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Self-association of hyperbranched poly(sulfone-amine) in water: studies with pyrene-fluorescence probe and fluorescence label

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Abstract

Both pyrene-fluorescence probe and fluorescence label techniques are used to investigate the association behaviors of hyperbranched poly(sulfone-amine) (HPSA) in aqueous solution. In the presence of HPSA, excimer emission peak evidently appeared, while no excimer peak was observed in the emission spectra in the absence of HPSA. The excitation spectrum monitored at excimer emission red shifts by about 38–40 nm compared to that monitored at monomer emission, which shows that the excimer is formed by preassociated pyrene chromophores. In the same concentration of pyrene, monomer emission of pyrene decreases but excimer emission increases with increasing the concentration of HPSA; the ratio of excimer-to-monomer emission intensity (I_E/I_M) gradually increases, reaches a critical point at 5–7 g/l, and sharply increases with the concentration. Pyrene-labeled hyperbranched poly(sulfone-amine) (Py-HPSA) was synthesized from 4-(1-Pyrene)butyroyl chloride and HPSA. The monomer emission and excimer emission of Py-HPSA show the concentration-quenching effect, while I_E/I_M increases monotonously, approaches a critical point, and then suddenly increases with increasing the concentration of Py-HPSA. Influences of acidity and solvents on the fluorescence emission were studied. In high concentrations of hyperbranched polymer, pH and DMSO significantly influence the emission of pyrene, and excimer peak disappears at 72% of DMSO fraction.

Keywords: Association; Fluorescence; Hyperbranched

1. Introduction

Pyrene has earned a reputation as a good fluorescence probe or fluorescence label for its features like excimer formation, long-lived excited state, and the sensitivity of monomer emission and the ratio of excimer-to-monomer emission (I_E/I_M) to the variation of microenvironment [1]. Through pyrene-fluorescence probe or fluorescence label, the formation of micelles and association behaviors for linear polymers in aqueous solution has been widely studied [2]. Water-soluble or amphiphilic macromolecules such as poly(vinyl alcohol) [3], poly(methacrylic acid) [4], poly(*N*-isopropylacrylamide) [5], polyacrylamide [6], poly(ethylene oxide) [7], poly(acrylic acid) [8], hydroxypropyl cellulose [9], copoly(maleic acid–ethyl vinyl ether) [10], poly(aspartic acid) [11], polynorbornene [12], and their copolymers or derivatives are often used as probing or labeled subjects. Generally, hydrophobic modified linear polymers or copolymers with hydrophobic units tend to aggregate into hydrophobic domains.

Comparing with the linear polymers, hyperbranched polymers [13] with good solubility, low viscosity and abundant functional groups have three-dimensional global architectures. Due to their unique size, shape and properties, hyperbranched polymers are drawing more and more attention of scientists especially in the fields of self-assembly and self-association [14–16]. By reductive amination of poly(ethylenimine) with 1-pyrenecarboxyaldehyde, Winnik and coworkers [17] obtained hyperbranched polymer labeled with pyrene chromophores, and then they [18] studied the interaction of the pyrene-labeled polymer with sodium dodecyl sulfate in aqueous solution. Frank, et al. [19] characterized pyrene-labeled highly branched polystyrenes through fluorescence quenching techniques, and they [19] found that the branched samples had reduced quenching rate constants, and the fraction of

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accessible chromophores decreased for higher generation polymers.

This work found that hyperbranched poly(sulfone-amine) made from divinyl sulfone and 1-(2-aminoethyl)piperazine without hydrophobic modification can associate via hydrogen bonds. Furthermore, both fluorescence probe and label techniques are applied to detect the self-association of the hyperbranched polymer.

