

Polysulfobetaines and Corresponding Cationic Polymers. IV. Synthesis and Aqueous Solution Properties of Cationic Poly(MIQSDMAPM)

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SYNOPSIS

A cationic poly(methyl iodide quaternized styrene–dimethylaminopropylmaleimide) copolymer [poly(MIQSDMAPM)] was synthesized by imidizing styrene–maleic anhydride (SMA) copolymer. Its aqueous solution properties were studied by measurements of reduced viscosity, intrinsic viscosity, and a flocculation test. The reduced viscosity and intrinsic viscosity of this cationic polyelectrolyte were related to the types and concentration of the added salt. “Soft” salt anions were more easily bound to the quaternary ammonium cation (R_4N^+) of poly(MIQSDMAPM) than “hard” salt anions. Halide anions are hard anions; consequently, hard cations were more easily attracted to halide anions, and reduced the binding degree of halide anion on the quaternary ammonium group (R_4N^+). Some salt ions were observed to strongly attract the quaternary ammonium group of the cationic polymeric side chain and resulted in agglomeration of the polymers. A comparison of various flocculants as to the effect of flocculation was made in this study. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Cationic quaternary polyelectrolytes have been widely used in the adhesive, coating, textile, hair conditioner, flocculant, and other related industries.^{1–7} The functional groups on the side chain of the cationic polymers are usually ammonium (primary, secondary, tertiary, and quaternary amines), sulfonium, or phosphonium groups.⁸ These cationic monomers with quaternary ammonium groups are usually the quaternary ammonium group sites on the polymeric side chain.^{8–18} For example, Salamone et al. reported the synthesis of vinylimidazolium salts and their polymeric aqueous solution properties.^{9,10} The synthesis, aqueous solution properties, and application of cationic polyelectrolytes derived from acrylates were also recently reported.^{11–18} The effect of various salt ions on the interaction of polyelectrolytes in the aqueous solution was investigated and the site-binding interaction of salt ions and polymer using Huggins constant k' was also inves-

tigated.^{19–33} The counterion size was found to affect the degree of side binding for salt ion attracting polymers.

The cationic polyelectrolytes derived from styrene–maleic anhydride (SMA) copolymer were reported by Isaacson and Young³⁴ and Pratt et al.⁷ Isaacson and Young reacted SMA copolymer with dimethylaminopropylamine and subsequently quaternized the dimethylamino group to yield a polyquaternary salt proposed as a flocculant for oil slicks. Pratt et al.⁷ proposed this polyquaternary ammonium salt to flocculate an aqueous suspension of solid inorganic particles.

Synthesis and aqueous solution properties of poly[(trimethyl acrylamidopropyl) 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 articles.^{32,33,35,36} The previous poly(DMAAPS) article concluded that soft salt anions and cations are more effective solubilizers than hard salt anions and cations,³³ but the poly(TMAAI) article showed that soft salt anions were more easily bound on the quaternary am-

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monium (R₄N⁺) of poly(TMAAI) than those of hard salt anions.³⁶ The synthesis and dilute aqueous solution properties of styrene-*N,N'*-dimethylmaleiminopropyl ammonium propane sulfonate (SDMMAPS) copolymer were studied in our laboratory.³⁷ Investigations of aqueous solution properties for corresponding cationic copolymer, methyl iodide quaternized styrene-dimethylaminopropylmaleimide (MIQSDMAPM) copolymer, especially the intrinsic viscosity in the presence of various salts, are the main interest in this article. Finally, the cationic polyelectrolyte is applied in the flocculation test of a bentonite sol system.

EXPERIMENTAL

Preparation of SMA Copolymer

A 0.25-L volume flask was equipped with a stirrer, a cooler, and a thermometer. Styrene (7.727 g), maleic anhydride (7.273 g), and methyl ethyl ketone (MEK, 50 mL) were added. The contents were stirred at 80°C for complete dissolution. To the solution α,α' -azobisisobutyronitrile (AIBN, 0.1 wt %) as an initiator was added and the solution was stirred at the same temperature for 5.5 h. The product was precipitated with diethyl ether and dried for 24 h at 80°C under vacuum to remove MEK, washed with dry diethyl ether several times, and dried under reduced pressure to obtain SMA copolymer. The polymer was analyzed by elemental analysis.

ANAL. Calcd for C₁₂H₁₀O₃: C, 71.28%; H, 4.98%; O, 23.74%. Found: C, 70.78%; H, 5.04%; O, 24.18%.

