Poly(sulfobetaine)s and Corresponding Cationic Polymers. XI. Synthesis and Aqueous Solution Properties of a Cationic Poly(methyl iodide quaternized ethyl vinyl ether/N,N-dimethylaminopropyl maleamidic acid) Copolymer

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ABSTRACT: A copolymer prepared by the copolymerization of ethyl vinyl ether and maleic anhydride underwent amidoacidation with N,N-dimethylaminopropylamine. The obtained ethyl vinyl ether/dimethylaminopropyl maleamidic acid copolymer was then reacted with methyl iodide to yield poly(methyl iodide quaternized ethyl vinyl ether/N,N'-dimethylaminopropyl maleamidic acid) (MIQED-MAPMA). The greatest difference from other polyelectrolytes was the carboxylic group on the polymer chain unit of MIQEDMAPMA. Its aqueous solution properties in various salts and at various pH values were studied by measurements of the reduced viscosity and intrinsic viscosity. The reduced viscosity and intrinsic viscosity of this cationic polyelectrolyte were related to the types and concentrations of the added salts. The tendency of the salt effect was similar to that of other polyelectrolytes; that is, soft salt anions were more easily bound to the quaternary ammonium (R_4N^+) of MIQEDMAPMA than hard salt anions. Some salt ions strongly attracted the quaternary ammonium of the cationic polymeric side chain for the agglomeration of the polymers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2261–2269, 2003

Key words: polyelectrolytes; viscosity; solution properties

INTRODUCTION

The production of cationic water-soluble homopolymers and copolymers with acrylamide has grown rapidly in past years because of their diverse commercial applications. These polymers are widely used as fine retention in paper making,[1–3] as flocculants in wastewater treatment,[4–6] as dispersants,[7] and as stabilizers for emulsion polymerization in cosmetics and pharmaceuticals.[8–12] Cationic polymers can be grouped into three types of compounds: ammonium (primary, secondary, tertiary, and quaternary), sulfonium, and phosphonium.[13] Of these, the ammonium-based polymers are the most popular. Therefore, in recent years, polyelectrolyte monomer/polymer synthesis efforts have increasingly been concentrated on quaternary polycationics.[14–23] The effect of various salt ions on the interactions of polyelectrolytes in aqueous solutions has been investigated by several scholars, and the site-binding interactions of salt ions and polymers, defined by the Huggins equation and Huggins constant k', has also been investigated.[24–37] The counterion size has been found to affect the degree of site binding for salt-ion-attracting polymers.

A series of poly(sulfobetaine)s and their corresponding cationic polymers, prepared from zwitterionic sulfobetaine and corresponding cationic monomers with different electron-withdrawing groups and with variations in the methylene units between the charged groups, were researched in our laboratory. The solution properties of cationic polyelectrolytes such as poly(trimethyl acrylamido propyl ammonium iodide) (TMAAI), poly-(methyl iodide quaternized styrene/dimethylaminopropyl maleimide) (MIQSDMAPM), and poly(methyl iodide quaternized acrylamide/N,N-dimethylaminopropyl maleimide) (MIQADMAPM) were reported in previous articles.[38–40] The TMAAI article showed that soft salt anions were more easily bound on the quaternary ammonium of TMAAI than hard salt anions.[38]

We could not find in the literature the synthesis and aqueous solution properties of poly(methyl iodide quaternized ethyl vinyl ether-N,N-dimethylaminopropyl maleamidic acid) (MIQEDMAPMA). Therefore, investigations of aqueous solutions of this copolymer, especially with respect to the reduced viscosity and intrinsic viscosity ($[\eta]$) in the presence of various salts and varied pH values, were the main foci of this study.

EXPERIMENTAL

Materials

Ethyl vinyl ether (EVE), N,N-dimethyl amino propyl amine (DMAPA), methyl ethyl ketone (MEK), dimethyl sulfoxide (DMSO), and methyl iodide (MI)

were reagent-grade and were used as received. Maleic anhydride (MA; mp = 56°C) and benzoyl peroxide (BPO) were purified by recrystallization in benzene. Methanol and acetone were distilled twice. Deionized water has a resistivity of 18 MΩ.

Characterization techniques

IR spectra were recorded with a Jasco FT/IR 7000 spectrophotometer (Tokyo, Japan) with a KBr window in the range of 400–4000 cm^{-1}. An elemental analysis of carbon, hydrogen, and nitrogen for poly(ethyl vinyl ether/maleic anhydride) (EMA), poly(ethyl vinyl ether/ dimethylaminopropyl maleamidic acid) (EDMAPMA), and MIQEDMAPMA copolymers was conducted with a PerkinElmer 2400 (Shelton, CT).

Preparation of EMA

MA (29.4 g, 0.3 mol), benzene (270 mL), and BPO (1.0 wt % based on total monomers) as an initiator were introduced into a 500-mL, three-necked flask equipped with a stirrer, a cooler, and a thermometer. The contents were stirred at 60°C for complete disso- lution. EVE (21.6 g, 0.3 mol), mixed with 30 mL of benzene, was added dropwise into the solution, and after the addition was completed, the solution contin- ued to react for 12 h at the same temperature under a nitrogen atmosphere. Then, the solution was filtered so that the precipitate could be collected. The precip- itate was repeatedly dissolved and precipitated from acetone with petroleum ether and dried under vac- uum; EMA as a white powder was obtained. The yield was 65%. The polymer was analyzed by elemental analysis.

