Metal-Coordination Complexes Mediated Physical Hydrogels with High Toughness, Stick–Slip Tearing Behavior, and Good Processability

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Supporting Information

ABSTRACT: It is challenging to develop hydrogels with a combination of excellent mechanical properties, versatile functions, and good processability. Here we report a physical hydrogel of poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)) cross-linked by carboxyl−Fe3+ coordination complexes that possesses high stiffness and toughness, fatigue resistance, and stimulation-triggered healing along with shape memory and processing abilities. The copolymers have randomly dispersed AAm and AAc repeat units, making the physical cross-links with different strength. The strong coordination bonds and their associations serve as permanent cross-links, imparting the elasticity, whereas the weak ones reversibly rupture and re-form, dissipating the energy. Furthermore, a stick–slip instability is observed during the tearing test, which should be associated with the specific nature of metal-coordination bonds that are strong yet fragile. Because of the dynamic nature of coordination bonds, both tensile and tearing mechanical properties are rate dependent. By tuning the bond strength via pH, the gels show distinct mechanical properties, shape memory ability, and even reversible sol–gel transition. The system also shows good processability; the copolymer solutions can be processed into tough gels with different structures by three-dimensional printing technology. These versatile, tough, yet processable hydrogels should be a promising material as structural elements in various applications.

1. INTRODUCTION

Tough hydrogels have received tremendous interest due to their promising applications as structural biomaterials, soft actuators, etc.1–3 In recent years, scientists have developed several kinds of mechanically robust hydrogels such as double-network (DN) gels, nanocomposite (NC) gels, and dual-cross-link gels.3–9 For example, the DN gels comprising brittle and ductile networks show high toughness, in which the fracturing of first brittle network effectively dissipates energy of the integrated gels.4 However, these gels containing permanent or quasi-permanent network structure usually have poor processability and recyclability. To address this issue, dynamic noncovalent bonds are incorporated as the cross-links to develop tough physical gels with an effective energy dissipation mechanism.10–18 For example, Gong et al. have developed tough physical gels based on the formation of polynion complex (PIC) between polyanion polyampholytes or oppositely charged polyelectrolytes with balanced charge.17,18 The tensile strength and fracture energy of PIC gels are 4 MPa and 8 × 10³ J/m², respectively. Liu and co-workers have synthesized physical hydrogels by forming stable hydrogen bonds,14 which possess breaking stress and strain in tension of 1.2 MPa and 1500%, respectively. Because of the dynamic nature of ionic and hydrogen bonds, these physical gels have processability and self-healing ability.19–21 The general toughening mechanism in physical gels is proposed and attributed to the wide distribution of bonding strength: the relatively strong associations serve as permanent cross-links to maintain the integrity of gels, whereas the relatively weak associations behave as reversible sacrificial bonds to dissipate the energy.3,17 Following this toughening principle, we may design novel tough physical gels with desired properties by incorporating other kinds of dynamic bonds.

The metal–ligand coordination bond, one kind of noncovalent interaction with a wide spectrum of bonding strength,
is prevalent in biological systems giving rise to tunable adhesion, toughness, and stiffness.22,23 Fratzl et al. have found that the coordination between ferric ions and catechol ligands contributes to the stiffness, toughness, and self-healing capacity of mussel byssal threads.23 Inspired by this scenario in nature, dynamic physical gels incorporating metal-coordination bonds have been developed, which show specific viscoelastic and mechanical properties.24–26 For example, Holten-Andersen and co-workers have developed bioinspired self-healing gels with catechol−Fe3+ coordination complexes as physical cross-links.24 However, their mechanical performances, especially the toughness, were still far away from biological gels such as cartilages. It should be of great significance to design tough and versatile physical gels based on dynamic metal-coordination bonds. To achieve this goal, there should be two requirements: (i) relatively high binding strength of metal−ligand coordinate bonds and (ii) effective energy dissipation mechanism for toughening.

