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Facile fabrication method of hydrophobic-associating cross-linking hydrogel with outstanding mechanical performance and self-healing property in the absence of surfactants

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ABSTRACT

A cationic surfactant monomer, dimethyldodecyl(2-acrylamidoethyl)ammonium bromide (AMQC₁₂) was synthesized. A family of hydrophobic-associating cross-linking hydrogels (HAC-gels) fabricated via the self-assembly of amphiphilic multiblock copolymers of acrylamide and AMQC₁₂ can be synthesized by free-radical aqueous solution micelle copolymerization in the absence of surfactants using the one-pot method. The HAC-gels possessed outstanding mechanical performance, with optimal tensile strength, compressive strength, and elongation at break of 250 kPa, 14 MPa, and 1850%, respectively. Meanwhile, the HAC-gels exhibited self-healing property, and tetrahydrofuran (THF) significantly accelerated their self-healing process. The recovery hysteresis of hydrophobic-associating hydrogels prepared in the presence of surfactants can be eliminated because of homogeneity of the hydrogel network and the dynamic and mobile properties of physical cross-linking junctions. Investigations on the mechanical property and structure evolution of hydrogels revealed that the hydrophobic-associating interaction was the driving force of self-assembly of amphiphilic multiblock copolymers. Furthermore, spherical micelles and macroscopic cross-linking network can be easily switched reversibly by regulating copolymers concentration.

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1. Introduction

Recently, hydrogels have attracted considerable attention because of their challenging applications in controlled release [1], tissue engineering [2,3], chemical separation [4], and intelligent sensors [5]. Moreover, regulating the subtle structure and suppression of network heterogeneity can improve the fragile of hydrogels and provide them with multifunctionality.

The fabrication methods of hydrogels with excellent performance can be divided into two categories. The first category produces chemical cross-linking hydrogels, including topological hydrogels (TP gels) [6,7], double network hydrogels (DN gels) [8], nanocomposite hydrogels (NC gels) [9,10], and macromolecular microsphere composite hydrogels (MMC gels) [11,12]. The second category produces physical cross-linking hydrogels, including those formed through electrostatic force [13,14], hydrogen bonding [15], $\pi-\pi$ stacking interaction [16] and hydrophobic interaction [17].

Amphiphilic multiblock copolymers with hydrophobic and hydrophilic block segments can form unique micelle structures with hydrophobic cores decorated by petals of hydrophilic blocks (i.e., flower-likes micelles) in dilute aqueous solution [18]. Theoretically, a string of flowers, even macroscopic network with hydrophobic cores as cross-linking points, can occur by increasing the concentration of amphiphilic multiblock copolymers [19] Taking advantage of the concept of the self-assembly of amphiphilic multiblock copolymer, some supermolecular gels based on low-molecularweight block copolymer gelators and physical cross-linking hydrogel via hydrophobic-associating interaction in the presence of surfactants (HA gels) have been successfully realized [20,21]. However, the complicated synthesis process of multiblock copolymers and the extremely poor mechanical property of macroscopic self-assembled hydrogels limit their development. Meanwhile, the presence of surfactants causes the intensive chain transfer effects and purification problems [22,23], and the residual surfactants in the gel structure elicit adverse effects on gel properties.





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Recently, Friedrich [24,25] has focused on the synthesis of a dual cross-linking (containing hydrophobic-associating physical and chemical cross-linking) hydrogel via copolymerization of NIPAAm and surfactant monomer (surfmer) under γ irradiation in the absence of surfactants. The synthesized hydrogel displayed good mechanical performance. However, massive grafting reaction points in the backbone of the polymer were induced by γ irradiation, and a chemical cross-linking network structure appeared. This chemical cross-linking structure inevitably affected the mechanical performance of the hydrogel because it destroyed the structure homogeneity of the hydrophobic-associating physical cross-linking hydrogel.

In this study, a water-soluble cationic surfmer dimethyldodecyl(2-acrylamidoethyl)ammonium bromide(AMQC12) containing an amphiphilic structure and polymerizable reactive groups was synthesized to avoid the use of surfactants and to raise the hydrophobic moiety level of amphiphilic multiblock copolymers. Subsequently, hydrophobic-associating cross-linking hydrogels (HAC-gels) were prepared via radical copolymerization of acrylamide (AAm) and cationic surfmer in the absence of surfactants using the one-pot method, in which the synthesis and selfassembly of amphiphilic multiblock copolymers were realized simultaneously. Meanwhile, spherical micelles and macroscopic hydrogels were easily switched reversibly by regulating copolymer concentration. The produced HAC-gels possess excellent mechanical performance and self-healing property. Meanwhile, the recovery hysteresis of the hydrophobic-associating hydrogels prepared in the presence of surfactants can be eliminated.

