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Fluorescence and Absorbance of Polystyrene in Dilute and Semidilute Solutions

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ABSTRACT: The fluorescence and absorbance of polystyrene in solution have been measured over a wide concentration range for several molecular weights and solvents. The absorbance at wavelengths below 280 nm for these molecular weights and solvents is found to be insensitive to the transition between dilute and semidilute solutions. Self-absorption of the fluorescence results in a much reduced observed monomer emission at high concentration. When this is corrected, the ratio of excimer to monomer fluorescence intensity, I_E/I_M, is essentially constant at low concentrations and at most increases only very slowly and smoothly at higher concentrations. No significant molecular weight or solvent effects on the concentration dependence of I_E/I_M are manifested for these molecular weights and solvents over the concentration range studied. Contrary to previous reports, fluorescence spectroscopy reveals no abrupt transition between dilute and semidilute solutions.

Introduction

Intermolecular excimer formation by polymers in solution is similar to intramolecular excimer formation by nonadjacent chromophores in that both rely on diffusion of significant portions of the polymer molecules rather than single-bond rotation for the photophysical reaction to occur. Recently, we reported a study in which we found that intramolecular excimer formation by nonadjacent chromophores, or remote intramolecular excimer formation, was insignificant in dilute solutions of polystyrene.[2] We now report on a study in which both the fluorescence and the absorption spectra of polystyrene are investigated over a wide range of concentration and in which the conditions are more favorable for remote intramolecular and intermolecular excimer formation.

A number of concentration studies on the fluorescence of polystyrene in solution have been reported. An early concentration study was done by Vala et al.,[3] who found that the ratio of excimer to monomer fluorescence intensity, I_E/I_M, was insensitive to small changes of concentration in a very dilute solution. Later, Nishihara and Kaneko[4] did an extensive study of polystyrene in six solvents. Contrary to Vala et al.,[3] they indicated that I_E/I_M increased linearly with concentration even at concentrations approaching infinite dilution. Roots and Nyström[5] reported the concentration dependence of the fluorescence of three molecular weights of polystyrene and found that the curve representing I_E/I_M showed an apparent upward curvature at $c[\eta] \simeq 1$ for all molecular weights. They concluded that fluorescence spectroscopy was of value in determining the critical concentration, c^*, for the transition from dilute to semidilute solution behavior. This concentration is, to within a numerical constant of order one, $1/[\eta]$.[6,7] They also claimed that the value of c^* determined by fluorescence depended on molecular weight as $c^* \sim M^{-0.8}$, in agreement with predictions from theoretical scaling arguments.[8,9] Renyuan,[10] also studying polystyrene fluorescence, reported two critical concentrations in the curve representing I_E/I_M; both critical concentrations were almost independent of molecular weight.

Clearly, there is little agreement among the various studies of the concentration dependence of polystyrene fluorescence. A possible contributor to this lack of agreement is that at high polymer concentration the effect of self-absorption of monomer fluorescence by the sample may become significant. If these self-absorption corrections are not made or are made improperly, the different geometries used in each of the studies may be responsible for the discrepancies.

Recently, two studies have reported on the concentration dependence of the absorption spectrum of polystyrene solutions. Destor et al.[11] made absorption measurements of poly(oxyethylene) in water and poly(vinyl acetate) in acetonitrile as well as of polystyrene in chloroform. For the first two polymers they found a critical concentration at which there was a break in the absorbance vs. concentration curve. They interpreted this concentration to be c^* and found $c^* \sim M^{-0.75\pm0.10}$. For polystyrene, the curve was linear at low concentrations ($c < 0.6\%$) but became progressively curved for the highest concentration used ($0.6\% < c < 1\%$). They explained their results as being due to changes in polarizability of the medium with increasing polymer concentration. The replacement of a solvent molecule by a monomer alters the polarity and consequently the absorption frequency and molar absorptivity. The diminished effect in polystyrene was interpreted to result from the reduced monomer–monomer interactions between the bulky phenyl groups and from the fact that the absorption bands originate from π–π^* transitions, which are not very sensitive to the medium's polarity. Lee, Waddell, and Casassa[12] have repeated these measurements. While they found seemingly critical con-

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centrations at which the slope changed in the absorbance curves of poly(oxyethylene) and poly(vinyl acetate), they showed that these critical concentrations were virtually independent of molecular weight. They also found that the absorbance of polystyrene in chloroform is linear in concentration up to 8 g/L. They contend that the data by Destor et al. were affected by instrumental artifacts.

