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Intermolecular Pyrene Excimer Formation in End-Labeled Polystyrene of M_w 7800: Role of the Mutual Diffusion Coefficient[1]

Jose M. G. Martinho,[2] Krzysztof Sienicki,[3] Douglas Blue, and Mitchell A. Winnik*

Contribution from the Department of Chemistry and Erindale College, University of Toronto, Toronto, Ontario, Canada M5S 1A1. *Received February 3, 1988*

Abstract: Fluorescence decay studies of excimer formation of polystyrene molecules of M_w 7800, **1**, capped on one end with a pyrene group are analyzed in such a way that the transient contribution to the diffusion-controlled reaction rate can be evaluated. The excimer formation rate coefficient $k_1(t,c)$ decays with time and also varies with the concentration c of **1** in the sample. The latter effect is consistent with the normal concentration dependence of the polymer mutual diffusion coefficient [$D = D_0(1 + k_Dc + ...)$]. By assuming a Smoluchowski form for k_1 [$k_1(t) = a(1 + bt^{-1/2})$] values for D and D_0 can be evaluated from the fluorescence decay data. These are entirely consistent with values recently reported for unlabeled polymer determined by QELS studies.

Photochemists and spectroscopists have been interested in the phenomenon of excimer formation since Förster and Kasper's initial observation[4] of a broad structureless emission in the fluorescence spectrum of pyrene at elevated concentrations. This interest has taken many forms. For those working in the area of solution chemistry of organic molecules, the kinetic behavior of excimers has been the topic receiving the greatest amount of attention.[5] Excimer formation is normally diffusion controlled. Measurements of the rates of excimer formation frequently provide a convenient way to study diffusion-controlled processes in solution.

When a molecule such as pyrene is chemically attached to some other species, the excimer kinetics reflect features of the dynamics of the species to which the pyrenes are attached. Thus, in a bichromophoric molecule such as meso or racemic 2,5-dipyrenylpentane, the kinetics of intramolecular excimer formation measure the rate of internal rotation and conformational change in the molecule.[6] In linear polymers containing pyrene groups at both chain ends, excimer formation measures the rate of large-amplitude chain motion leading to end-to-end cyclization.[7,8]

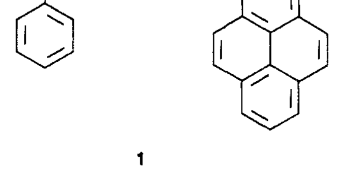
This paper examines pyrene excimer kinetics in solutions of a polystyrene sample containing a pyrene group at one end. This reaction is interesting from many points of view. First, excimer formation requires diffusion of the polymers containing the pyrene groups. The excimer formation rate coefficient carries information about the effect of the polymer chain on the diffusion of the reactants. Second, and more important, this reaction can be considered as a model for the termination step in free-radical polymerization.[9,10] The termination process involves the diffusion-controlled intermolecular reaction of free radicals located on the polymer chain end. This termination rate constant is believed to depend, albeit weakly, upon the chain lengths of the polymers involved in the reaction. This point is difficult to investigate directly, since in free-radical polymerization, chain growth competes with termination, and reactive chains of varying lengths are continually undergoing the termination processes of coupling and disproportionation.[10] Only in a spectroscopic study of a diffusion-controlled reaction can one establish conditions where chains of fixed length can be studied.[11]

The third reason why these experiments are important concerns the time dependence of diffusion-controlled rate coefficients. In the Smoluchowski formulation,[12,13] the diffusion-controlled rate coefficient $k_{\text{diff}}(t)$ can be expressed as

$$k_{\text{diff}}(t) = 4\pi N'_A R' D_m\{1 + R'/(\pi D_m t)^{1/2}\} \quad (1)$$

where N'_A is 10^{-3} times Avogadro's number, R' is an effective reactive radius, and D_m is the mutual diffusion coefficient of the reactants. At short times k_{diff} decreases as $t^{-1/2}$. This time dependence, important at short times, arises because reactants that are close together react faster than those further apart. At long times, the distribution function of reactive pairs attains its steady-state value: $k_{\text{diff}} = 4\pi N'_A R' D_m$. Equation 1 is derived for the case of small spherical molecules in a continuous medium. The situation for reactions between groups attached to polymer chains is less clear. In two important theoretical papers examining this process, de Gennes[14] argued that the time dependence of k_{diff} depends sensitively on the physics of polymer diffusion. For chains small enough and sufficiently separated that the polymer chains diffuse a distance larger than their radii of gyration before reacting, k_{diff} is predicted to follow Smoluchowski behavior (eq 1). For longer chains at higher concentration, where the chains are already overlapped, the situation changes. For very long chains, where entanglements force the chain to undergo repetitive diffusion, a very different time dependence for k_{diff} is predicted.[14]

