

Solution Properties of Ionic Hydrophobically Associating Polyacrylamide with an Arylalkyl Group

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ABSTRACT: Copolymers of acrylamide, 2-acrylamide-2-methylpropanesulfate (AMPS), and hydrophobic monomer *N*-arylalkylacrylamide (BAAM) were synthesized by free-radical micellar copolymerization. The effects of the copolymer, BAAM, AMPS, and NaCl concentrations and the pH value on the apparent viscosity of the copolymers were studied. The solution viscosities increased sharply when the copolymer concentration was higher than the critical associating concentration. The apparent viscosities of aqueous solutions of poly(*N*-arylalkylacrylamide-*co*-acrylamide-*co*-2-acrylamide-2-methylpropanesulfate) (PBAMS) increased with increasing BAAM and AMPS concentrations. PBAMS exhibited good salt resistance. With increasing pH, the apparent viscosities first increased and then decreased. Dilute

PBAMS solutions exhibited Newtonian behavior, whereas semidilute aqueous and salt solutions exhibited shear-thickening behavior at a lower shear rate and pseudoplastic behavior at a higher rate. Upon the removal of shear, the aqueous solution viscosities recovered and became even greater than the original viscosity, but the salt solution viscosities could not recover instantaneously. The elastic properties of PBAMS solutions were more dominant than the viscous properties, and this suggested a significant buildup of a network structure. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 316–321, 2005

Key words: polyelectrolytes; solution properties; viscosity; water-soluble polymers

INTRODUCTION

Hydrophobically associating water-soluble polymers (HAWSPs) are synthetic water-soluble polymers containing a small proportion of hydrophobic groups, usually in the form of pendent side chains or terminal groups, and they are attracting increasing interest for a wide variety of industrial applications, such as flocculants, thickening agents in oil recovery, latex paints, and cosmetics, because of the advantages of the polyelectrolytes and hydrophobic groups.^{1–11} In aqueous solutions, the hydrophobic groups aggregate to minimize their exposure to water and, therefore, form intermolecular or intramolecular associations, which result in the formation of hydrophobic microdomains. Above a certain polymer concentration (C_p^*), intermolecular hydrophobic interactions lead to the formation of a three-dimensional network of polymer chains, and this results in a rapid increase in the apparent viscosity.

The addition of salt enhances this interaction because of the increased polarity of the solvent, and so this kind of polymer exhibits good salt tolerance.^{12–14} Upon elevated shear action, the polymer network structures are disrupted. However, the associations between the polymer chains re-form, and the viscosity returns to its initial value. Consequently, irreversible mechanical degradation characteristic of high-molecular-weight polymers in high-shear applications can be avoided.^{15–17}

Until now, however, HAWSPs have not been applied widely. Many problems in their synthesis and performance have limited their usage. For example, C_p^* is too high, and the viscosities below C_p^* are not high enough to be used in practice. At high temperatures, the viscosities decrease because of the existence of weak bonds in the polymer chemical structure, which result in the breakage of hydrophobic side chains from the polymer backbone.¹⁴

Micellar copolymerization is the most convenient way of ensuring the solubilization of the hydrophobic monomer within the surfactant micelles and the copolymerization occurring in the continuous water medium.^{18–21} The most commonly used hydrophobic monomers are *n*-alkyl series, such as *N*-alkylacrylamide, *n*-alkyl(meth)acrylate, poly[ethoxy alkyl(meth)acrylate], and vinyl alkylates.^{7,9,14,16,20–22} Stud-

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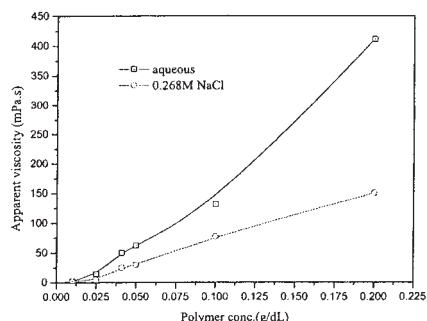


Figure 1 Apparent viscosity of PBAMS solutions as a function of C_p .

ies on hydrophobic monomers containing aryl groups are rare.^{18,23–25} Phenyl groups are well known to induce van der Waals interactions because of their planar and polarizable structure, and so the incorporation of an aromatic group into hydrophobic groups can stabilize the hydrophobic associations involved with alkyl chains. Furthermore, phenyl groups can act as spacers, increasing the rigidity of the structure.²¹ The UV-active property of aryl groups can also be used to characterize the microstructures of copolymers and the concentration of hydrophobes in copolymers.^{4,25} To enhance dissolution and provide potential tolerance to salt and pH changes, ionic monomers,^{26,27} such as carboxylate and sulfonate monomers, have been added to the molecular structures of HAWSPs, and they exhibit excellent viscosification effects in both aqueous and salt solutions.

