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Diffusion-Limited Phosphorescence Quenching Interactions in Polymer Solutions: Small Molecule–Small Molecule Interactions Interpreted by Free Volume Theory

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ABSTRACT: Diffusion-limited interactions between benzil and anthracene were studied by phosphorescence quenching in polystyrene–cyclohexane, polystyrene–toluene, poly(methyl methacrylate)–toluene, and polybutadiene–cyclohexane solutions. Values of the bimolecular diffusion-limited quenching rate constant, k_q, were obtained by measuring benzil phosphorescence lifetime as a function of anthracene concentration and applying a Stern–Volmer analysis. Besides polymer species and solvent, k_q was measured as a function of polymer molecular weight and concentration, up to 560 g/L. k_q was found to be independent of polymer molecular weight in polystyrene–cyclohexane solutions and exhibited a slight molecular weight dependence in polystyrene–toluene solutions. The polymer concentration dependence of k_q in polystyrene–cyclohexane and polystyrene–toluene solutions was found to mimic the polymer concentration dependence of the solvent self-diffusion coefficient; this result is consistent with the notion that $k_q/k_{q0} \sim D_s/D_{s0}$ where D_s is the solvent self-diffusion coefficient and the subscript 0 indicates the value at zero polymer concentration. A very similar polymer concentration dependence of k_q was obtained in poly(methyl methacrylate)–toluene solutions. The Vrentas–Duda free volume theory for D_s was found to predict the polymer concentration dependence of k_q quantitatively for polystyrene–toluene and approximately for poly(methyl methacrylate)–toluene solutions; over the range of polymer concentrations studied in polystyrene–cyclohexane solutions, the agreement between the Vrentas–Duda theory and experimental measures of k_q appears to be less satisfactory. The Fujita–Doolittle theory can also be used to fit experimental measures of k_q in selected cases; however, it is possible to obtain unphysical results if the Fujita–Doolittle theory is applied over too wide a range in polymer concentration.

Introduction

Diffusion of solvent and probe molecules in polymer solutions is a subject which has received great study.[2-42] Several theories or models have been put forth to explain the polymer concentration dependence of small-molecule diffusional processes including those by Fujita,[2] Vrentas and Duda,[3-7,42] and others.[8] These theories or models relate the mobility of small molecules to the level of free volume present in the polymer system. Much effort has been expended by experimentalists over the last several decades to comment on the applicability of these free volume models; these studies have involved the use of a variety of techniques including forced Rayleigh scattering,[18-20] pulsed-gradient spin–echo NMR,[9-12,37,38,41] stress relaxation methods,[39,40] and "thin smear" methods.[28-30]

As yet there is not complete agreement on the applicability and utility of these theories or models to describe diffusional processes in polymer systems. Fujita[2] has indicated that the application of his theory should be limited to cases in which polymer volume fraction equals or exceeds 0.85. However, this has not precluded many investigators[11-13] from fitting their data to his theory even in dilute polymer solutions. The application and testing of Vrentas and Duda's theory has, by necessity, been limited due to the large number of parameters involved in their theory and the small number of systems[14,17] for which these parameters have been determined or estimated. Furthermore, the early form of their theory[3,4] basically restricted its use to temperatures exceeding the polymer's glass transition temperature, T_g (where T_g is for the solvent-free systems). A recent modification[14-16] allows application of this theory and associated parameters for room temperature studies of polystyrene–toluene, polystyrene–ethylbenzene, and poly(vinyl acetate)–methanol systems.

A process which is intimately related to the subject of small molecule diffusion in polymer solutions is diffusion-limited interactions or reactions of small molecules. Phosphorescence quenching is a particularly useful tool in obtaining information on diffusion-limited interactions in polymer solutions. Fluorescence quenching has been much more commonly investigated than phosphorescence

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quenching in polymer solutions, but in the case of diffusion-limited quenching interactions, phosphorescence is much better suited for obtaining accurate data due to the much longer lifetimes of excited triplet states than excited singlet states. The long triplet lifetimes allow observation of a diffusion-limited interaction of a phosphorescence chromophore with a quenching molecule through a reduction in phosphorescence intensity or lifetime.

Diffusion-limited bimolecular quenching rate constants, k_q, may be obtained from phosphorescence quenching experiments. The relationship between k_q and the self-diffusion coefficients of the chromophore and quencher is given by the modified Smoluchowski equation:[43]

$$k_q = 4\pi\rho R(D_c + D_q) \qquad (1)$$

where R is the encounter radius between the chromophore and quencher, ρ is a steric factor, and D_c and D_q are self-diffusion coefficients of the chromphore and quencher, respectively. Recently, von Meerwall, Amis, and Ferry[11] have demonstrated that the self-diffusion coefficient of a ternary probe molecule (hexafluorobenzene) in a polymer solution (polystyrene/tetrahydrofuran) has the same polymer concentration dependence as the solvent self-diffusion coefficient over a broad range of polymer concentration (0 g/L $< c <$ 620 g/L). As we will demonstrate in our Results and Discussion section, this simple relationship also appears to hold for our system in which the ternary probes are benzil and anthracene and the solvent is toluene; from this we can determine that k_q/k_{q0} is equivalent to D_s/D_{s0}. (The subscript 0 denotes zero polymer concentration.) Thus, values of k_q obtained by phosphorescence quenching should not only be useful in simulating diffusion-limited small molecule–small molecule reactions in polymer solutions but should also be useful in testing the applicability of the various free volume theories to describe diffusional processes involving small molecules in polymer solutions.

While this is the first study to interpret diffusion-limited bimolecular quenching rate constants obtained over a wide range of polymer concentrations in terms of free volume theory, there have been previous phosphorescence quenching studies of diffusion-limited interactions of small molecules in polymer solutions. Most notable is the work by Horie and Mita[44] who studied phosphorescence quenching of benzil by anthracene in polystyrene–benzene solutions. Although they did not interpret their results in terms of free volume theory, they concluded rightly that the quenching interaction is influenced by the volume fraction of polymer segments in solution and that the polymer serves as an obstacle for diffusion of the chromophore and quencher.

In the present work, which eventually will include studies of polymer–small molecule and polymer–polymer diffusion-limited interactions, diffusion-limited bimolecular quenching rate constants for benzil and anthracene interactions are obtained for a variety of systems including several molecular weights of polybutadiene in cyclohexane, several molecular weights of polystyrene in cyclohexane and toluene, and poly(methyl methacrylate) in toluene. The general features of the polymer concentration dependence of k_q are shown to be predicted by the free volume theory. However, the specific quantitative applicability of the Fujita–Doolittle theory is seen to be limited to relatively narrow ranges of polymer concentration whereas the Vrentas–Duda theory, for the systems in which the values of the required parameters are known (polystyrene in toluene and poly(methyl methacrylate) in toluene), shows good quantitative agreement over the whole polymer concentration range under study.

