The concentration dependence of excimer fluorescence in polystyrene solutions

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The fluorescence of high- and low-molecular-weight polystyrene in a variety of solvent conditions has been measured as a function of polymer concentration up to $650\,\mathrm{g\,l^{-1}}$. Measurements made using both a right-angle emission geometry and a front-face emission geometry confirm that self-absorption of fluorescence, particularly monomer fluorescence, leads to measurement of the ratio of excimer to monomer fluorescence intensities, I_E/I_M, which overstates its true value at all but very low concentrations. When corrections are made for self-absorption effects, I_E/I_M is essentially constant at low concentrations and increases only very slowly and smoothly at higher concentrations. Contrary to previous reports, no transition from a fractional power dependence to a linear dependence on concentration for I_E/I_M has been observed at low polystyrene molecular weight.

(Keywords: polystyrene; excimer fluorescence; concentration dependence; solution)

INTRODUCTION

Fluorescence spectroscopy has been used as a tool to study intramolecular and intermolecular interactions as well as conformational properties of polymers in solution for several decades. A topic of major interest during this time has been the study of photophysical properties of vinyl aromatic polymers such as polystyrene[1-10] for which two types of emission are observed: a low-wavelength emission due to fluorescence from a single chromophore, the phenyl group in the case of polystyrene, known as monomer fluorescence; and a high-wavelength emission due to fluorescence from an excited-state complex of two chromophores, known as excimer fluorescence. The ratio of excimer to monomer fluorescence intensities, I_E/I_M, is the quantity most often used to characterize the fluorescence properties of vinyl aromatic polymers such as polystyrene.

While most polymer fluorescence studies are done in the dilute state, there has been increasing interest in applying these techniques to study polymers at high concentrations. This interest has led to some controversy concerning the concentration dependence of the fluorescence of polystyrene in solution. The earliest reported concentration study was by Vala *et al.*[1] in 1965 who reported that I_E/I_M was insensitive to concentration in very dilute polystyrene solutions. In 1969, Nishihara and Kaneko[2] found, in contrast to the conclusions by Vala *et al.*[1], that I_E/I_M increased linearly with concentration even in very dilute solutions. In 1979, Roots and Nyström[4] reported on the concentration dependence of several molecular weights of polystyrene and concluded that excimer fluorescence was able to determine the critical concentration c^* for the transition from dilute to semidilute solutions. However, in dilute solution they found little dependence of I_E/I_M on concentration in contrast to the results of Nishihara and Kaneko[2]. In 1983, Torkelson *et al.*[6] reported in a study of several molecular weights of polystyrene in both good and poor solvents that, when self-absorption of monomer fluorescence is taken into account, I_E/I_M is essentially constant at low concentrations and at most increases only very slowly at higher concentration. Furthermore, they concluded in contrast to the study by Roots and Nyström[4] that fluorescence spectroscopy does not reveal an abrupt transition at c^*. In 1986, Renyuan and Cao[7], who studied the concentration dependence of polystyrene fluorescence without accounting for self-absorption effects, reported that I_E/I_M starts from a constant value at low concentrations and then increases as a fractional power of polymer concentration both in good and θ-solvents. Furthermore, they reportedly found a significant difference in the concentration dependence of low-molecular-weight polystyrene (2000 MW and below) and higher-molecular-weight polystyrene (4000 MW and above).

In the present work, our purpose is to demonstrate convincingly that, in order to determine correctly the absolute value of I_E/I_M or the trend of I_E/I_M with concentration for vinyl aromatic polymers such as polystyrene in solution, it is necessary to make self-absorption corrections to the fluorescence intensities measured at any concentration except very dilute. This is true even when a front-face fluorescence geometry is employed, for although the use of a front-face geometry reduces self-absorption effects in comparison to the use of other geometries, it does not eliminate self-absorption effects. While previous work by one of us[6] was reported for only one emission geometry, we are reporting in this study results from two different fluorescence geometries, a right-angle geometry and a front-face geometry, which are distinct from the geometry employed in the previous study. Results are given for solutions of polystyrene ranging from 800 MW to 1.8×10^6 MW in several solvents to prove that the self-absorption effects are important regardless of the polymer molecular weight or solvent.

