

# Poly(sulfobetaine)s and Corresponding Cationic Polymers. X. Viscous Properties of Zwitterionic Poly(sulfobetaine) Derived from Styrene-(*N,N*-Dimethylaminopropyl maleamic acid) Copolymer in Aqueous Salt Solutions

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**ABSTRACT:** A styrene-[*N,N*-dimethyl (maleamic acid) propyl ammonium propane sulfonate] (SDMMAAPS) copolymer was synthesized through an amidoacidation reaction of styrene-maleic anhydride (SMA) alternating copolymer with *N,N*-dimethylaminopropylamine (ring-opening reaction), which was then reacted with propane sulfone. The effect of various salt solutions on the intrinsic viscosity of this ampholytic ADMMAAPS copolymer was investigated. The results showed that the effect of counter ions on the intrinsic viscosity of SDMMAAPS was not entirely similar to that of other zwitterionic poly(sulfobetaine)s. The greatest difference from other poly(sulfobetaine)s is the carboxylic

group on the polymer chain unit of SDMMAAPS. The Huggins constants for SDMMAAPS in aqueous salt solutions, however, were also quite different from those of other sulfobetaine copolymers, such as styrene-*N,N*-dimethyl (maleimido propyl) ammonium propane sulfonate] (SDMMAPS) copolymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 726–734, 2004

**Key words:** *N,N*-dimethyl (maleamic acid) propyl ammonium propane sulfonate; poly(sulfobetaine); reduced viscosity

## INTRODUCTION

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

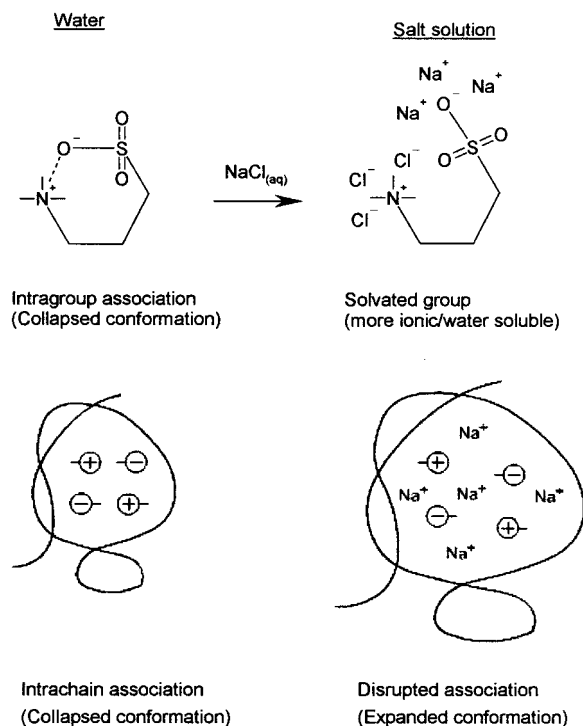
Zwitterionic monomers of sulfobetaines or carboxybetaines derived from dimethylaminoalkylacrylates and dimethylaminoacrylamides have been widely used in industry concerned with textiles, medical products, charged dispersing agents, protective colloids, and other related materials.<sup>1–9</sup> The synthesis and aqueous solution properties of these betaine monomers were reported by several investigators.<sup>10–25</sup>

During studies<sup>26–31</sup> of binding interactions of salt ions and polymers according to the Huggins constant  $k'$ , the counterion size was found to affect the degree of binding for salt ion-attracting polymers,<sup>12–16,19,22–24,32</sup>

that is, “soft” salt anions and cations are more effective solubilizers than “hard” anions and cations.<sup>33,34</sup>

A series of poly(sulfobetaine)s and corresponding cationic polymers prepared by zwitterionic sulfobetaine and corresponding cationic monomers with different electron-withdrawing groups and by varying the methylene units between the charged groups were researched in our laboratory. The solution properties of 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 studies.<sup>22,25,34,35</sup> In the presence of salts or electrolytes in aqueous solution, because of inter- or intraionic interactions, the degree of polymeric chain extension or recoiling causes changes in viscosity (**Scheme 1**). The previous poly(DMAAPS) study concluded that soft salt anions and cations bound easily to the quaternary ammonium and sulfonate group of poly(DMAAPS).<sup>25</sup> Recently, our studies have focused on polyampholytes prepared from copolymers having high purity and similar structural characteristics such as styrene-*N,N*-dimethyl maleimido propyl ammonium propane sulfonate (SDMMAAPS)<sup>36</sup> copolymers or acrylamide-*N,N*-dimethyl maleimido propyl ammonium propane sulfonate (ADMMAPS)<sup>37</sup> copolymers. The properties of these ampholytic SDMMAPS or ADMMAPS copolymers in

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aqueous salt solution were studied by measurement of cloud point and intrinsic viscosity.<sup>36,37</sup>

Even though the tendencies, in terms of minimum salt concentration (msc) for solubilization and intrinsic viscosity for poly(SDMMAPS) in various aqueous salt solutions, were similar to those of other zwitterionic poly(sulfobetaine)s, the Huggins constant for poly(SDMMAPS) in aqueous salt solutions showed an extreme distinction from that for sulfobetaine homopolymers, poly(DMAAPS), or copolymer poly(ADMMAPS).<sup>34,35,37</sup> This phenomenon was mainly attributed to the presence of the styrene segment, a hydrophobic group, pendent to the SDMMAPS copolymer. The structures of the related sulfobetaines are shown in Figure 1.

