

# Polysulfobetaines and Corresponding Cationic Polymers. VI. Synthesis and Aqueous Solution Properties of Cationic Poly(methyl iodide quaternized acrylamide-*N,N*-dimethylaminopropylmaleimide copolymer) [Poly(MIQADMAMP)]

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## SYNOPSIS

The copolymer prepared by copolymerizing with acrylamide and maleic anhydride was imidized with *N,N*-dimethylaminopropylamine. The obtained acrylamide-*N,N*-dimethylaminopropylmaleimide (ADMAMP) copolymer was then reacted with methyl iodide to yield a poly(methyl iodide quaternized acrylamide-*N,N*-dimethylaminopropylmaleimide) copolymer [poly(MIQADMAMP)]. Its aqueous solution properties were studied by measurements of reduced viscosity, intrinsic viscosity, and flocculation test in this study. 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(MIQADMAMP) than were "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 ( $R_4N^+$ ). The intrinsic viscosity behavior for cationic polyelectrolyte resulting from the electrostatic repulsive force of the polymer chain was contrasted with polyampholyte. The effect of various flocculants on flocculation in different pH values was accessed in this study. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The production of cationic water-soluble homopolymers and copolymers with acrylamide has grown rapidly in the past years because of their diverse commercial applications. These polymers are used for fine retention in paper making,<sup>1-3</sup> as flocculants and biocides in waste water treatment,<sup>4-6</sup> as dispersants,<sup>7</sup> as stabilizers for emulsion polymerization,<sup>8-10</sup> in cosmetics and pharmaceuticals,<sup>11,12</sup> and, in general, whenever aqueous solid-liquid separations are required.

Cationic polymers can be grouped into three categories: ammonium (primary, secondary, tertiary, and quaternary), sulfonium, and phos-

phonium compounds.<sup>13</sup> Of these, the ammonium-based polymers have been the most popular. Therefore, in recent years, polyelectrolyte monomer/polymer synthesis efforts have been increasingly concentrating on quaternary polycationics.<sup>14-23</sup> For example, Salamone et al. reported the synthesis of vinylimidazolium salts and their polymeric aqueous solution properties.<sup>14,15</sup> McCormick et al. reported the synthesis of copolymer of acrylamide with 2-acrylamido-2-methylpropanedimethylammonium chloride and their polymeric aqueous solution properties.<sup>16,17</sup> The synthesis, aqueous solution properties, and application of cationic polyelectrolytes derived from acrylates were also recently reported.<sup>18-23</sup>

The effect of various salt ions on the interaction of polyelectrolytes in an aqueous solution was investigated by several scholars, and the site-binding interaction of salt ions and polymers by the Huggins

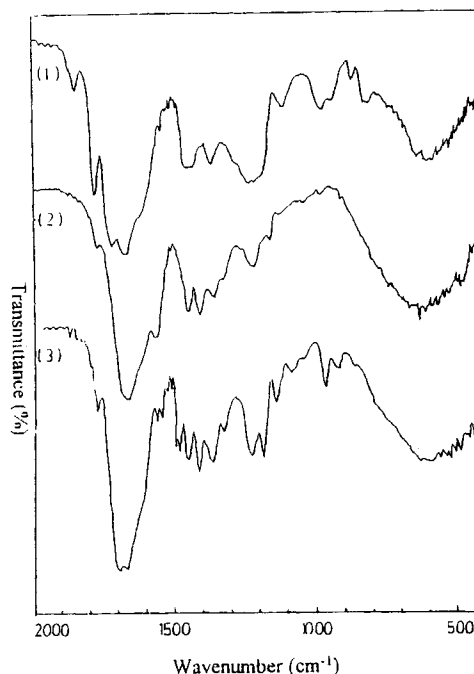
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equation and Huggins constant  $k'$  was also investigated by them.<sup>24-37</sup> The counterion size was found to affect the degree of site binding for salt ion-attracting polymers.

A series of polysulfobetaines and corresponding cationic polymers prepared by zwitterionic sulfobetaine and corresponding cationic monomers with different electrodrawing groups and by varying the methylene units between the charge groups were researched previously in our laboratory. The solution properties of cationic poly(trimethylacrylamidopropyl ammonium iodide) [poly(TMAAI)], poly[*N,N'*-dimethyl(acrylamidopropyl) ammonium propane sulfonate] [poly(DMAAPS)], poly[*N,N'*-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate] [poly(DMAPS)], and poly(methyl iodide quaternized styrene-*N,N'*-dimethylamino-propylmaleimide) (MIQSDMAPM) were reported in previous articles.<sup>38-41</sup> The previous poly(DMAAPS) article concluded that soft salt anions and cations bound easily to the quaternary ammonium and sulfonate group of poly(DMAAPS),<sup>40</sup> but the poly(TMAAI) article showed that soft salt anions were more easily bound on the quaternary ammonium of poly(TMAAI) than were those of hard salt anions.<sup>39</sup>

The tendency of the intrinsic viscosity for poly(MIQSDMAPM) in various aqueous salt solutions is similar to that of other polyquaternarys; the Huggins constant for poly(MIQSDMAPM) in an aqueous salt solution shows an extreme distinction from cationic homopolymers, especially cationic Poly(TMAAI).<sup>39</sup> This phenomenon is attributed mainly to the presence of the styrene segment, a hydrophobic group, in the pendent of the poly(MIQSDMAPM) copolymer.<sup>41</sup> Hence, the replacement of the styrene segment with acrylamide in the copolymer backbone was adopted in this study.

Investigations of aqueous solution properties for a corresponding cationic copolymer, MIQADMAPM, especially the intrinsic viscosity in the presence of various salts, are the main interest in



**Figure 1** IR spectra of (1) AA-MA, (2) ADMAPM, and (3) MIQADMAPM copolymers.

this article. Finally, the cationic polyelectrolyte is applied in the flocculation test of a bentonite sol system.

## EXPERIMENTAL

### Materials

Acrylamide (AA, mp 83–84°C) and maleic anhydride (MA, mp 56°C) were recrystallized from reagent-grade benzene and vacuum-dried at room temperature. Azobisisobutyronitrile (AIBN) was recrystallized from reagent-grade methanol prior to use. Deionized water used in this study has a resistivity of 18 MΩ.

**Table I** The Average Viscosimetric Molecular Weight ( $\bar{M}_v$ ) with the Different Solvents of Reaction

No.	Monomer Ratio (AA : MA)	Solvent	$[\eta]$ (dL/g) <sup>a</sup>	$K \times 10^6$	$\alpha$	$\bar{M}_v$
1	1 : 1	Benzene	0.096	10.5	0.66	$3.06 \times 10^4$
2	1 : 1	MEK	0.048	59.5	0.66	$2.55 \times 10^4$
3	1 : 1	Dioxane	0.060	10.5	0.66	$1.50 \times 10^4$

<sup>a</sup> The intrinsic viscosity  $[\eta]$  in 0.6N NaNO<sub>3</sub> solution at 25°C was determined using an Ubbelohde viscosimeter.