Although tough hydrogels cross-linked solely by metal-coordination bonds are rarely reported, this dynamic bond has been used to substantially improve the mechanical properties of physically or chemically cross-linked hydrogels.34–35 For example, Henderson et al. have used divalent metallic ions to reinforce the poly(methyl methacrylate) block of physically cross-linked gels.30 Thus, obtained single cross-linked gels have relatively high breaking stress and strain in tension reach 7 MPa and 800%, respectively. In stretching of the gels, the metal-coordination bonds break before those of chemical bonds, resulting in energy dissipation and high toughness. It seems that in terms of the toughening mechanism, a relatively strong physical or chemical cross-linking is needed to sustain the deformation of gels before the destruction of dynamic metal-coordination bonds.32–35 However, the existence of permanent or quasi-permanent network leads to poor processability, recyclability, and self-healing ability of the gels.

Recently, metal-coordination bonds have been applied to develop supramolecular elastomers with high stretchability and self-healing ability, in which poly(dimethylsiloxane) chains are physically cross-linked by coordination complex between Fe3+ and 2,6-pyridinedicarboxamide ligands.36,37 The dynamic metal-coordination bonds render the reversible unfolding and refolding of polymer chains, and thus high stretchability of the elastomers up to 4500% is achieved. On the basis of these results, we envision that it should be feasible to design robust yet dynamic physical hydrogels, where polymer chains are solely cross-linked by metal-coordination bonds.

Here we report one kind of tough physical hydrogel with versatile functions prepared by a facile approach: swelling a cast film of poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)) in FeCl3 aqueous solution to form supramolecular network cross-linked with carboxyl−Fe3+ coordination bonds. Thus, obtained hydrogels with water content of 35–85 wt % show excellent mechanical properties, with tensile modulus, breaking strain, breaking stress, and fracture energy being 0.1–80 MPa, 150–1100%, 0.5–18 MPa, and 100–1300 J/m², respectively. More interestingly, a stick−slip instability is observed during the tearing tests of gels. The mechanical properties characterized by tensile and tearing tests are strongly rate dependent, indicating the dynamic nature of the supramolecular network. Furthermore, the mechanical properties of such gels and even reversible gel−sol transition can be mediated by adjusting the pH, which are important for recycling and processing of these materials. Because of the dynamic nature of metal-coordination bonds, the gels show a combination of self-recovery, stimuli-triggered healing, and shape memory properties. These physical gels with excellent mechanical performances, good processability, and versatile functions should be an ideal material to construct structural elements and find applications in different areas.

2. EXPERIMENTAL SECTION

Materials. Acrylic acid (AAc), acrylamide (AAm), and potassium persulfate (KPS) were used as received from Aldrich Chemistry Co., Ltd. Iron(III) chloride hexahydrate, hydrochloric acid, and sodium hydroxide were used as purchased from Sinopharm Chemical Reagent Co., Ltd. Millipore deionized water was used in all the experiments.

Synthesis of Gels. Copolymers of poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)) with different compositions were synthesized by free radical polymerization of precursor aqueous solution containing prescribed amount of AAc, AAm, and KPS at 70 °C for 6 h (Table S1). Thus, the obtained product was a highly viscous liquid, which was precipitated in acetone and dried for use. The solid copolymers were redissolved in water with polymer concentration of 5 wt %. Homogeneous and transparent aqueous solutions can be obtained after 5 days, which were used for casting. Prescribed amounts of solutions were poured onto a glass mold; after solvent evaporation at room temperature, the films were immersed in 0.1 M FeCl3 aqueous solution for 8 h, which produced robust hydrogels by forming metal-coordination bonds between the Fe3+ ions and carboxylic groups. The as-prepared gels were reswelled in a large amount of pure water for 1 day to obtain equilibrated hydrogels with thickness of ~100–200 μm. The as-prepared and equilibrated gels are coded as AG-f and EG-f, in which f is the molar fraction of AAc in feed.