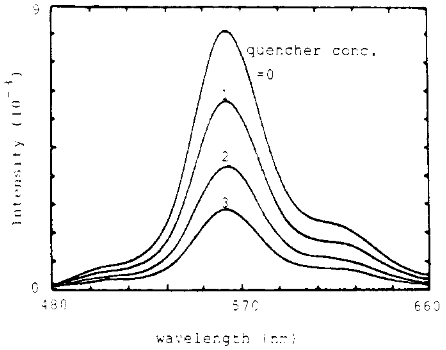

Figure 1. Steady-state phosphorescence spectra of benzil in toluene as a function of quencher concentration. Benzil concentration = 10^{-3} M. Quencher concentrations indicated in the figure are in units of 10^{-6} M.

Experimental Section

Polybutadiene (PB) of molecular weight 4500 and 200 000–300 000 was obtained from Aldrich Chemical. Poly(methyl methacrylate) (PMMA) with M_n = 46 500 and M_w = 93 300 was purchased from Scientific Polymer Products. Monodisperse polystyrene (PS) of molecular weight 4000, 47 500, and 670 000 was purchased from Pressure Chemical. All polymers were cleaned prior to use by dissolving in toluene and precipitating in methanol. This was repeated several times, and the polymer was dried in a vacuum oven for over a week. Reagent grade benzil and anthracene and spectrophotometric grade cyclohexane and toluene were purchased from Aldrich Chemical and were used as received.

Sample solutions were obtained by weighing polymer into 5-mL volumetric flasks and adding the desired amount of benzil and quencher dissolved in solvent. The solutions were shaken mechanically until homogeneous. Benzil concentration was maintained at 10^{-3} M, and anthracene concentration was maintained at about 10^{-5} to 10^{-6} M. Prior to measurement of the phosphorescence lifetime or the steady-state phosphorescence spectrum, all solutions were taken through seven freeze–pump–thaw cycles in order to remove dissolved oxygen which strongly quenches benzil phosphorescence. The adequacy of using seven freeze–pump–thaw cycles was tested by measuring the lifetime of biacetyl in acetonitrile and in cyclohexane. The lifetimes obtained (359.1 μs in acetonitrile and 182.2 μs in cyclohexane) agree well with literature values.[45]

Excitation of the samples was achieved by a xenon lamp pulse at 400 nm. The phosphorescence decay of benzil at 560 nm as well as the complete phosphorescence spectrum of benzil was detected with a SPEX fluorescence spectrophotometer with a phosphorescence attachment. The phosphorescence quenching rate constant, k_q, was calculated by using the Stern–Volmer equation[43]

$$1/\tau = 1/\tau_0 + k_q[Q] \qquad (2)$$

where τ and τ_0 are the phosphorescence lifetimes obtained from decay curves in the presence and absence of quencher, respectively. Generally, four samples with different quencher concentrations were prepared for each polymer concentration of interest and k_q was determined by the method of least squares. In Figures 4–9 all error bars are shown on the basis of calculations of the student t distribution with an 80% confidence level. In the cases of data without error bars, the calculated errors are less than the size of the symbols denoting the data. All samples were measured at room temperature.

Results and Discussion

A. Determination of Bimolecular Quenching Rate Constants. Figure 1 shows the steady-state phosphorescence spectrum of benzil in toluene as a function of anthracene concentration. Anthracene is clearly an effective quencher of benzil phosphorescence as the intensity decreases by about a factor of 2 when 2 × 10^{-6} M anthracene is added to the benzil–toluene solution.

Figure 2 shows the decay of benzil phosphorescence at 560 nm as a function of anthracene concentration. For all

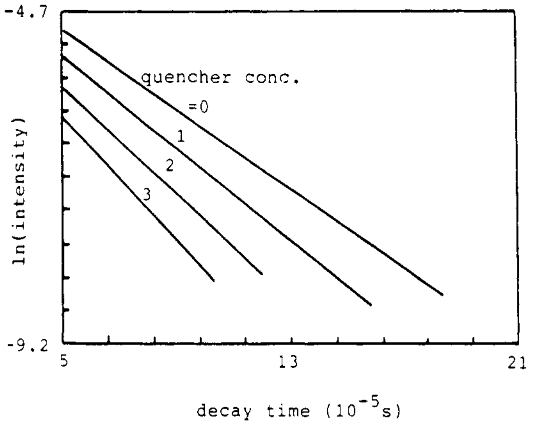

Figure 2. Decay of benzil phosphorescence at 560 nm as a function of quencher concentration. Benzil concentration in toluene = 10^{-3} M. Quencher concentrations indicated in the figure are in units of 10^{-6} M.

Table I
Values of τ_0/τ and I_0/I for the System Benzil (10^{-3} M) and Anthracene in Toluene

anthracene concn, 10^{-6} M	τ_0/τ	I_0/I	anthracene concn, 10^{-6} M	τ_0/τ	I_0/I
0	1	1	3	1.58	3.23
1	1.19	1.38	4	1.74	4.16
2	1.38	2.12			

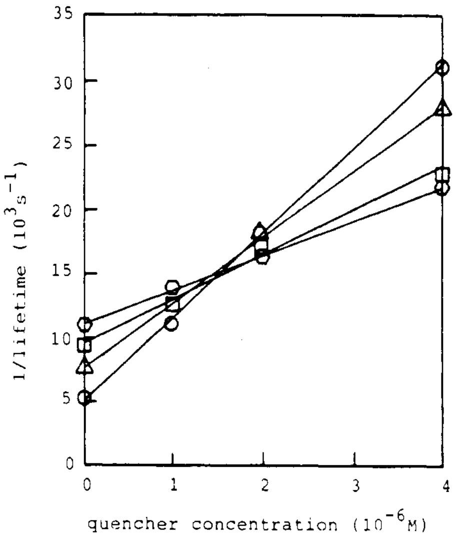

Figure 3. Stern–Volmer plot showing the inverse benzil phosphorescence lifetime as a function of quencher concentration in polystyrene–toluene solutions. Polystyrene concentration: (○) 0 g/L; (△) 50 g/L; (□) 120 g/L; (○) 200 g/L.

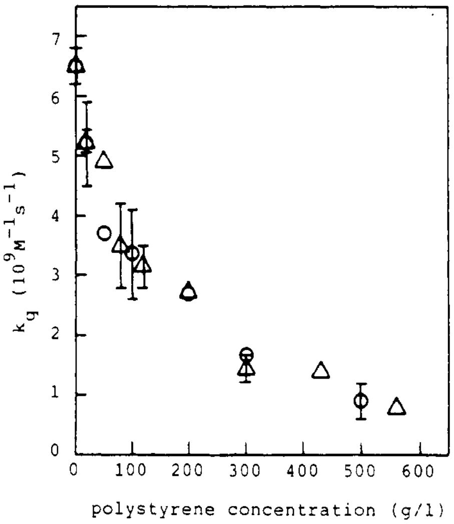

Figure 4. Benzil phosphorescence quenching rate constant as a function of polystyrene concentration in cyclohexane. Polystyrene molecular weights: (○) 4000; (△) 47 500.

four samples, the phosphorescence decay follows simple decay kinetics: ln $I \sim t/\tau$ where I is the phosphorescence intensity, t is the decay time, and τ is the benzil phosphorescence lifetime in the solution under study. As with the steady-state phosphorescence intensity, the lifetime of benzil phosphorescence decreases with increasing anthracene concentration.