### Synthesis of Acrylamide–Maleic Anhydride (AA–MA) Copolymer

AA (7.108 g, 0.1 mol), MA (9.806 g, 0.1 mol), and benzene (MEK, dioxane; 250 mL) were introduced into a 300 mL three-necked flask equipped a stirrer, a condenser, and a thermometer. The contents were stirred at 80°C for complete dissolution. To the solution was then added azobisisobutyronitrile (AIBN) (0.20 g, added by step) as an initiator and it was stirred at the same temperature for 3 h under a nitrogen atmosphere. In this case, the polymer precipitated from the solution as polymerization continued. The precipitated product was washed with acetone several times after the polymerization was completed and the hygroscopic white solid was obtained. The yield of the copolymers was more than 60 wt %. The fraction of products was placed into a large volume of the mixture of methanol–water (1 : 1), which is a solvent for these monomers and the AA homopolymer. The insoluble copolymer was then filtered and dried in a vacuum to constant weight at room temperature. A large excess of methanol (more than 1 : 10) was added to the filtrate to check for the absence of the AA homopolymer.<sup>42</sup>

### Imidization of AA–MA Copolymer

The AA–MA copolymer (8.00 g) was slurried with 60 mL of dimethyl sulfoxide (DMSO) at 80°C until the polymer particles were finely dissolved in DMSO and remained homogeneous during the following reaction. To this, 9.67 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 a gentle reflux for 1 h and then subjected to distillation until the reaction system reached 180°C and sparged with nitrogen for 30 min for conducting the dehydration reaction. To identify the structure of the ADMAPM copolymer (whether the dehydration reaction was completed), the 10 mL sampling mixture was drawn and poured into a large volume of methanol to precipitate, and the precipitated product was collected by filtration. The sample was then dissolved in deionized water and precipitated repeatedly with methanol three times and washed with acetone several times, respectively, and then dried at 80°C for 24 h under vacuum to obtain the ADMAPM copolymer. The ADMAPM copolymer was used to investigate the imidization degree by elemental analysis.

### Synthesis of Methyl Iodide Quaternized Acrylamide–*N,N*-Dimethylaminopropylmaleimide Copolymer [Poly(MIQADMAMP)]

The imidized copolymer mixture was subsequently cooled to a 5°C temperature with an ice bath, followed by the dropwise addition of the methyl iodide (14.38 g) with stirring for 1 h under a nitrogen atmosphere. The temperature of the exothermic reaction was maintained at 5°C. After completion of the addition, the mixture was stirred at the same temperature for several hours and then allowed to stand overnight. The resulting reaction mixture was precipitated by pouring the solution slowly into a large volume of reagent-grade methanol under stirring, and a formed brown precipitate was filtered and determined to be a methyl iodide quaternized acrylamide-*N,N*-dimethylaminopropylmaleimide copolymer [poly(MIQADMAMP)]. The crude yield of the poly(MIQADMAMP) copolymer was found to be greater than 74%. For purification, the crude ADMMAPS copolymer was dissolved in deionized water and precipitated repeatedly with methanol three times and washed with acetone several times until all the DMSO was removed, and the hygroscopic, yellow–white solid was then dried under a vacuum at 80°C for 24 h.

### Characterization Techniques

IR spectra were recorded with a Jasco FT/IR 7000 spectrophotometer using a KBr window in the range 400–2000 cm<sup>-1</sup>. Elemental analysis for carbon, hydrogen, and nitrogen of the ADMAPM and ADMMAPS copolymers was conducted with a Perkin-Elmer 2400.

### Viscometric Measurements

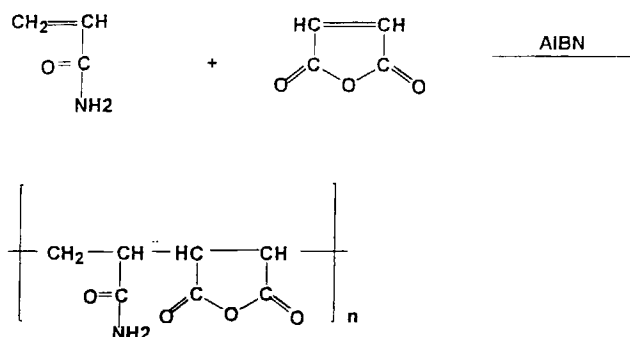
Viscometric measurements were carried out with an Ubbelodhe viscometer (flow time 129.25 s for pure water) at 30 ± 0.01°C. The polymer samples were dissolved in a salt solution of varying concentration to yield stock solutions of approximately 1.0 g polymer per 100 mL solvent.

Viscosity data were calculated according to the Mark–Huggins equation:

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

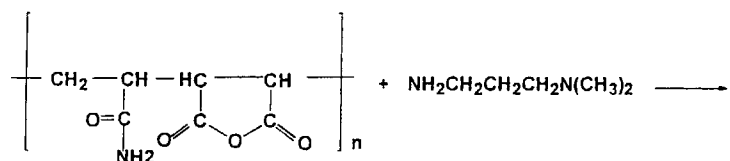
where  $\eta_{sp}$  is the specific viscosity;  $C$ , the concentration of the polymer;  $[\eta]$ , the intrinsic viscosity; and  $k'$ , the Huggins constant.

## (A) Synthesis of acrylamide-maleic anhydride (AA-MA) copolymer

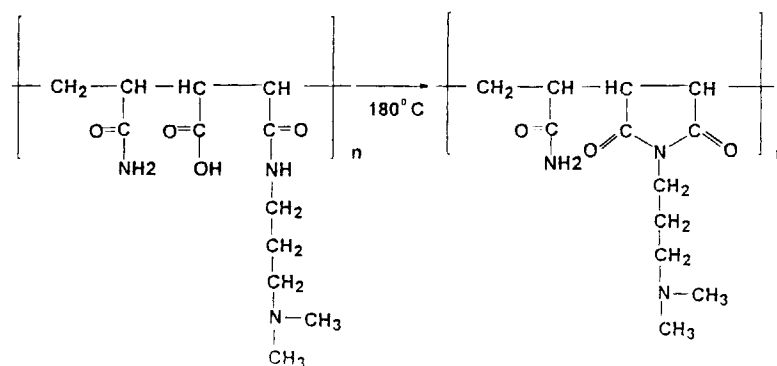


(I)

