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Temperature-Responsive Properties of Poly(acrylic acid-*co*-acrylamide) Hydrophobic Association Hydrogels with High Mechanical Strength

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ABSTRACT: A novel type of hydrophobic association hydrogels (HA-gels) was prepared through micellar copolymerization of acrylic acid (AA), acrylamide (AAm) as basic monomers and a small amount of octylphenol polyoxyethylene ether acrylate with seven ethoxyl units (OP7-AC) as hydrophobic association monomer. The HA-gels exhibited desirable mechanical property and stably reversible phase transition between opaque and transparency. The influences of adding urea and varying AA:AAm molar ratio on the phase transition behavior were discussed, which indicated that the phase transition was introduced by forming or dissociating of hydrogen bonding between amide and carboxyl groups. The introduction of hydrophobic units (OP7-AC) to poly(acrylic acid-*co*-acrylamide) (P(AA-AAm)) copolymer would result in the adulterating and cross-linking effects on the transition temperature. The former sharply reduced the transition temperature while the later gradually raised it. The transition temperature became linearly dropping with the increasing sodium dodecyl sulfate (SDS) content in the HA-gels. Therefore, the phase transition temperature can be finely adjusted by means of changing AA:AAm ratio, concentration, OP7-AC and/or SDS dosages in the synthesis of HA-gels.

Introduction

Stimuli-responsive hydrogels have been attracting a great deal of researchers' attention, both in academic fields and practical applications, because they undergo substantial and abrupt phase transition in response to external stimulus, such as temperature, pH, ionic strength, electric field, etc. These intriguing properties have prompted worldwide researchers to investigate such gels for applications in drug-delivery,[1,2] chemical separations,[3] tissue engineering,[4,5] enzyme immobilization[6,7] and sensors.[8,9]

As the environmental temperature fluctuations occur naturally and the environmental temperature changes are easy to design and control, much attention has been focused on temperature-responsive hydrogels in recent years. There are two kinds of thermo-responsive hydrogels: negatively and positively responsive hydrogels. In the past decades, negatively temperature-responsive volume phase transition hydrogels have been studied most extensively. The typical negatively temperature-responsive hydrogels are poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels which can undergo a reversible volume phase transition in response to small temperature changes around its lower critical solution temperature (LCST: 32 °C).[10−16] Below this temperature, the gels are swollen, hydrated, and hydrophilic, while above the LCST, the gels become collapsed, dehydrated, and hydrophobic. The volume phase transitions of these gels are driven by hydrophobic interactions between the macromolecules, and their phase transition behaviors can be controlled by incorporating more hydrophilic or hydrophobic monomers in the gels composition.

In certain applications, the positively temperature-responsive phase transition behavior is preferred. These hydrogels are mainly composed of acrylamide/acrylic acid copolymers or the interpenetrating polymer networks of polyacrylamide and poly(acrylic acid). Their phase transitions are driven by hydrogen bonding between the macromolecules.[17] The hydrogels form intermolecular complexes via hydrogen bonding at temperature lower than the upper critical solution temperature (UCST) while dissociate above the UCST. Many works have focused on the gel-volume phase transitions in the IPN hydrogels which were composed of PAAm and PAA.[18−23] As the hydrogels prepared from random copolymerization of acrylic acid and acrylamide, it is found that the hydrogels showed dull swelling/deswelling behavior but possessed dramatic optical transmittance transformation with the change of temperature.[24−26]

The hydrogels prepared with conventional method generally have poor mechanical strength which will restrict their applications in some area. In order to improve their mechanical strength, some novel hydrogels have been developed: topological hydrogels,[27] double network hydrogels,[28] nanocomposite hydrogels[29,30] and macromolecular microsphere composite hydrogels.[31] They have showed excellent mechanical strength, however, it is the insufficiency that they need some complex preparation processes and cannot be reformed.

Recently, new hydrophobic association hydrogels (HA-gels) with high mechanical strength and reforming as well as self-healing capability were reported by our group.[32−34] The HA-gels can be simply synthesized with micellar copolymerization containing water-soluble main monomer, a small amount of hydrophobic monomer, and surfactant. In this paper, as a part of our research on the HA-gels systems, we focus on the synthesis and phase transition behaviors of the P(AA-AAm) HA-gels. The hydrogels are made from AA, AAm, a small amount of OP7-AC, and SDS. The effects of urea, SDS and composition of HA-gels on the transparence transition behaviors driven by temperature are detailedly investigated.

