Water soluble copolymers: 46. Hydrophilic sulphobetaine copolymers of acrylamide and 3-(2-acrylamido-2-methylpropanedimethyl-ammonio)-1-propanesulphonate

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The free radical copolymerization of acrylamide (AM) with 3-(2-acrylamido-2-methylpropane-dimethylammonio)-1-propanesulphonate (AMPDAPS) has been studied in the range from 99 to 25% AM in the feed. Copolymer compositions obtained by elemental analysis and ^{13}C n.m.r. reflect the monomer feed concentrations. The value of $r_1 r_2$ has been determined to be 0.60 for the AM-AMPDAPS pair. Copolymer microstructures, including run numbers and sequence distributions, were calculated from the reactivity ratios. Molecular weights for the series range from 3.0×10^6 to 21.5×10^6 g mol^{-1}. Second virial coefficients decrease from 2.67 to 0.21 ml mol g^{-2} as charge density increases. Intrinsic viscosities decrease with increasing AMPDAPS content, but increase with increasing temperature (in the range of 25–60°C) and added electrolytes (NaCl and/or CaCl$_2$). The solution behaviour of the homopolymer of AMPDAPS is independent of pH. The observed properties are consistent with the charge density of the polymers and the sulphobetaine structure of the AMPDAPS monomer.

(Keywords: copolymers; free radicals; acrylamide)

INTRODUCTION

Synthetic polyampholytes can be prepared from zwitterionic monomers which exhibit the requisite net charge of zero at appropriate pH. The positive charge is provided by a quaternary ammonium functionality and the negative charge is provided by a carboxylate or sulphonate group (betaine and sulphobetaine). A number of investigations have focused on the unusual properties of zwitterionic polyampholytes.

Ladenheim and Morawetz reported the reaction poly(4-vinyl pyridine) with ethyl bromoacetate followed by hydrolysis of the ester to give high charge density polyampholytes[1]. Hart and Timmerman prepared sulphobetaine polyampholytes by reacting poly(2-pyridine) with sultones or by polymerizing the sultone derivative of 4-vinylpyridine[2]. Salamone *et al.* synthesized a variety of sulphobetaines based on vinylimidazole[3].

Galin and co-workers conducted an elegant study of poly(sulphobetaines) with various structures[4–7]. They described the synthesis of a series of polyampholytes by the quaternization of vinylamines with 1,3-propanesultone. Utilizing the Mark–Howink–Sakurada relationship, the existence of specific dipolar intramolecular interactions between lateral zwitterions was established. They concluded that in the presence of electrolytes, a polyampholyte behaved like a random coil of moderate flexibility in a thermodynamically very poor solvent.

Schulz *et al.*[8] have examined the phase behaviour and solution properties of the homopolymer of the commercially available monomer *N*-(3-sulphopropyl)-*N*-methacroyloxyethyl-*N*,*N*-dimethylammonium betaine (SPE). Negative A_2 values were found for the polyampholyte in solutions of low ionic strength; positive values were found as the ionic strength increased. Highly alternating copolymers of *N*-vinylpyrrolidone (NVP) with SPE which showed polyampholyte behaviour in solution were also researched[9].

Wielma studied the synthesis and solution properties of zwitterionic betaine and sulphobetaine polymers with one, two or three methylene units between the charged groups[10]. Varying degrees of ionization were achieved for the carboxylate groups by controlling the pH. At high pH values the polymers behaved as polyampholytes while at low pH values, polyelectrolyte behaviour was observed. It was concluded that strong intramolecular coulombic interactions were the dominant factor in the solubility behaviour of zwitterionic polymers.

Previous research in our laboratories focused on polyampholyte co- and terpolymers prepared by incorporation of cationic and anionic monomers[11–15]. Rheological characteristics, particularly pH and electrolyte responsiveness, can be readily changed by micro-structural manipulation during synthesis. Recently we have initiated studies of polyampholytes prepared from zwitterionic monomers which would have similar structural characteristics[15–19]. In this paper we report the synthesis and characterization of a series of

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copolymers of acrylamide with the novel amphoteric monomer 3-(2-acrylamido-2-methylpropanedimethyl-ammonio)-1-propanesulphonate (AMPDAPS).

EXPERIMENTAL

Materials and monomer synthesis

AMPDAPS was synthesized by the ring opening reaction of 1,3-cyclopropanesultone (PS) with 2-acrylamido-2-methylpropanedimethylamine (AMPDA; *Figure 1*). 1,3-Cyclopropanesultone (Aldrich) was used without further purification. The synthesis of AMPDA has been previously reported by our laboratories[19]. In a typical monomer synthesis, 0.144 mol AMPDA and 0.156 mol PS were reacted in 500 ml propylene carbonate under N_2 at 55°C for 4 days. During this period the product formed as a white precipitate. This was then filtered and washed with diethyl ether until all the propylene carbonate was removed. AMPDAPS (m.p. 220–224°C) was obtained in 80% yield. Analysis for $C_{12}H_{24}N_2O_4S$. Calculated: C, 49.29%; H, 8.29%; N, 9.58%; S, 10.96%. Found: C, 49.07%; H, 8.27%; N, 9.56%; S, 11.12%. I.r.: N–H, 3280 cm^{-1}(m); C=C–H 2990 cm^{-1}; aliphatic C–H, 2940 cm^{-1}; amide C=O, 1660 cm^{-1}(s) and 1550 cm^{-1}(s); S–O, 1200 cm^{-1}(s).

