Water-Soluble Polymers. 60. Synthesis and Solution Behavior of Terpolymers of Acrylic Acid, Acrylamide, and the Zwitterionic Monomer 3-[(2-Acrylamido-2-methylpropyl)dimethylammonio]-1-propanesulfonate

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Received November 24, 1993; Revised Manuscript Received March 10, 1994®

ABSTRACT: Terpolymers of acrylic acid (AA), acrylamide (AM), and the zwitterionic monomer 3-[(2-acrylamido-2-methylpropyl)dimethylammonio]-1-propanesulfonate (AMPDAPS) have been prepared by the free-radical polymerization in a 0.5 M NaCl aqueous solution using potassium persulfate as the initiator. The feed ratio of AMPDAPS:AA:AM was varied from 5:5:90 to 40:20:20 mol %, with the total monmer concentration held constant at 0.45 M. Terpolymer compositions were obtained by ^{13}C NMR. Low-angle laser light scattering provided molecular weights and second virial coefficients which varied from (3.0 to 7.9) × 10^6 and (2.23 to 2.95) × 10^{-4} mL mol g^{-2}, respectively. The solubilities of the resulting terpolymers are dependent on pH as well as the amount of AMPDAPS and AA present in the feed. At pH 4 and for higher incorporation of AA and AMPDAPS in the feed (>25 mol %), the terpolymers are insoluble in deionized water and 0.25 M NaCl. At pH 8, all terpolymers are soluble in deionized water and salt solutions. The dilute and semidilute solution behavior of the terpolymers were studied as a function of composition and added electrolytes. Polyelectrolyte behavior was observed for all terpolymers at pH 8 as evidenced by a viscosity decrease in the presence of added electrolytes. The terpolymers exhibit higher viscosities in the presence of NaSCN versus NaCl. Comparison of the solution behavior of the terpolymers to copolymers of AM and AA as well as copolymers of AMPDAPS and AM has been made.

Introduction

The synthesis of electrolyte-tolerant water-soluble polymers that contain ionic pendent groups has been the subject of study in our laboratories for the past several years.[1-8] Polyelectrolytes display high viscosities in deionized water at low concentrations and thus are commercially used as viscosifying agents in numerous applications. However, in the presence of added electrolytes, charge–charge repulsions are shielded, resulting in a considerable decrease in viscosity and, in some cases, phase separation. In striving to synthesize polymers that show tolerance in the presence of added electrolytes, we have recently focused our attention on polyampholytes, polymers which possess both cationic and anionic pendent groups. Polyampholytes have shown an enhancement in viscosity in the presence of added electrolytes as intramolecular Coulombic attractions are shielded.[9-21] In our laboratories, high charge density copolymers of cationic and anionic monomers have been synthesized. The rheological behavior of these polymers is dictated by the charge ratio of the cationic and anionic groups. If there is a charge imbalance, the polymers behave as polyelectrolytes and display a decrease in viscosity in the presence of added electrolytes. However, when there are equimolar anionic and cationic monomers, polyampholytic behavior is observed and viscosity increases as the ionic strength of the medium is increased. Low charge density polyampholytes have also been synthesized in which a neutral monomer such as acrylamide has been terpolymerized with cationic and anionic monomers. These polymers intermolecularly associate in deionized water and can form gels that may be used as "superabsorbers".[17]

Polyampholytes have also been synthesized from zwitterionic monomers in which the cationic charge is provided by a quaternary ammonium functionality and the anionic charge is provided by a carboxylate or sulfonate group. These monomers are unique in that they exhibit a net charge of zero at appropriate pH. A number of investigations have focused on the unusual solution behavior of zwitterionic polyampholytes.[22-34]

The goals of this research are to synthesize polymers that will display either polyampholytic or polyelectrolytic behavior depending on the pH of the environment. Special attention has been focused on polymers that contain the carboxylic acid group which may be neutralized to the carboxylate group by adjusting the pH of the medium. Thus, the synthesis and solution behavior of terpolymers of acrylic acid, acrylamide, and a sulfobetaine monomer will be discussed.

Experimental Section

Materials. Acrylamide (AM) from Aldrich was recrystallized twice from acetone and vacuum-dried at room temperature. Acrylic acid (AA) from Aldrich was distilled prior to use. 3-[(2-Acrylamido-2-methylpropyl)dimethylammonio]-1-propanesulfonate (AMPDAPS) was synthesized by the ring-opening reaction of 1,3-cyclopropanesultone with (2-acrylamido-2-methylpropyl)dimethylamine as previously reported.[19] Potassium persulfate from J. T. Baker was recrystallized twice from deionized water. All other materials were used as received.

Synthesis of Terpolymers of 3-[(2-Acrylamido-2-methylpropyl)dimethylammonio]-1-propanesulfonate, Acrylamide, and Acrylic Acid. The terpolymers of AMPDAPS, AM, and AA (the AADAPS series) were synthesized by free-radical polymerization in a 0.5 M NaCl aqueous solution under nitrogen at 30 °C using 0.1 mol % potassium persulfate as the initiator at a pH of 8. The use of 0.5 M NaCl as a reaction medium was to keep consistent with methods employed in ref 19. The feed ratio of AMPDAPS:AA:AM was varied from 5:5:90 to 40:40:20 mol %, with the total monomer concentration held constant at 0.45 M.

