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Macromolecular microstructure, reactivity ratio and viscometric studies of water-soluble cationic and/or zwitterionic copolymers

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Abstract

Copolymers of cationic trimethyl(4-methacrylamidophenyl)ammonium methyl sulfate (TMMAPhAMS) or zwitterionic 3-dimethyl(4-methacrylamidophenyl)ammonato propane sulfonate (DMMAPhAPS) monomer with methacrylamide (MAA) have been prepared by free radical polymerization using 4,4′-azobis-cyanovaleric acid as an initiator in aqueous solution. Copolymer compositions were obtained by elemental analysis. The monomer reactivity ratios were calculated by the Fineman–Ross and Kelen–Tüdos methods. The $r_1 r_2 = 0.17$ for TMMAPhAMS/MAA copolymer and $r_1 r_2 = 0.34$ for DMMAPhAPS/MAA copolymer, using the Fineman–Ross treatment, exhibit a slight tendency toward alternation. The microstructure of the cationic copolymer series (TMMAPhAMS/MAA) is more alternating than that of the zwitterionic series (DMMAPhAPS/MAA). A similar phenomenon was observed using the Kelen–Tüdos treatment. The statistical distribution of monomer sequences was calculated by the Pyun method. From the microstructure data, the alternation and the blockiness amounts were determined. The dilute-solution properties of the two copolymer series have been studied in related to their composition and added electrolytes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure; Copolymer; Zwitterion

1. Introduction

The synthesis of electrolyte-tolerant, water-soluble polymers that contain ionic pendant groups has been the goal of academic and industrial laboratories in recent years. Among these types of polymers, the poly(sulfobetaine)s have already been described in the vinylpyridine ([1] and references therein), vinylimidazole [2–4] and tertiary amino methacrylate series [5,6]. Aqueous polyelectrolytes of anionic and cationic types have been extensively studied and comprehensively described in numerous books and reviews [7–10]. All these polymers have applications in water treatment, remediation, drag reduction, petroleum recovery, viscosification, formulation of coatings, cosmetics and pharmaceutics [11–13]. Also, Szita et al. [14] and Spriestersbach et al. [15] reported that betaine monomers are copolymerizable with acrylonitrile and can be applied to the dyeing of textiles. Mizuguchi and his co-workers also used this polymerizable monomer to improve the physical properties of emulsion [16].

Previously, we had synthesized several phenyl-containing cationic water-soluble polymers and zwitterionic water-soluble polymers [17]. The solubility and viscometry of the phenyl-containing water-soluble homopolymers have been discussed. The hydrophobic group of these polymers interrupts the intra- and inter-ionic associations and causes the polymer to be soluble in deionized water [17].

In this paper, we report the synthesis and characterization of a series of copolymers of methacrylamide (MAA) with phenyl-containing monomers (TMMAPhAMS or DMMAPhAPS). The reactivity ratios and values of copolymerization parameters (Q, e) of the poly(TMMAPhAMS/MAA) and poly(DMMAPhAPS/MAA) series were determined. The microstructure, such as mean sequence length and distribution of the monomer units, were also discussed. The purpose of the present work is also to study the compositional effects of incorporation of ionic groups on the properties of the resulting copolymers. In particular, the viscosity responsiveness of the copolymers has been studied as a function of added electrolytes.

2. Experimental

2.1. Materials

The monomer MAA was obtained from Acros Chemical

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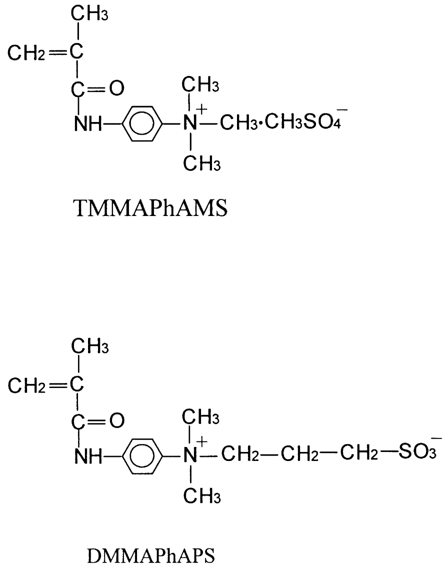
TMMAPhAMS

DMMAPhAPS

Scheme 1.

Co. Methylacryloryl chloride was prepared by refluxing a mixture of thionyl chloride (Merck) and methacrylic acid (Riedel-de Haën) which was followed by distillation. *N*,*N*-Dimethyl-1,4-phenylenediamine was purchased from Merck and used as received without further purification. The dimethyl sulfate (Merck) was distilled under reduced pressure (60–61°C/5 mmHg) before use. The 1,3-propane sulfone was used as-received (TCI). The organic solvents were purified using standard methods.

2.2. Monomer synthesis

N,*N*-Dimethylaminophenyl methacrylamide (DMAPMA), TMMAPhAMS and DMMAPhAPS were synthesized as reported previously [17]. The structures of TMMAPhAMS and DMMAPhAPS were shown in Scheme 1 and confirmed by ^{1}H NMR and ^{13}C NMR [17].

2.3. Copolymer preparation

The copolymers of ionic monomer (TMMAPhAMS or DMMAPhAPS) with MAA were prepared in an aqueous solution under reaction conditions shown in Tables 1 and 2.

