



ELSEVIER

Polymer 43 (2002) 6221–6229

**polymer**[www.elsevier.com/locate/polymer](http://www.elsevier.com/locate/polymer)

# Photophysical and aqueous solution properties of thermosensitive anionic potassium-2-sulfopropylmethacrylate/*N*-isopropylacrylamide/1-pyrenemethylmethacrylate terpolymer

Der-Jang Liaw\*, Ching-Cheng Huang, Tze-Shyuan Wang

*Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Section 4, Keelung Road, 106 Taipei, Taiwan, ROC*

Received 14 February 2002; received in revised form 25 June 2002; accepted 30 July 2002

## Abstract

This study describes the effect of salt on the aqueous solution property of the anionic terpolymer (SPM/NIPAM/PyMMA) of potassium-2-sulfopropylmethacrylate (SPM), *N*-isopropylacrylamide (NIPAM), and 1-pyrenemethylmethacrylate (PyMMA) in terms of fluorescence and dynamic light scattering. A plot of the thermally induced changes in  $I_1/I_3$  and  $I_E/I_M$  ratios for pyrene-labeled SPM/NIPAM/PyMMA with various temperatures was showed.  $I_E/I_M$  value (the ratio of intensities of the excimer and the monomer fluorescence emission) of SPM/NIPAM/PyMMA, which reflects the interactions of pyrene groups and the probability of dimeric pyrene, was investigated. The ratio of intensity of the first to the third vibronic bands ( $I_1/I_3$ ) in the fluorescence spectra of pyrene-labeled SPM/NIPAM/PyMMA depends on the polarity in the media, where pyrene exists. The  $I_E/I_M$  value of anionic terpolymer in aqueous solution varied with various surfactant (SDS) concentrations. Hydrodynamic diameters of anionic SPM/NIPAM/PyMMA in aqueous solution were also measured with various surfactant (SDS) concentrations. The same trends were obtained in fluorescence and dynamic light scattering measurements. At the lowered pH, the protonation of anionic terpolymer enhances hydrophobic association of polymer chains. The  $I_1/I_3$  ratio decreases with increasing temperature, but the  $I_E/I_M$  ratio increases. © 2002 Published by Elsevier Science Ltd.

**Keywords:** Thermosensitive anionic polymer; Fluorescence; Dynamic 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]. Moreover, attention is given to aqueous solution properties, photophysics, photochemistry, and the applications of the water-soluble copolymers containing hydrophobic residues and charged units [7–14]. Many investigators have used fluorescent-labeled water-soluble polymers to study phase separation [7], aggregation [8], latex film formation [9], electron transfer phenomena [10–13] or photoredox reaction [14]. Amphiphilic polymer contains hydrophobic and hydrophilic segment in the same polymer. These kinds of polymers have

found application in a variety of areas [15], from thickeners in food, rheology-controlling substances in coating fluids and latex-based paints [16], to additives in enhanced oil recovery or water treatment [17]. The physical properties of amphiphilic polymers depend to a large extent on their chemical composition. Also they are extremely sensitive to the relative amount of hydrophobic to hydrophilic moieties. In the area of life sciences too, synthetic amphiphilic polymers have found unique applications [18]. The preparation and properties of functional amphiphilic polymers designed to act as heat-sensitive modulators of membranes have been described [19]. *N*-isopropylacrylamide (NIPAM) was used to modify the surface of capsules. The grafted poly(*N*-isopropylacrylamide) [poly(NIPAM)] acted as a thermoreversible valve, blocking the escape of permeants from the capsule above critical temperature. The macroscopic behavior was attributed to a heat induced collapse of individual macromolecular chains which phenomenon is the thermoreversible phase. Poly(NIPAM) is extremely soluble in water at room temperature, but precipitates from the solution at 32 °C [20]. Copolymers of

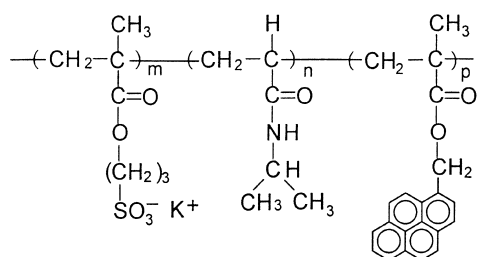
\* Corresponding author. Tel.: +886-2-273-35050/76638; fax: +886-2-237-81441/76644.

E-mail address: liaw@ch.ntust.edu.tw (D.J. Liaw),  
liaw8484@yahoo.com.tw (D.J. Liaw),  
liaw8484@hotmail.com (D.J. Liaw).

NIPAM and *n*-alkylacrylamides were chosen as promising candidates for membrane-anchored thermosensitive polymers [21]. Fluorescence studies of pyrene-labeled hydrophobically modified poly(NIPAM) were reported [21,22]. In particular, the studies focus on the incorporation of the alkyl chains and the interactions of the polymers with surfactants [21,22]. Furthermore, contribution of hydrogen bonding to the association of liposomes and an anionic hydrophobically modified poly(NIPAM) was proposed [23].

Previous works have examined a series of polybetaines and their corresponding cationic polyelectrolytes with different electron withdrawing groups and varied methylene units between the charged groups [24]. Previous reports have also thoroughly examined the difference in dilute aqueous solution properties of water-soluble polymer such as viscosity, cloud point, degree of binding, and hydrodynamic diameter [25–29]. These properties provide a reasonable assessment of the macroscopic behavior; however, a detailed analysis is required using a more sensitive characterization. When naphthalene labels were incorporated into the acrylamide-containing water-soluble polymer, photophysical properties and the behavior of polymers in aqueous solution could now be clearly defined [29,30]. Furthermore, a series of new phenyl-containing cationic water-soluble monomers and their polymers, such as cationic poly(trimethylmethacrylamidophenyl ammonium methylsulfate) (TMMAPhAMS) and zwitterionic poly(*N,N*-dimethylmethacrylamidophenyl ammonium propane sulfonate) (DMMAPhAPS), were synthesized [31, 32]. Also, the solubilities, viscometrics, surface activity and hydrodynamic diameter of these water-soluble polymers have been discussed [28]. A series of copolymers of methacrylamide (MAA) with phenyl-containing monomers (TMMAPhAMS or DMMAPhAPS) were prepared [33]. The monomer reactivity ratios were calculated by the Fineman-Ross and Kelen-Tüdös methods [33].

