

Water-soluble copolymers: 22. Copolymers of acrylamide with 2-acrylamido-2-methylpropanedimethylammonium chloride: Aqueous solution properties of a polycation

C. L. McCormick, K. P. Blackmon and D. L. Elliott

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406, USA

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The viscometric, turbidimetric and potentiometric properties of copolymers of acrylamide (AM) with 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) were studied in aqueous solutions. The AMPDAC polymers exhibit poor salt tolerance and large, negative viscosity/temperature coefficients. Furthermore, the polymers were found to be sensitive to changes in pH. The AMPDAC polymers undergo phase separation in the presence of dianions as a function of temperature and AMPDAC composition.

(Keywords: acrylamide copolymers; solution properties; polycation)

INTRODUCTION

Our previous efforts have involved the study of several anionic copolymer systems¹⁻⁶. Copolymers of acrylamide (AM) with 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) represent cationic analogues of these previously reported systems. In the previous paper⁷ we reported the synthesis and molecular characterization of the AM-AMPDAC copolymers; we now discuss the aqueous solution properties of these polymers.

EXPERIMENTAL

Materials

Copolymers of acrylamide with AMPDAC were prepared at 30°C in aqueous solution at a pH of 5 using potassium persulphate as the initiator. Details of the synthesis and molecular characterization have been reported in the previous paper⁷.

Reagent-grade sodium chloride and anhydrous sodium carbonate from J. T. Baker were used without purification. All aqueous salt solutions were prepared using deionized water.

Characterization

The copolymer compositions of the AM-AMPDAC polymers were determined from elemental analysis and ¹³C n.m.r. Microstructures of the copolymers (Table 1) were calculated using the statistical method⁸ as described in the previous paper.

Viscosity measurements

Stock solutions of sodium chloride (0.043, 0.086, 0.257 and 0.514 M) were prepared by dissolving the appropriate amount of salt in deionized water contained in volumetric flasks. The desired quantities of the dry copolymers were then dissolved in the salt solutions.

Solution viscosities were measured with a Cannon-Ubbelohde four-bulb shear dilution capillary viscometer (size 100). The shear rate constants and viscometer constants were provided by the manufacturer. The Carreau model⁹ was utilized to obtain zero-shear viscosities, and the Huggins equation¹⁰ was used to obtain zero-shear intrinsic viscosities, $[\eta]_0$, by extrapolation of the reduced viscosity, η_{sp}/c , to infinite dilution.

Turbidimetry measurements (ref. 11)

Reagent-grade anhydrous sodium carbonate was dried at 150°C for 2 days prior to use. Polymer solutions of 1.5 g/l were prepared by dissolving the appropriate amount of polymer in deionized water. Sodium carbonate concentrations were adjusted by addition of solid salt. Water lost by evaporation was replaced after each measurement.

A standard phototurbidimeter was used for the phase behaviour measurements. The sample of polymer solution (30–36 ml) was stirred by a magnetic stirrer and heated at a rate of 1°C/min. A thermometer was used to record the temperature (minimum reading: 0.1°C). The decrease in transmittance was used to determine the onset of precipitation. The critical temperature (T_c) was taken as the temperature at which precipitation was first observed when heating the solution. The process was found to be reversible with temperature; however, two slightly different critical temperatures were observed depending upon whether the solution was cooled or heated. The average of the two observed temperatures was taken as the critical temperature, T_c . The experiments were found to be repeatable to within $\pm 0.5^\circ\text{C}$.

