Dual behavior of polyelectrolyte and ionomer for an ionizable polymer containing sulfonate groups in DMSO/THF mixtures

Zhen Tong*, Biye Ren, Feng Gao

Research Institute of Materials Science, South China University of Technology, Guangzhou 510640, People's Republic of China

Abstract

A dansyl labeled polyelectrolyte (ADDan60) was prepared by copolymerization of ionizable monomer 2-(acrylamido)-2-methylpropanesulphonic acid (AMPS) with *N,N*-dimethylacrylamide (DMAA) and *N*-[2−[[[5−(*N,N*-dimethylamino)-1-naphthalenyl]-sulfonyl]amino]ethyl]-2-propenamide (DANSAEP, 0.2 mol%). Reduced viscosity η_{sp}/c, electrolytic conductivity κ, and fluorescent spectrum of ADDan60 in DMSO/THF mixtures were measured as functions of the volume fraction V_{THF} of THF. In the region of $V_{THF} < 0.7$, the emission maximum λ_{em}, relative intensity R_F of ADDan60 in DMSO/THF to that in DMSO, and anisotropy ratio r indicated that the polymer maintained its solvation layer not to change so much as the bulk solvent and exhibited a polyelectrolyte behavior, as observed from η_{sp}/c and κ. Once V_{THF} was beyond 0.70, the solvation layer was changed leading to the ion pair formation in an avalanche manner, which induced chain aggregation and phase transition due to the dipole attraction. The results suggest a behavior transition in ionizable polymers from polyelectrolyte into ionomer induced by medium polarity. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte; Ionomer; Fluorescence

1. Introduction

The volume phase transition in polymer gels has being intensively studied for about two decades since the discovery by Tanaka in 1980 of the hydrolyzed polyacrylamide gels swollen in water/acetone mixtures [1]. The fundamental molecular force driving such a discontinuous volume change is usually classified into four categories: van der Waals interaction, hydrophobic interaction, hydrogen bonding, and electrostatic interaction [2]. However, all gels showing the volume phase transition in response to changes in their surrounding environment contain charges on their network chains [3] and all of the reported transitions occur in aqueous solutions with only one exception [4]. These results indicate that the electrostatic interaction plays the most important role in initiating the volume phase transition of the polymer gels among the above four factors [5].

Recently Tong and Liu [6] found that highly charged polyelectrolyte gels of chemically crosslinked 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) and *N,N*-dimethylacrylamide (DMAA) underwent the volume phase transition in a water/acetone mixture as the acetone

concentration was above a certain level. The acetone concentration resulting in the volume phase transition rises only from 78 to 85 vol% when the AMPS content in the gels increases from 8.99 to 60.76 mol%. The volume phase transition of these gels can be also induced by increasing the volume fraction of tetrahydrofuran (THF) in simple organic mixtures of dimethyl sulfoxide (DMSO) and THF [7,8]. Similarly, to increase THF in this organic mixture beyond the above threshold can induce the precipitation of the corresponding linear polyelectrolytes from their homogeneous solution of DMSO/THF [9]. These facts imply that both the macroscopic volume phase transition and precipitation are caused by the decrease in the solvent polarity. As the polarity is decreased, the dissociative anion on the side chain associates with the mobile counterion bringing about ion pairs. Then, some ion pairs aggregate through the dipole–dipole attraction to form a so-called multiplet among different molecular chains or different segments of the same molecule as additional physical crosslinks [10,11]. Therefore, the dominant interaction in the system will alter from the repulsive to the attractive and the polyelectrolyte will behave like an ionomer with chain associations. Therefore, the media polarity change will cause the transition in the state of the polymers having ionizable groups.

The question arises, following what process the multiplet

* Corresponding author. Fax: +86-20-8711-2886.
  E-mail address: mcztong@scut.edu.cn (Z. Tong).

DANSAEP
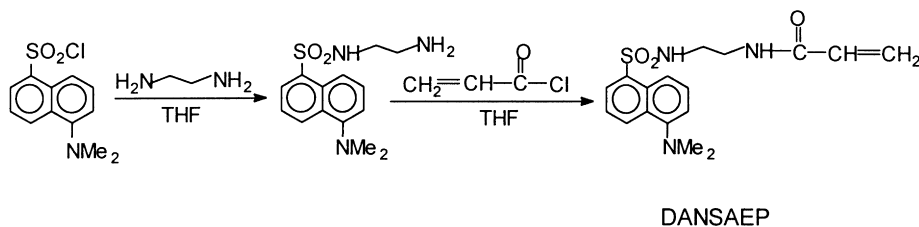
Scheme 1.

forms in a dilute polyelectrolyte solution. Does it form gradually and individually or suddenly and synchronously in response to the medium polarity change? As for the situation in mixed solvents, one has to take the solvent quality into account since the good solvent shows a higher affinity to a given polyelectrolyte. The composition of the solvation layer surrounding the chains is not expected to be the same as that of the bulk solvent due to the preferential absorption of the polymer.