Imidization of SMA Copolymer

Five grams of a SMA copolymer having a viscosity average molecular weight of about 390,000 were slurried with 20 mL of *N,N*-dimethylformamide (DMF) at 80°C until the resin particles were completely dissolved in DMF, and then 15 g of 3-dimethylaminopropylamine was added dropwise for 1 h. Heat was applied gradually until the addition was completed, and the solution was stirred under gentle reflux for 1 h and then subjected to distillation until the reaction product reached 200°C. The product was precipitated with distilled water, and then a 300 mm Hg vacuum was applied to remove the last traces of free amine. The product styrene-dimethylaminopropylmaleimide (SDMAPM) was subject to elemental analysis.

ANAL. Calcd for C₁₁H₁₇O₂N₂: C, 71.26%; H, 7.74%; N, 9.78%. Found: C, 70.84%; H, 7.72%; N, 9.19%. Imidization degree = 91.63 (mol %).

Preparation of MIQSDMAPM

The polymeric imide SDMAPM (3.77 g) was dissolved in 50 mL of distilled acetone and treated with liquid methyl iodide (2.7 g) in an ice bath for 2 h. To prevent excessive loss of methyl iodide, a condenser was used to return liquid methyl iodide to the reaction medium. The mixture was stirred at 10°C overnight. Then the yellow solution was removed by filtration before the precipitated product was washed with dry acetone several times and dried under darkness and reduced pressure for 24 h. The quaternary ammonium salt MIQSDMAPM was obtained and analyzed by elemental analysis.

ANAL. Calcd for C₁₂H₂₀O₂N₂I: C, 51.29%; H, 5.86%; N, 6.53%. Found: C, 51.12%; H, 6.55%; N, 5.88%. Degree of quaternization = 90.96 (mol %).

Viscometric Measurements

Viscometric measurements were carried out with an Ubbelohde viscometer, which has a flow time of 72 s with deionized water (18 M Ω), at 30.00 \pm 0.01°C. The polymer samples were dissolved in the salt solution and the polymer salt solution was adjusted to yield a stock solution of approximately 0.08 g/25 mL solvent. Viscosity data were calculated with the Mark-Huggins equation

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

Flocculation Measurement

The extent of flocculation was determined by measuring the transmittance of the supernatant. The tests, termed jar tests, were carried out in 1-L graduate cylinders (the basal area and height of the cylinders for every flocculation test are the same). Different concentrations of bentonite solution (1 L) were added to the cylinder. A stirring bar was vertically inserted into the cylinder, and the solution was stirred at a constant speed of about 150 rpm. Varying amounts of different flocculants were added to the cylinder, and the solution was then stirred for 10 min. Once the solution had remained undisturbed for 10 min, the sludge volume was tested and the turbidity of upper limpid aqueous solution was measured with an Orbeco-Hellige Series 965 Digital Di-

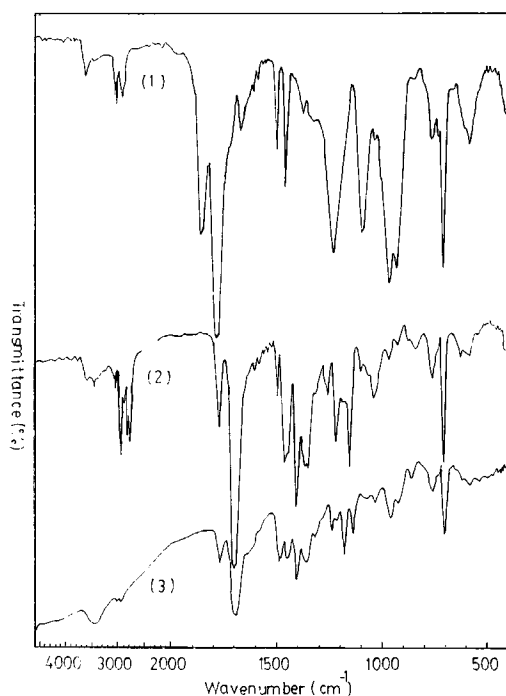


Figure 1 IR spectra of SMA(1), SDMAPM(2), and MIQSDMAPM(3) copolymers.

positive charges because the iodide ions became ionized in an aqueous solution. In this situation, the behavior of reduced viscosity exhibited a typical plot in pure water as shown in Figure 2(a). This result shows that the reduced viscosity in a higher concentration region decreases with an increase in polymeric concentration due to the interaction of the polymer chain. After a maximum at the concentration (C) of 0.1 g/dL is reached, the reduced viscosity then decreases. These phenomena were also observed by Salamone et al.^{9,10} and Eisenberg and Pouyet¹¹ to be true with various polyelectrolytes. As shown by plotting of reciprocal reduced viscosity versus square root of polymeric concentration [Fig. 2(b)], the concentration dependence of the reduced viscosity conforms to the Fuoss equation $\eta_{sp}/C = A / (1 + B\sqrt{C})$, where A corresponds to intrinsic viscosity $[\eta]$, B is a constant related to an interaction of counterions with polyion, and C is polymeric concentration in the lower polymeric concentration region.

