

# Viscosity Behavior and Surface and Interfacial Activities of Hydrophobically Modified Water-Soluble Acrylamide/*N*-Phenyl Acrylamide Block Copolymers

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**ABSTRACT:** In this study, the viscosity behavior and surface and interfacial activities of associative water-soluble polymers, which were prepared by an aqueous micellar copolymerization technique from acrylamide and small amounts of *N*-phenyl acrylamide (1.5 and 5 mol %), were investigated under various conditions, including the polymer concentration, shear rate, temperature, and salinity. The copolymer solutions exhibited increased viscosity due to intermolecular hydrophobic associations, as the solution viscosity of the copolymers increased sharply with increasing polymer concentration, especially above a critical overlap concentration. An almost shear-rate-independent viscosity

(Newtonian plateau) was also displayed at high shear rates, and typical non-Newtonian shear-thinning behavior was exhibited at low shear rates and high temperatures. Furthermore, the copolymers exhibited high air-water and oil-water interfacial activities, as the surface and interfacial tensions decreased with increasing polymer concentration and salinity. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2290–2300, 2003

**Key words:** micelles; copolymerization; water-soluble polymers; viscosity; tension

## INTRODUCTION

In recent years, associative water-soluble copolymers, which are characterized by hydrophobic moieties, have become the subject of extensive research because of their interesting rheological features.<sup>1–21</sup> The non-ionic water-soluble copolymers of acrylamide, prepared with low amounts of a hydrophobic comonomer, constitute an important class of these associating polymers that have recently attracted a great deal of interest.<sup>10–25</sup> These mainly hydrophilic polymers contain a small portion of hydrophobic groups, usually as pendant side chains or terminal groups. When these polymers are dissolved in aqueous solutions, the hydrophobic groups aggregate to minimize their exposure to water in a fashion analogous to that of surfactants above a critical overlap concentration ( $C^*$ ). Therefore, the hydrophobic groups associate in polar solvents, and this results in a sharp increase in solution viscosity. Several rheological aspects of polyacrylamide systems have been reported.<sup>10,19–23,25</sup> However, there are few systematic investigations concerning other characteristic features, such as the surface and interfacial activities of these kinds of polymers. These

associative polymers can also exhibit high surface and interfacial activities simultaneously because of their amphiphilic structure (i.e., the presence of hydrophobic moieties in the mainly hydrophilic polymer chain).

Amphiphilic polymers form monomolecular or polymeric micelles in aqueous solutions in a fashion analogous to that of surfactants above  $C^*$ ,<sup>8,9,21</sup> therefore, they have an enhanced ability to adsorb at an interface, and this can lead to a sharp reduction in the surface tension (ST) and interfacial tension (IFT) of a polymer solution. This combination of rheological features (i.e., thickening properties) and surface and interfacial activities is of great technological interest, especially in a number of important commercial applications, such as enhanced oil recovery (EOR), drag reduction, flocculation, super absorbency, latex paints, hydraulic fluids, protein separation, industrial thickeners, controlled drug release, and biological and medical devices.<sup>1–7</sup> For example, in EOR, the basic idea behind these polymers is to increase the viscosity of the aqueous phase and consequently improve the sweep efficiency with high molecular weight polymers. However, the use of high molecular weight polymers could plug the formation and cause severe injection problems.<sup>8</sup>

The hydrophobically modified water-soluble acrylamide/*N*-phenyl acrylamide copolymers under investigation can exhibit thickening properties equivalent to those observed for higher molecular weight homopolymers because of their intermolecular hydro-

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phobic interaction in aqueous solutions, especially above  $C^*$ . This can include shear thinning or thixotropy. In this way, it is possible to avoid irreversible mechanical degradation, which can occur for very high molecular weight samples when they are subjected to high shear stresses.<sup>26</sup> Moreover, because of the nonpolyelectrolyte nature of these polymers, aqueous solutions of these hydrophobically associating polymers are less salt-sensitive.<sup>19,21</sup> The rheological behavior of these compounds is of great technological importance, especially in applications of water-based systems that involve viscosity control.<sup>27</sup>

In view of these expected features of the copolymers, there has been an increasing interest in the synthesis and solution properties of these copolymers, such as enhanced viscosity for mobility control and low IFT between water and oil in petroleum reservoirs for EOR operations. The synthesis, mechanism, and kinetics of the free-radical copolymerization of hydrophobically modified acrylamide block copolymers have been studied extensively.<sup>10–25</sup> Different hydrophobic groups have been incorporated into polyacrylamide with micellar copolymerization, and detailed studies on the mechanism of the reactions and the rheology of their aqueous solutions have been conducted.<sup>3–28</sup> The copolymers can be prepared by the micellar radical copolymerization of *N*-phenyl acrylamide in an aqueous solution of acrylamide to form a water-soluble copolymer. The technique has been shown to be well suited to the preparation of copolymers with high molecular weight, adequate hydrophobe incorporation, and improved thickening properties.<sup>23,28–36</sup>

In this article, the results of a more detailed investigation into the solution properties, such as the rheological behavior and surface and interfacial activities, of hydrophobically associated water-soluble copolymers of acrylamide and *N*-phenyl acrylamide (at 1.5 and 5 mol % incorporation of *N*-phenyl acrylamide) prepared by the micellar copolymerization technique are presented. To the best of our knowledge, the preparation and solution properties of this acrylamide/*N*-phenyl acrylamide block copolymer have never been studied and reported before. The solution viscosity behavior of the copolymers is discussed with respect to the polymer concentration, shear rate, temperature, and NaCl concentration. Furthermore, the ST and IFT behaviors of these polymers are also studied with respect to the copolymer and NaCl concentrations.

## EXPERIMENTAL

### Materials

The source and purification of the monomers and other reagents have been reported elsewhere.<sup>17–19</sup> *n*-Decane, used in the IFT measurements, had a purity of 99.6% and was supplied by BDH (UK). It was distilled

twice before use. Doubly distilled water was also used in the ST and IFT measurements.