The synthesis and msc of styrene-(*N,N*-dimethyl maleamic acid propyl ammonium propane sulfonate) copolymer [poly(SDMMAPS)] were reported in a previous study.<sup>38</sup> The investigation of the reduced viscosity and intrinsic viscosity for the present copolymer in various aqueous salt solutions is the main purpose of this study.

## EXPERIMENTAL

### Material

Styrene, *N,N*-dimethyl amino propyl amine (DMAPA), dimethyl sulfoxide (DMSO), methyl ethyl ketone (MEK), and propane sultone were used as received. Maleic anhydride (MA, mp 56°C) and azo-

bisobutyronitrile (AIBN) were purified by recrystallization in methanol. Methanol and acetone were distilled twice. Deionized water had a resistivity of 18 MΩ.

### Preparation of styrene and maleic anhydride copolymer (SMA)

The SMA copolymer was prepared as described in the previous study.<sup>38</sup> The yield was 98%. The polymer was analyzed by elemental analysis. ANAL. calcd for C<sub>12</sub>H<sub>10</sub>O<sub>3</sub> (MW 202): C, 71.28%, H, 4.98%, O, 23.74%. Found: C, 70.22%, H, 5.61%, O, 24.12%.

### Amidoacidation of SMA copolymer for preparing SDMAPMA

The styrene-*N,N*-dimethylaminopropyl maleamic acid (SDMAPMA) prepared through amidoacidation of SMA was reported in the previous study.<sup>38</sup> The yield was 85%. The product of SDMAPMA was analyzed by elemental analysis. ANAL. calcd for (C<sub>17</sub>H<sub>24</sub>O<sub>3</sub>N<sub>2</sub>): C, 67.10%, H, 7.89%, N, 9.21%. Found: C, 65.92%, H, 8.75%, N, 8.18%; amidoacidation degree = 88.8%.

### Preparation of poly(SDMMAPS)

The above polymeric amidic acid, SDMAPMA (4.5 g), was dissolved in 80 mL of DMSO at 80°C and stirred until it was completely dissolved. When the temperature cooled to 50°C, 2.3 g of propane sultone mixed with 30 mL DMSO was added dropwise for 1 h. After the addition was completed, the solution continued to react for 8 h, then was allowed to stand overnight. The precipitated viscous product was collected by filtration, then washed with methanol to remove propane sultone, and then dried under reduced pressure for 24 h to obtain the SDMMAPS copolymer product with 80% yield. The orange-yellow, hygroscopic product poly(SDMMAPS) was obtained and analyzed by elemental analysis. ANAL. calcd for [C<sub>20</sub>H<sub>30</sub>O<sub>6</sub>SN<sub>2</sub> (MW 426)]: C, 56.33%, H, 7.04%, N, 6.57%. Found: C, 57.64%, H, 7.42%, N, 5.78%; degree of quaternization = 87.9% (based on elemental analysis).

### Viscometric measurements

Viscometric measurements were carried out with an Ubbelohde viscometer (Cannon-Ubbelohde, State College, PA) having a flow time 72.89 s with deionized water (18 MΩ), at 30.00 ± 0.01°C. The polymer samples were dissolved in the salt solution and the polymer salt solution was adjusted to yield a stock solution

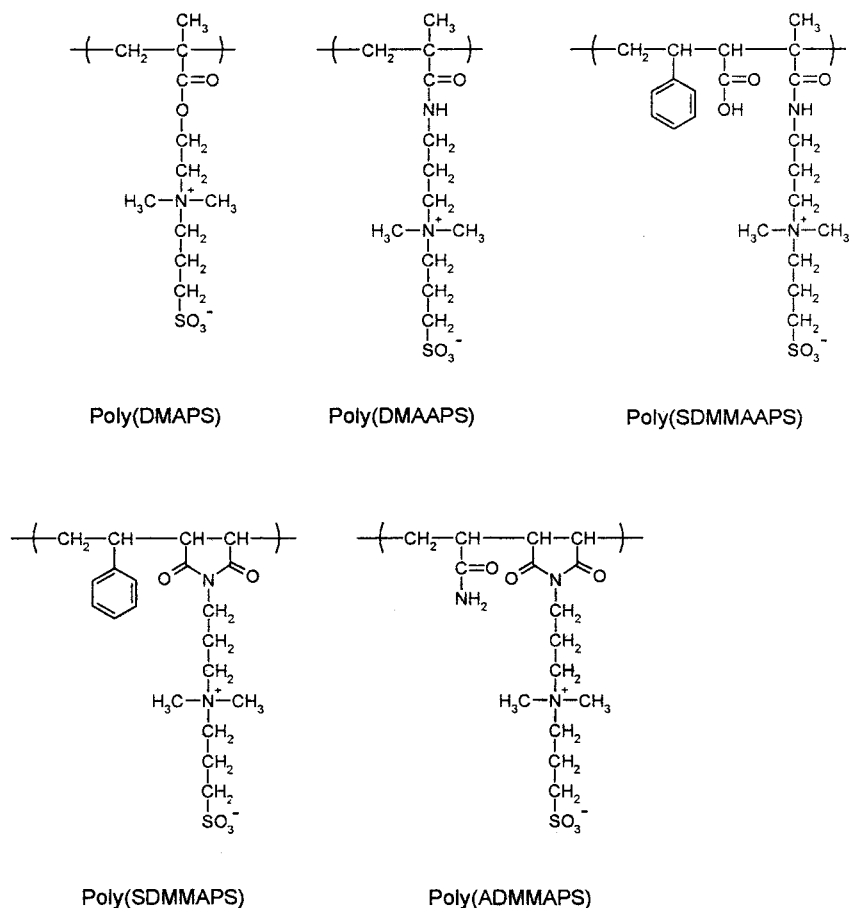


Figure 1 Structures of the related poly(sulfobetaine)s.

of approximately 0.3 g/dL solvent. Viscosity data were calculated with the Mark-Huggins equation:

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

where  $\eta_{sp}$  is the specific viscosity,  $C$  is the concentration of polymer,  $[\eta]$  is the intrinsic viscosity, and  $k'$  is the Huggins constant.