Experiments reported here describe the kinetics of excimer formation in oligomeric polystyrene **1** (M_w 7800) containing a pyrene substituent at one end. Pyrene excimer formation is normally described in terms of a two-state model (the Birks'



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[1] Transient effects in diffusion controlled reaction. 6. For the previous paper in this series, see: Martinho, J. M. G.; Tencer, M.; Campos, M.; Winnik, M. A. *Macromolecules*, in press.

[2] Permanent address: Centro de Quimica—Fisica Molecular, Complexo 1, I.S.T., Av. Rovisco Pais, 1096 Lisboa Codex, Portugal.

[3] Permanent address: Institute of Technical Physics and Applied Mathematics, Technical University of Gdansk, Poland.

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model),[5] Scheme I, in which the excimer formation rate, described by k_1, is considered to be diffusion controlled, but the possible time dependence of this rate coefficient is ignored.[5,7,15] In this scheme, k_{-1} describes excimer dissociation. The terms k_M and k_E describe, respectively, the pyrene "monomer" decay rate in the absence of excimer formation and the excimer decay rate in the absence of its dissociation.

Scheme I

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

The experimental data appear to fit this model reasonably well when the monomer $[I_M(t)]$ and excimer $[I_E(t)]$ fluorescence decay profiles are analyzed separately. It is only when we analyze these data simultaneously in terms of a new convolution relationship that we find serious discrepancies between the data and the predictions of Scheme I. These differences disappear if the time dependence of $k_1(t)$ is taken into account. Using eq 1 to describe $k_1(t)$, we obtain values for D_m and R', and for k_1, the limiting value of $k_1(t)$ at long times.

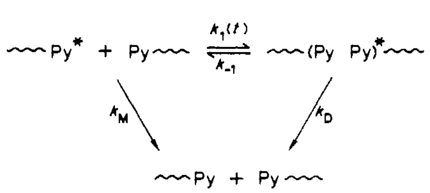
The results are full of surprises, all of which are readily understood from the perspective of polymer diffusion in good (toluene) and poor (cyclohexane) solvents. The most interesting of these is that k_1 decreases with increasing concentration of **1** for samples in cyclohexane. One normally expects in the excimer formation rate expression $k_1[\mathrm{Py}\sim][\mathrm{Py}\sim^*]$ that k_1 would not vary with the $[\mathrm{Py}\sim]$ reactant concentration. Here the kinetics have the added feature that D_m depends sensitively on the concentration $[c]$ of polymer, which in turn varies with the concentration of **1**. In cyclohexane D_m decreases with c, whereas in toluene no concentration dependence is observed: For experiments in toluene, two terms that both contribute to the concentration dependence of D_m exactly cancel.

Experimental Section

Polystyrene-CH_2CH_2OH was prepared by standard vacuum line anionic polymerization techniques in tetrahydrofuran using *sec*-butyllithium as the initiator. The reaction was terminated with excess ethylene oxide followed by protonation with acetic acid. The polymer was purified by repeated precipitation from toluene solution into methanol. The pyrene end group was attached by reaction of excess 4-(1-pyrene)butyryl chloride with a carefully dried polymer sample in toluene containing dry pyridine. The reaction was allowed to proceed for 3 days at ambient temperature and was quenched by addition of silica gel which reacts irreversibly with unreacted pyrenebutyryl chloride. The polymer was purified by successive reprecipitations from toluene into methanol and analyzed by gel permeation chromatography using Ultrastyragel columns and tandem differential refractive index and UV-vis detectors. In this way we could demonstrate that all pyrene groups in the sample were attached to the polymer. Based upon polystyrene standards the sample had M_n 5900 and M_w/M_n 1.33.

