

# Interaction between the Strong Anionic Character of Strong Anions and the Hydrophobic Association Property of Hydrophobic Blocks in Macromolecular Chains of a Water-Soluble Copolymer

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Received 12 January 2004; accepted 9 August 2004

DOI 10.1002/app.21505

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The copolymerization of acrylamide, sodium 2-acrylamido-2-methyl propane sulfonate, and styrene was carried out in a microemulsion medium, and ternary copolymers based on polyacrylamide, which contained both strong anionic groups ( $-\text{SO}_3\text{Na}$ ) and hydrophobic blocks (polystyrene), were synthesized. The structures and compositions of the copolymer were characterized by various means (Fourier transform infrared, ultraviolet, and elemental analysis). The aqueous solution properties were investigated with a fluorescence probe technique and apparent viscosity measurements, and the interactions between the strong anionic character of the anionic groups and the hydrophobic association behavior of the hydrophobic blocks was intensively examined. After the simultaneous addition of the strong anionic groups and hydrophobic association blocks to the main chains of polyacrylamide, the synergism of the electroviscosity effect of the strong anionic groups and

the hydrophobic association effect of the hydrophobic blocks obviously enhanced the apparent viscosity of aqueous copolymer solutions, and the synergism of greater salt tolerance of the strong anionic groups and the strengthened hydrophobic association of the hydrophobic blocks in brine solutions resulted in increased salt resistance for the copolymer. However, the presence of strong anionic groups ( $-\text{SO}_3^-$ ) in the macromolecules weakened the intermolecular hydrophobic association effect of the copolymer in aqueous solutions to a certain degree; that is, the strong anionic groups produced a certain negative influence on the hydrophobic association effect of the hydrophobic blocks. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 714–722, 2005

**Key words:** copolymer of acrylamide; strong anion; hydrophobic association; synergism; negative influence

## INTRODUCTION

Polymer flooding is more effective in current chemical flooding techniques for enhanced oil recovery, especially in China.<sup>1</sup> Polymer flooding can be applied successfully in most oil fields. Polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) are well-known water-soluble polymer used as flooding polymers in tertiary oil recovery. However, there are some disadvantages in using these polymers,<sup>2</sup> such as a loss of viscosity due to shear degradation, poor resistance to temperature and salt, and phase separation as divalent metal cations are encountered. Obviously, PAM and HPAM are not suitable for the high-salt and high-temperature geological conditions of petroleum reservoirs. To overcome these deficiencies of PAM and HPAM, in recent years, many researchers have studied flooding polymers with properties of salt tolerance and temperature resistance.<sup>3</sup> In the first way,

PAM is hydrophobically modified through the addition of a small concentration of hydrophobic groups and blocks to the hydrophilic backbone of PAM; that is, hydrophobic association acrylamide (AM) polymers are synthesized.<sup>4–6</sup> In the semidilute regime, during the hydrophobic interactions of the hydrophobic groups and blocks, transient networks form via the intermolecular association of the hydrophobic groups and blocks. This association results in an increase in the hydrodynamic size of the polymer, and this efficiently enhances the viscosity of aqueous solutions. An increase in the temperature is advantageous to hydrophobic association, and an increase in the polarity of aqueous solutions by salinity is also advantageous to hydrophobic association.<sup>7</sup> Hydrophobically modified PAM is characterized by enhanced viscosity, improved brine resistance, and temperature resistance. Moreover, adding strong anionic groups to the main chains of PAM is also an effective way of improving flooding polymer properties.<sup>3</sup> Strong anionic groups cause chain expansion because of electrostatic repulsion, and this leads to higher viscosity; they also impart better solubility to the polymer. Furthermore,

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these strong anionic groups have better salt tolerance, so the salt resistance of the polymer can be improved. As for the design of molecules, polymers with better properties can be obtained by a combination of these two methods; that is, it is possible to make PAM macromolecules that contain both strong anionic groups and hydrophobic groups or blocks in the main chains simultaneously. Therefore, there are two kinds of effects (electrostatic repulsion and hydrophobic association) in macromolecular chains. Some researchers have prepared analogous ternary copolymers of AM,<sup>7-9</sup> but mutual interactions between the strong anionic character of strong anionic groups and the hydrophobic association property of hydrophobic segments have not been researched deeply. In this study, ternary copolymers of AM, sodium 2-acrylamido-2-methyl propane sulfonate (NaAMPS), and styrene (St) were synthesized in a microemulsion medium that contained sulfonate groups ( $-\text{SO}_3\text{Na}$ ) and polystyrene (PSt) blocks simultaneously, and the interactions between the strong anionic character of the groups ( $-\text{SO}_3^-$ ) and the hydrophobic association behavior of the blocks (PSt) in macromolecular chains in aqueous copolymer solutions were emphatically examined. The results showed a mutual synergy function between them and a negative influence of strong anionic groups ( $-\text{SO}_3^-$ ) on the hydrophobic association behavior of blocks (PSt) to a certain degree.

## EXPERIMENTAL

### Materials

AM (Merck, Germany) was recrystallized twice from chloroform. St (Aldrich, Milwaukee, WI) was purified by vacuum distillation before use. 2-Acrylamido-2-methyl propane sulfonic acid (AMPS; Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan) was not purified further. Potassium persulfate and sodium thiosulfate (Aldrich) were used as the initiator system without further purification. Sodium dodecyl sulfate (SDS; Aldrich) was used as a surfactant without further purification. Phenylfluorone (PFN; Shanghai Reagent Factory, Shanghai, China), used as a fluorescence probe, was spectrally pure. Water was deionized and then distilled.