2. Experimental section

2.1. Materials

N, N-dimethylethylenediamine (98%) and 1-bromododecane (99%) were purchased from Aladdin Co. (Shanghai, P. R. China) and used as received. Acryloyl chloride from Shanghai RC Chemicals Co., Ltd. (Shanghai, P. R. China) was vacuum distilled to remove any inhibitor. AAm (Aldrich Co.) was recrystallized twice using acetone and then vacuum dried at 30 °C. 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044, AR grade) was purchased from Wako Pure Chemicals Industries Ltd. (Osaka, Japan) and used as the initiator without further purification. Formamide (AR grade) and tetrahydrofuran (THF, AR grade) from Beijing Chemical Works (Beijing, P. R. China) were used as received. Water was purified by a Millipore Milli-Q system (Millipore, USA).

2.2. Synthesis

2.2.1. Preparation of surfmer

AMQC₁₂ was synthesized as follows according to a previously published method [26,27] (Scheme 1).

2.2.2. Synthesis and self-assembly of amphiphilic multiblock copolymers

A macroscopic hydrogel constructed by the self-assembly of amphiphilic multiblock copolymers can be synthesized via free-radical micelle copolymerization in the absence of surfactants in aqueous solution using the one-pot method. AAm and AMOC₁₂ with AMQC12-to-AAm ratios of 1.5/98.5, 2.0/98.0, and 2.5/97.5 mol/ mol were dissolved completely in deionized water by agitation. The total monomer concentration was controlled at 20 wt% to ensure sufficient molecular weight of amphiphilic multiblock copolymers. Then, the mixture solution was poured into plastic tubes (5 mL centrifuge tubes for tensile sample preparation and 10 mL plastic syringes for compressive ones) and then placed in an ice bath. After the initiator VA-044 (0.5 mM) was added using a syringe and stirred evenly, the reaction was streamed into nitrogen for at least 10 min and then sealed. Finally, micelle copolymerization was conducted in a 30 °C water bath for 24 h and hydrogels with excellent mechanical property were prepared. The hydrogels were named as HAC-x-y, where x denotes the AMQC₁₂ content (mol %) and y denotes the total monomers concentration.

The as-synthesized HAC-gels were insoluble in large amounts of water for several months. However, they were dissolved in large quantities of formamide for several days because of the strong polarity of formamide that destroyed the hydrophobic-associating interaction of amphiphilic multiblock copolymers. Thus, the HAC-gels were diluted in 5 wt% with formamide and agitated until they were completely. Then, a large amount of acetone was employed to precipitate the copolymers. Finally, white powder was obtained after vacuum drying at 30 °C for 24 h.

2.3. Characterization

2.3.1. Polymer composition

The proton nuclear magnetic resonance (¹H NMR) spectra of $AMQC_{12}$ and amphiphilic multiblock copolymers were obtained using a Bruker AV 600 NMR spectrometer (Bruker Group Company, Germany) in deuterium oxide.

2.3.2. Determination of critical gel concentration (CGC)

The zero-shear viscosity (η_0) of the aqueous solution of amphiphilic multiblock copolymers with various concentrations was measured via rheological experiments. Steady-state shear flow experiments were performed using a Physica MCR300 stress-controlled rheometer (Physica, Company, Germany) with a concentric cylindrical geometry (CC17, cup radius = 9.33 mm and bob radius = 8.33 mm). All measurements were performed at 30 °C using the TEZ180-C cylinder system in rotation Mode. The η_0 values were obtained and used to investigate the self-assembly structure evolution of amphiphilic multiblock copolymers.

2.3.3. Measurement of micellar size

The size of the micelles was determined by dynamic light scattering (DLS) using a vertically polarized He–Ne laser (DAWN EOS, Wyatt Technology, U.S.A.). The scattering angle was fixed at 90° and the measurement was carried out at 25 °C.