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CORRECTIONS FOR SELF-ABSORPTION IN RIGHT-ANGLE AND FRONT-FACE GEOMETRIES

Since the fluorescence is radially dispersed at some non-zero depth in the polymer solution both in right-angle and front-face geometries, it must pass some non-zero distance through the solution on its way to the emission detector. As a result, the fluorescence undergoes absorption by the solution which is a function of the wavelength of fluorescence, the concentration of the solution, and the optical design of the instrument, e.g. front-face *versus* right-angle emission geometries.

In this study, values of I_E/I_M measured with two different emission geometries, right-angle and front-face, were corrected for self-absorption effects. The right-angle emission geometry is shown in *Figure 1* where w represents the excitation slit width (2.5 mm in this study) and l represents the light path of the cuvette (10 mm). Thus, $x_1=(l-w)/2=3.75$ mm and $x_2=(l+w)/2=6.25$ mm. From Beer's law, the corrected intensity, $I_{\mathrm{corr}}(\lambda)$, and the detected intensity, $I_{\mathrm{det}}(\lambda)$, are related by:

$$I_{\mathrm{det}}(\lambda)=I_{\mathrm{corr}}(\lambda)\times 10^{-\varepsilon_\lambda c x} \qquad (1)$$

where ε_λ are the decadic absorptivities of the polymer at a given wavelength λ, c is the mass concentration, $I_{\mathrm{det}}(\lambda)$ and $I_{\mathrm{corr}}(\lambda)$ are measured and corrected fluorescence intensities, respectively, and x is the distance the fluorescence travels through the sample. Thus, the corrected I_E/I_M is given by:

$$\frac{I_{\mathrm{E\,corr}}}{I_{\mathrm{M\,corr}}}=\left(\frac{I_{\mathrm{E\,det}}}{I_{\mathrm{M\,det}}}\right)\frac{\int_{x_2}^{x_1}10^{\varepsilon_E c x}\,\mathrm{d}x}{\int_{x_2}^{x_1}10^{\varepsilon_M c x}\,\mathrm{d}x} \qquad (2)$$

The front-face geometry is shown in *Figure 2* where x is the penetration depth of the incident light and α is the angle of reflection (22.5°). The value of x depends on the optical design of the instrument. In our study, we have assumed that $x=1.0$ mm, and we have obtained very consistent results in our corrected, normalized values of I_E/I_M using this value of penetration depth. The corrected I_E/I_M is given to excellent approximation by:

$$\frac{I_{\mathrm{E\,corr}}}{I_{\mathrm{M\,corr}}}=\left(\frac{I_{\mathrm{E\,det}}}{I_{\mathrm{M\,det}}}\right)10^{(\varepsilon_E-\varepsilon_M)cx/\cos\alpha} \qquad (3)$$

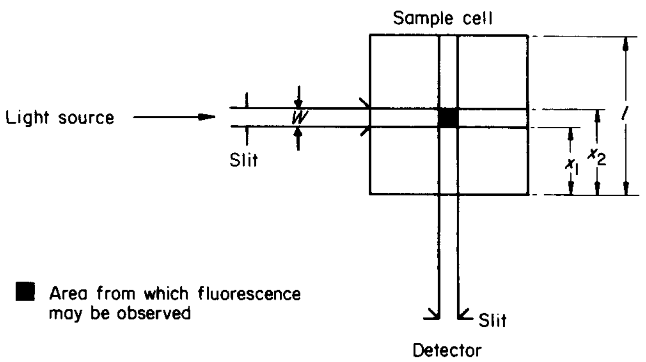

Figure 1 Right-angle emission geometry

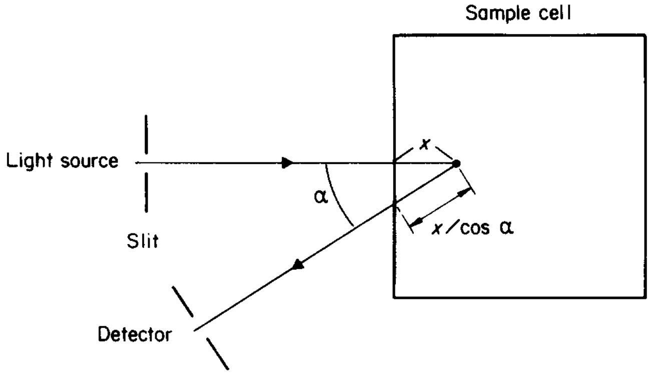

Figure 2 Front-face emission geometry

EXPERIMENTAL

The polymer samples were standard polystyrenes (PS) of narrow molecular weight distribution (Pressure Chemical Co.)with molecular weights of 800, 2000, 4000, 670 000 and 1800 000. Spectrophotometric quality cyclohexane and 1,2-dichloromethane from Aldrich were used without further purification.

