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Water soluble polymers: 69. pH and electrolyte responsive copolymers of acrylamide and the zwitterionic monomer 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate: synthesis and solution behaviour

Erich E. Kathmann, Leslie A. White and Charles L. McCormick*
The University of Southern Mississippi, Department of Polymer Science, Southern Station, Box 10076, Hattiesburg, MS 39406-0076, USA
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A novel carboxybetaine monomer, 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (AMPDAB), has been synthesized and copolymerized with acrylamide in an aqueous NaBr solution. The feed ratio of AM (M_1)/AMPDAB(M_2) was varied from 90/10 to 0/100 mol%. Low conversion samples were collected and copolymer compositions were determined with ^{13}C n.m.r. by integration of the carbonyl resonances. Reactivity ratios were determined and the nonlinear least-squares method yielded values of $r_1 = 1.01$ and $r_2 = 0.99$, indicating random incorporation of monomers into the final copolymer. Molecular weights were determined and range from 3.9 to 12.0×10^6 g mol^{-1}. The solution behaviour of the above copolymers was studied as a function of pH and added electrolytes. With the exception of the copolymers containing 60 and 75 mol% AMPDAB, homogeneous solutions were obtained in deionized water. At high pH, the polyzwitterions show an enhancement in viscosity as the concentration of added electrolyte is increased. In deionized water, as the pH of the aqueous media is lowered, the copolymers exhibit a dramatic increase in viscosity as the carboxylate groups are protonated and charge-charge repulsions of the quaternary ammonium groups induce polyelectrolyte behaviour. The solution behaviour is compared to structurally similar sulfobetaines which do not exhibit any responsiveness to changes in pH. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polyampholyte; polyelectrolyte; zwitterionic; carboxybetaine; sulfobetaine; water soluble polymers)

INTRODUCTION

The synthesis of electrolyte-tolerant, water-soluble polymers that contain ionic pendant groups has been the goal of academic and industrial laboratories for the past several years. Such polymers have applications in water treatment, remediation, drag reduction, petroleum recovery, viscosification, formulation of coatings, cosmetics, and pharmaceutics. In striving to synthesize polymers that show tolerance in the presence of added electrolytes, we have recently focused our attention on polyampholytes, polymers which posses both cationic and anionic pendent groups[1–6]. The ionic groups may be located on separate monomer units or may be incorporated into one zwitterionic monomer. Polyampholytes can exhibit enhancements in viscosity and solubility in the presence of added electrolytes due to shielding of coloumbic attractions[7–14]. This behaviour renders these systems useful in areas which require performance in the presence of additives such as electrolytes and surfactants.

Previous work in our laboratories dealt with the synthesis and characterization of copolymers of acrylamide and the sulfopropylbetaine monomer, 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulfonate (AMPDAPS)[4]. The solution behaviour was dependent on the amount of AMPDAPS incorporated into the copolymers. When 25 mol% or less of AMPDAPS was incorporated, the copolymers were soluble in deionized water and displayed a tendency to intermolecularly associate. Peiffer and Lundberg reported the tendency for intermolecular associations of other low-charge density polyampholytes[15]. Higher incorporation of AMPDAPS ($\geq$60 mol%) led to water insoluble copolymers that required the addition of a critical amount of electrolyte to achieve solubility in aqueous solution. This behaviour is typical of poly-(vinylsulfobetaines) and has been observed in numerous studies[16–18].

Another class of zwitterionic polymers are poly(vinylcarboxybetaines) in which the anionic group is a carboxylate functionality. The carboxylate moiety can be protonated at low pH values, allowing behaviour as polycations or polyampholytes depending on the pH of the aqueous medium. Ladenheim and Morawetz[19] synthesized the first poly(vinylcarboxybetaines) by reacting poly(4-vinylpyridine) with ethylbromoacetate followed by hydrolysis of the ester functionality. Topchiev *et al.*[20]

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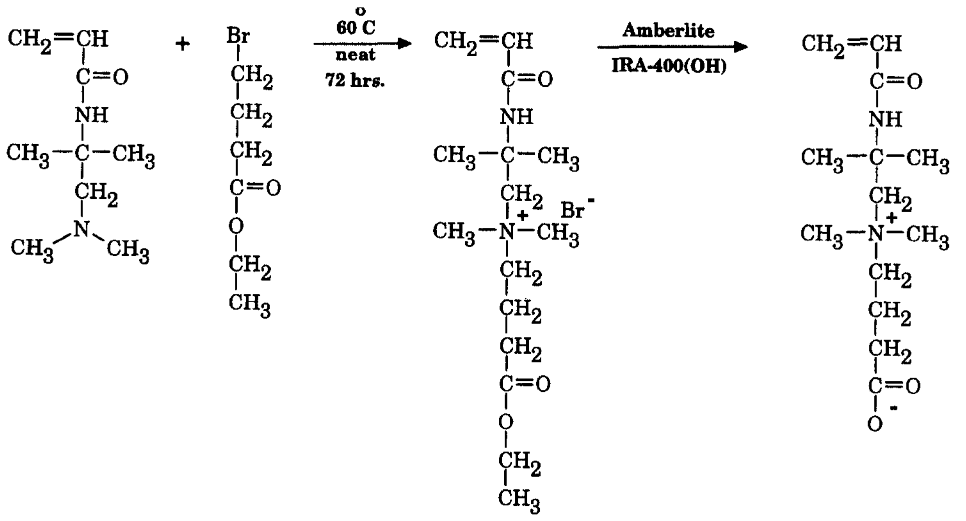
[*] To whom correspondence should be addressed



