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Water-Soluble Copolymers. 64. Effects of pH and Composition on Associative Properties of Amphiphilic Acrylamide/Acrylic Acid Terpolymers

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ABSTRACT: Acrylamide (AM)/acrylic acid (AA) copolymers and AM/AA/*N*-(4-hexylphenyl)acrylamide (HPAM, 0.5 mol %) terpolymers with varied AA content have been synthesized by micellar copolymerization. Co- and terpolymers with 5−37 mol % AA and similar hydrodynamic volumes were prepared. Solution viscosity studies of the copolymers as a function of pH and copolymer concentration in deionized water and NaCl solution indicate normal polyelectrolyte behavior. In aqueous solutions, intra- or intermolecular hydrophobic associations may be favored by variation of terpolymer composition. Three-dimensional plots of both I_3/I_1 (from pyrene probe fluorescence) and viscosity as functions of pH and terpolymer concentration demonstrate the responsive nature of associations in water and in 0.5 M NaCl. Terpolymers containing approximately 9 and 21 mol % AA exhibit intermolecular (open) associations at ≤pH 5 and in the presence of NaCl. The terpolymer containing approximately 37 mol % AA, however, exhibits no intermolecular associations in deionized water even at low pH. Pyrene fluorescence studies of this terpolymer indicate a significantly apolar environment sensed by the probe at pH 4, suggesting that intramolecular (closed) microdomains are formed. Conceptual models based on hydrophobic, ionic, and hydrogen-bonding interactions in these systems are presented.

Introduction

Water-soluble acrylamide co- and terpolymers are appropriate for a variety of industrial applications.[1] Addition of small quantities (≤1 mol %) of hydrophobic groups via micellar copolymerization can lead to AM copolymers with enhanced solution properties[2−8] including viscosification due to intermolecular associations above a critical overlap concentration (C^*). Importantly, this C^* is well below the entanglement overlap of the AM homopolymer[4−6] or random copolymers with similar hydrophobe content.[8,9] Fluorescence label studies on co- and terpolymers prepared by micellar polymerization indicate that the unique "blocky" microstructure which arises from the microheterogeneous nature of micellar polymerization is a determining factor for intermolecular associations.[8−10] Intermolecular aggregates formed by these "microblocky" copolymers have also been examined using external fluorescence probes, and organized microdomains have often been compared to those of common surfactant micelles.[5,7]

Introduction of charged groups to hydrophobically modified copolymers, either through hydrolysis or by copolymerization with ionic monomers, can increase solubility and provide systems responsive to changes in ionic strength and pH.[4,5,11−15] These polyelectrolyte systems exhibit decreased associative behavior and microdomain organization compared to their nonionic counterparts, often requiring higher levels of hydrophobe incorporation or addition of high concentrations of electrolyte to induce intermolecular aggregation.[4,5,11−14] Explanation of these properties has been incomplete. Increased polymer solubility and interchain ionic repulsions are speculated to be responsible for decreased intermolecular association.[4,13,14] One study[13] examined associative effects as a function of the level of hydrolysis in AM/ethylphenylacryamide copolymers through viscosity and fluorescence probe measurements. Differences in associative behavior as a function of degree of hydrolysis and NaCl concentration were reported, but the onset of aggregation in these systems was not explored; copolymer concentrations were well above C^*. Also lacking are studies that examine associative properties as a function of pH.

The purpose of this work is to investigate the viscosity and microdomain organization of hydrophobically modified polyelectrolytes as a function of pH, salt concentration, polymer concentration, and polymer composition for a fixed level of hydrophobe. To facilitate these studies, we have synthesized two polymer series: control copolymers of AM and AA and terpolymers of AM, AA, and *N*-(4-hexylphenyl)acrylamide (HPAM). Viscometric properties of the co- and terpolymers are examined as functions of polymer concentration and solution pH in the presence and absence of NaCl. To our knowledge, there have been no literature studies examining AM/AA copolymers utilizing such three-dimensional topological plots. These studies provide useful data for interpreting the associative properties of hydrophobically modified analogs. Topological investigations of viscosity as described above and pyrene I_3/I_1 measurements are conducted on the terpolymers to examine the onset of intermolecular aggregation. These studies provide insight into the factors governing intermolecular associations and provide useful structure/property relationships for the design of pH- or electrolyte-responsive associations.

Experimental Section

Materials. All materials were purchased from either Aldrich or Fisher and used as received unless otherwise noted. 4-Decylaniline (DA), acrylic acid (AA), and acryloyl chloride (AC) were distilled under vacuum prior to use. Acrylamide (AM) was recrystallized from acetone, and potassium persulfate was recrystallized from water. Pyrene was recrystallized three times from absolute ethanol. *N*-(4-Hexylphenyl)acrylamide (HPAM) was synthesized by the same procedure as its butylphenyl[11] and decylphenyl[14] analogs, utilizing DA and AC in the presence of an acid scavenger. Analysis for HPAM—Anal.

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Scheme 1. Synthesis of Copolymers C1–C4 and Terpolymer T1–T4 by Micellar Polymerization at 50 °C

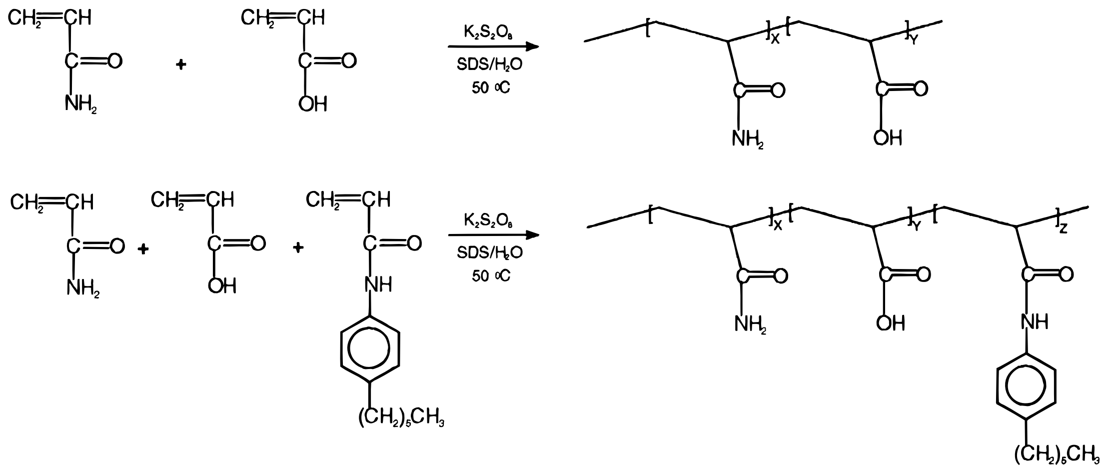


Table 1. Compositional and Hydrodynamic Data for P1–P8

sample	AM:AA feed ratio[a]	mol % of AM[b]	mol % of AA[b]	mol % of HPAM[c]	% conv[d]	d_H (nm)[e]	d_H (nm)[f]
C1	95.0:5.0	91.7	8.3		81	45	21
C2	90.0:10.0	88.9	22.2		91	70	43
C3	80.0:20.0	75.8	24.2		83	71	60
C4	70.0:30.0	64.8	35.2		83	70	66
T1	94.5:5.00	94.5	4.9	0.6	58	67	
T2	89.5:10.0	90.9	8.5	0.6	73	66	
T3	79.5:20.0	78.4	21.0	0.6	67	67	
T4	69.5:30.0	62.1	37.4	0.5	57	65	

[a] Composition in reaction feed. [b] From ^{13}C NMR/element analysis. [c] From UV spectroscopy. [d] Estimated gravimetrically. [e] Hydrodynamic diameter from DLS in 1.0% SDS (±12 nm). [f] Hydrodynamic diameter from DLS in 0.5 M NaCl (±10 nm).

