

# Solution and Interfacial Behavior of Hydrophobically Modified Water-Soluble Block Copolymers of Acrylamide and *N*-Phenethylacrylamide

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**ABSTRACT:** Hydrophobically modified water-soluble block copolymers were prepared by aqueous micellar copolymerization of acrylamide and small amounts (2 and 3 mol %) of a hydrophobe (*N*-phenethylacrylamide) that is characterized by a long spacer that places the aromatic ring far away from the backbone, with the objective of investigating the copolymers' rheological behavior and surface and interfacial activities under various conditions such as polymer concentration, shear rate, temperature, and salinity. As expected, the block copolymers exhibit improved thickening properties attributed to intermolecular hydrophobic associations as the solution viscosity of the copolymers increases sharply with increasing polymer concentration. Additional evidence for intermolecular association is provided by the effect of NaCl, the presence of which substantially enhances the viscosity. An almost shear rate-independent viscosity (Newtonian plateau) is also exhibited at high shear rate and a typical non-Newtonian shear thinning behavior appears at low shear rates and high temperatures. Furthermore, the block copolymers exhibit high air-liquid surface and liquid-liquid interfacial activities as the surface and interfacial tensions decrease with increasing polymer concentration, indicating strong adsorption of the copolymer at the interface. The surface and interfacial tensions exhibited by the copolymers were found to be relatively insensitive to the concentration of salt (NaCl). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 467–476, 2001

**Key words:** acrylamide block copolymers; micellar copolymerization; hydrophobically associating polymers; water-soluble polymers; solution viscosity; surface and interfacial tensions

## INTRODUCTION

Water-soluble polymers modified with a few mole percentage of a hydrophobic comonomer have re-

cently become the subject of extensive research.<sup>1–8</sup> In particular, the use of copolymers of acrylamide with various hydrophobic comonomers has proved to be of great interest.<sup>9–19</sup> Above a certain polymer concentration (CMC), the hydrophobic groups in these polymers tend to associate in aqueous solution by intermolecular hydrophobic interaction, leading to formation of polymolecular assemblies driven by the effort of the hydrophobic blocks to aggregate in their at-

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tempt to avoid the strongly hydrophilic aqueous medium. As a consequence, these block copolymers exhibit thickening properties equivalent to those observed for higher molecular weight homopolymers. These polymers thereby exhibit particular rheological properties in solution, resulting from the reversible dissociation process of the physical links occurring under shear.

For instance, hydrophobically associating polymers can show interesting behavior as a function of shear rate and shear time, such as shear thinning or thixotropy. This characteristic behavior allows the copolymer to avoid the irreversible mechanical degradation that occurs for very high molecular weight polymers when subjected to high shear stresses.<sup>20</sup> Moreover, unlike polyelectrolytes, aqueous solutions of these hydrophobically associating copolymers are less sensitive to salt because of their neutral nature.<sup>13,15</sup> The rheological behavior of these compounds is of great technological importance, especially in applications of water-based systems that involve viscosity control.<sup>21</sup>

Furthermore, in view of the amphiphilic structure (i.e., presence of hydrophobic moieties in the mainly hydrophilic polymer chain) of hydrophobically associating copolymers, high surface and interfacial activities with hydrocarbons are exhibited by the aqueous solutions of these copolymers. Amphiphilic polymers form monomolecular or polymeric micelles in aqueous solutions<sup>7,8,15</sup> and thus have enhanced ability to adsorb at an interface. This can lead to a sharp reduction in surface and interfacial tensions of the polymer solution. The combination of rheological behavior (i.e., thickening properties) and both surface and interfacial activities of these polymers can be 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 separations, industrial thickeners, controlled drug release, and biological/medical purposes.

As a consequence, in the past few years, there has been an increasing interest in the synthesis and solution properties of these copolymers. A class of particularly interesting hydrophobically associating copolymers is the block copolymers of acrylamide and hydrophobic comonomers. Interest in these copolymers stems from availability of constituting monomers and simplicity of synthesis procedure, which can be easily scaled up for mass production. Moreover, these copolymers

have the potential to exhibit thickening properties and both surface and interfacial activities. The copolymerization process, used in this study, essentially concerns acrylamide-based copolymers.<sup>9–19</sup> The properties and associative behavior of copolymers of acrylamide with comonomers of different sizes, hydrophobicity, and rigidity were investigated. In this study, we are interested in studying the influence of the hydrophobe spacer size on solution and interfacial properties of acrylamide block copolymers. The hydrophobe used in this study, *N*-phenethylacrylamide, is characterized by a relatively long spacer that places the bulky aromatic ring far away from the backbone of the copolymer. The block copolymer can be prepared by micellar radical copolymerization of *N*-phenethylacrylamide in an aqueous solution of acrylamide, to form a water-soluble multiblock copolymer. The technique has been shown to be well suited for the preparation of high molecular weight block copolymers having improved thickening properties.<sup>17,22–24</sup>

