Water-soluble polymers: 59. Investigation of the effects of polymer microstructure on the associative behaviour of amphiphilic terpolymers of acrylamide, acrylic acid and *N*-[(4-decyl)phenyl]acrylamide

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Water-soluble terpolymers of acrylamide, acrylic acid and *N*-[(4-decyl)phenyl]acrylamide have been synthesized by a micellar polymerization technique. Neutralization of the acid groups after polymerization yields hydrophobically modified polyelectrolytes. The ratio of the surfactant to the hydrophobic comonomer (SMR) was varied in successive polymerizations to yield a series of terpolymers with varied amphiphilic microstructures. Although each terpolymer in the series was identical in overall composition and molecular dimensions, profound differences in associative behaviour were observed. Terpolymers synthesized at low SMR exhibit large enhancements in viscosity owing to hydrophobic associations in 0.5 M NaCl. Those synthesized at high SMR behave in a similar fashion to a control acrylamide/acrylic acid copolymer. While viscometric studies indicate associative thickening behaviour, pyrene probe fluorescence studies fail to indicate the presence of well-organized hydrophobic microdomains.

(Keywords: amphiphilic terpolymers; micellar polymerization; hydrophobic associations)

INTRODUCTION

Hydrophobically modified water-soluble polymers are of increasing interest as aqueous thickening agents in areas such as enhanced oil recovery, formulation of water-based coatings and in personal care[1–4]. Such amphiphilic systems may be tailored to yield associative thickeners which rely on intermolecular hydrophobic associations above a critical overlap concentration (C^*). In aqueous solution C^* often appears well below the critical entanglement concentration of the unmodified or parent polymer of equivalent molecular weight. One particularly useful synthetic method for preparing copolymers and terpolymers which possess these properties is the micellar polymerization method of Turner *et al.*[5]. Copolymers of acrylamide (Am) and hydrophobic acrylamido or acrylate monomers prepared by this method have been the subject of study in our laboratories[6–9] as well as in others[10–14]. Furthermore, study of the micellar polymerization process has become increasingly important owing to the unique microstructure which results[7–9,14–16,24].

Elucidation of the mechanism of micellar polymerization has proven difficult for a number of reasons. A major limitation of earlier studies with n-alkylacrylamides as the hydrophobic comonomers[5,6,17] was the difficulty in accurately determining the number of hydrophobic groups incorporated into the polymer. Insufficient concentration of hydrophobic monomer was present for analysis by traditional methods such as nuclear magnetic resonance (n.m.r.) or elemental analysis. Incorporation of a hydrophobic comonomer that contains a chromophore allows detection by ultraviolet spectroscopy[11,12,14,18]. However, microstructural placement of the hydrophobic units is not easily ascertained from these systems.

For a number of years academic and industrial researchers postulated the existence of a 'microblocky' segmental structure; however, only recently has strong evidence been gained with fluorescent labels linking viscosity enhancement with microstructure. In our laboratories, for example, we have utilized fluorescent monomers which serve as the sole hydrophobic entity to prepare associative copolymers. Copolymers of acrylamide and a pyrene sulfonamide containing comonomer (APS) prepared by the micellar polymerization method have a 'blocky' microstructure relative to a random distribution in polymers synthesized by solution polymerization[7,8]. High values of excimer to monomer intensity, I_E/I_M, in the former indicate a higher local chromophore concentration and, therefore, a more 'blocky' microstructure. Also, rheological studies indicate that such an arrangement is responsible for viscosity enhancement (intermolecular associations above C^*)[7].

In a similar system with a hydrophobic monomer bearing a naphthalene chromophore, the surfactant to

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hydrophobic monomer molar ratio (SMR) was varied[9]. I_E/I_M for the naphthyl groups decreased with increasing SMR, indicating that the sequence of the hydrophobic monomers could be controlled by adjusting the initial number of hydrophobic monomers per micelle. While the naphthyl groups did not impart sufficient hydrophobicity to the copolymers for marked associative behaviour, an increase in bulk solution viscosity was noted for copolymers synthesized at a lower SMR.

Although the non-ionic copolymer systems described above provide useful properties, they possess distinct disadvantages. Dissolution from the dry state is difficult, often requiring weeks for rehydration. This practical limitation has resulted in a refocusing on hydrophobically modified polyelectrolytes[17,18]. These terpolymers consist of Am and various amounts of one of several anionic comonomers and small amounts of *N*-(n-decyl)acrylamide[17] or the *N*-aryl-substituted acrylamide *N*-[(4-butyl)phenyl]acrylamide[18]. These low to moderate charge density polyelectrolytes offer increased solubilities over non-ionic thickening agents and provide pH or electrolyte responsive properties. However, owing to electronic interferences between the anionic groups and the negatively charged sodium dodecyl sulfate micelles during polymerization, much lower levels of hydrophobe incorporation are achieved[18]. For significant control of rheological properties, it is necessary to elucidate further the mechanism of the micellar polymerization process.

