

Synthesis, Characterization, and Solution Properties of an Acrylamide-Based Terpolymer with Butyl Styrene

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ABSTRACT: The terpolymers (PASA) with acrylamide (AM), butyl styrene (BST), and sodium 2-acrylamido-2-methylpropane sulfonate (NaAMPS) were synthesized by the micellar free radical copolymerization technique. The polymer composition was determined by the elemental analysis, and the block structure of PASA was characterized directly by DSC measurement. Incorporation of NaAMPS into the terpolymers may improve the water solubility and intermolecular association, and the feed amount of BST, sodium dodecyl sulfate (SDS) amount, and the total monomer concentration in the polymerization can influence

apparently the viscosities of PASA. The polymer exhibits excellent viscosification effect, salt-thickening, temperature-thickening, thixotropy, pseudoplastic behavior or shear-thickening relative to the BST content in PASA, excellent anti-aging property at 85°C, and a dramatic increase in solution viscosity by the addition of little amount of SDS. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 4027–4038, 2007

Key words: acrylamide; butyl styrene; micellar free radical copolymerization; hydrophobically associating; solution properties

INTRODUCTION

Partially hydrolyzed polyacrylamide (HPAM) is widely applied in enhanced oil recovery (EOR), and its role is to increase the viscosity of the aqueous phase to improve sweep efficiency during EOR processes.¹ The viscosification of the traditional polymer relies on its high molecular weight, the expansion, and physical entanglement of polymer chains due to the repulsion of carboxylate groups and hydrogen bonds of amido groups. However, high shear rate causes the breakage of the polymer chains, resulting in the irreversible decrease of viscosity. In addition, the solution viscosity of HPAM decreases abruptly in the brine solution with the increase of salinity, attributed to shielding of ionic groups, and amido groups in HPAM hydrolyze rapidly to form carboxylate groups above 70°C. Therefore, HPAM is com-

monly used in the oil reservoirs with low temperature and salinity.

Hydrophobically associating water-soluble polymers are water-soluble polymers containing a small amount of hydrophobic groups. When dissolved in water, the hydrophobic groups can associate together via intermolecular interaction above the critical concentration ((C_p^*)) to form physical network structures, resulting in substantial viscosity increase, and the associations are reinforced by addition of salt.² With increasing shear rate, the network structures are disrupted and the apparent viscosities of polymer solutions decrease. However, upon removal of shear the associations can reform and the viscosities completely recover their original values. Because of these unique solution properties the hydrophobically associating polymers have potential application in EOR.^{3–6}

Presently, numerous studies on hydrophobically modified polymers have been concentrated on the copolymers containing acrylamide (AM) and one of hydrophobic monomers, which are mainly the derivatives of AM, acrylic esters, and its derivatives^{7–11} and are easy to hydrolyze under acidic or basic conditions at high temperature, resulting in the abrupt decrease in the viscosities of polymer solutions. The copolymers are difficult to dissolve in water, and the

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viscosities at low polymer concentration are not high enough to be applied in some areas, especially in EOR with high temperature and chemically unneutral underground oil layer environment.^{12,13}

In previous studies, the novel PASA terpolymer with AM, butyl styrene (BST) as the hydrophobic monomer, and sodium 2-acrylamido-2-methylpropane sulfonate (NaAMPS) was reported, which was prepared by free radical micellar copolymerization. The associating microstructures of PASA in the aqueous and brine solution were explored by AFM² and directly observed by environmental scanning electron microscope.¹⁴ The results showed that the strong intermolecular hydrophobic interaction of BST units with phenyl groups leads to the formation of physical networks and the high solution viscosity value at a low polymer concentration. To obtain the optimum polymerization conditions of PASA and improve the solution properties and thermal stability of hydrophobically associating water-soluble polymers, in the article, the polymerization parameters were studied, UV, FTIR, ¹HNMR, the composition, and block structure of the polymer were characterized, and the viscosities of PASA polymers were investigated as a function of polymer concentration, temperature, shear rate, salt concentration, surfactant, and aging time.

EXPERIMENTAL

Reagents

AM was recrystallized twice from CHCl₃, 2-acrylamido-2-methylpropane sulfonate (AMPS) was purchased from Lubrizol Co. (Ohio, USA), and used directly. BST was prepared in the laboratory.¹⁵ Other reagents were of analytical grade and used without further purification.

Synthesis of copolymers

The PASA terpolymers were prepared by the free radical micellar copolymerization,^{16,17} using sodium dodecyl sulfate (SDS) as the surfactant and potassium persulphate as the initiator. The typical micellar copolymerization process was as follows. A 100-mL, three-necked, round flask was equipped with a mechanical stirrer, nitrogen inlet and outlet. Into the reaction flask, 4.0 g (0.0563 mol) AM, 0.364 g (1.757 × 10⁻³ mol) AMPS, 2.55 g (8.842 × 10⁻³ mol) SDS, 39.951 mL distilled water were added, respectively, and NaOH was used to control the pH value of the reaction solution within 6–7. The mixture was stirred for 15 min, and then 0.075 g (4.685 × 10⁻⁴ mol) BST was added into the reaction flask. The flask was purged with N₂ for half an hour until a clear homogeneous mixture was observed. The solution was

heated to 50°C and then the initiator K₂S₂O₈ was added with the concentration 0.1 wt % relative to the total monomer feed. The polymerization proceeded for 12 h, after which the reaction mixture was diluted with 10 volumes of distilled water, followed by precipitation into two volumes of reagent-grade acetone while stirring. The polymers were washed with acetone twice and extracted with ethanol by the Soxhlet extraction instrument for 2 days to remove all traces of water, surfactant, residual monomers, and initiator. Finally, the polymers recovered by filtration were dried under reduced pressure at 50°C for 3 days.

In absence of BST, the copolymer (PAA) of NaAMPS with AM was synthesized. Molar ratio of AM/NaAMPS was 90/10, and the other reaction conditions and purified method were the same as mentioned earlier.

Polymer characterization

Elemental analysis

The elemental analysis of the polymers were conducted by CARLO ESRA-1106 elemental analyzer (Milan, Italy) to determine carbon, nitrogen, hydrogen, and sulfur content.

UV spectral analysis

The UV spectrum was obtained with a UV-240 spectrophotometer (Shimadzu, Japan). The purified PASA polymer was dissolved in pure water and the polymer concentration was 0.1 g dL⁻¹.

Fourier transform infrared

The FTIR spectrum was conducted with a NICOLET-560 FTIR spectrophotometer (Madison, WI) and its resolution capacity was 1 cm⁻¹ and scanning number was 32. The KBr pellets were prepared with the purified polymer sample.

Proton nuclear magnetic resonance

The purified PASA copolymer solution in D₂O was studied at room temperature by a 400-MHz INOVA-400 instrument (Varian Company, California, USA) to determine if BST hydrophobic units are incorporated into the polymer molecules.

DSC measurement

The glass transition temperature of PASA was measured by a Netzsch DSC204 instrument (Germany). N₂ was used as the experimental atmosphere, and the heating rate is 20°C/min in the range of 25–300°C.

