

# Properties of Hydrophobically Modified Polyacrylamide with Low Molecular Weight and Interaction with Surfactant in Aqueous Solution

Shuhui Wu, Robert A. Shanks, Gary Bryant

School of Applied Sciences, RMIT University, Melbourne, Victoria 3001, Australia

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**ABSTRACT:** Hydrophobically modified polyacrylamide (HMPAM), with a molecular weight of  $10^4$  g/mol, was studied using a range of rheological methods and dynamic light scattering (DLS). DLS measurements indicate that the association of the modified polymer begins at low concentration. The modified polymer with high substitution forms transient networks below the critical concentration, but the networks are disrupted by the micelles formed by the polymer itself, and the networks do not contribute to viscosity enhancement. The modified polymers exhibited surface activity, and so they may be regarded as nonionic polymeric surfactants rather than thickeners. On the other hand, HMPAM is shown to interact with the surfactant SDS while

PAM is inert to SDS. In the hydrophobic domains, it undergoes a surfactant-induced association process; in the hydrophobe-surfactant transition regions, the surfactant binds to the polymer in a noncooperative way and forms a polymer-surfactant complex. Contracted polymer chains begin to extend because of electrostatic repulsion, which can overcome the association at surfactant domains. The conformation of HMPAM polymer chains could be controlled by adding a specific amount of surfactant. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4348–4360, 2006

**Key words:** association; rheology; light scattering; solution properties; surfactants

## INTRODUCTION

Associative polymers are hydrophilic polymers modified with one or more hydrophobic groups. They have wide application in paints, foods, pharmaceutical products, and in enhanced oil recovery. The hydrophobic groups can associate to minimize their exposure to water, eventually a network is formed and the viscosity of the solution can increase markedly. For these reasons, associative polymers can be used as thickeners.

There are two types of associative polymers. One type is the group of telechelic polymers, with hydrophobes located at the polymer chain terminal positions. An example of this type is hydrophobic ethoxylated urethane (HEUR), which has molecular weight of the order of  $10^4$  g/mol, and is prepared by a substitution method.<sup>1–3</sup> The other type is the comb-like polymers, with hydrophobes distributed randomly along the polymer backbone, such as hydrophobically modified alkali soluble emulsions (HASE)<sup>4–6</sup> and hydrophobically modified polyacrylamides (HMPAM).<sup>7–9</sup> The molecular weight of these polymers is of the order of  $10^5$  to  $10^6$  g/mol, and the polymers are prepared by

a copolymerization method. These two types of polymers have different association processes and rheological behavior.

A strictly alternating method was developed to synthesize comb-like polymers.<sup>10–12</sup> Using this method, comb-like copolymers can be prepared with a broad range of molecular weights, from  $10^4$  to  $10^5$  g/mol. This type of polymer can be used to study the difference between comb-like polymers and telechelic polymers (with the same backbone and molecular weight), or the differences among comb-like polymers with different molecular weights. The rheological behavior of associative polymers is very complicated, and is influenced by association type, molecular weight, backbone structure, hydrophobe structure, and even spacer number.<sup>13</sup>

Recently a new modification method has been developed in our laboratory. Using a simple substitution method, polyacrylamide (PAM) had been substituted with octyl and hexyl groups to form a comb-like hydrophobically modified PAM (HMPAM), without changing the backbone.<sup>14,15</sup> The modified comb-like polymer in this study has a molecular weight of  $10^4$  g/mol, of the same order as telechelic polymers. The molecular weight is small when compared with that of HMPAM prepared by copolymerization methods. The substituted groups, octyl and hexyl, are weak hydrophobes. For this reason, the properties of HMPAM in this study are different to that of other comb-like

Correspondence to: R. A. Shanks (Robert.shanks@rmit.edu.au).

associative polymers prepared by copolymerization methods. In this study, a combination of rheology, dynamic light scattering, and surface chemistry methods were applied to characterize the distinctive properties and solution structure of the modified polymers, with particular emphasis on the rheological behavior.

When the PAM hydrophilic backbone is modified with hydrophobic groups, the molecules become amphiphilic, and consequently become surface active. As the polymers studied have small molecular weights and as they are of amphiphilic nature, they can be considered to be somewhere between a polymer and a surfactant. This behavior is investigated here by studying the interaction between sodium dodecyl sulfate (SDS) and both PAM and HMPAM. Although recently, new methodologies and instrumentation have developed rapidly (such as pulsed magnetic field gradient (PFG) NMR,<sup>16–19</sup> light scattering,<sup>20–24</sup> fluorescence,<sup>24–27</sup> and neutron and X-ray scattering<sup>28</sup>), other classical and fundamental methods (such as phase equilibria, surface tension,<sup>17,29</sup> and viscometry) are most frequently used to study the interaction of polymers and surfactants, as these experiments are precise and readily available. In this paper, surface tension measurements and phase equilibrium are used to investigate the interaction between HMPAM and SDS.

## EXPERIMENTAL

### Materials

Polyacrylamide (PAM), as a 50 wt % aqueous solution with weight average molecular weight ( $M_w$ ) of 10,000 g/mol and density of 1.189 g/mL, was purchased from SigmaAldrich (Australia). The solution was diluted to a concentration of about 10%, then lyophilized to obtain dry PAM solid. Sodium dodecylsulphate (SDS, 99% purity) was used as received.

Hydrophobically modified PAM (HMPAM) was obtained by a transamidation method that has been described elsewhere.<sup>14,15</sup> The amide group in the polymer backbone has been *N*-substituted in water solution, where the substituting amine is water soluble, such as hexylamine (C6) and octylamine (C8). For the octyl group, substitution ratios were chosen as 1, 3, or 5% (mole ratio) to PAM monomer units. The symbols for the modified polymers used are listed in Table I.

### Solution preparation

SDS additives were dissolved in water with a variety of concentrations (g/L). Dry PAM or HMPAM was dissolved in water or SDS aqueous solutions. Solution concentrations are expressed as a weight fraction of solid polymers.

TABLE I  
Designation of Modified Polymers

	Substitution group	Substitution ratio (%)
PAM	–	–
C6 1	Hexyl	1
C8 1	Octyl	1
C8 3	Octyl	3
C8 5	Octyl	5

### Dilute solution viscosity measurements

A Ubbelohde viscometer was used to measure the relative viscosity of the solutions. The method and theory are described elsewhere.<sup>30</sup>

### Rheology of concentrated solutions

Rheological properties of 50 wt % of PAM, C8 1, C8 3, and C8 5 solutions were measured using a Fluids Spectrometer II (RFS II) from Rheometrics, with a parallel plate measuring system. Silicone oil was placed at the edge of the two plates to prevent solvent evaporation. First, a dynamic strain sweep was measured at 1 rad/s to determine the linear viscoelastic region. The storage modulus  $G'$  and loss modulus  $G''$  were measured over the frequency range 0.1–100 rad/s. Phase angles were also recorded. A strain amplitude of 0.2 rad was applied for all samples. For continuous shear measurement, the steady state viscosity ( $\eta$ ) was measured over the shear rate range of 0.1–100 s<sup>-1</sup>.