Scheme 1 Synthetic pathway for the prepation of 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (AMPDAB)

reported the polymerization of a carboxybetaine monomer and solution behaviour of the resulting homopolymer. Polymerization rates and viscosity studies were dependent on the pH of the aqueous medium. More recently, Wielema *et al.*[21] reported the synthesis of several monomeric carboxybetaines with varying alkyl groups between charged centres. By adjusting the pH, polyelectrolyte or polyampholyte behaviour was observed depending on the degree of ionization of the carboxylate functionality.

In this paper we report the synthesis and characterization of a series of copolymers of acrylamide with a novel carboxybetaine monomer. The purpose of the present work is to study the compositional effects of carboxybetaine comonomer incorporation on the properties of the resulting copolymers. In particular, the viscosity responsiveness of the copolymers has been studied as a function of pH and added electrolytes. The results are compared to the behaviour of structurally similar poly(vinylsulfobetaines) and interpreted in terms of the differing anionic pendent groups in the respective copolymers.

EXPERIMENTAL

Materials

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

Monomer synthesis (4-carboxypropyl)2-acrylamido-2-methylpropanedimethylammonium bromide (Scheme 1)

The synthesis of (4-carboxypropyl)-2-acrylamido-2-methylpropanedimethylammonium bromide (AMPDAB) involved a similar procedure employed by Laughlin and others to synthesize various carboxybetaine surfactants[22-24]. 2-Acrylamido-2-methylpropanedimethylamine, AMPDA[25,26] (0.5 mol) was dissolved in ethyl 4-bromobutyrate (0.55 mol) and the reaction allowed to proceed for 72 h at 60°C. The solid that formed was then dissolved in methanol and precipitated in diethyl ether. The precipitate was filtered, thoroughly dried, and recrystallized from 2-propanol. Following recrystallization, the product was dissolved in water and passed over Amberlite IRA-400(OH) ion-exchange resin. The water was removed under reduced pressure at 50°C to yield the zwitterionic product as an oil. The product was dissolved in water, chilled on an ice bath, and one equivalent of HBr was added. The water was once again removed under reduced pressure at 50°C to yield the cationic monomer. The product was subsequently recrystallized in ethanol, dissolved in methanol, and precipitated into diethyl ether to yield pure AMPDAB (yield 70–80%). M.p. 185–187°C (dec). Analysis for $C_{11}H_{21}N_2O_3Br$: Calculated—C, 46.4%; H, 7.4%; N, 8.3%. Found—C, 47.5%; H, 7.3%; N, 8.3%. *FT*i.r. (KBr pellet) acid O–H, 3600–2600 cm^{-1}; aliphatic C–H, 2970 cm^{-1}; acid C=O, 1732 cm^{-1}; amide C=O, 1653 cm^{-1} and 1556 cm^{-1}; acid C–O, 1259 cm^{-1}. ^{13}C n.m.r. (D_20 with 3-(trimethylsilyl)-1-propane-sulfonic acid, sodium salt (DSS) as the reference: 20.03, 29.47, 32.36, 54.33, 56.04, 68.06, 69.31, 130.37, 132.53, 170.45, and 177.96 ppm. Peak assignments are given in *Figure 1.*

Synthesis of copolymers of 4-(2-acrylamido-2-methylpropanedimethylammonio)butanoate with acrylamide (Scheme 2)

The homopolymer of AMPDAB and the copolymers of AMPDAB with AM (the DABAM series) were synthesized by free radical polymerization in a 0.5 M aqueous NaBr solution under nitrogen at 30°C using 0.1 mol% potassium persulfate as the initiator. The feed ratio of AM/AMPDAB was varied from 90/10 to 0/100 mol% with the total monomer concentration held constant at 0.45 M. 0.5 M NaBr in the reaction medium was used as a precaution to insure that polymers with high AMPDAB content remained homogeneous during polymerization.

