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Tough polypseudorotaxane supramolecular hydrogels with dual-responsive shape memory properties†

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Cyclodextrin–polypseudorotaxane hydrogels have attracted extensive attention for their potential application in biomedical fields. Herein, we develop a facile strategy for the *in situ* formation of mechanically tough polypseudorotaxane hydrogels through photoinitiated copolymerization of poly(ethylene glycol) methyl ether methacrylate, acrylamide and sodium acrylate in α-CD solution at 60 °C. For the first time, we manage to screen the host–guest interaction between α-CD and PEG before copolymerization in the presence of a temporary hydrogen bonding weakening monomer (acrylamide) at a suitable temperature (60 °C). This shielding effect weakens gradually during polymerization, thus leading to the formation of polypseudorotaxane aggregations and a tough physical hydrogel. The hydrogel can bear a large compressive strain (80%) without rupture, and exhibits excellent antifatigue properties. Furthermore, this hydrogel could be endowed with thermal/ascorbic acid activated shape memory performance after being treated with $FeCl_3$ solution. This simple method will contribute to the design and application of smart supramolecular hydrogels.

1. Introduction

Cyclodextrins (CDs) are a group of cyclic oligosaccharides, which consist of 6, 7 and 8 glucose units for α-, β-, and γ-CD, respectively.[1] They can interact with various kinds of available guests such as adamantane, azobenzene and ferrocene to form host/guest complexes with a guest : host ratio = 1 : 1.[2–4] Considerable interest has been focused on CD-based sol–gel transition and self-assembly systems,[5–7] which are responsive to diverse stimuli such as temperature,[8–11] light,[12–15] redox[16,17] and metal ions.[18] Particularly, poly(ethylene glycol) (PEG) is a special guest of α-CD for polypseudorotaxane supramolecular hydrogels with biological compatibility and potential biomedical applications.[2,19–25] However, most of the α-CD/PEG polypseudorotaxane supramolecular hydrogels were prepared *via* mixing α-CD with a presynthesized polymer containing PEG segments, which resulted in poor mechanical strength such as the lack of ability of bearing compression and deformation, except for a few studies with slide-ring joints structure for energy dissipation.[26,27] This can be attributed to the fact that, in comparison with native PEG, polypseudorotaxane chains exhibit significantly increased stiffness and intermolecular interactions, and therefore the polypseudorotaxanes are almost insoluble in water and tend to precipitate, resulting in heterogeneity inside gels. It indicates that, for the *in situ* preparation of polypseudorotaxane supramolecular hydrogels during the polymerization process, the host–guest interaction between α-CD and PEG should be screened at first, which is difficult to realize at present. Thus, polypseudorotaxane supramolecular hydrogels with desirable mechanical strength and multi-stimuli responsive properties have rarely been reported to date.

In this study, we report a novel mechanically tough α-CD/PEG polypseudorotaxane supramolecular hydrogel (CD–PPR hydrogel) through photoinitiated copolymerization of poly(ethylene glycol) methyl ether methacrylate, acrylamide and sodium acrylate in α-CD solution at 60 °C. For the first time, acrylamide is chosen as a temporary hydrogen bonding weakening agent for α-CDs to prevent the formation and aggregation of polypseudorotaxanes. Neither acrylamide nor high temperature alone can effectively screen the host–guest interaction between α-CD and PEG. Interestingly, in the presence of acrylamide monomers and a suitable temperature (60 °C), the host–guest interaction between α-CD and PEG can be screened effectively to incorporate enough polypseudorotaxanes inside the final hydrogel to afford a highly compressible tough hydrogel. During polymerization, acrylamide monomers are gradually immobilized onto the polymer chains and the shielding effect weakens correspondingly. As a result, the formation and

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aggregation of polypseudorotaxanes occur, which act as physical joints and lead to a highly compressible tough hydrogel. The hydrogel can be compressed at an 80% strain without rupture and shows excellent antifatigue properties. Furthermore, this hydrogel could be endowed with thermal/ascorbic acid activated shape memory performance after being treated with $FeCl_3$ solution. To the best of our knowledge, this is the first time such a facile method for *in situ* formation of a mechanically tough polypseudorotaxane supramolecular hydrogel has been developed. We hope that our research could provide valuable understanding for the design and application of supramolecular and shape memory hydrogels.

2. Experimental section

Materials

Acrylamide (AM), ascorbic acid and iron(III) chloride hexahydrate were obtained from Sinopharm Chemical Reagent Co. Ltd. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n \sim 950$), α-CD, sodium acrylate (SA) and photoinitiator Irgacure 2959 were purchased from Sigma-Aldrich. PEGMA was purified by dissolving it in tetrahydrofuran, followed by passing through an inhibitor remover before use. Ultrapure deionized water from a Millipore water-purification system was used.

Hydrogel preparation

The hydrogels were prepared through photoinitiated free radical polymerization at 60 °C. In detail, 1.20 g AM, 1.59 g SA and 2.21 g α-CD were dissolved in 8 mL deionized water in a vial at 60 °C. Then 2 mL PEGMA solution (containing 0.24 g PEGMA) and 0.024 g photoinitiator Irgacure 2959 (0.3 mol% of total monomers) were added into the vial (molar ratio of AM : SA : PEGMA = 49 : 49 : 2). After bubbling N_2 for 5 minutes, the solution was injected into a glass mold and immersed in a water bath at 60 °C, followed by 1.5 hours of UV irradiation at 365 nm using a 5 watt lamp. The polymerization was allowed to proceed for another 4.5 hours, affording a CD–PPR hydrogel with a water content of 65%. In order to prepare hydrogels with different α-CD coverage, varied amounts of α-CD were added.