### Dynamic light scattering

For dynamic light scattering (DLS) the sample was illuminated by a laser beam, and the fluctuations in the scattered light, which are related to the motion of the particles, were measured. The theory is briefly outlined here. The fundamental quantity measured is the intensity autocorrelation function,  $g^{(2)}(\tau)$ , which is related to the normalized electric field autocorrelation function,  $g^{(1)}(\tau)$ , by

$$g^{(2)}(\tau) = 1 + B|g^{(1)}(\tau)|^2 \quad (1)$$

where  $B$  is an instrumental constant of order 1. For a dilute, monodisperse suspension of noninteracting particles the electric field autocorrelation function is described by

$$|g^{(1)}(\tau)| = \exp(-\Gamma\tau)\Gamma = \left(\frac{4\pi n}{\lambda_0} \sin\left(\frac{\theta}{2}\right)\right)^2 D \quad (2)$$

where  $\Gamma$  is the decay constant of the fluctuations,  $D$  is the particle diffusion coefficient,  $n$  is the refractive

index of the suspending liquid,  $\theta$  is the scattering angle and  $\lambda_0$  is the wavelength of the laser in vacuum.

For spherical particles the Stokes–Einstein relationship relates the diffusion constant  $D$  to the particle radius  $r$

$$D = \frac{k_B T}{6\pi\eta r} \quad (3)$$

Where  $T$  is the absolute temperature,  $k_B$  is the Boltzmann constant and  $\eta$  is the viscosity.

Dynamic light scattering (DLS) was performed using an ALV-compact goniometer. Samples were illuminated with a helium-neon laser with a wavelength of 633 nm. Measurements were carried out at 25°C, and the scattering angle was set at 30°. Autocorrelation functions were measured using an ALV-5000 correlator card, and analysis was carried out using the inbuilt software. For the samples presented here, multi-exponential fits with 1, 2, or 3 components were used. The refractive index of solutions was measured using an ATAGO illuminator, Japan. The relative viscosity of the dilute solutions (under 25 wt %) was measured using an Ubbelohde viscometer as described earlier, and the relative viscosity ratio was used to multiply the viscosity value of water. The absolute viscosity of concentrated 50 wt % solutions was measured using the rheometer. The samples were filtered prior to measurement using 0.8  $\mu\text{m}$  Millipore filters. Highly concentrated, 50 wt % solutions were difficult to filter, and these were measured without filtration.

### Surface tension measurement

The apparent surface tension was measured by the suspended drop method, using a Contact angle system (OCA20, Particle and Surface Science Pty Ltd.) at room temperature. Each sample was measured 5 times and the mean was quoted as the result. For phase-separated samples, the supernatant was measured.

### Phase equilibria

The turbidity of polymer–surfactant systems was determined by visual observation of each solution at room temperature, with the simple classification of clear, turbid, or phase-separated.

### Optical microscopy

A Nikon Labophot II microscope was used to study the emulsion and the phase separated solutions. A few drops of liquid were gently placed in the well of a glass slide, which was placed under the microscope for observation. Dye was mixed with the liquid to

**TABLE II**  
The Intrinsic Viscosity  $[\eta]$  and Huggins Constant  $k_H$  of Polymers

	$[\eta]$ (dL/g)	$k_H$
PAM	0.1101	0.99
C8 1	0.1125	0.92
C8 3	0.1328	0.6
C8 5	0.1293	0.66

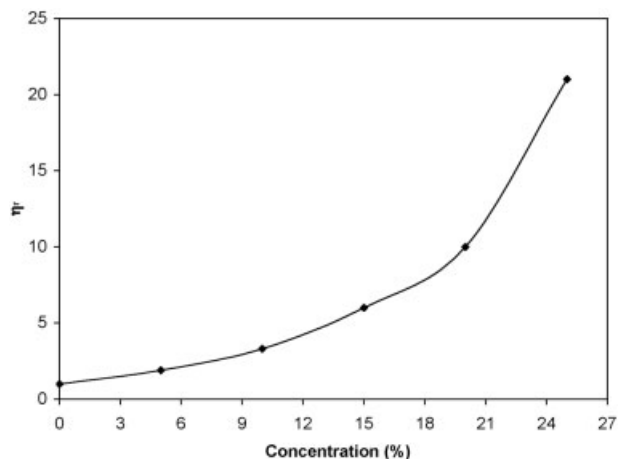
increase image contrast. Images were captured using a Sony video camera connected to a Macintosh computer with IPLab image analysis software (Spectra Analytics Co.).

## RESULTS AND DISCUSSION

### Dilute solution viscosity

Table II summarizes the results of Ubbelohde viscometer measurements. The intrinsic viscosity  $[\eta]$  (dL/g) of the modified polymers is almost identical to that of PAM. Normally the intrinsic viscosity of a modified polymer is lower than that of its unmodified analogue because of reduced intramolecular interactions in dilute regions. The results show similar values for the different samples (the slightly higher value of HM-PAM may be due to association of hydrophobes). The HMPAM used has low molecular weight. Other HMPAMs, prepared by micellar copolymerization methods, can have molecular weights up to  $10^6$  g/mol. The molecular weight of the monomer unit of PAM is 71 g/mol. For a polymer with 10,000 g/mol molecular weight, the average polymerization degree is 140. Modified polymers with 1% substitution have one or two hydrophobes on each polymer chain, so only intermolecular associations can occur. For a polymer chain that has 140 average repeat units, with some side-chains containing 8 carbons, the length–radius ratio is very low, the molecules are quite elongated. Compared with polymers that have high molecular weight, the length–radius ratio is very high, the chains are more coiled. When the polymer chains are short, modified polymers with high substitution ratio tend to have high elongation, which makes it difficult for the chains to bend to form intramolecular associations. As the intrinsic viscosity is related to the effective hydrodynamic volume of the molecules in solution, the results indicate that an elongated polymeric backbone produces a similar hydrodynamic volume to that of the unmodified polymer.

The Huggins constants of the modified polymers (shown in Table II) are lower than that of PAM, which indicates a better polymer–solvent interaction.<sup>30</sup> Because of the presence of hydrophobes in aqueous solution, the Huggins constant of a modified polymer is expected to be higher than that of its unmodified



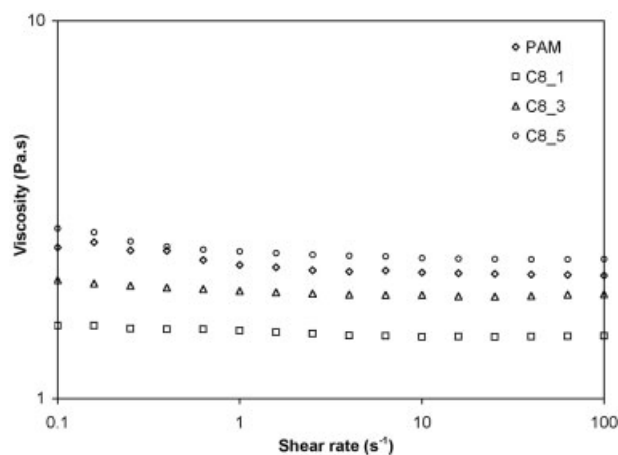
**Figure 1** Relative viscosity ratio of PAM versus polymer concentration.