Fluorescence technique is considered as a powerful tool to monitor the change in the environment surrounding the chromophore for both polymer solution and gel [12–14]. The chromophore attached to polymer chains can directly reflect the situation of the microenvironment of the labeled polymer, such as local polarity, viscosity, and segment mobility. Early in 1975, Strauss and Vesnaver [15,16] investigated the correlation between the emission spectra of the dansyl chromophore and the ionization degree of the carboxylate group and the equilibrium in the conformational transition of the dansyl-labeled maleic anhydride copolymer with alkyl vinyl ethers in solution. Chen and Morawetz [17] studied the complexation equilibrium and kinetics of the conformation transition and association of dansyl-labeled poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) with the polymer acting as the hydrogen bond acceptor by measuring the fluorescence intensity of the dansyl residues attached to PAA or PMA. Horie et al. [18,19], observed the changes in microenvironment and kinetics during the volume phase transition of dansylated polyacrylamide (PAAm) or poly(N-isopropylacrylamide) (PNIPA) gels in mixed solvent by fluorescence spectra, anisotropy, and fluorescence lifetime. Morishima et al. [20], investigated micelle formation induced by hydrophobic aggregation of amphiphilic polyelectrolytes containing AMPS segments in aqueous solutions with several fluorescent methods, including steady-state fluorescence, no-radiation-energy-transfer, fluorescence decay, etc.

In order to reveal microscopically the influence of polarity on the aggregation behavior of highly charged strong polyelectrolytes, the dansyl chromophore was chemically incorporated into a copolymer containing AMPS similar to those used previously [9]. First, the reduced viscosity of the AMPS copolymer in DMSO/THF mixtures was measured as a function of the THF volume fraction V_{THF} to determine the chain conformation of polyelectrolytes. Then, the dissociation state of sulfonate groups in the

copolymer was detected by the electrolytic conductivity over the same V_{THF} range. Finally, we recorded the fluorescent spectra of the dansyl-labeled polyelectrolyte to observe the change in the chain microenvironment accompanying the change in the dissociation state. Thus, we get a comprehensive understanding of the relation between the local polarity and the aggregation transition of a polyelectrolyte into an ionomer.

2. Experimental

2.1. Materials

Dansyl chloride (Aldrich) and 2-acrylamido-2-methyl-propanesulphonic acid (AMPS, Fluck) were used without further purification. N,N-dimethylacrylamide (DMAA, Kohjin, Japan) and acryloyl chloride (Aldrich) were distilled before use. The silica gel powder for the separation chromatography column was of 200–400 mesh and activated at 300°C for 6 h. Other reagents and solvents were all purchased from commercial sources and purified according to standard procedures [21]. Highly pure water was obtained through deionization and filtration with a Millipore purification apparatus.

2.2. Preparation of dansyl labeled polyelectrolyte

Dansyl monomer N-[2–[[[5–(N,N–dimethylamino)–1–naphthalenyl]-sulfonyl]amino]-ethyl]-2-propenamide (DANSAEP) was synthesized according to the method described previously [22] (Scheme 1). The product was purified by chromatography and characterized with ^{1}H and ^{13}C NMR spectra in CDCl$_3$ on a Bruker DRX-400 spectrometer (400 MHz).