Solution apparent viscosity and intrinsic viscosity measurement

Polymer solutions were prepared by dissolving the purified polymer in the distilled water or NaCl aqueous solution. The apparent viscosities were measured by a Brookfield DVIII R27112E viscometer at the shear rate of 6 s^{-1} at 25°C . The intrinsic viscosities were measured by a 0.6-mm Ubbelohde capillary viscometer at $(30.0 \pm 0.1)^\circ\text{C}$ and 1 mol L^{-1} sodium nitrate is used as the solvent.

Atomic force microscope measurement

The atomic force micrographs were made by SPA400 AFM (Seiko, Japan), and all measurements were performed in Tapping Mode. All samples were covered on the mica flakes and dried naturally.

Compositional calculations

The molar compositions of PASA were determined using eqs. (1)–(7), where A , B , and P are the moles of AM, BST, and NaAMPS in 100 g terpolymer, respectively. The coefficients are the number of carbon, nitrogen, hydrogen, and sulfur in each monomer. After obtaining A , B , and P for each polymer sample, mole percent compositional data were calculated.

$$\%C/12.01 = 3A + 12B + 7P \quad (1)$$

$$\%N/14.01 = 1A + 1P \quad (2)$$

$$\%H/1.01 = 5A + 16B + 12P \quad (3)$$

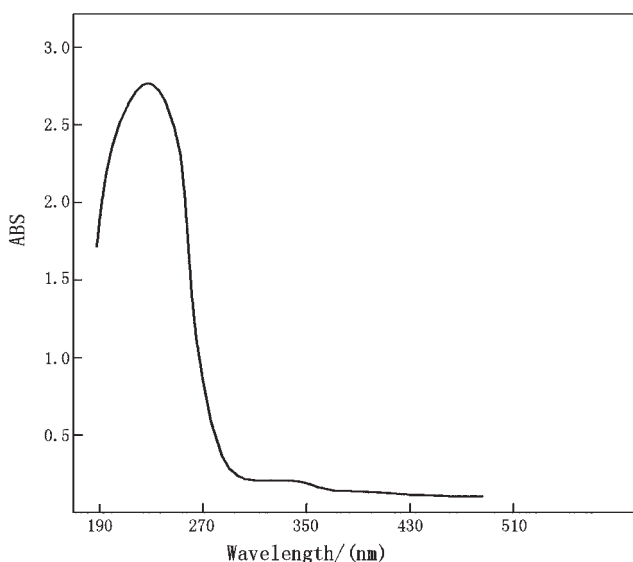


Figure 1 UV spectrum of PASA copolymer.

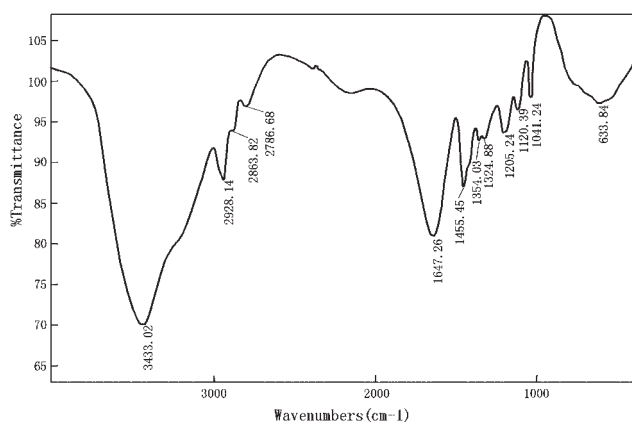


Figure 2 IR spectrum of PASA copolymer.

$$\%S/32.01 = 1P \quad (4)$$

$$\text{mol}\%AM = 100A/(A + B + P) \quad (5)$$

$$\text{mol}\%BST = 100B/(A + B + P) \quad (6)$$

$$\text{mol}\%NaAMPS = 100P/(A + B + P) \quad (7)$$

RESULTS AND DISCUSSION

Characterization of PASA

Ultraviolet

Figure 1 displays the UV spectrum of PASA. The characteristic absorption peak at 230 nm attributed to the phenyl group proves that BST hydrophobic units are incorporated into the polymer molecules.

Fourier transform infrared

The typical FTIR spectrum of the PASA copolymer is shown in Figure 2. The characteristic FTIR absorption peaks of PASA are as follows: $-\text{NH}$ stretch, 3433 cm^{-1} ; $\text{C}=\text{O}$ stretch, 1647 cm^{-1} ; $-\text{CH}_3$, $-\text{CH}_2$,

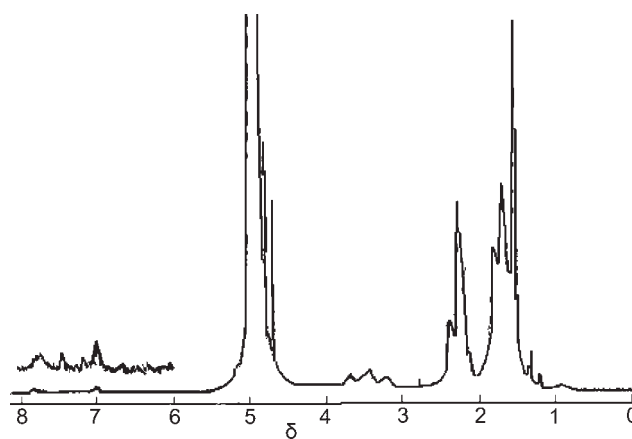


Figure 3 ^1H -NMR spectrum of PASA copolymer.

