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Water-Soluble Copolymers. 37. Synthesis and Characterization of Responsive Hydrophobically-Modified Polyelectrolytes

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ABSTRACT: Hydrophobically-modified, water-soluble polyelectrolytes have been prepared by a micellar technique from acrylamide, *n*-decylacrylamide, and a third monomer, sodium 3-acrylamido-3-methylbutanoate, sodium acrylate, or sodium 2-acrylamido-2-methylpropanesulfonate. These terpolymers exhibit rheological behavior dependent upon the terpolymer composition, nature of the charged monomer, ionic strength, and pH. Although the hydrophobic monomer is incorporated in low concentration, the associative effects are profound, with some compositions maintaining high viscosity in NaCl concentrations of up to 0.514 M. Hydrophobic associations in terpolymers with the carboxylate anion are stronger than those in structurally analogous terpolymers containing the sulfonate anion, especially at high NaCl concentrations. Within the carboxylate series, copolymers with the carboxylate group closer to the polymer backbone exhibit greater viscosity increases with added electrolyte above the critical overlap concentration, C^*. Presence of carboxylate or sulfonate groups farther from the macromolecular backbone disrupts to a greater extent such hydrophobic associations.

Introduction

Studies in our laboratories have focused on developing macromolecules that can maintain or increase the viscosity of aqueous solutions in the presence of mono- or multivalent electrolytes.[1-10] Such polymers may have important commercial applications in enhanced oil recovery, drag reduction, flocculation, superabsorbency, and personal care and coatings formulations. Hydrophilic polymers containing a small number of water-insoluble groups can undergo microphase separation and associations in aqueous solution.[11-17]

Recent work by our research group involved the synthesis and characterization of copolymers of acrylamide with *n*-alkylacrylamides with alkyl lengths of 8, 10, and 12 carbons. These polymers exhibit microheterogeneous associative behavior with the incorporation of <1 mol % of *n*-alkylacrylamide.[18,19] While such copolymers yield high-viscosity solutions in the presence of added electrolytes above a critical concentration, they are difficult to hydrate from the dry state. To enhance dissolution and provide potential responsiveness to salt or pH changes, terpolymers containing acrylamide (AM), 0.5 mol % of *n*-decylacrylamide (C10AM) as the hydrophobic monomer, and sodium 3-acrylamido-3-methylbutanoate (NaAMB), sodium acrylate (NaA), or sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) were synthesized.[20-22] Two carboxylate monomers and one sulfonate monomer were selected to evaluate the differences in pK_B of pendent anions and to observe the influence of the distance of the charged group from the polymer backbone. Rheological properties were determined by low-shear viscometry in deionized water and sodium chloride solutions.

Experimental Section

Materials. Acrylamide (AM), obtained commercially from Aldrich Chemical Co., was recrystallized twice from acetone, dried under vacuum, and stored in a desiccator prior to use (mp 81–84 °C). Acrylic acid, also obtained from Aldrich, was purified by vacuum distillation in the presence of cupric sulfate to remove inhibitor prior to use. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) was obtained from Fluka Chemical Co. and recyrstallized twice from a mixture of methanol and 2-propanol. *n*-Decylacrylamide[18] (C10AM) and 3-acrylamido-3-methylbutanoic acid (AMBA)[23] were synthesized and purified by previously reported methods. The monomers (Figure 1) were polymerized in their sodium salt forms.

Potassium persulfate from J. T. Baker Co. was recrystallized twice from deionized water prior to use. Sodium dodecyl sulfate, received from Aldrich Chemical Co., was used without further purification. Reagent grade sodium chloride from Fisher Scientific Co. was used without further purification. All aqueous solutions were prepared using deionized water.

