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ORIGINAL CONTRIBUTION

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Photophysical and viscometric properties of naphthalene-labeled acrylamide/*N,N*-dimethyl maleimido propyl ammonium propane sulfonate copolymer

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Abstract The synthesis, viscometric, and fluorescence properties of a water-soluble zwitterionic sulfobetaine copolymer, poly(ADMMAPS)/NA, are reported. When fluorescent hydrophobes (naphthyl group) are incorporated into the zwitterionic copolymer, the photophysical response may effectively probe solution behavior on the microscopic level. Experimental results indicate that I_E/I_M steadily increases with increases in polymer concentration. I_E/I_M in aqueous solution is greater than that in aqueous potassium chloride solution. Dynamic light scattering (QELS) measurements show that hydrodynamic diameters of the naphthalene-labeled zwitterionic sulfobetaine copolymer increase with an increasing salt concentration. Viscosity studies reveal that the polymer coil expanded as more salt is added. In fluorescence quenching study, the reduction in the quenching efficiency of Tl^+ with salt addition can arise from enhanced compartmentalization of naphthalene labels as added electrolyte enhances intrapolymer micellization. The intrapolymer micelle is easily formed, indicating that the thallium ion has difficulty reacting with bound naphthalenes located in the polymer coil. The naphthalene-labeled zwitterionic sulfobetaine copolymer is depicted as a compacted polymer coil conformation in deionized water because of intra- and inter-associations. Consequently, salt addition breaks up the associations and enhances the intrapolymer micellization. The microscopic and macroscopic behaviors of zwitterionic sulfobetaine copolymer differ a lot from those of the corresponding cationic copolymer.

Key words Fluorescence emission technique – dynamic light scattering – intrinsic viscosity

Introduction

The production and studies of water-soluble homopolymers and copolymers with acrylamide have rapidly grown in recent years because of their diverse commercial applications [1–4]. The internal salts of betaine substances such as carboxybetaine and sulfobetaine are widely used in textile, medical, dispersing agents, and other branches of industry [5–9]. Several investigators studied the aqueous solution properties of betaines [10–21]. Topchiev et al. investigated the kinetic features of the radical polymerization of an unsaturated carboxybetaine in various pH ranges [13]. Asonova et al. also reported that such a polycarboxybetaine had a varied intrinsic viscosity as a function of pH [12]. Also, Salamone et al. thoroughly examined the solution properties of sulfobetaine homopolymers, particularly in the vinylimidazole series [14–19].

More recently, many works have focused on fluorescently labeled water–soluble polymers to correlate the microscopic, photophysical response with a macroscopic event such as phase separation [22], aggregation [23, 24], or latex film formation [25]. Photophysical analysis of those fluorescently labeled polyelectrolytes has demonstrated that salt-dependent intermolecular and intramolecular associations are both macroscopic and microscopic.

Several researchers have examined a series of zwitterionic poly(betaine)s and their corresponding polyelectrolytes with different electron-withdrawing groups and methylene units between the charge groups [26, 27]. Previous works have dealt with the dilute aqueous properties of the cationic polyelectrolytes [28, 29], an anionic polyelectrolyte [30] and polyampholytes [31, 32]. These investigations thoroughly examined the differences between various polyelectrolytes with ionic group types. Dilute aqueous properties such as viscosity studies, and degree of binding, all provide a reasonable assessment of the macroscopic solution behavior; however, a detailed analysis requires using a more sensitive characterization technique. The naphthalene labels are incorporated into the poly(dimethyl sulfate quaternized acrylamide/*N*,*N*-dimethylaminopropylmaleimide copolymer) to be studied [33]. The synthesis, viscometric, and fluorescence properties of the cationic water-soluble naphthalene-labeled copolymer was reported.

