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Transient Effects in Intermolecular Diffusion-Controlled Polymer–Polymer Reactions

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ABSTRACT: The kinetics of intermolecular excimer formation have been studied for a sample of polystyrene (M_n = 120 000; M_w/M_n = 1.3) end-capped with a pyrene group and dissolved in toluene. At concentrations necessary for excimer formation to be studied, the polymer concentration c ranged from 0.11 to 0.51 g/mL. Simultaneous analysis of monomer and excimer fluorescence decay curves using a new convolution method permitted the time dependence of the diffusion-controlled rate coefficient $k(t)$ to be examined and various theoretical forms for $k_2(t)$ to be tested. The data do not support recent ideas put forth by de Gennes (*J. Chem. Phys.* **1982**, *76*, 3316, 3322) but are in accord with a simple time-dependent Smoluchowski model. Values of the chain-end diffusion coefficient calculated from this analysis are very similar (10^{-7}–10^{-9} cm^2 s^{-1}) to those reported in the literature for center-of-mass diffusion of polystyrene samples of this length and these polymer concentrations.

Introduction

The rate of diffusion-controlled encounter between the ends of two polymer chains is a topic of important practical concern and significant theoretical interest. This rate describes the termination process in free-radical polymerization reactions.[3] A proper description of the kinetics of free-radical polymerization depends upon an understanding of the factors (chain length, entanglements) that affect this rate. The parameter of interest is the rate coefficient $k_2(t)$ for the end-encounter process.

Diffusion-controlled rate parameters are time-dependent. The seeming contradiction of a rate "constant" decaying in time is well-understood in many systems.[4,5] It comes about when the intrinsic rate of reaction of two species A and B is much greater than their rate of diffusion. Proximate AB pairs react very quickly, whereas those separated by small distances react somewhat more slowly. Eventually only A and B species are left, which are far apart. They are no longer distributed uniformly in solution, and the rate of their reaction is limited by the rate of their mutual diffusion.

When the Smoluchowski equation,[4-6] describing diffusion, is solved for diffusion in three dimensions, one finds that $k_{\text{diff}}(t)$ decays initially (the transient part) from a very large value to one (the steady-state value k_{diff}), which remains constant in time. For the hypothetical case of reactions which involve diffusion in only one dimension, one can predict that k_{diff} falls off monotonically with time with no steady-state solution to the diffusion equation. One of the features characterizing diffusion in one dimension is that a particle diffusing from one point to another must traverse every point between them. This feature, denoted "compact diffusion" by de Gennes,[7] differs from noncompact diffusion in three dimensions, where there are so many pathways for diffusion from point 1 to point 2 that most of the intervening points of space are never visited. The existence of steady-state values of k_{diff} is associated with noncompact diffusion. The time profile itself of $k_{\text{diff}}(t)$ is intimately connected with the nature of the diffusion of the interacting species.

In the case of the termination process in free-radical polymerization reactions, the important question concerns the nature of the diffusion of the interacting polymer chains. One expects the rate coefficient $k_2(t)$ to be time-dependent. An important issue is whether at long times $k_2(t)$ relaxes to a steady-state value. This paper presents the first experimental measurements from which the form of this time dependence can be evaluated.

Ideally, experiments to determine $k_2(t)$ should be performed on monodisperse polymer chains, involving reactions known to be diffusion-controlled, under circumstances where other factors such as chain length and bulk polymer concentrations do not change. Fluorescence and phosphorescence quenching experiments involving polymers containing appropriate substituents at one end are the most direct way to obtain $k_2(t)$ values. For example, Mita, Horie, and Takeda (MHT)[8,9] examined quenching of benzil phosphorescence (lifetime τ = 30–100 μs) in end-labeled polystyrene (~PS~Bz) via energy transfer to anthracene (~PS~An). They treated their data in terms of a time-independent second-order rate constant, k_2.

Normally a discussion of diffusion-controlled reactions of polymer chains ends begins with a consideration of the translational diffusion coefficient of a chain end segment, D_e.[3,8] The magnitude of D_e, one believes, should depend upon the probing distance d, regulated by the time scale of the measurement, since the time dependence of the mean-squared displacement of a polymer segment differs for a time scale smaller or larger than the relaxation time T_R of the polymer coil.[10] When d is large enough for the measurement time to be larger than T_R, D_e should coincide with the translational diffusion coefficient D_s of the center of mass of the polymer.

