Synthesis and Solution Properties of Hydrophobic Associating Polymers*

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Abstract Acrylamide/2-acrylamido alkane sulfonic acid hydrophobic associating copolymers were synthesized by micellar copolymerization. Effects of hydrophobe content, polymer concentration, salinity and surfactant on rheological behavior of copolymers were investigated and the conformation of polymers in solution was studied by means of environmental scanning electronic microscopy and dynamic light scattering. The experimental results showed that in the dilute regime the hydrophobic parts could interact intramolecularly, while in the regime where the polymer concentration was higher than the critical association concentration, intermolecular hydrophobic association became predominant. Within the limit of the solubility, the critical association concentration of the polymer decreased with the increase of the salinity. The experimental results of the solution conformation indicated the presence of the three-dimensional network structure in deionized water and the size of the mesh in the network varied with the polymer concentration. In NaCl solution, above the critical association concentration, an increase in polymer concentration enhanced the intermolecular association and also enlarged the hydrodynamic radius. It would result in the improvement of the thickening power of polymers.
Keywords hydrophobic associating polymer, salt tolerance, viscosity, conformation

1 INTRODUCTION

The use of water-soluble polymer is an economic way for enhanced oil recovery, partially hydrolyzed polyacrylamide (HPAM) has already been commercially used in Daqing oilfield. The carboxylate groups in the chains of HPAM are very sensitive to salt, especially when encountering high value metal ions (such as Ca^{2+}, Mg^{2+}), phase separation easily happens. For this reason, the viscosity in salt solution will lose significantly, and the property of shear stability will become very weak. The higher the molecular weight, the more easily the chains degrade. Thus the specific molecular structure indicates that HPAM can only be used in moderate temperature and salinity for enhanced oil recovery. Furthermore, the three large oilfields in China using polymer for oil recovery are all faced with the problem of being short of aqueous water used for injection. This suggests that if solutions should be made with the sewage treated from the formation, the amount of HAPM used would be increased greatly and the profit of oil recovery would reduce. Therefore the research and development of the salt-resistance water-soluble polymers for oil recovery have become very urgent.

Hydrophobic associating polymers (HAPs) are water-soluble polymers containing a small proportion of hydrophobic groups in polymer chains, which have been focused in recent years[1−4]. In polymer solutions, the molecules are prone to yielding the in-tramolecular and intermolecular association for the effects of hydrophobic groups. Above the critical association concentration, a kind of transitional network is formed mainly for the intermolecular association, which may lead to a significant increase in solution apparent viscosity[5−7]. Especially in salt solution, the addition of electrolyte strengthens the hydrophobic effect, while the apparent viscosity will not decrease but increase greatly. Therefore, good salt-tolerance property is exhibited, which makes it promise to be a new kind of polymers that can make up the defects of HPAM's low apparent viscosity in salt solutions. Furthermore, particular rheological properties of HAP help them exhibit good prospect in sewage treatment, thickening agent in coating and paints[8−10], drag reduction[11], drug release and so on.

However, hydrophobic associating polymers are not perfect and have not been widely used. One problem is the existence of critical association concentration, which makes the apparent viscosity vary greatly above the critical association concentration. When the apparent viscosity increases greatly with the polymer concentration, there will be difficulty in injecting. Moreover, the apparent viscosity could not be easily controlled, before the problems are solved completely.

In this paper, using 2-acrylamido alkane sulfonic acid (AMC_nS) as hydrophobic monomer, acrylamide/2-acrylamido alkane sulfonic acid hydrophobic associating copolymers are synthesized by

free radical micellar copolymerization. The solution properties, the conformation of the polymers in solution and their affecting factors are investigated in detail. Based on this, the thickening mechanism of intermolecular association is discussed.