Polymer Synthesis. The incorporation of water-soluble and water-insoluble monomers into the polymer backbone was accomplished by a micellar polymerization method.[16] In this technique use of a surfactant is necessary to solubilize the hydrophobic monomer. Sodium dodecyl sulfate (SDS) was chosen as the surfactant in this instance. Each reaction was conducted in a 500-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, and condenser. The appropriate amount of ionizable monomer was placed in deionized water, and the pH was adjusted to 9 with NaOH to form the water-soluble salt. This amount was recorded and the

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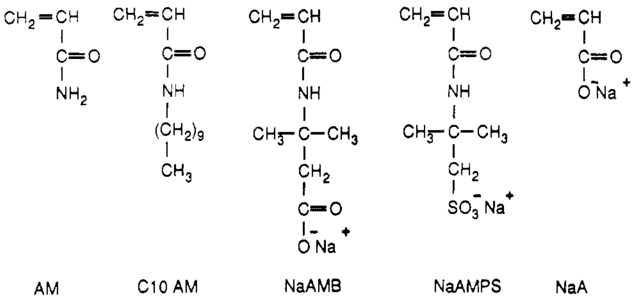

Figure 1. Structures of monomers used to prepare terpolymers.

Table I
Copolymer Comparison of C10AM Terpolymers from Elemental Analysis Neglecting C10AM

sample	feed ratio M_1:M_2[a]	elem anal. % C	elem anal. % N	polym comp, mol % M_1	polym comp, mol % M_2
NaAMPS-40[b]	59.5:40	39.39	10.12	68.8	31.2
NaAMPS-25	74.5:25	42.01	11.18	65.6	34.4
NaAMPS-10	89.5:10	45.17	14.37	83.7	16.3
NaAMPS-5	94.5:5	41.25	14.64	92.5	7.5
NaAMB-40	59.5:40	48.90	12.34	67.0	33.0
NaAMB-25	74.5:25	45.67	12.80	76.9	23.1
NaAMB-10	89.5:10	48.80	16.17	89.6	10.4
NaAMB-5	94.5:5	45.85	16.09	93.9	6.1
NaA-40	59.5:40	41.50	11.94	73.9	26.1
NaA-25	74.5:25	42.43	13.19	79.7	20.3
NaA-10	89.5:10	45.00	15.33	87.2	12.8
NaA-5	94.5:5	45.11	16.11	94.4	5.6

[a] M_1 = AM; M_2 = NaAMPS, NaAMB, or NaA. [b] Feed composition of ionizable monomer.

solution diluted to a final volume of 230 mL (13.0 mol). The acrylamide monomer was dissolved in this solution, placed in a round-bottom flask, and was deaerated with purified nitrogen for 30 min. Surfactant (7.93 g, 2.8×10^{-2} mol) and 0.109 g (5.2×10^{-4} mol) of C10AM monomer were then added, and the solution was heated to 50 °C with stirring under a nitrogen atmosphere. Potassium persulfate (0.005 g, 1.8×10^{-5} mol) dissolved in 5 mL of deionized water was added for a total water volume of 235 mL and a total monomer concentration of 0.44 M. The polymerizations were conducted for 4–6 h followed by dilution with an equal amount of water and precipitation into acetone. The polymers were washed extensively in acetone and then dried under vacuum for 24 h. Molecular weights for four acrylamide homopolymers prepared under the above conditions were determined to be from 1.0×10^6 to 1.5×10^6 by light scattering. Associative interactions precluded meaningful molecular weight measurements for the hydrophobically-modified terpolymers; however, molecular weights would be expected to be in the same range.

Polymer Composition. Elemental analyses for carbon, hydrogen, and nitrogen content of the terpolymers were conducted by M-H-W Laboratories of Phoenix, AZ. In addition, sulfur analyses of representative samples (of polymers not containing NaAMPS) were performed to confirm the absence of residual surfactant (Table I). The low amount of C10AM incorporated into the polymer could be neglected in elemental analysis calculations without inducing significant error.

Viscometry. Stock solutions of sodium chloride (0.085, 0.170, 0.257, 0.342, and 0.514 M) were prepared by dissolving the appropriate amount of salt in deionized water contained in volumetric flasks. Polymer samples were dissolved by gentle shaking on an orbital shaker for 14 days to allow complete hydration before further dilutions of these stock solutions were made.

Viscosity experiments were conducted on the Contraves LS 30 low-shear rheometer at a shear rate of 6 s^{-1} at 30 °C. The upper limit of the Contraves is 250 cP at a shear rate of 6 s^{-1}. Several polymers exceeded this value in the concentration range investigated. These polymer solutions were gels, and a value of 250 cP was assigned to them for graphical purposes.