In this paper, we report on the fluorescence of polystyrene in both dilute and semidilute solution regimes. Measurements are made in a good solvent, dichloroethane, and in a poor solvent, cyclohexane. The absorbance of polystyrene is reported over the same concentration range as for fluorescence, and absorption corrections to the fluorescence spectra are made. This is a factor that we feel has not been properly treated in previous work. The results and their implications with respect to c^* and to intramolecular and intermolecular excimer formation are discussed. The results do not reveal a critical concentration c^*.

Experimental Section

Spectroscopic-quality cyclohexane, 1,2-dichloroethane, and ethyl acetate, and reagent grade diethyl phthalate were used without further purification. The polymer samples were standard polystyrenes with narrow molecular weight distribution (Pressure Chemical Co.) of molecular weight 17 500, 100 000, 300 000, and 900 000.

Solutions were prepared by weighing polystyrene into 5-, 10-, and 25-mL volumetric flasks and diluting with solvents. Sufficient time (>24 h) was allowed for solution. With samples of high concentration, gentle heating (<60 °C) was employed to facilitate dissolution.

All absorption measurements were made with a Cary Model 15 spectrophotometer. Over the wavelength region required (i.e., 230–350 nm), stray light was sufficiently low to permit reliable measurements of absorbance to ≃2.5. The fluorescence samples, contained in 0.1- or 1.0-cm path length cells (Suprasil), were excited at 253.7 nm using a Hg resonance lamp in conjunction with a Cl_2 gas filter and a quartz prism monochromator (Beckman DU). The fluorescence was collected from the back face of the cell by a similar monochromator and detected by a photomultiplier (EMI 6256B) and electrometer; a CCl_4 filter was positioned between the analyzing monochromator and photomultiplier to remove residual 253.7-nm light. The excimer (E) and monomer (M) bands were monitored at 335 and 283 nm (or 286 nm), respectively.

At concentrations where the corrections for the absorption of monomer and excimer fluorescence were important, the exciting light was almost entirely absorbed at the front face of the sample cell. Thus, the ratio of $(I_E/I_M)_{corr}/(I_E/I_M)_{meas}$ was taken as equal to $10^{-(\epsilon_M-\epsilon_E)cl}$, where ϵ_E and ϵ_M are the decadic absorptivities of the polymer at 335 and 283 nm (or 286 nm), respectively, c is the polymer concentration, and l is the path length of the cell. Corrections to the formula above for the slight penetration of the exciting beam into the cell and for the finite band-pass of the analyzing monochromator (<6 nm) were shown to be negligible. The values of $\epsilon_E c$ and $\epsilon_M c$ used in the formula were those measured for each sample. Values of $\epsilon_M - \epsilon_E$ for the 1.0 × 10^5 MW PS in dichloroethane samples were approximately 0.0038 ± 0.00025 and 0.0020 ± 0.0015 L/g cm at 283 and 286 nm, respectively.

Since the polystyrene emission spectrum did not change significantly over the range of concentrations studied, no corrections were required for the spectral response of the analyzing system. All solutions were air-equilibrated and measurements were made at 25 °C.

Results and Discussion

The absorption spectrum of a dilute solution of polystyrene (MW = 1 × 10^5) is shown in Figure 1 and appears to be essentially independent of molecular weight from ≃2 × 10^4 to 9 × 10^5.