In this study, we examined the solution behavior of copolymers of acrylamide (AM), 2-acrylamide-2-methylpropanesulfate (AMPS), and hydrophobic monomer *N*-aryllalkylacrylamide (BAAM); they were prepared by free-radical micellar copolymerization. The solution behavior of the polymers was examined as a function of the polymer concentration (C_p), BAAM, AMPS, and salt concentrations, pH, and shearing. The linear viscoelastic properties and dilute solution properties were also studied.

EXPERIMENTAL

Materials and sample preparation

AM was recrystallized twice from CHCl_3 . AMPS was obtained from Lubrizol Co. and was recrystallized twice from a mixture of methanol and 2-propanol. BAAM was synthesized through the reaction of 4-alkylaniline (purchased from Aldrich Co. and redistilled at 133–134°C and 14 mmHg) with acryloyl chloride (self-produced and vacuum-distilled at 30–32°C and 140 mmHg) in *n*-hexane. Ammonium persulfate and sodium bisulfite were recrystallized from deionized water. Other analytically pure agents were used without further purification.

The copolymers of AM, AMPS, and BAAM [poly(*N*-aryllalkylacrylamide-*co*-acrylamide-*co*-2-acrylamide-2-methylpropanesulfate) (PBAMS)] were prepared by micellar copolymerization^{18,19} with sodium dodecyl sulfate (SDS) as the surfactant and ammonium persulfate/sodium bisulfite as the redox free-radical initiator. Each reaction was conducted in a 100-mL, three-necked, round flask equipped with a mechanical stirrer and nitrogen inlet and outlet. First, AMPS was added to the reaction flask and dissolved in double-distilled water (the pH value was adjusted to 8–9). Then, AM, SDS, and BAAM were added. The mixture was stirred under N_2 until a clear, homogeneous mixture was observed. The total monomer concentration in water was constant at 10 g/dL, and the initiator concentration was 0.1% (w/w) with respect to the monomer feed. After the addition of the initiator, the polymerization was conducted at 30°C for 12 h, and it was followed by the dilution of the mixtures with water and precipitation into excess acetone. The polymers were washed with acetone and extracted with ethanol overnight for the removal of all traces of the water, surfactant, and residual monomer before they were dried under reduced pressure at room temperature for 24 h.

All aqueous solutions were made in double-distilled water. Salt solutions were made by the direct addition of quantitative solid NaCl into aqueous solutions. All

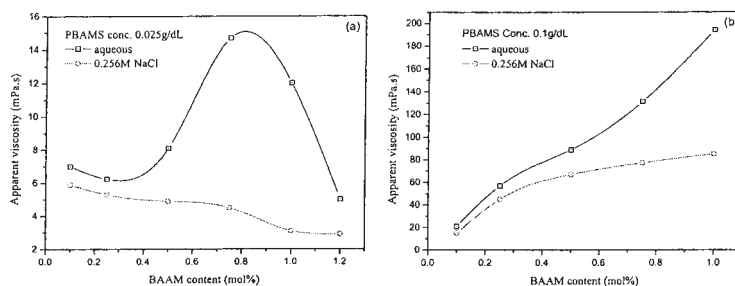


Figure 2 Apparent viscosity of PBAMS solutions as a function of the concentration of hydrophobic monomer BAAM for different solution systems.

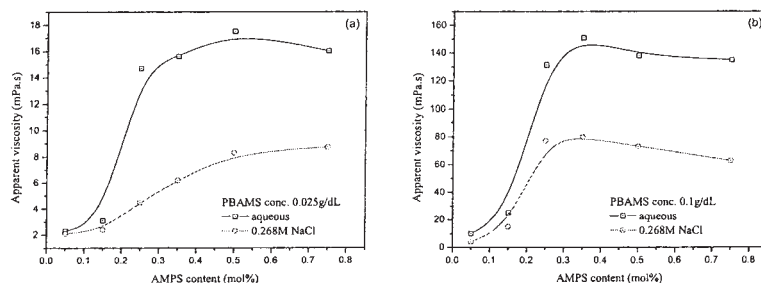


Figure 3 Apparent viscosity as a function of the concentration of ionic monomer AMPS for different solution systems.

solutions were gently shaken with an orbital shaker for at least 5 days before the measurements.