In a typical synthesis, specified quantities of each monomer were dissolved in small volumes of deionized water. The separate solutions were then combined and one equivalent of sodium hydroxide per equivalent of AMPDAB was added and the pH adjusted to 8. The necessary quantity of NaBr was added to achieve a 0.5 M NaBr solution. The reaction mixture was then sparged with nitrogen and initiated with 0.1 mol% potassium persulfate. A low conversion sample was acquired for reactivity ratio studies. The reaction was terminated around 50% conversion due to the high viscosity of the

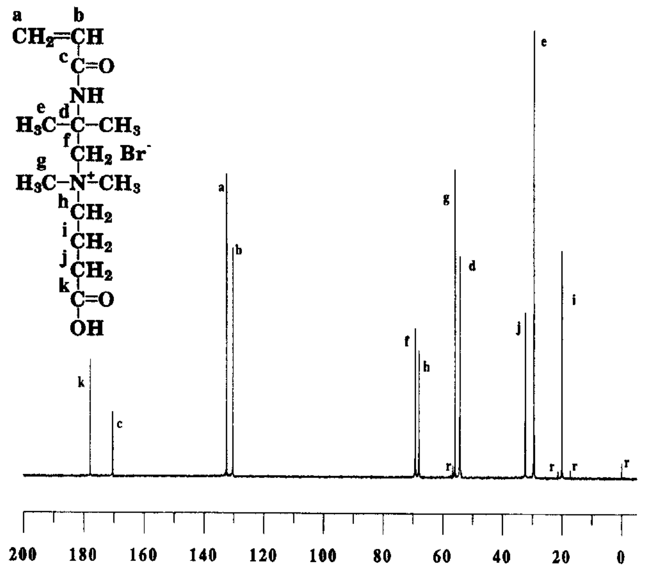
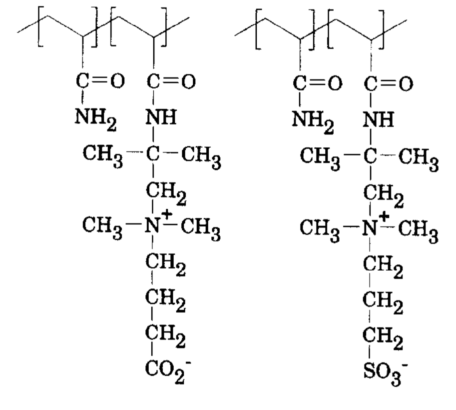


Figure 1 ^{13}C n.m.r. of 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (AMPDAB)



DABAM series DAPSAM series

Scheme 2 Structural composition of copolymers acrylamide with 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (the DABAM series) and with 3-(2-acrylamido-2-methylpropyldimethylammonio) propanesulfonate (the DAPSAM series)

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 12000 to 14000 g mol^{-1}.

Synthesis of the copolymer of 3-(2-acrylamido-2-methylpropanedimethylammonio)1-propanesulfonate with acrylamide (Scheme 2)

The polymerization procedure for DAPSAM-25 was conducted in 0.5 M NaCl in a similar manner as previously reported[4].

Copolymer characterization

^{13}C n.m.r. spectra of the copolymers were obtained at 50.3 MHz on a Bruker AC200 spectrometer using 15–20 wt% aqueous (D_20) polymer solutions with DSS as a reference. A recycle delay of 8 s, 90° pulse length, and gated decoupling to remove all NOE were used for quantitative spectral analysis. 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.

Viscosity measurements

Polymer solutions were made by dissolving designated amounts of polymer in the stock electrolyte solutions. The solutions were then isoionically diluted to appropriate concentrations and allowed to age for seven to ten days before being analysed with a Contraves LS-30 rheometer. Duplicate runs were conducted and reproducibility found to be within ±3–7% dependent on the magnitude of the viscosity values. Intrinsic viscosities were evaluated using the Huggins equation.

RESULTS AND DISCUSSION

Monomer synthesis

The novel carboxybetaine monomer, AMPDAB, was synthesized utilizing a method commonly used to prepare small molecule surfactants with carboxybetaine head groups. The advantages of the method vs typical base hydrolysis procedures (using alkali hydroxides) are the relatively mild conditions and the absence of inorganic electrolyte by-products which, due to the limited solubility of zwitterions in organic solvents, may be difficult to remove. In brief, the synthesis involves quaternization of the monomeric tertiary amine by the reaction with ethyl 4-bromobutyrate. The bromide ion affiliated with cationic product is replaced by the hydroxide ion after percolation through an anionic exchange resin of the hydroxide form (OH^-). The associated hydroxide ion promotes hydrolysis of the ester functionality with ethanol as the by-product to yield the zwitterionic product. Due to the hygroscopic nature of the product, however, the monomer had to be isolated as a bromide salt by addition of the equivalent of HBr. A ^{13}C n.m.r. spectrum of the monomer is shown in *Figure 1*.

Compositional and reactivity ratio analysis

Based on previous studies, the number and distribution of charged groups incorporated into polyampholytes dictate the solution behaviour of the resulting polymers. Inter- and intramolecular associations as well as solubility have been shown to be directly related to the charge density of the systems[4,15]. To investigate this issue for the novel poly(vinylcarboxybetaines) of this study, a series of copolymers was synthesized and reactivity ratios determined. The compositions of low conversion copolymer samples were determined by integration of the carbonyl peaks observed by ^{13}C n.m.r. spectroscopy (*Table 1*). Reactivity ratios for the AM(M_1)/AMPDAB(M_2) comonomer pair were determined by the methods of Fineman–Ross[27], Kelen–Tudos[28], and non-linear least squares (NLS)[29]. The Fineman–Ross method yielded values of $r_1 = 0.88$ and $r_2 = 0.92$, the Kelen–Tudos method yielded values of $r_1 = 0.88$ and $r_2 = 0.93$, and the NLS method yielded values of $r_1 = 1.01$ and $r_2 = 0.99$. The experimentally determined copolymer composition as a function of feed composition is shown in *Figure 2*, the dashed line represents ideal random incorporation. The random incorporation is in agreement with that previously observed by our group for a similar zwitterionic monomer[4].