A comparison of τ_0/τ and I_0/I as a function of anthracene concentration for the systems shown in Figures 1 and 2 is presented in Table I. τ and τ_0 are the phosphorescence lifetimes in the presence and absence of quencher, respectively, and I and I_0 are the steady-state phosphorescence intensities in the presence and absence of quencher, respectively. It is clear that these quantities are not equivalent at a given quencher concentration. This indicates that both dynamic and static quenching processes are present in this system. The lower values of τ_0/τ are indicative of only the dynamic quenching involving diffusion-limited interactions of benzil and anthracene whereas the I_0/I values are indicative of the combined effects of static and dynamic quenching.

If only dynamic quenching is present in a system, τ_0/τ is equivalent to I_0/I and k_q may be calculated by Stern–Volmer analysis from either eq 2 shown above or eq 3:

$$I_0/I = 1 + k_q\tau_0[Q] \tag{3}$$

However, in the case where both static quenching (which may be caused by some ground-state complexation between the chromophore and quencher thus yielding the chromophore unable to phosphoresce) and dynamic quenching are present, the use of eq 3 overestimates k_q, while eq 2 will yield accurate values of k_q. This point is important in that the k_q values reported by Horie and Mita[44] for benzil phosphorescence quenched by anthracene in polystyrene–benzene solutions were calculated based on determinations of I_0/I. Thus, while their qualitative conclusions about how the quenching interaction is influenced by the volume fraction of polymer segments in solution are absolutely right, their results cannot be used in any quantitative comparison with free volume theories describing how small molecule diffusional processes in polymer solutions are affected by polymer concentration.

Figure 3 shows that the Stern–Volmer relationship given by eq 2 is obeyed in these polymer solutions. It is noteworthy that as polystyrene concentration is increased in the solutions, the slope and thus the value is k_q obtained by Stern–Volmer analysis decreases significantly. τ_0 is also observed to decrease significantly as polymer concentration is increased. This is caused by a nondiffusion-controlled interaction between benzil and polymer and is the subject of a separate paper.[46]

Figures 4–6 present the dependence of k_q calculated from plots such as those in Figure 3 on polymer concentration for a variety of polymer–solvent combinations and a range of polymer molecular weights. In all cases, there is a dramatic decline in k_q with increasing polymer concentration which is in agreement with the conclusion reached by Horie and Mita[44] that the polymer serves mainly as an obstacle for diffusion and interaction of benzil and anthracene.

Figure 4 shows the dependence of k_q on polystyrene molecular weight and concentration in polystyrene–cyclohexane solutions. Up to 560 g/L polystyrene concen-

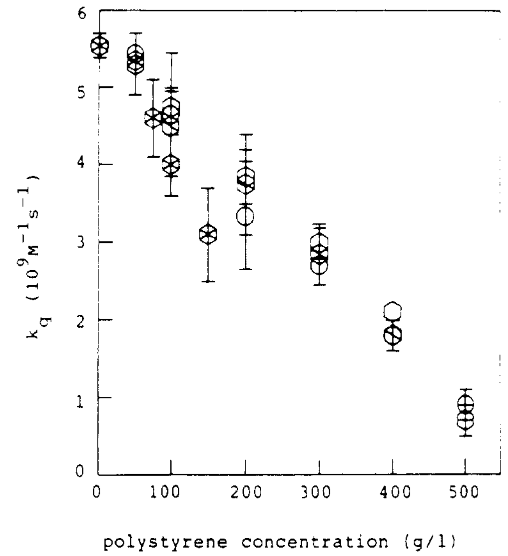

Figure 5. Benzil phosphorescence quenching rate constant as a function of polymer concentration in toluene. Polystyrene molecular weights: (⬡) 4000; (⦸) 47 500; (⊗) 670 000. Poly(methyl methacrylate) molecular weight: (○) 46 400.

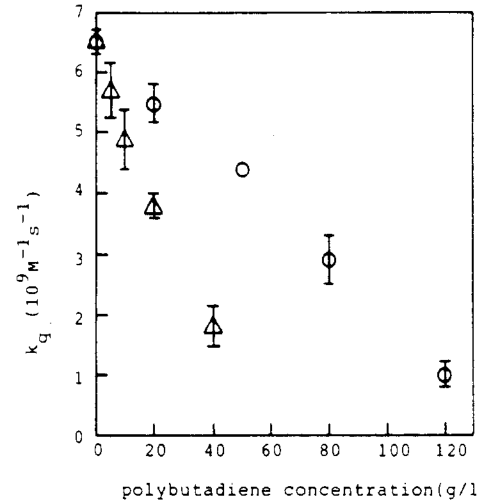

Figure 6. Benzil phosphorescence quenching rate constant as a function of polybutadiene concentration in cyclohexane. Polybutadiene molecular weights: (○) 4500; (△) 200 000–300 000.

tration, there appears to be virtually no molecular weight dependence on k_q although the concentration dependence is pronounced, with k_q falling from 6.4×10^9 M^{-1} s^{-1} at zero polymer concentration to less than 1×10^9 M^{-1} s^{-1} at 560 g/L of polystyrene. The concentration dependence is greatest at low polymer concentrations with k_q dropping by 3×10^9 M^{-1} s^{-1} with the first 100 g/L of polystyrene; this exceeds the decline in k_q obtained by increasing polystyrene concentration from 100 to 560 g/L.

It should be noted that Horie and Mita[47] have studied phosphorescence quenching of benzil by anthracene in pure cyclohexane. By use of eq 2 they determined that at 20 °C $k_q = 3.9 \times 10^9$ M^{-1} s^{-1} and at 30 °C $k_q = 4.1 \times 10^9$ M^{-1} s^{-1}. Their values are about 35–40% lower than the value of k_q obtained in pure cyclohexane in this study. (The value of k_q in pure cyclohexane obtained in this study is nearly identical with a value of k_q determined by Horie and Mita[48] using eq 2 for benzil phosphorescence quenched by anthracene in pure benzene.) Even at concentrations of 50 g/L polystyrene in cyclohexane, the values of k_q obtained in this study exceed those reported by Horie and Mita in pure cyclohexane. We have repeated our determination of k_q in pure cyclohexane on several occasions over a 1-year period and are confident in our value.

