4160 *Macromolecules* 1992, *25*, 4160–4166

Diffusion-Limited Polymer–Small Molecule Interactions: A Study of Phosphorescence Quenching

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Received August 7, 1991; Revised Manuscript Received April 24, 1992

ABSTRACT: Diffusion-limited interactions between benzil- and anthracene-labeled polystyrene were studied by phosphorescence quenching in polystyrene–toluene solutions. Values of the bimolecular diffusion-limited quenching rate constant, k_q, were obtained by measuring the benzil phosphorescence lifetime as a function of anthracene moiety concentration and applying a Stern–Volmer analysis. In the case of interactions of benzil with anthracene which was labeled randomly to phenyl groups along the polystyrene chain (RAPS), k_q is approximately one-third the value of k_q for the benzil–anthracene interaction over a broad range of *unlabeled polystyrene concentration, from 0 to at least 400 g/L*. This indicates that the physics controlling the polystyrene concentration dependence of the benzil–anthracene interaction also controls the polystyrene concentration dependence of the benzil–RAPS interaction in toluene solution. For both interactions, the Vrentas–Duda free volume theory for D_s, the solvent self-diffusion coefficient, predicts quantitatively the polymer concentration dependence of k_q, with $k_q/k_{q0} = D_s/D_{s0}$ where the subscript 0 denotes the value at zero polymer concentration. In contrast to the significant effect of polymer concentration, k_q was found to have little dependence on the polymer molecular weight. Benzil–RAPS interactions are compared to interactions of benzil with anthracene which is labeled at the terminus of the polystrene chain (TAPS), showing that the differences in the photophysical properties of RAPS and TAPS should be considered, along with other factors, in making conclusions about the effect of anthracene moiety placement on these interactions.

Introduction

Diffusion-limited interactions between polymers and small molecules in polymer solutions have been the subject of considerable study over the last 2 decades.[1–28] By investigating the effects of solvent, temperature, polymer molecular weight, and polymer concentration on these interactions, several important phenomena and properties such as photodegradation,[14–17] photooxidation,[18,19] structure of polymer colloids,[20,21] and propagation reactions in high-conversion, free-radical polymerization[1,2] can be better understood. Phosphorescence quenching is a well-known diffusion-limited interaction[28–32] that is appropriate in investigating the effects of environment on diffusion-limited interactions. Horie and Mita successfully used phosphorescence quenching to study diffusion-limited interactions in polymer systems; the interactions studied by them include small molecule–small molecule,[33] polymer–small molecule,[11,13,34,35] and polymer–polymer.[13,34–37] More recently, Yu and Torkelson[38] have investigated small molecule–small molecule interactions in polymer solutions by phosphorescence quenching while Gebert and Torkelson[39] are using similar approaches to study polymer–polymer interactions in related systems.

The rate constant of a diffusion-limited reaction or interaction may be related to the sum of the diffusion coefficients of the molecular or moieties undergoing interaction. For polymer–small molecule interactions, since the diffusion coefficients of polymers or moieties located on polymers are in general much less than those of small molecules, the interaction rate may be expected to be dominated by the diffusion of small molecules. Kirsh et al.[12] studied the interaction between small molecules and polymers by fluorescence quenching. They found that values of the quenching rate constant for polymer–small molecule interactions were approximately half those of small molecule–small molecule interactions. Given that a polymer diffuses much more slowly than a small molecule and assuming that the diffusion coefficients of the chromophore and quencher are approximately the same, the modified Smoluchowski equation[28,29] shown below predicts that the quenching rate constant, k_q, of a polymer–small molecule interaction should be approximately half that of a small molecule–small molecule interaction:

$$k_q = 4\pi R\rho(D_c + D_q) \tag{1}$$

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 chromophore and quencher, respectively.

Many theories have been used to describe the diffusion of small molecules in polymer solutions including the Fujita–Doolittle theory[40] and the Vrentas–Duda theory.[41–46] In studies of the effect of polymer concentration on diffusional processes in polymer solutions, the Vrentas–Duda free-volume theory has been shown to be adequate for modeling both the self-diffusion coefficient of solvent in polymer solutions[44,47,61,62] and the phosphorescence quenching rate constant of small molecule–small molecule interactions in certain polymer solutions.[38] In the current study, the application of Vrentas–Duda free-volume theory will be extended to model the concentration dependence of polymer–small molecule interactions in polystyrene–toluene systems.

It should be noted that for the interaction between a small molecule and a specific moiety attached to a polymer, the effect of the position of the moiety on the polymer may not be negligible. Phosphorescence quenching is potentially a most appropriate method to study the effect of moiety placement as the quenching interaction is specific to a particular quencher–chromophore pair. Horie and Mita[11,35] studied the phosphorescence quenching of benzil with an anthracene label located either at the chain end (one or both chain ends) or at the center of polystyrene in different solvents. They found that there was a

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0024-9297/92/2225-4160$03.00/0

significant decrease in the interaction of benzil with an anthracene unit located at the chain center as compared to the anthracene unit located at the chain end. This decrease was greater in poor solvent than in good solvent. They attributed this difference to a much smaller diffusion coefficient of the benzil inside the polymer coil as compared to that outside the coil.