Solutions of **1** in toluene and cyclohexane were placed in round (5-mm-o.d.) Pyrex tubes, degassed by the freeze-pump-thaw technique (5 cycles), and sealed under a vacuum better than 2×10^{-5} Torr. Concentrations of **1** ranged from 4.9×10^{-4} to 1.2×10^{-2} M. Fluorescence spectra were run on a Spex Fluorolog 2 spectrofluorometer without correction for the wavelength sensitivity of the system. Decay curves were obtained by the time-correlated single-photon counting technique.[16] The excitation source was a coaxial flash lamp (Edinburgh Instruments, Model 199F). The excitation wavelength was selected by a Jobin-Yvon Model H-20 monochromator, and that of the fluorescence by a SPEX Minimate Model 1760 monochromator. The excitation wavelength was 345 nm, the monomer fluorescence was observed at 376 nm and the excimer fluorescence at 520 nm. The analysis of the excited monomer and excimer decay curves was performed with the δ-pulse convolution method.[17] 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 1,4-bis(5-phenyloxazol-2-yl)benzene in cyclohexane (τ = 1.1 ns) were used for analysis of the excimer and monomer decay curves, respectively.

Scheme II



The Model. Pyrene excimer kinetics are commonly interpreted in terms of the mechanism given in Scheme I.[5] In Scheme II we modify the classical Birks' scheme by considering explicitly the time dependence of the diffusion-controlled excimer formation rate coefficient $k_1(t)$.

If this time dependence is ignored $[k_1(t) = k_1]$, the description of fluorescence decay of monomer $I_M(t)$ and excimer $I_D(t)$ intensities following δ-pulse excitation is given by the classical equations[5]

$$I_M(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \tag{2}$$

$$I_D(t) = A_3 \exp(-\lambda_1 t) - A_4 \exp(-\lambda_2 t) \tag{3}$$

and the decay parameters are related to the rate constants through the expressions

$$2\lambda_{1,2} = A_X + A_Y \mp \{(A_Y - A_X)^2 + 4k_1k_{-1}[\mathrm{Py}]\}^{1/2} \tag{4}$$

$$A_2/A_1 = (A_X - \lambda_1)/(\lambda_2 - A_X) \tag{5a}$$

$$A_3/A_4 = 1.0 \tag{5b}$$

where $A_X = k_M + k_1[\mathrm{Py}]$ and $A_Y = k_{-1} + k_D$.

In the experiments reported here, the $I_E(t)$ and $I_M(t)$ data fit eq 2 and 3 reasonably well. Some minor problems occur at early times. An example is presented in the following section of the paper. One commonly ignores the problems at short times using eq 4 and 5 to obtain values for k_1, k_{-1}, and k_E. It should be noted that, at very low concentrations, $\lambda_1 = k_M$.

The case of a time dependent $k_1(t)$ can be treated explicitly on the assumption that for the excimer reformation after dissociation, $k_1(t)$ maintains the same time-dependent form.[18] Under these circumstances the concentration time profiles of monomer $[\mathrm{M}^*](t)$ and excimer $[\mathrm{E}^*](t)$ can be given in the form of the Laplace transforms:

$$[\mathrm{M}^*](t) = L^{-1}\{[\mathrm{M}^*]^{(1)}(s)/(1 - \beta)\} \tag{6}$$

$$[\mathrm{E}^*](t) = L^{-1}\{[\mathrm{E}^*]^{(1)}(s)/(1 - \beta)\} \tag{7}$$

where

$$[\mathrm{M}^*]^{(1)}(s) = L^{-1}\{f_M\} \tag{8a}$$

$$[\mathrm{E}^*]^{(1)}(s) = L^{-1}\{k_1(t)[\mathrm{M}]f_M \otimes f_E\} \tag{8b}$$

$$f_M = \exp\left\{-k_M t - \int_0^t k_1(t')[\mathrm{M}]\,\mathrm{d}t\right\} \tag{8c}$$

$$f_E = \exp\{-(k_E + k_{-1})t\} \tag{8d}$$

$$\beta = L\{k_1(t)[\mathrm{M}]f_M \otimes k_{-1}f_E\} \tag{8e}$$

where $\otimes$ denotes convolution integral.

Under the assumption of a δ-pulse excitation, eq 6 and 7 can be transformed, using properties of the convolution integral, to the expression[18]

$$I_E(t) = k_1(t)[\mathrm{M}]I_M(t) \otimes f_E \tag{9}$$

To analyze data in terms of eq 9, one assumes a functional form for $k_1(t)$ (e.g., $k_1(t) = a(1 + bt^{-1/2})$ and uses an appropriate methodology to obtain best fit parameters for a, b, and $(k_E + k_{-1})$.[19] A subtle point, which we elaborate below, is that Scheme I implicitly assumes that $k_1(t)$ is concentration independent. For diffusion-controlled reactions involving labeled polymers, this assumption is not valid, since the mutual diffusion coefficient depends upon c. Proper data analysis indicates that $k_1(t,c)$ depends upon polymer concentration.

