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Characterization, Solution Behavior, and Microstructure of a Hydrophobically Associating Nonionic Copolymer

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Abstract To obtain an oil-displacement polymer with good thermal stability and solution properties, self-assembling acrylamide (AM)/4-butylstyrene (BST) copolymers (PSA) were synthesized by the micellar copolymerization technique. The resulting polymer was characterized by elemental analysis and UV and FT-IR spectroscopy. Conventional DSC measurement was used successfully to characterize the hydrophobic microblock structure of PSA, and two glass transition temperatures were found in the polymer: at 203 °C for the AM segments and at 106 °C for the hydrophobic BST segments. The initial decomposition temperature (234 °C) of the polymer is higher than that of polyacrylamide (210 °C). The DSC and TG results suggest that incorporation of BST into PSA enhances the molecular rigidity and thermal stability of the polymer. The apparent viscosity of a PSA solution greatly depends on the amount of BST in the polymer, and the polymer exhibits salt-thickening, temperature-thickening, thixotropy, pseudo-plastic behavior, anti shearing, and good anti-aging properties at 80 °C. In addition, the apparent viscosities of PSA solutions are increased remarkably by the addition of a small amount of surfactant. AFM measurements show that large block-like aggregates and small compact aggregates are formed in aqueous solutions of 0.4 g·dL^{-1} PSA because of strong intermolecular hydrophobic associations, despite the low molecular weight, and their sizes increase upon addition of a small amount of salt.

Keywords Acrylamide · Atomic force microscopy (AFM) · Differential scanning calorimetry (DSC) · Hydrophobic association · Micellar copolymerization · Solution properties · 4-Butylstyrene

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1 Introduction

Partially hydrolyzed polyacrylamide (HPAM) is widely applied to increase the viscosity of the aqueous phase in order to reduce the fluidity ratio of water-to-oil and to improve sweep efficiency during the enhanced oil recovery (EOR) process [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 the amido groups. However, when high shear rates are applied they cause breakage of the polymer chains, resulting in an irreversible decrease of viscosity. In addition, an increase of salinity causes the solution viscosity of HPAM solutions to decreases abruptly because of shielding of ionic groups, and the amido groups in HPAM hydrolyze rapidly to form carboxylate groups above 70 °C. Therefore, HPAM is commonly used in the oil reservoirs of low temperature and salinity.

Hydrophobically associating acrylamide-based copolymers with a small number of hydrophobic groups have been extensively studied in recent years [2, 3]. When dissolved in an aqueous solution above the critical concentration (C_p^*), the polymer molecules aggregate to form reversible supermolecular structures via intermolecular association of hydrophobic groups, resulting in a dramatic increase in the apparent viscosity, and degradation upon shearing does not occur because of the low molecular weight [4]. The hydrophobic monomers are mainly derivatives of acrylamide, acrylic esters and their derivatives [5–9], which are easy to hydrolyze under acidic or basic conditions at high temperature, which then results in an abrupt decrease in the viscosity of the polymer solution. For the polymers, the viscosities at low polymer concentration are not high enough for some applications, especially in EOR that involves high temperature and a non-neutral underground oil-layer environment [10]. In addition, acrylamide/styrene copolymers were reported previously [11–13]. However the viscosity of these polymer solutions was low, because of weak interactions of the phenyl groups used as hydrophobic units. Consequently, the technical applications of hydrophobically modified water-soluble polymers have been restricted.

To obtain a polymeric thickener with high viscosity and good thermal stability in aqueous solutions, we herein synthesized a novel acrylamide (AM)/4-butylstyrene (BST) copolymer (PSA) by micellar polymerization. The PSA polymer was characterized by UV and FT-IR spectroscopy and elemental analysis. The influence of BST on the thermal stability of the PSA polymer was studied by TG and DSC, and the solution viscosities of the PSA polymers were investigated as functions of the amount of BST in the polymer, temperature, shear rate, salt concentration and surfactant. Atomic force microscopy (AFM) was used to observe the microstructures of PSA in aqueous and brine solutions to reveal the association of BST as a hydrophobic monomer.

2 Experimental

2.1 Reagents

AM was recrystallized twice from chloroform. 4-Butylstyrene was synthesized according to the procedure of reference [14]. Other reagents were analytically pure and used without further purification.

2.2 Instrumentation

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

The FT-IR spectrum was measured with a NICOLET-560 FT-IR spectrophotometer (USA) using KBr disks. The spectroscopic resolution was 1 cm^{-1} and the scanning number was 32.

The NMR spectra of purified 4-butylstyrene in $CDCl_3$ was measured with a 400 MHz INOVA-400 instrument (America Varian Company, USA).

The glass transition temperature of PSA was measured with a NETZSCH DSC204 instrument (Germany). N_2 was used as the experimental inert atmosphere, and the heating rate was 20 $^\circ\mathrm{C}\cdot\mathrm{min}^{-1}$ for the temperature range of 25 to 300 °C.

The thermogravimetric curve of PSA was obtained with a PE TGA7 thermogravimetric analyzer (Perkin-Elmer Co.). N_2 was used as an inert atmosphere, and the heating rate was 10 $^\circ\mathrm{C}\cdot\mathrm{min}^{-1}$ for the temperature range 40 to 700 °C.

The apparent viscosities of polymer solutions were measured with a Brookfield DVIII R27112E viscometer at a shear rate of 6 s^{-1} at 35 °C and the measurement time for all samples was two minutes. The intrinsic viscosities were measured with a 0.6 mm bore Ubbelohde capillary viscometer at $(30.0 \pm 0.1)\,^\circ\mathrm{C}$ and 1 $\mathrm{mol}\cdot\mathrm{L}^{-1}$ sodium nitrate was used as the solvent.

The atomic force micrographs were made with a SPA400 AFM (Seiko, Japan), and all measurements were performed in the tapping mode. All samples were covered with mica sheets and dried naturally.