In the present study, phosphorescence quenching rate constants for interactions involving benzil with an anthracene moiety attached randomly to a phenyl unit off the polystyrene backbone were determined in dilute and semidilute polystyrene–toluene solutions as a function of inert (unlabeled) polystyrene matrix concentration and molecular weight. The Vrentas–Duda free-volume theory modeled adequately the concentration dependence of these interactions. Comments are also made with regard to differences observed between interactions involving benzil and randomly anthracene-labeled polystyrene (RAPS) and those involving benzil and terminally anthracene-labeled polystyrene (TAPS).

Experimental Section

Monodisperse polystyrene of 4000, 35 000, 47 500, 90 000, 152 000, 207 000, 670 000, and 1 800 000 molecular weight from Pressure Chemical was used as the inert polymer matrix. Benzil phosphorescence lifetime was measured in polymer solution with purified and unpurified matrix polymer; as no significant difference was found, the polystyrene was used without further purification.

The detailed procedure for synthesizing, purifying, and characterizing RAPS is described elsewhere.[48] RAPS used in this study was approximately 35 000 MW (nearly monodisperse polystyrene was used as the starting material) and had an average of 1 anthracene unit/77 repeat units as determined by UV–visible absorbance spectroscopy.

Terminally anthracene-labeled polystyrene (TAPS) was prepared by adding 9-(chloromethyl)anthracene to a living polystyryl monoanion prepared by anionic polymerization. Anionic polymerization was performed under N_2 gas with a modified "capped-bottle" technique[39,49–51] using *n*-butyllithium as the initiator and cyclohexane as the solvent. TAPS was purified and dried by the same method as RAPS but with dichloromethane used for dissolution. The number-average molecular weights of the two TAPS samples were determined by gel permeation chromatography[52] to be 18 000 (M_w = 24 000) and 101 000 (M_w = 114 000) using a Waters Baseline 180 chromatography workstation. The weight fraction of labeled polystyrene was found to be 0.54 for the 18K TAPS and 0.17 for the 101K TAPS by using UV–visible absorbance spectroscopy.[51]

Sample solutions were prepared by weighing the desired amount of inert polymer into a 5-mL volumetric flask with 1×10^{-3} M benzil concentration and adequate quencher polymer, RAPS or TAPS, in toluene solution. Typically, the concentrations of RAPS or TAPS used as quencher were 0.01–0.1 g/L. Samples were shaken for several hours and sat for at least 1 day to obtain a homogeneous solution. Prior to phosphorescence measurement, all samples were treated by seven freeze–pump–thaw cycles in order to remove dissolved oxygen; samples then remained for several hours at room temperature and were then shaken to obtain a "relaxed" polymer solution. The procedure of shaking the samples to "relax" them is necessary to accelerate removal of the effects of phase separation and aggregation of polystyrene chains during the freezing of polystyrene–toluene solutions.[53]

The phosphorescence lifetime of benzil at ambient temperature was measured by a SPEX fluorescence spectrophotometer with a phosphorescence attachment. The quenching rate constant, k_q, was calculated by the Stern–Volmer equation[30]

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

where τ and τ_0 are the phosphorescence lifetimes obtained from the decay curves in the presence and absence of quencher, respectively. [Q] is the quencher concentration which is the anthracene moiety concentration of RAPS or TAPS. The method to obtain τ and the analysis of k_q are the same as those in the study of diffusion-limited interactions done by Yu and Torkelson[38] and Gebert and Torkelson.[39] Sample excitation was achieved by a xenon lamp pulse at 400 nm while the phosphorescence decay of benzil was observed at 560 nm. Generally, five or six 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 1–4 all error bars are calculations based on Student's distribution (the *t* distribution) at an 80% confidence level. For data without error bars, the calculated errors are less than the size of the symbols.

