

Aqueous solution and photophysical properties of cationic poly(trimethyl methacrylamidophenyl ammonium methylsulfate) and zwitterionic poly(*N,N*-dimethylmethacrylamidophenyl ammonium propane sultone)

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Abstract

Water-soluble polymers, cationic poly(trimethyl methacrylamidophenyl ammonium methylsulfate) [poly(TMMAPhAMS)] and zwitterionic poly(*N,N*-dimethylmethacrylamidophenyl ammonium propane sultone) [poly(DMMAPhAPS)], derived from *N,N*-dimethylaminophenyl methacrylamide (DMPMA) were studied in terms of their solubility, viscosity, ultraviolet absorption, fluorescence properties, quasielastic light scattering and surface activity. The critical solution temperature of poly(DMMAPhAPS) and poly(TMMAPhAMS) observed was below 0°C showing that both have good solubility. These water-soluble polymers exhibited both ultraviolet absorption and fluorescence emission properties. The ultraviolet absorption of poly(DMMAPhAPS) (245 nm) showed a 2 nm red shift as compared to that of poly(TMMAPhAMS) (243 nm), suggesting that the microenvironment around the phenyl moiety of poly(DMMAPhAPS) is more hydrophobic in poly(TMMAPhAMS). With increasing salt concentration, the average hydrodynamic diameter of cationic poly(TMMAPhAMS) decreases from 640 to 200 nm, while that of poly(DMMAPhAPS) increases from about 300 to 750 nm. The surface tension of zwitterionic poly(DMMAPhAPS) decreases continuously in an almost linear dependence on logarithm concentration at higher polymer concentrations ($>2.5 \times 10^{-3}$ M), with no break indicative of micelle formation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorescence emission; Critical solution temperature; Light scattering

1. Introduction

In recent years, commercial applications of water-soluble polymers have been introduced, particularly as dispersing agents, surface-modifiers, and in the textile, pharmaceutical and other related industries [1–6]. Several research groups have studied the aqueous solution properties of polybetaines [7–14]. For example, Asonova et al. reported that a water-soluble polycarboxybetaine had a various reduced viscosity as a function of pH [9]. Topchiev et al. investigated the kinetic features of the radical polymerization of an unsaturated carboxybetaine in different pH ranges [10]. Salamone et al. thoroughly examined the solution properties of sulfo-betaine homopolymers, particularly in the vinylimidazole series [11,12]. Kang et al. reported that the adhesive-free

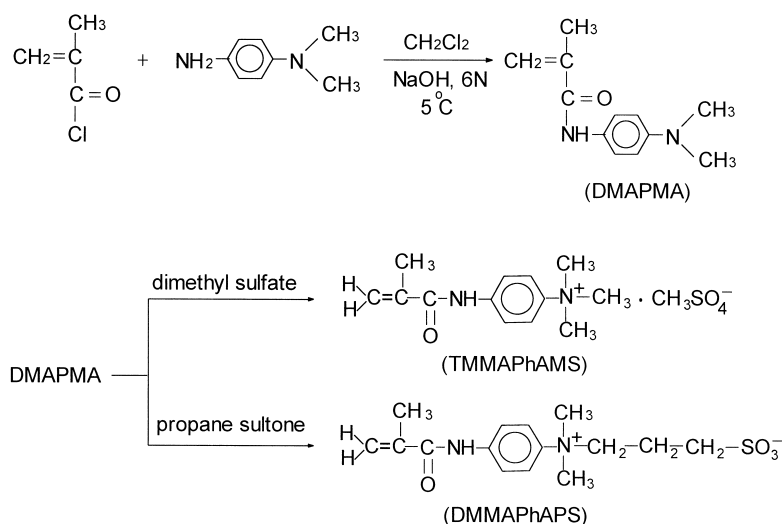
adhesion between two polymer films could be achieved with surface graft copolymerization water-soluble betaine [15,16]. Many investigators have used fluorescent-labeled water-soluble polymers to study phase separation [17], aggregation [18], latex film formation [19], electron transfer phenomena [20–23] or photoredox reaction [24].

In the past, researchers examined a series of poly(betaine)s and their corresponding cationic polyelectrolytes with different electron-withdrawing groups and varied ethylene units between the charge groups [25,26]. Some studies were conducted on the dilute aqueous solution properties of cationic polyelectrolytes [27,28], anionic polyelectrolytes [29] and polyampholytes [30,31]. Dilute aqueous solution properties such as viscosity and degree of binding to ionic groups within polymer chain can provide a reasonable assessment of the macroscopic solution; however, a detailed analysis requires the use of a more sensitive characterization.