Data and Data Analysis. Monomer and excimer decay curves of solutions of **1** in toluene and in cyclohexane were measured at various

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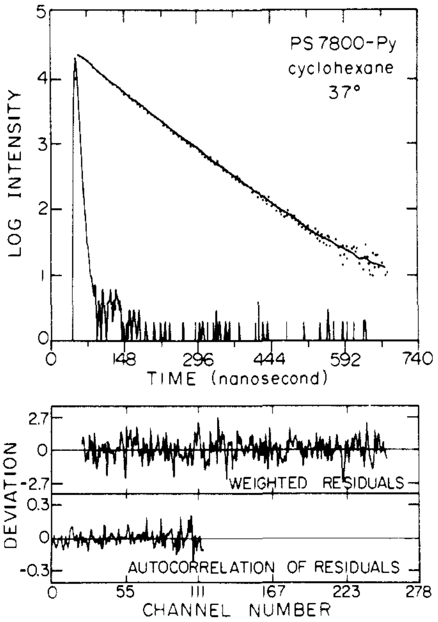

Figure 1. $I_M(t)$ decay profile for polystyrene-Py (**1**) (1.2×10^{-2} M) in cyclohexane at 37 °C. The best fit to eq 2 gives $\tau_2^M = 38.2$ ns, $\tau_1^M = 76.5$ ns, $A_2/A_1 = 4.23$, and $\chi^2 = 1.05$.

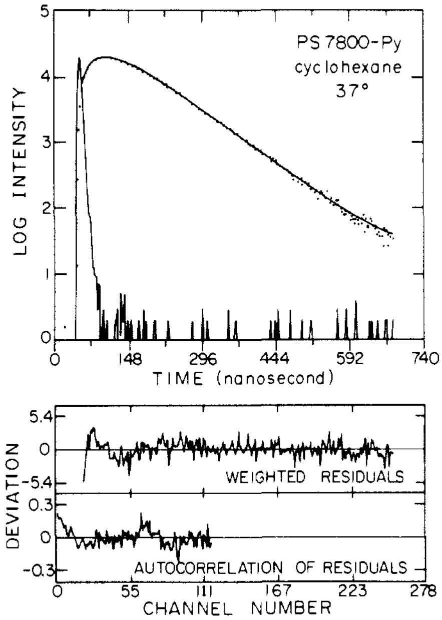

Figure 2. $I_E(t)$ decay profile for the same sample as Figure 1. Here $\tau_1^E = 79.3$ ns, $\tau_2^E = 40.7$ ns, $A_4/A_3 = 0.949$, and $\chi^2 = 1.46$.

temperatures ranging from 10 to 60 °C. These decay curves are remarkably consistent with the predictions of the classical Birks' scheme,[5] eq 2–5. An example is shown in Figures 1 and 2 for a solution of **1** at 1.2×10^{-2} M in cyclohexane at 37 °C. The decay parameters ($\lambda^{-1} = \tau$) from the two sets of measurements are virtually identical (here $\tau_1^M = 76.5$ ns, $\tau_2^M = 38.2$ ns; $\tau_1^E = 79.3$ ns, $\tau_2^E = 40.7$ ns). The statistical parameters are acceptable (χ^2, the distribution of weighted residuals, and their autocorrelation function). The only hint of a problem with the model is that $|A_3/A_4|$ is less than unity (here 0.949).

The same kind of behavior was observed for excimer formation with simple pyrene derivatives[19] in fluid solvents. However, the deviations from the Birks' kinetics predictions are smaller (e.g., the ratio of the preexponential factors of the excimer decay curve is ~0.98). This behavior was also observed by Boens et al.[20] in the study of the intermolecular excimer formation of 1-methylpyrene in vesicles. These authors also invoked a time-dependent excimer formation rate coefficient to interpret the experimental results.

