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Water-Soluble Copolymers. 43. Ampholytic Copolymers of Sodium 2-(Acrylamido)-2-methylpropanesulfonate with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride

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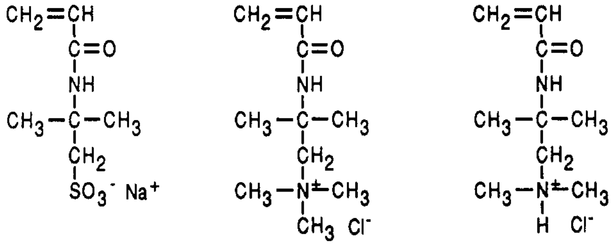
ABSTRACT: Copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) with [2-(acrylamido)-2-methylpropyl]trimethylammonium chloride (AMPTAC) have been prepared by free-radical polymerization in a 0.5 M NaCl aqueous solution using potassium persulfate as the initiator. Copolymer compositions were obtained by ^{13}C NMR and elemental analysis. An r_1r_2 value of 0.31 indicates an alternating microstructure for NaAMPS and AMPTAC monomer units. Molecular weights, second virial coefficients, diffusion coefficients, and average diameters were found using classical and quasielastic low-angle laser light scattering. As the compositions of the copolymers approach equal molar concentrations of NaAMPS and AMPTAC, polyampholyte behavior is observed. The second virial coefficients can be used to distinguish the polyelectrolyte/polyampholyte transition as a function of copolymer composition. The dilute-solution properties of the copolymers, as well as those of the NaAMPS and AMPTAC homopolymers, have been studied as related to composition, pH, temperature, and added electrolytes.

Introduction

Water-soluble copolymers showing tolerance to added electrolytes have been the subject of research in our laboratories in recent years. Of particular interest have been hydrophilic polyampholytes that exhibit enhanced viscosity with added salts.[1-9] Such copolymers containing acidic and basic moieties were reported as early as the 1950s. For example, Alfrey and Morawetz reported the synthesis of vinyl polyampholytes from copolymerization of 2-vinylpyridine and methacrylic acid.[10] These polyampholytes behaved as polyanions in alkaline solution and as polycations in acidic solution. Ehrlich and Doty copolymerized 2-(dimethylamino)ethyl methacrylate with methacrylic acid, varying the composition of the latter from 23 to 57 mol %.[11] The solution and light scattering properties of the copolymer which had 53.7 mol % methacrylic acid were studied at the isoelectric point. The polymer coils possessed negative second virial coefficients A_2, indicating that the hydrodynamic volume of the coils was reduced by intramolecular attractions between the positive and negatively charged groups.

More recently Salamone et al. studied polyampholytes made by pairing anionic and cationic monomers and then polymerizing them into highly alternating copolymers.[12-16] The observed solution behavior was consistent with that of high charge density polyampholytes. We reported polyampholytes containing the cationic monomer [2-(acrylamido)-2-methylpropyl]dimethylammonium hydrochloride (AMPDAC).[3-6] The cationic copolymers at low pH were subject to dehydrochlorination to reduce segmental repulsions, making structure/behavior assessment more difficult. The quaternary cationic monomer [2-(acrylamido)-2-methylpropyl]trimethylammonium chloride (AMPTAC) was synthesized to solve this problem.[8,18] This monomer not only features a quaternized ammonium moiety which remains charged regardless of pH but an amide group which is protected from hydrolysis by geminal methyl groups. This paper reports copolymers of NaAMPS and AMPTAC (Figure 1). In this series the monomers will retain their respective charges over a wide pH range; therefore, the monomer ratio will dictate polymer net charge and the resulting solution properties.



NaAMPS AMPTAC AMPDAC

Figure 1. Structures for the monomers sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS), [2-(acrylamido)-2-methylpropyl]trimethylammonium chloride (AMPTAC), and [2-(acrylamido)-2-methylpropyl]dimethylammonium hydrochloride (AMPDAC).