The dependence of the absorbance at 260 nm on polystyrene concentration, c, is presented in Figure 2. Contrary to the results reported by Destor et al.,[11] but in agreement with those of Lee et al.,[12] we find no curvature to concentrations of at least 10 g/L nor any dependence on molecular weight. Similar results are shown for λ = 254 nm. The absorptivities at these two wavelengths are ϵ_{260} = 2.02 L/g cm and ϵ_{254} = 1.62 L/g cm.

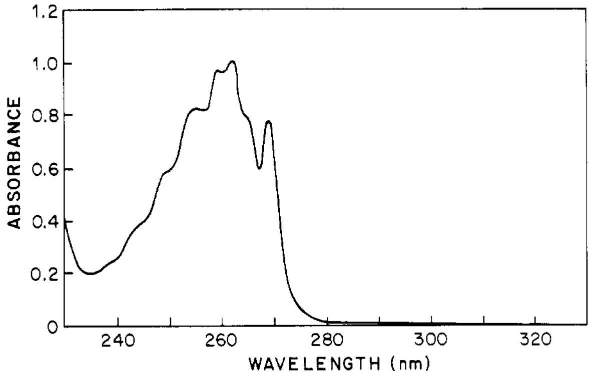

Figure 1. Absorption spectrum of 100 000 MW polystyrene in 1,2-dichloroethane as measured in a 1-cm cell. The concentration is 0.488 g/L.

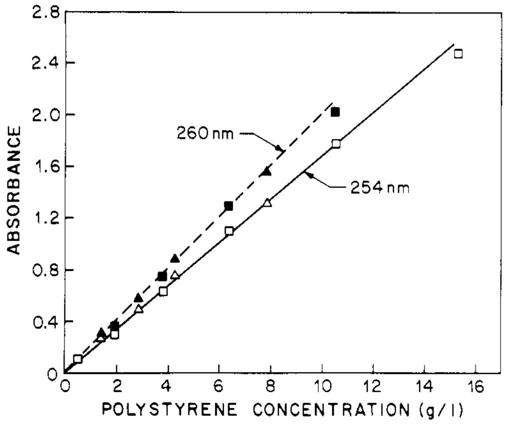

Figure 2. Concentration dependence of polystyrene absorbance at 260 and 254 nm as measured in a 0.1-cm cell. The solvent is 1,2-dichloroethane. Data for 260 nm: (■) 100 000 MW; (▲) 900 000 MW. Data for 254 nm: (□) 100 000 MW; (△) 900 000 MW.

Table I
Critical Concentration, c^* [a]

solvent	MW	T, °C	$c^* = 1/[\eta]$, g/L
1,2-dichloroethane	100 000	25	23.9
	900 000	25	5.6
cyclohexane	100 000	28	37.3
		34	36.9

[a] Calculation of c^* uses Mark-Houwink-Sakurada parameters obtained from ref 30.

Table I lists the values of c^* for various samples of polystyrene calculated assuming $c^* = 1/[\eta]$ (which is expected to underestimate the true value). From Table I it is clear that to determine whether or not $c = c^*$ manifests itself by some change in the absorption coefficient requires that measurements be made to somewhat higher concentrations than employed by Destor et al.[11] or Lee et al.[12] For this purpose we have determined the optical density at wavelengths that give smaller extinction (i.e., 235 and 275 nm) up to concentrations as high as ≃150 g/L. Our results are presented in Figure 3 and clearly give no indication of any obvious onset of polymer overlap. Similarly, we have been unable to confirm the observation of Ito and Shishido[13] that for 3.92 × 10^5 MW polystyrene in diethyl phthalate there is a Beer's law deviation for λ = 310 nm