Effect of Various Salts on Intrinsic Viscosity of Poly(MIQSDMAPM) in Aqueous Solution

The addition of salt to the aqueous solution of polyelectrolyte causes the polymeric chain to contract and decreases the intrinsic viscosity as mentioned

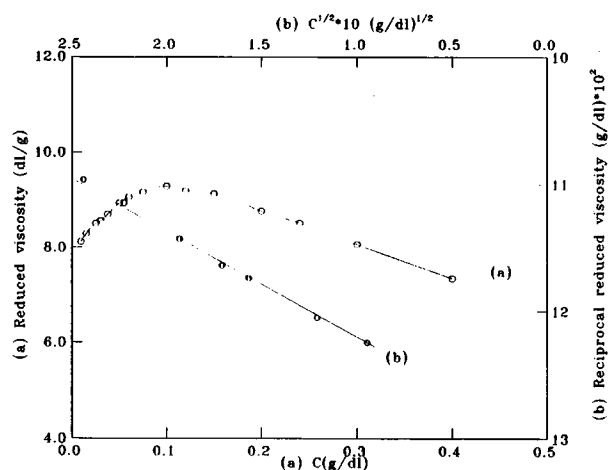


Figure 2 Reduced viscosity of poly(MIQSDMAPM) in water. (a) Dependence of reduced viscosity on polymer concentration. (b) Dependence of reciprocal reduced viscosity on square root of polymer concentration.

above. Investigation of the influence of various salts on this effect and interpretation of charged neutralization and Pearson theory will therefore be presented in the following section.

Influence of Different Cations with a Common Anion (Cl^-) on Intrinsic Viscosity of Poly(MIQSDMAPM)

The intrinsic viscosity $[\eta]$ and Huggins constant k' can be calculated from Figures 3 and 4, and eq. (1).

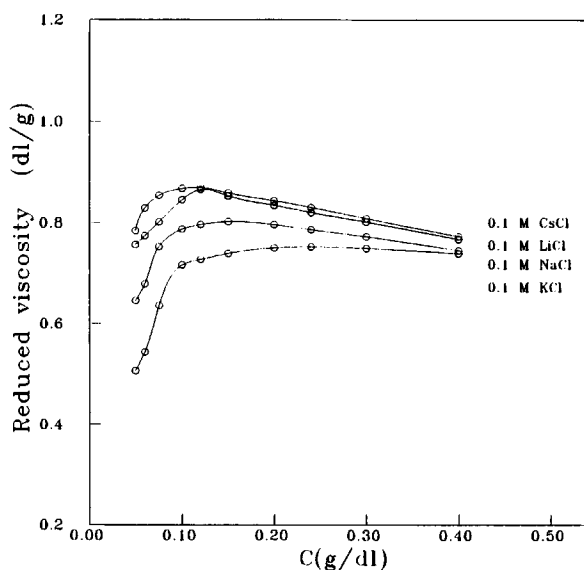


Figure 3 Reduced viscosity of poly(MIQSDMAPM) as a function of concentration for salts containing a common anion.

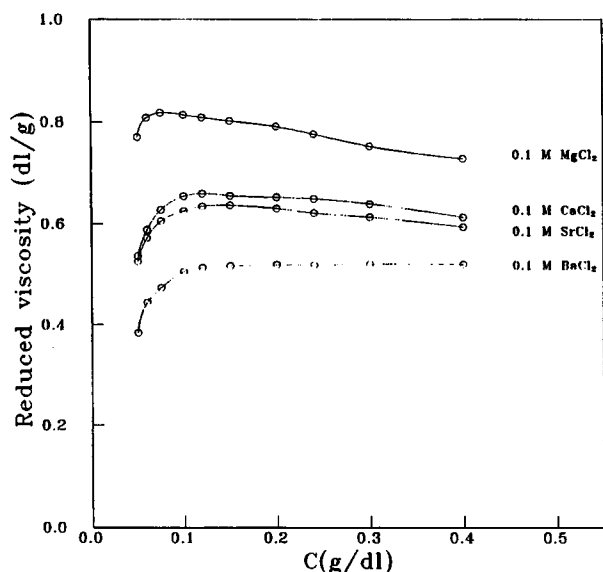


Figure 4 Reduced viscosity of poly(MIQSDMAPM) as a function of concentration for salts containing a divalent cation.

