

# Synthesis, Characterization, Rheological Behavior, and Shear Response of Hydrophobically Modified Polyacrylamide and Network Structure of Its Microhydrogel

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**ABSTRACT:** Octylphenol polyoxyethylene acrylate (OP-10-AC) was synthesized, and then OP-10-AC was copolymerized with acrylamide (AM) to form hydrophobically modified polyacrylamide P(AM/OP-10-AC) through micellar copolymerization. OP-10-AC content and rheology behavior of P(AM/OP-10-AC) were investigated in detail. Especially, under the conditions of different test methods, P(AM/OP-10-AC) showed interesting shear responsive behavior. The results of rheology study show that OP-10-AC content, polymer solution concentration, salt solution concentration, and different test methods powerfully influenced shear viscosity of aqueous solutions of P(AM/OP-10-AC). In addition, according to the dynamic shear exper-

imental results, the critical hydrogel concentration range (CHCR) could be confirmed for aqueous solutions of P(AM/OP-10-AC). Above CHCR, these polymer solutions were essentially a kind of microhydrogels, which could explain the effect of concentration and hydrophobe content on their shear viscosity and viscoelasticity from the microstructure's point of view. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 66–76, 2012

**Key words:** hydrophobically modified polyacrylamide; micellar copolymerization; rheological behavior; network structure

## INTRODUCTION

Water-soluble hydrophobically modified polyacrylamide (HMPAM) has been extensively investigated in the last thirty years. Research interest stems mainly from two areas: solutions and hydrogels. Interest in HMPAM solutions has arisen primarily from controlling viscosity at different shear rates (rheology) in many technologies. A useful strategy for enhanced control of rheology in these systems takes advantage of HMPAM which build viscosity through transient polymer association.<sup>1</sup> Therefore, these systems have received a great deal of attention due to their unique rheological characteristics and applications, such as cosmetics, coatings, drilling fluids, and chemically enhanced oil recovery.<sup>1–9</sup> HMPAM consists of a water-soluble polymer containing a small number of hydrophobic groups. For different synthesis methods, the hydrophobic groups may be randomly distributed along the chain or

they may be grouped in blocks.<sup>5,7,10,11</sup> To overcome the solubility of hydrophobic monomer in water, by now, most of HMPAM were prepared by micellar copolymerization. For HMPAM synthesized by this technique, Dowling et al.<sup>11</sup> and Ezzell et al.<sup>12</sup> confirmed blocky structure based on direct experimental evidence, that is, hydrophobe units were distributed along the polymer backbone in a microblock manner. The characteristic features of HMPAM prepared by a micellar polymerization technique were reviewed in detail elsewhere.<sup>7</sup> In the 1980s, to skip the complicated post-treatment process, surfactant macromonomer (abbreviations: surfomer) can be used instead of the hydrophobic monomer and surfactant in conventional micellar copolymerization.<sup>13,14</sup> The characteristic of surfomer was discussed in detail elsewhere.<sup>15</sup>

The incorporation of a small amount of hydrophobic monomer in a hydrophilic polymer backbone results in the unique rheological characteristics of these systems in aqueous solution, which results mainly from association of the hydrophobe units rather than simple entanglement of polymer chains. Therefore, they were extensively developed in the 1980s because of the large market potential that

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existed, and their properties in pure solution have been thoroughly investigated.<sup>2,7,11,14,15-17</sup> For many industrial applications such as enhanced oil recovery and latex paint technology, the interaction of HMPAM with small molecule surfactants is of fundamental importance; as a consequence, it has always received increasing attention and become the subject of extensively research.<sup>8,18-24</sup> This interest stems from the need to accurately control the solution rheological behavior under a variety of shear conditions. In addition, hydrophobic interactions between HMPAM and viscoelastic surfactant have also been investigated.<sup>22,25-27</sup>

Over the years, work on HMPAM hydrogels has been motivated by interest in controlled drug release.<sup>22</sup> Additionally, it is well known that design of hydrogels with good mechanical properties is crucially important in many application areas of soft materials. To improve the mechanical strength of HMPAM hydrogels, Abdurrahmanoglu et al.<sup>28</sup> prepared high-toughness PAM hydrogels by hydrophobic modification; unfortunately, they have not entered advanced ranks in hydrogels with high mechanical strength. In 2009, the successful preparation of physical hydrophobic association hydrogels (HA-gels) with good mechanical strength solved this question.<sup>29</sup> In contrast with other hydrogels with high mechanical strength,<sup>30-33</sup> not only did HA-gels exhibit outstanding transparency and mechanical properties but also possessed the capability of reforming due to dissociation and reassociation of crosslinking points, such as self-healing, molding, and unusual swelling behavior.<sup>9,29,34,35</sup> Moreover, temperature-responsive properties<sup>36</sup> and pH-responsive properties<sup>37</sup> of HA-gels with high mechanical strength were also reported. However, although a significant amount of literature is dedicated to solutions and hydrogels of HMPAM, much less attention has been paid to the shear responsive behavior of HMPAM solutions under the different test methods and the transformation from solutions to microhydrogels.

In this work, a new surfomer, octylphenol polyoxyethylene acrylate (OP-10-AC), was synthesized and characterized, and then novel HMPAM was successfully prepared through micellar copolymerization of acrylamide (AM) with a small amount of OP-10-AC in an aqueous solution at 30°C, namely P(AM/OP-10-AC). Under the conditions of steady shear and dynamic shear, rheology behavior of P(AM/OP-10-AC) aqueous solution was investigated in detail. Especially, under the conditions of different shear methods, the interesting shear-responsive behavior of P(AM/OP-10-AC) was observed, and our aim was to investigate the conversion of polymer hydrophobic groups between intramolecular and intermolecular associations by this method.

Additionally, for P(AM/OP-10-AC), the critical hydrogel concentration range (CHCR) from solutions to microhydrogels and parameters of network structure for microhydrogels were also investigated according to the dynamic shear experimental results.

## EXPERIMENTAL

### Materials

Octylphenol polyoxyethylene ether (OP-10) (Tianjin Guangfu Fine Chemical Research Institute, China), acryloyl chloride (AC) (Shanghai Haiqu Chemical Co., China), triethylamine (TEA), and sodium bisulfite (SB) (Tianjin Fuchen Reagent Factory, China) were all used as received and without further purification. AM and potassium persulfate ( $K_2S_2O_8$ ) (Tianjin Fuchen Chemical Reagent Factory, China) were recrystallized from distilled water and dried under vacuum at room temperature. Other reagents (Beijing Chemical Works, China) were used without further purification.