Table II
$R(\lambda_E/\lambda_M)$ of 100 000 MW Polystyrene in 1,2-Dichloroethane, Uncorrected and Corrected for Absorbance

concn, g/L	uncorrected				corrected			
	1-cm cell		1-mm cell		1-cm cell		1-mm cell	
	R(335/ 283)	*R*(335/ 286)	*R*(335/ 283)	*R*(335/ 286)	*R*(335/ 283)	*R*(335/ 286)	*R*(335/ 283)	*R*(335/ 286)
0.38	0.99	1.00			0.9_9	1.0_0		
0.49	1.00	1.00			1.0_0	1.0_0		
0.64	1.01	1.01			1.0_0	1.0_0		
1.91	1.10	1.10	0.99	0.99	1.0_4	1.0_5	0.9_9	0.9_9
3.77	1.12	1.10	1.00	1.01	0.9_8	1.0_2	1.0_0	1.0_1
7.00	1.11	1.09	1.05	1.04			1.0_4	1.0_4
10.5	1.15	1.11	1.06	1.04			1.0_5	1.0_3
20.0	1.43	1.27	1.07	1.05			1.0_4	1.0_4
33.2	1.48	1.26	1.09	1.07	1.0_9	1.0_6	1.0_5	1.0_5
45.9	1.70	1.36	1.10	1.08	1.0_9	1.0_9	1.0_7	1.0_7
56.2	1.85	1.42	1.14	1.10	1.1_1	1.0_8	1.1_0	1.0_8
65.4	1.93	1.49	1.17	1.13	1.1_0	1.0_3	1.1_2	1.1_1
78.8	2.20	1.66	1.19	1.12	1.0_7	1.1_5	1.1_3	1.1_0
125	2.93	1.98	1.27	1.15	1.0_6	1.1_5	1.1_6	1.1_1
175	4.59	2.83	1.40	1.22	1.1_6	1.3_4	1.2_3	1.1_4
227	6.42	3.42	1.56	1.33	1.0_2	1.3_9	1.3_2	1.2_2
275	11.5	5.35	1.84	1.49	1.0_2	1.4_4	1.4_3	1.2_9

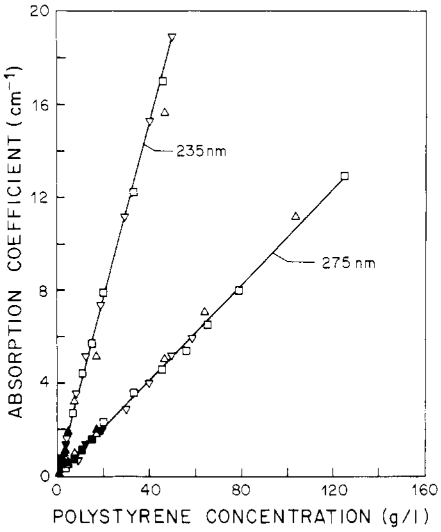

Figure 3. Concentration dependence of the absorption coefficient of polystyrene at 235 and 275 nm. Data for dichloroethane solutions: (□) 100 000 MW, 0.1-cm cell; (△) 900 000 MW, 0.1-cm cell; (■) 100 000 MW, 1-cm cell; (▲) 900 000 MW, 1-cm cell. Data for cyclohexane solutions: (▽) 100 000 MW, 0.1-cm cell; (▼) 900 000 MW, 1-cm cell.

beginning at c = 33 g/L. Our measurements for this system (using 3.0×10^5 MW polystyrene) indicate that most of the absorption reported by these authors at 310 nm is due to the solvent and when this is subtracted there is inadequate residual absorption for any reliable conclusion.