The synthesis, viscometrics, and fluorescence properties

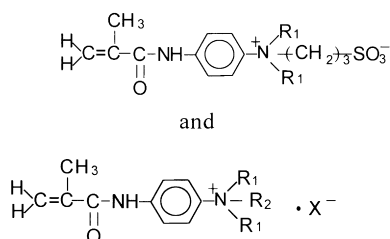
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Scheme 1.

of these water-soluble naphthalene-labeled acrylamide-based copolymers have been reported [32,33]. Similar studies were carried out on naphthalene-labeled styrene and maleic anhydride copolymers [34]. A series of new phenyl-containing sulfobetaines and their corresponding cationic monomers derived from *N,N*-dialkylamino phenyl methacrylamide,



in which $R_1 = -\text{CH}_3$ or $-\text{C}_2\text{H}_5$, $R_2 = -\text{CH}_3$, $-\text{C}_2\text{H}_5$ or $-(\text{CH}_2)_3\text{C}(=\text{O})\text{O}-\text{C}_2\text{H}_5$,

$X^- = \text{I}^-$, Br^- or CH_3SO_4^- , were performed and the NMR signals of the aliphatic group to be near the lines due to the quaternary ammonium group of sulfobetaine monomers with the assistance of their respective cationic monomers were clearly identified [35]. Furthermore, a series of copolymers of methacrylamide (MAA) with the phenyl-containing monomers [trimethylmethacrylamidophenyl ammonium methylsulfate (TMMAPhAMS) and *N,N*-dimethylmethacrylamidophenyl ammonium propane sultone (DMMAPhAPS)] were synthesized and characterized. The reactivity ratios and copolymerization parameters (Q , e) values of TMMAPhAMS/MAA and DMMAPhAPS/MAA copolymer series were determined. The microstructure such as mean sequence length and the distribution for the monomer units were also discussed [36].

In this study, we will report the viscometrics, surface activity and photophysical properties of the phenyl-containing cationic water-soluble polymer [poly (TMMAPhAMS)]

and corresponding zwitterionic water-soluble polymer [poly(DMMAPhAPS)], particularly the effect of salt on the photophysical and solution properties of poly(DMMA-PhAPS) and cationic poly(TMMAPhAMS).

2. Experimental

2.1. Materials

Methacryloyl chloride was prepared by refluxing a mixture of thionyl chloride (from Merck) and methacrylic acid (from RDH), followed by distillation [37–39]. *N,N*-Dimethyl-1,4-phenylenediamine was purchased from Merck and used as-received without further purification. The dimethyl sulfate (from Merck) was distilled under reduced pressure (60–61°C/5 mmHg) before use. Propane sultone was used as-received (from TCI). The organic solvents were purified using standard methods.

2.2. Synthesis of monomers

2.2.1. *N,N*-Dimethylaminophenylmethacrylamide (DMAPMA)

DMAPMA was synthesized according to the Scheme 1 [35]. M.p. 124–126°C. IR (KBr) ν (cm^{-1}): $\nu_{\text{N-H}}$ (3200), $\nu_{\text{C=O}}$ (1670), $\nu_{\text{C=C}}$ (1620). Elemental analysis: Calculated. C: 70.58%, H: 7.84%, N: 13.72%. Found. C: 70.25%, H: 7.70%, N: 13.56%.

2.2.2. Trimethylmethacrylamidophenyl ammonium-methyl sulfate (TMMAPhAMS) and *N,N*-dimethylmethacrylamidophenyl ammonium propane sultone (DMMAPhAPS)

The monomers, TMMAPhAMS and DMMAPhAPS, were synthesized from DMAPMA and corresponding compounds, dimethyl sulfate and propane sultone, respectively [35].

2.3. Preparation of polymers

2.3.1. Poly(TMMAPhAMS)

TMMAPhAMS monomer (0.02 mol) and 4,4'-azobis-4-cyanovaleric acid (ACVA) (2×10^{-4} mol) were introduced into a 100 ml ampoule. To this, 50 ml of distilled water was added to make a 0.4 M aqueous solution. The ampoule contents were then sealed in vacuum utilizing the freeze–thaw technique. The ampoule was then placed in an oil bath at 60°C for 24 h. The viscous solution was then precipitated with acetone. The crude polymer was reprecipitated from water to acetone, to eliminate the unreacted monomer, dried for 24 h at 60°C under vacuum, and weighed. A dried, brittle, and blue polymer was subsequently obtained. The yield was 92% and the intrinsic viscosity was calculated to be 1.0 dl/g in 0.1 M KCl solution with Ubbelohde viscometer at 30°C. The ^1H NMR peaks of polymer attributed to the acrylic group of monomer at 5.46 and 5.67 ppm disappeared.