analogue. However, the trend is reversed here and it is proposed that this is due to the association of the hydrophobic domains. A similar reversed trend has also been observed in unmodified/modified methacrylic acid-ethyl acrylate copolymer systems. An explanation was that the blocky ethyl acrylate segments in the polymer backbone were able to self-aggregate to reduce the total hydrophobic domain sites.<sup>31</sup>

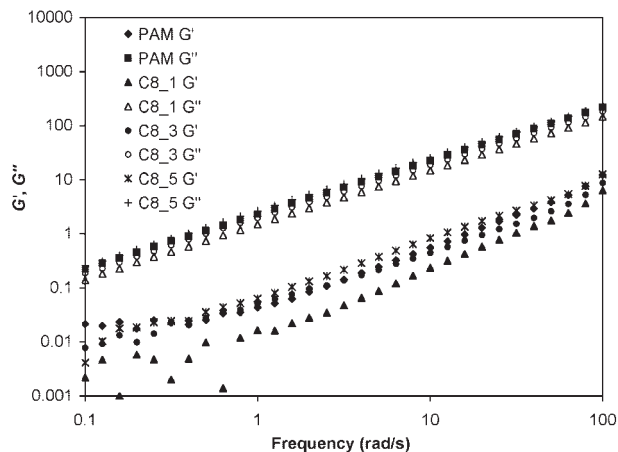
The critical concentration  $C^*$  of PAM, calculated as the reciprocal of intrinsic viscosity, was below 10 g/dL (about 10 wt %). Figure 1 shows the PAM concentration (wt %) versus relative viscosity ratio. The curve shows that  $C^*$  is between 15 and 20 wt %, which is higher than the calculated value.

### Rheology of concentrated solutions

Figure 2 shows the steady viscosity of polymer solutions (50 wt %) versus the shear rate. The figure shows



**Figure 2** Steady shear viscosity of polymers at weight fraction 50% versus shear rate.



**Figure 3** Dynamic storage modulus  $G'$  and loss modulus  $G''$  versus frequency for weight fraction 50% polymer.

that the viscosity of C8 1 and C8 3 is even lower than PAM, while C8 5 is slightly higher than that of PAM. Even though there are slight differences, the viscosities are of the same order. For other hydrophobically modified systems, the viscosity of the modified polymer can be a few orders higher than that of the unmodified polymer in the semidilute region.

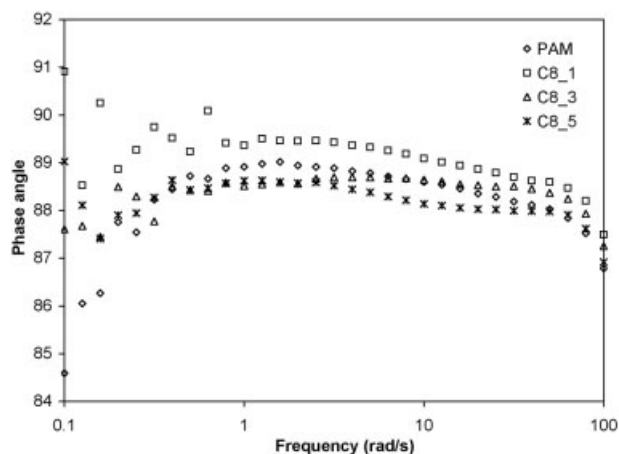
Figure 3 shows the dynamic shear modulus versus shear rate for each of the polymers at a concentration of 50 wt %. The C8 1 sample has the lowest  $G'$  and  $G''$ , while C8 3 is almost the same as that of PAM, and both  $G'$  and  $G''$  of C8 5 are slightly higher than that of PAM. All the values are of the same order, indicating that the modified polymers do not have significant viscosity enhancement. Table III summarizes the exponents of the power law for the four different HMPAMs. Exponents of  $G'$  are very small, and the exponents of  $G''$  are in the order of C8 5 > PAM > C8 3 > C8 1, close to 2. Table III indicates that all four solutions are viscous liquids. Figure 4 shows the phase angle of the samples. C8 1 has the highest phase angle though the other three are similar. The dynamic result is well correlated with the steady state result in Figure 2. Combining the results from Figures 2–4, the solution of C8 1 shows the most “liquid-like” properties and C8 5 the least.

There are two types of hydrophobic modified polymers: telechelic, with hydrophobes at terminal positions, molecular weights of order  $10^4$  g/mol, such as

**TABLE III**  
Exponents of the Power Law for Polymers

	$G'$	$G''$
PAM	0.103	2.2
C8 1	0.051	1.44
C8 3	0.072	1.83
C8 5	0.107	2.35





**Figure 4** Phase angle of weight fraction 50% polymer solutions versus frequency.

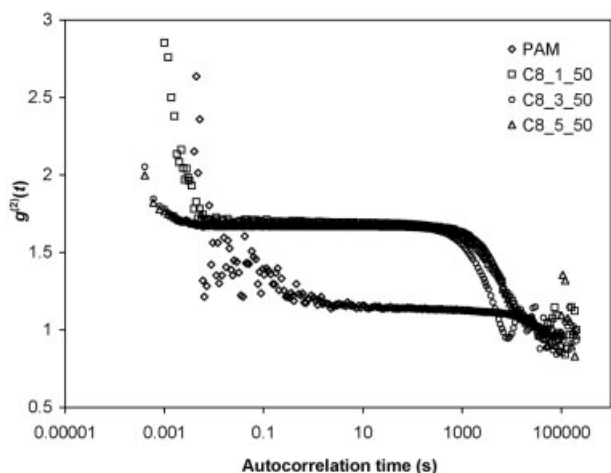
HEUR; and comb-like polymers, with the hydrophobes distributed randomly along the backbone, molecular weights in the range  $10^5$  to  $10^6$  g/mol, such as HASE and HMPAM (prepared by copolymerization method). For telechelic polymers with low molecular weight entanglement is usually ignored, while a Rouse-like relaxation process is observed, and the chains relax independently.<sup>2</sup> For comb-like polymers, which have high molecular weight, chains become entangled in the semidilute region, while a hindered reptation relaxation process is observed, with chains disengaging from association junctions first, followed by a reptation process. Chain entanglement and hydrophobic association are believed to co-contribute to viscosity enhancement.<sup>6,9,32,33</sup> The modified polymers studied here are analogous to comb-like polymers. The dynamic modulus showed that  $G'$  was two orders lower than  $G''$ ; the effect of entanglement can be ignored. Therefore only hydrophobic association contributes to the viscosity.