In Figure 4 we present the recorded fluorescence spectra of 1×10^5 MW polystyrene in 1,2-dichloroethane at 227 and 0.488 g/L in a 1-cm cell. By comparison with the fluorescence of ethylbenzene in this solvent, we have concluded, in agreement with the results of Ishii et al.,[14] that at λ = 335 nm the emission is essentially of pure excimer origin and at λ = 283 and 286 nm is not less than 95% and 94%, respectively, of monomer origin. For the purposes of this investigation, λ = 335 nm and λ = 283 nm (or 286 nm) were used to monitor the excimer and monomer emission intensities, respectively, and no attempt was made to correct for the slight contamination of the monomer by the excimer band. Both the large increase in excimer to monomer ratio at high polystyrene concentration and the slight red shift ($\simeq$4 nm) of the spectral

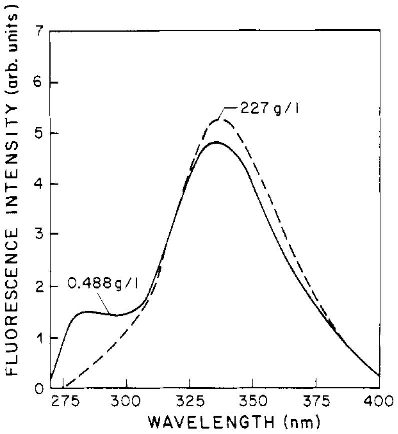

Figure 4. Fluorescence spectra of 100 000 MW polystyrene in 1,2-dichloroethane as measured in a 1-cm cell. Spectra are uncorrected for self-absorption effects.

maximum that is apparent in Figure 4 are strongly reduced in cells of smaller path length.

The ratio $R(\lambda_E/\lambda_M) = I_E(\lambda_E)/I_M(\lambda_M)$ (normalized to unity at c = 0) is shown in Figure 5 (uncorrected for absorption effects) for two representative molecular weights of polystyrene (1×10^5 and 9×10^5) in 1,2-dichloroethane using a 1-cm cell with λ_E = 335 nm and λ_M = 283 nm. These data are in substantial agreement with similarly uncorrected results of Roots and Nyström[5] (although their data for 1.1×10^5 MW polystyrene show a somewhat more abrupt change in R with c). However, contrary to the interpretations placed on this behavior by these authors, we present in Tables II–IV evidence that the major contribution to the variation in R with polymer concentration and polymer molecular weight is attributable to absorption of the monomer fluorescence both by the polymer itself and by different levels of absorbing impurities in the different molecular weight preparations. In Table II both uncorrected and corrected values of R are shown for 1×10^5 MW polystyrene in 1,2-dichloroethane in both 1.0- and 0.10-cm cells and at λ_M = 283 and 286 nm. The large disparity in the uncorrected values of R for the two cell lengths and the two monomer wavelengths is to be noted as is the nearly complete removal of this disparity after correction. Similar results for 100 000 MW polystyrene in cyclohexane and for 900 000 MW polystyrene in 1,2-dichloroethane are presented in Tables III and IV, respec-

Table III
$R(\lambda_E/\lambda_M)$ of 100 000 MW Polystyrene in Cyclohexane, Uncorrected and Corrected for Absorbance

	uncorrected				corrected			
	1-cm cell		1-mm cell		1-cm cell		1-mm cell	
concn, g/L	R(335/ 283)	R(335/ 286)	R(335/ 283)	R(335/ 286)	R(335/ 283)	R(335/ 286)	R(335/ 283)	R(335/ 286)
0.30	0.97	0.98			0.9_7	0.9_8		
0.56	1.00	1.00			1.0_0	1.0_0		
1.02	1.02	1.03			1.0_0	1.0_1		
1.73	1.05	1.05			1.0_2	1.0_2		
3.78	1.08	1.07	1.00	1.02	1.0_1	1.0_2	0.9_9	1.0_0
8.38	1.20	1.19	1.05	1.04	1.0_5	1.0_7	1.0_4	1.0_2
12.2	1.32	1.22	1.09	1.07	1.0_9	1.0_4	1.0_6	1.0_5
18.8	1.53	1.35	1.12	1.08	1.0_8	1.0_5	1.0_8	1.0_5
29.7	1.83	1.60	1.11	1.09	1.0_4	1.0_4	1.0_5	1.0_5
40.0	2.35	1.86	1.15	1.13	1.0_7	1.0_3	1.0_7	1.0_7
49.6	2.82	2.15	1.16	1.13	1.0_5	1.0_3	1.0_5	1.0_4
58.5	3.44	2.48	1.21	1.16	1.1_2	1.0_6	1.0_9	1.0_8