2.3.2. Poly(DMMAPhAPS)

The synthesis of poly(DMMAPhAPS) was carried out in the same manner as for poly(TMMAPhAMS) using monomer DMMAPhAPS (0.02 mol). The yield was 94% and the intrinsic viscosity was calculated to be 0.88 dl/g in 0.1 M KCl solution with Ubbelohde viscometer at 30°C. The ^1H NMR peaks of polymer attributed to the acrylic group of monomer at 5.48 and 5.70 ppm disappeared.

2.4. Characterization methods

Viscometric measurements were carried out with a Ubbelohde viscometer (the viscometer has a flow time of 139.25 s in pure water) at $30 \pm 0.01^\circ\text{C}$. The intrinsic viscosities $[\eta]$ could be obtained by extrapolating the curves of Huggins plot. Melting points were measured in capillaries on a Büchi apparatus (Model Büchi 535). IR spectra were recorded in the range 4000–400 cm^{-1} for the synthesized monomers and polymers using KBr disks (JASCO IR-700 spectrometer). Elemental analysis was made (Perkin–Elmer 2400 instrument). NMR spectra were recorded using a JEOL EX400 (^1H at 399.96 MHz and ^{13}C at 100.58 MHz). UV absorbance spectra were obtained on a Beckman DU-65 spectrophotometer.

2.5. Critical solution temperature measurements

The critical solution temperature measured by heating or cooling was accurate within $\pm 4^\circ\text{C}$. The concentration of the polymer ranged from 0.01 to 10 wt%.

2.6. Quasielastic light scattering (QELS) measurements

The polymer solution used in QELS measurements were carefully filtered prior to placement into the light scattering apparatus.

The quasielastic light-scattering instrument used in these experiments was the OTSUKA DLS7000. All QELS

measurements were performed at 25°C in the 0.1 g/dl polymer aqueous solution.

2.7. Surface tension measurements

All surface tension measurements were performed on DCA-322 at room temperature in various polymer concentrations.

3. Results and discussion

3.1. Solubility of monomers and polymers

The solubilities of the monomers and polymers in some standard solvents were measured. The DMAPMA is soluble in methanol, ethanol, acetone, acetonitrile, tetrahydrofuran, ethylacetate, dimethyl formamide and dimethyl sulfoxide and insoluble in hexane, toluene and water. The cationic monomer (TMMAPhAMS) and polymer (poly(TMMAPhAMS)) are easily soluble in water and in methanol, ethanol, acetonitrile, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) at 60°C but insoluble in acetone, tetrahydrofuran and ethylacetate. The zwitterionic monomer DMMAPhAPS is soluble in water, acetonitrile, DMF and DMSO at 60°C but insoluble in methanol, ethanol, acetone, tetrahydrofuran and ethylacetate. The poly(DMMA-PhAPS) is easily soluble in water but insoluble in other organic solvents. Since the cationic monomer and polymer are ionized in aqueous solution, they were more soluble than the zwitterionic monomer and polymer.

Conventional poly(sulfobetaine)s normally show an upper critical solution temperature (UCST), a lower critical solution temperature (LCST), or a closed loop of insolubility in phase behavior diagrams [36]. Previous studies have addressed the aqueous solution properties of the naphthalene-labeled styrene-*alt*-sulfobetaine copolymer, poly(SDMPAPS)/NA [34]. The result showed that the UCST was at 17°C and a closed loop of insolubility between 0.2 and 20 wt% aqueous poly(SDMPAPS)/NA solution in the phase diagram. The critical solution temperature of poly(SDMPAPS)/NA was below 0°C in the salt aqueous solution. The low UCST of poly(SDMPAPS)/NA is due to both the low molecular weight of poly(SDMPAPS)/NA and the hydrophobic group in poly(SDMPAPS)/NA that interrupts the intramolecular association [34]. In this study, the phase solubility of poly(DMMAPhAPS) was confirmed over a wide range of polymer concentration (0.01–10 wt%). As the critical solution temperature curve was not observed above 0°C in phase behavior diagram, the critical solution temperature of poly(DMMAPhAPS) was below 0°C. The solubility behavior results from the hydrophobic groups interrupting intramolecular associations (by ionic and H-bonding interactions) which cause insolubility of poly(sulfobetaine) in aqueous solution. These phenomena are similar to the phase behavior of styrene-containing poly(SDMPAPS)/NA [34]. When salt (KCl) was added to