The viscous solution of P(AAm-co-AAc) (13 wt %, f = 15%) was extruded out of a nozzle with different diameters into 0.1 M FeCl3 solution to prepare gel fibers. The solution was also used to prepare gel grids by three-dimensional printing technology; it was printed on a glass substrate and subsequently swelled in 0.1 M FeCl3 solution. The printed gel fibers and grids were then swelled in water to obtain toughened equilibrated samples.

Characterizations. The formation of metal-coordination bonds was confirmed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR; Bruker Vector 22) and UV−vis spectroscopy (PerkinElmer Lambda 35). The surfaces of as-prepared and equilibrated gel films swelled in FeCl3 solution or acidic solution with different pH were examined using an FTIR spectrometer. For the UV−vis spectra measurements, 0.1 M FeCl3 solution was gradually added to 3 mL of 2 mg/mL P(AAm-co-AAc) (f = 10%) to investigate the influence of pH on the metal-coordination complexes, 6 M HCl solution was gradually added to a mixture solution of 3 mL of 2 mg/mL P(AAm-co-AAc) (f = 10%) solution and 60 mL of 0.1 M FeCl3 solution. After each addition, the sample was gently shaken before the measurement of the UV−vis spectrum. The water content of as-prepared and equilibrated gels, q, was calculated according to θ = (w1 − w2)/w2, where w1 and w2 are the mass of gels in the swollen and dried states, respectively.

Tensile tests of gels were performed on a commercial tensile tester (Reger Co., Ltd., RWT10) at room temperature. The samples were cut from gel sheets into dumbbell shape with initial gauge length 12 mm (L0) and width of 2 mm and were loaded with stretch rate of 100 mm/min. The nominal stress and strain, σ and ε, were recorded as the applied load divided by the original cross-sectional area of the samples and the clamp displacement divided by L0. The tensile modulus (E) was calculated from the initial slope of the stress−strain curve with strain below 10%. The breaking strain (εb), stress (σb), and tensile
work ($W_f$) were extracted from the stress–strain curves for at least three separate tests. Tearing tests were also performed at room temperature to characterize the fracture energy of the gels. The gel samples were cut into rectangular shape (35 mm × 12 mm) with 10 mm initial notch at the midpoint of the short edge. Two arms of the specimen were clamped, and the two clamps were separated at a tearing rate (i.e., the pulling velocity of the cross-head) of 100 mm/min. The tearing energy $G$ was calculated from the averaged loading force $F$ according to the equation $G = 2F/w$, where $w$ is the gel thickness. The morphology of fractured surface was observed using a phase contrast microscope.

The tensile and tearing tests were also performed at different initial deformation rates to characterize the dynamic nature of the physical gels. Corresponding $E$, $E_y$, $\sigma$, and $G$ were obtained from three parallel tests at the specific deformation rate.

The rheological behaviors of equilibrated gels were analyzed by using an ARG-2 rheometer (TA Instruments, USA). The disc-shaped equilibrated gels ($f = 15\%$) with thickness of ∼1 mm and diameter of 20 mm were adhered to the plates with glue and surrounded by silicone oil. Strain sweeps of the gels were performed from 0.01 to 10% at frequency of 1 rad/s and temperature of 10 or 90 °C. Temperature sweep was performed from 10 to 90 °C (heating rate: 5 °C/min) at strain of 0.05% and frequency of 1 rad/s. Frequency sweeps were performed to the samples at different temperatures with strain of 0.05%. Master curves of storage modulus $G'$, loss modulus $G''$, and loss factor tan $\delta$ were obtained by time–temperature superposition shifts at a reference temperature of 26 °C. Based on the Arrhenius plot of temperature-dependent shift factors, the apparent activation energy $E_a$ was calculated from the slope of the curve.

3. RESULTS AND DISCUSSION

Synthesis of Hydrogels. Copolymers of P(AAm-co-AAc) were prepared by polymerization of acrylamide (AAm) and acrylic acid (AAc) with different compositions (Scheme 1a).