Table 1 Reaction parameters for the copolymerization of acrylamide (M_1) with 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (M_2)

Sample	Feed ratio (mol%) (AM/AMPDAB)	Rxn. time (h)	% Conv.	AMPDAB found^a (mol %)
DABAM-10	90.0 : 10.0	2.0	7.3	11.2
DABAM-25	75.0 : 25.0	0.3	8	22.4
DABAM-40	60.0 : 40.0	0.3	14	40.7
DABAM-60	40.0 : 60.0	0.3	12	61.1
DABAM-75	25.0 : 75.0	0.4	13	73.3
DABAM-100	0.0 : 100.0	—	—	100.0^b

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

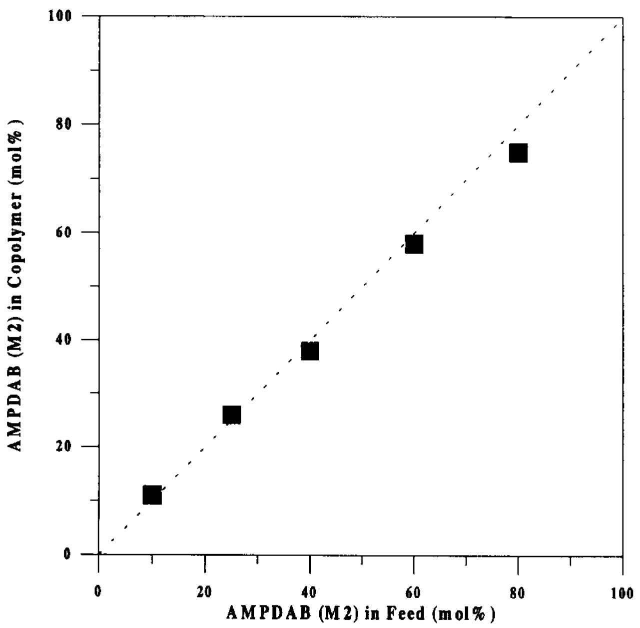


Figure 2 Mole percent AMPDAB incorporated into the copolymers as a function of comonomer composition in the feed

Table 2 Structural data for the copolymers of acrylamide (M_1) with 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (M_2)

Sample number	M_1 in copolymer (mol%)	Blockiness mol% M_1–M_1	Blockiness mol% M_2–M_2	Alternation mol% M_1–M_2	Mean seq. length M_1	Mean seq. length M_2
DABAM-10	88.8	78.7	1.1	20.2	9.39	1.10
DABAM-25	77.6	59.7	4.5	35.1	3.80	1.30
DABAM-40	59.3	34.1	15.5	50.5	2.40	1.59
DABAM-60	38.9	14.1	36.3	49.6	1.62	2.33
DABAM-75	26.7	6.4	53.0	40.6	1.31	3.66

Table 3 Classical light scattering data for the copolymers of acrylamide (M_1) with 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (M_2)

Sample	AMPDAB found^a (mol%)	$M_w \times 10^{-6}$ (g mol^{-1})	$A_2 \times 10^4$ (ml · mol g^{-2})	DP $\times 10^{-4}$
DABAM-10	11.2	12.0	6.0	13.4
DABAM-25	22.4	10.2	0.8	8.7
DABAM-40	40.7	9.8	0.6	6.7
DABAM-100	100^b	3.9	0.8	1.5
DAPSAM-25	25.8^c	12.4	0.6	9.8

^{a} Determined from ^{13}C n.m.r.
^{b} Theoretical value
^{c} mol% AMPDAPS found

The methods of Igarashi[30] were employed to determine the microstructural composition and are presented in *Table 2*. Similar values for all three categories (blockiness, alternation and mean sequence length) are observed for DABAM-25 and -75 as well as DABAM-40 and -60. For example, DABAM-40 has a mean sequence length of 2.4 for M_1 and 1.59 for M_2 while DABAM-60 has a mean sequence length of 1.62 for M_1 and 2.33 for M_2. Again, these values are consistent with a random microstructure.

Low angle laser light scattering

Table 3 shows the weight-average molecular weights determined by classical low-angle laser light scattering at 25°C in 1 M NaCl. The molecular weights for the DABAM series vary from 3.9 to 12.0×10^6 g mol^{-1}. The values decrease as more AMPDAB is incorporated into the copolymer feed. Also shown in *Table 2* is DAPSAM-25. This copolymer possesses a sulfonate group instead of a carboxylate group as the anionic moiety. Both DABAM-25 and DAPSAM-25 have similar molecular weights allowing meaningful comparisons and assessments of the effects of the anionic moiety on the solution behaviour of polyzwitterions.