2. Experimental section

2.1. Materials

Hyperbrancehd poly(sulfone-amine) (HPSA) was synthesized by direct polyaddition of 1-(2-aminoethyl)piperazine (AP) to divinyl sulfone (DV) [20]. The number-average molecular weight (M_n), molecular weight distribution (M_w/M_n), and degree of branching (DB) of HPSA were 23,650 (measured by GPC as water the solvent), 1.28, 53.2% (determined by the ^{1}H NMR), respectively. Pyrene and 4-(1-pyrene)butytic acid (PyBA) were purchased from Aldrich, and used as received. Thionylchloride, toluene, *n*-hexane, chloroform, triethylamine, dimethyl sulfoxide (DMSO), and methanol were purchased from domestic market, and distilled twice before use. Aqueous solutions of labeled polymer samples were made up by using distilled deionized-water. The concentration of pyrene aqueous solution used in the measurements of fluorescence probe is 8.5×10^{-7} mol/l. Polymer solutions used for pyrene-probing were made up by adding corresponding amount of polymer sample into the solution of the prepared pyrene aqueous solution. So the concentration of free pyrene is same for the solutions with different polymer content.

2.2. Synthesis of PyBC

4-(1-Pyrene)butyroyl chloride (PyBC) is synthesized according to the reference reported by Parlesak and coworker [21]. Into a three-necked round-bottom flask 9.0 mmol of PyBA, 15 ml of dried toluene, and 20 ml of thionylchloride were added. The reaction container was placed in an oil bath at 75 °C for 12 h. After removal of the solvent by reduced-pressure distillation, the mixture was recrystallized four times in dried *n*-hexane. 1.8 g (yield 69.3%) of brown product was obtained.

2.3. Synthesis of Py-HPSA

A typical example for synthesis of pyrene-labeled hyperbranched poly(sulfone-amine) (Py-HPSA) is given as follows. To a solution of HPSA (6 g) in 10 ml of chloroform and 0.5 ml of triethylamine, 0.0276 g of PyBC was added. The mixture was kept at 40 °C for 12 h, then poured into 500 ml of methanol. After purification of the crude product by three-times reprecipitation, 4.5 g (yield 74%) of brown solid was obtained. The degree of pyrene substitution determined by UV–vis absorption measurements using PyBA as the standard was one pyrene group per 240 SA units (SA = DV + AP).

2.4. Protonation of Py-HPSA

A typical example is given as follows. The resulting Py-HPSA-1 (0.5 g) was added to aqueous 6N hydrochloric acid (10 ml) with stirring. After dissolving perfectly, the mixture was poured into 300 ml of methanol, yield 0.75 g of solid product. IR (cm^{-1}) (KBr): 3450–3250 m, 2750–2250 s, 1290 s, 1131 s. ^{1}H NMR (D_2O): δ 7.85–8.33 (trace, Ar), 4.75 (H_2O), 3.92–4.05 (br, s), 3.72–3.9 (br, s), 3.4–3.7 (br, s), 3.38 (br, s), 2.8 (w, CH_2NH), 2.08 (NH), 1.33 (w, CH_2).

2.5. Characterization

Nuclear magnetic resonance (NMR) measurements were performed on a 500 MHz Bruker NMR spectrometer with D_2O as solvent. Fourier-transform infrared (FTIR) measurements were carried out on a Bruker Equinox 55 spectrometer with a disc of KBr. The molecular weight of the product was obtained on the HP 1100 gel permeation chromatograph (GPC) with water as solvent and PEO as standards, and the column used was G6000 PW (XL). Ultraviolet–visible (UV–vis) spectra were measured on a PE Lambda 20 spectrophotometer in chloroform solution. Potentiometric titration was carried out on a PHS-3C apparatus in water solution.