Scheme 1. Schematic for the Synthesis of Copolymers (a) and Preparation of Physical Gels (b); An Illustration of Structural Change from Polymer Solution to Physical Gel by Forming Metal-Coordination Bonds Is Shown in (b)

The free radical polymerization should produce copolymers with randomly dispersed AAm and AAc repeat units. Aqueous solutions of the copolymer were cast on a glass substrate. After solvent evaporation at room temperature, the cast films were immersed in 0.1 M FeCl₃ aqueous solution, leading to formation of robust physical hydrogels. These as-prepared gels were transformed into a large amount of pure water to achieve the equilibrium state (Scheme 1b). The as-prepared and equilibrated gels are coded as AG-f and EG-f, in which $f$ is the molar fraction of AAc in feed. When $f \leq 8\%$, the cast films are dissolved in FeCl₃ solution because of insufficient carboxylic groups for cross-linking. The as-prepared gels change from light-yellow to brown colors, with increasing $f$ (Figure 1a). After swelling in water, the color of gels deepens, accompanied by slight volume contraction. The gels contain 35–85 wt % water, which decreases with the increase in $f$ (Figure 1b).

The cast film can also be cross-linked by an Al³⁺ ion. However, the thus-obtained gel is much weaker than that cross-linked by Fe³⁺ ion. On the other hand, the cast film is dissolved in the solutions of Mg²⁺, Ca²⁺, Zn²⁺, and Ni³⁺ ions. It seems that Fe³⁺ ion has the highest coordination strength and stability in the system of P(AAm-co-AAc). However, other combinations of ligand and metallic ion with robust binding strength should be also competent as dynamic cross-linkers to develop tough physical hydrogels.30

The formation of supramolecular network of gels is apparently associated with the formation of metal-coordination bonds between ferric ions and carboxylic groups of the copolymers, which is confirmed by FTIR and UV–vis spectra (Figure 2).36,39 The peaks at 1600–1700 and 1400–1500 cm⁻¹ are assigned to the asymmetric and symmetric stretching vibrations of carbonyl groups; the difference between polymer solution and hydrogels suggests the formation of metal-coordination bonds (Figure 2a).36,40 The formation of coordination bonds is also reflected in UV–vis spectra (Figure 2b). P(AAm-co-AAc) solution shows a trace absorbance in the range of 400–600 nm; FeCl₃ solution shows a weak absorbance, which increases with the concentration of Fe³⁺ due to the increasing amount of hydrated metal ions. However, in the presence of copolymer, the addition of FeCl₃ solution results in evident absorption with a shoulder peak at ∼458 nm, indicating the formation of coordination bonds.
Similar to other types of metal–ligand interactions such as histidine– and catechol–metal coordination bonds, the stability constant of carboxyl–Fe$^{3+}$ chelates is influenced by the pH, which alters the ionization of carboxylic group and the coordination styles (mono-, bis-, or tris-ligand–metal complexes).24,25,40 The slight volume contraction from the as-prepared gels to the equilibrated ones should originate from the distinct conditions with different pH. The pH of 0.1 M FeCl$_3$ solution surrounding the as-prepared gels is $\sim$2 (Figure S1), whereas the pH of water for equilibrated gels is $\sim$5. In weakly acidic environment (pH = 4−5), tris-carboxyl–Fe$^{3+}$ coordination with the highest stability constant should dominate. The influence of pH on the coordination complexes is also verified by FTIR and UV–vis spectra (Figure S2). Furthermore, the equilibrated gels slightly expand their volumes in acidic solutions with 1.7 $\leq$ pH $\leq$ 3.5, indicating the partial destruction of the coordinate complexes (Figure S3). The gels are dissolved in acidic solution with pH $\leq$ 1 to form ferric hydroxide precipitates (Figure S4). The pH-mediated stability of hydrogels results in reversible sol–gel transition (Figure S5), which facilitates the reuse and fabrication of gels into different shapes.19−21 In the following section, we prepare hydrogel sheets from cast films and investigate their mechanical properties and functions.

