

Water-Soluble Copolymers. XLV. Ampholytic Terpolymers of Acrylamide with Sodium 3-Acrylamido-3-Methylbutanoate and 2-Acrylamido-2-Methylpropanetrimethylammonium Chloride

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SYNOPSIS

Water-soluble, low charge density polyampholytes have been synthesized by free-radical terpolymerization of acrylamide (AM) with sodium 3-acrylamido-3-methylbutanoate (NaAMB) and 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC). Terpolymer compositions obtained by ^{13}C -NMR reflect monomer feed concentrations. Molecular weights and second virial coefficients range from 3.43 to 19.4×10^6 g/mol and from 1.63 to 3.61 mL mol/g $^{-2}$, respectively, as determined by low-angle laser light scattering. Ionic associations were explored by investigating the dilute solution properties as a function of terpolymer concentration, terpolymer charge density, and added electrolytes. Terpolymers with 0.5, 2.5, and 5.0 mol % of both of the cationic (AMTAC) and anionic (NaAMB) monomers were soluble in deionized water, whereas those with 10 and 15 mol % of each monomer required electrolyte addition. The higher-density terpolymers undergo a 700% increase in intrinsic viscosity upon changing NaCl concentration from 0.05 to 1 M. Polyelectrolyte behavior could be induced by decreasing solution pH below the $\text{p}K_a$ of the NaAMB mer. Intermolecular ionic associations resulting in gel networks were studied utilizing dynamic mechanical analysis. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Only a limited number of synthetic polyampholytes have been reported in the literature that possess the carboxylate moiety as the anionic group. Early studies incorporated methacrylic acid and various ammonium species that provided high charge density polymers that were polyampholytes at their isoelectric points.¹⁻³ The polymers were polyanions in alkaline solution and polycations in acid solution. Nonaka and Egawa⁴ treated potassium polymethacrylate with 3-chloro-2-hydroxypropanetrimethylammonium chloride to obtain polymers with various amine/acid ratios. Merle et al.⁵ compared polyampholytes prepared by the hydrolysis or acidolysis of poly(*N,N*-dimethylaminoethyl methacrylate to

polymers made by the copolymerization of *N,N*-dimethylaminoethyl methacrylate and methacrylic acid.

Polyampholytes with regular structures have also been reported that incorporated the carboxylate group, but solution properties were rarely mentioned.⁶⁻⁸ Zwitterionic polyampholytes have been made with the carboxylate as part of a betaine functionality.⁹ Wielma studied the synthesis and solubility of zwitterionic polymers with carboxylate moieties.⁹ Varying degrees of ionization were achieved for the carboxylate groups by controlling the pH. At high pH values, the polymers behaved as polyampholytes, whereas at low pH values, polyelectrolyte behavior was observed.

Previously we reported ampholytic terpolymers containing the carboxylate group as the negatively charged moiety.¹⁰⁻¹² Sodium 3-acrylamido-3-methylbutanoate (NaAMB) was polymerized with 2-acrylamido-2-methyldimethylammonium hydrochloride

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ride (AMPDAC) and acrylamide (AM) as a neutral spacer. The superabsorbing terpolymers formed highly swollen gels even with added electrolytes due to strong intermolecular interactions. By contrast, structurally homologous terpolymers synthesized with the sulfonate monomer were soluble in deionized water and exhibited viscosity increases as electrolytes were added.¹³ Both intra- and intermolecular associations were observed in agreement with other literature reports on similar structures.¹⁴ In this study, we report electrolyte-soluble ampholytic terpolymers of acrylamide with the anionic monomer NaAMB and the cationic monomer AMPTAC.

EXPERIMENTAL

Materials and Monomer Synthesis

Sodium 3-acrylamido-3-methylbutanoate (NaAMB) monomer was synthesized via a Ritter reaction of equimolar amounts of 3,3-dimethylacrylic acid with acrylonitrile as reported by Hoke and Robins¹⁵ and as modified by McCormick and Blackmon.¹⁶ Synthesis of 2-acrylamido-2-methylpropanetrimethylammonium chloride (AMPTAC) by a multistep procedure has been previously reported.^{12,17} Briefly, 2-acrylamido-2-methylpropanedimethylamine was reacted with a 10-fold excess of methyl iodide in refluxing diethyl ether, then ion-exchanged to yield AMPTAC.