For long chains at elevated polymer concentrations, entanglements prevail. D_s is determined by the reptation time of the entangled chain.[11] In free-radical polymerization reactions, entanglements are responsible for the retardation of the termination process at high conversion, leading to the autoacceleration phenomenon commonly referred to as the "gel effect" or "Tromsdorff effect".[12] In their analysis of this phenomenon, Tulig and Tirrell[13] assumed that k_2 could be described by a Smoluchowski equation[6] which contains the reptation diffusion coefficient: $k_2 = (\text{const})D_s^{\text{rep}}R_e$, where R_e is the capture radius of the termination reaction.

de Gennes has recently examined the theory of intermolecular diffusion-controlled reactions between groups attached to polymer chains. He demonstrated that the physics of the chain motion governs the form of $k_2(t)$. This rate coefficient is predicted to exhibit a time dependence whose form depends upon the chain length N and concentration c of the polymer in solution. When the space explored by the chain end increases less rapidly than t (compact exploration), $k_2(t)$ decays to zero as t^{-u} with no steady-state solution. In other circumstances, the reactants explore space noncompactly, and $k_2(t)$ decays to its steady-state value.

In order to examine the short-time behavior of $k_2(t)$, where the time dependence should be most pronounced,

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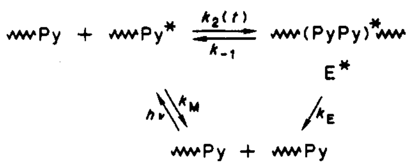
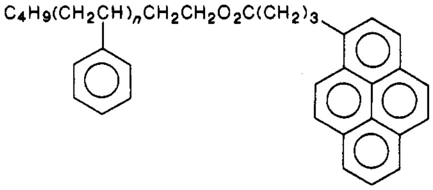
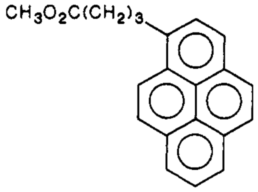
Scheme I



we undertook a study of intermolecular excimer formation[14] in a polystyrene sample end-labeled with pyrene (M_n = 120 000; M_w/M_n = 1.3; ~PS~Py). The mechanism of excimer formation[13] is given in Scheme I, where k_M and k_E are the reciprocal lifetimes of the locally excited pyrene "monomer" and excimer, respectively, and k_{-1} describes the excimer dissociation process. When k_2 is not a function of time, Scheme I predicts (i) that the monomer emission $I_M(t)$ decays as a sum of two exponential terms, (ii) that the excimer emission $I_E(t)$ can be described as the difference of two exponential terms with the same decay times as $I_M(t)$, and (iii) that the ratio of preexponential factors in the $I_E(t)$ profile equals −1.0.



~PS~Py



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The polymer solutions we examine (c = 0.11–0.51 g/mL) straddle c^* (here estimated to be ca 0.2 g/mL), and the chains are sufficiently long to experience entanglements. The theory of semidilute polymer solutions identifies two distinct diffusion processes in this concentration regime. The cooperative diffusion[15] (D_{coop}) is associated with long-wavelength fluctuations of the polymer concentration and is measured by quasi-elastic light scattering. Self-diffusion (D_s) describes the center-of-mass (reptative) diffusion of a labeled chain in the presence of identical but unlabeled chains. It is measured by tracer techniques including forced Rayleigh scattering, fluorescence recovery after pattern photobleaching, and pulsed-gradient NMR. Scaling laws in the semidilute region give the relationships[11]

$$R_G(c) = R_G(c/c^*)^{-1/4} \quad (1)$$

$$D_s \sim N^{-2}c^{-7/4} \quad (2)$$

where (1) describes the decrease in radius of gyration due to excluded volume screening in good solvents for $c > c^*$ and (2) describes the decrease of self-diffusion as a function of chain length and concentration. It was once believed that the N^{-2} dependence of D_s was due to reptative diffusion in the presence of entanglements and that the screening length, taken as the distance between entanglement points, could be calculated from measured values of D_{coop}[8,15]

$$D_{coop} = k_BT/(6\pi\eta_0\xi) \quad (3)$$

where k_B is the Boltzmann constant and η_0 is the solvent viscosity. For PS in benzene, MHT used the data of Adam and Delsanti[15] to calculate ξ = 16 Å for c = 0.2 g/mL, which corresponds to ca. 24 monomers between entanglement points.