Potentiometry measurements

All measurements of pH were made using a Corning 130 pH-mV meter with an Orion pH electrode and an

Table 1 Structural data for the copolymers of acrylamide (AM) with 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC)

Sample number	Composition (mol%) ^a		'Blockiness' (mol%) ^b		Alternation (mol%) ^b AM-AMPDAC	Mean sequence length	
	AM	AMPDAC	AM-AM	AMPDAC-AMPDAC		μ_{AM}	μ_{AMPDAC}
AMPDAC-10-1	89.95	10.05	80.1	0.2	19.7	9.6	1.0
AMPDAC-25-1	80.00	20.00	61.1	1.1	37.8	3.9	1.1
AMPDAC-40-1	69.15	30.85	41.8	3.5	54.7	2.4	1.1
AMPDAC-60-1	52.84	47.16	18.3	12.6	69.1	1.6	1.3

^aFrom elemental analysis^bStatistically calculated using reactivity ratios

Orion double-junction reference electrode. The meter was standardized using a two-point calibration method (pHs 7.0 and 10.0). All measurements were conducted at $25 \pm 0.05^\circ\text{C}$.

Copolymer concentrations were 1.5 g/l. Titrations were performed at constant ionic strength (0.36 M KCl), as well as with no ionic strength adjustment. Solutions of potassium hydroxide of about 0.1 M were prepared and standardized using potassium acid phthalate. The titrations were conducted under nitrogen atmosphere.

The degree of ionization α , defined as the fraction of acid groups dissociated, was determined for each addition of titrant. For observed values between 4.5 and 8.5, no correction was needed, and α was calculated as C_N/C_{NH} , where C_N is the concentration of non-protonated amine groups and C_{NH} is the total concentration of unprotonated and protonated groups in the sample^{12,13}. For pH values below 4.5 or above 8.5, correction for free acid groups was found to be negligible. Values of the dissociation constant (pK_a) were calculated using the modified Henderson-Hasselbalch equation¹⁴:

$$\text{pH} = \text{pK}' + n \log(\alpha/1 - \alpha) \quad (1)$$

Plots of pH vs. $\log(\alpha/1 - \alpha)$ were made to determine pK' and n values for each sample titration. All pK_a values reported are apparent pK_a values.

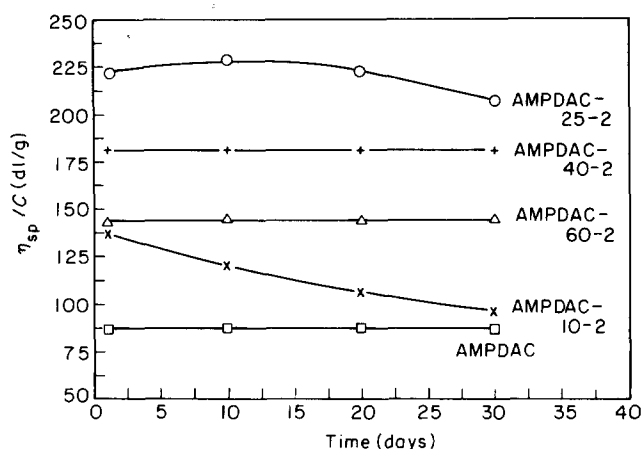
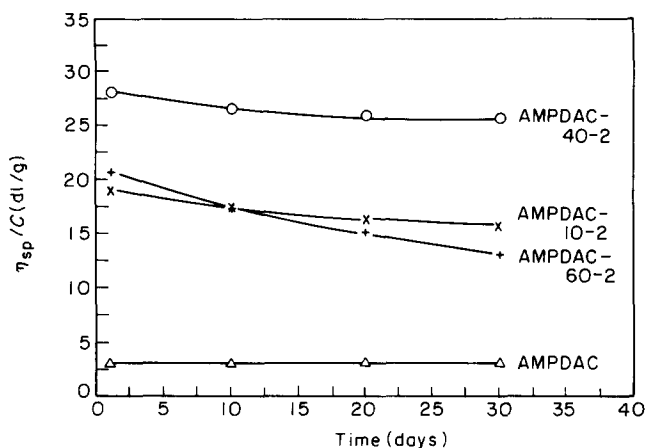
RESULTS AND DISCUSSION

Ageing effects

Ageing studies were conducted on the AM-AMPDAC copolymers and the AMPDAC homopolymer to assess the solution stability as a function of time. The effects of ageing are seen in an initial viscosity increase during dissolution followed by a gradual decrease. Such an ageing effect has been observed for aqueous solutions of polyacrylamide¹⁵ and partially hydrolysed polyacrylamide¹⁶, as well as cationic polymers¹⁷. The gradual viscosity decrease may be attributed to conformational changes resulting from changes in inter- and intrachain hydrogen bonding.