### Polymerization

The comonomer *N*-phenyl acrylamide was prepared as described in the literature.<sup>26</sup> The acrylamide/*N*-phenyl acrylamide copolymer containing 5 mol % of the hydrophobic monomer was prepared as follows. An aqueous solution of acrylamide (10 g) in water (200 mL) was degassed with gentle bubbling of  $N_2$  for 30 min in a round-bottom flask covered with a septum cap. The surfactant, hexadecyl triethyl ammonium bromide (CTAB; 6 g), was added; this was followed by the injection of *N*-phenyl acrylamide (1.09 g; 5 mol %) into the mixture while stirring continued at 50°C until a clear solution was obtained. The polymerization was then initiated by the injection of a potassium persulfate solution ( $K_2S_2O_8$ ; 0.50 g), and the reaction mixture was stirred at 50°C for 42 h. The resulting polymer was precipitated by the slow pouring of the solution into stirred methanol (1 L). The polymer after filtration was again dissolved in water (180 mL) and reprecipitated in methanol (1 L). The process was repeated four times to remove traces of the surfactant. The polymer was then dried at 55–65°C under vacuum for approximately 8 h or until a constant weight of the polymer was obtained, and then it was kept in a desiccator. The yield of the reaction ranged between 55 and 79%.

The ratio of the monomers in the copolymer was determined by  $^1H$ -NMR spectroscopy. The NMR measurements were carried out with a JEOL LA 500-MHz spectrometer (Japan). With the integration of the aromatic proton signals (ca.  $\delta = 7$  ppm) and the aliphatic signals, the ratio was found to be almost identical to the feed ratio. The nine hydrogens of the three methyl groups of CTAB appeared as a sharp singlet at  $\delta = 3.13$  ppm in the  $^1H$ -NMR spectrum. The absence of this singlet ensured the complete removal of CTAB.

The aforementioned procedure was similarly applied for the preparation of the acrylamide/1.5 mol % *N*-phenyl acrylamide copolymer. Detailed reaction conditions and some characteristic data of the copolymers are given in Table I. The reaction scheme and molecular structures of the monomers and hydrophobically modified copolymer are depicted in Figure 1.

### Experimental measurements of the viscosity, ST, and IFT

Concentrated stock solutions containing 5 wt % copolymer were prepared at least 24 h before the solution measurements. The dissolution processes lasted 24 h. Final solutions of the desired composition were obtained by dilution of the appropriate stock solution with distilled water. Saline solutions were prepared by the dissolution of appropriate amounts of solid NaCl in the diluted polymer solution.

TABLE I  
Reaction Conditions and Some Characteristic Data of the Copolymers

| Comonomer (mole %) | Acrylamide (AA) (g) | Comonomer (g) | H <sub>2</sub> O (mL) | CTAB (g) | Potassium persulfate (PPS) (g) | CTAB acrylamide (w/w)% | PPS/AA (w/w)% | Reaction time (hr:min) | Yield (g) | Yield (%) |
|--------------------|---------------------|---------------|-----------------------|----------|--------------------------------|------------------------|---------------|------------------------|-----------|-----------|
| 5                  | 10                  | 1.090         | 200                   | 6        | 0.50                           | 60                     | 5.04          | 42:00                  | 6.10      | 55.00     |
| 1.5                | 10                  | 0.315         | 200                   | 8        | 1.28                           | 80                     | 12.8          | 8:00                   | 8.16      | 79.10     |

The solution viscosities of the copolymers (1.5 and 5 mol % of the acrylamide/*N*-phenyl acrylamide copolymer) were measured for different polymer concentrations and salinities with a Brookfield digital rotational viscometer (Middleboro, MA) with an SC4-18 spindle accessory at shear rates ranging from 0.4 to 79.4 s<sup>-1</sup> and at temperatures ranging from 25 to 90°C.

The air-water STs and oil (*n*-decane)/aqueous solution IFTs of the copolymers (i.e., copolymers of acrylamide and 5 mol % *N*-phenyl acrylamide) were determined for different polymer concentrations with the plate and ring methods, respectively, of a K12 processor tensiometer (Kruss, Germany). *n*-Decane was used as the oil phase. The IFTs of the *n*-decane/aqueous polymer (i.e., the copolymer of acrylamide and 1.5 mol % *N*-phenyl acrylamide) solution were measured for a polymer concentration of 2.0 wt % with NaCl salt concentrations ranging from 0.1 to 9.0 wt %. All ST and IFT measurements were performed at 25°C.

All the measurements were at least duplicated and sometime repeated three times. The results were reproducible to ±5% and are reported (Figs. 2–11) as the average values of these measurements with a standard deviation of ±5%.

## RESULTS AND DISCUSSION

The solution properties of the hydrophobically modified water-soluble acrylamide/*N*-phenyl acrylamide

copolymers were studied under different conditions as part of a continuing research program investigating the relationship between polymer structures and their solution viscosity behaviors and air-water and oil-water interfacial activities. These were investigated with the objective of designing polymers with optimized structures for high solution viscosity and high surface and interfacial activities for applications in areas such as EOR.

### Rheological behavior of the copolymers

Figures 2–7 show the effects of the polymer concentration, shear rate, and temperature on the solution viscosity of the hydrophobically modified copolymer of acrylamide and 5 mol % *N*-phenyl acrylamide. Figure 8 depicts the dependence of the NaCl concentration on the solution viscosity of the 1.5 mol % acrylamide/*N*-phenyl acrylamide copolymer.

