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Guoqing Jiang[a][b]; Chang Liu[a]; Xiaoli Liu[a]; Guohui Zhang[a]; Meng Yang[a]; Qingrui Chen[a]; Fengqi Liu[a]
[a] College of Chemistry, Jilin University, Changchun, China [b] Exploration and Development Research Institute, Daqing Oilfield Company Limited, Daqing, China

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Self-healing Mechanism and Mechanical Behavior of Hydrophobic Association Hydrogels with High Mechanical Strength

GUOQING JIANG[1,2], CHANG LIU[1], XIAOLI LIU[1], GUOHUI ZHANG[1], MENG YANG[1], QINGRUI CHEN[1] and FENGQI LIU[1,*]

[1] *College of Chemistry, Jilin University, Changchun 130012, China*
[2] *Exploration and Development Research Institute, Daqing Oilfield Company Limited, Daqing 163712, China*

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Hydrophobic association hydrogels (HA-gels) were prepared through micellar copolymerizationof acrylamide (AM) and a small amount of octyl phenol polyethoxy ether acrylate (OP-4-AC) in an aqueous solution containing sodium dodecyl sulfate (SDS) at 50°C. The resulting HA-gels exhibited excellent mechanical properties and transparency. However, the most striking properties were that HA-gels possessed the capability of self-healing. The mechanical properties of HA-gels were investigated by uniaxial stretching. The results showed that the mechanical properties of HA-gels could be varied greatly by changing OP-4-AC content in the range of OP-4-AC used. On the basis of the rubber elastic theory and using uniaxial stretching data, the effective network chain density and the average distance between the cross-linking points were calculated for HA-gels. For tensile measurements of altering crosshead speed, the modulus of HA-gels increased sharply with increasing crosshead speed. The stress-relaxation behavior of HA-gels consisted of two stages. Similar to rubbery, HA-gels exhibited obvious thermoelastic behavior and also showed a good rubberlike elastic property.

Keywords: Hydrogels, micellar copolymerization, self-healing capability, mechanical behavior, stress-relaxation, thermoelastic behavior

1 Introduction

Hydrogels are one of the most promising types of polymers being used for new material development and have been investigated extensively from both basic and application points of view. Accordingly, hydrogels are widely applied to various fields, such as biomimetic actuators (1, 2), drug delivery systems (3, 4), immobilization of biocatalysts (5, 6), binding and removal of heavy metal ions (7–9), bioseparators (10, 11) and proton transport (12, 13). However, the lack of two properties restricts their applications: self-healing capability and weak mechanical strength. Therefore, searching for hydrogels with high mechanical strength and self-healing capability has been a classic and everlasting research topic. In recent years, many efforts have been focused on the enhancement of the mechanical strength of hydrogels. As a result, four strategies were developed, forming topological gels (14), double network gels (15), nanocomposite gels (16) and macromolecular microsphere composite gels (17). In particular, these hydrogels are extremely promising because they possessed good mechanical strength and rubberlike. However, the absence of the self-healing capability resulting from their permanent cross-linking structure and the complex synthesis process tend to hinder their industrial and biomedical applications.

Recently, in order to overcome the limitations of above-mentioned hydrogels, we succeeded in synthesizing a new type of physically cross-linked hydrogels: hydrophobic association hydrogels (HA-gels) with good mechanical strength and self-healing capability (18). HA-gels were prepared by micellar copolymerization (19–22) of acrylamide (AM) and a small amount of octyl phenol polyethoxy ether acrylate (OP-4-AC) as the hydrophobic monomer in an aqueous solution containing sodium dodecyl sulfate (SDS). As we all know, the solution properties of hydrophobically modified polyacrylamide (HMPAM) has been extensively studied over the past two decades (20, 23–28); however, very little work has been done on the bulk hydrogels with mechanical strength. The HA-gels were composed of HMPAM, SDS and water, in which the associated micelles acted as effective cross-linker. The associated micelles were formed by hydrophobic associations of SDS and hydrophobic groups belonging to two or more HMPAM chains. Because of the large distance between the

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*Address correspondence to: Fengqi Liu, College of Chemistry, Jilin University, Changchun 130012, China. E-mail: liufengqi@jlu.edu.cn

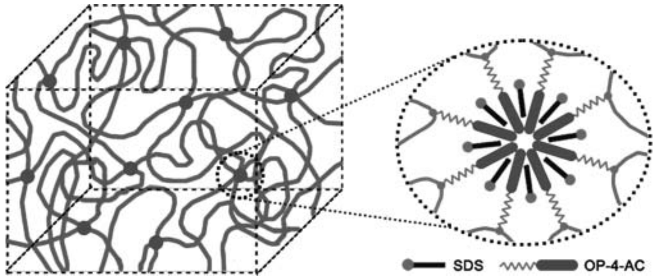


Fig. 1. Schematic illustration of the structural model with associating networks in the HA-gels, which consists of associated micelles and flexible polymer chains connected by neighboring associated micelles. For simplicity, only a small number of polymer chains are described in the structural model.