Table 1
Results of copolymerization of TMMAPhAMS (M_1) and MAA (M_2) ([ACVA]: 5.0×10^{-3} mol l^{-1} at 60°C; solvent: water; total monomer: 5.0×10^{-1} mol l^{-1}; total volume: 10 ml)

Sample	Feed ratio for TMMAPhAMS/MAA	N (%) in copolymer	[M_1] (mol%) in copolymer[a]
TM-90	90:10	8.97	79.93
TM-70	70:30	9.91	54.25
TM-50	50:50	10.48	43.61
TM-30	30:70	11.21	33.21
TM-10	10:90	13.38	13.99

[a] From elemental analysis.

Table 2
Results of copolymerization of DMMAPhAPS (M_1) and MAA (M_2) ([ACVA]: 5.0×10^{-3} mol l^{-1} at 60°C; solvent: water; total monomer: 5.0×10^{-1} mol l^{-1}; total volume: 10 ml)

Sample	Feed ratio for DMMAPhAPS/MAA	N (%) in copolymer	[M_1] (mol%) in copolymer[a]
DM-90	90:10	8.85	88.38
DM-70	70:30	9.25	74.08
DM-50	50:50	10.28	48.84
DM-30	30:70	10.55	44.00
DM-10	10:90	13.24	15.31

[a] From elemental analysis.

TMMAPhAMS, MAA, 1 mol% of 4,4′-azobis-cyanovaleric acid (ACVA) and distilled water were introduced into a 100 ml polymerization ampoule. The contents of the ampoule were then sealed in vacuum after utilization by the freeze–thaw technique. The copolymers were purified by reprecipitation from water into acetone. After complete drying, the copolymers were under Ar atmosphere. The water-free samples were obtained. The copolymer compositions were determined by nitrogen analysis. The copolymer compositions have also been checked by ^{1}H NMR spectra of the copolymers (the mole fractions of copolymers were estimated from the relative peak area of aliphatic proton resonance and phenylene proton resonance) [18–20]. All the resonance peak positions do not change with feed molar ratio. Phenyl proton resonance generally appears as the peak at 7.4–7.7 ppm whose relative intensities do not depend on polymer composition. Aliphatic proton resonance, whose relative peak area accounts well for the mole fraction of methacrylamide in the polymer, appears at 0.5–4.0 ppm. That is, the mole fraction of DMMAPhAPS or TMMAPhAMS in copolymer, estimated from the relative peak area of phenyl proton resonance is always in good accordance with that from the peak area of aliphatic proton resonance at 0.5–4.0 ppm. The ^{1}H NMR results approach the results of N-content element analysis. For example, TM-30 exhibits 32.6 mol% of M_1 (TMMAPhAMS) (determined from ^{1}H NMR) [18–20] and 33.2 mol% of M_1 (TMMAPhAMS) (determined from element analysis) in the copolymer. DM-50 exhibits 47.7 mol% of M_1 (DMMAPhAPS) (determined from ^{1}H NMR) [12] and 48.8 mol% of M_1 (DMMAPhAPS) (determined from element analysis) in the copolymer. Good agreement was observed between the cationic and zwitterionic copolymer compositions, by ^{1}H NMR and element analysis. The monomer reactivity ratios were calculated by the Fineman–Ross [21] and Kelen–Tüdos [22] methods.

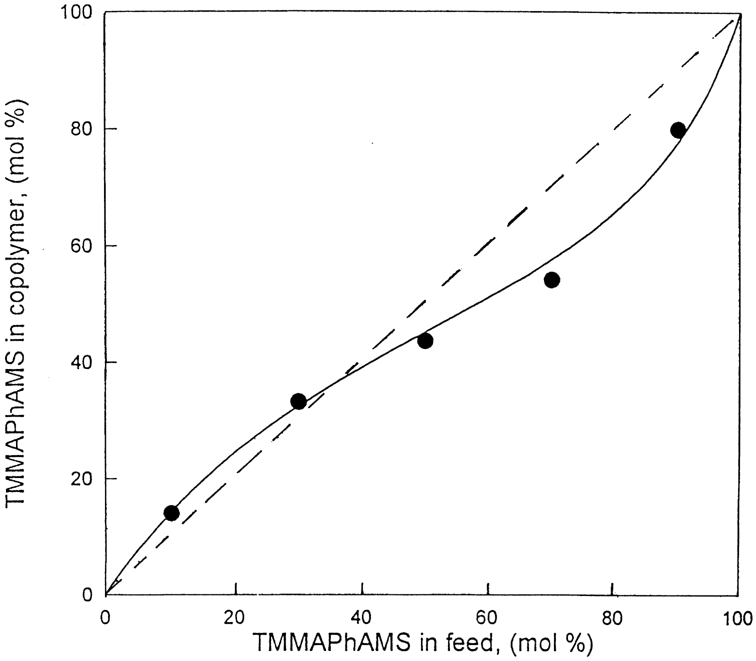

Fig. 1. Mol% of TMMAPhAMS incorporated into the copolymers as a function of the comonomer feed ratio.