Experimental Section

Materials and Monomer Synthesis. 2-(Acrylamido)-2-methylpropanesulfonic acid (NaAMPS) was obtained from Fluka and purified by recrystallization from a methanol/2-propanol solvent system. Methyl iodide from Aldrich was used without further purification. Synthesis of [2-(acrylamido)-2-methylpropyl]trimethylammonium chloride (AMPTAC) by a multistep procedure has been previously reported.[18] Briefly, [2-(acrylamido)-2-methylpropyl]dimethylamine was reacted with a 10-fold excess of methyl iodide in refluxing diethyl ether and then ion-exchanged to yield the product AMPTAC. Potassium persulfate from J. T. Baker was recrystallized twice from deionized water prior to use.

Synthesis of Copolymers of Sodium 2-(Acrylamido)-2-methylpropanesulfonate with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride. The homopolymers of NaAMPS and AMPTAC and the copolymers of *A*MP*T*AC with Na*A*MP*S* (the ATAS 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. The synthesis and purification procedures have been reported previously.[17,18] The feed ratio of NaAMPS/AMPTAC was varied from 90:10 to 30:70 mol %, with the total monomer concentration held constant at 0.45 M. Aqueous NaCl solutions as the reaction medium ensured that the copolymers remained homogeneous during polymerization.

All copolymers were soluble in deionized water except for ATAS-50. This copolymer precipitated from solution during dialysis and remained insoluble until NaCl was added. This "hydrogel" was washed repeatedly with deionized water to remove

Table I
Reaction Parameters for the Copolymerization of Sodium 2-(Acrylamido)-2-methylpropanesulfonate (NaAMPS) with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride (AMPTAC)

sample	feed ratio for NaAMPS/AMPTAC	reaction time, h	convn, %	weight % C	weight % N	weight % S	AMPTAC in copolymer, mol % *a*	AMPTAC in copolymer, mol % *b*
ATAS-10-1	90:10	3.3	22.3	31.26	5.79	9.86	14.7 ± 0.4	
ATAS-10-2	90:10	3.8	38.3					21.3 ± 1.3
ATAS-25-1	75:25	1.5	16.2	42.52	7.79	8.38	36.1 ± 1.1	
ATAS-25-2	75:25	3.3	42.0					36.1 ± 2.2
ATAS-40-1	60:40	1.4	28.9	45.55	8.80	7.58	45.4 ± 1.4	
ATAS-40-2	60:40	3.5	34.6					40.0 ± 2.4
ATAS-50-1	50:50	3.3	15.0	46.92	9.37	6.84	51.7 ± 1.6	
ATAS-50-2	50:50	16	61.2					51.0 ± 3.1
ATAS-70-1	30:70	1.5	14.2	47.40	9.81	4.65	65.7 ± 2.0	
ATAS-70-2	30:70	2.5	24.7					62.0 ± 3.7
ATAS-0	100:0	5.8	58.6				0[c]	0[c]
ATAS-100	0:100	5.5	41.2				100[c]	100[c]

[a] Determined from elemental analysis. [b] Determined from ^{13}C NMR. [c] Theoretical.

any remaining salt or monomer and was then lyophilized. Conversions were determined gravimetrically. Table I lists reaction parameters for the copolymerization of AMPTAC with NaAMPS and the homopolymerizations of NaAMPS and AMPTAC. FT-IR (copolymer ATAS-50): 3440 (s, NH) 3296 (s, NH); 3063–2935 (m, CH) 1655 (s, C═O) 1549 (C═O); 1208 cm^{-1} (s, SO). ^{13}C NMR (copolymer ATAS-50): NaAMPS, δ 178.8 (C═O); AMPTAC, δ 178.2 (C═O), 57.8 (quaternary CH_3), 37.8 (chain CH_2), 45.0 (chain CH), 29.4 (gem methyls CH_3).

Copolymer Characterization. Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were conducted by M-H-W Laboratories of Phoenix, AZ, on the low-conversion copolymer samples. Copolymer compositions were confirmed using ^{13}C NMR by integration of the amide carbonyl peaks.[19] ^{13}C NMR spectra were obtained using 10 w/w % aqueous (D_2O) polymer solutions with DSS as the reference. FT-IR spectra were obtained using a Perkin-Elmer 1600 Series FT-IR spectrophotometer. 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.

