

## Entanglement of Polymer Chains in Concentrated Region by Fluorescence Probe Technique

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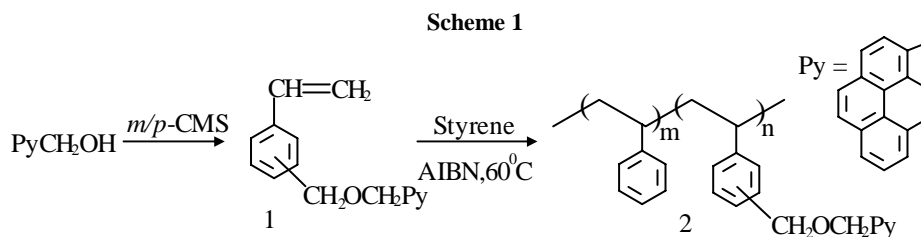
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**Abstract:** The fluorescence of polystyrene labeled with pyrenyl groups has been investigated in concentrated solutions. The ratio of excimer to monomer intensities ( $I_e/I_m$ ) of pyrenyl labels is found to vary with increasing polymer concentration ( $C$ ) and display fractional dependence on the  $C$ . A critical concentration,  $C_m$  at about 0.32g/ml, is first manifested. The results are interpreted by interchain interaction and entanglement of polymer chains.

**Keywords:** Fluorescence spectroscopy, entanglement, critical concentration.

Fluorescence probe technique has been used to study conformational properties as well as dynamics and morphology in polymer systems in the past decades<sup>1</sup>. The ratio of excimer to monomer intensities is most often used to characterize the fluorescence properties of polymer. Qian *et al.*<sup>2</sup> demonstrated by excimer formation of phenyl groups that the polymer concentration was ranged by two critical concentrations of  $C_s$  and  $C^+$ . It is shown that the ratio of excimer to monomer intensities merely increases linearly with concentration in concentrated region. Since excimer formation is a diffusion-controlled encounter process<sup>3</sup>, entanglement of polymer chains may play an important role on excimer formation in concentrated region. In the present work, we studied the excimer formation with a styrene copolymer containing pendant pyrenyl groups (**Scheme 1, 2**) in concentrated region. This polymer is considered to be sensitive for probing interchain interaction and entanglement of polymer chains.



### Experimental

*m/p*-(1-) Pyrenylmethylenoxymethylene-styrene (**Scheme 1, 1**) was synthesized from (1-) pyrenylmethanol with *m/p*-chloromethyl styrene (*m/p*-CMS) in the presence of

NaH in dry DMF, and purified by silica gel column chromatography. The characterization was performed by  $^1\text{H}$ NMR, FT-IR and Elemental Analysis<sup>4</sup>.

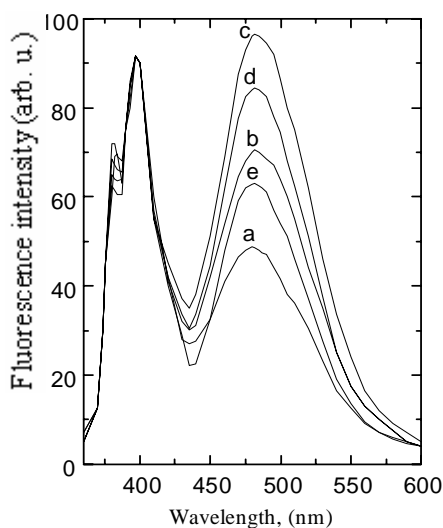
Pyrene-labeled polystyrene (**Scheme 1, 2**) was synthesized by copolymerization of styrene and **1** initiated with AIBN at 60°C. The polymer was purified by multiple reprecipitation until all unreacted components had been removed. The content of pyrenyl groups attached to polystyrene chains is  $2.02 \times 10^{-4}$  mol/g determined by UV absorption. The average molecular weight of the polymer is 42000 with molecular weight distribution index of 2.7. The characterization of pyrenyl labeled polymer and preparation of polymer solutions and films for fluorescence measurements were described in detail in our previous work<sup>4</sup>.

Fluorescence spectra were collected with a Hitachi F-3010 fluorescence spectrophotometer. The emission spectra were measured at 90 (degrees) to the excitation light beam (30 degrees to the axis of quartz cell) (front-face geometry) from a thin layer of illuminated concentrated solution close to the wall of the solution cell with an excitation wavelength of 340 nm, slits set at 1.5 nm. The spectra were normalized at 397 nm. All spectra (collected at least in triplicates) were uncorrected.  $I_e/I_m$  is the intensity ratio of excimer to monomer of  $I_{480\text{nm}}$  to  $I_{397\text{nm}}$ <sup>4</sup>.