Figure 5 shows the dependence of k_q on polystyrene molecular weight and concentration and poly(methyl methacrylate) concentration in toluene solutions. There are two similarities between Figures 4 and 5. The first is that as with the polystyrene–cyclohexane system, the values of k_q obtained in the 4000 MW and 47 500 MW polystyrene in toluene are very similar. At most, the values of k_q obtained with the 47 500 MW polystyrene in toluene are just slightly below the values obtained with the 4000 MW polystyrene in toluene. The second similarity is that at 500 g/L, k_q is approximately the same as that obtained in a 500 g/L polystyrene solution in cyclohexane.

In all other respects, the results in Figure 5 differ from those in Figure 4. First, in the absence of polymer k_q is more than 10% lower in toluene than in cyclohexane; this difference is outside the range of experimental uncertainty. Calculation of reduced rate constants, $k_q\eta/T$, to attempt to correct for effects of solvent viscosity does not result in closer agreement between the results obtained in the two solvents. This subject has been discussed by Birks[43] and is treated in another paper.[49] It should be noted that Horie and Mita[48] found a range of $k_q\eta/T$ from about 7 to about 10 J/K·mol from benzil phosphorescence quenched by 9-methylanthracene in benzene, cyclohexane, and butanone for three different temperatures. Second, instead of exhibiting a very pronounced curvature as in Figure 4, the k_q data for the poly(methyl methacrylate) samples and the two lower molecular weight polystyrene samples exhibit a nearly linear dependence on polymer concentration. And last, while the solutions of the two lower molecular weight polystyrene samples yield nearly identical values of k_q at a given polymer concentration, the 670 000 MW polystyrene solutions yield slightly lower values of k_q. A comparison of these results with k_q values for 670 000 MW polystyrene–cyclohexane solutions could not be done as 670 000 MW polystyrene does not dissolve appreciably in cyclohexane at room temperature.

Figure 6 shows the dependence of k_q on polybutadiene molecular weight and concentration in cyclohexane solutions. This system provides a dramatic contrast to the other systems investigated in this study. The interaction between benzil and anthracene is much more strongly affected by polybutadiene concentration than by either polystyrene or poly(methyl methacrylate) concentration. Furthermore, a much greater molecular weight dependence is observed in this system than in the polystyrene–toluene system. The reasons for the dramatic effects obtained in the polybutadiene–cyclohexane are as yet not fully understood.

With the exception of the polybutadiene results, the general trends observed for k_q are fairly consistent with the trends observed in other studies for D_s, the solvent self-diffusion coefficient. von Meerwall et al.[11] have reported either no or little polymer molecular weight dependence of D_s for polymer concentrations similar to those used in this investigation. This suggests that polymer entanglements play little or no role in self-diffusion of small molecules in polymer solutions. When a molecular weight dependence is observed,[50] it is usually exhibited by higher diffusivities in very low molecular weight polymer solutions. In our case, k_q was independent of molecular weight at low and intermediate molecular weights while at very high molecular weight a slightly larger effect of polymer concentration was observed.

B. Analysis by the Vrentas–Duda Theory. The effect of polymer concentration on k_q/k_{q0} is similar to the effect observed on D_s/D_{s0}. In Figure 7a,b, experimental

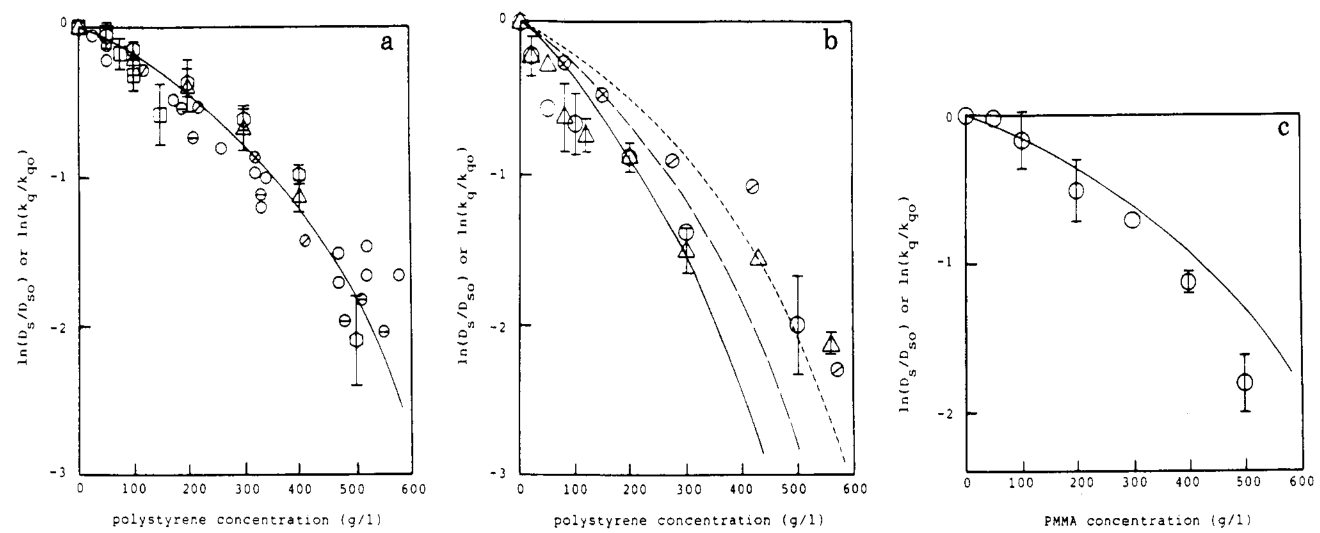

Figure 7. (a) Comparison of experimental data for ln (D_s/D_{s0}) and ln (k_q/k_{q0}) with the Vrentas–Duda free volume theory for the polystyrene–toluene system. The smooth curve represents the prediction resulting from the Vrentas–Duda theory. Self-diffusion data for 18 000 MW (⊘) and 280 000 MW (⊖) polystyrene are from ref 38, and other self-diffusion data (○) are from ref 36. Quenching rate constant data: (○) 4000 MW PS; (△) 47 500 MW PS; (□) 670 000 MW PS. (b) Comparison of experimental data for ln (D_s/D_{s0}) and ln (k_q/k_{q0}) with the Vrentas–Duda free volume theory for the polystyrene–cyclohexane system. $\hat{V}^*_s$ is estimated to be 0.93 in all cases. The smooth curves represent the Vrentas–Duda predictions with $K_{11}(K_{21} + T - T_{g_1})/\gamma$ taking the values 0.326 (- - -), 0.253 (— — —), and 0.200 (—). Self-diffusion data (⊘) are from ref 38. Quenching rate constant data: (○) 4000 MW PS; (△) 47 500 MW. (c) Comparison of experimental data for ln (k_0/k_{q0}) with the prediction of ln (D_s/D_{s0}) by the Vrentas–Duda free volume theory for the poly(methyl methacrylate)–toluene system. The smooth curve represents the prediction resulting from the Vrentas-Duda theory.

values of ln (D_s/D_{s0}),[36,38] where D_s is the self-diffusion coefficient of solvent in polystyrene solution (toluene is the solvent in Figure 7a while cyclohexane is the solvent in Figure 7b), are compared to values of ln (k_q/k_{q0}) as a function of polymer concentration. In figure 7c, experimental values of ln (k_q/k_{q0}) for poly(methyl methacrylate)–toluene solutions are plotted as a function of polymer concentration; no comparison is made to ln (D_s/D_{s0}) as experimental values of D_s are not available in the literature for this system.