In this study, we present results of a more detailed investigation on solution properties such as rheological behavior and both surface and interfacial activities of hydrophobically associating water-soluble multiblock copolymers of acrylamide and *N*-phenethylacrylamide (2 and 3 mol % of *N*-phenethylacrylamide as the hydrophobic monomer were incorporated), prepared by the micellar copolymerization technique. To our knowledge, preparation and solution properties of this acrylamide/*N*-phenethylacrylamide block copolymer have never been studied and reported before. The solution viscosity behavior of the polymer was investigated with respect to the polymer concentration, shear rate, temperature, and NaCl concentration. Furthermore, because very few studies have been conducted on surface and interfacial tension properties of this kind of polymers, a detailed investigation of both surface tension (ST) and interfacial tension (IFT) behaviors of these polymers was carried out with respect to the polymer concentration and NaCl concentration.

## EXPERIMENTAL

### Materials

The source and the purification of monomers and other reagents were reported elsewhere.<sup>15</sup> *n*-Decane used in the IFT measurements was supplied

**Table I** Reaction Conditions and Some Characteristic Data of the Copolymers<sup>a</sup>

CM (mol %)	AA (g)	CM (g)	H <sub>2</sub> O (ml)	CTAB (g)	CTAB/AA (w/w %)	PPS/AA (w/w %)	RT (h)	Yield (g)	Yield (%)
2	10	0.504	200	8	80	2.5	48	9.4796	90.25
3	10	0.762	200	8	80	2.5	72	8.2332	76.5

<sup>a</sup> CM = comonomer (*N*-phenethylacrylamide); AA = acrylamide; CTAB = (hexadecyl triethyl ammonium bromide) surfactant; PPS = potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>); RT = reaction time.

by BDH (Poole, UK) with a purity of 99.6% and was distilled twice prior to use. Doubly distilled water was also used in the surface and interfacial tension measurements.

Acrylamide used is from Merck-schuchardt (Germany); Phenethylamine, acryloyl chloride, CTAB, and D<sub>2</sub>O used were purchased from Fluka Chemie AG (Buchs, Switzerland); Et<sub>3</sub>N and THF are from BDH Ltd. (Poole, UK); ether hexane and methanol were purchased from Fluka A.G. (Chemische, Fabrika); MgSO<sub>4</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> used were bought from Fischer Scientific Co. (USA).

### Physical Methods

The melting point is uncorrected. The IR spectrum was recorded on a Perkin-Elmer 16F PC FTIR spectrometer (Perkin Elmer Cetus, Norwalk, CT). <sup>1</sup>H-NMR spectra were measured on a JEOL LA 500-MHz spectrometer (JEOL, Peabody, MA).

### Synthesis of *N*-Phenethylacrylamide

The comonomer *N*-phenethylacrylamide was synthesized using a modified procedure as described in the literature.<sup>19</sup>

Thus, a solution of phenethylamine (6.67 g, 0.055 mol) and Et<sub>3</sub>N (6.07 g, 0.060 mol) in Na-dried tetrahydrofuran (THF, 50 cm<sup>3</sup>) at 0–5°C was added to a solution of acryloyl chloride (0.055 mol) in dry THF (50 cm<sup>3</sup>) over a period of 45 min. The reaction mixture was stirred at 10°C for 2 h, after which the solvent THF was removed at 40°C, as much as possible, by a gentle stream of N<sub>2</sub>. The residue was transferred to a separatory funnel with the help of ether (150 cm<sup>3</sup>) and water (50 cm<sup>3</sup>). The organic layer was washed with water (2 × 50 cm<sup>3</sup>), dried (MgSO<sub>4</sub>), concentrated, and crystallized from an ether/hexane mixture at low temperature in the freezer to give the monomer *N*-phenethylacrylamide as colorless needles (6.6 g, 69%), mp 55–56°C.

$\nu_{\max}$  (Kbr): 3284, 3082, 3024, 2964, 2934, 2856, 2798, 1652, 1620, 1556, 1496, 1454, 1408, 1364, 1310, 1248,