Viscosity Measurement. Stock solutions of sodium chloride (0.10, 0.20, 0.30, 0.50, and 0.75 M NaCl) were prepared by dissolving the appropriate amount of salt in deionized water. Polymer stock solutions were then made by dissolving a specified amount of polymer in solvent from these salt solutions. The solutions were then diluted to required concentrations and allowed to age for 2–3 weeks before being analyzed with a Contraves LS-30 rheometer. Triplicate samples were prepared of each concentration to reduce experimental error. Intrinsic viscosities were evaluated using the Huggins equation.[20]

Results and Discussion

The ATAS series of copolymers was synthesized by varying the ratio of NaAMPS and AMPTAC from 90:10 to 30:70 mol % in the feed. Reaction parameters and the resulting copolymer compositions determined by elemental analysis or ^{13}C NMR are given in Table I. The number appended to the acronym ATAS refers to the amount of AMPTAC in the feed. This series differs from the previously studied ADAS series[3,4] in which AMPDAC was the cationic monomer. The quaternary ammonium group of AMPTAC has been shown to be a stable cationic moiety which remains charged over a wide pH range.[18] When AMPDAC was used in the ADAS copolymers, the exact number of cations present was never precisely known due to loss of HCl from the tertiary amine hydrochloride in aqueous solution. The AMPTAC monomer and ATAS copolymers have no facile route for charge elimination other than counterion condensation, making them better suited for structure/property studies.

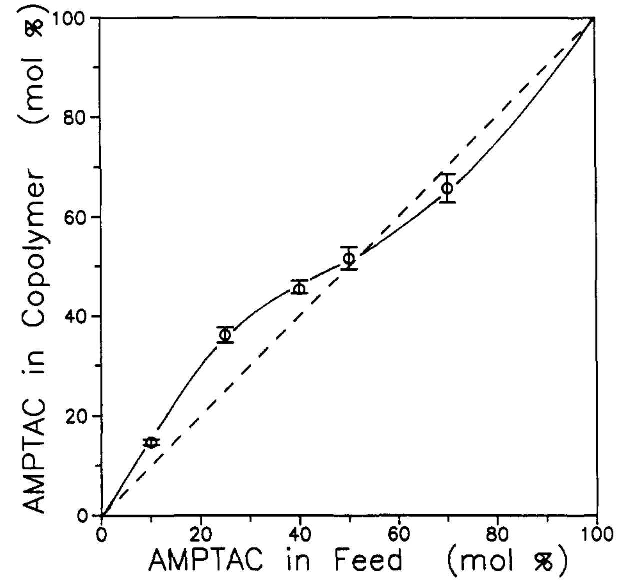


Figure 2. Mole percent AMPTAC incorporated into the ATAS copolymers as a function of the comonomer feed ratio. The dashed line represents an ideal random incorporation.

Compositional Studies. Elemental analysis was used to determine the copolymer compositions from nitrogen and sulfur content represented by eqs 1 and 2. The

$$\% \text{ N}/14.01 = A + 2B \tag{1}$$

$$\% \text{ S}/32.06 = A \tag{2}$$

coefficients A and B are the number of moles of NaAMPS and AMPTAC, respectively, in a normalized amount of copolymer, e.g., 1 g. The mole percent of each monomer in the copolymer may then be determined using eq 3 and 4.

$$\text{mol \% NaAMPS} = A/(A + B) \times 100\% \tag{3}$$

$$\text{mol \% AMPTAC} = B/(A + B) \times 100\% \tag{4}$$

Integration of ^{13}C NMR amide carbonyl peaks also gave the mole percent of NaAMPS and AMPTAC in the copolymers. This information agrees favorably with that derived from elemental analysis. The low- and high-conversion data differ significantly only for ATAS-10 in which compositional drift would be expected for an alternating copolymerization as indicated by the values of r_1 and r_2. The copolymer compositions as a function of feed composition are shown in Figure 2. A copolymeri-

Table II
Reactivity Ratios for the ATAS and ADAS Copolymer Series Determined Using the Methods of Kelen–Tüdős and Fineman–Ross

method	ATAS r_1	ATAS r_2	ATAS r_1r_2	ADAS r_1	ADAS r_2	ADAS r_1r_2
Kelen–Tüdős	0.50 ± 0.02	0.62 ± 0.02	0.31	0.22 ± 0.02	0.31 ± 0.04	0.07
Fineman–Ross	0.58 ± 0.06	0.87 ± 0.09	0.50	0.22 ± 0.03	0.33 ± 0.05	0.07