Synthesis of Terpolymers of NaAMB with AMPTAC and AM

Terpolymers of AMPTAC with NaAMB and AM (the ATABAM series) were synthesized by free-radical polymerization in a 0.5M NaCl aqueous so-

lution under nitrogen at 30°C using 0.1 mol % potassium persulfate as the initiator. The feed ratio of AM:NaAMB:AMPTAC was varied from 99.0 : 0.5 : 0.5 to 70 : 15 : 15 mol % with the total monomer concentration held constant at 0.45M. The synthesis and purification procedures have been reported previously.^{17,18} Table I lists reaction parameters for the terpolymerization of AM with NaAMB and AMPTAC. IR: Terpolymer: ATABAM 15-15, N—H 3401-3200 cm⁻¹ (s); C—H 2930 cm⁻¹ (m); C=O 1685-1653 cm⁻¹ (s); N⁺—R₄ 966 cm⁻¹. ¹³C-NMR: ATABAM 5-5, AM C=O, 180.8 ppm; NaAMB C=O, 176.9 ppm; AMPTAC C=O, 178.3 ppm; chain CH, 43.1 ppm; chain CH₂, 36.1 ppm; gem CH₃, 27.9 ppm.

Terpolymer Characterization

Terpolymer compositions were determined from ¹³C-NMR by integration of the acrylamido carbonyl peaks.¹⁹ ¹³C-NMR spectra were obtained using 10 wt/wt % aqueous (D₂O) polymer solutions with DSS as the reference. FTIR spectra were acquired using a Perkin-Elmer 1600 Series FTIR 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. A Langley-Ford Model LF1-64 channel digital correlator was used in conjunction with the KMX-6 to obtain quasi-elastic light-scattering data. All measurements were conducted at 25°C in 1M NaCl.

Viscosity Measurement

A 1 g/dL stock solution of each terpolymer was made in deionized water. Aliquots were taken and

Table I Reaction Parameters for Terpolymerization of AM with NaAMB, and AMPTAC

Sample No.	Feed Composition (mol %) AM : NaAMB : AMPTAC	Reaction Time (h)	Conversion (%)	Terpolymer Composition ^a (mol %) AM : NaAMB : AMPTAC
ATABAM 0.5-0.5	99.0 : 0.0 : 0.5	2.5	20.8	99 ^b : 0.5 ^b : 0.5 ^b
ATABAM 2.5-2.5	95.0 : 2.5 : 2.5	4.0	41.0	89.1 : 5.1 : 5.8
ATABAM 5.0-5.0	90.0 : 5.0 : 5.0	4.0	47.8	85.9 : 7.9 : 6.2
ATABAM 10-10	80.0 : 10.0 : 10.0	6.0	22.3	80.5 : 9.7 : 9.8
ATABAM 15-15	70.0 : 15.0 : 15.0	4.0	25.6	74.6 : 11.5 : 14.0
ATABAM 10-5	85.0 : 10.0 : 5.0	3.0	20.2	75.7 : 13.6 : 10.7
ATABAM 5-10	85.0 : 5.0 : 10.0	3.0	14.5	85.3 : 4.5 : 10.2

^a Determined by ¹³C-NMR.

^b Theoretical.

diluted with salt solutions to designated ionic strength and a polymer concentration of approximately 0.3 g/dL. These were further diluted to give polymer solutions with concentrations above and below C^* (0.025–0.3 g/dL). After aging for 2–3 weeks, the solutions were 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

Dynamic Mechanical Analysis

A Rheometrics RMS-800 dynamic mechanical spectrometer was used to examine G' (storage modulus) and G'' (loss modulus) as a function of frequency for 1 g/dL solutions of ATABAM 2.5–2.5 in various salt concentrations. Measurements were obtained using a Couette test geometry with 50% constant strain at 25°C.

RESULTS AND DISCUSSION

The previously studied ADABAM terpolymer series that contained AM, NaAMB, and AMPDAC (Fig. 1) formed highly swollen gels in aqueous solutions even in the presence of electrolytes. Strong hydrogen bonding between the carboxylate and the tertiary ammonium hydrochloride groups led to intermolecular cross-links that persisted even in 1M NaCl. Substitution of the protonated tertiary amine monomer AMPDAC by a quaternized monomer AMPTAC allows formation of soluble ampholytic terpolymers.