In a typical synthesis, specified quantities of each monomer were dissolved in small volumes of a 0.5 M NaCl solution. The separate solutions were then combined and diluted to a 0.45 M monomer concentration with a 0.5 M NaCl solution. One

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® Abstract published in *Advance ACS Abstracts,* May 1, 1994.

0024-9297/94/2227-3156$04.50/0

equivalent of sodium hydroxide per equivalent of acrylic acid was then added and the pH adjusted to 8. The reaction mixture was sparged with nitrogen and then initiated with 0.1 mol % potassium persulfate. The reaction was usually terminated at <55% conversion due to the high viscosity of the reaction medium and as a precaution against copolymer drift. The polymers were precipitated in acetone, redissolved in deionized water, and then dialyzed using Spectra/Por 4 dialysis bags with molecular weight cutoffs of 12 000–14 000. Half of the samples were dialyzed against deionized water adjusted to pH 4, while the other half were dialyzed against deionized water adjusted to pH 8. Polymers containing 25 mol % or more of AMPDAPS and AA in the feed (AADAPS-25 and AADAPS-40) precipitated during dialysis against deionized water adjusted to pH 4. After dialyzing for 2 weeks, the polymers were isolated by lyophilization. Conversions were determined gravimetrically. IR: AADAPS-40 copolymer isolated at pH 4 (KBr pellet): 3600–2600 (b d, *O-H*), 3280 (s, *N-H*), 3050, 2980 (m, *C-H*), 1700, 1655, 1637 *C=O*), 1560 (m, *N-H*), 1460 (m, *C-O-H*), 1208 (s, *C-O*), 1189, 1042 cm^{-1} (s, *S-O*).

Synthesis of Copolymers of 3-[(2-Acrylamido-2-methylpropyl)dimethylammonio]-1-propanesulfonate with Acrylamide and Acrylic Acid with Acrylamide. The polymerization procedures for copolymers of AMPDAPS with AM have been previously reported by Salazar and McCormick.[19] Copolymers of AM and AA were prepared using similar techniques for the terpolymer synthesis.

Copolymer Characterization. ^{13}C NMR spectra of the polymers were obtained at 50.3 MHz on a Bruker AC 200 spectrometer using 10–15 wt % aqueous (D_2O) polymer solutions with DSS as a reference. A recycle delay of 6 s, 90° pulse length, and gated decoupling to remove all NOE were used for quantitative spectral analysis. FTIR spectra were obtained using a Mattson Galaxy 2020 series spectrometer. Molecular weight studies were performed on a Chromatix KMX-6 low-angle laser light scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. For quasielastic light scattering a Langley-Ford Model LF1-64 channel digital correlator was used in conjunction with the KMX-6. All measurements were conducted at 25 °C in 1 M NaCl at a pH of 8.

Viscosity Measurements. Stock solutions of sodium chloride were prepared by dissolving the appropriate amount of salt in deionized water adjusted to either pH 4 or pH 8 in volumetric flasks. Polymer stock solutions were made by dissolving amounts of polymer in the salt solutions. The solutions were then diluted to appropriate concentrations and allowed to age for 7–10 days before being analyzed with a Contraves LS-30 rheometer. Intrinsic viscosities were evaluated using the Huggins equation.

Results and Discussion

Compositional Analysis. The terpolymers of AMPDAPS, AM, and AA (the AADAPS series) were synthesized by varying the feed ratios of AMPDAPS:AA:AM from 5:5:90 to 40:40:20 mol %. Copolymers of AM and AA (the AAAM series) were synthesized by varying the feed ratio of AA:AM from 10:90 to 25:75 mol %. Copolymers of AMPDAPS and AM (the DAPSAM series) have been synthesized previously.[19] All polymers reported in this paper are shown in Chart 1. The polymer compositions were determined by integration of the carbonyl resonances and agree favorably with past results. A typical NMR spectrum is shown in Figure 1. AMPDAPS and AM incorporation in both the AADAPS and DAPSAM series approximates the feed composition, indicating little preference for addition of either monomer. AA incorporation in both the AADAPS and AAAM series was found to be approximately half the feed composition, denoting a partiality toward the addition of the acrylamido-type monomers. The reaction parameters and the resulting copolymer compositions are given in Table 1.

Low-Angle Laser Light Scattering. Table 2 shows the weight-average molecular weights determined by low-angle laser light scattering at 25 °C in 1 M NaCl. The molecular weight for the AADAPS series varies from (3.0 to 7.9) × 10^6. The second virial coefficients (A_2) for the AADAPS series have values between those of the DAPSAM series and the AAAM series. This is expected due to the presence of the strongly hydrated carboxylate functionalities in the AADAPS terpolymers.