Table III
Structural Data for the Copolymers of Sodium 2-(Acrylamido)-2-methylpropanesulfonate (NaAMPS, M_1) with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride (AMPTAC, M_2)

sample	AMPTAC in copolymer,[a] mol %	blockiness, mol % M_1–M_1	blockiness, mol % M_2–M_2	alternation for M_1–M_2, mol %	mean sequence length M_1	mean sequence length M_2
ATAS-10	14.7	71.4	0.8	30.5	5.5	1.1
ATAS-25	36.1	35.1	7.3	54.0	2.5	1.2
ATAS-40	45.4	22.9	13.6	63.2	1.8	1.4
ATAS-50	51.7	16.3	19.6	64.1	1.5	1.6
ATAS-70	65.7	6.4	37.8	54.5	1.2	2.5

[a] Determined from elemental analysis.

zation in which an ideally random copolymer would be formed is represented by the dashed line.

Reactivity Ratio and Microstructure Studies. Reactivity ratios for the ATAS series were determined from the feed ratios of the monomers and the resultant copolymer compositions obtained by elemental analysis. The traditional methods of Fineman–Ross[21] and Kelen–Tüdős[22] were employed to determine the monomer reactivity ratios from the low-conversion copolymer samples. The Fineman–Ross method gave reactivity ratios of NaAMPS (M_1) and AMPTAC (M_2) of $r_1 = 0.58$ and $r_2 = 0.87$. The Kelen–Tüdős method produced reactivity ratios of 0.50 and 0.62 r_1 and r_2, respectively, and $r_1r_2 = 0.31$ (Table II). The copolymer compositions as a function of feed composition for the ATAS series are shown in Figure 2. The experimental data suggest the ATAS copolymers, like the previously reported series ADAS, are highly alternating.

Microstructural information was obtained statistically using the equations of Igarashi[23] and Pyun[24] and is presented in Table III. The Igarashi method calculates the fractions of NaAMPS–NaAMPS, AMPTAC–AMPTAC, and NaAMPS–AMPTAC units in the copolymers as a function of reactivity ratios and copolymer compositions. The Pyun method calculates the mean sequence length of the monomers in each copolymer. The data clearly indicate the alternating tendency of the monomer sequences. The ATAS copolymers, however, do not possess the degrees of alternation obtained for the ADAS copolymers. For example, ADAS-50 had a 15 mol % higher alternation value than the analogous ATAS-50. This is indicative of NaAMPS/AMPDAC having a stronger interaction than the NaAMPS/AMPTAC ion pair.

Light Scattering Studies. Classical and quasielastic light scattering data for the ATAS series are presented in Table IV. The polymers have molecular weights from 1.47×10^6 for the ATAS-100 homopolymer to 7.92×10^6 for ATAS-40-2. The second virial coefficients (A_2) were found to exhibit dependence on copolymer composition. ATAS-50-2 with a 50:50 mol % charge composition is better solvated in the presence of electrolytes than the copolymers with charge imbalances. ATAS-25-2 has a negative A_2 value while ATAS-50-2 has an A_2 value of 0.763×10^{-4} mL·mol/g^2. Similar results had been observed for the ADAS copolymers in which ADAS-50 had the highest A_2 value for the series. The data are consistent with the expected polyelectrolyte/polyampholyte transitions depending on the extent of AMPTAC incorporation in the copolymers. Higgs and Joanny have presented theoretical predictions which agree with our results.[25]

The narrow distributions of experimental values for the diffusion coefficients (D_0) and average hydrodynamic diameters (d_0) are consistent with the viscosity behavior of the copolymers in electrolyte solutions. In 1 M NaCl, the ATAS copolymers are neither chain extended nor chain constricted due to charge screening. In deionized water, large differences would be expected for polyampholytes, i.e., ATAS-50-2, and polyelectrolytes, i.e., ATAS-10-2 and ATAS-70-2 (Table IV), where strong electrostatic effects would dominate. Experimental difficulties, unfortunately, preclude meaningful light scattering studies of the high charge density polyampholytes in deionized water. Viscometric studies, however, support the above discussion.