## (B) Imidization of AA-MA copolymer



(I)



(II)A

(II)B

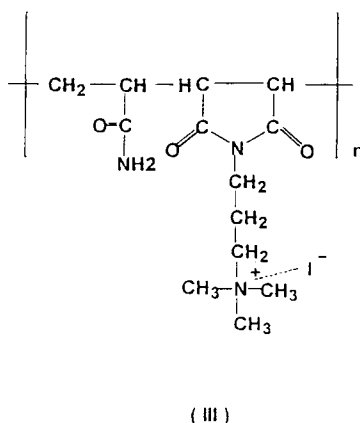
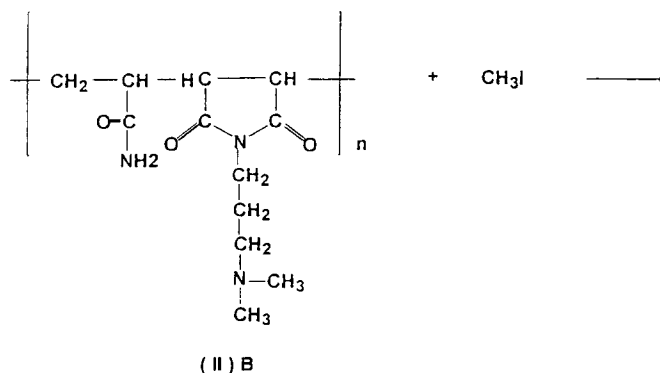
**Scheme 1** Synthesis of methyl iodide quaternized acrylamide-dimethylaminopropyl-maleimide copolymer (MIQADMAMP).

### Flocculation Measurements

The extent of flocculation was determined by measuring the turbidity of the supernatant. The tests called the "Jar Test" 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 direct-reading turbidimeter by using the turbidity suspension standards (8 and 40 NTU for range 0-

(C) Synthesis of methyl iodide quaternized acrylamide-  
dimethylaminopropylmaleimide copolymer (MIQADMAPM)



Scheme 1 (Continued from previous page)

9.99 and 9.99–99.9, respectively) and deionized water (0 NTU) for the calibration standards. The turbidity suspension standard was prepared by the following procedure: (1) Solution I—Dissolve 1.000 g hydrazin sulfate,  $(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ , in distilled water and dilute to 100 mL in a volumetric flask. (2) Solution II—Dissolve 10.00 g hexamethylenetetramine,  $(\text{CH}_2)_6\text{N}_4$ , in distilled water and dilute to 100 mL in a volumetric flask. (3) In a 100 mL volumetric flask, mix 5.0 mL of Solution I and 5.0 mL of Solution II. Let stand 24 h at  $25 \pm 3^\circ\text{C}$ . The turbidity of this suspension is 400 nephelometric units (NTU). (4) Dilute the 400 NTU turbidity standard solution to 40 and 8 NTU prior to use.

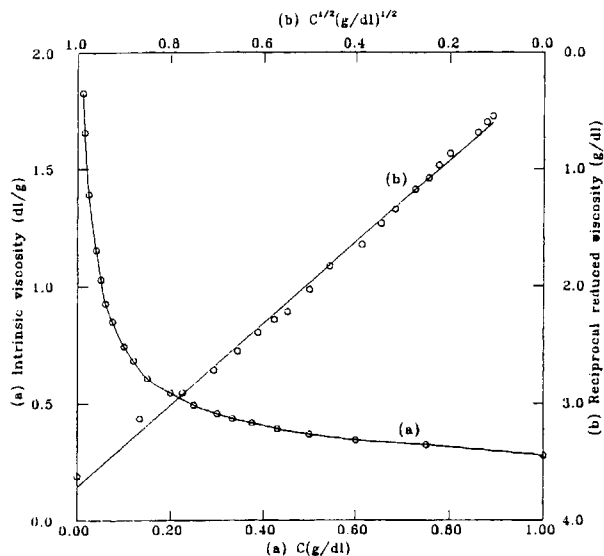
The nephelometric method is based on a comparison of the intensity of light scattered by a standard reference suspension under the same conditions. The higher the intensity of the scattered light, the higher the turbidity.

## RESULTS AND DISCUSSION

### Synthesis of AA–MA Copolymers

The copolymer of AA and MA was carried out in the AIBN as an initiator at  $80^\circ\text{C}$  in the different solvents—benzene, MEK, and dioxane. The monomer ratio, average viscosimetric molecular weight ( $\bar{M}_v$ ), and the constants  $\alpha$  and  $K$  (from the Mark-Houwink's equation,  $[\eta] = K\bar{M}_v^\alpha$ ) for AA–MA copolymers are given in Table I.<sup>43</sup>

The results shown in Table I indicate that the molecular weight of AA–MA was solvent-dependent. The structure of the AA–MA copolymer is an alternating copolymer by characterizing from the literature data<sup>44</sup> (the copolymerization reactivity ratios were given as 0.75 for AA and 0.00 for MA) and the IR spectrum [Fig. 1(1)]. The characteristic absorption peaks of the IR spectra for MA and AA units are  $1775$ ,  $1720$ , and  $1216 \text{ cm}^{-1}$  and  $1671$  and  $1363$



**Figure 2** Reduced viscosity of poly(MIQADMAPM) in water: (a) dependence of reduced viscosity on polymer concentration; (b) dependence of reciprocal reduced viscosity on square root of polymer concentration.

$\text{cm}^{-1}$ , respectively. The polymerization reaction is shown in Scheme 1(A).

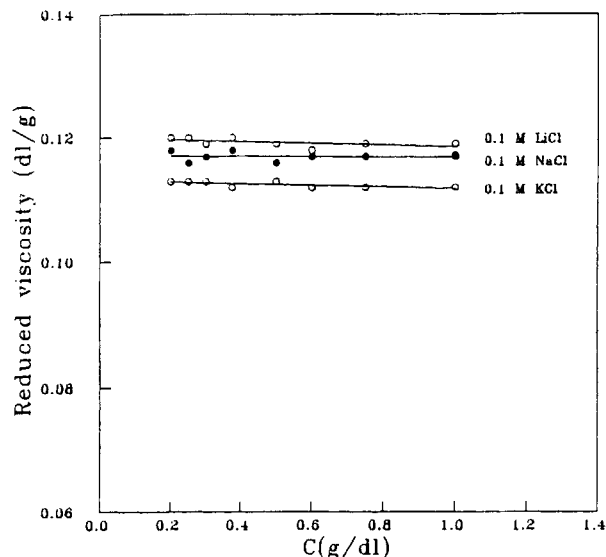
#### Synthesis of Methyl Iodide Quaternized Acrylamide-*N,N*-Dimethylaminopropylmaleimide Copolymer [poly(MIQADMAPM)]