Table I. Kinetic Parameters for Excimer Formation of **1** in Toluene and in Cyclohexane as a Function of Temperature

T/°C	$10^{-9}k_1$, M^{-1} s^{-1}	b, ns$^{1/2}$	10^6D_m, cm^2 s^{-1}	R', Å
		Toluene		
10.0	0.78	0.51	2.4	4.4
20.0	0.97	0.40	3.1	4.1
30.0	1.20	0.39	3.8	4.2
40.0	1.30	0.40	3.9	4.4
50.0	1.50	0.39	4.4	4.5
60.0	1.70	0.32	5.4	4.1
		Cyclohexane		
10.0	0.53	3.41	0.5	13.7
15.0	0.60	2.12	0.8	10.4
25.0	0.74	1.46	1.1	8.7
30.0	0.86	1.22	1.4	8.1
31.5	0.89	1.37	1.3	8.8
33.1	0.91	1.27	1.4	8.5
34.5	0.94	1.20	1.5	8.3
37.0	1.01	1.24	1.5	8.6
40.0	1.08	0.99	1.9	7.6
50.5	1.33	0.79	2.5	7.0
60.0	1.61	0.69	3.1	6.9

All the results indicate that the influence of the transient contribution of $k_1(t)$ is particularly visible on the rising portion of the excimer decay curve. This is manifested by a ratio of the preexponential factors different from 1.0 and/or different lifetimes recovered from the excited monomer and excimer decay curves. The monomer decay curve only shows significant deviations from a double-exponential fit when the number of counts on the peak maximum is greater than 50 000.

Taking at each temperature and for each solvent the exponential decay parameter $\lambda_M = k_M$ for a solution of **1** at 2.0×10^{-6} M, values of k_1, k_{-1}, and k_D can be calculated from the decay profile parameters and their fit to eq 2–5. These values are presented in the left-hand column of Table I. An alternative method for evaluating rate constants, plotting ($\lambda_1 + \lambda_2$) vs [**1**] and $\lambda_1\lambda_2$ vs [**1**], leads to linear traces. Rate constants calculated from the slopes of these lines for samples in cyclohexane are incorrect because in this solvent and in this range of temperatures k_1 varies with the concentration of **1**.

Experimental decay curves in our laboratory are obtained by using as an excitation source a flash lamp with an intensity profile $L(t)$. In the data analysis, the parameters of eq 1 and 2 are obtained by convoluting these expressions with $L(t)$ and using a computer to obtain the best fit when compared to the respective experimentally determined monomer [$I_M{}^{\text{exp}}(t)$] and excimer [$I_D{}^{\text{exp}}(t)$] decay profiles. This problem disappears when fitting the data to eq 9 assuming a time-independent k_1, since it is rigorously true that

$$I_D{}^{\text{exp}}(t) = k_1 \times I_M{}^{\text{exp}}(t) \otimes \exp(-A_y t) \qquad (10)$$

When considering the time-dependence of $k_1(t)$, the problem reappears in a subtle form, since the derivation of eq 9 presumes sample excitation by a δ-pulse.[18,19] We write the convolution relation in the form

$$I_D{}^{\text{exp}}(t) = L(t) \otimes k_1(t)\, I_M(t) \otimes \exp(-A_y t) \qquad (11)$$

and analyze experimental data as though the lamp were essentially a δ-pulse operating at the centroid of the lamp maximum.[19] The values of the excited monomer decay curve are multiplied by a or by $k_1(t)$, depending upon whether the channels are before or after the lamp centroid. The application of eq 11 to the excimer and monomer experimental decay curves has associated a scaling factor to normalize the results of the convolution procedure to the number of counts of the excimer decay curve. As a consequence, one obtains only the value of b plus ($k_E + k_{-1}$) from the data analysis.

When the data in Figures 1 and 2 are analyzed in terms of eq 10, serious deficiencies in the quality of the data analysis can be seen in both the distribution of the weighted residuals and in the autocorrelation function (see, for example, Figure 3). The convolution analysis magnifies the sensitivity of the experiment to the transient contribution to the diffusion-controlled process of excimer formation.[19] If we assume, however, that $k_1(t)$ has the form $a(1 + bt^{-1/2})$, we recover very good fits to data. Figure 4 shows the best fit of the decay curves of Figures 1 and 2 using relation 11.