Groot and Agterroff used a "bead-spring" model to simulate the viscoelastic properties of common comb-like polymers.<sup>34</sup> The beads had binary associations, either free or paired. Because of entanglement, dissociation of individual associations did not break the connectivity of the networks, and the normal comb-like associative polymer had a broad relaxation time distribution.<sup>35</sup> Only bridge structures (hydrophobes in the same polymer chains distributed in different micelles) could support stress.<sup>2</sup> Lack of entanglement of polymers in the present study provides many fewer opportunities for hydrophobes in the same chain to enter different micelles and form bridge structures. Low molecular weights can lead to a broad range of dilute regions, and polymer chains cannot interact significantly below  $C^*$ . It is well known that thickener behavior is obtained in semidilute regions. The modified polymers studied here do not form a network

sufficiently to increase the viscosity of the systems studied.

The modified polymers can be dissolved in water even at concentrations as high as 50 wt %. Although the viscosity and dynamic shear modulus do not change significantly, the modified polymers can self-assemble because of their amphiphilic structure (this was confirmed by dynamic light scattering and surface tension measurement). A number of polymer chains form single flower-like micelles. Semenov's model predicted a two-phase solution composed of close-packed micelles and a polymer-lean solvent phase.<sup>36</sup> The interaction of micelles contains two terms: one is a bridging attraction and the other is an osmotic repulsion. The bridging attraction can lead to phase separation when the polymer cannot interact properly with the solvent. On the other hand, osmotic repulsion can lead to dispersion of polymers in solution. Heitz and coworkers used an alternative strategy to synthesize comb-like associative polymers with the same backbone and modification ratio, but with different molecular weights. They found that phase separation occurred for the high molecular weight polymers while the lower ones did not separate.<sup>11,12</sup> The authors debated that the bridging between micelles was only favored when the length of the polymer chain was too long for one micelle to accommodate an entire polymer chain. If a polymer chain contained hydrophobes more than the aggregation number of a micelle, phase separation could occur. The aggregation number of micelles in our systems was not studied, but it may be of the order of 20–50 according to other results.<sup>11,24,37–39</sup> This value is higher than the average number of hydrophobes in the highest substituted polymer C8\_5 (about 7). Free chain ends extending into the solution provide a steric barrier that prevents bridging association. This explains why the modified polymer can still be dissolved at such high concentration (50 wt %), while maintaining a similar viscosity to the unmodified PAM.

For the telechelic polymer HEUR, the situation is different. Viscoelastic properties of HEUR are sensitive to hydrophobe structure and functionality but not to polymer chain length. Thuresson et al.<sup>22</sup> used mixtures of PEO diblock (DB) and triblock (TB) copolymers to study rheological properties. The DB was PEO with a hydrophobic tail on one end, which was a nonionic surfactant when the TB was PEO, with hydrophobic tails on both ends, the same as HEUR. They found that only the TB contributed to formation of a transient network, while the connectivity was provided by bridging chains. For the DB, the copolymers could form large clusters of various size that were slightly interconnected to each other. The functionality of DB was not enough to form bridging chains (crosslinking junctions). The systems studied here are different, with hydrophobes randomly attached to the



**Figure 5** Autocorrelation function  $g^{(2)}(t)$  of polymers at weight fraction 50%.

backbone. Intramolecular association, analogous to the loop structure of a unimer in a telechelic polymer, does not contribute to viscosity improvement; while intermolecular association, not really an analogue to bridge structure, can lead to formation of clusters with larger size, but the large particle size does not imply efficient bridge structures. Only when the hydrophobes on the same chain join different micelles it is possible to form a network. Polymer chain entanglement can provide the opportunity to form an efficient network. Meanwhile, there is a balance between attractive and repulsive forces. When repulsion overcomes attraction, the viscosity of the solution can be increased while maintaining polymer dissolution. But when the attraction is larger than the repulsion, phase separation occurs and the rheological behavior is suspension-like.<sup>40</sup> There are far fewer opportunities for the low molecular weight polymers to form bridge structures, while viscosity cannot be increased significantly. In contrast, the repulsion of polymer clusters is large enough to maintain polymer dissolution. Regaladao and coworkers<sup>9</sup> studied the rheology of HMPAM (prepared by copolymerization), and found molecular weight was an important parameter at very high concentration. However, the results obtained here suggest that, for comb-like polymers, there may be a critical molecular weight after which viscosity enhancement can occur.

### Dynamic light scattering (DLS)

Figure 5 is the autocorrelation function  $g^{(2)}(t)$  of PAM and HMPAM at 50 wt %. PAM decays at short delay times, while the three HMPAM decay at a much longer delay time. This indicates that networks are formed in the HMPAM solution, but not for the PAM, even at this high concentration. For PAM with molec-

ular weight of  $10^4$  g/mol, the particle size of a unimer is of order of 1–2 nm. For comparison, the particle size of a nonassociated HEUR, with molecular weight of  $2 \times 10^4$  g/mol, is 4.2 nm<sup>24</sup>; and for a HASE unimer, with a molecular weight of  $2.2 \times 10^5$  g/mol, it is about 20 nm.<sup>23</sup>

Table IV shows the hydrodynamic radii for the modified polymers at various concentrations. In some cases two-component-fits gave the best results, and in these cases the approximate fraction of smaller particles is shown in parentheses. For each polymer the particle size is of the order of 100–200 nm at 5 wt % concentration, which indicates that tens of molecules associate. One aggregate does not necessarily contain only one micelle (the possible aggregate number is about 20–50, see discussion mentioned earlier), few micelles may aggregate together, but network is not formed. For polymer C8 1, the size of the particles does not change significantly until 25 wt %, followed by an increase in the apparent size by an order of magnitude at 50 wt %. In addition, there is no significant contribution from any second component over the whole concentration range. The situation for solutions of C8 3 and C8 5 was quite different. For C8 3 the particle size showed a large increase at 15 wt %, and two components were needed to fit the data, indicating a bimodal size distribution. For C8 5 there was a similar increase at 10 wt %. The very large particle size suggests that a transient network is formed, with C8 5 forming this network at a lower concentration and higher ratio. In both cases, the concentrations where these networks formed were below  $C^*$ . When the concentration was increased by a further 5 wt %, the size decreased to a value comparable with that of the C8 1 polymer. At a concentration of 50 wt %, all three polymers appeared to form a network.

**TABLE IV**  
Hydrodynamic Radii (nm) of HMPAM at Various Polymer Concentrations

Weight fraction (%)	C8 1	C8 3	C8 5
5	117	166	220–226 50–100 (16)
10	129–142	150–250 87 (16) <sup>a</sup>	2000–3000
15	130–170	2000–3000 96 (52)	
20	140–240	150–170	170–220
25	180–220	120–140	160–180
50	950–1600	680–1100	600–1000

<sup>a</sup> Values in parentheses indicate the approximate concentration (%) of particles for the bimodal samples.

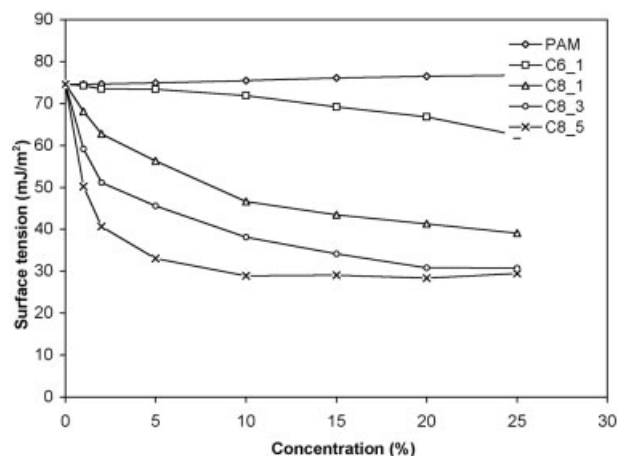
Above 25 wt %, in the semidilute region, the polymer chain interactions were well developed even without entanglement.