Hydrogel characterization

X-ray diffraction patterns were obtained using freeze-dried hydrogel samples with Cu Kα X-ray (λ = 1.54 nm) in a step of 0.02°. The voltage and current of X-ray tubes were 30 kV and 15 mA, respectively. ^{1}H NMR spectra were recorded on a Bruker Advance 400 M NMR spectrometer at 60 °C with D_2O as solvent.

Rheological measurements were carried out on a TA AR-G2 rheometer using parallel plates of 40 mm diameter and a plate to plate distance of 1200–1700 μm. Frequency sweep measurements were carried out over the frequency range of 0.1 to 100 rad s^{-1} at a fixed strain of 0.03% within a linear regime, which is determined through strain sweep measurements (Fig. S1, ESI†). In order to investigate the thermoplasticity of hydrogels, during the temperature sweep step, the temperature was raised from 10 °C to 90 °C and lowered from 90 °C to 10 °C with a ramp rate of 5 °C min^{-1}. Similar to a previous report,[28] during the whole process, a thin layer of silicon oil was applied to the edge of the disk-like hydrogel sample to avoid water evaporation.

Compression tests were carried out using a TA DMA Q800 dynamic mechanical analyser. The cylindrical hydrogel samples (diameter 2 cm and length 1 cm) were placed between self-leveling plates at a cross-head speed of 0.4 mm min^{-1}.

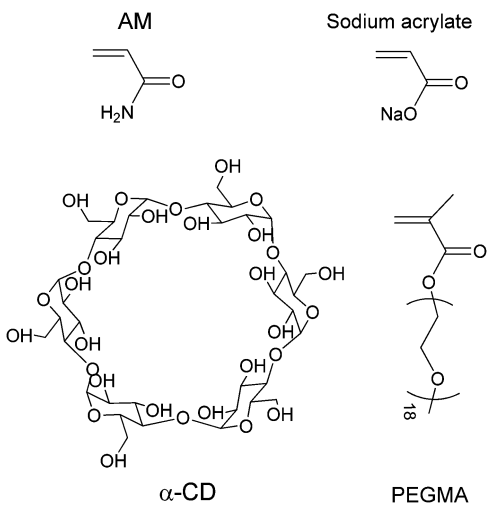
Shape memory behaviour

A linear cylindrical hydrogel with a diameter of 5.0 mm and a length of 6 cm was immersed in 1 M $FeCl_3$ solution for 20 minutes to introduce an additional network into the hydrogel *via* complexation of Fe^{3+} and carboxyl groups. Then the shape memory performance was evaluated according to previous reported methods.[29,30] For thermal-induced shape memory, the straight hydrogel was curled into a "V" angle at 75 °C and then cooled to room temperature to fix the deformation with an angle of θ_f. Afterwards, the deformed hydrogel was immersed in a 75 °C water bath to observe the shape recovery process. The corresponding angle θ_t at a certain time was recorded to determine the shape recovery ratio using the equation $R = (\theta_t - \theta_f)/(180 - \theta_f)$. The ascorbic acid-induced shape memory was explored in a similar way. The hydrogel was immersed in 1 M $FeCl_3$ solution to fix the temporary shape, and immersed in 1 M ascorbic acid solution to recover the initial shape.

3. Results and discussion

3.1 Synthesis of CD–PPR hydrogels

The hydrogels were prepared through free radical polymerization at 60 °C. As is well known, PEG can penetrate the beaker-like tunnel of α-CD and the resulting inclusions are insoluble in water at room temperature due to strong hydrogen bonding between α-CDs.[31] Herein, through polymerization at high temperature (60 °C), we have successfully copolymerized AM, sodium acrylate and PEGMA in the presence of α-CD (Scheme 1). Experimentally, as shown



Scheme 1 Chemical structures of monomers in the solution feed for polymerization.

in Fig. 1a, as the polymerization went on, the transparent system at first became viscous and later on turned white and opaque, indicating the formation of α-CD/PEG inclusions. In FTIR spectra (Fig. S2, ESI†), the absence of a band at 1640 cm^{-1} corresponding to the double bond of the PEGMA monomer demonstrates successful incorporation of PEGMA into the polymer.[32] Moreover, the α-CD/PEG inclusion in the hydrogel is demonstrated by XRD patterns. In Fig. 1b, the emerging peak at $2\theta = 19.8^{\circ}$ indicates the existence of channel-structured α-CD/PEG inclusions.