### Synthesis of OP-10-AC

The synthesis procedure of OP-10-AC basically followed the work reported by Jiang et al.<sup>29</sup> First, a transparent aqueous solution consisting of 64.67 g (0.10 mol) OP-10, 12.14 g (0.12 mol) TEA, and 80 mL tetrahydrofuran (THF) was prepared. This solution was added to a three-neck flask equipped with electromagnetic stirrer in an ice-water bath. Next, 10.86 g (0.12 mol) AC in 20 mL of THF was added dropwise to the former solution under the stirring conditions, and the water bath temperature remained below 5°C. After dropwise addition was complete, the mixture was further stirred for 5 h. Then, to separate triethylamine hydrochloride that was the sediment of the reaction system, the appropriate amount of acetone was added to the mixture, and the upper clear liquid containing OP-10-AC was distilled under reduced pressure to remove THF and the acetone. Finally, the residual triethylamine hydrochloride was separated from the product by centrifugation and the final product, OP-10-AC, was dried to constant weight in vacuum at 40°C. The reaction scheme is shown in Scheme 1.

### Synthesis of P(AM/OP-10-AC)

P(AM/OP-10-AC) was prepared by micellar copolymerization of AM and a small amount of OP-10-AC as the hydrophobic monomer was added in an aqueous solution using KPS and SB as the initiator.<sup>13,14</sup> First, distilled water used as a solvent was deoxygenated for 30 min by a nitrogen purge. Then, according to a special proportion, AM, OP-10-AC,



**Scheme 1** The reaction scheme of OP-10-AC synthesis.

and distilled water were added to a flask with mechanical stirrer and a nitrogen inlet and outlet. The weight concentration of AM was 5 wt %, and the molar percentage of OP-10-AC relative to AM was variable. The mixture was treated with mechanical mixing until a homogeneous solution was prepared. Finally, the solution was heated by a water bath under nitrogen purge at 30°C for 1 h. After this period of time, the initiator was added and the temperature maintained at 30°C under nitrogen for 8 h.

After reaction, the solution in the flask was poured into an excess of methanol using a precipitating agent. The polymers, which were isolated by precipitation, were dried to constant weight in a vacuum oven at 30°C. Then, the polymers were stored in a drying device. For comparison, polyacrylamide (PAM) was also prepared under the same conditions. For P(AM/OP-10-AC) prepared, the content of compositions in the initial reaction solution is listed in Table I.

### Characterization of OP-10-AC

Fourier transform infrared (FTIR) spectrum of OP-10-AC was obtained using an Avatar 360 FTIR spectrophotometer (Nicolet Inc., USA) by the conventional KBr disk tablet method. The measurement of the critical micellization concentration (CMC) of OP-10-AC was performed using ZL-2 automatic surface tensiometer (Zibo Kefeng Instrument Co., Ltd., China) by ring method.

### Characterization of P(AM/OP-10-AC)

The molecular weights of copolymers were characterized relatively with intrinsic viscosity according to the method published elsewhere.<sup>15</sup> However, it deserves noting that this treatment is only an approximate method because of the effect of interaction of hydrophobic groups on the determination of the viscosity-average molecular weight of HAPAM. For all of the copolymers, the molecular weight estimated by this method is between  $3.7 \times 10^5$  and  $4.2 \times 10^5$  g/mol. In the present study, these polymers can be assumed to have similar molecular weight. The measurements of OP-10-AC content in copolymers were performed using Vario EL III elementary analyzer (Elementar Analysensysteme GmbH, Germany), which was validated by AV-600 nuclear magnetic resonance (NMR) equipment (Bruker-Spectrospin Ag, Switzerland).

### Sample nomenclature

In the present study, according to the test results of elemental analysis, P(AM/OP-10-AC) is expressed as HMX%, where HM stands for copolymer and X% stands for molar percentage of OP-10-AC content in copolymer. When P(AM/OP-10-AC) aqueous solutions were prepared, the solutions are expressed as HMX%-Y% in which Y% stands for weight concentration of copolymer. Furthermore, when copolymer aqueous solutions containing KCl were prepared, the solutions are expressed as HMX%-Y%-Z% in which Z% stands for weight concentration of KCl.

### Rheological measurements

Steady shear and dynamic shear rheological measurements were performed using an AR-G2 rheometer (TA Instruments Corp., USA) with a plate-and-plate geometry (diameter 25 mm, gap 0.6 mm). All tests were done at 20°C. In static shear measurements, solution viscosity of the samples was measured at shear rates ranging from 0.01 to 1000 s<sup>-1</sup> depending on the viscosity of the sample. In the frequency ranging from 0.01 to 100 rad s<sup>-1</sup>, dynamic shear measurements were conducted in the linear viscoelastic regime of the samples, as determined previously by dynamic stress sweep measurements. In these experiments, the test sample was gently loaded into the plate tool and given about 20 min to allow the stresses to relax and attain thermal equilibrium before starting measurements.

For rheological measurements, P(AM/OP-10-AC) solutions were prepared by dissolution of copolymers in distilled water at room temperature. Copolymers were allowed to hydrate and swell for 24 h;

**TABLE I**  
Content of Compositions in Initial Reaction Solution for P(AM/OP-10-AC)

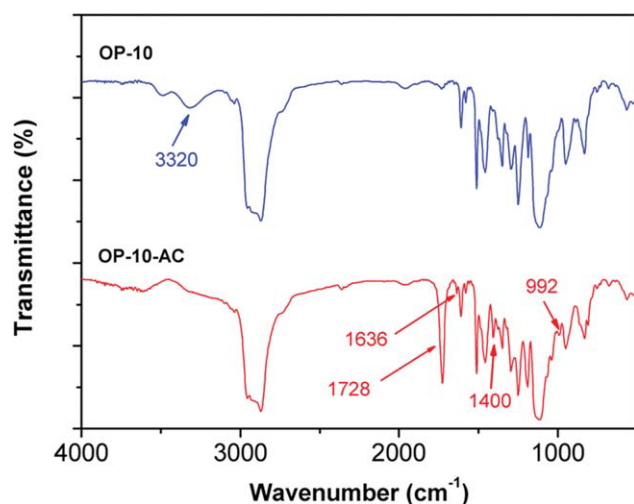
Feed ratio <sup>a</sup> (mol %)	AM (g)	OP-10-AC (g)	KPS <sup>b</sup> (g)	SB <sup>c</sup> (g)
0	33.00	0	0.16	0.053
0.5	33.00	1.63	0.17	0.055
1	33.00	3.25	0.18	0.058
1.5	33.00	4.88	0.19	0.061
2	33.00	6.50	0.20	0.064
3	33.00	9.76	0.21	0.069

The total mass of the initial reaction solution was 660.00 g.