Calcd for $C_{15}H_{21}NO$ (MW 231.33): C, 77.88; H, 9.15; N, 6.05; O, 6.92. Found: C, 77.78; H, 9.16; N, 6.06; O (not anal.), 7.00. Mp 95–96 °C. IR (KBr pellet (cm^{-1})): N–H, 3285; vinyl and aromatic C–H, 3133 and 3082; aliphatic CH_3 and CH_2, 2957 and 2940; carbonyl, 1665. ^{13}C NMR (DMSO-d_6 (ppm)): aliphatic CH_3, 13.9; aliphatic CH_2, 22.1–34.6; vinyl carbons, 126.3 and 132.0; aromatic carbons, 119.3, 128.3, 136.7, 137.3; carbonyl, 162.9.

Terpolymer Synthesis and Purification. Terpolymers **T1–T4** were synthesized via the micellar polymerization method of Turner et al.,[2] illustrated in Scheme 1. The total monomer concentration was 0.44 M. The HPAM content in the feed was held constant at 0.5 mol %, and the AM:AA feed ratios were 94.5:5.0, 89.5:10.0, 79.5:20.0, and 69.5:30.0. SDS was used as the surfactant to solubilize the hydrophobic comonomer, and potassium persulfate was used as a free-radical initiator. The surfactant to hydrophobe ratio, [SDS]/[HPAM], and the monomer to initiator ratio, [monomer]/[$K_2S_2O_8$], were held constant at 40 and 3000, respectively. Deionized water (240 mL) was purged with N_2 for 30 min. SDS (6.3 g) was added with stirring under a N_2 purge. HPAM (0.13 g) was then added with continued stirring for approximately 1 h or until the solution cleared. The AM:AA ratio was varied as indicated in Table 1, and the pH of the reaction feed varied from 3.5 to 4.5, depending on the AA feed ratio. $K_2S_2O_8$ was dissolved into 10 mL of deoxygenated, deionized water and added to the solution. The reaction was allowed to proceed under N_2 for 6 h. Polymers were precipitated into 1000–1200 mL of acetone. The polymers were washed with fresh acetone and dried overnight. The terpolymers were ground to a fine powder and dissolved in water (approximately 0.25 g/dL) on an orbital shaker for 1–2 weeks. The pH of these solutions was adjusted to approximately 7.5, and samples were returned to the shaker for 1–2 days. The polymer solutions were dialyzed against deionized water in Spectra Por No. 4 dialysis tubing with a molecular weight cutoff of 12 000–14 000 for 8 days. The purified samples were then freeze-dried to a constant weight. Copolymers **C1–C4** were synthesized and purified by an identical procedure using no HPAM monomer.

Structural Analysis. Co- and terpolymer compositions were determined by UV spectroscopy, elemental analysis, and/or ^{13}C NMR by methods discussed previously.[14] Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

UV spectra were obtained with a Hewlett-Packard Model 8452A photodiode-array spectrophotometer. A molar absorptivity of 10 700 M^{-1} cm^{-1} at 250 nm was used to calculate the composition of HPAM residues in the terpolymers.

^{13}C NMR spectra were obtained with a Bruker AC 200 spectrometer. Delay times of 5–6 s were used for gated-decoupled experiments. ^{13}C NMR spectra showed the expected chemical shifts for the backbone carbons at approximately 38–48 ppm as well as the two carbonyl resonances for acid (185.8 ppm) and amide (182.7 ppm) carbonyls.

IR spectra were obtained in KBr pellets with a Mattson Model 2020 FT-IR spectrophotometer.

Steady-state pyrene fluorescence studies were performed with an Edinburgh Analytical Instruments FS900CDT steady-state T-geometry fluorometer. Slit widths were maintained at ≤0.5 mm. An excitation wavelength of 338 nm was used. I_1 and I_3 were recorded at 372 and 384 nm, respectively. Steady-state spectra were analyzed using software provided by the manufacturer, and I_3/I_1 measurements were reproducible to within ±0.1 unit in the terpolymer solutions.

Viscosity measurements were conducted on a Contraves LS-30 low-shear rheometer at 25 °C and a shear rate of 6 s.$^{-1}$ At least three measurements were taken for each sample. An upper limit of 250 cP may be obtained on the Contraves LS-30 at this shear rate. This value was arbitrarily assigned to samples that exceeded this upper limit for means of comparison.

Dynamic light scattering studies were conducted with a Spectra-Physics 127 laser operating at 632.8 nm and a Brookhaven Instruments model BI-200SM automatic goniometer interfaced with a Brookhaven BI-2030AT autocorrelator and personal computer. Data were collected at an angle of 90°, and effective hydrodynamic diameters (d_H) were calculated using the algorithm CONTIN and associated software provided by the manufacturer. Multiple analyses (3–5) were performed to ensure reproducibility.

Sample Preparation. Samples for viscosity measurements and pyrene probe studies were made by preparing polymer stock solutions of 0.20 g/dL in deionized water and adjusting the pH to 4, 5, 6, and 7 ± 0.05 with microliter amounts of concentrated HCl or NaOH solutions. The solutions were allowed to mix on an orbital shaker before dilutions were made. Dilutions of 0.16, 0.12, 0.08, 0.04, and 0.02 g/dL were made and the pH of each dilution was adjusted to the desired value. Care was taken to ensure that a minimum amount of added acid or base was used to adjust the solution pH, since the neutralization process produces excess ions which may affect solution properties in deionized water. For salt studies, dry NaCl was added to each solution. Solutions for pyrene probe measurements were made by adding 1−2 μL of a concentrated stock solution of pyrene in methanol to each dilution. Final pyrene concentrations of approximately 1×10^{-6} mol/L were obtained.

Samples for dynamic light scattering measurements were prepared by dissolving the appropriate amount of polymer in the desired prefiltered solvent (0.5 M NaCl or 1.0% SDS) to give solutions of 2.0×10^{-4} g/mL polymer. After dissolution, the pH of the solution was adjusted to the proper pH (7.0 ± 0.05 in NaCl and 4.2 ± 0.1 in 1.0% SDS) using microliter amounts of NaOH and HCl solutions. Polymer solutions were filtered through loops with Millipore 0.45 μm filters to remove dust. Typical filtration times were 14−48 h.

Results and Discussion

Terpolymer Composition. Hydrophobically modified polyelectrolytes, **T1**−**T4**, were synthesized via micellar polymerization as shown in Scheme 1. The polymerization feed was varied as indicated in Table 1 to yield terpolymers of varying AA content. AM/AA copolymers of similar composition, **C1**−**C4**, were synthesized under identical conditions (Table 1).