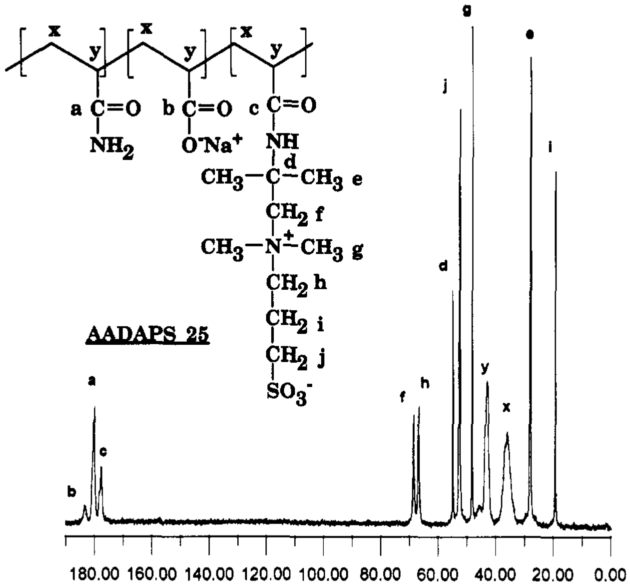
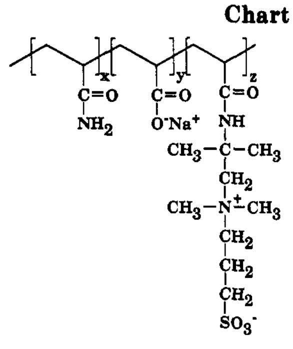
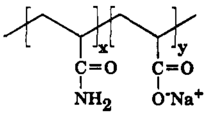


Figure 1. ^{13}C NMR of AADAPS-25.

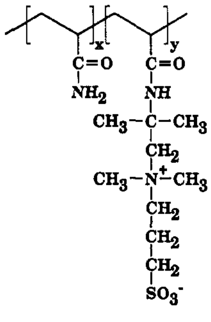
Chart 1



AADAPS Series



AAAM Series



DAPSAM Series

Quasi-elastic light scattering was used to obtain the mean diffusion coefficients (D_0) and diameters (d_0) shown in Table 2. As molecular weight and degree of polymerization increase, D_0 decreases and d_0 increases on average although solvent quality (A_2 values) as well as steric factors must also be considered. AADAPS-25 and DAPSAM-25, both having similar molecular weights, demonstrate enhanced solvation of AADAPS-25 due to the presence of carboxylate functionalities, resulting in a larger hydrodynamic volume.

Table 1. Reaction Parameters for AADAPS, AAAM, and DAPSAM Polymers

Reaction Parameters for AADAPS Terpolymers

sample	feed ratio (mol %) (*X*/*Y*/*Z*)	reaction time (h)	conv (%)	found[a] (mol %) AMPDAPS	AA	AM
AADAPS-5	90.0/5.0/5.0	4.0	53.0	5.0	3.2	91.8
AADAPS-10	80.0/10.0/10.0	4.0	48.0	10.2	4.6	85.2
AADAPS-25	50.0/25.0/25.0	4.0	46.0	31.1	13.3	55.6
AADAPS-40	20.0/40.0/40/0	5.5	50.0	50.4	25.4	24.2

Reaction Parameters for AAAM and DAPSAM Copolymers

sample	feed ratio (mol %) (*X*/*Y*)	reaction time (h)	conv (%)	found[a] (mol %) AMPDAPS	AA	AM
AAAM-10	90.0/10.0	4.0	65.0		5.8	94.2
AAAM-25	75.0/25.0	6.0	38.0		12.2	87.8
DAPSAM-10[b]	90.0/10.0	4.5	22.1	9.6		90.4
DAPSAM-25[b]	75.0/25.0	23.0	44.9	27.7		72.3

[a] Determined from ^{13}C NMR. [b] Reference 19.

Table 2. Classical and Quasi-Elastic Light Scattering Data for AADAPS, AAAM, and DAPSAM Polymers

sample no.	d*n*/d*c*	M_w ($\times 10^{-6}$)	A_2 ($\times 10^4$ mL mol g^{-2})	$D_0 \times 10^8$ (cm^2/s)	d_0 (Å)	DP × 10^{-4}
AADAPS-5	0.186	3.0	2.77	4.07	1150	3.61
AADAPS-10	0.175	5.4	2.95	4.10	1150	5.69
AADAPS-25	0.193	7.9	2.23	3.91	1370	5.55
AADAPS-40	0.181	4.7	2.23	4.00	1180	2.50
AAAM-10	0.172	4.0	5.76	4.09	1180	5.49
AAAM-25	0.189	1.9	9.49	4.12	1060	2.53
DAPSAM10	0.138	7.00	1.49	4.01	1380	7.50
DAPSAM25	0.139	8.20	1.33	3.97	1180	6.35

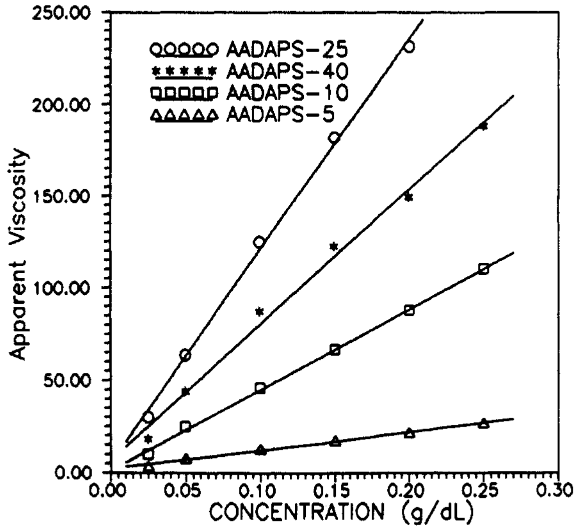


Figure 2. Apparent viscosities of AADAPS terpolymers in deionizing water. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8.)