## RESULTS AND DISCUSSION

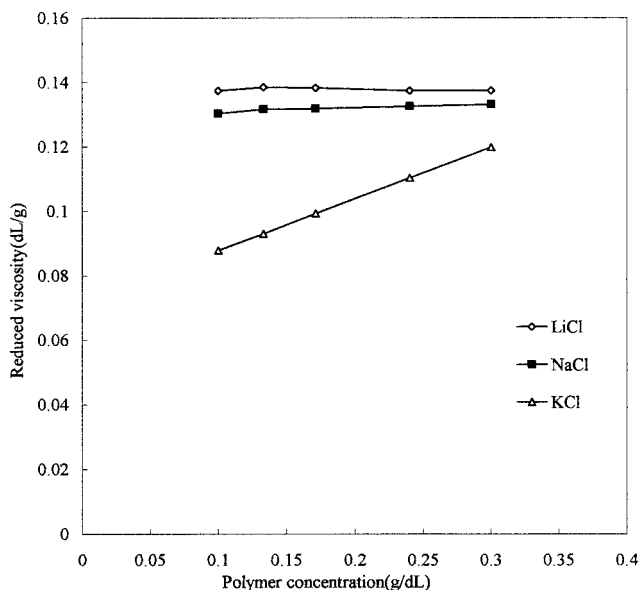
### Characterization of SMA, SDMAPMA, and SDMMMAAPS copolymers

SMA copolymer was confirmed by elemental analysis as an alternating copolymer.<sup>36</sup> The SMA copolymer had an average molecular weight ( $\bar{M}_v$ ) 87,000 determined using the Mark-Houwink equation,  $[\eta] = K\bar{M}_v^\alpha$ , where  $K = 3.98 \times 10^{-4}$  and  $\alpha = 0.596$ ,<sup>39</sup> at 25°C in tetrahydrofuran (THF). It was then converted to SDMAPMA and SDMMMAAPS. The characteristic absorption peaks of IR spectra are 1856, 1779, 1224, 800–600; 3600–2400, 1725, 1640–1550; and 1183, 1042  $\text{cm}^{-1}$  for SMA, SDMAPMA, and SDMMMAAPS, respectively.<sup>38</sup>

### Viscosity measurement

Polyampholytes are a class of polymers containing positive and negative charges on the same macromolecular chain. Higher intrinsic viscosities, observed with increasing solution ionic strength, are related to the type and concentration of the added salt. Poly(SDMMMAAPS) copolymer is an ampholytic copolymer behaving as an ionically crosslinked network in water or low concentration of salt in the solution. Schulz et al.<sup>17</sup> reported that these intramolecular aggregates are of both the intragroup and intrachain type. The intramolecular aggregates are broken up by external electrolytes (e.g., NaCl), with a consequent modest expansion of the polymer coil. This occurrence results in an increase of intrinsic viscosity (see **Scheme 1**).

The intrinsic viscosity is a good measure of the hydrodynamic volume of polymers. When salts are added to the SDMMMAAPS aqueous solutions to make the polymer dissolve, the polymeric chain expands. Therefore, the determination of the intrinsic viscosity of the SDMMMAAPS copolymer in the presence of different electrolytes reflects the influence of these salts on the hydrodynamic volume of the polymer chain.

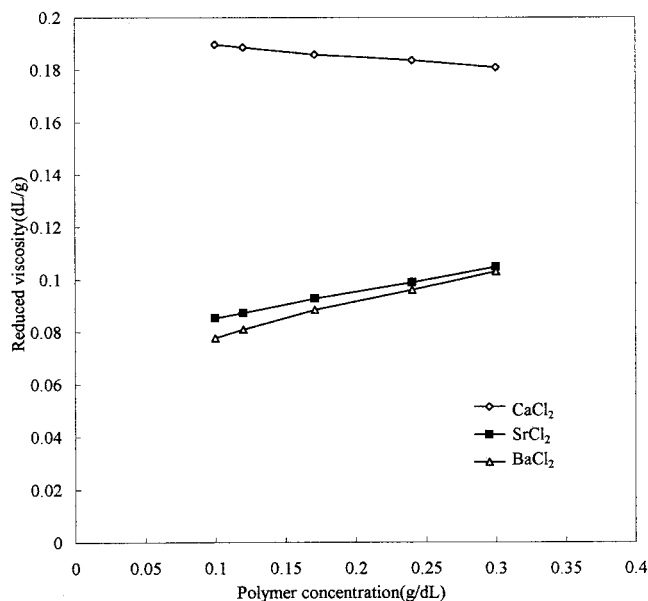


**Figure 2** Reduced viscosity of poly(SDMMAAPS) as a function of polymer concentration in 0.5M aqueous solution of salts with various monovalent cations.

To study this effect, the intrinsic viscosity was measured in various aqueous salt solutions.