In this paper we report the synthesis and solution properties of terpolymers of Am, acrylic acid (AA) and *N*-[(4-decyl)phenylacrylamide (DPAm) polymerized in the presence of specified concentrations of sodium dodecyl sulfate (SDS). The structures of these monomers are shown in *Figure 1*. This work complements the studies using fluorescent-labelled hydrophobic monomers in which we originally identified the surfactant to hydrophobe molar ratio as the defining parameter for the control of the microstructural architecture of hydrophobically modified water-soluble copolymers and terpolymers[9]. The purpose of this study is two-fold. First, we wish to extend the concepts of the micellar polymerization to more complex systems, including those which utilize ionizable monomers. Second, we wish to explore the electrolyte responsive nature of these hydrophobically modified polyelectrolytes by tailoring of the microstructure through manipulation of the SMR during polymerization. In this study we present further evidence that the 'initial polymerization conditions' dictated by the SMR have profound effects on the associative behaviour of the resulting microblocky terpolymers.

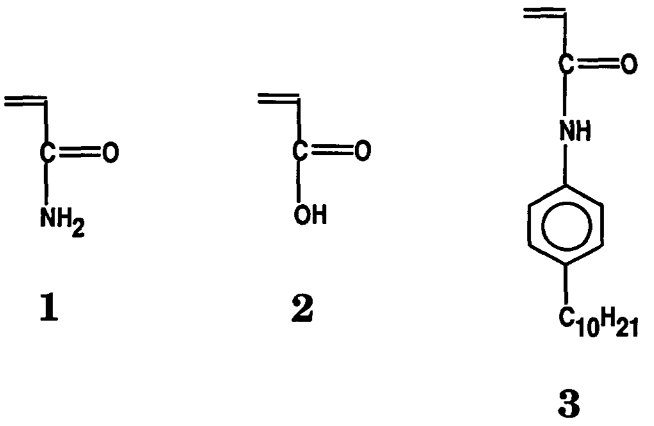

Figure 1 Monomers for micellar polymerizations: acrylamide (Am) **1**; acrylic acid (AA) **2**; *N*-[(4-decyl)phenyl]acrylamide (DPAm) **3**

EXPERIMENTAL

Instrumentation and analysis

Elemental analysis was performed by M-H-W Laboratories (Phoenix, AZ). High performance liquid chromatography (h.p.l.c.) was performed with a Hewlett–Packard model 1050 equipped with a photodiode-array detector. A Waters C18 column was employed with methanol as the mobile phase. Ultraviolet (u.v.) spectra were obtained with a Hewlett–Packard model 8452A photodiode-array spectrophotometer. Infra-red (i.r.) spectra were obtained with a Mattson model 2020 Fourier transform i.r. spectrophotometer. ^{13}C nuclear magnetic resonance (n.m.r.) spectra (in deuterated dimethyl sulfoxide (d_6-DMSO)) were obtained with a Bruker AC200 spectrometer. Steady-state pyrene fluorescence studies were performed with a Spex Fluorolog 2 fluorescence spectrophotometer equipped with a DM3000F data system ($\lambda_{EX} = 335$ nm, $I_1 = 372$ nm, $I_3 = 384$ nm). Viscosity measurements were conducted on a Contraves LS-30 low shear rheometer at 25°C and a shear rate of $6\,s^{-1}$ unless otherwise noted. An upper limit of 250 cP ($IP = 0.1\,N\,s\,m^{-2}$) may be obtained on the Contraves LS-30 at this shear rate. This value was arbitrarily assigned to samples which exceeded this upper limit for means of comparison. Surface tension measurements were performed with a Kruss K12 processor tensiometer using the Wilhemy Plate method. Refractive index increments (d*n*/d*c*) were obtained with a KMX-16 laser differential refractometer. Light-scattering studies were conducted with a Spectra-Physics 127 laser operating at 632.8 nm. Data points for classical scattering were taken at multiple angles with a Brookhaven Instruments model BI-200SM automatic goniometer interfaced with a personal computer, and Zimm plots were constructed using the software provided by the manufacturer. Dynamic light-scattering studies were performed at 90° and the signals were processed with a Brookhaven Instruments BI-2030AT autocorrelator. Effective hydrodynamic diameters were calculated using the algorithm CONTIN and associated software provided by the manufacturer. Multiple analyses were performed to ensure reproducibility.

Materials

Acrylamide (AM) (electrophoresis grade), 4-decylaniline (DA), triethylamine (TEA), succinic anhydride (SA) and sodium dodecyl sulfate (SDS) were purchased from Aldrich and used as received. Acrylic acid (AA) and acryloyl chloride (AC) were purchased from Aldrich and distilled under vacuum prior to use. Potassium persulfate was purchased from Aldrich and recrystallized from water. Pyrene was purchased from Aldrich and recrystallizd three times from ethanol. H.p.l.c. indicated a purity of >99.9%.