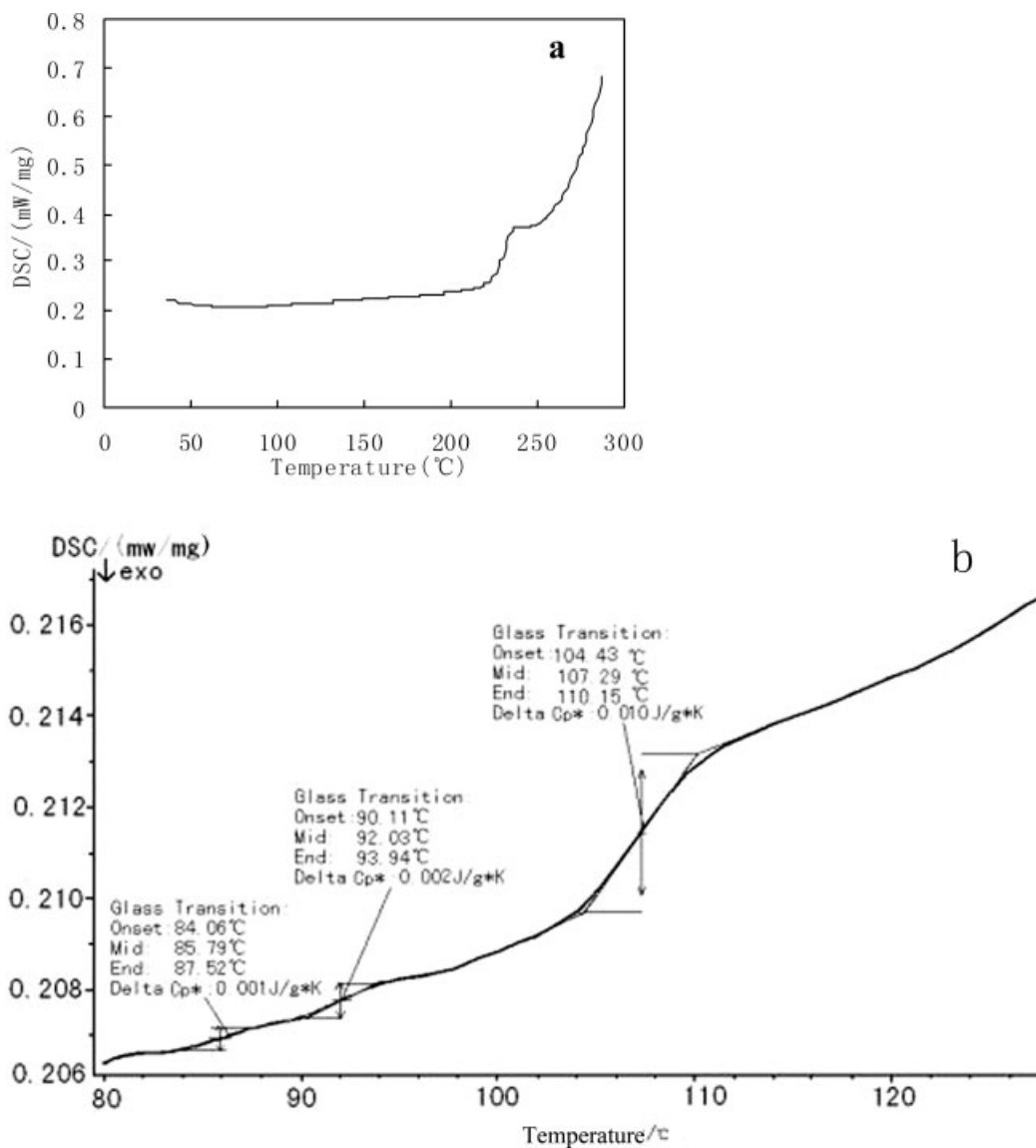


Figure 4 Temperature of glass transition of PASA copolymer.

—CH stretch, 2928 cm^{-1} , 2863 cm^{-1} , 2787 cm^{-1} ;
—CH₃, —CH₂—, —CH bending, 1455 cm^{-1} ,
 1354 cm^{-1} , 1325 cm^{-1} ; =C—H in phenyl stretch,
 3090.39 cm^{-1} ; —C=C— in phenyl stretch, 1647 cm^{-1}
(overlap with C=O), 1455 cm^{-1} (overlap with —CH₃,
—CH₂— bending); —SO₃⁻: 1205 cm^{-1} , 1120 cm^{-1} ,
 1041 cm^{-1} , 634 cm^{-1} .

Proton nuclear magnetic resonance

Figure 3 presents the ¹HNMR spectrum of PASA in D₂O. All the resonances of protons are as follows: 4H (—CH of phenyl), δ 7.028–7.787 ppm; 2H (—CH₂ of BST main chain), δ 2.105 ppm; 1H (—CH of BST main chain), δ 2.772 ppm; 6H (—CH₃ of NaAMPS side chain), δ 1.674 ppm; 2H (—CH₂ of AMPS side

TABLE I
Elemental Analysis of PASA

	Elemental composition of PASA			
	C (wt %)	H (wt %)	N (wt %)	S (wt %)
Total monomer feed data	49.96	6.92	15.67	3.67
Measurement data of PASA	49.34	6.85	14.59	5.00

TABLE II
Molar Composition of PASA

	Molar composition of PASA		
	BST (mol %)	AM (mol %)	NaAMPS (mol %)
Monomer feed composition	2.50	87.50	10.00
Terpolymer composition	2.80	82.62	5.00

TABLE III
Synthesis Conditions, Yield, and Viscosity of PASA^a

Sample	Reaction conditions			BST content in PASA (mol %)	Yield (%)	Intrinsic viscosity (dL g ⁻¹)	Apparent viscosity in 0.855 mol L ⁻¹ NaCl (mPa s)
	M1 : M2 : M3 ^b	SDS ^c (wt %)	Monomers ^d (wt %)				
PASA-PS1	96.2 : 3 : 0.8	6.0	10	–	82.0	–	6.7
PASA-PS2	93.2 : 6 : 0.8	6.0	10	–	79.3	–	14
PASA-PS3	89.2 : 10 : 0.8	6.0	10	1.07	76.2	6.50	27
PASA-PS4	84.2 : 15 : 0.8	6.0	10	–	69.0	–	5.2
PASA-SD1	89.2 : 10 : 0.8	2.0	10	0.61	28.1	3.84	–
PASA-SD2	89.2 : 10 : 0.8	5.0	10	1.22	57.8	5.61	–
PASA-SD3	89.2 : 10 : 0.8	7.0	10	1.14	68.4	2.72	–
PASA-M1	89.2 : 10 : 0.8	4.0	7	0.76	52.8	3.42	2.9
PASA-M2	89.2 : 10 : 0.8	9.5	15	1.19	83.1	7.20	12
PASA-M3	89.2 : 10 : 0.8	13.0	20	1.23	86.0	5.98	8.7
PASA-BS1	88.5 : 10 : 1.5	6.0	10	1.62	80.6	4.14	36.6
PASA-BS2	87.5 : 10 : 2.5	6.0	10	2.80	77.4	1.71	42.5
PASA-BS3	87 : 10 : 3.0	6.0	10	3.56	58.0	1.46	5.1

^a Polymer concentration: 0.15 g dL⁻¹.

^b M1, acrylamide; M2, NaAMPS; M3, BST feed molar compositions.

^c The mass percent composition in water.

^d Total monomer concentration (the mass percent composition in water).

chain), δ 3.439 ppm; 2H (–CH₂ of NaAMPS main chain), δ 1.781 ppm; 1H (–CH of AMPS main chain), δ 2.355 ppm; 2H (–CH₂ of AM main chain), δ 1.500 ppm; 1H (–CH of AM main chain), δ 2.246 ppm; H (–NH₂ of AM side chain and –NH of AMPS side chain), δ 4.716–4.967 ppm. The results show that the synthesized product is the terpolymer of AM, BST, and NaAMPS.

Differential scanning calorimetry

In the reported literature,¹⁷ the block structure of hydrophobic segments was examined by fluorescent probe, whereas, in the article, the traditional DSC technique was used to characterize the chain structure of hydrophobically associating polymers. The glass transition temperatures (T_g) of PASA-BS2 are shown in Figure 4, where (a) is amplified in the range of 80–130°C to obtain (b). As exhibited in Figure 4, the polymer has four temperatures of glass transition which are 231.63°C for random hydrophilic segments containing AM and NaAMPS, and 107.09°C, 92.03°C, and 85.79°C for block BST hydrophobic segments, respectively. The DSC results indicate that BST units are incorporated into PASA chains to form block structures. In addition, the synthesized products are completely dissolved in water, there is no white BST homopolymer in the polymer solution, NaAMPS is easily copolymerized with AM,¹² and there is only one T_g for the hydrophilic segments in PASA. The results show that the polymer is a terpolymer of AM, NaAMPS, and BST, and not a mixture. The T_g s of homopolyacrylamide,

p(AM-NaAMPS),¹⁸ and AM segments in p(AM-BST)¹⁹ are 163, 195, and 203°C, respectively, which are lower than that of hydrophilic segments in PASA (231.63°C) which is resulted in the polarity and rigidity of NaAMPS units and the steric effect of aromatic ring in BST units. Different T_g of BST segments suggests that the amounts of BST solubilized in SDS micelles are different in the reaction process, resulting in different length of hydrophobic segments. The result is consistent with the mechanism of micellar copolymerization. In the process, the hydrophobic monomer is solubilized within surfactant micelles, whereas AM is dissolved together with the initiator K₂S₂O₈ in the aqueous solution.¹⁷ When the reaction proceeds, the hydrophobe/surfactant