In Table I we present the values of the parameters obtained at various temperatures for samples in toluene and cyclohexane. We observe that the transient term b obtained for experiments in cyclohexane is at least 2 times larger than the value in toluene at the same temperature. This is expected, since there should be a greater contribution of the transient

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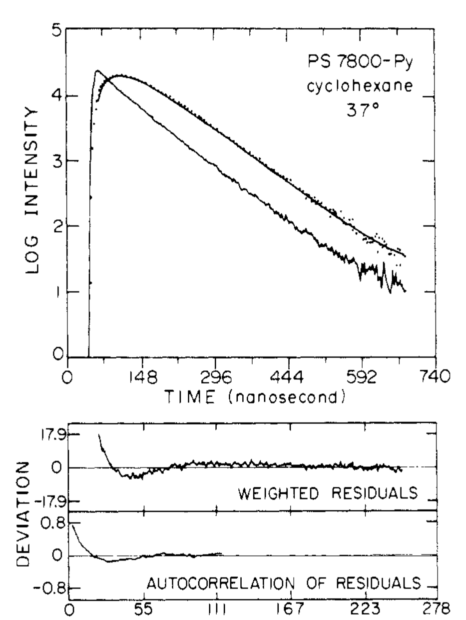

Figure 3. Fit of the data of Figures 1 and 2 to eq 10 assuming k_1 is not a function of time.

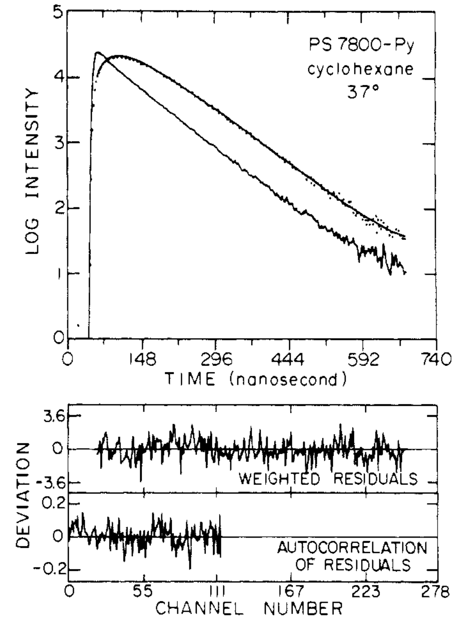

Figure 4. Fit of the data of Figures 1 and 2 to eq 11 assuming $k_1(t) = a(1 + bt^{-1/2})$. Here $b = 1.24\ \text{ns}^{1/2}$, $A_y^{-1} = 50.0$ ns, $\chi^2 = 1.37$.

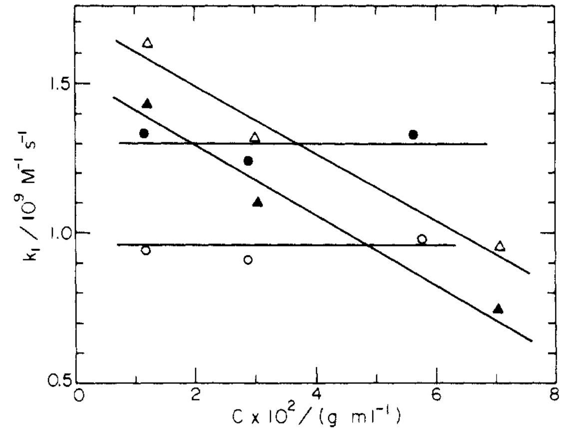

Figure 5. Plot of k_1 vs c where c represents the concentration of **1** (in g mL^{-1}). The data refer to the following solvents and temperatures: (△) cyclohexane, 34.5 °C; (●) toluene, 40 °C; (▲) cyclohexane, 25 °C; (○) toluene, 20 °C.

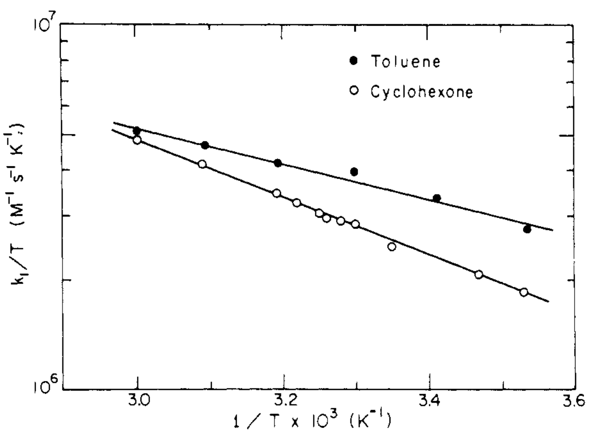

Figure 6. Plots of ln (k_1/T) vs $1/T$ for excimer formation in **1**. (○) in cyclohexane and (●) in toluene.

term to the diffusion-controlled process in the solvent of higher viscosity.