Monomer synthesis

The synthesis of *N*-[(4-decyl)phenyl]acrylamide (DPAm) **3** was accomplished by a procedure adapted from previous methods[18]. DA (0.021 mol) and TEA (0.027 mol) were dissolved in 100 ml diethyl ether and cooled to 2°C in an ice/water bath. AC (0.027 mol) was placed in an addition funnel and added dropwise with stirring over a period of approximately 40 min. A precipitate (TEA·HCl) formed as the AC was added. The reaction mixture was allowed to stir in the ice/water bath for 45 min after the addition of AC was complete, then allowed to warm to room temperature, with stirring, overnight. The precipitate was collected by filtration, washed with 100 ml ether and discarded. The filtrate was extracted three times with 10% HCl, once with 10% $NaHCO_3$ and the ether layer was dried over $MgSO_4$. The ether layer was filtered and the solution volume was reduced by evaporation at reduced pressure to 70–80 ml. This solution was then cooled to −25°C for approximately 4 h. White to off-white crystals were isolated by vacuum filtration and dried overnight under vacuum at room temperature (2.4 g, 40% yield; m.p. 97–98°C). H.p.l.c. analysis indicated this material to be 99.7% pure. The analytical results are as follows. Calculated for $C_{19}H_{29}NO$ (MW 287.44): %C, 79.39; %H, 10.17; %N, 4.89; %O, 5.57. Found: %C, 79.26; %H, 10.07; %N, 4.89; %O (not analysed), 5.78. I.r. (KBr pellet) (cm^{-1}): N–H, 3285; vinyl and aromatic C–H, 3133 and 3082; aliphatic CH_3 and CH_2, 2920 and 2949; carbonyl, 1665. ^{13}C n.m.r. (d_6-DMSO) (ppm): aliphatic CH_3, 13.8; aliphatic CH_2, 22.1–34.6 (eight peaks resolved); vinyl carbons, 126.1 and 132.0; aromatic carbons, 119.3, 128.3, 136.7 and 137.3; carbonyl, 162.8.

Model compound synthesis

The syntheses of *N*-[(4-decyl)phenylamido]proprionic acid (DPAPA, not depicted) and its water-soluble potassium salt were performed as previously described[18]. Succinic anhydride (SA) (0.01 mol) was slurried in 100 ml diethyl ether. 4-Decylaniline (DA) (0.01 mol) was dissolved in 20 ml diethyl ether, placed in an addition funnel and added dropwise at room temperature over a period of approximately 15 min. As the DA solution was added, the SA dissolved, followed by formation of a white precipitate. White crystals were isolated by vacuum filtration. The filtrate was chilled in an ice bath and more crystals were isolated. The product was dried under vacuum at room temperature (2.2 g, 70% yield; m.p. 153–154°C). H.p.l.c. analysis showed that this material was approximately 99.5% pure. The analytical results are as follows. Calculated for $C_{20}H_{30}NO_2{\cdot}H_2O$ (MW 334.46): %C, 71.81; %H, 9.04; %N, 4.19; %O, 14.96. Found: %C, 71.58; %H, 9.05; %N, 4.15; %O (not analysed), 14.96. I.r. (KBr pellet) (cm^{-1}): 3320, 3185, 3115, 3044, 2922, 2850, 1697, 1661, 1597, 1531, 1412, 1325 and 1188. ^{13}C n.m.r. (d_6-DMSO) (ppm): aliphatic CH_3, 13.9; aliphatic CH_2, 22.1–34.6 (eight peaks resolved); aromatic carbons, 118.9, 128.3, 136.8 and 137.0; carbonyls, 169.7 (amide) and 173.8 (acid).

The potassium salt of DPAPA was made by dissolving approximately 4×10^{-5} mol in 100 ml deionized water containing an equivalent amount of KOH. Dilutions of this stock solution were made with deionized water and the molar absorptivity ε was determined to be 10 666 $M^{-1}\,cm^{-1}$ at 250 nm.

Polymer synthesis and purification

Polymer synthesis was accomplished using the micellar polymerization method of Turner *et al.*[5]. The total monomer concentration was 0.44 M, with the following feed ratios: Am, 0.695; AA, 0.30; DPAm, 0.005. Sodium dodecyl sulfate (SDS) was used as the surfactant to solubilize the hydrophobic comonomer, and potassium persulfate was used as a free radical initiator. The surfactant/hydrophobic monomer molar ratio (SMR) was varied from 40 to 100 and $[K_2S_2O_8]/[\text{monomer}]$ was kept constant at 1/3000. The method previously published from our laboratories[17,18] was followed except as noted. The acrylic acid monomer was reacted in its acidic form and neutralized after polymerization. Polymerization was conducted at pH 4–5 for 3–3.5 h at 50°C. Polymers were isolated by precipitation into acetone, followed by drying and redissolution into water. After one week of dissolution, the pH was adjusted to between 7 and 8 and the polymers were dialysed against deionized water in SpectraPor no. 4 dialysis tubing (MW cut-off 10 000–14 000) for at least one week. The samples were then lyophilized to a constant weight.

Sample preparation

Samples for viscosity measurements were made by preparing stock solutions of 0.20 $g\,dl^{-1}$ of polymer in deionized H_2O and adjusting the pH to approximately 7.5–7.7 using microlitre amounts of NaOH and HCl solutions. The solutions were shaken on an orbital shaker for at least one week before dilutions were made. For samples containing added salt, the dry NaCl was added to the polymer solutions. Samples were equilibrated for a minimum of 24 h.