We delicately employ an acrylamide monomer as a temporary weakening agent of hydrogen bonding to prevent the formation of α-CD/PEG polypseudorotaxanes before polymerization. The driving forces for the formation of polypseudorotaxanes are hydrogen bonds between α-CDs and hydrophobic interactions between the hydrophobic internal cavity of α-CD and $-CH_2OCH_2-$ moieties

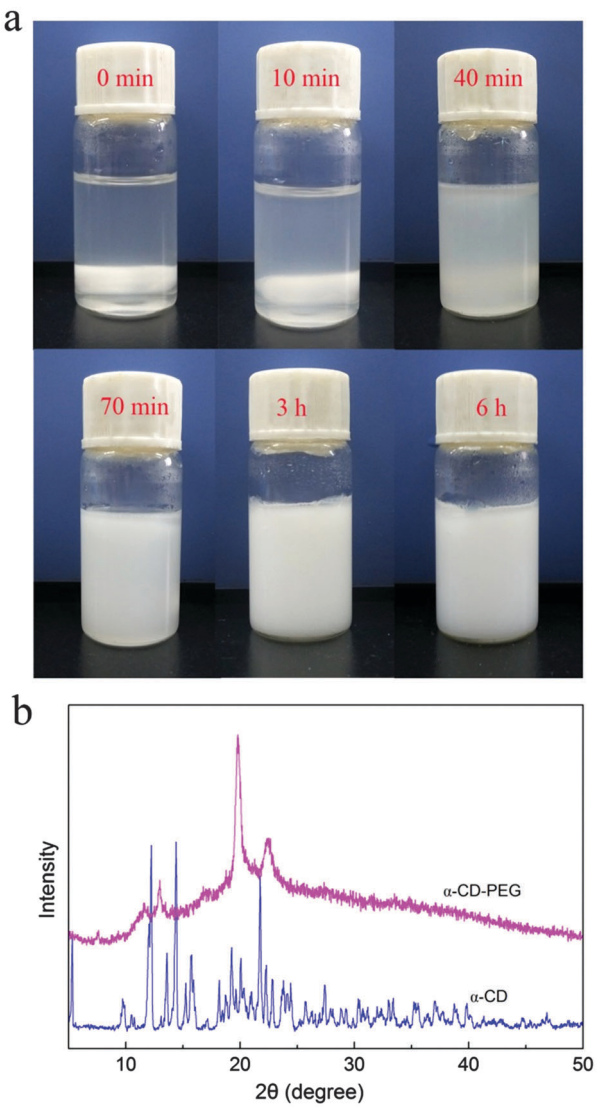


Fig. 1 (a) Digital photographs of solution/hydrogel at varied time from polymerization initiation and (b) XRD patterns of α-CD and freeze-dried CD–PPR hydrogel.

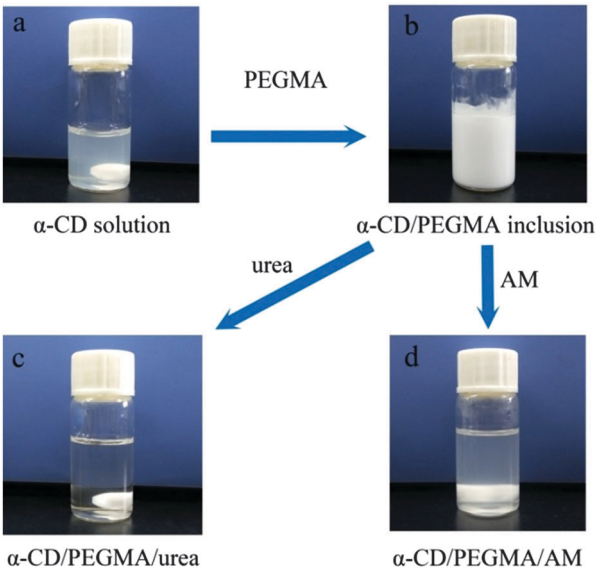


Fig. 2 Digital photographs of aqueous solutions at 60 °C: (a) 21 wt% α-CD transparent solution; (b) after the addition of PEGMA solution, a white precipitate appeared; (c) after the addition of urea into (b), the mixture turned into a transparent solution; and (d) after the addition of AM into (b), the mixture turned into a transparent solution.

of PEG.[31,33,34] As reported earlier, the urea can weaken the strong intermolecular hydrogen bonds between α-CDs and prevent the formation of polypseudorotaxane aggregations.[35,36] Before polymerization, with a chemical structure similar to urea, free acrylamide monomers can weaken the hydrogen bonding between α-CDs, preventing the formation of polypseudorotaxanes. This mechanism is illustrated by the following experiments. As shown in Fig. 2, 1.1 g α-CD was added into 4 mL water at 60 °C and a transparent solution was obtained. When 1 mL solution of 12 w/v% PEGMA was added, a white precipitate appeared, demonstrating the formation of polypseudorotaxanes, which was also illustrated by the XRD pattern of the precipitate (Fig. S3, ESI†). However, further addition of AM could make the white precipitate disappear, demonstrating the dissociation of polypseudorotaxane aggregations. Similarly, the addition of urea showed the same effect as AM to dissolve the precipitate. In the hydrogel preparation process, with the proceeding of polymerization, acrylamide monomers are immobilized onto the polymer chain and cannot effectively screen the hydrogen bonding between CDs, leading to the formation of polypseudorotaxanes. ^{1}H NMR spectra also further illustrate this mechanism. In Fig. 3a, the ^{1}H NMR spectra of the monomer feed containing α-CD, AM and PEGMA exhibit clearly split proton peaks of α-CD rather than a broad peak, indicating that the molecular mobility of α-CD is not retarded.[13,14] Moreover, ^{1}H NOESY spectra in Fig. 3b clearly show that there are no NOE correlation peaks between the protons of PEGMA and H3/H5 of α-CD, which point to the internal cavity of α-CDs, indicating that α-CDs do not thread onto PEGMA chains before polymerization at 60 °C in the presence of AM.[37] These experiments demonstrate that both high temperature and acrylamide are vital to obtain a homogeneous solution in the hydrogel preparation process.

