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ORIGINAL CONTRIBUTION

Studies on rheological behaviour of hydrophobically associating polyacrylamide with strong positive salinity sensitivity

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Abstract Hydrophobically associating polymer has been obtained by homogeneous copolymerization of acrylamide and an anionic surface-active monomers (surfmer) of acrylamide-type, sodium 2-acrylamido-tetradecane sulfonate ($NaAMC_{14}S$) in aqueous solution, and under different concentration conditions of $NaAMC_{14}S$ above its critical micellar concentration (CMC) and below CMC, two structure types of copolymers P ($AM–NaAMC_{14}S$) were prepared in which main chains $NaAMC_{14}S$ were distributed in microblock and in random manner, respectively. The hydrophobically associating property and rheological behaviour of the copolymers were studied with viscosimetry and then by fluorescence probe method. It was found that the apparent viscosity of the aqueous solution of the copolymers with microblock structures exhibits strong positive salinity sensitivity, whereas the positive salinity sensitivity of the apparent viscosity of the aqueous solution of the copolymers with random structure only appears generally and the apparent viscosity was diminutively increased because of salinity-promoting hydrophobic association. For those copolymers with microblock structures, the apparent viscosities of their brine solution are much higher than that of their pure water solution. In $CaCl_2$ solution (2 wt%), as the copolymer concentration attains 0.2 wt%, the apparent viscosity enhances dramatically with the increase in concentrations, and as the copolymer concentration was 0.3 wt%, the apparent viscosity can enhance by almost two orders of magnitude (from 32 to 1,000 mPa·s) as compared with in pure water solution. Thus, for copolymer P ($AM–NaAMC_{14}S$) with microblock structure, the peculiar positive salinity sensitivity, i.e. salinity thickening, is displayed distinctly. The unusual positive salinity sensitivity of copolymers P ($AM–NaAMC_{14}S$) with microblock structure was also revealed by fluorescence probe method, and the value I_1/I_3 of pyrene in the brine solution of the copolymers was smaller than that in pure water solution of the copolymers. This unique salinity sensitivity is a reflection of the unusual microstructure of the copolymers. The experiment results are interpreted in terms of the effects of the surfmer distribution manner in the copolymer main chain and bonding way of the ionic surfmer to the copolymer main chain on the forming intermolecular association.

Keywords Anionic surface-active monomers · Acrylamide-type · Acrylamide · Homogeneous copolymerization · Hydrophobic association · Rheological behaviour

Introduction

Water-soluble associating polymers have been extensively studied over the past two decades in both academic and industrial laboratories [1, 2]. In particular, hydrophobically associating polyacrylamide (HAPAM), in which a relatively small amount (generally less than 2 mol%) of hydrophobic groups is incorporated in the acrylamide backbone, has received increasing attention on account of their unique rheological characteristics and applications, in oil recovery, drilling fluids, coating and so on [3–6]. However, one major difficulty in the synthesis of HAPAM originates from the insolubility of the hydrophobic comonomers in water. Simply dispersing these insoluble monomers as fine particles in the aqueous medium under stirring (heterogeneous copolymerization) is not a satisfactory process. Thus, by far, most researchers adapted micellar copolymerization

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techniques. In the micellar copolymerization system an aqueous surfactant is added to ensure the solubilization of the hydrophobic comonomer within the micelles [7, 8], and it is actually a microheterogeneous copolymerization system [7]. The addition of surfactants results in some negative influences [9–11] such as low molecular weights caused by the chain transfer effects of surfactants and impurity within surfactants and complex post treatment processes to remove the surfactants. Thereby, it is needed to search for new routes to prepare HAPAM. Polymerizable surfactants are a kind of functional surfactants, and their molecules not only have amphiphilic structure composed of hydrophobic tail and hydrophilic head group but also contain polymerizable vinyl double bonds [12, 13]. The special molecular architecture imparts unique physicochemical properties: analogous to common surfactants, they have surface activity; similar to general vinyl monomers, they can be initiated by initiators and polymerized. Thus, they are called surface-active monomers, shortened as surfmers by academia. The amphipathic property and polymerizability of surfmers lead to their wide application prospect in many science and technology fields. For example, surfmers can be used to prepare vesicle to perform biological simulation, to prepare functional polymer microspheres, to construct soft template to synthesize functional inorganic nano-materials and inorganic/organic composite nano-materials. They can be applied to emulsion polymerization as polymerizable emulsifiers, and so on [14–17]. To overcome a variety of drawbacks of general emulsion polymerization in which usual surfactants are used, in recent years, many researchers have studied and developed a variety of surfmers of maleate and acrylates type [18, 19]. These surfmers are applied to emulsion polymerizations, and the properties of latex and film products have been improved greatly. At present, studies for surfmers are still focused on improving emulsion polymerization.