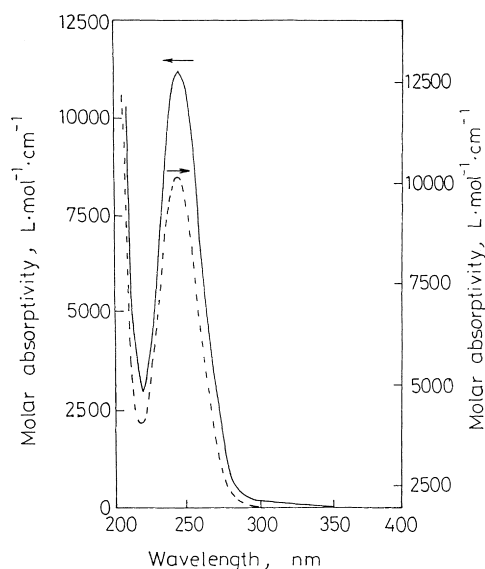


Fig. 1. UV absorption spectrum of polymers. poly(TMMAPhAMS), ---; poly(DMMAPhAPS), —. Polymer concentration was 10^{-4} M and solvent was water.

poly(DMMAPhAPS) aqueous solution, the critical solution temperature was lowered [40–44]. Therefore, the critical solution temperature of poly(DMMAPhAPS) was certainly below 0°C in salt solution.

3.2. Ultraviolet absorption and fluorescence emission

Strong ultraviolet absorptions of poly(DMMAPhAPS) and poly(TMMAPhAMS) containing phenyl group were observed as shown in Fig. 1. The maximum absorption for the moieties (phenyl group) of poly(DMMAPhAPS) (245 nm) shows a 2 nm red shift as compared to that of poly(TMMAPhAMS) (243 nm) suggesting that the microenvironment around the phenyl moiety of poly(DMMAPhAPS) is more hydrophobic than that of poly(TMMAPhAMS) [22]. This could be due to the compact structure of poly(DMMAPhAPS) caused by the associations of the group of R_4N^+ and SO_3^- . When the association occurs, the ionic condition of poly(DMMAPhAPS) would be neutralized and the phenyl moieties of poly(DMMAPhAPS) would be close to each other, resulting in the relatively more hydrophobic microenvironment.

Polymers containing the dimethylaminophenyl group exhibit characteristic fluorescence spectra in polar solvents, showing two emission bands (450 and 350 nm) corresponding to two kinds of excited states [45,46]. The a^* band for charge-transfer state appears at a longer wavelength region relative to the b^* band for non-charge-transfer state [45,46]. In this study, Fig. 2A shows the fluorescence emission spectra of poly(TMMAPhAMS) and poly(DMMAPhAPS) in aqueous solution. Two fluorescence bands of poly(DMMAPhAPS) are also observed at around 450 and 350 nm, but only one fluorescence band at 350 nm is seen for poly(TMMAPhAMS). The fluorescence emission of

poly(TMMAPhAMS) at 350 nm would be attributed to the fluorescence from the non-charge-transfer excited state [45,46]. The two fluorescence bands of poly(DMMAPhAPS) at around 450 and 350 nm may be resulting from charge-transfer state (a^* band) and non-charge-transfer excited state (b^* band), respectively. The charge-transfer excited state (a^* band) could not be observed in the fluorescence spectrum of poly(TMMAPhAMS) because there is no lone pair electron in the aminonium group of poly(TMMAPhAMS) chains. However, the charge-transfer excited state (a^* band) could be observed in its fluorescence spectrum around 450 nm for poly(DMMAPhAPS). That is, the charge-transfer (a^* band) would be formed in the zwitterionic poly(DMMAPhAPS) aqueous solution, but not in the cationic poly(TMMAPhAMS) aqueous solution. The phenomena might be due to the intra- and/or interchain association resulting from ammonium groups and sulfonate groups of zwitterionic polymer chains [30,31]. The charge-transfer may take place because of intra- and/or interchain association of polymer chains as a result of the sulfonate group easily approaching the phenylene group, which is in the neighborhood of the cationic ammonium group. Morishima et al. [23] have also observed a similar phenomenon in the amphiphilic polyelectrolytes poly(9-vinylphenanthrene-*co*-sodium 2-acrylamido-2-methylpropanesulfonate) (Aph) and 4,4'-bipyridinium-1,1'-bis(trimethylenesulfonate) (SPV) system described as a back-electron transfer model [23]. Furthermore, the fluorescence spectra excited at 295 nm in various poly(DMMAPhAPS) concentrations was shown in Fig. 2B. As the polymer concentration increases, the intensities of both non-charge-transfer excited state (b^* band) and charge-transfer excited state (a^* band) in fluorescence spectra increased, particularly the intensity of non-charge-transfer excited state (b^* band). The intensity ratio R