Experimental Part

Materials. Acrylic acid (AA), octylphenol polyoxyethylene ether (OP7, where 7 means the total number of ethoxy units in a molecule), dichloromethane (DCM), tetrahydrofuran (THF), urea and sodium dodecyl sulfate (SDS) were provided by Tianjin Guangfu Fine Chemical Research Institute. Acrylamide

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Scheme 1. Reaction Scheme of OP7-AC

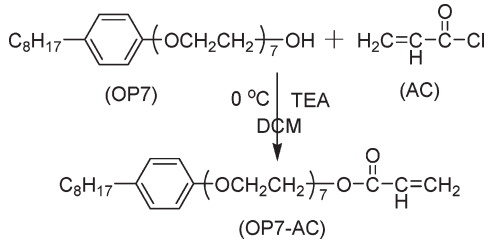


Table 1. Raw Material Compositions

samples	AA:AAm[a]	% urea[b]	% AA + AAm[c]	% OP7-AC[d]	% SDS[e]
a-series	0:10−10:0	0	15.0	3.0	3.0
b-series	5:5	0−10.0	15.0	3.0	3.0
c-series	5:5	0	10.0−20.0	3.0	3.0
d-series	5:5	0	15.0	0−6.0	3.0
e-series	5:5	0	15.0	3.0	1.5−7.5

[a] The molar ratio of AA to AAm. [b] The weight percentage of urea in the total solution. [c] The weight percentage of AA and AAm in the total solution. [d] The molar percentage of OP7-AC to the summation of AA and AAm. [e] The weight percentage of SDS in the total solution.

(AAm), potassium persulfate (KPS) and triethylamine (TEA) were purchased from Tianjin Fuchen Chemical Reagent Factory. Acryloyl chloride (AC) was purchased from Shanghai Haiqu Chemical Co.. AA was distilled under reduced pressure before use. AAm and KPS were recrystallized with distilled water. OP7 was dried over phosphorus pentoxide for 48 h in a vacuum desiccator. DCM was dried by distillation from phosphorus pentoxide before use. THF and TEA were purified by refluxing with metallic sodium followed by distillation. The other reagents were used without further purification.

Synthesis of OP7-AC. First, 200 mL of DCM, 51.5 g (0.10 mol) of OP7, and 11.6 g (0.115 mol) of TEA were added to a three-neck flask equipped with an electromotion stirrer. Stirring the mixture at 0 °C for 15 min until a homogeneous solution was obtained, and then 11.3 g (0.125 mol) of AC in 40 mL of DCM was added dropwise to the flask under stirring at 0 °C. After the addition was complete, the reaction was carried out for another 4.5 h at 0 °C and 16 h at room temperature in sequence. Then triethylamine hydrochloride was filtrated from the reaction system by a G4 type Buchner funnel and DCM was removed by rotary evaporation at 22 °C. Then, 150 mL of THF was added into the product and stirred uniformly, then rotary evaporated again after the residual triethylamine hydrochloride was filtrated. The final product, OP7-AC, was dried to constant weight with quantitative yields (94.75%) in vacuum at 20 °C. The reaction scheme is shown in Scheme 1.

Synthesis of P(AA-AAm) HA-Gels. The P(AA-AAm) HA-gels were synthesized by micellar copolymerization. A certain amount of AAm, AA, OP7-AC, SDS, and H_2O were added to a 20 × 200 mm test tube (the raw material compositions are shown in Table 1). The mixture was stirred until a homogeneous solution was achieved. Then 0.01 g/g KPS aqueous solution was added into the solution. The dosage of initiator KPS was 0.5% gross weight of monomer AA, AAm and OP7-AC. Nitrogen was bubbled through the mixture to remove oxygen for 20 min. A quartz cell (10 × 10 × 45 mm) was immersed into the reaction solution, followed by sealing up the tube and reacting at 50 °C for 12 h. After the HA-gel was obtained, the test tube was broken down, and the exterior gel outside of the cell was cleaned out. The interior gel with quartz cell was measured for transmittance without further purification.

Tensile Mechanical Strength Measurements. The samples for tensile tests were obtained with the method described previously.[32] The tensile mechanical strength of the P(AA-AAm) HA-gels (7 mm o.d. × 70 mm length) were tested by Shimadzu Autograph AG-I with 1KN load cell (Shimadzu Corp., Kyoto, Japan). The sample length between the jaws was 25 mm and the cross-head speed was 100 mm·min^{-1}.