Samples for pyrene probe experiments were prepared by adding microlitre amounts (typically 1–2 μl) of a stock solution (pyrene in methanol) necessary to give a final pyrene concentration of 10^{-6} M to polymer solutions of the desired concentration and ionic strength. These solutions were allowed to equilibrate for a minimum of 24 h.

Samples for d*n*/d*c* and light-scattering measurements were prepared by dissolving the appropriate amount of polymer in the desired solvent. After a minimum of one week, the pH of the solution was adjusted to between 7.1 and 7.5 using microlitre amounts of NaOH and HCl solutions. Solutions were filtered through 0.2 or 0.45 μm Millipore filters.

RESULTS AND DISCUSSION

Terpolymer synthesis and composition

The amphiphilic polyelectrolytes of this study were prepared from acrylamide (Am) **1**, acrylic acid (AA) **2**, and *N*-[(4-decyl)phenyl]acrylamide (DPAm) **3** (*Figure 1*). The Am monomer has a high k_p^2/k_t and is the hydrophilic component along with the pH and electrolyte responsive AA units. DPAm was synthesized by a procedure similar to that reported previously for *N*-[(4-butyl)phenyl]acrylamide[18]. This monomer has both the hydrophobic character and chromophore desired. The DPAm model compound *N*-[(4-decyl)phenylamido]proprionic acid (DPAPA, not depicted) was synthesized by a procedure similar to that previously reported for *N*-[(4-butyl)phenylamido]proprionic acid[18]. The molar absorptivity ε of this model compound in water was determined to be 10 666 $M^{-1}\,cm^{-1}$ at 250 nm. Polymerizations were carried out under micellar reaction conditions in SDS/H_2O utilizing potassium persulfate as the initiator. A control copolymer of Am/AA **4** was synthesized in the presence of surfactant. The feed compositions are shown in *Table 1*. Identical feed ratios were used for the terpolymers **5**–**8** and the terpolymer microstructure was varied by changing the surfactant concentration as

Table 1 Compositional data for the Am/AA copolymer **4** and the Am/AA/DPAm terpolymers **5–8**

Sample	SMR	Feed ratio AM/AA	AM content (mol%)	AA content (mol%)	DPAm content (mol%)	Conversion (%)
4	Unmodified	70/30	60.4	39.6	0	25
5	40	69.5/30	62.2	37.4	0.4	53
6	60	69.5/30	63.6	35.9	0.5	53
7	80	69.5/30	64.9	34.7	0.4	57
8	100	69.5/30	64.8	35.9	0.5	52

Table 2 DPAm molecules per micelle as a function of SMR and [SDS] for terpolymers **5–8** ([DPAm] $=2.2\times10^{-3}$ M, CMC $=6.5\times10^{-3}$ M and $N=60$)

Sample	SMR	[SDS] (M)	DPAm molecules per micelle
5	40	0.088	1.62
6	60	0.132	1.05
7	80	0.176	0.78
8	100	0.220	0.62

Table 3 Dynamic light-scattering results for the copolymer **4** and the terpolymers **5–8** in 1.0% SDS

Sample	SMR	$10^8 D_0$[a] (cm^2 s^{-1})	d_H (nm)
4	Unmodified	1.89	256[b]
5	40	2.38	203
6	60	1.94	249
7	80	1.88	257[a]
8	100	2.26	214

[a] Limiting diffusion coefficient

[b] Diameter distribution was bimodal

discussed below. Compositions of the terpolymers **5–8** and copolymer **4** (*Table 1*) in this study were determined by a combination of elemental analysis (EA) and u.v. spectroscopy using the previously published methods[18]. The amount of acrylic acid in the polymers is slightly greater than the feed composition, consistent with reactivity ratio predictions[19]. Polymerization at low pH eliminates ionic interferences between the charges on the growing polymer radical and the negatively charged SDS micelles. In the case of the terpolymers, percentage conversions were approximately the same (52–57%).

The statistical distribution of hydrophobic groups in micellar systems can be accurately described using the Poisson distribution[20], provided that the critical micelle concentration CMC and aggregation number N of the surfactant are known. In our systems, the CMC of SDS (at 50°C) was determined to be 6.5×10^{-3} M in deionized water containing 0.306 M Am and 0.132 M AA. These conditions closely approximate the polymerization conditions in this study. An aggregation number of 60 was assumed for SDS in this study.

From the above values, the number of DPAm molecules per micelle can be calculated using the equation

$$n=\frac{N[\text{DPAm}]}{[\text{SDS}]-\text{CMC}} \tag{1}$$

Table 2 shows the surfactant concentrations and the calculated average numbers of DPAm molecules per micelle for the terpolymers **5–8** in this series. Surfactant to monomer ratios of 40, 60, 80 and 100 were used in the polymerizations. A molar ratio of SDS to DPAm of approximately 60/1 corresponds to a 1/1 hydrophobe to micelle ratio or a statistical distribution of one hydrophobic monomer per micelle; at a lower SMR there would be more than one hydrophobic monomer per micelle on the average. The surfactant to hydrophobe ratios in this study are well below the ones used by Peer[15] and in the low range of the values used by Candau *et al.*[14].