#### Influence of cations with common anion ( $\text{Cl}^-$ ) on the intrinsic viscosity of the SDMMAAPS copolymer

The influence of various electrolytes having a common anion ( $\text{Cl}^-$ ), on the intrinsic viscosity of the SDMMAAPS copolymer, is shown in Figures 2 and 3 and Table I. The intrinsic viscosity of this copolymer in the aqueous salt solutions (0.5M) decreases in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  for LiCl, NaCl, and KCl; and  $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$  for  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ , and  $\text{BaCl}_2$ , respectively. This phenomenon conforms to the results of the msc determinations reported in a previous study.<sup>38</sup> However, this result is different from that obtained with poly(DMAPS),<sup>25</sup> poly(DMAAPS),<sup>34,35</sup> poly(SDMMAAPS),<sup>36</sup> and poly(ADMMAAPS).<sup>37</sup> In general, the ions with a lower charge density ( $\text{K}^+$ ) easily approach the sulfobetaine groups and disrupt the ionically crosslinked network with the trend in the order of  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$  for LiCl, NaCl, and KCl; and  $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$  for  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ , and  $\text{BaCl}_2$ , respectively (site-binding effect); however, the Pearson's principle<sup>40</sup> also happens in this system. That is, the  $-\text{COO}^-$  from  $-\text{COOH}$  side groups of poly(SDMMAAPS) is a hard base preferring to bind with a hard acid such as  $\text{Li}^+$  (or  $\text{Ca}^{2+}$ ), which has a small radius: the smaller the radius of the cation ionized from the salts containing various mono- or divalent cations, the stronger the binding ability on  $-\text{COOH}$ . This action makes the  $-\text{COOH}$  side group transform into a  $-\text{COO}^-$  group,



**Figure 3** Reduced viscosity of poly(SDMMAAPS) as a function of polymer concentration in 0.5M aqueous solution of salts with various divalent cations.

which produces a strong electrostatic repulsive force to make polymer chains fully expand according to the decreasing order of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  and  $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$  for LiCl, NaCl, and KCl; and  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ , and  $\text{BaCl}_2$ , respectively ( $\text{H}^+$ -abstraction effect). This effect is predominant in contrast to that of the ion-binding site on the sulfonate group ( $\text{SO}_3^-$ ) [or the quaternary ammonium group ( $\text{R}_4\text{N}^+$ ) of poly(SDMMAAPS)], which reduces the likelihood of abstracting  $\text{H}^+$  from the  $-\text{COOH}$  side group.

The Huggins constants  $k'$ , calculated from Figures 2 and 3 and eq. (1) (results shown in Table I), increase with a decrease in the intrinsic viscosity and are positive. This tendency is different from that observed from SDMMAPS, which also has a styrene segment in the polymer chain, although the Huggins constants of poly(SDMMAAPS) were negative.<sup>36</sup> This interesting property may be attributed to interactions between the

**TABLE I**  
Effect of Various Monovalent Cations and Divalent Cations on the Viscosity Behavior of Poly(SDMMAAPS) at 30°C

Salt solution (0.5M)	Slope	$[\eta]$	$k'$	$R^2$
LiCl	0.00	0.14	-0.14	— <sup>a</sup>
NaCl	0.01	0.13	0.72	0.87
KCl	0.16	0.07	31.3	1.00
$\text{CaCl}_2$	-0.04	0.19	-1.13	0.99
$\text{SrCl}_2$	0.10	0.08	17.0	1.00
$\text{BaCl}_2$	0.13	0.07	29.0	1.00

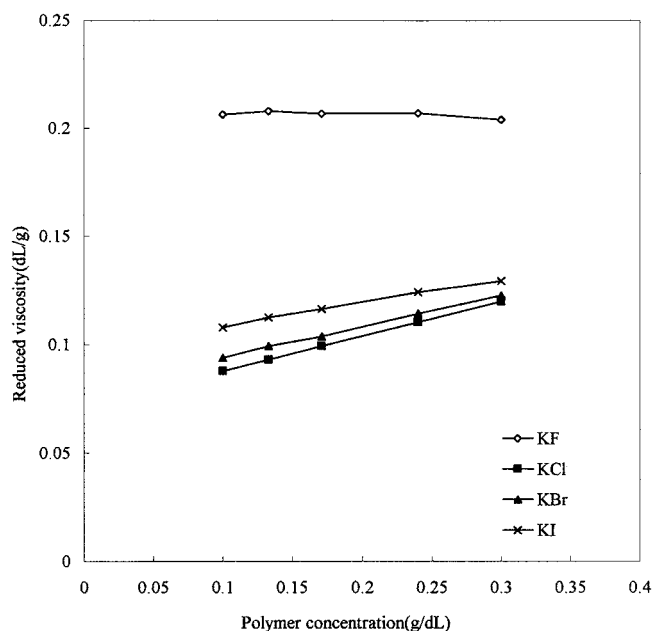
<sup>a</sup> Denotes the reduced viscosity not affected by the salt concentration.



styrene segment (which is hydrophobic) and the carboxylic side group (which is hydrophilic) in the poly(SDMMAAPS) copolymers. This hydrophobic-hydrophilic property induces the polymeric chain to coil like a surfactant micellar structure in aqueous solutions, with the hydrophilic DMMAAPS units located toward the outside layers of the micelles. This would make the Huggins constant increase because the interactions between the DMMAAPS units would be increased.

#### Influence of halide anions with a common cation ( $K^+$ ) on the intrinsic viscosity of SDMMAAPS

The intrinsic viscosities of SDMMAAPS, under the influence of various anions with a common cation ( $K^+$ ), are shown in Figure 4 and Table II. The intrinsic viscosity in aqueous solution (0.5M) increases in the order  $Cl^- < Br^- < I^- < F^-$  for KCl, KBr, KI, and KF, respectively. This tendency also conforms to the result of the msc reported in a previous study<sup>38</sup> and the results obtained for poly(SDMMAAPS).<sup>36</sup> The reason is that the ions with lower charge densities such as  $I^-$  are more easily polarized as they approach the quaternary ammonium group ( $R_4N^+$ ) on the DMMAAPS unit and become more easily site-bound. This site-binding effect on the sulfobetaine group of poly(SDMMAAPS) becomes predominant in contrast to the  $H^+$ -abstraction effect, making the carboxylic side group ionize into an anionic carboxylate polyelectrolyte. The intrinsic viscosity thus increases as the degree of salt ion binding to the DMMAAPS unit increases ( $Cl^- < Br^-$



**Figure 4** Reduced viscosity of poly(SDMMAAPS) as a function of polymer concentration in 0.5M aqueous solution of salts with various halide anions.