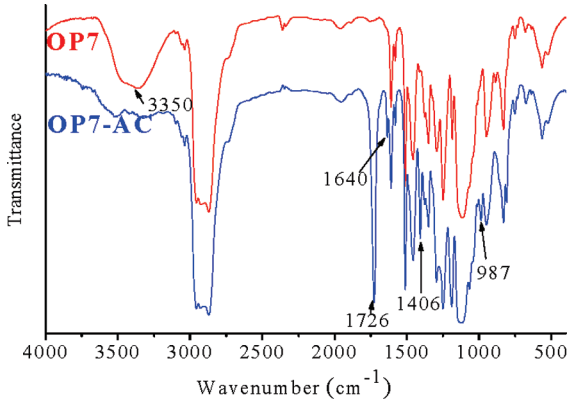


Figure 1. FTIR spectra of OP7 and OP7-AC.

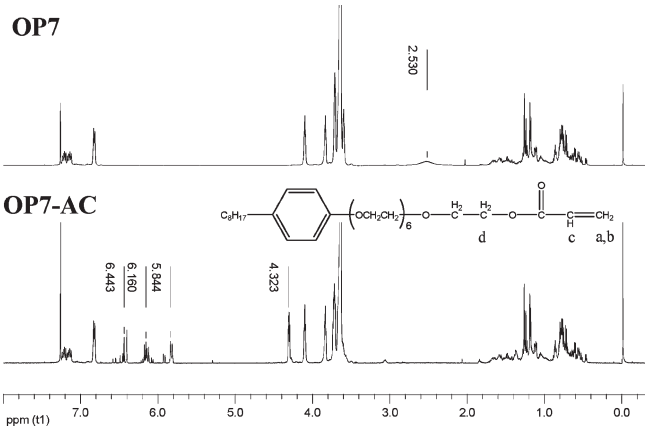


Figure 2. ^{1}H NMR spectra of OP7 and OP7-AC.

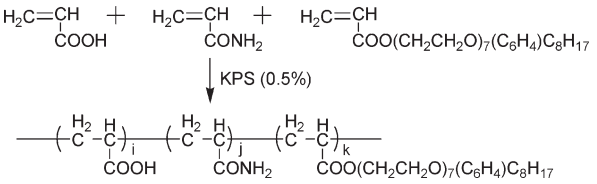
Transmittance Measurements. The transparence transitions of the P(AA-AAm) HA-gels were tested with a Shimadzu UV-2450 spectrophotometer equipped with a temperature controlling set. The temperature was changed from 1 to 67 °C, and the transmittance value at 600 nm was recorded every 2 °C. The time interval between each temperature increment was 15 min. To examine the reversibility of the phase transition of the P(AA-AAm) HA-gels, the temperature was alternately changed between 10 and 40 °C for several cycles by using a6 sample (AA:AAm = 5:5).

Results and Discussion

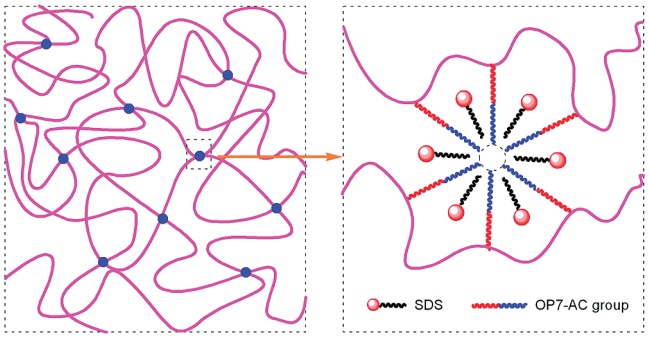
Characterization of OP7-AC. Figure 1 shows the Fourier transform infrared (FTIR) spectra of OP7 and OP7-AC. The FTIR spectra were recorded in the range of 4000−400 cm^{-1} by using a Bruker VECTOR22 spectrophotometer. From the IR spectra, it is obvious that OP7 shows a broad peak at 3350 cm^{-1} corresponds to stretching vibration of −OH, however, it disappeares on the spectrum of OP7-AC. The strong and acute peak at 1726 cm^{-1}, which is different from the peak at 1760 cm^{-1} for AC, proves that the OH groups of OP7 have reacted with AC. Moreover, the peak at 1640 cm^{-1} corresponds to stretching vibration of C=C, the peak at 1406 cm^{-1} corresponds to the shear-vibration of $=CH_2$ and the peak at 987 cm^{-1} corresponds to out-of-plane bending vibration of $=CH_2$ are observed on the spectrum of OP7-AC.

Figure 2 shows the ^{1}H NMR spectra of OP7 and OP7-AC. The ^{1}H NMR spectra were recorded by using a Bruker AVANCE500 nuclear magnetic resonance spectrometer. In the OP7-AC ^{1}H NMR spectrum, intense resonance peaks appear at 5.8, 6.1, and 6.4 ppm, which are assigned to the protons linked to C=C (a, b, c). The peak at 4.3 ppm corresponds to

Scheme 2. Reaction Scheme of P(AA-AAm) HA-Gels



Scheme 3. Schematic Illustration of the Structural Model with Associating Networks in the HA-Gels



the methylene protons which links to ester group (d), while the peak at 2.5 ppm disappears which belongs to the hydroxyl proton in the OP7 spectrum. The IR and ^{1}H NMR spectra indicate that the polymerizable hydrophobic monomer OP7-AC has been successfully synthesized.