The ageing effects for the AM-AMPDAC copolymers and AMPDAC homopolymer were studied utilizing a size 100 Cannon-Fenske capillary viscometer at 30°C . Figure 1 shows the ageing effect for the polymers in deionized water. Only slight decreases in the reduced viscosities were observed for most of the polymers over the 30 day ageing period; however, AMPDAC-10-2 (9.8 mol% AMPDAC) experienced a viscosity reduction of 30%.

Figure 2 shows the ageing effect on the polymers in 0.257 M NaCl solutions. The viscosity decreases were

**Figure 1** Ageing of AM-AMPDAC copolymers and AMPDAC homopolymer in deionized water at 30°C **Figure 2** Ageing of AM-AMPDAC polymers in 0.257 M NaCl at 30°C

generally larger in the salt solutions than in the pure water solutions, ranging from 9% for AMPDAC-40-2 to 37% for AMPDAC-60-2. Apparently, the copolymers undergo greater conformational changes in NaCl solutions resulting in smaller hydrodynamic volumes as a function of time. Interestingly, the homopolymer of AMPDAC exhibited no ageing behaviour in pure water or salt solution.

Effects of added electrolytes

The effects of added sodium chloride on the zero-shear intrinsic viscosities of the AM-AMPDAC polymers are shown in Figure 3. As expected, the plots of $[\eta]_0$ vs. $I^{-1/2}$ were found to be linear^{18,19}. The viscosities were found to decrease with increasing NaCl concentration due to shielding of ionic charges along the polymer chain. AMPDAC-10-2, which contains 9.8 mol% AMPDAC,

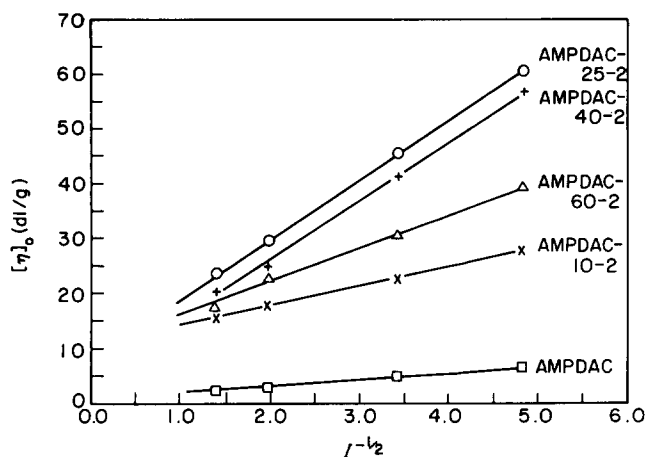


Figure 3 Zero-shear intrinsic viscosity as a function of ionic strength (NaCl)^{-1/2} for the AM-AMPDAC polymers at 30°C

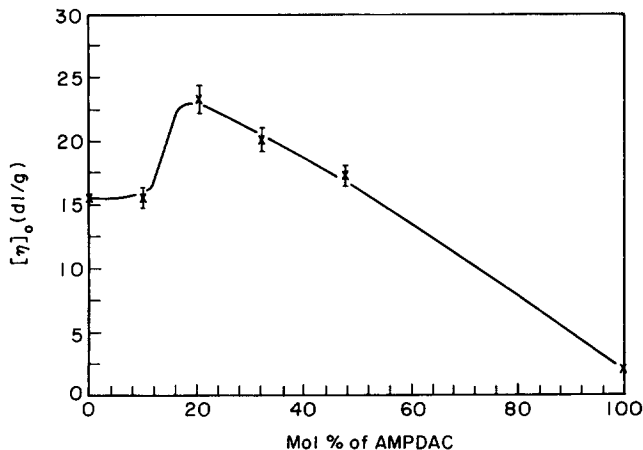


Figure 4 Compositional effect on zero-shear intrinsic viscosity in 0.514 M NaCl for AM-AMPDAC polymers