Co- and terpolymer compositions were determined by UV spectroscopy, elemental analysis, and/or ^{13}C NMR as discussed previously.[14] HPAM incorporation in each terpolymer is consistent with the feed composition of HPAM (0.5−0.6 mol %). Under the conditions outlined in the Experimental Section, a level of approximately 1.6 HPAM monomers per SDS micelle was maintained. Over the 6 h reaction time, hydrophobe compositional drift[13b] should not be a concern; therefore, we expect hydrophobic "microblocks" similar to those previously reported for $\mathbf{T}_1$−$\mathbf{T}_4$. The AM:AA content in the co- and terpolymers agrees with values of the feed ratios within experimental error except for the 70:30 AM:AA polymers, **C4** and **T4**. The latter polymers have AA contents consistent with previous studies on similar systems,[14−16] showing slightly higher AA incorporation.

Dynamic Light Scattering (DLS) Studies. DLS studies were first performed on copolymers **C1**−**C4** in 0.5 M NaCl at 25 °C. Hydrodynamic diameters (d_H) were determined from the limiting diffusion coefficients, D_0, using the Stokes equation:

$$D_0 = \frac{kT}{3\pi\eta_0 d_H} \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature, and η_0 is the viscosity of the solvent. Values of d_H appear in Table 1. These values scale with increasing charge density and are consistent with previous DLS studies on AM/AA co- and terpolymers.[16]

We have found that DLS in 1.0% SDS (w/v) is a useful method for comparison of molecular dimensions of hydrophobically modified polyelectrolytes. The presence of SDS above its critical micelle concentration (cmc) prevents terpolymer aggregation and adsorption onto the microfilter membranes that are utilized to remove dust from the sample.[14] DLS experiments on copolymers **C1**−**C4** in 1.0% SDS were performed, and d_H values were determined for comparison with those for terpolymers **T1**−**T4**. These studies were performed at pH 4.2 ± 0.1 to minimize the effect of differing carboxylate compositions in the co- and terpolymers. Results for the copolymers appear in Table 1 and indicate similar hydrodynamic diameters for **C2**−**C4**. These data are consistent with measurements in 0.5 M NaCl. The dimensions of **C1** appear to be the smallest of the series in both 0.5 M NaCl and 1.0% SDS.

DLS studies on terpolymers **T1**−**T4** were not possible in 0.5 M NaCl due to strong adsorption onto the microfilter membranes. We were also unable to use water/dioxane or water/DMF mixed solvents for light scattering measurements as previously reported for other hydrophobically modified associating systems[13] due to insufficient d*n*/d*c* values. Therefore, studies were carried out in 1.0% SDS. Hydrodynamic diameter values of 65−67 nm for **T1**−**T4** are similar to those of copolymers **C1**−**C4** (Table 1). Of course, hydrodynamic volume is affected by SDS, but we expect similar molecular weights and hydrodynamic volumes for the **C1**−**C4** and **T1**−**T4** series under identical synthetic conditions. These values are in the same range as those previously reported for fluorescently labeled AM/AA copolymers.[10]

Viscometric Studies. Viscometric properties of the co- and terpolymer with the lowest AA contents (**C1** and **T1**) exhibited characteristics similar to AM homopolymer or copolymers with similar hydrophobic modification; little response to pH or electrolyte concentration is observed. Therefore, attention will be focused on the co- and terpolymers with higher AA content.

Effects of AA Content and Added Electrolyte. Since **C2**−**C4** and **T2**−**T4** possess different charge densities at high pH, the viscometric properties were examined as a function of ionic strength under dilute conditions. Therefore, reduced viscosity measurements were conducted on 0.05 g/dL solutions of **C2**−**C4** and **T2**−**T4** as a function of ionic strength $I^{-0.5}$ at pH 7.0.

Reduced viscosity of the copolymers is linear with $I^{-0.5}$, and the magnitudes of the slopes scale roughly with charge density (Figure 1, top). **C2** (11% AA) shows the smallest slope; **C3** (24% AA) and **C4** (35% AA) exhibit greater slopes. The terpolymers **T2**−**T4** (Figure 1, bottom) exhibit approximately the same slopes, however, indicating that hydrophobic modification may affect the polyelectrolytic nature of the chain in the presence of NaCl. Also, viscosity values for the terpolymers are higher than those for the copolymers, possibly attributable to intermolecular hydrophobic associations in solution.

Effects of pH and Polymer Concentration. Viscometric studies were performed on each copolymer (**C2**−**C4**) and terpolymer (**T2**−**T4**) in deionized water and in 0.5 M NaCl as a function of polymer concentration and solution pH. Polymer concentrations ranged between 0.20 and 0.02 g/dL; pH values were 4.0, 5.0, 6.0, and 7.0 ± 0.05. A shear rate of 6 s^{-1} was employed, and the temperature was maintained at 25 °C.

The topological features of the apparent viscosity−pH−polymer concentration relationships in deionized water are shown in Figures 2−4. Data for the unmodified copolymers are shown in the upper portion of each figure and for the terpolymers in the lower portion. Analogous topological data for the co- and terpolymers in 0.5 M NaCl are shown in Figures 5−7.

The copolymers exhibit the expected viscosity behavior for poly(carboxylic acid)s, revealing maxima in viscosity at high concentration and pH values. The magnitude of viscosity maxima in deionized water (at 0.20 g/dL) scales with polyelectrolyte charge density. **C2** (11% AA) exhibits a maximum viscosity of approximately 8.5 cP at pH 7 (Figure 2), and **C3** (24% AA) exhibits a maximum viscosity of approximately 55 cP at pH 6 (Figure 3). The increase in viscosity from pH 7 to 6 may be due to intramolecular hydrogen bonding, which stiffens the polymer chain.[17,18] **C4** (35% AA)

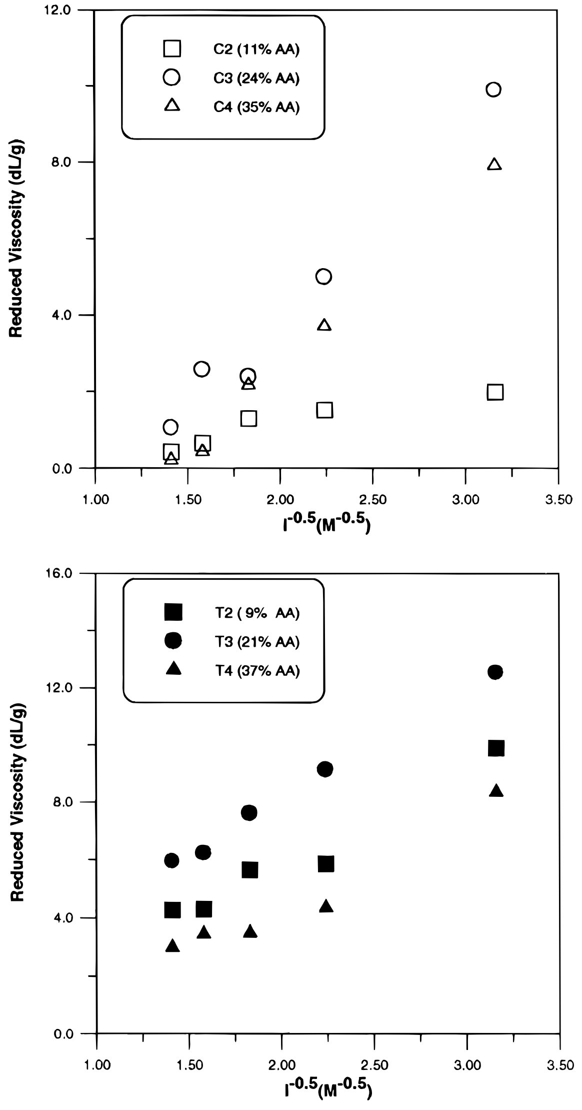


Figure 1. Reduced viscosity measurements as a function of ionic strength $I^{-0.5}$ at pH 7.0 for **C2**–**C4** (top) and **T2**–**T4** (bottom). Polymer concentration: 0.05 g/dL.