As shown in Figure 2 for shear rates of 0.4 and 0.8 s<sup>-1</sup>, the hydrophobically modified polymer exhibited a slight increase in viscosity up to a polymer concentration of 1.5 wt % followed by a sharp increase in viscosity with increasing polymer concentration for the two low shear rates considered. *C*\* of the copolymer could clearly be observed between 1.5 and 2.0 wt % polymer concentrations. The remarkable increase in the viscosity, especially above the 1.5 wt % polymer concentration, was attributed to the strong and large

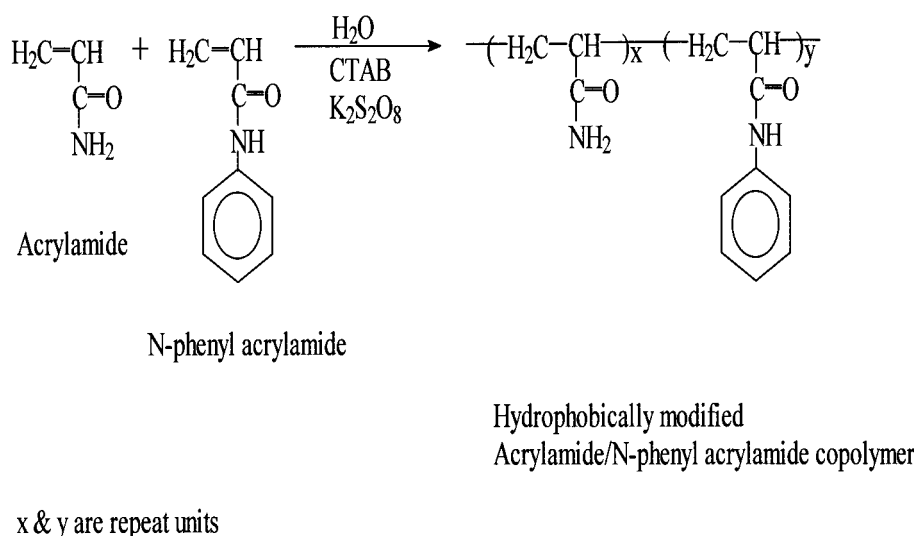
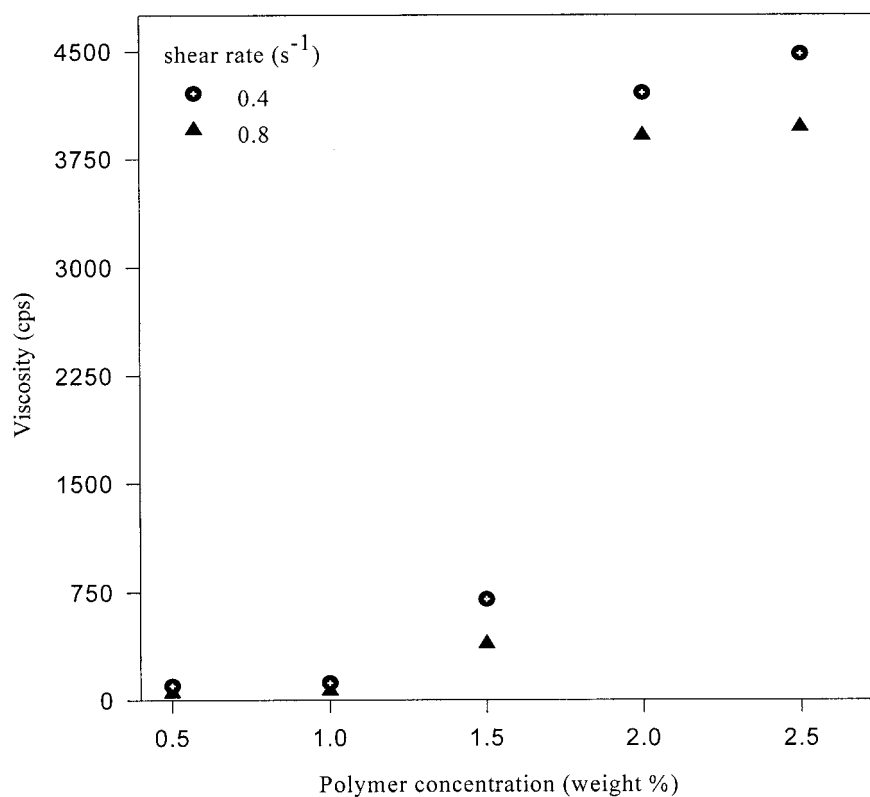
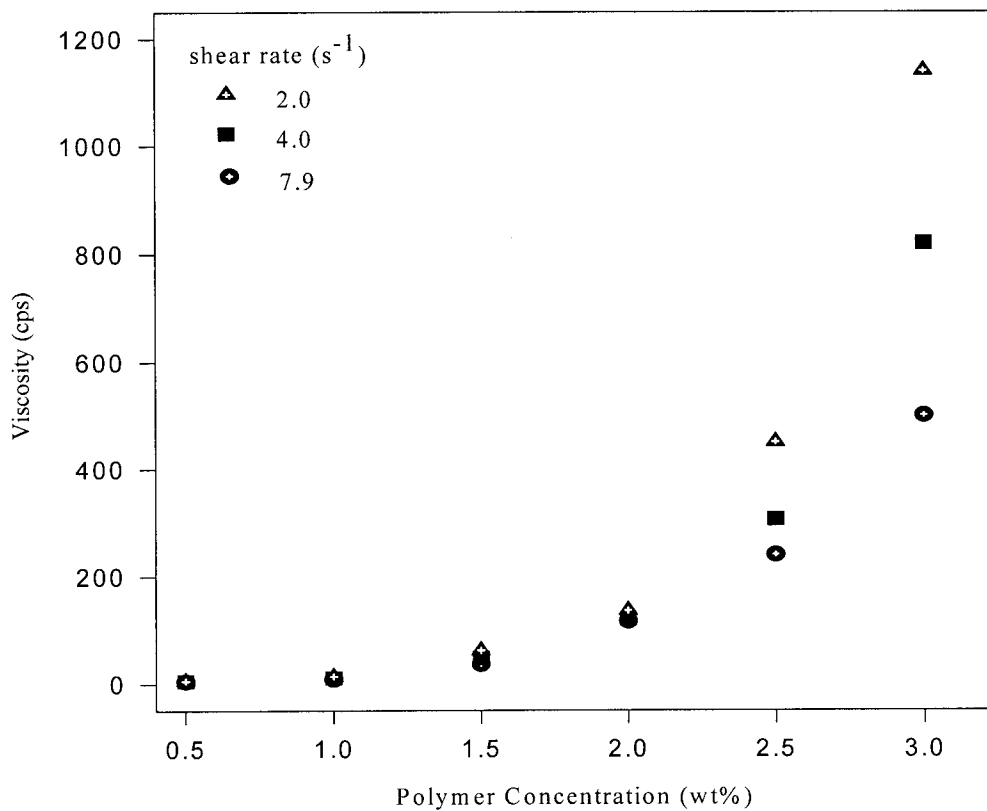