2 EXPERIMENTAL

2.1 Materials

Hydrophobic monomer (2-acrylamido alkane sulfonic acids) was prepared in our laboratory, whose formula is

$$
\begin{array}{c}
H_2C = CH \\
| \\
C = O \\
| \\
NH \\
| \\
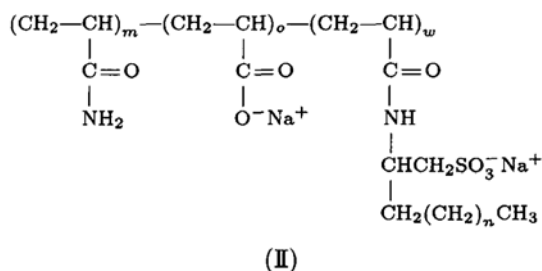CH-(CH_2)_n CH_3 \\
| \\
CH_2 \\
| \\
SO_3H
\end{array}
$$

(I)
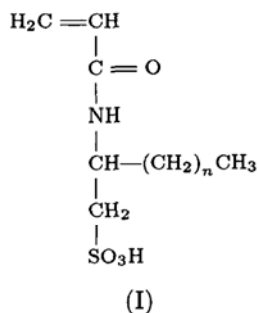
Acrylamide, sodium chloride, and sodium carbonate anhydrous were analytical pure grade agents used without further purification.

All other regents and nitrogen gas were obtained from commercial sources, and the water was distilled three times with an all-glass apparatus.

2.2 Synthesis of AM-AMC$_n$S Copolymers

The copolymers of acrylamide (AM) with AMC$_n$S (I) were prepared by free radical micellar copolymerization. The reaction was conducted in a 250 ml flask equipped with a mechanical stirrer, a thermometer and a nitrogen inlet and outlet. A given amount of acrylamide was dissolved in deionized water followed by 25 min purified nitrogen purge, then anhydrous sodium carbonate was added to control the pH value and hydrophobe monomer dissolved by surfactant sodium dodecyl benzene sulfonate (SDBS) was added. After the addition of potassium peroxydisulfate as free radical initiator, the polymerization was conducted at 20°C under nitrogen atmosphere. Twenty minutes later, the flask was shut and then the system was put in an adiabatic environment until its temperature reached the summit, then hydrolyzed at 70°C for 4 h. Finally it was cooled off and taken out. Its formula is

$$
\begin{array}{ccc}
(CH_2-CH)_m-(CH_2-CH)_o-(CH_2-CH)_w \\
| & | & | \\
C=O & C=O & C=O \\
| & | & | \\
NH_2 & O^-Na^+ & NH \\
& & | \\
& & CHCH_2SO_3^- Na^+ \\
& & | \\
& & CH_2(CH_2)_n CH_3
\end{array}
$$

(II)

2.3 Measurements

The polymer solutions were prepared by dissolving the dried polymer in deionized water or salt solution. Of the salt solutions, some were NaCl solutions of different concentration, and the other was Daqing salt water with their components given by Table 1.

Table 1   The component of Daqing salt water

Component	Na$_2$SO$_4$	KCl	CaCl$_2$	MgCl$_2$·6H$_2$O	NaHCO$_3$
Content, mg·L^{-1}	251.5	191.0	180.0	251.0	3717.5

Intrinsic viscosities were measured by a Ubbelohde viscometer at (30 ± 0.1)°C. Apparent viscosity of polymer solutions was measured by Brookfield DV-II viscometer (shear rate 7.74 s^{-1}). All apparent viscosities were measured at (40 ± 0.1)°C.

The conformation of the polymers in solution was studied by means of environmental scanning electronic microscopy (ESEM) (produced by Philips Electroscan Corporation). In this technique, one or two drops of polymer solution was added to the given sampler and the sample was cooled by the electronic cooling apparatus of ESEM, which was put into the chamber under vacuum, and the temperature and vacuum degree were adjusted to let the ice sublime. Then the changed conformation of the polymer solutions can be recorded. After all the ice sublimated, the conformation was kept on the surface of the fundus.

Based on the measurements of dynamic light scattering (DLS), the distribution of hydrodynamic radius of the polymer solution was detected with Zatasizer 3000HS PCS V1.4. Using He-Ne as lamp-house, the temperature was 25°C, wavelength 633.0 nm, and detector angle 90°.