Terpolymers of potassium-2-sulfopropylmethacrylate (SPM), *N*-isopropylacrylamide (NIPAM), and 1-pyrenemethylmethacrylate (PyMMA) were chosen as promising candidates for thermosensitive polymers as following:



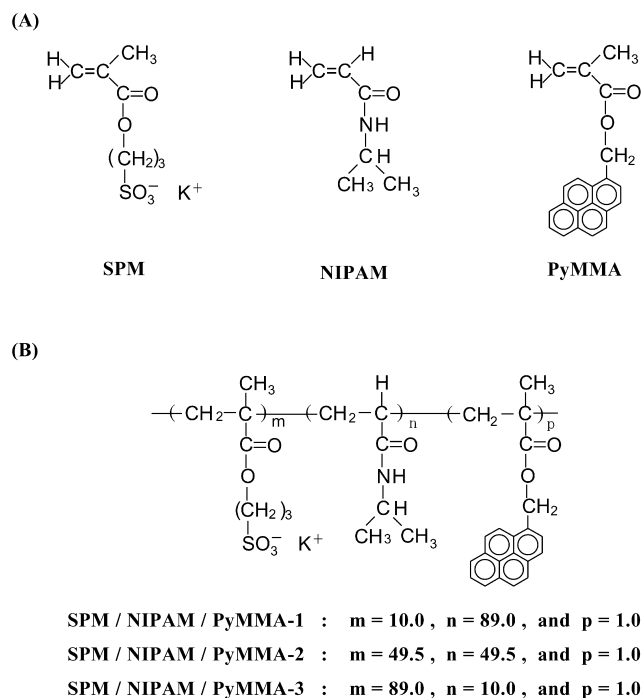
The photophysical and solution properties of these terpolymers are based on the results obtained from fluorescence and dynamic light scattering analysis.

## 2. Experimental section

### 2.1. Preparation of pyrene-labeled potassium-2-sulfopropylacrylate/*N*-isopropylacrylamide/1-pyrenemethylmethacrylate (PyMMA)

Methacryloyl chloride was prepared by refluxing a mixture of thionyl chloride and methacrylic acid, followed by distillation [34]. In a 100 ml flask equipped with a stirrer, thermometer, 1-pyrene methanol ( $1 \times 10^{-3}$  mol), NaOH ( $1 \times 10^{-3}$  mol) and dried THF (20 ml) were charged under argon atmosphere and the contents were stirred below 5 °C. A mixture of methacryloyl chloride ( $1.1 \times 10^{-3}$  mol) and dry THF was added dropwise for 1 h. Following the addition, the mixture was stirred for 10 h at the same temperature. The solution was then condensed under reduced pressure to remove THF. Methanol was added to precipitate the desired product. The contents were poured into a large excess of water to precipitate the resulting compound. The precipitated white crystals were collected by filtration and dried under reduced pressure for 24 h. The pyrene-containing monomer, 1-pyrenemethylmethacrylate (PyMMA), was obtained.

The pyrene-labeled polymers were prepared by free radical polymerization initiated by  $K_2S_2O_8$ . A glass ampoule containing monomers [SPM (89 mol% on the basis of the monomers), NIPAM (10 mol% on the basis of the monomers), and pyrene-containing monomer (PyMMA) (1 mol% on the basis of the monomers)] and  $K_2S_2O_8$  ( $10^{-4}$  mol) in *N,N*-dimethylformamide (30 ml) and water (10 ml) (3/1) cosolvent was degassed by three freeze-pump-thaw cycles on a vacuum line. The sealed ampoule was maintained at 60 °C in a water bath. After polymerization, the mixture was poured into a large excess of acetone to precipitate the resulting polymers. The polymers were purified by three precipitations from deionized water into acetone and dried under vacuum at 70 °C. The corresponding pyrene-labeled SPM/NIPAM/PyMMA-1 terpolymer was obtained. The yield was 94%. The  $^1H$  NMR peaks of polymer attributed to the acrylic group of monomer at 5.48 and 5.70 ppm were disappeared. Similarly, the monomer solution containing SPM (49.5 mol% on the basis of the monomers), NIPAM (49.5 mol% on the basis of the monomers), and pyrene-containing monomer (PyMMA) (1 mol% on the basis of the monomers) was used to prepare SPM/NIPAM/PyMMA-2 and the monomer solution containing SPM (10 mol% on the basis of the monomers), NIPAM (89 mol% on the basis of the monomers), and pyrene-containing monomer (PyMMA) (1 mol% on the basis of the monomers) was used to prepare SPM/NIPAM/PyMMA-3, respectively (Scheme 1). A series of such terpolymers prepared from terpolymerization of NIPAM, SPM and PyMMA in 89.0:10.0:1.0, 49.5:49.5:1.0, and 10.0:89.0:1.0 molar ratios were obtained.



Scheme 1. Structures of the monomers and polymers used in this study.

## 2.2. Characterization methods

$^1\text{H}$  NMR spectra were recorded using a JEOL EX400 at 399.96 MHz. Viscometric measurements were carried out with Ubbelohde viscometer (the viscometer had a flow time of 67.20 s in pure water) at  $30 \pm 0.01$  °C. The polymer samples were dissolved in the salt concentration to yield a stock solution of solvent. The polymer solution used in the QELS measurements was carefully filtered prior to placement into the light scattering instrument (OTSUKA DLS 7000). All QELS measurements were performed at room temperature in polymer aqueous solution. The fluorescence spectra were recorded by a Shimadzu RF-5031 spectrophotometer. All the fluorescence measurements were performed at room temperature.

## 3. Results and discussion

### 3.1. Effect of temperature on photophysical properties

Ionic group incorporation was shown to affect the photophysical and aqueous solution properties of thermo-sensitive polymer. Emission of pyrene-labeled polymer was investigated by fluorescence measurement to elucidate the aqueous solution's behavior. When the fluorescent hydrophobe (pyrene group) is incorporated into the polymer, the photophysical response may effectively probe the aqueous solution behavior on the microscopic level. As the degree of hydrophobic association increases, interactions between the isolated, covalently bound fluorescent hydrophobe allows the formation of dimeric conformations that subsequently

leads to excimer formation. The inter-polymer hydrophobic association is observed with an increase in excimer relative to that of 'monomer' emission, where  $I_E/I_M$  is the ratio of intensities of the excimer and the monomer fluorescence and reflects the interactions of pyrene groups and the probability of excited dimeric pyrene. The ratio of the first to the third vibronic bands ( $I_1/I_3$ ) in the fluorescence spectra of pyrene is known to depend on the polarity in the media, where pyrene exists, the  $I_1/I_3$  ratio being larger in less polar media [7–14].

Fluorescence spectra of the pyrene-labeled SPM/NIPAM/PyMMA-1 were observed in aqueous solution (Fig. 1(A)). The maximum peak at 377 nm ( $I_1$ ), and, 388 nm ( $I_3$ ) arise from the fluorescence emission of the isolated pyrene (monomer emission). The structureless, broad band centered at 472 nm results from emission of excited dimeric pyrene (excimer emission). Fluorescence