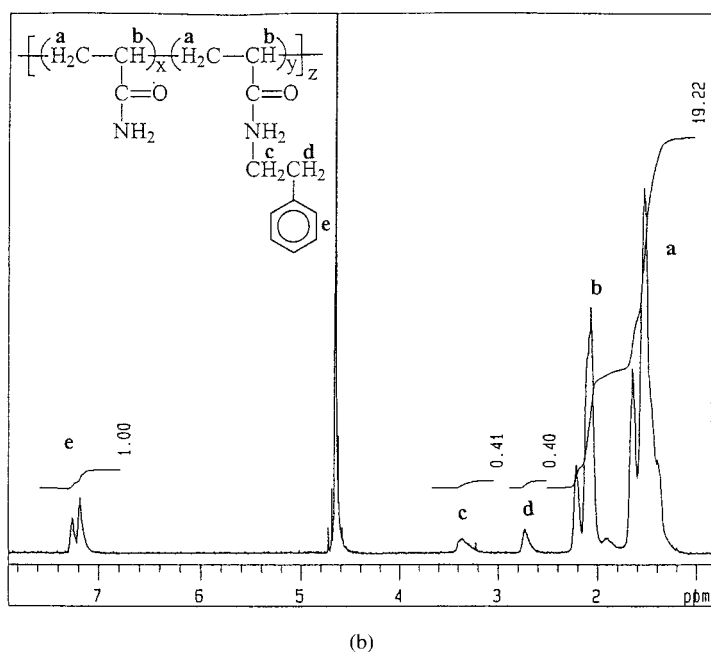
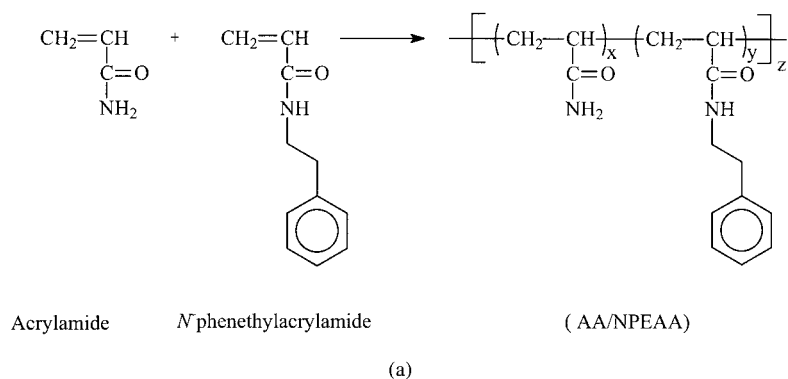
1066, 990, 996, 806, 746, and 698 cm<sup>-1</sup>;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>, TMS): 2.86 (2H, t, *J* 7.0 Hz), 3.60 (2H, q, *J* ~ 6.8 Hz), 5.61 (1H, d, *J* 10.3 Hz), 5.66 (1H, br, s), 6.03 (1H, dd, *J* 10.3, 17.0 Hz), 6.25 (1H, d, *J* 17.0 Hz), 7.30 (5H, m).

### Synthesis of Copolymers

Acrylamide/*N*-phenethyl acrylamide block copolymer containing 2 mol % of the hydrophobe was prepared as follows. An aqueous solution of acrylamide (10 g) in water (200 mL) was degassed with gentle bubbling of N<sub>2</sub> for 30 min in a 500-mL round-bottom flask covered with septum cap. The surfactant CTAB (hexadecyl trimethyl ammonium bromide; 8 g) followed by *N*-phenethylacrylamide (0.504 g; 2 mol %) were added to the mixture, under constant stirring at 50°C, until a clear solution was obtained. Polymerization was then initiated by the addition of potassium persulfate solution (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; 0.250 g) and the reaction mixture was stirred at 50°C for 48 h. The resulting polymer was precipitated by slowly pouring the solution into constantly 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 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 kept in a desiccator.

The above procedure was similarly applied for the preparation of 3 mol % acrylamide/*N*-phenethylacrylamide copolymer. Detailed reaction conditions and some characteristic data of the copolymers are shown in Table I. The reaction scheme and molecular structures of monomers and hydrophobically modified copolymer are depicted in Figure 1(a) and (b).

The ratio of the two monomers in the copolymer was determined by <sup>1</sup>H-NMR spectroscopy of the polymer samples measured in D<sub>2</sub>O using a JEOL LA 500 MHz spectrometer. Using integration of the signals of the aromatic proton (~ 87.25 ppm), the methylene protons ( $\delta$ 3.36 and 82.73