The values of the largest particle sizes (2000–3000 nm) are larger than the filter pore size. The interpretation is that the reversible association junctions were broken during filtration, and re-formed after passing through the filter.<sup>23</sup>

The DLS analysis shows that the HMPAM in this study does associate even though there is no significant increase in viscosity. The particle size was quite consistent over the whole range of concentration. The questions that need to be answered are: why is there no significant change in viscosity even though a network is formed? And why do the particle sizes of C8\_3 and C8\_5 decrease again at high concentration? As Figure 1 showed, the critical concentration  $C^*$  was between 15 and 20 wt %, and this value is higher than that for which C8\_3 and C8\_5 showed an increased particle size. Below  $C^*$ , the polymer chains cannot interact efficiently; the junctions of networks are very weak reversible associations instead of chemical bonds. In this situation, the system cannot support stress any more efficiently than the unmodified PAM.

Rheology and DLS reflect different aspects of the solution properties. DLS shows that association does occur in the modified polymer, while rheology shows that the association has not contributed to a significant viscosity enhancement as for associative thickeners. The association is caused by the amphiphilic nature of the molecules. Surfactants are also amphiphilic, and their molecules are associated to form micelles in aqueous solution, but they do not lead to viscosity increases. PEO diblock copolymer (DB) is a nonionic surfactant, and studies of DB, triblock copolymer (TB), and their mixture showed that TB polymer played a crucial role in the establishment of a strong network at high concentration.<sup>22</sup> As previously discussed, C8\_1 polymer contains only one or two hydrophobes per chain, which is analogous to DB, and it therefore could not contribute to network formation even though it was associated. While C8\_3 and C8\_5 are analogous to TB, there are excess hydrophobes to form bridge structures. The data shows that C8\_5 is more efficient as it forms a network at lower concentration, compared with C8\_3. At higher concentrations, the networks become re-dissolved in the micelles themselves, and the connectivity is disrupted. The values of the particle size (except where networks were forming) were consistent over the whole range of concentrations. After modification, the polymers have surfactant properties, and the molecules can self-assemble into micelles, with bridge structures forming below  $C^*$  in polymers with a high substitution ratio, but then re-dissolving in the micelles themselves.

The viscoelastic properties of associative polymers are very sensitive to surfactants. The classical behavior



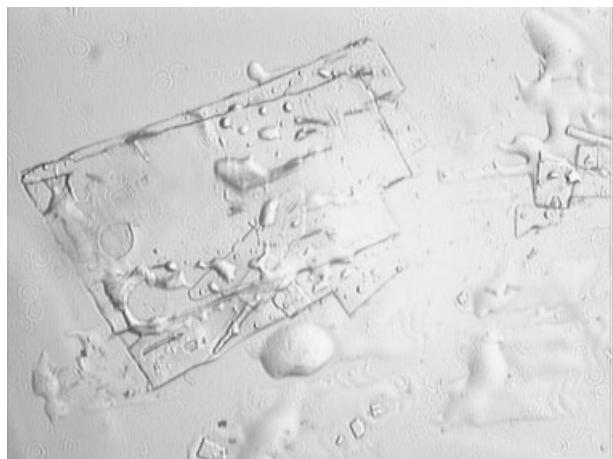
**Figure 6** Surface tension versus polymer concentration in pure water solution.

of associative polymers and surfactant interactions is that there is a viscosity maximum at a critical surfactant concentration. Below this concentration, the apparent viscosity of the associative polymer–surfactant solution increases because the surfactant increases the strength and number of associations; above the critical concentration, excess surfactant would dissolve the hydrophobes, and network connectivity would be disrupted. The viscosity can drop even below the level when surfactant is absent.<sup>41–44</sup> The polymers studied here had both surfactant properties and associative polymer properties. So, once the polymers associate, the particle size increases and this can lead to enhancement of viscosity. On the other hand, as the polymer behaves like a surfactant, it will prevent network formation, thus lowering the viscosity. The balance between these competing effects may explain why the total viscosity is of the same order as that of PAM.

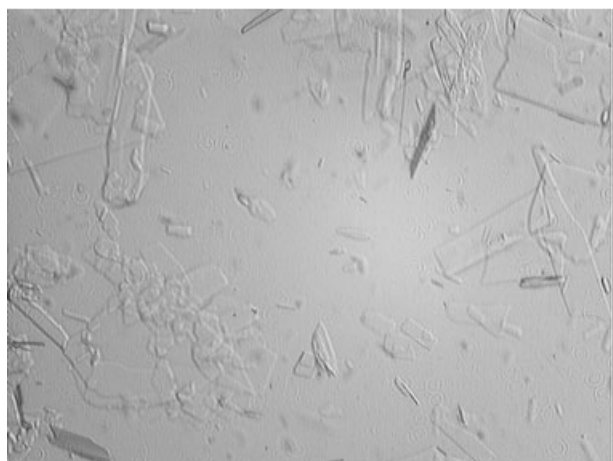
### Surface activity

After being modified with hydrophobic groups, PAM changes from a purely hydrophilic polymer into an amphiphilic polymer, and becomes surface active. Figure 6 shows that PAM has weak surface activity. For C6\_1, the hydrophobes are not hydrophobic enough to form micelles, though they decrease the surface tension. For octyl modified PAM, the surface activity increased with hydrophobe content, and the surface tension decreased from 75 mJ/m<sup>2</sup> to a plateau at about 30 mJ/m<sup>2</sup> at high polymer concentrations. Other evidence of surface activity was the HLB (hydrophile-lipophile balance) value of the modified polymer. HLB is equal to mol % of hydrophilic group divided by 5, give a arbitrary range between 20 (hydrophilic) and 0 (lipophilic).<sup>45</sup> The HLB value of HMPAM is about 10, indicating its amphiphilic nature. Thus, HMPAM could be regarded as a polymeric nonionic surfactant,





(a)



(b)

**Figure 7** Images of phase separation at HMPAM-SDS systems ( $\times 100$ ).

where the hydrophilic groups of the surfactant are the amide groups along the polymer backbone.

#### Interaction with SDS in hydrophobe domains

Although PAM interacts weakly with SDS, HMPAM can interact more strongly with SDS. The important parameter for the interaction is the ratio between surfactant and hydrophobes ( $N_{\text{SDS}}/N_h$ ). When  $N_{\text{SDS}}/N_h$  is below 1, the SDS and HMP solution is located in the hydrophobe domain regions. The polymer concentration was from 5 to 25 wt %, while the SDS concentration was between 0.5 and 2.5 g/L, consistent with experiments in other domains.