Acrylamide (AM; Aldrich) was recrystallized twice from acetone and vacuum dried at room temperature. Potassium persulphate (J. T. Baker) was recrystallized twice from deionized water.

Synthesis of copolymers of AMPDAPS with AM

The homopolymer of AMPDAPS and the copolymers of AMPDAPS with AM (the DAPSAM 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 persulphate as the initiator. The feed ratio of AM:AMPDAPS was varied from 99:1 to 25:75 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 polymers with high AMPDAPS content remained homogeneous during polymerization.

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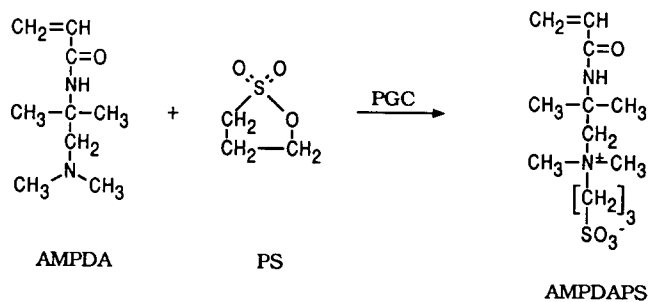
a precaution against copolymer drift. The polymers were precipitated in acetone, redissolved in deionized water, then dialysed using Spectra/Por 4 dialysis bags with molecular weight cutoffs of 12 000–14 000 g mol^{-1}. After isolation by lyophilization the polymers were stored in desiccators with a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

When more than 40 mol% AMPDAPS was incorporated in the copolymers, swelling but not dissolution could be achieved in deionized water. These 'hydrogels' 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 copolymerization of AMPDAPS with AM and the homopolymerization of AMPDAPS. I.r.: DAPSAM-100 homopolymer: N–H 3200 cm^{-1} (s); C–H 3050 cm^{-1} (m) and 2980 cm^{-1} (m); C=O 1650 cm^{-1} (s); S–O 1200 cm^{-1} (s). Typical copolymer: DAPSAM-75, N–H 3290 cm^{-1}(s); C–H 3050 cm^{-1} (m) and 2980 cm^{-1} (m); C=O 1670 cm^{-1} (s); S–O 1200 cm^{-1} (s).

Copolymer characterization

Elemental analyses for carbon, hydrogen and nitrogen were conducted by M-H-W Laboratories (Phoenix, AZ) on both the low and high conversion copolymer samples. ^{13}C n.m.r. spectra of the DAPSAM polymers were obtained using 5–10 wt% aqueous (D_2O) polymer solutions with DSS as the reference. The procedure for quantitatively determining copolymer compositions from ^{13}C n.m.r. has been discussed in detail elsewhere[20]. *F*Ti.r. spectra for all materials synthesized were obtained using a Perkin-Elmer 1600 Series *F*Ti.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 at pH 7.0 ± 0.1.

Viscosity measurements

Stock solutions of sodium chloride were prepared by dissolving the appropriate amount of salt in deionized water in volumetric flasks. Polymer stock solutions were made by dissolving designated amounts of polymer in the salt solutions. The solutions were then diluted to appropriate 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[21]. The modified Einstein–Simha equation was used to calculate the intrinsic viscosities for DAPSAM-40-3 as a function of temperature[22].

RESULTS AND DISCUSSION

Compositional analysis

The copolymers of AMPDAPS with AM (the DAPSAM series) were synthesized by varying the feed ratios of AM:AMPDAPS from 99:1 to 25:75 mol%. Reaction parameters and the resulting compositions for the polymers are given in *Table 1*. Copolymer compositions were determined from ^{13}C n.m.r. and

Figure 1 Synthesis of 3-(2-acrylamido-2-methylpropanedimethyl-ammonio)-1-propanesulphonate (AMPDAPS)

Table 1 Reaction parameters for the copolymerization of acrylamide (AM) with 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate (AMPDAPS)

Sample number	Feed ratio AM:AMPDAPS	Reaction time (h)	Conversion (%)	C (wt%)	N (wt%)	AMPDAPS in copolymer (mol%)[a]	AMPDAPS in copolymer (mol%)[b]
DAPSAM-1	99:1	5.0	28.8	–	–	1[c]	1[c]
DAPSAM-5	95:5	5.0	27.4	–	–	5[c]	5[c]
DAPSAM-10-1	90:10	2.8	12.9	45.47	14.59	11.9 ± 0.4	10.0 ± 0.6
DAPSAM-10-2	90:10	4.5	22.1	–	–	–	9.6 ± 0.6
DAPSAM-10-3	90:10	3.0	23.4	–	–	–	10.0 ± 0.8
DAPSAM-25-1	75:25	4.5	3.4	43.74	12.04	26.0 ± 0.8	26.0 ± 1.6
DAPSAM-25-2	75:25	23	44.9	41.04	11.13	27.7 ± 0.8	–
DAPSAM-40-1	60:40	2.0	9.2	44.11	10.77	42.1 ± 1.3	38.3 ± 2.3
DAPSAM-40-2	60:40	4.8	16.7	43.95	10.77	38.9 ± 1.2	–
DAPSAM-40-3	60:40	3.3	38.2	–	–	–	40.0 ± 2.4
DAPSAM-60-1	40:60	2.0	9.2	44.39	9.96	57.9 ± 1.7	57.3 ± 3.4
DAPSAM-60-2	40:60	4.8	16.7	44.44	9.93	58.8 ± 1.7	–
DAPSAM-75-1	25:75	3.0	12.2	44.35	9.39	71.9 ± 2.2	69.2 ± 4.2
DAPSAM-75-2	25:75	7.0	24.7	44.43	9.47	70.1 ± 2.2	–
DAPSAM-100	0:100	10	56.8	–	–	100[c]	100[c]

