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to a complex distribution of quenching rates for k_1 and k_{-1} on the order of $k_{\rm DM}$,[21] to collapse to Scheme I for values of k_1 and k_{-1} which are large relative to $k_{\rm DM}$.

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Registry No. (**1a**)(VAc) (copolymer), 83561-73-3; (**1b**)(VAc) (copolymer), 110864-45-4; (**1c**)(VAc) (copolymer), 110864-46-5; **2**, 110864-47-6; (**2**)(MMA) (copolymer), 115797-69-8; (**2**)(styrene) (copolymer), 110864-48-7; (**3**)(VAc)(dimethyl furmarate) (copolymer), 115797-68-7; **4a**, 83561-76-6; **4b**, 83572-93-4; **5a**, 115826-84-1; **5b**, 115797-43-8; **6**, 115797-42-7; **7**, 115797-44-9; itaconyl chloride, 1931-60-8; 1-naphthylmethanol, 4780-79-4; *trans*-cyclohexane-1,2-dicarboxylic anhydride, 14166-21-3; *cis*-5-norbornene-*endo*-2,3-carboxylic anhydride, 129-64-6; *cis*-hexahydrophthalic anhydride, 13149-00-3.

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Intermolecular Excimer Kinetics of Methyl Pyrenebutyrate in Polystyrene/Toluene Mixtures[1]

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ABSTRACT: The kinetics of excimer formation are examined for methyl 4-(1-pyrene)butyrate (1) in polystyrene/toluene mixtures containing up to 50% polystyrene by weight. By virtue of a convolution analysis of the fluorescence decay data, we recover the transient component b of the diffusion-controlled excimer formation rate coefficient, $k_1(t) = a(1 + bt^{-1/2})$. The steady-state value a was obtained by using a normal Birks' analysis of the decay curves. From these values, the diffusion coefficient of 1 is obtained as a function of polymer concentration, c. The dependence of D on c fits the simple obstacle model for diffusion.

Introduction

Pyrene excimer formation, first observed by Förster and Kasper,[3] has become a classic reaction for studying the influence of environment on diffusion-controlled processes. For example, excimer formation from pyrene dissolved in lipid membranes has been used to monitor their fluidity changes.[4] Intramolecular excimer formation in chain molecules containing pyrene groups at both ends provides a means of studying molecular and macromolecular cyclization dynamics.[5]

Here we examine a different kind of problem. We are interested in the influence of inert polymeric additives on the rate of diffusion-controlled reactions in solution. The presence of the polymer as a solute has a large effect on the bulk solution viscosity but a much smaller effect on small molecule diffusion. This influence is expressed via a change in the microscopic friction coefficient which retards diffusion. In the "obstacle model",[6] the polymer chains serve as impediments along diffusion trajectories, and in the "free volume model",[7] they reduce the free volume accessible for molecular motion.

Our objective in these experiments is not to provide any kind of definitive test of these models. These models treat self-diffusion coefficients, D_s, which are accessible through pulsed gradient NMR measurements[8] and other methods.[9] Here, we are interested in diffusion-controlled reactions and, in particular, the transient term associated with the time evolution of the distribution function of the reactants. From this data, we can extract the mutual diffusion coefficient, D_m, of the reactants and the effective reactive distance, R', characterizing pyrene excimer formation. R' varies inversely with D_m (vide infra) and becomes equal to the intrinsic reactive distance in the limit of $D_m \to 0$. Adding unlabeled polymer is a convenient way of varying D_m for the reacting species while keeping the temperature constant.

These data become available through a novel method we developed for fluorescent decay curve analysis of two interrelated fluorescent states, here excimer and excited monomer. In this case, the two decay curves are connected

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by the time-dependent excimer formation rate coefficient that is diffusion controlled. The excimer formation reaction is reversible. As a consequence, one cannot obtain an analytical solution for the excimer and excited monomer decay curves in real space, although expressions can be written in Laplace space. Our method overcomes these difficulties by simultaneous analysis of the two decay curves and allows one to obtain parameters for the transient part of the excimer formation rate coefficient. The method is rigorously correct within the assumptions of the model. One of our major objectives here is to explore the limitations of the method and the model on which it is based.