Solutions were prepared by weighing polymer into either 5, 10, or 25 ml volumetric flasks or cuvettes directly in the case of very high concentrations and diluting with solvent. Over 24 h was allowed for dissolution. With samples of high concentration, a magnetic stirrer and gentle heating were employed to facilitate dissolution.

Decadic absorptivities of the polymers, obtained in digital readout, were measured with an IBM 9410 UV/Visible spectrophotometer. Fluorescence spectra were measured with a SPEX fluorescence spectrophotometer. Fluorescence emission was measured both at 90° to the excitation light beam (right-angle geometry) and 22.5° to the excitation light beam (front-face geometry) for each sample. Slit widths for the excitation and emission beams were 2.5 mm and 5 mm, respectively, for right-angle geometry, and 1.25 mm and 5 mm, respectively, for front-face geometry. All sample measurements were made using a 1 cm path length Suprasil cuvette and excitation light with a wavelength of 253.7 nm. The excimer emission was monitored at 335 nm; the monomer emission was monitored at three wavelengths: 286, 283 and 280 nm. All samples were air-equilibrated. Spectra were measured at 27 ± 1°C, and in the case of 800 and 670 000 MW samples at 50 ± 1°C.

RESULTS AND DISCUSSION

Figure 3 and *Table 1* present the uncorrected and corrected (for self-absorption effects) values of I_E/I_M for 2000 MW PS in a good solvent, dichloromethane, at room temperature, normalized to values at infinite dilution. *Figure 3* gives uncorrected and corrected normalized values of I_E/I_M for the right-angle geometry only while *Table 1* gives uncorrected and corrected results for both the right-angle and front-face geometries. It is clear that, while self-absorption is greater for the right-angle geometry and is most important when monomer emission is measured at low wavelengths, even in a front-face geometry corrections for self-absorption must be made at polystyrene concentrations exceeding $20\,\mathrm{g\,l^{-1}}$. Failure to make such corrections will result in significant overestimation in the absolute values of I_E/I_M and in the concentration dependence of I_E/I_M.

The corrected values of normalized I_E/I_M shown in *Figure 3* and *Table 1* are in excellent agreement with each other for a given concentration regardless of the monomer emission wavelength or sample geometry employed in making the measurement. For example, at 95.0 g l^{-1}, the average value of normalized I_E/I_M is 1.21 with no value less than 1.19 or greater than 1.23. This excellent agreement is even more striking given that such large corrections in normalized I_E/I_M values, e.g. from 5.20 to 1.23, were made using equations (1) and (2). The excellent agreement obtained in corrected values supports the use of the corrections given by equations (1) and (2).