Dilute Solution Behavior. Effects of Copolymer Composition and pH. To study the effects of pH on the terpolymers, 0.25-g/dL stock solutions were prepared from the terpolymer samples dialyzed at pH 4 and pH 8. Of the samples dialyzed against pH 4, only two of the samples were soluble in deionized water: AADAPS-5 and AADAPS-10. AADAPS-25 was insoluble in deionized water and 0.25 M NaCl; however, the copolymer was soluble in 1 M urea. AADAPS-40 was insoluble in all of the above solvents.

The solubility behavior is a culmination of two effects: (1) charge–charge interaction between the AMPDAPS mer units and (2) hydrogen bonding between the amide and carboxylic acid units. The insolubility of polyampholytes in deionized water has been observed numerous times and is clearly due to strong Coulombic attractions. In our group, copolymers of AM and AMPDAPS have been studied.[19] Those copolymers containing 60 mol % or more of AMPDAPS were insoluble in water and required the addition of a critical concentration of NaCl before solubility could be achieved. In the case of AADAPS terpolymers, the solubility is greatly reduced by substituting acrylamide units with acrylic acid units during synthesis.

The behavior of acrylamide/acrylic acid copolymers has been studied by numerous groups.[35–41] Precipitation has been observed for polymers containing more than 30 mol % acrylic acid in 0.05 M HCl due to strong hydrogen bonding between the acid and amide groups.[38] Similar behavior has been observed in AADAPS terpolymers and is further supported by the solubilization of AADAPS-25 which requires 1 M urea. The presence of urea may disrupt hydrogen bonding between the carboxylic acid and amide groups and allows solubilization of the terpolymer.

Although polymer samples AADAPS-5 and AADAPS-10 were soluble in deionized water as well as salt solutions, viscosity data yielded little information due to the extremely low values that were obtained ($\eta_{red} < 0.5$). Extremely compact conformations are indicated in both deionized water and 0.514 M NaCl. As for the samples dialyzed against pH 8, all were soluble in both deionized water and salt solutions.

Effects of Added Electrolytes on the AADAPS Series. The effects of added salts on the viscosities of the AADAPS terpolymers were observed at a shear rate of 5.96 s^{-1}. The apparent viscosities of the AADAPS terpolymers in deionized water at pH 8 are shown in Figure 2. As expected, the terpolymers display high viscosities due to a net negative charge on the chain which causes the polymer to behave as a polyelectrolyte. Viscosity tends to increase with increasing sodium acrylate mer units except for the discrepancy between AADAPS-40 and AADAPS-25, perhaps due to molecular weight differences or increased rigidity from cyclic interactions between amide and carboxylate groups. Our group and others have found that the highest intrinsic viscosities for copolymers of acrylamide and sodium acrylate occur when there is roughly an equal ratio of acrylamide to sodium acrylate units due to the cyclization mechanism noted above.[35,36] This nearest-neighbor effect may be broken up by the AMPDAPS mer units in AADAPS-40 which contains 50 mol % AMPDAPS.

The AADAPS terpolymers act as anionic polyelectrolytes with a reduction in the intrinsic viscosity as a function

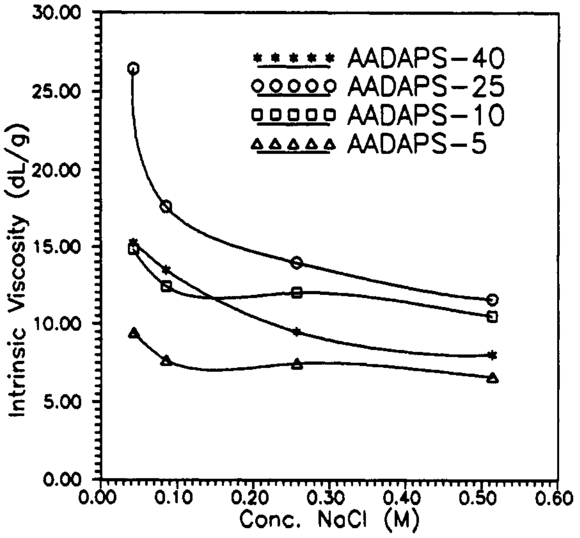


Figure 3. Dependence of intrinsic viscosity of AADAPS terpolymers as a function of NaCl concentration. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8.)