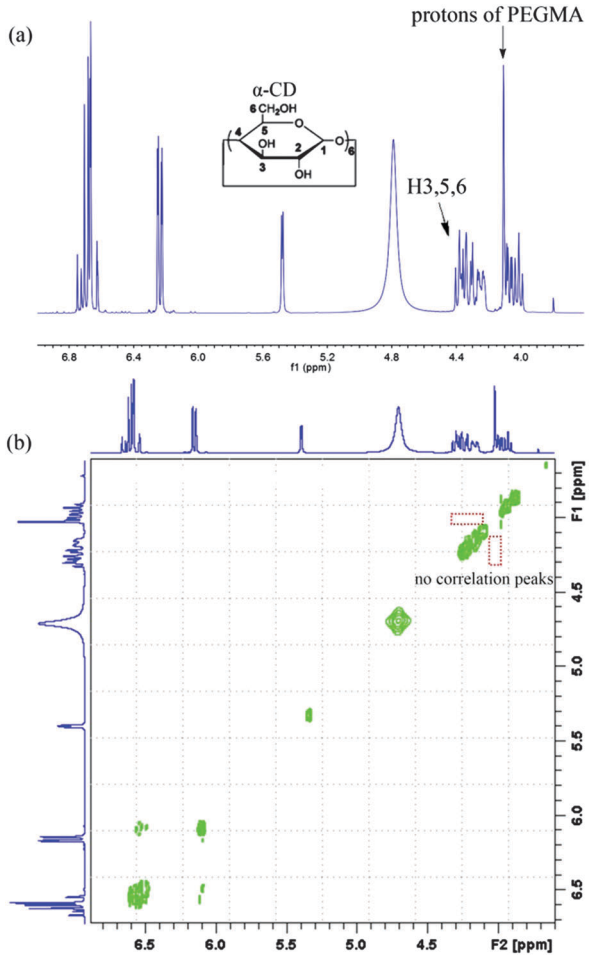


Fig. 3 (a) ^{1}H NMR spectra of monomer feed solution at 60 °C and (b) ^{1}H–^{1}H NOESY spectra of monomer feed solution at 60 °C.

Polypseudorotaxane aggregates and a precipitate will appear either at room temperature or without the presence of acrylamide.

3.2 Mechanical properties of CD–PPR hydrogels

The prepared supramolecular hydrogels exhibit tough compressive mechanical strength. As shown in Fig. 4, the CD–PPR hydrogel can bear a deformation strain as high as 80% without rupture and recover back after the release of compressive stress. The hydrogel also demonstrates antifatigue properties. The cyclic loading–unloading experiments showed that, with a fixed maximum strain of 40%, the hydrogel could recover the original strength and exhibited almost overlapping hysteresis loops with an interval of 5 minutes between each loading–unloading cycle. After 10 cycles, the recovery ratio is larger than 96% and the stress relaxation is smaller than 2%, indicating the hydrogel's robust mechanical and antifatigue properties.[38] These tough mechanical properties can be attributed to multiple hydrogen bonds between polypseudorotaxane chains and crystalline formation of columnar α-CDs.[20] The mechanism for the excellent mechanical properties is as follows.

Firstly, the tough compressible mechanical properties are attributed to the polypseudorotaxane joints in the hydrogel, where the amount of polypseudorotaxanes is much greater than that in previous reports, thus providing much more joints for energy dissipation. In the process of hydrogel preparation, the applied high temperature not only contributes to the disruption of hydrogen bonding to prevent the formation of polypseudorotaxane aggregates before polymerization, but also helps to dissolve and integrate a large amount of α-CD into the hydrogel to endow a final hydrogel with more polypseudorotaxane cross-linking and network. Different from chemical cross-linkers, physical cross-linking consisting of multiple hydrogen bonds is a good candidate for energy dissipation.[39] To be specific, in this article, the physical polypseudorotaxane cross-linking based on hydrogen bonding is an effective means of dissipating the deformation energy applied to the system. When the hydrogel is compressed, the polypseudorotaxanes will slide with each other and a large amount of compressive energy is dissipated by hydrogen bonds between columnar polypseudorotaxanes, endowing the hydrogel with tough compressive mechanical properties. After the stress is released, the repulsive interaction between columnar polypseudorotaxanes vertical to the compressive force drives the hydrogel to recover its original shape.

Secondly, the reversible nature of physical cross-linking interactions between polymer chains contributes to the self-recovery ability of the hydrogel after the release of stress and endows the hydrogel with antifatigue properties. After the release of stress, the reorganization nature of physical polypseudorotaxane cross-linking based on hydrogen bonding helps the hydrogel to restore to its original status.[40] For each cycle, the hysteresis loop remains almost the same, indicating that after 5 minutes of rest, the network structure recovers its original status. This viscoelastic system, as one example of physical hydrogels, can disperse applied energy and exhibit different loading and unloading strain–stress curves, indicating the hysteresis phenomenon in the system, which was not observed in chemically cross-linked hydrogels.