### Equipment

The Fourier transform infrared (FTIR) spectrum of the copolymer was recorded with a PerkinElmer 1700 spectrometer. Elemental analysis, used to determine the sulfur concentration, was conducted on a Elementar Vario EL analyzer (Germany). Fluorescence emission spectra were recorded on a Shimadzu RF-540 fluorescence spectrophotometer (Japan). The apparent viscosity ( $\eta_a$ ) was measured with an NDJ-1 rotational

rheometer from the Shanghai Balance Instrument Factory (Shanghai, China).

### Synthesis of the AM/NaAMPS/st ternary copolymer

In a beaker, a certain amount of AMPS was dissolved in an appropriate amount of distilled water; it was neutralized with equal moles of an aqueous NaOH solution in ice water, the pH was adjusted to about 8, and NaAMPS was formed. In another beaker, a certain amount of SDS was dissolved in an aqueous AM solution. The two solutions were mixed, and the total concentration of the monomers was kept at 5 wt %. Then, St was added according to a feed ratio, and a clear microemulsion was formed by slight agitation. In the microemulsion system, the aqueous solution of AM and NaAMPS was the continuous phase, and St was dispersed in the aqueous medium as microemulsion drops. The microemulsion system was transferred into a four-necked flask equipped with a thermometer, a mechanical stirrer, an  $\text{N}_2$  inlet, and a water condenser. After  $\text{N}_2$  purging for 30 min, the temperature was increased to 40°C, and a redox initiator (as an aqueous solution), composed of 1:1 (mol/mol)  $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_3$ , was added to the flask. The reaction system was maintained at 40°C under a continuous flow of  $\text{N}_2$ . After 10 h, the polymerization was terminated, and the polymers were precipitated by the slow pouring of the reaction mixture into a constantly stirred sixfold excess of acetone. After filtration, the polymer was dissolved again in water, was again precipitated with acetone, and was filtered. The operation was repeated three to four times to remove the surfactant thoroughly. The obtained polymer was dipped into toluene for 48 h to extract the PSt homopolymer and then was dried under reduced pressure at 50°C for 6 h and conserved in a desiccator.

A series of AM/NaAMPS/St ternary copolymers with various compositions were prepared through variations in the feed of St at a fixed feed ratio of AM and NaAMPS (90:10 mol/mol). For comparison, under microemulsion polymerization conditions identical to those used for the AM/NaAMPS/St ternary copolymers, a series of binary block copolymers (PAM-*b*-PSt) were prepared, and a random copolymer {poly(acrylamide-*co*-sodium 2-acrylamido-2-methyl propane sulfonate) [P(AM-*co*-NaAMPS)]} was also prepared with the same feed ratio of AM to NaAMPS (90:10 mol/mol). PAM and HPAM (hydrolysis degree = 40%) were also prepared.

### Characterization of the structure and composition of the copolymers

For the measurement of the infrared spectrum of the ternary copolymer, a powder of the prepared ternary

TABLE I  
Binary Copolymers Synthesized at Different Feed Ratios

Copolymer	AM/St (wt %)	Amount of $K_2S_2O_8$ + $Na_2S_2O_3$ (wt %) <sup>a</sup>	St (wt %) <sup>b</sup>	$[\eta]$ (mL/g)	$k_H$
C2-1	99.5:0.5	0.2	0.46	468.2	0.409
C2-2	99.2:0.8	0.2	0.75	460.8	0.512
C2-3	99.0:1.0	0.2	0.96	456.7	0.556
C2-4	98.5:1.5	0.2	1.45	442.6	0.495
C2-5	97.0:3.0	0.2	2.94	430.5	0.405
C2-6	96.0:4.0	0.2	3.92	418.3	0.361

Polymerization temperature = 40°C; polymerization time = 6 h.

<sup>a</sup> Weight fraction of initiator in the total feed.

<sup>b</sup> Weight fraction of St in the copolymer by the results of UV analysis.

copolymer was mixed with KBr and was pressed into a piece, and the infrared spectrum was recorded on a spectrometer. For the measurement of the composition of the copolymer, with the elemental analysis method, the content of NaAMPS in the copolymer was determined by an analysis of the content of S, and the concentration of St was measured with ultraviolet (UV) spectroscopy according to a procedure described previously.<sup>10</sup> In this way, the composition of the copolymer was determined.

#### Determination of the intrinsic viscosity ( $[\eta]$ ) and huggins constant ( $k_H$ )

Viscosity measurements were performed in aqueous NaCl solutions (2 mol L<sup>-1</sup>) at 30.0 ± 0.1°C with an Ubbelohde viscometer at a polymer concentration of 0.2–0.04 wt %.  $[\eta]$  was obtained by the extrapolation to a zero concentration of the linear plots of the reduced viscosity versus the polymer concentration.  $[\eta]$  was used to represent the molecular weights of the polymers relatively.  $k_H$  was obtained during the determination of  $[\eta]$ , and  $k_H$  was used to evaluate and compare the hydrophobic association behaviors of polymers.