It has been shown[19,42] that the self-diffusion coefficient of a probe molecule, D_p, can be related to the self-diffusion of the solvent, D_s, in a polymer–solvent–probe system by

$$\ln\left(\frac{D_p}{D_{p0}}\right) = \left(\frac{\hat{V}^*_p M_{jp}}{\hat{V}^*_s M_{js}}\right) \ln\left(\frac{D_s}{D_{s0}}\right) \tag{4}$$

where $\hat{V}^*_p$ and $\hat{V}^*_s$ are the specific critical hole free volumes of probe and solvent required for a jump, respectively, and M_{jp} and M_{js} are the corresponding molecular weights of a jumping unit. As k_q is proportional to the sum of self-diffusion coefficients of chromophore and quencher, we can reasonably assume that $k_q \sim D_p$, where $D_p = D_A + D_B$ and D_A (D_B) represents the self-diffusion coefficient of the anthracene (benzil), and that $k_q/k_{q0} = D_p/D_{p0}$. Therefore, ln (k_q/k_{q0}), which equals ln (D_p/D_{p0}), is a function of ln (D_s/D_{s0}).

In the case of the polystyrene–toluene solutions, the values of ln (D_s/D_{s0}) appear to lie intermediate between the values of ln (k_q/k_{q0}) obtained for high molecular weight polystyrene samples and those obtained for low and medium molecular weight polystyrene samples. The toluene solution data are particularly convincing as there is a good correspondence between the polystyrene concentration dependence of ln (k_q/k_{q0}) as determined in our study and the dependence of ln (D_s/D_{s0}) as determined by two independent experimental studies.[36,38] Only one experimental study[38] of D_s for polystyrene–cyclohexane solutions has been reported over the concentration range of interest. Over most of the concentration range studied, the ln (D_s/D_{s0}) data appear to lie somewhat above the ln (k_q/k_{q0}) data (with the exception of $c > 500$ g/L). It would be of interest to obtain a third set of experimental data on either D_s/D_{s0} or k_q/k_{q0} for polystyrene–cyclohexane in order to determine whether Blum's data[38] slightly underestimate the polystyrene concentration dependence or whether our data slightly overestimate the dependence.

Table II
Parameters Used in the Vrentas–Duda Free Volume Theory (Eq 4 and 5)

	PS–toluene[a]	PMMA–toluene	PS–cyclohexane
$\hat{V}^*_s$, cm^3/g	0.917	0.917[a]	0.93[c]
$\hat{V}^*_p$, cm^3/g	0.850	0.77[b]	0.85[a]
ξ	0.54	0.55[b]	0.56[c]
K_{11}/γ, cm^3/g·K	1.57×10^{-3}	1.57×10^{-3} [a]	
$K_{21} - T_{g_1}$, K	−90.5	−90.5[a]	
K_{12}/γ, cm^3/g·K	5.82×10^{-4}	2.82×10^{-4} [b]	5.82×10^{-4} [a]
$K_{22} - T_{g_2}$, K	−327	−301[b]	−327[a]

[a] Data are obtained from ref 16. [b] Data are obtained and calculated from ref 6 and 16. [c] Estimated.

On the basis of eq 4, there is a linear relationship between ln (k_q/k_{q0}) and ln (D_s/D_{s0}); from Figure 7a,c, these two quantities seem to be the same. It has also been found[41,42] from two solvent–probe–polymer systems, C_6F_6 (hexafluorobenzene)–$C_{12}H_{26}$ (*n*-dodecane)–*cis*-4-polybutadiene and C_6F_6–$C_{36}H_{74}$ (*n*-hexatriacontane)–*cis*-4-polybutadiene, that the values of $\hat{V}^*_p M_{jp}/\hat{V}^*_s M_{js}$ were equal to 1. Therefore, we can assume as a good approximation that the values of $\hat{V}^*_p M_{jp}/\hat{V}^*_s M_{js}$ in our system are also equal to 1. This then allows us to equate $k_q k_{q0}$ with D_s/D_{s0}.

The systems investigated in this study for which all of the necessary parameters in the Vrentas–Duda theory have been published or can be easily obtained from the literature are polystyrene–toluene[16] and poly(methyl methacrylate)–toluene. (See Table II for the parameters required by the Vrentas–Duda theory which we obtained from various sources in the literature.) Thus, a comparison of the Vrentas–Duda predictions for D_s/D_{s0} and our experimental values of k_q/k_{q0} can be easily made for those two systems, and the utility of phosphorescence quenching measurements and diffusion-limited quenching rate constants for obtaining quantitative information on diffusional processes in polymer solutions can be critically tested.

For a binary solution consisting of polymer and solvent at a given temperature, Vrentas and Duda have derived the polymer concentration dependence of D_s for polymer concentrations ranging from infinitely dilute to bulk:[3,4]

$$D_s = D_{0s} \exp\left[-\frac{\gamma(\omega_s \hat{V}^*{}_s + \omega_p \xi \hat{V}^*{}_p)}{\hat{V}_{FH}} \right] \qquad (5)$$

where ω_s and ω_p are the weight fractions of solvent and polymer, respectively, $\hat{V}^*{}_s$ and $\hat{V}^*{}_p$ are the specific critical hole free volumes for the solvent and the polymer jumping unit, respectively, $\hat{V}_{FH}$ is the average hole free volume per gram of solution, γ is an overlap factor which is introduced because the same free volume is available to more than one molecule, D_{0s} is a temperature-dependent preexponential factor, and ξ is as defined in ref 3 and 4. The specific hole free volume may be expressed as follows:[17]

$$\frac{\hat{V}_{FH}}{\gamma} = \frac{K_{11}}{\gamma}\omega_s(T - T_{g_1} + K_{21}) + \frac{K_{12}}{\gamma}\omega_p(T - T_{g_2} + K_{22}) \qquad (6)$$

where K_{11} and K_{21} are free-volume parameters of the solvent, K_{12} andd K_{22} are free-volume parameters of the polymer, and T_{g_1} and T_{g_2} are glass transition temperatures of the solvent and polymer, respectively. (It should be noted that in calculating D_s/D_{s0} it is critical to use the latest revision of parameter values given in reg 17 rather than the values reported earlier by Vrentas and Duda; failure to do so results in a much poorer correlation between the Vrentas–Duda predictions of D_s/D_{s0} and experimental values of k_q/k_{q0}).