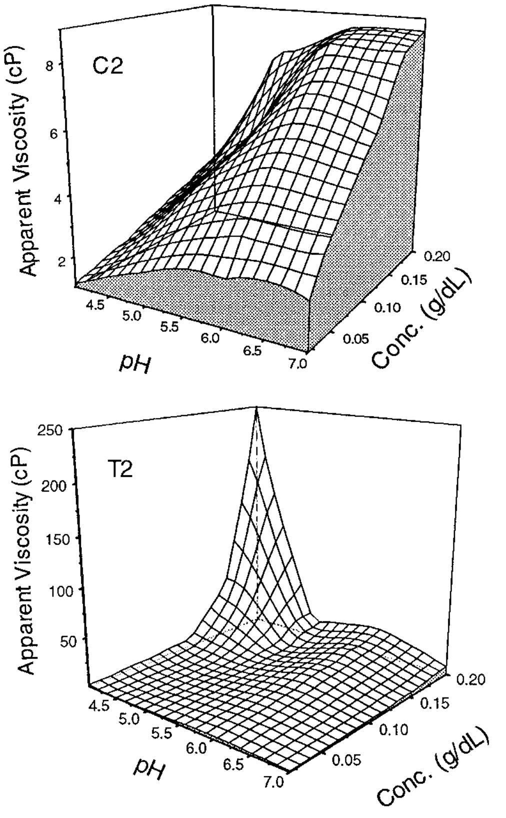


Figure 2. Apparent viscosity of **C2** (11% AA, 89% AM, top) and **T2** (9% AA, 90% AM, 0.6% HPAM, bottom) as a function of solution pH and polymer concentration in deionized water. A shear rate of 6 s^{-1} was employed, and the temperature was maintained at 25 °C.

exhibits the highest viscosity maximum of approximately 85 cP at pH 7 (Figure 4). Viscosities for **C2**, **C3**, and **C4** in 0.5 M NaCl (Figures 5–7) are lower by an order of magnitude due to electrostatic screening by the excess counterions; the viscosity increase with increasing pH is, therefore, much less dramatic. These studies provide a useful baseline by which to gauge the viscometric and associative behavior of the hydrophobically modified terpolymers **T2**–**T4**.

Topological apparent viscosity–pH–concentration data for **T2**–**T4** in deionized water (Figures 2–4) and 0.5 M NaCl (Figures 5–7) exhibit some interesting features. Figures 2 and 3 show the topological data for **T2** (9% AA) and **T3** (21% AA), respectively, in deionized water. Notable differences in viscosity behavior of these terpolymers and their respective control copolymers, **C2** (11% AA) and **C3** (24% AA), are observed. Large increases in apparent vicosity are observed with decreasing pH and increasing terpolymer concentration in both plots. No associative behavior is noted at pH 6 and 7 in either case; viscosity increases in a linear fashion with terpolymer concentration. However, at pH 4 and 5, marked curvature in the viscosity–concentration dependence indicates intermolecular associations for both **T2** and **T3**. At pH 4, both terpolymers have viscosities surpassing 250 cP due to extensive intermolecular associations. The onset of association or critical overlap concentration, *C**, appears to be at a lower polymer concentration for **T3**, below 0.10 g/dL. The onset of association for **T2** is at a concentration slightly greater than 0.10 g/dL. The amount of HPAM in all the terpolymers was determined to be identical (0.5–0.6 mol %) within experimental error, and data from DLS indicate similar dimensions for **T2** and **T3**. Therefore, the differences in *C** are likely due to compositional effects.

The viscosity–pH–concentration plot for terpolymer **T4** (37% AA) in deionized water is shown in Figure 4. Although some curvature in the apparent viscosity versus concentration dependence is present at pH 4, no notable increase in viscosity is evident at any of the pH values investigated, in contrast with data for **T2** and **T3**. If extensive hydrophobic associations are present in **T4** in deionized water, they are intramolecular (closed) in nature. This finding is consistent with studies by Klenina and Lebedeva,[19] who noted poor solubility of AM/AA copolymers of greater than 30 mol % AA at low pH. These studies suggest that above this AA composition, intramolecular hydrogen bonding is stronger than the polymer–water interactions, resulting in poor polymer solvation. Intermolecular association for **T4** at low pH may therefore be overwhelmed by intramolecular hydrogen bonding.

The concentration range studied in this work is identical to that of previous studies on hydrophobically modified AM copolymers,[2–7] in which the onset of intermolecular associations was noted. For the AA-containing terpolymers **T2**–**T4**, no intermolecular association is evident in deionized water at pH 6 and 7.

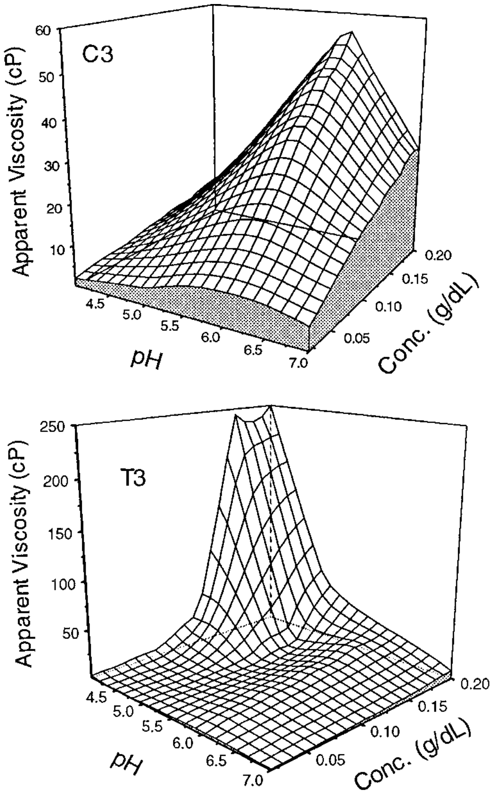


Figure 3. Apparent viscosity of **C3** (24% AA, 76% AM, top) and **T3** (21% AA, 78% AM, 0.6% HPAM, bottom) as a function of solution pH and polymer concentration in deionized water. A shear rate of 6 s^{-1} was employed, and the temperature was maintained at 25 °C.

Intermolecular associations in **T2** and **T3** have apparently been disrupted by ionization of the carboxylic acid groups. Further discussion of the nature of these "pH-triggered" associations in solution is presented in subsequent sections.

Figures 5–7 show topological viscosity–pH–concentration data for **T2**–**T4** in 0.5 M NaCl. Viscosities for each sample are lower at pH 6 and 7 as compared to values in deionized water due to the addition of NaCl. Electrostatic shielding of the polyelectrolyte charges causes collapse of the individual polymer coils, but intermolecular associations result at sufficient terpolymer concentrations for **T2** (Figure 5) and **T3** (Figure 6) at pH 5–7. Each polymer exhibits a C^* at approximately 0.15 g/dL (except at pH 4). The induction of intermolecular associations at high pH by the addition of NaCl is consistent with results reported for *N*-(4-decylphenyl)acrylamide-modified terpolymers.[14] Associations may be more efficient at high pH in NaCl solutions as compared to deionized water due to the screening of inter- and intracoil polyelectrolyte charges as well as enhanced water structuring in the presence of NaCl. Also, collapse of the polymer coils may result in more hydrophobic groups at the surface which aggregate to minimize contact with water.