**Figure 1** Structure of the acrylamide/*N*-phenethylacrylamide copolymer.

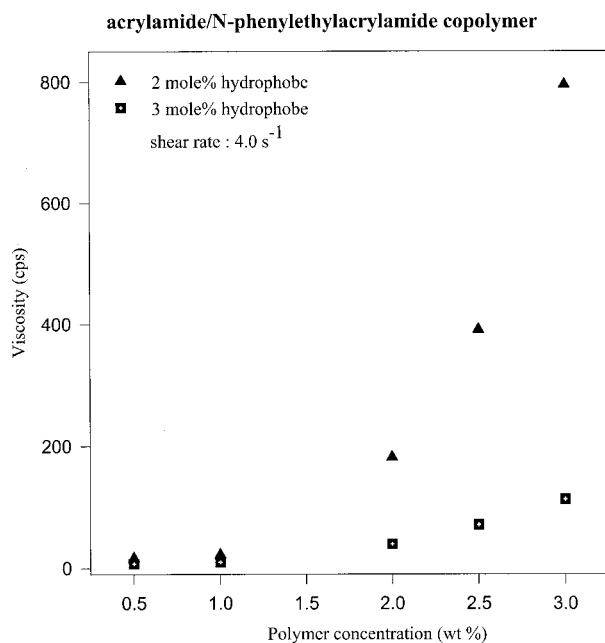
ppm), and the signals of the aliphatic protons attached to the backbone ( $\sim \delta 2$  ppm), the ratio was found to be identical to the feed ratio. Figure 1 shows that there is 3.1 mol % hydrophobe incorporation for a feed of 3.0 mol %. The <sup>1</sup>H-NMR spectra also confirmed the absence of even traces of the surfactant molecule (CTAB). The nine hydrogens belonging to the three methyl groups of hexadecyl trimethyl ammonium bromide (surfactant) appear as a large, sharp singlet at  $\delta 3.13$  ppm. The <sup>1</sup>H-NMR spectrum [Fig. 1(a)] of the copolymer prepared from a feed of 3 mol % hydrophobe indicates the absence of the singlet at  $\delta 3.13$ , thereby ensuring complete removal of the surfactant.

There is ample precedence in the literature that the micellar polymerization, the procedure adapted in the current work, would lead to

multiblock copolymers consisting of long sequences of acrylamide separated by short sequences of the hydrophobic comonomers, which occupy the micellar phase.<sup>17,24</sup> A chain initiated in the aqueous solution keeps on adding acrylamide units until it encounters a micelle full of the hydrophobic comonomer. The chain adds the hydrophobic monomer until all hydrophobe is exhausted from the micelle, forming a short hydrophobic block. Consequently, the chain adds more acrylamide from the aqueous phase, forming another block of acrylamide. The process is repeated many times to form a multiblock copolymer.

#### Measurement of Viscosity

The solution properties of the block copolymers, such as viscosity and both surface and interfacial



**Figure 2** Effect of polymer concentration on the viscosity of 2 and 3 mol % acrylamide/*N*-phenethylacrylamide copolymers for shear rate of  $4.0 \text{ s}^{-1}$  and at  $25^\circ\text{C}$ .

tensions, were investigated with respect to the polymer concentration, shear rate, temperature, and salinity. In this study, concentrated stock solutions were prepared at least 24 h prior to the measurements. The dissolution processes lasted for 2–3 days. Final solutions of the desired compositions were obtained by dilution of the appropriate stock solution with distilled water. Saline solutions were prepared by dissolving appropriate amounts of solid NaCl in the diluted polymer solution.

The solution viscosities of the block copolymers (2 and 3 mol % copolymers of acrylamide and *N*-phenethylacrylamide) were measured for different polymer concentrations and salinities using a digital Brookfield rotational viscometer with SC4-18 spindle accessory, at a shear rate ranging from  $0.4$  to  $79.4 \text{ s}^{-1}$  and at a temperature ranging from  $25$  to  $95^\circ\text{C}$ .

#### Measurement of Surface Tension and Interfacial Tension

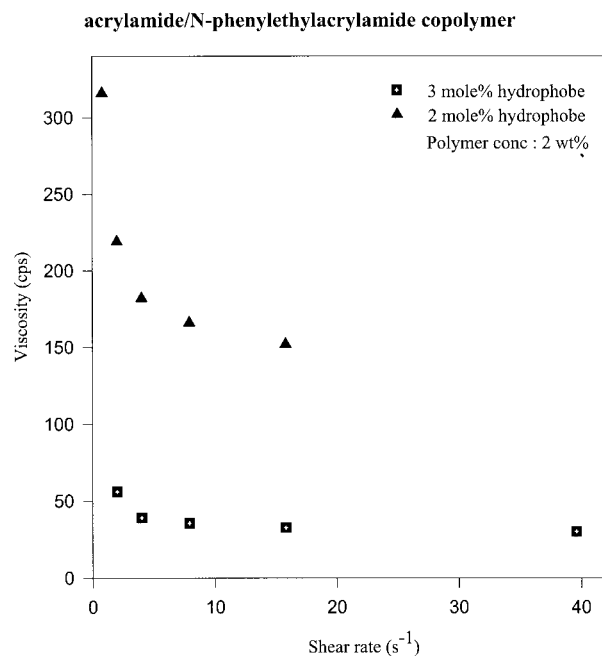
The air–liquid surface tensions of the copolymers were determined for different polymer concentrations (for 2 and 3 mol % copolymer of acrylamide and *N*-phenethylacrylamide) using the plate method of the Processor tensiometer K12 (Kruss). The oil (*n*-decane)–aqueous solution IFTs of the

copolymers were determined for different polymer concentrations (for 2 and 3 mol % copolymer of acrylamide and *N*-phenethylacrylamide), using the ring method of the same tensiometer used for surface tension measurement. *n*-Decane was used as the oil phase. The IFTs of the *n*-decane–aqueous polymer solution were measured for a polymer concentration of 2.0 wt % (for 2 mol % copolymer of acrylamide and *N*-phenethylacrylamide) with NaCl salt concentration ranging from 0.1 to 9.0 wt %. All surface and interfacial tension measurements were performed at  $25^\circ\text{C}$ .