**TABLE II**  
Effect of Various Halide Anions and Acid Groups on the Viscosity Behavior of Poly(SDMMAAPS) at 30°C

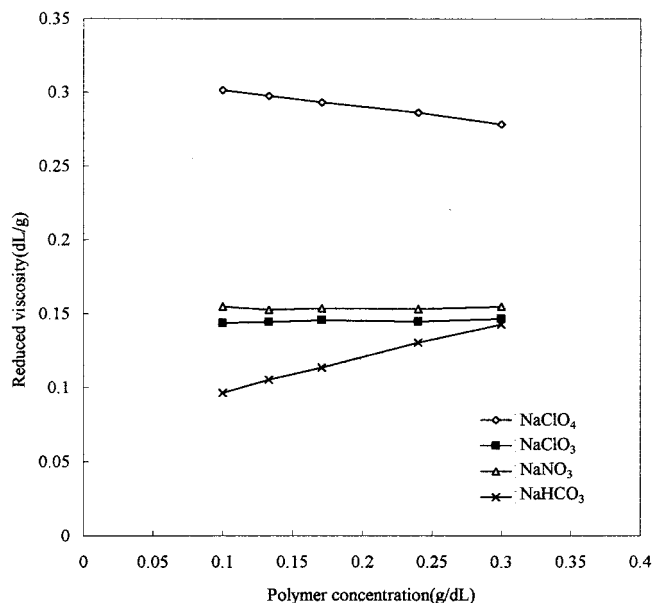
Salt solution (0.5M)	Slope	$[\eta]$	$k'$	$R^2$
KF	-0.01	0.21	-0.28	— <sup>a</sup>
KCl	0.16	0.07	31.3	1.00
KBr	0.14	0.08	22.6	1.00
KI	0.11	0.10	11.1	0.99
NaClO <sub>4</sub>	-0.11	0.31	-1.16	1.00
NaClO <sub>3</sub>	0.01	0.14	0.54	— <sup>a</sup>
NaNO <sub>3</sub>	0.11	0.10	11.8	— <sup>a</sup>
NaHCO <sub>3</sub>	0.23	0.07	42.3	1.00
Na <sub>2</sub> CO <sub>3</sub>	-0.23	0.30	-2.64	1.00
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	-0.09	0.23	-1.65	1.00
Na <sub>2</sub> SO <sub>3</sub>	-0.04	0.16	-1.49	— <sup>a</sup>
Na <sub>2</sub> SO <sub>4</sub>	0.01	0.10	0.91	— <sup>a</sup>

<sup>a</sup> Denotes the reduced viscosity not affected by the salt concentration.

$< I^-$ ). The fluoride ion, however, is very small and is a strong hard base, and is therefore not easily polarized. The  $F^-$  ion thus has no capability of site-binding on the sulfobetaine group to open the inner salt ring of poly(SDMMAAPS) but strongly attracts  $H^+$  from  $-COOH$  side groups and causes the  $-COOH$  side group to totally transform into the  $-COO^-$  group, which produces electrostatic repulsive force to lead to full expansion of the polymer chain in aqueous salt solution. Therefore, the  $F^-$  anion effects a greater apparent intrinsic viscosity of poly(SDMMAAPS) than that of any other halide anions in aqueous salt solution (strong anionic polyelectrolyte effect). The Huggins constants (shown in Table II) decrease with an increase of the intrinsic viscosity. This phenomenon is consistent with that observed from ADMMAAPS,<sup>37</sup> which contains a hydrophilic acrylamide segment in the polymer chain unit, but differs from SDMMAPS,<sup>36</sup> which contains a hydrophobic styrene segment in the polymer chain unit. This result is also similar to that found in the msc determinations.<sup>38</sup>

#### Influence of various acid groups with a common cation ( $Na^+$ ) on the intrinsic viscosity of SDMMAAPS

The intrinsic viscosities of SDMMAAPS in the presence of various monovalent acid groups with a common cation ( $Na^+$ ) are shown in Figure 5 and Table II. The intrinsic viscosity of SDMMAAPS copolymer in aqueous solution (0.5M) decreases in the order  $ClO_4^- > NO_3^- > ClO_3^- > HCO_3^-$  for NaClO<sub>4</sub>, NaNO<sub>3</sub>, NaClO<sub>3</sub>, and NaHCO<sub>3</sub>, respectively. This is because the monovalent acidic groups possessing very low charge density are easily polarized to pull much closer to side-chain groups of  $R_4N^+$  and COOH of inter- and intramolecular aggregates of poly(SDMMAAPS). This allows the copolymer to bind together to produce a



**Figure 5** Reduced viscosity of poly(SDMMAAPS) as a function of polymer concentration in 0.5M aqueous solution of salts with various monovalent acid groups.