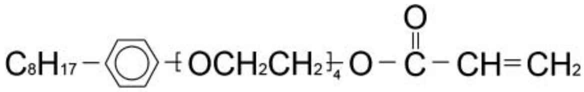
associated micelles, all polymer chains between the cross-linking points in HA-gels were sufficiently long and flexible. These polymer chains were effectively cross-linked by associated micelles. We proposed the model structure for HA-gels depicted in Figure 1. The model is based on a fairly narrow distribution of chain lengths between associated micelles. As a result of the unique network structure, we found that HA-gels could break through the limitations described above. Similar to the above-mentioned four types of hydrogels, HA-gels exhibited also excellent mechanical properties. However, it is noted that HA-gels possessed the capability of self-healing due to dissociation and re-association of cross-linking points. Especially, no external cross-linker was used for the formation of their network structure and the preparation process of HA-gels was very simple. Furthermore, HA-gels are also possessed of thermoelastic behavior, and their mechanical behavior can be described by applying the rubber elastic theory. In addition, dried-gels, which were prepared by stretching HA-gels to a certain elongation for a period of time in the air, can be used as shrinkable or thermal sensitivity materials.

In the communication reported previously (18), construction and various properties of HA-gels were briefly discussed by Fourier transform infrared, uniaxial stretching and swelling behavior. These results showed HA-gels possessed the unique network structure and mechanical properties of HA-gels strongly depended on the content of compositions in initial reaction solution. HA-gels with variously available properties, such as thermoresponsive HA-gel, nano-spheres composite HA-gel and fluorescent HA-gel were also reported. In this paper, the network structure of HA-gels was further analyzed based on the rubber elasticity theory. Moreover, the self-healing mechanism and the mechanical behavior of HA-gels were further discussed in detail.

2 Experimental

2.1 Materials

OP-4-AC was prepared according to the synthetic procedure reported previously (18) and its chemical structure is given in Scheme 1. AM and potassium persulfate (KPS) were purchased from Tianjin Fuchen Chemical Reagent Factory, China. Other reagents were purchased from Beijing Chemical Works, China. All these reagents were used as received except AM and KPS which were recrystallized from distilled water before use and dried under vacuum at room temperature. All solutions used in experiments were prepared in distilled water.



OP-4-AC

Sch. 1. Chemical structure of octyl phenol polyethoxy ether acrylate (OP-4-AC).

2.2 Synthesis of HA-gels

The synthetic procedure of HA-gels is the same as that reported previously (18). In order to prepare various HA-gels with different compositions, the OP-4-AC content in the initial solution were varied over a wide range. In the present study, HA-gels are expressed as A_n gels, where n stands for molar percentage of OP-4-AC relative to AM in the initial reaction solution and weight concentrations of SDS and AM were 3 wt% and 10 wt%, respectively. All the total mass of the initial reaction solution was 30.00 g. Nomenclature and the content of compositions in the initial reaction solution for A_n gels are listed in Table 1. For example, the experimental procedure used for A_2 gel was as follows: first, a transparent aqueous solution consisting of AM (3.00 g), OP-4-AC (0.37 g), SDS (0.90 g), and distilled water (24.04 g) were prepared. Then, the aqueous solution of initiator (KPS 0.0169 g in water 1.69 mL) was added to the former solution. Next, the solution was added to a test tube and drove out dissolved oxygen with N_2 for 10 minutes under normal pressure, and then the tube was sealed. After being placed at room temperature for 1 h, micellar copolymerization was carried out in a water bath at 50°C for 5 h. As a result, HA-gels were prepared.

Table 1. Nomenclature and the content of compositions in initial reaction solution for A_n gels

A_n gels	*AM (g)*	*OP-4-AC (g)*	*SDS (g)*	*KPS[a] (mL)*	*H_2O (g)*
$A_{0.5}$	3.00	0.09	0.90	1.55	24.46
$A_{0.7}$	3.00	0.13	0.90	1.57	24.40
$A_{0.9}$	3.00	0.17	0.90	1.58	24.35
A_1	3.00	0.18	0.90	1.59	24.33
A_2	3.00	0.37	0.90	1.69	24.04
A_3	3.00	0.55	0.90	1.78	23.77
A_4	3.00	0.72	0.90	1.86	23.52
A_5	3.00	0.92	0.90	1.96	23.22

[a] Concentration of KPS was 0.01g/mL.