The α-CD coverage ratio on PEG chains and the amount of polypseudorotaxanes greatly influence the mechanical properties of hydrogels. As shown in Fig. 5, with the same maximum compressive stress (90 kPa), hydrogels with a designed α-CD coverage ratio of 33%, 66% and 100% exhibit a strain of 85%, 59% and 39%, respectively. Meanwhile, the hydrogel with a higher α-CD coverage ratio can reach a higher strain recovery after the release of stress, which is indicative of increasing robustness of hydrogels with more polypseudorotaxane cross-linking. In other words, with increasing α-CD content and polypseudorotaxane cross-linking, the hydrogel becomes more resilient and exhibits better deformation recovery ability.[41]

Interestingly, by contrast, simply mixing poly(acrylamide-*co*-sodium acrylate-*co*-poly(ethylene glycol) methyl ether methacrylate) with α-CD affords only a much weaker hydrogel. This can be ascribed to the following factors. (1) As PEG and α-CD quickly form aqueous insoluble polypseudorotaxane aggregations, it is difficult to dissolve enough PEG and α-CD at room temperature to endow hydrogel with sufficient hydrogen bonds to dissipate compressive stress. However, in the preparation

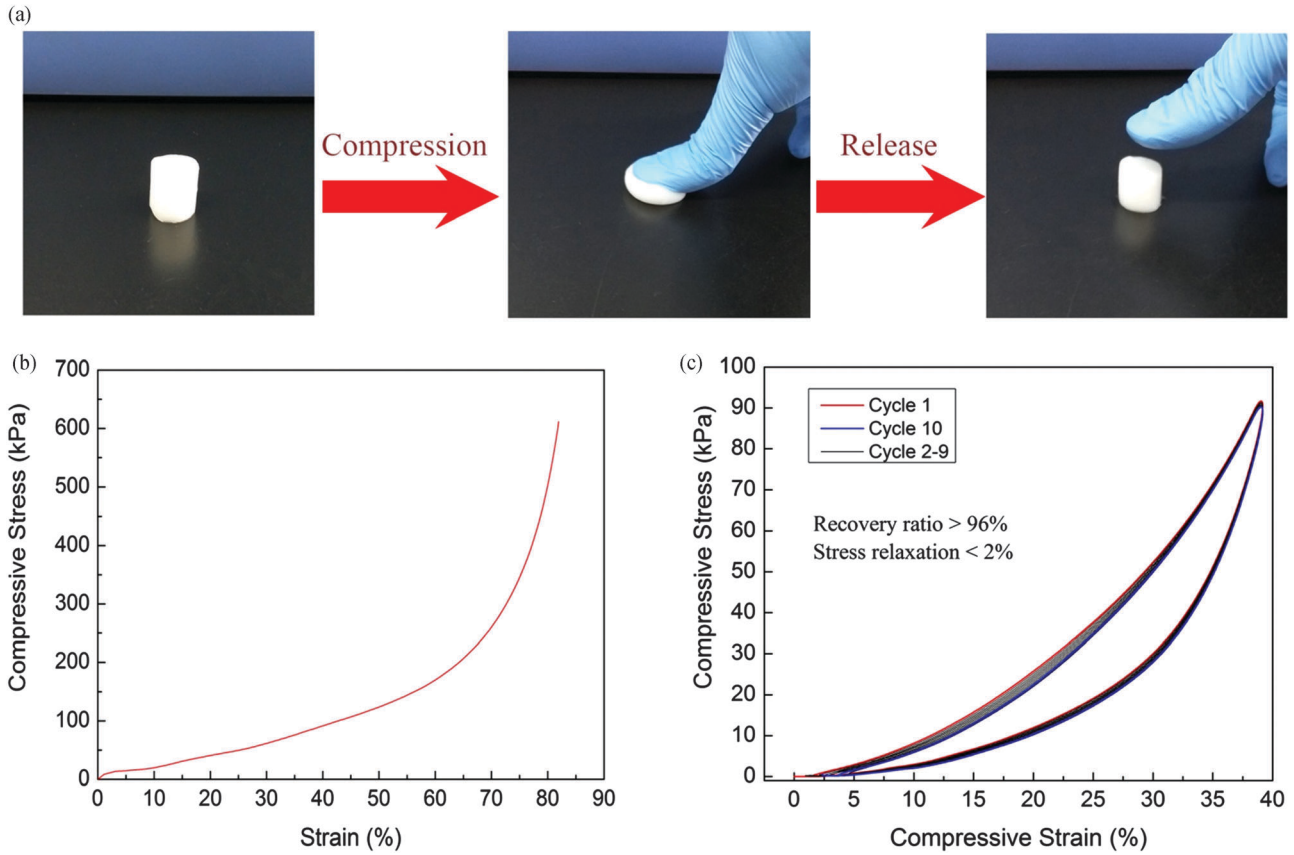


Fig. 4 Mechanical performance of compressible CD–PPR hydrogels. (a) Photographs showing that the cylindrical CD–PPR hydrogel can recover its original shape after strong compression. (b) The hydrogel can stand a compressive strain of 80% without rupture. (c) Ten successive compression cycles of hydrogel in compression test with a time interval of 5 minutes between each cycle.