Some investigations were made to determine whether HAPAM with high performance can be prepared via homogeneous copolymerizations of AM and water-soluble surfmers in aqueous solution. Some investigators have performed some studies in this field [20, 21], and we also have carried out investigations [22, 23]. These studies have revealed the copolymerization mechanism of surfmer and AM as follows: when the concentration of surfmer is above its critical micellar concentration (CMC), surfmers are incorporated into polyacrylamide main chains in the manner of microblocks; whereas when the concentration of surfmer is below its CMC, the copolymer is random. The method of homogeneous copolymerizations of AM and surfmers is a novel route to prepare a new family of HAPAM, and the method has advantage in several aspects. Firstly, the common small molecular surfactants need not be added because of the solubility of surfmers in water. Secondly and mainly, the sequence structure of surfmers in polyacrylamide backbone can be controlled well according to their micellar parameters, such as CMC and aggregation numbers (N_{agg}). If surfmers are distributed on polyacrylamide backbones in microblock manners, the dense hydrophobic pendant chains will tend to be more effectively associating and will lead to bulky intermolecular association networks. As a consequence, the hydrophobic associating polyacrylamide will exhibit strong thickening properties and excellent shear resistance due to the reversible dissociation process of the physically cross-linking networks under shear. Those surfmers of maleate and acrylates type mentioned above are all not suitable for preparing HAPAM with temperature tolerance due to easy hydrolysis of ester groups. In previous studies, we synthesized an anionic surface-active monomer of acrylamide-type, sodium 2-acrylamido-tetradecane sulfonate ($\mathrm{NaAMC_{14}S}$) [22], prepared HAPAM via homogeneous copolymerization in aqueous solutions and studied the mechanism of copolymerization of AM and $\mathrm{NaAMC_{14}S}$ [23]. Based on these studies, in this paper, the rheological behaviour of HAPAM is researched. During performing experiments, it was found for the first time that the solution apparent viscosity of the copolymers with microblock structures possesses strong positive salinity sensitivity, i.e. salinity thickening property. Previously, it was only reported that the solution apparent viscosities of HAPAM containing acrylic acid are pH-responsive [23, 24], whereas HAPAM with strong positive salinity response has not been reported. Our finding not only is significant theoretically in the studies on the relationship between the structures and rheological behaviours for HAPAM but also has potential technological values in oil recovery or drilling applications and other important commercial applications.

Experimental

Materials and equipment

We ourselves synthesized $\mathrm{NaAMC_{14}S}$. Acrylamide (Merck) was twice recrystallized from chloroform acetone. Ammonium persulphate (Aldrich) was used as initiator without further purification. Pyrene (Aldrich) was recrystallized twice by ethanol before use. Water used in this study was deionized and then distilled. All other chemicals were of analytical purity grade.

The apparent viscosity of polymer solutions were measured using a NDJ-1 rotation viscometer (Shanghai balance plant), and the fluorescence emission spectra of probe pyrene in aqueous solutions were determined on a Hitachi F-2500 fluorescence spectrophotometer. A THZ-82 constant temperature shaker equipped with gas bath made in China was used.

Synthesizing copolymer of AM and $NaAMC_{14}S$ by homogeneous copolymerization

The aqueous solution of two monomers, AM and $NaAMC_{14}S$, was prepared according to a certain mass ratio in a four-neck flask equipped with a mechanical stirrer, a thermometer, an inlet of N_2 and a water condenser. The total concentration of the monomers was controlled at 5 wt%, N_2 was purged for 30 min so as to exclude air, the temperature was increased up to 45 °C, and the initiator $(NH_4)_2S_2O_8$ was added. Under stirring and protection of N_2, the reaction was carried out at a constant temperature of 45 °C for 4 h (if the polymerization time was too long, the reaction system would become very sticky and so much as gelatinizing). After finishing the reaction, the copolymer product was precipitated using ethanol as precipitator, was dipped and washed many times with ethanol and, finally, was dried under vacuum. By varying the feed ratio of two monomers and making $NaAMC_{14}S$ concentration above and below its CMC, the copolymerizations were carried out, and then the copolymers with different microstructures and compositions were obtained. For comparison, homogeneous polymer polyacrylamide (PAM) was prepared under the same conditions as copolymerization.