ELEM. ANAL. Calcd. for $C_8H_{10}O_4$ [weight-average molecular weight (M_w) = 170]: C, 56.47%; H, 5.88%. Found: C, 54.30%; H, 5.92%.

Amidoacidation of the EMA copolymer for the preparation of EDMAPMA

EMA (10 g) was mixed with 170 mL of MEK in a 500-mL, round-bottom flask at 55°C, and the mixture was stirred until EMA was completely dissolved. When the temperature cooled down to 45°C, 6.5 g of 3-dimethylaminopropylamine, mixed with 30 mL of MEK, was added dropwise to the flask for 1 h. After the addition was completed, the solution continued to react for 6 h, and then the solution was filtered so that the precipitate could be collected. The precipitate was washed with MEK twice and then dried under vac- uum; a hygroscopic orange-white product was ob- tained. The yield was 80%. The product EDMAPMA was subjected to elemental analysis.

ELEM. ANAL. Calcd. for $C_{13}H_{24}O_4N_2$ (M_w = 304): C, 57.35%; H, 8.82%; N, 10.29%. Found: C, 56.25%; H, 8.40%; N, 9.16%. Amidoacidation degree: 89%.

Preparation of MIQEDMAPMA

The aforementioned polymeric amidic acid, ED- MAPMA (6 g, 0.021 mol), was dissolved in 150 mL of DMSO at 90°C and stirred until it was completely dissolved. When the temperature cooled down to 30°C, 3.3 g of MI, mixed with 20 mL of DMSO, was added dropwise for 1 h. After the addition was com- pleted, the solution continued to react for 8 h; it re- mained still for 12 h and then precipitated with tetra- hydrofuran (THF). The product was repeatedly dis- solved and precipitated from methanol with THF and then dried at 80°C for 24 h under vacuum; a quater- nary ammonium salt product was obtained with an 80% yield. The product, red and hygroscopic MIQED- MAPMA, was obtained and was analyzed by elemen- tal analysis.

ELEM. ANAL. Calcd. for $C_{14}H_{27}O_4N_2I$ (M_w = 414): C, 40.58%; H, 6.52%; N, 6.76%. Found: C, 40.70%; H, 6.78%; N, 6.77%. Degree of quaternization: 100%.

Viscometric measurements

The viscometric measurements were performed with an Ubbelohde viscometer, which had a flow time of 72.89 s with deionized water (18 MΩ) at 30.00 ± 0.01°C. The polymer samples were dissolved in a salt solution, and the polymer salt solution was ad- justed to yield a stock solution of approximately 1 g/dL of solvent. The viscosity data were calculated with the Mark–Huggins equation:

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

where η_{sp} is the specific viscosity and C is the concen- tration of the polymer.

RESULTS AND DISCUSSION

Characterization of the EMA, EDMAPMA, and MIQEDMAPMA copolymers

The EMA copolymer, prepared from EVE and MA, was confirmed to be an alternating copolymer with $M_w > 2.4 \times 10^5$ g/mol.[41,42] It (as described in Scheme 1) was then converted into EDMAPMA and MIQED- MAPMA. The IR spectra of EMA, EDMAPMA, and MIQEDMAPMA are shown in Figure 1. The charac- teristic absorption peaks are 1856, 1779, 1224, and 1300–1000 cm^{-1} for EMA; 3600–2400, 1725, and 1640– 1550 cm^{-1} for EDMAPMA; and 963 cm^{-1} for MIQED- MAPMA.
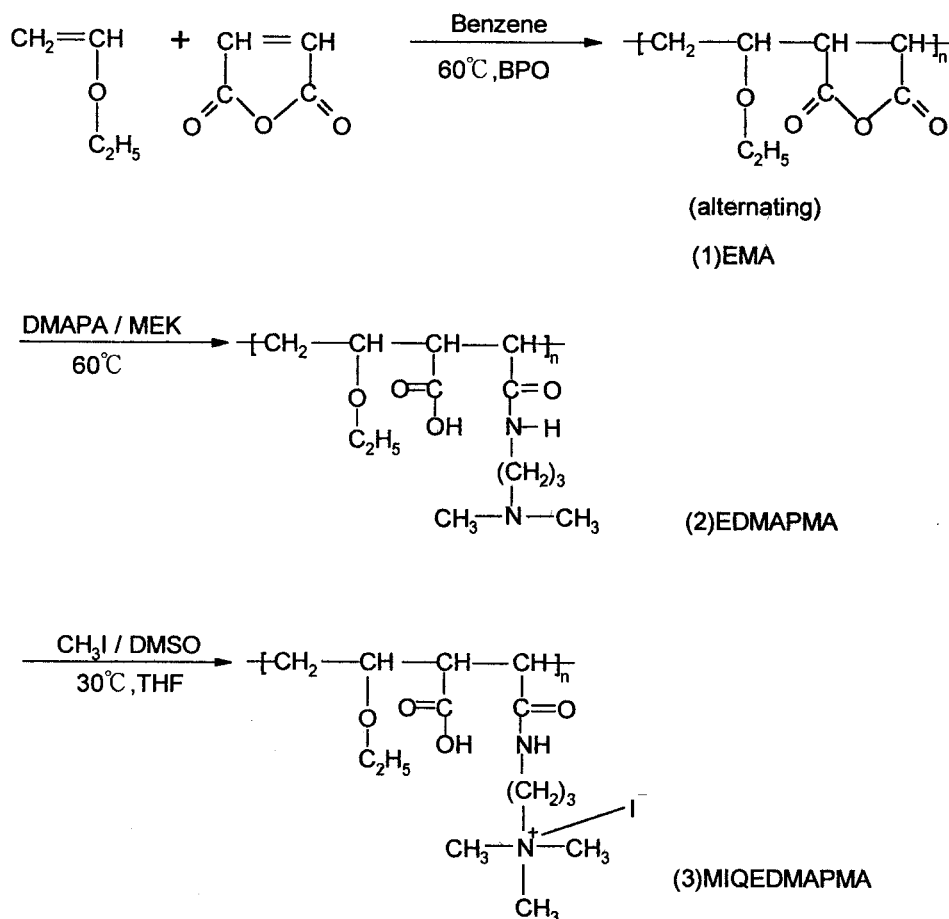
Scheme 1 Synthesis of (1) EMA, (2) EDMAPMA, and (3) MIQEDMAPMA.