exhibited the greatest degree of salt tolerance with a viscosity decrease of 44.3% over the studied range of salt concentrations. The remaining copolymers and the AMPDAC homopolymer showed viscosity decreases of 55–65% over the studied range of salt concentrations. The hydrophobicity of the dimethyl ammonium moiety may be responsible for such salt sensitivity. The magnitudes of these viscosity decreases are comparable to those observed for the relatively hydrophobic copolymers of AM with sodium-3-(*N*-propyl)acrylamido-3-methylbutanoate (NaPAMB)²⁰, an analogous anionic series.

Effects of copolymer composition

The effects of copolymer composition on the zero-shear intrinsic viscosities of the AM-AMPDAC polymers in 0.514 M NaCl and on the apparent viscosities of the polymers in deionized water are shown in Figures 4 and 5, respectively. Even though the weight-average molecular weights (more particularly, the weight-average degrees of polymerization, DP_w) of the AM-AMPDAC copolymers are similar, it is still difficult to assess the relative contributions of molecular weight and composition on the viscosities in salt solutions. However, several observations should be set forth: AMPDAC-25-2 (20.2 mol% AMPDAC) exhibits a higher zero-shear intrinsic viscosity than AMPDAC-10-2 (9.8 mol% AMPDAC), but also possesses a higher degree of polymerization. AMPDAC-40-2 (32.0 mol% AMPDAC) also exhibits a higher viscosity than AMPDAC-10-2, but

possesses a lower degree of polymerization; thus, a compositional effect must be contributing to the differences in viscosity. AMPDAC-60-2 (47.8 mol% AMPDAC) possesses the highest DP_w of the series, but not the highest intrinsic viscosity; therefore, copolymer composition (and microstructure) must be the primary consideration in this behaviour. The homopolymer of AMPDAC exhibited the lowest intrinsic viscosity and possessed the lowest molecular weight.

It was not possible to obtain intrinsic viscosities for the AM-AMPDAC polymers in deionized water due to the overwhelming polyelectrolyte effect. Thus, a comparison of viscosities at 100 s⁻¹ and a polymer concentration of 0.015 g/dl was made (Figure 5). A maximum in viscosity was observed for AMPDAC-40-2. The relatively large hydrodynamic size of AMPDAC-40-2 may be attributed to an optimum in charge density allowing for maximum chain extension in the absence of added electrolytes.

Effects of temperature

The effects of temperature on the zero-shear intrinsic viscosities of the AM-AMPDAC copolymers in 0.257 M NaCl are shown in Figure 6. Furthermore, the viscosity/temperature coefficients of $[\eta]_0$ for the range of 30°C–70°C are listed in Table 2. Relatively large negative viscosity/temperature coefficients were observed for the AM-AMPDAC copolymers, with the maximum in viscosity loss being noted for AMPDAC-40-2. The

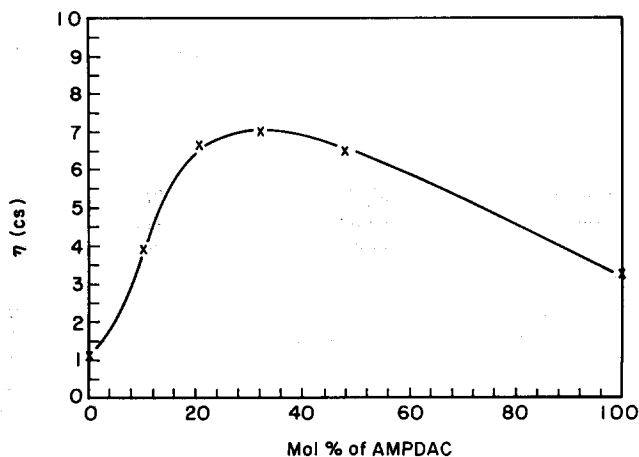


Figure 5 Compositional effect on viscosity in deionized water at 30°C for AM-AMPDAC polymers (conc. = 0.015 g dl⁻¹, shear rate = 100 s⁻¹)