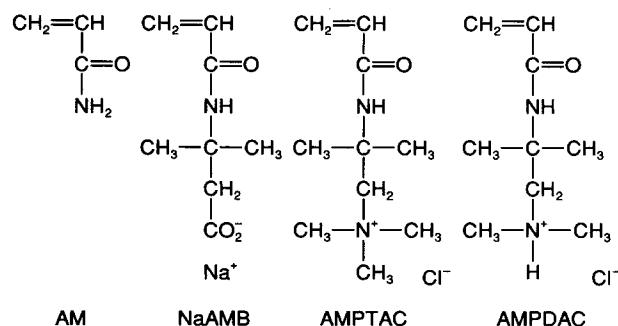


Figure 1 Structures for the monomers Acrylamide (AM), Sodium 3-Acrylamido-3-methylbutanoate (NaAMB), 2-Acrylamido-2-methylpropanetriammonium Chloride (AMPTAC), and 2-Acrylamido-2-methylpropanedimethylammonium Hydrochloride (AMPDAC).

Compositional Studies

Compositions for the ATABAM series of terpolymers were determined by integration of ¹³C-NMR acrylamido carbonyl peaks (Table I). Much like the previously studied ATASAM series,²¹ synthesis of the terpolymers in 0.5M NaCl led to random incorporation of the charged groups such that the resulting compositions approximate the feed compositions. The presence of added electrolytes during polymerization shields the charged groups from each other so that monomer pairing is not favored. Such random distribution of ionic mers along the backbone would be predicted to result in significantly different properties when compared to terpolymers with large numbers of neighboring group associations. The terpolymers ATABAM 10–5 and 5–10 were synthesized with charge imbalances in the feed, resulting in polyelectrolyte solution behavior.

Light-scattering Studies

Low-angle laser light scattering was employed to obtain the molecular weight and second virial coefficient (A_2) data shown in Table II. The molecular weights range from 3.43 to 19.4×10^6 g/mol for ATABAM 0.5–0.5 and ATABAM 10–5, respectively. The terpolymers ATABAM 10–10, 15–15, and 5–10 have very similar degrees of polymerization and therefore can be used for comparative structure/property assessments. Except for ATABAM 0.5–0.5, the A_2 values range from 1.63 to 2.06×10^{-4} mL mol/g² for the charge-balanced systems. ATABAM 0.5–0.5 remains well solvated in 1M NaCl as indicated by the A_2 value of 3.63 mL mol/g².

Quasi-elastic light scattering was used to obtain the diffusion coefficients (D_0) and hydrodynamic volumes (d_0) shown in Table II. ATABAM 10–10 has the largest d_0 value of 2160 Å, reflecting good solvation and high molecular weight. ATABAM 5–5 possesses a molecular weight and hydrodynamic volume approximately equal to that of ATABAM 0.5–0.5, although its second virial coefficient is much smaller. A similar effect is observed for ATABAM 10–5, which has 73% the molecular weight of ATABAM 5–10, yet, due to the presence of three times as much NaAMB, has approximately the same hydrodynamic volume.

Viscometric Studies

Effects of Terpolymer Composition

The terpolymers ATABAM 2.5–2.5, 5–5, 10–10, and 15–15 exhibit polyampholyte behavior as expected

Table II Classical and Quasi-elastic Light-Scattering Data for Terpolymers of AM with NaAMB with AMPTAC

Sample No.	dn/dc	$MW \times 10^{-6}$ (g/mol)	$A_2 \times 10^4$ (ml mol/g ²)	$D_0 \times 10^8$ (cm ² /g)	d_0 (Å)	$DP \times 10^{-3}$
ATABAM 0.5-0.5	0.1543	3.43	3.61	4.98	1024	4.82
ATABAM 2.5-2.5	0.1372	13.9	1.66	3.13	1873	15.0
ATABAM 5-5	0.1386	3.45	1.63	4.76	1003	4.02
ATABAM 10-10	0.1395	10.8	2.06	2.64	2159	11.0
ATABAM 15-15	0.1308	12.2	1.75	3.13	1630	11.5
ATABAM 5-10	0.1460	11.2	1.84	3.61	1330	10.8
ATABAM 10-5	0.1399	19.4	1.85	3.89	1440	21.1

for equal (or near equal) concentrations of NaAMB and AMPTAC. ATABAM 0.5-0.5, 2.5-2.5, and 5-5 have charge densities low enough to allow solubilization in the absence of added electrolytes. At slightly higher charge densities, however, ATABAM 10-10 and 15-15 are insoluble in deionized water. The net charge of ATABAM 5-10 and 10-5 polyelectrolytes allow solubility in electrolyte-free water.