Characterizing molecular weight of copolymers

Using the aqueous solution of NaCl with a concentration of 1 mol/l as solvent and at a constant temperature of 30.0± 0.1 °C, the viscosities of the aqueous solution of polymers were measured with an Ubbelohde viscometer, the intrinsic viscosities [η] of polymers were obtained with dilution extrapolation method, and the molecular weight of polymers were expressed relatively with the intrinsic viscosities [η].

Measuring apparent viscosity of aqueous solutions of polymers

Polymer samples were weighed accurately, swelled in distilled water for 3 days, and then were placed on a constant temperature shaker and were shaken for 7–10 days so that the polymers were dissolved entirely. After these, the solution was diluted with distilled water, and a polymer aqueous solution with a concentration of 1 wt% was prepared. At the same time, $CaCl_2$ aqueous solution with a concentration of 10 wt% was also prepared. By using the above two solutions and distilled water, pure water solutions and brine solutions of polymers with different concentrations were prepared. The apparent viscosities of various polymer solutions were determined at a constant temperature of 25.0±0.1 °C with a rotary viscometer, respectively.

Measuring fluorescence spectra of probe pyrene in polymer solutions

Polymers were dissolved in the saturated aqueous solution of pyrene (the concentration of pyrene was about 7×10^{-7} mol l^{-1}); then, these polymer solutions were diluted with the saturated aqueous solution of pyrene; and finally, the polymer solutions containing probe pyrene and with different concentrations were prepared. The fluorescence spectra of probe pyrene in various polymer solutions were determined with excition at 335 nm, with a slit width of 2.5 nm and in a scanning range of 350–450 nm.

Results and discussions

Structures and compositions of copolymers

Basic structures of copolymers

According to the procedure and conditions described in "Synthesizing copolymer", the copolymers of AM and $NaAMC_{14}S$ were prepared via homogeneous copolymerization in aqueous solutions. There are two kinds of monomeric units in the macromolecules, and the basic chemical structure of the copolymer P (AM–$NaAMC_{14}S$) is expressed in Fig. 1.

Copolymers with different compositions and microstructures

Under the same polymerization conditions, by varying the monomer feed ratios, copolymers with different microstructures (random and microblock structures) and different compositions (with different content of $NaAMC_{14}S$) were synthesized, and the relative data are given in Table 1.

The CMC of $NaAMC_{14}S$ at 40 °C is 8.2×10^{-4} mol·l^{-1} [22], whereas the total monomer concentration is 5 wt%. Therefore, in the reaction system for preparing copolymer

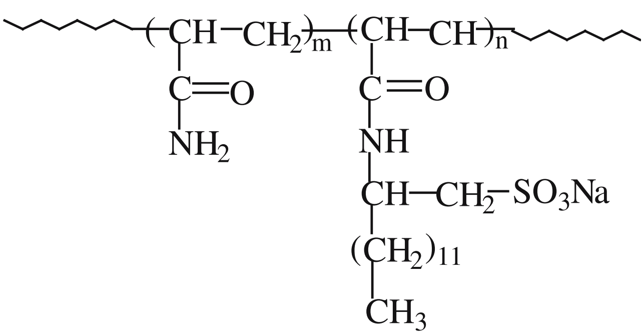

Fig. 1 Basic chemical structure of the copolymer of $NaAMC_{14}S$ and AM

Table 1 Copolymers synthesized under different feed ratio

Copolymer	Feed ratio ($NaAMC_{14}S$/AM [wt/wt])	Amount of[a] $(NH_4)_2S_2O_8$ (wt%)	[η][b] (ml/g)
CP-0.0 (PAM)	0.0:100	0.08	853
CP-0.6	0.6:99.4	0.08	840
CP-1.5	1.5:98.5	0.08	825
CP-2	2.0:98.0	0.08	815

[a] Weight fraction of initiator $K_2S_2O_8$ in the total feed

[b] [η] intrinsic viscosity (ml/g)

CP-0.6, the concentration of $NaAMC_{14}S$ is below its CMC, and in the reaction systems for preparing copolymer CP-1.5 and CP-2, the concentrations of $NaAMC_{14}S$ are above their CMC. According to the explored copolymerization mechanism of surfmers and AM [20, 21, 23], CP-0.6 should be a random copolymer, whereas CP-5 and CP-2 should have microblock structures, that is, $NaAMC_{14}S$ are distributed on polyacrylamide backbones in a microblock manner, and the length of the microblock is approximately equal to the aggregation number of $NaAMC_{14}S$ in the micelles of aqueous solution. The difference between CP-1.5 and CP-2 only is the contents of the microblocks on the macromolecular chains. The chain architecture of the copolymer with the microblock structure is illustrated schematically in Fig. 2. It is still seen in Table 1 that although the intrinsic viscosities of these copolymers decrease slightly with the increase in the proportion of $NaAMC_{14}S$ in the feed, the differences of intrinsic viscosities are very small because of the same added amounts of initiator.