#### Measurement of $\eta_a$ of aqueous and brine solutions of the polymers

A certain amount of the polymer was dissolved in distilled water, no agitation was applied during the 2 days of dissolution (the swelling of the polymer), and homogenization was ensured by magnetic stirring for another day. Aqueous solutions with a series of concentrations were prepared by dilution. An NDJ-1 rotational rheometer was used to determine  $\eta_a$  of the aqueous solutions at a shear rate of 6 s<sup>-1</sup> and at 25°C. Curves of  $\eta_a$  versus  $c$  (concentration of the copolymer) were plotted, and the rheological behaviors of solutions of different polymers with different compositions were compared.

Aqueous CaCl<sub>2</sub> solutions of polymers with different CaCl<sub>2</sub> concentrations were prepared, and they all contained the same concentration of the polymer (0.3 wt %). Their  $\eta_a$  values were measured, and the viscosity properties of brine solutions of different polymers with different compositions were compared.

#### Measurement of the fluorescence spectra of the probe

Samples of the binary copolymers and ternary copolymers were dissolved in saturated aqueous solutions of PFN ([PFN] ≈ 1 × 10<sup>-6</sup> mol · L<sup>-1</sup>), and aqueous copolymer solutions with different concentrations were prepared by dilution with saturated aqueous solutions of PFN. Fluorescence emission spectra of PFN in these aqueous solutions (excitation wavelength = 360 nm) were determined with a Shimadzu RF-540 fluorescence spectrophotometer.<sup>11</sup>

## RESULTS AND DISCUSSION

#### Binary copolymers and ternary copolymers with various compositions

Under the same microemulsion polymerization conditions, through variations in the feed ratio of the monomers, binary copolymers (PAM-*b*-PSt) and ternary copolymers (AM/NaAMPS/St) with various compositions were synthesized (series C2 and C3, respectively), and correlative data are listed in Tables I and II.

During the preparation of aqueous solutions of the copolymers, the dissolution rates of the terpolymers were observed to be more rapid than those of the binary copolymers generally. Obviously, after the addition of strong anionic groups (—SO<sub>3</sub><sup>-</sup>) to the macromolecular main chains, strong solvation could improve the dissolution properties of PAM.

#### Structures and compositions of the copolymers

The FTIR spectrum of the AM/NaAMPS/St ternary copolymer synthesized in a microemulsion medium is

TABLE II  
Ternary Copolymers Synthesized at Different Feed Ratios

Copolymer	Feed ratio		Amount of $K_2S_2O_8$ + $Na_2S_2O_3$ (wt %) <sup>b</sup>	St (wt %) <sup>c</sup>	NaAMPS (wt %) <sup>d</sup>	[ $\eta$ ] (mL/g)	$k_H$
	AM/NaAMPS (mol:mol)	St (wt %) <sup>a</sup>					
C3-1	90:10	0.5	0.2	0.42	23.4	479.6	0.388
C3-2	90:10	0.8	0.2	0.73	23.3	475.1	0.485
C3-3	90:10	1.0	0.2	0.93	23.2	470.5	0.530
C3-4	90:10	1.5	0.2	1.41	23.5	463.2	0.471
C3-5	90:10	3.0	0.2	2.90	23.2	440.9	0.385
C3-6	90:10	4.0	0.2	3.90	23.3	426.7	0.346

Polymerization temperature = 40°C; polymerization time = 6 h.

<sup>a</sup> Weight fraction of St in the total feed.

<sup>b</sup> Weight fraction of initiator in the total feed.

<sup>c</sup> Weight fraction of St in the terpolymer by the results of UV analysis.

<sup>d</sup> Weight fraction of NaAMPS in the terpolymer by the results of elemental analysis.

shown in Figure 1. The absorptions at 1655 and 1450  $cm^{-1}$  are characteristic of the benzene ring, and the absorptions at 765 and 705  $cm^{-1}$  are characteristic of a single substitute of the benzene ring. The amide bond can be observed at 3350 and 1658  $cm^{-1}$ . The stretching vibration of the C=O bond of the amide group appears at 1658  $cm^{-1}$  and overlaps the characteristic absorption of benzene ring at 1655  $cm^{-1}$ , and the stretching vibration of the  $-NH_2$  group appears at 3350  $cm^{-1}$ . The characteristic absorption bands of the  $-SO_3Na$  group can be observed at 1192 and 1045  $cm^{-1}$ . The stretching vibration of the C=O bond in the NaAMPS units appears at 1192  $cm^{-1}$ , and the stretching vibration of the S=O bond of sulfonate groups appears at 1045  $cm^{-1}$ . The FTIR spectrum of the ternary copolymer shows absorption bands typical of the constituent monomeric units, and so the prepared product is indicated to be a copolymer of three kinds of monomers, that is, the AM/NaAMPS/St ternary copolymer.

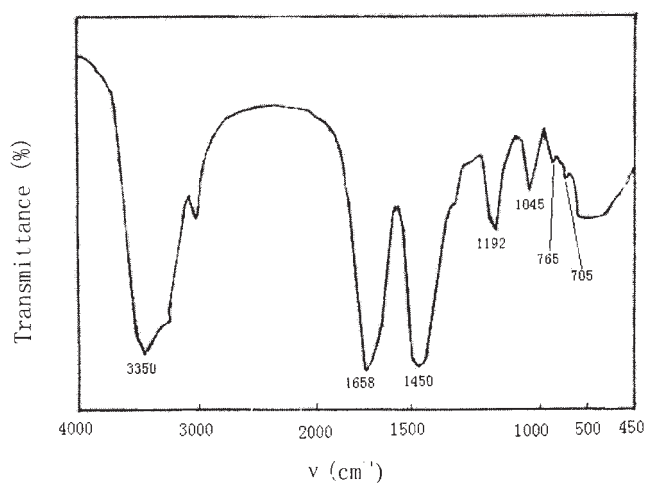


Figure 1 FTIR spectrum of the AM/NaAMPS/St ternary copolymer.