2.4. Characterization methods

Viscometric measurements were carried out with a Ubbelohde viscometer (the viscometer has a flow time of 132.25 s in pure water) at 30 ± 0.01°C. Melting points were measured in capillaries on a Büchi apparatus (model Büchi 535). IR spectra were recorded in the range of 4000–400 cm^{-1} for the synthesized monomers and polymers using KBr disks (JASCO IR-700 spectrometer). Elemental analysis was performed with a Perkin–Elmer 2400 instrument. NMR spectra were recorded using a JEOL EX400.

3. Results

3.1. Compositional and reactivity ratios analysis

The copolymer compositions, as a function of feed composition, are shown in Figs. 1 and 2. The dashed line represents a copolymerization in which an ideally random copolymer would be formed.

Reactivity ratios for the poly(TMMAPhAMS/MAA) series and the poly(DMMAPhAPS/MAA) series were determined from the feed ratios of the monomers and the resultant copolymer compositions were obtained by elemental analysis. Fig. 3 is a Fineman–Ross plot used to determine the reactivity ratio for TMMAPhAMS (M_1) and MAA (M_2). The reactivity ratio r_1 and r_2 for the monomer pair M_1 and M_2, respectively, can be determined by

$$\frac{F(f-1)}{f} = r_1\left(\frac{F^2}{f}\right) - r_2 \tag{1}$$

where $f = \text{d}[M_1]/\text{d}[M_2]$, $F = [M_1]/[M_2]$.

The reactivity ratio r_1 was determined to be 0.30 from the slope and $r_2 = 0.58$ from the intercept. The Kelen–Tüdos approach was similarly used for the evaluation of reactivity ratios for the same monomer pair according to

$$\nu = r_1\xi - \frac{r_2(1-\xi)}{\alpha} \tag{2}$$

where $\nu = G/(\alpha + H)$ and $\xi = H/(\alpha + H)$.The transformed variables G and H are given by

$$G = \frac{[M_1]/[M_2]\{(\text{d}[M_1]/\text{d}[M_2]) - 1\}}{\text{d}[M_1]/\text{d}[M_2]}$$
$$H = \frac{([M_1]/[M_2])^2}{\text{d}[M_1]/\text{d}[M_2]} \tag{3}$$

The parameter α is calculated by taking the square root of the product of the lowest and highest values of H for the copolymerization series. Graphical evaluation for poly(TMMAPhAMS/MAA) yields values of $r_1 = 0.29$ and $r_2 = 0.59$. From Fig. 4, it is clear that the observed data in the Kelen–Tüdos plot are linear, indicating that these copolymerizations follow the conventional copolymerization kinetics under a prerequisite, and that the reactivity of a polymer radical is determined only by the terminal monomer unit [23]. The calculated reactivity ratios for the copolymerization of TMMAPhAMS with MAA are listed in Table 3. Similar values of r_1 and r_2 were found by using Fineman–Ross and Kelen–Tüdos treatments.

Copolymerization of the zwitterionic monomer (DMMAPhAPS) with MAA was also carried out in deionized water solution at low conversion. The result is shown in Table 4. Similarly, reactivity ratio studies were carried out for the

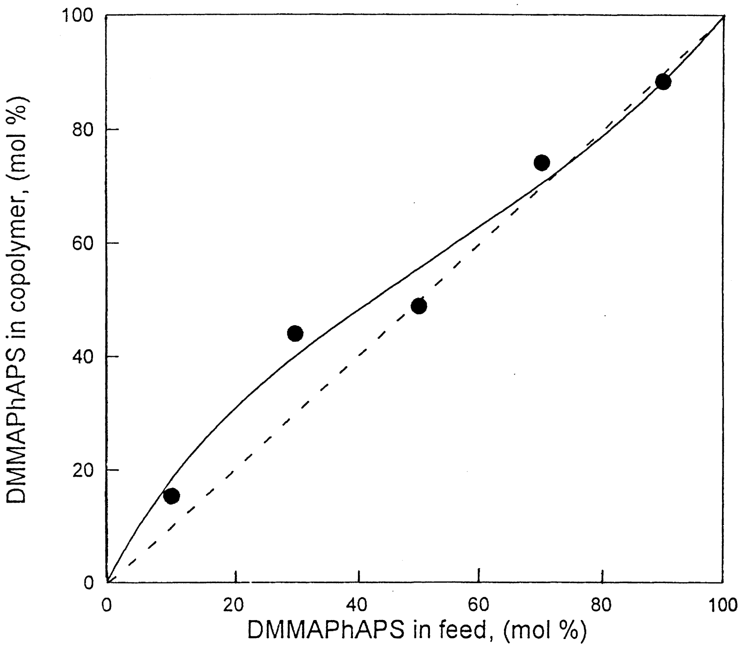

Fig. 2. Mol% of DMMAPhAPS incorporated into the copolymers as a function of the comonomer feed ratio.

copolymerization of DMMAPhAPS (M_1) with MAA (M_2) using Fineman–Ross (Fig. 5) and Kelen–Tüdos (Fig. 6) methods.