3 RESULTS AND DISCUSSION

3.1 Behavior in dilute solution

The behavior of the dilute solution of HAP was evaluated by intrinsic viscosity η. The effects of hydrophobe content and hydrophobe length on η are showed in Table 2, where n, p and q represent different hydrophobe length. The results show that with the increase of hydrophobe content and hydrophobe length, η decreases. This means that in dilute solutions, intramolecular association is very strong, which leads to the contraction of polymer chains and results in the decrease of η. Fig. 1 shows the effect of salt on the intrinsic viscosity of the polymer solution. The intrinsic viscosity of the polymer solution decreases with the increase of NaCl concentration, because the addition of NaCl shields the electrostatic repulsive force among carboxylate groups in polymer molecular chains. With increasing NaCl concentration, the interaction of car-

boxylate becomes weak and the polymer chains become more contracted; on the other hand, the polarity of solution increases, leading to stronger intramolecular hydrophobic association. The two factors result in the decrease of η.

Table 2   Intrinsic viscosity of HAP containing different hydrophobe content and hydrophobe length

Sample	Hydrophobe monomer	Hydrophobe mole content, %	η, dL·g^{-1}
HAPA-0.08	AMC$_n$S	0.08	9.394
HAPA-0.09	AMC$_n$S	0.09	6.063
HAPA-0.10	AMC$_n$S	0.10	5.050
HAPA-0.11	AMC$_n$S	0.11	4.678
HAPB-0.09	AMC$_p$S	0.09	12.995
HAPB-0.10	AMC$_p$S	0.10	9.768
HAPC-0.09	AMC$_q$S	0.09	13.855
HAPC-0.10	AMC$_q$S	0.10	13.260
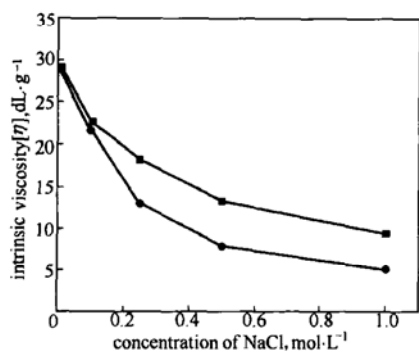
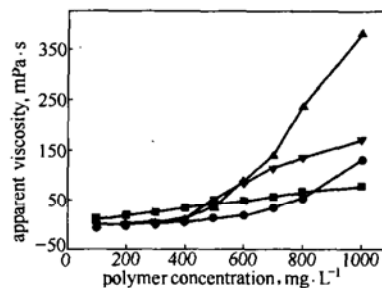
Figure 1   Effect of NaCl concentration on intrinsic viscosity of HAP
■ HAPA-0.08;   ● HAPA-0.10

3.2 The effect of NaCl concentration on the critical association concentration

Figure 2 shows the concentration dependence of apparent viscosity for polymer solutions in different NaCl concentration. As polymer concentration increases, apparent viscosity first increases slowly. When the polymer concentration reaches some definite value, a turning point appears in the curves. This polymer concentration is called the critical association concentration, above which the apparent viscosity increases rapidly because the association among the hydrophobe groups is mainly the intermolecular association and many chains form the dimensional network, so that the hydrodynamic volume of polymer chains enlarge drastically. Fig. 2 also shows that in the range of NaCl concentration investigated, the higher the NaCl concentration, the lower the critical association concentration (when NaCl concentrations are 2×10^3 mg·L^{-1}, 4×10^3 mg·L^{-1}, and 3×10^4 mg·L^{-1}, the critical association concentration are 600 mg·L^{-1}, 500 mg·L^{-1}, and 400 mg·L^{-1} respectively). This is because the polarity of solvent is increased by NaCl, so that the association among the hydrophobe groups

is strengthened. Below the critical association concentration, the intramolecular association leads to a decrease of apparent viscosity by the contraction of polymer chains. Above the critical association concentration, intermolecular association becomes dominant and causes an increase of apparent viscosity, so the difference between apparent viscosity below and above the critical association concentration will cause the critical association concentration to move toward the smaller value. McCormick and Johnson[12] found the same conclusion in investigating the solution properties of acrylamide/N-alkylacrylamide. Furthermore, there is no critical association concentration for HAP in deionized water, probably because the polarity is very low for deionized water and the quantity of intermolecular association increases uniformly with the polymer concentration and makes the critical association concentration unobvious. We also found that when the NaCl concentration reached some value, the apparent viscosity of the solution reduced instead. This occurred mainly because the hydrophobic interaction was reinforced with the addition of NaCl, but when the hydrophobic interaction was too strong, it would affect the solubility and if the NaCl concentration increased continuously, phase separation would appear.