[a] Determined from elemental analysis
[b] Determined from ^{13}C n.m.r.
[c] Theoretical value
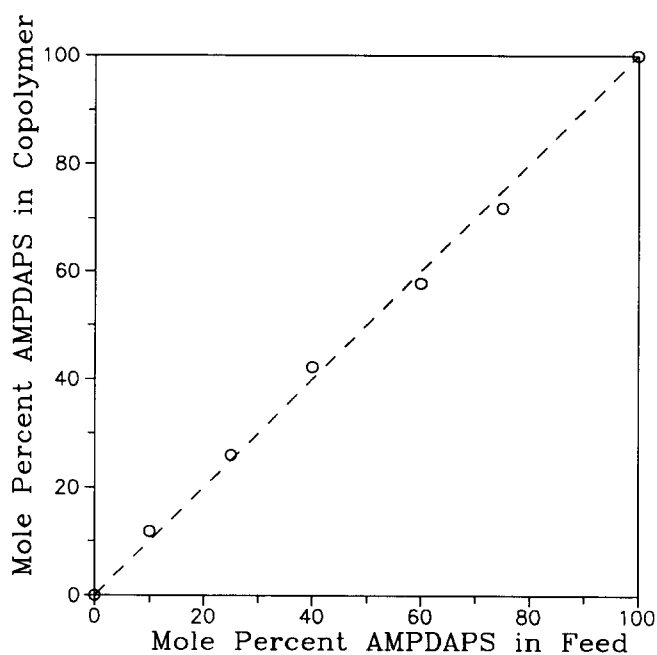
Figure 2 Mole percent AMPDAPS incorporated into the copolymers as a function of comonomer feed ratio

elemental analysis data. Integration of ^{13}C carbonyl peaks gave the mol% of AM and AMPDAPS in the copolymers, which agrees favourably with that derived from elemental analysis. The copolymer compositions as a function of feed composition for the DAPSAM series are shown in *Figure 2*. The copolymerization curve follows closely that of an ideally random system represented by the dashed line.

Reactivity ratio and microstructure studies

Reactivity ratio values for the AMPDAPS series were determined from monomer feed ratios and resultant copolymer compositions obtained at low conversions. Fineman–Ross[23] and Kelen–Tüdös[24] methods were used to determine the monomer reactivity ratios. The Fineman–Ross method yielded reactivity ratios for AM and AMPDAPS of $r_1 = 0.79$ and $r_2 = 0.73$. The Kelen–Tüdös method gave reactivity ratios of 0.79 and 0.75 for r_1 and r_2, respectively and $r_1 r_2 = 0.60$. The experimental data indicate random comonomer incorporation with a slight alternating tendency.

To elucidate the microstructural features of these copolymers, the equations of Igarashi[25] and Pyun[26] were employed. The fractions of AM–AM, AMPDAPS–AMPDAPS, and AM–AMPDAPS units (the mol% blockiness, the mol% alternation, and the mean sequence length) in the copolymers were calculated from the reactivity ratios and the copolymer compositions (*Table 2*). The mean sequence lengths of AM and AMPDAPS reverse in value when the amount of AMPDAPS in the copolymers increases from 25 and 40 mol% to 60 and 75 mol%. This behaviour is indicative of a random microstructure.

Low angle laser light scattering

Weight-average molecular weights were determind by classical low-angle laser light scattering. *Table 3* shows the data obtained at 25°C in 1 M NaCl. The molecular weights vary from 3.0×10^6 to 21.5×10^6 g mol^{-1}. For polymers prepared under similar conditions (initiator concentration, reaction conversion, etc.), the more AMPDAPS in the feed, the lower the molecular weight of the resulting polymer. The similar molecular weights of DAPSAM-10 and -25, and DAPSAM-60 and -75 allow meaningful assessments of the effects of copolymer composition on solution behaviour.
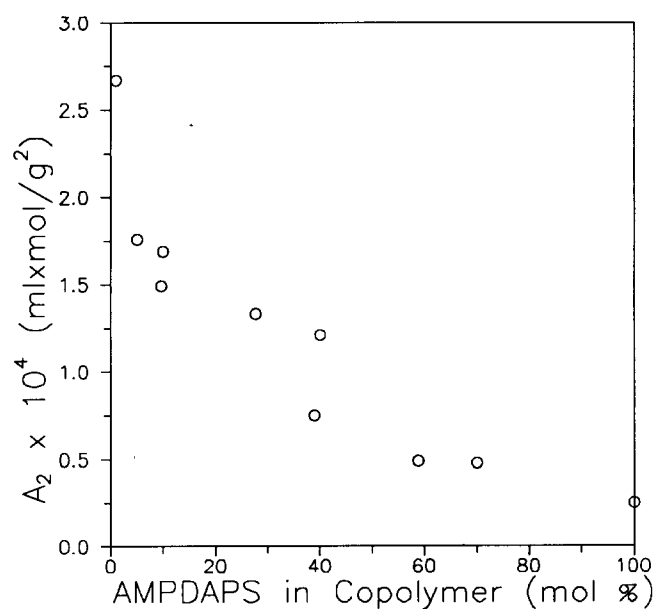
The second virial coefficients (A_2) decrease with increasing AMPDAPS content in the copolymers, as shown in *Figure 3*. This is the opposite of polyelectrolytes which have increasing A_2 values with increasing charge

