

Note

ON SELF-ABSORPTION CORRECTION IN EXCIMER FLUORESCENCE MEASUREMENTS OF POLYMER SOLUTIONS*

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Abstract The effect of self absorption on the ratio of excimer to monochromophore emission intensities, I_e/I_m , has been explored by experimentally changing the solution layer thickness of the emission light path traversed in the solution in the right-angle geometry. The result shows that data obtained by front-face geometry are better than those obtained by right-angle geometry even after correction to zero solution thickness. The correction formula based on geometric optics given by Tsai and Torkelson is not adequate.

Keywords Excimer fluorescence, Self absorption, Polystyrene solution

Excimer fluorescence of aromatic chromophore containing polymers, for example polystyrene (PS), has been studied for decades. A fractional power dependence of the ratio of excimer fluorescence intensity to monochromophore fluorescence intensity, I_e/I_m , on the solution concentration C was found^[1] for $C \geq C_s$, where C_s is the dynamic contact concentration, below which I_e/I_m is constant independent of the solution concentration. This fractional power dependence of I_e/I_m on solution concentration has been termed a polymer effect of excimer emission^[2] as it is unique for chromophore containing flexible chain polymers in solution. Tsai and Torkelson^[3], however, disputed this polymer effect and attributed the effect to self absorption of the fluorescence emission by the solution. They used a correction formula for self absorption of the emission in solution based on geometrical optics. In view of the importance of self absorption in the excimer fluorescence of PS solutions, a detailed study of the experimental correction for self absorption has been carried out to examine the validity of the Tsai and Torkelson's correction formula. The method is based on the effect of changing the solution layer thickness traversed by the emission light beam and extrapolating the values of I_e/I_m to zero solution thickness. On examining their published Figs. 4 and 5^[3] one finds that the unnormalized values of I_e/I_m are so high that $I_e/I_m \geq 8$, which is not in accord with the values published so far in the literature, including the Refs. [1] and [2] cited in their paper. Maybe this was the reason that they tabulated their values of I_e/I_m all normalized to the value at infinite dilution, which is apparently greater than 8. When their conclusion that self absorption correction is important, for $C > 2$ g/dL in front-face geometry and for $C > 0.3$ g/dL in right-angle geometry regardless of molar mass and solvent, is applied to our previously published experimental results of PS in good solvent, dichloroethane^[4], and in θ -solvent, cyclohexane at 35.4°C^[2], except for solutions of low molar mass PS samples, the polymer effect of I_e/I_m was observed in all concentrations lower than 2 g/dL using the front-face geometry, so that self absorption correction should be unimportant. Even the Fig. 4 of Tsai and Torkelson's paper^[3] indicates a fractional power dependence of I_e/I_m (corrected, unnormalized) on C for the PS sample of molar mass 4000. Thus

* This work was supported by the National Key Projects for Fundamental Research, "Macromolecular Condensed State", of Ministry of Science and Technology, China.

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Received March 17, 2000

their view of the polymer effect of excimer emission being an artifact could not be considered as valid.

EXPERIMENTAL

The anionic polystyrene (PS) sample, $M_w = 3.65 \times 10^5$, $M_w/M_n = 1.07$ by size exclusion chromatography, used in this work was supplied by Nanjing University. The sample has an intrinsic viscosity $[\eta] = 1.048$ dL/g in CH_2Cl_2 at 25.0°C . Spectrophotometric grade 1,2-dichloromethane (E. Merck) and cyclohexane (Acros) were used without further purification. Solutions were prepared by weighing the PS sample into 5 mL volumetric flasks and the solvent was poured in. The dissolution was complete in 48h and the solution volume was adjusted. The solutions in cyclohexane were kept at 35°C .