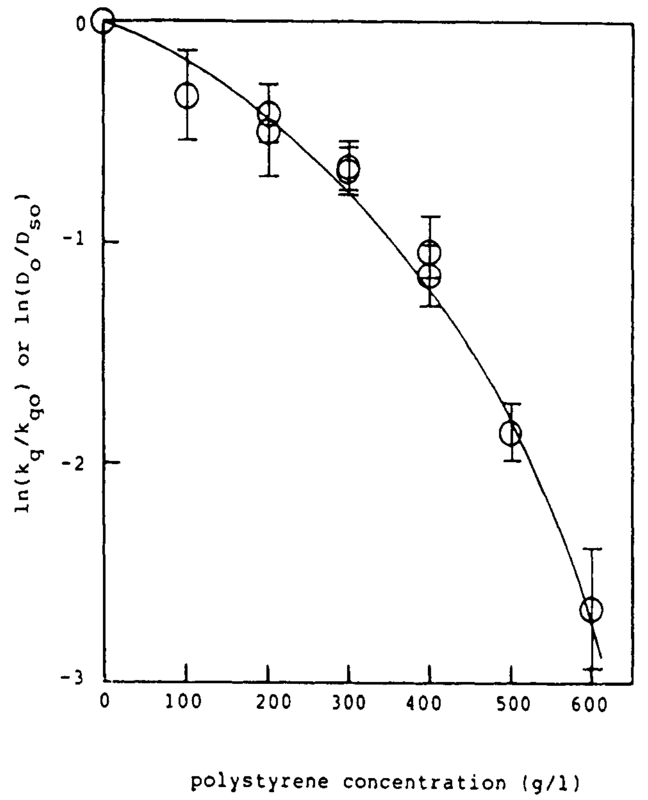

Figure 1. Comparison of experimental data for ln (k_q/k_{q0}) for the benzil–RAPS interaction with ln (D_s/D_{s0}) predicted by the Vrentas–Duda free volume theory for the polystyrene–toluene system. The smooth curve is the prediction of the Vrentas–Duda theory.

Results and Discussion

A. Benzil–RAPS Diffusion-Limited Interactions. k_q for the benzil–RAPS diffusion-limited interaction was measured in nearly monodisperse 4000 MW inert polystyrene matrix solutions using toluene as the solvent; the inert polystyrene concentration ranged from 0 to 600 g/L. Results are shown in Table I and Figures 1 and 2. Table I compares the k_q's obtained from the polymer–small molecule interactions with those of small molecule–small molecule (benzil–anthracene) interactions[38] in solutions at the same polystyrene concentration. The values of k_q in parentheses in Table I are from a second experimental run showing very good precision. (The excellent precision of the measurements suggests that the true error associated with the data is smaller than that estimated by use of Student's distribution at an 80% confidence level in calculating the error associated with individual k_q determinations.)

Table I illustrates several interesting points concerning small molecule–polymer diffusion-limited interactions. The first is that the attachment of the anthracene moiety to the polymer in the production of RAPS results in a reduction of k_q to approximately one-third the value of k_q

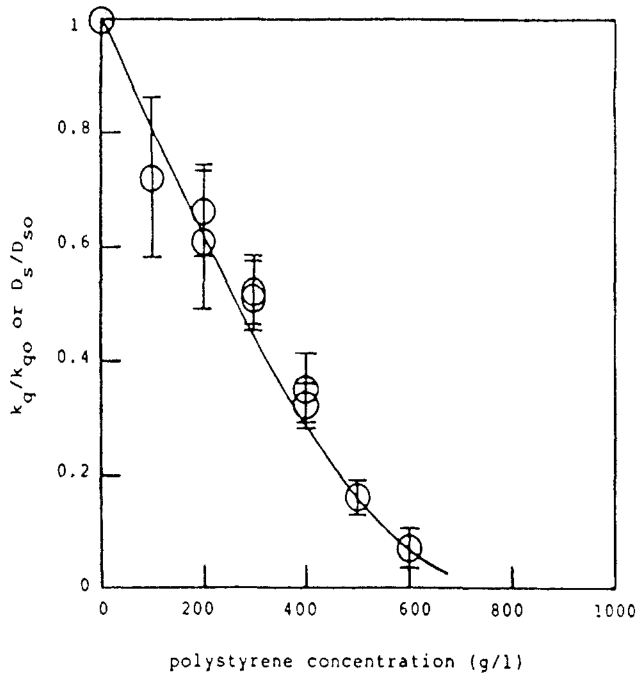

Figure 2. Comparison of experimental data for k_q/k_{q0} for the benzil–RAPS interaction with D_s/D_{s0} predicted by the Vrentas–Duda free volume theory for the polystyrene–toluene system. The smooth curve is the prediction of the Vrentas–Duda theory.

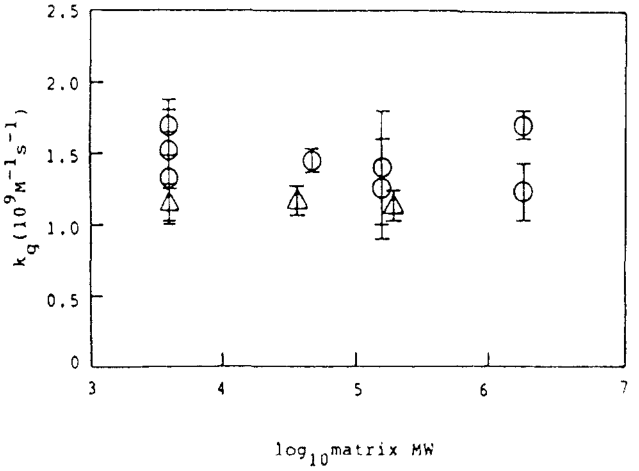

Figure 3. Values of k_q for benzil–RAPS interaction in polystyrene–toluene solution with different inert polystyrene molecular weight. Polymer concentration: (○) 50 g/L; (△) 150 g/L.