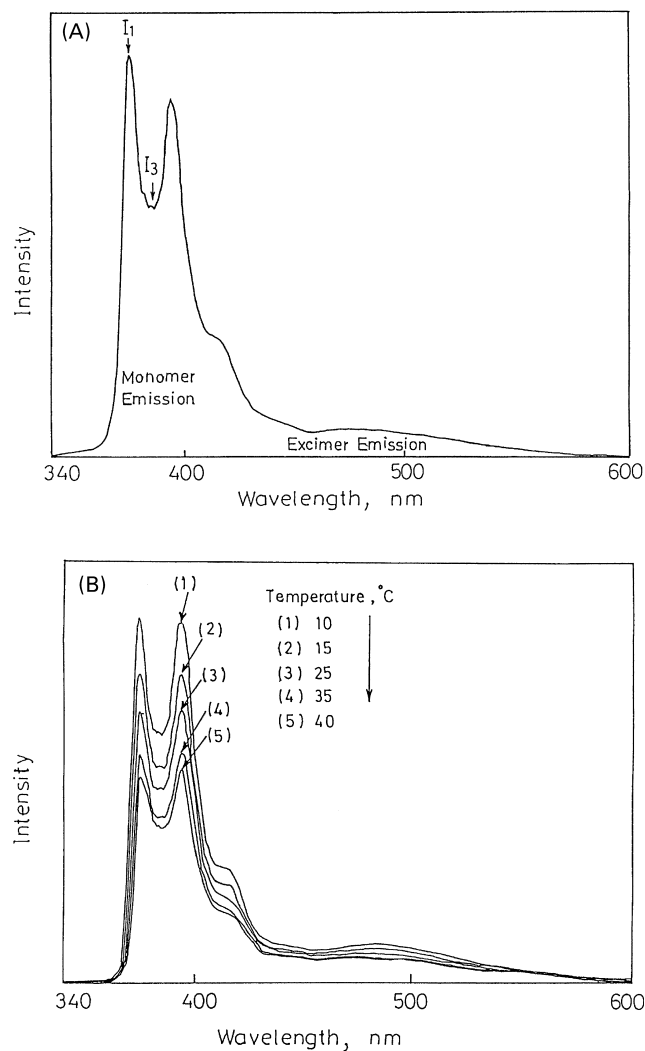


Fig. 1. (A) Excimer emission ( $I_E$ ) and monomer emission ( $I_M$ ) of SPM/NIPAM/PyMMA-1 terpolymer in deionized water. (B) Excimer emission ( $I_E$ ) and monomer emission ( $I_M$ ) of SPM/NIPAM/PyMMA-1 terpolymer in deionized water at various temperatures,  $I_M$ : fluorescence intensity at 377 nm;  $I_E$ : fluorescence intensity at 472 nm. Excitation wavelength: 330 nm.

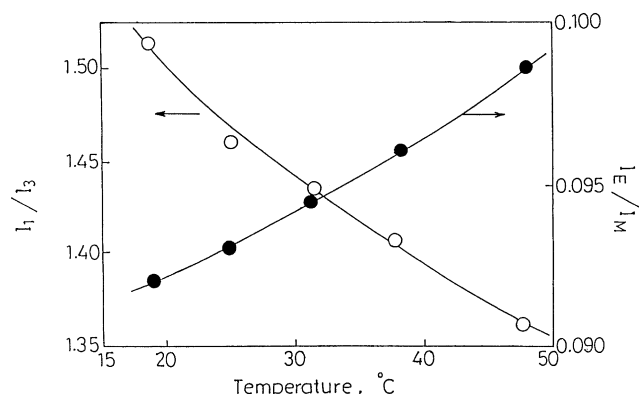


Fig. 2.  $I_E/I_M$  and  $I_1/I_3$  of aqueous solution of SPM/NIPAM/PyMMA-1 terpolymer ( $1.2 \times 10^{-2}$  g dl $^{-1}$ ) as a function of temperature.  $I_E$ : fluorescence intensity at 472 nm;  $I_1$  or  $I_M$ : fluorescence intensity at 377 nm;  $I_3$ : fluorescence intensity at 388 nm. Excitation wavelength: 330 nm. (●)  $I_E/I_M$  and (○)  $I_1/I_3$ .

spectra of SPM/NIPAM/PyMMA-1 terpolymer in aqueous solution depend on temperature (Fig. 1(B)). The intensity decreases with increasing temperature. This phenomenon was due to the incorporation of thermosensitive NIPAM segments. Fig. 2 shows a plot of the thermally induced changes in  $I_1/I_3$  and  $I_E/I_M$  ratios for SPM/NIPAM/PyMMA-1. The  $I_1/I_3$  ratio decreases with increasing temperature, but the  $I_E/I_M$  ratio increases. These behaviors exhibit an increase in formation of dimeric pyrene and a decrease in polarity of microenvironment around pyrenes when the temperature was increased. The hydrophobic association of NIPAM segments increases with increasing temperature so that the pyrene group within polymer chains would be close to each other. The dimeric pyrene was formed easily. Winnik et al. [21] reported that the differences of the thermally induced changes in  $I_E/I_M$  for pyrene-labeled poly(*N*-isopropylacrylamide) and hydrophobically modified poly(*N*-isopropylacrylamide) [21]. Heating induces the intra-polymeric aggregation, resulting in the formation of a phase that provides a hydrophobic environment to the pyrene chromophores [21]. Pyrene was isolated and buried within hydrophobic microdomain [21]. Therefore,  $I_E/I_M$  values decrease and  $I_1/I_3$  values decrease with an increasing temperature [21]. In this study, modified *N*-isopropyl-

acrylamide-containing SPM/NIPAM/PyMMA series are prepared and these terpolymers provide repulsion between anionic sulfonate group and anionic sulfonate group, which interrupt the formation of hydrophobic microdomain. Pyrene would not be limited in the hydrophobic microdomain resulted from polymeric aggregations, but the hydrophobic association would induce the formation of dimeric pyrene [21].  $I_E/I_M$  values increase and  $I_1/I_3$  values decrease with an increasing temperature.

Fig. 3(A) and (B) show a proposed model of the thermally induced changes in conformation for SPM/NIPAM/PyMMA. The polymer chains exhibit an expanded conformation at low temperature (Fig. 3(A)). Pyrene label is far from the other. Low  $I_E/I_M$  values were observed. Furthermore, relative high  $I_1/I_3$  values were also observed, resulting in a relative high polarity of microenvironment near counter cations (Fig. 3(A)). The conformation will be compacted with an increasing temperature. The  $I_1/I_3$  ratio decreases with increasing temperature, but the  $I_E/I_M$  ratio increases (Figs. 2 and 3(B)). That is, the hydrophobic association of NIPAM segments increases with increasing temperature, resulting in the aggregation of polymer chain. The pyrene group within polymer chains became close to each other (Fig. 3(B)).

### 3.2. Interactions of surfactant with anionic terpolymer

The interaction between polymers and surfactants in aqueous solutions were also of interest for both theoretical and practical purpose [7]. The interactions of cationic, anionic and neutral surfactants with water-soluble polymer have been studied [22]. Poly(NIPAM) and pyrene-labeled poly(NIPAM) interact with surfactant in patterns typical of neutral water-soluble polymer [21]. The polymers form mixed micelles with ionic surfactants above a critical surfactant concentration which depends on structural parameters, such as the charge of the surfactant and head group and hydrophobic tail of the surfactant. Excess addition of surfactant results in a large increase in the amount of bound surfactant while the concentration of free surfactant remains almost constant [21]. Surfactant clusters form along the polymer chain. In the case of poly(NIPAM) and SDS micelles, it may indicate less water penetration into the mixed micelles than in the SDS micelles themselves. Winnik et al. [21] reported that neutral surfactant interact only weakly with poly(NIPAM). The sharp decrease in pyrene excimer emission from pyrene-labeled poly(NIPAM) in the presence of neutral surfactant at a concentration slightly lower than its cmc is an evidence of binding of the surfactant to the polymer [21]. Binding occurs even at extremely low surfactant concentration [21]. At saturation the polymer/surfactant aggregates consist of clusters into which one (or several) hydrophobic chain is sequestered by the surfactant molecules. The surfactant binds to poly(NIPAM) derivatives by a cooperative mechanism at a critical surfactant concentration lower

