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Intrachain and Interchain Interactions in Polystyrene: Dilute and Semidilute Solutions

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Abstract: Excimer formation in pyrenyl labeled polystyrene has been investigated in dilute solution region. The change of the intensity ratio of excimer to monomer (I_e/I_m) with increasing concentration (C), is interpreted by intrachain and interchain interactions. The double logarithmic plot of I_e/I_m vs C displays two critical points, C_s at about 2.5×10^{-3}g/ml and C^+ at about 3.2×10^{-2} g/ml. In dilute region $C < C_s$, excimer formation may be controlled by intrachain interaction.

Key words: Excimer fluorescence, dilute solution, chain interaction, critical concentration.

The studies of polymer solution properties from dilute to concentrated solution by fluorescence technique have attracted more attentions in recent decades[1,2]. In order to investigate intrachain and interchain interactions in dilute solution region, pyrene was used as labels attached to polystyrene, which was intensely fluorescent with a long fluorescent lifetime[3]. In the present work, the polystyrene attached with pyrenyl groups had an unfavourable structure to the nearest neighbor excimer formation with the pyrenyl groups separated by more than three atoms along the chain[4,5]. It contains about 2 pyrenyl groups per 100 phenyl rings. The sample was considered to be more sensitive for probing intrachain and interchain interactions in dilute solution. In this report, we studied excimer formation of pyrenyl groups in dilute regime.

Experimental

Pyrenyl-labeled polystyrene was synthesized by copolymerization of styrene and *m/p*-(1-)pyrenylmethyleneoxymethylene-styrene initiated with AIBN at 60°C. The polymer was purified by reprecipitation till unreacted components had been removed. The content of pyrenyl groups attached to polystyrene chains is 2.02×10^{-4}mol/g determined by UV absorption. The average molecular weight of the polymer is 42000. Polystyrene solutions were prepared by weighing the polymer into 5ml, 10ml or 25ml volumetric flasks and diluting with toluene. Over 24 hours was allowed for dissolution.

The fluorescence spectra of pyrenyl labeled polystyrene solutions were collected with Hitachi F-3010 fluorescence spectrophotometer. A front-face fluorescence emission was measured from a thin illuminated layer solution with an excitation wavelength of

340 nm, slits set at 1.5 nm. All spectra (collected at least in triplicate) are uncorrected and normalized at 397 nm. I_e/I_m is the intensity ratio of excimer to monomer I_{480nm}/I_{397nm}. The excitation spectra were taken with emission wavelength set at 390nm, 470nm, slits set at 1.5nm. UV absorption was taken with Shimadzu UV-Vis Recording Spectrophotometer.

Results and Discussion

The typical fluorescence spectra of pyrene-labeled polystyrene solutions are shown in **Figure 1.** Typical normalized fluorescence sprctra of pyrenyl labeled polystyrene solutions with concentrations (a) 1.05×10^{-3} g/ml, (b) 0.048 g/ml, (c) 0.135 g/ml in toluene.

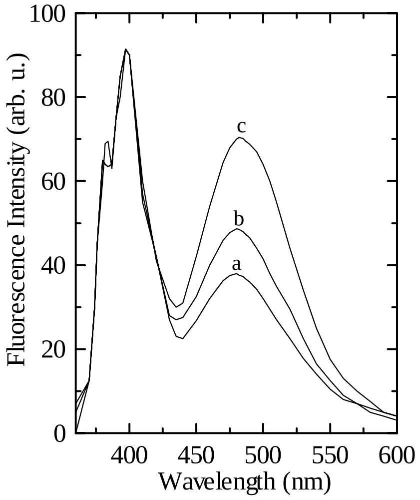


Figure 1. The emission centered at 397 nm is monomer emission of pyrenyl groups. The emission with a peak at 480nm is excimer emission from “face to face” pyrenyl groups at excited state. UV absorption of the polystyrene solution agrees with that of pyrene with a maximum at 345.5nm. The excitation spectra of monomer monitored at 390nm shows no shift from that of excimer emission at 470nm. The results show that the emission centered at 480nm can be attributed to dynamic excimer. It is reasonable to assume that the quantum efficiencies of excimer and monomer do not vary for the same polymer solution with different concentrations[6].