In this study, we incorporate naphthalene labels into the acrylamide/*N*,*N*-dimethylmaleimido propyl ammonium propane sulfonate copolymer. The synthesis, viscometric, and fluorescence properties of a novel water-soluble zwitterionic sulfobetaine copolymer, naphthalene-labeled poly(acrylamide/*N*,*N*-dimethylmaleimido propyl ammonium propane sulfonate copolymer), poly(ADMMAPS)/NA, are reported. Moreover, the molecular level probes (dynamic light scattering and fluorescence emission techniques) are used to understand more thoroughly the microscopic and macroscopic properties of the zwitterionic sulfobetaine copolymer in deionized water and salt solutions. Our primary interest is drawn towards the difference in the viscometric, and photophysical properties between zwitterionic sulfobetaine copolymer and its corresponding cationic copolymer. Furthermore, proposed schematic models were used to accurately describe their properties.

Experimental

Synthesis of naphthalene-labeled acrylamide/*N*,*N*-dimethyl maleimido propyl ammonium propane sulfonate copolymer, poly(ADMMAPS)/NA

The copolymer naphthalene-labeled acrylamide/*N*,*N*-dimethylaminopropylmaleimide copolymer, poly(ADMMAPM)/NA [33], mixture was dissolved in dimethylsulfoxide (DMSO) and subsequently cooled to 0 °C temperature with an ice bath, followed by dropwise addition of the 1,3-propanesultone with stirring for 1 h under a nitrogen atmosphere [Scheme 1]. Temperature of the exothermic reaction was maintained at 0 °C. After the addition was completed, the mixture was stirred at the same temperature for several hours and then allowed to stand overnight. The subsequent reaction was slowly added into a large volume of reagent-grade methanol under stirring. Subsequently, the brown precipitate formed was filtered and determined to be a naphthalene-labeled acrylamide/*N*,*N*-dimethylmaleimido propyl ammonium propane sulfonate copolymer, poly(ADMMAPS)/NA. The crude yield of the poly(ADMMAPS)/NA copolymer was found to be greater than 80%. For purification, the crude poly(ADMMAPS)/NA 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. Finally, the hydroscopic, yellow solid was then dried under a vacuum at 80 °C for 24 h. From the measurement of element analysis $x = 0.45$, $y = 0.05$, $z = 0.50$ were obtained [Scheme 1].

Viscometric measurements [28, 32]

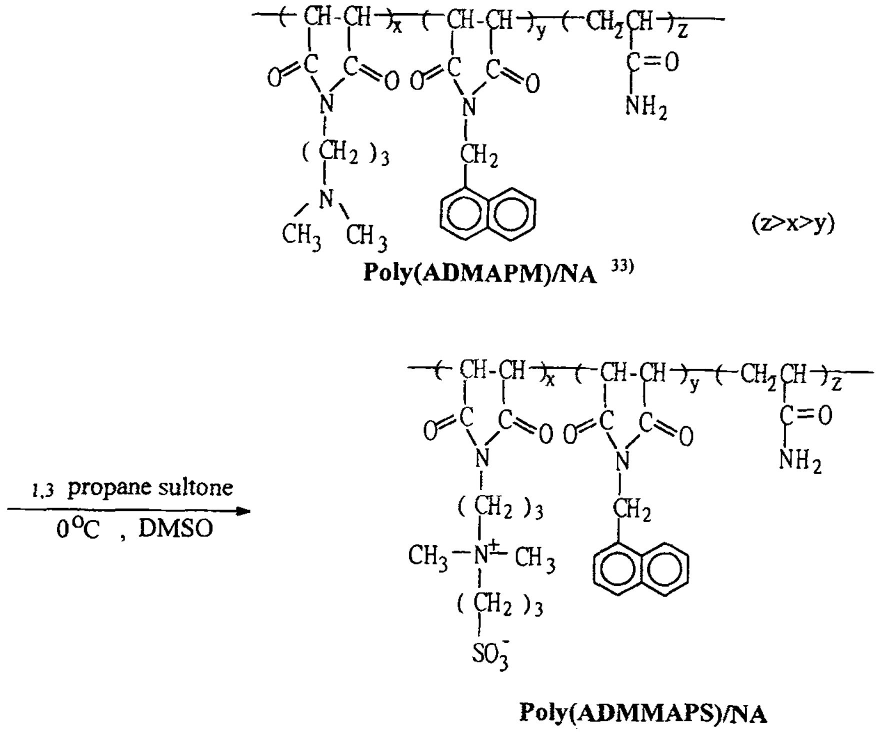
Viscometric measurements were taken with a Ubbelohde viscometer (the viscometer has a flow time of 79.19 s in the pure water) at 30.00 ± 0.01 °C. The polymer samples were dissolved in the salt concentration to yield a stock solution of approximately 1 g/100 ml solvent.