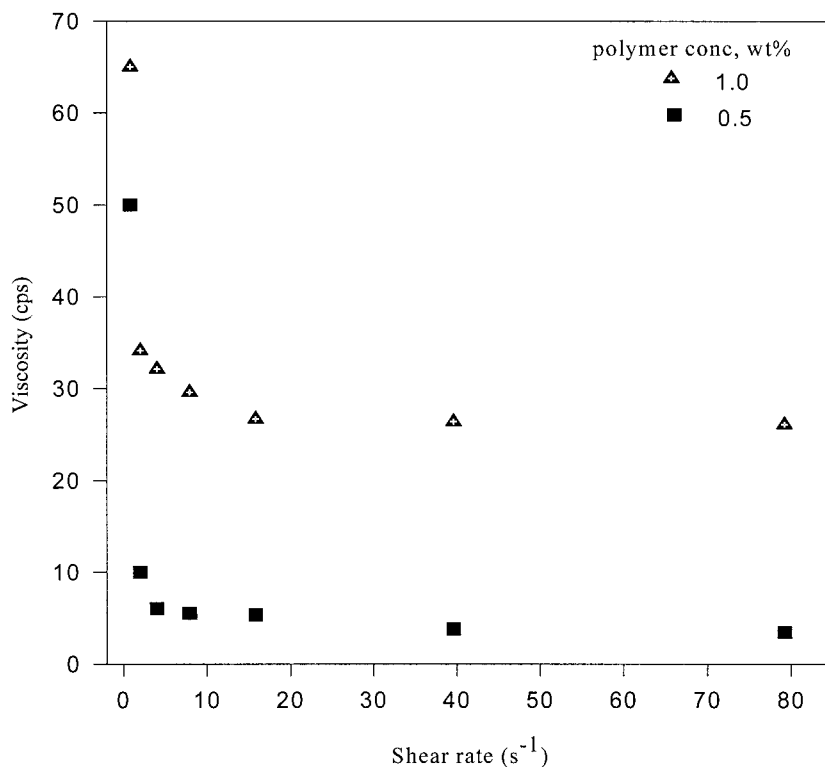
Figure 1 Reaction scheme and molecular structures of the monomers and hydrophobically modified copolymer.



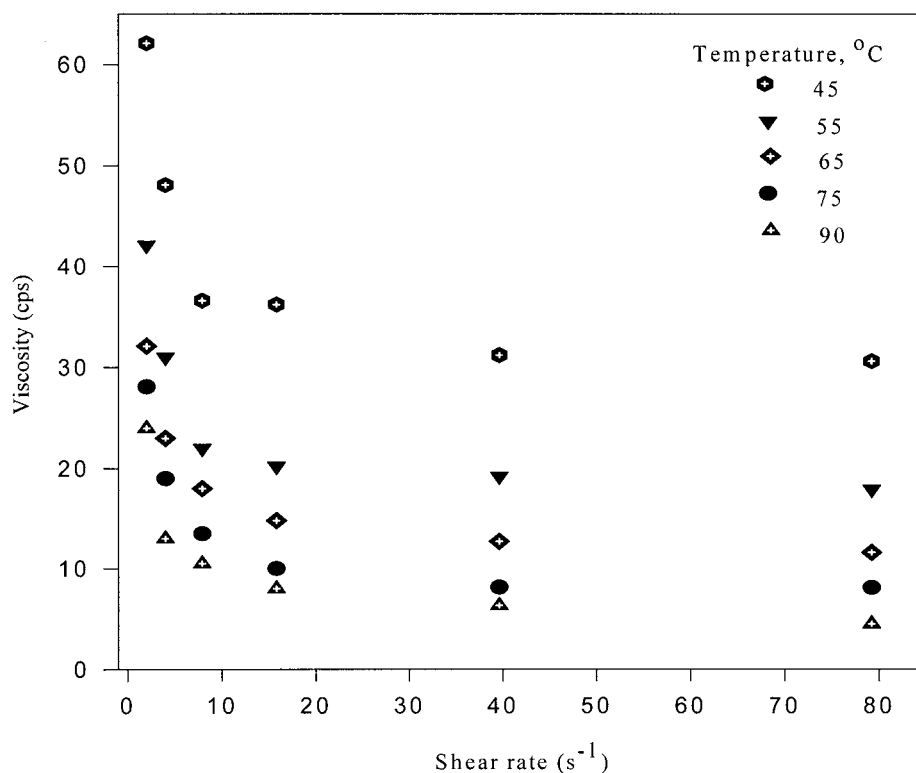
**Figure 2** Effect of the polymer concentration on the viscosity of the acrylamide/5 mol % *N*-phenyl acrylamide copolymer for two different shear rates at 25°C.