The content of St in the copolymer was measured with UV spectrometry, and the content of NaAMPS in the copolymer was determined with elemental analysis. The measurement results are given in Tables I and II.

### Synergism effect of the strong anionic character and hydrophobic association property

#### Synergism effect in aqueous solutions

The  $\eta_a$  values of aqueous solutions of the AM/NaAMPS/St ternary copolymer, the PAM-*b*-PSt binary block copolymer, and the PAM homopolymer were measured with a rotational rheometer. Figures 2 and 3 show curves of  $\eta_a$  versus the concentration of aqueous ternary copolymer solutions and aqueous binary copolymer solutions, respectively.

At the same concentration, the  $\eta_a$  values of aqueous PAM-*b*-PSt solutions were greater than those of aqueous PAM solutions, especially at higher concentra-

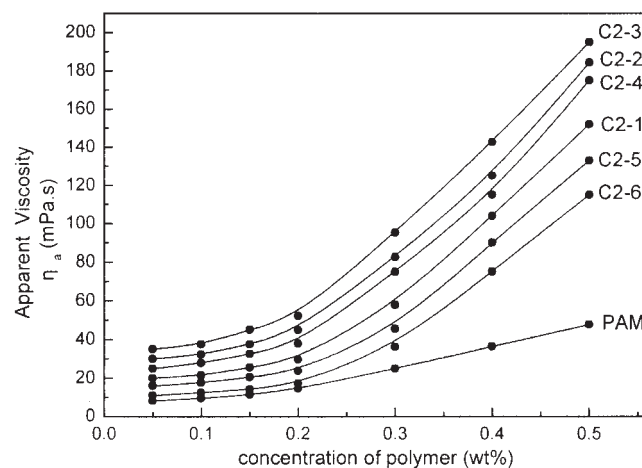
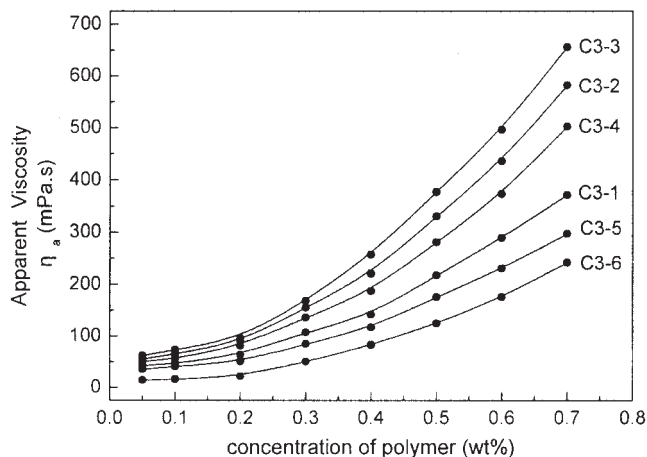


Figure 2  $\eta_a$  of binary copolymer solutions versus the concentration at a shear rate of 6  $s^{-1}$ .



**Figure 3**  $\eta_a$  of ternary copolymer solutions versus the concentration at a shear rate of  $6 \text{ s}^{-1}$ .

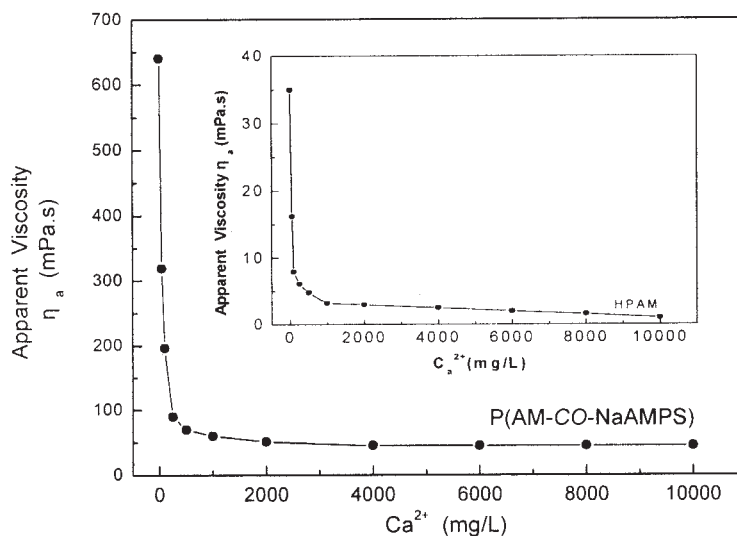
tions; the  $\eta_a$  values of the aqueous AM/NaAMPS/St ternary copolymer solutions were even greater than those of PAM-*b*-PSt, which contained the same amount of St as the ternary copolymer (comparing C3-3 and C2-3 and comparing C3-4 and C2-4). For PAM-*b*-PSt, above the critical association concentrations, the intermolecular hydrophobic association predominated in intermolecular and intramolecular hydrophobic associations and led to transient physical networks, which increased the hydrodynamic volume of the macromolecular chains and greatly enhanced the viscosity.<sup>12</sup> The polymerization mechanism in the microemulsion for the synthesis of the AM/NaAMPS/St ternary copolymer was expected to be the same as that for the synthesis of PAM-*b*-PSt,<sup>11</sup> so the chain microstructure of the AM/NaAMPS/St ter-