Parts a and c of Figure 8 compare the predicted values of D_s/D_{s0} from the Vrentas–Duda theory to experimental values of D_s/D_{s0} and/or k_q/k_{q0} for polystyrene–toluene and poly(methyl methacrylate)–toluene solutions, respectively. In the figure the smooth curves represent the predictions from the Vrentas–Duda theory. (For the poly(methyl methacrylate)–toluene system, predictions from the Vrentas–Duda theory were determined by their parameter values for toluene[16] and data we obtained from the literature[6] for poly(methyl methacrylate). See Table II.) Excellent agreement is obtained for the polystyrene–toluene system and approximate agreement (particularly good below 300 g/L) is obtained for the poly(methyl methacrylate)–toluene system. We have also plotted the predictions of the Vrentas–Duda theory in Figure 7a,c, and the same conclusions are evident from that figure. This supports our claim that $\hat{V}^*{}_2 M_{j2}/(\hat{V}^*{}_1 M_{j1})$ from eq 4 is approximately equal to one in both polymer–toluene solutions.

For the polystyrene–toluene system, the prediction from theory lies intermediate between the values of k_q/k_{q0} obtained for the 670 000 MW polystyrene samples and those obtained for the 4000 MW and 47 500 MW samples. Given the slight molecular weight dependence of the experimental k_q/k_{q0} data and the fact that the parameters in the Vrentas–Duda theory were calculated for polystyrene of an indeterminate (but likely intermediate or high) molecular weight, the agreement between theory and experiment is as close as could be expected over the range of polystyrene concentration studied. It is interesting to note that Blum's data[38] for D_s/D_{s0} in the polystyrene–toluene system also track the Vrentas–Duda predictions. Blum[12] has compared other diffusion data to the Fujita–Doolittle theory and reached the conclusion that the Fujita–Doolittle theory explained the polymer concentration dependence, but he made no comparison with the Vrentas–Duda theory.

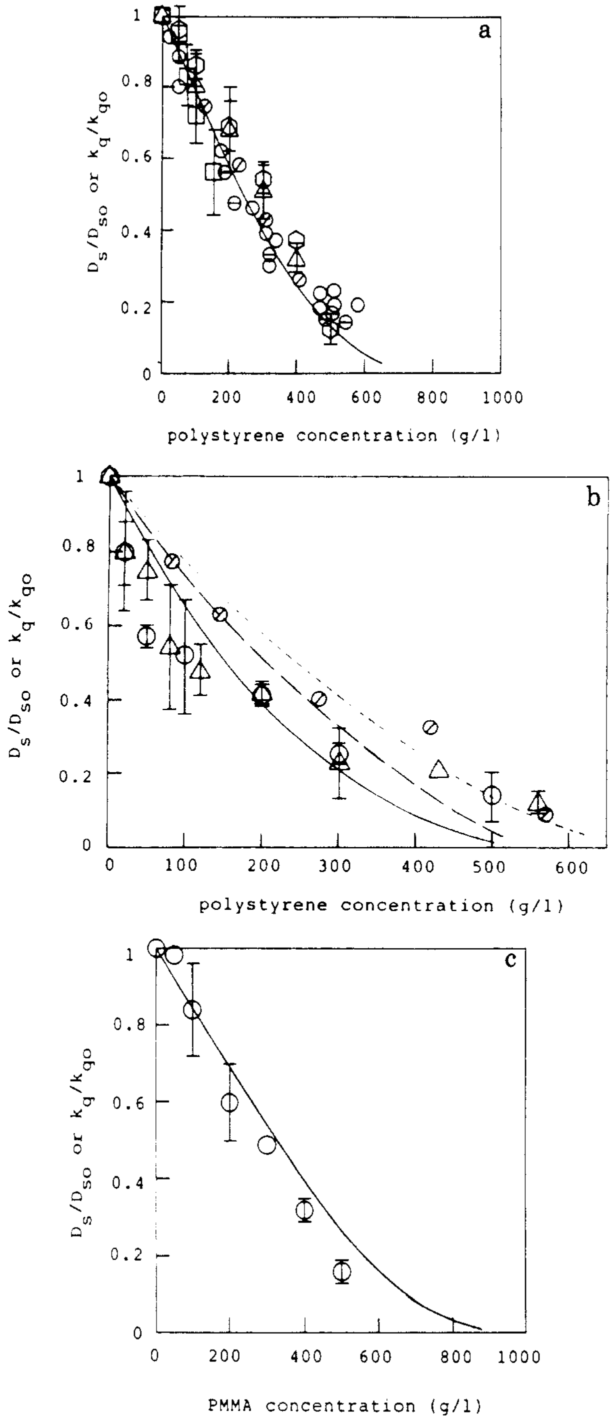

Figure 8. (a) Comparison of experimental data for D_s/D_{s0} and k_q/k_{q0} with the Vrentas–Duda free volume theory for the polystyrene–toluene system. The smooth curve represents the prediction of Vrentas–Duda theory. The symbols of self-diffusion data (⊘, ⊖, ⦶) and quenching rate constant data (○, △, □) are the same as in Figure 7a. (b) Comparison of experimental data for D_s/D_{s0} and k_q/k_{q0} with the Vrentas–Duda free volume theory for the polystyrene–cyclohexane system. The smooth curves represent the Vrentas–Duda predictions with the same parameters as Figure 7b. Symbols of self-diffusion data (⊖) and quenching rate constant data (○, △) are the same as Figure 7b. (c) Comparison of experimental data for k_q/k_{q0} with the prediction of D_s/D_{s0} by the Vrentas–Duda free volume theory for the poly(methyl methacrylate)–toluene system. The smooth curve represents the prediction.

It should be noted that the Vrentas–Duda analysis would not be able to adequately predict the polystyrene concentration dependence of k_q/k_{q0} at extremely high concentrations if such bimolecular quenching rate constant data were available. With the latest version of the Duda–Vrentas parameters for the polystyrene–toluene system[15] $\hat{V}_{FH} < 0$ for $\omega_p \geq 0.95$ at room temperature. Obviously, eq 4 is meaningful only when $\hat{V}_{FH} > 0$. This suggests that even more fine tuning in the values of the Vrentas–Duda parameters for the polystyrene–toluene system may be necessary in order to use the Vrentas–Duda theory at very high polystyrene concentrations.