The carbon, nitrogen and hydrogen contents of the polymers were determined with a CARLO ESRA-1106 Elemental Analyzer (Italy). The molar compositions of PSA were determined using Eqs. 1 to 5, where A and B are the number of moles of AM and BST, respectively, in 100 g of terpolymer. The coefficients are the numbers of carbons, nitrogen and hydrogen atoms in each monomer unit. After obtaining A and B for each polymer sample, mol-% compositions were calculated.

$$\%\text{-C}/12.01 = 3A + 12B \tag{1}$$

$$\%\text{-N}/14.01 = 1A \tag{2}$$

$$\%\text{-H}/1.01 = 5A + 16B \tag{3}$$

$$\text{mol-}\%(\mathrm{AM}) = 100A/(A + B) \tag{4}$$

$$\text{mol-}\%(\mathrm{BST}) = 100B/(A + B) \tag{5}$$

2.3 Synthesis of 4-Butylstyrene

4-Butylchlorobenzene (0.2 mole) and an equal number of moles of vinyltributyltin were dissolved in 100 mL of dioxane and placed in a 500 mL flask. In the presence of 2.0720 g of $Pd_2(dba)_3$ and 8.2880 g of $P(t\text{-}Bu)_3$ as catalysts, and 2 g of CsF as an additive, the reaction mixture was stirred for 24 h at 100 °C. 4-Butylstyrene was then distilled from the crude product under vacuo. The purity and yield were 93% and 80%, respectively. The observed ^{1}H NMR (400 MHz) shifts δ (ppm) are: 4H (–CH of phenyl), 7.353; 2H (=CH_2), 5.193 and 5.709; 1H (=CH), 6.700; 9H (–CH_2^a CH_2^b $CH_2^cCH_3^d$), 2.654 ($2H_a$), 1.739 ($2H_b$), 1.406 ($2H_c$), and 0.907 ($3H_d$).

2.4 Synthesis of Copolymers

The PSA copolymers were synthesized by free radical micellar copolymerization [15]. A 100 mL three-necked round bottom flask was equipped with a mechanical stirrer, and a nitrogen gas inlet and outlet. AM (5.0 g, 0.0704 mole) and sodium dodecyl sulfate (SDS) (1.2274 g, SDS) were dissolved in 20.69 mL of distilled water and the solution was placed in the flask. Hydrochloric acid was used to control the pH of the reaction solution to between 6 and 7. The mixture was stirred for 15 min., and BST (0.1716 g, 1.0724×10^{-3} mole) was then added to the reaction flask. The flask was purged with N_2(g) for half an hour until a clear homogeneous mixture was observed. The reactant solution was then heated to 50 °C, with stirring, in a tempering kettle under N_2(g), and 5.720 mL of 0.005 $\mathrm{mol \cdot L^{-1}}$ $K_2S_2O_8$ solution was then added to the reactant solution. After the polymerization proceeded for 16 h at 50 °C, the reaction mixture was diluted with five volumes of distilled water, and two volumes of acetone were then added with stirring to precipitate the polymers. The polymers were washed with acetone twice and extracted with ethanol using a Soxhlet extractor, for two days to remove all traces of water, surfactant, residual monomers and initiator. Finally, the polymers were dried under vacuo at 50 °C for three days.

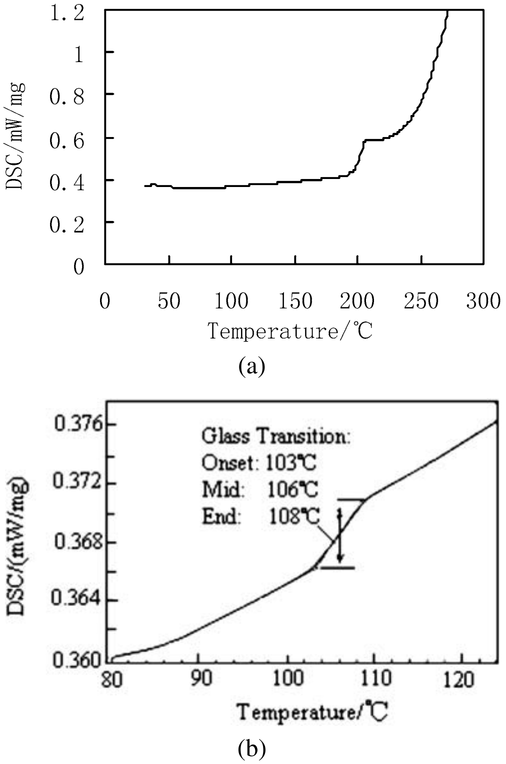
In the absence of BST, polyacrylamide (PAM) was synthesized using the same reaction conditions and purification method as mentioned above.

For the UV spectrum of PSA, there is a characteristic absorption peak at 240 nm attributed to the phenyl group, indicating that the 4-butylstyrene hydrophobic units are incorporated into the polymer molecules. FT-IR peaks of PSA ($\mathrm{cm^{-1}}$) are: –N–H stretch, 3430.78; C=O stretch, 1654.50; $–CH_3$, $–CH_2$, and –CH stretches, 2928.60, 2861.89 and 2788.61; $–CH_3$, $–CH_2$, and –CH bending, 1455.08, 1417.45 and 1323.28; =C–H phenyl stretch, 3090.39; and =C–H phenyl bending, 827.75.