The calculated reactivity ratios for DMMAPhAPS and MAA are listed in Table 4. The copolymerization of the r_1r_2 value also showed a tendency toward alternation. From Tables 3 and 4, it is clear that the copolymerization of the cationic monomer (TMMAPhAMS) with MAA has lower r_1r_2 values than that of the zwitterionic monomer (DMMAPhAPS). The microstructure of the poly(TMMAPhAMS/MAA) and the poly(DMMAPhAPS/MAA) series is of great use in predicting solution properties. The statistical distribution of monomer sequences M_1–M_1, M_2–M_2 and M_1–M_2 may be calculated by the Igarashi method [24]

$$X = \phi_1 - \frac{2\phi_1(1-\phi_1)}{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1-\phi_1)]^{1/2}} \tag{4}$$

$$Y = (1-\phi_1) - \frac{2\phi_1(1-\phi_1)}{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1-\phi_1)]^{1/2}} \tag{5}$$

$$Z = \frac{4\phi_1(1-\phi_1)}{1 + [(2\phi_1 - 1)^2 + 4r_1r_2\phi_1(1-\phi_1)]^{1/2}} \tag{6}$$

The mole fractions of M_1–M_1, M_2–M_2 and M_1–M_2 sequences in the copolymer are designated X, Y and Z, respectively. Φ_1 is the mole fraction of M_1 in the copolymer. Mean sequence length, μ_1 and μ_2, can be calculated by the following equations, in consideration of the compositional drift:

$$\mu_1 = 1 + r_1\frac{[M_1]}{[M_2]} \tag{7}$$

$$\mu_2 = 1 + r_2\frac{[M_2]}{[M_1]} \tag{8}$$

Microstructure information was obtained statistically using these equations. The results are shown in Tables 5

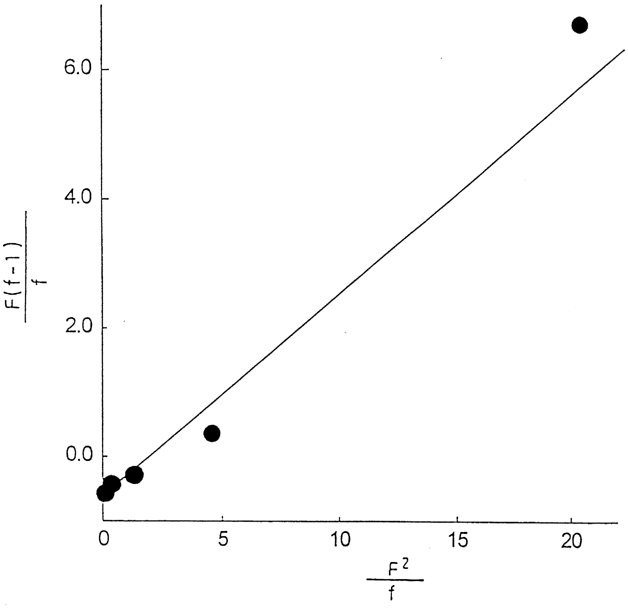

Fig. 3. Determination of reactivity ratios for the copolymerization of TMMAPhAMS with MAA by the Fineman–Ross method.

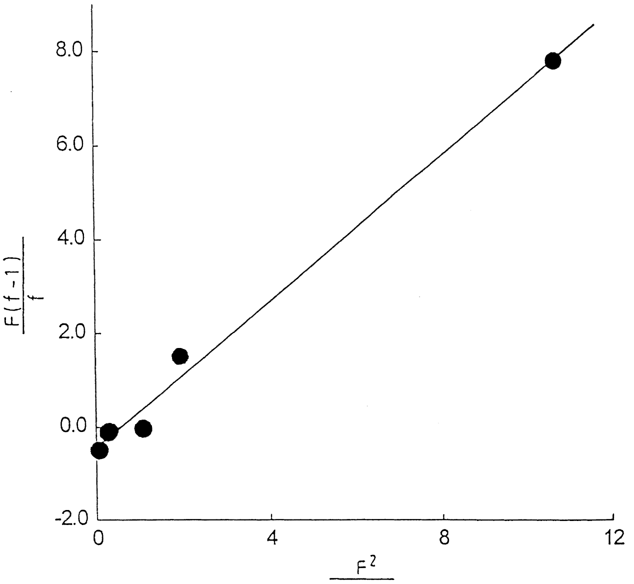

Fig. 4. Determination of reactivity ratios for the copolymerization of DMMAPhAPS with MAA by the Fineman–Ross method.

and 6. The Igarashi method calculates the fractions of blockiness and alternation units in the copolymers as a function of reactivity ratios and copolymer compositions. The Pyun [25] method calculates the mean sequence length of the monomers in each copolymer. The inter-monomer linkages and mean sequence length distributions for the poly(TMMAPhAMS/MAA) and the poly(DMMAPhAPS/MAA) series are listed in Tables 5 and 6, respectively. For the series of poly(TMMAPhAMS/MAA), the mean sequence length of TMMAPhAMS, $\mu_{\mathrm{TMMAPhAMS}}$, varied from 3.70 at a 79.93/20.07 mole ratio of TMMAPhAMS/MAA in the copolymer to 1.03, at a 13.99/86.01 mole ratio.