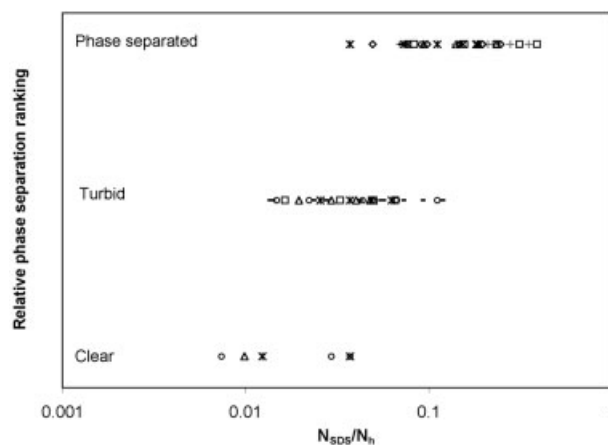
After mixing with SDS, the surface tension of solutions decreased rapidly to about 24–26 mJ/m<sup>2</sup>. The pure polymer solution was clear, but some HMPAM-SDS solutions became turbid, or phase separated. Small gel particles of about 0.2–0.3 mm in size ap-

peared in the solution, as are shown in Figure 7. Phase separation has previously been observed by dilution of a HMP system at an intermediate SDS concentration.<sup>19,46</sup> Figure 8 shows how phase conditions changed with  $N_{\text{SDS}}/N_h$  (below 1). Turbid solutions varied from slightly turbid to very turbid, although they had the same ranking. Figure 8 indicates that the solutions became turbid and phase-separated gradually when  $N_{\text{SDS}}/N_h$  increased from 0.01 to close to 1. Although the regions overlap, the trend is clear that the polymer chains become contracted when SDS was added, until finally precipitation occurs. The hydrophobes on the polymer chains are hydrophobic enough to solubilize individual surfactant in this surfactant-induced association process.

#### Interaction with SDS in transitional and surfactant domains

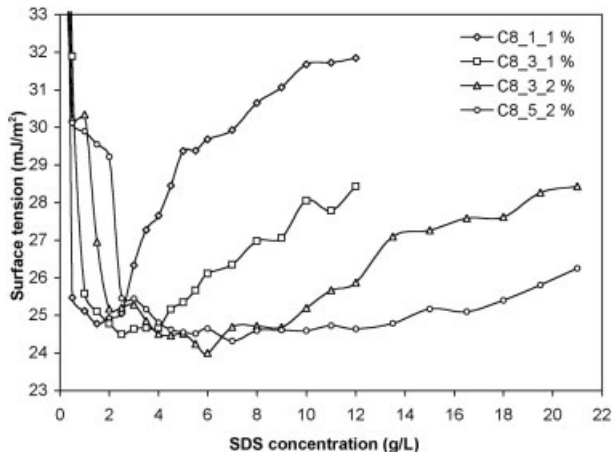
The transitional domains refer to when the ratio of surfactant and hydrophobes is stoichiometric (of the same order). The value of  $N_{\text{SDS}}/N_h$  was 1–4. Surfactant domains refer to  $N_{\text{SDS}}/N_h$  values over 4. For these experiments, the polymer concentration was chosen in the dilute region, 1 and 2 wt %, and SDS concentration started from 0.5 g/L.

Figure 9 illustrates surface tension versus SDS concentrations for the polymer solutions. It shows that the surface tension decreases rapidly on adding small amounts of SDS (see hydrophobe domains), to a minimum, then the surface tension began to increase on further addition of surfactant. There are four solutions in the figure, 1 wt % C8 1 (C8 1 1%) and C8 3 (C8 3 1%) solution, 2 wt % C8 3 (C8 3 2%) and C8 5 (C8 5 2%). The number of hydrophobe sites in C8 3 1%, C8 3 2%, and C8 5 2% solution were, respectively, 3, 6, and 10 times that of the C8 1 1% solution. The range of minimum surface

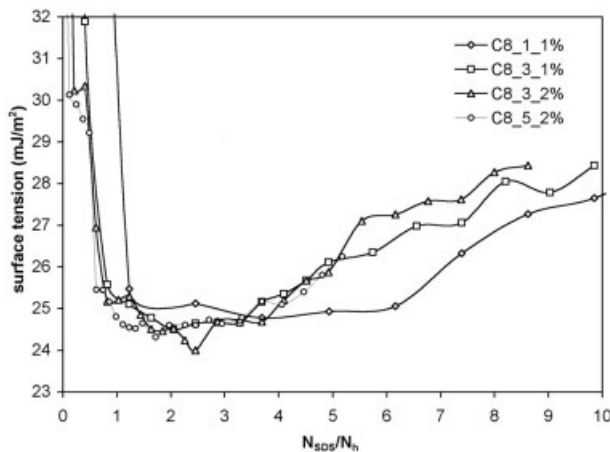


**Figure 8** Phase conditions of HMPAM-SDS systems versus value of  $N_{\text{SDS}}/N_h$  ( $< 1$ ).





**Figure 9** Surface tension of HMPAM-SDS systems versus SDS concentration.



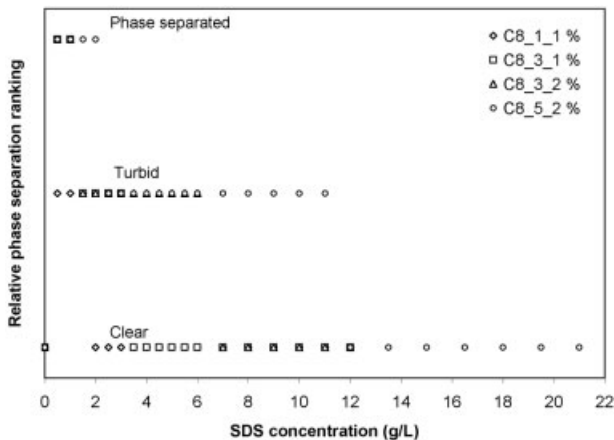
**Figure 11** Surface tension of HMPAM-SDS systems versus value of  $N_{SDS}/N_h$  ( $>1$ ).

tension was increased with the increase in the number of hydrophobe sites. Figure 10 ranks the phase condition of solutions versus SDS concentration. Comparison of Figure 9 with Figure 10 indicates that decrease in surface tension corresponds to phase separation. The minimum surface tension region corresponds to a turbid situation, and the surface tension increasing region corresponds to a one-phase region. Phase-change processes always followed from clear, slightly turbid, very turbid, phase separation, very turbid, slightly turbid to clear, it was a continual transition.