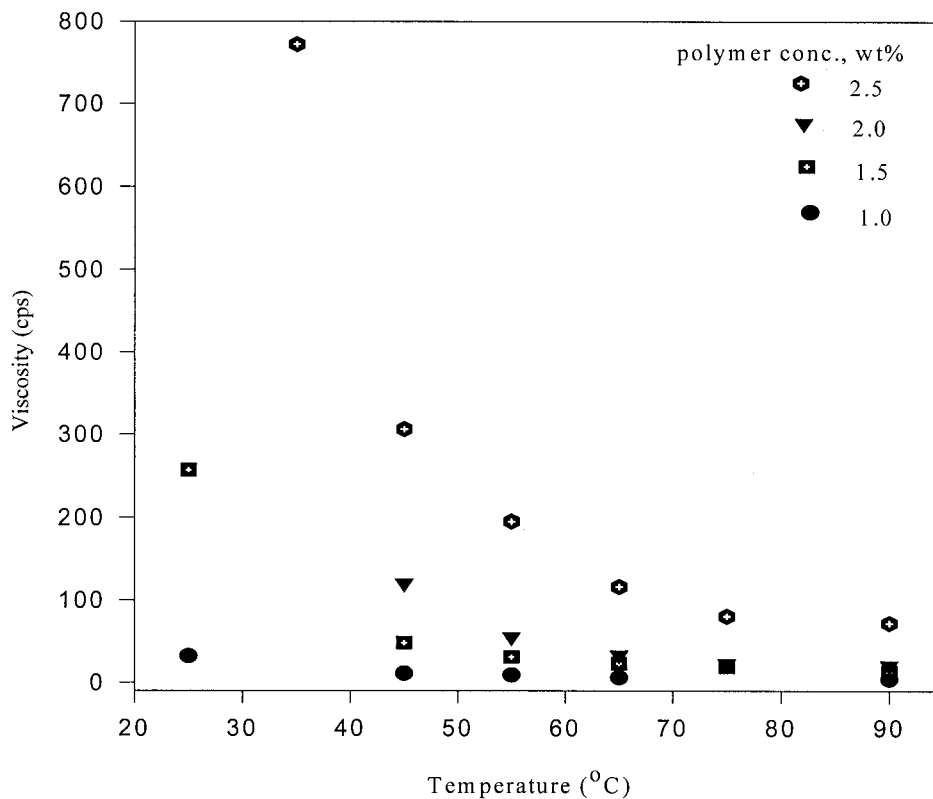
**Figure 3** Effect of the polymer concentration on the viscosity of the acrylamide/5 mol % *N*-phenyl acrylamide copolymer for three different shear rates at 25°C.



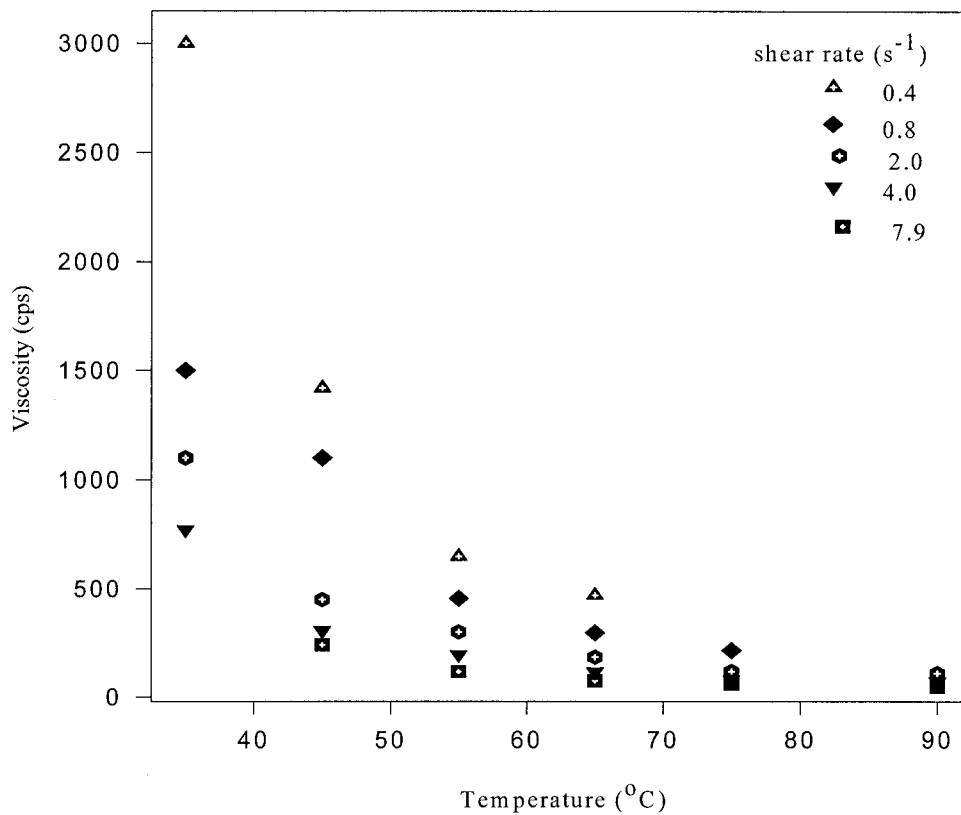
**Figure 4** Variations of the viscosity of the acrylamide/5 mol % *N*-phenyl acrylamide copolymer with the shear rate for two different polymer concentrations at 25°C.