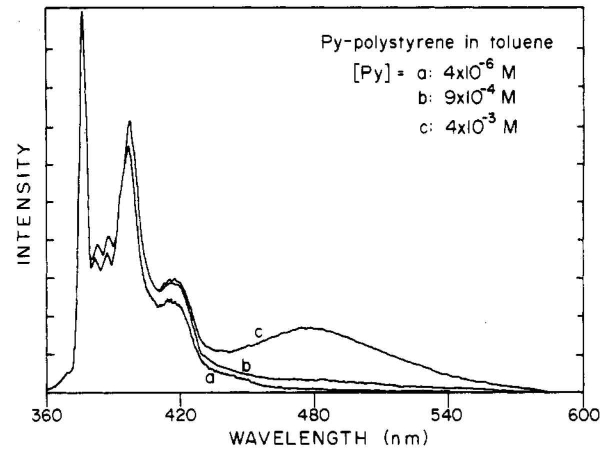

Figure 1. Fluorescence spectra of Py-polystyrene in toluene at the molar concentrations indicated on the figure. These correspond to weight concentrations of (a) 4.4×10^{-4}, (b) 0.11, and (c) 0.51 g/mL, respectively.

One now appreciates that in the melt, the critical molecular weight for entanglements is ca. 33 000 for polystyrene (about 330 monomer units) and that the entanglement length would increase upon dilution of the polymer with solvent. From this point of view, entanglements play at most a minor role in the chain dynamics of our most concentrated solution (c = 0.51 g/mL).

Experimental Section

A sample of polystyrene–CH_2CH_2OH was prepared by anionic polymerization, using *sec*-butyllithium to initiate (−78 °C) styrene polymerization in tetrahydrofuran solution, followed by termination with an excess of ethylene oxide. After protonation, the sample was reprecipitated 3 times from toluene into excess methanol. Analysis by gel permeation chromatography (10^5, 10^4, 10^3, and 500-Å columns) gave M_n = 123 000 (M_w/M_n = 1.3) vs. PS standards. Esterification with 4-(1-pyrene)butyryl chloride was carried out as previously described. End-group analysis by UV absorption indicated >90% pyrene groups. The molecule methyl 4-(1-pyrene)butyrate (1) was used as the reference.

Samples of (~PS~PY + toluene) and of (1 + PS [M_n = 100 000, M_w/M_n = 1.06] + toluene) were prepared in cylindrical Pyrex tubes, carefully outgassed, and sealed under vacuum. Fluorescence decay profiles were measured by the time-correlated single-photon counting method.[16] Samples were excited at 345 nm. Monomer decay was monitored at 376 nm, and the excimer time profile at 520 nm.

The delta function convolution method[17a] was used for analysis of the decay curves, in conjunction with degassed solutions of BBOT (2,5-bis[5-*tert*-butylbenzoxazol-2-yl]thiophene) in ethanol (τ = 1.47 ns) for excimer and POPOP (*p*-bis[2-(5-phenyloxazolyl)]benzene) in cyclohexane (τ = 1.1 ns) for monomer, as reference compounds.

Results and Discussion

Fluorescence spectra of ~PS~Py at three different concentrations are shown in Figure 1. The lowest concentration sample ([~PS~Py] = 4×10^{-6} M) shows no excimer. The extent of excimer formation is largest in the sample with [~PS~Py] = 4×10^{-3} M. Here the weight concentration (c) of polymer is c = 0.46 g/mL.

Decay Profiles. Monomer profiles, $I_M(t)$, could be fitted to one exponential term at very low sample concentrations ($c < 5 \times 10^{-4}$ M). At higher sample concentrations (cf. Figure 2), two exponential terms were necessary to fit the $I_M(t)$ data. The excimer decay profile, $I_E(t)$, of the same sample requires a minimum of three

