

Poly(sulfobetaine)s and corresponding cationic polymers: 3. Synthesis and dilute aqueous solution properties of poly(sulfobetaine)s derived from styrene-maleic anhydride

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The copolymer prepared by copolymerizing styrene and maleic anhydride was imidized with *N,N'*-dimethylaminopropyl amine. The styrene-*N,N'*-dimethylaminopropyl maleimide (SDMAPM) copolymer obtained was then reacted with propane sulfone to yield a styrene-*[N,N'*-dimethyl(maleimidopropyl)ammonium propane sulfonate] (SDMMAPS) copolymer. The cloud point and intrinsic viscosity of this ampholytic SDMMAPS copolymer were determined in aqueous salt solutions. The effects of counter ions on the cloud point and intrinsic viscosity of SDMMAPS were similar to their effects on these properties of other zwitterionic poly(sulfobetaine)s. The Huggins constants for SDMMAPS in aqueous salt solutions, however, were quite different than those of other sulfobetaine homopolymers, such as poly[*N,N'*-dimethyl(acrylamidopropyl) ammonium propane sulfonate], [poly(DMAAPS)]. The value of the constant was negative and increased as the intrinsic viscosity and salt concentration increased. This phenomenon is mainly attributed to the presence of the styrene segment, a hydrophobic group, in the SDMMAPS copolymer. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: sulfobetaine; styrene-*[N,N'*dimethyl (maleimido propyl) ammonium propane sulfonate] copolymer; intrinsic viscosity)

INTRODUCTION

Zwitterionic monomers derived from dimethylaminoalkylacrylates and dimethylaminoacrylamides have been widely used in industry concerned with textiles, medical products, charged dispersing agents, protective colloids, and other related materials¹⁻⁹. These ampholytic monomers can be divided into two types, i.e. the sulfobetaines and carboxybetaines¹⁰⁻²⁵. The synthesis and aqueous solution properties of these betaine monomers and their polymers were reported by several scholars, such as Asonova *et al.*^{11,12}, Topchiev *et al.*¹⁰, Hart *et al.*¹⁴, Schulz *et al.*¹⁵, Galin *et al.*^{18,19}, Salamone *et al.*²⁰⁻²², Liaw *et al.*²⁴, and Laschewsky and Zerbe¹⁷, etc. During studies²⁶⁻³¹ of the binding interaction between salt ions and such polymers, the counterion size was found to affect the degree of binding to the salt-ion-attracting polymer^{12,18-25,32}, i.e. 'soft' salt anions and cations are more effective solubilizers than 'hard' anions and cations^{15,33}.

Cationic polyelectrolytes derived from a styrene-maleic anhydride copolymer have been reported by Isaacson *et al.*³⁴ and Pratt *et al.*³⁵. Isaacson and Young reacted a styrene-maleic anhydride copolymer with dimethylaminopropylamine and, subsequently, quaternized the dimethylamino group to yield a polyquaternary ammonium salt, which was proposed as a flocculant for oil slicks. Pratt and Diefenbach used this polyquaternary

ammonium salt to flocculate an aqueous suspension of solid inorganic particles. The synthesis and aqueous solution properties of poly(trimethylacrylamidopropyl ammonium iodide), poly(TMAAI), poly[*N,N'*-dimethyl(acrylamidopropyl) ammonium propane sulfonate], poly(DMAAPS) and poly[*N,N'*-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate], poly(DMAPS), were reported in previous papers^{16,24,33,36}. The previous poly(DMAAPS) article concluded that soft salt anions and cations bind easily to the quaternary ammonium and sulfonate group of poly(DMAAPS), and the poly(TMAAI) article showed that soft salt anions were more easily bound to the quaternary ammonium ion of poly(TMAAI) than hard salt anions.

The poly(sulfobetaine)s derived from a styrene-maleic anhydride (SMA) copolymer have never been reported in the literature. The synthesis and aqueous solution properties of poly(sulfobetaine) derived from SMA, were investigated in this work. The cloud points and intrinsic viscosities of the polymers in the presence of various salts were determined.