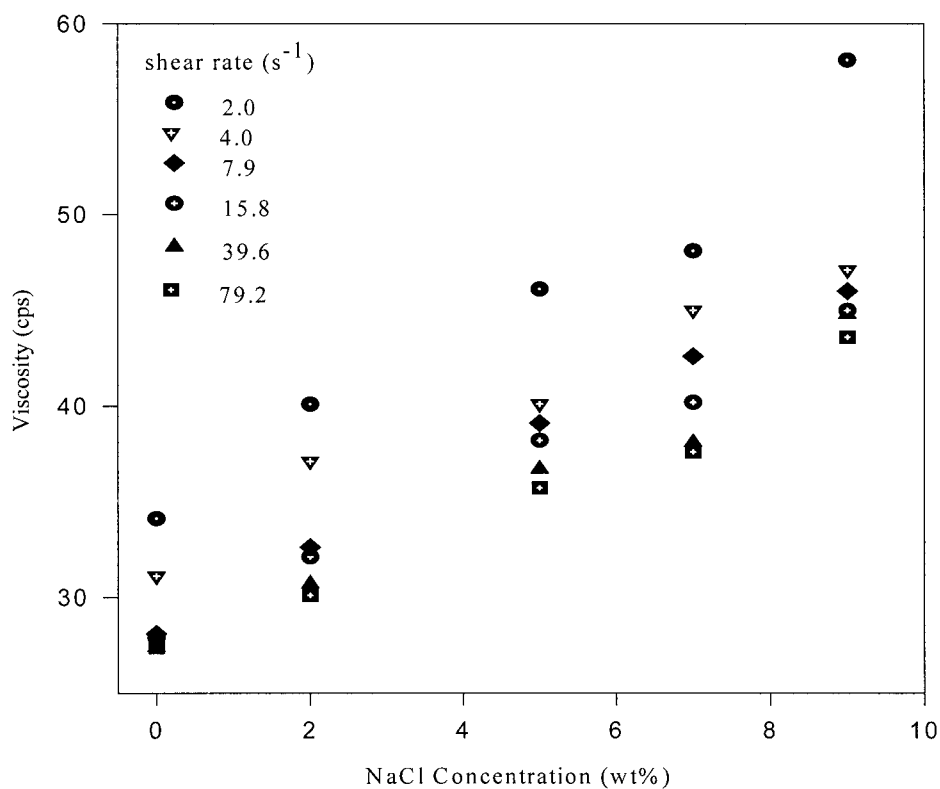
**Figure 5** Variations of the viscosity of the acrylamide/5 mol % *N*-phenyl acrylamide copolymer with the shear rate for various temperatures and for a polymer concentration of 1.5 wt %.



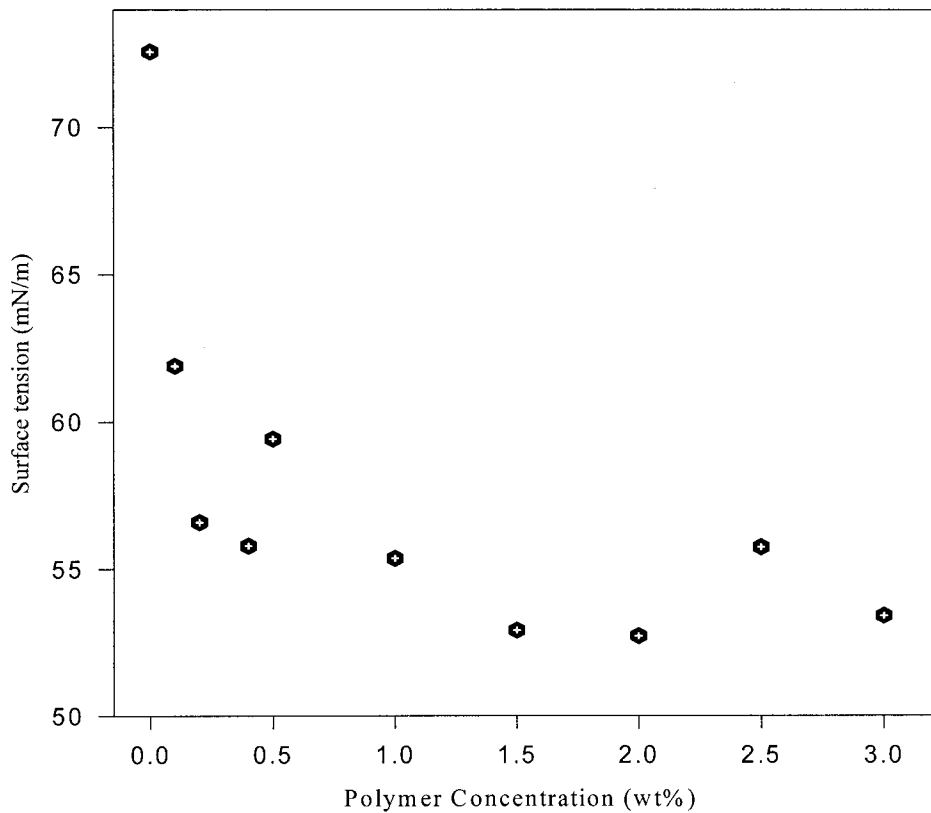
**Figure 6** Effect of the temperature on the viscosity of the acrylamide/5 mol % *N*-phenyl acrylamide copolymer for various polymer concentrations at a shear rate of  $4.0 \text{ s}^{-1}$ .



**Figure 7** Effect of the temperature on the viscosity of the acrylamide/5 mol % *N*-phenyl acrylamide copolymer for various shear rates and for a polymer concentration of 2.5 wt %.



**Figure 8** Effect of the NaCl salt concentration on the viscosity of the acrylamide/1.5 mol % *N*-phenyl acrylamide copolymer for various shear rates at 25°C.