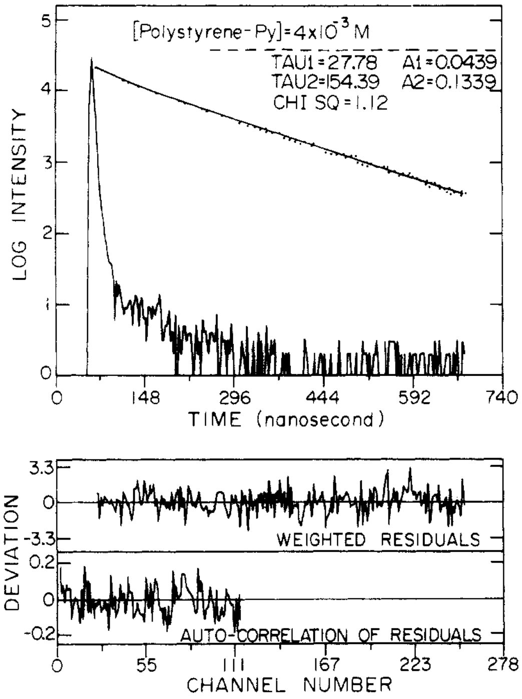

Figure 2. Fluorescence decay curve of monomer emission corresponding to sample c in Figure 1.

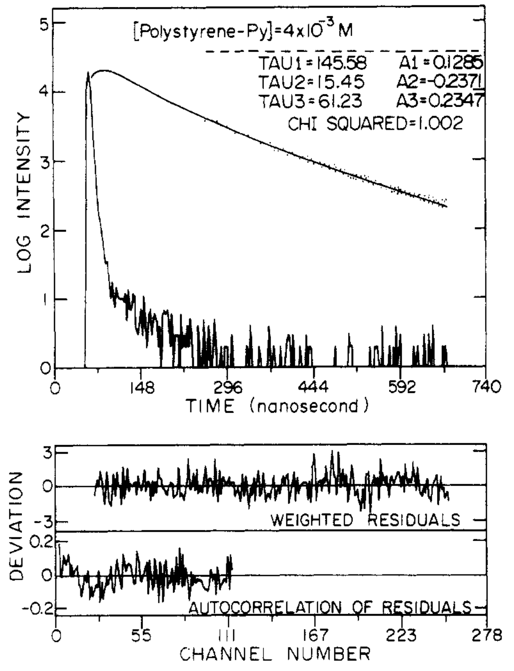

Figure 3. Fluorescence decay curve of excimer emission of the same sample as Figure 2.

exponential terms (cf. Figure 3) to be fitted. The lifetime of the rising component in the excimer decay is lower than that of the short component of the correspondent monomer decay curve. At lower polymer concentration (Figure 4), $I_E(t)$ could be fit to two exponentials, but the rising and decay portions had a ratio very different from unity. These results mean that data analysis in terms of Scheme I is not possible if one assumes that k_2 is not a function of time.

In order to assess whether these deviations are due to the time dependence of $k_2(t)$, one has to examine whether the $I_M(t)$ and $I_E(t)$ decay profiles can be fitted to equations which contain a predicted functional form for $k_2(t)$. This is possible when the diffusion-controlled processes are irreversible, i.e., when the dissociation step denoted by k_{-1} in Scheme I is unimportant. When, however, excimer dissociation is significant, it is no longer possible to find an analytical solution with which to fit $I_M(t)$ or $I_E(t)$.

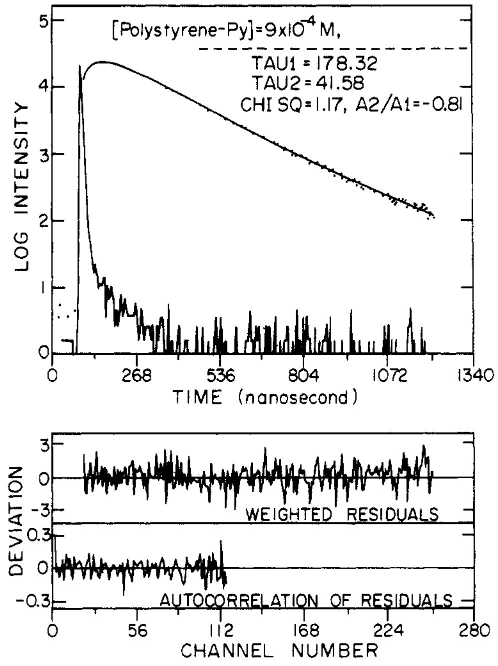

Figure 4. Fluorescence decay curve of excimer emission corresponding to sample b in Figure 1.

By use of Smoluchowski's equation for the excimer formation rate coefficient, the following expression is obtained for the monomer decay curve

$$I_M(t) = A \exp\{-(k_M + a[\mathrm{Py}])t - 2b[\mathrm{Py}]t^{1/2}\} \qquad (4)$$

where

$$a = \frac{4\pi D N_A R_e}{1000} \qquad b = \frac{4\pi D N_A R_e^2}{1000}(\pi D)^{-1/2} \qquad (5)$$

Here R_e is the capture radius for the reaction, N_A is Avogadro's number, and D is the mutual diffusion coefficient characterizing the diffusion-controlled process.