The second virial coefficients (A_2) for the DABAM series have been determined and are also presented in *Table 2*. With the exception of DABAM-10, all of the copolymers have A_2 values below 1×10^{-4} ml · mol g^{-2} in 1 M NaCl. This behaviour is representative of polyampholytic systems which normally have low A_2 values under these conditions.

SOLUTION BEHAVIOUR

Copolymer composition and solubility

The carboxybetaine monomer, AMPDAB, was copolymerized with AM in varying molar ratios to yield polyampholytic systems. These polymers behave as polyelectrolytes or a polyampholyte depending on the pH of the solution due to the presence of the carboxylate functionality incorporated into the AMPDAB mer unit. The presence of the carboxylate functionality, however, induces complex solution behaviour as discussed below. The viscosity behaviour of the above copolymers was studied with a Contraves LS-30 rheometer as a function of pH and added electrolytes at 25°C and a shear rate of 6 s^{-1}.

The solubility of the DABAM series is a function of the amount of AMPDAB incorporated into the copolymer. The numbers appended to DABAM in the following discussions indicate the mol% of AMPDAB present in the copolymer feed and therefore representative of the mol% incorporated into the copolymer. DABAM-10, -25 and -40 are readily solubilized in deionized water and salt solutions at all values studied. DABAM-60 and DABAM-75, however, are not completely soluble over the pH range (1–13). The copolymer stock solutions (0.3 g dl^{-1}) are optically clear solutions but visibly heterogeneous as noted by the presence of a number of small, microgel-like particles suspended in solution. The solutions are viscous, however, indicating complete dissolution of most of the sample. Furthermore, aggregates remain even when diluted to 0.01 g dl^{-1}. The addition of NaCl, NaSCN, and CsCl, or known protein denaturants

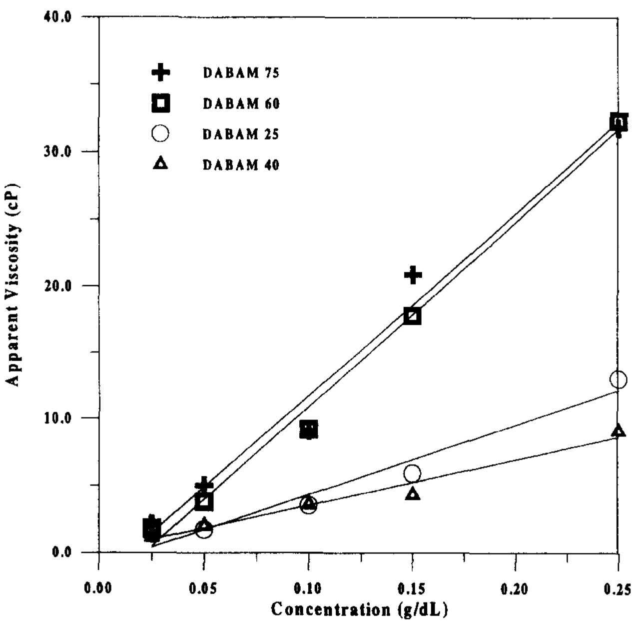


Figure 3 Apparent viscosity of DABAM copolymers at pH 7.5 as a function of copolymer concentration

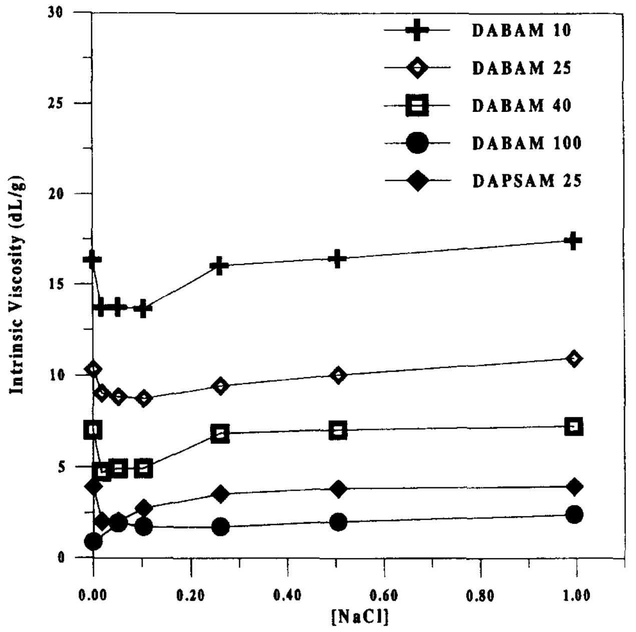


Figure 4 Intrinsic viscosity of DABAM copolymers as a function of NaCl concentration

(urea and guanidine hydrochloride) over a wide range of concentrations (0-3 M) fail to disperse the microgel particles. This implies some other mechanism for intermolecular aggregation other than electrostatic interactions. Polyzwitterions previously studied in our laboratories, based on sulfobetaine comonomers (DAPSAM series), did not display this behaviour and were molecularly dissolved in the presence of added electrolytes[4]. Interestingly, DABAM-100 is soluble in deionized water at all pH values investigated (pH 1–13). This suggests the incomplete solubility of DABAM-60 and -75 is due to the presence of the acrylamide comonomer. Whether this is a molecular weight effect or a conformational effect is not currently resolved and is under investigation.