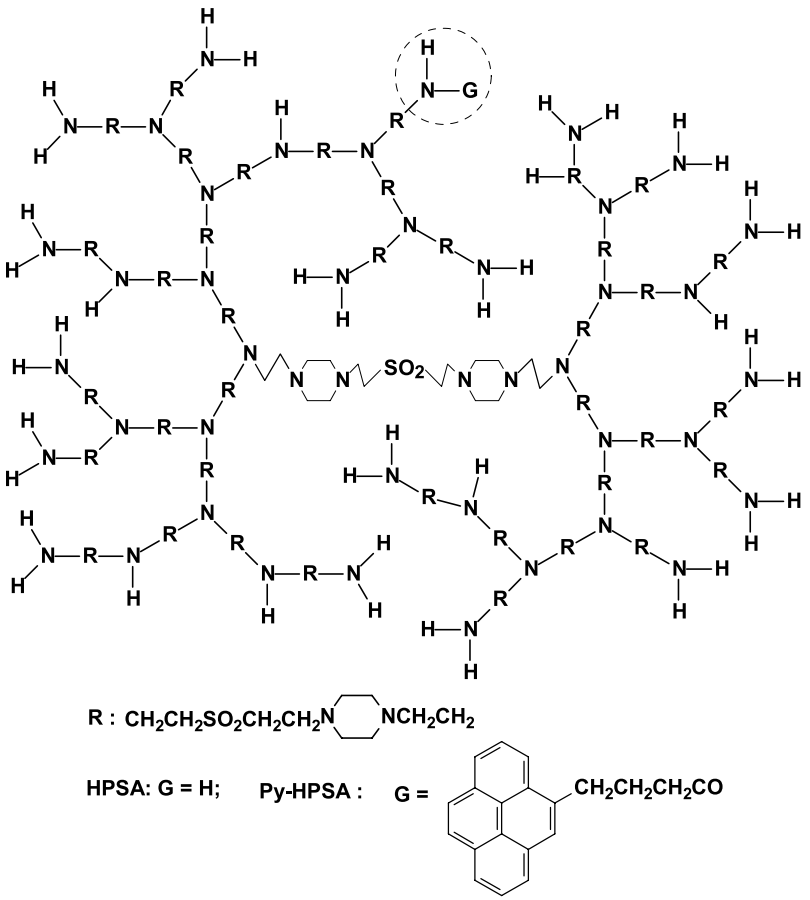
2.6. Fluorescence measurements

Fluorescence spectra were recorded at room temperature on a PE LS50B spectrophotometer in water solution. The excitation and emission slit widths are 5 and 3 nm, respectively. The value of I_E/I_M was the ratio of the emission intensity at 470 nm to the intensity at 377 nm (probe) or 385 nm (label). By adding a trace of concentrated aq. HCl or NaOH to the original tested polymer solution, water solutions with various pH were prepared, and then the concentration error resulting from the addition of acid or base was negligible.

3. Result and discussion

3.1. HPSA and Py-HPSA

Scheme 1 shows the schematic structures of hyperbranched poly(sulfone-amine) (HPSA) and Pyrene-labeled hyperbranched poly(sulfone-amine) (Py-HPSA) used in this paper. HPSA contains large amount of tertiary, secondary and primary amino groups in its backbones or terminal units. Py-HPSA was fabricated by reaction of 4-(1-Pyrene)butyroyl chloride with HPSA. Fluorescence probe



Scheme 1. The molecular structure of HPSA and Py-HPSA.

is easily disturbed by the probed surroundings [22], and the concentration of fluorescence chromophore varied with the concentration of the labeled molecules, resulting in partial errors for the detected objects. Therefore, both fluorescence probe and label techniques are utilized to investigate the association behavior of HPSA.

3.2. Emission and excitation spectra

Fig. 1 shows the emission and excitation spectra of pyrene in HPSA aqueous solution. Monomer and excimer emission are observed. Comprising with the spectrum of free pyrene, the monomer emission has no considerable difference, but the excimer emission red shifts from 450 to 470 nm. No excimer peak was observed in the spectrum of pyrene aqueous solution without HPSA, which preliminarily indicates that association occurs in the HPSA solution.