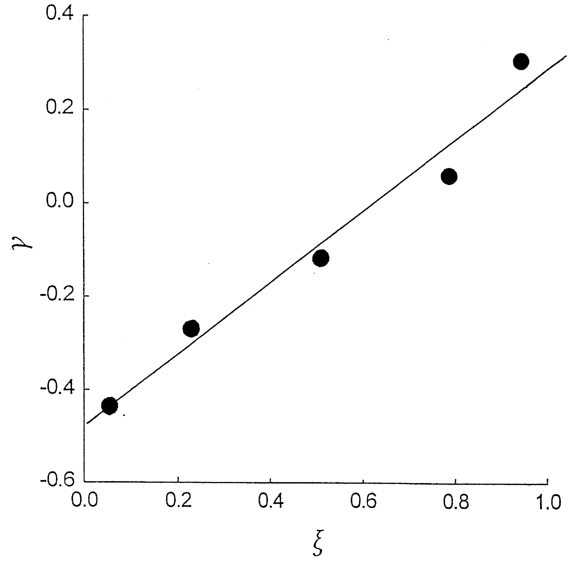

Fig. 5. Kelen–Tüdos plot for the determination of reactivity ratios for the copolymerization of TMMAPhAMS with MAA.

Table 3
Monomer reactivity ratios and copolymerization parameters of TMMAPhAMS (M_1) with MAA (M_2) determined using the methods of Fineman–Ross and Kelen–Tüdos

Method	Reactivity ratios			Copolymerization parameter	
	r_1	r_2	$r_1 \times r_2$	Q_1[a]	e_1[a]
Fineman–Ross	0.30	0.58	0.174	0.49	− 0.08
Kelen–Tüdos	0.29	0.59	0.171	0.48	− 0.09

[a] Calculated by methacrylamide, $Q_2 = 1.46$, $e_2 = 1.24$ from Brandrup J, Immergut EH, editors. Polymer Handbook, 2nd Edition, New York: Wiley, p. II-395, 1975.

For these compositions, values of μ_{MAA} were 1.06 and 6.22, respectively. In comparison, the poly(DMMAPhAPS/MAA) series had $\mu_{\mathrm{DMMAPhAPS}}$ values of 8.02 and 1.09 at 88.38/11.62 and 15.31/84.69 mole ratios of the poly(DMMAPhAPS/MAA) series. Values of μ_{MAA} were 1.05 and 4.87, respectively.

3.2. Viscometric studies

The dilute-solution behavior of these copolymers was studied with respect to their composition and added electrolytes. The reduced viscosities of the poly(TMMAPhAMS/MAA) series in NaCl aqueous solution and in deionized water solution, plotted as a function of composition are shown in Fig. 7. An increase in the reduced viscosity develops as the molar ratio of TMMAPhAMS and MAA approaches unity. Fig. 8 shows the reduced viscosity of the zwitterionic poly(DMMAPhAPS/MAA) series in deionized water and salt aqueous solution. Lower reduced viscosities of the poly(DMMAPhAPS/MAA) series than those of the cationic poly(TMMAPhAMS/MAA) series in aqueous solutions were observed. When salt is added, the reduced viscosity increased with increasing salt concentration. The series of TMMAPhAMS/MAA are ionized in deionized water solution and the mutual repulsion of their charges causes expansion of the polymer chain. These phenomena were also observed by Wiley et al. [26,27], Salamone et al. [28], Schulz et al. [29] and Liaw et al. [30–32] for various polymer electrolytes. In addition,

Table 4
Monomer reactivity ratios and copolymerization parameters of DMMAPhAPS (M_1) with MAA (M_2) determined using the methods of Fineman–Ross and Kelen–Tüdos

Method	Reactivity ratios			Copolymerization parameter	
	r_1	r_2	$r_1 \times r_2$	Q_1[a]	e_1[a]
Fineman–Ross	0.78	0.43	0.34	0.94	0.20
Kelen–Tüdos	0.81	0.48	0.39	0.88	0.27

[a] Calculated by methacrylamide, $Q_2 = 1.46$, $e_2 = 1.24$ from Brandrup J, Immergut EH, editors. Polymer Handbook, 2nd Edition, New York: Wiley, p. II-395, 1975.

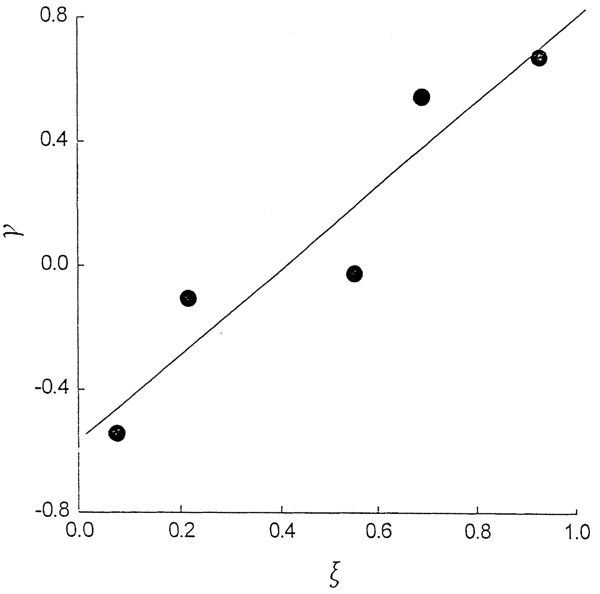

Fig. 6. Kelen–Tüdos plot for the determination of reactivity ratios for the copolymerization of DMMAPhAPS with MAA.

when salt is added to the poly(DMMAPhAPS/MAA) series, the reduced viscosity increased with increasing NaCl concentration.