Viscosity measurements

Polyelectrolytes normally exhibit properties in solution that are quite different from those of general polymers. They are ionized in aqueous solutions, and the mutual repulsion of their charges causes expansions of the chain. The size of the polyelectrolyte random coil is a function of the concentrations of the polymer and added salt because both influence the degree of ionization. The viscosity is strongly affected by chain expansion. The reduced viscosity may even increase markedly as the polymer concentration decreases, with a resultant increase in the degree of ionization of the polymer. However, the addition of a 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 it also reduces the thickness of the layer of bound counterions around the chain. Those effects cause the chain to contract.[43] In our experiments, the MIQEDMAPMA side chains bore positive charges because the iodine ions became ionized in an aqueous solution. In this situation, the reduced viscosity exhibited typical behavior 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 the polymeric concentration because of the interaction of the polymer chains and in a lower concentration region sharply increases with a decrease in the polymeric concentration. These phenomena were also observed by Salamone and coworkers[14,15] and Fuoss and coworker[44,45] and in our previous study[40] for various polyelectrolytes. As shown by the plotting of the reciprocal reduced viscosity versus the square root of the polymeric concentration [Fig. 2(b)], the concentration dependence of the reduced viscosity conforms to the Fuoss equation:[44]

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

where A corresponds to $[\eta]$, B is a constant related to the interaction of counterions with polyions, and C is the polymer concentration in the lower polymeric concentration region.

Effect of various salts on $[\eta]$ of MIQEDMAPMA in aqueous solutions

The addition of salt to an aqueous solution of the polyelectrolyte causes the polymeric chain to contract
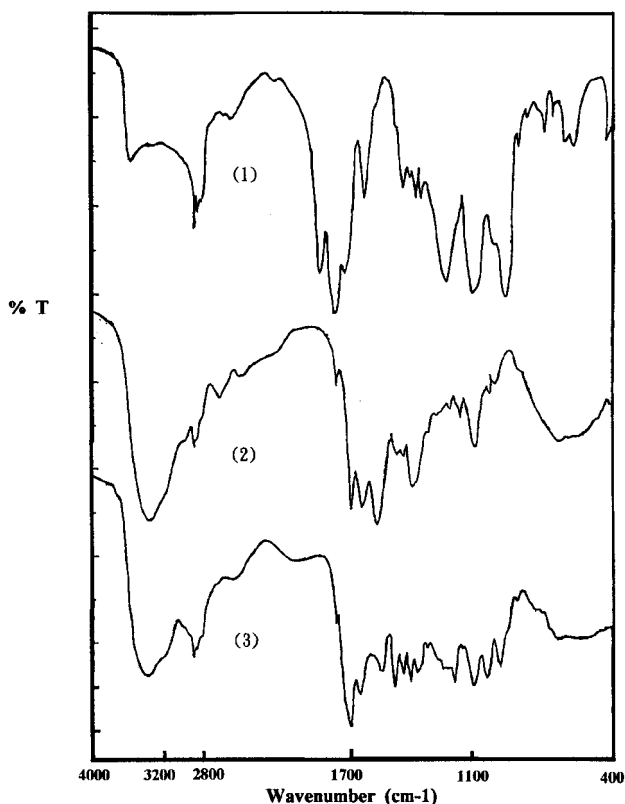
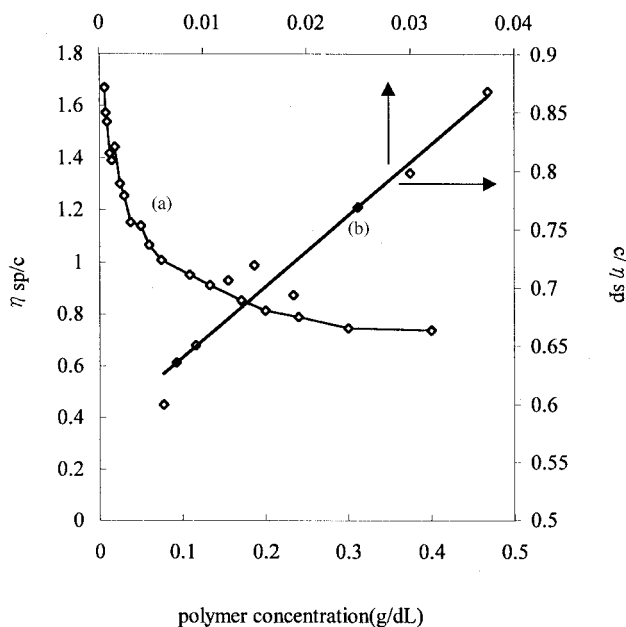**Figure 1** IR spectra of (1) EMA, (2) EDMAPMA, and (3) MIQEDMAPMA.