3 Results and Discussion

3.1 DSC Measurements

The block structure of the hydrophobic segments was determined previously by a fluorescent probe [15]. In that paper, the chain structure of the hydrophobically associating polymers was successfully characterized by the DSC technique. A high heating rate is favorable for obtaining the fine glass transition. Therefore, in this study, the heating rate was 20 $\mathrm{°C \cdot min^{-1}}$ to observe the glass transition temperatures (T_g) of the microblock BST segments. As shown in Fig. 1, where (a) is enlarged in the range of 80 to 120 °C to obtain (b), there are two glass transition temperatures: one at 203 °C for the AM hydrophilic segments and a second at 106 °C for the microblock BST hydrophobic segments for PSA–BS1. The DSC result indicates that the BST units are incorporated into the PSA chains to form microblock structures that favor intermolecular hydrophobic association [15]. In addition, the polymers are completely dissolved by water, and there is no white homopoly(4-butylstyrene) in the polymer solution. The results show that the polymer is a copolymer of AM and BST, and not a mixture of polyacrylamide and poly(4-butylstyrene). The T_g (203 °C) of the hydrophilic segments in PSA is higher than that of homo-polyacrylamide (163 °C), which suggests that the rigidity of the polymer chains has increased. This is due to the steric effect of the aromatic ring of the BST units. On the other hand, the T_g of the BST segments is dependent on the length of the hydrophobic segments, which in turn is determined by the amount of BST solubilized in the SDS micelles during the reaction. The T_g of homopoly(4-butylstyrene) with a high molecular weight is 118 °C. The DSC result is consistent with the mechanism for micellar copolymerization, which is that the hydrophobic monomer is solubilized within the surfactant micelles and AM is dissolved together with the initiator $K_2S_2O_8$ in the aqueous phase [15].



(a)

(b)

Fig. 1 Glass transition temperature of a PSA copolymer, heating rate: 20 °C·min^{-1}: (**a**) main scale of 20 °C·min^{-1}; (**b**) enlarged graph of (**a**) in the range of 80 to 120 °C

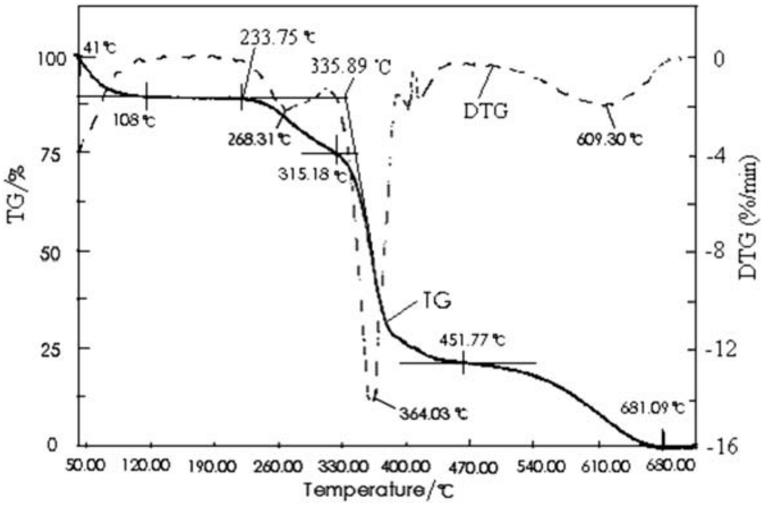


Fig. 2 TG analysis curve of a PSA copolymer

3.2 TG Measurements

The heat-resistant property of the PSA polymer was measured with the thermogravimetric analyzer, and the curves are shown in Fig. 2 where the broken line is a differential thermogravimetric curve that displays the decomposition rate of PSA. The thermogravimetric curve consists of five sections: (1) a weight loss of 9.885% from 41 to 102 °C, which resulted from volatilization of water molecules from the polymer. (2) The weight is constant from 102 to 233.75 °C. (3) The polymer begins to decompose at 233.75 °C, and the imine reaction occurs for a small number of amido groups and the weight loss is 12.967% between 233.75 to 315.18 °C. The polymer decomposes fastest at 268.31 °C. (4) Between 315.18 to 451.77 °C, a large number of amido groups decompose and the main chains of the polymer degrade, leading to the large loss of weight (54.021%). The decomposition rate is the highest at 364.03 °C. (5) In the range of 451.77 to 681.09 °C, the loss of weight is 21.707%. The decomposition rate then becomes slow, and the degradation of the polymer chains and the decomposition of (4-butyl)phenyl groups dominate. Finally, only 0.845% of the polymer remains at 681.09 °C. The initial decomposition temperature (233.75 °C) for the polymer is obviously higher than that (210 °C) of the homo-polymer polyacrylamide [16], indicating that the thermal stability of the hetero-polymer is good because of the incorporation of the rigid benzene ring into the polymer.

3.3 Solution Behavior of PSA

The polymerization conditions, compositions and properties of some of the samples are shown in Tables 1 and 2. The reaction temperature of all samples was 50 °C, and the pH of the reacting solutions is between 6 and 7. For micellar polymerization, the viscosity of the polymer solution is greatly influenced by both the length and number of hydrophobic blocks in the polymer chains, which is determined by the hydrophobe/surfactant ratio. As shown in Table 1, the maximum viscosity is attained at 4 wt% SDS when the total monomer concentration is 15 wt%, but at a lower surfactant concentration of 3 wt% it was observed that many

Table 1 Synthesis conditions, apparent viscosity and yield of PSA copolymers

Sample	Reaction conditions			Apparent viscosity (mPa·s)	Yield (%)
	M1: M2[a]	SDS[b] (wt%)	Monomers[c] (wt%)		
PSA-SD1	98.8 : 1.2	3.0	15	38.2	70.5
PSA-SD2	98.8 : 1.2	4.0	15	127.0	84.5
PSA-SD3	98.8 : 1.2	5.0	15	78.7	81.6
PSA-SD4	98.8 : 1.2	6.0	15	28.0	76.3
PSA-M1	98.8 : 1.2	2.7	10	23.5	66.7
PSA-M2	98.8 : 1.2	5.6	20	208.0	87.2
PSA-M3	98.8 : 1.2	7.2	25	42.0	91.5
PSA-BS1	98.5 : 1.5	5.6	20	296.0	89.2
PSA-BS2	98.2 : 1.8	5.6	20	96.0	88.4
PSA-BS3	98.0 : 2.0	5.6	20	53.0	85.5
PSA-BS4	97.5 : 2.5	5.6	20	33.0	82.0