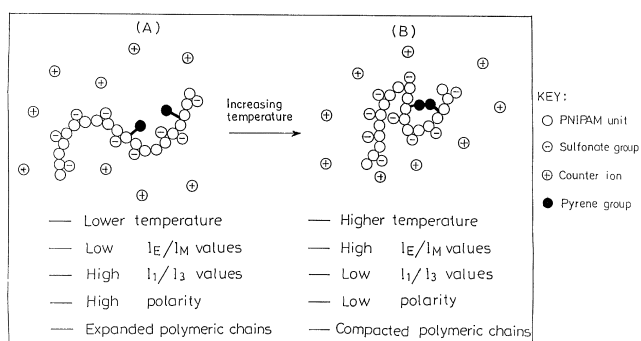


Fig. 3. Proposed model of the interaction in the aqueous SPM/NIPAM/PyMMA solution at various temperatures.



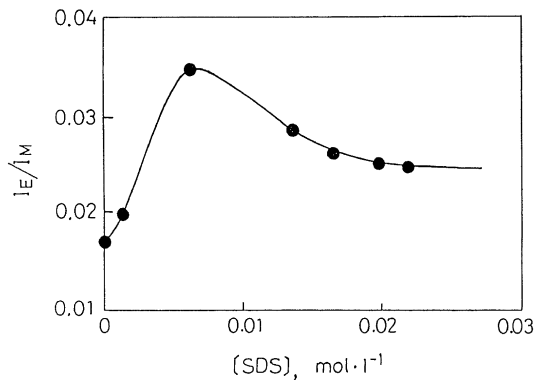


Fig. 4.  $I_E/I_M$  of anionic SPM/NIPAM/PyMMA-1 in aqueous solution at different surfactant (SDS) concentrations.  $I_M$ : fluorescence intensity at 377 nm;  $I_E$ : fluorescence intensity at 472 nm. Excitation wavelength: 330 nm.

than the surfactant cmc. Mixed polymer/surfactant clusters are formed [21]. McCormick et al. [36] reported that  $I_E/I_M$  value displays a maximum in mixed solutions of pyrene-labeled ionic polymer and surfactant. Micellar bridging was formed through hydrophobic inter-polymer associations [36]. In this investigation, the anionic surfactant (sodium dodecyl sulfonate; SDS) ( $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3^- \text{Na}^+$ ) was used to study the interactions between thermosensitive polymers and surfactants in aqueous solutions. The addition of surfactant to aqueous solutions of anionic terpolymer can either induce or break the inter-polymer aggregation. The nature of the association is dictated by surfactant concentration and charge.  $I_E/I_M$  values of anionic SPM/NIPAM/PyMMA-1 terpolymer in aqueous solution depend on SDS concentrations (Fig. 4). A maximum of  $I_E/I_M$  value was observed (0.035; SPM/NIPAM/PyMMA-1) in Fig. 4. The  $I_E/I_M$  value increased with the first addition of SDS ( $0-6 \times 10^{-3} \text{ mol l}^{-1}$ ).  $I_1/I_3$  value was 1.79 at  $6 \times 10^{-3} \text{ mol l}^{-1}$  SDS concentration. When more surfactant amounts were added ( $>6 \times 10^{-3} \text{ mol l}^{-1}$ ), the  $I_E/I_M$  values decreased distinctly with an increase in the surfactant concentration from the maximum value ( $I_E/I_M = 0.035$ ) to a limiting value ( $I_E/I_M = 0.025$ ) for SDS higher than ca.  $2 \times 10^{-2} \text{ mol l}^{-1}$  (Fig. 4), a concentration significantly higher than the cmc of SDS ( $8.2 \times 10^{-3} \text{ mol l}^{-1}$ ) [21].  $I_1/I_3$  value was almost kept constant at 1.8 (not shown in figures).

In the surfactant-free solution, anionic terpolymer exhibits an expanded conformation in aqueous solution, which is due to the repulsion between anionic sulfonate groups. Pyrene groups dispersed into the expanded conformation. When the surfactant was added, micellar bridging occurs through hydrophobic association between pyrene labels with surfactant. The micellar bridging enhances the formation of excimer. Mixed inter-polymer micelles with surfactant were formed and a maximum of  $I_E/I_M$  value ( $I_E/I_M = 0.035$ ; SPM/NIPAM/PyMMA-1) was observed (Fig. 4). Further addition of surfactant molecules (Fig. 4) results in the decrease in the  $I_E/I_M$  value with increasing surfactant molecules, which interrupt the micel-

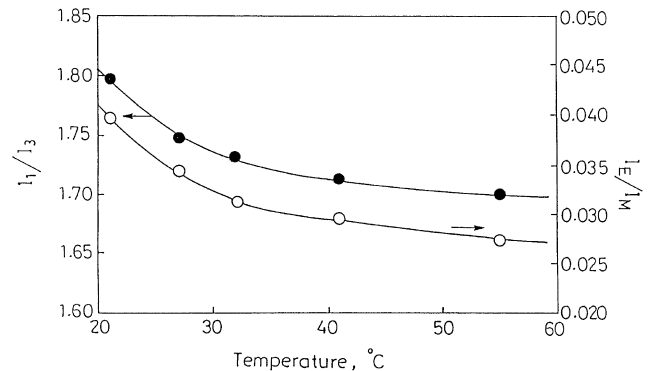


Fig. 5.  $I_E/I_M$  and  $I_1/I_3$  of mixed aqueous solution of SPM/NIPAM/PyMMA-3 terpolymer ( $1.2 \times 10^{-2} \text{ g dl}^{-1}$ ) and anionic surfactant (SDS) ( $6 \times 10^{-3} \text{ mol l}^{-1}$ ) as a function of temperature.  $I_E$ : fluorescence intensity at 472 nm;  $I_1$  or  $I_M$ : fluorescence intensity at 377 nm;  $I_3$ : fluorescence intensity at 388 nm. Excitation wavelength: 330 nm. (●)  $I_1/I_3$  and (○)  $I_E/I_M$ .

lar bridging. The pyrene group was isolated and surrounded with hydrophobic tails of surfactant molecules. That is, while adding large amount of surfactant, the mixed inter-polymer micelle was disrupted and turned to mixed intra-polymer micelles with surfactants. After high surfactant concentration was reached, all the mixed inter-polymer micelles changed to the mixed intra-polymer micelles. The  $I_E/I_M$  value for SPM/NIPAM/PyMMA-1 remained constant at 0.025 (Fig. 4). The same trends were also observed for SPM/NIPAM/PyMMA-2 and SPM/NIPAM/PyMMA-3.