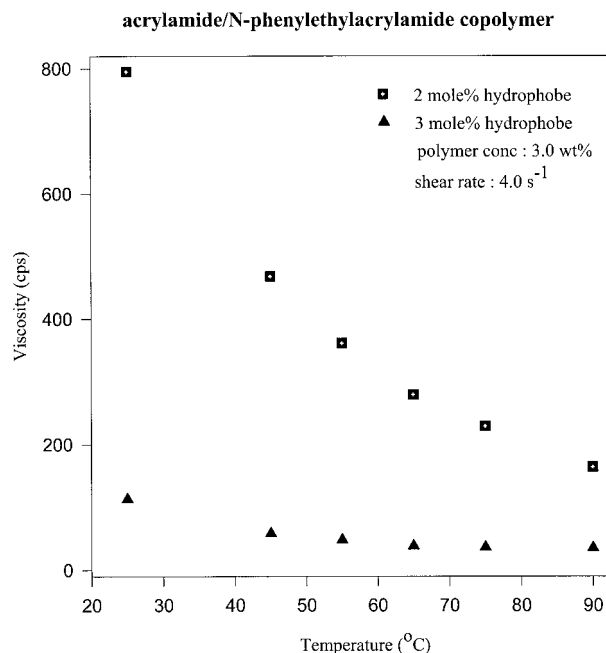
All of the measurements were carried out at least in duplicate and sometimes three times and the results were reproducible to  $\pm 5\%$  and reported (Figs. 2–8) as the average value of these measurements with a standard deviation of 5%.

## RESULTS AND DISCUSSION

The solution properties of hydrophobically associating water-soluble acrylamide/*N*-phenethylacrylamide block copolymers were studied under different conditions as part of a continuing research program to investigate the relationship between polymer structures and their solution



**Figure 3** Variations of viscosity of 2 and 3 mol % acrylamide/*N*-phenethylacrylamide copolymer with shear rate for polymer concentration of 2.0 wt % and at  $25^\circ\text{C}$ .



**Figure 4** Effect on the viscosity of 2 and 3 mol % acrylamide/*N*-phenethylacrylamide copolymer of temperature for polymer concentration of 3.0 wt % and at a shear rate of  $4.0 \text{ s}^{-1}$ .

viscosity behaviors, and air-liquid and liquid-liquid interfacial activities. These were investigated with the objective of designing polymers with optimized structure for high solution viscosity, and simultaneously high surface and interfacial activities that could be applied in such areas, for example, as enhanced oil recovery, drag reduction, and industrial thickeners.

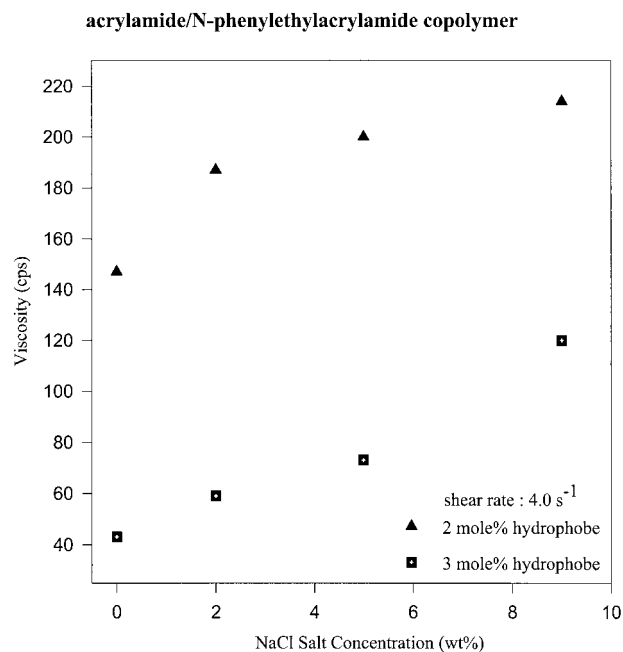
### Viscosity Behavior of the Copolymers

Figures 2–4 depict the dependencies of polymer concentration, shear rate, and temperature on the solution viscosity of hydrophobically modified 2 and 3 mol % block copolymers of acrylamide and *N*-phenethylacrylamide. Figure 5 shows NaCl concentration dependence of the solution viscosity for 2 and 3 mol % acrylamide/*N*-phenethylacrylamide copolymers.