The apparent viscosities of the copolymers in deionized water at pH = 7.5 are shown in *Figure 3*. Due to obvious microheterogeneity, the viscosities for DABAM-60 and -75 were determined at least five times and found to be consistent to within ±7% of the reported values. DABAM-60 and DABAM-75 display higher viscosities than DABAM-25 and DABAM-40. This is probably a result of the more aggregative nature of the copolymers containing a higher incorporation of AMPDAB as previously discussed. Molecular weights could not be determined for DABAM-60 and -75.

Effects of added electrolytes

Intrinsic viscosities were determined for DABAM-10, -25, -40, and -100, as well as DAPSAM-25, in varying ionic strengths of NaCl at pH 8 (*Figure 4*). At this pH, essentially all of the AMPDAB mer units are zwitterionic. The copolymers of DABAM-10, DABAM-25, and DABAM-40 display complex solution behaviour. At low concentration of NaCl, there is an initial decrease in the intrinsic viscosity likely due to the elimination of intermolecular interactions with the increasing ionic strength. This behaviour has been observed previously for other low charge density polyampholytic systems[4,15,19,31]. Upon addition of a critical concentration of NaCl, the polymers display polyampholytic behaviour as evidenced by an increase in intrinsic viscosity as intramolecular attractions are reduced. DABAM-100 exhibits an increase in intrinsic viscosity as the ionic strength increases, indicating the shielding of intramolecular coulombic attractions. As mentioned earlier, DABAM-100 is soluble in deionized water in contrast to the sulfobetaine homopolymer previously studied in our group, DAPSAM-100, which requires the addition of a critical concentration of NaCl for dissolution. The only structural difference in these two polymers is the nature of the anionic group; DABAM-100 possesses a carboxylate functionality while DAPSAM-100 possesses a sulfonate functionality. The differences in solubility are likely due to the more hydrophilic nature of the carboxylate functional group as compared to the sulfonate group. This behaviour has been observed for small molecule zwitterionic surfactants[23,24,32]. The more hydrated the carboxylate moiety is, the weaker the attraction with neighbouring ammonium groups, and therefore an enhancement in solvation for the polymer coil. Another interesting feature is that DABAM-25 exhibits a much higher intrinsic viscosity than DAPSAM-25, even though the two copolymers have similar molecular weights and A_2 values.

The reduced viscosities were also examined as a function of increasing electrolyte concentration of various salts. *Figure 5* displays the results of this study for DABAM-25 and DAPSAM-25. Both copolymers show an enhancement in viscosity as the concentration of electrolyte is increased in accord with polyampholytic behaviour. In addition, the aqueous solutions which have soft counterions (Cs^+ and SCN^-) yield higher viscosity values than those which possess relatively hard counterions (Na^+ and Cl^-). This behaviour is in accord with the Hoffmeister effect[33] and has been observed for other polyzwitterionic systems[16–18]. Salamone *et al.* have proposed that this effect is a result of specific counterion condensation[17]. Other effects, such as the influence the added ions have on water structure, should also be considered.

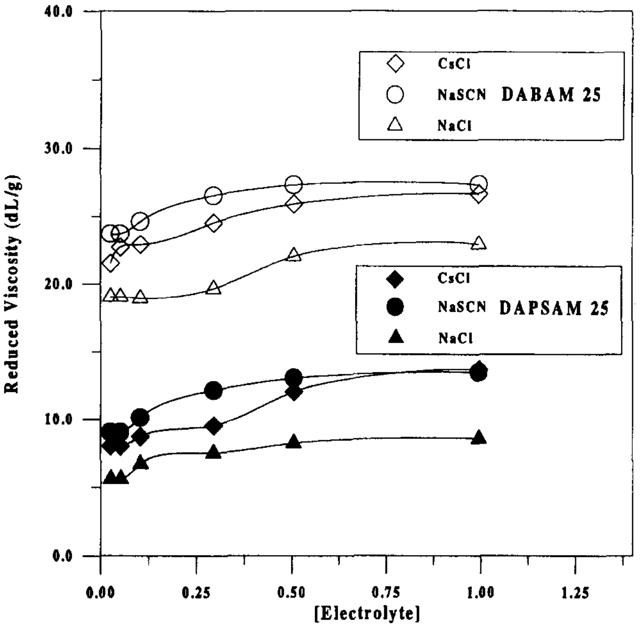


Figure 5 Reduced viscosity as a function of increasing ionic strength of various salts. (Polymer concentration of 0.1 g dl^{-1})