Results and Discussion

Electrostatic interactions and hydrophobic effects for copolymers of the type prepared in this study may lead to microheterogeneous phase separation of important consequence in aqueous solution. The electrostatic interaction of carboxylate or sulfonate groups along the backbone generally increase the hydrodynamic volume while hydrophobic moieties aggregate in aqueous solution by intramolecular (closed) or intermolecular (open) associations dependent upon polymer microstructure, concentration, and molecular weight. Proper selection of synthetic conditions can lead to technologically important systems responsive to changes in pH or electrolyte concentration.

Feed Composition. Three series of terpolymers were prepared by a modified micellar polymerization technique reported in the patent literature by Turner, Siano, and Bock.[16] The reaction conditions (Table I) were chosen to have feed compositions of 0.5 mol % of the hydrophobic monomer C10AM, specified (5, 10, 25, and 40 mol %) concentration of the anionic monomer, NaAMB, NaAMPS, or NaA, and the remainder AM. Our initial objectives were to achieve an associative viscosifier with properties of the uncharged C10AM/AM copolymer previously prepared[19] but with pH or electrolyte responsiveness. Additionally, it was our desire to assess the roles of the carboxylate and sulfonate groups on hydrophobic domain disruption.

Terpolymer Composition. Data from elemental analysis show agreement between feed ratios and copolymer composition up to 20 mol % of the anionic monomer (Table I). Above 20 mol %, the incorporation likely decreases as electrostatic repulsions between structopendent charged groups of the growing polymer chain and charged monomer units become significant. While the incorporation of C10AM cannot be determined by conventional methods such as elemental analysis or NMR, Valint et al.[24] have shown >85% incorporation of a chromophore-labeled hydrophobic monomer by ultraviolet spectroscopy. Terpolymers with ionizable monomer feed compositions of 5 and 25 mol % are representative samples of a low-charge-density and a high-charge-density terpolymer, respectively. Terpolymers (Table I) are named according to the type and concentration of ionic monomer present. For example, the terpolymer with a feed composition of 0.5 mol % C10AM, 94.5 mol % AM, and 5 mol % NaAMB is referred to as NaAMB-5.

Solution Studies. Apparent viscosity (η_{app} in centipoise) is plotted as a function of polymer concentration (grams per 100 mL or g/dL) and of solution ionic strength ([NaCl]) in three-dimensional plots to clearly illustrate solution behavior. Reduced viscosity (η_{red} in deciliters per gram) is plotted as a function of polymer concentration for each polymer sample at specific NaCl concentrations to further illustrate rheological changes (Figures 2–7).

NaAMPS Terpolymers. Both NaAMPS-5 and NaAMPS-25 show typical polyelectrolyte behavior at low solution ionic strengths (Figures 2 and 3). The apparent viscosities of both systems are high at low ionic strength, characteristic of typical hydrated polyelectrolytes. Viscosity then decreases with increasing ionic strength as the charged groups are shielded by the addition of NaCl. However, above a critical polymer concentration (C^*), η_{app} and η_{red} of NaAMPS-5 increase with increasing solution ionic strength above 0.26 M NaCl, atypical of traditional polyelectrolytes (Figure 2). The low-charge-density polymer (Figure 2b) shows a linear increase in η_{red} only for the low ionic strength solution. At higher ionic strength, η_{red}