nary copolymer was expected to be similar to that of PAM-*b*-PSt. That is, PSt hydrophobic blocks were distributed in the hydrophilic main chains,<sup>10-13</sup> which consisted of AM and NaAMPS for the AM/NaAMPS/St ternary copolymer. On the one hand, these hydrophobic blocks made the macromolecules associate hydrophobically and increase the viscosity of aqueous solutions;<sup>12</sup> on the other hand, there was an NaAMPS group concentration of about 10 mol % in the macromolecular chains, these sulfonate groups caused chain expansion because of strong electrostatic repulsion (which led to increased hydrodynamic volume), and the solution viscosity was enhanced further. Therefore, under the synergy of the two aforementioned effects, the viscosity of aqueous solutions of the AM/NaAMPS/St ternary copolymer was enhanced greatly.

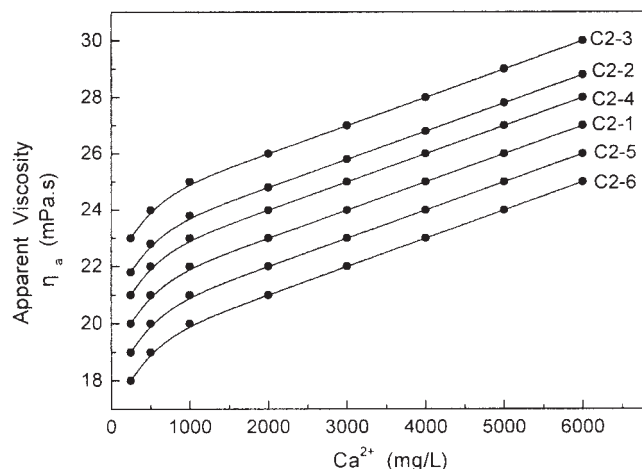
#### Synergism effect in $\text{CaCl}_2$ solutions

The dependence of the  $\text{CaCl}_2$  solution viscosity of the polymers on the  $\text{CaCl}_2$  concentration for random copolymer P(AM-*co*-NaAMPS) and HPAM, for binary block copolymer PAM-*b*-PSt, and for ternary copolymer AM/NaAMPS/St is shown in Figures 4, 5, and 6, respectively.

For random copolymer P(AM-*co*-NaAMPS) and HPAM (in Fig. 4), the  $\eta_a$  values of their solutions initially decreased rapidly as the salinity or hardness increased at a low solution ionic strength, and typical behaviors of polyelectrolytes were displayed. This was due to a shielding effect of the electrolyte ions, which reduced the repulsion between anions in macromolecular chains and caused chain contraction.<sup>3</sup> From this perspective, the polymers containing sulfo-

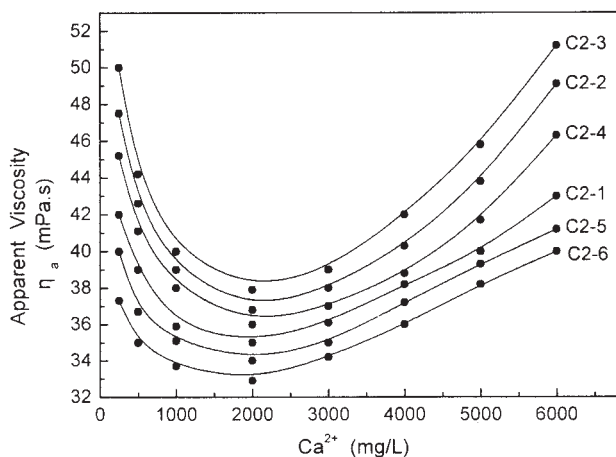


**Figure 4** Effect of the  $\text{CaCl}_2$  concentration on  $\eta_a$  of aqueous solutions of HPAM and random copolymer P(AM-*co*-NaAMPS). The polymer concentration was 0.3 wt %, and the shear rate was  $6 \text{ s}^{-1}$ .

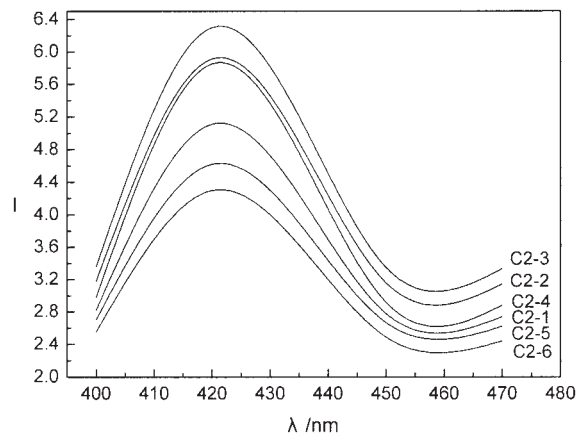


**Figure 5** Effect of the  $\text{CaCl}_2$  concentration on  $\eta_a$  of aqueous solutions of binary block copolymer PAM-*b*-PSt (series C2). The polymer concentration was 0.3 wt %, and the shear rate was  $6 \text{ s}^{-1}$ .