After addition of *N,N*-dimethylaminopropylamine to an AA-MA copolymer solution (DMSO as solvent) and then refluxing 1 h to form an acrylamide-maleamic acid (ring-opened reaction) [Scheme 1(B)-IIA], the system was heated to  $180^\circ\text{C}$  to carry out a dehydration reaction (ring-closed reaction) to obtain ADMAPM [Scheme 1(B)-IIB]. The identification of the copolymer was confirmed by IR spectrum data; the characteristic absorption peak of the MA group ( $\nu_{\text{C=O}}$ ) at  $1216\text{ cm}^{-1}$  disappeared after the AA-MA copolymer was dehydrated at  $180^\circ\text{C}$  [see Fig. 1(2)]. The degree of imidization was evaluated by elemental analysis of nitrogen. The product of ADMAPM was subject to elemental analysis.

ANAL: Calcd for  $(\text{C}_{12}\text{H}_{19}\text{O}_3\text{N}_3)$ : C, 56.90%; H, 7.56%; N, 16.58%.

Found: C, 56.85%; H, 7.46%; N, 16.47%. The imidization degree was 98.10 (mol %).

ADMAPM was then quaternized by a single reaction which generated the ionic structure (MIQADMAPM) [Scheme 1(C)]. The structure of MIQADMAPM was also characterized by an IR spectrum [see Fig. 1(3)]. The IR spectrum of the MIQAD-

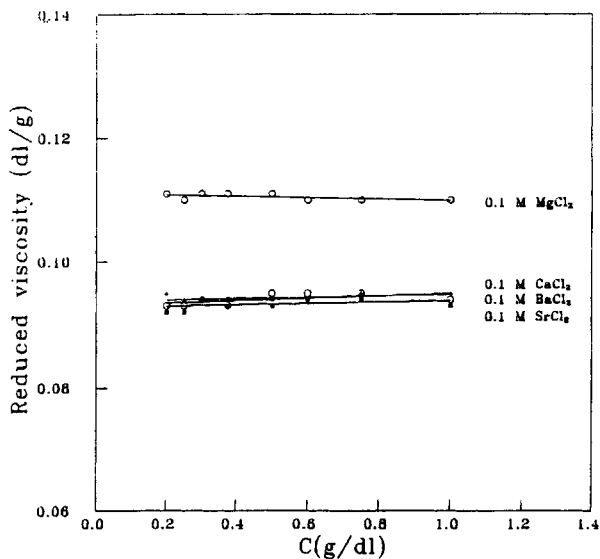


**Figure 3** Reduced viscosity of poly(MIQADMAPM) as a function of concentration for salts containing a common anion.

MAPM copolymer presents the characteristic absorption of the quaternary group ( $\nu_{\text{R}_4\text{N}^+}$ ) at  $967\text{ cm}^{-1}$ . The degree of the formation of the quaternary was calculated by elemental analysis of nitrogen.

ANAL: Calcd for  $(\text{C}_{13}\text{H}_{22}\text{O}_6\text{N}_3\text{I})$ : C, 39.59%; H, 5.60%; N, 10.60%.

Found: C, 40.07%; H, 5.94%; N, 10.56%. The degree of the quaternization was 96.72 (mol %).



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

**Table II** Effect of Various Monovalent Cations on the Viscosity Behavior of Poly(MIQADMAMPM) at 30°C

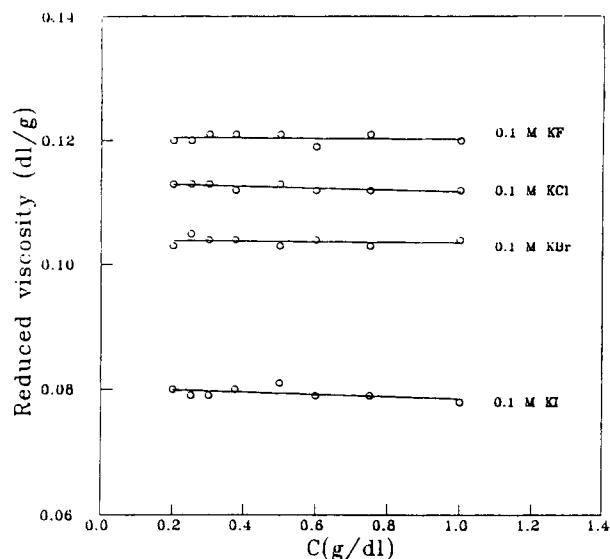
Salt Solution (0.1M)	Slope × 100	[ $\eta$ ] (dL/g)	$k'$
LiCl	-0.10	0.120	-0.07
NaCl	0.00	0.117	0.00
KCl	-0.10	0.113	-0.08

### Viscosity Measurements

Polyelectrolytes normally exhibit properties in solution that are quite different from general polymers when they are ionized in aqueous solution; the mutual repulsion of their charges causes the chain to expand. The size of the polyelectrolyte random coil is a function of the concentrations of the polymer and added salt, since both influence the degree of ionization. The property of viscosity is strongly affected by chain expansion. The reduced viscosity may even increase markedly as polymer concentration decreases, with a consequent increase in the degree of ionization of the polymer. On the other hand, the addition of low molecular weight electrolyte (salt) to the aqueous solution increases the ionic strength of the solution outside the polymer coil relative to that inside and also reduces the thickness of the layer of "bound" counterions around the chain. Those effects cause the chain to contract.<sup>45</sup> In our experiments, the poly(MIQADMAMPM) side chains would bear positive charges since 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 Fig. 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 and the reduced viscosity in a lower concentration region increases with a decrease of polymeric concentration. These phenom-

**Table III** Effect of Various Divalent Cations on the Viscosity Behavior of Poly(MIQADMAMPM) at 30°C

Salt Solution (0.1M)	Slope × 100	[ $\eta$ ] (dL/g)	$k'$
MgCl <sub>2</sub>	-0.10	0.111	-0.01
CaCl <sub>2</sub>	0.10	0.094	0.11
SrCl <sub>2</sub>	0.10	0.093	0.12
BaCl <sub>2</sub>	0.20	0.093	0.23