**Mechanical Properties.** As shown in Figures 3a and 3b, both the as-prepared and equilibrated gels show good mechanical performances. The tensile modulus ($E$) and breaking stress ($\sigma_b$) increase with $f$, whereas the breaking strain ($\varepsilon_b$) decreases with $f$; the extension work ($W_b$), usually used to quantify the toughness, achieves the maximum value at $f$ of 15%−20% (Figure 3c). The mechanical properties of thus-obtained physical gels are fully comparable to the hybrid gels using metal-coordination bonds to reinforce a permanent or quasi-permanent network.30−35 Compared with the as-prepared gels, the equilibrated gels have larger $E$, $\varepsilon_b$, and $W_b$, yet smaller $\sigma_b$, due to the formation of a more compact network. This difference should arise from the variation of pH, which
influences the chelating styles and stability constant of the coordinate complexes. This speculation is verified by the mechanical tests of the as-prepared and equilibrated gels after being swelled in solutions with different pH. The gels incubated in solution with pH = 2.4 and 5 show similar tensile curves to that of original as-prepared and equilibrated gels, respectively (Figure S6). The gels in pH = 1.7 solution become softer and more ductile than the as-prepared gel. Therefore, the mechanical properties of gels can be facially tuned over a wide range by pH, which mediates the strength of coordination bond. The concentration of FeCl$_3$ solution, $C_{Fe^{3+}}$, also influences the mechanical properties of both as-prepared and equilibrated gels (Figure S7). Too low $C_{Fe^{3+}}$ leads to insufficient cross-linking and thus poor mechanical properties, whereas too high $C_{Fe^{3+}}$ results in less compact coordinate complexes and small stability constant due to the decrease in pH. Considering the overall mechanical performances of as-prepared and equilibrated gels, $C_{Fe^{3+}}$ of solution in which cast films are incubated is kept constant as 0.1 M.

Because of the dynamic nature of metal-coordination bonds, the mechanical properties of gels depend on the deformation rate. As shown in Figure 4a, the stress–strain ($\sigma$–$\varepsilon$) curves of EG-15% shift upward as the stretch rate increases, and the yielding occurs at an constant strain, $\sim$100%. $E$ and $\sigma_y$ increase, yet $\varepsilon_b$ decreases with the stretch rate (Figure 4b). $W_a$ achieves its maximum value at stretch rate of 100 mm/min. The effect of stretch rate on the tensile mechanical properties is similar to that of $f$ (Figure 3c), indicating that at high stretch rate some metal-coordination bonds or their associations with moderate strength change to those with high strength and serve as permanent cross-links to resist the deformation.

Besides tensile tests, tearing tests were also performed to characterize the fracture resistance of the gels. As shown in Figure 5a, all the equilibrated gels with different $f$ show periodic stick–slip instability during the tearing (Movie S1), which was previously observed in rubber materials and some chemical gels only. The normalized force (applied force/thickness of gel) versus displacement curves include two distinct processes, with a moderate increase and an abrupt decrease in force. When the slope of $F(x)$ is positive, the crack front remains stationary and the deformation (i.e., shearing) around the front is increased by the applied tearing. When the slope is negative, the crack quickly propagates to relax the localized stress around the crack front. The periodic initiation and arrest of crack produce a periodic fractured surface. The fracture surface of the equilibrated gel with $f = 15\%$ at 100 mm/min tearing rate shows periodic fibrous morphology, of which the period length, $\sim$200 $\mu$m, is approximately half the periodic displacement of the $F(x)$ curve (Figure 5b). The fibrous structure with ridges parallel to the direction of crack propagation should be related to the “pull-out” of chains from the cross-linking junctions with coordinate complexes during the severe shearing at the crack tip. The tearing fracture energy, $G_{out}$, is derived from the averaged stretch force, $F_{avg}$, by $G_{out} = 2F_{avg}/w$, in which $w$ is the thickness of gel films. The gels show high $G_{out}$ about 300–1300 J/m$^2$, which increases with $f$ (Figure 5c). The values are comparable to that of DN gels yet lower than that of PIC gels.