Network Structure and Mechanical Property of P(AA-AAm) HA-gels. The Scheme 2 shows the reactants and the chemical compages of a polymer chain in P(AA-AAm) HA-gels. Compared with the traditional chemical hydrogels, double functional groups monomers as cross-linking agents were not introduced into the preparation process of P (AA-AAm) HA-gels. OP7-AC as a hydrophobic monomer was solubilized by SDS and formed associated micelles during the process of stirring the mixture of AAm, AA, OP7-AC, SDS, and H_2O. Then in the process of copolymerization, OP7-ACs in a micelle were copolymerized to two or more P(AA-AAm) chains,[35] and the associated micelles acting as cross-linking points cross-linked the P(AA-AAm) chains and formed three-dimensional polymer network.[32,33] Scheme 3 illustrates the proposed network model with hydrophobic associating in the HA-gels.

HA-gels exhibited outstanding mechanical property. Figure 3a shows the stress−strain curves of P(AA-AAm) HA-gels (samples in a-series). The PAAm HA-gel showed the highest tensile strength while the PAA HA-gel showed the highest elongation. Along with increasing AA components in P(AA-AAm) HA-gels, the tensile strength becomes reduction and the break elongation tends toward augment. The deformations for all samples can recover before fracture. Figure 3b shows the fracture energies calculated from the tensile curves, indicating that introducing AA will somewhat weaken the mechanical strength. However, the fracture energies are still more than 0.35 J and are evidently higher than fragile hydrogels prepared conventionally with monoalkene and bialkene monomers copolymerization.

Phase Transition Behavior. When a light beam passes through a dispersed medium, it will occur light transmitting, light scattering or light reflecting. If the diameter of the particle is much smaller than the light wavelength (λ), light is transmitted. If the diameter of the particle is much larger than λ, light is reflected. And light scattering occurs when λ is larger than the size of particle in the dispersed phase. Therefore, the

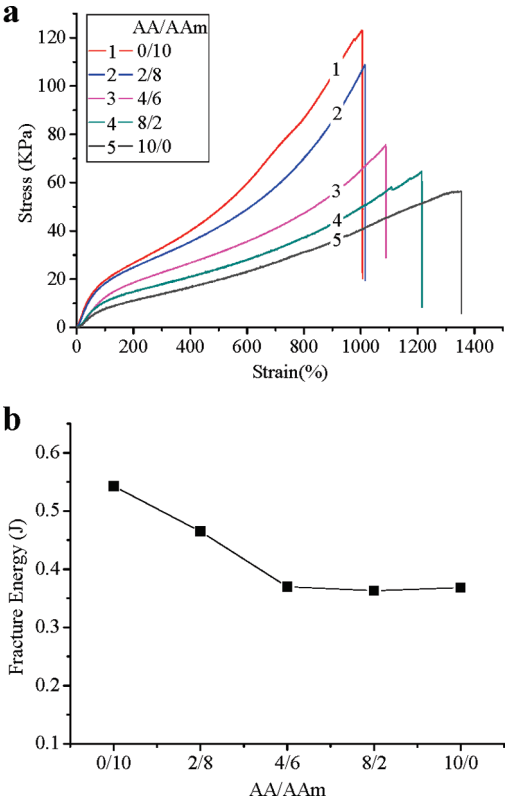


Figure 3. Mechanical properties of P(AA-AAm) HA-gels with different AA/AAm ratios: (a) stress−strain curves; (b) fracture energies.

density of transmitted light is affected greatly by the size of the particle dispersed in the medium. For P(AA-AAm) HA-gels, microphase separation occurred when temperature decreased and the microphase in HA-gels played the same role as the particle in a dispersed medium. Therefore, we measured the optical transmittance at 600 nm to estimate the phase transition temperature of the P(AA-AAm) HA-gels.