The lack of high viscosity for **T2** and **T3** at pH 4 in 0.5 M NaCl is likely due to the collapse of the polymer coils due to protonation of the AA groups and increased hydrophobic associations due to the presence of NaCl. A "salting-out" effect on the terpolymers may prohibit bridging or open associations under these conditions. However, no precipitation is noted for these solutions. Alternatively, intramolecular hydrogen bonding, similar to that postulated for **T4**, could be promoted because of the compact nature of the polymer coils in 0.5 M NaCl.

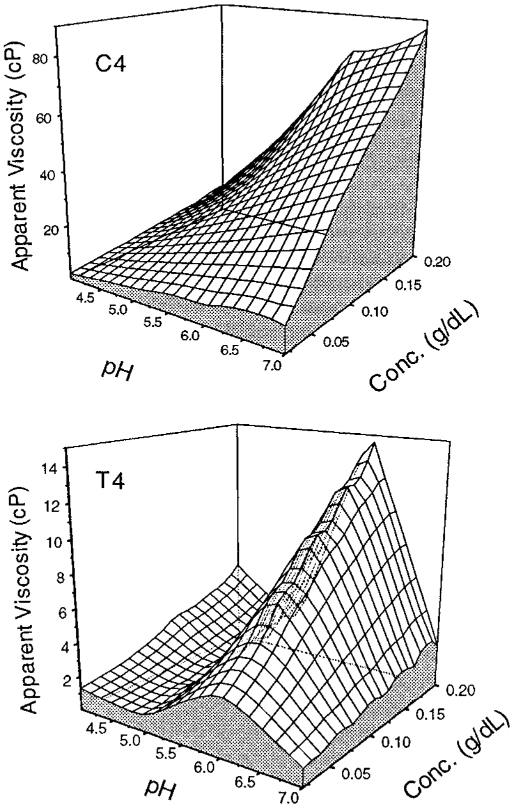


Figure 4. Apparent viscosity of **C4** (35% AA, 65% AM, top) and **T4** (37% AA, 62% AM, 0.5% HPAM, bottom) as a function of solution pH and polymer concentration in deionized water. A shear rate of 6 s^{-1} was employed, and the temperature was maintained at 25 °C.

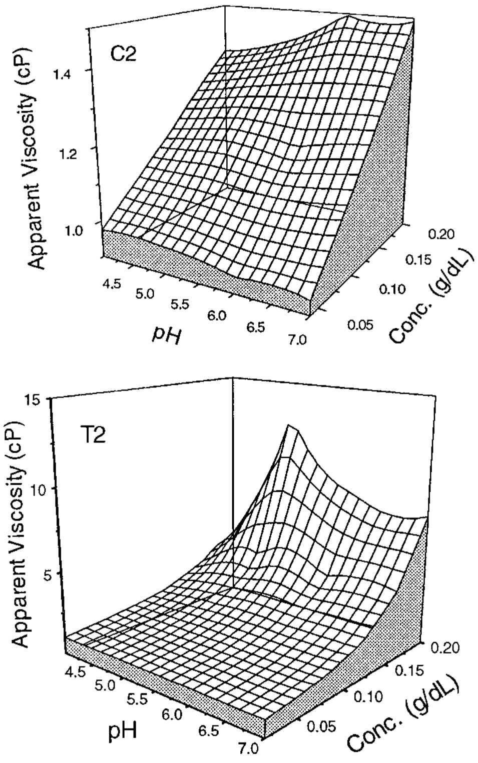


Figure 5. Apparent viscosity of **C2** (11% AA, 89% AM, top) and **T2** (9% AA, 90% AM, 0.6% HPAM, bottom) as a function of solution pH and polymer concentration in 0.5 M NaCl. A shear rate of 6 s^{-1} was employed, and the temperature was maintained at 25 °C.

The topological data for **T4** in 0.5 M NaCl (Figure 7) exhibit some curvature indicative of intermolecular

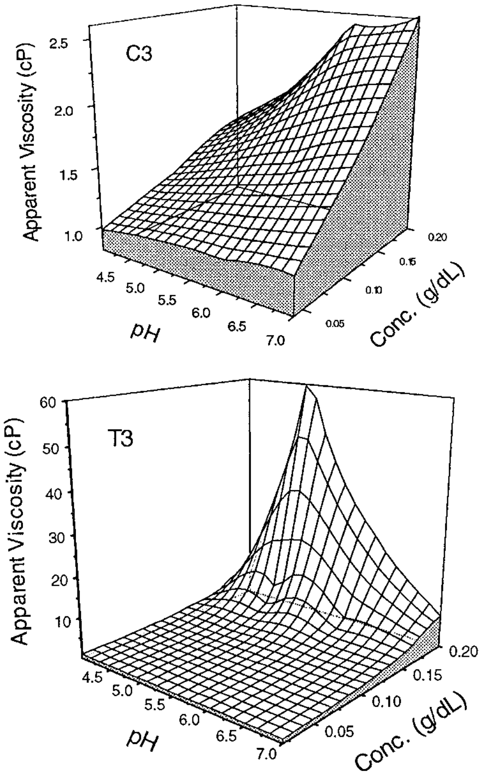


Figure 6. Apparent viscosity of **C3** (24% AA, 76% AM, top) and **T3** (21% AA, 78% AM, 0.6% HPAM, bottom) as a function of solution pH and polymer concentration in 0.5 M NaCl. A shear rate of 6 s^{-1} was employed, and the temperature was maintained at 25 °C.

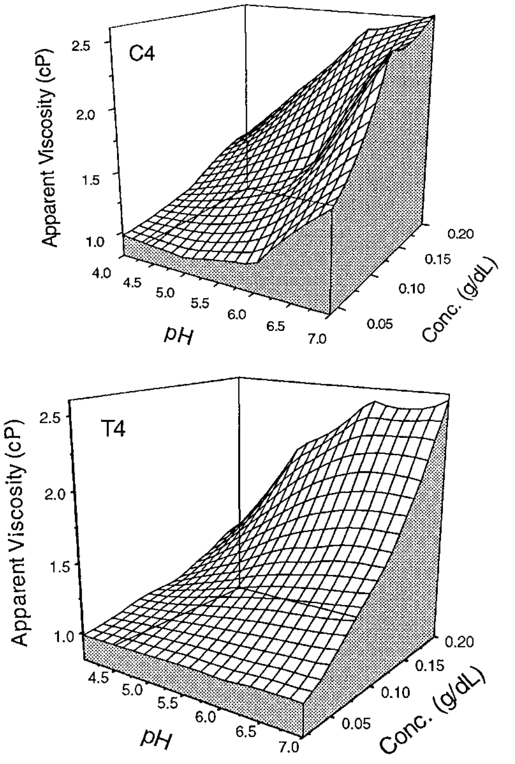


Figure 7. Apparent viscosity of **C4** (35% AA, 65% AM, top) and **T4** (37% AA, 62% AM, 0.5% HPAM, buottom) as a function of solution pH and polymer concentration in 0.5 M NaCl. A shear rate of 6 s^{-1} was employed, and the temperature was maintained at 25 °C.