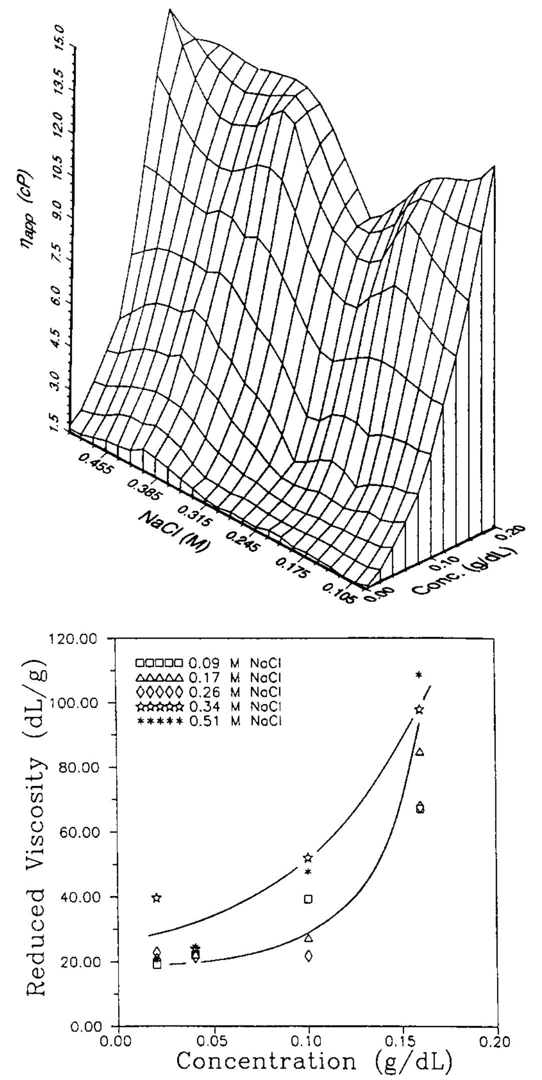

Figure 2. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaAMPS-5 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaAMPS-5 terpolymer at five different solution ionic strengths.

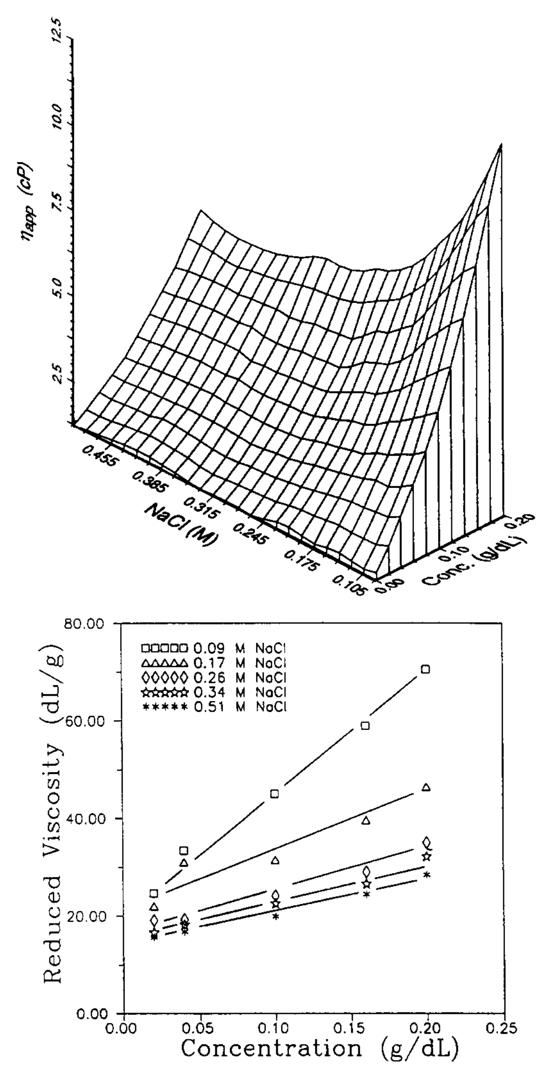

Figure 3. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaAMPS-25 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaAMPS-25 terpolymer at five different solution ionic strengths.

increases rapidly, indicative of interpolymer associations. The high-charge-density NaAMPS-25 polymer shows linear behavior at all ionic strengths investigated; apparently the increased charge density effectively prevents hydrophobic aggregation (Figure 3) by disrupting water structure ordering necessary for associative thickening behavior.

NaAMB Terpolymers. The NaAMB terpolymers exhibit unusual behavior as demonstrated by an increase in apparent viscosity with increasing solution ionic strength (Figures 4a and 5a). The NaAMB-5 terpolymer does not show associative behavior at NaCl concentrations less than 0.17 M. The electrostatic repulsions of the NaAMB groups are sufficient to prevent interpolymer aggregation through hydrophobic associations. At 0.26 M NaCl, however, a rapid increase in apparent viscosity is observed above 0.10 g/dL, indicative of associative behavior. In 0.51 M NaCl, no further aggregation occurs above 0.10 g/dL. However, because the coil is further collapsed by the large excess of NaCl, apparent viscosity is lower than that of the polymer in 0.34 M NaCl. This also is clearly illustrated in the reduced viscosity plots for the NaAMB-5 polymer, where linear behavior is observed only for the 0.17 M NaCl solution. Above 0.17 M NaCl, η_{red} again increases nonlinearly, indicating associative behavior (Figure 4b).