Also, a maximum of  $I_E/I_M$  value was observed for SPM/NIPAM/PyMMA-3 at the surfactant concentration of ca.  $6 \times 10^{-3} \text{ mol l}^{-1}$  (not shown in figures).  $I_E/I_M$  and  $I_1/I_3$  values of mixed aqueous solution of SPM/NIPAM/PyMMA-3 terpolymer ( $1.2 \times 10^{-2} \text{ g dl}^{-1}$ ) and anionic surfactant (SDS) ( $6 \times 10^{-3} \text{ mol l}^{-1}$ ) were functions of temperature (Fig. 5). The surfactant concentration of  $6 \times 10^{-3} \text{ mol l}^{-1}$  exhibits a micellar bridging conformation for SPM/NIPAM/PyMMA-3 as mentioned above. Both  $I_1/I_3$  and  $I_E/I_M$  values decrease uniformly with increasing temperature (Fig. 5). These behaviors imply that the pyrene group was separated from each other and the polarity of microenvironment around pyrenes was decreased when the temperature was increased in aqueous surfactant (SDS) solution. The hydrophobic association of NIPAM segments increases with increasing temperature so that the pyrene groups within polymer chains will be buried in the hydrophobic NIPAM segments, which interrupt the micellar bridge conformation. The dimeric pyrene was not formed easily. The hydrophobic segments lowered the polarity of microenvironment. A proposed model was shown in Fig. 6(A) and (B). At the surfactant concentration of micellar bridging conformation, mixed inter-polymer micelles of surfactant and hydrophobic pyrene groups from different polymeric chains form cross-links [21]. An expanded polymer chain of SPM/NIPAM/PyMMA series exist in aqueous solution at low temperature (Fig. 6(A)). When temperature was increased, heating induce a collapsed

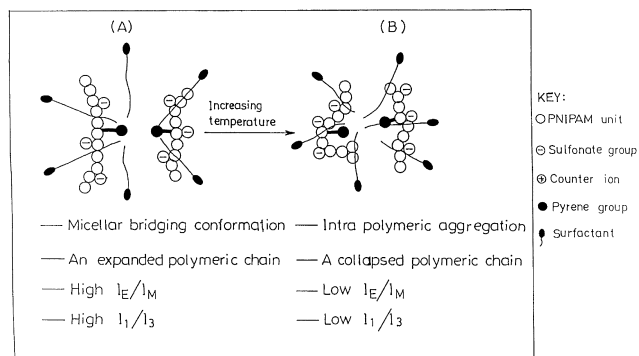


Fig. 6. Proposed model of the interaction in the aqueous mixed solution of SPM/NIPAM/PyMMA and surfactant at various temperatures.

polymeric chains and intra-polymeric aggregation (Fig. 6(B)), resulting in the formation of a phase that provides a hydrophobic environment to the pyrene groups. Relatively low  $I_1/I_3$  and low  $I_E/I_M$  values were observed (Figs. 5 and 6(B)).

Hydrodynamic diameter of anionic terpolymer (SPM/NIPAM/PyMMA-2) in aqueous solution depends on surfactant (SDS) concentrations (Fig. 7). Fluorescence spectra of anionic terpolymer (SPM/NIPAM/PyMMA-2) in aqueous solution with various SDS concentrations exhibit a maximum  $I_E/I_M$  value at SDS concentration of  $6.6 \times 10^{-3} \text{ mol l}^{-1}$ . Also, a maximum of hydrodynamic diameter (2300 nm) was observed at SDS concentration of  $6.6 \times 10^{-3} \text{ mol l}^{-1}$ . The diameter increased with the first addition of anionic surfactant (SDS) ( $0-6.6 \times 10^{-3} \text{ mol l}^{-1}$ ). When more surfactant amounts were added ( $>6.6 \times 10^{-3} \text{ mol l}^{-1}$ ), the diameter decreased distinctly with an increasing in the surfactant concentration (Fig. 7). In the surfactant-free solution, anionic terpolymer exhibits an expanded conformation (Fig. 8(A)) in aqueous solution, which results in relatively low diameter. When the surfactant was added, micellar bridging occurs through hydrophobic association between pyrene labels with SDS (Fig. 8(B)). A mixed inter-polymer micelle with surfactant was formed (Fig. 8(B)). Therefore, relatively high hydrodynamic diameter was observed (Figs. 7 and 8(B)). With

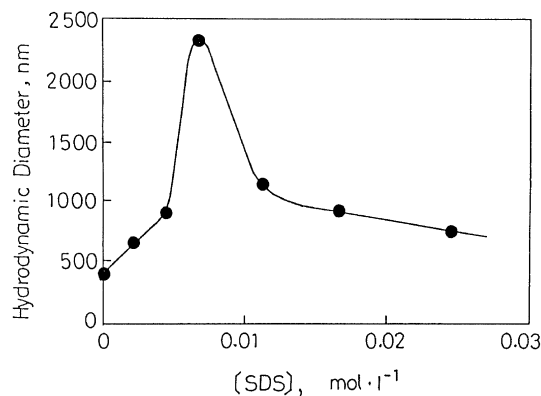


Fig. 7. Hydrodynamic diameter of SPM/NIPAM/PyMMA-2 in aqueous solution at various surfactant (SDS) concentrations.

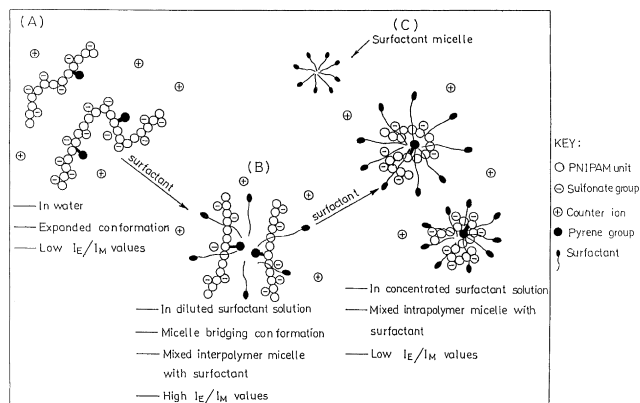


Fig. 8. Proposed model of the interaction in aqueous SPM/NIPAM/PyMMA solution at various surfactant concentrations.

further addition of surfactant molecules, the hydrodynamic diameter decreases with increasing surfactant molecules, which interrupt the micellar bridging (Fig. 8(C)). The mixed inter-polymer micelle was disrupted and turned to mixed intra-polymer micelle with surfactant (Fig. 8(C)). After high surfactant concentration was reached, all the mixed inter-polymer micelles changed to mixed intra-polymer micelle as mentioned above (Fig. 8(C)). The hydrodynamic diameter will almost keep constant at ca. 750 nm (Fig. 7). Similar trends were also observed in fluorescence study (Fig. 4).