Polymer concentration in aqueous solution: 0.30 g·dL^{-1}

[a] M1, acrylamide; M2, BST feed molar compositions

[b] mass percent composition in water

[c] Monomers = total monomer concentration, the mass percent composition in water

Table 2 Composition and properties of PSA copolymers

Sample	Elemental composition			Molar composition M1: M2[a]	T_g/°C		Intrinsic viscosity (dL·g^{-1})
	C (wt%)	N (wt%)	H (wt%)		Hydrophilic segments	Hydrophobic segments	
PSA-SD1	51.39	19.41	7.16	99.27 : 0.73	192.0	/	2.70
PSA-SD2	51.86	19.17	7.19	98.72 : 1.28	201.4	103.6	3.48
PSA-SD3	51.93	19.14	7.20	98.64 : 1.36	199.1	102.8	3.01
PSA-SD4	51.58	19.31	7.18	99.05 : 0.95	197.6	102.0	2.44
PSA-M1	51.31	19.45	7.16	99.36 : 0.64	186.4	/	2.85
PSA-M2	51.89	19.16	7.20	98.69 : 1.31	202.3	104.0	3.71
PSA-M3	52.03	19.09	7.21	98.53 : 1.47	204.5	107.8	3.20
PSA-BS1	52.14	19.03	7.23	98.40 : 1.60	203.0	106.0	4.05
PSA-BS2	52.41	18.90	7.24	98.08 : 1.92	204.1	106.8	3.91
PSA-BS3	52.69	18.75	7.26	97.74 : 2.26	204.7	107.5	3.35
PSA-BS4	53.17	18.51	7.30	97.17 : 2.83	206.2	108.1	2.90

[a] M1, acrylamide; M2, BST molar compositions in copolymers

droplets of hydrophobic monomer are dispersed in the reacting solution, which greatly disturbs the micellar polymerization. However, excessive surfactant produces a large number of bubbles, resulting in a low hydrophobic monomer content and low yield of the polymer. Compared with the intrinsic viscosity of HPAM, which is generally higher than 15 dL·g^{-1}, the intrinsic viscosities of the PSA polymers are lower. This result shows that the thickening property of PSA solutions mainly depends on intermolecular hydrophobic associations. By increasing the amount BST in the feed, the intrinsic viscosity of the polymer decreases because of steric obstruction of the hydrophobic monomer, indicating that the molecular weight of the polymer is reduced, and the glass transition temperatures of the hydrophilic and hydrophobic segments increase because of the increase in the length of the microblock BST segment. The molar compositions of the polymers are higher than the corresponding monomer feed compositions for BST (except for PSA-SD1, PSA-SD4 and PSA-M1), which is due to the local concentration effect of BST solubilized within the surfactant micelles.

3.3.1 Effect of the Amount of BST on Viscosity

The thickening ability of the hydrophobically associating water-soluble polymer is greatly dependent on both the length and number of hydrophobic blocks in the polymer chains as determined by the amount of hydrophobe. As shown in Fig. 3, the optimum BST amount is 1.5 mol-%. For PSA-BS1, the solution viscosity increases sharply with increasing polymer concentration above 0.1 g·dL^{-1}, which is the critical association concentration (C_p^*). For PSA-BS2, PSA-BS3, and PSA-BS4, the solution viscosities are lower because of the larger amount of BST. For comparison, the concentration dependence of the solution viscosity for PAM is also shown in Fig. 3, but the PAM polymer displays only a linear relationship between solution viscosity and polymer concentration. At a constant surfactant concentration but with increasing amount of BST from 1.2 to 1.5 mol-%, intermolecular hydrophobic associations are reinforced above C_p^*, resulting in the obvious increase in solution viscosity. However, higher BST contents in the copolymers resulted in poor solubility in water and strong intramolecular associations. Consequently, solution viscosities decreased remarkably.

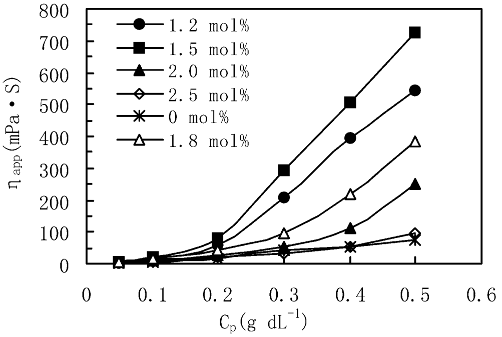


Fig. 3 Influence of the amount of BST on the apparent viscosity of aqueous PSA solutions

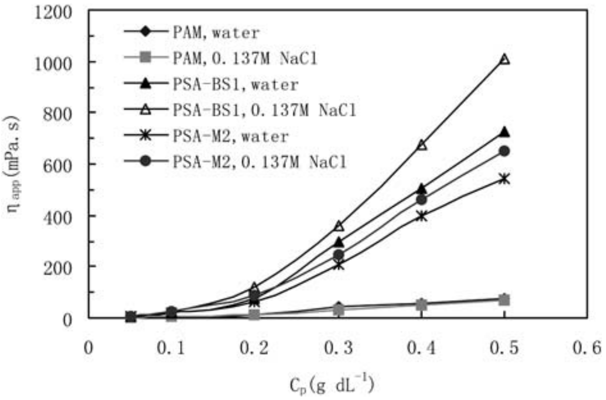


Fig. 4 Influence of the amount BST on the apparent viscosity of PSA in brine solutions where the NaCl concentration is 0.137 mol·L^{-1}

Intermolecular hydrophobic associations and the viscosification effect of the polymers in brine solution are strengthened because of the increase in solution polarity from addition of NaCl (Fig. 4). The phenyl group from BST can induce van der Waals interactions due to its planar and polarizable structure, and improve the rigidity of the hydrophobic unit. In addition, the length of the hydrophobic carbon chain in BST is longer than that of the phenyl group in styrene. Hence, the incorporation of (4-butyl)phenyl groups into the PSA polymer leads to strong intermolecular hydrophobic associations and high viscosities for the polymer solution at low polymer concentrations.