Fluorescence emission technique

Naphthalene fluorescence spectra and the behavior of fluorescence quenching were measured on the spectrofluorometer. In this technique, the emission's intensity in the absence of the quencher (I_0) to that in the presence of the quencher, I, is related to the quenching constant (K_{sv}) and the quencher concentration ($[Q]$) by the relationship

$$\frac{I_0}{I} = 1 + K_{sv}[Q] . \tag{1}$$

Scheme 1



All solutions were prepared with deionized water, and the quencher was purified by recrystallization from an adequate solvent.

Results and discussion

Characteristics of naphthalene-labeled acrylamide/*N*,*N*-dimethyl maleimido propyl ammonium propane sulfonate copolymer, poly(ADMMAPS)/NA [Scheme 1]

The IR spectrum of poly(ADMMAPS)/NA copolymer indicates the characteristic absorption of the quaternary group ($\nu_{R_4N^+}$) at 967 cm^{-1} and the sulfonate group ($\nu_{s=o}$) to be at 1044 cm^{-1}. ^{1}H-NMR (D_2O): δ 3.6 ($-C\underline{H}_2-$naphthyl), 1.6–2.0 ($-CH_2-C\underline{H}_2-CH_2-N^+(CH_3)_2-(CH_2)_3-SO_3^-$), 3.1–3.3 ($-\underline{CH}_2-N^+(CH_3)_2-C\underline{H}_2-$), 2.69 ($-CH_2-N^+(C\underline{H}_3)_2-CH_2-$), 6.85 ppm (naphthyl group protons). ^{13}C-NMR: δ 42 ($-\underline{C}H_2-$naphthyl), 50.67 ($-CH_2-N^+(\underline{CH}_3)_2-CH_2-$), 62.9 ($-\underline{C}H_2-N^+(CH_3)_2-$), 182.0 ppm (C=O).

Viscosity Studies

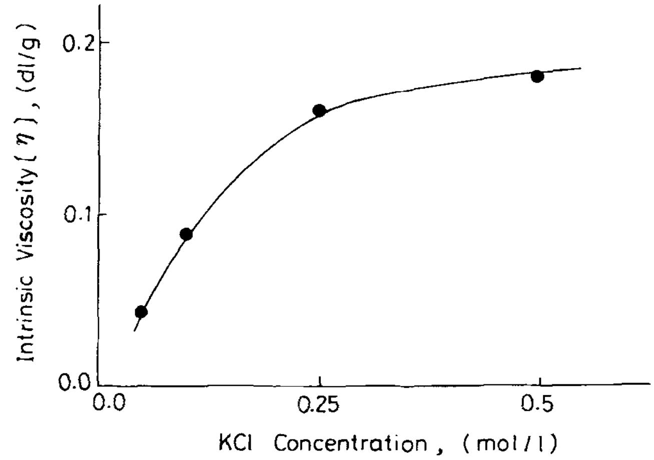


Fig. 1 Intrinsic viscosities of poly(ADMMAPS)/NA in the various concentration of KCl aqueous solution

Figure 1 plots the intrinsic viscosities, obtained by extrapolating the curves of the Huggins plot (the relationship between reduced viscosity and polymer concentration) at constant simple electrolyte concentration [KCl] to zero concentration of the poly(ADMMAPS)/NA, as a function of the ionic strength of the medium. The intrinsic viscosities in the various concentrations of KCl solutions containing fixed poly(ADMMAPS)/NA were determined.