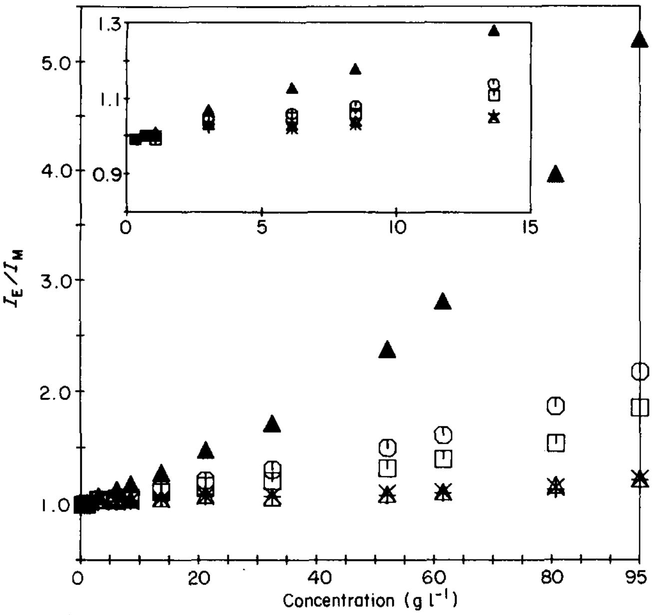

Figure 3 I_E/I_M values as a function of PS concentration for 2000 MW PS in dichloromethane measured in right-angle geometry: (□) I_{335}/I_{286}; (○) I_{335}/I_{283}; (▲) I_{335}/I_{280}; (+) corrected I_{335}/I_{286}; (×) corrected I_{335}/I_{283}; (△) corrected I_{335}/I_{280}. I_E/I_M is normalized to unity at $c=0$. Insert is low-concentration data

Similarly excellent agreement in corrected values of normalized I_E/I_M at a given concentration were obtained for all other molecular weight–solvent combinations used in this study: 4000 MW PS in dichloromethane, 1800000 MW PS in dichloromethane, 800 MW PS in cyclohexane, 800 MW PS in cyclohexane at 50°C, and 670000 MW PS in cyclohexane at 50°C. *Tables 2* and *3* present uncorrected and corrected results for both right-angle and front-face geometries for 1800000 MW PS in dichloromethane and 800 MW PS in cyclohexane. Regardless of molecular weight or solvent, corrections for front-face geometry measurements are seen to be important when the polystyrene concentration exceeds 20 g l^{-1}; in a right-angle geometry such corrections are important when polystyrene concentration exceeds 2 or 3 g l^{-1}. It is striking in *Table 3* that even at 168 g l^{-1}, corrected values of normalized I_E/I_M are in excellent agreement even though some of the corrections were massive, e.g. from 16.19 to 1.35. At concentrations exceeding 168 g l^{-1}, it was not possible to obtain a precise reading of uncorrected I_E/I_M in right-angle geometry with a monomer emission wavelength of 280 nm as the observed monomer emission was so small. Thus, the only values reported above that concentration were measured using the front-face geometry. With front-face geometry measurements, corrected values of normalized I_E/I_M are observed to be in excellent agreement regardless of monomer emission wavelength chosen even up to 646 g l^{-1} polystyrene concentration.

In the study reported by Renyan and Cao[7], results of I_E/I_M uncorrected for self-absorption were reported for both low MW (740, 1370, 1730 and 4200) and high MW (6.09×10^6) PS as a function of polystyrene concentration. Emission measurements were made either

Table 1 Normalized I_E/I_M of 2000 MW polystyrene in dichloromethane uncorrected and corrected for absorbance

Conc. (g l^{-1})	Geometry[a]	Uncorrected I_{335}/I_{286}	Uncorrected I_{335}/I_{283}	Uncorrected I_{335}/I_{280}	Corrected I_{335}/I_{286}	Corrected I_{335}/I_{283}	Corrected I_{335}/I_{280}
0.34	FF	1.00	1.00	1.00	1.00	1.00	1.00
	RA	0.99	0.99	0.99	0.99	0.99	0.99
0.72	FF	1.00	1.00	1.00	1.00	1.00	1.00
	RA	1.00	1.00	1.00	1.00	1.00	1.00
1.08	FF	0.99	0.99	1.00	0.99	0.99	1.00
	RA	0.99	1.00	1.01	0.99	1.00	1.00
3.02	FF	1.00	1.01	1.02	1.00	1.01	1.01
	RA	1.04	1.04	1.07	1.02	1.03	1.03
6.12	FF	1.02	1.02	1.03	1.01	1.02	1.01
	RA	1.05	1.06	1.13	1.02	1.02	1.03
8.48	FF	1.03	1.04	1.06	1.02	1.03	1.03
	RA	1.06	1.08	1.18	1.03	1.03	1.04
13.62	FF	1.06	1.08	1.11	1.05	1.06	1.06
	RA	1.11	1.14	1.28	1.06	1.05	1.05
21.14	FF	1.08	1.09	1.14	1.06	1.06	1.07
	RA	1.16	1.21	1.48	1.07	1.07	1.08
32.50	FF	1.10	1.13	1.20	1.08	1.08	1.08
	RA	1.21	1.31	1.72	1.07	1.08	1.06
52.00	FF	1.14	1.16	1.25	1.09	1.08	1.06
	RA	1.32	1.50	2.38	1.08	1.10	1.09
61.52	FF	1.15	1.18	1.31	1.09	1.09	1.08
	RA	1.40	1.61	2.81	1.10	1.11	1.11
80.66	FF	1.22	1.29	1.52	1.14	1.16	1.17
	RA	1.54	1.87	3.97	1.13	1.15	1.17
94.98	FF	1.29	1.36	1.66	1.19	1.20	1.22
	RA	1.86	2.18	5.20	1.22	1.23	1.23