Figure 2   Apparent viscosity as a function of polymer concentration in different concentrations of NaCl
■ deionized water;   ● 2000 mg·L^{-1} NaCl;
▲ 4000 mg·L^{-1} NaCl;   ▼ 3×10^4 mg·L^{-1} NaCl

3.3 Effect of NaCl concentration on apparent viscosity

The effects of salt on the apparent viscosity of the polymer solution are showed in Fig. 3 for polymer concentration of 1000 mg·L^{-1}. The changing trend of apparent viscosity with NaCl concentration at different hydrophobe contents is roughly the same. The difference is that the higher the hydrophobe content the smaller the initial decrease of the apparent viscosity. For example, the apparent viscosity of HAP-0.1 in deionized water is 77 mPa·s, then it reduces to 67.3 mPa·s in 1000 mg·L^{-1} NaCl, and increases to 420 mPa·s in 5000 mg·L^{-1} NaCl. η changes little after

NaCl concentration exceeds 4%. The apparent viscosity of HAP-0.08 reduces from 72.4 mPa·s in deionized water to 30.2 mPa·s and then increases, though the change in hydrophobe content is little. The effect of NaCl concentration on apparent viscosity of semi-dilution solution mainly demonstrates two effects. One is the increase of the polarity of solvent resulted from NaCl which leads to the reinforcement of the extent of intermolecular association; the other is the shield of the repulsive force, resulting in the contraction of the polymer chains. These two effects compete with each other. Whether the apparent viscosity increases or decreases depends on which factor is the primary one.
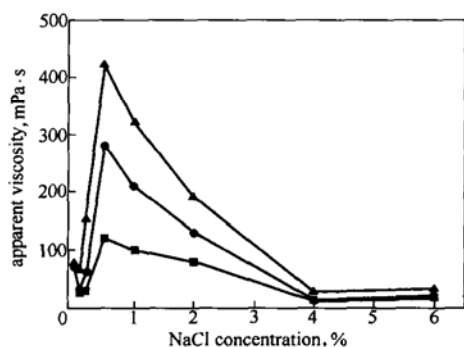

Figure 3 Effect of NaCl concentration on the apparent viscosity
■ HAPA-0.08; ● HAPA-0.09; ▲ HAPA-0.10

3.4 Surfactant

Table 3 shows the effect of concentration of surfactant SDBS on the apparent viscosity of solutions. As the surfactant concentration increases during synthesis, there is a maximum value of apparent viscosity. The addition of SDBS solubilizes the hydrophobe monomer and makes the hydrophobic groups incorporate into the polymer chains. The surfactant concentration plays a very important role on the solubility properties. If the surfactant concentration is very small, the solubility of HAP in salt water will decrease and the apparent viscosity decreases accordingly. With increasing hydrophobe content, the addition of surfactant increases and there is an optimum concentration of surfactant for each hydrophobe level. Under this condition, the apparent viscosity of the solution reaches the maximum value. When the amount of surfactant molecules is low, it will crosslink the hydrophobic groups of different polymer molecules and forms the mixed micells. Under this condition the surfactant plays a bridging and linking role, so the apparent viscosity increases. However, further addition of SDBS would lead to the formation of micelles with single hydrophobe group and weaken the microdomains of intermolecular association, so that the viscosities

decrease.