Figure 1 displays the low intrinsic viscosities of the naphthalene-labeled zwitterionic sulfobetaine copolymer in small concentration of potassium aqueous solution having resulted from the polymer chain's association. When more salt was added, the association was broken effectively and hydrodynamic volume increased. The addition of salt also caused the ionic condition of the zwitterionic sulfobetaine copolymer to be neutralized and the intrinsic viscosity to increase. This phenomenon might be due to the salt loosening the compacted structure through inter- and intra-molecular ionic interactions. Thus, a polymer will behave more freely in a salt solution. Restated, a higher salt concentration implies lower association and, thus, a higher intrinsic viscosity. This phenomenon was also observed by Liaw [31, 32], Lee [34] and Schulz [35]. The effect of the intrinsic viscosity in the various concentrations of salt solution for poly(ADMMAPS)/NA is contrary to that of naphthalene-labeled cationic polyelectrolyte [33].

Excimer emission studies

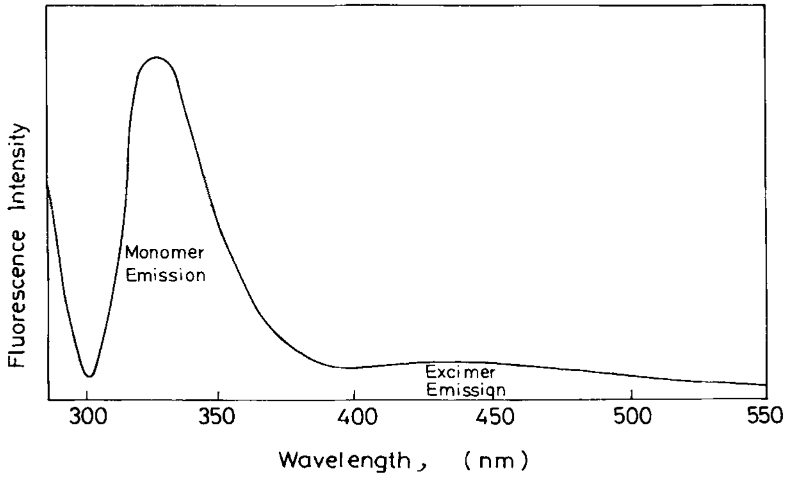
Naphthalene-labeled poly(ADMMAPS)/NA excimer emission was investigated by fluorescence measurement to elucidate the solution's behavior. Kramer reported that as the degree of hydrophobic association increases, interaction between isolated, covalently bound fluorescent hydrophobes allows the formation of dimeric, sandwich-like conformations that subsequently lead to excimer formation [36, 37]. Interpolymer hydrophobic association is observed as an increase in excimer relative to that of "monomer" emission, where I_E/I_M is the ratio of intensities of excimer and monomer fluorescence and reflects intra-/inter-chain interactions of naphthalene groups. Figure 2 presents a typical fluorescence spectrum of the naphthalene-labeled poly(ADMMAPS)/NA. The peak maxima at 330 nm arises from the fluorescence emission of isolated naphthalenes (monomer emission). The broad band centered around 440 nm results from emission of excited dimeric naphthalene (excimer emission). Figure 3 plots I_E/I_M as a function of polymer concentration in deionized water. Moreover, I_E/I_M steadily increases with the polymer concentration. As the polymer concentration increases, the intermolecular hydrophobic associations between naphthalene labels increase the population of excited naphthalene dimers. Therefore, an increase in I_E/I_M occurs. The same results were observed for both the poly(ADMMAPS)/NA and the naphthalene-labeled cationic poly(DSQADMAPM)/NA [33].