Viscometric Studies. The dilute-solution behavior of the ATAS series was studied with respect to composition, temperature, pH, and added electrolytes. Apparent viscosities of the polymers were measured at polymer concentrations below C^* using a Contraves LS-30 low-shear rheometer. The solutions were aged 2–3 weeks to allow equilibration of polymer conformations in solution. Intrinsic viscosities were calculated using the Huggins relationship.

The solution behavior of the homopolymer ATAS-100 was previously examined in the pH range of 3–11 in 0.1 M NaCl.[17] No dependence of the apparent viscosity was observed. Each copolymer of AMPTAC with the sulfonate monomer NaAMPS should be nondependent on changes in pH above 3 since the sulfonate group remains ionized.

Intrinsic viscosities for the copolymers ATAS-50 and -70 and the homopolymer ATAS-100 are relatively independent of temperature when measured in deionized water and in 0.5 M NaCl in the temperature range of 25–60 °C. Most polyelectrolytes exhibit reductions in viscosity as a function of increasing temperature due to the elimination of rotational restrictions. Increases in conformational freedom may be offset by water restructuring around the NaAMPS and AMPTAC ion pairs.

Effects of Copolymer Composition. The apparent viscosities of the ATAS copolymers in deionized water plotted as a function of composition are shown in Figure 3. A decrease in the apparent viscosity develops as the molar ratio of NaAMPS and AMPTAC approaches unity. The curve is discontinuous due to the insolubility of ATAS-50-2 in the absence of added electrolytes. This is the result of decreasing polymer hydrodynamic volume caused by increasing intramolecular associations. The ADAS copolymers displayed a similar effect.[3,4]

The effects of composition on the intrinsic viscosity in NaCl solutions are displayed in Figure 4. The homopolymer ATAS-0 and the copolymers ATAS-10-2, -25-2, -40-2, and -50-2 have comparable molecular weights which lead to similar viscosities in 0.75 M NaCl. In 0.1 M NaCl, the polyelectrolyte effect dominates solution viscosity and significant differences due to composition can be discerned. Copolymers with more NaAMPS than AMPTAC act as

Table IV
Classical and Quasielastic Light Scattering Data for Copolymers of Sodium 2-(Acrylamido)-2-methylpropanesulfonate (NaAMPS) with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride (AMPTAC)

sample	AMPTAC in copolymer,[a] mol %	dn/dc	$M_w \times 10^{-6}$	$A_2 \times 10^4$, mL·mol/g^2	$D_0 \times 10^8$, cm^2/g	d_0, Å	DP $\times 10^{-4}$
ATAS-0	0.0	0.1116	6.12	0.92	3.87	1270	2.23
ATAS-10-2	14.7	0.1190	8.22	0.49	4.19	1300	2.67
ATAS-25-2	36.1	0.1229	6.20	−0.02	4.73	1050	3.61
ATAS-40-2	45.4	0.1405	7.92	0.59	3.85	1290	2.75
ATAS-50-2	51.7	0.1445	7.68	0.76	4.63	1000	3.52
ATAS-70-2	65.7	0.1454	4.98	0.34	4.06	1250	3.42
ATAS-100	100.0	0.1458	1.47	2.11	6.37	920	0.67

[a] Determined from elemental analysis.

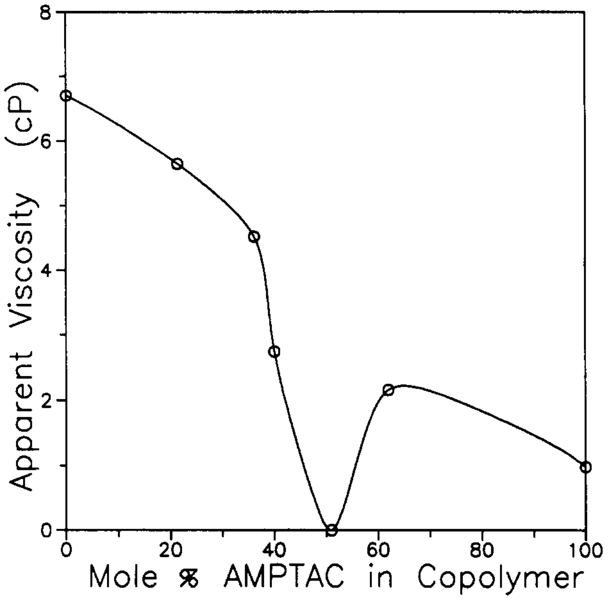


Figure 3. Effect of copolymer composition on the apparent viscosity of 0.025 g/dL ATAS polymer solutions in deionized water at 25 °C at a shear rate of 5.96 s^{-1}.