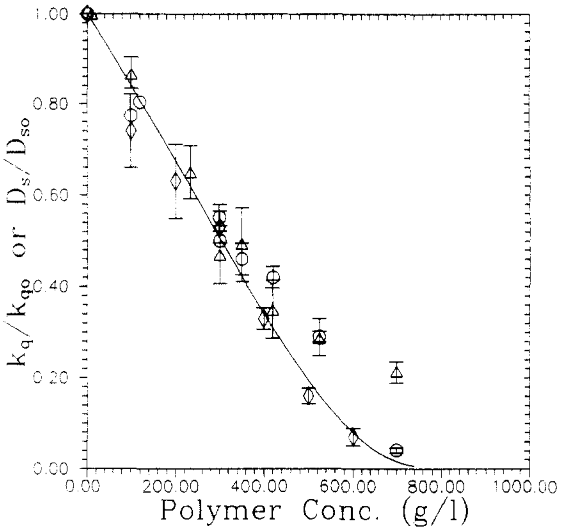

Figure 4. Comparison of experimental data for k_q/k_{q0} benzil–TAPS interaction with benzil–RAPS interaction as a function of polystyrene concentration: (◇) benzil–35K RAPS interaction; (○) benzil–18K TAPS interaction; (△) benzil–101K TAPS interaction. The smooth curve is the prediction of the Vrentas–Duda theory.

for the benzil–anthracene interaction. Assuming that the diffusion coefficient of the anthracene moiety on the RAPS molecule is reduced very significantly in comparison to the diffusion coefficient of anthracene, this suggests that the diffusion coefficient of anthracene in polystyrene–toluene solutions is approximately twice that of benzil in the polystyrene–toluene solutions, ignoring other effects. Recent k_q results[39a] obtained for benzil–anthracene interactions and benzil-labeled polystyrene–anthracene interactions in polystyrene–cyclohexane solutions show that, upon attachment of the benzil moiety to the polymer, k_q reduces to approximately two-thirds the value of k_q for the benzil–anthracene interaction. This result also suggests that anthracene diffuses approximately twice as fast as benzil in polystyrene–cyclohexane solutions.

The second point of interest in Table I is that the ratio of k_q for the benzil–RAPS interaction, k_q(B–RAPS), to k_q for the benzil–anthracene interaction, k_q(B–A), remains constant at approximately one-third over a very broad range of inert polystyrene concentration. This indicates that the physics controlling the polystyrene concentration dependence of the benzil–anthracene interaction also controls the polystyrene concentration dependence of the benzil–RAPS interaction in toluene solution. This necessarily implies that attachment of the anthracene moiety to polystyrene in the manner employed in synthesizing RAPS in no way alters the concentration dependence of the benzil–anthracene moiety interaction in toluene.

In the earlier analysis of the benzil-anthracene interaction, it was found[38] that the Vrentas–Duda free volume theory[41–46] for the solvent self-diffusion coefficient, D_s, correlated well with the polystyrene concentration dependence of k_q(B–A) measured in toluene solution. (Similar excellent agreement was found by Yu and Torkelson[38] between the concentration dependence of experimental measures[54,55] of D_s for polystyrene–toluene solutions and the concentration dependence of k_q(B–A).) As the analysis of k_q data by the Vrentas–Duda free volume theory has been fully covered in ref 38, a complete discussion of the analysis of k_q by the free volume theory will not be repeated here.

However, some important facts result from investigating the validity of a free volume theory to model the polymer concentration dependence of diffusion-limited interactions between probe molecules in a polymer–solvent–probe system. It is known[38,43,56–62] that the self-diffusion coefficient of a probe molecule, D_p, can be related to the self-diffusion coefficient of the solvent, D_s, in a polymer–solvent–probe system by

$$\ln (D_p/D_{p0}) = \{(V^*_p m_{jp})/(V^*_s M_{js})\} \ln (D_s/D_{s0}) \quad (3)$$

where V^*_p and V^*_s are the specific critical hole free volumes of probe and solvent required for a jump, respectively, M_{jp} and M_{js} are the corresponding molecular weights of a jumping unit, and D_{p0} and D_{s0} represent the values of D_p and D_s at zero inert polymer concentration. As k_q is proportional to the sum of the self-diffusion coefficients of the chromophore and quencher moieties, it can be reasonably assumed that $k_q \sim D_p$, where $D_p = D_A + D_B$; here D_A (D_B) represents the self-diffusion coefficient of the anthracene moiety (benzil). Thus, $k_q/k_{q0} \sim D_p/D_{p0}$. Therefore, ln ($k_q/k_{q0}$), which equals ln ($D_p/D_{p0}$), is a multiplicative constant of ln (D_s/D_{s0}).