[a] Front-face (FF) and right-angle (RA)

Table 2 Normalized I_E/I_M of 1800000 MW polystyrene in dichloromethane uncorrected and corrected for absorbance

Conc. (g l^{-1})	Geometry	Uncorrected			Corrected		
		I_{335}/I_{286}	I_{335}/I_{283}	I_{335}/I_{280}	I_{335}/I_{286}	I_{335}/I_{283}	I_{335}/I_{280}
0.39	FF	0.99	0.99	0.99	0.99	0.99	0.99
	RA	1.00	0.99	0.99	1.00	0.99	0.99
0.49	FF	1.00	1.00	1.00	1.00	1.00	1.00
	RA	1.00	1.00	1.00	1.00	1.00	1.00
0.73	FF	1.00	1.00	1.00	1.00	1.00	1.00
	RA	1.00	1.00	1.02	1.00	1.00	1.01
1.00	FF	1.00	1.01	0.99	1.00	1.00	0.98
	RA	1.02	1.02	1.03	1.01	1.01	1.01
2.01	FF	1.01	1.01	1.01	1.00	1.00	1.00
	RA	1.03	1.03	1.04	1.02	1.02	1.01
3.02	FF	1.02	0.99	1.02	1.01	0.99	1.01
	RA	1.03	1.04	1.06	1.01	1.01	1.01
5.00	FF	1.03	1.00	1.01	1.02	0.99	0.99
	RA	1.04	1.06	1.10	1.02	1.03	1.02
6.98	FF	1.02	1.01	1.03	1.01	1.00	1.00
	RA	1.06	1.06	1.14	1.03	1.02	1.03
10.07	FF	1.02	1.04	1.07	1.01	1.02	1.03
	RA	1.06	1.08	1.20	1.02	1.02	1.04
16.60	FF	1.09	1.11	1.14	1.07	1.08	1.09
	RA	1.15	1.20	1.38	1.08	1.09	1.09
20.80	FF	1.14	1.13	1.22	1.12	1.10	1.14
	RA	1.19	1.26	1.53	1.10	1.11	1.13
30.56	FF	1.17	1.20	1.35	1.14	1.15	1.20
	RA	1.30	1.41	1.89	1.16	1.18	1.21
54.36	FF	1.28	1.35	1.49	1.23	1.25	1.29
	RA	1.42	1.66	2.53	1.20	1.26	1.30

with a front-face geometry (30° angle) or 'at 90° to the excitation light beam from a thin layer of illuminated solution close to the wall of the solution cell'[7]. They indicated that they obtained good agreement in I_E/I_M values by the thin-layer right-angle scattering and by a front-face geometry involving a 30° surface reflection. Given the fact that the data reported in the present study gave evidence of significant self-absorption effects at $20\,g\,l^{-1}$ and higher for front-face geometry measurements involving a 22.5° surface reflection, it is important to compare the results of this study to those of Renyuan and Cao[7]. This comparison is especially important as Renyuan and Cao[7] have purported not only to show a significant concentration dependence, with I_E/I_M increasing by over 20% from infinitely dilute to about $68\,g\,l^{-1}$ of 740 MW PS, but to show as well a significant difference in the form of concentration dependence for samples with $MW \leqslant 1.73 \times 10^3$ as compared to the 4200 MW sample. For the 740, 1370 and 1730 MW samples studied by Renyuan and Cao[7], I_E/I_M is nearly linear in concentration while for higher MW samples I_E/I_M purportedly exhibits a fractional power dependence on concentration. They have used the apparent difference in concentration dependence of I_E/I_M with molecular weight to support their notion that polymer coils with $MW > 1730$ shrink in polymer coil dimension significantly as polymer concentration is increased[7,11].