The dansyl-labeled polyelectrolyte was prepared by radical copolymerization of AMPS, DMAA, and DANSAEP in water at 70°C, using 0.2 mol% of ammonium persulfate as the initiator. The total monomer concentration was 0.46 mol L^{-1} with 0.2 mol% of DANSAEP. The mixture was stirred for 16 h under nitrogen atmosphere and then the product was dialyzed for two weeks against distilled water to thoroughly remove impurities. The dialyzed solution was condensed, freeze-dried and finally vacuum-dried at 60°C to obtain the dansylated sample ADDan60 (yield about 80%). The content of 63.3 mol% AMPS in this copolymer was estimated from the N content determined by
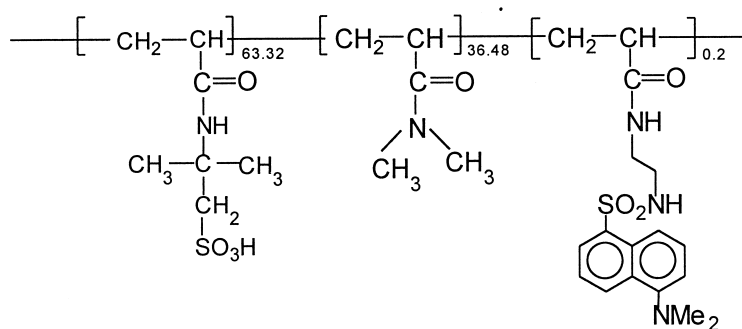
ADDan-60

Chart 1.

elemental analysis with a Heraeus CHN-O apparatus. The composition and structure of this copolymer is shown in Chart 1.

2.3. Measurements

The stock solution of ADDan60 in DMSO/THF mixtures was prepared by dissolving ADDan60 in pure DMSO then adding THF of desired solvent composition. The stock solution was diluted with the mixed solvent of the same composition.

The reduced viscosity of ADDan60 in DMSO/THF mixtures was measured with a modified Ubbelohde capillary viscometer at 25 ^ 0.05°C. The flow time for mixed solvents was longer than 100 sec.

The conductivity of ADDan60 in DMSO/THF mixtures was measured with a immerse-type conductometer of model DDS-11A at 25 ^ 0.05°C. For solutions with conductivity less than 10×10^{-6} Scm^{-1} bright platinum electrodes were used, while for solutions with conductivity higher than

10×10^{-6} Scm^{-1} platinum black electrodes were used. The electrode constant was established using the standard KCl solution.

Steady-state fluorescence spectra and fluorescence anisotropy of the dansyl monomer DANSAEP and dansyl-labeled copolymer ADDan60 in DMSO/THF were measured with a Hitachi F-4500 fluorescence spectrophotometer at 25°C. The excitation wavelength and the slit width were adjusted to 338 nm and 5 nm, respectively. The fluorescence anisotropy ratio r is defined as [23]

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \tag{1}$$

where $I_{\parallel}$ and $I_{\perp}$ are emission intensities measured parallel and perpendicular to the vertically polarized excitation, respectively.

3. Results and discussion

3.1. Reduced viscosity in DMSO/THF

According to the traditional methodology, the concentration dependence of the reduced viscosity η_{sp}/c reflects the chain conformation in the dilute solution. Fig. 1 shows η_{sp}/c of the copolymer ADDan60 against polymer concentration c in the DMSO/THF mixtures of different volume fractions V_{THF} of THF. Similar to what Liu et al. [9] recently reported for the AMPS/hydropropyl methacrylate copolymer in DMSO/THF, the reduced viscosity increases with decreasing polymer concentration at all tested solvent compositions. Based on the common interpretation, this is a typical polyelectrolyte phenomenon, which is usually observed in salt-free aqueous solutions, indicating that the sulfonate group is still ionized and the electrostatic repulsion makes the chain expand in the mixtures as long as V_{THF} is not beyond 0.7.

The η_{sp}/c values at constant polymer concentration c are plotted as a function of solvent composition V_{THF} in Fig. 2 for easy comparison. It is seen that as V_{THF} is raised the reduced viscosity continuously decreases with a gradual increase in the negative slope of η_{sp}/c vs. V_{THF} curves,
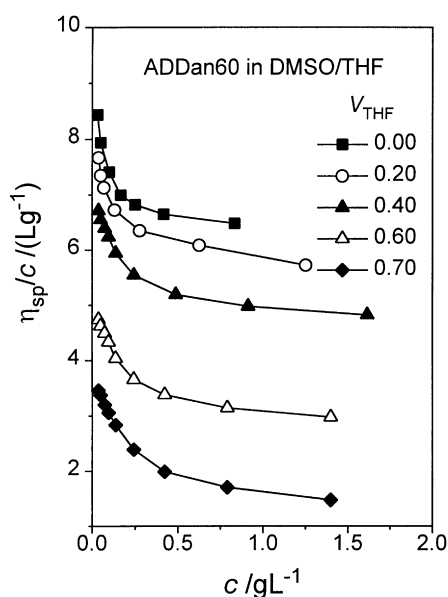