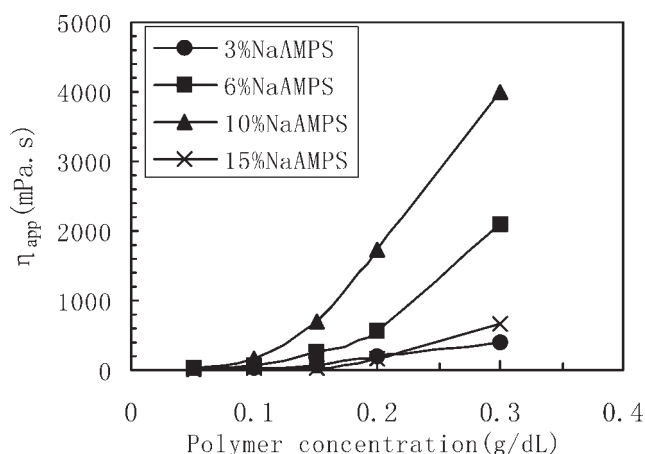


Figure 5 Influence of NaAMPS amount on apparent viscosity of PASA aqueous solution.

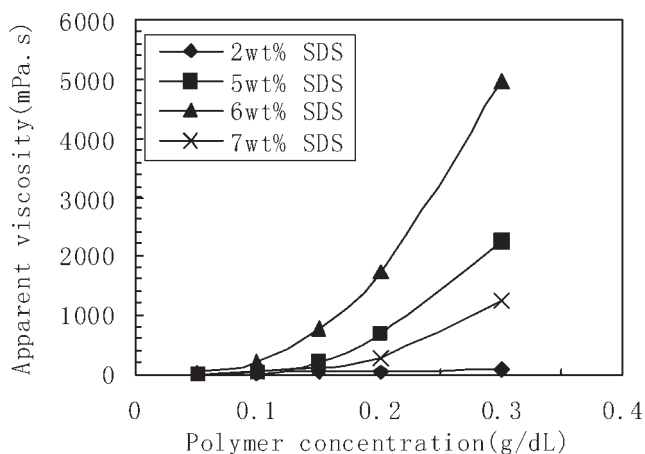


Figure 6 Influence of SDS concentration on apparent viscosity of PASA aqueous solution.

ratio decrease, leading to the decrease of the number of BST molecules per micelle and the shorter hydrophobic blocks of lower T_g . T_g of homopoly BST with high molecular weight is 118°C .

Composition study

Table I shows the element compositions of the total monomer feed and polymer. As shown in Table II, the molar composition of PASA-BS2 was determined using eqs. (1)–(7) and the elemental analysis data of the carbon or hydrogen, nitrogen, and sulfur content. The polymer molar composition data of BST and NaAMPS higher than the monomer feed data reveal that the reaction rates of BST and NaAMPS are higher than that of AM. According to the reaction mechanism of micellar free radical copolymerization^{17,20} and the DSC measurement, the PASA mole-

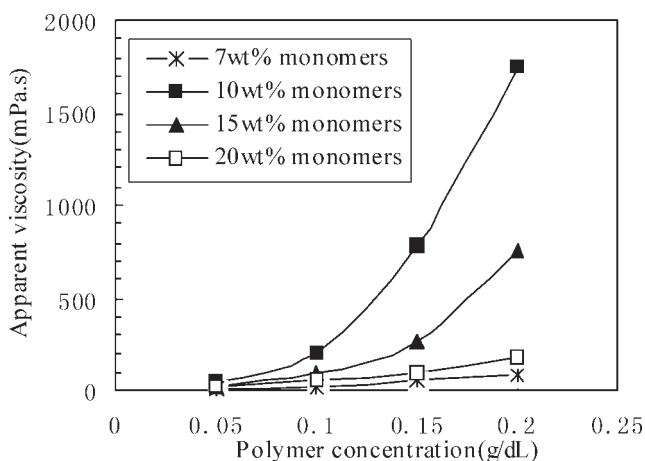


Figure 7 Influence of total monomer concentration on apparent viscosity of PASA aqueous solution.

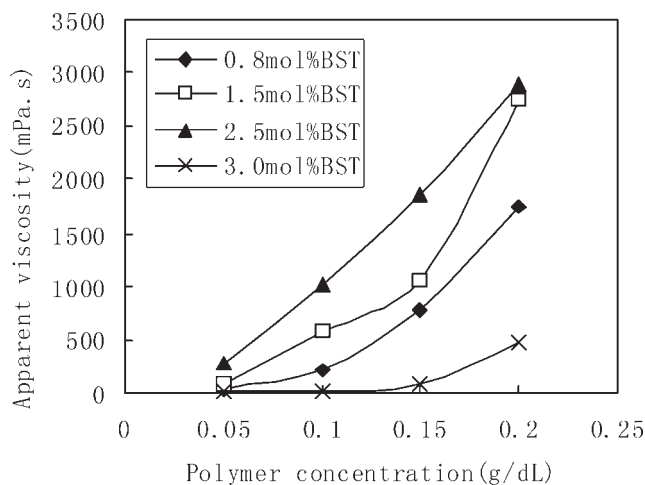


Figure 8 Influence of BST amount on apparent viscosity of PASA aqueous solution.

cules consist of the random hydrophilic segments of AM and NaAMPS and the block hydrophobic segments of BST. The reactivity ratios of AM and BST ($r_{\text{AM}} = 0.76$, $r_{\text{BST}} = 8.55$)¹⁹ and AM and NaAMPS ($r_{\text{AM}} = 0.98$, $r_{\text{AMPS}} = 0.49$)¹² also show that the homopolymerization tendency of BST is higher than that of AM and the copolymerization tendency of NaAMPS is higher than that of AM, resulting in the molar composition data of PASA. The local micellar concentration effect of the micellar copolymerization influences the reactivity ratio of AM and BST.

The molar composition of p(AM-NaAMPS) obtained by the elemental analysis of the carbon, nitrogen, and sulfur content is as follows: AM:NaAMPS = 84.27 : 15.73.

Synthesis studies

The polymerization conditions and some properties of all samples are shown in Table III, where the total

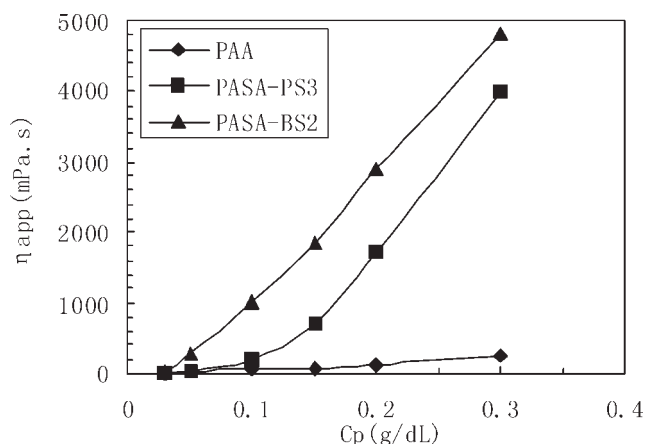


Figure 9 Effect of polymer concentration on the apparent viscosity of copolymer aqueous solution.