As shown in Figure 2 for a shear rate of  $4 \text{ s}^{-1}$ , the copolymer containing 2 mol % hydrophobe exhibits a sharp increase in viscosity with increasing polymer concentration. This observation is similar to that frequently observed for hydrophobically modified associative polymers.<sup>3,5,6,9,13–16,19,24</sup> This behavior is caused by the strong interchain associations that form large aggregates (a network struc-

ture of polymer chains) as the polymer concentration increases (greater than 2 wt %). At low polymer concentration, hydrophobic chains have little chance of interacting intermolecularly with each other, thus leading to the formation of small aggregates with a small hydrodynamic volume. Intramolecular associations are dominant compared to intermolecular associations in this dilute solution; thus the hydrophobic interactions produce a decrease in the hydrodynamic radius of the copolymer coil. However, as the copolymer concentration is increased (above the critical level), hydrophobic intermolecular associations are more probable, giving rise to a network structure of polymer chains (large aggregates) with large hydrodynamic volumes and, consequently, high solution viscosities. These physical network structures contribute significantly to the thickening behavior of this associative polymer. The smaller increase in viscosity observed for the 3% hydrophobe copolymer compared to the 2% hydrophobe copolymer is probably caused by the greater tendency of the higher hydrophobe copolymer to form intramolecular association that is facilitated by the long spacer and the greater abundance of hydrophobe.

For the hydrophobically associating polymer, an almost shear rate-independent viscosity

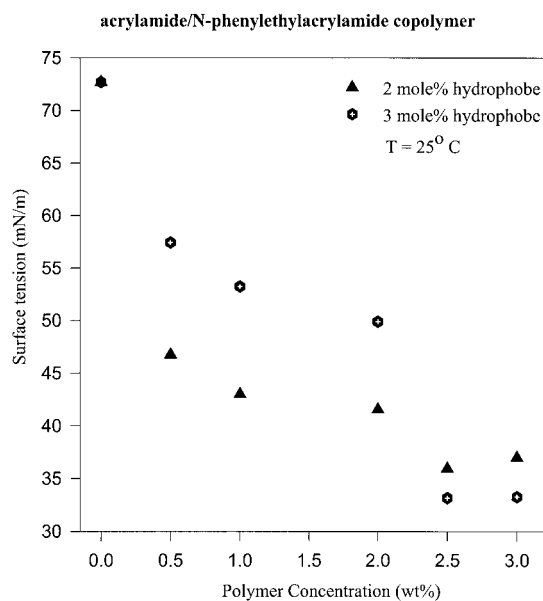


**Figure 5** Effect on the viscosity of 2 and 3 mol % acrylamide/*N*-phenethylacrylamide copolymer of NaCl salt concentration for a shear rate of  $4.0 \text{ s}^{-1}$  and at  $25^\circ\text{C}$ .

(Newtonian plateau) is observed at high shear rates, as depicted in Figure 3 for a polymer concentrations of 2.0 wt %. However, a sharp decrease in viscosity with shear rate (a typical shear thinning behavior) appears at low shear rates, as shown in the same figure. The shear thinning behavior can be attributed to the disorientation and disentanglement of the macromolecular chains under shear, which corresponds to the progressive rupture of the intermolecular associations upon increasing the shear rate. The development of viscosity behavior for associative polymers like the one under investigation relies on an increase in the apparent macromolecular aggregation among hydrophobic groups with increasing polymer concentration. Under high shear conditions, the hydrophobic interactions can be disrupted, giving rise to a decrease in the apparent molecular weight, and hence a decrease in solution viscosity. However, under low shear conditions the hydrophobic interchain associations will reform, restoring the high solution viscosity.<sup>6,9,15-17,19,24</sup>

Figure 4 displays the effect of temperature on the solution viscosity of the polymer for a concentration of 2 wt % and a shear rate of  $4 \text{ s}^{-1}$ . As expected, a sharp decrease in viscosity is observed with increasing temperature, especially for the low hydrophobe copolymer. The decline in viscosity with temperature is less pronounced for the 3% hydrophobe copolymer. The lowering of the solution viscosity with increasing temperature was previously reported for aqueous solutions of hydrophobically associating water-soluble polymers.<sup>6,8,9,15,19</sup> This effect could be attributed to the weakening of hydrophobic effect at elevated temperatures resulting from the increased mobility of the polymer chains (as a result of decrease in solvent viscosity), which gives rise to loss of interchain liaisons and/or an increase in copolymer solubility as the temperature increases.