## Results and Discussion

**Figure 1** exhibits the fluorescence spectra of pyrene-labeled polystyrene solutions at different concentrations. The spectra are normalized at 397 nm, the center of monomer emission of pyrenyl groups<sup>4</sup>. The excimer emission centered at 480 nm is different with various concentrations of polymer solutions. The ratio of excimer emission intensity ( $I_e$ ) to monomer emission intensity ( $I_m$ ) is dependent on the polymer concentration ( $C$ ), as

**Figure 1.** Typical normalized fluorescence spectra of pyrenyl labeled polystyrene solution in toluene with polymer concentrations of (a) 0.048 g/ml, (b) 0.135 g/ml, (c) 0.312 g/ml, (d) 0.325 g/ml, (e) 0.403 g/ml.



shown in **Figure 2**. The double logarithmic plot is also shown in **Figure 2**. A critical concentration of  $C_m$  *ca.* 0.32 g/ml is first manifested by means of fluorescence spectroscopy. With increasing concentration in the region of  $C < C_m$ ,  $I_e/I_m$  increases quickly. Then,  $I_e/I_m$  decreases sharply after  $C_m$  is reached. And a double linear logarithmic plot of  $I_e/I_m$  and  $C$  is obtained.

In pyrene labeled polystyrene concentrated solution, excimer can be found by intramolecular and intermolecular interactions, which is dependent on the concentration. As the  $C$  increases before  $C_m$  is reached, polymer chains interpenetrate each other, and the density of polymer segments will be a uniform distribution, which is proportional to the  $C$ . Pyrenyl groups approach each other to form intermolecular excimer configuration. So, the excimer formation can be mainly attributed to intermolecular interaction. In this region,  $I_e/I_m$  is a fractional power dependence on the  $C$  shown as follows:

$$I_e/I_m \propto C^\epsilon, \quad \epsilon = 0.37 \quad C < C_m$$

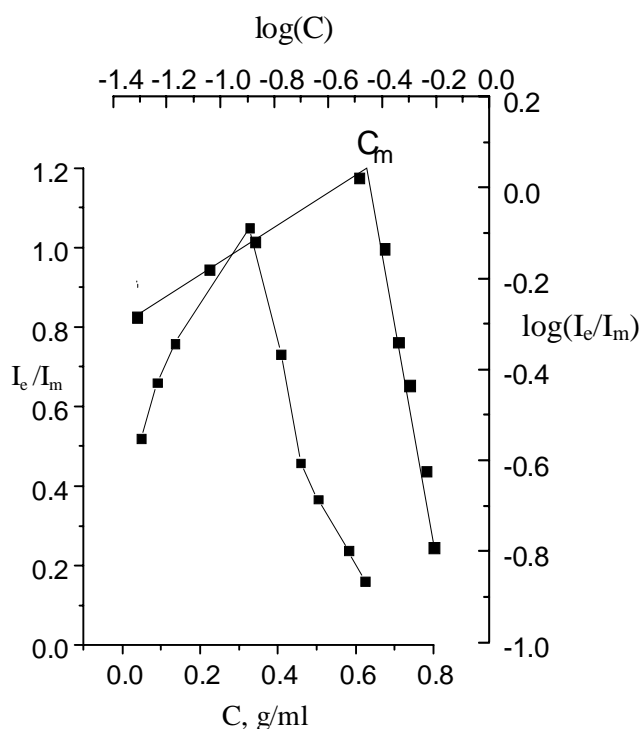
Surprisingly,  $I_e/I_m$  decreases sharply after  $C_m$ , and a fractional power dependence on concentration with a negative power is shown in **Figure 2** in the region of  $C > C_m$ .

$$I_e/I_m \propto C^\epsilon, \quad \epsilon = -3.73 \quad (1)$$

As a consideration of excimer formation controlled by diffusion,  $I_e/I_m$  is dependent on the concentration of pyrenyl groups ( $[M]$ ), which can be correlated to the kinetic excimer formation through the expression<sup>5</sup>

$$I_e/I_m = A[M]^\eta \quad (2)$$

**Figure 2.** Dependence of intensity ratio of  $I_e/I_m$  on the polymer concentration,  $I_e/I_m$ - $C$  (down) ;  $\log(I_e/I_m)$  - $\log(C)$  (up) .



where  $\eta$  is microviscosity around the label of pyrenyl groups, A is a constant. The microviscosity plays an important role in the excimer formation of pyrenyl groups, which may be related to the motion of polymer segments. In concentrated region of  $C < C_m$ , the motion of polymer segments is relatively free. The excimer formation will be controlled by the concentration of pyrenyl groups and interchain interaction in polymer solution. While  $C > C_m$  the entanglement of polymer chains will control the motion of polymer segments<sup>6</sup>, and pyrenyl groups attached to polymer chains will be difficult to approach each other to form excimer. As C increases after  $C_m$ , the microviscosity mainly controlled by motion of polymer segments will be increased sharply, which induces a sharp decrease of  $I_e/I_m$ . So, the abrupt decrease of  $I_e/I_m$  can be attributed to entanglement of polymer segments. Since the local concentration of pyrene labels ([M]) is proportional to the C, the following formula is obtained from formula 1 and 2.

$$\eta \propto C^{4.73}, \quad C > C_m$$

Therefore, we may define the region of  $C > C_m$  as super-concentrated polymer solution with a characteristic of entanglement of polymer segments.

### Conclusions

Excimer fluorescence of pyrenyl groups is demonstrated to be useful for probing interchain interaction and entanglement of polymer chains in concentrated solution region. A sharp transition of concentration value of  $C_m$  is first obtained. The critical point may be regarded as the beginning of entanglement of polymer chains in super-concentrated solution region.

### Acknowledgments

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