Figure 3 Reduced viscosity of MIQEDMAPMA versus the polymer concentration in a 0.25M aqueous solution of salts containing various monovalent cations.

and reduces [η]. An investigation of the influence of various salts on this effect and an interpretation of charged neutralization and Pearson theory is, therefore, presented in the next section.

Influence of different cations with a common anion (Cl$^-$) on [η] of MIQEDMAPMA

[η] and k' were calculated from Figures 3 and 4 and eq. (1). The data shown in Table I exhibit an increase in [η] in the order of Li$^+$ > Na$^+$ > K$^+$ for LiCl, NaCl, and KCl and in the order of Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} for MgCl$_2$ CaCl$_2$, SrCl$_2$, and BaCl$_2$, respectively, for MIQEDMAPMA in 0.25M aqueous salt solutions. These phenomena are in contrast to polyampholyte behavior.[46–48] These results coincide with the Pearson principle, which states that hard acid species prefer binding with hard base species but soft acid species prefer binding with soft base species.[49] The hard acid species, such as the chloride ion (Cl$^-$), are easily bound to small-radius hard bases such as the lithium ion (Li$^+$). Therefore, the lithium ion (or magnesium ion) is more easily attracted to the chloride ion than the sodium ion and potassium ion (or calcium ion and strontium ion). This result reduces the site-binding degree of the chloride ion (Cl$^-$) on the quaternary ammonium group (R$_4$N$^+$) and also decreases the degree of the chloride ion (Cl$^-$), which neutralizes the positive charge on polymeric side chains for MIQEDMAPMA. This result yields a higher [η] value in an aqueous salt solution.

Figure 2 Reduced viscosity of MIQEDMAPMA in pure water: (a) the dependence of the reduced viscosity on the polymer concentration and (b) the dependence of the reciprocal reduced viscosity on the square root of the polymer concentration.
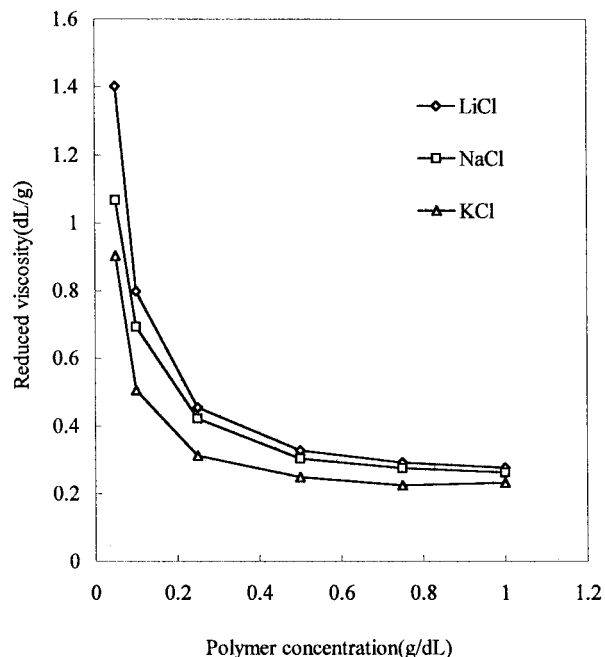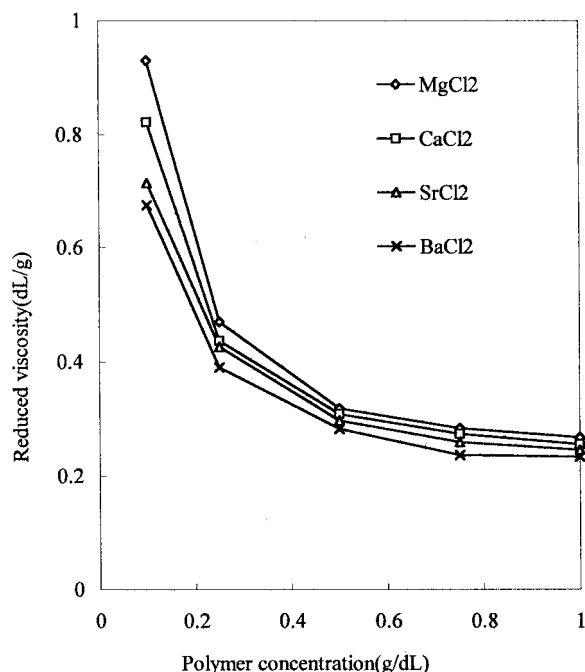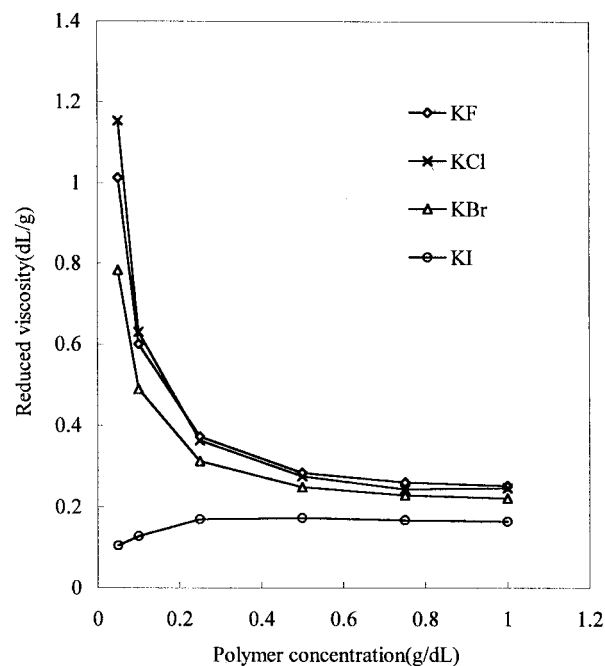
Figure 4 Reduced viscosity of MIQEDMAPMA versus the polymer concentration in a 0.25*M* aqueous solution of salts containing various divalent cations.