Measurements

The apparent viscosities were measured with an NXE-1 cone-plate viscometer (Thermo Electron Co., Karlsruhe, Germany) at a shear rate of 7.68 s^{-1} . Shearing testes were conducted with a Haake CV20N/RV20 rotational rheometer (CV20 system and PK45-4.0 spindles) (Chengdu Instrument Factory, Sichuan, China), and the shear rate range was $0\text{--}200 \text{ s}^{-1}$. The data were processed with Haake Rotation ROT 2.4 software. All viscosities were measured at $25 \pm 0.1^\circ\text{C}$ without special statement. The linear viscoelastic properties were measured with the same Haake rheometer, and the software was Haake Oscillation OSC 2.0.

The intrinsic viscosities were measured with a 0.6-mm Ubbelohde capillary viscometer at $30.0 \pm 0.1^\circ\text{C}$. The kinetic energy and shear rate were negligible. The density of the solutions was thought to be approximately the same as that of pure water. All solutions were filtered with a sand filter and kept overnight before the measurements.

RESULTS AND DISCUSSION

C_p

Figure 1 shows the relationship between the PBAMS concentration and the apparent viscosities of both

aqueous and 0.268 mol/L NaCl solutions. In both cases, almost the same solution behavior was observed. The solution viscosities increased with increasing C_p , especially above C_p^* , which corresponded to the formation of three-dimensional networks in solution. The C_p^* value was very low, and this meant that the intermolecular hydrophobic association could occur at very low concentrations. This was due to the introduction of ionic groups and, therefore, the electrostatic repulsion force. The results showed that the PBAMS copolymers had very good viscosification capacity and efficiency in comparison with similar copolymers without the AMPS unit.²⁸

Hydrophobic group concentration

The effects of the BAAM concentration on the apparent viscosities of aqueous and NaCl solutions were related to C_p (see Fig. 2). The apparent viscosities of PBAMS aqueous solutions increased with increasing BAAM concentration both at lower C_p values ($C_p < C_p^*$) and at higher C_p values ($C_p > C_p^*$). However, the apparent viscosities of the PBAMS NaCl solutions decreased little ($C_p < C_p^*$) or increased little ($C_p > C_p^*$) with increasing BAAM concentration. There existed a hydrophobic association effect and an electrostatic repulsion effect simultaneously inside the macromolecules. With increasing BAAM concentration, the hydrophobic association effect was reinforced, and the

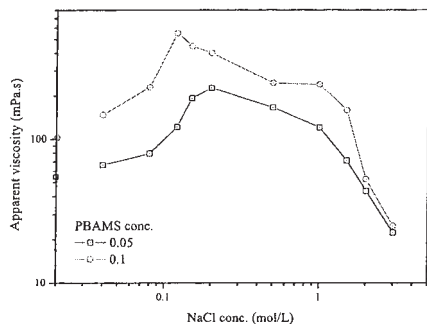


Figure 4 Apparent viscosity of PBAMS solutions as a function of the NaCl concentration.

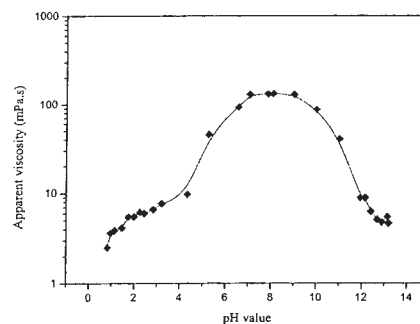


Figure 5 Apparent viscosity of PBAMS solutions as a function of the pH value.

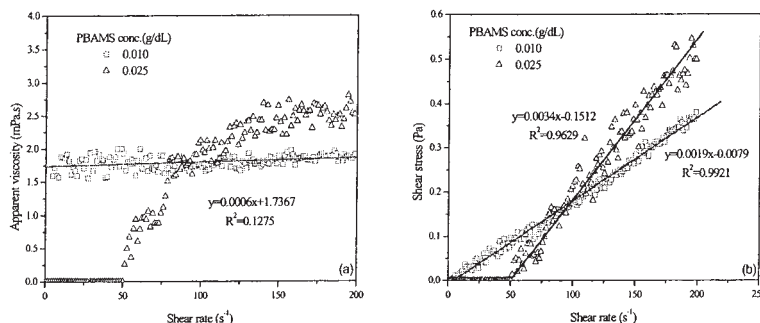


Figure 6 (a) Apparent viscosity and (b) shear stress of dilute PBAMS aqueous solutions as a function of the shear rate.

intermolecular association increased, so the apparent viscosities increased. The addition of NaCl shielded the electrostatic repulsion effect and reinforced the hydrophobic association which can be formed by the hydrophobes both inside a same macromolecules (intramolecular association) and in the different macromolecules (intermolecular association); therefore, the viscosities of dilute NaCl solutions decreased, and those of semidilute solutions increased slowly. Too much incorporation of hydrophobic monomer BAAM into the water-soluble polymers reduced the solubility of the polymers in water.^{29,30} PBAMS copolymers did not dissolve when the BAAM concentration was greater than 1.2 mol %.