Static excimer emission of pyrene observed in the experiment gives further evidence for the association of HPSA. Generally, static excimer or dynamic excimer might be formed in the pyrene-fluorescence emission. The former arises from preassociated pyrenes that has a red-shift excitation spectrum, and the latter from the excited pyrene and a ground-state pyrene group that has a same excitation spectrum as that of monomer emission [19]. Static excimer of pyrene is often used in the detection of association behaviors of polymers in aqueous solution [15,16,23–26]. As shown in Fig. 1, the excitation spectrum monitored at excimer emission red shifts by about 40 nm compared with that monitored at monomer emission, which implies that the excimer results from preassociated pyrene groups, or

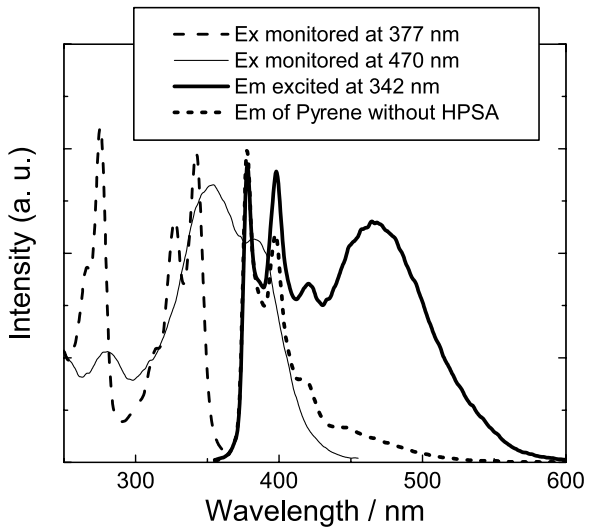


Fig. 1. Excitation and emission spectra of pyrene in HPSA aqueous solution and in water solution without HPSA.

supramolecular domains caused by association of HPSA exists in the water solution.

The fluorescence spectra of Py-HPSA are shown in Fig. 2. The monomer emission red shifts from 377 to 385 nm, and excitation peak of Py-HPSA red shifts by about 10 nm too. Again, static excimer emission is observed since the excitation spectrum monitored at 385 nm red shifts by about 38 nm. The outcome obtained from the measurements of fluorescence label and probe is in agreement with each other.

3.3. Concentration effects

Association behaviors of polymers would change with the concentration, resulting in the variation of fluorescence of the probe, which can be used reversibly to probe association behaviors. Fig. 3 shows the concentration effect of HPSA probed by pyrene at pH = 8.5. With increasing the concentration of HPSA, monomer emission of pyrene decreases while excimer emission increases in the same concentration of pyrene, and an equal-fluorescence point appears at 425 nm. Furthermore, the ratio of excimer-to-monomer emission intensity (I_E/I_M) gradually increases, reaches a critical point at 5–7 g/l (critical association concentration, CAC), and significantly increases with increasing the concentration of HPSA (Fig. 4). These data indicate that the self-association of HPSA depends on its concentration, and no considerable aggregation occurs until the concentration approaches CAC.

For Py-HPSA (Fig. 5), the monomer and excimer emission increase, pass through a maximum, and decrease with increasing the concentration of polymer, which is attributed to the self-quenching effect [27] of pyrene chromophores since the content of pyrene increases with the concentration of polymer. However, I_E/I_M increases monotonously with the concentration of Py-HPSA, and

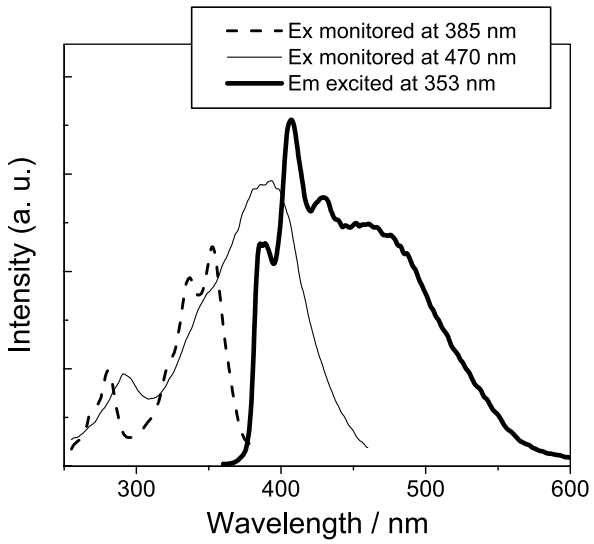


Fig. 2. Excitation and emission spectra of Py-HPSA in water solution.