Fig. 1. Reduced viscosity η_{sp}/c against ADDan60 concentration c of solution with indicated V_{THF} in DMSO/THF mixtures at 25°C.
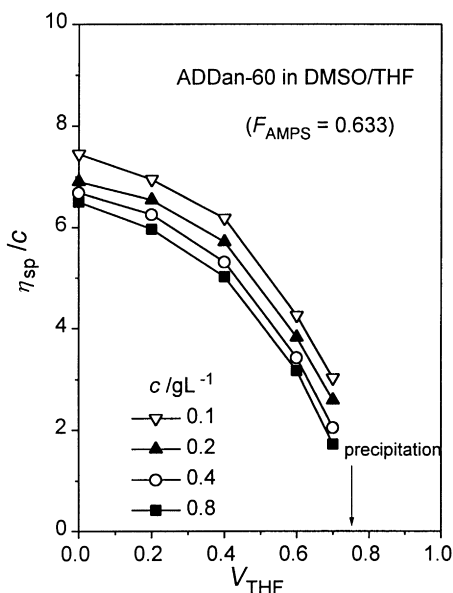
Fig. 2. Reduced viscosity η_{sp}/c against V_{THF} in DMSO/THF mixtures at indicated ADDan60 concentrations c at 25°C.
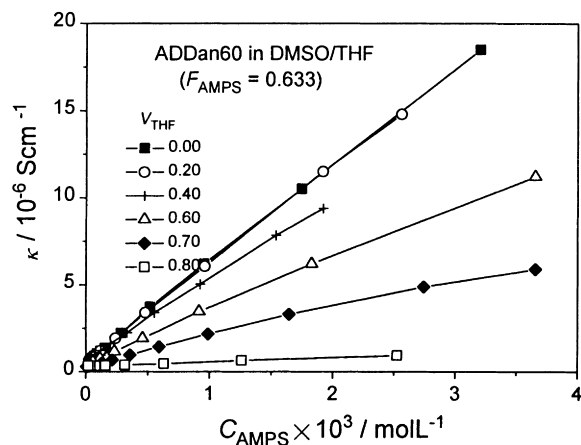

Fig. 3. The electrolytic conductivity κ in DMSO/THF mixtures against molar concentration C_{AMPS} of AMPS segment in ADDan60 with indicated V_{THF} at 25°C.

corresponding to the shrink of polyelectrolyte chains. When V_{THF} reaches 0.75, precipitation was observed in the concentrated solution of the sample ADDan60. There are two causes for this chain collapse on the addition of THF: the mixed solvent becomes poorer and the dissociated polyion associates with counterions to form ion pairs. At the present stage, it is impossible to divide the contributions of these two causes. According to the theory proposed by Khokhlov et al. [24,25], the ion-pair attraction occurs in an avalanche process to produce the so-called multiplet as additional physical crosslinkers. We consider that the fast decrease in the chain spatial size in a higher V_{THF} range and the precipitation appearing in the concentrated solution are mainly induced by this positive feedback process of multiplet formation.

3.2. Dissociation–association state transition

The association of ion pairs will cause the conductivity of a polyelectrolyte solution to decease approximately to zero. Fig. 3 shows the electrolytic conductivity κ of ADDan60 in different DMSO/THF mixtures varying with the molar concentration C_{AMPS} of the AMPS segment in the copolymer calculated from the copolymer composition and concentration. The polymer concentration is in the range of 1×10^{-3}– 0.97 gL^{-1}, lower than that used in viscosity measurement to avoid precipitation. The electrolytic conductivity κ is generally expressed as a function of the mobile ion concentration C_{ion} [26,27]

$$\kappa = \kappa_0 + \Lambda^0 C_{ion} + \psi(C_{ion}) \qquad (2)$$

where κ_0 is the solvent conductivity obtained by extrapolation to infinite dilution, Λ^0 is the limiting equivalent conductivity at infinite dilution of mobile ions, and

$\psi(C_{ion})$ represents the effect of the interionic interactions on the conductivity.

In the dilute region, the linear part can be seen at each V_{THF}, while the curve bends downwards at higher AMPS segment concentration indicating a little effect of $\psi(C_{ion})$. When $V_{THF} \leq 0.7$, κ increases with the increase in C_{AMPS} still showing dissociation of sulfonate groups in these mixtures. On the other hand, at $V_{THF} = 0.8$ κ becomes a constant close to the solvent conductivity independent of C_{AMPS}, showing no contribution to κ by the sulfonate groups in this mixture.