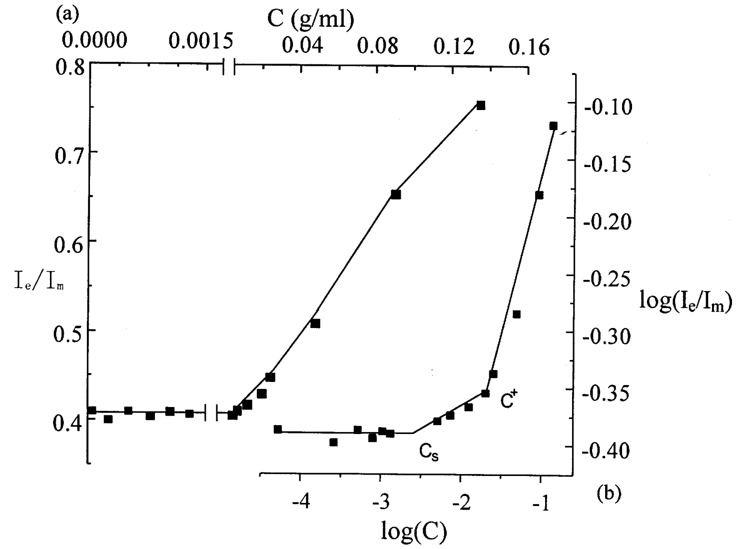
Figure 2(a) exhibits the polymer concentration (C) dependence of the intensity ratio of excimer to monomer (I_e/I_m). The double logarithmic plot is shown in **Figure 2(b)**. In the region $C < C_s$, I_e/I_m values are insensitive to modest changes in concentration. While $C_s < C < C^+$, a slight increase of I_e/I_m is revealed. However, I_e/I_m increase sharply in the region $C > C^+$.[8] Two critical concentration points named as C_s at about 2.5×10^{-3} g/ml and C^+ at about 3.2×10^{-2} g/ml can be obtained.

Excimer formation is widely considered to be a diffusion-controlled process[7]. The intensity ratio I_e/I_m is dependent on the concentration of pyrenyl groups ([Py]) and the microviscosity of the labels (η)[8]. Therefore, we can write for the intensity ratio by the following expression:

$$I_e/I_m = A[Py]/\eta \quad (1)$$

where, A is a constant that includes instrumental characteristics and factors that transform intensity of a single wavelength to integrated intensity. In pyrenyl-labeled polystyrene solution, excimer can be found in two ways:[9] (1) intrachain excimer formed by pyrenyl groups attached to the same polymer chain; (2) interchain excimer formed between two pyrenyl groups attached to different polystyrene chains. It is assumed that the intrachain and interchain excimer formation may be controlled by the concentration and the microviscosity of the labels.

Figure 2. I_e/I_m values as a function of polystyrene concentration (C) in toluene, a: I_e/I_m *vs* C; b: log (I_e/I_m) *vs* log(C). C_s at about 2.5×10^{-3} g/ml and C^+ at about 3.2×10^{-2} g/ml are critical concentrations.



In very dilute concentration range, polymer chains will be free coils in toluene[10,11]. In the region $C < C_s$, the repulsive forces between free flexible polymer coils may be negated. Thus, no interaction of polymer coils may take place upon addition of polymer. Intrachain excimer[9] is dependent on the microviscosity and the concentration of pyrenyl groups in the inner of free polymer coils. In this region, the microviscosity and the concentration of the labels in the coils may be constants. And I_e/I_m values are insensitive to changes in polymer concentration. The excimer formation is independent of the polymer concentration in very dilute polystyrene solution region. This demonstrates the nature of intrachain interaction in the excimer forming process. As polymer concentration increases in the region $C^+ > C > C_s$, I_e/I_m increases slowly. And a fractional power dependence of I_e/I_m on the C is obtained.

$$I_e/I_m \sim C^{\alpha}, \quad \alpha = 0.06 \quad (2)$$

The result may be interpreted with interchain interaction in the outside of polymer coils.

While polymer coils approach each other, interchain interaction in the outside of different polymer coils may induce the slight increase of I_e/I_m. So, the fractional power dependence may be interpreted as a manifestation of interchain interaction of polymer coils approaching each other in solution[12]. The critical point C_s may be regarded as the beginning of interchain interaction in polymer solution. In this region, we may assume that the local concentration of pyrenyl groups increases slowly and the microviscosity remains a constant as polymer concentration increases.

While concentration increases beyond C^+, polymer coils may overlap and interpenetrate each other[12]. Excimer formation may be mainly ascribed to interchain interaction. The local concentration of pyrenyl groups may increase linearly with polymer concentration. It is assumed that the microviscosity increase slowly, but the local concentration of labels increase sharply because of interpenetrating of polymer coils. The sharp increase of I_e/I_m may be attributed to the increase of local concentration of the labels. In this region, I_e/I_m is also a fractional power dependence on polymer concentration.

$$I_e/I_m \sim C^{\alpha}, \qquad \alpha = 0.37 \qquad (3)$$

The critical point C^+ may be regarded as the beginning of interpenetrating of polymer chains.

Conclusions

Excimer fluorescence of pyrenyl groups has been demonstrated to be useful for probing intrachain and interchain interactions in dilute solution region. The concentration dependence of the intensity ratio shows two sharp transitions of concentration values C_s and C^+ , which may be used to divide polymer solution into dilute, semidilute and concentrated solution regions. In very dilute solution region $C<C_s$, excimer formation is attributed to intrachain interaction. In semidilute region, the fractional power dependence of I_e/I_m on the C may be a manifestation of interchain interaction with increasing concentration. In the region $C>C^+$, the abrupt increase of I_e/I_m may reveal the interpenetrating of polymer chains.

Acknowledgments

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