Table 2 Structural data calculated for the copolymers of acrylamide M_1 (AM) with 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate M_2 (AMPDAPS)[a]

Sample number	M_2 in copolymer (mol%)[b]	Blockiness (mol%)		Alternation (mol%) M_1–M_2	Mean sequence length	
		M_1–M_2	M_2–M_2		M_1	M_2
DAPSAM-10-1	11.9	77.2	0.9	21.9	8.2	1.1
DAPSAM-25-1	26.0	53.0	5.0	42.0	3.4	1.3
DAPSAM-40-1	42.9	30.4	14.8	54.8	2.2	1.5
DAPSAM-60-1	57.9	14.7	30.5	54.8	1.5	2.1
DAPSAM-75-1	71.9	6.0	49.7	44.4	1.3	3.3

[a] Determined with $r_1 = 0.79$ and $r_2 = 0.75$
[b] Determined from elemental analysis

Table 3 Classical and quasielastic light scattering data for copolymers of acrylamide (AM) with 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate (AMPDAPS)

Sample number	AMPDAPS in copolymer (mol%)[a]	dn/dc	M_w ($\times 10^{-6}$ g mol^{-1})	A_2 ($\times 10^4$ ml mol g^{-2})	D_o ($\times 10^8$ cm^2 s^{-1})	d_o (Å)	DP ($\times 10^{-4}$)
DAPSAM-1	1[c]	0.1450	3.2	2.67	5.05	1170	4.43
DAPSAM-5	5[c]	0.1520	12.4	1.76	3.16	1650	15.1
DAPSAM-10-2	9.6	0.1385	7.0	1.49	4.01	1380	7.50
DAPSAM-10-3	10[b]	0.1436	21.5	1.69	3.20	1530	23.0
DAPSAM-25-2	27.7	0.1395	8.2	1.33	3.97	1180	6.35
DAPSAM-40-2	38.9	0.1224	15.1	0.75	3.62	1420	9.57
DAPSAM-40-3	40[b]	0.1546	17.5	1.21	3.24	1560	11.0
DAPSAM-60-2	58.8	0.1480	5.4	0.49	3.60	1430	2.71
DAPSAM-75-2	70.1	0.1293	6.2	0.48	4.90	1060	2.69
DAPSAM-100	100[c]	0.1322	3.0	0.25	6.28	870	1.03

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

Figure 3 Dependence of the second virial coefficient (A_2) on the composition of the DAPSAM polymers (determined in 1 M NaCl at 25°C)

density. In deionized water, copolymers with compositions greater than 40 mol% AMPDAPS are insoluble. Solubility is achieved in the presence of electrolytes; however, even in 1 M NaCl, A_2 values are less than those of DAPSAM-1 which approximates a neutral polyacrylamide sample.

Quasielastic light scattering (q.l.s.) data are presented in *Table 3* and illustrated in *Figures 4* and *5*. The mean polymer diffusion coefficients (D_o) and diameters (d_o) for all copolymer systems in 1 M NaCl show some dependence on the degree of polymerization and on the weight-average molecular weight. As degree of polymerization and molecular weight increase, D_o values decrease (d_o increase). The scatter in the data is, of course, due to solvation differences with compositional changes, a conclusion clearly supported by A_2 values.

Dilute solution properties

Effects of copolymer composition. The effects of copolymer composition on the intrinsic viscosities of the DAPSAM copolymers (*Table 2*) in 0.514 M NaCl are shown in *Figure 6*. The decrease in the intrinsic viscosities is due to decreases in molecular weight as well as increasing intramolecular interactions which constrict the polymer coils. The presence of the AMPDAPS monomer units is responsible for the latter, as demonstrated by the second virial coefficients. For DAPSAM-60 and -75, which have similar molecular weights and degrees of polymerization, increasing AMPDAPS concentration decreases the respective intrinsic viscosities. Schulz *et al.* postulated these interactions to be based on electrostatic attractions between opposite charges of different sulphobetaine units[8]. One might expect such effects to
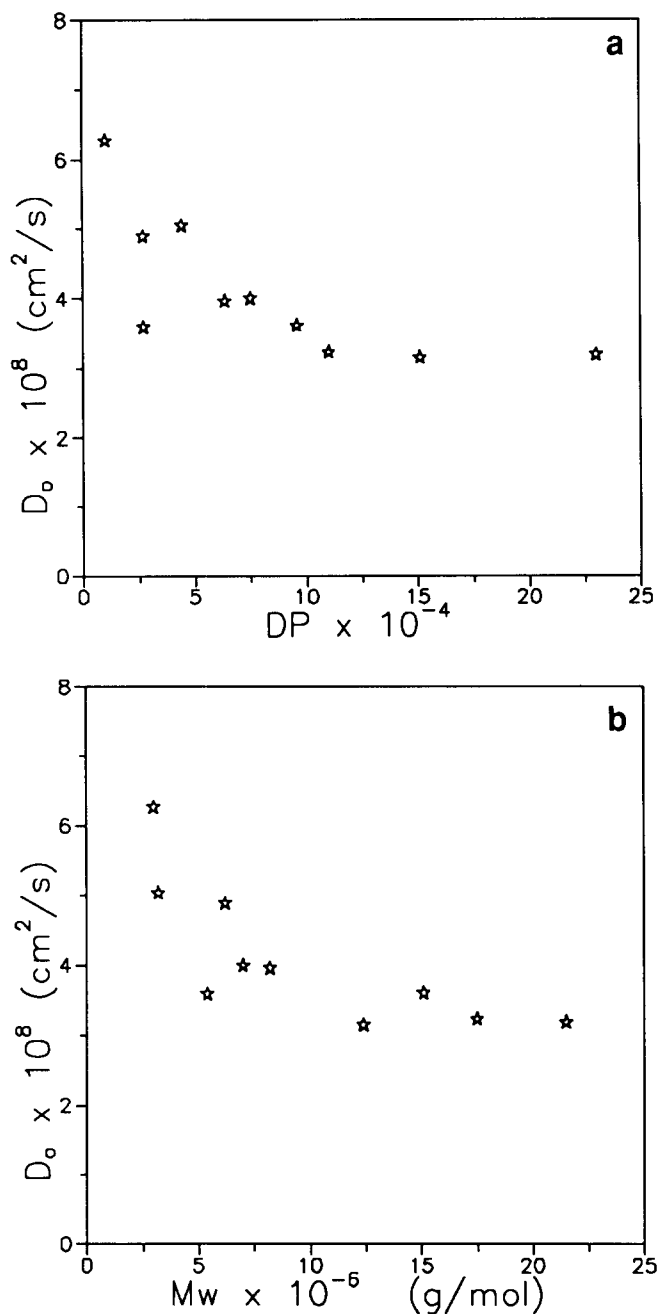
Figure 4 Dependence of the diffusion coefficient (D_o) on (a) degree of polymerization and (b) molecular weight of the DAPSAM copolymers (determined by q.l.s. in 1 M NaCl at 25°C)