Ionic group concentration

The incorporation of ionic groups into polymer chains enhances the solubility of terpolymers, and the electrostatic repulsion of ionic groups results in chain expansion, which may favor the intermolecular associations of hydrophobic groups. This is called a synergistic effect.³¹ As shown in Figure 3, the apparent viscosities of PBAMS aqueous and NaCl solutions increased with increasing AMPS concentration, but a greater concentration did not result in increased apparent viscosities.

Inorganic salt (NaCl)

The effect of NaCl on the apparent viscosities of PBAMS aqueous solutions was investigated and is shown in Figure 4. The viscosities of the polymer solutions increased with increasing NaCl concentration in the range of 0–0.2 mol/L, slightly decreased at concentrations of 0.2–1.0 mol/L, and then sharply decreased. The addition of salt enhanced the intermolecular association because of the increased polarity of the solvent. On the other hand, the strong polarity shielded the intermolecular repulsion and made the polymer molecule contract. These increases were attributed to the increase in the polarity of the solvent induced by electrolytes. These two effects competed with each other, so these polymers exhibited good salt resistance.

pH value

As shown in Figure 5, as the pH value of polymer solutions increased, the apparent viscosities first increased and then decreased. The solutions could have very good viscosities. At a lower pH, the sulfate groups of AMPS units existed as an acid type. With increasing pH, the sulfate groups ionized slowly, and the electrostatic repulsion effect appeared to lead to an expansion of polymer chains and an increase in the

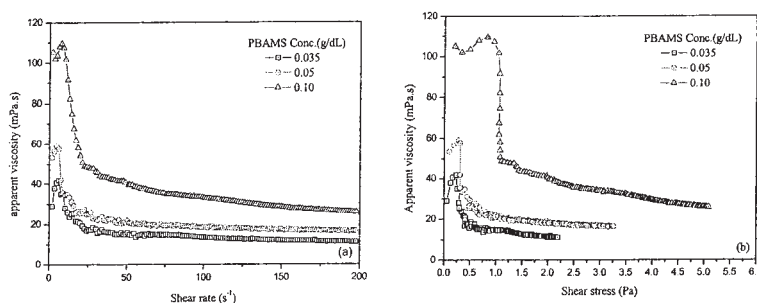


Figure 7 Shear viscosity of PBAMS aqueous solutions with different C_p values (a) as a function of the shear rate and (b) as a function of the shear stress.

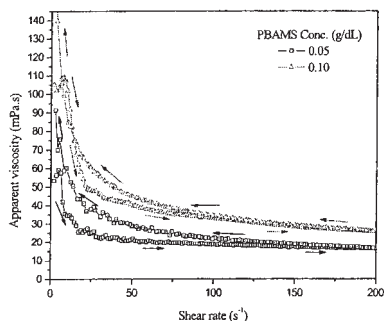


Figure 8 Effect of one cycle of the shear rate on the apparent viscosity of PBAMS aqueous solutions with different C_p values.

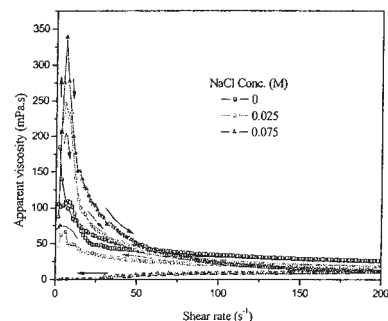


Figure 10 Effect of one cycle of the shear rate on the apparent viscosity of 0.15 g/dL PBAMS solutions with different NaCl concentrations.

solution viscosities. However, excessive Na^+ and OH^- shielded the repulsion and destroyed the intermolecular hydrophobic association, and this resulted in a reduction of the viscosities at a high pH value.