EXPERIMENTAL

Synthesis of styrene-maleic anhydride (SMA) copolymers

Styrene (7.295 g, 0.07 mol), maleic anhydride (6.865 g, 0.07 mol) and methyl ethyl ketone (MEK) 50 ml were introduced into a 250 ml volume flask equipped with a stirrer, a condenser, and a thermometer. The contents

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Table 1 Relationship between yield, average molecular weight and initiator content

	A	B	C	D
AIBN, wt%	0.45	0.22	0.05	0.02
$[\eta]$	0.388	0.481	0.669	1.026
Molecular weight, M_v	103 000	148 000	258 000	529 000
Yield, %	96	95	87	85

were stirred at 80°C until complete dissolution. Azobisisobutyronitrile (AIBN) (0.05 wt% based on monomers) was then added to the solution and stirred at the same temperature for 5.5 h under a nitrogen atmosphere. The mixture was then precipitated in diethyl ether. The product was then repeatedly dissolved and precipitated from MEK with diethyl ether and then dried at 80°C for 24 h under vacuum to obtain the styrene-maleic anhydride (SMA) copolymer. Four SMA copolymers with different molecular weights were obtained by changing the level of initiator and labelled as A, B, C and D, respectively.

Imidization of SMA copolymers

Each SMA copolymer sample (5 g) was stirred in 20 ml of *N,N'*-dimethylformamide (DMF) at 80°C until the polymer particles were dissolved. To this, a solution of 15 g of 3-dimethylaminopropylamine and 20 ml DMF was added dropwise for 1 h. Heat was applied gradually during the addition, and the temperature was raised to reflux. The solution was stirred under gentle reflux for 1 h and then subjected to distillation by heating to 200°C in order to carry out the dehydration reaction. The product was precipitated in distilled water. The polymeric product was then dried under vacuum to obtain styrene-dimethylaminopropyl maleimide (SDMAPM). The products were labelled as A1, B1, C1 and D1, respectively.

Synthesis of styrene-[*N,N'*-dimethyl(maleimido propyl) ammonium propane sulfonate] (SDMMAPS) copolymers

Each sample of SDMAPM copolymer (3 g) was dissolved in a 50 ml of dry acetone. To this, a mixture of propane sultone (1.479 g) and acetone (20 ml) was added dropwise for 1 h at room temperature. After completion of the addition, the mixture was stirred at the same temperature for several hours and then allowed to stand overnight. The precipitated product was collected by filtration, washed with acetone to remove unreacted copolymer and propane sultone, and then dried under reduced pressure for 24 h to obtain the SDMMAPS copolymer. The SDMMAPS copolymers were labelled as A2, B2, C2, and D2, respectively.

Cloud point determination

Each SDMMAPS copolymer (0.1 g) was dissolved in an appropriate aqueous salt solution (10 ml). Cloud point titrations to determine the point at which the polymer becomes insoluble in the aqueous salt solution (25 ± 5 ml) were performed by dissolving the material in an aqueous salt solution with sufficient salt content and titrating the stirred solution with deionized water to the first indication of turbidity.

Viscometric measurements

Viscometric measurements were carried out with an Ubbelodhe viscometer (flow time 76.23 s for pure water)

at $30 \pm 0.01^\circ\text{C}$. The polymer samples were dissolved in salt solutions of varying concentrations to yield stock solutions of approximately 0.2 g polymer per 100 ml solvent.

Viscosity data were calculated according to the Mark-Huggins equation

$$\eta_{sp}/C = [\eta] + K'[\eta]^2C \quad (1)$$

RESULTS AND DISCUSSION

Synthesis of SMA copolymers

Four SMA copolymers with different molecular weights were prepared by changing the amount of initiator. The molecular weight was determined using the Mark-Houwink equation, $[\eta] = KM^\alpha$, where $K = 3.98 \times 10^{-4}$ and $\alpha = 0.596^{37}$, at 25°C in tetrahydrofuran (THF) solution. The results shown in *Table 1* indicate that higher molecular weights were obtained with smaller amounts of initiator, but the yield was also decreased as the initiator content decreased. The structure of the SMA copolymers was confirmed to be that of an alternating copolymer by elemental analysis and i.r. analysis [*Figure 1(1)*]. The characteristic i.r. absorption peaks for anhydride are 1856, 1779, and 1224 cm^{-1} . Elemental analysis: calculated, C 71.28%, H 4.98%, O 23.74%; found, C 70.78%, H 5.04%, O 24.18%. The polymerization reaction is shown as *Scheme 1A*.