The real Λ^0 value cannot be estimated from the slope of the linear part of κ against C_{AMPS} plots in Fig. 3 because the abscissa C_{AMPS} does not stand for the actual concentration of mobile ions, which is depressed by the addition of THF into the mixed solvent. From the change in the slope of κ vs. C_{AMPS} curves, however, one can still recognize the decrease in the contribution of sulfonate groups to the solution conductivity due to the composition change in the solvent. These results suggest that so long as the medium polarity is below a certain level, the polyelectrolyte would transfer from electrostatic repulsion dominant into ion-pair attraction dominant. This transition concerns the change in the selective solvation layer of the copolymer, which can be detected by fluorescence of our dansyl labeled polyelectrolyte.

3.3. Emission spectra of the dansyl monomer DANSAEP

As a starting stage, the emission spectra of the dansyl monomer DANSAEP were measured as a function of V_{THF} in DMSO/THF as shown in Fig. 4. The emission appearing in $493 \sim 517 \text{ nm}$ range blue-shifts and the intensity increases with the increase of V_{THF} in the mixed solvent. The emission is attributed to the formation of the twisted intramolecular charge-transfer (TICT) state of dansyl groups and its wavelength is referred to as the emission maximum λ_{em} [18,19,22]. The TICT state is related to the
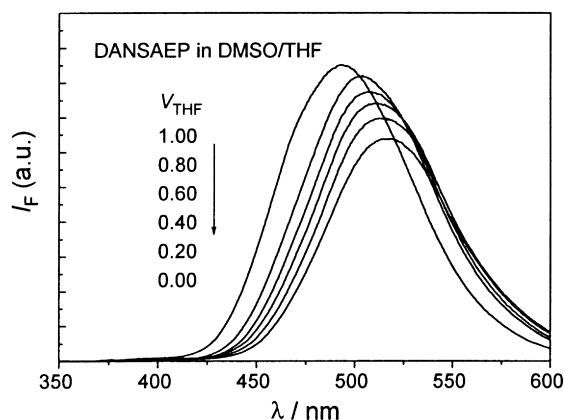
Fig. 4. Fluorescence spectra of the dansyl monomer DANSAEP in DMSO/ THF mixtures at the concentration of 1.5×10^{-5} molL^{-1} at 25°C.

Fig. 5. The emission maximum λ_{em} (circle) and relative emission intensity R_F (square) of the dansyl monomer DANSAEP against the V_{THF} in DMSO/ THF.

torsional motion of the dimethylamino group around the amino-naphthalene bond of the dansyl residue and is stabilized by interactions with adjacent solvent molecules [28]. The fluorescence maximum of the dansyl chromophore exhibits a large solvachromic shift from less-polar to polar solvents and provides useful information about its microenvironment polarity as well as its segment mobility [18,19,22]. For example, in less-polar hexane the fluorescence maximum λ_{em} is about 460 nm, while in water it significantly shifts to 530 nm [22].

As illustrated in Fig. 5, λ_{em} gradually decreases from 517 in pure DMSO to 493 nm in pure THF with increasing V_{THF} in DMSO/THF mixture. This blue-shift of λ_{em} manifests a continuous decrease in the polarity of the microenvironment around the chromophore accompanying the mixture composition. The relative intensity R_F of the emission in DMSO/ THF to that in DMSO is also plotted against V_{THF} in Fig. 5. R_F increases with an increase in V_{THF} over the whole composition range. The results indicate that the less polar and lower viscosity medium favors the formation and stabilization of the TICT state. Chen and Morawetz [17] reported that with the increasing concentration of polyoxyethylene (POE-600) in aqueous solution, the emission intensity of *N*-dansyl ethylene diamine was greatly enhanced together with the blue-shift of λ_{em} due to the establishment of a more hydrophobic environment.

3.4. Emission spectra of dansylated polyelectrolyte

The TICT fluorescent emission of the dansylated polyelectrolyte ADDan60 in DMSO/THF mixtures is displayed in Fig. 6. In contrast to DANSAEP, the fluorescence intensity of ADDan60 decreases with increasing V_{THF}.