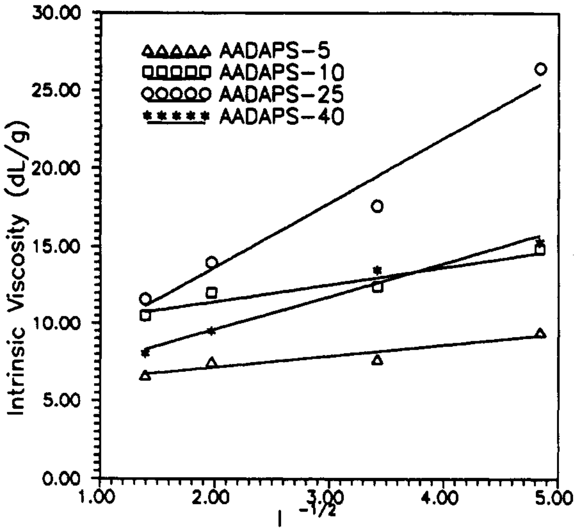


Figure 4. Intrinsic viscosities of AADAPS terpolymers as a function of the inverse square root of ionic strength. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8.)

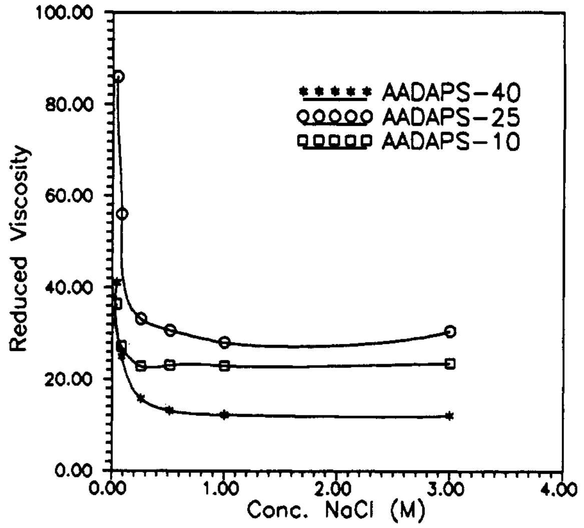


Figure 5. Reduced viscosity of AADAPS terpolymers versus NaCl concentration with a polymer concentration of 0.25 g/dL. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8.)

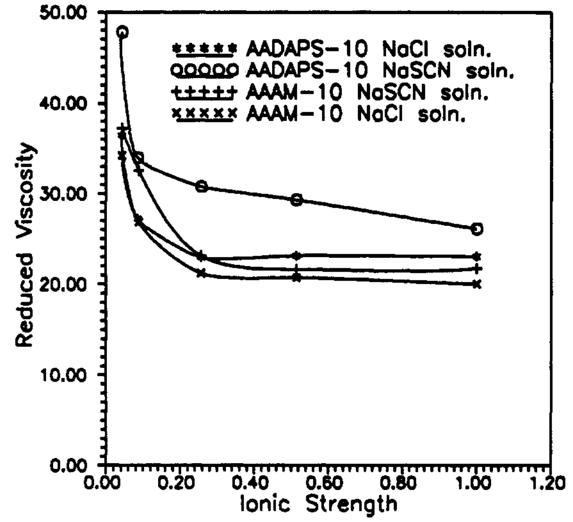


Figure 6. Reduced viscosity as a function of increasing ionic strength of various salts with a polymer concentration of 0.25 g/dL. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8.)

of increasing ionic strength as shown in Figure 3. As the concentration of NaCl increases, the anionic repulsions are shielded and the hydrodynamic volume decreases as the polymer chain relaxes into a more compact configuration. AADAPS-40 displays a lower intrinsic viscosity than AADAPS-10 at higher ionic strengths, probably indicative of a lower molecular weight. Polyelectrolyte behavior was further illustrated by plotting intrinsic viscosity as a function of the reciprocal square-root of the ionic strength (Figure 4). All samples display a linear dependence which is typical of polyelectrolytes. AADAPS-25 exhibits the highest slope and is, therefore, the most sensitive to changes in the ionic strength of the solution.

Figure 5 shows the reduced viscosity versus NaCl concentration at a polymer concentration of 0.25 g/dL. Once again typical polyelectrolyte behavior is observed even up to 3 M NaCl. Polyampholytes normally display an enhancement in viscosity as the ionic strength of the medium increases due to the shielding of intramolecular Coulombic attractions. As the ionic strength of the medium is increased, the electrostatic energy term plays a smaller and smaller role in the conformational stability of the chain while the rotational and hydrophobic terms as well as polymer solvation become the dominant factors in dictating the conformation of the polymer chain. The AADAPS terpolymers show no polyampholytic behavior at higher ionic strengths, and the hydrodynamic volumes of the polymers appear to remain fairly constant between 0.5 to 3 M NaCl.