Imidization of SMA copolymer

3-Dimethylaminopropylamine was added to the SMA copolymer solutions (DMF), which were then heated for 1 h to form styrene-maleamic acid copolymers (ring-opened reactions) (*Scheme 1B-IIA*). The solutions were heated to 200°C to carry out the dehydration reactions (ring-closed reactions) to obtain the styrene-dimethylamino propyl maleimide copolymers (SDMAPM) (*Scheme 1B-IIB*). The yield and the degree of imidization were evaluated by nitrogen elemental analysis (*Table 2*). The structures were characterized with i.r. [see *Figure 1(2)*]. The characteristic peaks for imide and tertiary amine are 1771 and 1696 cm^{-1} ; 1218 and 1151 cm^{-1} , respectively.

Synthesis of styrene-[*N,N'*-dimethyl(maleimido propyl) ammonium propane sulfonate] (SDMMAPS) copolymers

Propane sultone was added to the SDMAPM acetone solution to form SDMMAPS (*Scheme 1C*). The degree of the formation of sulfobetaine was determined by sulfur elemental analysis. The yields of SDMMAPS are listed in *Table 3*. The yields decreased with increasing molecular weight of the copolymers. On the other hand, the degree of sulfobetaine formation remained over 94%.

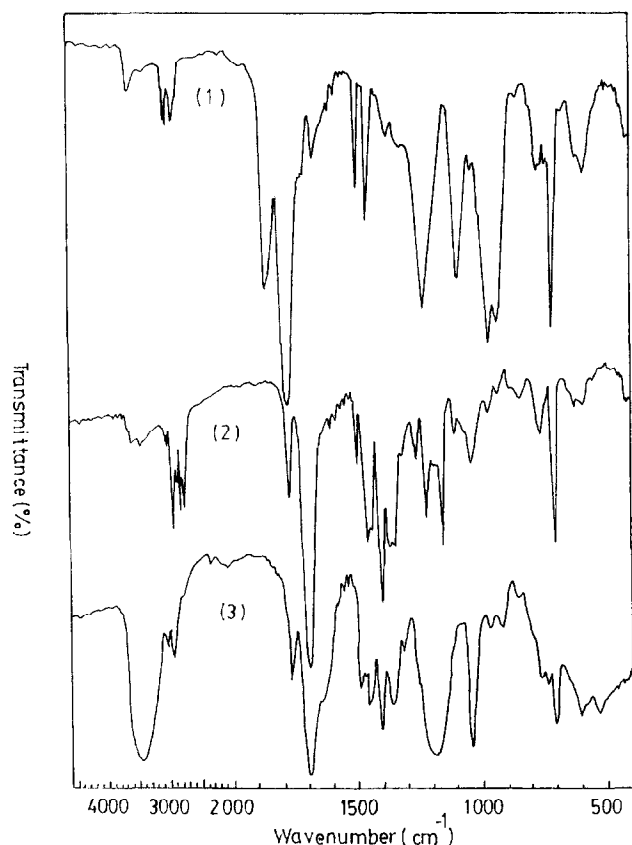


Figure 1 I.r. spectra of SMA (1), SDMAPM (2), and SDMMAPS (3)

The structure of SDMMAPS was also characterized by i.r. analysis [see Figure 1(3)]. The characteristic absorption peaks for imide and sulfonate groups are 1771 and 1696 cm^{-1} ; 1183 and 1042 cm^{-1} , respectively.

Determination of cloud point

The SDMMAPS copolymers were insoluble in water but formed transparent gels in aqueous solutions. The positive charges on the DMMAAPS units were attracted to the negative charge sites to form an ionically cross-linked network. For this reason, salts were added to the polymeric aqueous solutions to disrupt the ionic interaction and dissolve the polymers.

In the aqueous salt solutions of the SDMMAPS copolymers, the cations (or anions) of the salts were attracted to the binding sites on the sulfonate group (SO_3^-) [or the quaternary ammonium group (R_4N^+)] of SDMMAPS, thereby, collapsing the ionically cross-linked network and expanding the polymeric chain; the SDMMAPS copolymer then dissolved in the aqueous salt solution¹⁷⁻²⁵. The typical process of dissolution of SDMMAPS in a NaCl solution is shown in Scheme 2. In order to study the solution behaviour of the SDMMAPS copolymers, it was necessary to measure the minimum salt concentration needed for solubilization of the polymer.