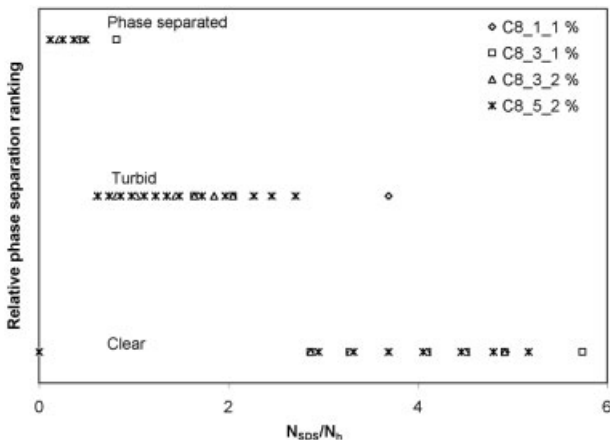
Figures 11 and 12 show the data from Figures 9 and 10 plotted as functions of the parameter  $N_{SDS}/N_h$ . They show that when  $N_{SDS}/N_h$  is below 1 (hydrophobe domains), the surface tension of the polymer solutions decreased rapidly, and the polymers began to precipitate (see hydrophobe domains section). When  $N_{SDS}/N_h$  is between 1 and 3, it was within the minimum region of apparent surface tension and the solutions gradually became clear. When  $N_{SDS}/N_h$  was

above 3, the surface tension began to increase and the solutions finally became single-phase clear solutions.

PAM interacts with SDS very weakly, and so the phenomena described earlier are due to the hydrophobes. There are three classifications of polymer-surfactant interactions.<sup>47</sup> The first is the interaction of an ionic surfactant with a hydrophilic polyelectrolyte. If the polyelectrolyte has the opposite charge, phase separation may occur with one layer of surfactant micelle and one layer of the oppositely charged polymer. If the polyelectrolyte has the same charge, the ionic surfactant will have a screening effect on it. For this category, the interaction is purely electrostatic, and no hydrophobic interaction is involved. A second category is surfactant interaction with slightly hydrophobic polymers, where the hydrophobicity of the polymers is not enough for them to self-assemble. The important parameter for this interaction is the critical aggregation concentration (*cac*). At concentrations below the *cac*, there is no interaction; at concentrations



**Figure 10** Phase conditions of HMPAM-SDS systems versus SDS concentration.



**Figure 12** Phase conditions of HMPAM-SDS systems versus value of  $N_{SDS}/N_h$  ( $>1$ ).

above the *cac*, the surfactant micelles begin to bind to the polymer chains to form polymer-surfactant complexes, a process called polymer-induced micellarization. A third category is when the surfactant interacts with hydrophobically modified polymer (HMP), where the hydrophobes are strong enough to form micelles by themselves, and they have the capacity to solubilize the individual surfactant molecules, resulting in mixed micelle complexes. This category exhibits the strongest hydrophobic interaction.

The binding ratio of surfactant to polymer is defined as  $\beta = C_{s,b}/C_h$ , where  $C_{s,b}$  is the concentration of bound surfactant and  $C_h$  is the concentration of hydrophobes.<sup>16,47-50</sup> When the binding ratio is very small ( $\beta \ll 1$ ), there is no polymer-surfactant interaction, there are only pure HMP micelles in the solution, and the polymer behavior is independent of surfactant concentration. When  $\beta \gg 1$ , cooperative binding occurs. This occurs for the second polymer-surfactant interaction category, where the polymer is slightly hydrophobic. At low surfactant concentrations there is no binding, so  $\beta$  is small; but as the concentration increases past the *cac*, the value of  $\beta$  increases markedly. A closed association model is used to describe the cooperative binding, assuming that the bound micelle has a fixed aggregation number. When  $\beta \sim 1$ , the number of bound surfactant has the same order of the hydrophobes. For the third category of polymer-surfactant interaction, where polymer contains strongly hydrophobic groups, the polymer can bind individual surfactants, and it will saturate with surfactant in the same order as the hydrophobic sites, making the  $\beta$  value close to 1. This process is described as a noncooperative process, and it is a continuous process, with the bound surfactant being always proportional to the number of hydrophobic sites, which is represented by a Langmuir isotherm model.<sup>51,52</sup>

With the surfactant concentration continuously increasing, the HMP-surfactant system moved from the hydrophobe domain through a transition region into the surfactant domain. It follows a process of "hydrophobic species" in the system, starting from free hydrophobe side-chains, pure hydrophobe aggregates, mixed aggregates, free surfactant to pure surfactant aggregates. Free hydrophobe side-chains only exist at infinite dilution. Pure hydrophobe aggregates and pure surfactant aggregates exist in very large hydrophobes or surfactant domain regions. There are different binding isotherms in the different regions. The most studied polymers are hydrophobically modified ethyl(hydroxyethyl)-cellulose ethers (HM-EHEC) or hydroxyethyl cellulose (HM-HEC).<sup>16,20,21,25-27,41,53,54</sup> Unmodified EHEC or HEC have slight hydrophobicity, and so the surfactant can bind to the polymer in a cooperative way above the *cac*. The corresponding HMP has more complicated binding behavior, which is believed to involve a two-step process. In the hy-

drophobe domains, the surfactant is bound to the polymer in a noncooperative way, while the system contains pure hydrophobe aggregates and hydrophobe-dominated mixed micelles. In the transition region, the transitional mixed micelles exist in solution. Above the *cac*, the surfactant starts to bind to the polymer in a cooperative way, complexes are formed, and the systems move into the surfactant domains. The mixture of mixed aggregates, free surfactant and pure surfactant aggregates coexist in this system. Other polymers, such as nonionic polyacrylamide (PAM), have very weak interaction with the surfactant SDS. The corresponding hydrophobically modified polymer, HMPAM, could absorb surfactant at hydrophobe sites in a noncooperative way, until it is saturated.<sup>17,55-59</sup>

Hydrophobes interact with SDS in a noncooperative way, which is a continuous process described by the Langmuir isotherm. It is proposed that the absorption is proportional to the number of nucleation sites-hydrophobes. Effing et al.<sup>56</sup> used surfactants with aromatic rings to study the interaction between HMPAM and anionic surfactants. They found that HMPAM was saturated with a limited amount of surfactant. Below a certain amount of surfactant, the polymer-surfactant system was described by a two-site model, composed of free surfactant and surfactant-bound polymer; above that amount of surfactant, the system was a three-site model with free surfactant, free surfactant micelles and surfactant-saturated copolymer. Other HMPAMs, which were studied by pulse field gradient NMR and surface tension methods, bound only low amounts of SDS (about 1-3 SDS per hydrophobe). Combined with the results obtained in this study, it is proposed that SDS and HMP form a complex with  $N_{SDS}/N_h$  from 1 to 3. In this region, the system experienced a minimum apparent surface tension, and the polymer chains contracted by hydrophobic association.

Phase separation of dilute EHEC and HMEHEC at intermediate SDS concentrations was reported by Nilsson et al.,<sup>19</sup> who also observed small gel-like particles, and the solubility of HMEHEC-SDS complex was decreased in the noncooperative region. A critical  $N_{SDS}/N_h$  value was responsible for surfactant-mediated gelation of HMHEC-surfactant systems, which was attributed to micelle-like aggregation bridged with multiple polymer chains. However if a gel forms entirely from solution in semidilute regions, polymer chains may form a network, and the gel phase will not appear as small particles. There is a balance between the hydrophobic attractive interactions and the electrostatic repulsive forces. Adding low amounts of SDS could increase the attractions, then adding more SDS could lead to repulsive forces being increased to overcome the attractions, resulting in the micelles being dissolved.