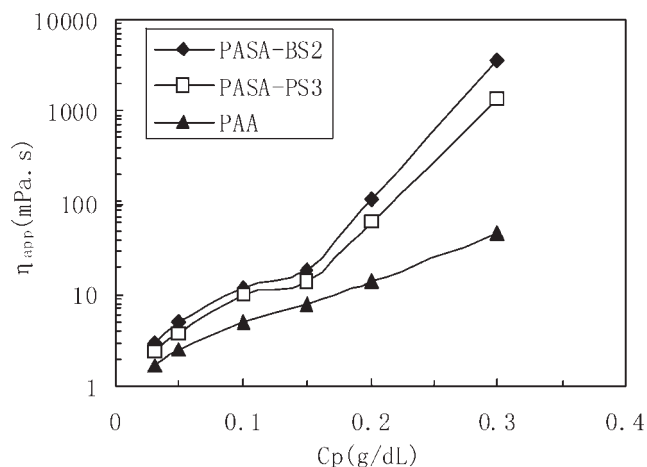


Figure 10 Effect of polymer concentration on the apparent viscosity of copolymer in 0.256 mol L^{-1} NaCl solution.

monomer concentration and SDS concentration are the mass percent composition in water, respectively, and BST content in PASA was determined by the combination of elemental analysis data and eqs. (1)–(7). In the following discussion of reaction conditions, every obtained optimum condition was used in the next condition study.

Effect of NaAMPS amount

As shown in Figure 5 and Table III, PASA with 10 mol % NaAMPS exhibits higher viscosity than the other three terpolymers in water and 0.855 mol L^{-1} NaCl solution. The incorporation of anion groups into polymer chains improves the water solubility of terpolymers, and charge–charge repulsions act to expand molecular chains, which favors intermolecu-

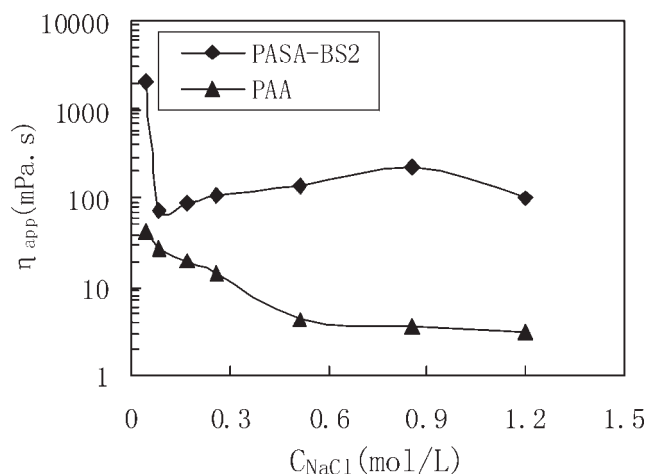


Figure 11 Effect of NaCl concentration on apparent viscosity of copolymer brine solution. Copolymer concentration: 0.2 g dL^{-1} PASA, 0.2 g dL^{-1} PAA.

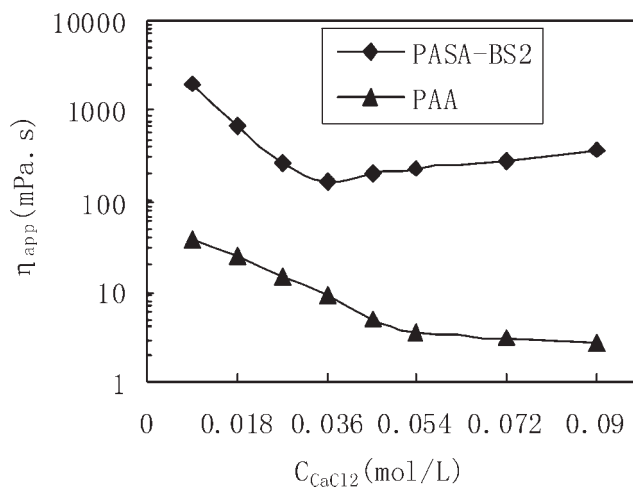


Figure 12 Effects of CaCl_2 concentration on apparent viscosity of copolymer brine solution. Copolymer concentration: 0.2 g dL^{-1} PASA, 0.2 g dL^{-1} PAA.

lar hydrophobic associations. Above the critical association concentration of polymer ((C_p^*)), the increase of NaAMPS amount from 3 to 10 mol % results in larger hydrodynamic volumes of terpolymers in aqueous and brine solution, and the rapid increase of solution viscosities. However, when NaAMPS amount further increases, excessive anionic groups along polymer chains interfere with hydrophobic aggregations. Therefore, the suitable NaAMPS amount is 10 mol %.

Effect of SDS amount

Figure 6 shows the effect of SDS amount on viscosities of terpolymers solution for the micellar polymerization. The thickening property of terpolymers

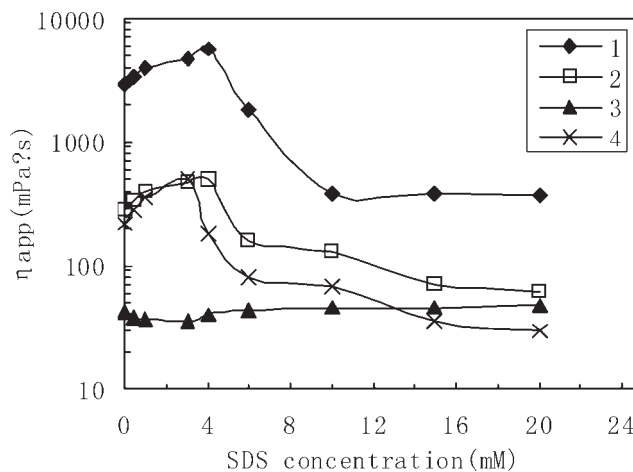


Figure 13 Effect of SDS on apparent viscosity of PASA solution. (1–3) PASA aqueous solution; (1) 0.2 g dL^{-1} PASA-BS2; (2) 0.05 g dL^{-1} PASA-BS2; (3) 0.03 g dL^{-1} PASA-BS2; (4) 0.2 g dL^{-1} PASA-BS2 in 0.855 mol L^{-1} NaCl solution.