For salt solutions containing common anions (Cl^- , ClO_4^-) but different cations, the data presented in Table 4 show that the solubility of SDMMAPS copolymer in aqueous salt solutions increased in the order $\text{NH}_4^+ < \text{Li}^+ < \text{Na}^+ < \text{K}^+$ and $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Ba}^{2+}$ for NH_4Cl , LiCl , NaCl , KCl or NH_4ClO_4 , NaClO_4 , KClO_4 , and MgCl_2 , CaCl_2 , BaCl_2 , respectively. The cloud points of

Table 2 Degree of imidization of SMA copolymers

	A1	B1	C1	D1
Yield, %	84	85.6	83.4	87.9
Elemental analysis of nitrogen				
Calc. (%)	9.71	9.71	9.71	9.71
Found (%)	9.20	9.19	9.22	9.23
Imidization degree (%)	94.7	94.6	95.0	95.1

Table 3 Yield and degree of sulfobetaine formation of SDMAPM

	A2	B2	C2	D2
Yield (%)	79.8	76	67.6	58.6
Elemental analysis of sulfur				
Calc. (%)	7.84	7.84	7.84	7.84
Found (%)	7.65	7.73	7.37	7.46
Degree of betaine formation (%)	97.5	98.5	94.0	95.1

Table 4 Minimum salt concentration of SDMMAPS copolymer in salt solution with a common anion

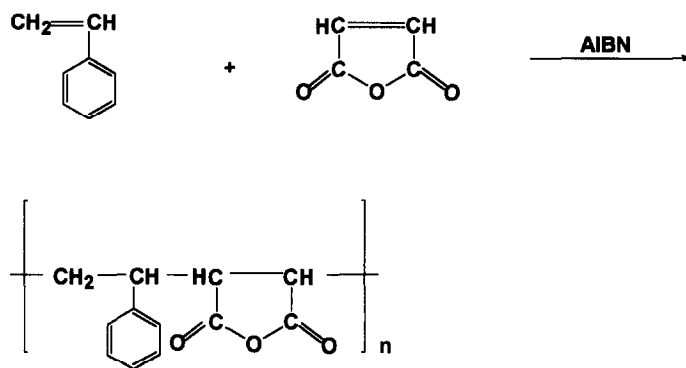
Electrolytes	Minimum salt concentration ($\times 10^{-1}$) (M)
NH_4Cl	1.38
LiCl	1.27
NaCl	1.16
KCl	1.13
NH_4ClO_4	0.11
NaClO_4	0.107
KClO_4	0.105
MgCl_2	0.599
CaCl_2	0.565
BaCl_2	0.537

Table 5 Minimum salt concentration of SDMMAPS copolymer in a salt solution with a common cation

Electrolytes	Minimum salt concentration ($\times 10^{-1}$) (M)
KCl	1.136
KBr	0.752
KI	0.364
KClO_4	0.105

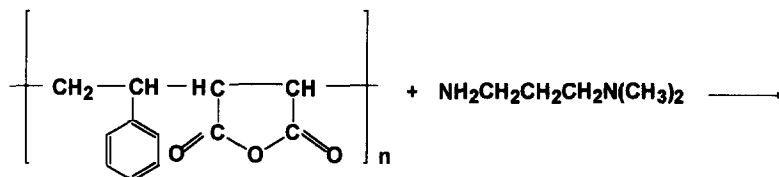
the copolymer solutions containing salts with a common cation (K^+) but different anion appear in Table 5. For these salts, the data indicate increased solubility of the copolymer in the order $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{ClO}_4^-$ for KCl , KBr , KI , and KClO_4 , respectively. These trends are similar to those for the sulfobetaine derived from poly(vinyl pyridine)¹⁴, poly(vinyl imidazole)²², poly(DMAPS)²⁴, and poly(DMAAPS)³³ and seem to relate to the site binding ability of anions of cations^{22,38-40}. But, the minimum salt concentration for SDMMAPS is higher than those of poly(DMAPS) and poly(DMAAPS) by one order of magnitude. This is due to the hydrophobic nature of the styrene unit in the copolymer, which lowers the solubility of SDMMAPS in the salt solution. However, the relative effects of the various counterions are not affected by the presence of the styrene unit in SDMMAPS. Those cations (anions) with a large radius bind easily to the sulfonate (quaternary ammonium) groups of the