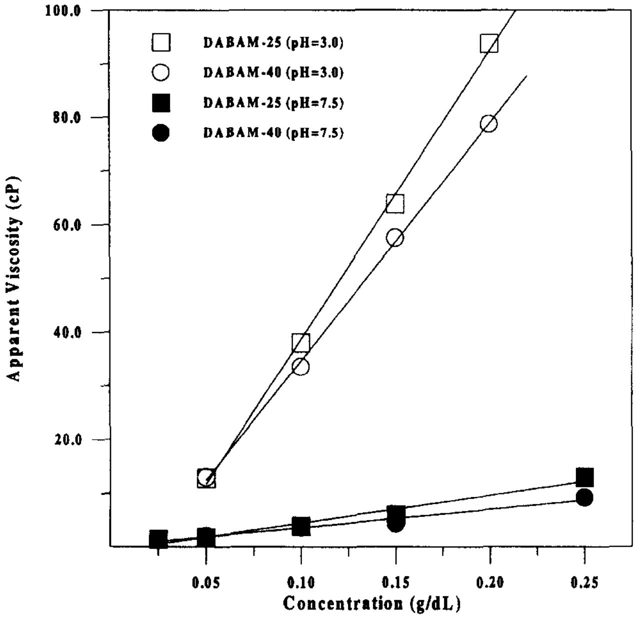


Figure 6 Apparent viscosities of DABAM copolymers at pH 3 and pH 7.5 as a function of copolymer concentration

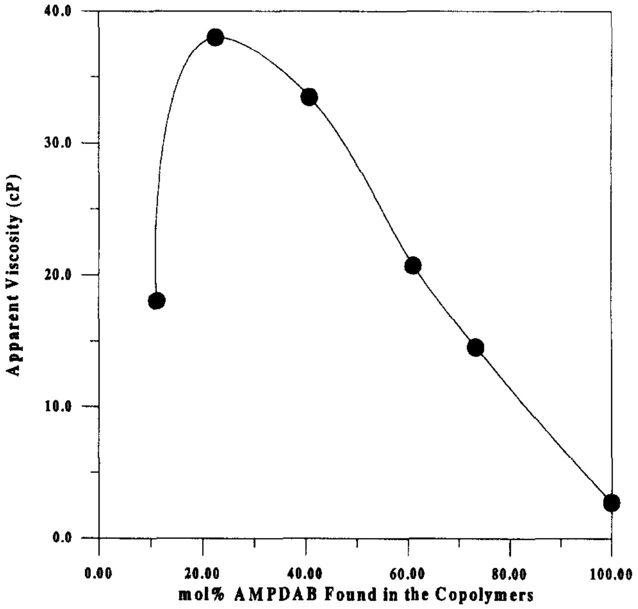


Figure 7 Apparent viscosities of DABAM copolymers as a function of the mol% AMPDAB found in the copolymers. (Determined at pH 3 and a polymer concentration of 0.1 g dl^{-1})

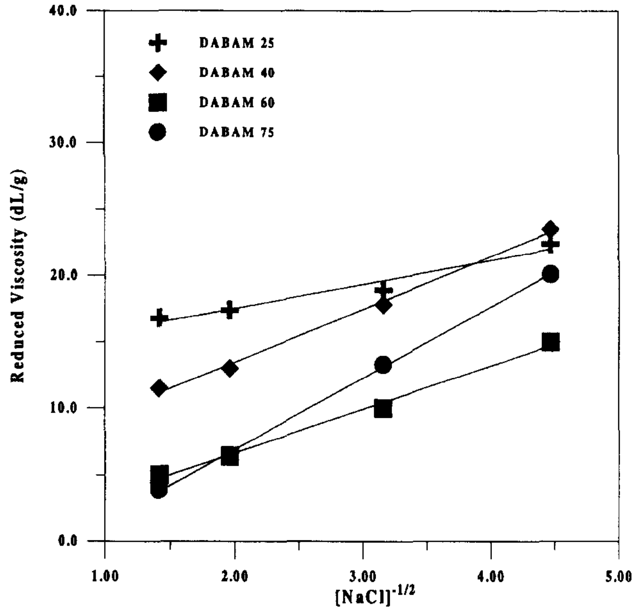


Figure 8 Reduced viscosity of DABAM copolymers as a function of the inverse square root of ionic strength. (Determined at pH 3 and a polymer concentration of 0.1 g dl^{-1})

Effects of pH

Figure 6 shows the effects of increasing polymer concentration on the apparent viscosity of DABAM-25 and -40 at pH 3 and pH 7.5. At low pH, the carboxylate group incorporated in the AMPDAB mer unit is protonated and the polymer acquires an overall positive charge due to the remaining ammonium group. The polycationic nature of the copolymer induces a larger hydrodynamic volume since charge–charge repulsions result in an extended conformation. As the pH is raised the carboxylic acid is ionized and the coulombic repulsions essentially become coulombic attractions. These attractions lead to a restricted conformation and much smaller hydrodynamic volumes as evidenced by the lower viscosity values. The effect of copolymer composition on the apparent viscosity at pH 3 is presented in *Figure 7*. The maximum viscosity occurs when approximately 20–30 mol% AMPDAB is incorporated into the copolymer and is likely the result of molecular weight differences as well as charge density effects.