I_E/I_M values decreased with an increase in the salt concentration. Such a decrease indicates that the positive charges and negative charges in copolymer are neutralized and the polymer coil loosen as more salt is added. As this occurs, the distance between naphthalene groups on the same polymer chain increases, and excimer formation becomes more difficult. Figure 4 summarizes the effect of added electrolyte on the degree of excimer emission at a low concentration of naphthalene-labeled zwitterionic sulfobetaine copolymer, i.e., the expanded polymer coil conformation enhanced by charge–charge interactions between the R_4N^+ groups and SO_3^- are shielded effectively in the presence of more salt. This fact suggests that naphthalene groups within the naphthalene-labeled zwitterionic sulfobetaine copolymer are separated from each other, in addition to decrease in excimer emission relative to monomer emission. The effect of the I_E/I_M values decreasing with increasing the concentration of salt for poly(ADMMAPS)/NA is contrary to that for cationic poly(DSQADMAPM)/NA [33].

Dynamic light scattering (QELS)

The other molecular level probe is dynamic light scattering (QELS) which could facilitate a better understanding of

Fig. 2 Fluorescence emission spectrum of poly(ADMMAPS)/NA. Excitation wavelength: 280 nm



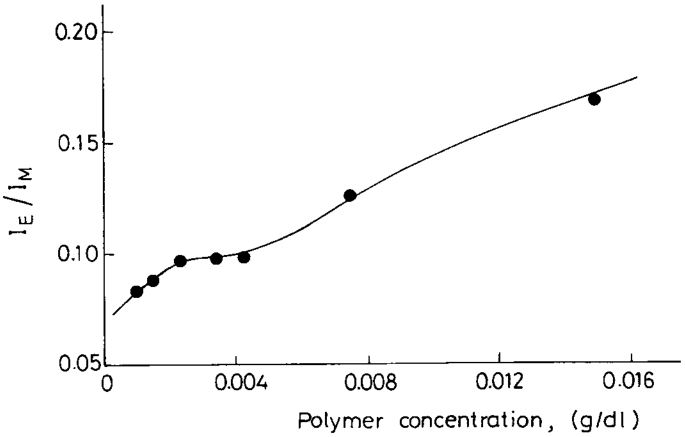


Fig. 3 Excimer emission/monomer emission (I_E/I_M) of poly(ADMMAPS)/NA in deionized water. I_M = fluorescence intensity at 330 nm; I_E = fluorescence intensity at 440 nm. Excitation wavelength: 280 nm

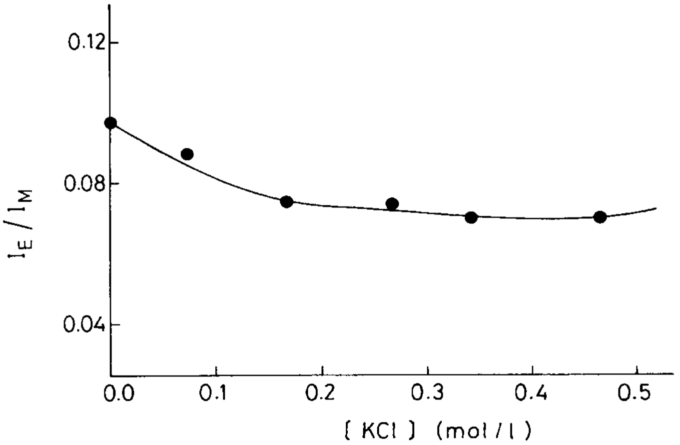


Fig. 4 I_E/I_M of poly(ADMMAPS)/NA as a function of aqueous NaCl concentration. I_M = fluorescence intensity at 330 nm; I_E = fluorescence intensity at 440 nm. Excitation wavelength: 280 nm