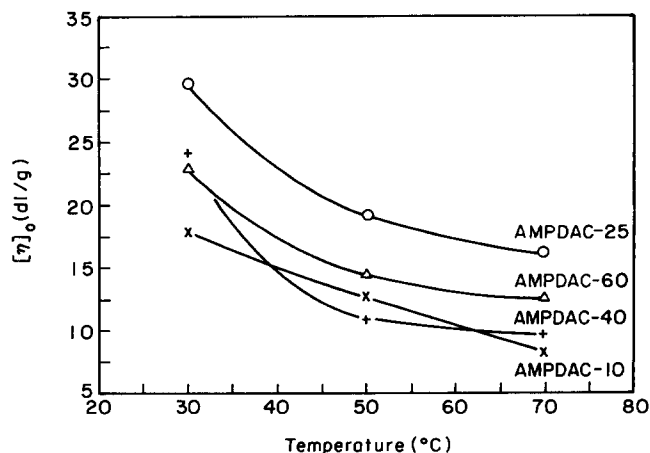


Figure 6 Zero-shear intrinsic viscosities of AM-AMPDAC copolymers in 0.257 M NaCl as a function of temperature

decrease in $[\eta]_0$ with increasing temperature indicates a decrease in the hydrodynamic volume of the polymer molecules, a result of changes in conformation and solvent association with increasing temperature.

Effects of pH

Table 3 illustrates the dependence of the intrinsic viscosities on pH for the AM-AMPDAC polymers in 0.514 M NaCl solutions. The zero-shear intrinsic viscosities increased with decreasing pH due to the

Table 2 Temperature coefficients of intrinsic viscosity for copolymers of acrylamide (AM) with 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) in 0.257 M NaCl(aq.)

Sample number	Temperature coefficient = $-(d\ln[\eta]_0/dT) \times 10^{2^\circ\text{C}^{-1}}$
AMPDAC-10-2	1.98
AMPDAC-25-2	1.51
AMPDAC-40-2	2.28
AMPDAC-60-2	1.49

Table 3 Zero-shear intrinsic viscosity data for copolymers of acrylamide (AM) with 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) in 0.514 M NaCl solutions of various pH values at 30°C

Sample number	Mol% AMPDAC	pH	$[\eta]_0$ (dl/g)
AMPDAC-10-2	9.8	6	15.6
		8	13.8
		10	12.2
AMPDAC-25-2	20.2	6	23.4
		8	19.1
		10	16.3
AMPDAC-40-2	32.0	6	20.2
		8	15.9
		10	13.2
AMPDAC-60-2	47.8	6	17.4
		8	14.5
		10	12.8
AMPDAC	100	6	2.2
		9	1.5

Table 4 Phase separation behaviour of the AMPDAC series

Sample	Mol% AMPDAC	Wt% Na ₂ CO ₃			
		0.25	0.50	1.5	3.5
AMPDAC-10	8	*	*	*	*
AMPDAC-25	20	*	*	*	*
AMPDAC-40	32	92.7	80.4	66.7	57.4
AMPDAC-60	49	50.2	43.5	41.3	41.5
AMPDAC-homo	100	<RT	<RT	<RT	<RT

* No phase separation observed up to 100°C

Table 5 Dissociation constants of the AMPDAC series using the modified Henderson-Hasselbalch equation

Sample	H ₂ O			0.36 M KCl		
	pK _a	ΔpK_a	<i>n</i>	pK _a	ΔpK_a	<i>n</i>
AMPDAC-10	8.19 ± 0.04	0.12	1.2	8.61 ± 0.02	0.10	1.1
AMPDAC-25	7.65 ± 0.04	0.33	1.6	8.68 ± 0.04	0.05	1.1
AMPDAC-40	7.63 ± 0.03	0.45	1.7	8.49 ± 0.04	0.05	1.1
AMPDAC-60	7.17 ± 0.04	0.38	1.7	8.46 ± 0.03	0.04	1.1
AMPDAC-hom	6.61 ± 0.04	0.80	2.1	8.18 ± 0.04	0.17	1.2

(All correlation coefficients are 0.99)

increasing degree of ionic character, leading to a more extended chain through electrostatic repulsions. The AMPDAC homopolymer precipitated at a pH above 9.5 since enough of the amine moiety was in the uncharged form to render the polymer insoluble.

