biological glue, ...) in our life.

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