2.3 Mechanical Testing

The measurements of tensile mechanical properties were performed on as-synthesized HA-gels of 7.0 mm diameter ×80 mm length with a Shimadzu Autograph AG-I with a 1 KN load cell (Shimadzu Corp., Kyoto, Japan) at 25°C. The specimen length between jaws was 25 mm and the tensile experiment was carried out at crosshead speed of 100 mm/min (except for the testing of altering crosshead speed). Initial cross-sectional area (38.48 mm^2) was used for calculating tensile stress.

3 Results and Discussion

3.1 The Effective Network Chain Density (N) and the Average Distance between the Cross-Linking Points (D_N)

HA-gels were prepared by a simple method. First, HMPAM was synthesized by micellar copolymerization of AM and OP-4-AC as the hydrophobic monomer, where the presence of SDS ensured the solubilization of the OP-4-AC. The HMPAM prepared by micellar copolymerization had microbloky structure; in other words, the hydrophobic monomer was distributed along the copolymer backbone in a microblocky manner (22, 29). After polymerization, hydrophobic associations of SDS and hydrophobic microblocks of HMPAM lead to the formation of associated micelles (21, 24). Then, these associated micelles promoted chain cross-linking by acting as cross-linking points, so three-dimensional polymer networks were constructed. As a consequence, HA-gels exhibited remarkable mechanical properties, see Figure 2. The HMPAM in HA-gels was also confirmed by IR studies (18).

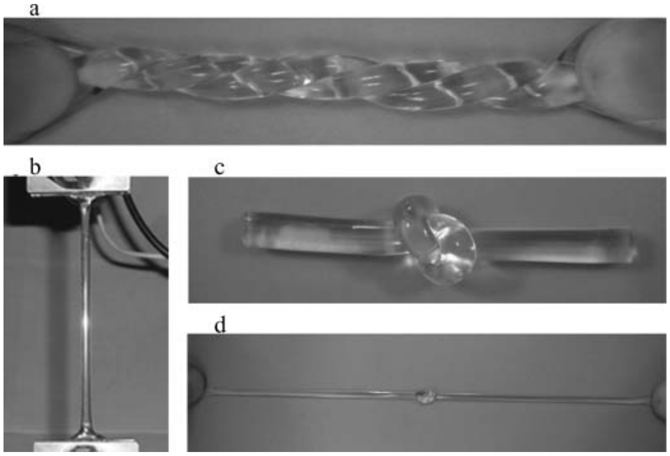


Fig. 2. Photographs of HA-gels with excellent mechanical toughness. A_2 gels can exhibit high level of deformation, such as (a) plaiting, (b) elongation, (c) knotting and (d) stretching after being knotted.

In order to describe the extension behavior of HA-gels, based on the rubber elasticity theory, the shear modulus (G) is evaluated from the uniaxial stretching data on the assumption of affine deformation and incompressible volume (30–32):

$$\tau = G(\alpha - \alpha^{-2}) \tag{1}$$

Here, τ is the stress defined as the force per cross sectional area of the undeformed specimen, α is the relative extension equal to L/L_0 in which L and L_0 are the length of the deformed and undeformed HA-gels specimen, respectively. If the τ is plotted vs. $(\alpha - \alpha^{-2})$, the slope of the curve at small strains is equal to G. Thus, the initial linear part of the curves ($\alpha < 2$) was used to fit straight lines and the slope of these lines was used to calculate G. The average molecular weight of the chain length between cross-linking points (M_C) was calculated from the G according to rubber elasticity theory using the following equation (33):

$$M_C = RTc/G \tag{2}$$

Here, R is gas constant, T is the absolute temperature and c is the polymer concentration. Furthermore, the knowledge of M_C allows calculation of D_N, the average distance between the cross-linking points using the "equivalent network model" (34):

$$D_N = \left(\frac{6M_C}{\pi c A}\right)^{1/3} \tag{3}$$

Here, A is Avogadro's number. In addition, the effective network chain density N in HA-gels can be also evaluated from the shear modulus (35):

$$G = NRT \tag{4}$$

Therefore, according to Equations 1–4, G, D_N and N were calculated and are listed in Table 2. As listed in Table 2, N increases and D_N decreases with increasing OP-4-AC content for all A_n gels. This indicates that the higher OP-4-AC content, the more difficulty the orientation of polymer chains between cross-linking points.