Shear effect

Figure 6 shows the effects of various shear rates on the shear viscosities and shear stress of dilute PBAMS aqueous solutions with two different concentrations. The 0.01 g/dL solution exhibited Newtonian behavior at all shear range. In Figure 6(b), the relationship between the shear rate and the shear stress is linear, and the slope of the line (1.9 mPa s) is near the viscosity (1.737 mPa s) in Figure 6(a). The behavior of the 0.025 g/dL solution is very interesting. Its viscosity and shear stress were zero at a low shear rate ($<51.42 \text{ s}^{-1}$) and then increased with an increasing shear rate; this may be due to the expansion of polymer chains under shearing.

The apparent viscosities of semidilute PBAMS aqueous solutions with different concentrations are shown in Figure 7(a,b) as a function of the shear rate and shear stress, respectively. The polymer solutions exhibited shear-thickening behavior at a lower shear rate and then pseudoplastic behavior at a higher rate; this is characteristic of associating polymers with a

comblike structure.^{32,33} The viscosity profiles of these solutions displayed one or more inflection points, which could be clearly discerned when plotted against the shear stress; this behavior is not usually observed in conventional entangled polymer systems. The decrease in the viscosity with increasing shear stress after a critical shear stress value was due to the disruption of the network junctions formed by the relatively weak hydrophobic interactions. The required critical stress depended on the strength of the associating hydrophobic junctions; the higher C_p was, the stronger the network was and the bigger the critical shear stress was. Surprisingly, upon the removal of shear, the solution viscosities recovered and were even greater than the original viscosity value (see Fig. 8). The results indicate that not only did the associations recover immediately after the removal of shear but the associations were also enhanced by the application of shear because of the increasing order of the hydrophobic microdomain and the longer distance hydrophobic associations.

The effect of shearing on the properties of PBAMS salt solutions is shown in Figure 9. The polymer salt solution still exhibited shear-thickening behavior at a lower shear rate and then shear-thinning behavior at a higher rate. The salt-thickening effect could also be seen from the low-shear-rate viscosity values. Unlike

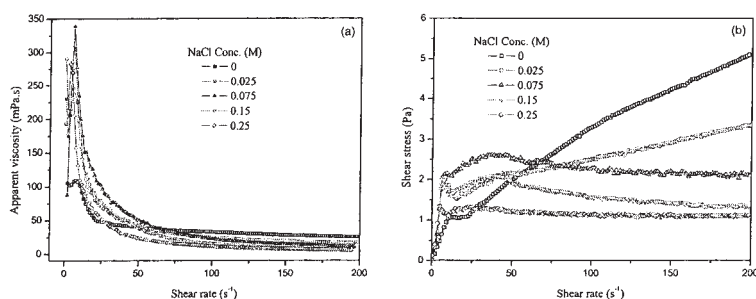


Figure 9 (a) Apparent viscosity and (b) shear stress as a function of the shear rate for 0.10 g/dL PBAMS solutions with different NaCl concentrations.

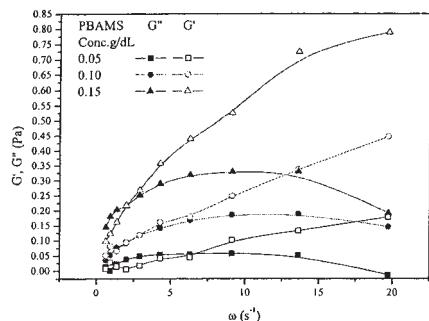


Figure 11 Effect of ω on the dynamic shear moduli of PBAMS aqueous solutions with different C_p values.

the linear increase in the shear stress of the PBAMS aqueous solution with increasing shear rate after the critical shear rate, the shear stress of the PBAMS salt solution decreased slowly when the NaCl concentration was greater than 0.075 mol/L. Because of the increasing polarity and shear force and the electrostatic shielding, the intermolecular hydrophobic domains were destroyed and changed into intramolecular associations; this resulted in the contraction of the polymer molecules and the reduction of the solution viscosities. When the shearing effect was removed, the solution viscosities could not recover instantaneously (see Fig. 10). The higher the NaCl concentration was, the more the viscosities were lost after shearing.

Linear viscoelastic properties

The relationship of the storage modulus (G') and the loss modulus (G'') of the PBAMS aqueous solutions with the angular frequency (ω) is shown in Figure 11. As ω increased, G' also increased, but G'' increased first and then decreased. In most cases, for these polymer solutions in a salt-free environment, the elastic properties were more dominant than the viscous properties; that is, G' was greater than G'' . This suggests that there was a significant buildup of a network structure, which was responsible for imparting significant elasticity to the polymer solutions. With increasing C_p , the G'/G'' ratio also increased, and this meant that stronger hydrophobic association junctions were formed. This resulted in the formation of stronger networks in the solutions.

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