The effects of added electrolytes on the solution behaviour of the DABAM copolymers at pH 3 are shown in *Figure 8*. As anticipated, there is a decrease in viscosity as the concentration of NaCl increases as charge–charge repulsions are shielded and the polymer coil contracts. Linear dependency of the reduced viscosity on the inverse square root of ionic strength is

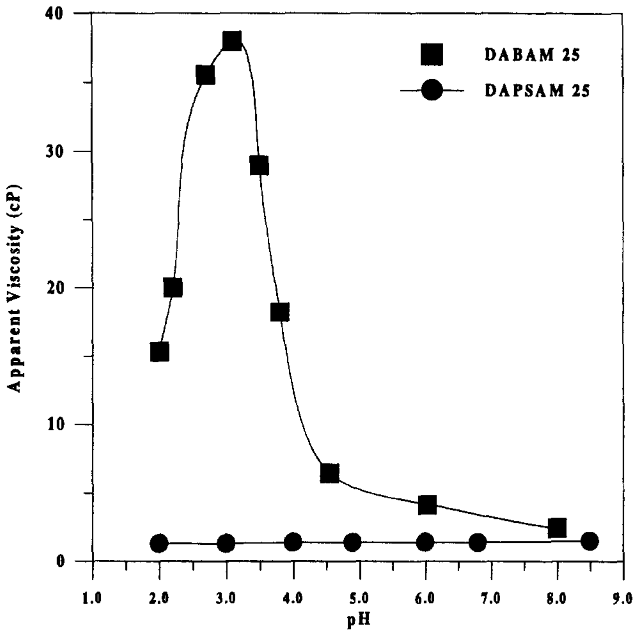


Figure 9 Apparent viscosities of DABAM and DAPSAM copolymers as a function of pH. (Polymer concentration of 0.1 $g\,dl^{-1}$)

typical behaviour for polyelectrolytes[34]. Furthermore, the magnitude of the slope gives an indication of the degree of conformational change induced by the addition of electrolytes. From *Figure 8*, DABAM-25 exhibits the smallest slope while DABAM-75 has the highest slope. This behaviour is, in part, due to enhanced hydrophobicity of the AMPDAB mer unit at low pH due to the conversion of the carboxylate group to the carboxylic acid group. Thus, through the addition of NaCl, not only are charge–charge repulsions shielded but also hydrophobic interactions are enhanced as water structuring events lead to a 'salting-out' effect. As more AMPDAB is incorporated into the copolymers, this effect is magnified.

The apparent viscosity as a function of decreasing pH was also examined for copolymers with different anionic substituents (*Figure 9*). DABAM-25, which incorporates the carboxylate functionality, exhibits a magnitude of order increase in the apparent viscosity as the pH is lowered from 8 to 3. DAPSAM-25 which contains the sulfonate functionality is relatively insensitive to changes in the pH of the aqueous solution. The dramatic pH responsiveness of the carboxybetaine mer units is in direct contrast with that of the sulfobetaine mer units. The sulfonate group is a much weaker base than the carboxylate group and cannot be protonated at pH values which will not degrade the polymer backbone. Thus, the AMPDAPS mer units of DAPSAM-25 remain in the zwitterionic state throughout the useful pH range. In contrast, DABAM-25, which contains carboxylate groups, may be converted from the zwitterionic to the cationic state by lowering of pH. At pH values less than 3, a reduction in the apparent viscosity is observed for DABAM-25. This behaviour probably results from a shielding of the cationic charges as the concentration of hydronium and chloride ions increases as the pH is lowered. The increase in hydrophobicity as more of the carboxylate groups are protonated is also partially responsible for loss of hydrodynamic volume in aqueous media.

CONCLUSIONS

A novel series of polyampholytes based on copolymers of acrylamide (AM) and 4-(2-acrylamido-2-methylpropyldimethylammonio) butanoate (AMPDAB) has been synthesized by free radical polymerization in 0.5 M NaBr. Reactivity ratios and copolymer microstructures were determined indicating random incorporation of the comonomers. Weight average molecular weights range from 3.9 to $12.0 \times 10^6\,g\,mol^{-1}$ as determined by low angle laser light scattering. The copolymers exhibit complex solubility and solution behaviour due to hydrogen bonding, charge–charge interactions, molecular weight, and configurational effects. The copolymers at pH 3 display polyelectrolyte behaviour due to the cationic nature of the polymer. At pH 8, the copolymers exhibit both intermolecular and intramolecular interactions depending on the amount of AMPDAB incorporated into the copolymer. The poly(vinyl carboxybetaines) are more soluble in deionized water than the analogous poly(vinyl sulfobetaines) as well as being more responsive to changes in the pH of the aqueous medium

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