Table 2. Mechanical properties and network structural parameters of A_n gels with different composition content

A_n gels	elongation at break (%)	tensile strength (KPa)	G (KPa)	N (mol/m^3)	D_N (nm)
$A_{0.5}$	–	–	2.33	0.94	15.00
$A_{0.7}$	–	–	2.91	1.17	13.93
$A_{0.9}$	–	–	4.34	1.75	12.20
A_1	1683.21	86.82	4.46	1.80	12.08
A_2	1460.39	179.67	8.48	3.42	9.75
A_3	1281.41	212.79	9.16	3.70	9.50
A_4	1154.51	192.34	9.55	3.85	9.37
A_5	982.01	174.93	10.21	4.12	9.17

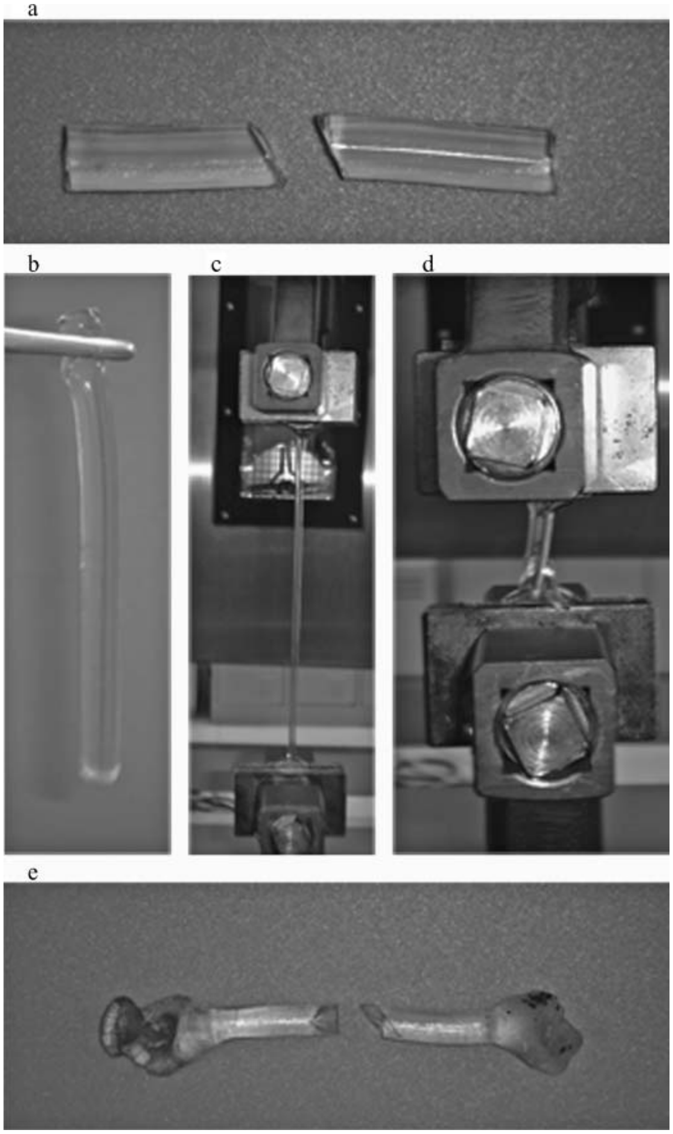


Fig. 3. HA-gels exhibit the capability of self-healing and the appearance of the self-healed specimen during the tensile measurements. The specimen was $A_{0.9}$ gel, (a) two parts came from cutting the original specimen, (b) the self-healed specimen, (c) in elongation, (d) and (e) show the self-healed specimen after break.

3.2 Tensile Measurements of Self-healed Specimen and Self-healing Mechanism

In aqueous solution of HMPAM and SDS, above a certain polymer concentration, intermolecular hydrophobic associations can cause the formation of a transitory three-dimensional network of polymer chains. Therefore, the solution of HMPAM exhibits particular rheological property, due to the reversible dissociation process of the physical cross-linking undergoing under shear (24, 26, 28). This property of structural reorganization of HMPAM endows HA-gels with the self-healing capability. Figure 3 shows exhibition of self-healing and appearance of the self-healed specimen during the tensile measurements. The hydrogel specimen was cut into two parts (Figure 3a), and then the self-healed specimen could be gotten by connecting the two parts *in situ* and closing it in a pipe at room temperature in a wet circumstance for 3 days (Figure 3b). In the process of tensile measurements, the fracture usually occurred at a point close to one jaw collet, but the fracture of the self-healed specimen occurred at original cut, see Figure 3c and d. It is noted that tensile fracture surface included only the part of the original cut surface, see Figure 3e. These results indicate that a part of the self-healed cut already possessed the same tensile strength as that of uncut part of the specimen during three-day self-healing experiment.