Figure 5 Reduced viscosity of MIQEDMAPMA versus the polymer concentration in a 0.25*M* aqueous solution of salts containing various halide anions.

Influence of different halide anions with a common cation (K^+) on [η] of MIQEDMAPMA

The data shown in Figure 5 and Table II show an increase of [η] for monovalent anions in the order of $F^- > Cl^- > Br^- > I^-$ for KF, KCl, KBr, and KI, respectively, for MIQEDMAPMA in 0.25*M* aqueous salt solutions. This is because the larger anion with a common positive charge (the charge density is smaller) is easily polarized and bound to the quaternary ammonium group (R_4N^+) on MIQEDMAPMA. The positive charge on polymeric side chains could, therefore, become effectively neutralized by the larger anion and reduce [η] of MIQEDMAPMA in 0.25*M* aqueous salt solutions. This result also conforms to the Pearson principle.

Influence of different acid groups with a common cation (Na^+) on [η] of MIQEDMAPMA

For various acidic groups, Figure 6 and Table III show an increase of [η] for MIQEDMAPMA in 0.25*M* aqueous salt solutions in the order of $ClO_4^- < NO_3^- \cong NaHCO_3^- < CH_3COO^-$ for $NaClO_4$, $NaNO_3$, $NaHCO_3$, and CH_3COONa, respectively. This tendency is similar to that of the halide anions (Fig. 5 and Table II). MIQEDMAPMA dissolved in 0.25*M* $NaClO_4$ aqueous solutions, and this resulted in lower [η] values than for other salts. This phenomenon is attributed to the strong attraction of the polymeric side chains of MIQEDMAPMA 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 TMAAI and MIQS-DMAPM; it caused these polymeric aqueous solutions to become turbid,[38,39] just as $Na_2S_2O_3$ did (discussed in the next section). The acetate ion (CH_3COO^-) is a weakly acidic group and is easily associated in the

TABLE I
Effect of Various Cations with a Common Anion on the Viscosity Behavior of MIQEDMAPMA at 30°C

| Salt solution (0.25*M*)	Slope	[η]	k'
LiCl	−0.103	0.375	−0.729
NaCl	−0.083	0.342	−0.708
KCl	−0.057	0.298	−0.642
$MgCl_2$	−0.101	0.366	−0.757
$CaCl_2$	−0.105	0.358	−0.821
$SrCl_2$	−0.103	0.345	−0.869
$BaCl_2$	−0.098	0.325	−0.931

TABLE 2
Effect of Various Halide Anions with a Common Cation on the Viscosity Behavior of MIQEDMAPMA at 30°C