Thus, on the basis of eq 3, there is expected to be a linear relationship between ln (k_q/k_{q0}) and ln (D_s/D_{s0}).

Table I
Comparison of the Concentration Dependence of k_q's for Benzil–Anthracene, Benzil–RAPS, and Benzil–TAPS Interactions in Polystyrene (PS)–Toluene Solutions

	k_q (10^9 L/mol·s)					
PS conc (g/L)	benzil–anthracene[a]	benzil–RAPS[b]	k_q(B–RAPS)[c]/ k_q(B–A)	benzil–TAPS[d]	benzil–TAPS[e]	k_q(B–TAPS)[f]/ k_q(B–A)
0	5.6	1.98	0.35	2.34 (2.31)[g]	2.45	0.42
100	4.48	1.47	0.33	1.81	2.12	0.44
200	3.83	1.24 (1.21)[g]	0.32			
300	3.02	1.04 (1.06)[g]	0.34	1.17 (1.29)[g]	1.15	0.40
400	2.05	0.65 (0.64)[g]	0.32	0.97	0.86	0.45
500		0.32				
525				0.68	0.70	
600		0.14				
700				0.10	0.52[h]	

[a] Data taken from ref 38. [b] 35K MW RAPS with 4K MW unlabeled matrix PS. [c] k_q (benzil–RAPS)/k_q (benzil–anthracene). [d] 18K MW TAPS with 4K MW unlabeled matrix PS. [e] 101K MW TAPS with 90K MW unlabeled matrix PS. [f] k_q (benzil–TAPS)/k_q (benzil–anthracene) – average values for all benzil–TAPS. [g] Results of a second run. [h] Results of a sample which may not be homogeneously mixed due to its extremely high viscosity. This may account for the anomalously high k_q value.

From Figure 1, these two quantities seem to be identical,[63] implying that to a good approximation $V^*_pM_{jp}/V^*_sM_{js}$ for the benzil–RAPS system is equal to 1. Given that in the benzil–RAPS system the physics of the diffusion-limited interaction is dominated by the self-diffusion coefficient of the benzil molecule, this indicates that V^*M_j for benzil and toluene are to a good approximation the same. It is interesting to note that in the previous study of benzil–anthracene diffusion–limited interactions Yu and Torkelson[38] also found that $V^*_pM_{jp}/V^*_sM_{js}$ is equal to 1. The fact that the results of this and a previous[39] study suggest that anthracene diffuses approximately twice as fast as benzil in the polystyrene–toluene solutions implies that the product $V^*_pM_{jp}$ in the benzil–anthracene system is actually a parameter which lumps effects from both anthracene and benzil diffusion, with the effect from the anthracene diffusion dominating the effect from the benzil diffusion. Using the fact from the current study that $V^*_pM_{jp}/V^*_sM_{js}$ is approximately 1 for benzil and toluene, it is then possible to conclude from the results of benzil–anthracene interactions[38] that $V^*_pM_{jp}/V^*_sM_{js}$ is approximately 1 for anthracene and toluene as well. This then allows the equating of k_q/k_{q0} with D_s/D_{s0} which is illustrated in Figure 2 using the correlative prediction of the Vrentas–Duda theory[46] for the toluene self-diffusion coefficient.[63] Figure 2 strongly reinforces the conclusion that not only is the application of the Vrentas–Duda theory valid for modeling diffusion-limited interactions between benzil and RAPS in a polystyrene–toluene solution but also the relationship between the concentration dependencies of k_q and D_s is particularly straightforward.

It is interesting to note that values of $V^*_pM_{jp}/V^*_sM_{js}$ have been found to be equal to 1 for several other probe–solvent–polymer systems[43] including C_6F_6 (hexafluorobenzene)–$C_{12}H_{26}$ (*n*-dodecane)–*cis*-polybutadiene and C_6F_6–$C_{36}H_{74}$ (*n*-hexatricontane)–*cis*-polybutadiene. Other values of $V^*_pM_{jp}/V^*_sM_{js}$ have also been determined for polystyrene–toluene–probe systems which can serve as a comparison to those determined here. Frick et al.[61,62] have determined that $V^*_pM_{jp}/V^*_sM_{js} = 1.77 \pm 0.07$ for the polystyrene–toluene–azobenzene system, somewhat greater than the values for benzil or anthracene probe systems. When a larger probe molecule of higher molecular weight is used, $V^*_pM_{jp}/V^*_sM_{js}$ becomes much greater than 1. This is the case for the polystyrene–toluene–methyl red system studied by Huang et al.[58] where $V^*_pM_{jp}/V^*_sM_{js} = 1.96 \pm 0.12$ and for the polystyrene–toluene–aberchrome 540 system studied by Frick et al.[61,62] where $V^*_pM_{jp}/V^*_sM_{js} = 4.92 \pm 0.17$.