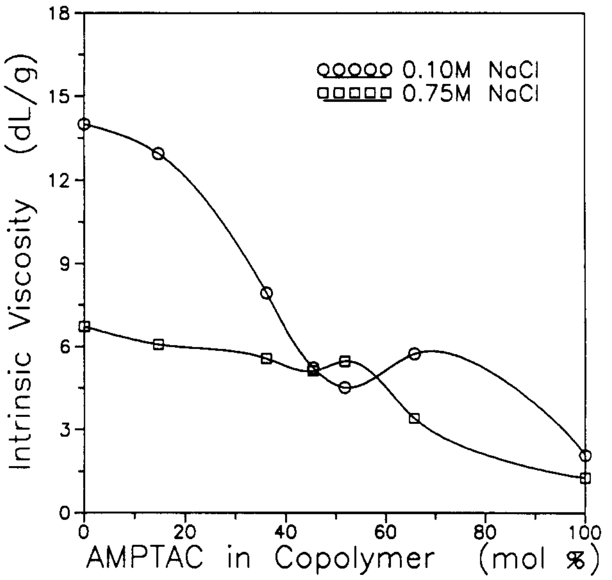


Figure 4. Intrinsic viscosity of the ATAS copolymer series as a function of the composition in 0.10 and 0.75 M NaCl determined at a shear rate of 5.96 s^{-1} at 25 °C.

polyanions. As the amount of AMPTAC in the copolymers increases to 50 mol %, the viscosity decreases as a result of increasing polyampholyte character. This behavior agrees with the second virial coefficient data. The copolymer ATAS-70-2 which has 65.7 mol % AMPTAC and the homopolymer ATAS-100 have low intrinsic viscosities due to polycationic character. The intrinsic viscosity of ATAS-50-2, which is insoluble in deionized water, increases with increasing ionic strength.

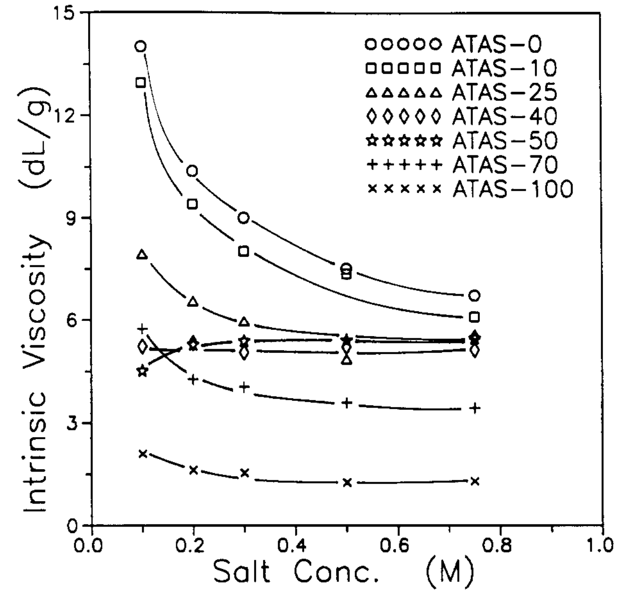


Figure 5. Intrinsic viscosities for the ATAS copolymers as a function of NaCl concentration determined at a shear rate of 5.96 s^{-1}.