the microscopic behavior of the naphthalene-labeled zwitterionic sulfobetaine copolymer in solutions. Herein, QELS was employed to obtain the whole chain dimensions and dynamics. Figure 5 plots the average hydrodynamic diameter of the naphthalene-labeled zwitterionic sulfobetaine copolymer as a function of an increasing salt concentration, as measured by QELS at 25 °C. The zwitterionic sulfobetaine copolymer in deionized water may be compacted by inter- and intra-association, resulting from the positive charge of R_4N^+ groups and SO_3^- groups. By adding KCl, the inter- and intra-association broke and intra-polymer micellization was enhanced. Adding, further salt led to an increase in the hydrodynamic diameter of intra-polymer micelle. Figure 5 summarizes those results. In general, the hydrodynamic diameter increases with increasing salt levels, going from about 205 nm in 0.025 M KCl to about 328 nm in 0.34 M KCl. Moreover, the largest increases in hydrodynamic diameter occur in the low salt regime. Such an occurrence corresponds to the excimer emission studies, as expected (Fig. 4). Restated, the higher salt concentration implies higher hydrodynamic diameter and, thus, higher macroscopic intrinsic viscosity (Fig. 1). Liaw [31, 32], Lee [34] and Schulz [35] also observed such a phenomenon of macroscopic intrinsic viscosity in other polysulfobetaine solutions. With the addition of salt, intra-polymer micellization was enhanced both in poly(ADMMAPS)/NA and in cationic poly(DSQADMMAPS)/NA, but the change in hydrodynamic diameter gave reversed results in both polymers [33].

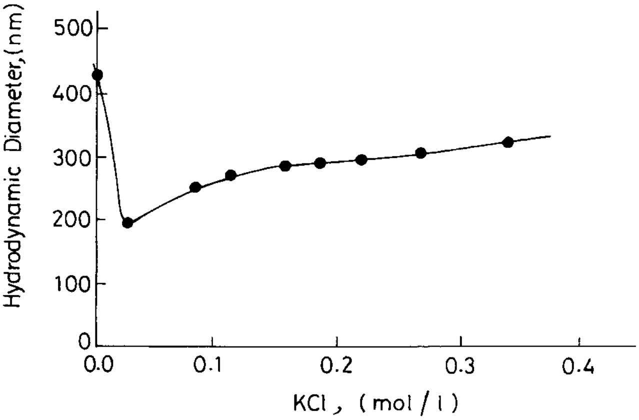


Fig. 5 QELS measurements on poly(ADMMAPS)/NA. [polymer] = 0.5 g/dL, temperature = 25 °C

Fluorescence quenching studies

Figure 6 shows fluorescence spectra of the naphthalene-labeled polysufobetaine in the presence of varying concentrations of $TlNO_3$ in deionized water [36, 38]. The intensity of monomer emission and excimer emission decreases with an increase in the $TlNO_3$ concentration, particularly at monomer emission (330 nm). Figure 7 shows the Stern–Volmer plot for thalliumnitrate quenching in potassium chloride solutions. K_{sv} values derived from Eq. (1), indicate that naphthalene labels reside in a rather hydrated environment. As salt is added, K_{sv} decreases. The reduction in the quenching efficiency of Tl^+ with salt addition could arise from enhanced compartmentalization of naphthalene labels as added electrolyte (KCl) enhances intrapolymer micellization. The intrapolymer micelle was easily formed, indicating that the thallium ion (Tl^+) has difficulty in reacting with bound naphthalenes located in the shrinked polymer coil. Thomas et al. [38] reported that it was indeed very difficult for ionic quenchers to traverse the polymer and react with bound fluorescent hydrophobes located in the polymer coil. A similar behavior of fluorescence quenching was also observed for the naphthalene-labeled poly(DSQADMAPM)/NA [33].

Here, we propose a model to account for the effects of KCl addition with respect to the macroscopic and microscopic behavior of a zwitterionic sulfobetaine copolymer (Fig. 8). In H_2O, zwitterionic sulfobetaine copolymer has extensive inter- and intra-association (Fig. 8a). The intra-association results from interactions between the quaternary amino group (R_4N^+) and the sulfonate group (SO_3^-) within the zwitterionic sulfobetaine copolymer side chain. Meanwhile, the inter-association results from interactions between the quaternary amino group (R_4N^+) and the sulfonate group (SO_3^-) at the different zwitterionic