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

ena were also observed by Fuoss and Strauss<sup>46,47</sup> and Salamone et al.<sup>14,15</sup> for various polyelectrolytes. As shown by the plotting of the reciprocal reduced viscosity vs. the square root of polymeric concentration [Fig. 2(b)], the concentration dependence of the reduced viscosity conforms to the Fuoss equation<sup>46</sup>:

$$\eta_{sp}/C = A/(1 + B \sqrt{c}) \quad (2)$$

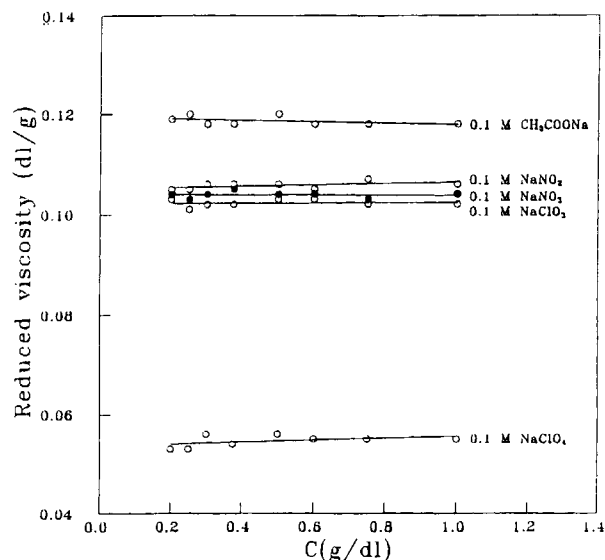
where  $A$  corresponds to intrinsic viscosity [ $\eta$ ],  $B$  is a constant related to an interaction of counterions with the polyion, and  $C$  is polymeric concentration in the lower polymeric concentration region.  $A$  and  $B$  calculated by the Fuoss equation were 4.33 and 15.07 (g/dL)<sup>-1/2</sup>, respectively.

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

The addition of salt to the aqueous solution of polyelectrolyte causes the polymeric chain to contract

**Table IV** Effect of Various Anions on the Viscosity Behavior of Poly(MIQADMAMPM) at 30°C

Salt Solution (0.1M)	Slope × 100	[ $\eta$ ] (dL/g)	$k'$
KF	0.00	0.121	0.00
KCl	-0.10	0.113	-0.08
KBr	0.00	0.104	0.00
KI	-0.20	0.080	-0.31



**Figure 6** Reduced viscosity of poly(MIQADMAMP) as a function of concentration for salts containing various acidic ions.

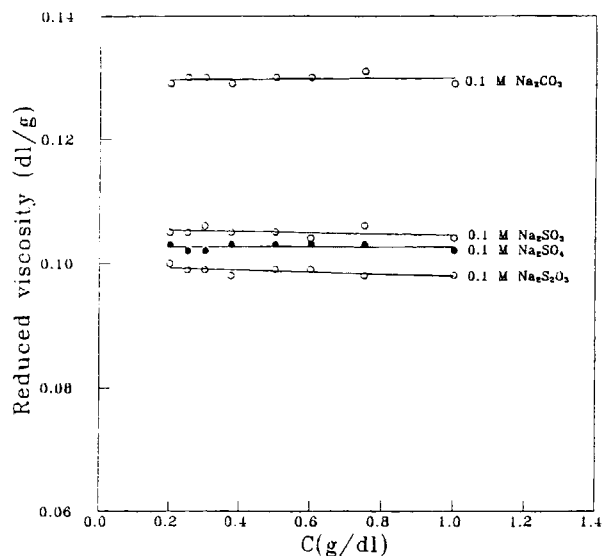
and decrease the intrinsic viscosity as mentioned above. Investigation of the influence of various salts on this effect and interpretation of charged neutralization and Pearson theory will therefore be presented in the following section.

#### Influence of Different Cations with a Common Anion ( $\text{Cl}^-$ ) on Intrinsic Viscosity of Poly(MIQADMAMP)

The intrinsic viscosity  $[\eta]$  and Huggins constant  $k'$  can be calculated from Figures 3 and 4 and eq. (1). The data shown in Tables II and III exhibit an increase in the intrinsic viscosity in the order of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  for  $\text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{KCl}$  and in the order of  $\text{Mg}^{+2} > \text{Ca}^{+2} \doteq \text{Sr}^{+2} \doteq \text{Ba}^{+2}$  for  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{SrCl}_2$ , and  $\text{BaCl}_2$ , respectively, for poly(MIQADMAMP) in a 0.1M aqueous salt solution. These phenomena are in contrast to polyam-

**Table V** Effect of Various Acidic Groups on the Viscosity Behavior of Poly(MIQADMAMP) at 30°C

Salt Solution (0.1M)	Slope $\times 100$	$[\eta]$ (dL/g)	$k'$
$\text{CH}_3\text{COONa}$	-0.10	0.191	-0.07
$\text{NaNO}_2$	0.10	0.105	0.09
$\text{NaNO}_3$	0.00	0.104	0.00
$\text{NaClO}_3$	0.00	0.102	0.00
$\text{NaClO}_4$	2.00	0.054	6.86



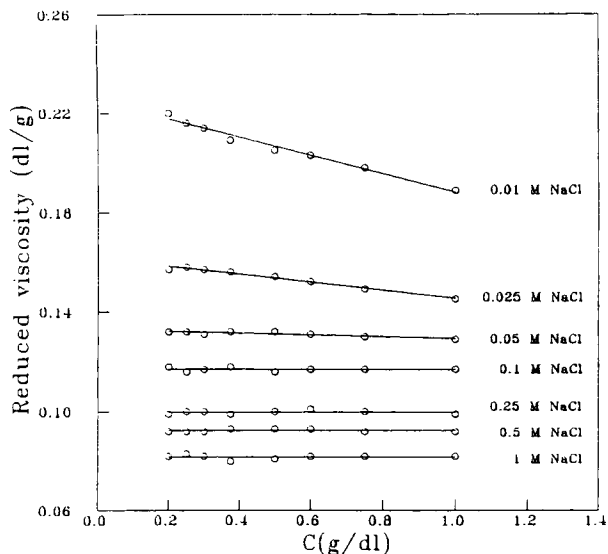
**Figure 7** Reduced viscosity of poly(MIQADMAMP) as a function of concentration for salts containing various divalent acidic ions.

pholyte behavior.<sup>37,40,48</sup> These results coincide with the Pearson principle, which 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).<sup>49</sup> The hard-acid species, e.g., the chloride ion ( $\text{Cl}^-$ ), are easily bound to small radius hard bases such as the lithium ion ( $\text{Li}^+$ ). Hence, the lithium ion (and magnesium ion) is more easily attracted to the chloride ion than is the sodium ion and potassium ion (calcium ion and strontium ion). This result would reduce the site binding degree of the chloride ion ( $\text{Cl}^-$ ) on the quaternary ammonium group ( $\text{R}_4\text{N}^+$ ) and also decrease the degree of the chloride ion ( $\text{Cl}^-$ ), which neutralizes the positive charge on polymeric side chains for poly(MIQADMAMP). This result yields a higher intrinsic viscosity in an aqueous salt solution.