<sup>a</sup> Molar percentage of OP-10-AC relative to AM.

<sup>b</sup> Weight percentage of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> relative to AM and OP-10-AC was 0.5%.

<sup>c</sup> Molar ratio of KPS relative to SB was 1.2 : 1.



**Figure 1** FTIR spectra of OP-10 and OP-10-AC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

then the solutions were gently stirred magnetically for 7 days to form homogeneous solutions. Prior to measurements, the copolymers solutions were still kept for more 48 h to remove air bubbles.

## RESULTS AND DISCUSSION

### Characterization of OP-10-AC

#### IR analysis of OP-10-AC

Figure 1 shows the IR spectra of OP-10 and OP-10-AC. From the IR spectrum of OP-10, it is obvious that OP-10 shows a broad peak at  $3320\text{ cm}^{-1}$  corresponding to stretching vibration of  $\text{—OH}$ . However, in the IR spectrum of OP-10-AC, the above-mentioned peak disappears. Moreover, it can be seen that the peak at  $1636\text{ cm}^{-1}$  corresponds to stretching vibration of  $\text{C=C}$ , and the peak at  $1728\text{ cm}^{-1}$  corresponds to stretching vibration of  $\text{C=O}$ . The peak at  $992\text{ cm}^{-1}$  corresponds to out-of-plane bending vibration of  $\text{=CH}$ , and the peak at  $1400\text{ cm}^{-1}$  corresponds to the shear vibration of  $\text{=CH}_2$ . The results demonstrate that OP-10-AC was successfully synthesized.

#### CMC of OP-10-AC

Figure 2 exhibits surface tension curves of OP-10-AC with different concentration. According to the surface tension curves, the obtained CMC of OP-10-AC is  $4.553 \times 10^{-5}\text{ mol/L}$ . In initial reaction solution for HMPAM, the smallest molar percentage of OP-10-AC relative to AM was 0.5 mol %. That is, the concentration of OP-10-AC in initial reaction solution was  $3.713 \times 10^{-3}\text{ mol/L}$ , which was much higher than the CMC of OP-10-AC. The result demonstrates that OP-10-AC can form micelles in all initial

reaction solutions. Therefore, it is clear that polymerization prepared HMPAM was micellar copolymerization.

### Characterization of P(AM/OP-10-AC)

#### Element analysis

Element analysis is one of the approaches adopted frequently in the composition analysis of organic matter, which can determine mass components of elements in polymers. According to methods of literature concerned,<sup>38,39</sup> the content of OP-10-AC can be easily calculated with the help of mass components of C, H, and N in P(AM/OP-10-AC) determined by element analysis. In the present study, elemental analysis data are listed in Table II, and mass fractions of N and C in copolymers can be expressed by eqs. (1) and (2):

$$N\% = \frac{14C_1}{W} \quad (1)$$

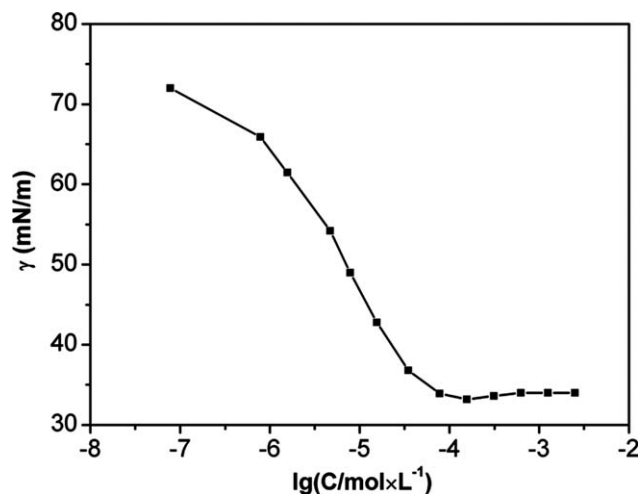
$$C\% = \frac{12(3C_1 + 37C_2)}{W} \quad (2)$$

Here, for the test sample,  $W$  is sample quality,  $C_1$  is amount of substance of copolymerizing unit containing OP-10-AC, and  $C_2$  is amount of substance of copolymerizing unit containing AM.

Using eqs. (1) and (2), eq. (3) can be obtained:

$$\frac{C_2}{(C_1 + C_2)} = \frac{14C\% + 36N\%}{(408N\% + 14C\%)} \quad (3)$$

According to eq. (3), elemental analysis data in Table II and sample nomenclature, the molar percentage of copolymerizing unit containing OP-10-AC in P(AM/OP-10-AC) can be calculated and sample



**Figure 2** Surface tension as a function of concentrations of OP-10-AC solutions.

TABLE II  
Elemental Analysis Data and Content of OP-10-AC in P(AM/OP-10-AC)

Feed ratio <sup>a</sup> (mol %)	Sample quality (mg)	N% (wt)	C% (wt)	H% (wt)	Content of OP-10-AC <sup>b</sup> (mol %)	Sample name <sup>c</sup>
0	—	—	—	—	—	HM0%
0.5	2.7290	17.38	46.07	7.40	0.25	HM0.25%
1	2.3590	17.02	45.88	7.47	0.39	HM0.39%
1.5	2.1930	16.35	45.50	7.62	0.66	HM0.66%
2	2.2400	16.09	46.20	7.58	0.94	HM0.94%
3	2.0350	15.21	47.06	7.74	1.62	HM1.62%

<sup>a</sup> Molar percentage of OP-10-AC relative to AM.