The NaAMB-25 terpolymer (Figure 5) behaves in a different manner from NaAMB-5. The higher polymer charge density results in a more expanded coil at low solution ionic strength. Initially, coil collapse due to ionic shielding occurs with increasing NaCl concentration followed by an increase in viscosity. The NaAMB-25 curve does not exhibit the maximum seen in the low-charge-density polymer system, suggesting insufficient electrolyte to effectively reduce charge–charge repulsions. Reduced viscosity solution behavior is linear for the high-charge-density NaAMB-25 polymer up to a concentration of 0.15 g/dL. Above this concentration the polymers associate and η_{red} increases exponentially.

NaA Terpolymers. An initial decrease and the leveling of apparent viscosity with increasing ionic strength at high concentration are observed for NaA-5 (Figure 6a). The polymer has nonlinear reduced viscosity solution behavior at all ionic strengths (Figure 6b). The higher-charge-density polymer (NaA-25) has low viscosity in low ionic strength solution, and apparent viscosity rapidly increases with increasing salt solution to form gels with viscosities greater than 250 cP (Figure 7a). Similar behavior is seen in the η_{red} plot; viscosity increases even more rapidly at higher ionic strength (Figure 7b).

Comparison of the NaAMPS, NaAMB, and NaA Terpolymers. NaAMPS terpolymers demonstrate associative behavior only at low charge densities and

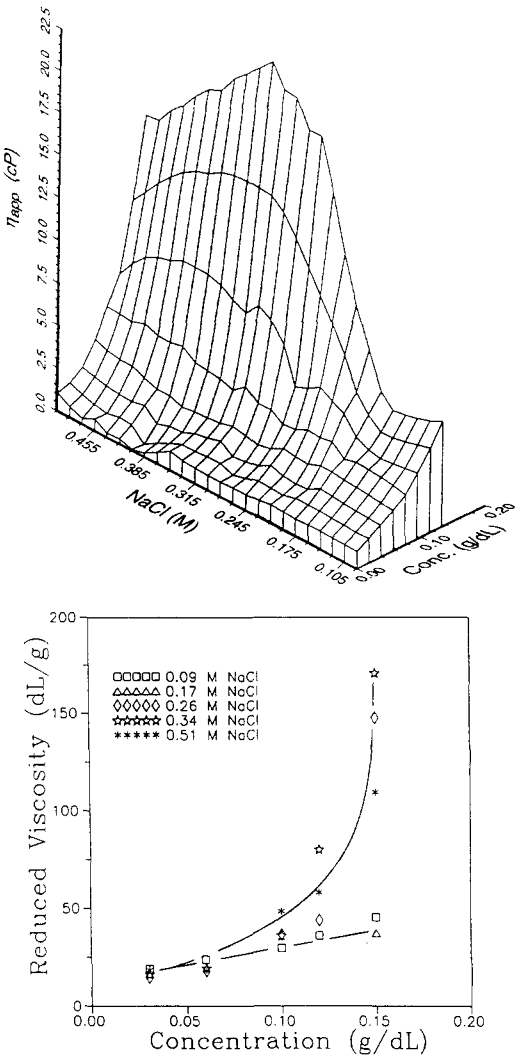

Figure 4. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaAMB-5 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaAMB-5 terpolymer at five different solution ionic strengths.