In H<sub>2</sub>O, pyrene labeled anionic polyelectrolytes (SPM/NIPAM/PyMMA-1, -2, and -3) have extensive inter-molecular and intra-molecular repulsion. The intra-molecular repulsion results from interactions between the sulfonate groups (SO<sub>3</sub><sup>-</sup>) within the SPM/NIPAM/PyMMA chains. Meanwhile, the inter-molecular repulsion results from interactions between the sulfonate groups (SO<sub>3</sub><sup>-</sup>) at the different SPM/NIPAM/PyMMA chains. An expanded conformation was formed (Fig. 8(A)) in water. SPM/NIPAM/PyMMA shows a relatively low  $I_E/I_M$  in surfactant-free solution (Figs. 4 and 8(A)). When surfactant molecules are added into the SPM/NIPAM/PyMMA aqueous solution, the pyrene labels would be buried in surfactant micelles, exhibiting less polarity of the local environment near pyrene (Fig. 8(B)). Particularly, when surfactants (SDS) are added to the aqueous SPM/NIPAM/PyMMA solution, the pyrene labels would be buried in the hydrophobic portions of the surfactant molecules. Then, the micellar bridging conformation was formed (Fig. 8(B)). The mixed inter-polymer micelles with surfactants are obtained, resulting in  $I_E/I_M$  increasing (Fig. 8(B)). As more surfactants are added, the surfactant molecules would disrupt micellar bridging conformation and mixed inter-polymer micelles (Fig. 8(C)). The inter-polymer micelles will become intra-polymer micelles (Fig. 8(C)).  $I_E/I_M$  ratios decrease with the concentrations of surfactant (Figs. 4 and 8(C)).

### 3.3. Effect of salt and acid on photophysical properties

Fig. 9 shows  $I_E/I_M$  and  $I_1/I_3$  ratios of anionic

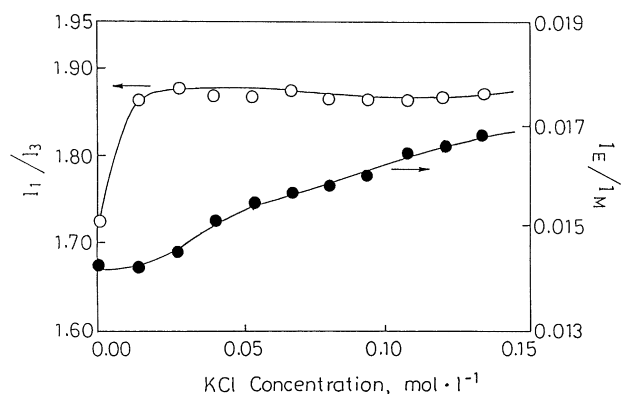


Fig. 9.  $I_E/I_M$  and  $I_1/I_3$  of anionic SPM/NIPAM/PyMMA-2 ( $3.6 \times 10^{-2} \text{ g dl}^{-1}$ ) in aqueous solution at various salt (KCl) concentrations.  $I_E$ : fluorescence intensity at 472 nm;  $I_1$  or  $I_M$ : fluorescence intensity at 377 nm;  $I_3$ : fluorescence intensity at 388 nm. Excitation wavelength: 330 nm. (●)  $I_E/I_M$  and (○)  $I_1/I_3$ .

SPM/NIPAM/PyMMA-2 in aqueous solution with various salt (KCl) concentrations.  $I_E/I_M$  of anionic terpolymer (SPM/NIPAM/PyMMA-2) in aqueous solution depends on salt (KCl) concentrations (Fig. 9). In the salt-free solution, anionic terpolymer exhibits an expanded conformation in aqueous solution, which is due to the repulsion between anionic sulfonate groups (Fig. 3(A)). When KCl salt was added, the  $I_E/I_M$  values increased with an increased salt concentration (Fig. 9). The repulsion between anionic sulfonate groups was neutralized and the collapsed conformation was formed. Pyrene group became close to each other. Relatively high  $I_E/I_M$  value would be observed.  $I_1/I_3$  value will keep constant at high KCl salt concentration.

Fig. 10(A) shows fluorescence spectra of SPM/NIPAM/PyMMA-1 terpolymer in aqueous salt (KCl) solution with various temperatures. The intensity decreases with increasing temperature. Fig. 10(B) and (C) show  $I_E/I_M$  and  $I_1/I_3$  values of mixed aqueous solution of terpolymer (SPM/NIPAM/PyMMA-1) and salt (KCl) as a function of temperature. Furthermore,  $I_E/I_M$  of mixed aqueous solution of terpolymer (SPM/NIPAM/PyMMA-1) and salt (KCl) was shown as a function of temperature (Fig. 10(B)). The  $I_1/I_3$  ratio decreases with increasing temperature (Fig. 10(C)), but the  $I_E/I_M$  ratio increases (Fig. 10(B)). These behaviors show that the pyrene group was close to each other and the polarity of microenvironment around pyrenes was decreased when the temperature was increased. Also, the hydrophobic association of NIPAM segments increased with increasing temperature so that the pyrene group within polymer chains got close to each other [21]. The dimeric pyrene was formed easily. These results are the same as (SPM/NIPAM/PyMMA-2) and (SPM/NIPAM/PyMMA-3).

$I_E/I_M$  and  $I_1/I_3$  values of aqueous acidic solution for SPM/NIPAM/PyMMA-3 were functions of temperature (Fig. 11). The  $I_1/I_3$  ratio decreases with increasing temperature, but the  $I_E/I_M$  ratio increases. These behaviors show that the pyrene group was close to each other and the polarity of microenvironment around pyrene was decreased

