Water soluble copolymers: 44. Ampholytic terpolymers of acrylamide with sodium 2-acrylamido-2-methylpropanesulphonate and 2-acrylamido-2-methylpropanetrimethylammonium chloride

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Low charge density ampholytic terpolymers of acrylamide with random distributions of sodium 2-acrylamido-2-methylpropanesulphonate and 2-acrylamido-2-methylpropanetrimethylammonium chloride have been synthesized by free radical polymerization in 0.5 M NaCl aqueous solutions. Terpolymer compositions were obtained by ^{13}C n.m.r. Low angle laser light scattering provided molecular weights and second virial coefficients which varied from 2.78×10^6 to 6.77×10^6 g mol^{-1} and 1.31 to 2.95 ml mol g^{-2}, respectively. Dilute solution properties of the terpolymers were measured with respect to composition, concentration and added electrolytes. Polyampholyte behaviour was observed for the polymer with as little as 0.5 mol% of each charged group and became significant when 7 mol% of each charged monomer was incorporated. At 12 and 15 mol% incorporation of each charged monomer, solution behaviour becomes complex consistent with the existence of intermolecular interactions at low ionic strengths and intramolecular associations at medium salt concentrations.

(Keywords: copolymer; terpolymer; free radical polymerization)

INTRODUCTION

Few studies have been reported for polyampholytes with low charge densities[1–8] although copolymers and terpolymers of this type have great potential as rheology modifiers. Applications include drag reduction, enhanced oil recovery, personal care and coatings formulations. The 'antipolyelectrolyte' effect or increased viscosity in salt solutions has not been commercially exploited. Microstructural charge placement, polymer concentration and ionic strength are important in determining viscosity behaviour. For polyampholytes with hydrophilic mers, the lower the charge density the greater the solubility in deionized water and the less added electrolyte necessary for dissolution[2–4,9].

Peiffer *et al.*[7,8] studied polyampholytes with low charge densities by incorporating the neutral monomer acrylamide (AM) along with methacrylamidopropyltrimethylammonium chloride and sodium styrene sulphonate yielding properties not readily attainable with the high charge density polyampholytes. Polymers were soluble in deionized water as well as in the presence of added electrolytes. In the absence of added electrolytes, the low charge density polyampholytes (< 10 mol%) showed intermolecular associations while the polymers with higher charge densities favoured intramolecular ionic associations. The rheology of high ionic strength aqueous solutions could be controlled by adjusting the net charge and the anion–cation charge density of the polyampholytes.

Our laboratories have previously explored polyampholyte behaviour using high charge density copolymers[10,11] and low charge density terpolymers[1,5,6]. Low charge density terpolymers (the ADASAM terpolymer series) were made using AM as a neutral hydrophilic monomer along with sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS) and 2-acrylamido-2-methylpropanedimethylammonium hydrochloride (AMPDAC) as the charged monomers (*Figure 1*). The terpolymers were soluble in deionized water and exhibited enhanced viscosity as electrolytes were added. Both intra- and intermolecular associations could be observed in rheological studies.

This paper reports the study of a new series of terpolymers (the ATASAM series) made with 2-acrylamido-2-methylpropanetrimethylammonium chloride

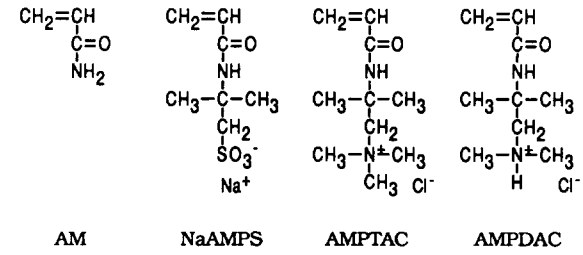

Figure 1 Structures for the monomers

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(AMPTAC) as the cationic monomer. This monomer features a quaternized ammonium functionality which is resistant to hydrolysis and readily copolymerizable[2,12]. The methods used to synthesize these terpolymers and their dilute solution behaviour are discussed and compared to the previously studied ADASAM series.

EXPERIMENTAL

Monomer synthesis

NaAMPS obtained from Fluka was purified by recrystallization from a methanol/2-propanol solvent system followed by drying under vacuum at room temperature. Synthesis of AMPTAC by a multistep procedure has been previously reported[12]. Briefly, 2-acrylamido-2-methylpropanedimethylamine was reacted with a 10-fold excess of methyl iodide in refluxing diethyl ether then ion-exchanged to yield the product AMPTAC.