The data shown in Tables I and II exhibit an increase in the intrinsic viscosity in the order of $\text{Cs}^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+$ for CsCl, LiCl, NaCl, and KCl, and in the order of $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ for MgCl_2 , CaCl_2 , SrCl_2 , and BaCl_2 , respectively, for poly(MIQSDMAPM) in 0.1M aqueous salt solution. These phenomena are in contrast to polyampholyte behavior.^{32,33,37} These results coincide with the Pearson principle that states that hard acid species prefer binding with a hard base species, but soft acid species prefer binding with a soft base species (the hard species, both acids and bases, tend to be smaller and only slightly polarizable species; soft acids and bases tend to be larger and more polarizable species).³⁹ The hard acid species, e.g., the chloride ion (Cl^-), are easily bound to small radius hard bases such as the lithium ion (Li^+). Hence, the lithium ion (and magnesium ion) is more easily attracted to the chloride ion than the sodium ion

Table I Effect of Various Monovalent Cations on Viscosity Behavior of Poly(MIQSDMAPM) at 30°C

Salt Solution (0.1 M)	Slope	$[\eta]$	k'
CsCl	-0.33	0.91	-0.40
LiCl	-0.30	0.89	-0.38
NaCl	-0.16	0.82	-0.24
KCl	0.07	0.72	0.13

Table II Effect of Various Divalent Cations on Viscosity Behavior of Poly(MIQSDMAPM) at 30°C

Salt Solution (0.1 M)	Slope	$[\eta]$	k'
MgCl_2	-0.30	0.85	-0.41
CaCl_2	-0.14	0.68	-0.30
SrCl_2	-0.12	0.65	-0.28
BaCl_2	0.03	0.51	0.11

and potassium ion (calcium ion and strontium ion). This result would reduce the site binding degree of the chloride ion (Cl^-) on the quaternary ammonium group (R_4N^+) and also decrease the degree of the chloride ion (Cl^-), which neutralizes the positive charge on the polymeric side chains for poly(MIQSDMAPM). This result yields a higher intrinsic viscosity in an aqueous salt solution.

Influence of Different Anions with a Common Cation (K^+ or Na^+) on Intrinsic Viscosity of Poly(MIQSDMAPM)

The data shown in Figure 5 and Table III show an increase of the intrinsic viscosity for monovalent anions in the order of $\text{F}^- > \text{Cl}^- > \text{Br}^-$ for KF, KCl, and KBr, respectively, for poly(MIQSDMAPM) in 0.1M aqueous salt solution. This is because the larger anion with the common positive charge

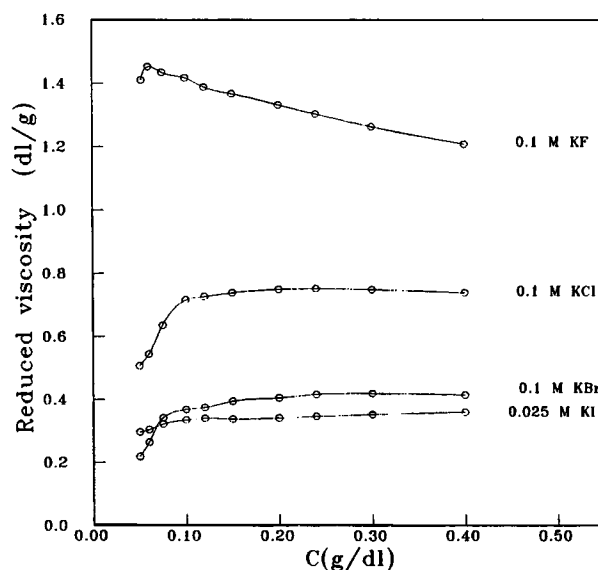


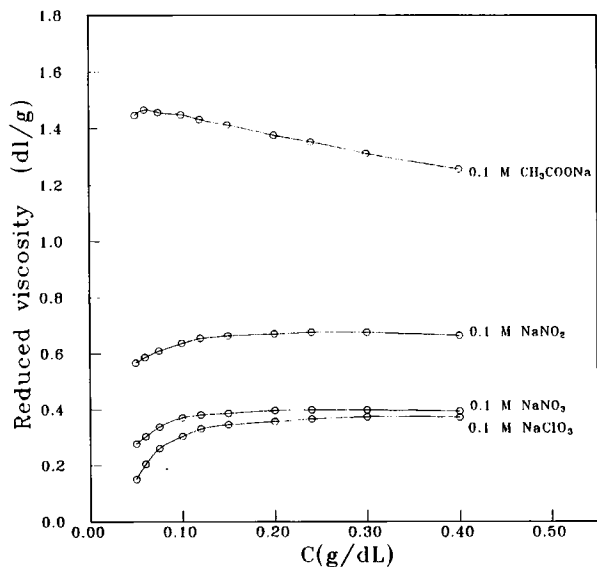
Figure 5 Reduced viscosity of poly(MIQSDMAPM) as a function of concentration for salts containing a common cation.