Additional evidence for intermolecular association is provided by the effects of NaCl salt addition on the viscosity of 2 wt % solutions of copolymers containing 2 and 3% hydrophobe at a shear rate of  $4 \text{ s}^{-1}$  shown in Figure 5. As depicted, the viscosity of the copolymer solution increases appreciably with increasing NaCl concentration. These results suggest that intermolecular association is favored by the addition of salt. The addition of salt makes the aqueous environment more hostile for the hydrophobic blocks, causing them to favor association with each other and, hence, promoting the formation of large macromolecular



**Figure 6** Surface tension (ST) versus polymer concentration for 2 and 3 mol % acrylamide/*N*-phenethylacrylamide copolymer at 25°C.

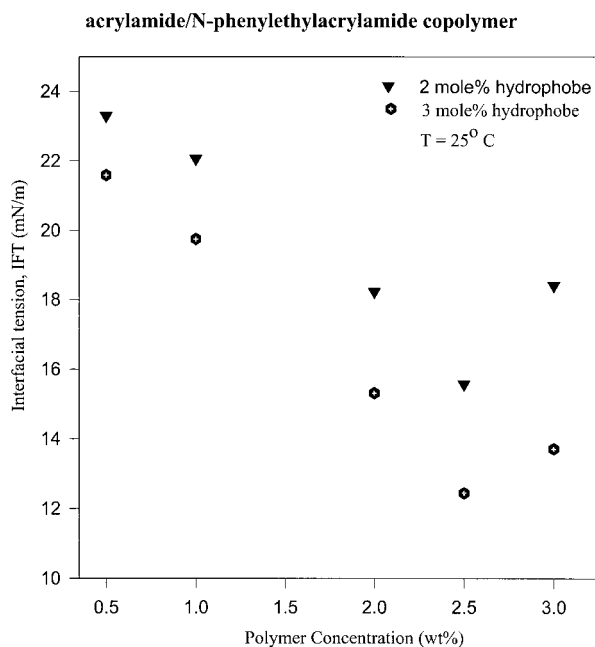
aggregates.<sup>19</sup> Salt reduces the number of available solvent molecules because many of the water molecules are associated with the salt ions and, consequently, fewer water molecules are available for dissolving the copolymer molecules. This forces the copolymer molecules to favor interacting with each other over interacting with the solvent molecules and, as a result, they tend to form intermolecular aggregates through the hydrophobic blocks at lower copolymer concentrations.

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

### Surface and Interfacial Tension Properties of the Copolymer Solutions

Another interesting feature, which has rarely been investigated,<sup>7,8,15</sup> concerns the surface and interfacial activities of the hydrophobically modified block copolymers. Thus, Figures 6 and 7 show the influence of polymer concentration on air-liquid surface and *n*-decane-aqueous polymer solution IFTs of the copolymers.

As shown in Figure 6 for the copolymers containing 2 and 3 mol % *N*-phenethylacrylamide, a gradual decrease in ST is observed up to a poly-



**Figure 7** Interfacial tension (IFT) versus polymer concentration for 2 and 3 mol % acrylamide/*N*-phenylethylacrylamide copolymer at 25°C.

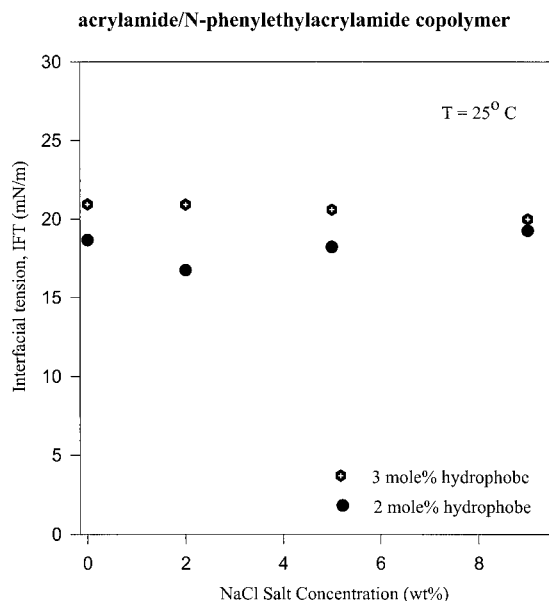
mer concentration of 2 wt %, followed by a sharp decrease. The decrease in the ST could be attributed to the increased adsorption of the available copolymer molecules at the air–aqueous solution interface as the copolymer concentration increases, leading to interfacial excess of the copolymer. At low copolymer concentrations, the copolymer molecules adsorb at the interface so that the hydrophobic blocks can avoid the unfavorable aqueous environment and escape to the air phase because of the unavailability of enough polymer molecules to form intermolecular aggregates. The sharp decrease at 2% might be caused by aggregation of the hydrophobe at the interface, causing a more concentrated effect of the hydrophobe on interfacial tension and at the same time leaving space for more copolymer molecules to adsorb at the surface, leading to higher interfacial excess and lower surface tension. At higher copolymer concentrations, the interface becomes saturated with copolymer molecules and the intermolecular aggregates start providing a favorable environment for the hydrophobes. Consequently, a less-pronounced decrease in ST is observed at higher polymer concentration.