Synthesis of terpolymers of AM with NaAMPS and AMPTAC

Terpolymers of AM with NaAMPS and AMPTAC (the ATASAM series) were synthesized by free radical polymerization in 0.5 M NaCl aqueous solutions under nitrogen at 30°C using 0.1 mol% potassium persulphate as the initiator. The feed ratio of AM:NaAMPS:AMPTAC was varied from 99.0:0.5:0.5 to 70:15:15 mol% with the total monomer concentration held constant at 0.45 M. The use of 0.5 M NaCl as the reaction medium ensured that the terpolymers remained in solution during polymerization.

In a typical synthesis, specified quantities of each monomer were dissolved in small volumes of NaCl solution. After the pH was adjusted to 7, the separate solutions were combined and diluted to a 0.45 M total monomer concentration. The reaction mixture was sparged with nitrogen for 20 min then initiated with 0.1 mol% potassium persulphate. The reaction was usually terminated at $<30\%$ conversion due to the high viscosity of the reaction medium and as a precaution against terpolymer compositional drift. The polymers were precipitated in acetone, redissolved in deionized water, then dialysed using Spectra/Por 4 dialysis bags with molecular weight cut-offs of 12 000–14 000 g mol^{-1}. After isolation by lyophilization, the polymers were stored in desiccators with a nitrogen atmosphere.

All terpolymers were soluble in deionized water except for ATASAM 10-10 and ATASAM 15-15. These terpolymers precipitated from solution during dialysis. These hydrogel-like materials were washed repeatedly with deionized water to remove any remaining salt, or monomer, and then lyophilized. Conversions were determined gravimetrically. *Table 1* lists reaction parameters for the terpolymerization of AM with NaAMPS and AMPTAC. *FT*i.r., typical terpolymer: ATASAM 15-15, N–H 3515 – 3200 cm^{-1} (s); C–H 2933 cm^{-1} (m); C=O 1674 – 1658 cm^{-1} (s); S–O 1208 cm^{-1} (s). ^{13}C n.m.r.: ATASAM 15-15, AM C=O 181.1 ppm; AMPTAC C=O 179.2 ppm; NaAMPS C=O 178.0 ppm; chain CH 45.0 ppm; chain CH_2 38.0 ppm; quat. CH_3 57.1 ppm; *gem* CH_3 29.5 ppm.

Terpolymer characterization

Terpolymer compositions were determined from ^{13}C n.m.r. by integration of the amide carbonyl peaks[13]. ^{13}C n.m.r. spectra were obtained using 10 wt/wt% aqueous (D_2O) polymer solutions with 3-(trimethylsilyl)-1-propanesulphonic acid, sodium salt (DSS) as the reference. *FT*i.r. spectra were acquired using a Perkin-Elmer 1600 series *FT*i.r. 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 were prepared by dissolving the appropriate amount of salt in deionized water. Polymer stock solutions were 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 analysed 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[14].

RESULTS AND DISCUSSION

The ATASAM terpolymers were synthesized by varying the ratio of AM:NaAMPS:AMPTAC from 99:0.5:0.5 to 70:15:15 mol% in the feed. Reaction parameters and the resulting compositions for the polymers are given in *Table 1*. The number appended to the acronym ATASAM refers to the concentration of NaAMPS and AMPTAC in the feed, respectively. This series differs from the

Table 1 Reaction parameters for the terpolymerization of AM with NaAMPS and AMPTAC

Sample number	Feed composition (mol%) AM:NaAMPS:AMPTAC	Reaction time (h)	Conversion (%)	Terpolymer composition[a] (mol%) AM:NaAMPS:AMPTAC
ATASAM 0.5-0.5	99.9:0.5:0.5	2.5	51.6	99[b]:0.5[b]:0.5[b]
ATASAM 2.5-2.5	95.0:2.5:2.5	2.5	25.0	95[b]:2.5[b]:2.5[b]
ATASAM 5.0-5.0	90.0:5.0:5.0	2.5	19.5	86.0:6.9:7.0
ATASAM 10-10	80.0:10.0:10.0	2.5	26.1	76.0:11.9:12.1
ATASAM 15-15	70.0:15.0:15.0	2.5	29.0	69.5:15.8:14.7
ATASAM 5-10	85.0:5.0:10.0	3.0	13.9	82.2:6.4:11.5

[a] Determined from ^{13}C n.m.r.
[b] Theoretical

previously studied ADASAM series in that AMPTAC replaces AMPDAC as the cationic monomer. The quaternary ammonium of AMPTAC has been shown to provide a hydrolytically stable cationic moiety which remains charged regardless of solvent pH[12].