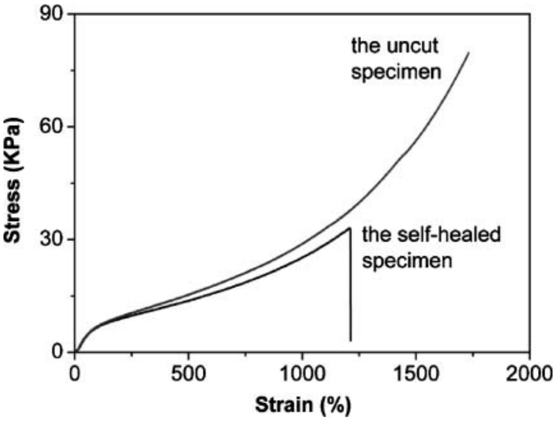


Fig. 4. Stress-strain curves of the self-healed hydrogel specimen and the uncut hydogel specimen. The specimens were both $A_{0.9}$ gels.

Figure 4 demonstrates the stress-strain curves of the self-healed hydrogel specimen and the uncut hydrogel specimen, and they were both $A_{0.9}$ gels. It is observed that the elongation and the tensile strength of the uncut hydrogel specimen were much larger than those of the self-healed hydrogel specimen. This result is in accordance with the self-healing mechanism of HA-gels. Figure 5 shows a schematic of the self-healing process. For all $A_n$gels, the SDS concentrations were 1.04×10^{-4} mol/mL; however, the SDS critical micelle concentration (CMC) is 9.2×10^{-6} mol/mL at 50°C (25,27,28). Therefore, SDS would form micelles in A_n gels. However, in the surface of hydrogels, SDS would form a close monolayer molecule membrane with orientation permutation. As shown in Figure 5, when the hydrogel specimen was cut into two parts (Figure 5b), the monolayer molecule membrane motioned above will occur on the cut surface. These SDS, which formed the monolayer molecule membrane, were from the associated micelles disintegrated in hydrogels. After the two parts were connected in situ and closed them in a pipe in a wet circumstance, the cylindrical micelle of SDS would be formed at the contact surface between two parts. Hydrophobic groups of HMPAM chains, which originally interacted with these associated micelles disintegrated in hydrogels by association, would hydrophobic associate with the cylindrical micelle to form new

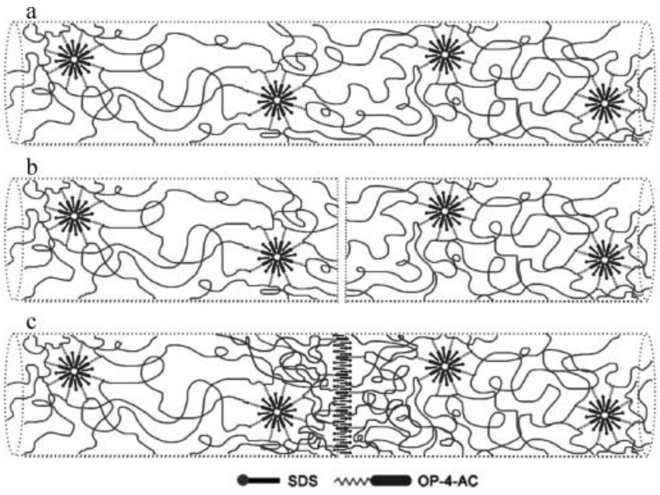


Fig. 5. Schematic of self-healing process for HA-gels. (a) Normal hydrogel specimen, (b) the specimen is cut into two parts and the blank in the middle of the specimen stands for the cut, and (c) the self-healed specimen.

associated micelle. As a result, the cut would be self-healed, see Figure 5c. However, because of the absence of long and flexible polymer chains in the cylindrical micelle, the elongation and the tensile strength of the self-healed hydrogel specimen were much lower than the uncut hydrogel specimen.