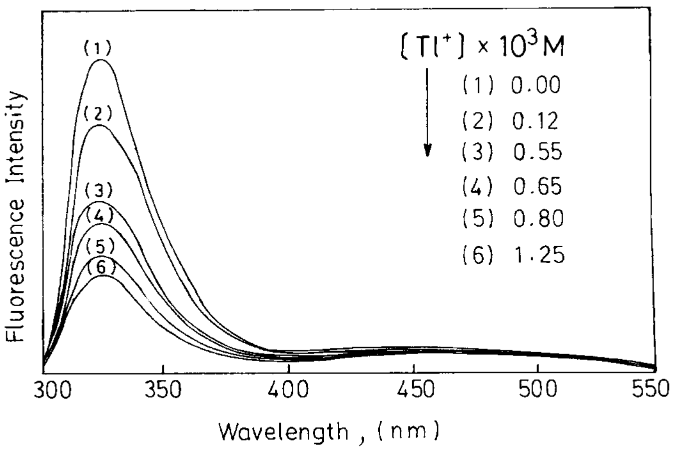


Fig. 6 Fluorescence spectra of poly(ADMMAPS)/NA in aqueous solution in the presence of varying concentration of Tl^+ ions

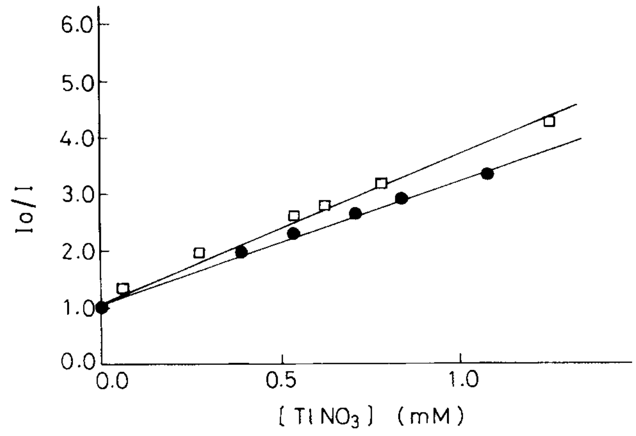


Fig. 7 Stern–Volmer plot of 0.03 g/d*L* poly(ADMMAPS)/NA quenching by thallium nitrate ($TlNO_3$) in deionized water (□) and in aqueous 0.025 M KCl (●). I_0 and I intensity values at 330 nm