The emission maximum λ_{em} and relative intensity R_F are plotted against V_{THF} in Fig. 7. In pure DMSO, λ_{em} of the dansyl chromophore in ADDan60 blue-shifts to 513 nm comparing with 517 nm for monomer DANSAEP, due to the contribution of the hydrophobic polymer backbone to the local polarity surrounding the chromophore on polymer
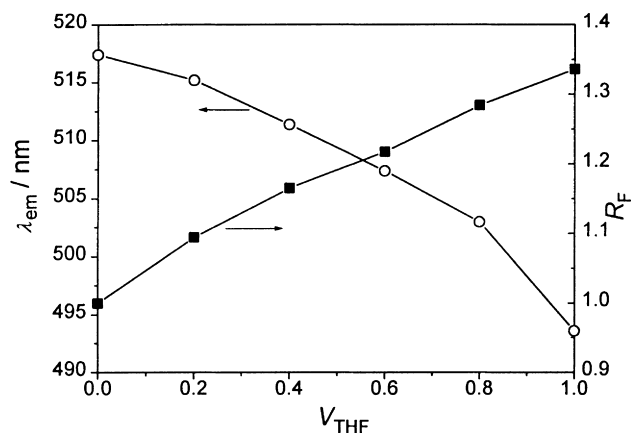
side chains. On the other hand, with increasing V_{THF} λ_{em} of ADDan60 blue-shifts 9 nm from pure DMSO to the mixture of $V_{THF} = 0.70$ (504 nm), smaller than 12 nm for the dansyl monomer DANSAEP over the same solvent composition range (517–505 nm). Since the emission maximum λ_{em} is sensitive to the local polarity, the results imply that the solvation layer of polyelectrolyte surrounding the dansyl chromophore does not vary so much as the bulk solvent when $V_{THF} \leq 0.70$. The polarity of the solvation layer is a synthetic effect from the bulk solvent, the polymer backbone, the residues on the polymer chain, and the additives in the solution. Due to the dominant contribution of the less-polar polymer backbones, the polyelectrolyte chain is capable of maintaining the local polarity in the surrounding microenvironment. This argument is confirmed by the emission maximum λ_{em} of about 510 nm for the solid ADDan60 sample[29], because this value is very close to the plateau level in the range of $V_{THF} \leq 0.70$. Furthermore, when V_{THF} exceeds 0.70 the solvation layer is destroyed as illustrated by the steeper decrease of λ_{em} with increasing V_{THF}.

Fig. 7 also demonstrates the solvent composition dependence of the relative emission intensity R_F for the dansyl labeled polyelectrolyte ADDan60 in DMSO/THF. In contrast to the DANSAEP, R_F is always less than 1 and slightly decreases with increasing V_{THF} up to 0.65, then a sharp decrease in R_F occurs when V_{THF} is above 0.70. The R_F value is a measure of the segment mobility since the TICT state is related to the torsional motion of the dimethylamino group linked to the naphthyl group [30,31]. Tazuke et al. [30,31] reported that the existence of poly(methyl methacrylate) main chain greatly suppressed the formation of the TICT state of the 4-(*N*-dimethylamino)-benzoate group bonded to poly(methyl methacrylate) side chain in ethyl acetate and in *n*-butyl chloride dilute solutions, even the chromophore was separated from the main chain with a long alkyl spacer. The abrupt decrease of R_F observed in Fig. 7 at $V_{THF} \sim 0.70$ indicates that the TICT process is
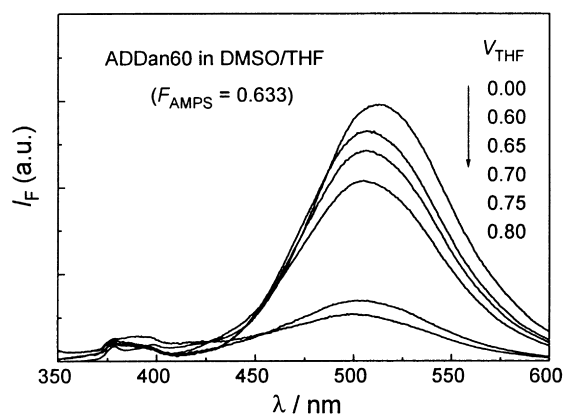
Fig. 6. Fluorescence spectra of the dansyl-labeled polyelectrolyte ADDan60 in DMSO/THF mixture at a concentration of 0.6 gL^{-1} at 25°C.