Hydrophobically associating properties of copolymers

Figure 3 presents the concentration dependence of apparent viscosities for the aqueous solutions of four polymers. At higher concentrations, the apparent viscosities for the copolymer aqueous solutions are much greater than that of PAM. For the copolymer of AM and $NaAMC_{14}S$, intermolecular association appears due to the hydrophobic interaction of the hydrophobic side chains of $NaAMC_{14}S$ between macromolecules and transient network structures with large hydrodynamic volume form, resulting in higher solution viscosities. It is apparent that the viscosities enhance sharply with concentration increases as the polymer concentrations attained approximately 0.2 g dl^{-1} for the three copolymers. This suggests that 0.2 g dl^{-1} (or a value around 0.2 g dl^{-1}) is a critical concentration for the copolymer of AM and $NaAMC_{14}S$, at which intramolecular association transforms into intermolecular association, i.e. critical association concentration (*cac*; the accurate values of *cac* for the three copolymers will be estimated in the following discussion). When the copolymer concentrations increase further, the intermolecular association degree is strengthened because of the shortening of the distance between macromolecules, and the viscosity enhanced rapidly. As compared with two copolymers, CP-1.5 and CP-2, the solution viscosity of copolymer CP-0.6 is much smaller. This not only is owing to a low content of $NaAMC_{14}S$ on the macromolecular main chains of copolymer CP-0.6 and a weaker intermolecular association but also is due to the random distribution of $NaAMC_{14}S$ on the main chains, and the latter is the main reason for the lower solution viscosity of CP-0.6. On the macromolecular main chains of CP-1.5 and CP-2, $NaAMC_{14}S$ distributes in

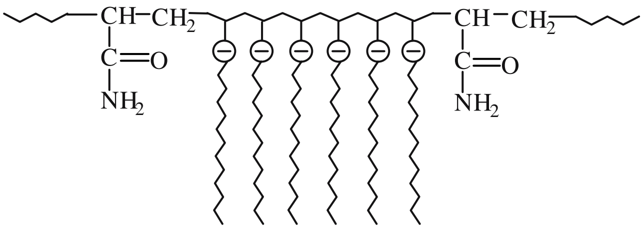

Fig. 2 Schematic illustration of chain architecture of copolymers with microblock structure

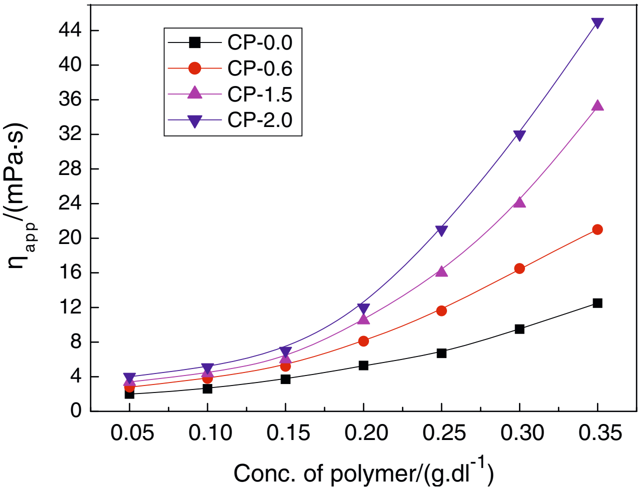

Fig. 3 Varying of the apparent viscosity of polymer solutions in pure water with polymer concentration. Temperature = 25.0 ± 0.1 °C; shear rate=6 S^{-1}

microblock manners, and the hydrophobic side chains can associate intermolecularly more effectively, leading to higher solution viscosities. This microstructure effect of copolymers on the rheological behaviour of the copolymers will be revealed more clearly in the following discussion.