The fracture behavior of tearing also depends on the tearing rate (i.e., the moving velocity of cross-head). As shown in Figures 5d and 5e, the normalized force–displacement curves $F(x)$ move downward as the tearing rate increases. Accordingly, $G_{out}$ decreases with the tearing rate, and the periodic step length between two stick–slip peaks and oscillation amplitude of fracture energy show a similar trend (Figure 5f). The interesting point is that the maximum fracture energy $G_{max}$ corresponding to the maximum force and crack initiation, decreases with the increasing tearing rate, whereas the minimum fracture energy $G_{min}$ corresponding to the minimum force and crack arrest, almost maintains a constant value (Figure S8). This is reasonable because the crack initiation is related to the energy dissipation around the crack front, whereas the crack is arrested after the localized stress has been effectively released, which should be independent of the deformation rate. The gels are soft and ductile at low loading speed (Figure 4b), which should result in a large damaged zone and effective energy dissipation around the crack tip. On the basis of rate dependence in $G_{max}$ and $G_{min}$, the rate-dependent oscillation amplitude (i.e., $G_{max} - G_{min}$) and periodic displacement can be understood. The larger $G_{max}$ corresponds to more tearing action and larger periodic step length (Figure 5f).

The dynamic mechanical behaviors of equilibrated gels are investigated by rheological measurements. Temperature-sweep shows that the physical gel (EG-15%) has low loss factor tan $\delta$ of $\sim$0.1 at low temperature ($\leq$50 °C), indicating the elastic nature, whereas the tan $\delta$ gradually increases with temperature to 0.3 at 90 °C (Figure S9). The temperature-dependent behaviors should be related to the hydrogen bonding between

**Figure 4.** Tensile stress–strain curves (a) of equilibrated gels with $f = 15\%$ at different stretch rates and corresponding mechanical properties (b). Error bars represent standard deviation of the mean.
Figure 5. Stick–slip tearing behaviors of the equilibrated gels with different compositions at the tearing rate of 100 mm/min (a–c) and the equilibrated gels with f = 10% at different tearing rates (d–f). (b) and (e) present the magnification of the curves of (a) and (d) of the gel with f = 10%, respectively. Corresponding averaged fracture energy $G_{av}$, periodic step length between two stick–slip peaks, and oscillation amplitude of fracture energy ($G_{max} - G_{min}$) are presented in (c) and (f). Error bars represent standard deviation of the mean. The inset of (b) is a micrograph of the fracture surface; white dotted lines are drawn to show the relationship between the periodic surface structure and displacement of stick–slip tearing.

Figure 6. Dynamic mechanical behaviors of the equilibrated gel with f = 15%. (a) Frequency dependence of the storage modulus $G'$, loss modulus $G''$, and loss factor tan $\delta$ of the gel. The frequency sweeps were performed from 0.1 to 100 rad/s at different temperatures and a strain amplitude of 0.05%; the master curves were obtained by time–temperature superposition shifts at a reference temperature of 26 °C. (b) Arrhenius plot for the temperature-dependent shift factors. The apparent activation energy was calculated from the slope of the curve.
the amino and carboxyl groups of the copolymers, which is verified by the DSC measurements.\textsuperscript{16} The DSC thermographs of as-prepared and equilibrated physical gels ($f = 25\%$), as well as the P(AAm-co-AAc) solution, show an exothermic peak at $\sim 50{^\circ}\text{C}$ (Figure S10). Frequency sweeps are performed to the gel of EG-15% at different temperatures; the spectra follow the principle of time−temperature superposition (Figure 6a). The Arrhenius plot for the shift factor $\alpha_T$ of the master curve is shown in Figure 6b, giving two apparent activation energy values $E_a$ of 92 and 298 kJ/mol. The wide range of $E_a$ arises from the wide distribution of strengths of the coordination and hydrogen bonds and their associations, which originates from the randomly dispersed AAm and AAc repeat units of the copolymers. During stretching, the weak bonds and associations rupture to dissipate energy, whereas the strong ones are retained to resist more deformation.\textsuperscript{17}