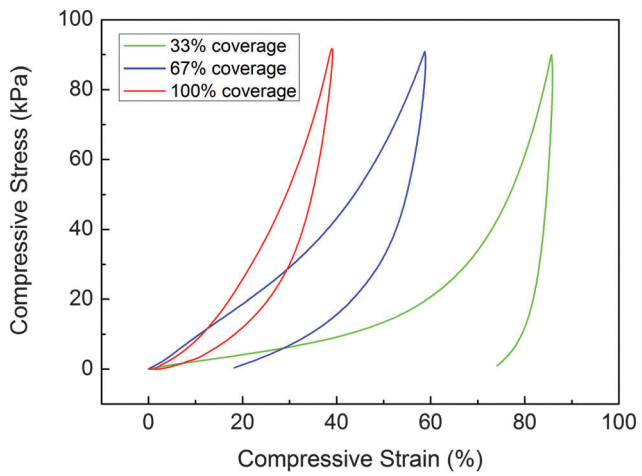


Fig. 5 Plot showing that under the same compressive stress, hydrogels with different α-CD coverage ratios on PEG chains exhibit different compressive strains.

process of present hydrogel, this problem is solved by combination of acrylamide and high temperature. (2) When mixing α-CD and synthesized poly(acrylamide-*co*-sodium acrylate-*co*-poly(ethylene glycol) methyl ether methacrylate), the rapid gelation and precipitation lead to massive heterogeneity in the system, contributing to brittle mechanical properties of the hydrogels.

3.3 Thermal-responsive shape memory performance

As is well known, at room temperature, α-CDs will thread onto PEG chains and lead to the formation of polypseudorotaxanes, where hydrogen bonding plays a key role.[20] Due to the temperature-sensitive nature of hydrogen bonding, the mechanical strength of the present hydrogel is thermal-responsive and can be employed to endow the present hydrogel with thermal-induced shape memory performance.

The thermal-responsive behaviour of the hydrogel was investigated through rheological properties of the hydrogel. As demonstrated in Fig. 6a, when subjected to a temperature sweep in the range of 10–90 °C, the loss modulus G'' remains constant in the whole temperature range whereas the storage modulus G' decreases drastically from 18.2×10^4 Pa to 5.2×10^4 Pa in the range of 45–90 °C. In contrast to the heating process, in the cooling process, G' recovers its original value at a much lower temperature (32 °C) and a hysteresis loop is observed, which was also found in other thermal-sensitive polymer systems.[39,42] This hysteresis loop is a kinetically indicative phenomenon of the resistance to disintegration of entangled polymer chains forming the hydrogel network. Frequency sweep at different

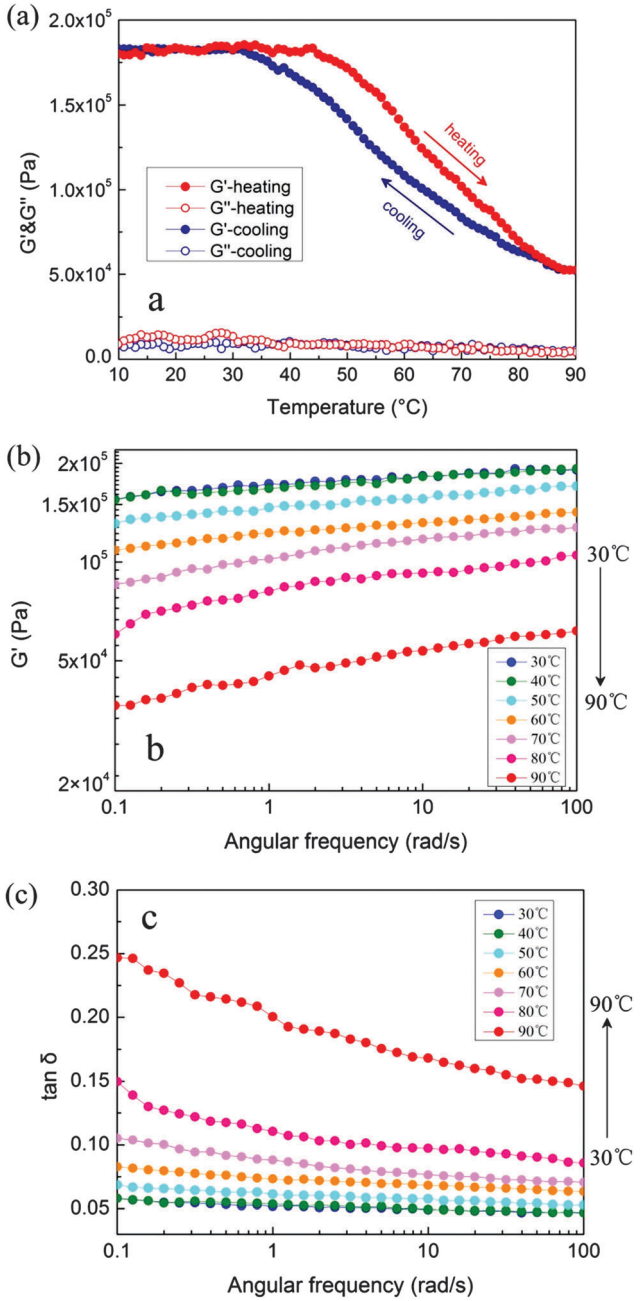


Fig. 6 (a) Temperature sweep of the CD–PPR hydrogel from 10 °C to 90 °C; (b) and (c) Frequency sweep at varied temperatures in terms of storage modulus G' and tan δ.

temperatures is carried out to further clarify the thermoplasticity of hydrogels. As seen from the frequency sweep (Fig. 6b), G' exhibits frequency dependence, which is indicative of the existence of supramolecular non-covalent interaction inside the hydrogel. At varied temperatures from 40 °C to 90 °C, the storage modulus G' decreases at high temperature. Moreover, as an indicator of the viscous nature of hydrogels, tanδ (tan $\delta = G''/G'$) increases at higher temperature (Fig. 6c), indicating high temperature's contribution to the viscous properties of hydrogels, which is attributed to the partial disruption of hydrogen bonds in the thermal-responsive junction zones inside the hydrogel.