Light-scattering studies

Attempts were made at the determination of molecular weight in several solvents. Candau *et al.*[14] indicated that formamide was a suitable solvent for hydrophobically modified polyacrylamides. However, we were unable to obtain accurate differential refractive index (dn/dc) values for the hydrophobically modified polyelectrolytes in our study, possibly complicated by osmotic effects in the low ionic strength medium. Also, light-scattering experiments were attempted in 0.5 M NaCl and 50/50 (v/v) water/methanol solutions; however, retention of the terpolymers by the filter membranes proved to be problematic. Addition of 1.0% SDS, however, lowered the solution viscosities and sufficiently stabilized the terpolymers for dynamic light-scattering studies.

In an attempt to establish the baseline molecular weight and scale of molecular size for this polymer series, classical light-scattering studies were performed on the unmodified copolymer **4** in 0.5 M NaCl (dn/dc = 0.2296); dynamic light-scattering studies were conducted on the copolymer and the terpolymers **5–8** in 1.0% SDS.

Classical light-scattering studies indicate a weight-average molecular weight (M_w) of 7.2×10^5 g mol^{-1}, a second virial coefficient (A_2) of 7.0×10^{-3} cm^3 mol g^{-2} and an estimated radius of gyration (R_G) of 68 nm for the unmodified copolymer in 0.5 M NaCl. Dynamic light-scattering data for the polymers in 1.0% SDS are presented in *Table 3*. Average hydrodynamic diameters range from approximately 200 to 250 nm with a standard error of ±31 nm. Diameter distributions are broad; the unmodified copolymer **4** and terpolymer **7** (SMR 80) exhibit bimodal (but continuous) distributions. These data indicate that the molecular dimensions of the copolymers and terpolymers are quite similar in solution. The source of the bimodal distributions is currently under investigation.

Viscometric studies

As noted in the preceding sections, the compositions of the terpolymers in this study are virtually identical and

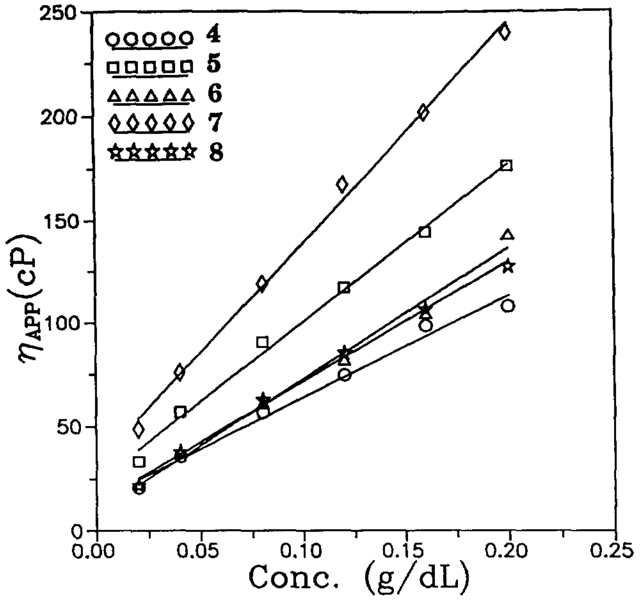

Figure 2 Apparent viscosities as a function of polymer concentration in deionized water at 25°C and a shear rate of $6\,s^{-1}$

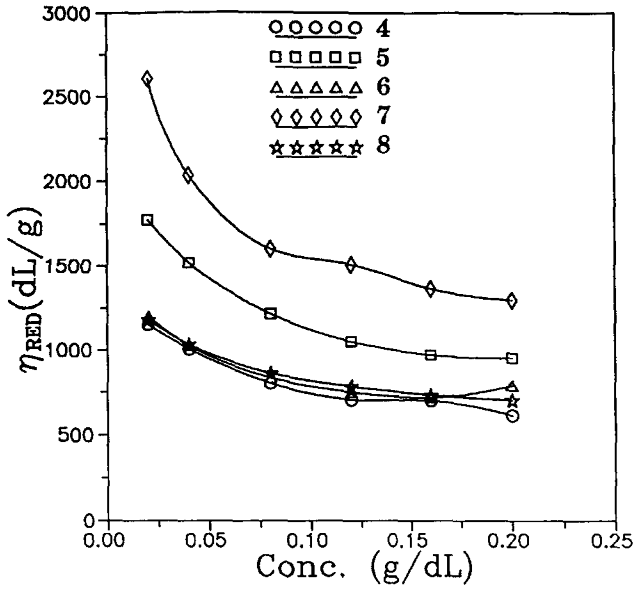

Figure 3 Reduced viscosities as a function of polymer concentration in deionized water at 25°C and a shear rate of $6\,s^{-1}$

the molecular dimensions in solution are similar. Therefore differences in terpolymer aggregation may be attributed to variation of the polymer microstructure based on the SMR during the respective polymerizations[7-9].