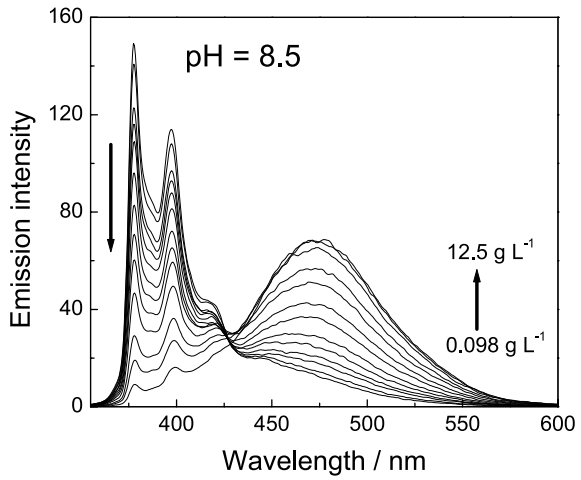


Fig. 3. Emission spectra of pyrene in various HPSA aqueous solutions at pH = 8.5.

sharply increases above a critical point. Similarly, the CAC for HPSA found by label technique is also 5–7 g/l.

3.4. Influence of pH

Acidity of solution always influences the polarity, hydrogen bonds and solubility, and then association state of polymers. For HPSA aqueous solution, pH has no significant influence on the emission intensity of pyrene at low concentration (<2 g/l) since there is no strong association for HPSA at this condition. In higher concentrations, however, the effect of pH is not negligible more. Fig. 6 shows the emission spectra at various pH in a HPSA concentration of 12.5 g/l. The intensity of monomer emission changes little, while that of excimer emission rapidly decreases with decreasing pH, which shows that the association of HPSA gets weaker with increasing acidity. At pH = 5.5, I_E/I_M is lower than that at pH = 8.5. This phenomenon may be caused by the partial deformation of

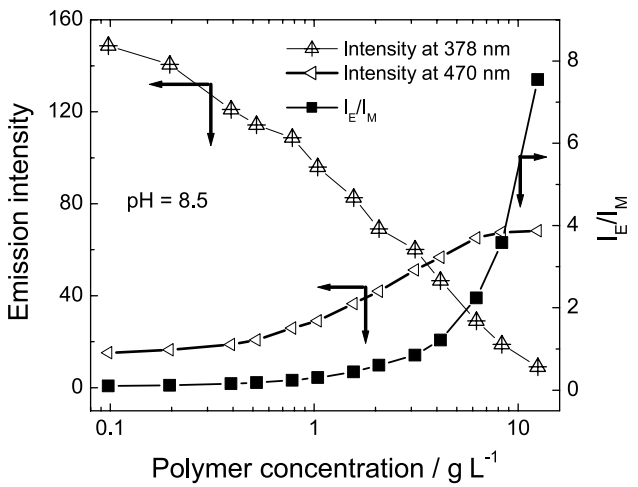


Fig. 4. Emission intensity and I_E/I_M of pyrene as a function of HPSA concentration at pH = 8.5.