nate groups and carboxylate groups were all sensitive to salt. However, after the ion-shielding effect ended, the former viscosity was much higher than the latter viscosity, and the viscosity of P(AM-*co*-NaAMPS) remained basically constant, whereas the viscosity of HPAM decreased sequentially with an increase in the  $\text{CaCl}_2$  concentration. There were two causes. The aquation of sulfonate groups ( $-\text{SO}_3^-$ ) in P(AM-*co*-NaAMPS) was much stronger than that of carboxylate groups ( $-\text{COO}^-$ ) in HPAM, and this led to a higher viscosity of the P(AM-*co*-NaAMPS) solution. Moreover, the complexing effect of the carboxylate groups of HPAM resulted in polymer precipitation in the presence of a high concentration of  $\text{Ca}^{2+}$ , and this led to a sequentially decreasing viscosity of the HPAM



**Figure 6** Effect of the  $\text{CaCl}_2$  concentration on  $\eta_a$  of aqueous solutions of the AM/NaAMPS/St ternary copolymer (series C3). The polymer concentration was 0.3 wt %, and the shear rate was  $6 \text{ s}^{-1}$ .



**Figure 7** Fluorescence emission spectra of the PFN probe in aqueous solutions of the binary block copolymer/PAM-*b*-PSt (series C2). The copolymer concentration was 0.5 wt %.

solution. Obviously, P(AM-*co*-NaAMPS), containing strong anionic groups, had better salt tolerance, that is, excellent salt resistance.

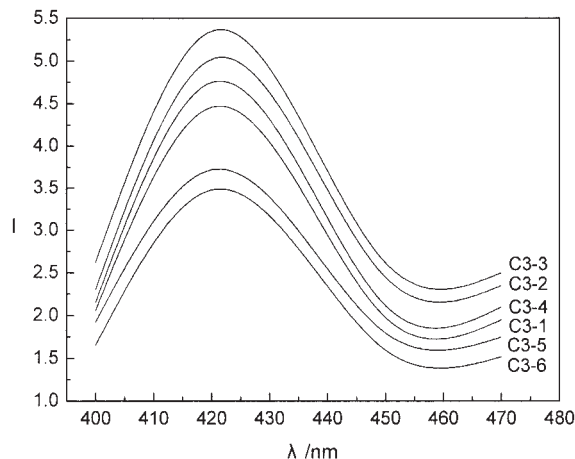
For binary block copolymer PAM-*b*-PSt (Fig. 5), the  $\eta_a$  values of brine solutions increased as the salinity or hardness increased. This was because hydrophobic association benefited from higher solution polarity.<sup>7</sup>

For the  $\eta_a$  values of brine solutions of the AM/NaAMPS/St ternary copolymer (Fig. 6), two rules were observed. First, in the total concentration region, the  $\eta_a$  values of the brine solutions were all higher than those of the binary block copolymer brine solutions. Second, the curve of  $\eta_a$  versus the  $\text{Ca}^{2+}$  concentration went down first and then went up after reaching a minimum. Actually, the curves in Figure 6 are the results of the combination of the curves of P(AM-*co*-NaAMPS) in Figure 4 and PAM-*b*-PSt in Figure 5, and this combination enhanced the  $\eta_a$  values of the ternary copolymer brine solutions on the whole. Obviously, because there were strong anionic groups ( $-\text{SO}_3^-$ ) and hydrophobic blocks (PSt) simultaneously in the macromolecular chains of the AM/NaAMPS/St ternary copolymer, salinity was beneficial to intermolecular hydrophobic association, and the sulfonate groups had better salt tolerance, so the synergy of two kinds of salt-resistance effects gave the ternary copolymer brine solutions higher values of  $\eta_a$ .

#### Negative influence of the strong anionic character on the hydrophobic association behavior

Weakening effect of the strong anionic character on the hydrophobic association property

This investigation used PFN as a fluorescence probe. The fluorescence emission spectra of the probe in aqueous solutions of series C2 copolymers and series C3 copolymers are shown in Figures 7 and 8, respectively.



**Figure 8** Fluorescence emission spectra of the PFN probe in aqueous solutions of the AM/NaAMPS/St ternary copolymer (series C3).

Comparing Figures 7 and 8, we found that the fluorescence emissions of the probe in the ternary copolymer solutions were all weaker than those of the probe in the binary copolymer solutions ( $C3-3 < C2-3$ ,  $C3-2 < C2-2$  ...). The PFN fluorescence probe was sensitive to the polarity of the environment,<sup>11</sup> and the weaker the polarity of the environment was, the stronger the fluorescence emission was. As mentioned previously, hydrophobic blocks (PSt) were distributed in the main chains of the AM/NaAMPS/St ternary copolymers and in the main chains of the PAM-*b*-PSt binary copolymers, so above a critical concentration, intermolecular aggregates prevailed over intramolecular ones (as shown later), and clusters of hydrophobic microdomains were formed. PFN is a hydrophobic substance, and it spontaneously enters into hydrophobic microdomains, so strong fluorescence emissions arise. That the fluorescence emissions of the probe in the ternary copolymer solutions were all weaker than those in the binary copolymer solutions was due to the negative influence of the strong anionic groups on the association of the hydrophobic blocks. An anion ( $-\text{SO}_3^-$ ) concentration of about 10 mol % in the macromolecular chains of the AM/NaAMPS/St ternary copolymer made the macromolecular chains in the aqueous solutions rigid or stiff<sup>8</sup> because of the mutual repulsion between the anions in identical macromolecules. Besides, there was also repulsion between different macromolecules because of charged anions. These two factors made it difficult for the macromolecules to be close to one another, the intermolecular hydrophobic association was weakened, hydrophobic microdomains became smaller, and the fluorescence emission of the probe appeared weaker.