Table IV
$R(\lambda_E/\lambda_M)$ of 900 000 MW Polystyrene in 1,2-Dichloroethane, Uncorrected and Corrected for Absorbance

	uncorrected				corrected			
	1-cm cell		1-mm cell		1-cm cell		1-mm cell	
concn, g/L	R(335/ 283)	R(335/ 286)	R(335/ 283)	R(335/ 286)	R(335/ 283)	R(335/ 286)	R(335/ 283)	R(335/ 286)
0.28	0.98	1.00			0.9_8	1.0_0		
0.42	1.01	1.02			1.0_1	1.0_2		
0.52	1.01	1.00			1.0_1	1.0_0		
0.60	1.02				1.0_2			
1.45	0.99	0.98						
2.89	1.09	1.09	1.00	1.01	0.9_9	1.0_0	1.0_0	1.0_1
4.25	1.21	1.17	1.00	0.99	1.0_0	1.0_0	0.9_9	0.9_8
7.87	1.27	1.21	1.01	1.01	1.0_1	1.0_1	1.0_1	1.0_1
17.1	1.73	1.51	1.04	1.04	1.0_6	1.0_9	0.9_9	1.0_0
46.6	2.94	2.17	1.14	1.10	1.1_3	1.0_8	1.0_5	1.0_4
63.9	3.46	2.53	1.20	1.17	1.0_6	1.0_9	1.0_7	1.0_8
103.7	6.88	4.66	1.41	1.31	1.0_6	1.2_2	1.1_5	1.1_2

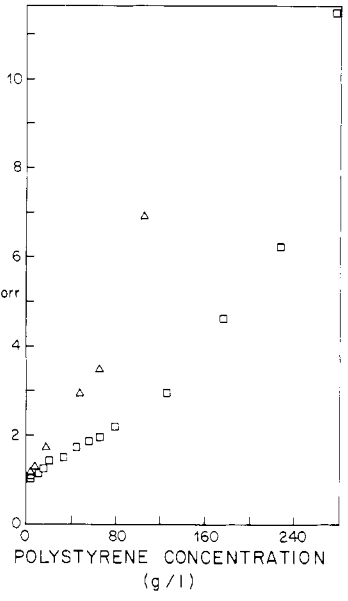

Figure 5. $R(335/283)$ for polystyrene in 1,2-dichloroethane as measured in a 1-cm cell. $R(\lambda_E/\lambda_M) = I_E(\lambda_E)/I_M(\lambda_M)$ normalized to unity at $c = 0$. Values of R are uncorrected for self-absorption effects. (□) 100 000 MW; (△) 900 000 MW.

tively. Results obtained for 17 500 MW polystyrene in dichloroethane were in substantial agreement with the results obtained for the other polystyrene samples. The corrected values for R (averaged over the two path lengths and the two monomer analysis wavelengths) are displayed graphically in Figure 6.