When  $N_{\text{SDS}}/N_h$  was over 3, the apparent surface tension began to increase and the solution became clear again. After the polymer was saturated with surfactant, these nonionic HMPAM formed a polymer–SDS complex, which had an apparent polyelectrolyte character. The “necklace” model has been proposed for polymer–surfactant complexes,<sup>48</sup> considering the polymer chain as a string and surfactant clusters as beads. The electrostatic repulsion expands the polymer chains, and surfactant clusters are evenly distributed along the backbone, with hydrophobes as nucleation sites. This molecular picture was represented by Biggs and coworkers.<sup>58</sup>

Phase behavior is another important aspect of the study of the interaction of polymer–surfactant systems. Phase studies have been reviewed exhaustively by Piculell et al., who pioneered research in this area.<sup>46,49,50,60</sup> In general, there are two types of phase separation: associative separation, where polymer and surfactant are enriched in the same phase; and segregative separation, where polymer and surfactant are separated into different phases.<sup>61</sup> It is believed that associative separation occurs when polymer–surfactant interactions dominate, while segregative separation occurs when polymer–solvent interactions dominate. Composite fractions, polymer and surfactant charge, hydrophilicity and temperature all influence the phase behavior. The Flory–Huggins theory is extensively used to describe phase behavior.<sup>62,63</sup> The experiments were not continued to very high SDS concentrations. Some researchers have proposed that phase separation could occur again.<sup>50</sup> Unlike intermediate SDS concentrations, where associative phase separation occurs (complex formation), the second phase separation should be a segregative separation, which is composed of a mixed aggregation phase and an excess pure surfactant aggregation phase. Adding SDS can increase the preference for interaction either with polymer or with water, the former promotes associative interaction, while the later promotes segregative separation. The general phase behavior for nonionic polymer-anionic surfactants consists of monophasic and biphasic association, monophasic and biphasic segregation processes.

### Questions about polymer–surfactant interaction

The hydrophobe domains range from 5 to 25 wt %, and are located in the dilute to semidilute regions, while in transitional regions and surfactant domains, the concentration of polymer was chosen as 1 and 2 wt %, totally in the dilute region. The behavior of HMP–SDS in hydrophobe domains may be different if it was performed at the same concentration as in transitional regions and surfactant domains. Viscosity studies with hydrophobically modified (hydroxypropyl)guar showed a very complicated behavior of polymer–sur-

factant interactions.<sup>64</sup> There were four regions identified: infinite polymer solution–surfactant before critical concentration, low polymer solution–surfactant before critical concentration, infinite polymer solution–surfactant after a critical concentration, and low polymer solution–surfactant after a critical concentration. Each was responsible for different behavior. In the current study, the low molecular weight leads to a very broad dilute region; the hydrophobe domains were studied over a broad range from the dilute region to the semidilute region, while SDS concentration was consistent with that of transitional and surfactant domains.

Another question is what was the composition of the precipitate? Was it pure polymer–surfactant complex or an aggregation of a few polymer chains? Or was it a mixture of complex and aggregation? NMR could be used to analyze the composition.

The third question is that after re-dissolution, it is not clear why the surface tension began to increase. In hydrophobe domains, the surfactant induced the polymer to associate, the polymer chains compacted (in dilute solution) or bridge attractions increased (in the semidilute region), leading to phase separation. The surface tension attained a minimum value when  $N_{\text{SDS}}/N_h$  was between 1 and 3, corresponding to a complex formation ratio. The small value of surface tension indicated the surface activity, the polymer chains were very compact, and more molecules were assembled at the air–liquid interface. Figure 11 showed that the surface tension of polymer with more hydrophobe sites was slightly higher. This may be due to a relatively lower excess of surfactant, which caused the polymer to have a lower screening effect, therefore the polymer chains were slightly more expanded. The questions posed here cannot however be answered by surface tension methods, and so other techniques need to be applied to further study HMPAM.

### CONCLUSIONS

From dilute solution viscosity measurements, it was found that the various HMPAMs with molecular weights of 10,000 g/mol had molecular sizes that were similar at infinite concentration because of the relative elongation of the backbone regardless of substitution.

Rheological study of PAM and HMPAM concentrated solutions showed that the modified polymers had the same order of steady viscosity and dynamic shear modulus as that of PAM. There was no significant viscosity enhancement of the modified polymer. Both PAM and HMPAM at 50 wt % form viscous solutions. Among three modified samples, C8 1 showed the most liquid-like behavior. It is proposed that molecular weight is a critical factor for comb-like polymers to provide thickener behavior.

Dynamic light scattering measurement showed that hydrophobically modified polymers are associated from low concentrations. The particle size of C8-1 was consistent over the range of 5 to 25 wt %, which suggested that the molecules self-assemble at a certain aggregation number. However for HMPAM C8-3 and C8-5, transient networks were formed at concentrations below  $C^*$ , though at higher concentrations these networks re-dissolved into micelles, formed by the polymer itself and were consequently disrupted. C8-5 could form bridge-chains easier than C8-3, and it formed a network at lower concentration and higher fraction when compared with C8-3. Over the whole range of concentration, a network was not established efficiently enough to result in viscosity enhancement.

Surface tension measurements and the emulsifying behavior of modified polymers showed that HMPAM was surface active, and so HMPAM can be regarded as a nonionic polymeric surfactant.

HMPAM could interact with the surfactant SDS. The ratio between surfactant and hydrophobes ( $N_{\text{SDS}}/N_h$ ) was an important parameter. In the hydrophobe domains, with  $N_{\text{SDS}}/N_h < 1$ , the surface tension of the polymer-surfactant system decreased rapidly with increasing  $N_{\text{SDS}}/N_h$ , and the solution changed from clear to turbid then finally phase separated, indicating that polymer chains contracted on addition of surfactant. This was identified as a surfactant-induced association process.

At  $N_{\text{SDS}}/N_h$  between 1 and 3 or 4, there was a hydrophobe-surfactant transition region, where the surface tension of the polymer-surfactant system had a minimum, the total system was separated into two phases at  $N_{\text{SDS}}/N_h$  of about 1, and gradually the system became clear at  $N_{\text{SDS}}/N_h$  of about 4. In this region, the surfactant was bound to polymer in a noncooperative way, surfactant and HMPAM formed a complex, until the hydrophobes were saturated with surfactant. The polymer chains were most contracted at  $N_{\text{SDS}}/N_h$  of about 1, and the chains expanded on adding surfactant. The "necklace" model was used to describe the complex; electrostatic repulsive force finally overcame the association and the solution became clear again.

At  $N_{\text{SDS}}/N_h$  above 3, the system became totally clear, and the surface tension began to increase on addition of surfactants, though the reason for this remains unclear.

In general, even though HMPAM itself can be regarded as a nonionic surfactant, it showed typical polymeric behavior when it interacted with surfactant. The polymer chains were first contracted on adding surfactant, and bound with surfactant to form a complex. Later the polymer chains became extended because of electrostatic repulsion overcoming associa-

tion. Adding a certain amount of surfactant could control the conformation of the polymer chains.

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