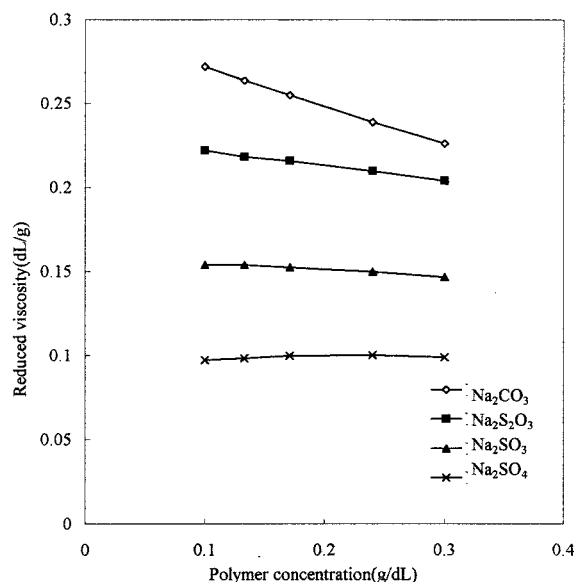
new ring of  $\text{NR}_4^+ - \text{COO}^-$ , which is characterized by a polyampholyte structure that behaves like a polycarboxybetaine. At the same time, the copolymer structure transforms into a strong anionic sulfonate ( $\text{SO}_3\text{H}$ ) polyelectrolyte that dissociates to produce electrostatic repulsive forces, resulting in full expansion of the polymer chain in aqueous salt solution. Based on this action, the  $\text{ClO}_4^-$  anion leads to the largest intrinsic viscosity for poly(SDMMAAPS) than for any other monovalent acid group in aqueous salt solution. The data in Table II indicate that the intrinsic viscosity decreases in the order  $\text{NO}_3^- > \text{ClO}_3^-$  for  $\text{NaNO}_3$  and  $\text{NaClO}_3$ , respectively. This tendency conforms to that obtained from the msc determination. Therefore, this result indicates that no structural transformation occurs under the influence of  $\text{NaNO}_3$  and  $\text{NaClO}_3$ , although the charge density of  $\text{NO}_3^-$  is smaller than that of  $\text{ClO}_3^-$ .

However, because of coupling with the  $-\text{COOH}$  side group, the  $\text{HCO}_3^-$  anion loses the ability to make the carboxylic side group ionize into an anionic carboxylate polyelectrolyte and keeps the ability of site-binding on the sulfobetaine group to open the inner salt ring of poly(SDMMAAPS); however, this site-binding effect is very small. Hence, the  $\text{HCO}_3^-$  anion causes poly(SDMMAAPS) to have the smallest intrinsic viscosity among the other monovalent acid groups in aqueous salt solution.

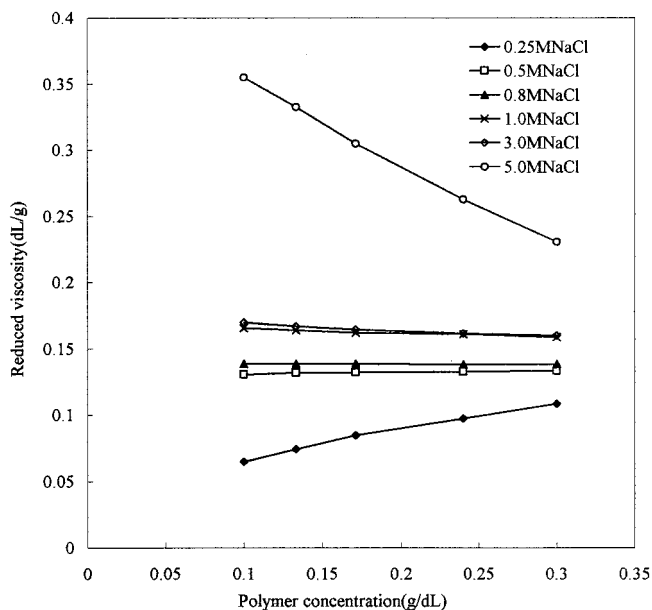
The intrinsic viscosities of SDMMMAAPS, under the influence of various divalent acid groups with a common cation ( $\text{Na}^+$ ), are shown in Figure 6 and Table II. The intrinsic viscosity in aqueous solution (0.5M) decreases in the order  $\text{CO}_3^{2-} > \text{S}_2\text{O}_3^{2-} > \text{SO}_3^{2-} > \text{SO}_4^{2-}$  for

$\text{NaCO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{NaSO}_3$ , and  $\text{NaSO}_4$ , respectively. This tendency also conforms to that obtained in the msc determination. Because both  $\text{CO}_3^{2-}$  and  $\text{SO}_3^{2-}$  are hard bases, and easily abstract  $\text{H}^+$  from  $-\text{COOH}$  side groups, and  $\text{SO}_3^{2-}$  has a smaller charge density than that of  $\text{CO}_3^{2-}$ ,  $\text{CO}_3^{2-}$  has a greater effect than that of  $\text{SO}_3^{2-}$  on intrinsic viscosity. This phenomenon indicates that the influence of  $\text{H}^+$ -abstraction to make the carboxylic side group ionize into an anionic carboxylate polyelectrolyte is much greater than that of site-binding on the sulfobetaine group to open the inner salt ring of poly(SDMMAAPS). However,  $\text{S}_2\text{O}_3^{2-}$  is a soft base relative to  $\text{CO}_3^{2-}$  and  $\text{SO}_3^{2-}$  and easily binds to the quaternary ammonium group ( $\text{R}_4\text{N}^+$ ) of poly(SDMMAAPS). This site-binding effect becomes predominant, in contrast to the effect of  $\text{H}^+$ -abstraction, to make the carboxylic side group ionize into an anionic carboxylate polyelectrolyte. Therefore,  $\text{S}_2\text{O}_3^{2-}$  has a lesser influence than that of  $\text{SO}_3^{2-}$  on intrinsic viscosity. As for  $\text{SO}_4^{2-}$ , it is necessary to draw a balance between two factors where  $\text{SO}_4^{2-}$  attracts sulfobetaine groups to open the inner salt ring of poly(SDMMAAPS) and at the same time abstracts  $\text{H}^+$  from the  $-\text{COOH}$  side groups to reduce the degree of site-binding on the sulfobetaine groups; therefore  $\text{SO}_4^{2-}$  has the smallest effect on the intrinsic viscosity of poly(SDMMAAPS).