$$\left(R = \frac{450 \text{ band}}{350 \text{ band}} = \frac{\text{charge transfer}}{\text{non-charge transfer}} = I_{a^*}/I_{b^*} \right)$$

of poly(DMMAPhAPS) in 0.1 g/dl polymer concentration is lower than that of poly(DMMAPhAPS) in 0.03 g/dl polymer concentration. This phenomenon was due to degree of freedom of sulfonate groups attached at side chain ends and phenylene groups buried in poly(DMMAPhAPS) coil. In dilute aqueous poly(DMMAPhAPS) solution, the groups of aminonium and/or sulfonate exhibit relatively large degree of freedom, which is of advantage to form charge-transfer within the loose polymer coil. At high polymer concentration, there may well be chain entanglement, which results in difficulty of charge-transfer taking place within the shrunk polymer coil. Though the high polymer concentration will also enhance intermolecular interactions, the entangled polymer chains will interrupt charge-transfer formation. The fluorescence spectra of poly(TMMAPhAMS) in various polymer concentrations were also measured. As the poly(TMMAPhAMS) concentration increases, the intensities of non-charge-transfer excited

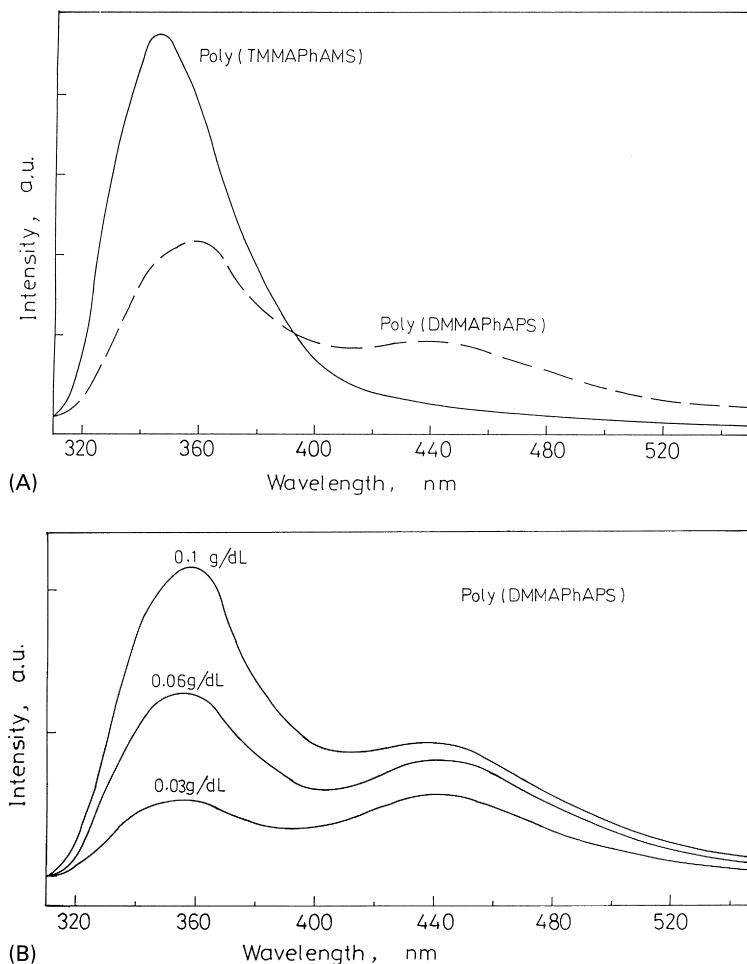


Fig. 2. (A) Fluorescence spectra of poly(DMMAPhAPS), --; and poly(TMMAPhAMS), —. (B) Relationships between fluorescence intensity and various poly(DMMAPhAPS) concentration in aqueous solution. ($\lambda_{\text{exc.}} = 295 \text{ nm}$).

state (b^* band) in fluorescence spectra also increase. The emission band of charge-transfer excited state (a^* band) was not observed in any poly(TMMAPhAMS) concentration range (0.03–0.1 g/dl).