Fluorescence spectra were recorded by a Hitachi F-4500 fluorescence spectrophotometer using $\lambda = 260$ nm excitation with both the excitation and emission slits set at 5 nm. All measurements were made with a 10×10 mm square solution cell, kept at $25 \pm 1^\circ\text{C}$ for PS solutions in 1,2-dichloromethane and at $35 \pm 0.5^\circ\text{C}$ for PS solutions in cyclohexane. Fluorescence emission was observed by front-face geometry at 30° to the excitation beam direction and by right-angle geometry. The effect of self absorption was studied for the right-angle geometry by moving the cell centre relative to the excitation light beam incident into the cell, so that the emission beam traversed different solution layer thicknesses. The cell was placed on a movable carriage with micro-screw adjustment and a scale reading to 0.1 mm as shown in Fig. 1. The cell was started at a position so that the excitation beam entered at the center of the cell, and then at 1, 2 and 4 mm from the cell centre, and the fluorescence emission was recorded at each position of the cell. This means that the emission beam traversed a solution layer thickness of 5, 4, 3 and 1 mm, respectively.

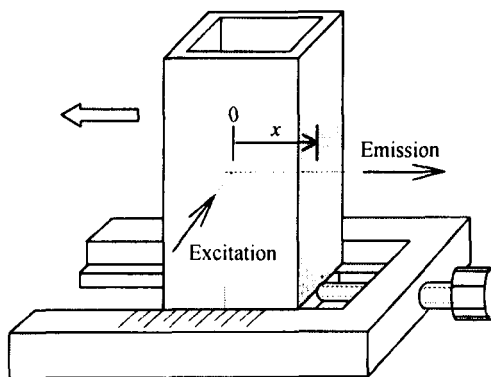


Fig. 1 The carriage for the solution cell for fluorescence measurement

RESULTS AND DISCUSSION

The effect of self absorption on the fluorescence spectra observed for a PS solution is to decrease the monochromophore fluorescence emission intensity at $\lambda = 285$ nm due to absorption by polystyrene (peaked at $\lambda = 264, 270$ nm) in the solution layer before the emitted light beam exits from the cell, while the excimer fluorescence emission intensity (peaked at $\lambda = 330$ nm) is little affected because the emission peak is some 60 nm apart from the absorption peak. The fluorescence spectra of the PS sample solution at $C = 5.2$ g/dL in 1,2-dichloromethane (DCM) on varying the solution layer thicknesses traversed by the emission light beam are illustrated in Fig. 2, where the curves are normalized to the same excimer emission intensity at $\lambda = 330$ nm. From this figure, the values of I_e/I_m could be extrapolated to zero solution layer thickness to get the corrected value of I_e/I_m . Linear plots of I_e/I_m versus solution layer thickness ($5 - x$) mm traversed by the emission light beam are used for the extrapolation as a first approximation, as shown in Figs. 3a, 3b for PS solution in DCM at 25°C and in cyclohexane (CH) at 35°C respectively.

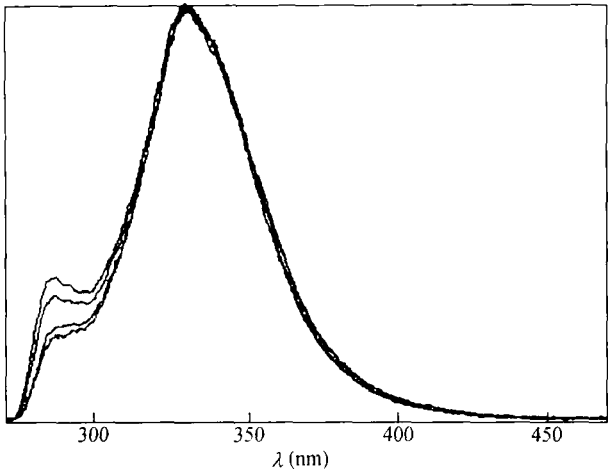


Fig. 2 Fluorescence spectra of PS solutions in DCM normalized for the emission intensity at $\lambda = 330$ nm
Solution concentration 5.18 g/dL; distance traversed by the emission beam in the solution cell, $(5 - x) = 1, 2, 4, 5$ mm for the curves from top to bottom