3.3.2 Effect of NaCl on Viscosity

The apparent viscosity is plotted as a function of NaCl concentration for the PSA polymers and PAM in brine solutions (Fig. 5). With increasing NaCl concentration, for PSA-BS1 and PSA-SD2, the apparent viscosities first increase and then decrease at a polymer concentration of 0.3 g·dL^{-1}. This is due to an increase in solution polarity induced by electrolytes, which results in reinforced intermolecular hydrophobic associations and good salt-thickening behavior. However, when the salt concentration further increases, the hydrophobic microstructures become more compact, and then the condensed aggregates associate to form larger aggregates, resulting in the phase separation of gels and a decrease in the apparent viscosity. The salt resistance of the PSA-SD2 polymer is higher than that of PSA-BS1 because of the lower hydrophobe content. For the 0.1 g·dL^{-1} PSA-BS1 solution, there are few aggregates, and monomeric molecules mainly exist in the dilute solution. Thus, the solution viscosity varies only slightly with an increase of salt concentration.

Fig. 5 Effect of the NaCl concentration on the apparent viscosity of PSA in brine solutions: ♦ 0.3 g·dL^{-1} PSA-BS1; ▲ 0.3 g·dL^{-1} PSA-SD2; □ 0.1 g·dL^{-1} PSA-BS1

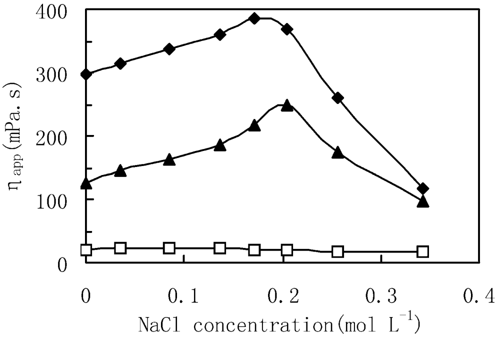
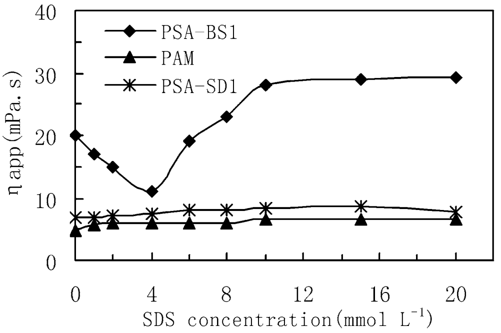


Fig. 6 Influence of the SDS concentration on the apparent viscosity of PSA in dilute aqueous solutions where the polymer concentration is 0.1 g·dL^{-1}



3.3.3 *Effect of Surfactant on Viscosity*

Figure 6 shows the influence of the SDS concentration on the apparent viscosity of the polymers in dilute solution at the concentration 0.1 g·dL^{-1}. By addition of SDS, the apparent viscosity of PAM without BST hardly varies in aqueous solution, and the solution viscosity of PSA-SD1 is also almost constant because very little of the hydrophobe is present in the molecules. For 0.1 g·dL^{-1} PSA-BS1, with increasing SDS concentration, the solution viscosity first decreases below 4 mmol·L^{-1}, then rises, and finally tends to become constant. In a 0.1 g·dL^{-1} PSA-BS1 solution, most of polymer chains exist in the form of the monomeric molecule, and intramolecular hydrophobic associations easily occur. The intramolecular associations are strengthened by addition of a small amount of surfactant, and molecule coils become more compact, leading to the decrease of solution viscosity. When the concentration of SDS reaches 4 mmol·L^{-1}, intramolecular associations become strongest, but then weakens with increasing the SDS concentration. However, above 8 mmol·L^{-1}, which is the critical micellar concentration (CMC) of SDS, hydrophobic segments are surrounded in SDS micelles, the intramolecular association is destroyed, and mixed micelles involving only hydrophobic segments are formed with further increasing of the SDS concentration (Fig. 7). Therefore, the viscosity becomes almost constant. In addition, electrostatic repulsions of SO_4^{2-} in mixed micelles acts to extend the polymer chains, contributing to the viscosity increase.

The effect of the SDS concentration on the apparent viscosities of copolymers in semidilute solution is shown in Fig. 8. In the studied concentration range of surfactant for PSA-BS1 and PSA-M2, the solution viscosities first increase remarkably, reach maxima (attributable to inter-polymer crosslinking through the bridging of the surfactant molecules with hydrophobic groups), and then decrease. Finally, the solution viscosities are almost invariant

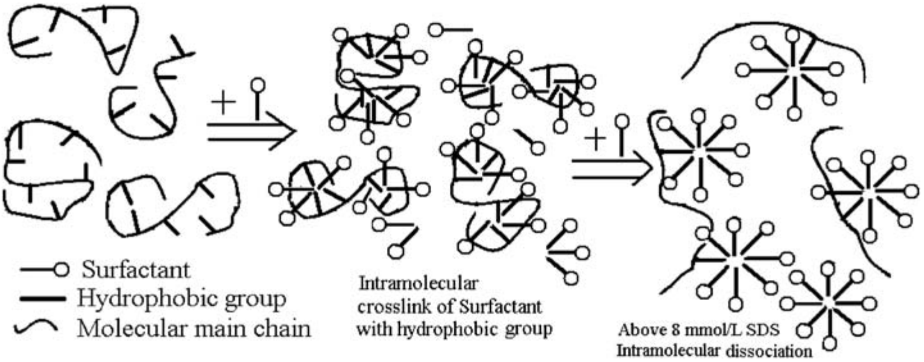
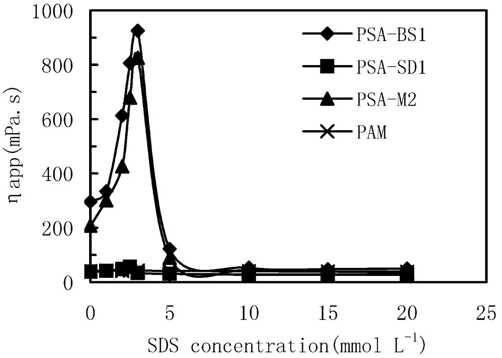