Effects of Added Electrolytes. The effects of sodium chloride on the intrinsic viscosities of the ATAS copolymers and ATAS-0 and ATAS-100 were determined at a shear rate of 5.96 s^{-1} at 25 °C (Figure 5). ATAS-0, the anionic homopolymer of NaAMPS, shows the greatest decrease in viscosity as the NaCl concentration increases. As more AMPTAC is incorporated into the copolymer, this effect becomes less pronounced due to the transition from polyelectrolyte to polyampholyte character. ATAS-40-2 lies near the polyampholyte composition region but still possesses a net charge. This leads to a small change in viscosity for ATAS-40-2 with increasing ionic strength. At equal molar concentrations of each monomer (ATAS-50-2), there is an increase in the viscosity. The copolymer ATAS-70-2 lies on the edge of the polyelectrolyte/polyampholyte transition and thus shows a small decrease in the intrinsic viscosity.

The intrinsic viscosity of each sample was plotted as a function of the inverse square root of the ionic strength (Figure 6). Polyelectrolytes show a direct linear dependence when plotted in this manner.[26] The polymers ATAS-0, -10-2, and -100 exhibit linear behavior and positive slopes. The copolymers ATAS-50-2 and -40-2 exhibit slightly negative slopes indicative of polyampholyte nature and consistent with the second virial coefficient data. Intermediate behavior is observed for ATAS-25-2 and ATAS-70-2.

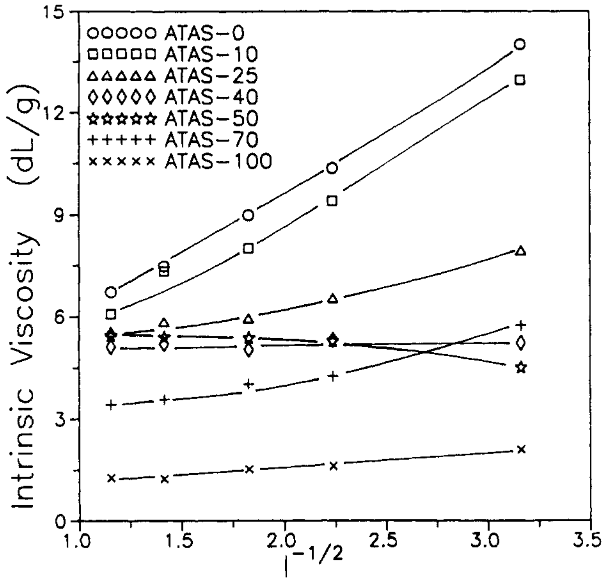


Figure 6. Intrinsic viscosities for the ATAS copolymers as a function of the inverse square root of the ionic strength.

Conclusions

Homopolymers of NaAMPS and AMPTAC and the copolymers of NaAMPS with AMPTAC (the ATAS series) have been synthesized by free-radical polymerization in 0.5 M NaCl. The presence of NaCl allows the polymerizations to remain homogeneous, yielding copolymers with microstructures less alternating than those of the previously studied ADAS series. Copolymer compositions were obtained by elemental analysis and ^{13}C NMR. Reactivity ratios determined by the methods of Fineman–Ross and Kelen–Tüdös yield $r_1r_2 = 0.31$. Molecular weights range from 1.47 to 7.92×10^6 for the AMPTAC homopolymer and the ATAS-40 copolymer, respectively. Second virial coefficients indicate a copolymer with an equal molar concentration of each monomer to be better solvated than copolymers with charge imbalances. Second virial coefficients and ionic strength changes may be used to detect polyampholyte/polyelectrolyte transitions with compositional changes. ATAS-0, -10, -25, -75, and -100 behave as polyelectrolytes, while ATAS-40 and -50 show polyampholyte behavior.

In the absence of added electrolytes, decreasing viscosities are observed as copolymer compositions approach equal molar values. This is attributed to decreasing polymer hydrodynamic volumes caused by increasing intramolecular associations. In 1 M NaCl the copolymers are neither chain extended nor chain constricted due to charge screening by the added electrolytes. The use of the quaternary ammonium monomer AMPTAC allows the synthesis of high charge density polyelectrolytes and polyampholytes with precisely known charge ratios, thus allowing accurate assessment of structure/property relationships.

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Registry No. NaAMPS, 5165-97-9; NaAMPS (homopolymer), 35041-59-9; AMPTAC, 51730-62-2; AMPTAC (homopolymer), 51730-63-3; (NaAMPS)(AMPTAC) (copolymer), 139101-46-5.