Aggregation of surfactants and associating polymers can be studied on the molecular level using fluorescence spectroscopy with pyrene as a probe, due to its sensitivity to the microenvironment polarity [24]. The formation of hydrophobic microdomains in aqueous media and the penetration of pyrene molecules into these domains lead to the drop of the ratios of fluorescence intensities of the first and the third emission peaks (I_1/I_3) from 2-1.6 to 1.2 [25]. This means that the characteristic value for pyrene in pure water is equal to 2-1.6 [26]. Figure 4 presents the ratios I_1/I_3 for PAM, CP-0.6, CP-1.5 and CP-2 as a function of polymer concentrations. The ratios I_1/I_3 of PAM in whole concentration region remains unchanged (about 1.8), whereas the ratios I_1/I_3 of copolymers are decreased when concentration increases. Especially in the range of higher concentrations, the ratios I_1/I_3 of copolymers are much lower than that of PAM. This indicates that the hydrophobic domains have formed in copolymer solutions due to the hydrophobic associating intramolecularly at lower concentrations and intermolecularly at higher concentrations. It can be found that the distinct decreases of the values I_1/I_3 for three copolymers appear at an approximate concentration, 0.2 g dl^{-1} (it is corresponding to the *cac* measured by viscometry). However, there are apparent differences of concentrations at which the ratios I_1/I_3 appear distinctly decreased for three copolymers. The distinct decreases of I_1/I_3 value for CP-2 and CP-1.5 appear at about 0.19 g dl^{-1}, and for CP-0.6, it appears at about 0.23 g dl^{-1}. They are the more accurate *cac* values for the three copolymers. It can also be found that in whole concentration range, the ratio I_1/I_3 for CP-2 and CP-1.5 is lower than that for CP-0.6, especially, over *cac*, the ratio I_1/I_3 for CP-2 and CP-1.5 decreases rapidly, and the ratio I_1/I_3 for CP-2 and CP-0.6 decreases from 1.72 to 1.42 and from 1.76 to 1.63, respectively. These differences should be attributed to different microstructures of the three copolymers. For copolymers CP-2 and CP-1.5, the distribution of NaAMC$_{14}$S on the main chains is in microblock manner, the hydrophobic side chains are closed, and stronger hydrophobic association ability is expected. After *cac* large and dense physically cross-linking networks via intermolecular association of hydrophobic side chains form easily. Therefore, the polarities of the hydrophobic microdomains in the solutions of CP-2 and CP-1.5 are weaker than that in the solutions of CP-0.6, and the ratios I_1/I_3 are much smaller.

Positive salinity sensitivity of viscosity

Apparent viscosity of copolymer solution in brine of CaCl$_2$

Copolymer solutions with different concentrations were prepared with brine containing CaCl$_2$ of 2 wt%, their apparent viscosities were determined, and the viscosities, as the function of the polymer concentration, are given in Fig. 5. From Fig. 5, a peculiar phenomenon can be found: as compared with the apparent viscosities of the pure water solutions of copolymers CP-1.5 and CP-2 (in Fig. 3), their apparent viscosities of the brine of CaCl$_2$ enhanced dramatically with the increase in the concentration; as the concentrations were over *cac* and the apparent viscosity of CP-2 solution with a concentration of 0.3 wt% enhanced actually by two orders of magnitude (from 32 to 1,000 mPa·s; the former is the viscosity of the pure water solutions), and a strong positive salinity-dependence of the rheological behaviour for the copolymer with microblock

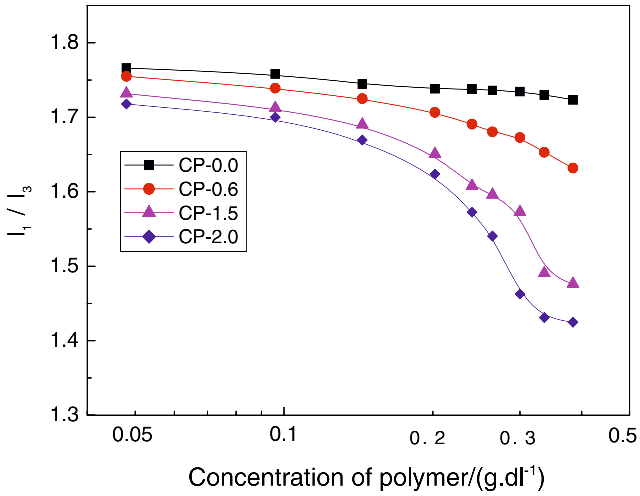

Fig. 4 Varying of the I_1/I_3 ratio of pyrene in polymer solutions in pure water with polymer concentration. Temperature=25 °C