3.3 Effect of OP-4-AC Content in HA-gels on Mechanical Properties

At first, we measured the elongation at break and tensile strength of A_n gels to confirm excellent mechanical properties and Table 2 summarizes the results of $A_n$gels with different OP-4-AC content throughout the range of OP-4-AC used in the initial reaction solution. Figure 6 shows stress-strain curves of A_n gels. It is obvious that modulus exhibited increases and the elongations at break showed monotonous decreased with an increase in OP-4-AC content; however, tensile strength of A_n gels first increased and then decreased with increasing OP-4-AC content.

As listed in Table 2, throughout the range of OP-4-AC used in the initial reaction solution, with increasing OP-4-AC content, the effective network chain density N increases and the average distance between the cross-linking points D_N decreases. It is well known that in most cross-linked polymer an increase in $N$is always accompanied by an increase in modulus and a decrease in D_N. This is because conformation changes of polymer chains were restricted with decreasing D_N. That is, the increase in modulus mainly results from the orientation effect of polymer chains. Thus, for A_n gels, modulus increased with increasing OP-4-AC content. Elongations at break commonly decreases with decreasing D_N due to the stress concentrations in the shorter chains present at any instant during the uniaxial stretching. Therefore, elongations at break showed decreases with increasing OP-4-AC content, see Table 2. With increasing OP-4-AC content, it is noted that the tensile strength reached a plateau value and began to decrease, see Table 2. There are two possible reasons for this phenomenon: the orientation on stretching of polymer chains in cross-linked network got more difficult and the number of polymer chains that bore maximum stress force also began to decrease. Another reason seems to be due to the increase of crack sensitivity that caused early fracture neighboring to the clamps (36). Other compositional factors such as SDS and AM also affect the mechanical properties, and these effects will be presented in another paper.

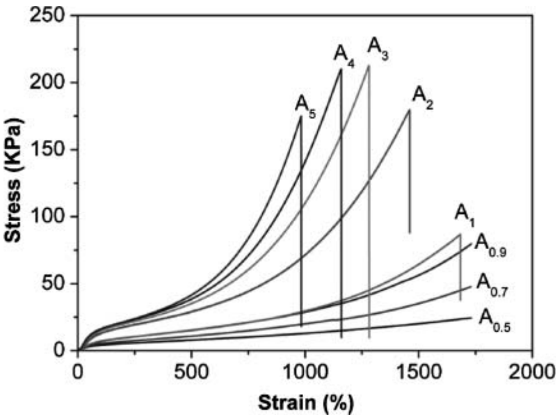


Fig. 6. Stress-strain curves of A_n gels with different octyl phenol polyethoxy ether acrylate (OP-4-AC) content ($A_{0.5}$ to A_5).

3.4 Tensile Measurements of Altering Crosshead Speed for HA-gels

Tensile measurements of altering crosshead speed were performed on three specimens of A_2 gels under the conditions of same elongations. Figure 7 illustrates the stress-strain curves for A_2 gels at crosshead speed of 100 mm/min,

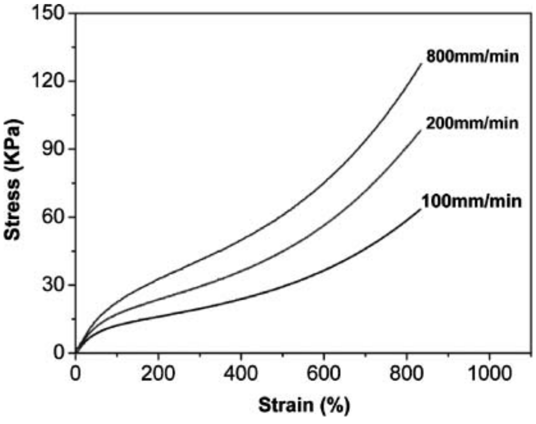


Fig. 7. Stress-strain curves of A_2 gels at crosshead speed of 100 mm/min, 200 mm/min, and 800mm/min, respectively.

200 mm/min, and 800mm/min, respectively. In Figure 7, the hydrogel becomes harder with increasing crosshead speed, showing an increased tensile modulus. According to the HA-gels structure model (Figure 1), the effective network chain density N and the average distance between the cross-linking points D_N are unchanged under the conditions of the same type of hydrogels. This phenomenon, which tensile modulus increased with increasing crosshead speed, is the result of the stretching orientation for the network chains. As mentioned above, the higher crosshead speed was, the shorter the time of orientation of polymer chains in cross-linked network was. Therefore, the orientation effect of polymer chains in cross-linked network was the main reason that tensile modulus of HA-gels showed outstanding increases with increasing crosshead speed.