The reduced viscosities were also examined as a function of the structure of the anion in the added electrolytes. Figures 6 and 7 display the differences in the reduced viscosity in NaCl and NaSCN solutions for AADAPS-10, AAAM-10, and AADAPS-25, AAAM-25. In agreement with the Hoffmeister series predictions, all polymers studied show an enhancement of reduced viscosity in NaSCN solutions compared to NaCl solutions; however, the effect is much less dramatic for AAAM copolymers. As noted by others[31-33] and in accord with the "hard-soft" acid–base theory, the SCN^- ion is a "softer" ion than the Cl^- ion and is thus able to bind tighter to the "soft" ammonium group. Salamone et al.[31] have proposed that tighter binding between the small anion and the ammonium group in sulfobetaine polymers reduces the draining ability of individual chains and thus an increase in viscosity is observed. It is further stated that, as the concentration of salt is increased, the viscosity rises rapidly at first due to site binding and then increases slowly as atmospheric binding becomes the only mode available for

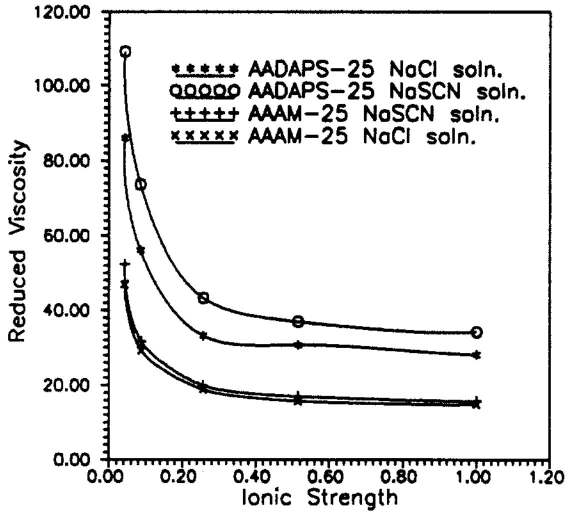


Figure 7. Reduced viscosity as a function of increasing ionic strength of various salts with a polymer concentration of 0.25 g/dL. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8.)

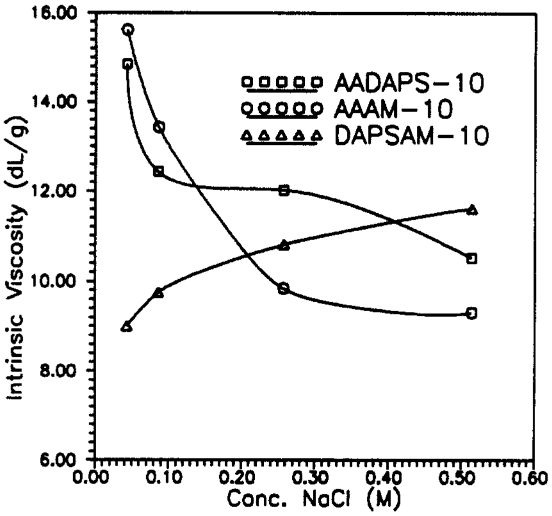


Figure 8. Dependence of intrinsic viscosity as a function of NaCl concentration. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8.)

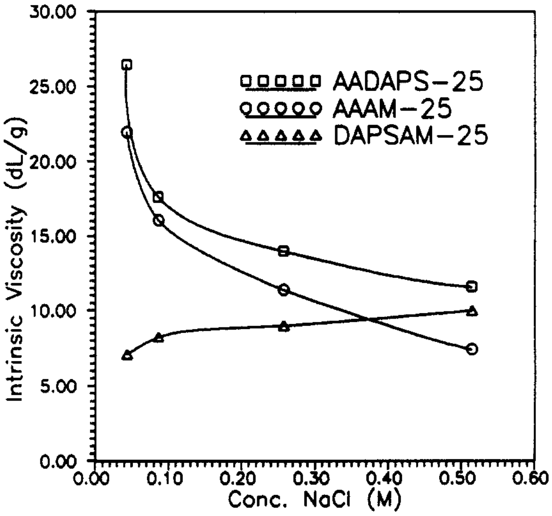


Figure 9. Dependence of intrinsic viscosity as a function of NaCl concentration. (Determined at 25 °C at a shear rate of 5.96 s^{-1} and pH 8.)

ionic interaction. Liaw et al.[33] suggested that, if the small anion binds tighter to the ammonium group than the small cation does to the sulfonate group in sulfobetaine polymers, a partial negative charge may develop along the polymer chain and thus lead to an increase in viscosity.

Our systems show that, at the lower ionic strengths, the differences in reduced visocsity between the NaSCN and NaCl solution are quite large. However, at higher salt concentrations the differences begin to narrow. This behavior is in agreement with the propositions put forth by Salamone and Liaw.[31,33] At lower concentrations of salt, the SCN^- anion binds tighter to the ammonium group than does the Cl^- anion, leading to an enhancement of the reduced viscosity. This "tighter" binding not only reduces the draining ability of the polymer chain but leads to an amplification of the net negative charge that is already present along the polymer chain due to the sodium acrylate mer units. At higher concentrations of salt, electrostatic repulsive forces are greatly diminished and the differences in viscosity between the NaCl and the NaSCN solutions are probably due to draining differences of the polymer in the different solutions as well as the enhanced "salting-in" of the polymer chain by NaSCN.