<sup>b</sup> Molar percentage of OP-10-AC content in P(AM/OP-10-AC).

<sup>c</sup> HM1.62% was not used in rheological measurements due to the limitation of rheometer measuring range.

names for copolymers prepared are also identified, and they are listed in Table II.

### NMR

The OP-10-AC content was also determined by <sup>1</sup>H-NMR spectroscopy in deuterium oxide (D<sub>2</sub>O) according to literature methods.<sup>8</sup> Figure 3 is an example of a spectrum for P(AM/OP-10-AC) containing 3 mol % OP-10-AC in the feed (HM1.62%). The OP-10-AC content was calculated from the relative integrated area of peak A corresponding to the protons of the terminal CH<sub>3</sub> groups of the alkyl chains compared to that of peak B corresponding to the protons of CH groups in the polymer backbone. For the present copolymer, assuming that there are *x* mol units of hydrophobic monomer (OP-10-AC) and *y* mol units of hydrophilic monomer (AM), then the area of *S<sub>A</sub>* of peak A corresponds to 3*x* mol protons from the OP-10-AC units, the area *S<sub>B</sub>* of the peak B corresponds to (*x*+*y*) mol protons from AM units and OP-10-AC units. Therefore, the OP-10-AC content in mol % = 100 *S<sub>A</sub>*/3*S<sub>B</sub>*. As a result, the OP-10-AC content for copolymer containing 3 mol % OP-10-AC in the feed (HM1.62%) is 1.69 mol %. This shows that the result from <sup>1</sup>H-NMR spectroscopy is identical with that of element analysis.

### Steady shear experiments

As is well known, the thickening ability of PAM solutions derives mainly from entanglement of polymer chains. Therefore, with increasing shear rate under a shear field, the pseudoplastic behavior of PAM solutions is largely due to orientation and disentanglement of polymer chains. However, the thickening ability of nonionic HMPAM solutions stems mainly from intermolecular association of the hydrophobe units which are dispersed along the polymer backbone and not just because of entanglement of polymer chains. Furthermore, for HMPAM, solution concentration and hydrophobe content will have a strong effect on their intermolecular hydrophobic association ability.<sup>5–8</sup>

### Effect of concentration and hydrophobe content on shear viscosity

Figure 4 shows the effect of the shear rate on the viscosity for solutions of HM0.39%–Y%. As shown in Figure 4, with an increase in concentration of HM0.39% solutions (Y%), viscosity exhibited increases. When Y% is less than 2%, the test sample exhibited typical pseudoplastic behavior, and flow curve of HM0.39–1% entered the second Newtonian fluid region after the shear rate exceeded 0.4 s<sup>-1</sup>. Furthermore, when Y% is higher than or equal to 2%, flow curves first exhibited shear thickening behavior in low shear rate range, and then showed a monotonous decrease with further increasing the shear rate. However, the whole flow curve for HM0.39–5% could not be obtained because of the limitation of rheometer measuring range.

Figure 5 shows the effect of the shear rate on the viscosity for solutions of HMX%–2%. As shown in Figure 5, with an increase in OP-10-AC content of HMX%–2%, all flow curves except that of HM0–2% (PAM solution) first exhibited shear thickening

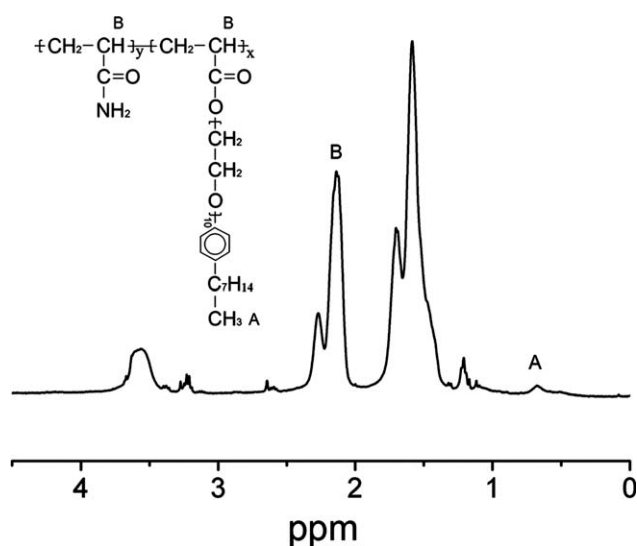
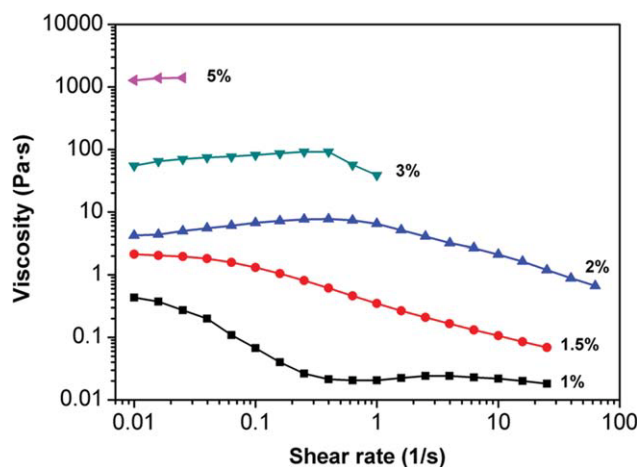


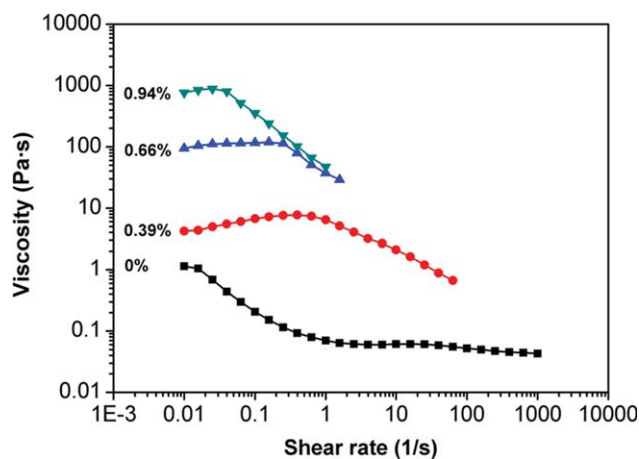
Figure 3 A representative <sup>1</sup>H-NMR spectrum for P(AM/OP-10-AC), containing 3 mol % OP-10-AC in the feed.