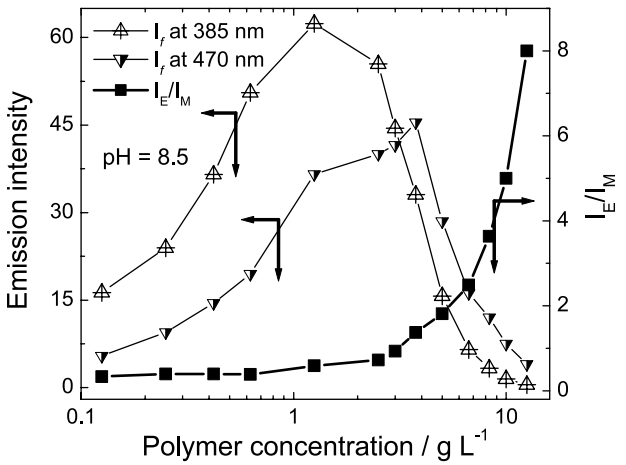


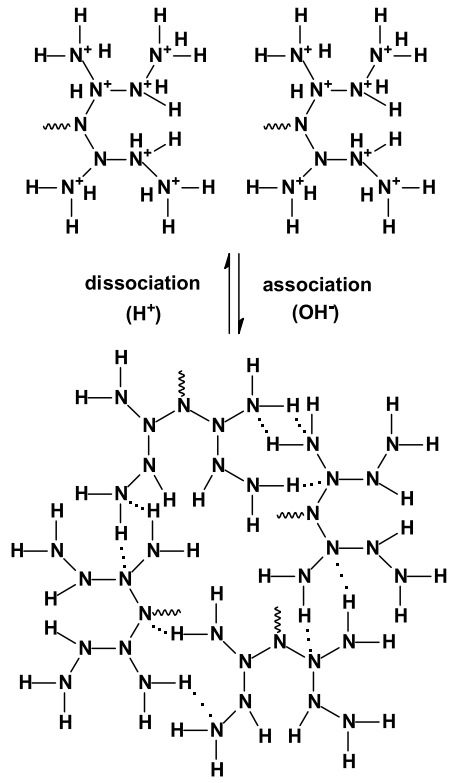
Fig. 5. Emission intensity and I_E/I_M of Py-HPSA as a function of Py-HPSA concentration at pH = 8.5.

hydrogen bonds among inter- or intra-molecules in the presence of acid (Scheme 2).

Potentiometric titration has been performed to investigate the protonation of the polymer electrolyte in the presence of acid. In the aqueous solution of HPSA, the hyperbranched poly(sulfone-amine) was in the state of deprotonation, and pH was higher than 7. So the corresponding potential was lower than zero. With decreasing the pH or increasing the acidity, the potential increased, and reached zero at about 7.3, and then got a positive value. Furthermore, the potential of the solution of HPSA was higher than that of pure acid without the polymer at the same pH. These data confirmed that the hyperbranched poly(sulfone-amine) was protonated in the presence of acid.

3.5. Influence of solvents

In the presence of organic solvents, the association behaviors of polymers in water solution may change [28]. Winnik and coworkers [17] reported that the emission of



Scheme 2. Schematic description for formation or deformation of hydrogen bonds among hyperbranched poly(sulfone-amine).

pyrene-labeled poly(ethylenimine) influenced by methanol. In our experiments, the influences of methanol and DMSO on the fluorescence were investigated. The influence of methanol on the emission is not considerable, while the influence of DMSO on the fluorescence is very strong. As seen in Fig. 7, the monomer emission of pyrene increases whereas excimer emission decreases with increasing volume fraction of DMSO, and excimer peak disappears at 72% of DMSO fraction. The results suggest that DMSO destroy the association microstructures of HPSA. In the

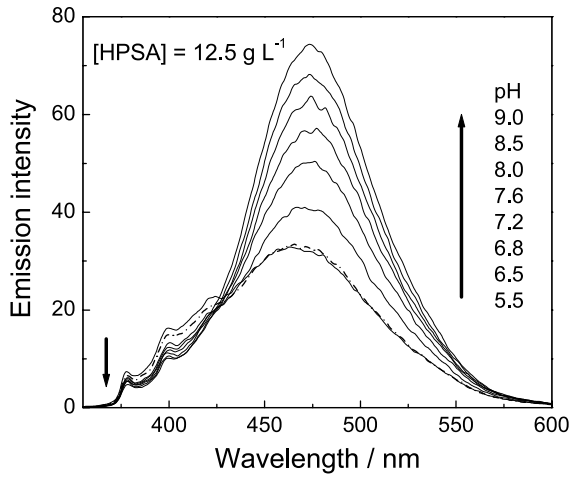


Fig. 6. Emission spectra of pyrene at HPSA concentration of 12.5 g/l with various pH.