4. Discussion

4.1. Macromolecular microstructure and reactivity ratio studies

The monomer reactivity studies of water-soluble monomer have grown rapidly in the past years because of their diverse commercial applications. Kathmann et al. [33] had synthesized copolymers of acrylamide (M_1) and zwitterionic monomer [4-(2-acrylamido-2-methylpropyldimethylammonio)butanoate] (M_2) to study reactivity ratios of the monomers. A nonlinear least-squares method yielded values of $r_1 = 1.01$ and $r_2 = 0.99$, indicating random incorporation of monomers into the final copolymer in salt solution. The salt in the reaction medium was used as a precaution to ensure that polymers with high zwitterionic monomer content remained homogeneous during polymerization. The collective positive charges on the zwitterionic monomer and polymer attracted the collective negative charges to form an ionically crosslinked network, thereby causing the monomer and polymer to show relatively poor solubility. Salts were added to the zwitterionic monomer or polymer aqueous solutions to shield the ionic associations between positive and negative charges as well as improve the water-solubility of zwitterionic monomers and polymers. That is, the salt in the reaction medium would shield the ionic interactions of the zwitterionic monomers/polymers during polymerization and indicate random incorporation of monomers into the final copolymer.

In our previous studies, the polymerization rate of ionic monomer in pure water was lower than that in salt aqueous solution because both ionic monomer and polymer were shielded in the reaction medium [34–36]. Copolymers of acrylamide with zwitterionic [3-dimethyl(acryloyloxyethyl)-ammoniumpropanesulfonate] (DAAPS) were prepared and r_1r_2 value was found to be 0.06. The result indicates an alternating microstructure for the acrylamide and zwitterionic monomer in salt-free aqueous solution [34–36]. In this study, the microstructure for the zwitterionic (DMMAPhAPS/MAA) series also possesses a tendency towards alternation. (The r_1r_2 value of DMMAPhAPS/MAA was 0.34.) However, the relatively high r_1r_2 values of the zwitterionic (DMMAPhAPS/MAA) series in salt-free solutions might have resulted from the hydrophobic association between the phenyl groups. The poly(DMMAPhAPS/MAA) series, remaining homogeneous in the salt-free reaction medium during polymerization, is also resulted from the hydrophobic phenyl groups that interrupt the zwitterionic association. These phenomena were also observed by Laschewsky et al. [37] and Liaw et al. [17,38] for the copolymerization of the cationic TMMAPhAMS/MAA series, which was also done in salt-free aqueous solution. As expected, an alternating microstructure for the TMMAPhAMS/MAA series was observed (the r_1r_2 value was 0.17). Kathmann et al. reported the same alternating result in the study of copolymerization of acrylamide with

Table 5
Structural data for the copolymer of TMMAPhAMS with MAA (T: trimethyl(4-methacrylamidophenyl)ammonium methyl sulfate (TMMAPhAMS). M: methacrylamide monomer.)

Sample	Composition (mol%)[a]		Blockiness (mol%)[b]		Alternation (mol%)[b]	Mean sequence length	
	T	M	T–T	M–M	T–M	μ_T	μ_M
TM-90	79.93	20.07	60.90	1.04	38.07	3.70	1.06
TM-70	54.25	45.75	19.40	10.90	69.71	1.70	1.25
TM-50	43.61	56.39	9.29	22.07	68.64	1.30	1.58
TM-30	33.21	66.79	3.96	37.54	58.49	1.13	2.35
TM-10	13.99	86.01	0.44	72.46	27.10	1.03	6.22

[a] From elemental analysis.
[b] Statistically calculated using reactivity ratios.

Table 6
Structural data for the copolymer of DMMAPhAPS with MAA (D: 3-dimethyl(4-methacrylamidophenyl)ammonato propane sulfonate (DMMAPhAPS). M: methacrylamide monomer.)

Sample	Composition (mol%)[a]		Blockiness (mol%)[b]		Alternation (mol%)[b]	Mean sequence length	
	D	M	D–D	M–M	D–M	μ_D	μ_M
DM-90	88.38	11.62	77.29	0.53	22.17	8.02	1.05
DM-70	74.08	25.92	51.49	3.33	45.19	2.82	1.18
DM-50	48.84	51.16	17.20	19.52	63.28	1.78	1.43
DM-30	44.00	56.00	12.95	24.95	62.09	1.33	2.00
DM-10	15.31	84.69	0.98	70.36	28.66	1.09	4.87

[a] From elemental analysis.

[b] Statistically calculated using reactivity ratios.

2-acrylamido-2-methylpropane dimethylammonium chloride (the r_1r_2 value was 0.19 in salt-free aqueous solution) [33].

4.2. Viscometric studies

The reduced viscosities of the zwitterionic poly(DMMAPhAPS/MAA) series and cationic poly(TMMAPhAMS/MAA) series were measured in deionized water and salt aqueous solution with various amounts of ionic monomer incorporation (Figs. 7 and 8). Furthermore, the reduced viscosities of the poly(DMMAPhAPS/MAA) series were lower than that of the cationic poly(TMMAPhAMS/MAA) series in both salt and salt-free aqueous solutions. These phenomena may be because of the formation of compact conformation of the poly(DMMAPhAPS/MAA) series and expansion conformation of the poly(TMMAPhAMS/MAA) series in aqueous solution. In salt-free aqueous solutions, the compact conformation of the poly(DMMAPhAPS/MAA) series resulted from the ionic associations between the cationic quaternary ammonium group and anionic sulfonate group. In addition, the expansion conformation of the poly(TMMAPhAMS/MAA) series resulted from the ionic repulsion between the cationic quaternary ammonium group and cationic quaternary ammonium group in polymer chains. With the addition of salt, the associations of the poly(DMMAPhAPS/MAA) series chains and the charge–charge repulsion of the poly(TMMAPhAMS/MAA) series chains decreased with an increasing $NaCl_{(aq)}$ concentration. Therefore, relatively high reduced viscosities of the poly(DMMAPhAPS/MAA) series were observed.