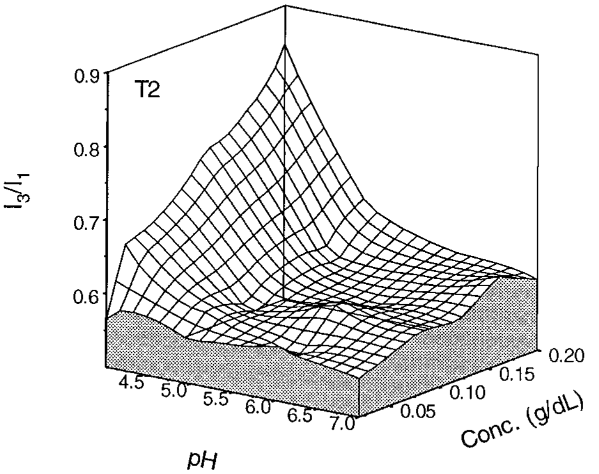


Figure 8. I_3/I_1 as a function of solution pH and terpolymer concentration in deionized water for **T2** (9% AA, 90% AM, 0.6% HPAM) at 25 °C.

associations at pH 5–7, but associative behavior is altered little by the presence of salt. The viscosity values are lower in general due to the presence of electrolyte. Although **T4** does not exhibit extensive associations in 0.5 M NaCl, it should be noted that an identical terpolymer bearing the larger decylphenyl hydrophobe[14] showed significant associations at pH 7 in 0.5 M NaCl.

Pyrene Probe Fluorescence Studies. In order to determine the extent and nature of the hydrophobic associations in **T2**–**T4**, pyrene probe fluorescence experiments were performed under conditions identical to those in the viscosity studies. The ratio of the fluorescence intensity of the third vibronic band to that of the first vibronic band (I_3/I_1) of pyrene is a useful indicator of the local dielectric constant surrounding the probe.[20] I_3/I_1 has values of approximately 0.5 in water, 0.7–0.9 in common short-chain alcohols, and ~1.5 in hydrocarbon media. I_3/I_1 values for pyrene solubilized in common surfactant micelles[20] or hydrophobic microdomains in amphiphilic polymer systems[21] are between those found in aqueous and hydrocarbon media.

The I_3/I_1–pH–concentration plot for **T2** in deionized water is shown in Figure 8. I_3/I_1 remains approximately equal, within experimental error, to its value in water from 0.02 to 0.20 g/dL concentration of terpolymer at pH 6 and 7. Below pH 5, I_3/I_1 increases significantly at high terpolymer concentration. A maximum value of ~0.85 is obtained at pH 4–0.20 g/dL (comparable to I_3/I_1 of pyrene in common surfactant micelles). Comparison of these data (Figure 8) with viscosity data for **T2** in water (Figure 2) indicates that the increase in I_3/I_1 corresponds to C^* at pH 4 (just above 0.10 g/dL).

I_3/I_1 data as a function of pH and terpolymer concentration for **T3** in deionized water (Figure 9) are similar to those of **T2**. The I_3/I_1 value above pH 5 remains close to that of water even at high terpolymer concentration. Below pH 5, I_3/I_1 approaches values found in surfactant micelles once sufficient terpolymer concentration is reached. Maximum values of I_3/I_1 for **T3** (0.80) and **T2** (0.85) are equal within experimental error, suggesting domain organization is similar under these conditions. Furthermore, these values are comparable to acrylamide polymers containing <0.5 mol % lauryl methacrylate above C^*.[7] Increased domain organization with protonation of the carboxylate groups is addressed below.

I_3/I_1–pH–concentration plots for **T4** in deionized water appear in Figure 10. The features of I_3/I_1 as a function of pH and terpolymer concentration are similar to those exhibited by **T2** and **T3** below pH 5. I_3/I_1

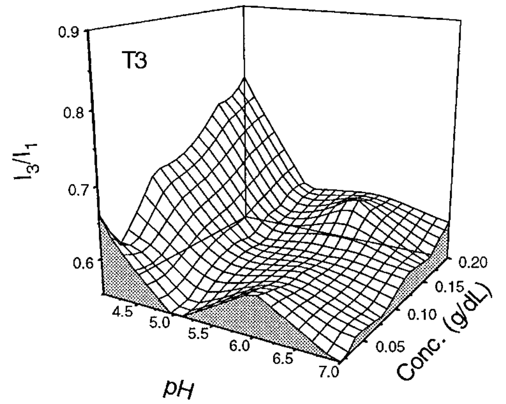


Figure 9. I_3/I_1 as a function of solution pH and terpolymer concentration in deionized water for **T3** (21% AA, 78% AM, 0.6% HPAM) at 25 °C.

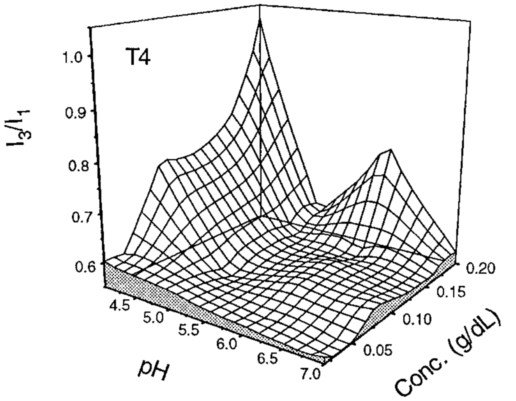


Figure 10. I_3/I_1 as a function of solution pH and terpolymer concentration in deionized water for **T4** (37% AA, 62% AM, 0.5% HPAM) at 25 °C.

reaches a value of 0.8 just below 0.10 g/dL terpolymer and increases to ~1.0 at 0.20 g/dL. This indicates a more hydrophobic environment at low pH, despite the fact that no C^* was evident from viscosity studies (Figure 4). Therefore, the hydrophobic microdomains sensed by the pyrene probe are likely of an intra- rather than an intermolecular nature. The higher values of I_3/I_1 at low pH may indicate stabilization of intramolecular associations by hydrogen bonding,[19] and the drop in I_3/I_1 with decreasing terpolymer concentration at pH 4 and 5 in water is likely due to significant partitioning of the probe into the aqueous phase as the concentration of intramolecular hydrophobic domains is decreased.[20]

The I_3/I_1 value of pyrene in solutions of **T4** increases between pH 7 and 5 as long as the terpolymer concentration exceeds 0.15 g/dL. This behavior mirrors the viscosity increase under the same conditions (Figure 4). The origin of the increase in both viscosity and I_3/I_1 under these conditions is unclear at present but is likely related to hydrogen bonding and the exclusion of water from the probe.

Topological data of I_3/I_1–pH–terpolymer concentration in 0.5 M NaCl for **T2** is shown in Figure 11. Data for terpolymers **T3** and **T4** show similar features. First, the dependence of I_3/I_1 on pH at high terpolymer concentration is less pronounced in NaCl solution, compared to deionized water (Figures 8–10). This is expected since the polyions are in a less extended conformation in the presence of excess counterions.

Also, I_3/I_1 is higher at pH 6 and 7 in 0.5 M NaCl than in water. This is significant in light of the fact that **T2** and **T3** exhibit intermolecular associations in 0.5 M NaCl even at high degrees of ionization. These results suggest perturbation of hydrophobic associations due to increasing ionization of the polymer chain may be overcome by addition of NaCl.