In other words electrostatic repulsive forces, resulting in expansion of the polymer chain in aqueous salt solution, makes the effect of  $\text{H}^+$ -abstraction from the  $-\text{COOH}$  side group play a more important role in the intrinsic viscosity determination than the effect of site-binding on the sulfobetaine group to open the inner salt ring formed by charge neutralization.



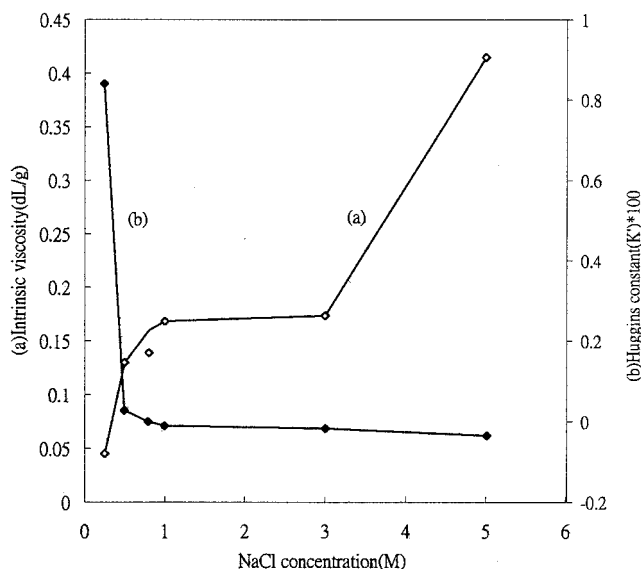
**Figure 6** Reduced viscosity of poly(SDMMAAPS) as a function of polymer concentration in 0.5M aqueous solution of salts with various divalent acid groups.



**Figure 7** Reduced viscosity of poly(SDMMAAPS) as a function of various concentration of NaCl.

#### Effect of NaCl concentration on the intrinsic viscosity of the SDMMAAPS copolymer

The effect of various concentrations of NaCl from 0.25 to 5.0M on the reduced viscosity and intrinsic viscosity of the poly(SDMMAAPS) copolymer is illustrated in Figures 7 and 8, respectively. There is a significant increase in the reduced viscosity and intrinsic viscosity with an increase of the NaCl concentration. According to Figure 7 and Table III, the degree of salt ions binding to the DMMAAPS unit increases with



**Figure 8** Intrinsic viscosity (a) and Huggins constant (b) of SDMMAAPS copolymer as a function of various concentrations of NaCl.

**TABLE III**  
Effect of NaCl Concentrations on the Intrinsic Viscosity and Huggins Constant of Poly(SDMMAAPS) at 30°C

NaCl (M)	Slope	$[\eta]$	$k' \times 10^2$	$R^2$
0.25	0.21	0.05	1.07	0.99
0.50	0.01	0.06	0.50	0.87
0.80	0.00	0.14	-0.00	— <sup>a</sup>
1.00	-0.03	0.17	-0.02	0.97
3.00	-0.05	0.17	-0.02	0.96
5.00	-0.62	0.42	-0.04	1.00

<sup>a</sup> Denotes the reduced viscosity not affected by the salt concentration.

increasing concentration of salt in the low-concentration region, that is, the amount of sodium ions binding to the sulfonate groups and chloride ions binding to the quaternary ammonium groups increases at low concentrations of salt (0.25–1.0M). When the concentration of salt is increased to 1.0M, increasingly more of the potential binding sites are occupied, resulting in decreased binding ability.<sup>25–31</sup> The reason is that the polymer and solvent interact until the concentration of NaCl approaches 1.0M. At this concentration, the binding sites are increasingly occupied and form a region of high charge local density. This concentration-induced binding saturation effect was also observed for other poly(sulfobetaine)s in aqueous salt solutions in previous studies.<sup>34–37</sup>

Meanwhile, although poly(SDMMAAPS) has styrene segments in the polymer chain unit, the Huggins constant (as shown in Fig. 8 and Table III) decreases from positive to negative as the intrinsic viscosity increases, which means the polymer–polymer interactions decrease with an increase in intrinsic viscosity at higher salt concentrations. The Huggins constants are extremely large and positive in dilute salt solutions. This phenomenon is consistent with poly(DMAAPS) and poly(DMAAPS) but different from poly(SDMMAAPS), which also has styrene segments in the polymer chain. The Huggins constants for poly(SDMMAAPS) were extremely large and negative in dilute polymer solutions. This interesting property is mainly attributed to the balance between the styrene segment, which is hydrophobic, and the carboxylic side group (–COOH), which is hydrophilic in the poly(SDMMAAPS) copolymer unit. This hydrophobic–hydrophilic balance causes the polymeric chain to have a surfactant-like micellar structure in aqueous solutions, with the poly(SDMMAAPS) hydrophilic units located toward the outside layers of the micelles (**Scheme 2**). This structure is much like that of SDMMAPS because poly(SDMMAAPS) easily foams when it is stirred in aqueous salt solution.