The strongest fluorescence emissions at a wavelength ( $\lambda$ ) of 420 nm in Figures 7 and 8 are plotted as a curve of the intensity versus the concentration of St

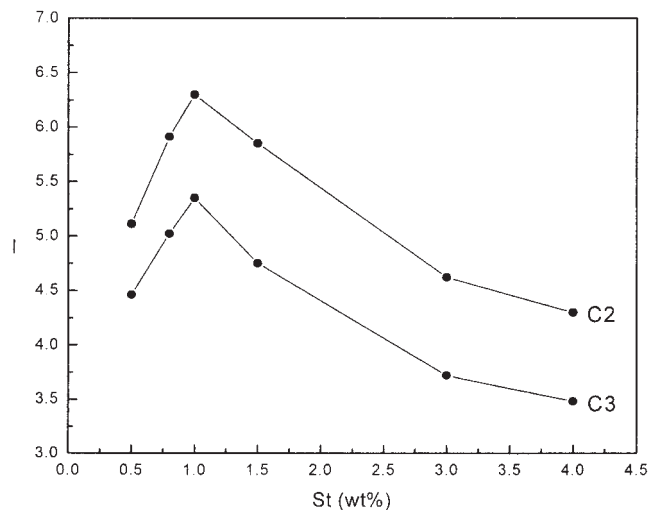
in the copolymer, as shown in Figure 9. The dependence of the fluorescence on the concentration of St was similar to the dependence of the viscosity on the concentration of St, and that has been described in detail in a previous study.<sup>12</sup> Figure 9 shows clearly that the hydrophobic association behaviors of the AM/NaAMPS/St ternary copolymers and PAM-*b*-PSt binary copolymers were quite different.

Figure 9 shows that the curve of the intensity versus the concentration of PSt for the ternary copolymer is below the curve for the binary copolymer; that is, the curve of C3 is below the curve of C2. The fluorescence emission of the probe in each ternary copolymer solution was weaker than that in the corresponding binary copolymer solution. This fact indicates fully that the hydrophobic association behavior of the AM/NaAMPS/St ternary copolymers was weakened by strong anionic groups in comparison with that of PAM-*b*-PSt.

Figure 10 shows plots of  $k_H$  versus the concentration of St in various copolymers (series C3 and series C2).  $k_H$  is a very important measure of polymer-polymer hydrophobic interactions; greater  $k_H$  values reflect stronger intermolecular associations for macromolecules, and smaller  $k_H$  values show weaker intermolecular associations.<sup>7</sup> The  $k_H$  values of the AM/NaAMPS/St ternary copolymers were smaller than those of PAM-*b*-PSt, and obviously this reduction resulted from the weakening effect of the strong anionic character of the  $-\text{SO}_3^-$  groups on the hydrophobic association behavior of the PSt blocks.

#### Influence of the strong anionic character on the critical association concentration

For the PAM-*b*-PSt binary copolymers, the dependence of the hydrophobic association behavior on the



**Figure 9** Maximum fluorescence emission intensity ( $I$ ) of the PFN probe at 420 nm in series C3 and C2 solutions.

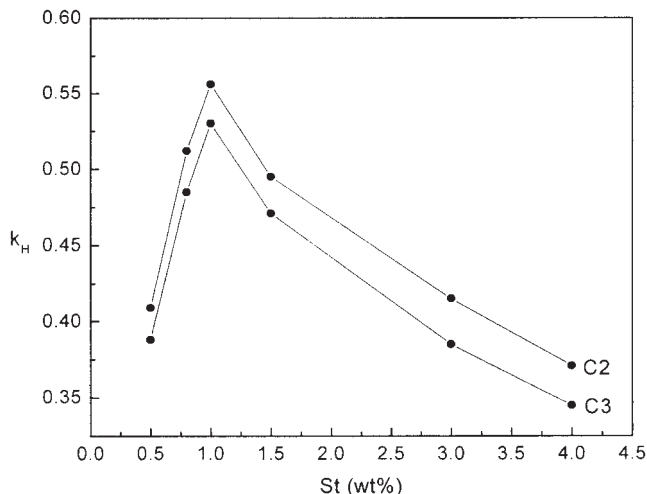


Figure 10  $k_H$  for series C3 and C2 copolymers.

concentration and the critical concentrations were investigated with previous detailed measurements of  $\eta_{sp}$ .<sup>12</sup> However, for the AM/NaAMPS/St ternary copolymers, the viscosity property was the result of a combination of the hydrophobic association and electroviscosity effects, as described previously, and so the dependence of the hydrophobic association behavior on the concentration and their critical concentrations could not be examined exactly. However, the fluorescence probe technique could be used for a correct assessment. Aqueous solutions with various concentrations of the AM/NaAMPS/St and PAM-*b*-PSt copolymers were prepared with saturated aqueous solutions of PFN, and the fluorescence emissions of the probes in these solutions at 420 nm were measured. Figure 11 presents plots of the intensity of the maximum fluorescence emission of the probe at  $\lambda = 420$  nm versus the concentration of the copolymers for series C3 (i.e., C3-3 and C3-4) and series C2 (i.e., C2-3 and C2-4).