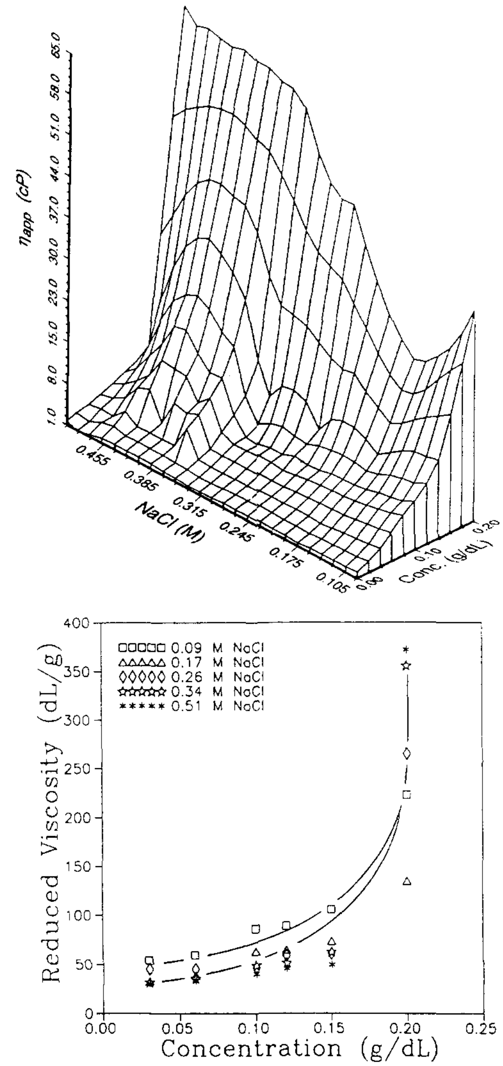

Figure 5. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaAMP-25 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaAMP-25 terpolymer at five different solution ionic strengths.

moderate-to-high ionic strength. However, for the NaAMB and NaA terpolymers, apparent viscosity increases linearly with sample concentration up to a critical value of solution ionic strength. Above this NaCl molarity, the viscosity exponentially increases with polymer concentration, indicative of intermolecular hydrophobic association. The salt concentration necessary for this transition is higher for the NaAMB polymer than for the NaA polymer. It is also apparent that the terpolymers containing NaA have much higher viscosities than the other systems investigated.

Conceptual Models. At low ionic strength and high charge density, the electrostatic repulsive forces dominate the polymer solution behavior and all the polymers act as polyelectrolytes with similar viscosities. Armstrong and Strauss[25] have depicted a typical polyelectrolyte as an extended chain with the ionic atmosphere projecting out radially to a distance on the order of the Debye–Hückel shielding length (κ^{-1}) where for a 1:1 simple electrolyte $\kappa^{-1} = 0.304/I^{1/2}$ (e.g., for a 0.1 M NaCl solution $\kappa = 0.1$ nm). The entire chain may be envisioned as enclosed by a tube with an average diameter of $2\kappa^{-1}$. Even in excess electrolyte, where the chain may form a random coil, the local geometry may be represented by the above model if the radius of curvature is greater than $2\kappa^{-1}$.

The presence of pendent C10AM hydrophobic groups along the polymer backbone apparently changes the aqueous solution behavior from that of a typical polyelectrolyte at higher ionic strengths; the nonpolar *n*-decyl groups are excluded from the polar environment,[26] resulting in network formation. The onset value of interaction at low C^* values has yet to be explained; however, Israelachvili et al.[27,28] and Pashley et al.[29] have demonstrated long-range attractive interaction of crossed cylinders of hydrophobically-modified mica surfaces. They reported attractive forces 10–100 times stronger than expected van der Waals force over distances up to 10 nm. These forces decay exponentially with a force proportional to $\exp(-D/1.0)$.

In our terpolymer systems, as the charge density decreases and solution ionic strength increases, the electrostatic potential along the polymer chain decreases, allowing long-range hydrophobic attractions well below that of C^* for unmodified polyacrylamides.[19,30] Israelachvili has predicted aggregation for charged, hydrophobically-modified colloid particles where the Debye–Hückel parameter approaches the decay length of 1.0 nm for hydrophobic associations corresponding to a solution ionic strength for NaCl of 0.1 M.[28] This is consistent with our finding that significant associative behavior occurs only at ionic strengths greater than or equal to 0.17 M NaCl.

Strauss et al. observed similar behavior with poly(4-vinylpyridine) derivatives[31,32] hydrophobically modified