Turbidimetry

The results of the turbidimetry measurements are shown in Table 4. Since the polyion in the AMPDAC series was cationic, divalent cations such as CaCl₂ had little effect on the phase behaviour of the copolymers. However, addition of sodium carbonate, which ionizes in solution to form a dianion, to solutions of the polymers was found to cause precipitation as a function of AMPDAC content in the polymers. AMPDAC-10 and AMPDAC-25, containing about 8 and 20 mol% AMPDAC, respectively, were found to remain soluble in sodium carbonate solutions up to 100°C and 7% Na₂CO₃. AMPDAC-40, AMPDAC-60 and the AMPDAC homopolymer were found to precipitate in the presence of sodium carbonate at lower temperatures with increasing AMPDAC in the copolymer.

The AMPDAC units, containing a tertiary amine functional group, are strongly nucleophilic and remain protonated to pHs up to 8.0–9.0. The positively charged units are thus susceptible to the formation of ionic bonds with anionic electrolytes, and increasing AMPDAC content in the polymers will increase the frequency of ionic bond formation. These bonds render the polymer insoluble, which leads to precipitation. Solutions of these copolymers are less stable to precipitation in the presence of simple electrolytes than the copolymers of acrylamide with anionic comonomers of analogous structure^{4,6,11}.

Potentiometry

The potentiometric titrations of the AMPDAC series were performed using techniques reported previously^{4,6,12,13}; however, potassium hydroxide was used as the titrant instead of HCl. The results of the potentiometric studies are shown in Table 5.

The AMPDAC copolymers, having an amine functional group, exhibit high pK_a values as expected. The general trend which can be observed in Table 5 is a decrease in pK_a values with an increase in AMPDAC content. This trend is a result of the charge-charge repulsion between the cationic groups in the chain. With increasing AMPDAC content, the ammonium ions are destabilized by the charge repulsion, and this instability is relieved by the increased lability and subsequent release of the protons (H⁺) in order to decrease the charge density on the chains. The increased lability of the protons of the ammonium salts with increasing AMPDAC content makes the amine moiety a weaker base resulting in lower pK_a values.

The Henderson-Hasselbalch n values are observed to be larger for the titrations in water due to the increased charge density in the absence of added electrolyte. The ΔpK_a values are also larger in water, and this can be attributed to the greater conformational changes the polymers undergo in water as they change from a random coil ($\alpha=0$) to a more rod-like extended chain ($\alpha=1$).

CONCLUSIONS

The aqueous solution properties of poly(acrylamide-co-2-acrylamido-2-methylpropanedimethylammonium chloride) were studied. The AM-AMPDAC copolymers showed greater ageing effects in NaCl solutions than in pure water solutions; however, the AMPDAC homopolymer exhibited no viscosity decrease with time. Furthermore, large reductions in viscosity were observed with increasing temperature and increasing pH. The AMPDAC polymers were found to be relatively sensitive to increasing ionic strength due to the hydrophobic contribution of the methyl groups on the amine functionality.

The AMPDAC polymers were found to exhibit phase separation in the presence of dianions (e.g. sodium carbonate) as a function of temperature and AMPDAC composition. In addition, the presence of an amine moiety, due to its basic nature, results in relatively high apparent pK_a values. The pK_a values were found to decrease with increasing AMPDAC content due to increasing charge density along the chain. The AMPDAC polymers displayed many similarities to previously studied analogous anionic systems in their viscometric properties; however, the cationic nature of the AM-AMPDAC copolymers did result in differences in potentiometric properties.

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