Compositional studies

Terpolymer compositions were determined by the integration of acrylamido carbonyl peaks obtained from ^{13}C n.m.r. This method gave the mol% AM, NaAMPS and AMPTAC in the terpolymers with the exception of ATASAM 0.5-0.5 and ATASAM 2.5-2.5 which were assumed to have compositions equivalent to their feed. Previous studies of AM copolymers with NaAMPS or AMPTAC showed low concentrations of charged monomers in the feed provided random incorporation regardless of the conversion[2,12,15]. The terpolymerizations were terminated at low conversion (<30% except for ATASAM 0.5-0.5) as an added precaution against compositional drift. Relatively good agreement between the feed compositions and the terpolymer compositions is shown in *Table 1*.

In these terpolymerizations it is unlikely that the charged units exist in pairs along the polymer chain. Previous studies have demonstrated that addition of sodium chloride lowers monomer–monomer and monomer–polymer electrostatic interactions during polymerization[2,16,17]. A similar shielding effect would be expected to eliminate monomer pairing thus producing polyampholytes with charged monomers distributed randomly along the polymer chain. It is also interesting that attempts to synthesize these polyampholytes without added electrolytes were not successful due to phase separation of the reaction mixture.

Light scattering studies

Classical and quasielastic light scattering data for the ATASAM series are presented in *Table 2*. Molecular weights range from 2.78×10^6 to 6.77×10^6 g mol^{-1}. Terpolymers with similar degrees of polymerization show decreasing second virial coefficient (A_2) values with increasing charge density. This trend is consistent with that of recently prepared sulphobetaine copolymers of AM with the zwitterionic monomer 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate[3,4].

The mean polymer diffusion coefficients (D_0) and hydrodynamic diameters (d_0) are consistent with degrees of polymerization and A_2 values. Decreasing solvation is indicated by decreasing A_2, lower d_0 and larger D_0 values. The terpolymer ATASAM 5-5 has a degree of polymerization similar to ATASAM 10-10 but has greater A_2 and d_0 values.

Viscometric studies

The dilute solution behaviour of the ATASAM series was studied in relationship to copolymer composition and added electrolyte concentration. Apparent viscosities of the polymers were measured at polymer concentrations below C^*, the critical overlap concentration, using a Contraves LS-30 low shear rheometer. The solutions were aged 2–3 weeks to allow complete solvation. Intrinsic viscosities were calculated using the Huggins relationship.

Effects of terpolymer composition. The terpolymers with approximately balanced molar concentrations of NaAMPS and AMPTAC exhibit polyampholyte behaviour. ATASAM 5-10 displays polyelectrolyte behaviour as a direct result of the charge imbalance. For ATASAM 0.5-0.5 and ATASAM 2.5-2.5 the charge density is not sufficient to produce major changes in viscosity, however slight increases in intrinsic viscosity were observed with increasing salt concentration.

Effects of added electrolytes. The effects of sodium chloride on the intrinsic viscosities of the ATASAM terpolymers were measured at a shear rate of 5.96 s^{-1} at 25°C as shown in *Figure 2*. ATASAM 5-5 displays a dramatic increase in viscosity with the addition of a small amount of sodium chloride. This is indicative of the elimination of intramolecular interactions and the resulting coil expansion.

The terpolymers ATASAM 10-10 and ATASAM 15-15 display complex behaviour with increasing salt concentration. The presence of a small amount of electrolyte is

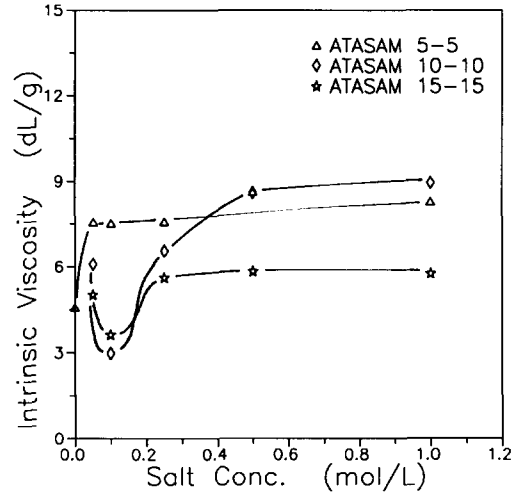

Figure 2 Effects of sodium chloride on the intrinsic viscosities of ATASAM terpolymers determined at a shear rate of 5.96 s^{-1} at 25°C