Viscometric studies were first carried out in deionized water at specified terpolymer concentrations. Plots of apparent and reduced viscosities as a function of polymer concentration (*Figures 2* and *3*) indicate that the terpolymers, as well as the unmodified Am/AA copolymer, behave as typical polyelectrolytes in deionized water. *Figure 2* indicates that the apparent viscosity increases in a linear fashion; curvature generally associated with intermolecular hydrophobic associations is not evident. The polymers exhibit high viscosities in deionized water owing to the large hydrodynamic volume typical of polyelectrolytes. Plots of reduced viscosity *versus* polymer concentration (*Figure 3*) illustrate that hydrophobic modification does not inhibit the classical polyelectrolyte behaviour; expanded hydrodynamic size results upon dilution.

The same general trends for each terpolymer in this study are observed in both *Figures 2* and *Figure 3*. Terpolymer **7** (SMR 80) has the highest hydrodynamic volume in water, followed by **5** (SMR 40). Terpolymers **6** (SMR 60) and **8** (SMR 100) each have a hydrodynamic volume approximately equal to that of the unmodified copolymer **4**. Also, as indicated by dynamic light scattering, similar hydrodynamic diameters for the control copolymer and the terpolymers in 1.0% SDS are found.

Addition of NaCl to hydrophobically modified polyelectrolytes would be expected to result in (1) the loss of hydrodynamic volume of the individual polymer coils by shielding of intracoil ionic repulsions and (2) the enhancement of hydrophobic associations. *Figure 4* shows plots of apparent viscosity *versus* polymer concentration in 0.5 M NaCl. At low polymer concentration, all the polymers exhibit very low viscosities and thus low hydrodynamic volumes, indicative of collapse of the individual polymer coils. Under these conditions, the terpolymers behave identically to the unmodified polymer at low concentration. At sufficient polymer concentration, three of the four terpolymers exhibit sharp increases in apparent viscosity owing to hydrophobic associations of individual polymer coils. At this ionic strength, a correlation between the SMR of the polymerization and the associative properties of the resulting terpolymers is noted. Terpolymers **5** and **6** with SMR values of 40 and 60 appear to be the most strongly aggregated, with the latter having the lowest C^* (ca. $0.13\,g\,dl^{-1}$). Terpolymers **5** and **7** (SMR 80) appear to have approximately the same C^* (ca. $0.16\,g\,dl^{-1}$), but **5** appears to be more strongly aggregated. It is important to note that **5** and **6** have higher viscosities than **7** above C^*, even though the latter has the highest hydrodynamic volume in water below C^*. Terpolymer **8** (SMR 100) exhibits the lowest viscosity;

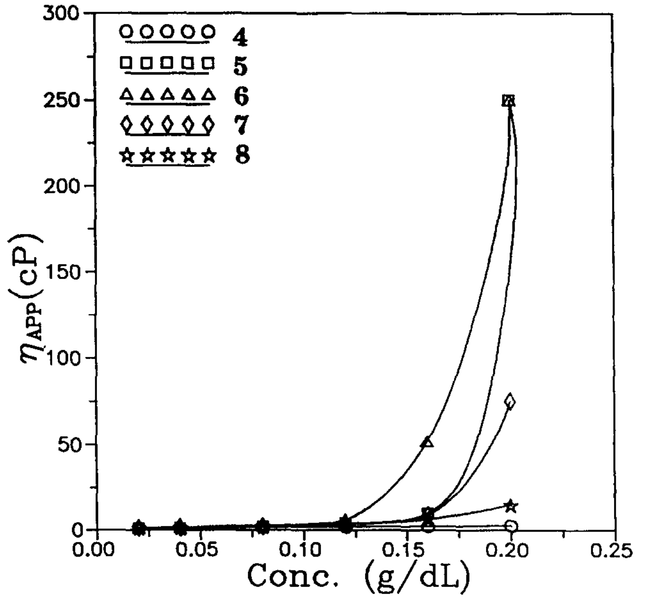

Figure 5 Apparent viscosities as a function of NaCl concentration at 25°C and a shear rate of $6\,s^{-1}$

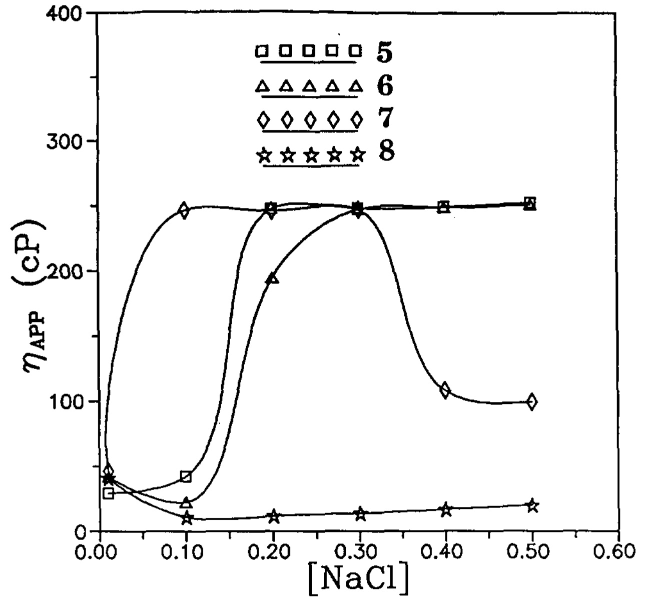

Figure 5 Apparent viscosities as a function of NaCl concentration at 25°C and a shear rate of $6\,s^{-1}$

its rheological properties are similar to those of the unmodified copolymer **4**.