The viscosity measurements are consistent with a model for poly(SDMMAAPS) copolymer where the chains are intramolecularly associated in dilute salt





dilute polymeric salt solutions, which means that the polymer-polymer interactions decrease with increasing intrinsic viscosity and salt concentration. This phenomenon is consistent with poly(DMAPS) and poly(DMAAPS), but different from poly(SDMMAPS), which also contains styrene segments in the polymer chain and possesses negative Huggins constants in dilute polymeric salt solutions. The intrinsic viscosity increases as the salt concentration is increased until the concentration for binding saturation of the salt is reached.

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## References

- Rohm and Hass Co. Br. Pat. 1,077,772, 1967.
- Bahr, U.; Wieden, H.; Rinkler, H. A.; Nischk, G. E. *Makromol Chem* 1972, 1, 161.
- Szita, J.; Bahr, U.; Wieden, H.; Marzolph, H.; Nischk, G. E. Belg. Pat. 659,316, 1965 and Amended, Br. Pat. 1,024,029, 1966.
- Spriestersbach, D. R.; Clarke, R. A.; Couper, M.; Patterson, H. T. U.S. Pat. 3,473,998, 1969.
- Ishikura, S.; Mizuguchi, R.; Takahashi, A. *Jpn. Kokai Tokkyo Koho* 80,386 and 80,387, 1977.
- Thomson, E.; Parks, E.; Allan, K. Eur. Pat. Appl. EP 209337, 1987.
- Hagen, J.; Bischoff, M.; Heing, W. Eur. Pat. Appl. EP 72,509, 1983.
- Ohme, R.; Rusche, R. J.; Seibt, J. H. Eur. Pat. Appl. EP 205,625, 1986.
- Seibt, H.; Ballschuk, D.; Ohme, R.; Zastrow, L. Ger. (East) DD 286,178, 1991.
- Ladenheim, H.; Morawetz, H. *J. Polym Sci* 1957, 26, 251.
- Hart, R.; Timmerman, D. *J Polym Sci* 1958, 28, 638.
- Salamone, J. C.; Volkson, W.; Raia, S. C. D. C.; Broggi, A.; Hsu, T. D. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1973, 14, 731.
- Salamone, J. C.; Volkson, W.; Israel, S. C.; Olson, A. P.; Raia, D. C. *Polymer* 1977, 18, 1058.
- Salamone, J. C.; Volkson, W.; Olson, A. P.; Israel, S. C. *Polymer* 1978, 19, 1157.
- Monroy Soto, V. M.; Galin, J. C. *Polymer* 1984, 25, 121, 254.
- Galin, M.; Marchal, E.; Mathis, A.; Meurer, B.; Monroy Soto, V. M.; Galin, J. C. *Polymer* 1987, 28, 1937.
- Schulz, D. N.; Kitano, K.; Danik, J. A.; Kaladas, J. J. In: *Polymers in Aqueous Media*; Glass, J. E., Ed.; *Advances in Chemistry Series 223*; American Chemical Society: Washington, DC, 1989; p. 165.
- Asonova, T. A.; Razvodovskii, Ye. F.; Zezin, A. B.; Kargin, V. A. *Dokl Akad Nauk SSSR* 1969, 118, 583.
- Asonova, T. A.; Razvodovskii, Ye. F.; Zezin, A. B. *Vysokomol Soyed* 1974, A 16, 777.
- Topchiev, D. A.; Mkrtchyan, L. A.; Simonyan, R. A.; Lachinov, M. B.; Kabanov, R. A. *Vysokomol Soyed* 1977, A19, 506.
- Laschewsky, A.; Zerbe, I. *Polymer* 1991, 32, 2070, 2081.
- Liaw, D. J.; Lee, W. F.; Whung, Y. C.; Lin, M. C. *J Appl Polym Sci* 1987, 34, 999.
- Itoh, Y.; Abe, K.; Senoh, S. *Makromol Chem* 1986, 187, 1691.
- Newman, J. K.; McCormick, C. L. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1992, 33, 1929.
- Lee, W. F.; Tsai, C. C. *Polymer* 1994, 35, 2210.
- Huggins, M. L. *J Am Chem Soc* 1942, 64, 2716.
- Sakai, T. *J Polym Sci* 1968, A-2, 1535.
- Liaw, D. J.; Shiau, S. J.; Lee, K. R. *J Appl Polym Sci* 1992, 45, 61.
- Strauss, U. P.; Leung, Y. *J Am Chem Soc* 1965, 1476.
- Tan, J. S.; Marcus, P. R. *J Polym Sci Polym Phys Ed* 1976, 14, 239.
- Osawa, F.; Imai, N.; Kagawa, I. *J Polym Sci* 1954, XIII, 93.
- Kagawa, I.; Gregor, H. P. *J Polym Sci* 1957, XXIII, 477.
- Schulz, D. N.; Peiffer, D. G.; Agarwal, P. K.; Larabee, J.; Kaladas, J. J.; Soni, L.; Handwerker, B.; Garner, R. T. *Polymer* 1986, 27, 1734.
- Lee, W. F.; Tsai, C. C. *Polymer* 1995, 36, 357.
- Lee, W. F.; Tsai, C. C. *J Appl Polym Sci* 1994, 52, 1447.
- Lee, W. F.; Lee, C. H. *Polymer* 1997, 38, 971.
- Lee, W. F.; Hwong, G. Y. *Polymer* 1996, 37, 4389.
- Lee, W. F.; Chen, Y. M. *J Appl Polym Sci* 2003, 89, 1884.
- Chow, C. D. *J Appl Polym Sci* 1976, 20, 1619.
- Huheey, J. E. *Inorganic Chemistry*; Harper and Row: New York, 1972.