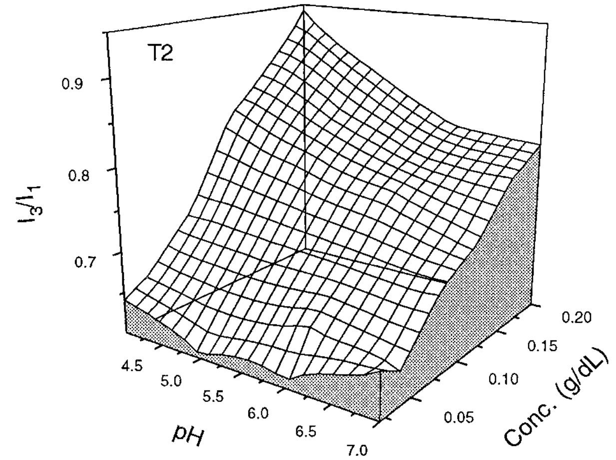


Figure 11. I_3/I_1 as a function of solution pH and terpolymer concentration in 0.5 M NaCl for **T2** (9% AA, 90% AM, 0.6% HPAM) at 25 °C.

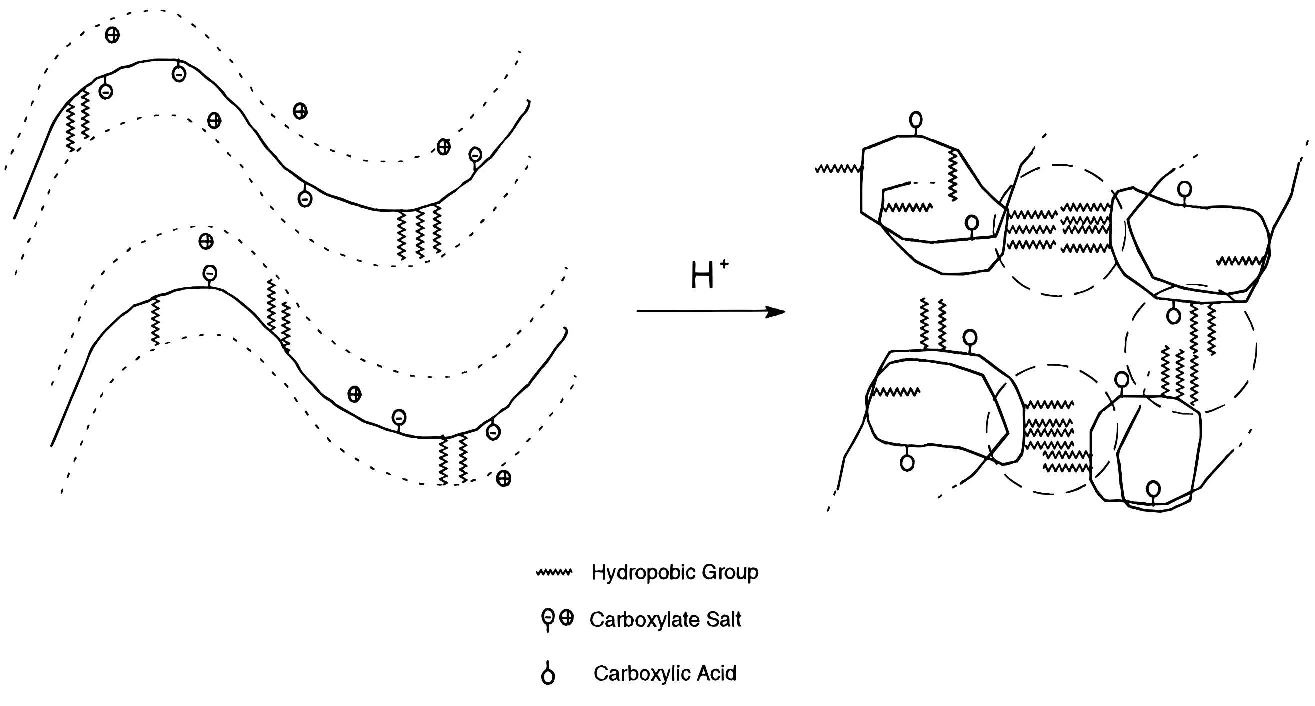
Terpolymer Solvation and Microdomain Organization. The remarkable effect of 0.5 mol % incorporation HPAM on solution properties that we observe experimentally by comparing the **T** and **C** series is attributable to macromolecular concentration and solvation. The presence of polymer sequences along the amphiphilic macromolecule which are “water averse” allows for long-range intra- and/or intermolecular microdomain formation. Such interactions have been extensively reviewed in both synthetic[22,23] and biological[22,24,25] amphiphilic polymers.

For both synthetic[23] and biopolymer systems,[24,25] it has been proposed that two modes of hydration of the amphiphilic polymer are operative: one is due to water restructuring as hydrophobic moieties release ordered water back into the bulk on aggregation; the second is due to hydration of polar or ionic entities along the macromolecular backbone. It is hypothesized that water molecules cannot participate in both modes of hydration and that increasing hydration of the hydrophilic portion of the chain results in disruption of nearby hydrophobic aggregates. Urry[24] has elegantly demonstrated this behavior by measuring the resulting changes in the lower critical solution temperature (LCST) for polypeptides with controlled changes in amino acid sequence and thus polarity, solvation, and hydrogen bonding. Similar changes in LCST have been observed for copolymers of *N*-isopropylacrylamide with acrylamide in our laboratories and others.

The seemingly complex behavior of the BPAM/AM/AA (**T** series) terpolymers as followed by three-dimensional viscosity–pH–concentration plots (Figures 9–11) can be readily interpreted in terms of the above by examining high (≥0.1 g/dL) and low (<0.1 g/dL) terpolymer concentrations at high and low pH values.

In general, little intermolecular (open) association is observed at high pH in deionized water. Only **T2** and **T3** exhibit a C^* in deionized water at low pH. I_3/I_1 measurements support the presence of intermolecular microdomains. **T4**, on the other hand, exhibits no C^*, but I_3/I_1 studies reveal well-organized intramolecular (closed) microdomains in aqueous solution. Addition of 0.5 M NaCl shifts C^* for **T2** and **T3** to higher concentrations. **T4** exhibits both closed and open association

Scheme 2. Conceptual Model for the pH-Responsive Intermolecular Associations of T2 and T3



in 0.5 M NaCl at low pH and high terpolymer concentration.

The above concepts are illustrated in Scheme 2. At high pH the terpolymers are depicted as rodlike entities due to intracoil charge−charge repulsions of the carboxylate ions. Intermolecular hydrophobic associations are prohibited by hydration of the polymer backbone and/or interchain ionic repulsions of the charged groups. As acid is added to the system, the carboxylate groups are masked, reducing hydrophilic hydration of the chain and intercoil ionic repulsions. The restructuring of water forces the hydrophobes from individual polymer chains into intermolecular (open) microdomains, resulting in viscosification of the solution.

Viscosity and I_3/I_1 studies of **T3** and **T4** indicate that intermolecular associations may result at high pH in the presence of electrolyte (0.5 M NaCl). At comparable pH values, **T3** and **T4** show increased I_3/I_1 at high terpolymer concentration as compared to I_3/I, in deionized water. This may be due to enhanced organization of the hydrophobic domains in solution brought about by the water-structuring effect of NaCl and/or removal of conformational restraints by collapse of the polymer coils due to shielding of polyelectrolyte charges. Apparently, these factors allow intermolecular hydrophobic association at sufficient terpolymer concentration in spite of the hydration of the carboxylate groups at high pH. Note that I_3/I_1 data indicate that the aggregates at high pH are more hydrated than at low pH.