be especially strong as microheterogeneous associations lead to local decreases in dielectric constant of the domains.

Effects of added electrolytes. The effects of sodium chloride on the intrinsic viscosities of the DAPSAM copolymers and the AMPDAPS homopolymer were determined at a shear rate of 1.75 s^{-1} as shown in *Figure 7*. The polymer solutions show increasing intrinsic viscosities as the amount of salt in the solutions increases. Some of the polymers do not dissolve unless salt is present. DAPSAM-60 and DAPSAM-75 require 0.0428 M NaCl, and DAPSAM-100 needs 0.257 M NaCl for dissolution. Attempts to remove the salt from the polymers by dialysis result in phase separation of the polymers from solution.

The initial decreases in intrinsic viscosity for DAPSAM-10 and DAPSAM-25 are due to the elimination of intermolecular interactions with increasing ionic strength. This behaviour has been observed with other polyampholyte systems[1,15,17,18]. DAPSAM-40, which possesses a higher charge density, experiences a disruption of intramolecular interactions with increasing ionic strength. In all cases the intrinsic viscosities increase significantly.

Figure 8 demonstrates the effects of adding the divalent salt calcium chloride to solutions of the DAPSAM copolymers and the AMPDAPS homopolymer. DAPSAM-60, -70, and the AMPDAPS homopolymer are insoluble up to a critical concentration.