(A) Synthesis of Styrene-Maleic anhydride (SMA) copolymer

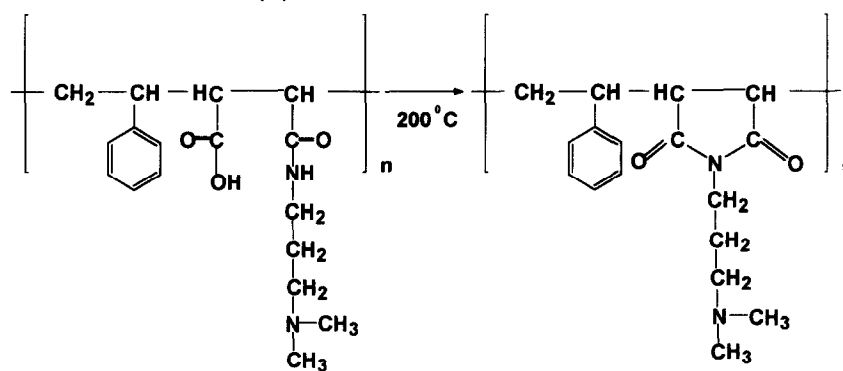


(I)

(B) Imidization of Styrene-Maleic anhydride copolymer



(I)



(II) A

(II) B

Scheme 1

DMMAPS units according to the above results. This result conforms to the Pearson principle that hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases^{15,41}.

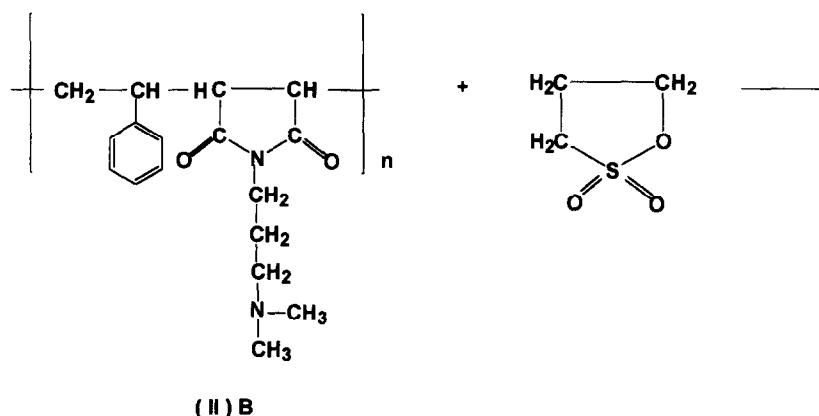
Viscosity measurement

The intrinsic viscosity is a good measure of the hydrodynamic volumes of polymers. When salts are added to the SDMMAPS aqueous solutions in order to make the polymer dissolve, the polymeric chain expands. Therefore, the determinations of the intrinsic viscosity of the SDMMAPS copolymer in the presence of different electrolytes reflects the influence of these salts on the hydrodynamic volume of the polymer chain. In order to study this effect, the intrinsic viscosity of the B2 sample (SMA molecular weight = 148 000) was measured in various salt solutions.

Influence of cations with common anions on the intrinsic viscosity of the SDMMAPS copolymer

The influence of various electrolytes having a common anion (Cl^-) on the intrinsic viscosity of the SDMMAPS copolymer is shown in Figure 2 and Table 6. The intrinsic viscosity of this copolymer in the aqueous salt solutions (0.5 M) increased in the order $\text{NH}_4^+ < \text{Li}^+ < \text{Na}^+ < \text{K}^+$ for NH_4Cl , LiCl , and KCl ; and $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Ba}^{2+}$ for MgCl_2 , CaCl_2 , and BaCl_2 , respectively. This phenomenon is similar to the results of the cloud point determination (Table 4). This indicates that ions with an ion charge density easily approach the sulfonate groups and disrupt the ionically crosslinked network. This result is similar to that obtained with poly(DMAPS)²⁴ and poly(-DMAAPS)³³, and other poly(sulfobetaine)s^{15,17-22}. The Huggins constant, k' , was calculated by means of Figure 2 and equation (1). The value of the Huggins constant

(C) Synthesis of Styrene-[N,N-dimethyl (maleimidopropyl) ammonium propane sulfonate] copolymer



Scheme 1 (Continued)