3.5 Stress-relaxation Behavior

In this study, the stress-relaxation behavior was investigated using two methods. First, we carried out stress relaxation tests after stretching the specimens to a certain elongation. The results showed that the stress underwent a quick dropping then tended to a constant value which increased with the increase of hydrophobic groups content for $A_n$gels, see Figure 8. This phenomenon is similar to that of chemically cross-linked rubberlike materials. According to the proposed model structure (Figure 1), with increasing OP-4-AC content, the effective network chain density N increased and the average distance between the cross-linking points D_N decreased. Therefore, the difficulty of the orientation of polymer chains in cross-linked network increased also with increasing OP-4-AC content for $A_n$gels, which is the result of the stress relaxation of polymer chains between cross-linked points.

On the other hand, the cross-linked points possessed the dissociation and re-association properties. Namely, if the time of stress-relaxation tests was long enough, the stress value should be zero. However, it is impossible for the stress relaxation tests to be unlimitedly prolonged because the water contained in the hydrogels will inevitably volatilize. After about 2 h, in fact, the stress relaxation curves tended to slowly rise during the stress relaxation experiment. To avoid the interfering of water volatilization, the experiment of stress relaxation were performed in a sealed container. The specimen was forced into a plastic syringe with pressing the plunger for a long time under the conditions of rising temperature, and then we took it out and observed its deformation after keeping it in the air for a certain period of time. The result showed that the deformation gradually tended to be irreversible. At last, it entirely copied the shape of the syringe cavum, see Figure 9. From the results above, we think that the stress-relaxation behavior of HA-gels consisted of two stages: stress relaxation of polymer chains between cross-linked points and structural reorganization of the cross-linked points. The stress-relaxation time of the latter was much higher than that of the former.

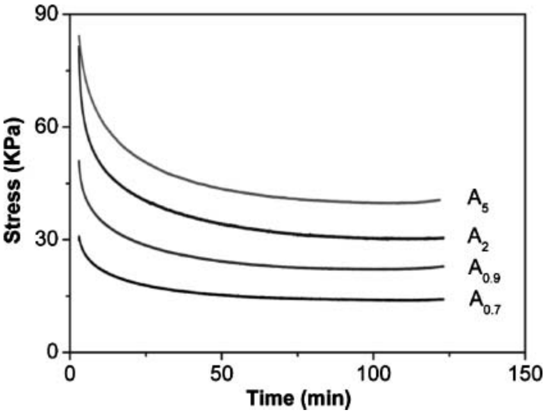


Fig. 8. Stress relaxation curves of A_n gels with different octyl phenol polyethoxy ether acrylate (OP-4-AC) content ($A_{0.7}$ to A_5). Elongation: 600% for A_5gel, 1000% for the others.

3.6 Thermoelastic Behavior of HA-gels

In the tensile testing described above, it was noticed that HA-gels showed high recovery even after extensive stretching. Moreover, HA-gels exhibited also obvious thermoelastic behavior, see Figure 10. Figure 10a shows the stress-temperature curves of a group of A_2 gels stretched different elongations. The intercept of the stress-temperature curves for Figure 10a, which was force-temperature coefficient ($\partial f/\partial T$), was plotted versus strain, and the $\partial f/\partial T$-strain curve was obtained, as shown in Figure 10b. It was

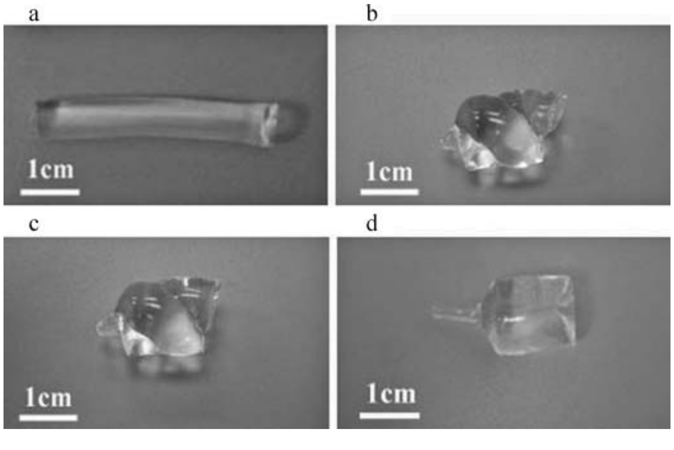


Fig. 9. The stress relaxation test of A_2 gel. (a) original specimen; (b) to (d), appearance of the specimen at different stress relaxation time. Processing conditions: specimen (b): pressing the original specimen into syringe and holding it at 40°C for 25 h; specimen (c): pressing specimen (b) into syringe and holding it at 40°C for 18 h; specimen (d): pressing specimen (c) into syringe and holding it at 80°C for 29 h.