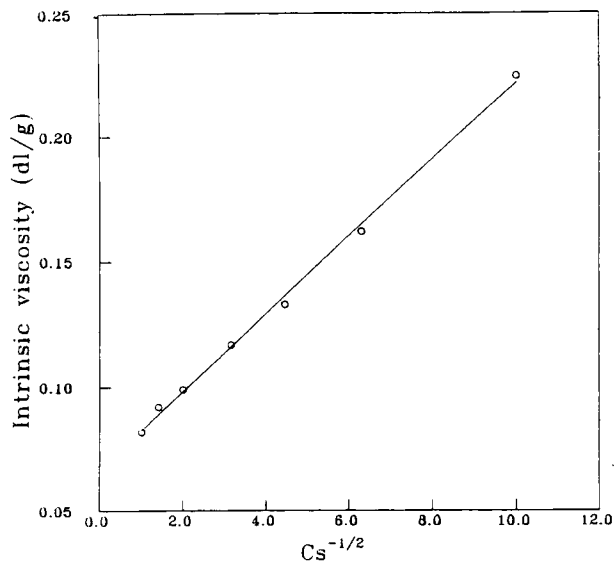
**Table VI** Effect of Various Divalent Acidic Groups on the Viscosity Behavior of Poly(MIQADMAMP) at 30°C

Salt Solution (0.1M)	Slope $\times 100$	$[\eta]$ (dL/g)	$k'$
$\text{Na}_2\text{CO}_3$	0.03	0.130	0.02
$\text{Na}_2\text{SO}_3$	-0.10	0.106	-0.09
$\text{Na}_2\text{SO}_4$	-0.01	0.103	-0.01
$\text{Na}_2\text{S}_2\text{O}_3$	-0.20	0.100	-0.20





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



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

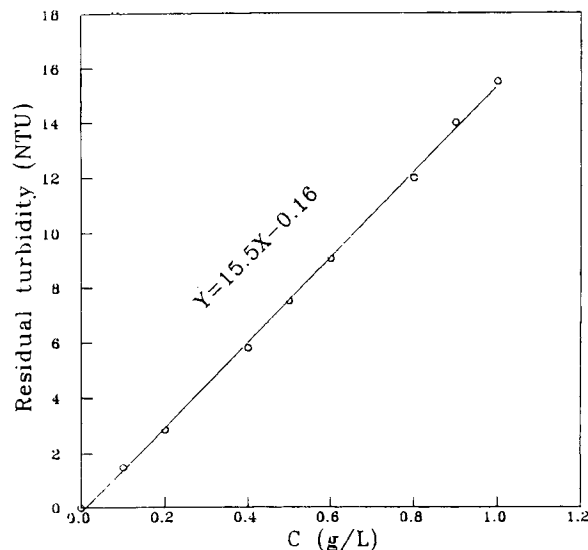
**Influence of Different Anions with a Common Cation (K<sup>+</sup> or Na<sup>+</sup>) on Intrinsic Viscosity of Poly(MIQADMAPM)**

The data shown in Figure 5 and Table IV show an increase of the intrinsic viscosity for monovalent anions in the order of F<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> for KF, KCl, KBr, and KI, respectively, for poly(MIQADMAPM) in a 0.1M aqueous salt solution. This is because the larger anion with a common positive charge (charge density is smaller) is easily polarized and bound to the quaternary ammonium group (R<sub>4</sub>N<sup>+</sup>) on poly(MIQADMAPM). The positive charge on polymeric side chains could therefore become effectively neutralized by the larger anion and reduce the intrinsic viscosity of poly(MIQADMAPM) in the 0.1M aqueous salt solution. This result also conforms to the Pearson principle.

**Table VII** Effect of NaCl Concentrations on the Intrinsic Viscosity and Huggins Constant of Poly(MIQADMAPM) at 30°C

NaCl Concentration	Slope × 100	[η] (dL/g)	k'
0.010M	-3.70	0.225	-0.73
0.025M	-1.60	0.162	-0.61
0.05M	-0.40	0.133	-0.23
0.10M	0.00	0.117	0.00
0.25M	0.00	0.099	0.00
0.5M	0.00	0.092	0.00
1M	0.00	0.082	0.00

For various acidic groups, Figure 6 and Table V show an increase of the intrinsic viscosity for poly(MIQADMAPM) in the 0.1M aqueous salt solution in the order of ClO<sub>4</sub><sup>-</sup> < ClO<sub>3</sub><sup>-</sup> < NO<sub>3</sub><sup>-</sup> < NO<sub>2</sub><sup>-</sup> < CH<sub>3</sub>COO<sup>-</sup> for NaClO<sub>4</sub>, NaClO<sub>3</sub>, NaNO<sub>3</sub>, NaNO<sub>2</sub>, and CH<sub>3</sub>COONa, respectively. This tendency is similar to the monovalent anions (Fig. 5 and Table IV). The poly(MIQADMAPM) dissolved in the 0.1M NaClO<sub>4</sub> aqueous solution and resulted in lower intrinsic viscosity than that of other salts. This phenomenon is attributed to the strong attraction of



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

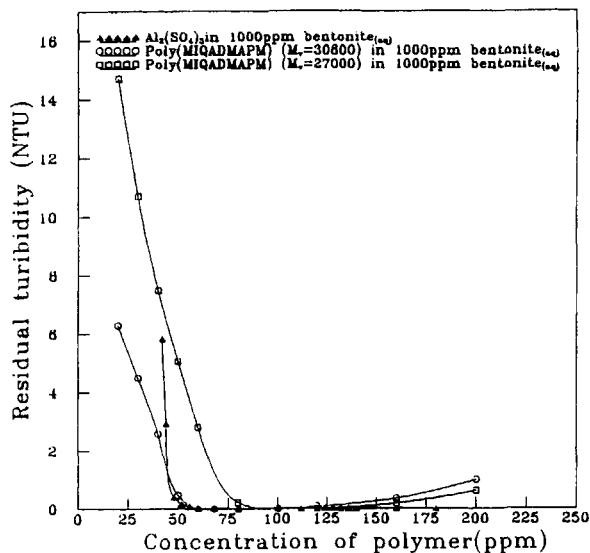


Figure 11 The residual turbidity vs. poly(MIQADMAMPM) and  $Al_2(SO_4)_3$  concentration in 1000 ppm bentonite aqueous solution.