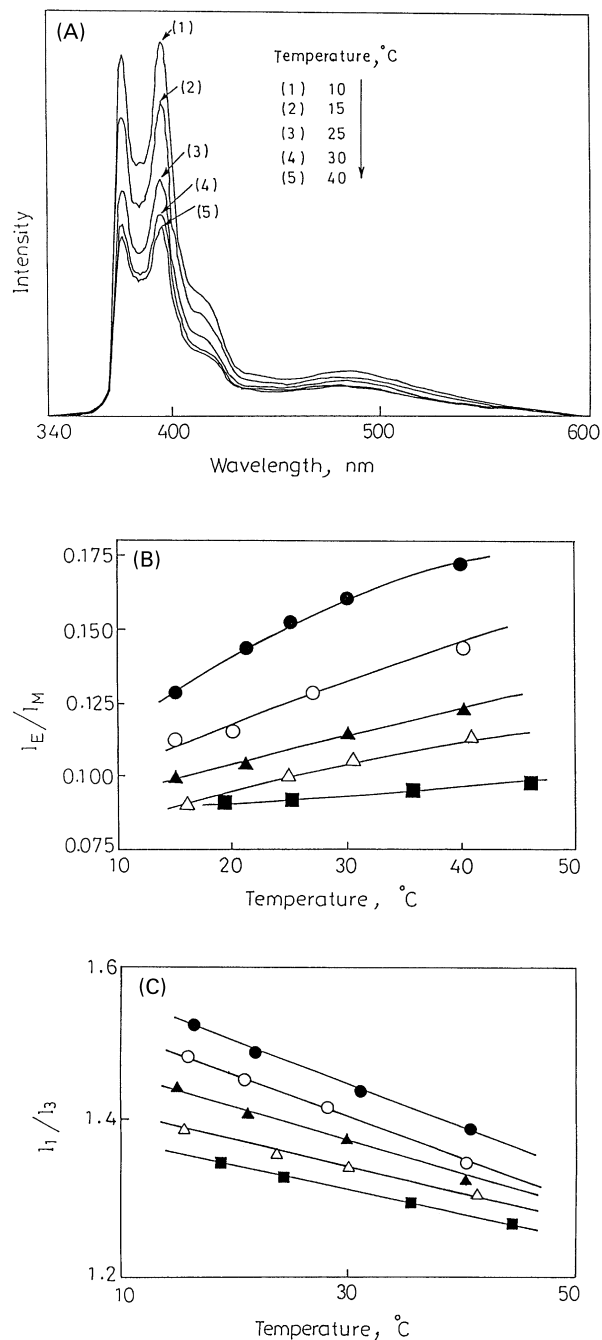


Fig. 10. (A) Excimer emission ( $I_E$ ) and monomer emission ( $I_M$ ) of SPM/NIPAM/PyMMA-1 terpolymer ( $4 \times 10^{-1} \text{ g dl}^{-1}$ ) in aqueous KCl solution at various temperatures. (B)  $I_E/I_M$  of mixed aqueous solution of SPM/NIPAM/PyMMA-1 and salt (KCl) as a function of temperature. (C)  $I_1/I_3$  of mixed aqueous solution of SPM/NIPAM/PyMMA-1 and salt (KCl) as a function of temperature. (KCl): (●)  $1 \times 10^{-1} \text{ g dl}^{-1}$ ; (○)  $5 \times 10^{-2} \text{ g dl}^{-1}$ ; (▲)  $1 \times 10^{-2} \text{ g dl}^{-1}$ ; (△)  $1 \times 10^{-3} \text{ g dl}^{-1}$ ; (■)  $0 \text{ g dl}^{-1}$ .  $I_E$ : fluorescence intensity at 472 nm;  $I_1$  or  $I_M$ : fluorescence intensity at 377 nm;  $I_3$ : fluorescence intensity at 388 nm. Excitation wavelength: 330 nm.

when the temperature was increased. The sulfonate groups were protonated with HCl addition (pH 2.51). The protonation of anionic terpolymer enhances hydrophobic association of polymer chains. Hydrophobic association of

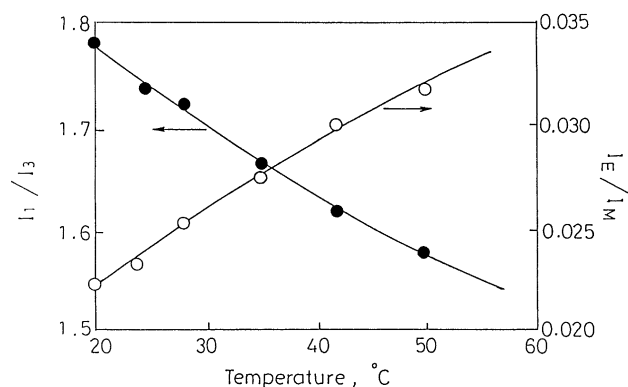


Fig. 11.  $I_E/I_M$  and  $I_1/I_3$  of acidic aqueous SPM/NIPAM/PyMMA-3 solution ( $1.2 \times 10^{-2} \text{ g dl}^{-1}$ ) (pH 2.50) as a function of temperature.  $I_E$ : fluorescence intensity at 472 nm;  $I_1$  or  $I_M$ : fluorescence intensity at 377 nm;  $I_3$ : fluorescence intensity at 388 nm. Excitation wavelength: 330 nm. (●)  $I_1/I_3$  and (○)  $I_E/I_M$ .

NIPAM segments increases with increasing temperature so that the pyrene group within polymer chains become close to each other. The dimeric pyrene was formed easily.

### 3.4. Solution properties and viscometric studies

In general, amphiphilic NIPAM-containing polymers were soluble in water near room temperature. As expected the aqueous solutions became turbid when heated, signaling the occurrence of a lower critical solution temperature (LCST). In the classic study of the LCST of water-soluble polymers, a general rule that the LCST should decrease with increasing hydrophobicity of the polymer was proposed [22]. Therefore, the LCST of amphiphilic poly(NIPAM) would be expected to decrease with increasing *n*-alkyl chain length and, for a given chain length, with increasing *n*-alkylacrylamide content [22]. However, Winnik et al. [22] reported that a depression of the LCST was observed for NIPAM copolymers containing  $C_{10}$  and  $C_{14}$  alkyl chains [22], but NIPAM copolymer containing  $C_{18}$  alkyl chain has an LCST lower than poly(NIPAM) and higher than the NIPAM copolymer containing  $C_{14}$  alkyl chain [22]. The unusual trend suggests that in solutions of the  $C_{18}$ -containing NIPAM copolymer the alkyl chains are not exposed to water but rather from a micellar structure protected from water and therefore do not make a hydrophobic contribution to the LCST [22]. In this study, anionic groups were incorporated into pyrene-labeled NIPAM-containing polymers. The LCST of anionic NIPAM-containing polymer series was expected to increase with increasing anionic content. However, aqueous solutions did not become turbid when heated from room temperature to 70 °C. There are no LCST in the SPM/NIPAM/PyMMA series solutions. These phenomena would be due to the interruption between ionic interactions and hydrophobic associations. Conventional poly(sulfobetaine) normally show an upper critical solution temperature (UCST), an LCST, or a closed loop of insolubility in phase behavior diagrams [35]. Previous

studies have addressed the aqueous solution properties of the naphthalene-labeled styrene–sulfobetaine copolymer, poly(SDMPAPS)/NA [30]. The hydrophobic group within poly(SDMPAPS)/NA interrupts the interaction between zwitterionic groups, resulting in a low critical solution temperature of poly(SDMPAPS)/NA solution [30]. Furthermore, the critical solution temperature of phenylene-containing zwitterionic polymer was below 0 °C, which results from the hydrophobic groups interrupting intramolecular associations (by ionic and H-bonding interactions) [32].

The dilute-solution behaviors of these anionic terpolymers were studied with respect to added electrolytes. The reduced viscosities of the SPM/NIPAM/PyMMA-3 series in KCl aqueous solution and in deionized water plotted as a function of polymer concentration are shown in Fig. 12. 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 group, which improves water solubility of polymers, and solution properties can become dependent on electrolyte concentration. Ionic polymers also exhibit a high sensitivity to added salt, which will influence the polymer conformation in aqueous solution. The salt-responsiveness inherent to ionic polymer solutions is a function of the ionic group type and placement. A relatively high viscosity observed indicated that an expanded conformation of the polymer chains was formed. In contrast, the formation of a polymer's compacted conformation implied that a relatively low viscosity would be observed (Fig. 12). The amount of ionic groups in 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 viscosity have been directly related to the charge density of the ionic polymer solution. In this study, SPM was copolymerized with NIPAM in varying molar ratios and further labeled

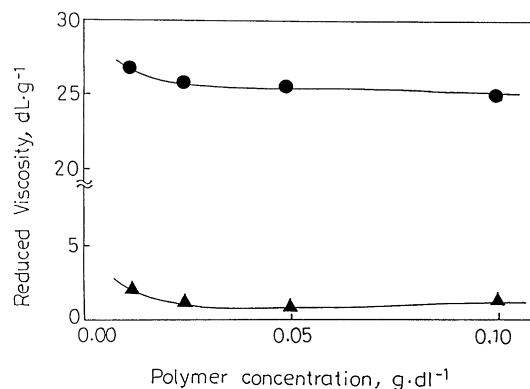


Fig. 12. Reduced viscosities of SPM/NIPAM/PyMMA-3 in deionized water and in salt solution. (●) in deionized water and (▲) in KCl salt solution ( $1 \times 10^{-1} \text{ mol l}^{-1}$ ).