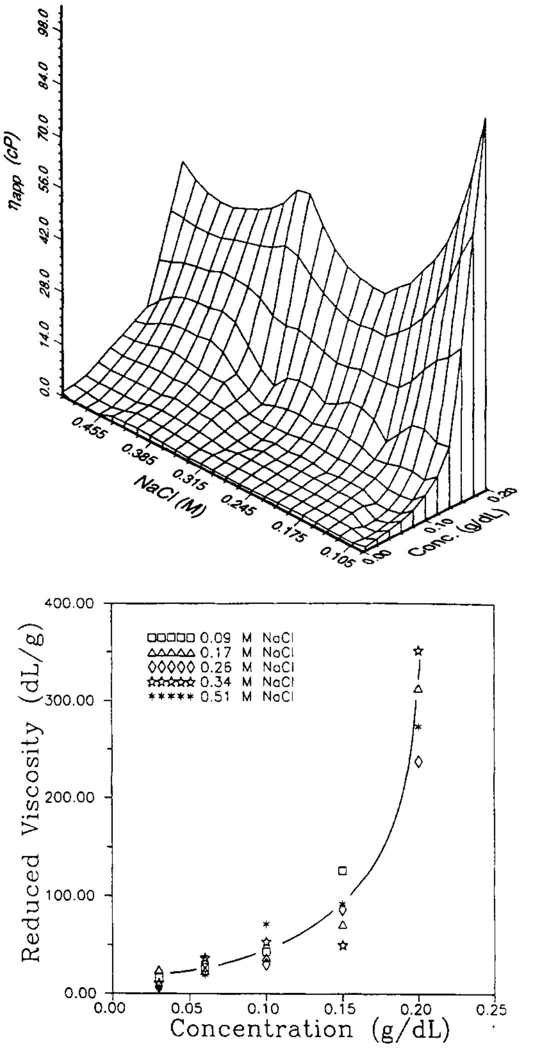

Figure 6. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaA-5 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaA-5 terpolymer at five different solution ionic strengths.

with ethyl and dodecyl side chains. Low hydrophobic group incorporation resulted in polymers that displayed intermolecular association above C^*; with increasing hydrophobic group incorporation, the polymers associated intramolecularly, resulting in polysoaps. Above a critical polymer concentration, sufficient hydrophobic groups were present to associate in either an inter- or an intramolecular fashion. The associations of bound hydrophobic groups were discussed in terms of a critical micelle concentration similar to that for small-molecule surfactants. At low dodecyl group incorporation, an insufficient number of hydrophobic groups are present on any individual polymer chain to form a stable ensemble. When a critical polymer concentration is reached, the polymer chains associate to form an intermolecular network in the aqueous system.

The association of polymer chains results in a rapid increase in apparent molecular weight (M_{app}). Below this critical molecular weight, η_{app} and η_{red} increase in a linear fashion, and reduced viscosity as a function of concentration may be plotted according to the Huggins equation.[33] Above a critical M_{app} (M_c) viscosity increases exponentially instead of linearly[34] as seen by the increases in both apparent and reduced viscosity (Figures 2–7).

The terpolymers containing NaAMPS are the least affected by changing ionic strength, reflecting the soft nature of the sulfonate anion. The carboxylate anions of

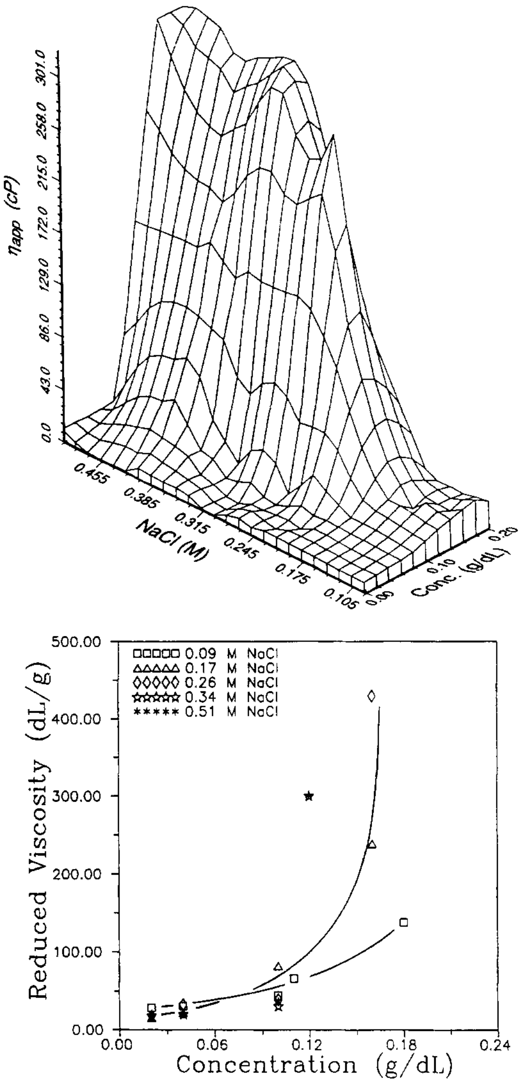

Figure 7. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaA-25 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaA-25 terpolymer at five different solution ionic strengths.