Our long-term interest is to study intermolecular excimer formation between pyrene groups attached to the ends of polymer chains. Here, we examine the specific case of excimer formation from methyl 4-(1-pyrene)butyrate (1) in toluene/polystyrene [PS] mixtures: 1 is chosen rather than pyrene itself because it serves as a model for a polymer-bound pyrene end group.

Kinetic Scheme

Pyrene excimer kinetics are normally analyzed in terms of the two-state (Birks') model given in Scheme I.

Scheme I

$$2\mathrm{Py} \underset{k_M}{\overset{h\nu}{\rightleftharpoons}} \mathrm{Py}^* + \mathrm{Py} \underset{k_{-1}}{\overset{k_1(t)}{\rightleftharpoons}} (\mathrm{PyPy})^* \xrightarrow{k_D} 2\mathrm{Py}$$

Here k_M^{-1} and k_D^{-1} are the molecular monomer and excimer lifetimes. The rate coefficient of the excimer dissociation process is described by k_{-1} and that of its formation by $k_1(t)$. Here we take explicit account of the time dependence of $k_1(t)$, reflecting the time evolution of the pair distribution function of reactive pairs at early times in the reaction. At long times, $k_1(t)$ decays to its steady-state, time-independent value, k_1. We specifically ignore the time dependence of k_{-1}[10] as well as the fact that excimer dissociation yields spatially correlated Py*/Py pairs, since these factors make the theory insolvable and the data analysis intractable. These assumptions are reasonable in the case where the extent of excimer dissociation is small and the viscosity is not too large.

For time-independent rate coefficients, a well-known solution exists for the evolution in time of the excited monomer [M*] and excimer [D*] concentrations[11] after a delta pulse excitation:

$$[\mathrm{M}^*] = \frac{[\mathrm{M}^*]_0}{\lambda_2 - \lambda_1}[(\lambda_2 - A_x)\exp(-\lambda_1 t) + (A_x - \lambda_1)\exp(-\lambda_2 t)] \quad (1)$$

$$[\mathrm{D}^*] = \frac{k_1[\mathrm{M}^*]_0[\mathrm{M}]}{\lambda_2 - \lambda_1}[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \quad (2)$$

$$2\lambda_{1,2} = \{(A_x + A_y) \mp [(A_x - A_y)^2 + 4k_1k_{-1}[\mathrm{M}]]^{1/2}\} \quad (3)$$

$$A_x = k_M + k_1[\mathrm{M}] \qquad A_y = k_D + k_{-1} \quad (4)$$

where [M] and $[\mathrm{M}^*]_0$ are the concentrations of 1 and of the initially excited molecules, respectively.

The steady-state values of the excited monomer and excimer intensities are given by

$$I_M = [\mathrm{M}^*]_0 \frac{q_{FM}}{1 + [\mathrm{M}]/[\mathrm{M}]_h} \quad (5)$$

$$I_D = [\mathrm{M}^*]_0 \frac{q_{FD}}{1 + [\mathrm{M}]_h/[\mathrm{M}]} \quad (6)$$

where q_{FM} and q_{FD} are the quantum efficiencies for excimer and monomer fluorescence and $[\mathrm{M}]_h$ is the half-value concentration, given by

$$[\mathrm{M}]_h = k_M(k_{-1} + k_D)/(k_D k_1) \quad (7)$$

A convolution relation can be established between eq 1 and 2, namely

$$[\mathrm{D}^*] = k_1[\mathrm{M}][\mathrm{M}^*] \otimes \exp(-A_y t) \quad (8)$$

where ⊗ denotes convolution integral. Normally, introducing a transient term into data analysis of a diffusion-controlled process is straightforward. A problem arises, however, when one has to consider the reverse of the diffusion-controlled process (e.g., excimer dissociation). One approach, by Weixelbaumer et al.,[12] resulted in a very complex mathematical treatment for monomer–excimer kinetics with a time-dependent rate coefficient, $k_1(t)$. Hauser and co-workers[13] have looked at this problem in detail. They point out that, for a time-dependent rate coefficient, the form of the equations one uses to describe the system is very important. One must account for the fact that excited states are created at different times. They proposed that the time dependence of the fluorescence intensity can be calculated by convolution relationship for any given time dependence of the excitation intensity. Similar equations were also obtained by Bojarski et al.[14] from a statistical description of donor–acceptor kinetics in nonradiative energy-transfer reactions.