A number of studies by other research groups have attempted to find evidence for the existence of
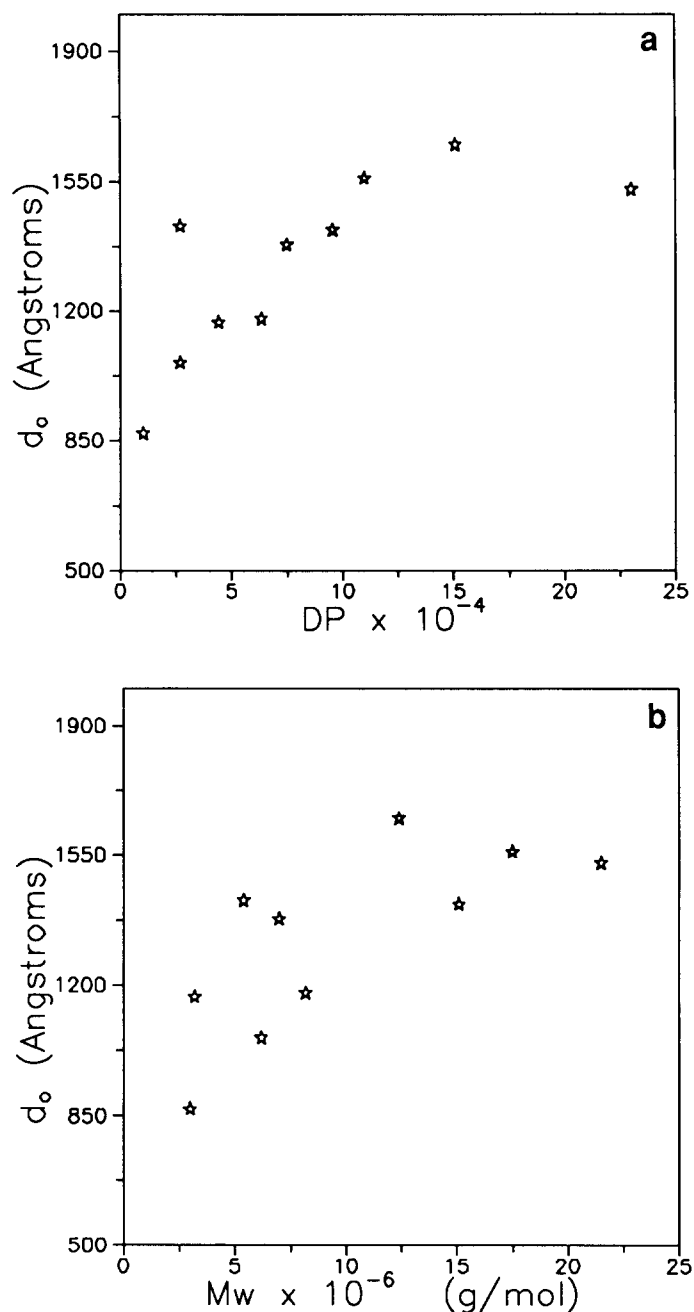
Figure 5 Dependence of copolymer mean diameter (d_o) on (a) degree of polymerization and (b) molecular weight (determined by q.l.s. in 1 M NaCl at 25°C)
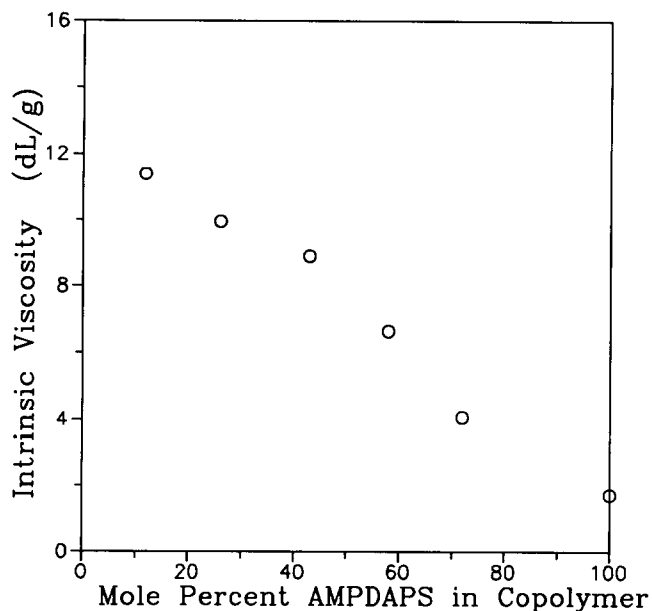
Figure 6 Intrinsic viscosity of DAPSAM copolymers as a function of AMPDAPS incorporated (determined in 0.514 M NaCl at a shear rate of 1.25 s^{-1})
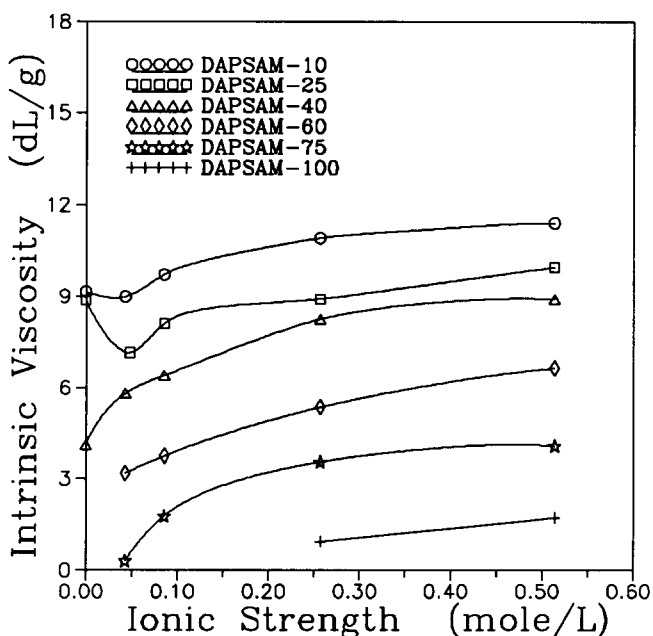

Figure 7 Dependence of the intrinsic viscosity of DAPSAM copolymers on NaCl ionic strength (determined at 25°C at a shear rate of 1.75 s^{-1})

hydrophobic domains within polyampholytes. For sulphobetaine and betaine polyampholytes, it is conceivable that intramer and intramolecular charge–charge associations may lead to such domains. Zheng *et al.* utilized reporter anionic probes to find a polyampholytic environment with the same relative hydrophobicity of methanol[7]. Wielma was unsuccessful in using fluorescent labels on polysulphobetaines to relate macroscopic behaviour, such as increases in solution viscosity, to changes in the microenvironment along the polyampholyte backbone[10].

Our research group is currently active in developing fluorescent probe and label technology[27,28]. For this study, however, a simple approach was utilized to assess the presence of hydrophobic domains in the DAPSAM polymers. Urea is a water structure breaker which solubilizes certain molecules by disrupting hydrophobic domains. It follows that if hydrophobic domains exist within polyampholytes, the presence of urea should alter solution behaviour.