First, with regard to the magnitude of the concentration dependence of I_E/I_M observed by Renyuan and Cao[7], their decision to forego any self-absorption corrections, even though their results from right-angle thin-layer measurements agree with front-face measurements at a 30° surface reflection, has resulted in an overestimation of I_E/I_M at high concentrations. From results previously reported by Torkelson *et al.*[6] as well as results in the current study, I_E/I_M in the range of 60 to $70\,g\,l^{-1}$ appears to be about 8 to 11% higher than at infinite dilution, regardless of molecular weight or solvent, when corrected for self-absorption effects instead of the more than 20% increase indicated by Renyuan and Cao[7] for the 740 MW PS/dichloroethane solution. It is interesting that uncorrected I_E/I_M values for 800 MW PS in front-face geometry from this study agree with the form of the concentration dependence reported by Renyuan and Cao for 740 MW PS. This strongly indicates that their data were significantly affected at higher concentrations by self-absorption effects.

Secondly, with regard to Renyuan and Cao's observation[7] of a different form of concentration dependence for their 4200 MW PS sample as compared to their lower MW samples, several comments must be made. It must be noted at the outset that their observed values of I_E/I_M at infinite dilution yield a molecular weight dependence unlike that observed by any previous investigator, with I_E/I_M for the 4200 MW PS sample being well below that observed for the 1370 MW and 1730 MW PS samples. All previous studies by Ishii *et al.*[12], Torkelson *et al.*[5], Soutar *et al.*[13], Itagaki *et al.*[14] and Gordon *et al.*[15] show a monotonic increase in I_E/I_M with increasing PS MW until MW exceeds 10000 or 20000. Thus, the result obtained by Renyuan and Cao[7] is somewhat puzzling; a possible explanation may lie in the fact that the 4200 MW PS sample came from a different source than the three lower MW polymers, and thus the 4200 MW may have a significantly different configurational population than the other three polymers.

Figure 4 shows corrected values of I_E/I_M (not normalized to infinite dilution) as a function of PS concentration for four different PS/solvent systems: 2000 MW PS/dichloromethane, 4000 MW PS/dichloromethane, 800 MW PS/cyclohexane (27°C) and 800 MW PS/cyclohexane (50°C). In this figure, it is clear that

Table 3 Normalized I_E/I_M of 800 MW polystyrene in cyclohexane uncorrected and corrected for absorbance