To calculate the values of R' and D_m (eq 1), we combine the values of $b = R'/(\pi D)^{1/2}$ and $k_1 = a = 4\pi N'_A R' D_m$ obtained as described above. The values of R' obtained for samples of **1** in cyclohexane are close to those we obtained previously for the encounter radius of excimer formation for methyl 4-(1-pyrene)butyrate, a model for the pyrene group attached to the chain and in **1**.[19,20] In toluene, the R' for **1** is a factor of 2 smaller.

There is a small technical difficulty in obtaining R' values from the cyclohexane samples at the two lowest temperatures. We believe that the value of b obtained here is too large because of a breakdown of eq 1 at short times when the transient effect contribution to the data is too strong.[13] If R' values here are set arbitrarily at 8.5 Å, the value of D_m calculated increases by ~30%.

Another source of concern is the polydispersity of the sample of **1**. In experiments where one of the rate coefficients (here k_1) varies with chain length (N), the data analysis should be affected by polydispersity, and the magnitude of the problem should depend upon how sensitively k_1 varies with N.[15]

Results published by Horie[11] and by Mahabadi[10] indicate that k_1 is very weakly dependent upon N, especially for chains of this length. It appears, therefore, that our results are not seriously affected by polydispersity. In order to confirm these results, we have recently repeated these measurements on a sample of **1** of M_n 9000 (M_w/M_n 1.06) and find essentially identical kinds of fits of the $I_M(t)$ and $I_E(t)$ data to eq 2, 3, 10, and 11 as reported here.[21]

Discussion

Values of the first-order rate constants obtained in the standard decay curve analysis (Table I) are unexceptional, and typical of pyrene excimer formation in small molecules. One curious feature of the data is that k_1 varies with the concentration of **1** (Figure 5) for samples in cyclohexane, but not for those in toluene. A second curious feature is that the activation energy associated with k_1 for samples in cyclohexane differs from that expected for simple diffusion-controlled reactions, whereas for samples in toluene, the anticipated result is obtained. For example, plots of ln (k_1/T) vs $1/T$ are linear (Figure 6) and yield activation energies of 2.2 ± 0.2 kcal/mol (toluene) and 3.6 ± 0.4 kcal/mol (cyclohexane). The corresponding activation energies obtained from Arrhenius plots of the reciprocal solvent viscosities are essentially identical (2.06 kcal/mol) for toluene, but significantly smaller (2.90 kcal/mol) for cyclohexane.

These differences originate in temperature, time, and concentration effects on $k_1(t,c)$, which become apparent when one examines the transient contribution to the rate coefficient for excimer formation. Analysis of the fluorescence decay curves in terms of the convolution relationship, eq 11, yields the mutual diffusion coefficient D_m and the effective capture radius R' characteristic of excimer formation for pyrene groups attached to the polymer chain end. In cyclohexane, D_m is concentration dependent and this dependency changes with temperature. To emphasize this feature, we show in Figure 7 an Arrhenius plot of the values of

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[21] Strukelj, M.; Winnik, M. A., unpublished data.

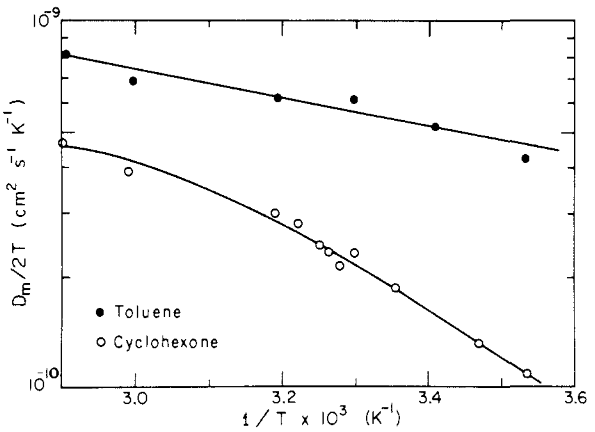

Figure 7. Plots of ln ($D_m/2T$) vs $1/T$ for values obtained from experiments in (○) cyclohexane and (●) in toluene.

$D_m/2T$ obtained for **1** in the two solvents. For samples in toluene, a good straight line can be drawn through the experimental points, and the data yield the same activation energy as found from k_1 values. The cyclohexane data, on the other hand, show a pronounced curvature.