**Figure 4** Viscosity as a function of shear rate for HM0.39%–Y%. The percent in figure denotes Y% of HM0.39%–Y%, which stands for weight concentration of HM0.39% solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

behavior in low shear rate range, and then showed a monotonous decrease with further increasing the shear rate. However, HM0–2% exhibited typical pseudoplastic behavior, and its flow curve entered the second Newtonian fluid region after the shear rate exceeded  $1 \text{ s}^{-1}$ .

As shown in Figures 4 and 5, viscosity of test samples exhibited increases with an increase in their concentration or OP-10-AC content. The reason for this is that the intermolecular hydrophobic association ability of test samples enhanced with increasing their concentration or OP-10-AC content, resulting in an increase of solution viscosity. For HM0.39–1% and HM0–2%, the reason, which their flow curves entered the second Newtonian fluid region, is that polymer chains were in a state of a high degree of orientation under a shear field. In low shear rate range, the shear thickening behavior of test samples should be viewed with some concern. It means that the interaction of their hydrophobic groups must be changed. We think that this shear thickening behavior should be mainly owed to the rearrangement of their hydrophobic association structure. That is, under the act of the shear stress, since polymer chains would gradually orientate, some intramolecular hydrophobic association microdomains were disrupted and hydrophobic groups which were from these microdomains were free. Therefore, with stretching of polymer chains, these free hydrophobic groups had a chance to reform intermolecular hydrophobic association microdomains with hydrophobic groups of other polymer chains in low shear rate range, resulting in the shear thickening behavior.<sup>40</sup> When the shear stress reached levels high enough to seriously disrupt the intermolecular hydrophobic association microdomains, these test

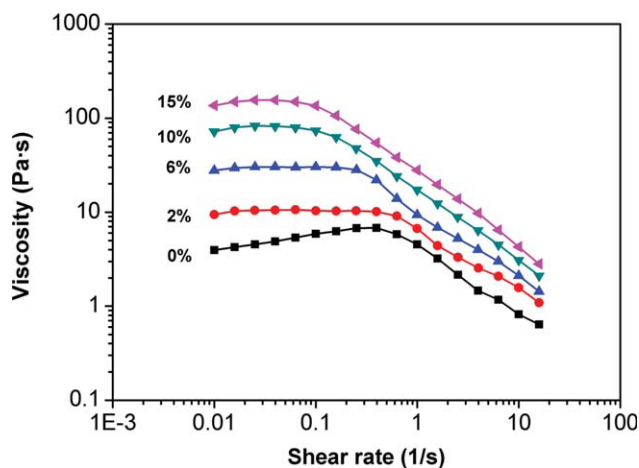


**Figure 5** Viscosity as a function of shear rate for HMX%–2%. The percent in figure denotes X% of HMX%–2%, which stands for molar percentage of OP-10-AC content in P(AM/OP-10-AC). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

samples exhibited typical pseudoplastic behavior. In addition, with increasing concentration or hydrophobe content, the shear rate value of beginning in shear thinning behavior decreased, which was because the proportion of intermolecular hydrophobic association microdomains to intramolecular hydrophobic association microdomains increased in the polymer solutions.

#### Effect of salt concentration on shear viscosity

In the present study, the effect of KCl concentration on shear viscosity of HM0.39% solutions was studied in the range of 0–15 wt %, where the HM0.39% concentration was kept constant at 2 wt %. As shown in Figure 6, KCl concentration has strong



**Figure 6** Viscosity as a function of shear rate for HM0.39–2%–Z%. The percent in figure denotes Z% of HM0.39%–2%–Z%, which stands for KCl weight concentration. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

effect on shear viscosity of HM0.39% solutions. As increasing the KCl concentration, the solution shear viscosity increased and the shear rate value of beginning in shear thinning behavior decreased. Furthermore, all test samples exhibited slight shear thickening behavior in low shear rate range.

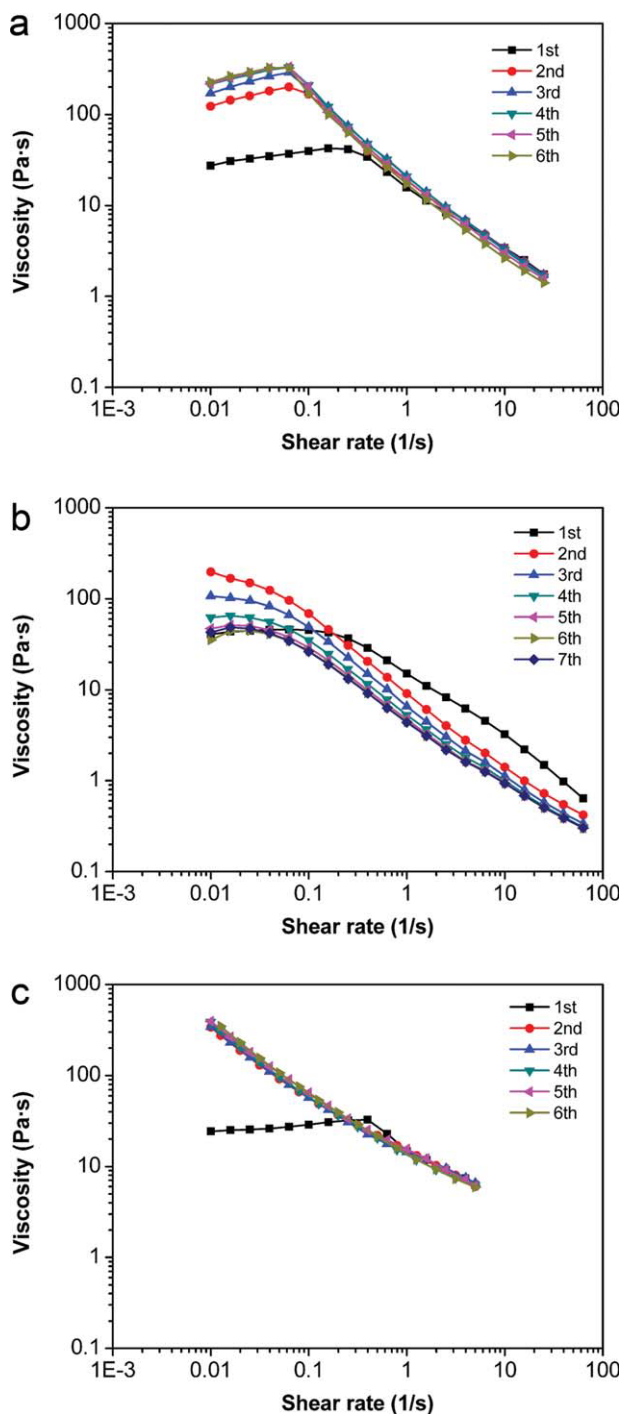
The effect of salt on hydrophobic association of HMPAM has been investigated for several decades and extensively documented.<sup>2,19,41,42</sup> For nonionic HMPAM solutions, salt can decrease the solubility of hydrophobic groups in distilled water; however, it also can promote the extent and strength of hydrophobic association, which can change weak hydrophobic association to strong hydrophobic association. For these reasons, increasing KCl concentration resulted in an increase in solution shear viscosity. For slight shear thickening behavior in Figure 6, as discussed earlier, this is doubtless due to the transition from intramolecular hydrophobic association microdomains to intermolecular hydrophobic association microdomains.<sup>40</sup>