Table III Effect of Various Anions on Viscosity Behavior of Poly(MIQSDMAPM) at 30°C

Salt Solution (0.1 M)	Slope	$[\eta]$	k'
KF	-0.72	1.48	-0.33
KCl	0.07	0.72	0.13
KBr	0.16	0.36	1.23
KI (0.025 M)	0.08	0.33	0.73

(charge density is smaller) is easily polarized and bound to the quaternary ammonium group (R_4N^+) on poly(MIQSDMAPM). The positive charge on the polymeric side chains could therefore become effectively neutralized by the larger anion and reduce the intrinsic viscosity of poly(MIQSDMAPM) in 0.1M aqueous salt solution. This result also conforms to the Pearson principle.

For various acidic groups, Figure 6 and Table IV show an increase of the intrinsic viscosity for poly(MIQSDMAPM) in 0.1M aqueous salt solution in the order of $ClO_3^- < NO_3^- < NO_2^- < CH_3COO^-$ for $NaClO_3$, $NaNO_3$, $NaNO_2$, and CH_3COONa , respectively. This tendency is similar to the monovalent anions (Fig. 5 and Table III). The poly(MIQSDMAPM) does not dissolve in 0.1M Na_2ClO_4 and KI aqueous solution. This phenomenon is attributed to the attraction of the polymeric side chains of poly(MIQSDMAPM) by salt counterions (ClO_4^- and I^-) and this attraction prevents the polymeric chain from expanding and agglomerating.

**Figure 6** Reduced viscosity of poly(MIQSDMAPM) as a function of concentration for salts containing acidic ions.**Table IV** Effect of Various Acidic Groups on Viscosity Behavior of Poly(MIQSDMAPM) at 30°C

Salt Solution (0.1 M)	Slope	$[\eta]$	k'
CH_3COONa	-0.63	1.51	-0.28
$NaNO_2$	0.08	0.65	0.19
$NaNO_3$	0.07	0.37	0.51
$NaClO_3$	0.20	0.31	2.08
$NaClO_4$	—	—	—

The acetate ion (CH_3COO^-) is a weakly acidic group and is easily associated in forming acetic acid in aqueous solution. Therefore, the ionic intensity is very small and cannot effectively neutralize the charges of the polycations. The intrinsic viscosity of poly(MIQSDMAPM) was, hence, higher than other anions in 0.1M aqueous salt solution. The results obtained from the different anions and various acids for poly(MIQSDMAPM) are also in contrast to polyampholytes.^{16,32,33,37}

For the various divalent acidic groups, the data (see Fig. 7 and Table V) show an increase of the intrinsic viscosity for poly(MIQSDMAPM) in 0.1M aqueous salt solution in the order of $CO_3^{2-} > SO_3^{2-} > SO_4^{2-} > S_2O_3^{2-}$ for Na_2CO_3 , Na_2SO_3 , Na_2SO_4 , and $Na_2S_2O_3$, respectively. This tendency conforms to the Pearson principle and is similar to the previous poly(TMAAI) results.³⁶

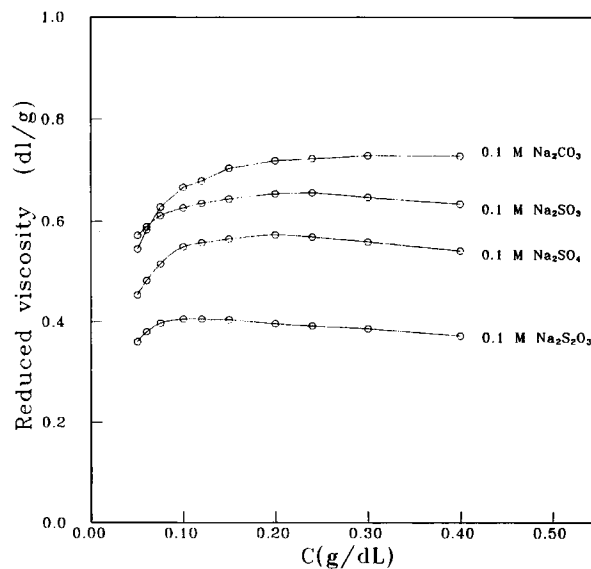
**Figure 7** Reduced viscosity poly(MIQSDMAPM) as a function of concentration for salts containing various divalent acidic ions.