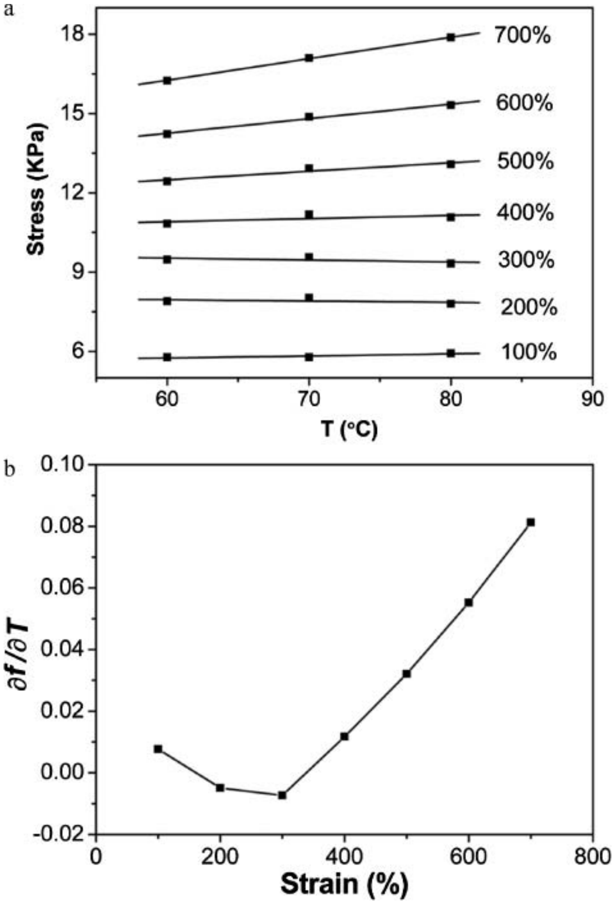


Fig. 10. Thermoelastic phenomena of HA-gels. The specimens were A_2 gels, (a) plot of stress and temperature relations under the conditions of fixed elongation; (b) curve of changes of force-temperature coefficient ($\partial f/\partial T$) with temperature.

found that the $\partial f/\partial T$ decreased with increasing elongations that were in the range of 0–300%; however, the $\partial f/\partial T$ enhanced with increasing elongations that were in the range of 300–700%. Thus, the higher elongations were, the more obvious thermoelastic behavior was. As mentioned above, it was revealed that HA-gels possessed thermoelastic inversion effect, which resulted fundamentally from thermal expansion of specimens.

Because of improving the experimental temperature, the lengths of specimens enhanced necessarily due to thermal expansion of specimens. As a result, elongations of specimens decreased, so the tensile stress was partially counteracted. It should be noted that the effect mentioned above was relatively small when elongations of specimens were in the range of 300–700%. On the contrary, if elongations of specimens were lower than 300%, the effect was especially serious. This result indicates that the tensile stress was partially counteracted due to thermal expansion in the range of 0–300% of elongations, so thermoelastic inversion effect emerged.

4 Conclusions

We have synthesized and characterized a novel type of hydrophobic association hydrogels (HA-gels) with a unique network structure, where the effective network chain density N increased and the average distance between the cross-linking points D_N can be controlled by altering compositions of hydrogels. HA-gels were synthesized in an aqueous solution by micellar copolymerization at 50°C. The associated micelles, which were composed of hydrophobic groups of HMPAM chains and SDS by hydrophobic association, acted as cross-linking points of network of HA-gels. HA-gels possessed the capability of self-healing due to the dissociation and re-association process of the associated micelles. For HA-gels, mechanical properties strongly depended on OP-4-AC content in the initial reaction solution. Nincreases and D_N decreases with increasing OP-4-AC content for all A_n gels. The tensile modulus enhanced and the elongations at break decreased with increasing OP-4-AC contents. In addition, for tensile measurements of altering crosshead speed, the modulus of A_n gels tended to enhance sharply on increasing crosshead speed. The stress-relaxation behavior of HA-gels consisted of two stages: stress relaxation of polymer chains between cross-linked points and structural reorganization of the cross-linked points. The stress-relaxation time of the latter was much higher than that of the former. Similar to rubbery, HA-gels exhibited high recovery even after extensive elongations and obvious thermoelastic behavior.

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