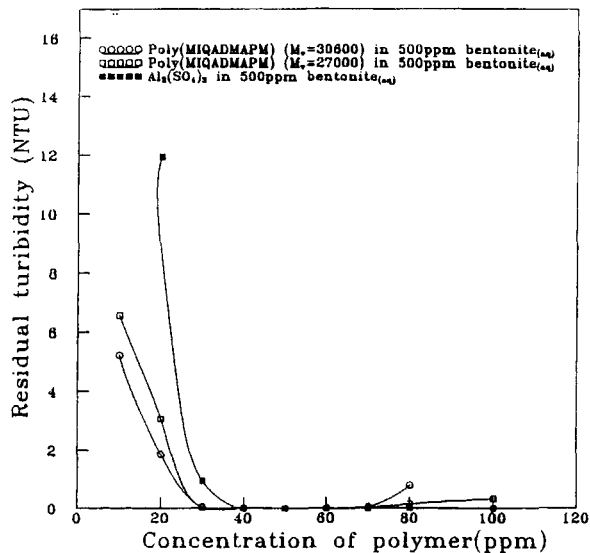


Figure 13 The residual turbidity vs. poly(MIQADMAMPM) and  $Al_2(SO_4)_3$  concentration in 500 ppm bentonite aqueous solution.

the polymeric side chains of poly(MIQADMAMPM) by the salt counterion ( $ClO_4^-$ ) and this strong attraction prevents the polymeric chain from expanding. This phenomenon has also been observed in our previous studies on poly(TMAAI) and poly(MIQSDMAPM) that caused these polymeric aqueous solution to become turbid.<sup>39,41</sup> 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(MIQADMAMPM) was, hence, higher than that of other anions in the 0.1M aqueous salt solution. The results obtained from the different anions and various acids for poly(MIQADMAMPM) are also in contrast to polyampholytes.<sup>21,37,40,48</sup>

For the various divalent acidic groups, the data (see Fig. 7 and Table VI) show an increase of the intrinsic viscosity for poly(MIQADMAMPM) in the 0.1M aqueous salt solution in the order of  $CO_3^{2-} > SO_3^{2-} > SO_4^{2-} > S_2O_3^{2-}$  for  $Na_2CO_3, Na_2SO_3, Na_2SO_4,$

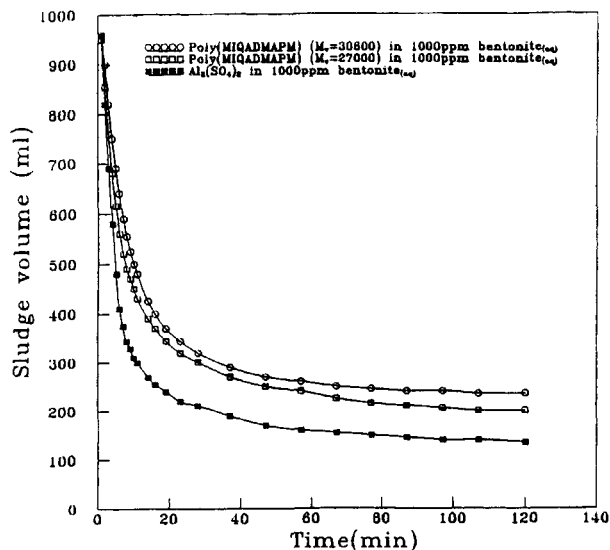


Figure 12 The sludge volume of varied coagulations (100 ppm) in 1000 ppm bentonite aqueous solution.

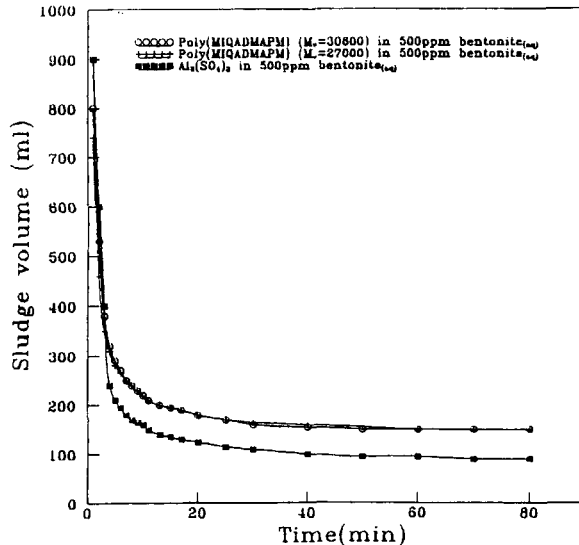
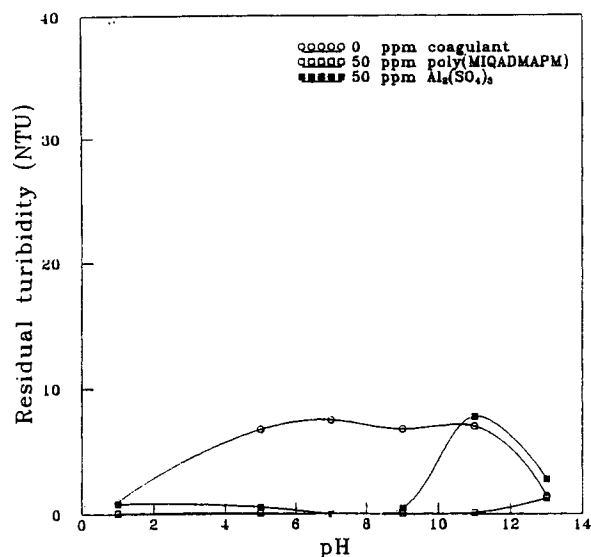


Figure 14 The sludge volume of varied coagulations (50 ppm) in 500 ppm bentonite aqueous solution.



**Figure 15** The residual turbidity vs. poly(MIQADMAMPM) and  $\text{Al}_2(\text{SO}_4)_3$  concentration in 500 ppm bentonite aqueous solution for varying pH value.

and  $\text{Na}_2\text{S}_2\text{O}_3$ , respectively. This tendency conforms to the Pearson principle and is similar to the previous TMAAI and MIQSDMAPM results.<sup>39,41</sup>