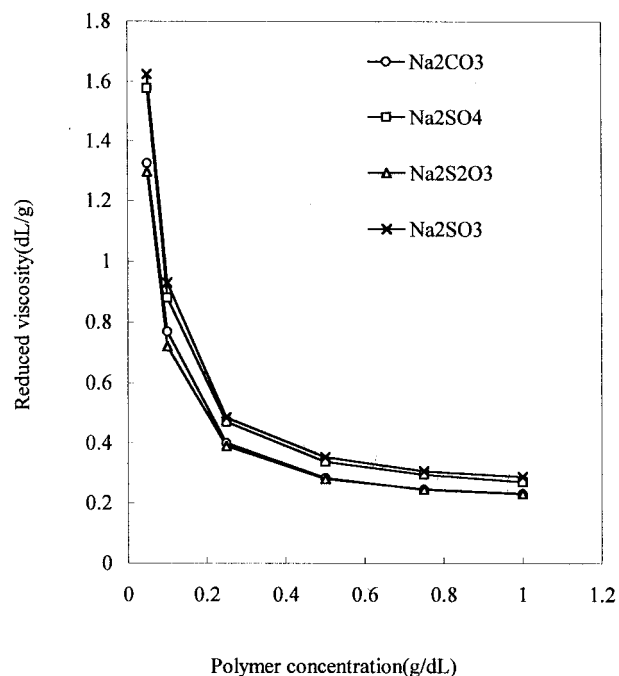| Salt solution (0.25*M*)	Slope	[η]	k'
KF	−0.064	0.313	−0.649
KCl	−0.057	0.298	−0.642
KBr	−0.056	0.275	−0.746
KI	−0.016	0.179	−0.506
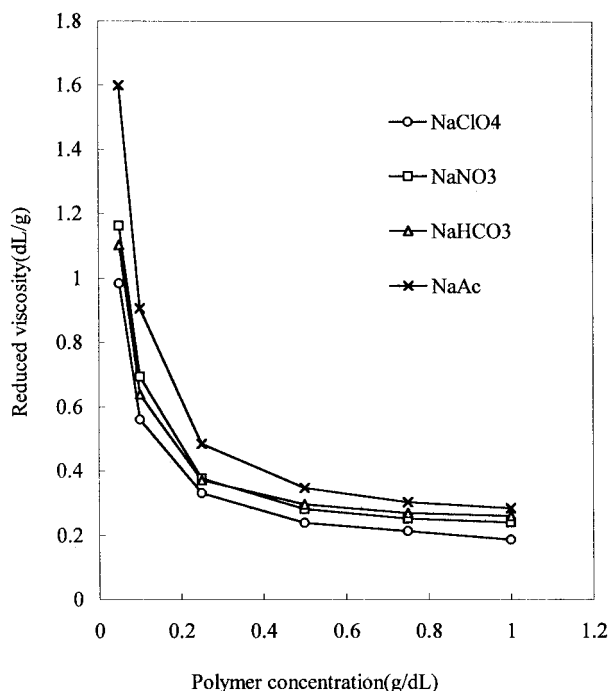
Figure 6 Reduced viscosity of MIQEDMAPMA versus the polymer concentration in a 0.25M aqueous solution of salts containing various monovalent acid groups.
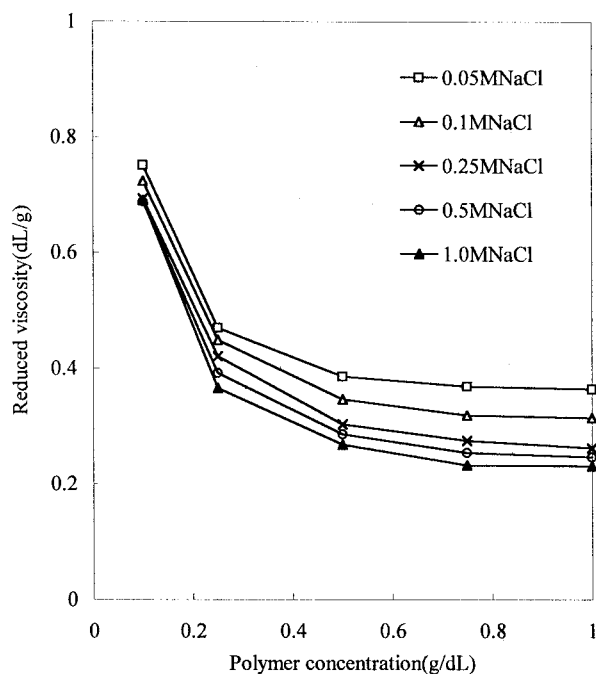

Figure 7 Reduced viscosity of MIQEDMAPMA versus the polymer concentration in a 0.25M aqueous solution of salts containing various divalent acid groups.

formation of acetic acid in an aqueous solution. Therefore, the ionic intensity is very small and cannot effectively neutralize the charges of the polycations. The [η] value of MIQEDMAPMA was, therefore, higher than that of other anions in 0.25M aqueous salt solutions. The results obtained from the different anions and various acids for MIQEDMAPMA also contrast with those of polyampholytes.[46-48]

For the various divalent acidic groups, the data (see Fig. 7 and Table III) show a decrease of [η] for MIQED-MAPMA in 0.25M aqueous salt solutions in the order of $SO_3^{-2} > SO_4^{-2} > S_2O_3^{-2} \cong CO_3^{-2}$ for Na_2SO_3, Na_2SO_4, $Na_2S_2O_3$, and Na_2CO_3, respectively. However, the [η] effect of CO_3^{-2} is close to that of $S_2O_3^{-2}$ because more counterions such as OH^- and HCO_3^- are produced and bound to the quaternary ammonium

group (R_4N^+) to reduce [η] of MIQEDMAPMA. This tendency conforms to the Pearson principle and is similar to previous results for TMAAI, MIQAD-MAPM, and MIQSDMAPM.[38-40]