3.3. Viscosity

Polyelectrolytes ionized in an aqueous solution exhibit an expansion conformation. By contrast, zwitterionic polymers are ionized in aqueous solution and their mutual associations of their positive and negative charges cause the polymers to shirk themselves with increasing ionic strength [7]. In order to test this notion, reduced viscosities η_{sp}/C (dl g^{-1}) for zwitterionic poly(DMMAPhAPS) and the corresponding cationic poly(TMMAPhAMS) in the absence and presence of KCl solutions were determined. Fig. 3 shows η_{sp}/C of poly(TMMAPhAMS) in various aqueous KCl solution concentrations C_s (M). The η_{sp}/C of poly(TMMAPhAMS) solution in different KCl concentrations as a function of polymer mass concentration C shows typical behavior of polyelectrolyte, increasing with decreasing C . The η_{sp}/C

of poly(TMMAPhAMS) solution decreases with salt addition at a fixed polymer concentration. Fig. 4 shows η_{sp}/C of zwitterionic poly(DMMAPhAPS) at various C_s .

The reduced viscosity in different concentrations also exhibits similar patterns. However, η_{sp}/C increases with the salt addition at a fixed poly(DMMAPhAPS) concentration. These behaviors of poly(TMMAPhAMS) and poly(DMMAPhAPS) is due to the addition of salt, which would cause the polymer conformation in aqueous solution to change, conforming to the above notion.

Cationic poly(TMMAPhAMS), when ionized in an aqueous solution, expands due to electrostatic repulsion among charge groups on the chain. By contrast, for zwitterionic polymers ionized in aqueous solution, mutual association of their positive and negative charges give rise to an antipolyelectrolyte effect in which the viscosity of the solution increases with increasing ionic strength [7]. With poly(TMMAPhAMS), the dependence of η_{sp}/C on C is similar at various salt concentrations C_s (M), although η_{sp}/C decreases with increasing C_s at fixed C . In the salt-free

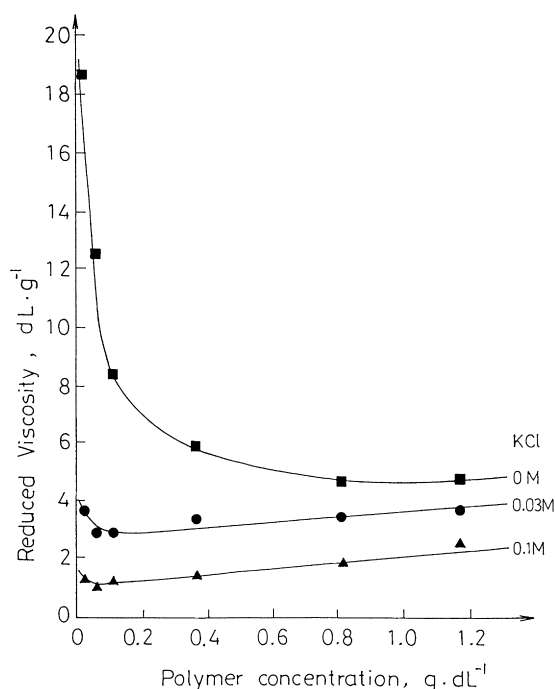


Fig. 3. Relationships between reduced viscosity of poly(TMMAPhAMS) and various KCl salt concentrations: (O) in 0.1 M KCl aqueous solution; (X) in 0.03 M KCl aqueous solution, and (B) in deionized water.