Charge density also controls the type of macromolecular associations present. ATABAM 2.5-2.5 displays very strong intermolecular associations that "gel" semidilute polymer solutions at low ionic strengths. The high charge density ampholyte terpolymers possess both inter- and intramolecular associations under the same conditions.

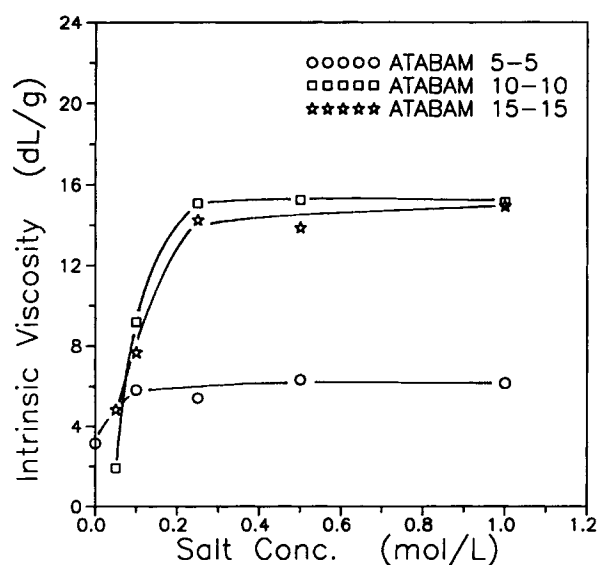


Figure 2 Intrinsic viscosities of ATABAM 5-5, 10-10, and 15-15 plotted as function of NaCl concentration determined at 25°C at a shear rate of 5.96 s⁻¹.

Effects of Added Electrolytes

Figure 2 displays the intrinsic viscosity of a number of the terpolymers as a function of NaCl concentration obtained using the Huggins equation.²⁰ The data are indicative of classic "antipolyelectrolyte" behavior. Increases in solution ionic strength disrupt intramolecular ionic associations, thus producing increases in polymer hydrodynamic volume. ATABAM 10-10 undergoes a 700% increase in intrinsic viscosity going from 0.05 to 1M NaCl. ATABAM 10-10 and 15-15, which have similar molecular weight, attain the same intrinsic viscosity in 1M NaCl.

The data parallel the behavior observed for the previously examined ADASAM low charge density terpolymers.¹³ For example, ADASAM 10-10 (76.7 mol % AM, 12.6 mol % NaAMPS, and 10.7 mol % AMPDAC) displayed a 330% increase in intrinsic viscosity from deionized water to 1M NaCl. The complex solution behavior of the ATASAM terpolymers was not observed.²¹

Effects of pH

The reduced viscosities for ATABAM 10-10 obtained in neutral and acidic pH values are shown in Figure 3. Above pH 7.5, the polymers behave as polyampholytes since all NaAMB units possess a negative charge. Intramolecular charge-charge interactions initially constrict the coils but disappear as solvent ionic strength is increased. At pH 3, the polymers behave as polyelectrolytes. The NaAMB units are protonated so that only the cationic charge of AMPTAC remains. Like typical polyelectrolytes, the coils expand in the absence of added electrolytes but collapse in their presence.

It is interesting that the polyelectrolyte form of ATABAM 10-10 has smaller dimensions in 1M NaCl than does the polyampholyte form. This may

be due to the relative hydrophobicity of the acid form of NaAMB. For example, copolymers of NaAMB with AM precipitate from aqueous solution below pH 5.¹² The presence of this relatively hydrophobic monomer may constrict the polymer to dimensions smaller than those of a random coil, thus producing the effect observed in Figure 3. Also, the extent of counterion condensation may differ for the two forms at high NaCl concentrations.