Fig. 8. The fluorescence anisotropy ratio r of DANSAEP (unfilled circle) and ADDan60 (filled circle) as functions of V_{THF} in DMSO/THF mixtures at 25°C.

greatly hindered by the polymer chain aggregation due to the dipole–dipole attraction of ion pairs.

Fig. 8 shows the variation of the anisotropy ratio r of DANSAEP and dansylated polyelectrolyte ADDan60 with V_{THF} in DMSO/THF mixtures. For the monomer DANSAEP, r remains a constant at about 0.20 over the entire range of the solvent composition. While for ADDan60, r is a constant when $V_{THF} < 0.65$, and then increases suddenly at $V_{THF} = 0.70$. This sharp increase of r manifests that the relaxation motion of local chain segments of the polyelectrolyte ADDan60 is greatly slowed down in this solvent mixture due to the restriction of the ion pair attraction. This observation is consistent with the change in the emission maximum λ_{em} and relative intensity R_F reported in the above paragraphs.

The fluorescent spectra of the ADDan60 in DMSO/THF mixtures can be understood in terms of the dual phenomena of polyelectrolyte and ionomer for an ionizable polymer [8,9,24,25]. The dissociation state of sulfonate groups on the polymer side chain directly depend on the medium
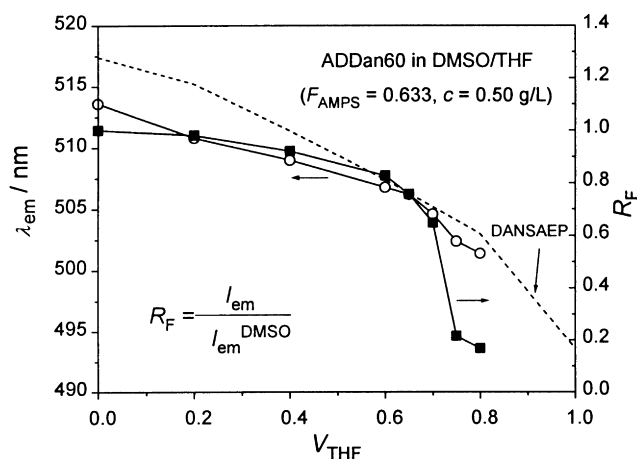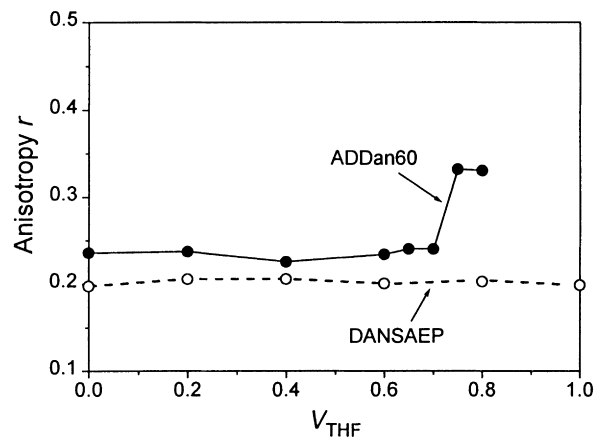
polarity. In pure DMSO the ionization is complete, while in the mixture of $V_{THF} \geq 0.7$ the sulfonate groups exist as ion pairs with protons. These two ionization states correspond to the two behaviors: polyelectrolyte and ionomer. For polyelectrolytes, the electrostatic repulsion among ionized groups plays a dominant role and makes the polymer chain extended. On the other hand, in ionomers the dipole–dipole attraction among the ion-pairs causes the chain aggregation. Therefore, these two behaviors have the same origin of interaction in the system, i.e. electrostatic interaction. As observed from the change in λ_{em}, R_F, and r, the polymer chain can retain its solvation layer without changing much within the region of $V_{THF} < 0.7$, resulting in the almost complete ionization of the sulfonate groups. When V_{THF} is beyond 0.70, the solvation layer is changed leading to the association of the sulfonate groups into ion-pairs. The dipole attraction among ion-pairs brings about the chain aggregation in an avalanche manner greatly reducing the chain mobility. It is this polyelectrolyte–ionomer transition that induces the macroscopic phase transition in polyelectrolyte gels and solutions.

Acknowledgements

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Fig. 7. The emission maximum λ_{em} (circle) and relative intensity ratio R_F (square) of ADDan as functions of V_{THF} in DMSO/THF mixtures at 25°C. Dashed line: λ_{em} of monomer DANSAEP.

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