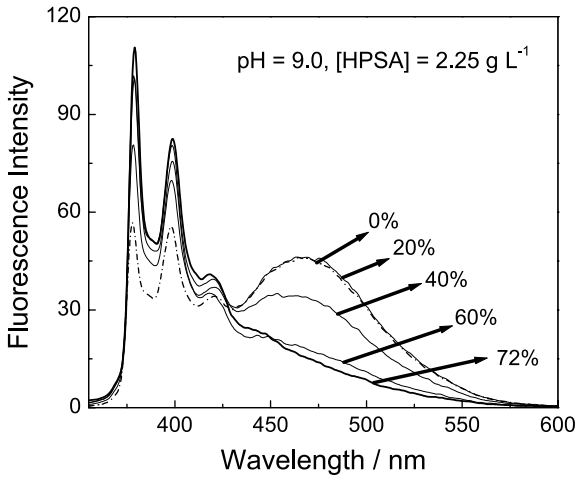


Fig. 7. Emission spectra of pyrene in HPSA solution with different fraction of DMSO.

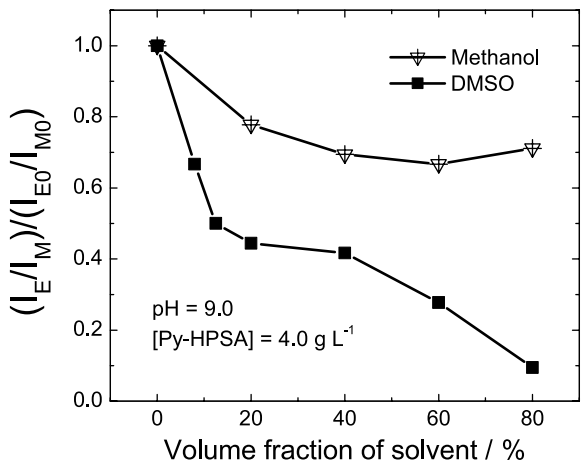


Fig. 8. Normalized ratio of excimer-to-monomer emission intensity (I_E/I_M) of Py-HPSA as a function of volume fraction of solvent.

existence of strong-polar organic solvent, the hydrogen bonds of HPSA are deformed, leading to disintegration of association structures.

Same phenomena are observed in the characterization of pyrene-labeled sample (Fig. 8). Comparing with the influence of methanol on the I_E/I_M of Py-HPSA, that of DMSO is much stronger.

4. Conclusions

The self-association behaviors of hyperbracnhed poly-(sulfone-amine) (HPSA) in water solutions were detected with pyrene-fluorescence probe and label techniques. Static excimer emission was observed in the measurements of fluorescence probe and label. When pyrene was a fluorescence probe, its monomer emission decreases whereas excimer emission increases with increasing the concentration of hyperbranched polymer, and its ratio of excimer-to-monomer emission intensity (I_E/I_M) gradually increases, approaches a critical concentration (CAC), and sharply increases with the concentration. Pyrene-labeled hyperbranched polymer (Py-HPSA) was obtained by reaction of 4-(1-Pyrene)butyroyl chloride with HPSA. The monomer emission and excimer emission of Py-HPSA get higher, and pass through a maximum point, then decrease with increasing the concentration of Py-HPSA, while I_E/I_M increases monotonously, reaches a critical point, and then significantly increases with increasing the concentration of Py-HPSA. No considerable association occurs below the critical concentration of the polymer. The characterizations of fluorescence probe and label showed that CAC for HPSA is 5–7 g/l. Acidity and strong-polar organic solvents such as DMSO can influence the association behaviors of HPSA in high concentrations. In a base condition, self-association of HPSA gets stronger. Comparing with DMSO, the influence of methanol on the association of HPSA is much weaker.

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