Shape memory polymers generally contain fixed cross-linking determining the permanent shape and transient cross-linking contributing to the fixity of the temporary shape. Usually the driving interactions of transient cross-linking are responsive to external stimuli, such as heat,[43,44] light,[13,45,46] pH[47,48] and chemicals,[29] resulting in corresponding stimulus-responsive shape memory polymers. With inside carboxyl groups and columnar α-CD domains, the present hydrogel is endowed with dual-responsive shape memory properties.

The polypseudorotaxane aggregation is the first cross-linking network in the hydrogel. By immersing the hydrogel into $FeCl_3$ solution, a second cross-linking based on Fe^{3+}-carboxyl complexation is introduced into the hydrogel. The temperature sweep of Fe^{3+} cross-linked hydrogel shows that with Fe^{3+}-carboxyl cross-linking, the temperature-sensitivity of the hydrogel is not altered and the storage modulus G' decreases from 3.4×10^5 Pa at 10 °C to 1.5×10^5 Pa at 90 °C (Fig. 7b).

The thermal-responsive properties attributed to the temperature-sensitive hydrogen bonding in polypseudorotaxane linking endow the hydrogel with thermal-responsive shape memory ability. In the shape fixity process, the straight columnar hydrogel was curled into a "V" shape with external force at 75 °C and allowed to cool to room temperature to be fixed at a temporary shape. As shown in Fig. 7, in the shape recovery process, the hydrogel was immersed in a 75 °C water bath to observe the shape recovery process. Fe^{3+}-carboxyl complexes role as fixed cross-linking determines the permanent shape of hydrogels. On the other hand, polypseudorotaxane aggregations *via* hydrogen bonding serve as temperature-sensitive switchable cross-linking, endowing the hydrogel with thermal-responsive shape memory ability.

High temperature can disrupt the hydrogen bonds in the hydrogel and thus the polypseudorotaxane cross-linking will be dissociated, losing the ability to fix the hydrogel at a temporary "V" shape. In the end, the hydrogel recovers its initial straight shape.

3.4 Ascorbic acid-responsive shape memory performance

A previous report confirmed that the carboxyl group could form strong complexation with Fe^{3+} but much weaker interaction with Fe^{2+}.[49] Since the Fe^{3+}-carboxyl complexation is redox-sensitive, the hydrogel also exhibits ascorbic acid-responsive shape memory behaviour. After immersion in $FeCl_3$ solution, the carboxyl groups in the hydrogel can form complexation with Fe^{3+} ions, introducing additional cross-linking into the hydrogel, which will act as switchable points for the ascorbic acid-responsive shape memory performance. The complexation between Fe^{3+} ions and carboxyl groups endows the hydrogel with enhanced mechanical strength. As shown in Fig. 8b, the storage modulus G' increases from 1.8×10^5 Pa to 3.4×10^5 Pa (ω = 6.28 rad s^{-1}). This mechanical enhancement enables the fixity of the temporary shape in $FeCl_3$ solution through Fe^{3+}-carboxyl complexation. The Fe^{3+} ions can be reduced to Fe^{2+} by ascorbic acid through redox reaction.[50] These redox-responsive