NaAMB and NaA polymers, on the other hand, show aggregation as ionic shielding causes collapse of the Debye–Hückel radius. The much higher viscosities of the NaA terpolymers may also be explained by the thickness of the Debye ionic layer. The NaAMB and NaAMPS mers are farther from the polymer backbone and may interfere with hydrophobic association more than the NaA mer. Additionally, the *gem*-dimethyl groups of the NaAMB and NaAMPS may have sufficient hydrophobic character to disrupt associations of the *n*-decyl groups into stable micelle-like domains (Figure 8).

Conclusions

Associative polymers of acrylamide and *n*-decylacrylamide with sodium 3-acrylamido-3-methylbutanoate, sodium acrylate, or sodium 2-acrylamido-2-methylpropanesulfonate have been prepared by a micellar technique. The NaAMPS terpolymers display typical polyelectrolyte behavior at low solution ionic strength and high charge density. The sulfonate groups are not sufficiently shielded by the Na counterions to prevent electrostatic repulsions and hydrophobic aggregation at charge densities of 25 mol %. The NaAMB and NaA terpolymers exhibit associative properties at lower ionic strengths and higher charge densities due to hydrophobic associations among the decyl

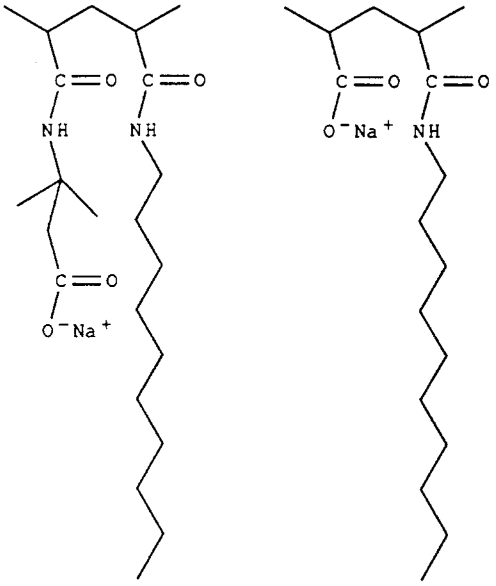

Figure 8. Schematic comparison of NaAMB terpolymer versus NaA terpolymer illustrates how hydrophobic associations might be disrupted by the more extended NaAMB ionic group resulting in less aggregation and lower viscosity.

groups along the polymer chain as the Debye–Hückel reciprocal shielding length (κ^{-1}) is reduced to the order of the decay length for long-range hydrophobic interactions.

Distance of the ionic group from the backbone seems to influence hydrophobic association also. The NaAMB and NaAMPS monomers allow charged groups to extend out farther from the polymer backbone, apparently preventing associations among the hydrophobic decyl groups at low solution ionic strengths and high polymer charge density. This is not observed for the NaA monomer with charge much closer to the backbone. As the polymer coils interact, a critical apparent molecular weight is reached and viscosity exponentially increases with increasing polymer concentration.

Although the goals of achieving facile dissolution of associative viscosifiers and understanding more fully the effects of ionic monomer composition on solution behavior have been realized, a number of significant problems remain unresolved. First, the precise composition of these *n*-alkyl type terpolymers is not determinable by current methods of analysis. Second, although preliminary data have been presented and discussed at major symposia,[17,18] the precise nature of micellar polymerization has not been elucidated, in particular sequence length of hydrophobic monomers produced by the method and its importance on macroscopic viscosity. Finally, molecular weight data for associative polymers, particularly those with blocky microstructures, are suspect since intermolecular associations during dissolution may not be completely disrupted. Therefore, comparisons can only be made (and then cautiously) on systems prepared under similar synthetic conditions. Each of these concerns will be addressed in subsequent papers in this series.[36,37]

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Registry No. AM/C10AM/NaAMB (copolymer), 126509-34-0; AM/C10AM/NaA (copolymer), 126461-18-5; AM/C10AM/NaAMPS (copolymer), 114859-64-2; NaCl, 7647-14-5.