We have shown,[15] using the convolution method of Hauser et al.,[13] that eq 8 maintains its validity even when the excimer formation rate coefficient is time dependent. Our derivation[15] assumes that, for monomer pairs produced by excimer dissociation, the excimer formation rate coefficient maintains its initial form. Equation 8 is very useful for the evaluation of the transient part of the rate coefficient and the A_y value.[16]

The rate coefficient for intermolecular excimer formation is diffusion controlled. The theory of diffusion-controlled reactions has been reviewed recently.[17] For diffusion in a continuous medium, the rate coefficient for times not near $t = 0$ is given by

$$k(t) = a(1 + bt^{-1/2}) \quad (9)$$

$$a = \frac{4\pi D_m N R'}{1000} \qquad b = R'/(\pi D_m)^{1/2} \quad (10)$$

where N is Avogadro's number, D_m the mutual diffusion coefficient for the reactive species, and R' an effective radius of reaction that considers the efficiency of the excimer formation at the encounter distance, R. These values are related by the expression

$$1/R' = 1/R + 4\pi D_m/k_c \quad (11)$$

where k_c is an intrinsic rate constant for excimer formation at the encounter radius.

Experimental Section

Methyl 4-(1-pyrene)butyrate (1) was prepared by esterification of pyrenebutyric acid with methanol and purified by chromatography and repeated crystallization. The polystyrene [PS] standard samples of $M_n = 35\,000$ ($M_w/M_n = 1.06$) and $M_n = 1\,000\,000$ ($M_w/M_n = 1.06$) were purchased from Pressure Chemical Company, Pittsburgh, PA. Toluene was freshly distilled from sodium metal under nitrogen.

Solutions of 1 in mixtures of toluene and polystyrene were prepared in two ways: for lower concentrations of PS by weighing the polymer, adding a known amount of a stock solution of 1 in toluene, and topping up to the desired volume; for higher concentrations of PS by weighing both the polymer and the toluene and assuming volume additivity. The samples were placed in round (5-mm-o.d.) Pyrex tubes, degassed by the freeze–pump–

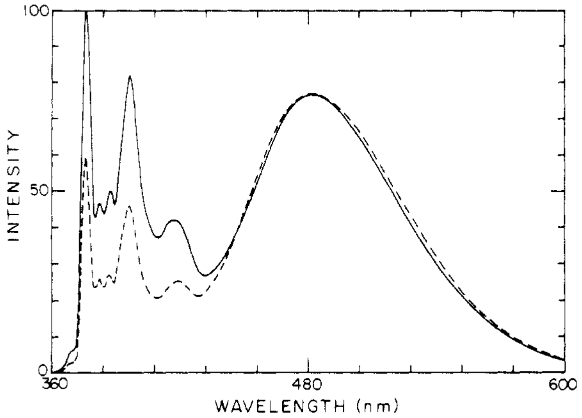

Figure 1. Fluorescence spectra of two solutions of 1 with [Py] = 1.03×10^{-2} M in mixtures of toluene/polystyrene. (—) PS(M = 100 000) concentration is 0.408 g mL^{-1}. (- - -) PS(M = 35 000) concentration is 0.149 g mL^{-1}.

thaw technique (five cycles) and sealed under a vacuum better than 2×10^{-5} Torr.

Fluorescence spectra were run on a Spex Fluorolog 2 spectrofluorimeter without correction for the wavelength sensitivity of the system. Decay curves were obtained by using the time-correlated single-photon counting technique.[18] Our apparatus has been described elsewhere.[19] The excitation wavelength was 345 nm, the monomer fluorescence was observed at 376 nm, and the excimer fluorescence was observed at 520 nm. The analysis of the decay curves was performed by using the delta pulse convolution method.[20,21] Reference decay curves of degassed solutions of BBOT (2,5-bis(5-(*tert*-butyl)-2-benzoxazolyl)-thiophene) in ethanol (τ = 1.47 ns) and POPOP (*p*-bis(5-phenyloxazol-2-yl)benzene) in cyclohexane (τ = 1.10 ns) were used for analysis of the excimer and excited monomer decay curves, respectively.