k_q for benzil–RAPS was also measured as a function of the polymer matrix molecular weights. Solutions with 50 g/L concentrations of nearly monodisperse polystyrene of 4000, 47 500, 152 000, 670 000, and 1 800 000 molecular weight and with 150 g/L concentrations of 4000, 35 000, and 207 000 molecular weight were prepared for the measurements. The effects of polymer matrix molecular weight are shown in Figure 3. It is found that there is no significant polymer matrix molecular weight dependence on the benzil–RAPS interaction over almost 3 decades of polymer molecular weight for 50 g/L solutions and 2 decades of polymer molecular weight for 150 g/L solutions. This agrees with the fact that the benzil–RAPS interaction is dominated by benzil diffusion and that small-molecule diffusion is not affected significantly by polymer matrix molecular weight. This is consistent with results obtained by Bai et al.[23] on small molecule–polymer interactions and with the very minor polymer molecular weight effects observed in the benzil–anthracene interactions studied earlier by Yu and Torkelson.[38]

B. Benzil–TAPS Diffusion-Limited Interactions. k_q for the benzil–TAPS diffusion-limited interaction was measured for two molecular weights of TAPS: 18 000 and 101 000. For the 18 000 MW TAPS sample, nearly monodisperse 4000 MW inert polystyrene was used for the matrix, while for the 101 000 MW TAPS sample, nearly monodisperse 90 000 MW inert polystyrene was used for the matrix. Inert polystyrene concentrations studied range from 0 to 700 g/L. Results are shown in Table I and Figure 4.

From Table I it is observed that, at zero inert polymer concentration, k_q(B–TAPS) for both samples of TAPS is slightly larger than k_q(B–RAPS). From the point of view of self-diffusion, these small differences are unexpected. If k_q is dominated by small-molecule self-diffusion, then k_q(B–TAPS) for both molecular weights of TAPS should be about the same as k_q(B–RAPS); if polymer self-diffusion plays any measurable role in k_q, then k_q(B–TAPS) for the 101 000 MW TAPS system should be smaller, not greater, than k_q(B–RAPS) and much smaller than k_q(B–TAPS) for the 18 000 MW TAPS system.

One potential explanation for the slightly higher values of k_q(B–TAPS) as compared to k_q(B–RAPS) is related to the notion that polymer chain ends are substantially more mobile than inner chain segments (to which the anthracene moieties are attached in the case of RAPS) due to the less restrictive chain connectivity requirements associated with chain ends. Thus, it would be expected that end labels would explore more volume than labels attached to interior

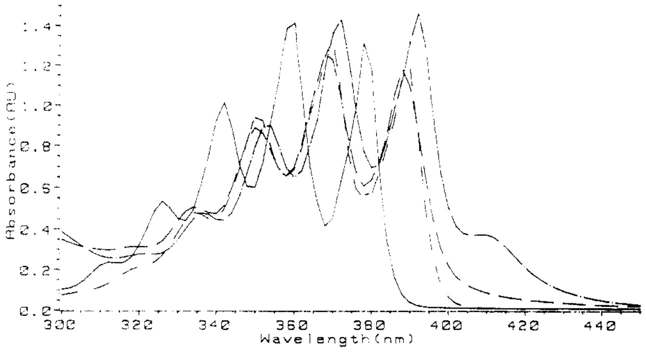

Figure 5. UV absorbance spectra of (— —) 35K MW RAPS, (- · -) 18K MW TAPS, (- - -) 9-methylanthracene, and (—) anthracene in toluene.

segments, resulting in slightly higher k_q values. If this explanation solely is used to account for the different k_q values for the RAPS and TAPS systems, the results in Table I suggest that the effective self-diffusion coefficient of anthracene attached to chain ends is reduced by 87% (from 2.0 to 0.26 times the free benzil self-diffusion coefficient) relative to its unattached (or free probe) value. This would imply that while the mobility of anthracene is strongly attenuated upon attachment to a chain end, it is not entirely negligible.

Another potential explanation for these differences relates to the result by Horie and Mita,[11,35] who observed a lower k_q for benzil interacting with an anthracene moiety labeled centrally on a polystyrene chain as compared to benzil interacting with end-labeled polystyrene. They explained these differences as being associated with different screening effects in the two polymers, with a much smaller effective diffusion coefficient for benzil inside the polymer coil as compared to outside the coil. At present we have no independent experimental data to indicate that the differences in our RAPS and TAPS results can be associated with differences in screening effects. However, we note that screening is likely to play some role in the observed differences.