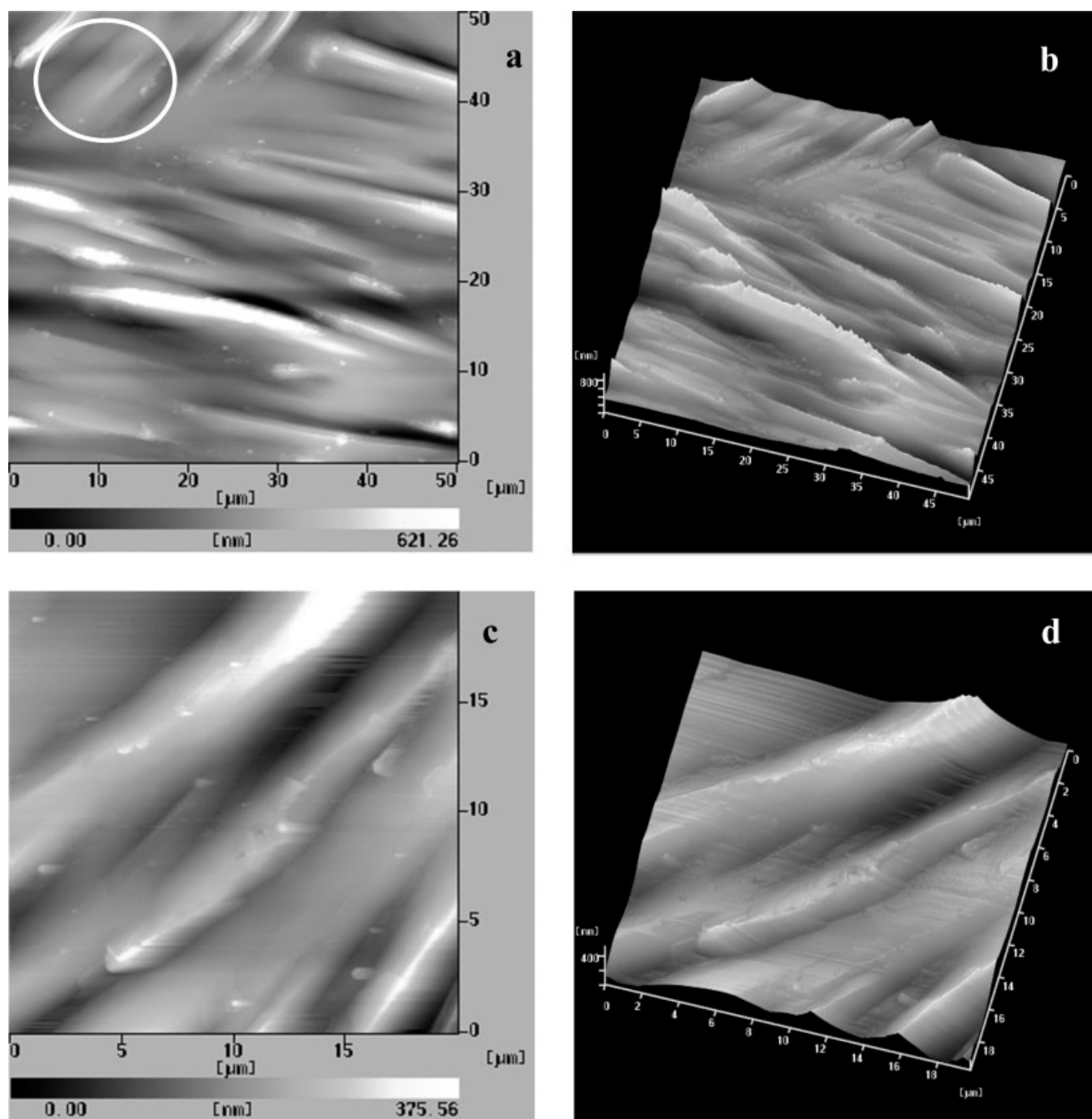


Figure 14 AFM images of 0.23 g dL⁻¹ PASA in water. (a) Two-dimension; (b) three-dimension image of (a); (c) local enlarged image of (a); (d) three-dimension image of (c).

is greatly influenced by both the length and the number of hydrophobic blocks in polymer chains, which are controlled by the number of hydrophobe molecules per micelle, determined by hydrophobe/surfactant ratio. As shown in Figure 6, the maximum viscosity is attained at 6 wt % SDS. At low surfactant concentration of 2 wt % SDS, it was observed that many small droplets of hydrophobic monomer dispersed in the reaction solution, which disturbed the micellar polymerization, resulting in the low

hydrophobe monomer content and low yield of the polymer (Table III).

Effect of monomers concentration

As shown in Figure 7, the optimum total monomer concentration used for the synthesis of terpolymers is 10 wt % at a constant surfactant/hydrophobe ratio. With increasing total monomer concentration from 7 to 10 wt %, molecular weight of terpolymers and the amount of incorporation of hydrophobic monomer

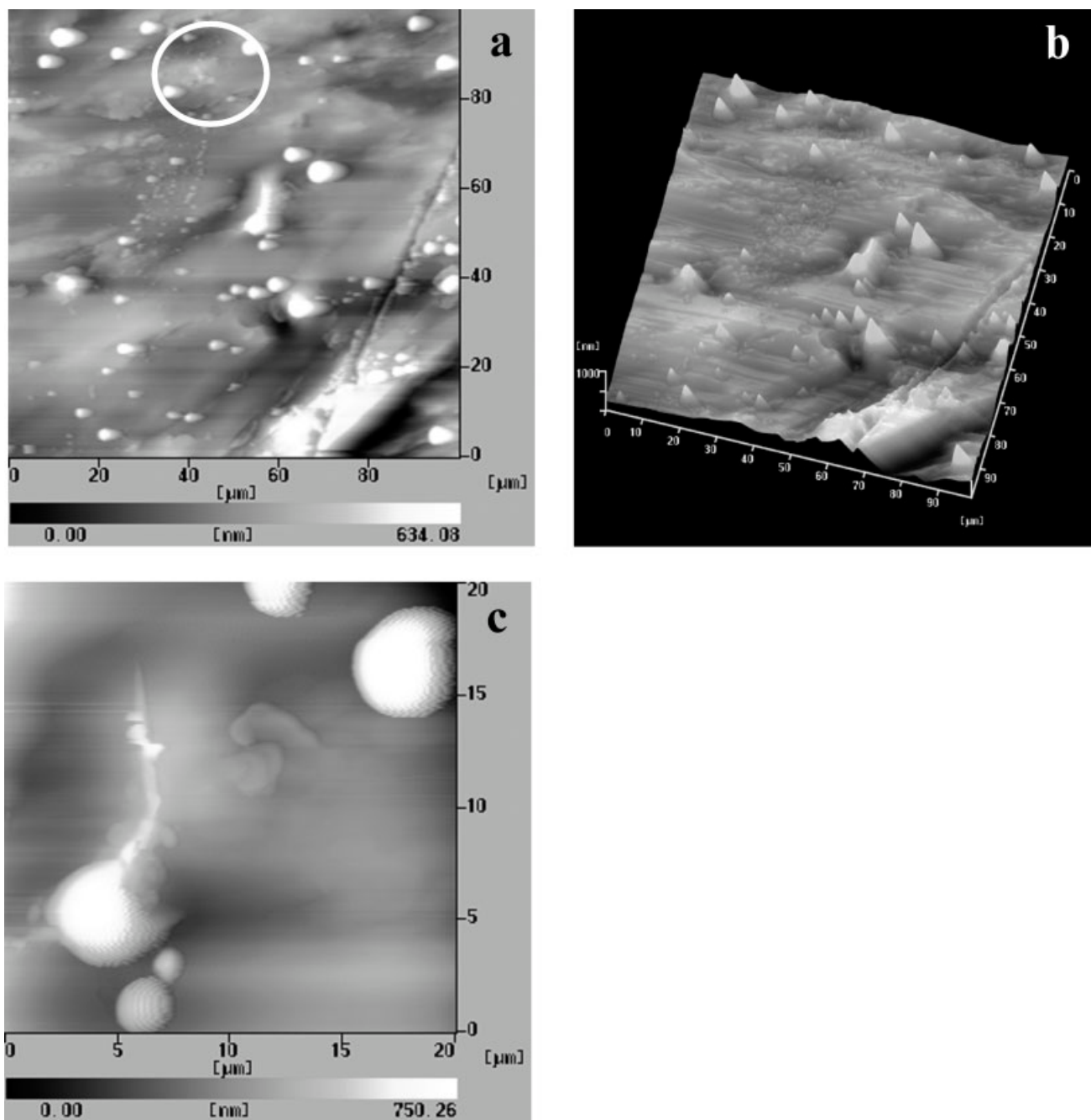


Figure 15 AFM images of 0.23 g dL⁻¹ PASA-BS2 in 4 mmol L⁻¹ SDS solution. (a) Two dimension; (b) three dimension; (c) local enlarged image of (a).