Solutions of the copolymers DAPSAM-10-3 and DAPSAM-40-3 were studied in deionized water, 1 M NaCl, 1 M urea, and a mixture of 1 M NaCl and 1 M urea. *Figures 9* and *10* show the reduced viscosity for each copolymer as a function of polymer concentration. For each copolymer, the solution in deionized water has
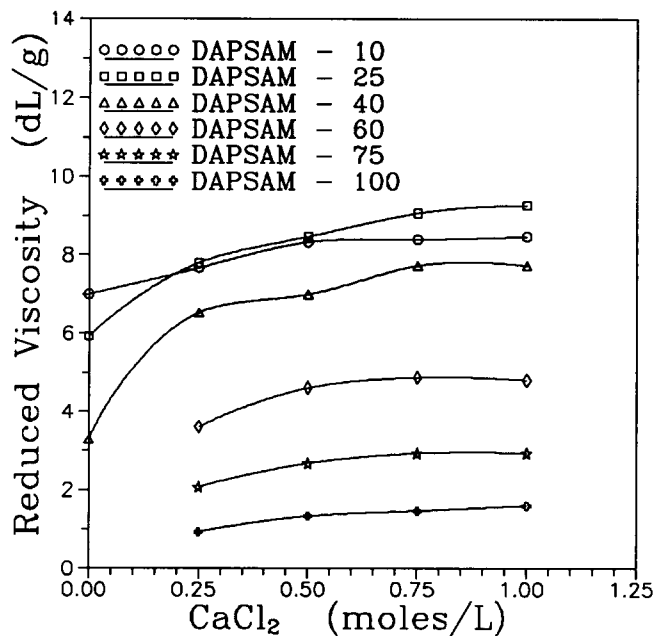

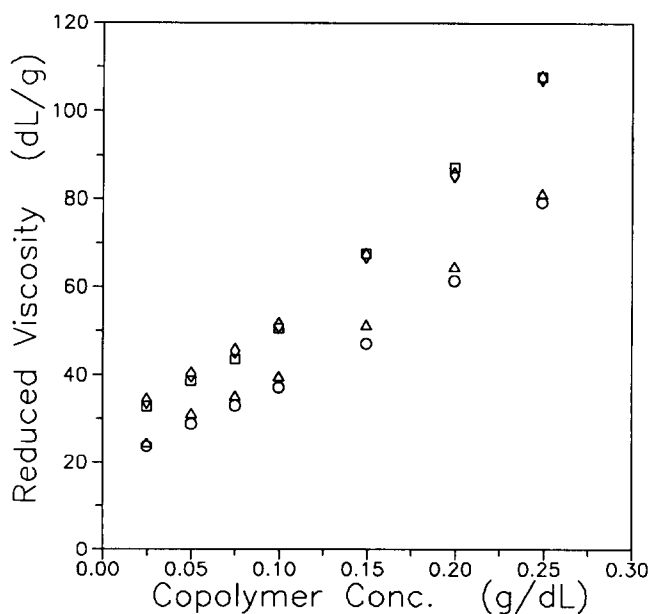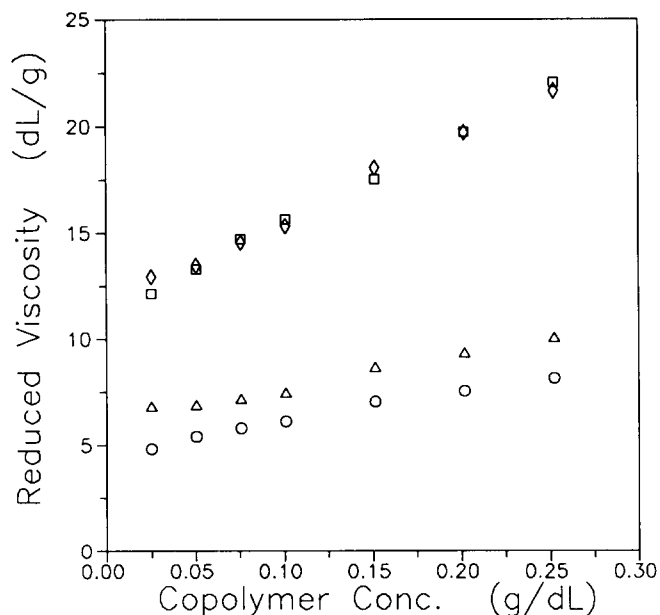**Figure 8** Reduced viscosity of DAPSAM copolymers as a function of CaCl$_2$ concentration (determined at 25°C at a shear rate of 1.75 s^{-1})

Figure 9 Changes in reduced viscosity of DAPSAM-10 as a function of solvent (determined at 25°C with a shear rate of 5.96 s^{-1}). O, Deionized water; □, 1 M NaCl; △, 1 M urea; ◇, 1 M NaCl + 1 M urea
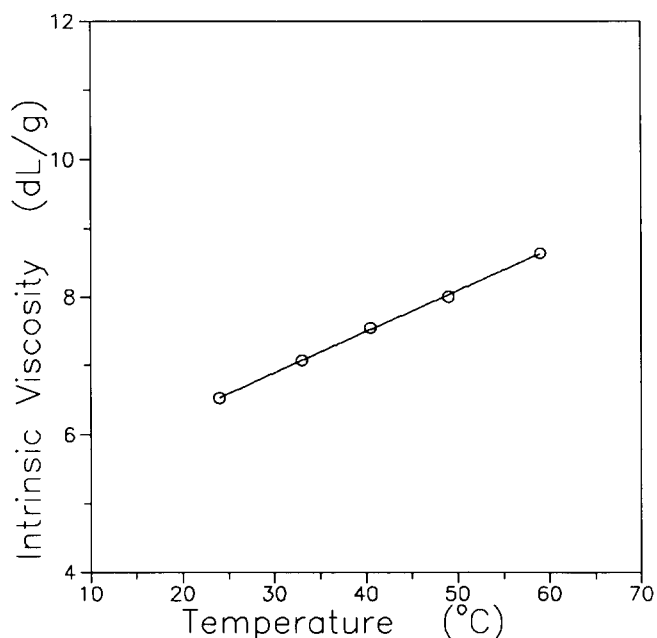
Figure 10 Changes in reduced viscosity of DAPSAM-40 as a function of solvent (determined at 25°C with a shear rate of 5.96 s^{-1}). ○, Deionized water; □, 1 M NaCl; △, 1 M urea; ◇, 1 M NaCl + 1 M urea