Effect of various salt concentrations in aqueous solutions on [η] of MIQEDMAPMA

The conformation of cationic polymers is governed by electrostatic repulsive forces 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. Therefore, the phenomenon of a decrease in the reduced viscosity with an increase in the salt concentration was rationalized. The effect of various NaCl concentrations between 0.05 and 1.0M on the reduced viscosity is shown in Figure 8 for MIQEDMAPMA. The reduced viscosity apparently decreased with an increase in the NaCl concentration. These phenomena are in sharp contrast to the inner salt of poly(sulfobetaine)s.[46-48]

When the salt concentration was increased, a partial amount of negative charges of salt became site-bound on the quaternary ammonium group (R_4N^+) on MIQEDMAPMA. The polymeric charges became neutralized by the counterions in the aqueous solution. This occurrence reduced the repulsion of polymeric side chains, decreasing the extent of tightly stretched chains and coiling the polymeric main chains. The

TABLE III
Effect of Various Acid Groups with a Common Cation on the Viscosity Behavior of MIQEDMAPMA at 30°C

Salt solution (0.25M)	Slope	[η]	k'
CH_3COONa	−0.126	0.406	−0.765
$NaHCO_3$	−0.071	0.328	−0.660
$NaNO_3$	−0.084	0.321	−0.818
$NaClO_4$	−0.105	0.291	−1.241
Na_2SO_3	−0.130	0.414	−0.761
Na_2SO_4	−0.133	0.401	−0.829
$Na_2S_2O_3$	−0.096	0.325	−0.909
Na_2CO_3	−0.108	0.334	−0.967

Figure 8 Reduced viscosity versus the polymer concentration for MIQEDMAPMA in aqueous NaCl solutions of various concentrations.

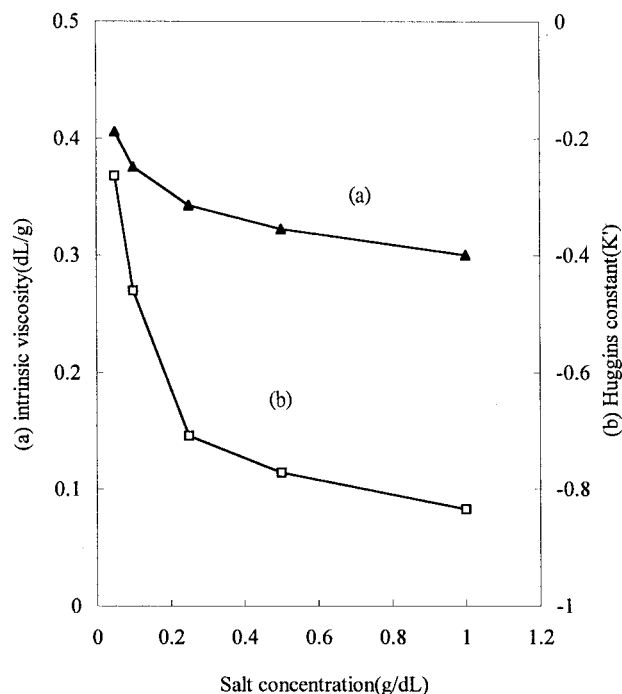**Figure 9** (a) $[\eta]$ and (b) k' of MIQEDMAPMA versus the concentration of NaCl.

chloride ions (Cl^-) binding on the quaternary ammonium group (R_4N^+) of MIQEDMAPMA were increased in high salt concentrations to form regions of high local charge density.

The slope, $[\eta]$, and k' values shown in Table IV were calculated with Figure 8 and eq. (1). The values of k' decreased with a decrease in $[\eta]$ as the concentration of the salt increased (also see Fig. 9). These phenomena might be due to the decrease of the intramolecular electrostatic repulsive force and the formation of the hydrophobic microdomains arising from local intramolecular aggregation of alkyl chains under higher salt concentrations. This phenomenon was also observed in our previous study of MIQADMAPM.[39]

$[\eta]$, obtained by the extrapolation of the curves in Figure 8 at a constant simple electrolyte concentration to a zero concentration of the polymer, is plotted in Figure 10 as a function of the reciprocal square root of the ionic strength ($I^{-1/2}$). A linear relationship obtained from Figure 9 conforms to the general law of polyelectrolytes.[50,51]

Effect of various pH values in aqueous solutions on $[\eta]$ of MIQEDMAPMA

Because MIQEDMAPMA contains side-chain groups of R_4N^+ and COOH like an amino acid structure,

TABLE IV
Effect of the NaCl Concentration or Ion Strength on $[\eta]$ and k' of MIQEDMAPMA at 30°C