into terpolymers increase. However, higher total monomer concentration results in terpolymers with poor solubility in water, which is due to high molecular weight and the distribution heterogeneity of hydrophobic units along molecules backbone caused by high reaction rate of hydrophobic monomer. It was found that the polymer obtained at the total monomer concentration of 20 wt % was difficult to be dissolved in water and condensed aggregates of the polymer associated with each other to form microgels in aqueous solution, resulting in low solution viscosity.

Effect of BST amount

The aqueous solution properties of hydrophobe-containing polymer strongly depend on the amount of hydrophobic units. As shown in Figure 8, the maximum viscosity is attained at 2.5 mol % BST. As shown in Table III, at a constant surfactant concentration, with increasing BST amount, both the length and the number of hydrophobic blocks in polymer chains increase, resulting in obvious increase of solution viscosities. However, excessive BST contents in

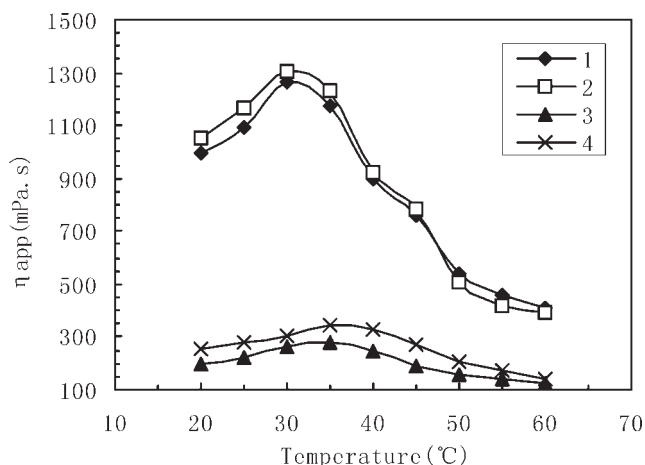


Figure 16 Apparent viscosity of PASA solution as function of temperature. (1) The first measurement of 0.1 g dL^{-1} PASA-BS2; (2) the second measurement of 0.1 g dL^{-1} PASA-BS2; (3) 0.2 g dL^{-1} PASA-BS2 salt solution; (4) 0.2 g dL^{-1} PASA-BS3 aqueous solution.

terpolymers cause strong intramolecular association or poor solubility in water.

Solution properties

Effect of polymer concentration on viscosity

Figures 9 and 10 show the viscosity dependence on polymer concentration for polymers with the hydrophobic monomer of BST and poly(AM-NaAMPS) (PAA) without BST in aqueous and 0.256 mol L^{-1} NaCl solution, respectively. A dramatic increase in solution viscosity with increasing polymer concentration is clearly exhibited above 0.05 g dL^{-1} for PASA-BS2 in Figure 9, indicating that the critical association concentration (C_p^*) of the polymer is about 0.05 g dL^{-1} . For PASA-PS3, C_p^* is 0.1 g dL^{-1} due to less BST amount. For comparison, the concentration dependence of the viscosity for PAA is also shown in Figure 9, but C_p^* of PAA is not observed in the concentration range investigated. The remarkable increase in solution viscosities of PASA polymers is attributed to the strong intermolecular associations. The same concentration effect was observed for the brine solution of polymers, and the critical concentration of PASA increases because of the ionic shielding on $-\text{SO}_3^-$ groups along the polymer chains (Fig. 10).

Effect of electrolytes on viscosity

The effects of salt on solution viscosity for PASA and PAA were shown in Figure 11. The solution viscosity of PASA decreases with the increase of NaCl concentration in the range of $0.0428\text{--}0.0855 \text{ mol L}^{-1}$

because of charge shielding of repulsive ionic interactions along the polymer chain. However, in the range of $0.0855\text{--}0.855 \text{ mol L}^{-1}$, the shielding effect tends to reach equilibration, and with an increase of salt concentration, the polarity of solution induced by electrolytes increases, resulting in the reinforced intermolecular association of the hydrophobic groups and the good salt-thickening behavior of the polymer solution. When the salt concentration further increases, the hydrophobic microstructures turn more compact, and then condensed aggregates associate with each other to form larger aggregates, resulting in the phase separation and the decrease of the apparent viscosity. PAA behaves differently from the PASA polymer, and shows the conventional polyelectrolyte behavior because of the shielding of charges, leading to the abrupt reduction of viscosity of PAA in the brine solution. In Figure 12, the similar polyelectrolyte effect is observed for PAA with the CaCl_2 concentration of $0\text{--}0.09 \text{ mol L}^{-1}$; with increasing CaCl_2 concentration, the solution viscosity of PASA first decreases below 0.036 mol L^{-1} CaCl_2 , and then increases. The results show that the electrostatic shielding effect of CaCl_2 is stronger than that of NaCl because of bivalent Ca^{2+} .

Effect of surfactant on viscosity

Figure 13 shows effect of anionic surfactant SDS on the solution viscosity of PASA-BS2 with different polymer concentration in aqueous and brine solution. For 0.2 g dL^{-1} PASA-BS2 in aqueous and 0.855 mol L^{-1} NaCl solution, solution viscosities increase dramatically by addition of SDS, attributed to interpolymer crosslinking through the formation of mixed micelles involving the hydrophobic groups from different polymer chains and the surfactant molecules. It was found that integrated crosslinking association was

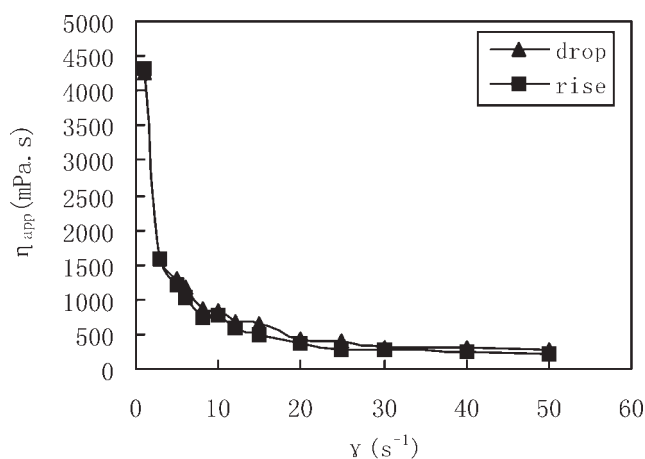


Figure 17 Apparent viscosity of 0.1 g dL^{-1} PASA-BS2 solution as function of shear rate.