Conc. (g l^{-1})	Geometry	Uncorrected			Corrected		
		I_{335}/I_{286}	I_{335}/I_{283}	I_{335}/I_{280}	I_{335}/I_{286}	I_{335}/I_{283}	I_{335}/I_{280}
0.54	FF	1.00	1.00	1.00	1.00	1.00	1.00
	RA	1.00	1.00	1.00	1.00	1.00	1.00
0.62	FF	0.99	1.01	1.00	0.99	1.01	1.00
	RA	0.99	0.99	1.00	0.99	0.99	0.99
0.88	FF	0.98	1.00	1.01	0.98	1.00	1.01
	RA	1.00	1.00	1.00	1.00	1.00	1.00
1.32	FF	1.00	1.00	1.00	1.00	1.00	1.00
	RA	1.00	1.00	1.00	1.00	1.00	1.00
2.32	FF	1.00	1.00	1.00	1.00	1.00	1.00
	RA	1.01	1.02	1.04	1.01	1.01	1.01
2.58	FF	1.00	1.00	1.00	1.00	1.00	1.00
	RA	1.00	1.02	1.05	1.00	1.01	1.02
4.85	FF	1.01	1.01	1.02	1.01	1.01	1.01
	RA	1.01	1.03	1.08	1.00	1.00	1.01
7.12	FF	1.02	1.02	1.04	1.02	1.01	1.02
	RA	1.02	1.04	1.10	1.00	1.00	1.01
7.41	FF	1.02	1.04	1.05	1.02	1.03	1.03
	RA	1.03	1.05	1.13	1.01	1.01	1.02
13.62	FF	1.05	1.05	1.07	1.03	1.03	1.03
	RA	1.06	1.10	1.24	1.01	1.02	1.02
22.39	FF	1.06	1.07	1.11	1.04	1.04	1.04
	RA	1.11	1.18	1.42	1.03	1.04	1.03
23.66	FF	1.07	1.08	1.14	1.05	1.05	1.06
	RA	1.13	1.19	1.47	1.04	1.04	1.05
36.34	FF	1.10	1.12	1.20	1.07	1.07	1.08
	RA	1.21	1.31	1.81	1.06	1.06	1.07
46.48	FF	1.12	1.13	1.25	1.08	1.07	1.08
	RA	1.27	1.40	2.12	1.07	1.07	1.08
52.25	FF	1.14	1.16	1.28	1.08	1.09	1.09
	RA	1.31	1.46	2.30	1.08	1.08	1.08
64.60	FF	1.16	1.18	1.33	1.09	1.09	1.09
	RA	1.38	1.59	2.81	1.09	1.09	1.10
78.71	FF	1.20	1.24	1.44	1.12	1.13	1.13
	RA	1.48	1.78	3.56	1.11	1.12	1.13
84.18	FF	1.23	1.31	1.56	1.15	1.18	1.20
	RA	1.55	1.92	4.03	1.14	1.17	1.18
124.5	FF	1.39	1.48	1.90	1.26	1.27	1.29
	RA	1.97	2.63	7.84	1.24	1.26	1.26
139.0	FF	1.44	1.60	2.00	1.29	1.34	1.30
	RA	–	–	–	–	–	–
168.0	FF	1.52	1.67	2.29	1.33	1.35	1.36
	RA	2.50	3.60	16.19	1.34	1.33	1.35
249.0	FF	1.68	1.90	3.02	1.38	1.39	1.39
	RA	–	–	–	–	–	–
440.0	FF	2.18	2.63	5.95	1.54	1.51	1.51
	RA	–	–	–	–	–	–
646.2	FF	3.18	4.15	13.49	1.90	1.83	1.80
	RA	–	–	–	–	–	–

4000 MW PS yields a greater value of I_E/I_M at infinite dilution in dichloromethane than 2000 MW PS and 800 MW PS at the same temperature, in contrast to the results of Renyuan and Cao[7] but in agreement with previous studies[5,12–15]. No significant difference in the form of the concentration dependence of I_E/I_M at low concentrations can be ascertained for the 4000 MW PS/dichloromethane system as compared to the other PS/solvent systems in this study, and no fractional power dependence in concentration is evident. The similarity in the form of the concentration dependence for these systems is not surprising. At these low molecular weights, in fact for PS <6000 MW[16,17], the polymers behave as though they were in a θ-solvent regardless of the solvent as they are too small to exhibit excluded volume effects. Thus, Renyuan and Cao's explanation of their fractional power dependence on concentration for their 4000 MW PS sample is clearly not even possible as polystyrene of such molecular weight is at its θ-dimension in an infinitely dilute solution regardless of the solvent chosen. Thus, no shrinkage of polymer coil dimensions can take place upon addition of polymer due to interaction between interchain segments.

Renyuan and Cao's expectation that I_E/I_M should be sensitive to coil shrinkage in vinyl aromatic polymers is itself incorrect. As data by Major and Torkelson[8] for poly(styrene sulphonate) convincingly show, I_E/I_M is approximately constant as the shape of a poly(styrene sulphonate) chain changes from a highly extended form to a loose coil. This implies that the overall conformation of a coil can change dramatically with little change in the conformational population responsible for excimer fluorescence.