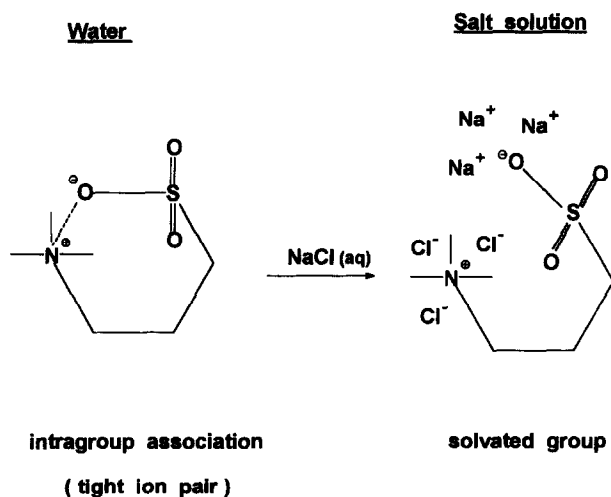
(shown in *Table 6*) increased as the intrinsic viscosity increased. This phenomenon is different from that observed with poly(DMAPS) and poly(DMAAPS). The constant had extremely large negative values in the dilute polymeric salt solutions. This abnormal property may be attributed to the styrene structure in the SDMMAPS copolymer, which leads the polymeric chain to form a surfactant-like micellar structure in aqueous solutions, with the hydrophilic DMMAPS units located towards the outside layers of the micelles. This would make the Huggins constant increase because the interaction between the DMMAPS units would be increased.

Influence of anions with a common cation on the intrinsic viscosity of SDMMAPS

The intrinsic viscosity of SDMMAPS under the effect of various anions with a common cation (K^+) are shown in *Figure 3* and *Table 7*. The intrinsic viscosity in aqueous solution (0.5 M) increases in the order $Cl^- < Br^- < I^-$ for KCl, KBr, and KI, respectively. The reason is that the

ions with low charge densities are easily polarized as they approach and become bound to the quaternary ammonium group (R_4N^+) on the DMMAPS unit. The intrinsic viscosity, hence, increased as the degree of salt binding to the DMMAPS unit³³ increased. The Huggins constant (shown in *Table 7*) also increased with an increase in the intrinsic viscosity. A similar tendency was also observed for the various acidic groups (see *Figure 3* and *Table 7*) in the order $ClO_4^- < NO_3^- < NO_2^-$ for $NaClO_4$, $NaNO_3$, and $NaNO_2$, respectively. These tendencies are similar to those found in the cloud point determinations (*Table 4*).

The cloud point and intrinsic viscosity results are in agreement with the Pearson principle. The quaternary ammonium group and the sulfonate group on the DMMAPS unit of SDMMAPS copolymer behave as a soft acid and a soft base, respectively. Thus, soft base (anions) from a salt (larger anionic radius) binds more easily to sites on the quaternary ammonium group on the DMMAPS unit of the copolymer than hard bases, and soft acids (cations) from a salt (larger cationic radius) bind



Scheme 2

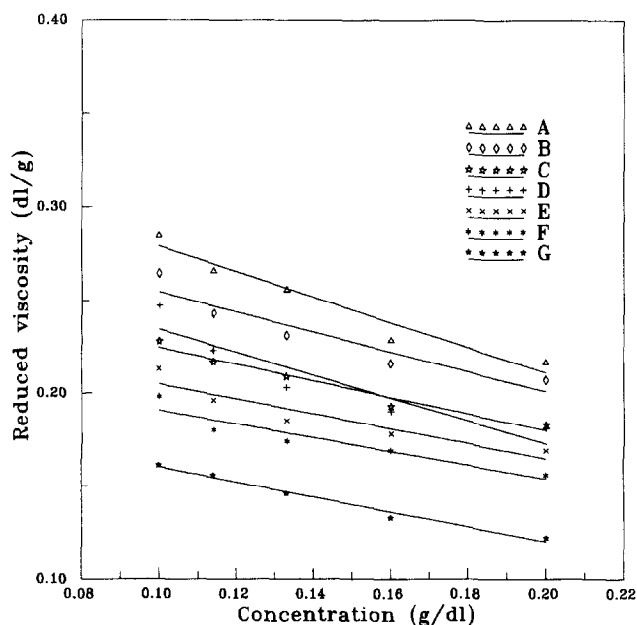


Figure 2 Reduced viscosity of SDMMAPS copolymer as a function of concentration for salts containing a common anion: (A) 0.5 M BaCl₂, (B) 0.5 M CaCl₂, (C) 0.5 M MgCl₂; (D) 0.5 M KCl, (E) 0.5 M NaCl, (F) 0.5 M LiCl, (G) 0.5 M NH₄Cl

Table 6 Effect of various salt solutions with a common anion on the intrinsic viscosity behaviour and Huggins constant for SDMMAPS copolymer at 30°C

Salt (0.5 M)	$[\eta]$	k'
NH ₄ Cl	0.193	-9.69
LiCl	0.228	-7.21
NaCl	0.240	-6.98
KCl	0.265	-6.12
MgCl ₂	0.288	-6.4
CaCl ₂	0.313	-5.52
BaCl ₂	0.334	-5.24