Viscosity of water-soluble polymers (such as cationic polyelectrolyte, anionic polyelectrolyte and polyampholyte) is not only related to the molecular weight but also reflects the change in polymer conformation in aqueous solution. Water-soluble polymers having ionic groups, which improve water solubility of polymers, and solution properties can become dependent on pH and/or electrolyte concentration. Ionic polymers also exhibit a high sensitivity to added salt, which will influence the polymer conformation in aqueous solution. The salt- and pH-responsiveness inherent to ionic polymer solutions is a function of the ionic group type and placement. The relatively high viscosity observed indicated that an expansion conformation of the polymer chains was formed. In contrast, a polymer's compact conformation implied that a relatively low viscosity would be observed. The amount of ionic groups in

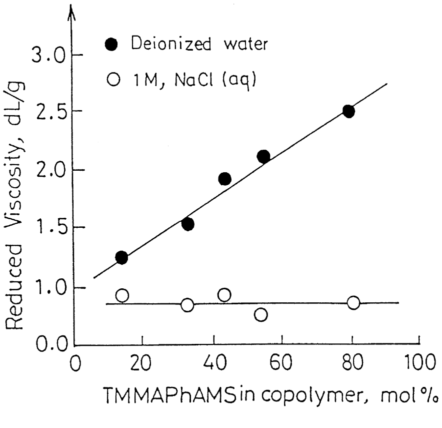

Fig. 7. Reduced viscosity of poly(TMMAPhAMS/MAA) series in deionized water solution and in 1M NaCl salt solution.

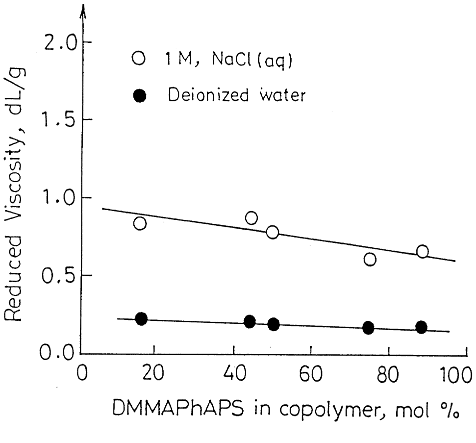

Fig. 8. Reduced viscosity of poly(DMMAPhAPS/MAA) series in deionized water solution and in 1M NaCl salt solution.

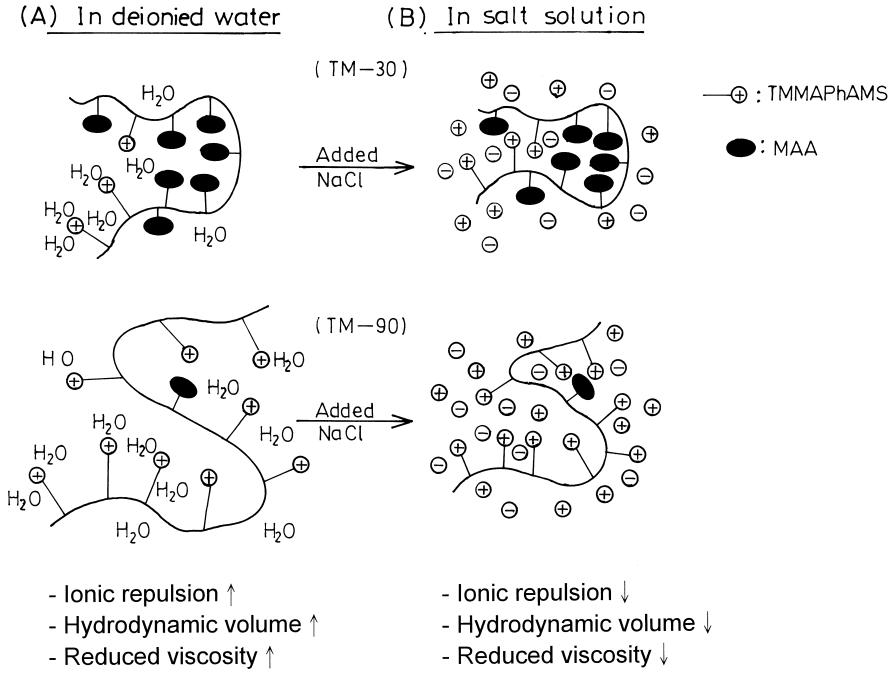

Fig. 9. Proposed model for effect of salt addition on poly(TMMAPhAMS/MAA) solution.