The 2% hydrophobe copolymer shows the same type of behavior as the 3% hydrophobe copolymer, although it lowers the surface tension more significantly than the 3% copolymer at copolymer

concentrations less than 2 wt %. This unexpected behavior can be explained by the lower ability of the 2% hydrophobe to form intramolecular associations that stabilize the copolymer in solution. As a result, the 2% hydrophobe copolymer tends to adsorb more strongly at the interface at all concentrations than the 3% copolymer, to avoid the aqueous environment, and consequently a lower surface tension is observed. For polymer concentrations exceeding 2 wt %, where copolymers are believed to self-aggregate at the surface, the surface tension of the 3% copolymer solution is lower because of its ability to form more stable inter- and intramolecular aggregates caused by the higher abundance of hydrophobes.

Figure 7 depicts the effect of polymer concentration on the IFT of the same copolymers shown in Figure 6. As expected, the IFT decreases as the polymer concentration increases. A minimum is observed at 2.5 wt % polymer concentration. The decrease in the IFT with polymer concentration could also be attributed to the same reasons given for decrease in ST. The increase in IFT at a polymer concentration higher than 2.5 wt % might be caused by a balance between bulk solution aggregation and interfacial adsorption. The copolymers are very efficient in reducing the interfacial tension of water compared to other hydrophobically associating acrylamide copolymers containing smaller hydrophobes.<sup>15</sup> For example, a 2 wt % acrylamide-*co*-styrene multiblock copolymer containing 6% hydrophobe shows an interfacial tension of 21 mN/m compared to 15.5 mN/m for the same weight percentage of phenethylacrylamide copolymer containing only 3% hydrophobe.<sup>15</sup> Acrylamide-*co*-benzylacrylamide copolymers containing 3% hydrophobe show an interfacial tension of 22 mN/m at the same polymer concentration.<sup>27</sup> This can be attributed to the long hydrophobic spacer, which gives the hydrophobes more freedom to extend away from the aqueous phase without causing significant change in the conformation of the copolymer. Unlike surface tension, the 3% hydrophobe copolymer reduces the interfacial tension more efficiently than the 2% hydrophobe copolymer. This phenomenon might be explained by the good solubilization ability of the hydrophobe by *n*-decane, which provides the hydrophobes with a more favored environment than the air phase (in the ST experiment) and the hydrophobic aggregates. As a result, the hydrophobes adsorb at the interface as much as they can in the absence of competition by hydrophobic aggregation. The lower interfacial tension of the





**Figure 8** Effect on the IFT of 2 and 3 mol % acrylamide/*N*-phenethylacrylamide copolymer of NaCl salt concentration for polymer concentration of 2.0 wt % at 25°C.

3% hydrophobe copolymer solution is a direct consequence of the greater abundance of hydrophobes.

Figure 8 shows the influence of NaCl concentration on IFT of 2 wt % copolymer solutions at 25°C. The IFT of the two copolymers is fairly insensitive to salt addition. This insensitivity is caused by the neutral nature of the copolymers. It is also caused by the saturation of the interface with the copolymers that, as was observed in Figure 7, is caused by the good solubility and ease of extension of the hydrophobe in the organic phase. As a consequence, the interface is not strongly influenced by the bulk behavior of the solution. The slight decrease in the IFT of the 2% hydrophobe copolymer at 2 wt % salt concentration is possibly a result of the presence of some impurities.

## CONCLUSIONS

The solution properties of hydrophobically associating water-soluble acrylamide/*N*-phenethylacrylamide block copolymers were studied under different conditions as a part of a continuing research program to investigate the relationship between polymer structures and their solution viscosity behaviors, and air-liquid and liquid-

liquid interfacial activities. These were investigated with the objective of designing polymers with optimized structure for high solution viscosity, and simultaneously high surface and interfacial activities for possible application in such areas as enhanced oil recovery (EOR). Because of the unique structural features of the copolymers, which are copolymerized with hydrophobic moieties that are characterized by a long spacer that promotes intermolecular hydrophobic associations and formation of polymolecular micelles, the copolymers were found to exhibit high air-liquid surface and liquid-liquid interfacial activities. A relatively high salt tolerance, typical of nonionic polymers, is also exhibited by the copolymers. Furthermore, an almost shear rate-independent viscosity (Newtonian plateau) is exhibited at high shear rates and a typical non-Newtonian shear thinning behavior appears at low shear rates and high temperatures. These pseudoplasticity, salt tolerance, and relatively favorable viscosity-temperature profiles are some of the attractive features of this hydrophobically associating copolymer that can make it of potential technological interest in oil recovery or drilling applications and other important commercial applications.

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