Comparison of the Effect of Added Electrolytes on the AADAPS, DAPSAM, and AAAM Series. Figures 8 and 9 examine the effect of increasing NaCl concentration on the intrinsic viscosities of all the polymer series. In Figure 8, a structural comparison between AADAPS-10 and AAAM-10 may tentatively be drawn since both have similar molecular weights and degrees of polymerization. It can be seen that, at low ionic strength, the pure polyelectrolyte has a higher intrinsic viscosity due to Donnan effects that have not been overcome. AADAPS-10 has a lower intrinsic viscosity because of Columbic attractions between the cationic and anionic groups present along the polymer chain. When the ionic strength increases, the Columbic attractions in AADAPS-10 are shielded sufficiently enough for the copolymer to adopt a more random configuration; however, there is still a decrease in the intrinsic viscosity due to the charge imbalance of the polymer. At higher ionic strengths there is a crossover of intrinsic viscosity values of the AADAPS-10 and AAAM-10 polymers, with AADAPS-10 maintaining a higher intrinsic viscosity. This behavior is probably a result of the inherent bulkiness of the AMDPAPS mer unit restricting the rotational freedom of the polymer chain rather than a solvation effect. DAPSAM-10 displays typical polyampholyte behavior, with the intrinsic viscosity increasing in the presence of added salt. DAPSAM-10 has the highest intrinsic viscosity in 0.5 M NaCl, likely due to the higher molecular weight compared to the other polymers. In Figure 9, a structural comparison between AADAPS-25 and DAPSAM-25 may tentatively be drawn since molecular weights and degrees of polymerization are similar. At low ionic strengths, AADAPS-25 has a higher intrinsic viscosity due to the charge imbalance of the polymer chain. At higher ionic strengths, AADAPS-25 still maintains a higher intrinsic viscosity than DAPSAM-25 due to the presence of the carboxylate functionalities which enhance the solvation of the polymer chain. This is in accord with the A_2 values discussed earlier.

Effects of Shear Rate. The effects of shear rate on the apparent viscosity of AADAPS-10 and AADAPS-25 were investigated in deionized water at both high and low polymer concentrations. The shear rates ranged from 0.94–127.47 s^{-1}. In Figure 10, the behavior of the terpolymers is shown at two different concentrations. Both terpolymers display pseudoplastic behavior as evidenced by the reduction in the apparent viscosity as shear rates increase. In 0.514 M NaCl, the terpolymers no longer

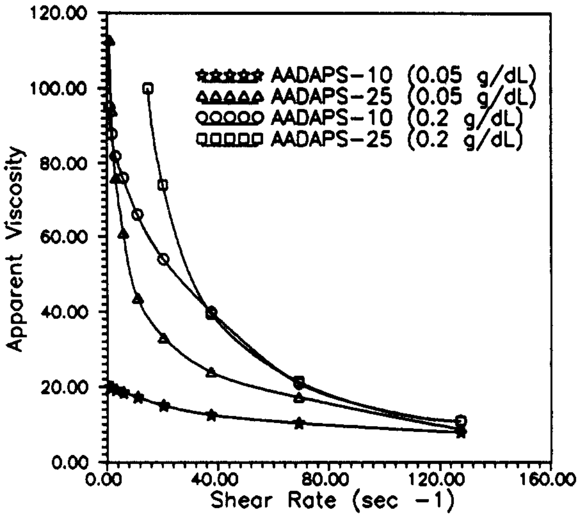


Figure 10. Effect of shear rate on the apparent viscosity of AADAPS-10 and AADAPS-25 in deionized water and different concentrations. (Determined at 25 °C and pH 8.)

display pseudoplastic behavior and viscosity is fairly constant over the range of shear rates studied.

Conclusions

Terpolymers of AA, AM, and AMPDAPS have been synthesized by free-radical polymerization in 0.5 M NaCl. In deionized water at pH 4, the solubility of the polymers is greatly reduced due to ionic interactions as well as hydrogen-bonding interactions. At pH 8, the polymers behave as typical polyelectrolytes displaying high apparent viscosities. As the ionic strength of the medium is increased, the intrinsic viscosity decreases due to shielding effects between like charges. The reduced viscosities are higher in NaSCN solutions compared to the NaCl solutions due to the higher binding ability between the SCN^- anion and the ammonium group on the AMPDAPS mer unit. AADAPS-10 displays a higher intrinsic viscosity than AAAM-10 in 0.5 M NaCl probably due to steric factors. AADAPS-25 displays a higher intrinsic viscosity due to solvation effects.

Acknowledgment. Financial support for portions of this research from the Department of Energy, the Office of Naval Research, and the Defense Advanced Research Project Agency is gratefully acknowledged.