solution, the extensive mutual repulsion among R_4N^+ groups in the polymer chain results in a relatively high hydrodynamic volume. When salt is added, the electrostatic charges of cationic polymer chain is now screened and the electrostatic repulsion among cationic R_4N^+ groups of the same chain as well as surrounding chains decreases, thus shrinking the chain. On the other hand, poly(DMMA-PhAPS) exhibits similar η_{sp}/C vs C profile at all C_s examined, but η_{sp}/C increases with increasing C_s at fixed C . These phenomena may be due to the addition of salt, which can loosen the compact structure caused by the inter- and intrachain associations between R_4N^+ groups and SO_3^- groups of poly(DMMA-PhAPS) chains; thus, poly(DMMA-PhAPS) can behave more freely in the salt solution. Therefore, the hydrodynamic volume increased and the reduced viscosity increased consequently. Furthermore, in the absence of KCl, zwitterionic poly(DMMA-PhAPS) solution shows relatively lower reduced viscosity than cationic poly(TMMAPhAMS), which is due to the inter- and intrachain associations between R_4N^+ groups and SO_3^- groups of poly(DMMA-PhAPS) chains.

3.4. Quasielastic light scattering (QELS)

The quasielastic light scattering (QELS) is one of the molecular level probes which facilitates a better understanding of the microscopic behavior of an ionic polymer in solutions. Herein, QELS was employed to obtain the whole chain dimensions and dynamics. Fig. 5 shows a

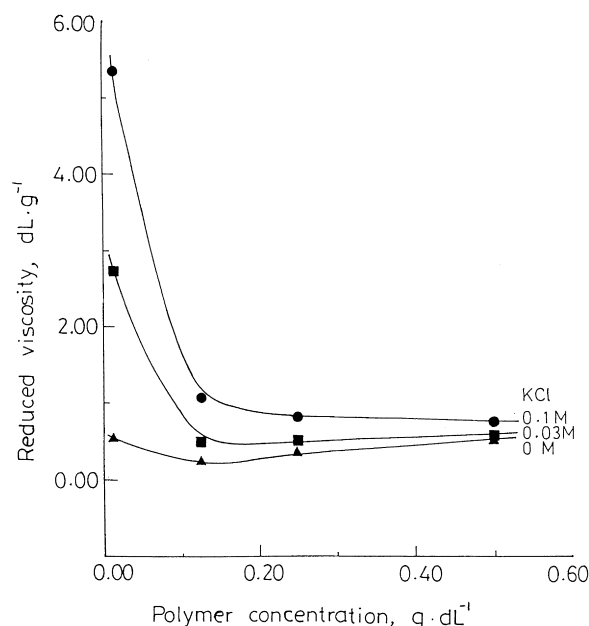


Fig. 4. Relationships between reduced viscosity of poly(DMMA-PhAPS) and various KCl salt concentrations: (X) in 0.1 M KCl aqueous solution, (B) in 0.03 M KCl aqueous solution, and (O) in deionized water.

plot of average hydrodynamic diameter R_H of poly(TMMAPhAMS) and poly(DMMA-PhAPS) as a function of salt (KCl) concentration, C_s (M) at 25°C. The result showed that the R_H of cationic poly(TMMAPhAMS) decreases with increasing C_s (levels of higher salt concentrations), falling from about 640 nm in 0.05 M $KCl_{(aq)}$ to about 200 nm in 0.4 M $KCl_{(aq)}$. However, R_H of zwitterionic poly(DMMA-PhAPS) increases with increasing C_s , rising from about 300 nm in 0.05 M $KCl_{(aq)}$ to about 750 nm in 0.4 M $KCl_{(aq)}$. These changes are consistent with those in η_{sp}/C discussed above.

3.5. Surface activity

The surface active behavior of poly(DMMA-PhAPS) and poly(TMMAPhAMS) was studied by surface tension measurement. The plot of surface tension vs logarithm of polymer concentration shows the marked differences in surface activity between the two polymers (Fig. 6). The surface tension of zwitterionic poly(DMMA-PhAPS) stays constant below 3.0×10^{-3} M. However, at higher concentrations ($>2.5 \times 10^{-3}$ M), it decreases continuously in an almost linear dependence on logarithm concentration, lacking a distinct break indicative of a critical micelle concentration. However, the cationic poly(TMMAPhAMS) shows no change in the surface tension even at higher polymer concentrations (3.0×10^{-2} M). That is, ionic polymers such as poly(TMMAPhAMS) cause only a minor depression of surface tension, whereas zwitterionic polymers such as poly(DMMA-PhAPS) cause considerable depressions [41–44]. These phenomena would be due to the electrostatic effects. The cationic polymers are subject to charge repulsion, in contrast