Fig. 7 Schematic representation of the effect of surfactant on intramolecular hydrophobic association

Fig. 8 Effect of the SDS concentration on the apparent viscosity of PSA polymers in semi-dilute aqueous solutions where the polymer concentration is 0.3 g·dL^{-1}



when the surfactant concentration is higher than the CMC of SDS. At low concentrations of SDS, aggregates, which involve the surfactant molecules and the hydrophobic groups from different copolymer molecules, can form and this leads to the observed increase in solution viscosity. However, by addition of excess SDS, micelle-like aggregates with an individual hydrophobic segment form that disrupt the intermolecular association. The viscosity maximum of PSA-BS1 is higher than that of PSA-M2 because it contains more hydrophobic groups. For PSA-SD1 with increasing concentration of SDS, the solution viscosity varies only slightly because the hydrophobe content of the polymers is not high enough to form mixed hydrophobic microdomains.

3.3.4 Effect of Temperature on Viscosity

As shown in Fig. 9 for PAM, as the temperature increases the solution viscosity regularly decreases because of the faster movement of the polymer chains and weaker hydrogen bonding. For 0.3 g·dL^{-1} PSA-BS1 and 0.3 g·dL^{-1} PSA-SD2 in aqueous solutions, the solution viscosities increase with increasing temperature from 20 to 40 °C, followed by a decrease above 40 °C. Compared with PSA-SD2, the enhancement of the solution viscosity of PSA-BS1 between 20 to 40 °C is higher because of the stronger inter-chain associations. These results indicate that an increase of temperature is favorable for inter-polymer hydrophobic association within a certain temperature range.

Hydrophobic hydration is exothermic whereas hydrophobic association is an endothermic process with an entropy increase in a low temperature range [17]. Water molecules

Fig. 9 Influence of temperature on the apparent viscosity of PSA aqueous solutions where the polymer concentration is 0.3 g·dL^{-1}

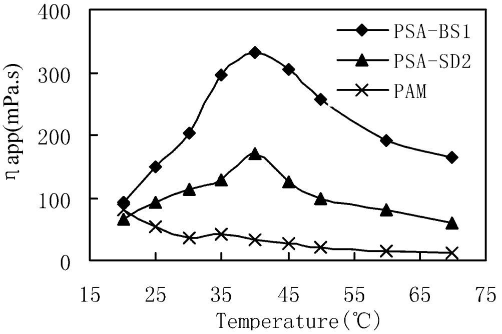
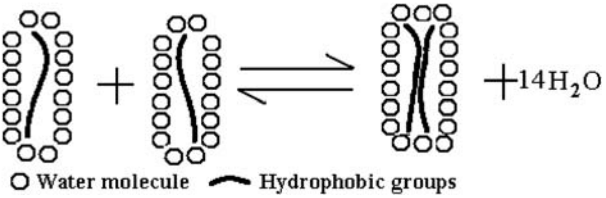


Fig. 10 Schematic representation of hydrophobic association



surrounding the hydrophobic groups are arranged orderly by their hydrogen bonds, which are called iceberg structures (Fig. 10). The structures are not stable because of their higher energy states, and hydrophobic groups are easily extruded from the aqueous environment and aggregate to form a stable thermodynamic state via van der Waals interactions. This is hydrophobic association. The iceberg structures collapse, which is endothermic, results in an increase of disordered states. Hydrophobic groups in hydrophobic micro domains are freer than in the aqueous environment, their aggregations with each other occur exothermically, and the energy is lower than that absorbed by the thaw of the iceberg structures. Thus, hydrophobic association is an endothermic process with an entropy increase in the low-temperature region. At higher temperatures, the iceberg structure decreases or becomes weaker because of the faster movement of water molecules and polymer chains, and values of entropy increase and the endothermic energy obviously decreases, resulting in exothermic hydrophobic association. Therefore, the solution viscosity decreases with increasing temperature.

3.3.5 Effect of Shear Rate on Viscosity

The plots of viscosity versus shear rate are displayed in Fig. 11 for PSA-BS1 in aqueous solutions at 35 °C. With increasing shear rate (curve 1), the viscosity decreases sharply, the rate of reduction then slows, and finally the viscosity tends to be constant because of the balance between intermolecular association and disassociation, which exhibits pseudo-plastic behavior. Upon gradually reducing the shear rate (curve 2), the viscosity becomes slightly lower than the primary viscosity at a given high shear rate and does not recover immediately, indicating that the intermolecular hydrophobic associations take places at a finite rate. After the first measured sample was allowed to set for 2 h, the remeasured viscosity (curve 3) was higher than the first measurements. This solution behavior is attributable to the expansion of polymer chains and the transition from intramolecular associations to intermolecular associations upon shearing, leading to more hydrophobic domains and an increase in the solution viscosity. These results imply that the intermolecular associations are reversible, all

Fig. 11 Influence of shear rate on the apparent viscosity of aqueous PSA solutions where the polymer concentration is 0.3 g·dL^{-1} PSA-BS1: *curve 1*, increasing shear rate; *curve 2*, decreasing shear rate; *curve 3*, measured 2 h after the first measurement