Table V Effect of Various Divalent Acidic Groups on Viscosity Behavior of Poly(MIQSDMAPM) at 30°C

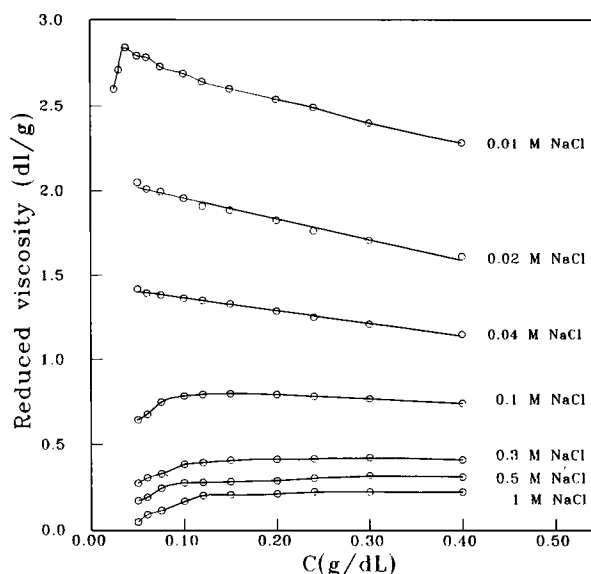
Salt Solution (0.1 M)	Slope	$[\eta]$	k'
Na ₂ CO ₃	0.20	0.66	0.46
Na ₂ SO ₃	0.02	0.64	0.05
Na ₂ SO ₄	-0.03	0.57	-0.09
Na ₂ S ₂ O ₃	-0.11	0.42	-0.62

Effect of Various Salt Concentrations in Aqueous Solution on Intrinsic Viscosity of Poly(MIQSDMAPM)

The presumed concept of chain contraction of the cationic polymers for salt ions attracting or site binding on the polymers was confirmed. Therefore, the phenomenon of a decrease in the reduced viscosity with an increase of salt concentration was rationalized. The effect of various NaCl concentrations between 0.01 and 1 mol/L on the reduced viscosity is illustrated in Figure 8 for the poly(MIQSDMAPM). A significant decrease in the reduced viscosity apparently occurred with an increase of the NaCl concentration. These phenomena are in sharp contrast with the inner salt of polysulfobetaines.^{32,33,37}

When the salt concentration is increased, a partial amount of negative charges of salt would become site bound on the quaternary ammonium group (R₄N⁺) on the poly(MIQSDMAPM). The polymeric charges would become neutralized by the counterions in the aqueous solution. This occurrence would reduce the repulsion of polymeric side chains resulting in both decreasing the extent of tightly stretched chains and coiling the polymeric main chains. The chloride ions (Cl⁻) binding on the quaternary ammonium group (R₄N⁺) of poly(MIQSDMAPM) were increased in high salt concentration to form regions of high local charge density.

The slope, intrinsic viscosity, and Huggins constant k' shown in Table VI could be calculated through Figure 8 and eq. (1). The slopes of the reduced viscosity against polymer concentration curves increase sharply with the increase in the concentration of simple electrolyte (NaCl). The slopes change from negative value to positive value when the concentration of the added salt reaches 0.3 M. The value for Huggins constants k' decreases with the lower concentration of the salt (<0.04 M) and then strongly increases with the increase of salt

**Figure 8** Reduced viscosity of poly(MIQSDMAPM) as a function of various concentration of NaCl.

concentration. The intrinsic viscosities increase as the concentration of the salt increases.

The above phenomena might be attributed to the addition of mobile simple electrolyte that can loosen the compact structure that results from the inter- and intramolecular ionic interactions, thus enabling the polymer to behave more freely in the salt solution.^{16,39} In other words, the higher the salt concentration, the lower the electrostatic repulsive force, and thus the lower the intrinsic viscosity. This result was also observed by Liaw et al.,¹⁶ Conway,⁴⁰ and Eisenberg and Pouyet.¹¹ The intrinsic viscosity $[\eta]$, obtained by extrapolating the curves in Fig. 8 at constant simple electrolyte concentration to zero concentration of the polymer, is plotted in Figure 9 as a function of the reciprocal square root of the ionic strength ($C s^{-1/2}$). A linear relationship ob-

Table VI Effect of NaCl Concentrations on Intrinsic Viscosity of Poly(MIQSDMAPM) at 30°C