Table 2 Classical and quasielastic light scattering data for terpolymers of AM with NaAMPS and AMPTAC[a]

Sample number	dn/dc	M_w ($\times 10^{-6}$) (g mol^{-1})	A_2 ($\times 10^4$) (ml mol g^{-2})	D_0 ($\times 10^8$) (cm^2 g^{-1})	d_0 (Å)	DP ($\times 10^{-3}$)[b]
ATASAM 0.5-0.5	0.1426	6.03	2.95	4.23	1037	8.48
ATASAM 2.5-2.5	0.1481	2.78	1.65	5.77	835	3.91
ATASAM 5-5	0.1510	5.07	2.00	3.81	1192	5.48
ATASAM 10-10	0.1395	5.87	1.57	4.49	1094	5.44
ATASAM 15-15	0.1344	6.77	1.31	4.33	1184	5.74
ATASAM 10-5	0.1376	3.88	1.56	4.13	1278	3.95

[a] Determined in 1.0 M NaCl at 25°C
[b] DP, degree of polymerization

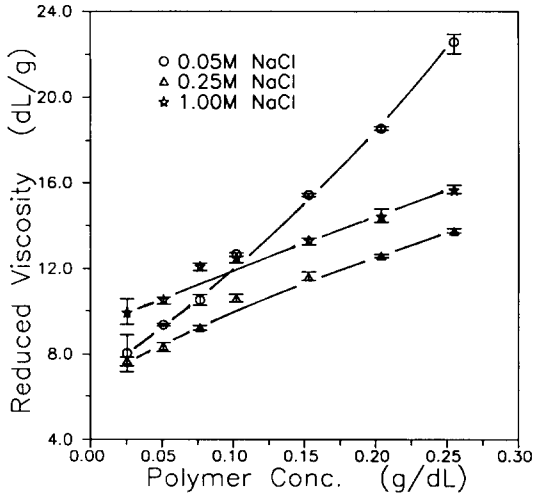

Figure 3 Reduced viscosities of the ATASAM 10-10 terpolymer as a function of polymer concentration at various ionic strengths determined at a shear rate of $5.96\,s^{-1}$ at 25°C. The bars represent the distribution of the data

required to solubilize both terpolymers. A slight increase in the ionic strength initially produces a decrease in intrinsic viscosity, likely due to the elimination of intermolecular molecular interactions with increasing ionic strength[2,7]. As the ionic strength increases further, the intrinsic viscosities increase as intramolecular interactions are reduced and chain solvation is enhanced.

Figure 3 displays the reduced viscosity of ATASAM 10-10 as a function of polymer concentration at three ionic strengths. Intermolecular interactions exist in 0.05 M NaCl as suggested by the large reduced viscosities above C^* ($\sim 0.13\,g\,dl^{-1}$ polymer concentration). Polymer aggregation is likely occurring at low salt concentration. In 0.25 M NaCl the reduced viscosities above C^* decrease as intermolecular interactions are disrupted. Remaining intramolecular interactions in 0.25 M NaCl are eliminated resulting in increased reduced viscosity at 1.0 M NaCl.

CONCLUSIONS

Synthesis of the ampholytic ATASAM terpolymers in NaCl solutions allowed the incorporation of charged monomers in equal amounts and in random sequences. Molecular weights and A_2 values varied from 2.78×10^6 to $6.77 \times 10^6\,g\,mol^{-1}$ and 1.31 to $2.95\,ml\,mol\,g^{-2}$, respectively. Solution properties were studied as functions of terpolymer composition as determined by ^{13}C n.m.r. and ionic strength. Polyampholyte behaviour was observed for the polymer with as little as 0.5 mol% of each charged group and became significant when 7 mol% of each charged monomer was incorporated. ATASAM 5-5 displayed an 80% increase in intrinsic viscosity in 1 M NaCl compared to deionized water. At 12 and 15 mol% incorporation of each charged monomer, the solution behaviour was complex with increasing ionic strength. These polymers were insoluble in deionized water but dissolved in 0.05 M NaCl. Increasing the ionic strength to 0.1 M NaCl led to a decrease in intrinsic viscosity, the result of elimination of intermolecular interactions, i.e. aggregates. Further increases in ionic strength led to disruption of intramolecular interactions and an increase in intrinsic viscosity.

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