**Figure 9** ST versus the polymer concentration for the acrylamide/5 mol % *N*-phenyl acrylamide copolymer at 25°C.

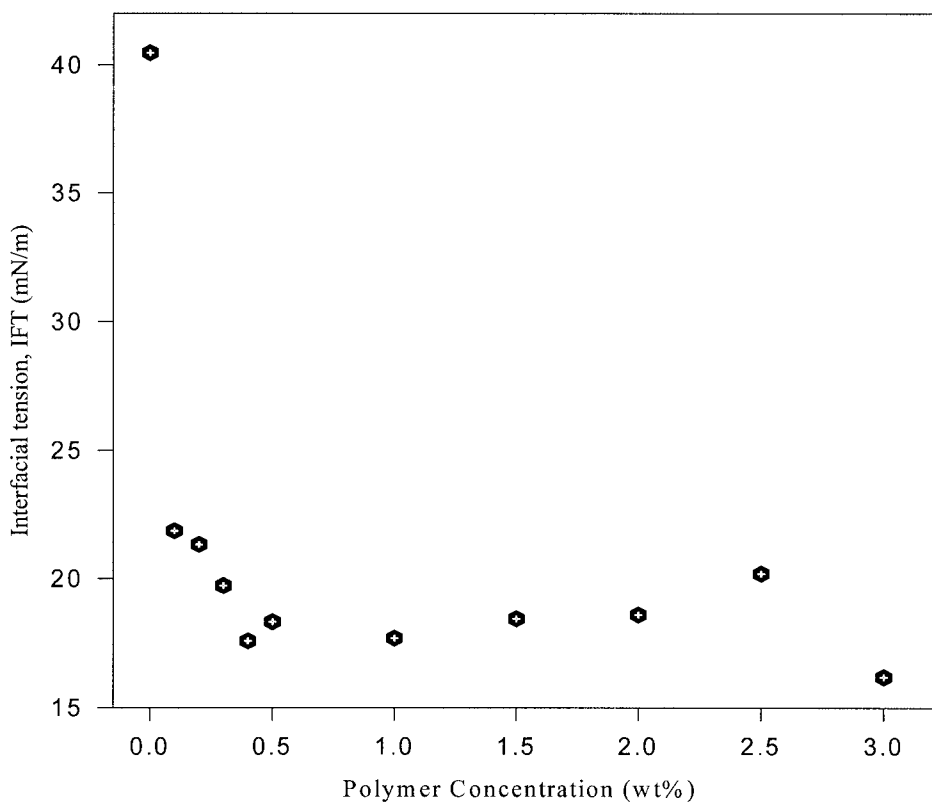


Figure 10 IFT versus the polymer concentration for the acrylamide/5 mol % *N*-phenyl acrylamide copolymer at 25°C.

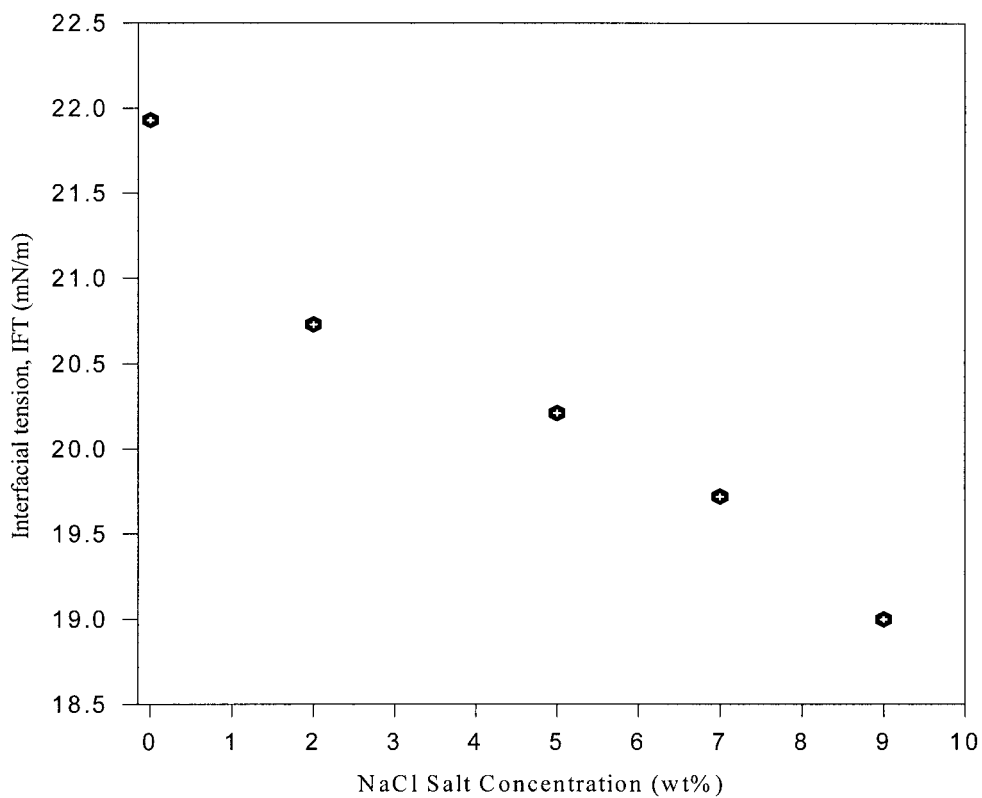


Figure 11 IFT versus the NaCl salt concentration of the 1.5 mol % acrylamide/*N*-phenyl acrylamide copolymer for a polymer concentration of 2.0 wt % at 25°C.



number of intermolecular associations, which gave rise to a network structure of polymer chains. However, below this concentration, intramolecular associations were dominant in comparison with intermolecular associations. For somewhat higher shear rates (i.e., 2.0, 4.0, and 7.9 s<sup>-1</sup>), as shown in Figure 3, a dramatic increase in the viscosity was observed with increasing polymer concentration. However, C\* shifted to higher concentrations with an increasing shear rate. These observations are similar to those frequently observed for hydrophobically modified associative polymers.<sup>1-13,22,26-29,32,36</sup> This behavior, which was anticipated, was probably due to the strong interchain associations forming large aggregates as the polymer concentration increased. At low polymer concentrations, the hydrophobic chains had little chance of interacting intermolecularly with one another, and this led to the formation of small aggregates with a small hydrodynamic volume. However, as the polymer concentration was increased (i.e., above a certain concentration), hydrophobic intermolecular associations were more probable, giving rise to a network structure of polymer chains with large hydrodynamic volumes and, consequently, high solution viscosity. These network structures contributed significantly to the thickening behavior of this associative polymer. Intermolecular aggregates broke under higher shear rates, and this resulted in the shift in the observed C\* values to higher polymer concentrations.