Results

Two series of samples were prepared for each PS sample. In the first set, the concentration of chromophore 1 is low enough ([Py] = 2×10^{-6} M) to prevent excimer formation. In the other, the concentration of 1 is 1.03×10^{-2} M and yields an easily observable amount of excimer formation.

In Figure 1 are presented the fluorescence spectra of two solutions of 1 in toluene with different amounts of polystyrene. We observe a large decrease in the relative intensity of the excimer emission with an increase in the polystyrene concentration. The ratio of the excimer to monomer intensities (I_D/I_M) is presented in Table I. These values were obtained by integration of the monomer and excimer fluorescence bands recovered from decomposition of the fluorescence spectra. The fluorescence spectra of a diluted solution in 1 and the same concentration in PS were used to recover the monomer emission. The decrease in the I_D/I_M ratios can be understood on the basis of a decrease of the excimer formation rate coefficient with increasing amount of polystyrene according to eq 5 and 6.

In order to analyze this effect, we performed time-resolved measurements. Values for $k_M^{-1} = \tau_M$ (Table I) were obtained from the decay curves of 1 at 2×10^{-6} M. When the PS concentration exceeded 10%, a double-exponential fitting routine was used to accommodate the small parasitic 10-ns emission from a PS-bound impurity.[21] At the higher concentration of 1, excimer and monomer emissions can be fitted, respectively, with a difference or a sum of two exponential terms. In Figures 2 and 3, we present the decay curves of a sample with a concentration in polystyrene (M = 100 000) of 0.202 g mL^{-1}. The ratio of the preexponential factors for the excimer decay curve is 0.975. The values of $\tau_2 = 1/\lambda_2$, for the best fit of the excimer and monomer decay curves, are 30.8 and 29.3 ns, respectively, while $\tau_1 = 1/\lambda_1$ = 53.6 ns from the excimer decay was fixed in the monomer analysis. Equations 1 and 2 predict identical values for τ_1 derived from monomer and excimer decay curves, as well for τ_2. Equation 2 predicts a ratio of 1.0 for the coefficients of the rise and decay components of $I_D(t)$. While the differences between predicted and observed behavior are small and often ignored, they are consistent throughout these experiments and become more pronounced as the PS concentration increases.

In a recent study of the temperature dependence of excimer formation in 1, we made similar observations[16a] and showed that these deviations were due to a small contribution of the transient term in $k_1(t)$. When the transient contribution is small, Birks' analysis of the decay curves according to eq 1 and 2 yields reasonable values of the time-independent rate coefficient, k_1. Stable values

Table I
Fluorescence Parameters for Solutions of 1 in Mixtures of Toluene/Polystyrene for Different Concentrations of Polystyrene, the Excimer Formation Rate Coefficient (*a*), and the Decay Parameter of the Excimer Emission (A_y) Obtained Assuming Birks' Kinetics

c^a	M^b	τ_M, ns	I_D/I_M	$10^{-9}a$, M^{-1} s^{-1}	A_y^{-1}, ns
0		195	6.07	3.9	41.6
0.051	ii	183	5.93	3.4	45.5
0.074	i	182	4.73	2.9	46.0
0.075	ii	180	4.92	3.0	42.7
0.105	ii	179	4.92	3.0	46.1
0.149	i	179	4.37	2.5	46.6
0.151	ii	174	4.38	2.5	46.6
0.202	ii	172	4.01	2.2	47.5
0.206	i	181	3.95	2.4	44.1
0.286	ii	173	3.35	1.8	48.4
0.401	ii	174	2.06	0.97	43.4
0.408	i	176	2.41	1.1	43.1

[a] Polystyrene concentration in g mL^{-1}. [b] Molecular weight of polystyrene: (i) M = 35 000, (ii) M = 100 000.