The different viscometric responses of the terpolymers result from differences in the apparent microstructures formed during polymerization[7–9]. Decreasing SMR results in an initially greater number of DPAm molecules per micelle. This should theoretically increase the length of the runs of hydrophobic monomers in the resulting polymers. In this system, where the number of hydrophobes per micelle initially present is approximately two or less, some hydrophobe migration or aggregate coalescence process would be necessary in order to obtain 'blocks' of a sufficient length. Large differences in association are exhibited by the terpolymers in this series, indicating that hydrophobe migration might occur to build blocks of larger than predicted size. Also, the differences in associative properties, and thus hydrophobe migration, appear to be augmented at lower SMR. These observations are in agreement with other studies which indicate that polymer heterogeneity is greatest at higher numbers of hydrophobes per micelle[14].

To study further the response of the Am/AA/DPAm terpolymers **5**–**8** to changes in ionic strength, viscometric studies at selected NaCl concentrations were performed at a constant terpolymer concentration of $0.20\,g\,dl^{-1}$ (above C^*). *Figure 5* relates apparent viscosity to NaCl concentration. Several features are notable. First, **5** and **6** do not exhibit large increases in viscosity below an NaCl concentration of approximately 0.2 M. Thereafter, the viscosity gains are significant. Terpolymer **7** exhibits a rapid increase in viscosity in the range 0.01–0.1 M NaCl. Viscosity remains high up to 0.3 M NaCl, after which it drops significantly. The viscosity of **8** has very little dependence on NaCl concentration and remains relatively low over the entire range of NaCl concentration. Above C^* and a critical salt concentration, the terpolymers synthesized at low SMR exhibit the highest viscosities. These results are in agreement with the studies in 0.5 M NaCl. However, the unusual behaviour of terpolymer **7** (SMR 80) as a function of ionic strength has yet to be explained.

The effects of shear on solution viscosity were also studied for terpolymers **5** and **6** in 0.5 M NaCl and above C^* ($0.16\,g\,dl^{-1}$). Plots of apparent viscosity *versus* shear rate appear in *Figure 6*. This study was conducted by first increasing the shear rate at 3 min intervals and then decreasing the shear at the same rate following the $94.5\,s^{-1}$ measurement. Apparent viscosities for terpolymer **6** are higher owing to stronger aggregation in 0.5 M NaCl, but the same trends are noted for both terpolymers. Solution viscosities for both terpolymers are greater along the decreasing portion of the shear cycle, indicating that more intermolecular contacts are induced with the application of shear. The original viscosity was recovered on standing (approximately one day), and the curves were reproducible within experimental error. These data are in agreement with earlier findings for hydrophobically modified acrylamide copolymers[6], implying that associations recover from shear very quickly and that increases in viscosity with the application of shear are caused by participation of a greater number of hydrophobic groups in hydrophobic associations in solution.

Pyrene fluorescence studies

In an attempt to gain insight into the nature of aggregation, pyrene probe experiments were performed. The ratio of the fluorescence intensity of the first band to that of the third band (I_1/I_3) has been related to the polarity of the local enviroment experienced by the pyrene probe. The third vibronic band in the fine structure of pyrene fluorescence is relatively insensitive to solvent polarity, while the first vibronic band shows a marked increase with increasing solvent polarity[21]. Typical values of I_1/I_3 are approximately 1.9 for water, 1.6–1.8 for polar organic solvents such as acetone and dimethylformamide, 1.2–1.3 for solvents such as tetrahydrofuran and chloroform and 0.6 for hydrocarbons such as hexane and cyclohexane. Values in common surfactant micelles are typically 1.1–1.2.

Plots of I_1/I_3 as a function of polymer concentration in 0.5 M NaCl are shown in *Figure 7* for the terpolymers

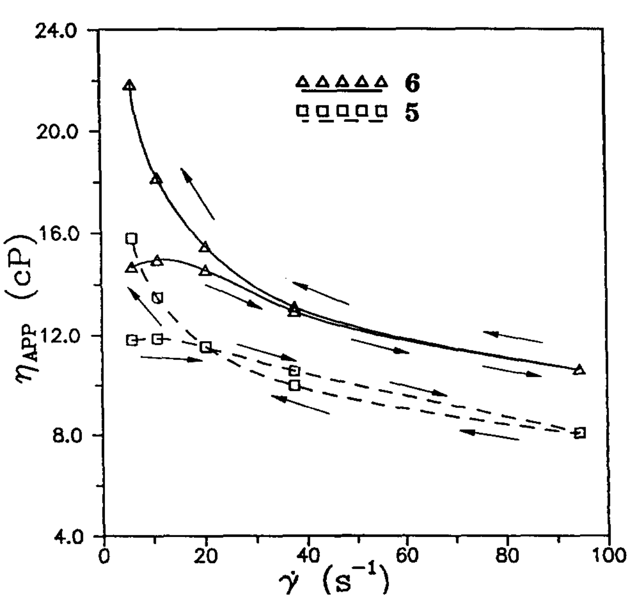

Figure 6 Apparent viscosities as a function of shear rate in 0.5 M NaCl at 25°C and $0.16\,g\,dl^{-1}$ polymer