Although there is insufficient information in the literature to obtain easily all the Vrentas–Duda parameters for the polystyrene–cyclohexane system (in particular, $\hat{V}^*_s$ and $K_{11}(K_{21} + T - T_{g_1})/\gamma$ are unknown), some approximations can be made to try to determine whether either our k_q/k_{q0} data or Blum's[38] D_s/D_{s0} data can be predicted from the Vrentas–Duda theory. In Table II, we have listed our best guess for $\hat{V}^*_s$ to be 0.93. This is close to the values of $\hat{V}^*_s$ given by Vrentas and Duda[6,17] for ethyl benzene ($\hat{V}^*_s = 0.946$), toluene ($\hat{V}^*_s = 0.917$), acetone ($\hat{V}^*_s = 0.95$), and methanol ($\hat{V}^*_s = 0.96$) and slightly above that for methyl acetate ($\hat{V}^*_s = 0.855$).

In previous studies by Vrentas and Duda,[14,16] $K_{11}(K_{21} + T - T_{g_1})/\gamma$ was found to be 0.326 for toluene, 0.318 for ethyl benzene, and 0.253 for methanol at 25 °C. When values for $K_{11}(K_{21} + T - T_{g_1})/\gamma$ over the range from 0.200 to 0.326 were plugged into eq 4 and 5, the predicted polystyrene concentration dependence of D_s/D_{s0} for polystyrene–cyclohexane solutions resulted as shown in Figure 8b. (We have also plotted the predictions of the Vrentas–Duda theory in Figure 7b.) In no case does the predicted concentration dependence of D_s/D_{s0} fit either Blum's data[38] for D_s/D_{s0} or our data for k_q/k_{q0} over the whole range of concentration studied. (No discussion of errors was given in ref 38, and thus it is unclear whether any of the three predictions using the Vrentas–Duda theory is within the range of error of Blum's data.) For the case when $K_{11}(K_{21} + T - T_{g_1})/\gamma = 0.253$, the predicted concentration dependence appears to fit Blum's data[38] up to about 300 g/L; however, above 300 g/L the predicted values are significantly lower than the values of D_s/D_{s0} from Blum's study.

This apparent slight disagreement between our estimates of the predicted values from the Vrentas–Duda theory and the experimental data on D_s/D_{s0} and k_q/k_{q0} should not be interpreted as meaning that the Vrentas–Duda theory is invalid in the case of polystyrene–cyclohexane solutions. Obviously, in order to make firm conclusions, further work must be done not only to obtain the exact parameters for use in the Vrentas–Duda theory but also to determine whether our data or Blum's data more accurately represent the true polystyrene concentration dependence on the cyclohexane self-diffusion coefficient.

C. Analysis by the Fujita–Doolittle Theory. Cohen and Turnbull[51,52] determined that the self-diffusion coefficient could be related to the free volume of a system by the following:

$$D_s = A \exp(-B/V_f) \tag{7}$$

where A and B are constants and V_f is the free volume of the system. For polymer–diluent systems, Fujita[2] proposed that

$$V_f = V_p + b\phi_s \tag{8}$$

where V_p is the free volume of the pure polymer, b is a constant, and ϕ_s is the volume fraction of the solvent. With this assumption of a linear relationship between free volume of the system and volume fraction of the solvent or diluent, Fujita derived the following relationship:[2]

$$\frac{1}{\ln (D_s/D_{sp})} = \frac{V_p}{B} + \frac{V_p^2}{Bb}\frac{1}{\phi_s} \tag{9}$$

where D_{sp} is solvent self-diffusion coefficient in the limit of zero solvent volume fraction (pure polymer).

A slight modification of eq 8 may be obtained by proposing a reference solvent volume fraction, ϕ_r:

$$V_f = V_r + a(\phi_s - \phi_r) \tag{10}$$

where V_r is the free volume at the reference state and a is a constant. With eq 10 the following relationship may be derived:

$$\frac{1}{\ln (D_s/D_{sr})} = \frac{V_r}{B} + \frac{V_r^2}{Ba}\left(\frac{1}{\phi_s - \phi_r}\right) \tag{11}$$

where D_{sr} is the solvent self-diffusion coefficient in the reference state. Equation 11 is equivalent to eq 9 if the reference state is taken to be the system at zero solvent concentration.

Figure 9 shows our attempts to fit our k_q data (substituting k_q for D_s in eq 11 for our polystyrene solutions) to a Fujita–Doolittle analysis. In both parts of the figure, the bimolecular quenching rate constant data fail to make sense based on the Fujita–Doolittle free volume theory.

In Figure 9a, a straight line dependence between 1/ln (k_q/k_{qr}) and $1/(\phi_s - \phi_r)$ is not obtained for the 47 500 MW polystyrene–cyclohexane solution with 560 g/L as the reference concentration ($\phi_r = 0.467$) nor for the 4000 MW polystyrene–cyclohexane solution with 300 g/L as the reference concentration ($\phi_r = 0.714$). (When higher polymer concentrations are chosen as reference states for the 4000 MW solution, a straight line dependence is not readily apparent but cannot be ruled out due to large error bars.) This is clearly contradictory to the dependence predicted by eq 11. We should also note that Blum's data[38] for D_s in polystyrene–cyclohexane solutions fail to yield a straight line when plotted according to eq 11. While it might be argued that Blum's data and/or our data may be slightly inaccurate given that the two sets of data disagree slightly with respect to their dependence on polystyrene concentration, it is nevertheless significant that neither set of data yields a straight line when a moderate or high polystyrene volume fraction is used as the reference state. A straight line dependence is obtainable only when a low polystyrene volume fraction is used for the reference state.

In Figure 9b, a straight line dependence based on eq. (11) is obtained for the 4000 MW and 47 500 MW polystyrene–toluene systems when the reference state is taken to be 400 g/L polystyrene ($\phi_r = 0.619$). A straight line dependence is obtained as well when a lower concentration (300 g/L) is used as the reference state. (It is significant that the straight line dependence is evident from the symbols alone and that the calculated errors may in fact overestimate the true error in the data.) However, when the intercepts are determined for the two reference states, an unphysical result may be obtained. According to eq 11, the intercept from Figure 9b can be interpreted as being proportional to the free volume of the reference state. As the intercept is smaller for the 300 g/L reference state than for the 400 g/L reference state, this implies that free volume increases as the polymer concentration is increased. Such a result does not make physical sense. While it may be argued that on the basis of the size of the error bars in Figure 9b, the difference in the two intercepts may not be significant, it is noteworthy that when we plotted self-diffusion data from other studies[10,12] according to eq 11,