with pyrene to yield water soluble anionic terpolymer systems. The chains of the SPM/NIPAM/PyMMA series have negative charges of the sulfonate species, and charge–charge repulsions force the polymer chains to expand. 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 anionic groups to decrease. The hydrodynamic volume of the anionic SPM/NIPAM/PyMMA series would decrease with a decreasing ionic repulsion between the anionic groups when salt was added. The reduced viscosities of the anionic SPM/NIPAM/PyMMA series were measured in deionized water and aqueous salt solution. For instance, the reduced viscosity of SPM/NIPAM/PyMMA-3 ( $\eta_{\text{red}} = 25 \text{ dl g}^{-1}$ , (SPM/NIPAM/PyMMA-3) =  $1 \times 10^{-1} \text{ g dl}^{-1}$ ) in deionized water was higher than that of SPM/NIPAM/PyMMA-3 ( $\eta_{\text{red}} = 1.2 \text{ dl g}^{-1}$ , (SPM/NIPAM/PyMMA-3) =  $1 \times 10^{-1} \text{ g dl}^{-1}$ ) in  $1 \times 10^{-1} \text{ mol l}^{-1}$  KCl solution. In salt-free aqueous solutions, the expanded conformation of the SPM/NIPAM/PyMMA series resulted from the ionic repulsion between the anionic sulfonate group and anionic sulfonate group in polymer chains. With salt added, the charge-charge repulsion of the SPM/NIPAM/PyMMA series chains decreased with an increasing  $\text{KCl}_{(\text{aq})}$  concentration. Therefore, the relatively low reduced viscosities of the SPM/NIPAM/PyMMA series were observed in the salt solution (Fig. 12).

#### 4. Conclusions

This study describes the effect of salt on the aqueous solution property of the anionic terpolymer in terms of fluorescence and dynamic light scattering. The  $I_1/I_3$  ratio decreases with increasing temperature, but the  $I_E/I_M$  ratio increases. When SDS are added into the anionic terpolymer aqueous solution, the pyrene labels would be buried in surfactant micelles, exhibiting less polarity of the local environment near pyrene. Particularly, when SDS is added to the aqueous anionic terpolymer solution, the ionic surfactant molecules would shield the ionic groups and the pyrene labels would be buried in the hydrophobic portions of the SDS molecules. Then, the micellar bridging causes and the inter-polymer micelles form, resulting in  $I_E/I_M$  increasing. When the inter-polymer micelles are formed, the  $I_1/I_3$  values start to decrease. As more SDS is added, the surfactant molecules would disrupt micellar bridging and inter-polymer micelles. The inter-polymer micelles will become intra-polymer micelles.  $I_E/I_M$  ratios decrease with the concentrations of SDS. The  $I_E/I_M$  and  $I_1/I_3$  ratios increase with increasing pH.

#### Acknowledgements

The authors would like to thank the National Science Council of the Republic of China for financial support.

#### References

- [1] Ezzell SA, Hoyle CE, Creed D, McCormick CL. *Macromolecules* 1992;25:887.
- [2] Hughes LE. US Patent 2,694,688; 1954.
- [3] Priestersbach DR, Clarke RA, Couper M, Patterson HT. US Patent 3,473,998; 1966.
- [4] Samour CM, Falxa ML. Patent 3,671,502; 1972.
- [5] Bahr U, Wieden H, Rinkler HA, Nischk GE. *Makromol Chem* 1972; 161:1.
- [6] Li ZF, Kang ET, Neoh KG, Tan KL, Huang CC, Liaw DJ. *Macromolecules* 1997;30:3354.
- [7] Winnik FM. *Polymer* 1990;31:2125.
- [8] Ringsdorf H, Simon J, Winnik FM. *Macromolecules* 1992;25:5353.
- [9] Itoh Y, Morishima Y, Nozakura S. *J Polym Sci, Chem Ed* 1982;20: 467.
- [10] Morishima Y, Itoh Y, Hashimoto T, Nozakura S. *J Polym Sci, Chem Ed* 1982;20:2007.
- [11] Morishima Y, Itoh Y, Nozakura S. *Makromol Chem* 1981;182:3135.
- [12] Morishima Y, Tominaga Y, Kamachi M, Furui T, Okada T, Hirata Y, Mataga N. *J Phys Chem* 1991;95:6027.
- [13] Morishima Y, Itoh Y, Nozakura S, Ohno T, Kato S. *Macromolecules* 1984;17:2264.
- [14] Zhao C, Wang Y, Hruska Z, Winnik FM. *Macromolecules* 1990;23: 4082.
- [15] *Polymers in aqueous media: advances in chemistry series no. 223*. Washington, DC: American Chemical Society; 1989.
- [16] Shaw KG, Leipold DP. *J Coat Technol* 1985;57:63.
- [17] Constein VG. *Polym Prepr* 1986;27:243.
- [18] Tirrell DA. *J Controlled Release* 1987;6:15.
- [19] Okahata Y, Noguchi H, Seki T. *Macromolecules* 1986;19:494.
- [20] Heskins M, Guillet JE. *J Macromol Sci* 1968;A2:1441.
- [21] Winnik FM, Ringsdorf H, Venzmer J. *Langmuir* 1991;7:905.
- [22] Ringsdorf H, Venzmer J, Winnik FM. *Macromolecules* 1991;24:1678.
- [23] Polozova A, Winnik FM. *Langmuir* 1999;15:4222.
- [24] Liaw DJ, Huang CC, Lee WF, Borbely J, Kang ET. *J Polym Sci, Chem Ed* 1997;35:3527.
- [25] Liaw DJ, Huang CC. *Polymer* 1997;38:6401.
- [26] Niu A, Liaw DJ, Sang HC, Wu C. *Macromolecules* 2000;33:3492.
- [27] Liaw DJ, Huang CC, Kang ET. *Langmuir* 1999;15:5204.
- [28] Liaw DJ, Huang CC, Kang ET. *J Polym Sci, Polym Phys Ed* 1998;36: 11.
- [29] Liaw DJ, Huang CC, Kang ET. *Colloid Polym Sci* 1997;275:922.
- [30] Liaw DJ, Huang CC, Sang HC, Kang ET. *Langmuir* 1998;14:3195.
- [31] Liaw DJ, Huang CC. *Macromol Chem Phys* 2000;201:1101.
- [32] Liaw DJ, Huang CC, Sang HC, Kang ET. *Polymer* 2001;42:209.
- [33] Liaw DJ, Huang CC, Sang HC, Wu PL. *Polymer* 2000;41:6123.
- [34] Kamachi M, Satoh J, Liaw DJ, Nozakura S. *Macromolecules* 1977;10: 501.
- [35] Schulz DN, Peiffer DG, Agarwal PK, Larabee J, Kaladas JJ, Soni L, Handwerker B, Garner RT. *Polymer* 1986;27:1734.
- [36] Kramer MC, Welch CG, Steger JR, McCormick CL. *Macromolecules* 1995;28:5248.