#### Shear response under different test methods

In this study, the shear-responsive behavior of P(AM/OP-10-AC) solutions was also investigated using three test methods, in which the test samples were HM0.39–2%–6%, namely, the weight concentrations of HM0.39% and KCl were 2 wt % and 6 wt %, respectively. The effect of different test methods on shear viscosity, as shown in Figure 7, indicated that P(AM/OP-10-AC) solutions possessed complicated and changeable rheology properties.

Figure 7(a) shows the variation of viscosity with shear rate using repeated shear test with 10 min interval from low to high frequency. As shown in Figure 7(a), with increasing number of repetitions, the shear viscosity first sharply increased and then attained a stable value in low shear rate range. It is clear that all hydrophobic association microdomains were disrupted after the first shear test; however, new hydrophobic association microdomains would be reformed within 10 min interval. Moreover, the proportion of intermolecular hydrophobic association microdomains to intramolecular hydrophobic association microdomains was greater than that of untested sample because polymer chains were in a state of a high degree of orientation after the first shear test. As a result, the shear viscosity of the second shear test was greater than that of the first shear test in low shear rate range. With increasing number of repetitions, the proportion mentioned above gradually tended toward stability; therefore, the shear viscosity of the fifth shear test and the sixth shear test were almost constant in low shear rate range.

Figure 7(b) shows the variation of viscosity with shear rate using repeated shear test without interval



**Figure 7** Viscosity as a function of shear rate for HM0.39–2%–6% under the conditions of different test methods. (a) Repeated shear test with 10 min interval from low frequency to high frequency. (b) Repeated shear test without interval from low frequency to high frequency. (c) Repeated circulating shear test without interval. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

from low frequency to high frequency. As shown in Figure 7(b), with increasing number of repetitions, the shear viscosity first sharply increased, and then decreased, finally attained a stable value in low

shear rate range. Moreover, the shear viscosity decreased with increasing number of repetitions after the shear rate exceeded about  $0.3 \text{ s}^{-1}$ . This rheological behavior in Figure 7(b) is correlated with variation of hydrophobic association microdomains and disentanglement of polymer chains. For this test method, because the test sample was always kept in a shear field and there was no interval between neighboring tests to adjust the conformation of polymer chains, the variation of hydrophobic association microdomains was different from that of the first test method. Under this condition, we think that hydrophobic association microdomains reformed were almost intermolecular hydrophobic association microdomains in low shear rate range; therefore the shear viscosity of the second shear test was greater than that of the first shear test. In addition, with increasing number of repetitions, the entanglement extent of polymer chains was in the trend of lowering gradually, which could gradually decrease in the number of intermolecular hydrophobic association microdomains reformed and the shear viscosity after the shear rate exceeded about  $0.3 \text{ s}^{-1}$ . However, when the entanglement extent of polymer chains was quite high, the number of intermolecular hydrophobic association microdomains reformed also attained a stable value in low shear rate range. As a result, with increasing number of repetitions, decreasing range of the shear viscosity gradually decreased from the second shear test to the fifth shear test, and the flow curve of the sixth shear test approximately accorded with the seventh shear test.

Figure 7(c) shows the variation of viscosity with shear rate using repeated circulating shear test without interval. First the shear test was performed from low to high frequency and then the shear test was performed from high to low frequency, which was a circulating shear test. That is, there were three repeated circulating shear tests without interval in Figure 7(b). From low to high frequency, for the first shear test, the flow curve first exhibited shear thickening behavior in low shear rate range, and then showed a monotonous decrease with further increasing the shear rate; for the third shear test and the fifth shear test, with increasing shear rate, the shear viscosity exhibited a monotonous decrease. However, for the second shear test, the fourth shear test and the sixth shear test from high frequency to low frequency, with decreasing shear rate, the shear viscosity exhibited monotonous increase. According to the discussion earlier, the reason for the flow curve of the first shear test was very clear. Their rheological behavior was also correlated to variation of hydrophobic association microdomains. For the shear test from high to low frequency, we think that hydrophobic association microdomains reformed should be intermolecular hydrophobic association

microdomains and were gradually constructed with decreasing shear rate, resulting in monotonous increase of shear viscosity. For the shear test from low to high frequency, the shear viscosity decreased with increasing shear rate, which is mainly because there was not the transition from intramolecular hydrophobic association microdomains to intermolecular hydrophobic association microdomains.

From the discussion above, the effect of different test methods on shear viscosity of P(AM/OP-10-AC) was rather complex. By now, no direct data have been determined here to prove the variation of hydrophobic association microdomains under these test methods, so the effect of different test methods on shear viscosity of HMPAM still remains a hypothesis, and detailed investigation is in progress.