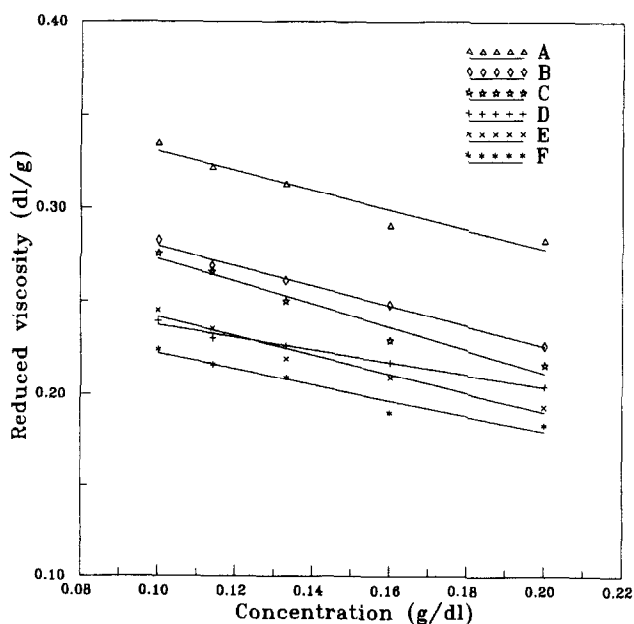


Figure 3 Reduced viscosity of SDMMAPS copolymer as a function of concentration for salts containing a common cation: (A) 0.5 M NaClO₄, (B) 0.5 M NaNO₃, (C) 0.5 M NaNO₂, (D) 0.5 M KI, (E) 0.5 M KBr, (F) 0.5 M KCl

Table 7 Effect of various salt solutions with a common cation on the intrinsic viscosity and Huggins constant for SDMMAPS copolymer at 30°C

Salt (0.5 M)	$[\eta]$	k'
KCl	0.265	-6.12
KBr	0.295	-5.52
KI	0.340	-5.24
NaNO ₂	0.278	-5.34
NaNO ₃	0.339	-4.98
NaClO ₄	0.381	-3.53

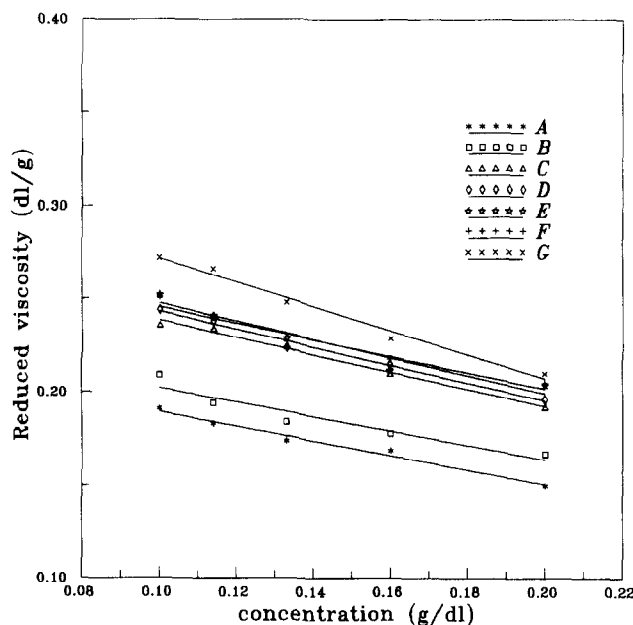


Figure 4 Reduced viscosity of SDMMAPS copolymer as a function of concentration for NaCl: (A) 0.3 M, (B) 0.5 M, (C) 0.7 M, (D) 1.0 M, (E) 2.0 M, (F) 4.0 M, (G) 5.0 M

more easily on the sulfonate group than hard acids. These results conform to those obtained with poly-(sulfobetaine)s derived from acrylates, acrylamides, or vinylimidazole, etc.^{18-22,24,33}