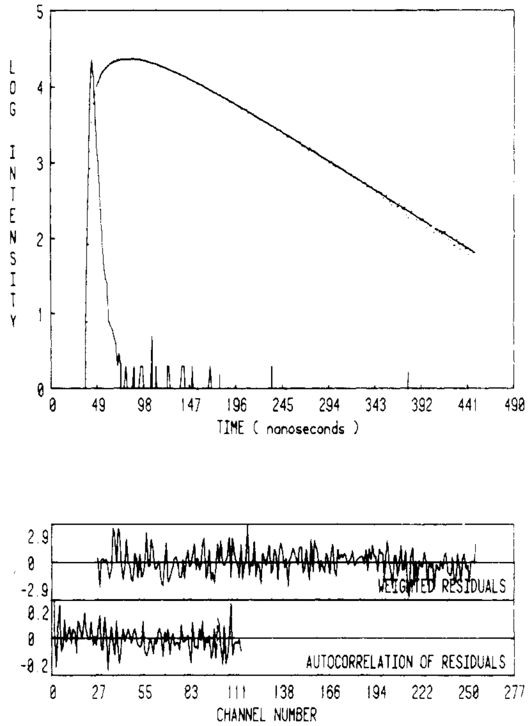

Figure 2. Double-exponential fit of the excimer decay curve of a 1.03×10^{-2} M solution of 1 in a mixture of toluene/polystyrene, with a concentration in PS(M = 100 000) of 0.202 g mL^{-1}. τ_2^D = 30.8 ns; τ_1^D = 53.6 ns; A_2^D/A_1^D = 0.975; χ^2 = 1.1.

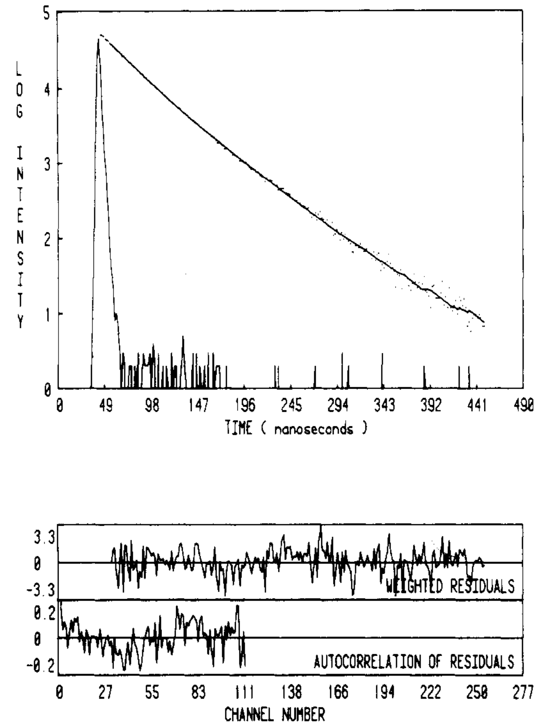

Figure 3. Double-exponential fit of the monomer decay curve of solution of Figure 2. $\tau_2^M = 32.2$ ns; $\tau_1^M = 53.6$ ns; $A_2^M/A_1^M = 1.74$; $\chi^2 = 1.3$.

of the parameters are obtained by beginning the $I_M(t)$ analysis a few channels after the lamp maximum. In this way, we used eq 1–4 to obtain the a and A_y values presented in Table I (for k_M, the reciprocals of the τ_M values presented in Table I were used).

The analysis of Scheme I when there is a transient term in $k_1(t)$ is very complicated. Recently a solution was obtained in Laplace space.[15] The analysis of experimental fluorescence decays in this space, however, is not very accurate.[18b] A better method using the convolution relation (eq 8) was successfully applied[16a] to the study of excimer formation of 1 in toluene at different temperatures.

The experimental decay curves are obtained using as excitation a flash lamp with intensity profile $L(t)$. For a time-independent excimer formation rate coefficient ($a = k_1$), the convolution relation (eq 8) should be written, apart for some constants, as

$$I_D(t) = aI_M(t) \otimes \exp(-A_y t) \tag{12}$$

A test of the mechanism of Scheme I, ignoring the possible time dependence of $k_1(t)$, is given in Figure 4, where the best fit to a monomer–excimer pair of decay curves is analyzed in terms of eq 12. The fit is poor, as is shown in both the weighted residuals and the autocorrelation of the residuals. The deviations from the fit are most serious at early times when the transient effect would be expected to be most important, and any contribution from k_{-1} is very small.

Therefore, for the time-dependent excimer formation rate coefficient, the convolution relation should be written in the form

$$I_D(t) = L(t) \otimes k_1(t)I_M^\delta(t) \otimes \exp(-A_y t) \tag{13}$$

where $I_M^\delta(t)$ is the monomer decay that should be observed when using a delta pulse.