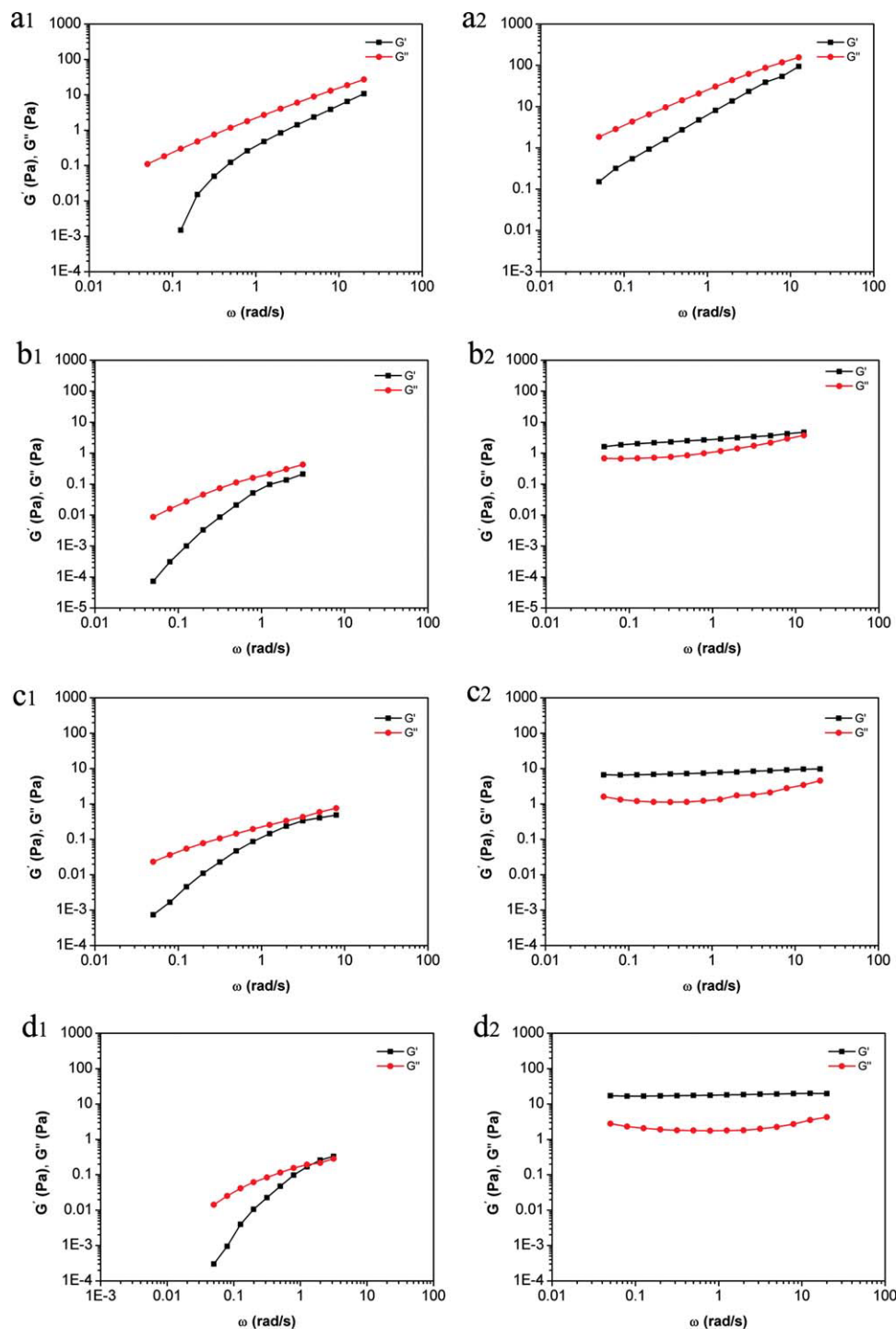
### Dynamic shear experiments

#### Measurements of CHCR

Figure 8 shows storage modulus  $G'$  and loss modulus  $G''$  as a function of angular frequency  $\omega$  in the linear viscoelastic regime for aqueous solutions of HMX%-Y%. As shown in Figure 8(a1-a2), for HM0-6% and HM0-10%,  $G''$  was always greater than  $G'$ , which indicates that flow characteristics of the test samples was dominated by viscous flow in the test frequency range. In addition,  $G'$  and  $G''$  increased with increasing frequency. It is well known that viscoelasticity of PAM solutions (HM0% solutions) stems mainly from entanglement of polymer chains. Therefore, with increasing frequency, the time of adjusting conformation of polymer chains was reduced in HM0% solutions, and the orientation and disentanglement of polymer chains got more difficult, resulting in an increase of  $G'$  and  $G''$ .

As in Figure 8(a1-a2), flow characteristics of HM0.39-2% (Fig. 8b1), HM0.66-2% (Fig. 8c1), and HM0.94-1% (Fig. 8d1) showed the viscoelastic behavior with dominating viscous property in the test frequency range, and  $G'$  and  $G''$  increased with increasing frequency. However, as shown in Figures 8b2, 8c2, and 8d2, in the test frequency range,  $G'$  was greater than  $G''$ , which indicates that flow characteristics of the test samples was dominated by elasticity; with increasing frequency,  $G'$  only exhibited a slight increase, and  $G''$  first exhibited a slight decrease in lower frequency range, and then showed a gentle increase with further increasing the frequency; these results clearly indicate that these test samples exhibited mechanical behavior of elastic bodies, which showed that the three-dimensional network structure crosslinked by intermolecular hydrophobic association microdomains had been constructed in the test systems, that is, these polymer solutions were essentially a kind of microhydrogels.<sup>43,44</sup>





**Figure 8**  $G'$  and  $G''$  as a function of frequency in the linear viscoelastic regime for aqueous solutions of HMX%–Y%. (a1) HM0–6% and (a2) HM0–10%. (b1) HM0.39–2% and (b2) HM0.39–3%. (c1) HM0.66–2% and (c2) HM0.66–3%. (d1) HM0.94–1% and (d2) HM0.94–2%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

In Figures 8b2, 8c2, and 8d2, the trend of  $G'$  was correlated to variation of hydrophobic association microdomains. In the linear viscoelastic regime, a small quantity of intramolecular hydrophobic association microdomains were disrupted under the act of the dynamic shear stress, and free hydrophobic groups, which were from intramolecular hydropho-

bic association microdomains disrupted, had a chance to reform intermolecular hydrophobic association microdomains with hydrophobic groups of other polymer chains, resulting in an increase of crosslinking density of the three-dimensional network structure. As a result, the trend of  $G'$  showed a slight increase with increasing frequency. For the

dynamic response  $G''$  to frequency, this is because there were two different molecular motions in the test system, namely the relaxing movement of polymer chains and the motion of the three-dimensional network structure. In low frequency range of test frequencies, the main molecular motion of the test system was the relaxing movement of polymer chains, and polymer chains could orientate sufficiently under alternating stress, therefore  $G''$  decreased with increasing frequency. In the high frequency range of test frequencies, the motion of the three-dimensional network structure concealed the relaxing movement of polymer chains and played a dominant role; moreover, the crosslinking density of the three-dimensional network structure would increase with increasing frequency as mentioned above; for these reasons, the trend of  $G''$  showed a gentle increase with increasing frequency.