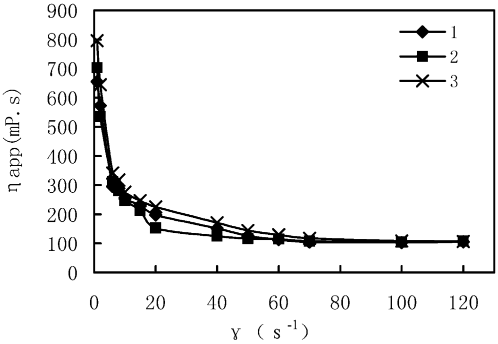


Table 3 Apparent viscosities of PSA copolymers in brine solution after ageing at 80 °C (mPa·s)

Sample	Ageing time (d)							
	0	1	5	15	30	45	60	90
PSA-BS1	109.3	95.7	84.1	73.8	66.4	60.3	57.1	53.8
PSA-M2	87.6	70.9	63.3	58.5	52.4	48.1	43.8	39.3

Polymer concentration: 0.2 g·dL^{-1}, NaCl concentration: 0.137 mol·L^{-1}

aggregates break at high shear rates, and molecular chains orientate in the fluid flow field. In addition, the results also show that the polymer does not degrade and the molecular structure is stable upon shearing.

3.3.6 Aging Effect

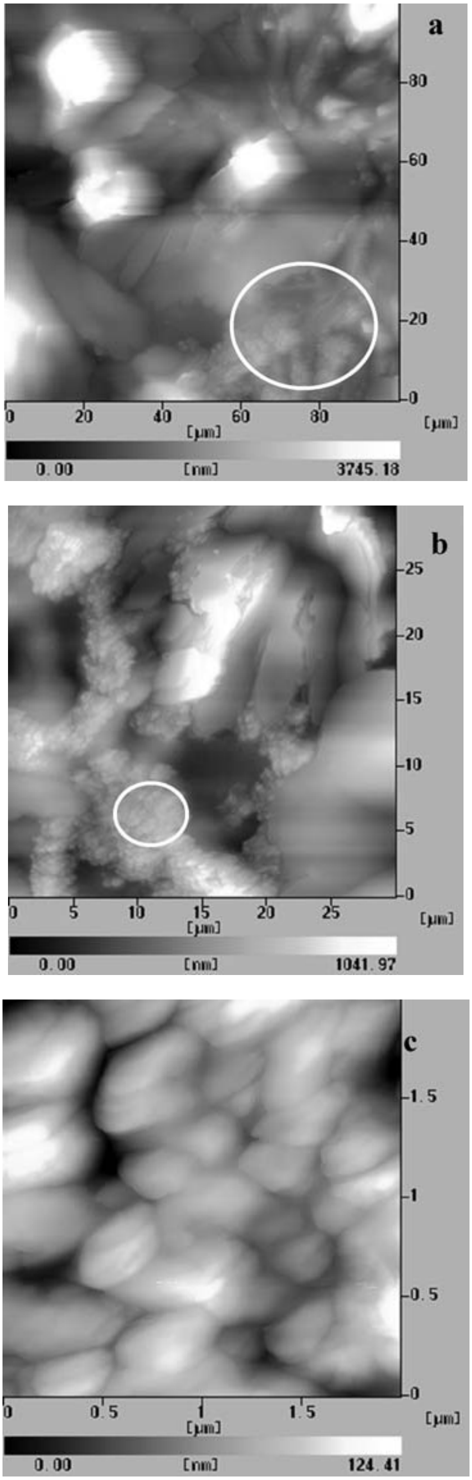
Table 3 shows the aging effect of 0.2 g·dL^{-1} PSA-BS1 and PSA-M2, in 0.137 mol·L^{-1} NaCl solution saturated with oxygen, at 80 °C. After aging for 90 days at 80 °C, the viscosity retention ratio of a PSA-BS1 brine solution is 49.2%, which is higher than that (22.2%) of 0.15 g·dL^{-1} for poly (acrylamide/N-(4-butyl)phenyl acrylamide) in 0.256 mol·L^{-1} NaCl solution after aging for 7 days at 80 °C [18]. This result shows that the anti-aging property of the polymer is good in brine solution at 80 °C because of the incorporation of BST into the copolymer chains. The rigid phenyl groups of BST are linked directly to main chains that can stabilize the hydrophobic units and effectively interfere with the hydrolysis of amido groups in the polymers. This aging result is consistent with the DSC and TG results.

4 The Associating Microstructure of PSA in Solutions

4.1 Aggregation in Aqueous Solutions

The aggregation morphology of a 0.4 g·dL^{-1} PSA-BS1 aqueous solution is shown in Fig. 12, where (a) is locally enlarged to obtain (b), which is then locally enlarged to form (c). Numerous aggregates with different shapes and sizes are formed via intermolecular hydrophobic associations, and small compact aggregates associate with each other through van der Waals interactions and hydrogen bonding. These results indicate that there is a heterogeneous distribution of the hydrophobic groups in the copolymer molecules, and that small compact

Fig. 12 AFM images of 0.4 g·dL^{-1} PSA-BS1 in aqueous solution: (**a**) two-dimension image; (**b**) local enlarged image of (**a**); (**c**) local enlarged image of (**b**)