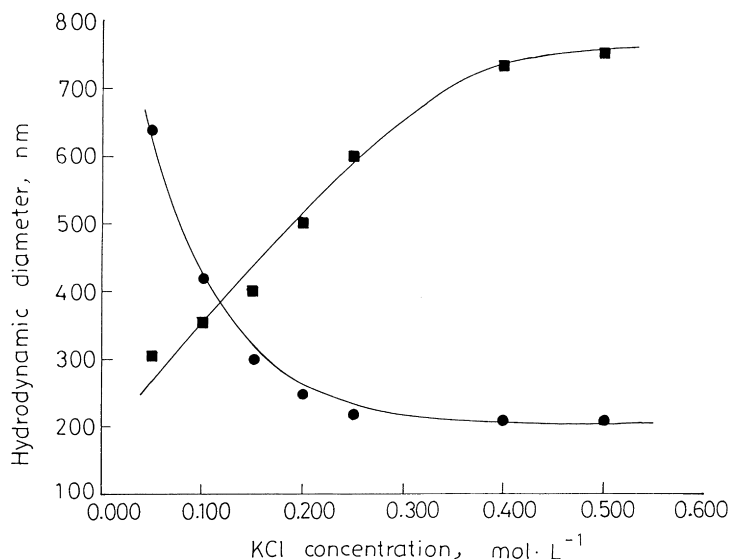


Fig. 5. Relationships between hydrodynamic diameters and various KCl salt concentrations in 0.1 g/dl aqueous polymer solution: (B), poly(DMMAPhAPS); and (x), poly(TMMAPhAMS).

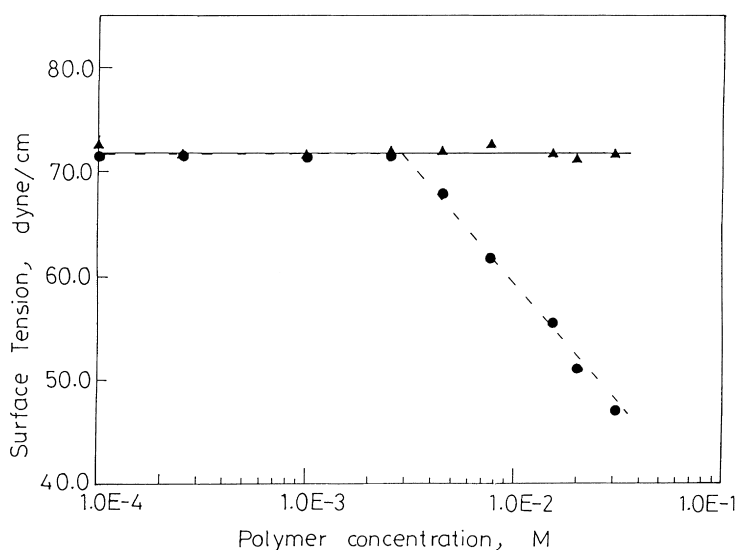


Fig. 6. Relationships between surface tension and different polymer concentrations in aqueous solution: —, poly(TMMAPhAMS) (O); ---, poly(DMMAPhAPS) (x).

to the zwitterionic polymer, thus the tendency to aggregate and to pack density is lower. Also, the sulfobetaine headgroup within poly(DMMAPhAPS) is less hydrophilic than cationic headgroup within poly(TMMAPhAMS) [42].

4. Conclusions

The monomers, trimethylmethacrylamidophenyl ammonium methylsulfate (TMMAPhAMS) and *N,N*-dimethylmethacrylamidophenyl ammonium propane sultone (DMMAPhAPS), were synthesized from *N,N*-dimethylaminophenylmethacrylamide (DMAPMA) and corresponding

compounds, dimethyl sulfate and propane sultone, respectively. The phase solubility of poly(DMMAPhAPS) was confirmed over a wide range of polymer concentration (0.01–10 wt%) was the result of the hydrophobic groups interrupting intramolecular associations in aqueous solution. Strong ultraviolet absorptions of poly(DMMAPhAPS) and poly(TMMAPhAMS) were observed. The band around 450 nm was only observed in fluorescence spectrum of zwitterionic poly(DMMAPhAPS), but not in the cationic poly(TMMAPhAMS) aqueous solution. Reduced viscosity studies showed that as the concentration of salt increased, the reduced viscosity of zwitterionic poly(DMMAPhAPS) would increase while that of cationic poly(TMMAPhAMS)

would decrease. The surface tension of zwitterionic poly (DMMAPhAPS) decreases continuously in an almost linear dependence on logarithm concentration at higher polymer concentrations.

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