NaCl Concn (M)	Slope	$[\eta]$	k'
0.01	-1.50	2.85	-0.18
0.02	-1.22	2.08	-0.28
0.04	-0.76	1.44	-0.37
0.1	-0.16	0.82	-0.24
0.3	0.09	0.39	0.59
0.5	0.14	0.26	2.07
1	0.14	0.18	4.32

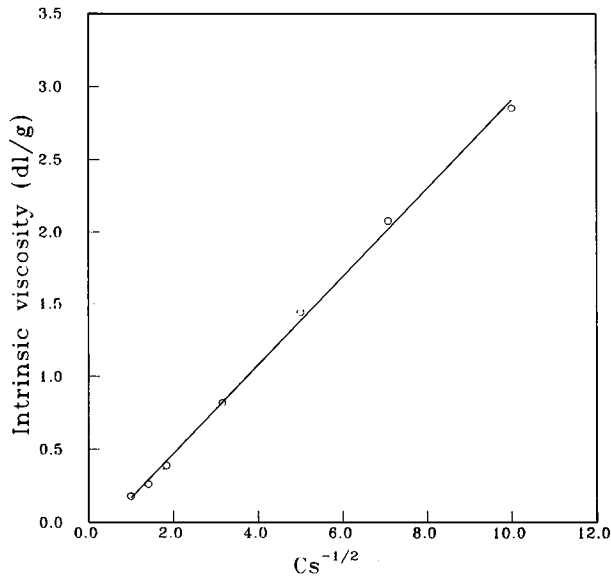


Figure 9 Intrinsic viscosity of poly(MIQSDMAPM) as a function of reciprocal square root of ionic strength.

tained from Figure 9 conforms to the general law of polyelectrolytes.^{41,42}

Flocculation Measurement

The charged surface of colloids forms the electrical double layer in aqueous solution, because either the ions have cohered on the surface of colloids or the charges have ionized from the deficiently crystalline structure of the colloids. The charges of the colloidal surface for general clay produce a negative charge that causes the mutual repulsion of the colloids in forming turbid suspension aqueous solution and causes them to not be flocculated. For conventional flocculation methods, the added trivalent cations can neutralize the charge of colloids for the sake of both reducing the mutual repulsion of the charges on the colloidal surface and coagulating the colloids. The colloids would become flocculated whenever polyelectrolyte was introduced into the suspension aqueous solution. The flocculation mechanism of polyelectrolyte coagulant was previously investigated by Hiemenz⁴³ and Benefield et al.⁴⁴ who explained the phenomenon of flocculation in light of chemical bridging.

Effect of Flocculation for Poly(MIQSDMAPM) and Al₂(SO₄)₃

Bentonite particles in an aqueous suspension absorb visible light, thereby reducing the turbidity of the suspension. The turbidity of the bentonite suspen-

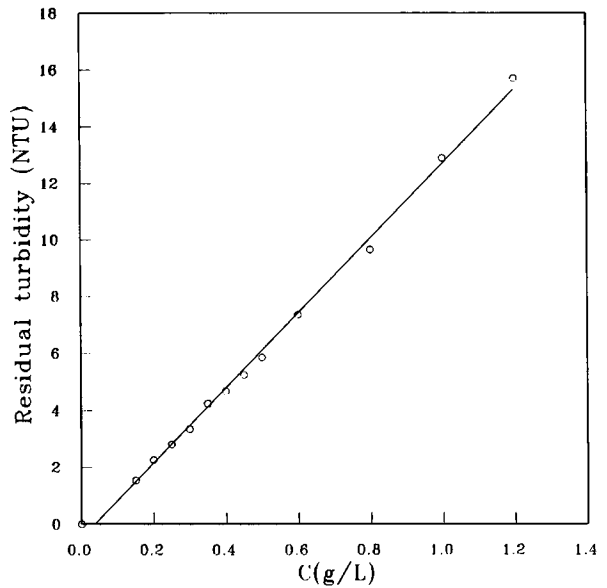


Figure 10 Calibration curve for residual turbidity and varied bentonite concentration.

sion shown in Figure 10 decreases as the bentonite concentration increases; however, this turbidity is a linear regression between the turbidity of the suspension and bentonite concentration.