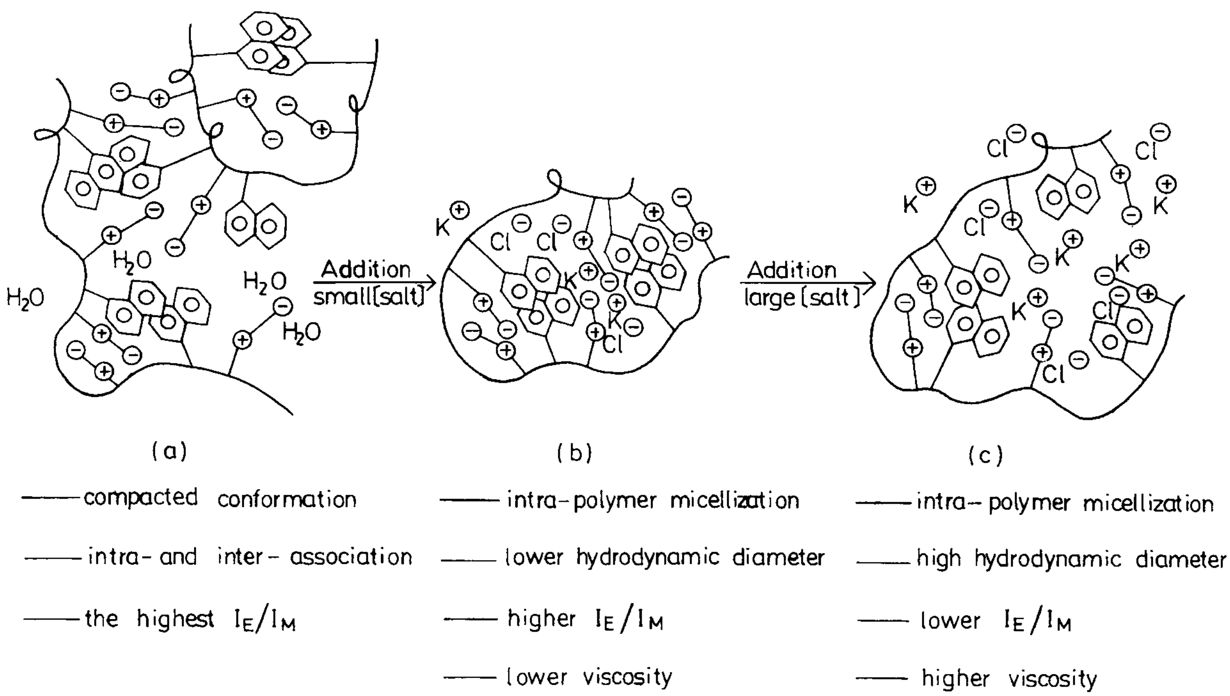


Fig. 8 Proposed mechanism of salt-triggered collapse of a fluorescently labeled polymeric micelle

sulfobetaine copolymer side chains. Adding a small concentration of $KCl_{(aq)}$ would neutralize the positive charge and negative charge at the side chain of the zwitterionic sulfobetaine copolymer and decrease the association between the quaternary amino groups and the sulfonate groups (SO_3^-) (Fig. 8b). This disrupts the inter- and intra-association, thereby causing the compacted conformation of polymer coils (the hydrodynamic diameter is high) break and enhance intra-polymer micellization in the solution. Because of the breaking of the intra- and inter-associations, naphthalene groups within the naphthalene-labeled zwitterionic sulfobetaine copolymer in a salt aqueous solution are separated from one another and the I_E/I_M value would decrease in salt-aqueous solution compared to that in H_2O. While adding the larger salt concentration, the positive charge of R_4N^+ group and negative charge of SO_3^- group within the intra-polymer micelle was effectively neutralized, the inter- and intra-association was broken effectively and the hydrodynamic diameter of intra-polymer micelle increased (Fig. 8C). With the increase in hydrodynamic diameter of intra-polymer micelle, the I_E/I_M values decreased and the macroscopic viscosity increased.

In H_2O, the structure of cationic copolymer is an expanded conformation due to extensive inter- and intra-repulsions [33] whereas zwitterionic sulfobetaine copolymer has a compacted conformation due to extensive inter- and intra-associations. As salt is added, intra-polymer micellization was enhanced both for the cationic copolymer and the zwitterionic sulfobetaine copolymer. As the concentration of salt increases, the hydrodynamic diameter of cationic copolymer decreases while that of zwitterionic sulfobetaine copolymer increases. These results could be attributable to the shielding of Coulombic interactions between the ionic groups of polymers. Neutralizing the ionic groups of polymers, the distance of bound naphthalenes within cationic copolymer decreases but increases within zwitterionic sulfobetaine copolymer. Thus, the I_E/I_M value of cationic copolymer increases whereas that of zwitterionic sulfobetaine copolymer decreases [33].

Conclusions

In this paper, we have described the synthesis, viscometric, and fluorescence properties of a zwitterionic sulfobetaine water-soluble copolymer which fluorescent hydrophobes (naphthyl group) are incorporated into the polymer chain. I_E/I_M steadily increases with increasing polymer concentration and I_E/I_M values for a given polymer concentration are lower in salt. Dynamic light scattering (QELS) measurements indicate that the naphthalene-labeled zwitterionic sulfobetaine copolymer's hydrodynamic diameters increase with an increasing salt concentration. The zwitterionic sulfobetaine copolymer is depicted as a compacted polymer coil conformation in deionized water because of intra- and inter-associations.

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