For the copolymer, an almost shear-rate-independent viscosity (Newtonian plateau) was observed at high shear rates, as shown in Figure 4, for polymer concentrations of 0.5 and 1.0 wt % and, as shown in Figure 5, for temperature ranging from 45 to 90°C. However, a sharp decrease in the viscosity with the shear rate (typical shear-thinning behavior) was observed at low shear rates, as shown in the same figures. The shear-thinning behavior could be attributed to the disorientation and disentanglement of the macromolecular chains under high shear, which corresponded to the progressive rupture of the intermolecular associations with an increasing shear rate. The development of the viscosity behavior for associative polymers such as the one under investigation relies on an increase in the apparent macromolecular aggregation among hydrophobic groups (moieties) with increasing polymer concentration. Under high shear conditions, the hydrophobic interactions can be disrupted, and this gives rise to decrease in the apparent molecular weight and, therefore, a decrease in the solution viscosity. However, under low-shear conditions, the hydrophobic interchain associations will reform, restoring the high solution viscosity.<sup>19,22,28-30,32,36</sup> A similar relationship between the viscosity and temperature can be observed in Figure 5. At low temperatures, a sharp decrease in the viscosity was initially observed at

low shear rates, and this indicated that intermolecular assemblies formed at low temperatures were disturbed by the high shear. Increasing the temperature resulted in the rupture of the intermolecular aggregates, which led to the less pronounced effect of the shear rate observed at high temperatures on the viscosity.

Figures 6 and 7 depict the effect of temperature on the solution viscosity of the copolymer for different polymer concentrations and shear rates, respectively. As expected, a sharp decrease in the viscosity was observed with increasing temperature, especially at high polymer concentrations and low shear rates. The decline in viscosity with temperature was less pronounced at low polymer concentrations and high shear rates. The lowering of the solution viscosity with increasing temperature has been reported for aqueous solutions of hydrophobically associating water-soluble polymers.<sup>19,21,22,28,32</sup> This behavior could be attributed to the weakening of the hydrophobic effect at elevated temperatures due to the increased mobility of the polymer chains (as a result of a decrease in the solvent viscosity); it gave rise to a loss of interchain liaisons and/or an increase in the copolymer solubility as the temperature increased.

The dependency on the solution viscosity of the copolymer of acrylamide and 1.5 mol % *N*-phenyl acrylamide with the NaCl concentration is shown for different shear rates in Figure 8. As depicted, the viscosity of the copolymer solution increased dramatically with increasing NaCl concentration at all shear rates considered. This observation suggests that intermolecular association was probably favored by the addition of salt. A similar effect has been reported in previous studies of this kind.<sup>19,21,22,28,32</sup>

The pseudoplasticity, the salt tolerance, and the relatively favorable viscosity-temperature profiles are some of the attractive features of these hydrophobically modified copolymers that make them of potential interest in oil recovery or drilling applications.

### ST and IFT properties of the copolymers

Because very few studies<sup>20,21,28</sup> had been conducted on the surface and interfacial activities of hydrophobically modified copolymers, we conducted detailed studies on these features. Figures 9-11 display the influence of the polymer and NaCl salt concentrations on air-liquid STs and *n*-decane/aqueous polymer solution IFTs of the copolymers.

Figure 9 shows a sharp decrease in ST up to a polymer concentration of 0.4 wt % followed by a slight increase in ST up to a polymer concentration of 0.5 wt % for the copolymer of acrylamide and 5 mol % *N*-phenyl acrylamide. After this point, a dramatic decrease was observed with increasing polymer concen-

tration. The decrease in ST, especially at higher polymer concentrations (>0.5 w%), could be attributed to the increased adsorption of the available polymer molecules at the air/aqueous solution interface as the polymer concentration increased.

Figure 10 shows the effect of the polymer concentration on IFT of the same copolymer shown in Figure 9, and as expected, IFT decreased as the polymer concentration increased. However, a minimum was observed at a 0.4 wt % polymer concentration, and a maximum was seen at 0.5 wt %. The decrease in IFT with the polymer concentration could also be attributed to the same reason given for the decrease in ST, as shown in Figure 9. The small peak observed in ST and IFT (i.e., Figs. 9 and 10, respectively) at a 0.5 wt % polymer concentration could be attributed to the migration of the hydrophobic segments from the interface to the bulk of the solution for the formation of macromolecular aggregates. A further increase in the polymer concentration resulted in the availability of more hydrophobes at the interface after the intermolecular aggregates formed, thereby resulting in the observed decrease in ST and IFT at higher polymer concentrations.

As shown in Figure 11 for the copolymer of acrylamide and 1.5 mol % *N*-phenyl acrylamide, a sharp decrease in IFT was observed with increasing NaCl concentration. This behavior is unusual for nonionic polymers such as the ones under investigation, as they usually exhibit little change in the surface activity with salt. In fact, it has been reported that, in contrast to polyelectrolyte polymers, ST of zwitterionic polysoaps is increased by the addition of salt because of their antipolyelectrolyte behavior.<sup>36</sup> This decrease in IFT with salinity, which is favorable and sought for EOR operations, is also one of the attractive features of these hydrophobically modified copolymers that make them of potential interest for oil recovery or drilling applications.

## CONCLUSIONS

Hydrophobically modified water-soluble polymers were prepared by an aqueous micellar copolymerization technique from acrylamide and small amounts of *N*-phenyl acrylamides with the objective of investigating the copolymer viscosity behavior and surface and interfacial activities under various conditions. The hydrophobic moieties of the copolymers promoted intermolecular hydrophobic associations and the formation of polymolecular micelles, which exhibited increased viscosity and enhanced air-liquid surface activities and liquid-liquid interfacial activities, especially with increasing polymer concentration and salinity. A relatively high salt tolerance, typical of nonionic polymers, was also exhibited by the copolymers. Furthermore, an almost shear-rate-independent vis-

cosity (Newtonian plateau) was exhibited at high shear rates, and a typical non-Newtonian shear-thinning behavior appeared at low shear rates and high temperatures. The pseudoplasticity, salt tolerance, and relatively favorable viscosity-temperature profiles are some of the attractive features of these hydrophobically modified copolymers that make them of potential technological interest for oil recovery or drilling applications and other important commercial functions.

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