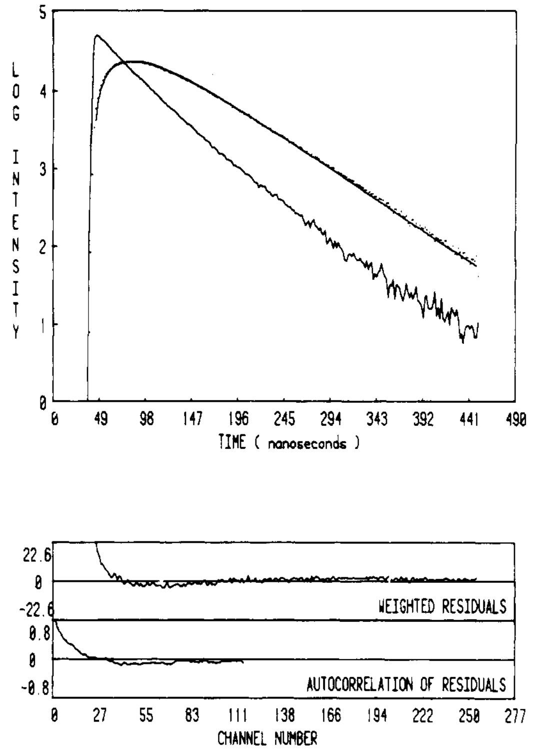

Figure 4. Time-independent fit of the excimer decay of the solution of Figure 2 using eq 12. $A_y^{-1} = 44.8$ ns; $\chi^2 = 8.6$.

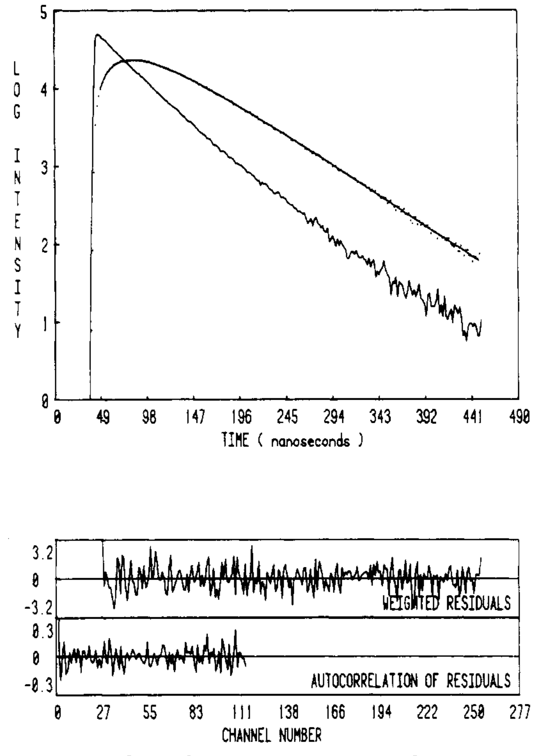

Figure 5. Time-dependent fit of the excimer decay curve of the solution of Figure 2 using eq 13. $b = 0.48$ ns$^{1/2}$; $A_y^{-1} = 47.1$ ns; $\chi^2 = 1.1$.

In order to relate the experimental values of the excimer and monomer decays, we assume a delta pulse excitation at the lamp centroid to consider the transient contribution of $k_1(t)$. This is a testable hypothesis for laboratories with a picosecond excitation source and something we plan to examine in the future. Here, we fit data to eq 13 by multiplying values of $I_M(t)$ decay curve by a or $k_1(t)$ depending upon whether the channels are situated before or after the lamp centroid. Data analysis begins two or three channels after the lamp centroid to minimize possible errors due to our assumptions.

Reanalysis of the curves given in Figure 4 with eq 13 gives the very reasonable fit shown in Figure 5. Values