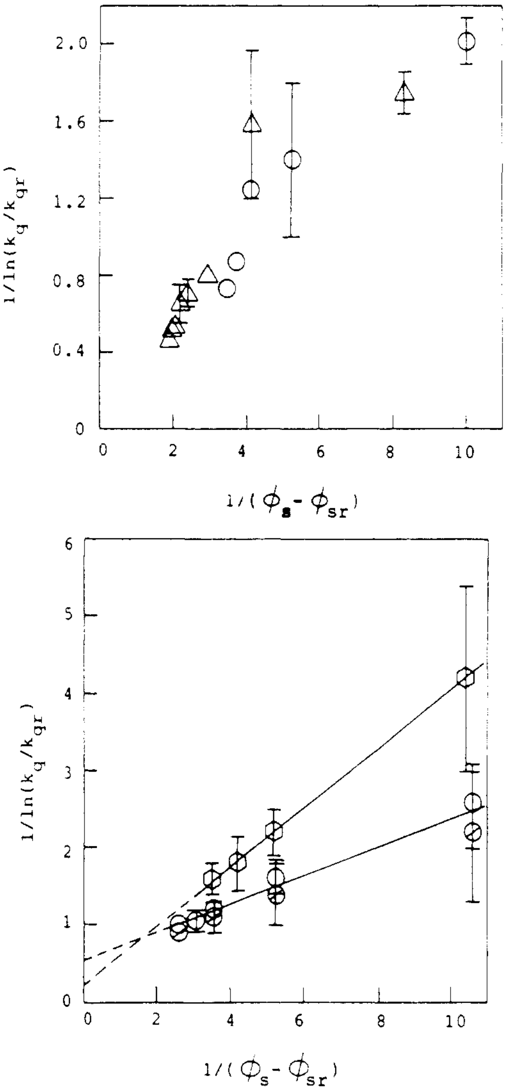

Figure 9. (a) Fujita–Doolittle free volume analysis applied to k_q values obtained for polystyrene–cyclohexane solutions: (△) 47 500 MW PS with 560 g/L as the reference state; (○) 4000 MW PS with 300 g/L as the reference state. (b) Fujita–Doolittle free volume analysis applied to k_q values obtained for polystyrene–toluene solutions: (○) 4000 MW PS with 300 g/L as the reference state; (○) 4000 MW PS with 400 g/L as the reference state; (⊘) 47 500 MW PS with 400 g/L as the reference state.

similar unphysical results were obtained. Interestingly, the conclusion reached in these other studies was that the data fit Fujita–Doolittle theory (even though unphysical results could be obtained). This shows that simply obtaining a straight line dependence according to eq 11 with one reference state is not sufficient to claim agreement with the Fujita–Doolittle theory. We note that Fujita[2] himself indicated that his theory should be applicable only at very high polymer concentrations ($c > 85\%$), and it appears that the results of this study and reinterpretation of other studies bear out the fact that indiscriminate use of the Fujita–Doolittle theory is not advisable over a wide range of low and intermediate polymer concentrations.

Summary

Phosphorescence quenching techniques have been used successfully to determine the effects of polymer species, molecular weight, concentration, and solvent on diffusion-limited interactions in polymer solutions. The normalized bimolecular quenching rate constants, k_q/k_{q0}, obtained in these studies were observed to scale with the normalized solvent self-diffusion coefficient, D_s/D_{s0}. The Vrentas–Duda theory for solvent self-diffusion coefficients was compared to experimental data from several of our polymer solutions and was found to predict the basic polymer concentration dependence of k_q. In contrast, application of the Fujita–Doolittle theory to our data led to either an unsatisfactory correlation or possibly unphysical predictions about the polymer concentration dependence of free volume. Our studies are currently being extended to small molecule–polymer and polymer–polymer diffusion-limited interactions in polymer solutions in order to quantify how placement of a label on a polymer chain affects the interaction. It is anticipated that k_q will be much lower for these interactions not only because of the reduced diffusion of the label when attached to the polymer but also because of screening effect by the polymer chain itself.

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Registry No. Benzil, 134-81-6; anthracene, 120-12-7; polybutadiene, 9003-17-2; polystyrene, 9003-53-6; poly(methyl methacrylate), 9011-14-7.

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Chain Conformation in Ternary Polymer Solutions

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ABSTRACT: This paper presents a theoretical study on chain conformation of a solute polymer P in a mixture of different chemical species A and B, where A is a good solvent and B is a nonsolvent or an incompatible polymer. In the case of B being a nonsolvent, particular attention is drawn in the vicinity of the critical point of the A/B solvent mixture. On the basis of a lattice theory extended to inhomogeneous three-component polymer systems, it is found that the polymer chain P is swollen in the concentration region close to the critical demixing point. We present quantitative calculation and compare it with the experimental results obtained for the poly(tetrahydrofuran)/methanol/cyclohexane system. In the case of B being an incompatible polymer, polymer P collapses as the concentration of polymer B is increased. The nature of the transition is theoretically studied. We find that the transition is easier when the B chain becomes longer and is sharper when the length of the B chain relative to that of P becomes smaller.

1. Introduction

Recent experimental data[1] show that a polymer dissolved in a mixture of a good solvent and a poor one swells near its critical demixing point. On the other hand, theoretical analyses[2] of ternary polymer solutions suggested that effective interaction induced by critical fluctuation is, for most practical situations, attractive irrespective of the solvent nature. It was also theoretically claimed[3] that, in the case of a mixture of two good solvents, there is a collapse just above the critical point and a reswelling exactly at T_c. This poses a rather puzzling situation. As for single-polymer conformation in three-component solutions, coil-to-globule transition induced by the existence of incompatible polymers has recently received considerable attention.[4-11] Very little is known, however, about the influence of the concentration on the nature of the transition.

The present paper describes spatial dimensions of a polymer chain (P) dissolved in a mixture of a good solvent (A) and a nonsolvent (B). While A is always assumed to be a monomolecular solvent, B is allowed to be a polymer. We assume, however, that N, the degree of polymerization (DP) of P, is larger than n, that of B.

We study, from a unified point of view, the following two environments:

(i) In the case where B is a low molecular weight species we focus our attention to the region in the vicinity of the critical demixing point of an A/B mixture. We find that in the critical region, where the free energy of the mixed solvent is in a limit of stability, the P chain swells to nearly twice its size in the pure A solvent. This fact indicates that instability in the background medium induces effective repulsion between the polymer segments.

(ii) In the case where the DP of B is larger, we focus our attention on the concentration region where B polymers begin to overlap. It is shown that the P chain shrinks to a compact globule for sufficiently large B concentration. The transition from a swollen random coil to a compact globule due to the existence of B chains becomes easier as n becomes larger, while it becomes sharper as n/N becomes smaller.

For the first problem, de Gennes[2] predicted through certain intuitive arguments that the indirect interaction between two segments of a polymer chain, for most practical situations, results in an attractive and long-range interaction. Hence a polymer chain must contract in the critical region. The viscometric measurement by Dondos and Izumi,[1] however, showed quite opposite behavior of a polymer chain, poly(tetrahydrofuran) (PTHF), in the mixed solvent methanol/cyclohexane. Reduced viscosity of PTHF exhibited clear peaks at the critical concentration for temperatures near the critical value when methanol fraction was increased. We therefore examine this problem once again from a statistical-mechanical point of view. For

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