The morphology of the micelles was characterized by transmission electron microscopy (TEM, Hitachi H-800) at an acceleration voltage of 100 kV. A suspension droplet was made to drip on a



Scheme 1. Synthesis route of AMQC₁₂.

Tuble 1
Reaction parameters and mechanical properties for HAC-gels.

Specimen	Feed composition/mol%		c _m ^a /wt%	Tensile properties			Compressive properties		
	AM	AMQC12		$E_{\rm t}/{\rm kPa^b}$	$\sigma_{\rm t}/{\rm kPa}$	$\varepsilon_{\rm t}/\%$	$E_{\rm c}/{\rm MPa^{\rm c}}$	$\sigma_{\rm c}/{\rm MPa}$	ε _c /%
HAC-1.5-20	98.5	1.5	20	8.25	111.83	1461.7	0.169	10.31	84.2
HAC-2.0-20	98.0	2.0	20	8.33	152.25	1514.0	0.186	12.47	89.0
HAC-2.5-20	97.5	2.5	20	8.60	246.89	1849.5	0.189	13.98	93.8

^a $c_{\rm m}$ refers to the concentration of monomer.

^b E_t is the tensile elastic modulus for the elongation 100%–200%.

^c E_c is the compressive elastic modulus for the compression 10%–30%.

copper grid for 1 min. The liquid was blotted off using a filter paper, and the grid was air dried before measurement.

The hydrogels were freeze-dried for 48 h and their morphology was investigated using a JSM-840 scanning electron microscope (JEOL Company, Japan).

2.3.4. Tensile tests

Tabla 1

Tensile measurements were performed on cylindrical hydrogel specimens (10 mm in diameter and 30 mm in length) using a Shimadzu Autograph AG-I with a 1 kN load cell (Shimadzu Corp., Kyoto, Japan) at room temperature. The sample length between jaws was 15 mm, the crosshead speed was 100 mm/min, and the initial cross section (78.54 mm²) was used to calculate the tensile stress and elastic modulus. The initial cross section was obtained from the increment in the load detected between elongations of 100% and 200%.

2.3.5. Compressive tests

Compressive tests were performed using an Instron 5869 with a 5 kN load cell (Instron Corp., Boston, USA). Cylindrical specimens with a diameter of 11 mm and a thickness of 14 mm (the thickness-to-diameter ratio was more than 1.2) were used. The crosshead speed was 2 mm/min, and the initial cross section (94.99 mm²) was used to calculate compressive stress. The initial compressive elastic moduli were calculated using the ratio of the compressive stress and strain in the compression range of 10%–30%.

2.3.6. Self-healing property tests

The as-prepared cylindrical hydrogels with a diameter of 10 mm and a length of 30 mm were cut into two parts. A small quantity of solvent was dropped onto the specimen sections. Tensile tests of the healed samples at various healing times were performed using a Shimadzu Autograph AG-I with a 1 kN load cell (Shimadzu Corp., Kyoto, Japan). Self-healing efficiency was evaluated by the tensile strength and elongation at break of the healed samples, and the morphology of the sections was recorded by an optical camera.

3. Results and discussion

3.1. Mechanical performance of HAC-gels

In our proposal, the water-soluble cationic surfmer $AMQC_{12}$ [the critical micelle concentration of AMQC₁₂ is only 4.9×10^{-3} mol/L (25 °C) [28]] that contains amphiphilic structure and polymerizable double bond was designed to avoid the use of surfactants and to increase the hydrophobic moiety level of amphiphilic multiblock copolymers. The solubility of AMQC₁₂ can reach 2.5 g (25 °C), stemming from the quaternary ammonium group in its structure. The structure of AMQC₁₂ was confirmed via ¹H NMR (Supplementary Information S1). Based on the synthesis of AMQC₁₂, the HAC-gels constructed via the self-assembly of amphiphilic multiblock copolymers of AAm and AMQC₁₂ can be synthesized by free-radical aqueous solution micelle copolymerization in the absence of surfactants using the one-pot method. During copolymerization, the total monomer concentration was controlled at 20 wt% to prevent sufficiently high molecular weights of amphiphilic multiblock copolymers. The structure of the copolymer was characterized via ¹H NMR (Supplementary Information S2). Then, the mechanical performance of the HAC-gels was investigated and the results accompanying the reaction parameters of those were listed in Table 1 and Fig. 1.