Table II
Transient Term of the Excimer Formation Rate Coefficient (b), Decay Parameter of the Excimer Emission (A_y) Obtained by Using the Convolution Relation (Equation 13), the Reaction Radius (R'), and Mutual Diffusion Coefficient (D_m) in Mixtures of Toluene/Polystyrene

c^a	M^b	b, ns$^{1/2}$	A_y^{-1}, ns	R', Å	10^6D_m, cm^2 s^{-1}
0		0.17	42.9	3.6	15.0
0.051	ii	0.24	45.8	4.3	10.4
0.074	i	0.25	46.2	4.2	8.9
0.075	ii	0.27	46.0	4.5	8.8
0.105	ii	0.33	46.1	5.1	7.7
0.149	i	0.33	46.6	4.8	6.9
0.151	ii	0.33	46.6	4.8	6.9
0.202	ii	0.48	47.1	6.0	4.9
0.206	i	0.46	43.9	6.0	5.3
0.286	ii	0.56	47.5	6.2	3.9
0.401	ii	1.00	48.6	7.4	1.7
0.408	i	1.20	47.4	6.9	2.2

[a] Polystyrene concentration in g mL^{-1}. [b] Molecular weight of polystyrene: (i) M = 35 000, (ii) M = 100 000.

of b and A_y obtained in this way are recovered in Table II. Note that values of a are unavailable from this analysis because of a normalization step in the fitting procedure.

The values of A_y recovered from the classic Birks' analysis (Table I) compare very well with the values recovered when using the convolution procedure. From the values of a obtained when using the usual Birks' analysis and b from the convolution procedure, the mutual diffusion coefficient, D_m, and the effective reaction radii, R', shown in Table II were calculated. The estimated error in these parameters is ca. ±10%. The variation of $D = D_m/2$ with polymer concentration is in agreement with the theory of diffusion in polymers.[17] This means that, even with the approximations involved in the convolution process, the recovery of the parameters is reasonable.

Analysis

According to the theory of partially diffusion-controlled reactions, the values of R' and D_m are related by eq 11. We plot the variation of $1/R'$ versus D_m in Figure 6. A reasonably straight line can be drawn through the experimental points. The intercept yields a value of $R = 8.5 \pm 0.6$. This value is close to the value of 7.6 ± 0.7 we obtained from variable-temperature studies of **1** in toluene.[16a] From the slope, we calculate a value of $k_c = (1.2 \pm 0.7) \times 10^{-11}$ cm^3 s^{-1}, which coincides with the value obtained in the temperature studies. This value is lower than the expected value from the kinetic theory of gases, probably due to steric effects of the side chain of our chromophore and/or to short-range cage effects not considered here.

We observe a decrease in the diffusion coefficient with an increase of polystyrene concentration. This variation does not depend on molecular weight, at least for the two molecular weight samples examined.

As is well-known in polymer science, this result cannot be explained on the basis of the macroscopic viscosity of the medium. Here, for example, in our most concentrated sample of the higher molecular weight polystyrene, the solution viscosity increases by 1000 times over that of toluene, whereas D_m decreases by a factor of 50. Diffusion of small molecules in polymer/solvent mixtures is normally examined in light of the free volume model[7,22] or the obstacle model.[6] A review of this topic has recently been published.[23] The free volume model describes the mobility of molecules in a mixture in terms of their sensitivity to the average specific hole free volume of the system.[7] The specific hole free volume of a solvent is usually much greater than that of a typical polymer, and the addition of solvent to bulk polymer leads to an increase in average free volume of the mixture. Dramatic effects are often observed at low solvent concentrations, with the solvent diffusion coefficient undergoing large increases with increasing solvent concentration. The most common and most meaningful applications of the free volume model are to solutions rich in polymer.

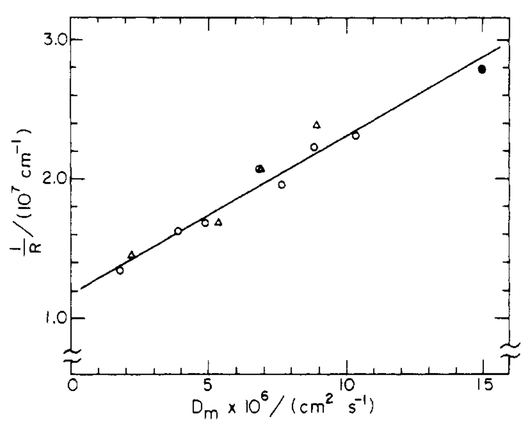

Figure 6. Plot of $1/R'$ versus the mutual diffusion coefficient, D_m, according to eq 11. (△) Toluene; (○) toluene/PS(M = 100 000); (●) toluene/PS(M = 35 000).