Using an approach described by Ediger and co-workers,[64] it is possible to estimate in dilute solution the local concentration of polymer segments in the immediate neighborhood of the chain center to be approximately 30% of the bulk polymer concentration for the molecular weights of polystyrene employed here and in the studies by Horie and Mita.[11,35] On the basis of our previous small molecule–small molecule (benzil–anthracene) interaction studies,[38] an increase in the polystyrene concentration from 0 to 30 wt % in toluene solution results in a reduction of k_q by 40–50%. This type of reduction in k_q was observed by Horie and Mita[11,35] in center-labeled systems relative to end-labeled systems in dilute solution. Thus, it appears that not only the bulk concentration of the polymer but also the local concentration of chain segments must be considered in interpreting k_q data. Qualitatively, the local concentration of polymer segments in the vicinity of an anthracene moiety should obey the following order: centrally labeled > RAPS > TAPS. It should be noted that even very modest increases in the local concentration of chain segments in the vicinity of an anthracene moiety in RAPS systems as compared to TAPS systems could produce the type of differences in k_q illustrated in Table I.

Finally, a third explanation of our results may be related to the different photophysical characteristics of RAPS and TAPS as evidenced by the difference in their absorbance spectra, shown in Figure 5. As explained in section C of this paper, such differences may be associated, at least in part, with a difference in the effective encounter radius for the benzil and anthracene moiety interaction. As is evident from eq 1, any change in the photophysical characteristics of the anthracene moiety due to differences in labeling techniques which changes R will also provide a concomitant change in k_q.

Figure 4 and Table I compare k_q's of the benzil–TAPS interaction to those of the benzil–RAPS interaction as functions of inert polystyrene concentration. It is apparent that at least up to 500 g/L there is fairly good agreement in the concentration dependence between the two TAPS systems and the RAPS system.

In the 600–700 g/L concentration range, the 101 000 MW TAPS system apparently has a much larger k_q/k_{q0} than either the 18 000 MW TAPS system or the 35 000 MW RAPS system. This discrepancy is potentially due to inhomogeneity in the 101 000 MW, 700 g/L polymer solution sample.[65] Obtaining a well-mixed sample is often difficult at high polymer concentrations and high polymer molecular weights where the very high viscosity of the solutions interferes with the mixing. (This is made all the more difficult here in this study where the solutions are treated to multiple freeze–pump–thaw cycles; polystyrene–toluene solutions phase separate[53] before reaching their freezing temperature in the freeze–pump–thaw processing.) Some researchers[60–62] have allowed their highly concentrated polymer solution samples to sit at elevated temperature for several weeks before a truly uniform sample was achieved. We have opted not to use such measures here because the thermal stability of the benzil and anthracene probes in solution under such conditions is questionable.[51,66] This may prove to be a limiting factor in studying diffusion-limited interactions in extremely concentrated, high molecular weight polymer solutions using the phosphorescence quenching technique.

From Figure 4 and Table I, it is also observed that, at least up to the 400–500 g/L concentration range, the concentration dependence of the benzil–TAPS interaction correlates as well with the Vrentas–Duda theory for solvent self-diffusion as the benzil–RAPS interaction. Thus, at least for the labeling techniques and solvent employed here, the observed dynamics of the interaction are not strongly dependent on label location. However, given some of the strong effects of label location observed by Horie and Mita[11,35] using end- and center-labeled polystyrenes, future studies of small molecule–polymer interactions will be undertaken employing randomly, terminally, and centrally labeled polystyrene as functions of molecular weight and thermodynamic solvent quality. These studies will determine the relative roles of label photophysical characteristics and polymer screening effects on observed differences in the interaction dynamics of such systems. Polymer–small molecule interactions will also be undertaken involving anthracene- and benzil-labeled polymers.[39a] This may eliminate or lessen the difficulties arising in comparing the results of polymer–small molecule interactions found with the RAPS and TAPS materials here, associated with differences in their photophysical characteristics.

C. Effect of Photophysical Characteristics of Anthracene-Labeled Polystyrene. As suggested in the previous section, the somewhat larger values (at any polymer concentration) of k_q(B–TAPS) as compared to k_q(B–RAPS) may be associated, at least in part, with differences in the photophysical characteristics of the TAPS and RAPS molecules. These differences are evident in Figure 5. Shown in Figure 5 are the singlet absorption

Table II
Emission and Absorption Maxima for Substituted Anthracenes[a]

	singlet absorption $(S_0 \rightarrow S_1)$[67]		singlet emission $(S_1 \rightarrow S_0)$[67]		triplet absorption $(S_0 \rightarrow T_1)$[29]	
anthracene	λ_{max}	$\Delta\lambda_{max}$	λ_{max}	$\Delta\lambda_{max}$	λ_{max}	$\Delta\lambda_{max}$
unsubstituted	357.0	0.0	400.0	0.0	672.5	0.0
9-nitro					683.5	11.0
9-methyl	366.0	9.0	410.0	10.0	691.6	19.1
9,10-dimethyl			427.5	27.5		
9,10-diphenyl	373.0	16.0	430.0	30.0		
RAPS[b]	366.0	9.0	414.0	14.0		
TAPS[b]	372.0	15.0	417.0	17.0		

[a] Units of absorption and emission maxima and shifts are in nanometers. [b] Experimental results from this study.