the carboxylate ion and a corresponding increase in viscosity is observed for the polymer in deionized water. The presence of salt negates the polyelectrolyte effect and disrupts zwitterionic intramolecular interactions. The solution viscosities of the DAPSAM-100 homopolymer are independent of pH in 0.512 M NaCl. Resistance of the AMPDAPS monomer to hydrolysis is due to the presence of geminal methyl groups next to the amide functionality. This protecting group has been used in other hydrolytically stable monomers such as sodium 2-acrylamido-2-methylpropanesulphonate (NaAMPS)[29] and sodium 3-acrylamido-3-methyl-butanoate (NaAMB)[30].

the lowest viscosity. The addition of 1 M urea increases reduced viscosity by only a small amount relative to that produced by the addition of 1 M NaCl. The combination of NaCl and urea yields the same viscosity increase as that attained by 1 M NaCl alone. As a reference, homopolyacrylamide solution shows no change in viscosity in the presence of salt or urea. The slight increase in reduced viscosity for both DAPSAM-10-3 and DAPSAM-40-3 in the presence of urea is most likely due to enhanced hydrogen bonding between the polymers and the solvent. The major effect dominating rheological behaviour appears to be charge screening upon addition of NaCl, yielding better solvated chains. Transition from dilute to semidilute behaviour is more readily observed for the DAPSAM-10-3 sample which is initially less compact than DAPSAM-40-3.
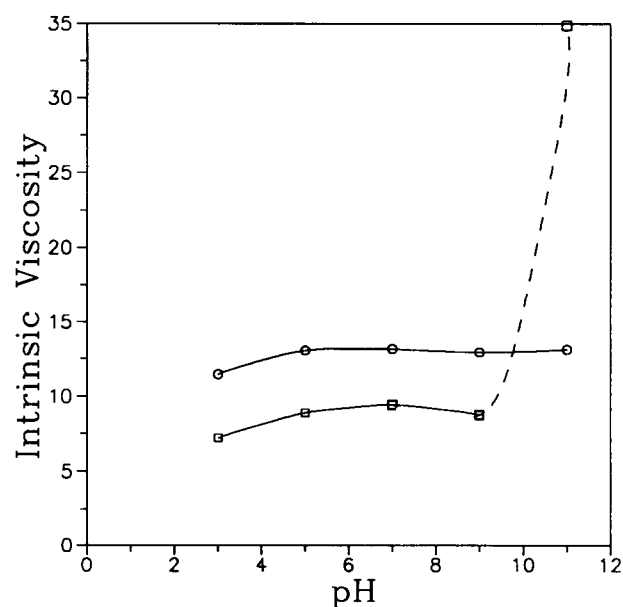
Effects of temperature. Intrinsic viscosities for DAPSAM-40-3 increase with increasing temperature (*Figure 11*). The copolymer was tested in deionized water in the range 25–60°C. Most neutral polymers and polyelectrolytes exhibit reductions in viscosity as a function of increasing temperature. In deionized water this betaine exists in a compact conformation as evidenced by second virial coefficients and viscosity data. Temperature increases obviously allow accessibility to more extended conformations and better solvation. Copolymers which were insoluble in deionized water, however, could not be solubilized by the application of heat, apparently as a result of strong intramolecular ionic effects. Interestingly, the DAPSAM copolymers are phase stable to 100°C in the presence of added electrolytes.

Effects of pH. Although acrylamide can be used as a comonomer to obtain very high molecular weights, hydrolysis can be problematic. *Figure 12* shows the effects of pH on DAPSAM-25 in deionized water and in 0.512 M NaCl. At high pH the acrylamide unit is hydrolysed to

Figure 11 Intrinsic viscosity of the DAPSAM-40-3 copolymer as a function of temperature (determined in deionized water at a shear rate of 5.96 s^{-1})

Figure 12 Intrinsic viscosity of DAPSAM-25 as a function of pH in: □, deionized water; ○, 0.512 M NaCl (determined at 30°C with a shear rate of 1.25 s^{-1})

CONCLUSIONS

The new sulphobetaine monomer 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulphonate (AMPDAPS) has been synthesized and incorporated into a series of copolymers (the DAPSAM series) with AM as the comonomer. The polymers were examined by ^{13}C n.m.r., *FT*i.r., elemental analysis and low angle laser light scattering. Elemental analysis data from low conversion samples gave $r_1 r_2 = 0.60$ for the AM–AMPDAPS monomer pair. Copolymer microstructures were statistically determined from reactivity ratios and found to be random with a slight alternating tendency. Weight-average molecular weights in the range of 3.0×10^6 to 21.5×10^6 g mol^{-1} have been determined for the polymers. Second virial coefficients were found to decrease in value as the zwitterion content of the copolymers increased.

Increasing concentrations of AMPDAPS decrease the intrinsic viscosities of the copolymers. Copolymers containing more than 40 mol% AMPDAPS are insoluble in deionized water but readily dissolve in the presence of NaCl. The copolymers display increased viscosity upon addition of NaCl and CaCl$_2$; intramolecular interactions are responsible for this effect. Intrinsic viscosities increase in the temperature range 25–60°C.

ACKNOWLEDGEMENTS

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