There is a critical concentration on each  $I$ - $c$  (maximum fluorescence emission intensity ( $I$ ) of the pfn probe at 420 nm versus the concentration ( $c$ ) of the copolymer) curve. Below the concentration, the fluorescence emission was very weak and varied slowly with the concentration, and above the concentration, the fluorescence emission rapidly increased with the concentration. At a low concentration, the hydrophobic blocks on separate copolymer chains had little interaction, and the intramolecular association effect was predominant; this led to the contraction and coiling of chains. Therefore, the hydrophobic microdomains were small, and the fluorescence emission of the probe was weak. Above the critical concentration, intermolecular associations prevailed over intramolecular associations, and stronger intermolecular hydrophobic association significantly contributed to the formation of hydrophobic microdomains. After that, in-

termolecular hydrophobic association increased rapidly with the concentration, and hydrophobic microdomains were enlarged swiftly; therefore, the fluorescence intensity increased rapidly with the concentration. From this, it is suggested that before and after this critical concentration of the  $I$ - $c$  curve, the chains of the copolymers basically hydrophobically associated with two different forms, and this concentration could be called the critical association concentration.

Moreover, the critical association concentrations of the AM/NaAMPS/St ternary copolymers were greater than those of the PAM-*b*-PSt binary copolymers; the former was about 0.3%, and the latter was about 0.2%. This fact shows again the negative influence of the strong anionic groups on the hydrophobic association behavior of the hydrophobic blocks. As previously described, the rigidity or stiffness of the chains and the repulsion between the chains made it difficult for the macromolecules of the AM/NaAMPS/St ternary copolymers to be close to one another and associate in a low-concentration region. Only after the concentration increased further it was possible for the macromolecules to be close to one another; the negative influence of the strong anionic groups on the hydrophobic association behavior of the hydrophobic blocks was overcome, and intermolecular association formed. Therefore, greater critical association concentrations were led to the AM/NaAMPS/St ternary copolymers. This was consistent with the work of Braun et al.<sup>14</sup>

## CONCLUSIONS

After the addition of strong anionic groups ( $-\text{SO}_3\text{Na}$ ) and hydrophobic blocks (PSt) simultaneously to the main chains of PAM, interactions occurred between the strong anionic character and

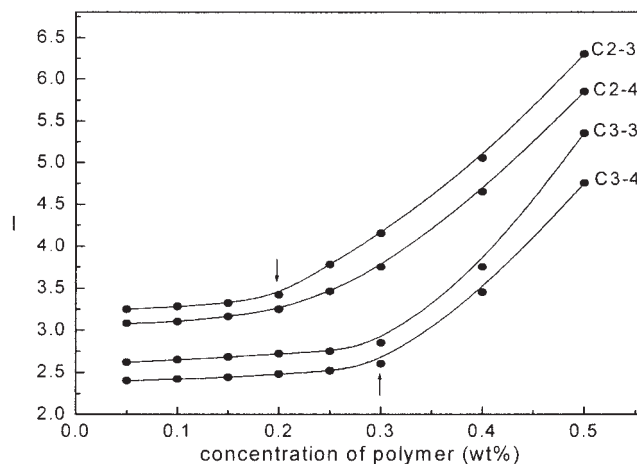


Figure 11 Dependence of the maximum fluorescence emission intensity ( $I$ ) at 420 nm on the copolymer concentration.



the hydrophobic behavior. The synergism of the electroviscosity effect of the anions and the hydrophobic association behavior of the hydrophobic blocks resulted in an apparent enhancement of the aqueous solution viscosity of the copolymers, and the synergism of the better salt tolerance of the strong anions and the strengthening effect of the salinity on the hydrophobic association of the hydrophobic blocks led to an obvious increase in the salt resistance of the copolymers. Moreover, the addition of anionic sulfonate groups improved polymer solubility in water. However, the presence of strong anions weakened the intermolecular associating property of hydrophobic blocks to a certain degree; that is, it produced a certain negative influence on the hydrophobic association property of the hydrophobic blocks.

## References

1. Hua, D.-K.; Yang, C.-Z. *J Petrol Sci Eng* 1990, 22, 181.
2. Nasr-Ei-Din, H. A.; Hawkins, B. F.; Green, K. A.; Schulz, D. N.; Maurer, J.; Bock, J. *J Polym* 1987, 28, 2111.
3. Taylor, K. C.; Nasr-Ei-Din, H. A. *J Petrol Sci Eng* 1998, 19, 265.
4. Hill, A.; Candau, F.; Selb, J. *Macromolecules* 1993, 26, 4521.
5. Schulz, D. N.; Bock, J. *J Macromol Sci Chem* 1991, 28, 1235.
6. Biggs, S.; Hill, A.; Candau, F. *J Phys Chem* 1992, 96, 1505.
7. McCormic, C. L.; Nonaka, T.; Johnson, C. B. *J Polym* 1988, 29, 731.
8. Valint, P. L.; Bock, J. U.S. Pat. 5,089,578 (1992).
9. McCormic, C. L.; Middleton, J. C.; Cummins, D. F. *Macromolecules* 1992, 25, 1201.
10. Gao, B.; Yang, Y.; Ge, Z. *Chin J Anal Chem* 2002, 30, 69.
11. Gao, B.; Yang, Y.; Jiu, H. *Chin J Acta Polym Sinica* 2001, 5, 608.
12. Gao, B.; Xu, R.; Wu, N. *Chin J Acta Polym Sinica* 2003, 3, 368.
13. Ge, Z.; Gao, B.; Yang, Y. *Chin J Acta Polym Sinica* 2002, 6, 712.
14. Braun, O.; Selb, J.; Candau, F. *Polymer* 2001, 42, 8499.