References and Notes

(1) McCormick, C. L.; Blackmon, K. P.; Elliott, D. L. *Polymer* **1986**, *27*, 1971.
(2) McCormick, C. L.; Blackmon, K. P.; Elliott, D. L. *Polymer* **1986**, *27*, 1976.
(3) McCormick, C. L.; Blackmon, K. P.; Elliott, D. L. *Macromolecules* **1986**, *19*, 1516.
(4) McCormick, C. L.; Blackmon, K. P. *J. Macromol. Sci., Chem.* **1986**, *A23* (12), 1469.
(5) McCormick, C. L.; Salazar, L. C. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29* (3), 193.
(6) McCormick, C. L.; Salazar, L. C. *J. Polym. Sci., Polymer. Chem. Ed.* **1993**, *31*, 1099.
(7) McCormick, C. L.; Bock, J.; Schulz, D. N. *Mark-Bikales-Overberger-Menges Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley and Sons: New York, 1989; Vol. 17, p 730.
(8) Molyneux, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC Press: Boca Raton, FL, 1989; Vol. II.
(9) Alfrey, T.; Morawetz, H. *J. Am. Chem. Soc.* **1952**, *74*, 436.
(10) Ehrlich, G.; Doty, P. *J. Am. Chem. Soc.* **1954**, *76*, 3764.
(11) Salamone, J. C.; Tsai, C. C.; Watterson, A. C. *J. Macromol. Sci., Chem.* **1979**, 665.
(12) Salamone, J. C.; Tsai, C. C.; Olsen, A. P.; Watterson, A. C. *Advances in the Chemical Sciences: Ions in Polymers*; American Chemical Society: Washington, DC, 1980; Vol. 187, p 337.
(13) Peiffer, D. G.; Schulz, D. N. *Polymer* **1985**, *26*, 1058.
(14) McCormick, C. L.; Johnson, C. B. *Macromolecules* **1988**, *21*, 686.
(15) McCormick, C. L.; Johnson, C. B. *Macromolecules* **1988**, *21*, 694.
(16) McCormick, C. L.; Johnson, C. B. *Polymer* **1990**, *31*, 1100.
(17) McCormick, C. L.; Johnson, C. B. *J. Macromol. Sci., Chem.* **1990**, *A27* (5), 539.
(18) McCormick, C. L.; Salazar, L. C. *Water-Soluble Polymers: Synthesis, Solution Properties, and Applications*; American Chemical Society: Washington, DC, 1991; Vol. 467, p 119.
(19) McCormick, C. L.; Salazar, L. C. *Polymer* **1992**, *33*, 4617.
(20) McCormick, C. L.; Salazar, L. C. *Macromolecules* **1992**, *25*, 1896.
(21) McCormick, C. L.; Salazar, L. C. *J. Appl. Polym. Sci.* **1993**, *48*, 1115.
(22) Ladenheim, H.; Morawetz, H. *J. Polym. Sci.* **1957**, *26* (113), 251.
(23) Hart, R.; Timmerman, D. *J. Polym. Sci.* **1958**, *28* (*118*), 638.
(24) Salamone, J. C.; Volksen, W.; Israel, S. C.; Olson, A. P.; Raia, D. C. *Polymer* **1977**, *18*, 1058.
(25) Monroy Soto, V. M.; Galin, J. C. *Polymer* **1984**, *25*, 121.
(26) Monroy Soto, V. M.; Galin, J. C. *Polymer* **1984**, *25*, 254.
(27) Galin, M.; Marchal, E.; Mathis, A.; Meurer, B.; Monroy Soto, V. M.; Galin, J. C. *Polymer* **1987**, *28*, 1937.
(28) Zheng, Y. L.; Knoesel, R.; Galin, J. C. *Polymer* **1987**, *28*, 2297.
(29) Schulz, D. N.; Kitano, K.; Danik, J. A.; Kaladas, J. J. *Polym. Mater. Sci. Eng.* **1987**, *147*, 149.
(30) Wielma, T. Ph.D. Dissertation, University of Groningen, Groningen, The Netherlands, 1989.
(31) Salamone, J. C.; Volksen, W.; Olsen, A. P.; Israel, S. C. *Polymer* **1978**, *19*, 1157.
(32) Schulz, D. N.; Peiffer, D. G.; Agarwal, P. K.; Larabee, J.; Kaladas, J. J.; Soni, L. L.; Handwerker, B.; Garner, R. T. *Polymer* **1987**, *27*, 1734.
(33) Liaw, D. J.; Lee, W. F.; Whung, Y. C.; Lin, M. C. *J. Appl. Polym. Sci.* **1987**, *37*, 999.
(34) McCormick, C. L.; Salazar, L. C. *Polymer* **1992**, *33*, 4384.
(35) Chen, G. S. Ph.D. Dissertation, The University of Southern Mississippi, Hattiesburg, MS, 1982.
(36) Park, L. S. Ph.D. Dissertation, The University of Southern Mississippi, Hattiesburg, MS, 1982.
(37) Kulicke, W. M.; Horl, H. H. *Colloid Polym. Sci.* **1985**, *263*, 530.
(38) Klenna, O. V.; Lebedeva, L. G. *J. Polym. Sci.* (*U.S.S.R.*) **1983**, *25* (10), 2380.
(39) Muller, G.; Laine, J. P.; Fenyo, J. C. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 659.
(40) Fenyo, J. C.; Laine, J. P.; Muller, G. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 193.
(41) McCarthy, K. J.; Burkhardt, C. W.; Parazak, D. P. *J. Appl. Polym. Sci.* **1987**, *33*, 169.