Effect of Urea Content. It has been reported that the chains in P(AA-AAm) IPN hydrogels existed in the forms of collapsed coils because of hydrogen bonds.[21] The collapsed coils could be disrupted by adding salt or enhancing the temperature. To verify that the phase transition of the P(AA-AAm) HA-gels is induced by hydrogen bond, a certain amount of urea was added to the initial reaction solution. And the influences of urea on the temperature dependence of the transmittance for P(AA-AAm) HA-gels (b-series) are shown in Figure 4. The transmittance of the P(AA-AAm) HA-gel without any urea was 0% below 10 °C and near 100% above 30 °C. With increase of urea, the phase transition temperature of the P(AA-AAm) HA-gel became decrease. When urea content was equal or more than 10 wt %, the transmittance for the P(AA-AAm) HA-gel had reached 100% above 0 °C, meaning that the complexes dissociated completely. The urea is well-known to strongly disturb hydrogen bonding and hydrophobic interaction,[21] while raising temperature tends to enhance the hydrophobic association,[16] which means the change of transparency for P(AA-AAm) HA-gels is mainly due to intermolecular hydrogen bonds rather than the microdomains of hydrophobic association. In fact, although hydrophobic microdomains as cross-linking points had been introduced, the clear HA-gels without any phase transition were observed in our previous work, in which only AAm as water-soluble monomer was used.[32−34] In view of the effect of disturbing hydrogen bonds, the more urea in P(AA-AAm) HA-gels, the less hydrogen bonds formed, leading to lower transition temperature.

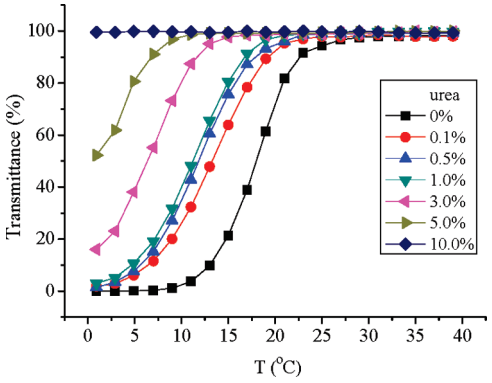


Figure 4. Influence of urea on the temperature dependence of the transmittance for P(AA-AAm) HA-gels.

Effect of AA:AAm Ratio. Figure 5a shows the influence of AA:AAm molar ratios on the phase transition process of P(AA-AAm) HA-gels. Besides the HA-gels made with onefold AAm or AA as main monomers, the P(AA-AAm) HA-gels were entirely transparent when AA:AAm ratios were less than 2:8. When the AA:AAm ratios varied from 3:7 to 9:1, the phase-transitions appeared. For expedient comparison, the temperature at 75% transmittance is selected as the transition temperature. It was observed that the transition temperature first increased then decreased along with the increasing AA components (Figure 5b). Above phenomena indicate that the hydrogen bonding between carboxyl groups of AA units and amide groups of AAm units must play an important role although several other types of hydrogen bonding are possible in P(AA-AAm) HA-gels.

It was observed that the highest transition temperature for the HA-gels occurred at 6:4 (AA:AAm) rather than 5:5, which could be due to a few carboxyl groups had been wasted in forming hydrogen bonding with ethoxy groups on the hydrophobically associated side chain. To confirm this guess, the OP7-AC was ridded from the system, and it was observed that the highest transition temperature of the sample did occur at 5:5 AA:AAm molar ratio (Supporting Information, Figure S1). The schematic representation of hydrogen bonding in P(AA-AAm) HA-gels is shown in Schematic 4. A similar result has been obtained by Kubota et al.[26]

Additionally, because the presence of hydrogen bonding between AA and ethoxy group on OP7-AC, some OP7-AC units were likely to be pulled from solubilized SDS micelles into the water phase during the synthesis of P(AA-AAm) HA-gels. Consequently, the cross-linking effect of hydrophobic association was impaired, that is, the network of HA-gels became more and more imperfect as the AA fraction increased. It seems to be an important factor resulting in the change of mechanical properties of HA-gels showed in Figure 3.

Effect of AA+AAm Concentration. The temperature dependences of the transmittance of the HA-gels with various AA+AAm concentrations (c-series) is shown in Figure 6. It is obvious that the phase transition of the HA-gels was affected by the AA+AAm concentration. Along with the AA+AAm concentration increasing, the transition temperature of the HA-gels increased and the phase transition became sharper. When the AA+AAm concentration increased from 10 to 20 wt %, the increment of temperature at 75% transmittance was about 15 °C. P(AA-AAm) molecular chains were more compact in the concentrated system, and the amount of hydrogen bonds between carboxyl and amide group in per unit volume increased too. Higher temperature will be required to destroy the stronger hydrogen bonds.