polymers would influence the conformation of ionic polymer in aqueous solution. The number and distribution of charged groups incorporated into polymers dictate the solution behavior of the resulting polymers. That is, the conformation of polymer chains as well as their viscosity has been directly related to the charge density of the ionic polymer solution. In this study, TMMAPhAMS was copolymerized with MAA in varying molar ratios to yield water-soluble cationic copolymer systems. The chains of the poly(TMMAPhAMS/MAA) series have positive charges of the quaternary ammonium species, and the charge–charge repulsions force the polymer chains to expand. The amounts of cationic groups incorporated into the poly(TMMAPhAMS/MAA) series enhance the expansion conformation of the poly-(TMMAPhAMS/MAA) chains and show relatively large hydrodynamic volume and highly

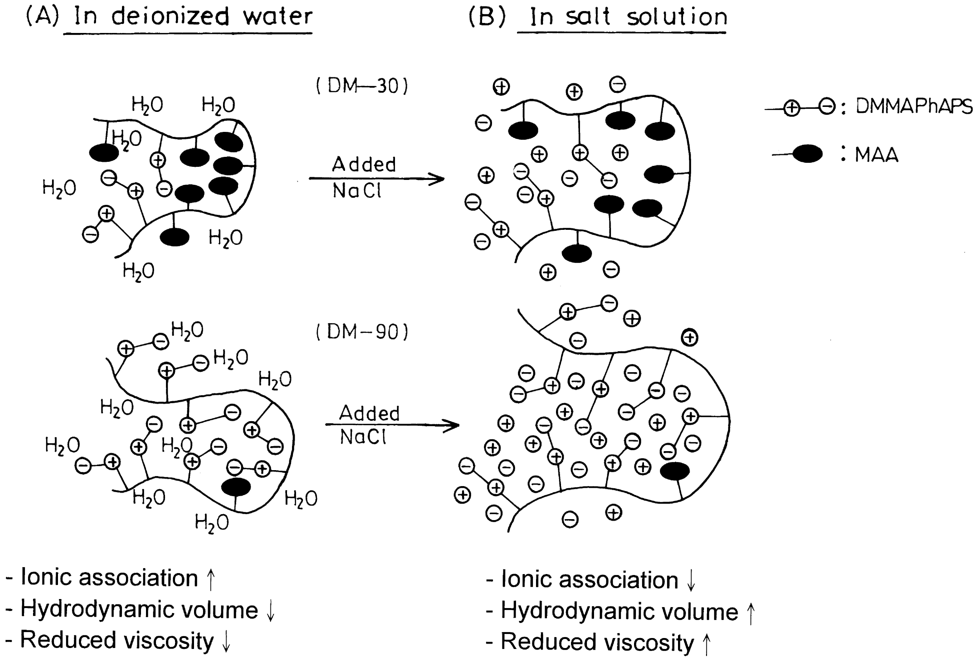

Fig. 10. Proposed model for effect of salt addition on poly(DMMAPhAPS/MAA) solution.

reduced viscosity. For instance, the reduced viscosity of TM-90 ($\eta_{red} = 2.6$ dl/g) was higher than that of TM-30 ($\eta_{red} = 1.6$ dl/g) in deionized water (Figs. 7 and 9A).

In contrast, the poly(DMMAPhAPS/MAA) chains have ionic associations between a positive charge of the quaternary ammonium group and a negative charge of the sulfonate group. Thus, the ionic associations force the poly(DMMAPhAPS/MAA) chains to show a compact conformation. The amount of zwitterionic groups incorporated into the poly(DMMAPhAPS/MAA) series has less effect on the hydrodynamic volume of the poly(DMMAPhAPS/MAA) series in aqueous solution (Figs. 8 and 10A).

Nevertheless, high incorporation of the zwitterionic groups would cause the inter- and/or intra-ionic associations of poly(DMMMAPhAPS/MAA) to become complicated. The solution properties and conformation of water-soluble polymers are changed with the solvent quality at various salt concentrations. Adding salt also causes the polymer's ionic condition to be screened out and the ionic interactions between the cationic groups and/or zwitterionic groups to decrease. The hydrodynamic volume of the cationic poly(TMMAPhAMS/MAA) series would decrease with a decreasing ionic repulsion between the cationic groups when salt was added. Thus, a relatively low viscosity was observed (Figs. 7 and 9B). Also, the hydrodynamic volume of the zwitterionic poly(DMMAPhAPS/MAA) series would increase with decreasing ionic associations between the zwitterionic groups. Large hydrodynamic volumes and, therefore, enhanced viscosities of the poly(DMMAPhAPS/MAA) series were observed (Figs. 8 and 10B).

5. Conclusions

Poly(TMMAPhAMS/MAA) and poly(DMMAPhAPS/MAA) series have been prepared by free radical polymerization in deionized water solution. Reactivity ratios and copolymer microstructures were determined and indicated alternation incorporation of both comonomers. The poly(TMMAPhAMS/MAA) series ($r_1 r_2 = 0.17$) is more alternating than the poly(DMMAPhAPS/MAA) series ($r_1 r_2 = 0.34$). The increase in reduced viscosity suggests an increase in ionic repulsion as the amount of TMMAPhAMS incorporated into the poly(TMMAPhAMS/MAA) series increases. The nature of added electrolyte influences the solution behavior of both copolymer series. With addition of electrolytes, the shielding of the ionic interaction between the cationic groups and/or zwitterionic groups caused the relatively low viscosity in the poly(TMMAPhAMS/MAA) series aqueous solutions and the relatively high viscosity in the poly(DMMAPhAPS/MAA) series aqueous solutions.

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