spectra of TAPS, RAPS, 9-methylanthracene, and anthracene in toluene. In the case of RAPS, the shapes of the major absorbance peaks resemble those[67] of anthracene and 9-methylanthracene, with the absorbance spectrum of RAPS red-shifted about 10 nm from that of anthracene and about the same as that of 9-methylanthracene. In contrast, the absorbance spectrum of TAPS has a red shift of about 5 nm as compared to the absorbance spectrum of 9-methylanthracene and exhibits an additional (but weaker) peak at about 410 nm not present in the absorbance spectra of anthracene, 9-methylanthracene, or RAPS. This difference in the absorbance spectra of TAPS and 9-methylanthracene has been confirmed from earlier syntheses and characterizations of TAPS and of isoprene–styrene diblock copolymers with anthracene attached at the terminal styrene unit.[39,51]

As the benzil phosphorescence quenching by the anthracene moiety is due to triplet–triplet energy transfer,[11,13,34] it is not possible to argue directly that the differences in the absorbance spectra shown in Figure 5 of TAPS and RAPS are responsible for different encounter radii R of the benzil and anthracene moieties, thereby resulting in different k_q's. In triplet–triplet energy transfer, the ability of energy to be transferred (related to R and k_q in phosphorescence quenching) is associated with the overlap of the phosphorescence spectrum of the donor (benzil) with the absorption spectrum (from ground state to excited triplet state[29]) of the acceptor (anthracene moiety). The absorption spectra shown in Figure 5 represent ground-state to excited singlet state absorption and not ground-state to excited triplet state absorption.

However, as can be seen from Table II red shifts in singlet absorption spectra of the type shown in Figure 5 are associated with red shifts in ground-state to triplet-state absorbance. Table II illustrates the fact that if a functional group on a molecule such as anthracene causes a red shift in the singlet absorption spectrum, one can expect that this substituted molecule will also exhibit red shifts in both the singlet emission and triplet absorption spectra. For example, anthracene and 9-methylanthracene which exhibit different absorbance spectra in Figure 5 also have a different ground-state to triplet-state absorbance; for anthracene[29] the ground-state to first excited triplet state peaks are located at 565, 613, 655, and 672 nm, whereas for 9-methylanthracene[29] the related peaks are red-shifted to 580, 631, 673, and 692 nm. Given that the peak in benzil phosphorescence is at about 560 nm, this red shift of the ground-state to triplet-state absorbance band of 9-methylanthracene should result in a smaller quenching rate constant for benzil–9-methylanthracene as compared to benzil–anthracene. The quenching rate constants measured for benzil interacting with anthracene and 9-methylanthracene in toluene solution at ambient temperature are 5.6×10^9 and 4.47×10^9 L/mol·s, respectively.

Horie and Mita also found differences in k_q of benzil phosphorescence quenched by anthracene (5.9×10^9 L/mol·s) and 9-methylanthracene (3.7×10^9 L/mol·s) at 20 °C in benzene solution[13] as well as in cyclohexane solution[35] (3.9×10^9 L/mol·s for anthracene and 2.8×10^9 L/mol·s for 9-methylanthracene). They ascribed[13] this difference to a steric contribution of the methyl group in 9-methylanthracene. While this may be a contributing factor, the significant red shift (away from the benzil phosphorescence peak, thus reducing overlap) in the ground-state to first excited triplet state absorption spectrum of the 9-methylanthracene as compared to anthracene should contribute to a reduction in k_q (and R) observed both by us and Horie and Mita.

Given the differences in the absorbance spectra of RAPS and TAPS shown in Figure 5, it is likely that the two systems have different ground-state to first excited triplet state absorbance spectra. Thus, small but reproducible differences in the k_q values for the RAPS and TAPS systems of the type observed in Table I should be expected purely on photophysical grounds.

Summary

The diffusion-limited interaction between a small-molecule, benzil-, and anthracene-labeled polystyrene (RAPS and TAPS) was investigated with the photophysical technique of phosphorescence quenching. For both RAPS and TAPS the quenching rate constant was found to decrease with increasing polymer concentration according to Vrentas–Duda free volume theory. The quenching rate constant was independent of polymer molecular weight both in magnitude and behavior over a wide range of polymer concentration. The quenching rate constants obtained for the TAPS systems are slightly larger than those obtained for the RAPS systems. The higher k_q's in the TAPS systems are attributable at least in part to the effects of the higher mobility of the chain ends and the screening effects resulting in a reduced interaction of benzil with interior chain segments. However, the difference in the photophysical characteristics of RAPS and TAPS also may be expected to contribute to the observed higher k_q's in the TAPS systems.

Acknowledgment. The support provided by the National Science Foundation (Contract CBT-8505299 and funding through the Presidential Young Investigator program), Northwestern University, Amoco Foundation (for a faculty initiation grant), and 3M (nontenured faculty research initiation grant) is greatly appreciated. The assistance of Mr. Steven R. Gilbert in synthesizing the RAPS is gratefully acknowledged. We also acknowledge the helpful comments of a reviewer.

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