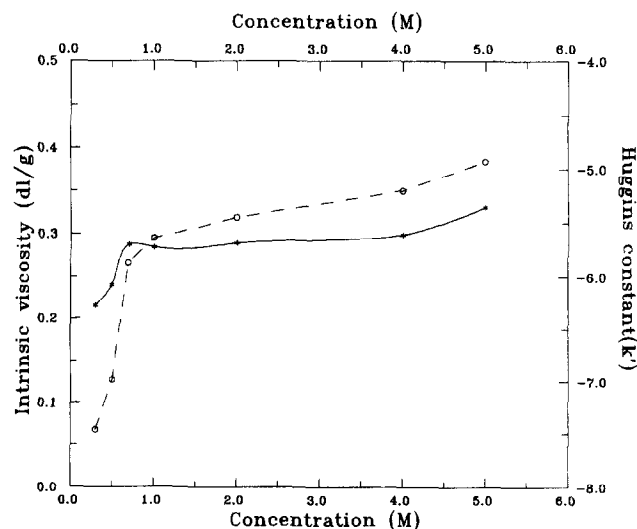


Figure 5 Intrinsic viscosity (*) and Huggins constant (O) of SDMMAPS copolymer as a function of concentration of NaCl

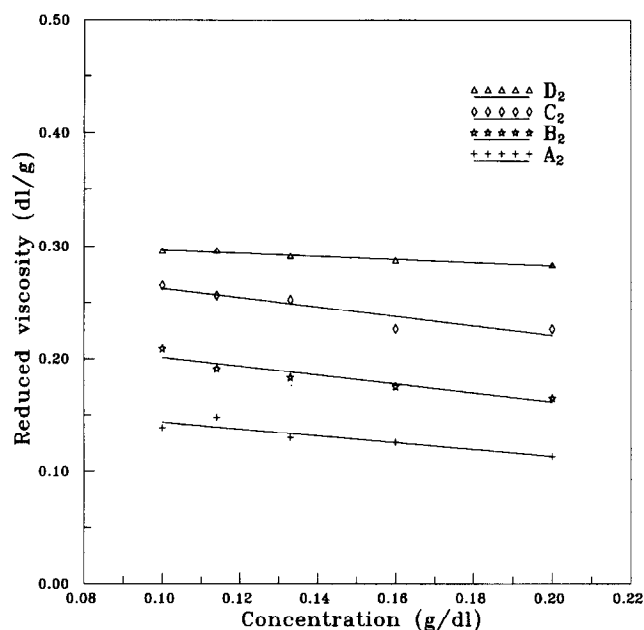


Figure 7 Reduced viscosity of various molecular weight of SDMMAPS copolymers in 0.5 M NaCl

occupied, resulting in a decreased tendency of site binding^{24,26-31}. The reason is that the polymer and solvent interacted until the concentration of NaCl approached 0.7 M. At this concentration, the binding sites were increasingly occupied and formed a region of local density of charge. This concentration of saturated binding was also observed in poly(DMAAPS) aqueous salt solution reported in previous work³³.

Thus, macroscopic viscosity measurements are consistent with a model for SDMMAPS copolymers where the chains are intramolecularly associated in dilute salt solutions. These intramolecular aggregates are both of the intragroup and intrachain type. Such intramolecular aggregates are broken up by external electrolytes (e.g. NaCl), with a consequent modest expansion of the polymer coil (Figure 6). Thus, the solution properties for sulfobetaine zwitterionic copolymers with styrene follow trends similar to those reported for sulfobetaine zwitterionic homopolymers^{14,15,18,22} and N-vinyl pyrrolidone sulfobetaine copolymers⁴².

Effect of molecular weight of SDMMAPS on reduced viscosity

The relationships between reduced viscosity and polymer concentration are shown in Figure 7 for four samples of SDMMAPS copolymers with different molecular weights. The intrinsic viscosity in the 0.5 M NaCl solution increased as the molecular weight of the copolymers increased (e.g. D₂ > C₂ > B₂ > A₂). This result conforms to the Huggins-Houwink equation, $[\eta] = kM^\alpha$. Thus, the longer polymeric chains expanded to occupy larger hydrodynamic volumes in the dilute aqueous salt solutions.

CONCLUSIONS

The behaviour of SDMMAPS in aqueous solutions was different from that of other poly(sulfobetaine)s in some

respects. For example, the minimum salt concentrations required to dissolve the polymer were one order of magnitude higher than that for sulfobetaine homopolymers. The Huggins constant was negative in the aqueous salt solutions and increased as the viscosity increased. This phenomenon may be due to the hydrophobic styrene units, which make the polymeric chain aggregate in a micellar conformation in aqueous solution. This conformation results in an increase in the Huggins constant as the concentration of the salt increases. The intrinsic viscosity also increases as the salt concentration is increased until the saturated binding concentration of the salt is reached.

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