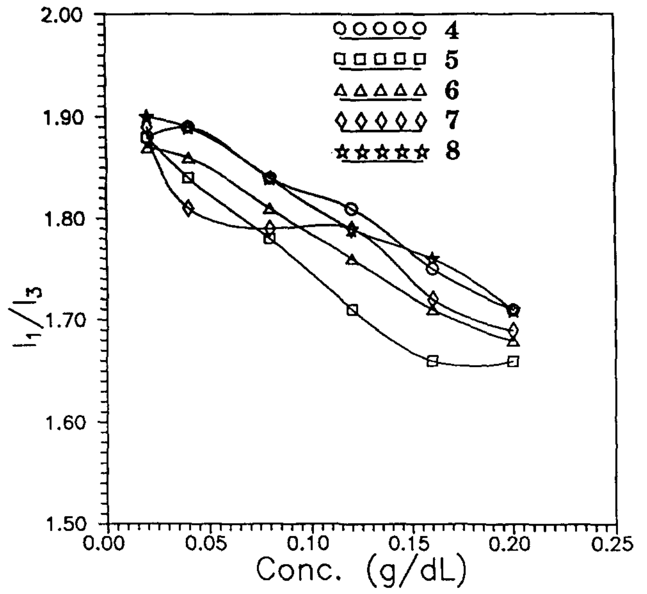

Figure 7 I_1/I_3 values as a function of polymer concentration in 0.5 M NaCl

5–8 and the unmodified Am/AA copolymer **4**. Values (1.85–1.90) at low polymer concentration indicate that the probe is solvated in an aqueous environment. As the polymer concentration is increased to 0.20 g dl^{-1}, the I_1/I_3 values for the unmodified copolymer **4** and the terpolymer **8** became quite similar, decreasing to approximately 1.73. The I_1/I_3 values for the remaining terpolymers decrease with increasing concentration to slightly lower values, the lowest value being for terpolymer **5** at 1.65. This value is near to that of pyrene in acetone. These data indicate some change in probe environment with increasing polymer concentration, but the absolute value of I_1/I_3 indicates a relatively polar environment. These results are in contrast to previous studies on non-ionic, hydrophobically associating polymers[13,22] in which values of 1.1–1.2 (similar to common surfactant micelles) were obtained. No dramatic changes in the curves are evident as the polymers approach C^*. Associations may be open and somewhat hydrated; this is consistent with fluorescence studies on labelled polyacrylamides which have been previously published[8]. Also, studies with other probes on partially hydrolysed copolymers of acrylamide and a hydrophobic comonomer have indicated that the presence of ionic groups may lead to microdomains which are more polar than their non-ionic counterparts[23]. While it appears that some correlation between I_1/I_3 and SMR and thus the microstructure of the terpolymers may exist, the differences in values are slight. This observation leads us to conclude that pyrene probe fluorescence is not sufficiently sensitive to allow the elucidation of the nature of the associations present in these systems.

CONCLUSIONS

Am/AA/DPAm terpolymers **5–8** and an unmodified Am/AA copolymer **4** were synthesized with variation in the [SDS]/[DPAm] ratio (SMR). These polymers have similar compositions, with the AM content being 60–65 mol%, the AA content being 35–40 mol% and the DPAm content being approximately 0.4–0.5 mol%. Classical light-scattering studies on the Am/AA copolymer **4** in 0.5 M NaCl indicate a molecular weight of 720 000 g mol^{-1}, and dynamic light-scattering studies in 1.0% SDS indicate that the hydrodynamic diameters of the terpolymers are similar, ranging from 200 to 250 nm. The terpolymers show similar viscosity behaviour to that of the unmodified polymer in the dilute concentration regime in 0.5 M NaCl. Differences in the solution properties at higher concentrations are attributed to microstructural differences arising from variation of the surfactant concentration in the micellar polymerization process. The terpolymers synthesized at low SMR show the strongest associative behaviour above C^* in 0.5 M NaCl. Those synthesized at high SMR behave much like the unmodified polymer. Terpolymers **5** and **6** exhibit the best associative behaviour, Terpolymer **7** has moderate associations, while **8** has viscometric behaviour similar to that of the unmodified Am/AA copolymer **4**. It is expected that at a lower SMR there is a larger number of DPAm molecules per micelle, resulting in a more 'blocky' polymer microstructre. However, the lack of significant changes in probe solubilization leads us to conclude that pyrene probe fluorescence studies are not sufficiently sensitive to indicate differences in local polarity for the terpolymers above C^*. While this study neither provides direct evidence of microstructural placement nor an estimate of hydrophobe block length, it clearly demonstrates that manipulation of the synthetic parameters in micellar polymerization allows one to tailor the associative properties of hydrophobically modified polyelectrolytes. Studies on polyelectrolytes prepared by micellar polymerization containing fluorescent labels to probe more effectively the microstructure of hydrophobically modified polyelectrolytes will be reported in a forthcoming paper.

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