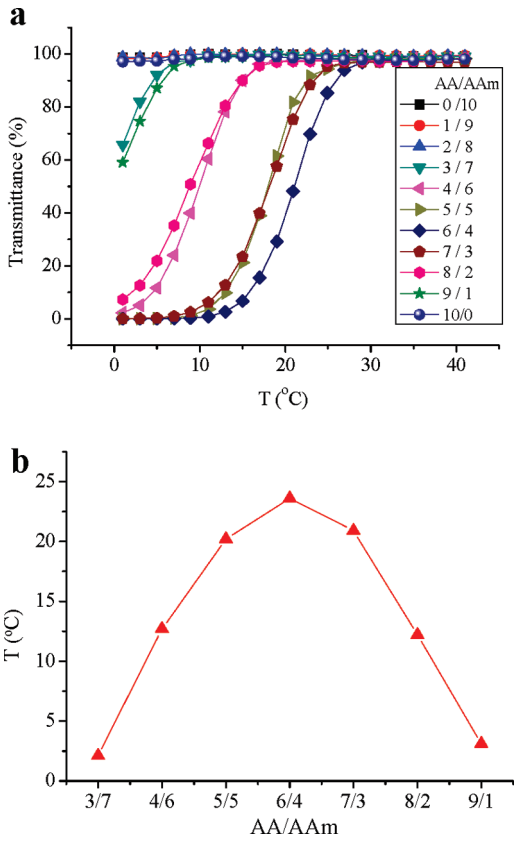
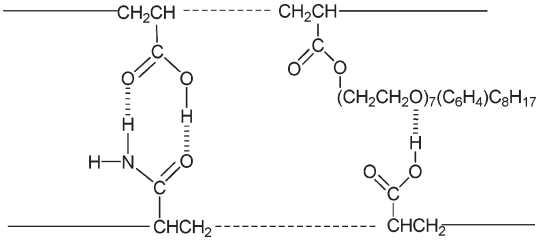


Figure 5. Influence of monomer composition on the phase transition temperature: (a) dependence of transmittance on AA:AAm ratios; (b) dependence of temperature (transmittance = 75%) on AA:AAm ratios.

Scheme 4. Schematic Illustration of Hydrogen Bonding in P(AA-AAm) HA-Gels



Effect of OP7-AC Dosage. In order to further investigate the relationship between the phase transition and the inherent structure of P(AA-AAm) HA-gels, two series (d and e) samples were synthesized with different ratios of OP7-AC and SDS. For series-d samples, the OP7-AC dosage changed from 0 to 6%, while SDS and other agent contents were invariable as usual. Figure 7a shows the transmittances of series-d samples as a function of temperature. It is obvious that the OP7-AC dosage largely affects the phase transition.

The temperature at 50% transmittance as a function of the OP7-AC dosage is shown in Figure 7b. Along with the increasing of the OP7-AC dosage, the transition temperature decreased sharply at first, then gradually dropped, after then tardily increased. The lowest transition temperature (12.5 °C) occurred as 1.5% OP7-AC was used, while the sample without OP7-AC had the highest transition temperature (62 °C), implying that the strongest interaction of hydrogen bonding existed in the pure P(AA-AAm) copolymer solution.

There are two opposite effects should be considered for us to explain the influence of introduced OP7-AC on the phase

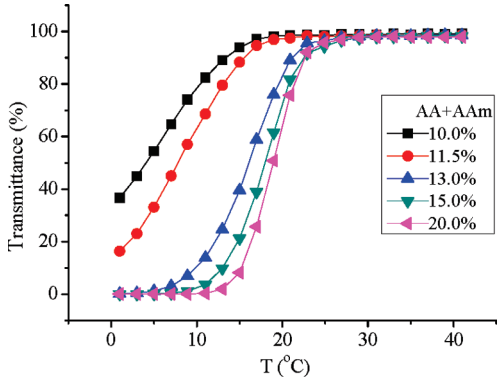


Figure 6. Influence of AA+AAm concentration on the phase transition temperature.

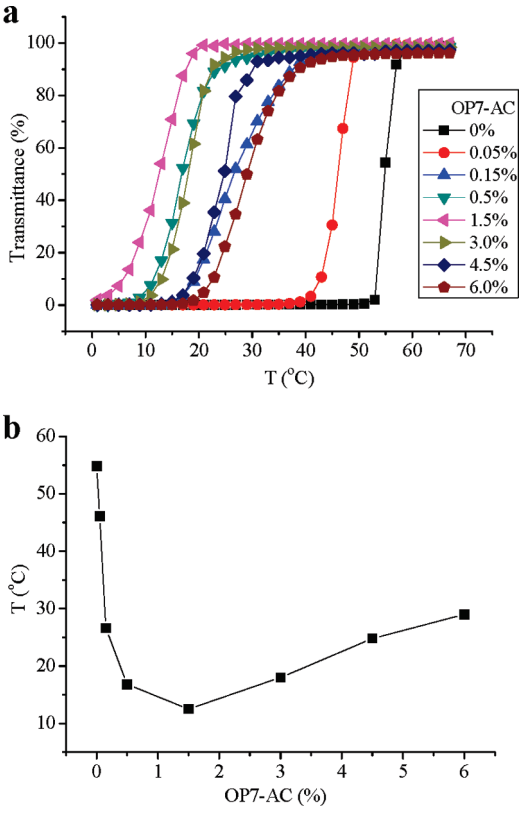


Figure 7. Influence of OP7-AC on the phase transition temperature: (a) dependence of transmittance on OP7-AC; (b) dependence of temperature (transmittance = 50%) on OP7-AC.