The above results demonstrate that mechanically tough physical hydrogels can be developed by cross-linking the polymer chains with metal−ligand coordinate complexes. These physical gels with metal-coordination complexes show robust mechanical performances comparable to previously developed tough gels with permanent or quasi-permanent cross-linking. Two Ashby charts for a variety of soft materials are presented in Figure S11 to show the excellent mechanical properties of P(AAm-co-AAc) gels in this work.\textsuperscript{52,53} In terms of strength and stiffness, our gels with broad tunability of mechanical properties outperform most existing tough hydrogels, including DN gels and polyampholyte gels. However, the P(AAm-co-AAc) gels only have moderate fracture energy, $G_{av} \sim 300−1300$ J/m$^2$, probably because of the specific nature of metal-coordination bond, which is of high strength yet very fragile.\textsuperscript{36} This might also account for the observed stick−slip phenomena, in which the crack once initiated by tearing action will quickly propagate with a certain length.

Functions and Processability. As described above, the dynamic and adaptive coordination bonds should endow the gels with versatile functionalities.\textsuperscript{27,28} During the cyclic tensile tests, the stress−strain curves of the gel exhibit large hysteresis loop between loading and unloading, indicating vast energy dissipation in breaking the internal structure of the gel (Figure 7a). Notable residual strain after the unloading demonstrates the viscoelastic deformation. However, after a sufficient period of waiting time, the residual strain gradually vanishes, indicating the recovery of viscoelastic deformation. Meanwhile, the loading−unloading loop gradually approaches the first cycle. The residual strain and hysteresis ratio (calculated as the area ratio of the second hysteresis to the first) depend on the waiting time after the unloading and reach respectively 4% and 78% after 4 h (Figure 7b). The self-recovery behavior is related to the re-formation of metal-coordination bonds broken during the loading process,\textsuperscript{32,35} resulting in high fatigue resistance of the gels against dynamic deformation.\textsuperscript{36}

The stability of coordination complexes is influenced by pH, indicating its dynamic nature. Because of the adaption of

![Figure 7](image_url). Cyclic tensile loading−unloading curves (a) of the equilibrated gel with $f = 15\%$ after different waiting time and the corresponding residual strains and hysteresis ratios (b). The sample was loaded to a strain of 250% and then unloaded with deformation rate of 100 mm/min.

![Figure 8](image_url). (a) Photos to show the stimuli-triggered healing process. The cut surfaces of equilibrated gel ($f = 10\%$) were brought into contact and dripped with one drop of 1 M HCl solution. After 10 min, the sample was sequentially swelled in 0.1 M FeCl$_3$ solution for 2 h and pure water for 12 h. The healed sample can sustain stretching to more than 3 times its original length. (b) Tensile stress−strain curves of the original and healed gels. Stretch rate: 100 mm/min.
coordination bonds and reversible sol–gel transition of the system of P(AAm-co-AAc) and Fe$^{3+}$ ions, the gel exhibits stimulation-triggered healing ability.24,27 As shown in Figure 8a, the fractured gels (EG-10%) can be healed with assistance of highly acidic solution to soften and activate the fracture surfaces, followed by reswelling in FeCl$_3$ solution and pure water for cross-linking and mechanical enhancement, respectively. The healed gel shows $\varepsilon_b$ of 480% and $\sigma_b$ of 4.5 MPa (Figure 8b). This $\sigma_b$ is the highest value, to our knowledge, for the healed gels. Since the mechanical properties, especially the elastic modulus, of the gels are tunable by changing the pH value of the incubated solution, shape fixation and recovery of gels can be realized by switching the pH. As shown in Figure 9a, the tough equilibrated gel is softened by swelling it in acidic solution with pH = 1.7, leading to the fading of gel color from brown to light yellow. This gel is deformed into a helical shape, followed by immersing it into 0.1 M FeCl$_3$ solution and pure water, leading to shape fixation and mechanical enhancement of the gel (Movie S2). The dramatic increase in modulus from 50 kPa at pH of 1.7 to 10.5 MPa at pH of 5 enables the fixation of temporary shape (Figure 9b).49–52 The helical shape can be relaxed by reswelling the gel in acidic solution with pH of 1.7. Such shape fixation and relaxation are reversible and can be repeated for at least three times.