To the best of our knowledge, hydrophobe level is a key factor affecting the mechanical properties of the HAC-gels because hydrophobic-associating microdomains are developed to fabricate a cross-linking network. In the present study, the mechanical properties of the HAC-gels with various hydrophobe contents (from 1.5 mol% to 2.5 mol%) are shown in Fig. 1. Fig. 1a shows that the tensile strength and elongation at break of the HAC-gels



Fig. 1. Effect of hydrophobe content on the mechanical properties of HAC-gels. (a) Tensile stress-strain curves. (b) Compressive stress-strain curves. Insert shows the determination method of the fracture point during the compression test.

significantly increased with hydrophobe content, reaching the maximum values of 247 kPa and 1850%, respectively, at 2.5 mol% hydrophobe content (HAC-2.5-20).

Fig. 1b shows the typical compressive stress—strain curves of the HAC-gels. For all specimens, the compressive stresses gradually increased with increasing strain until the strain crossed 70% and then abruptly increased. In the stress—strain curves of each gel, an extremely minor fall (inset of Fig. 1b) followed by a sharp rise was observed. The vertex before the second rise was identified as the fracture point. Then, the corresponding stress and strain were considered as the breaking strength and deformation at break, respectively. Similar to the results of the tensile test, the breaking strength and deformation at break of the HAC-gels during the compression measurement increased with increasing hydrophobe content. The optimal values were approximately 14 MPa and 94%, respectively, at 2.5 mol% hydrophobe content (HAC-2.5-20).

Considering the cross-linking effect of the hydrophobic microdomains on the hydrogel structure, higher hydrophobe level indicates higher cross-linking density and better mechanical performance of the HAC-gels. As the driving force of the selfassembly of the amphiphilic multiblock copolymers, the hydrophobic-associating interaction of the hydrophobic microdomains can significantly improve the homogeneity of the hydrogel network and provide dynamic and mobile properties to the hydrogels [29]. When the hydrogels are subjected to external force, the hydrophobic microdomains can deform at a large scale or even dissociate into many small-scale microdomains to dissipate energy [30]. After the removal of imposed forces, small-scale hydrophobic microdomains aggregate again because of the dynamic feature of hydrophobic-associating interaction. Thus, the HAC-gels exhibit excellent tensile and compressive performance.

Corresponding to their mechanical property development, the morphological evolution of the HAC-gels was evident because of the presence of a hydrophobe. As shown in Fig. 2, all gel specimens exhibited similar porous structures, and the mean aperture declined with increasing hydrophobe content. Therefore, higher hydrophobe level suggests higher cross-linking density and better mechanical performance of the HAC-gels. On the other hand, a fact should be faced that uneven porous structure of all HAC-gels, as shown in Fig. 2, hints that heterogeneous distribution of hydrophobe in HAC-gels in nature state. However, the dynamic and mobility of hydrophobic-associating physical cross-linking junctions can absorb and dissipate large amount of energy when HACgels surfers from deformation. Thus, the mechanical performance of HAC-gels can be significantly proved by introduction of hydrophobe.

Recovery hysteresis is still one of the serious defects in hydrophobic-associating hydrogels [31], which limits their application. However, HAC-gels can recover to their original shape immediately after the removal of the load, which exhibits obvious elastic deformation feature. In the present study, HAC-2.5-20 first stretched to 1600% strain at 2 mm/min and then recovered immediately to its original condition. Then, it immediately stretched until it fractured. As shown in Fig. 3a, the two stress–strain curves almost overlapped in the strain range of 0%–1600%, and the breaking strength and elongation at break of the specimen were close to those of HAC-2.5-20 (Fig. 3a). This finding suggests that the first stretch did not damage the inner structure of the specimen.

Similar results were also obtained in repeated compression measurement of HAC-2.5-20 (Fig. 3b). The first three measurements were terminated at 80% strain, and the specimen maintained the compressed state for 10 min. After the gel was released, it immediately recovered to its original shape. Finally, the gel was compressed until it fractured. The stress—strain curves of this repeated compression process exhibited almost the same trend (inset of Fig. 3b). This finding indicates that the original state of the gel's structure was maintained during compression.