Viscosity is at a minimum for **T2** and **T3** at pH 4 in 0.5 M NaCl (Figures 5 and 6) but at a maximum in deionized water (Figures 2 and 3). One might expect that hydrophobic associations would be at a maximum at pH 4 in 0.5 M NaCl for reasons stated above. The lack of high viscosity for **T2** and **T3** at pH 4 in 0.5 M NaCl is unclear since I_3/I_1 values are actually enhanced under these conditions (Figure 11). One possibility is a "salting-out" effect on the terpolymers as they approach the uncharged state. However, no precipitation is noted for these solutions. Alternatively, intramolecular hydrogen bonding, similar to that postulated for **T4**, could be promoted due to the compact nature of the polymer coils in 0.5 M NaCl. In this case, water would be excluded from the hydrophobic domains.

In the case of **T4**, significant intermolecular associations may be ruled out from viscosity data; I_3/I_1 data suggest intramolecular hydrophobic associations at low pH. Values of ∼1.0 at low pH and high terpolymer concentration in deionized water and in 0.5 M NaCl are measured. This value equals or exceeds the highest value of I_3/I_1 for pyrene in the hydrophobic interior of surfactant micelles, suggesting a high degree of microdomain organization. The drop in I_3/I_1 with decreasing terpolymer concentration at pH 4 and 5 in water (Figure 10) is likely due to significant partitioning of the probe into the aqueous phase as the concentration of intramolecular hydrophobic domains is decreased.[20] I_3/I_1 data under these conditions in 0.5 M NaCl show a similar decrease.

Conclusions

AM/AA/HPAM **T2**−**T4** terpolymers with identical HPAM content, sequence distribution, and molecular size but varying AA content were synthesized by micellar polymerization. Associative properties were investigated at pH 4.0, 5.0, 6.0, and 7.0 by low-shear viscosity and pyrene probe fluorescence studies in deionized water and 0.5 M NaCl. At pH 6 and 7 in deionized water, no hydrophobic associations are noted for any of the terpolymers due to hydration of the carboxylate residues in solution. Apparently, hydration of the carboxylate residues disrupts the structuring of water that drives hydrophobic associations. At pH 4 and 5, two copolymers containing 9 and 21 mol % AA show extensive intermolecular hydrophobic associations. Masking of the carboxylate charges at low pH allows the natural structuring of water around the hydrophobic HPAM residues, thus driving intermolecular association.

No intermolecular associations for a terpolymer containing 37% AA are noted even at pH 4. However, well-organized hydrophobic microdomains are indicated at low pH by pyrene I_3/I_1 measurements. This leads to the conclusion that intramolecular hydrophobic associations are stabilized by strong hydrogen bonding. These intramolecular hydrophobic microdomains appear to be unaltered in the presence of 0.5 M NaCl.

Addition of NaCl to solutions of the terpolymer containing 9 and 21 mol % AA results in intermolecular associations even at high pH. Collapse of the polymer coils and screening of intra- and intercoil electrostatic repulsions by excess electrolyte and/or the water-structuring effect of NaCl allow hydrophobic association even though hydration of the carboxylate residues remains high. Finally, loss in viscosity is noted at pH 4 for these two terpolymer systems in 0.5 M NaCl. This is thought to occur by either a "salting-out" effect on the terpolymers or the promotion of intramolecular hydrophobic associations stabilized by hydrogen bonding.

These studies clearly demonstrate how controlling composition, solution pH, ionic strength, and terpolymer concentration can lead to materials with pH- and electrolyte-responsive associations.

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References and Notes

(1) McCormick, C. L.; Bock, J.; Schultz, D. N. In *Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons, Inc.: New York, 1989; Vol. 17, pp 730−784.

(2) Turner, S. R.; Siano, D. B.; Bock, J. U.S. Patent 4,520,182.

(3) Valint, P. L.; Bock, J.; Ogletree, J.; Zushuma, S.; Pace, S. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 67.

(4) Bock, J.; Siano, D. B.; Valint, P. L.; Pace, S. J. In *Polymers In Aqueous Media*; Glass, J. E., Eds.; Advances in Chemistry 223; American Chemical Society: Washington, DC, 1989; p 411.

(5) Siano, D. B.; Bock, J.; Myer, P.; Valint, P. L. In *Polymers in Aqueous Media*; Glass, J. E., Ed.; Advances in Chemistry 223; American Chemical Society: Washington, DC, 1989; p 425.

(6) McCormick, C. L.; Nonaka, T.; Johnson, C. B. *Polymer* **1988**, *29*, 731.

(7) Flynn, C. E.; Goodwin, J. W. In *Polymers as Rheological Modifiers*; Schultz, D. N., Ed.; ACS Symposium Series 462; American Chemical Society: Washington, DC, 1991; p 190.

(8) Ezzell, S. A.; McCormick, C. L. *Macromolecules* **1992**, *25*, 1881.

(9) Ezzell, S. A.; Hoyle, C. E.; Creed, D.; McCormick, C. L. *Macromolecules* **1992**, *25*, 1887.

(10) Branham, K. D.; McCormick, C. L. In *Multi-Dimensional NMR, FT-IR/Raman, and Fluorescence Spectroscopy of Polymers;* Urban, M., Provder, T., Eds.; ACS Symposium Series 598; American Chemical Society: Washington, DC, 1994; Chapter 32.

(11) McCormick, C. L.; Middleton, J. C.; Cummins, D. F. *Macromolecules* **1992**, *25*, 1201−1206.

(12) McCormick, C. L.; Middleton, J. C.; Grady, C. E. *Polymer* **1992**, *33*, 4184.

(13) (a) Biggs, S.; Selb, J.; Candau, F. *Polymer* **1993**, *34*, 580. (b) Biggs, S.; Hill, A.; Selb, J.; Candau, F. *J. Phys. Chem.* **1992**, *96*, 1505.

(14) Branham, K. D.; Davis, D. L.; Middleton, J. C.; McCormick, C. L. *Polymer* **1994**, *35*, 4429.

(15) Mortimer, D. A. *Polym. Int.* **1991**, *25*, 29.

(16) Branham, K. D.; Shafer, G. S.; Hoyle, C. E.; McCormick, C. L. *Macromolecules*, accepted for publication.

(17) Klein, J.; Heitzmann, R. *Makromol. Chem.* **1978**, *179*, 1895.

(18) Kulicke, W.-M.; Horl, H.-H. *Colloid Polym. Sci.* **1985**, *263*, 530.24.

(19) Klenina, O. V.; Lebedeva, L. G. *Polym. Sci. U.S.S.R. (Single Transl.)* **1983**, *25*, 2380.

(20) Kalyanasundarum, K. *Photochemistry in Microheterogeneous Systems*; Academic Press, Inc.: Orlando, FL, 1987.

(21) Varadaraj, R.; Branham, K. D.; McCormick, C. L.; Bock, J. In *Macromolecular Complexes in Chemistry and Biology*; Springer-Verlag: New York, 1993; p 15.

(22) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; John Wiley & Sons: New York, 1973.

(23) Molyneaux, P. *Water Soluble Synthetic Polymers*; CRC Press: Boca Raton, FL, 1984; Vol. I, pp 6−7.

(24) (a) Urry, D. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 819. (b) Urry, D. W.; Peng, S. Q. *J. Am. Chem. Soc.* **1995**, *117*, 8478.

(25) Dill, K. *Protein Sci.* **1995**, *4*, 561.

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