The sol–gel transition also merits the recycle of gels as well as good processability. The destroyed gels can be dissolved in strongly acidic solutions and reconstruct into tough gels by decreasing the pH (Figure S4). The viscous P(AAm-co-AAc) aqueous solutions can also be directly extruded into FeCl$_3$ solution to trigger the sol–gel transition, thereby obtaining tough gel fibers.19,53 As shown in Figure 10a, gel fibers with diameter of 0.5–2 mm were prepared by extruding P(AAm-co-AAc) solution (13 wt %, $f = 15\%$) out of a nozzle into 0.1 M FeCl$_3$ solution. These gel fibers show good mechanical properties (Figure S12), which are comparable to those of bulk gels prepared from the cast films. This result indicates that tough fibrous gels can be continuously prepared by the spinning approach. The P(AAm-co-AAc) solution can also be used to construct gel into complex structures by three-dimensional (3D) printing technology. The concentrated solution is highly viscoelastic, which can sustain the shape after being extruded out of the nozzle for a short period of time. This time window enables 3D printing the viscous “ink” into specific shapes, followed by swelling the sample in FeCl$_3$ solution to obtain tough printed gels (Figure 10b). Other functional materials such as magnetic nanoparticles can be facially incorporated into these gels with different shapes.54

![Figure 9](image1.png)

**Figure 9.** Photos to show the shape memory behavior (a) and the corresponding stress–stress curves (b) of the gel ($f = 15\%$) mediated by pH switching. The equilibrated gel incubated in acidic solution (pH = 1.7) was shaped and then swelled in 0.1 M FeCl$_3$ solution for 1 h and water (pH = 5) for 4 h; the structure was maintained after removing the external force. The gel recovered to the original flat shape after swelling in solution with pH = 1.7 for 2 h. Inset in (b) shows the tensile modulus of the gel at different pH. Stretch rate: 100 mm/min.

![Figure 10](image2.png)

**Figure 10.** (a) Gel fibers prepared by extruding the copolymer solution out of a nozzle with different diameters into FeCl$_3$ solution. (b) 3D printed gel grids of the copolymer solution on a glass substrate, followed by swelling the sample into solution. The “ink” for printing is 13 wt % P(AAm-co-AAc) ($f = 15\%$) solution. Scale bar: 1 cm.
4. CONCLUSIONS

We have developed tough physical hydrogels of P(AAm-co-AAc) cross-linked with metal–ligand coordination complexes. These gels show remarkable mechanical performances and versatile functions, including high stiffness, toughness, self-recovery, and shape memory properties. A stick–slip tearing instability is first observed in physical hydrogels. The high toughness of gels originate from the wide distribution of bonding strength of coordination complexes as well as the hydrogen bonding between carboxyl and amino groups: the strong dynamic bonds and their associations serve as permanent cross-links to maintain the integrity of gels, whereas the relatively weak ones behave as reversible and sacrificial bonds to dissipate energy. Because of the dynamic nature of coordination bonds, the mechanical properties are strongly rate dependent in both stretching and tearing. The mechanical performances of gels are tunable in a wide range by controlling the composition of copolymers, concentration of metallic ions, and pH values of the solutions where the gels are incubated. The sol–gel transition endows the gels with good recyclability and processability; the copolymer solutions can be extruded out of a nozzle to construct tough gel fibers and grids by 3D printing technology. Such versatile, tough, yet processable physical hydrogels with remarkable features should be a promising material with broad applications such as in load-bearing artificial organs and soft actuators.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b02150.

Table S1 and Figures S1–S12 (PDF)

Stick–slip instability during the tearing test of equilibrated P(AAm-co-AAc) gel (AVI)

Shape retention of the robust equilibrated gel with a helical structure (AVI)

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Notes
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