#### Effect of Various Salt Concentrations in Aqueous Solution on the Intrinsic Viscosity of Poly(MIQADMAMPM)

The conformation of cationic polymers is governed by electrostatic repulsions and hydrophobic interactions. Therefore, it depends on the ionic strength of the macromolecular solutions. The presumed concept of chain contraction of the cationic polymers for salt ions attracting or site-binding on the polymers was confirmed. Hence, 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(MIQADMAMPM). The behavior of the copolymer is the same as that of classical polyelectrolyte: By increasing the ionic strength of the solutions, the macromolecular chains contract themselves and the intrinsic viscosities decrease. These phenomena are in sharp contrast with the inner salt of polysulfofetaines.<sup>37,40,48</sup> When the salt concentration is increased, a partial amount of negative charges of the salt would become site-bound on the quaternary ammonium group ( $\text{R}_4\text{N}^+$ ) on the poly(MIQADMAMPM). The polymeric charges would become neutralized by the counterions in the aqueous solution. This occurrence would reduce the

repulsion of polymeric side chains that results in both decreasing the extent of tightly stretched chains and coiling the polymeric main chains. The chloride ion ( $\text{Cl}^-$ ) binding on the quaternary ammonium group ( $\text{R}_4\text{N}^+$ ) of poly(MIQADMAMPM) was increased in high salt concentration to form regions of high local charge density. Moreover, the higher the ionic strength, the higher the Huggins constant (see Table VII). When salt is added ( $<0.1M$ ), the higher values of  $k'$  (from negative value to zero) showed the existence of hydrophobic macrodomains due to the weak polymer-solvent interactions. In fact, by increasing the ionic strength of the solutions, the intramolecular electrostatic repulsions decrease and the correlative decrease of the intrinsic viscosity show that these hydrophobic microdomains arise from local intramolecular aggregation of alkyl chains. With the slopes of the curves representing the dependence of the reduced viscosity on the concentration ( $>0.1M$ ) of polyelectrolyte being relatively small, one can suppose that the reduced viscosity is only slightly concentration-dependent. In other words, increasing the concentration of polyelectrolyte from 0.2 to 1.0 g/dL makes an insignificant contribution to the compensation of polymer-solvent and polymer-polymer interactions.

The above phenomena might be attributed to the addition of a mobile simple electrolyte, which 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.<sup>21,50</sup> 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 Conway<sup>51</sup> and Eisenberg and Pouyet.<sup>16</sup> The intrinsic viscosity  $[\eta]$ , obtained by extrapolating the curves in Figure 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 obtained from Figure 9 conforms to the general law of the polyelectrolyte.<sup>52,53</sup>

#### Flocculation Measurements

The charged surface of colloids forms the electrical double layer in an aqueous solution, because either the ions have cohered on the surface of colloids or the charges have ionized from the deficiently crystalline structure of colloids. The charges of the colloidal surface for general clay produce negative charges that cause the mutual repulsion of the colloids in forming a turbid suspension aqueous solu-

tion that cannot be flocculated. For conventional flocculational 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 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 Ruehawein and Ward, who explained the phenomenon of flocculation in light of chemical bridging.<sup>54,55</sup>

### Effect of Flocculation for Poly(MIQADMAMP) and $\text{Al}_2(\text{SO}_4)_3$

Bentonite particles in an aqueous suspension scatter visible light which consequently increases the turbidity of the suspension as the bentonite concentration increases (see Fig. 10). However, this turbidity is a linear regression between the turbidity of the suspension and bentonite concentration.

The influence of different coagulants on the turbidity and sludge volume of the suspension solution with 1000 ppm (or 500 ppm) bentonite concentration is shown in Figures 11–14. From the observed data, the bentonite particles become flocculated when the flocculant concentration reaches 60 ppm (40 ppm) and 60 ppm (30 ppm) for  $\text{Al}_2(\text{SO}_4)_3$  and poly(MIQADMAMP) in 1000 ppm (500 ppm) bentonite solution. The residual bentonite concentration in the upper limpid aqueous solution is less than 10 ppm for  $\text{Al}_2(\text{SO}_4)_3$  and poly(MIQADMAMP) in 1000 ppm (500 ppm) bentonite solution. As shown in Figures 11 and 12, the residual turbidity decreases with increasing polymer concentration below the saturation level of adsorption. Optimum flocculation, corresponding to the complete removal of turbidity in the supernatant, is then achieved. Beyond the optimum flocculation, higher polymer dosages redisperse the bentonite suspensions. This event occurs since poly(MIQADMAMP) neutralizes the charges of colloids, which subsequently both reduces the distance of colloids and also forms 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 until the optimum polymer dosages, and any exceeding polymer dosages would decrease the coagulation of colloids due to the stabilization of colloids. Poly(MIQADMAMP) is therefore capable (Figs. 13 and 14) of more slowly coagulating the suspension than is  $\text{Al}_2(\text{SO}_4)_3$  in the initial period with 1000 ppm bentonite concentration. (The settling of various

coagulants is very rapid at 500 ppm bentonite concentration.) The bulk sludge settled by the poly(MIQADMAMP) coagulant is condensed with difficulty. The sludge volume is therefore (Figs. 13 and 14) larger than that settled by  $\text{Al}_2(\text{SO}_4)_3$ .

The effects of flocculation for different molecular weights of the poly(MIQADMAMP) coagulant are shown to be similar from Figure 13. From the observed data, the colloids are indicated to be readily coagulated and settled by the different molecular weights [poly(MIQADMAMP)] from  $\bar{M}_v = 27,000$  and  $\bar{M}_v = 30,600$  of AA-MA copolymers).

### The Effect of Flocculation on Various PH Aqueous Solutions

The influence of different PH values—adjusted by HCl and NaOH in an aqueous solution—on flocculation is very evident. The hydrogen ion ( $\text{H}^+$ ) and sodium ion ( $\text{Na}^+$ ) are observed (Fig. 15) to neutralize the charge of bentonite particles to flocculate the colloids as pH value ranges from 1 to 13. With this experiment, the colloids could be effectively coagulated and settled by poly(MIQADMAMP) in a large range of pH values (1–11). The supernatant would become turbid for coagulation by  $\text{Al}_2(\text{SO}_4)_3$  as the pH value reaches 11. This phenomenon would be attributed to the appearance of the aluminum hydrate ion [ $\text{Al}(\text{OH})_4^-$ ] at high pH value and result in the mutual repulsion between the colloid particles.

## CONCLUSION

The aqueous solution properties of cationic polyelectrolyte were evidently changed as salts were added to polymeric aqueous solution. As the radius of the salt ion was increased, the degree of attraction for poly(MIQADMAMP) 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 the Huggins constant  $k'$  increased (the Huggins constant  $k'$  was influenced by polymer-solvent and polymer-polymer interactions). The poly(MIQADMAMP) can coagulate the suspension more effectively and rapidly than can  $\text{Al}_2(\text{SO}_4)_3$  in a low coagulant concentration (500 ppm); however, the sludge volume with the poly(MIQADMAMP) flocculant is larger than that with  $\text{Al}_2(\text{SO}_4)_3$ . The colloids could be effectively coagulated and settled by poly(MIQADMAMP) in a large range of pH values.

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Received July 29, 1995

Accepted September 26, 1995