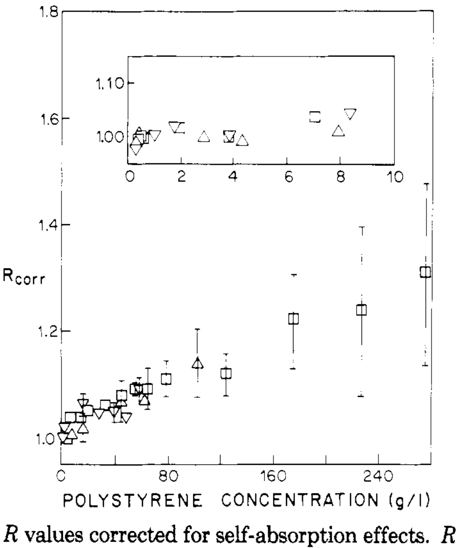

Figure 6. R values corrected for self-absorption effects. $R(\lambda_E/\lambda_M) = I_E(\lambda_E)/I_M(\lambda_M)$ normalized to unity at $c = 0$. Values are averaged over the two path lengths and the two monomer analysis wavelengths employed. (See Tables II–IV.) Error bars represent simple standard deviations for the four measurements; symbols without error bars have standard deviations roughly equal to the size of the symbols. Insert is low-concentration data. Data for 1,2-dichloroethane solutions: (□) 100 000 MW; (△) 900 000 MW. Data for cyclohexane solution: (▽) 100 000 MW.

As is apparent from Figure 6, R is essentially invariant at low concentrations and increases at most only very slowly and smoothly at higher concentrations. In fact, had we originally intended to quantify a low level of increase in R, we would have used an apparatus optimized for detecting such effects. In any case, this apparent residual increase in R with polymer concentration is independent of molecular weight and shows no obvious indication of the onset of intermolecular polymer overlap. Several effects could contribute to a residual increase in R. These include contributions from intermolecular excimer formation and from an enhancement of remote and/or adjacent intramolecular excimer formation due to coil contraction as the polystyrene concentration increases.

For intermolecular excimer formation to occur, two chromophores from different polymer molecules must come into a nearly coplanar sandwich-like structure with a separation less than ~ 3.7 Å.[15,16] In a semidilute solution, the average distance between interpolymer contacts, ξ, is believed to depend on $c^{-3/4}$ in a good solvent[17-20] so that the number of binary contacts in a unit volume is then proportional to $c^{9/4}$. If the change in R were due solely to intermolecular excimers, then ΔR ($\Delta R = R - 1.00$), the increment in the number of intermolecular excimers formed per monomer unit, should be proportional to the product $c^{9/4}c^{-1} = c^{5/4}$. However, upon using this prediction with the results shown in Figure 6, one sees that ΔR is not proportional to $c^{5/4}$. At 40 g/L, $\Delta R = 0.06$, and a $c^{5/4}$ dependence predicts $\Delta R = 0.67$ at 275 g/L, which is more than twice the value of ΔR actually observed. Thus other effects must contribute to the residual increase in R.

The phenomenon of chain contraction with increasing polymer concentration is well documented,[17,21,22] and this contraction may contribute to an increase in remote excimer formation with increasing concentration. However, other work has shown that remote excimer formation is insignificant even in polystyrene chains that are near precipitation.[2,23] Accordingly, it is unlikely that remote excimer formation is an important contributor to the increase in R. The decrease in coil dimensions may also affect vicinal excimer formation through changes in local conformation. This could increase R by facilitating the diffusional formation of excimer. Studies of polystyrene model compounds[24] have shown that isotactic configurations are much more favorable for excimer formation than syndiotactic configurations; furthermore, it has been shown[25,26] that isotactic polystyrene has a considerably greater $I_{\mathrm{E}}/I_{\mathrm{M}}$ than atactic polystyrene. It may be concluded from these studies that the vast majority of vicinal excimer formation in an atactic polystyrene molecule is due to isotactic dyads, where the excimer-forming conformation is approximately trans–trans.[24] Yoon et al.[27] have indicated that the ratio of trans to gauche conformations increases as the radius of gyration of an isotactic polystyrene molecule decreases. If this is also true for short isotactic sequences in an atactic polystyrene chain, then a decrease in coil dimensions would result in a higher number of vicinal excimer-forming sites and thus an increase in R. This increase in R should be small as a moderate change in overall coil dimensions may be obtained with only a small effect on the local dyadic population.[28] A decrease in coil dimensions could also increase R by facilitating energy migration to an excimer-forming site.[29] The current understanding of these effects is insufficient to allow a quantitative determination of the relative contributions of additional vicinal excimer formation and energy migration to the small residual increase in R.

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