The obstacle model of Mackie and Meares[6] treats the polymer molecules added to a solution as inert obstacles. These increase the trajectory and hence the diffusion time for small molecules in the mixture. This model is widely used to describe diffusion of solvent and other small molecules through gels and membranes,[24] since in these systems the tortuosity of the path is thought to be a major consideration in determining the permeation rate. It has also been applied with success by Nakagawa et al.[25] to describe the diffusion of p-chloronitrobenzene and fractionated phenol resins in solutions containing mixtures of different solvents with polystyrene and poly(vinyl acetate). The feature of the obstacle model most attractive to us is not the underlying physics but rather our concern with the assumptions we have made in calculating D_m values from our fluorescence decay data. The obstacle model has no adjustable parameters. It is useful in polymer mixtures rich in solvent. A good fit of our data to the model provides an additional level of confidence to the meaningfulness of our data.

A key criterion for successful application of the obstacle model is the absence of specific interactions between the diffusant and the polymer. In our experiments, this feature is likely to be satisfied.

In the obstacle model, the diffusion coefficients of a small molecule in the pure solvent, D_0, and in solutions containing the polymer, D, are related by

$$D/D_0 = [(1 - c\bar{v}_p)/(1 + c\bar{v}_p)]^2 \qquad (14)$$

where $\bar{v}_p$ is the partial specific volume of the polymer and c is its concentration in grams per milliliter. In Figure 7a we plot our results according to eq 14, setting $D = D_m/2$ for **1**. The best fit obtained when using a weighted nonlinear least-squares analysis gives $\bar{v}_p = 1.24$ cm^3 g^{-1}. This value of $\bar{v}_p$ does not compare well with the known value for polystyrene ($\bar{v}_p = 0.92$ cm^3 g^{-1}).[26] It is not difficult to spot the origin of the problem: the transient contribution to $I_M(t)$ persists most and is easiest to analyze, when D is small. As a consequence, the value of D known with least confidence is D_0. Here, the value of D_0 is too large. An error in D_0 distorts the plot of eq 14. Choosing the alternative value of $D_0 = 6.0 \times 10^{-6}$ cm^2 s^{-1} obtained by an Arrhenius extrapolation of our previous temperature-dependence studies,[13a] we obtain a better fit shown in Figure

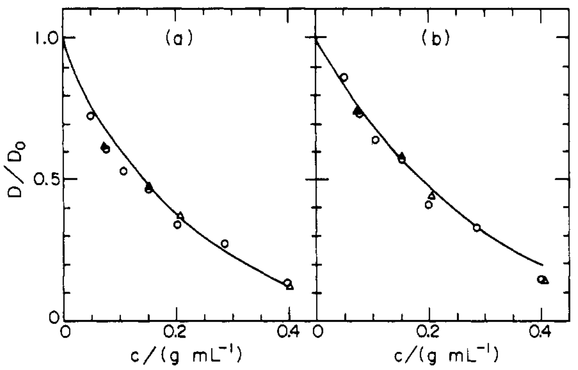

Figure 7. Variation of the diffusion coefficient of 1 with the concentration of polystyrene (a) using $D_0 = 7.5 \times 10^{-6}$ cm^2 s^{-1} and (b) using $D_0 = 6.0 \times 10^{-6}$ cm^2 s^{-1}. (△) Toluene/PS(M = 100 000); (○) toluene/PS(M = 35 000).

7b with a value of $\bar{v}_p = 0.92$ cm^3 g^{-1}.

The importance of the work presented here is that it demonstrates the viability of the convolution method for analyzing the transient contribution to monomer–excimer kinetics. It provides a fluorescence technique for studying diffusion-controlled reactions in complex systems where diffusion is slow compared to dilute solutions in fluid solvents. From the data analysis, one obtains the mutual diffusion coefficient for the reactive species and the capture radius for the reaction.

Conclusions

The results presented in this paper indicate that the kinetics of excimer formation in solutions containing different amounts of polystyrene can be well explained if we assume a time-dependent rate coefficient for the excimer formation process. We observe an increase in the transient term of the rate coefficient with the amount of polystyrene added due to the decrease of the diffusion coefficient and the increase of the effective radius of reaction. The meaningfulness of the diffusion coefficients obtained is demonstrated by showing that they give a good fit to the obstacle model previously used to describe the diffusion in polymer/solvent mixtures.

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