It is interesting to note that although values of I_E/I_M (not normalized) are dependent on temperature in cyclohexane solutions as shown in *Figure 4*, the

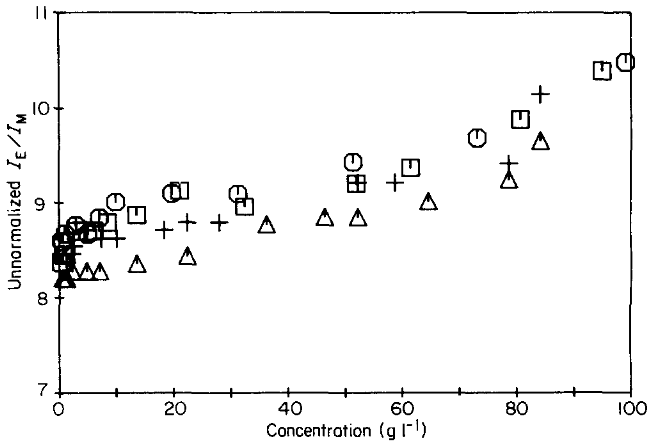

Figure 4 Corrected, unnormalized values of I_E/I_M as a function of PS concentration for oligomeric PS measured in right-angle geometry: (□) 2000 MW in dichloromethane; (○) 4000 MW in dichloromethane; (△) 800 MW in cyclohexane; (+) 800 MW in cyclohexane at 50°C

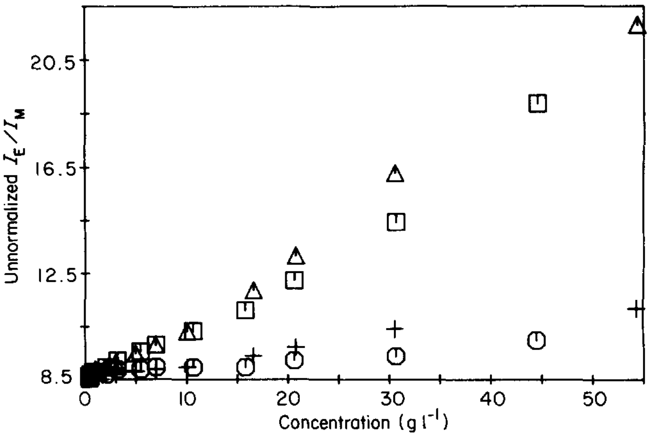

Figure 5 Corrected and uncorrected values of unnormalized I_{335}/I_{280} for two high-molecular-weight PS samples measured in right-angle geometry: (□) uncorrected I_{335}/I_{280} for 670 000 MW in cyclohexane at 50°C; (○) corrected I_{335}/I_{280} for 670 000 MW in cyclohexane; (△) uncorrected I_{335}/I_{280} for 1 800 000 MW in dichloromethane; (+) corrected I_{335}/I_{280} for 1 800 000 MW in dichloromethane

concentration dependence observed in values of normalized I_E/I_M is very similar at 27 and 50°C. Thus, as long as significant excimer fluorescence is present in the limit of infinite dilution due to intramolecular interactions, the effects of polymer concentration and intermolecular interactions on excimer fluorescence appear to be reasonably small in solutions of polystyrene, regardless of the temperature.

Figure 5 illustrates corrected and uncorrected values of unnormalized I_E/I_M for very high-molecular-weight polystyrene samples, 670 000 MW PS in cyclohexane at 50°C and 1 800 000 MW PS in dichloromethane at room temperature. Unlike results reported by Renyuan and Cao[7] for 6.09 × 10^6 MW PS in cyclohexane at 35.4°C and in dichloromethane at 25°C, these data show only a slight, nearly linear dependence of corrected I_E/I_M on concentration. Thus, even at very high molecular weight, no 'polymer effect' of the type described by Renyuan and Cao is evident from this study. However, the report by Renyuan and Cao was very interesting and provocative since it does appear that the concentration effect observed above 20 g l^{-1} PS is slightly greater for the 1800 000 MW sample than for all the other MWs of polystyrene investigated in this study.

It is interesting to note the excellent agreement in the concentration dependence of corrected values of normalized I_E/I_M from this study with the results of work by Torkelson *et al.*[6] in which corrected values of normalized I_E/I_M were obtained from emission measurements at the back face of the cell (180° to the excitation light). The fact that excellent agreement in normalized values of I_E/I_M after correction for self-absorption effects can be obtained from studies done using three different geometries provides convincing evidence for the validity of the self-absorption corrections discussed in this paper. As a result, it is apparent that when measurements of either the absolute value of I_E/I_M or the change in I_E/I_M with concentration are made, self-absorption corrections should be considered in all but very dilute solutions, even if a front-face emission geometry is employed in the measurements.

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