Table 3 Effect of surfactant concentration on the apparent viscosity of 1000 mg·L^{-1} HAP solutions during synthesis

Mass concentration of SDBS,%	1.12	1.20	1.28	1.37	1.44
Apparent viscosity, mPa·s	280	430	360	300	240

## 3.5 ESEM detection of HAP

Figure 4 shows the ESEM photographs at different concentration of HAP in deionized water, indicating that the polymer truly form three dimensional network in deionized water, and the network is affected by the polymer concentration. The extent of density of meshes in network varies with polymer concentration. As shown in photographs, the lower the polymer concentration, the more sparse the meshes. This further indicates that the number and extent of hydrophobe association depend greatly on the polymer concentration. Fig. 4 also shows that the meshes in network consist of chain bundles, formed through the interaction of hydrophobic groups, and there are pitch points among the meshes. Chain bundles, meshes and pitch points are combined to from dimensional network. Moreover, even though the polymer concentration was only 100 mg·L^{-1}, there are networks in solution. This indicates that at this concentration, lots of hydrophobic groups are associated together and form the intermolecular association. Whether the polymer concentration is high or low, networks exist. This further shows that there is no critical association concentration in deionized water, consistent with the result of rheological experiments.

3.6 DLS results

In order to get further related information on HAP in salt solution, the hydrodynamic radii of two different concentrations of HAP in 5000 mg·L^{-1} NaCl solution were investigated. Fig. 5 shows that the distribution of hydrodynamic radii has two peaks. The lower peak was probably related to the single polymer chains[13], while the higher one attributes to intermolecular association. The size of association depends on the polymer concentration. With increasing polymer concentration, the size of association drifts to larger size. The experimental results show that when the polymer concentration is 500 mg·L^{-1}, the hydrodynamic radius is 110.1 nm, and while the polymer concentration is 700 mg·L^{-1}, it is 214.0 nm. This indicates that the extent of intermolecular association depends mainly on polymer concentration and leads to the increase of viscosity. We also found that in the experiment for dilute solution the refraction and density between dispersed phase and dispersion medium was too low to detect the signal of DLS. Therefore
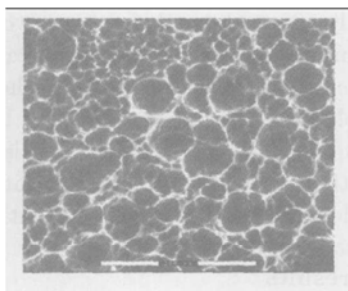
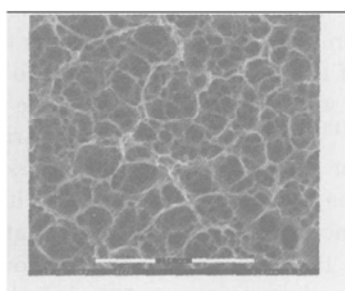further investigations should be conducted to confirm this work.
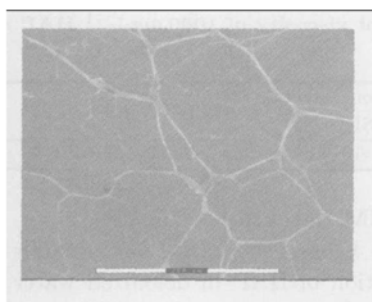
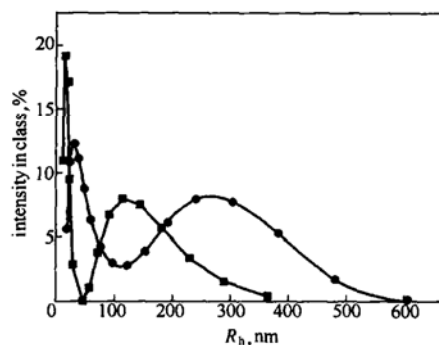(a) 100 mg·L^{-1} HAP, (×200)
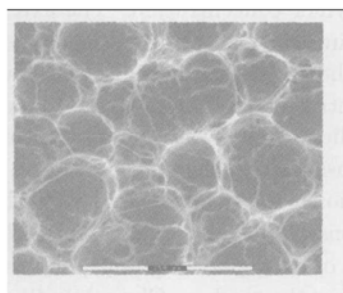
(b) 500 mg·L^{-1} HAP, (×200)

(c) 1000 mg·L^{-1} HAP, (×230)

(d) 4000 mg·L^{-1} HAP, (×200)

Figure 4   ESEM photographs of HAP aqueous solutions

Figure 5   The size distribution of HAP in NaCl solutions
■ 500 mg·L^{-1} HAP; ● 700 mg·L^{-1} HAP

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