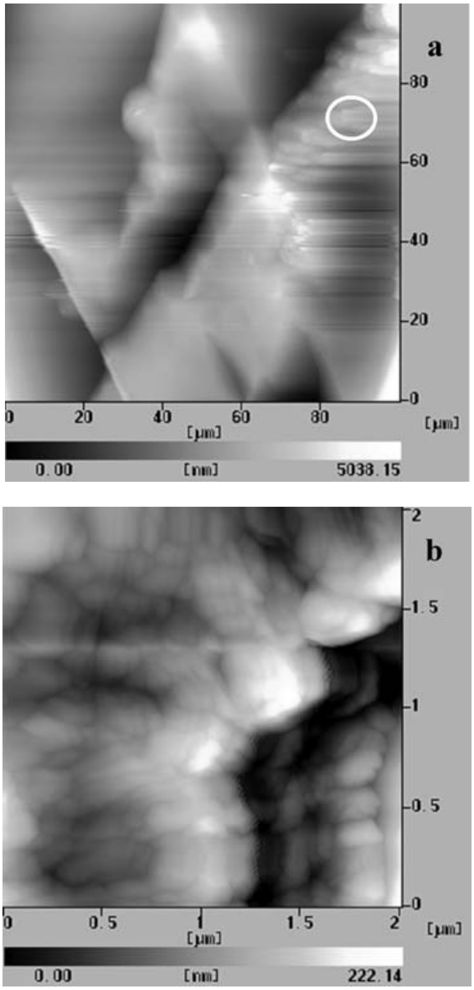


Fig. 13 AFM image of 0.4 g·dL^{-1} PSA-BS1 in a 0.034 mol·L^{-1} NaCl solution: (**a**) two-dimension image; (**b**) local enlarged image of the top section in (**a**); (**c**) local enlarged image of the right section in (**a**)

aggregates are formed by the polymer chains with more hydrophobic groups. Although the intermolecular hydrophobic associations of (4-butyl)phenyl groups are strong, continuous three-dimensional network structures are not observed in Fig. 12. This is attributed to there being no ionic groups to extend the molecules in nonionic polymer chains, leading to a coiled molecular conformation.

4.2 Aggregation in Brine Solutions

As shown in Fig. 13 for 0.4 g·dL^{-1} PSA-BS1 in a 0.034 mol·L^{-1} NaCl solution, larger associative blocks are formed by the addition of a small amount of salt, resulting in an increase of the solution viscosity. In addition, a small amount of more compact aggregates with smaller sizes are exhibited in Fig. 13b, resulting from the formation of more condensed hydrophobic micro domains. As observed in Fig. 14, when increasing the NaCl concentration from 0.034 to 0.513 mol·L^{-1}, the polymer morphologies change from huge blocks to small compact aggregates that associate to form gels. The results indicate that when the polarity of a brine

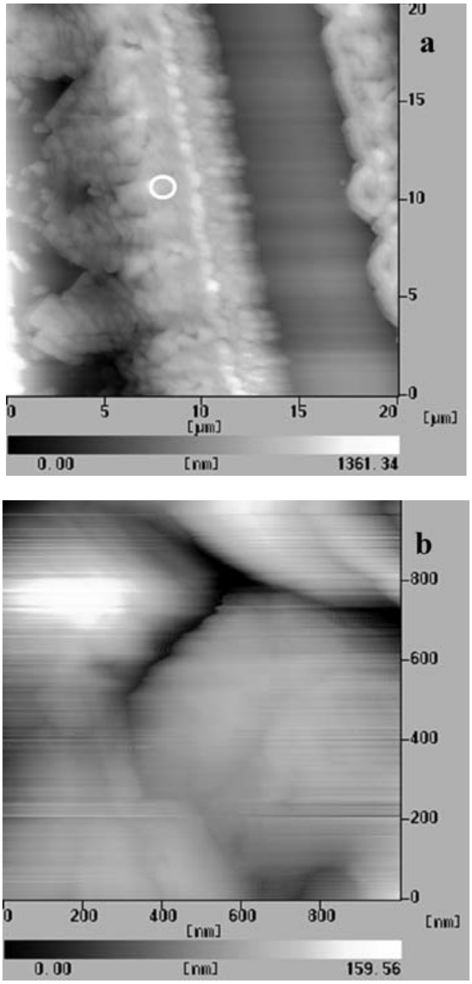


Fig. 14 AFM images of 0.4 g·dL^{-1} PSA-BS1 in a 0.513 mol·L^{-1} NaCl solution: (**a**) two-dimension image; (**b**) local enlarged image of (**a**)

solution is large, intermolecular associations of hydrophobic groups are strong enough to result in the phase separation of gels and the decrease in apparent viscosity. The AFM result is in good agreement with the plot of the apparent viscosity versus the NaCl concentration.

5 Conclusions

Hydrophobic acrylamide-modified copolymers (PSA) with 4-butylstyrene (BST) were synthesized by the micellar copolymerization technique. The block structures of PSA were conveniently measured by DSC, indicating that the incorporation of BST enhances molecular rigidity. TG analysis shows that the initial decomposition temperature of PSA is 234 °C, higher than that of the homo-polyacrylamide, suggesting that the copolymer has better thermal stability than homo-polyacrylamide. The amount of BST remarkably affects the apparent viscosity of PSA solutions because of strong intermolecular hydrophobic associations, and with increasing concentration of polymer with the optimum BST content, the solution viscosities increase dramatically in aqueous and brine solutions above C_p^* despite the low molecular weight of PSA. The polymer exhibits good salt-thickening behavior below a NaCl concentration of 0.137 mol·L^{-1}, temperature-thickening, thixotropy, pseudo-plastic behavior, and anti-shearing. The solution viscosities of the polymers increase, apparently through the crosslinking of a small amount of surfactant with the hydrophobic groups. The PSA polymer with a rigid benzene ring shows good anti-aging property in brine solutions at 80 °C, which is consistent with the DSC and TG results. AFM measurements show that large block-like aggregates are formed in an aqueous solution of 0.4 g·dL^{-1} PSA. The microstructures of the polymer become much larger by addition of small amounts of salt, resulting in an increase in solution viscosity. However, by addition of larger amounts of NaCl, small compact aggregates are formed and phase separation of gels occurs, leading to the decrease of the apparent viscosity. The AFM results reveal the relationship between associating microstructure and thickening property of the polymer solutions.

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