Dynamic Mechanical Analysis

The intermolecular associations of ATABAM 2.5-2.5 are strong enough to produce gels with elastic properties in solvents of low ionic strengths. The storage modulus G' and the loss modulus G'' were examined on a Rheometrics RMS-800 spectrometer using a couette test configuration. Solutions of varying ionic strengths at constant polymer concentrations (1 g/dL) were analyzed at 50% strain in the frequency range of 0.1-100 rad/s. The frequencies at which G' and G'' intersect, i.e., $\tan \delta = G''/G' = 1$, are plotted as a function of ionic strength in Figure 4. At NaCl concentrations above 0.05 M, the frequency at which $\tan \delta$ is unity becomes independent of ionic strength. This implies the complete disappearance of intermolecular associations.

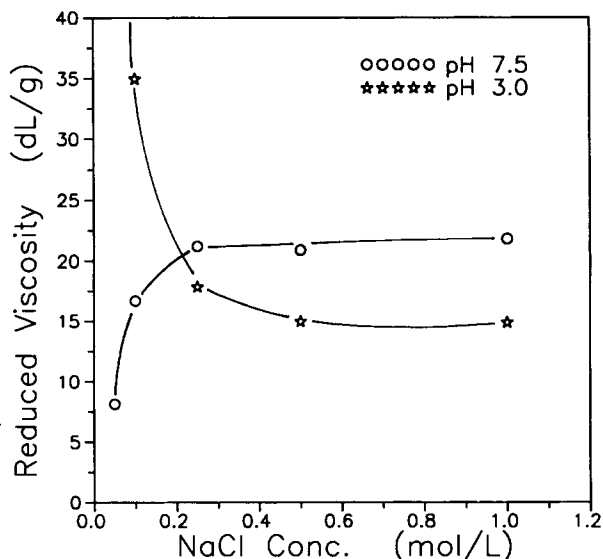


Figure 3 Reduced viscosity for ATABAM 10-10 in the polyampholyte form (pH 7.5) and in the polyelectrolyte form (pH 3.0). Determined with a polymer concentration of 0.10 g/dL at 25°C at a shear rate of 5.96 s⁻¹.

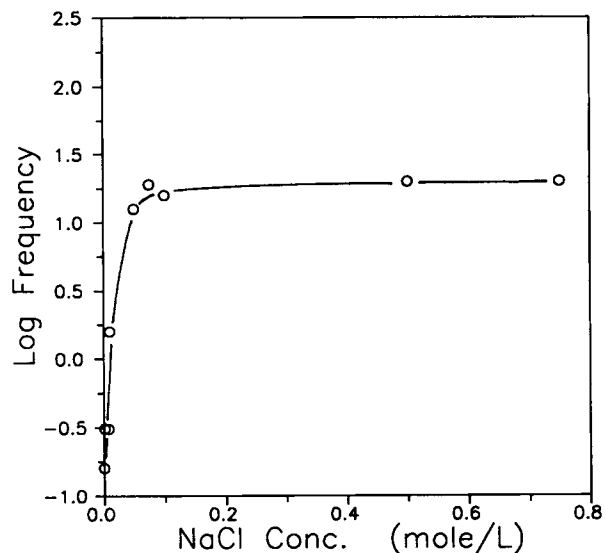


Figure 4 Log frequency at which $\tan \delta$ is unity as a function of NaCl concentration for 1 g/dL solutions of ATABAM 2.5-2.5.

CONCLUSIONS

The ATABAM series of low charge density polyampholytes has been synthesized by free-radical terpolymerization of AM with NaAMB and AMPDAC. Unlike the analogous terpolymers containing the tertiary amine hydrochloride monomer AMPDAC, this series dissolves in aqueous solutions provided enough salt is present to disrupt ionic associations. The terpolymers have been characterized by ¹³C-NMR, FTIR, and classical and quasi-elastic low-angle laser light-scattering techniques. The terpolymer compositions reflect the monomer feed concentrations. Molecular weights range from 3.43 to 19.4 × 10⁶ g/mol for the series.

Increases in solution ionic strength disrupt intramolecular ionic associations, thus producing increases in polymer hydrodynamic volume. ATABAM 10-10 undergoes a 700% increase in intrinsic viscosity, going from 0.05 to 1 M NaCl. Intermolecular ionic associations, studied utilizing dynamic mechanical analysis, were observed to be very sensitive to the presence of added electrolytes.

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