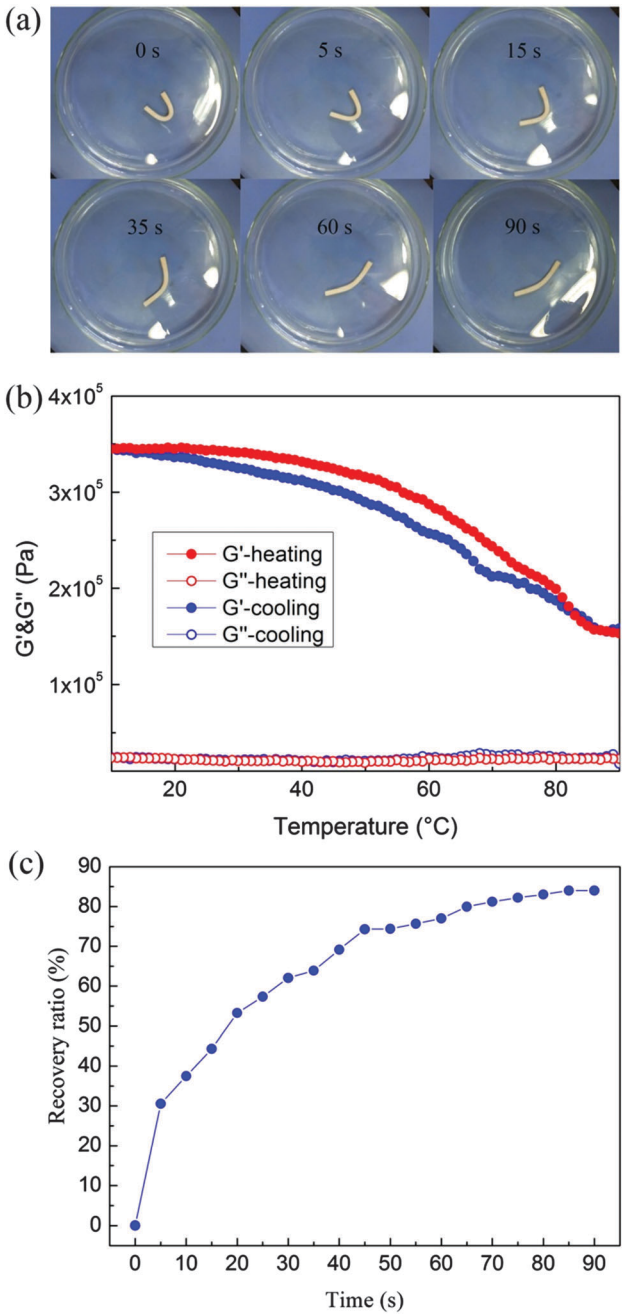


Fig. 7 (a) Photographs of thermal-responsive shape memory performance. (b) Temperature sweep of G' and G'' of Fe^{3+} cross-linked CD–PPR hydrogel. (c) Shape recovery ratio as a function of time.

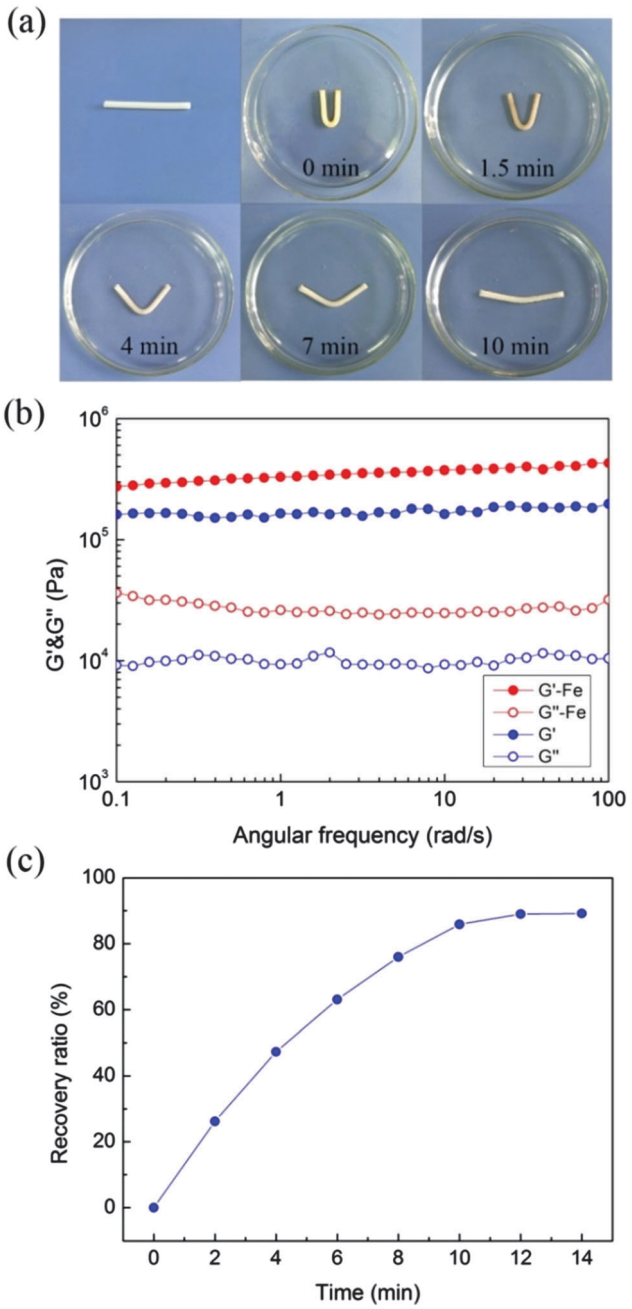


Fig. 8 (a) Photographs of ascorbic acid-responsive shape memory performance. (b) G' and G'' of the CD–PPR hydrogel before and after the introduction of Fe^{3+} into the hydrogel. (c) Shape recovery ratio as a function of time.

properties of Fe^{3+}-carboxyl interaction endowed the hydrogel with ascorbic acid-induced shape memory. Experimentally, after immersing the curled CD–PPR hydrogel in 1 M $FeCl_3$ solution for 20 minutes, with the introduction of an additional network into the hydrogel, the original straight hydrogel was fixed at a "V" shape, with its colour changing from white to slight yellow endowed by Fe^{3+} ions. Then the hydrogel was immersed in 1 M ascorbic acid solution to observe the shape recovery process. The colour of the hydrogel was observed to gradually change from yellow back to white, indicating the reduction of Fe^{3+} to Fe^{2+} and the dissociation of Fe^{3+}-carboxyl complexation. Without Fe^{3+}-carboxyl complexation, the hydrogel lost the ability to sustain its temporary "V" shape and recovered its permanent straight shape in 12 minutes.

4. Conclusions

We have prepared a polypseudorotaxane supramolecular hydrogel *via in situ* formation of polypseudorotaxanes employing temporary hydrogen bonding weakening the monomer acrylamide to prevent

rapid precipitation of α-CD/PEG inclusions. The present tough polypseudorotaxane supramolecular hydrogel demonstrates highly compressible and antifatigue mechanical properties. The hydrogel can also be endowed with thermal and ascorbic acid dual-responsive shape memory ability. We hope this report could push forward the research frontier of supramolecular hydrogels and endow them with more potential applications in biomedical fields.

Acknowledgements

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