The dynamic shear experiments results show that there was CHCR for HMX% solutions. According to Figure 8 and the above discussion, CHCR of HM0.39%-Y% and HM0.66%-Y% should be between 2 wt % and 3 wt %, and CHCR of HM0.94%-Y% should be between 1 wt % and 2 wt %; however, HM0%-Y% did not possess CHCR because there was no three-dimensional network structure in their solutions under the range of test concentration.

#### Parameters of network structure for microhydrogels

From the beginning of the science of polymer networks, it has been a major goal to control the effective network chain density  $\nu_0$  (number of effective cross-linked chains per unit volume) and the molecular weight of the chain length between crosslinking points  $M_c$ .<sup>32</sup> Therefore,  $\nu_0$  and  $M_c$  are the most important network structural parameters for hydrogels and has a critical influence on their properties. For a network of Gaussian chains,  $\nu_0$  in hydrogels is related to the equilibrium shear modulus  $G_0$  as in Refs. 34,45–47.

$$G_0 = A\nu_0RT \quad (4)$$

Here, the structure factor  $A$  equals 1 for an affine network,  $R$  is the gas constant,  $T$  is the absolute temperature,  $G_0$  was taken as the plateau modulus at  $G'$  versus  $\omega$  curves where the plateau appeared and  $G''$  was much smaller than  $G'$ . The estimated  $\nu_0$  values are listed in Table III together with the  $G_0$  values.

So, the chain length between crosslinking points  $N$  can be also evaluated by:<sup>28</sup>

$$N = \frac{M_c}{M_r} \quad (5)$$

Here,  $M_c = \frac{\rho}{\nu_0}$ ,<sup>28,48</sup> assuming the conversion of the monomer to P(AM/OP-10-AC) is complete,  $\rho$ , which

**TABLE III**  
Structure Parameters of HMX%-Y% Aqueous Solutions with Three-Dimensional Cross-Linked Network

Sample	$G_0$ (Pa)	$\nu_0$ (mol/m <sup>3</sup> )	$\rho$ (g/cm <sup>3</sup> )	$N$ ( $\times 10^4$ )
HM0.39%-3%	1.63	0.00067	0.031	65.14
HM0.39%-6%	31.44	0.013	0.064	6.92
HM0.39%-10%	103.50	0.042	0.11	3.69
HM0.66%-3%	6.68	0.0027	0.031	16.18
HM0.66%-6%	53.80	0.022	0.064	4.09
HM0.66%-10%	131.90	0.054	0.11	2.87
HM0.94%-2%	17.27	0.0071	0.020	3.97
HM0.94%-3%	54.80	0.022	0.031	1.98
HM0.94%-6%	170.50	0.070	0.064	1.29

is the density of the polymer in polymer solutions, can be easily calculated depending on the content of compositions in initial reaction solution.  $M_r$  is average molecular weight of repeated units in polymer. In this study, copolymerizing units containing OP-10-AC may be neglected because their number is small relative to AM units. As a result,  $N$  is evaluated using the molecular weight of AM units ( $M_r = 71.08$  g/mol).  $\rho$  and  $N$  are also listed in Table III.

According to Table III, when the solution concentrations were greater than their respective CHCR, for HM0.39%-Y%, HM0.66%-Y%, and HM0.94%-Y%,  $N$  decreased and  $\nu_0$  increased with increasing solution concentration; for HMX%-Y% with the same solution concentration,  $N$  decreased and  $\nu_0$  increased with increasing OP-10-AC content. Depending on the results, the reasons, the effect of concentration, and hydrophobe content on shear viscosity and viscoelasticity above CHCR, can be explained by variation of microstructure of the microhydrogels. Above CHCR, with increasing solution concentration or OP-10-AC content,  $\nu_0$  increased and  $N$  decreased, that is, crosslinking density of the three-dimensional network structure increased, so their shear viscosity and viscoelasticity increased.

## CONCLUSIONS

Using octylphenol polyoxyethylene acrylate (OP-10-AC) as a hydrophobic monomer and acrylamide as hydrophilic monomer, novel hydrophobically modified water-soluble copolymer P(AM/OP-10-AC) (HMX%, see sample nomenclature above) was prepared by micellar copolymerization. Elemental analysis confirmed the content of OP-10-AC in copolymer, which was verified by the result of NMR spectroscopy. Rheological properties of HMX% were investigated in aqueous solutions. For HMX%, its concentration, hydrophobe content, and salt concentration had a strong influence on shear viscosity. Some test samples exhibited shear thickening behavior in low shear rate range. We think the thickening

was due to stretching of polymer chains under a shear field, enabling some polymer hydrophobic groups to be converted from intra- to intermolecular associations. Furthermore, the P(AM/OP-10-AC) solutions exhibited interesting shear-responsive behavior under the conditions of different test methods, which verified the conclusion above. In addition, according to the results of dynamic shear experiments, all HMX% solutions except that of HM0% (PAM solution) possessed critical hydrogel concentration range (CHCR) in the whole experimental concentration range. Above CHCR, these polymer solutions were essentially a kind of microhydrogels. On the basis of the statistical molecular theory of rubber elastic, micellar copolymerization theory and using dynamic shear experiments data, the effective network chain density and the chain length between crosslinking points were evaluated for all microhydrogels. Therefore, for the microhydrogels containing HMX%, the effect of concentration and hydrophobe content on shear viscosity and viscoelasticity can be explained by variation of the microstructure.

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