NaCl (M)	$I^{-1/2}$	Slope	$[\eta]$	k'
0.05	4.4721	−0.044	0.4057	−0.265
0.1	3.1623	−0.065	0.3752	−0.461
0.25	2	−0.083	0.3423	−0.708
0.5	1.4142	−0.080	0.3222	−0.772
1	1	−0.075	0.3002	−0.834
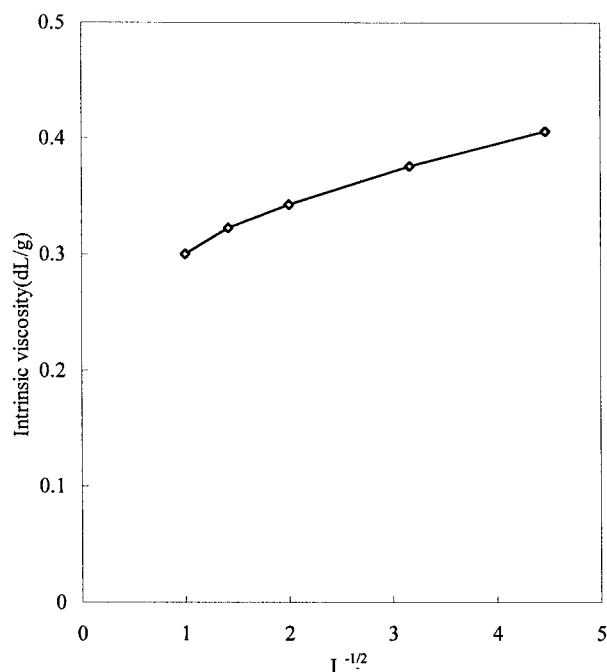
Figure 10 k' of MIQEDMAPMA as a function of $I^{-1/2}$.
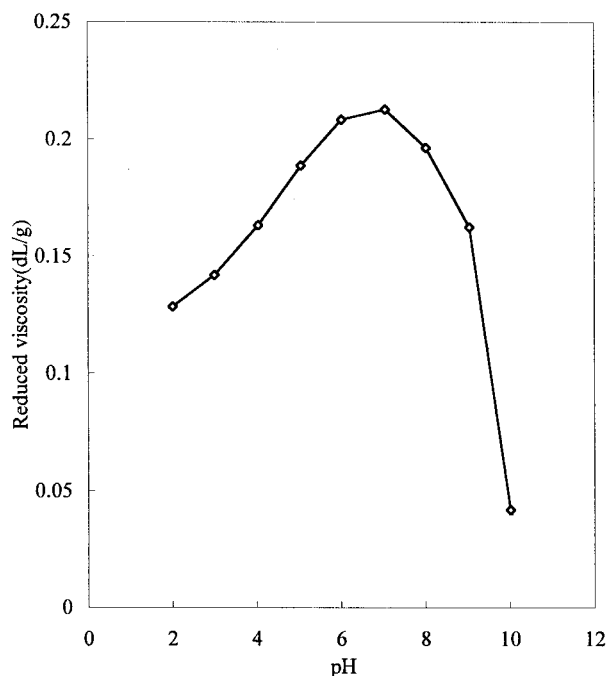
Figure 11 Reduced viscosity versus the pH for MIQED-MAPMA in a 0.2 g/dL aqueous solution.

which perhaps have zwitterionic properties in acidic or basic aqueous solutions or perhaps have an inner ring of NR_4^+—COO^-, a polyampholyte structure arises from interpolymer and intrapolymer chain attraction. Such a structural transformation for MIQED-MAPMA makes the polyelectrolyte property convert into a polyampholyte property under certain circumstances. The data exhibited in Figure 11 show that there exists a maximum reduced viscosity at pH 7. This phenomenon indicates that MIQEDMAPMA has a maximum net charge repulsion under this condition. This behavior was also observed for poly(methyl iodide quaternized styrene-dimethylaminopropyl male-amidic acid) (MIQSDMAPMA) in our previous work.[52]

CONCLUSIONS

The aqueous solution properties of cationic polyelectrolytes were evidently changed as salts were added to polymeric aqueous solutions. As the radius of the salt ion was increased, the degree of attraction between MIQEDMAPMA and salt, and the degree of polymeric recoiling, increased. Simultaneously, the reduced viscosity and $[\eta]$ decreased. As the salt concentration was increased, $[\eta]$ and k' decreased (k' was influenced by polymer–solvent and polymer–polymer interactions). The structural transformation of MIQEDMAPMA in aqueous salt solutions containing various acid groups occurred, converting the polyelectrolyte property into a

polyampholyte property. Moreover, the polymer aqueous solution exhibited a maximum reduced viscosity at pH 7, even though the tendency of the reduced viscosity and $[\eta]$ values of MIQEDMAPMA in various aqueous salt solutions was similar to that of other cationic polyelectrolytes. k' of MIQEDMAPMA in aqueous salt solutions was extremely different from k' of MIQSDMAPM and MIQADMAPM copolymers and TMAAI homopolymers and was especially different from previous work on the MIQSDMAPMA copolymer with the replacement of the styrene segment by vinyl ether in the MIQEDMAPMA copolymer backbone. This phenomenon was attributed mainly to the presence of the ethyl vinyl segment and carboxylic group of the anionic polyelectrolyte, two hydrophilic groups, in the pendent of the MIQEDMAPMA copolymer.

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