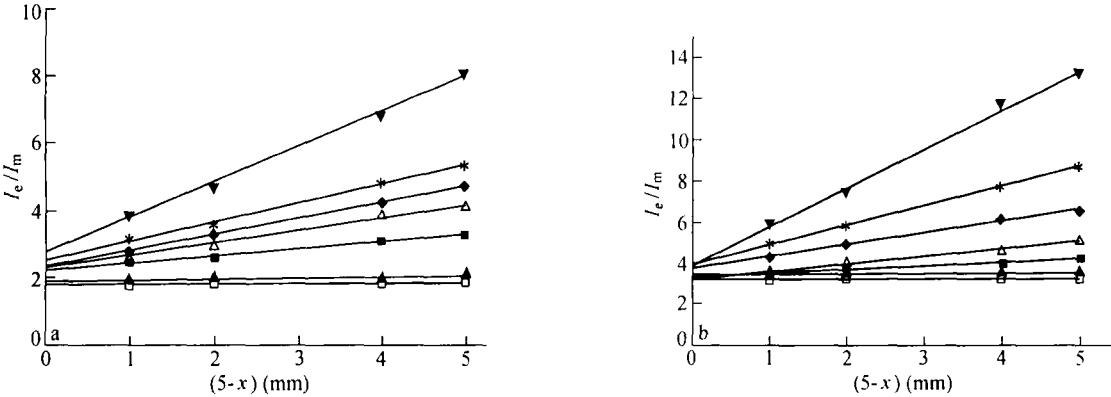


Fig. 3 Plot of I_e/I_m versus $(5 - x)$ for PS in (a) DCM at 25°C and (b) CH at 35°C
Solution concentrations from top to bottom: (a) 7.8, 6.0, 5.4, 4.4, 3.1, 7.8×10^{-2} , 5.4×10^{-4} g/dL; (b) 4.5, 2.6, 2.0, 1.0, 0.49, 0.13, 1.3×10^{-2} , 3.8×10^{-2} g/dL

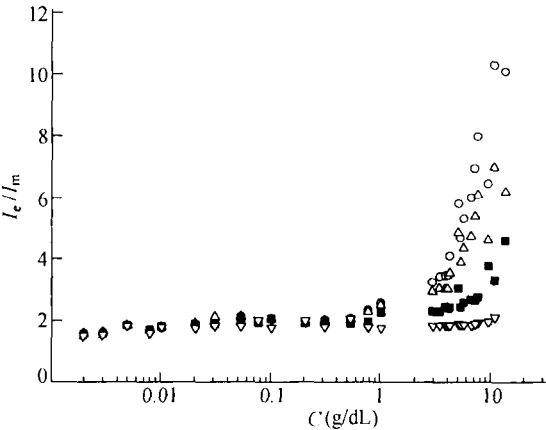


Fig. 4 Comparison of I_e/I_m versus $\lg C$ plots for (○) uncorrected values, (△) values corrected by Tsai and Torkelson's formula, (■) values corrected by extrapolation and (▽) values from surface refraction

The experimental data of uncorrected I_e/I_m , those corrected for self absorption according to the formula given by Tsai and Torkelson^[3], and the values extrapolated to zero solution layer thickness from measurements using the right-angle geometry for PS solutions in DCM are compared in Fig. 4, together with the experimental data obtained by front-face geometry. It is seen that the data from front-face geometry give the lowest values of I_e/I_m , and the extrapolated values are close to those obtained by front-face geometry for $C < 1$ g/dL; for solutions of higher concentrations the extrapolated values are still not adequately corrected for self absorption. The I_e/I_m values corrected by Tsai and Torkelson's formula are far from adequately corrected. From Fig. 4 it is safe to conclude that for $C < 0.1$ g/dL the self absorption correction for the data from right angle geometry can be neglected. Data obtained from front-face geometry do give correct values of I_e/I_m . Consequently the present authors still maintain the opinion that the polymer effect of excimer emission of polymer solutions is a physical reality, not an experimental artifact.

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