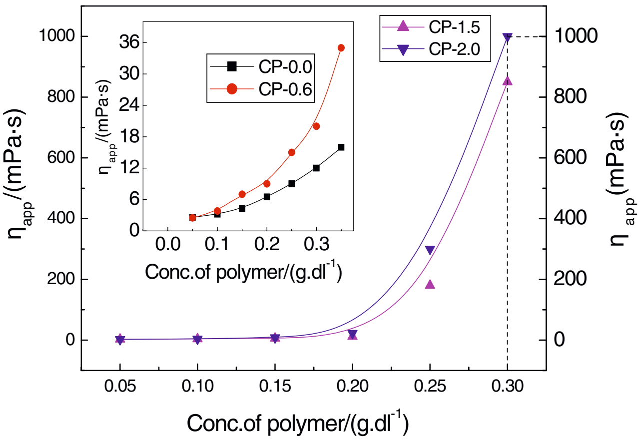

Fig. 5 Varying of apparent viscosity of polymer solution in brine containing 2 wt% of CaCl$_2$ with polymer concentration. Temperature=25 °C; shear rate=6 S^{-1}

microstructure is displayed distinctly. This strong positive salinity sensibility of HAPAM is found for the first time. Whereas for the random copolymer CP-0.6, the above phenomenon has not been observed. The fluorescence spectra of pyrene in these solutions were determined, and the ratios I_1/I_3 as the function of copolymer concentrations are presented in Fig. 6. As compared with the case of pure water solutions (in Fig. 4), the ratios I_1/I_3 for copolymer CP-1.5 and CP-2 in brine of $CaCl_2$ decrease more greatly as the concentrations are over *cac*. The ratio I_1/I_3 for CP-2 at a concentration of 0.3 wt% is down to 1.35, whereas the corresponding value in pure water solution is equal to 1.46 (in Fig. 4). The above facts show that the polarities of the hydrophobic microdomains in brine of copolymers CP-1.5 and CP-2 are much weaker than that in pure water solutions.

Generally, the increase in the polarity of aqueous solutions due to the addition of salt will promote hydrophobic association, and will make the solution's apparent viscosity of associating polymers to increase. However, the promoting effect is limited, and the explanation for the above peculiar phenomenon that the apparent viscosities of the brine solution of copolymers CP-1.5 and CP-2 are of strong positive salinity-response needs to be given from the point of view of macromolecular microstructures. On one hand, for the copolymers CP-1.5 and CP-2, $NaAMC_{14}S$ is distributed on the main chains of macromolecules in microblock manner (the length of each microblock should be approximately equal to the aggregation number of monomer $NaAMC_{14}S$ in micelles according to the copolymerization mechanism [20, 21, 23]), and on the other hand, the anionic surfactants are covalently bound to the main chain at the charged head, sulfoacid groups $-SO_3^{2-}$ (that is, ion head groups are closed to the main chain), their hydrophobic tails are apart from the main chain, and both the two structure factors lead to a favourable situation for intermolecular associations. However, the electrostatic repulsion between anions $-SO_3^{2-}$ exerts an impeditive effect on the hydrophobic associations. When $CaCl_2$ is added into the copolymer solutions, the contrary ions Ca^{2+} will combine fast with the sulfoacid groups $-SO_3^{2-}$, and the divalent cations Ca^{2+} will produce a strong effect of electrostatic shield, resulting to larger and denser physically cross-linking networks. The hydrodynamic volume of the supermolecular structure increases sharply, so the apparent viscosity of brine solution of the copolymer enhances remarkably. At the same time, the polarity of the inner networks becomes very weak, so the ratio I_1/I_3 decreases to a smaller value as compared with the case in the pure water solution. Besides, as shown in Fig. 5, the salinity-dependence of the brine solution of copolymer CP-1.5 is poorer than that of CP-2 because of a fewer content of microblocks of $NaAMC_{14}S$ unit on the macromolecular chains.

In Fig. 7, the plots of the apparent viscosity of the brine solutions of copolymers with a concentration of 0.3 wt% versus $CaCl_2$ concentration are given. Figure 7 again clearly indicates the strong positive salinity sensitivity of the viscosities of the copolymers with microblock structures. The apparent viscosities of the brines for CP-1.5 and CP-2 are enhanced greatly with the increase of $CaCl_2$ concentration, whereas for random copolymer CP-0.6, the viscosity of the brine changes slightly with $CaCl_2$ concentration. So far, the above salinity-dependent viscosity enhancement of aqueous solutions of hydrophobically associating polyacrylamide has not been reported, and only the pH-dependence of viscosity behaviours of HAPAM-containing acrylic acid [27, 28] has been reported in literatures.