The influence of different coagulants on the turbidity with 1000-ppm bentonite concentration is shown in Figure 11. The bentonite particles are indicated from the observed data to become flocculated when the flocculant concentration reaches 60 and 40 ppm for Al₂(SO₄)₃ and poly (MIQSDMAPM) in

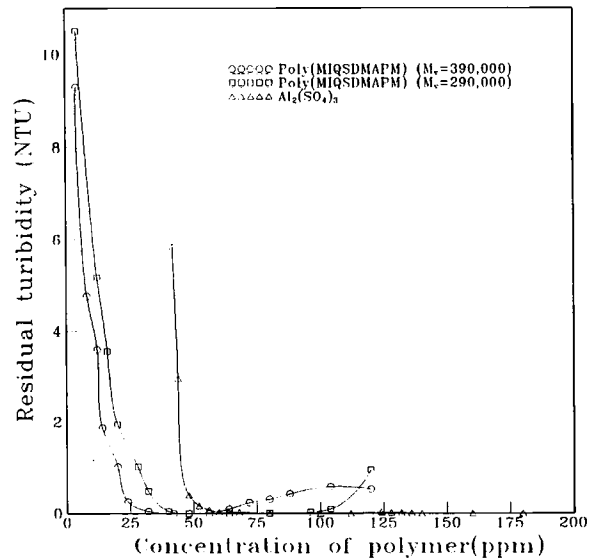


Figure 11 The residual turbidity vs. poly(MIQSDMAPM) concentration.

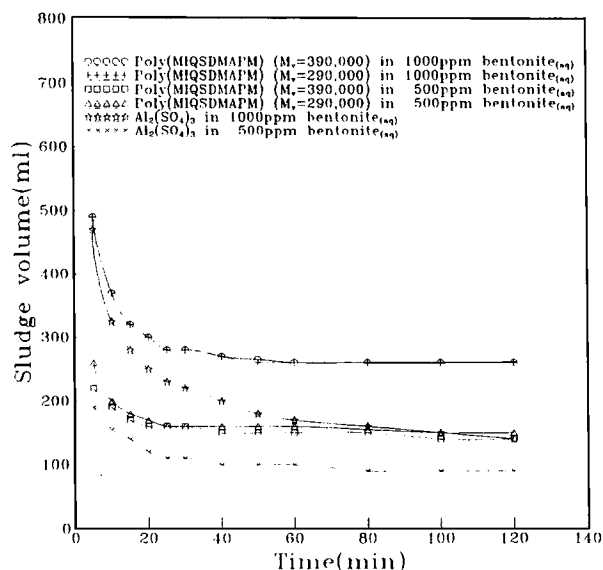


Figure 12 The sludge volume of varied coagulations (60 ppm) in bentonite aqueous solution.

a 1000-ppm bentonite solution. The residual bentonite concentration in the upper limpid aqueous solution is about 30 ppm and 20 ppm for $\text{Al}_2(\text{SO}_4)_3$ and poly(MIQSDMAPM) in a 1000-ppm bentonite solution, respectively. This event occurs because poly(MIQSDMAPM) neutralizes the charges of colloids that subsequently both reduce the distance of colloids and form large particles by secondary forces (Van der Waals forces). Additionally, the polymeric chains entangle the colloidal particles so as to increase the coagulation of colloids. Poly(MIQSDMAPM), as shown in Figure 12, is capable of coagulating the suspension more slowly than $\text{Al}_2(\text{SO}_4)_3$ in the initial period with a 1000-ppm bentonite concentration. (The settling of various coagulants is very rapid at 500-ppm bentonite concentration.) The bulk sludge settled by poly(MIQSDMAPM) coagulant is condensed with difficulty. The sludge volume, as shown in Figure 12, is larger than that settled by $\text{Al}_2(\text{SO}_4)_3$.

The effects of flocculation for different molecular weights of the poly(MIQSDMAPM) coagulant are shown to be similar (Fig. 12). The colloids are indicated from the observed data to be readily coagulated and settled by the different molecular weights (290,000 and 390,000) of poly(MIQSDMAPM).

CONCLUSION

The aqueous solution properties of cationic poly-electrolyte were evidently changed as salts were

added to the polymeric aqueous solution. As the radius of the salt ion was increased, the degree of attraction for poly(MIQSDMAPM) and salt, and the degree of polymeric recoiling increased. Simultaneously, the reduced viscosity and intrinsic viscosity decreased. As the salt concentration was increased, the intrinsic viscosity decreased and Huggins constant k' increased (Huggins constant k' was influenced by polymer-solvent and polymer-polymer interaction). The poly(MIQSDMAPM) can coagulate the suspension more effectively and rapidly than $\text{Al}_2(\text{SO}_4)_3$ in low coagulant concentration; however, the sludge volume with poly(MIQSDMAPM) flocculant is larger than that with $\text{Al}_2(\text{SO}_4)_3$. The colloids can be effectively coagulated and settled by poly(MIQSDMAPM).

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