Therefore, we can speculate a structure evolution mechanism of the HAC-gels under deformation. When hydrogels carry external load, the deformation and disassociation of hydrophobicassociating microdomains and homogeneous dynamic cross-linking



Fig. 2. SEM images of the HAC-gels with various hydrophobe contents. (a and b) HAC-1.5-20, (c and d) HAC-2.0-20, and (e and f) HAC-2.5-20.



Fig. 3. Perfect elastic recovery of HAC-2.5-20. (a) Stress-strain curves of the tension in the repeated tensile experiments. (b) Stress-strain curves of the compression in the repeated compression tests.

network ensure that the gels possess excellent mechanical strength and deformation capacity. After the external load was removed, the uniformly distributed hydrophobic-associating junctions returned to their original position, as confirmed by the complete coincidence of the stress–strain curves of the tensile and compression tests. Thus, the HAC-gels exhibit outstanding mechanical performance and perfect elastic recovery capacity.

3.2. Self-healing property of HAC-gels

The HAC-gels were formed via the self-assembly of amphiphilic multiblock copolymers. The hydrophobic-associating interaction of the hydrophobic multiblock was the driving force of the formation of macroscopic cross-linking network. Thus, the self-healing feature of the HAC-gels can be expected from the dynamicity and mobility of physical cross-linking junctions. In the present study, the self-healing capacity of HAC-2.5-20 was assessed by the tensile test of the healed gel. First, HAC-2.5-20 was cut into two parts, and a small amount of THF was dropped onto the sections of the specimen. Then, tensile tests were performed under various healing times (Fig. 4). When THF was used to induce the self-healing of HAC-2.5-20 gel, the gel can self-repair and recover its high mechanical properties. When the healing time was only 1 d, the tensile

strength and elongation at break of the healed gel were approximately 55 kPa and 850%, respectively. When the healing time was increased, the healing efficiency of the gel obviously increased. When the healing time was 7 d, the tensile strength and elongation at break reached 93 kPa and 1360%, respectively, with recovery ratios of approximately 38% and 74%, respectively. In our design, THF was employed to control the self-healing of the HAC-gels because it can rapidly induce more hydrophobe onto the surface of the fractured gel and reform more hydrophobic microdomains. However, the self-healing efficiency of the HAC-gels must be improved further to satisfy practical applications.

3.3. Fabrication mechanism of HCA-gels

Finally, the fabrication mechanism of the HCA-gels, i.e., the mechanism of self-assembly structure evolution of amphiphilic multiblock copolymers, was assumed to follow the results of the aforementioned analysis. When AAm, cationic surfmers, and initiator were dissolved in aqueous solution, the surfmers formed micelles in the scale of tens of nanometers, which can ensure the formation of amphiphilic multiblock copolymers following the mechanism of micellar copolymerization (Scheme 2a) [32]. Meanwhile, the microblock length of amphiphilic multiblock



Fig. 4. Self-healing measurements of HAC-2.5-20. (a) Specimen being cut in two parts. (b) Healed specimen induced by THF. (c) Tensile properties of the specimen; the "scar" on the section is indicated by the red circle. (d) Tensile stress—strain curves of the specimen under various healing times. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Scheme 2. Mechanism of the micelle polymerization and self-assembly structure evolution of amphiphilic multiblock copolymers.

copolymer can be adjusted by the content of cationic surfmers. During copolymerization, amphiphilic multiblock copolymers appeared and exhibited individual extended chain configuration [33] in the dilution (Scheme 2b). As the copolymerization continued, amphiphilic multiblock copolymers with sufficient molecular weight gradually appeared and formed various selfassembly structures. Moreover, the self-assembly structure of amphiphilic multiblock copolymers from the spherical micelles (Scheme 2c, the TEM photograph is supplied in Supplementary Information S2) to the macroscopic cross-linking network of the



Fig. 5. Sol-gel transition of HCA-gels triggered by the stimuli of copolymer concentration. (a) Free-flow viscous liquid. (b) Free-standing gel. (c) TEM image of spherical micelles and particle size analysis. (d) SEM image of HAC-gel morphology.



Fig. 6. Determination of the CGC of HAC-gels via the zero-shear viscosity (η_0) of various amphiphilic multiblock copolymer solutions.