Based on the above description, it seems that the positive salinity sensitivity of the viscosities of the copolymers of

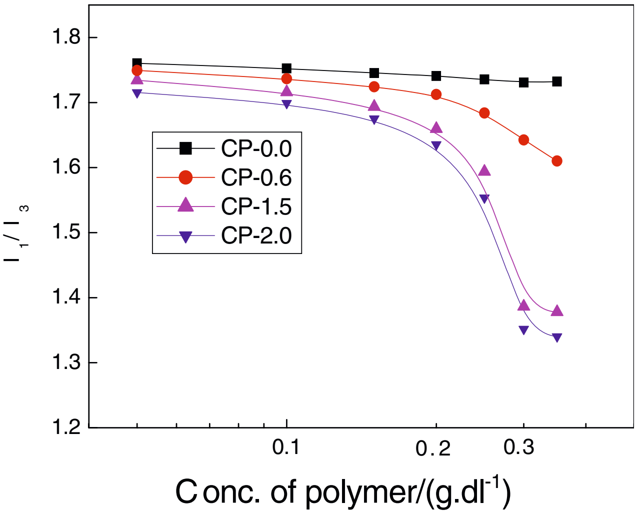

Fig. 6 Varying of I_1/I_3 ratio of pyrene in polymer solution in brine containing 2 wt% of $CaCl_2$ with polymer concentration. Temperature= 25 °C

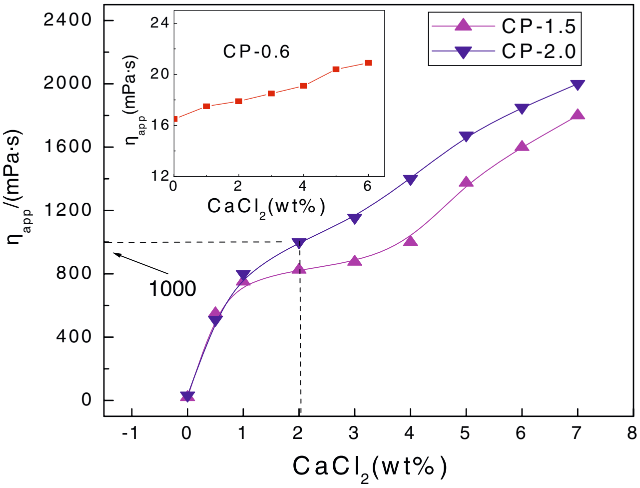

Fig. 7 Effect of concentration of $CaCl_2$ on apparent viscosity of polymer aqueous solution. Polymer concentration=0.3 wt%; shear rate=6 S^{-1}

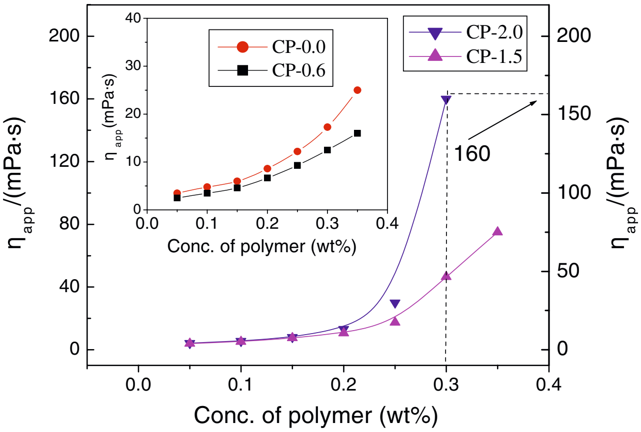

Fig. 8 Varying of apparent viscosity of polymer solution in brine containing 2 wt% of NaCl with polymer concentration. Temperature= 25 °C; shear rate=6 S^{-1}

ionic surfmer and AM is decided by two-structure factors: one factor is the distributing manner of surfmers on copolymer main chains, and the other one is the way by which surfmers are linked to copolymer main chains. About the effect of the relative positions of the charged heads and hydrophobic groups of surfmers with respect to the copolymer main chains on the association properties, other researchers also have similar description and report [29]. Hence, for hydrophobic association polymers prepared from ionic surfmers and AM, the relative positions of the charged heads and hydrophobic groups with respect to the copolymer main chains are important to influence the rheological behaviour of the polymer.