transition of HA-gels. One is adulterating effect, that is, embedding OP7-AC units into the copolymer chain will disturb the formation of the hydrogen bonds between carboxyl and amide group, meanwhile waste a few carboxyl groups to form hydrogen bonds with the ethoxy groups, which makes destroying the hydrogen bonds easy, so that the transition temperature will decrease. The other is cross-linking effect brought by hydrophobic association microdomains, which will restrict the motion of polymer chains, accordingly, makes destroying the hydrogen bonds difficult, so the transition temperature will increase. The result showed in Figure7 suggests that predominant effect depends on the OP7-AC dosage in the HA-gels. When OP7-AC dosage was less than 1.5%, the adulterating effect was predominant. More than this critical value, the cross-linking effect played the main role.

Both intensities of these two effects should increase with the increasing OP7-AC content in the HA-gels. Meanwhile the intensity of the cross-linking effect should get quicker increasing, since the transition temperature had tended to increase if OP7-AC dosage was more than the critical value mentioned above. On the other hand, if the OP7-AC units introduced are too few to form effective hydrophobic association microdomains, the cross-linking effect will not exist. This means that there is another critical value of OP7-AC dosage, under which no cross-linking effect occurs. However, the adulterating effect always works throughout the range of OP7-AC added.

Let C_c and C_r denote the two critical values of OP7-AC content; here, the subscripts "c" and "r" mean "cross-linking" and "reversal" respectively. That is, as the OP7-AC content reaches C_c, the cross-linking effect begins, and as it further reaches to C_r, the change of transition temperature begins reversal. We can imagine that the range of OP7-AC content from zero to a certain amount is separated into three sections by C_c and C_r ($C_c \leqslant C_r$). When the OP7-AC content is less than C_c, only the adulterating effect exists, so the transition temperature will sharply decrease with increasing OP7-AC content. When the OP7-AC content is more than C_c but less than C_r, both of two effects work while the adulterating effect is predominant, so the transition temperature will tend to slowly drop. When the OP7-AC content is more than C_r, the cross-linking effect becomes predominant, so the transition temperature will tend toward rise. The phase transition phenomena showed in Figure 7 can be well illuminated by this consideration, and it seems that C_c is about 0.5% and C_r is about 1.5% for the series-d P(AA-AAm) HA-gels.

It should be mentioned that we have found that the introduction of SDS into pure P(AA-AAm) copolymer aqueous solution would largely increase its transition temperature. As to the system without SDS, the phase transition occurred at about 23.8 °C rather than 54.8 °C as showed in the Figure 7. The transition temperature would linearly increase with SDS increases (Supporting Information, Figure S2). However, this effect did not influence the qualitative discussion about the adulterating effect of HA-gels. The detail investigation about the effect of surfactants on the phase transition temperature of P(AA-AAm) copolymers without hydrophobic association cross-linking is beyond our subject in this paper and will report elsewhere.

Effect of SDS Content. During the preparation of P(AA-AAm) HA-gels, OP7-AC was solubilized by SDS. While without SDS in the system, the phase separation occurred after raw material mixing and homogeneous hydrogel could not be prepared. For the e-series HA-gels, the SDS content cannot be less than 1.5%.

On the basis of the principle of micellar copolymerization,[36−44] the hydrophobic monomers solubilized in SDS or other surfactants micelles will form microblocky structures embedded into hydrophilic polymer chains after polymerization. In the condition of invariable OP7-AC dosage, increasing SDS content means increasing micelle amount, which will result in further dispersion of OP7-AC and reducing its amount in each micelle. It allows us to predicate that, with the increasing SDS content, more hydrophobic microblocks will be formed and each microblock will become short in the HA-gels systems. This microstructural variation should be reflected in the phase transition behavior and mechanical property of HA-gels. It has shown that the tensile modulus tends to decrease as more SDS is added in HA-gels,[33] indicating that the effective cross-linking density of the network has decreased. More hydrophobic microblocks embedded in the polymer chains will enhance the adulterating effect, while