HAC-gels (Scheme 2d) can be easily switched reversibly by regulating copolymer concentration. Herein the hydrophobic effect of dynamic hydrophobic-associating microdomains is major driving force of the formation of HAC-gels network due to the absence of cross-linking agent. The sufficient flexibility of the bridge hydrophilic polymer chains and the excellent homogeneity of the hydrogel network can significantly improve the mechanical property of hydrogels. Thus, the HAC-gels exhibit outstanding compressive and tensile performance. Meanwhile, the mechanical performance of HAC-gels can be regulated by the change of cationic surfmers level during the synthesis of HAC-gels in that the crosslinking density of HAC-gels network can be considered as a function of cationic surfmers level. The HAC-gels also possessed selfhealing property owing to the dynamic reversibility of the hydrophobic-associating interaction, which is the driving force of the self-assembly of amphiphilic multiblock copolymers and the formation of HAC-gels cross-linking network.

3.4. Self-assembly structure evolution of amphiphilic multiblock copolymers

As aforementioned, the HAC-gels were fabricated based on the hydrophobic-associating interaction of amphiphilic multiblock copolymers. Thus, they can be dissolved into strong polar solvents (such as formamide). These copolymers can be employed to investigate the self-assembly structure evolution of amphiphilic multiblock copolymers by controlling their concentration. When the concentration of copolymers was much lower than the CGC, free-flowing liquid was observed (Fig. 5a). The results of TEM and DLS also showed the presence of considerable particles at the 40 nm-60 nm scales (Fig. 5b and inset of Fig. 1b). This result suggests that spherical micelles were fabricated via the self-assembly of amphiphilic multiblock copolymers in dilute aqueous solution. However, after the concentration of copolymers crossed the CGC, free-standing gel appeared (Fig. 5c). This observation suggests that a macroscopic network was produced because of the cross-linking effect of hydrophobic-associating microdomains (Fig. 5d).

To demonstrate further the self-assembly structure evolution of amphiphilic multiblock copolymers, the η_0 (zero-shear viscosity) values of the copolymer solution, which was obtained from a platform of the rheological curve [34], were investigated as a function of copolymer concentration (Fig. 6). Fig. 6 shows that the viscosity evolutionary trends of amphiphilic multiblock copolymers containing various hydrophobe levels were similar under

various copolymer concentrations. First, η_0 increased with copolymer concentration and then sharply increased when the concentration crossed the CGC. The CGC of amphiphilic multiblock copolymers obviously shifted to the lower concentration region with increasing hydrophobic moiety level. The CGCs of HAC-2.5-20, HAC-2.0-20, and HAC-1.5-20 were 0.3, 0.8, and 1.0 g/dL, respectively. This evolutionary trend, which is similar to the critical association concentration of the hydrophobically associating watersoluble polymers [35], suggests that a transition from intramolecular association to intermolecular interaction occurs when copolymer concentration increases. Moreover, this result shows that the hydrophobic-associating interaction of amphiphilic multiblock copolymers is the driving force of the fabrication of their various self-assembly structures containing spherical micelles and macroscopic cross-linking network. These two types of selfassembly structures of amphiphilic multiblock copolymers, which correspond to a sol-gel transition, can be reversibly switched only by regulating copolymer concentration.

4. Conclusions

In this paper, a facile fabrication method of HAC-gels with outstanding mechanical performance and self-healing property was described based on the self-assembly of amphiphilic multiblock copolymers induced via the hydrophobic-associating interaction of hydrophobic microdomains. The synthesis of amphiphilic multiblock copolymers and the fabrication of macroscopic crosslinking network can be realized by the one-pot method in absence of surfactants. During the mechanical property test of hydrogels, the optimal tensile strength, compressive strength, and elongation at break reached 250 kPa, 14 MPa, and 1850%, respectively. Meanwhile, the recovery hysteresis of the HAC-gels prepared in the presence of surfactants can be eliminated owing to the homogeneity of the hydrogel network and the dynamic and mobile properties of physical cross-linking junctions.

The investigation on the HAC-gel fabrication mechanism and self-assembly structure evolution of amphiphilic multiblock copolymers shows that spherical micelles and macroscopic crosslinking network can be reversibly switched by regulating copolymer concentration, which corresponds to a sol-gel transition.

The excellent properties and peculiar structure evolution of the HAC-gels provide them with challenging application prospects and open an avenue in materials science. However, although the self-healing process of the HAC-gels can be accelerated using THF, the issue on the development of HAC-gels to satisfy practical application requirements remains challenging.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.07.079.

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