Apparent viscosity of copolymer solution in brine of NaCl

Figure 8 gives the variations in the viscosities of the copolymer solutions in the brine of 2 wt% NaCl with copolymer concentration. Similarly, in Fig. 8, the positive salinity sensitivity of the viscosity of the copolymer with microblock structures also is displayed clearly. When the concentrations are over *cac*, the apparent viscosities of the solutions of copolymers CP-1.5 and CP-2 enhanced rapidly with the increase in the concentration, and the apparent viscosity of CP-2 solution with a concentration of 0.3 wt% enhanced from 32 mPa·s (in pure water) to 160 mPa·s (in brine of NaCl). Whereas for the random copolymer CP-0.6, the above phenomenon also has not been observed.

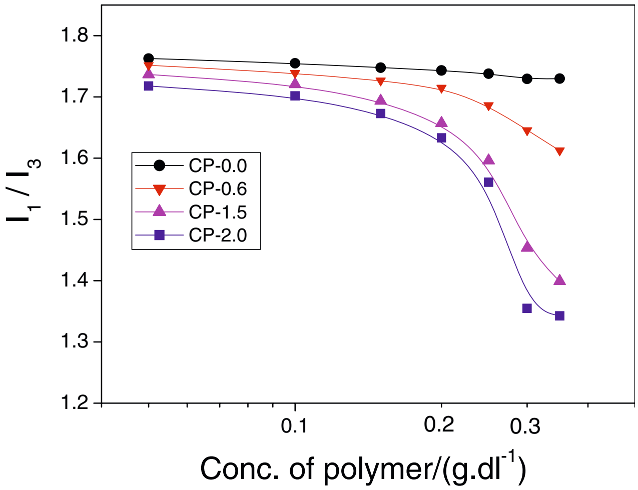

Fig. 9 Varying of I_1/I_3 ratio of pyrene in polymer solution in brine containing 2 wt% of NaCl with polymer concentration. Temperature= 25 °C

As compared with the case in the brine of $CaCl_2$, the salinity dependence of viscosity enhancement for copolymers CP-1.5 and CP-2 in the brine of NaCl is obviously poorer. The reason for this is that, as compared with bivalent Ca^{2+}, the electrostatic shield effect of monovalent Na^+ as contrary ion for the repulsion between anions, $-SO_3^{2-}$, is weaker, and the effect to promote hydrophobic association of NaCl is smaller, so that the viscosity of copolymer solution in brine of NaCl is much lower than that in the brine of $CaCl_2$.

The fluorescence spectra of pyrene in copolymer solutions in the brine of NaCl were also measured. The ratios I_1/I_3 as a function of polymer concentration are shown in Fig. 9. For copolymers CP-1.5 and CP-2, when the concentration is over *cac*, the decreases of ratios I_1/I_3 are more rapid than that in pure water solution, and at the concentration of 3 wt% for copolymer CP-2, the ratio I_1/I_3 is 1.37 lower than 1.46, which is the corresponding value in pure water solution. This fact also reveals that the polarity of the hydrophobic microdomains in NaCl solution of copolymer CP-2 is much smaller than that in its pure water solution, and the salinity sensitivity of the viscosities of the copolymers with microblock structures once again is displayed.

Conclusions

Based on probing into the copolymerization mechanism of AM and anionic surfmer $NaAMC_{14}S$, homogeneous copolymerizations of the two monomers were performed in aqueous solutions, and copolymers with two structures, random and microblock structures, were prepared below and above the CMC of $NaAMC_{14}S$, respectively. The solution viscosity of the copolymer with microblock structures exhibits strong positive salinity sensitivity. This macroscopic rheological character is dependent on two kinds of microstructure factors: (1) distribution manner of microblocks in which $NaAMC_{14}S$ distributes on polymer main chains makes the hydrophobic side chains closed and is favourable for forming large association networks; (2) $NaAMC_{14}S$ are covalently bound to the polymer main chain at the ionic head groups, their hydrophobic tails are apart from the main chain, and this structure is favourable for forming dense association networks. Furthermore, via electrostatic shield effect of cations of salt for the repulsion of ionic head groups, these hydrophobic tails can form large and dense association networks via intermolecular hydrophobic associating, and the hydrodynamic volume of the supermolecular structure increases dramatically, resulting in strong positive salinity-dependent viscosity enhancement.

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