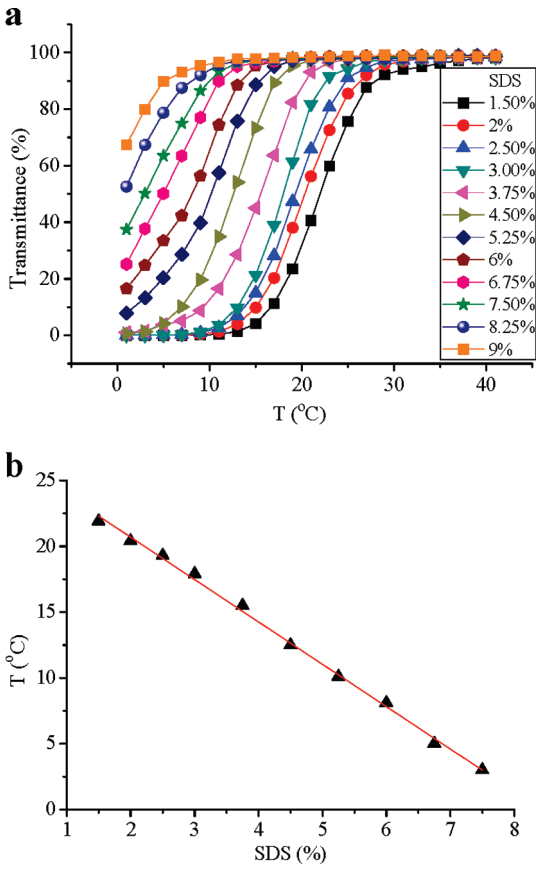


Figure 8. Influence of SDS on the phase transition temperature: (a) dependence of transmittance on SDS; (b) dependence of temperature (transmittance = 50%) on SDS.

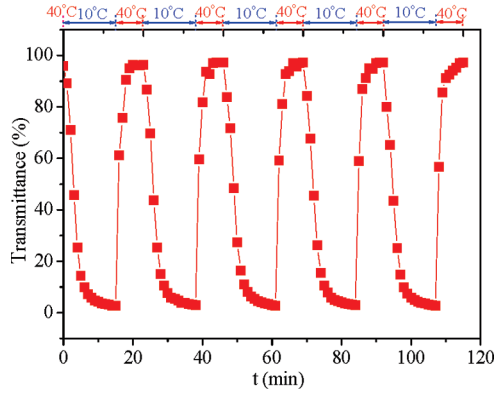


Figure 9. Oscillatory phase transition behavior of P(AA-AAm) HA-gel.

shortening microblocks will weaken the cross-linking effect due to more SDS surround the hydrophobic group. The both will reduce the transition temperature of HA-gels.

Figure 8 shows the effect of SDS on the transition temperature of the e-series HA-gels. It reveals that the transition temperature linearly dropped with increasing SDS content, which quite accorded with above deduction. It was noticed that, when more SDS was introduced into the present system, the transition temperature rather dropped than rose as mentioned in above section, implying that the adulterating effect was more important so long as enough hydrophobic monomers were used in the synthesis of HA-gels.

Oscillatory Phase Transition. To confirm the reversibility of the phase transition of the P(AA-AAm) HA-gels, the transmittance change for one of a-series samples (AA:AAm = 5:5) was examined between 10 and 40 °C. Which have covered the entire range of the transition temperature. Transmittance changes with alternate temperature changes are shown in Figure 9. The highest transmittance observed at 40 °C and the transmittance decreased when the temperature was changed to 10 °C and vice versa. The transmittance change showed a sharp shape and could not be weakened by multiple temperature changes. This reversibility as well as the unique mechanical strength mentioned above may allow P(AA-AAm) HA-gels to be an useful functional material.

Conclusions

P(AA-AAm) HA-gels were prepared through micellar copolymeration of AA, AAm, and a few OP7-AC in an aqueous solution containing SDS. The P(AA-AAm) HA-gels exhibited desirable mechanical property and stably reversible phase transition behavior. The result of adding urea indicated that the phase transition was induced by forming or dissociating hydrogen bonding between amide and carboxyl groups. The introduction of hydrophobic units (OP7-AC) to P(AA-AAm) copolymer would result in the adulterating and cross-linking effects on the transition temperature. The former sharply reduced the transition temperature but the later gradually raised it. The phase transition temperature can be finely adjusted in a wide range by means of changing AA:AAm ratio, concentration, OP7-AC and/or SDS dosages in the synthesis of HA-gels.

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Supporting Information Available: Figures S1 and S2, showing influence of AA:AAm on the phase transition temperature of P(AA-AAm) HA-gels without OP7-AC and influence of SDS on the phase transition temperature of P(AA-AAm) copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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