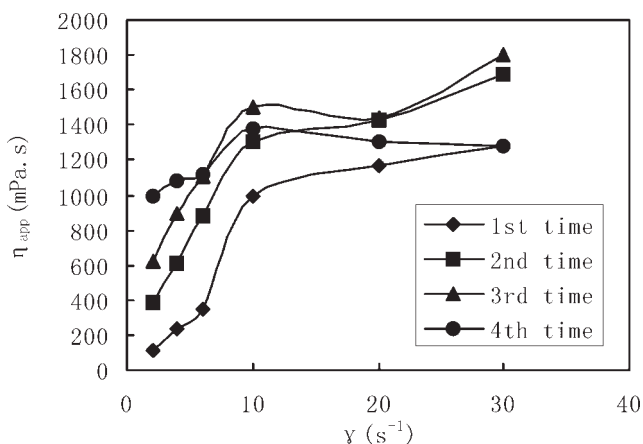


Figure 18 Apparent viscosity of 0.3 g dL⁻¹ PASA-BS3 aqueous solution as function of shear rate.

formed upon connection of SDS by means of AFM measurement (Figs. 14 and 15). Further addition of SDS makes solution viscosities decrease, and when SDS concentration is above 15 mmol L⁻¹, solution viscosities vary slightly. Excessive surfactant disrupts the intermolecular association and micelle-like aggregates with individual hydrophobic segment form. The similar viscosity dependence on SDS concentration is investigated for 0.05 g dL⁻¹ PASA-BS2. For 0.03 g dL⁻¹ PASA-BS2 in water, by addition of small amounts of SDS, the solution viscosity decreases slightly, and then tends to be constant with the concentration of SDS higher than 4 mmol L⁻¹.

Effect of temperature on viscosity

The apparent viscosities versus temperature for PASA-BS2 and PASA-BS3 are shown in Figure 16. For 0.1 g dL⁻¹ PASA-BS2 in water, the viscosity increases from 995 to 1260 mPa s with increasing from 20 to 30°C through the first measurement, and then reduce from 1260 mPa s (30°C) to 457 mPa s (55°C), the viscosity retention ratio is 36%. After the measured sample is placed for an hour, the second viscosity is higher than the first viscosity, attributed to the expansion of polymer chains upon heating and shearing, which is favorable to intermolecular association. For 0.2 g dL⁻¹ PASA-BS2 in 0.855 mol L⁻¹

NaCl solution, the viscosity retention ratio from 30°C (265 mPa s) to 55°C (138 mPa s) is 52%, attributed to the formation of compact aggregates which withstands effectively the increase in temperature by addition of NaCl. Compared with PASA-BS2, the solution viscosity retention ratio of 0.2 g dL⁻¹ PASA-BS3 in water from 30°C (302 mPa s) to 55°C (170 mPa s) is 56% because of the stronger interchain associations generated by more longer hydrophobic segments in polymer molecules.

Effect of shear rate on viscosity

Figure 17 shows the viscosity versus shear rate for 0.1 g dL⁻¹ PASA-BS2 aqueous solution at 25°C. With increasing shear rate, the viscosity initially decreases dramatically, then gradually tends to be constant, which exhibits pseudoplastic behavior. Upon reducing the shear rate gradually, the viscosity is lower slightly than the primary viscosity at a given shear rate and do not recover immediately. The result implies that the intermolecular associations are reversible, all aggregates break at high shear rate, and molecular chains orientate in fluid field.

As shown in Figure 18, for the aqueous solution of 0.3 g dL⁻¹ PASA-BS3 with high BST content, the shear-thickening behavior is displayed through four consecutive measurements in the investigated range of shear rate. The phenomenon may be due to the transition of intramolecular associations to intermolecular associations upon shear, resulting in the increase of solution viscosity.

Aging effect

Table IV shows the aging effect of 0.1 g dL⁻¹ PASA-BS2 in water and 0.256 mol L⁻¹ NaCl solution with saturated oxygen at 45°C. After aging for 120 days at 45°C, the viscosity retention ratio of 0.1 g dL⁻¹ PASA-BS2 in water is 93.8% and the viscosity of the polymer in brine solution almost remain unchanged. As shown in Table V, all the three samples exhibit excellent antiaging property at 70°C. After aging for 30 days, 0.2 g dL⁻¹ PASA-BS2 in 0.855 mol L⁻¹ NaCl solution was further aged for 30 days at 85°C, and the viscosity increased from 221 to 351.6 mPa s.

TABLE IV
Apparent Viscosity of 0.1 g dL⁻¹ PASA-BS2 Solutions after Aging at 45°C (mPa s)

	Apparent viscosity						
	0 ^a	1	5	15	30	60	120
Aqueous solution	1020	1020	1012	997	982	974	956
0.256 mol L ⁻¹ NaCl solution	108	109	107	111	113	107	112

^a 0, 1, 5, 15, 30, 60, and 120 are the aging times (d), respectively.

TABLE V
Apparent Viscosity of Terpolymer Solutions in 0.855 mol L⁻¹ NaCl
after Aging at 70°C (mPa s)

	Apparent viscosity				
	0 ^a	1	5	15	30
0.1 g dL ⁻¹ PASA-PS3	12.6	12.4	13.5	15.7	16.2
0.1 g dL ⁻¹ PASA-BS3	7.5	7.2	6.9	8.3	9.0
0.2 g dL ⁻¹ PASA-BS2	221.0	235.6	241.8	259.5	270.9

^a 0, 1, 5, 15, and 30 are the aging times (d), respectively.

The excellent thermal stability of terpolymer solutions is attributed to the incorporation of BST and NaAMPS into terpolymer chains. Rigid groups of BST and NaAMPS are stable and effectively interfere with the hydrolysis of amido groups in the polymers. On the other hand, the terpolymer chains aggregate together via a strong intermolecular hydrophobic association in the brine solution and form compact aggregates at 25°C. During aging period at high temperature, further expansion of polymer chains and the transition of intramolecular associations to intermolecular associations are favorable to the formation of crosslinking structures, resulting in the increase of solution viscosity.

CONCLUSIONS

The terpolymers (PASA) with AM, BST, and NaAMPS were synthesized by micellar free radical technique. The elemental analysis result shows that the polymer molar composition data of BST is higher than the feed molar composition due to the local concentration effect of BST solubilized in micelles. The block-structure of PASA was characterized directly by DSC measurement, which suggests that the length of hydrophobic segments is not homogeneous. The use of NaAMPS improves the water solubility and intermolecular association of terpolymers due to chain expansion formed by the electrostatic repulsions. The feed amount of BST affects remarkably the viscosity of PASA because of hydrophobic interaction. SDS amount and total monomer concentration in the polymerization also influence apparently the viscosification effect of PASA.

The viscosities of PASA increase dramatically in aqueous and brine solution with increasing polymer concentration above the critical association concentration. The polymer exhibits salt-thickening, temperature-thickening, thixotropy, pseudoplastic behavior,

and shear-thickening for PASA with high BST content at low shear rate. Integrated crosslinking association is formed by the addition of a small amount of SDS, resulting in the remarkable increase of viscosity of PASA solution. The PASA solution with high NaCl concentration exhibited excellent antiaging property at 85°C and the apparent viscosity increased substantially after aging.

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