The mutual diffusion coefficient of a polymer chain at low concentrations c is given by the expression[22]

$$D = D_0(1 + k_D c + ...) \qquad (12)$$

where D_0 is the value of D at infinite dilution. The coefficient k_D, defined in eq 12, is related to other polymer properties, as

$$k_D = 2A_2 M_w - k_f - \bar{v}_2 \qquad (13)$$

where A_2 is the second Virial coefficient and $\bar{v}_2$ the partial specific volume of the polymer. The term k_f describes the concentration dependence of the monomeric friction coefficient[22]

$$f = f_0(1 + k_f c + ...)$$

Since k_f and $\bar{v}_2$ are positive quantities, k_D is negative in poor solvents where $(k_f + \bar{v}_2) > 2A_2M_w$. At the θ temperature, by definition, $A_2 = 0$.

Toluene is a good solvent for polystyrene over the entire range of our experiments. Quasi-elastic light scattering (QELS) experiments indicate that k_D for polystyrene chains of this length in toluene has a value very close to zero.[23] The magnitude of the $2A_2M_w$ term in eq 13 must be essentially equal to the sum $(k_f + \bar{v}_2)$. Our experiments in cyclohexane straddle the θ temperature (34.5 °C), and k_D is negative. The value A_2 changes sensitively with temperature, taking increasingly positive values above $T = \theta$ and negative values at $T < \theta$. The curvature in the Arrhenius plot of D_m values for samples of **1** at finite concentrations reflects temperature effects on both the solvent viscosity and the magnitude of k_D.

We can make a rough comparison of the diffusion coefficient obtained here with values reported by Huber et al.[23] from QELS measurements. For experiments in toluene at 20 °C, we set $D_0 = D_m/2$, since k_D is zero, to obtain $D_0 = 1.6 \times 10^{-6}$ cm^2 s^{-1} for our sample of M_w 7800. The QELS results[23] are reported for polystyrene samples of M_w 4000 ($D_0 = 2.58 \times 10^{-6}$ cm^2 s^{-1}) and M_w 10 700 (1.51×10^{-6} cm^2 s^{-1}). These results are consistent with one another. While the QELS results are more accurate, the agreement shows that our method of analyzing the fluorescence decay data is reasonable and that $k_1(t)$ for excimer formation can be well described by the Smoluchowski expression.

A final comment is in order about the magnitude of the effective capture radius R' in these reactions. R' is related to the true capture radius R in the Smoluchowski model through the expression

$$R' = pR$$

where p is the reaction probability per encounter. For small molecule reactions, p increases as D_m decreases. We find from model studies a limiting value of $R = 8.0 \pm 0.5$ Å for pyrene excimer formation in methyl 4-(1-pyrene)butyrate. R' values for **1** in cyclohexane are close to this value for experiments carried out between 25 and 37 °C, suggesting that excimer formation occurs on every diffusive encounter. At higher temperatures, where D increases, p decreases.

Reactions of **1** in toluene are characterized by $R' = 4$Å, implying that only half the diffusive encounters lead to excimer formation. This result may indicate easier chain interpenetration for these short polystyrene chains in a good solvent as opposed to a θ solvent. Or it may point to a limitation of the Smoluchowski model, which was developed to describe diffusion-controlled reactions between hard spheres in a continuous medium.

Summary

Fluorescence decays studies of excimer formation of polystyrene molecules of M_w 7800, **1**, capped on one end with a pyrene group are analyzed in such a way that the transient contribution to the diffusion-controlled reaction rate can be evaluated. The excimer formation rate coefficient $k_1(t,c)$ decays with time and also varies with the concentration c of **1** in the sample. The latter effect is consistent with the normal concentration dependence of the polymer mutual diffusion coefficient [$D = D_0(1 + k_D c + ...)$]. By assuming a Smoluchowski form for k_1, [$k_1(t) = a(1 + bt^{-1/2})$], values for D and D_0 can be evaluated from the fluorescence decay data. These are entirely consistent with values recently reported for unlabeled polymer determined by QELS studies.

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[22] Yamakawa, H., *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.

[23] (a) Huber, K.; Burchard, W.; Akcasu, A. Z. *Macromolecules* **1985**, *18*, 2743. (b) Huber, K.; Bantle, S.; Lutz, P.; Burchard, W. *Macromolecules* **1985**, *18*, 1416.