In one sample of ~PS~Py ([Py] = 9.0×10^{-4} M, c = 0.11 g/mL), the excimer emission is weak (Figure 1). Here the excimer dissociation contribution to $I_M(t)$ can be reasonably neglected. For this sample, a good fit can be obtained for $I_M(t)$ to eq 4.

From the values of a and b, we obtain $D = 2 \times 10^{-7}$ cm^2 s^{-1} and R_e = 10 Å. These values are known with poor precision. At low [Py], a in eq 4 is determined as the small difference between two large numbers, and at higher [Py], excimer dissociation prevents proper analysis of the $I_M(t)$ decay.

Recently we published[18] a new convolution relationship between $I_M(t)$ and $I_E(t)$ which provides an exact solution to the reaction kinetics irrespective of whether $k_2(t)$ is time-dependent or not. This relationship magnifies the manifestation in the data of the transient contribution to diffusion-controlled reactions. It makes it possible to examine different models giving different functional forms for $k_2(t)$. It is this relationship that allows us for the first time to examine de Gennes' predictions about the time dependence of $k_2(t)$ for intermolecular reactions of groups attached to the ends of polymer chains. This equation[18] relates the excimer concentration at time t ($[E^*]_t$) to that of the locally excited pyrene monomer concentration ([Py*]), where ⊗ in eq 6 denotes convolution.

$$[E^*]_t = k_2(t)[\mathrm{Py}][\mathrm{Py}^*]_t \otimes \exp\{-(k_E + k_{-1})t\} \qquad (6a)$$

This equation is quite general. The analytical form of $k_2(t)$ can be chosen in accordance with the theoretical

Table I
Experimental Data and Calculated D and k_2 Values for Pyrene Excimer Formation ~PS~PY in Toluene Solution at 22 °C

10^3[Py], M	c, g/mL	d, Å	B/A^b	C,^{b} ns$^{-1/2}$	$10^{-7}D$,^{c} cm^2 s^{-1}	$10^{-7}k_2$,^{d} M^{-1} s^{-1}	$10^{-7}(k_E + k_{-1})$, s^{-1}
0.90	0.11	123	2	0.79	4.3	26	2.0
3.8	0.46	76	25	0.79	0.053	0.32	2.7
4.2	0.51	73	30	0.89	0.047	0.28	2.8

[a] $d = N_A[\mathrm{Py}]^{-1/3}$. [b] Best fit parameters to eq 6 and 10. [c] From eq 13. [d] From eq 14.

models available. By a fitting procedure, the parameters of $k_2(t)$ and $(k_E + k_{-1})$ can be obtained.

What one does in practice is to fit the monomer and excimer decay profiles simultaneously, using the corresponding relationship

$$I_E(t) = k_2(t)[\mathrm{Py}]I_M(t) \otimes \exp\{-(k_E + k_{-1})t\} \qquad (6b)$$

If the model chosen for $k_2(t)$ is not in accord with the data, strong deviations in the fit become pronounced, particularly at early times.

We begin the analysis of $k_2(t)$ by identifying the distance and time scales characteristic of the polymer reaction. A useful measure of the distance probed in the reaction may be defined as

$$d = \{N_A[\mathrm{Q}]\}^{-1/3} \qquad (7)$$

where [Q] is the molar concentration of quencher. In the MHT experiments,[4] d = 400–500 Å. For a polymer of M_w = 150 000, $R_G \sim 170$ Å in benzene and toluene. Thus, MHT examine a system with $d/R_G \sim 2$–3. In terms of the entanglement distance ξ, at c = 0.2 g/mL, the MHT experiment probes $d/\xi \sim 30$. In our experiments, d = 75–125 Å; therefore, d/R_G = 0.5–0.7, and $d/\xi \sim 6$. These differences are a consequence of the longer time scale of the phosphorescence quenching experiment (100 μs to 1 ms) compared to 1 μs for excimer formation.

For the point of view of theory,[7] there are two characteristic time scales which pertain to these measurements. The longer is the Rouse time $T_R = W^{-1}N^2$, where W is the monomer jump frequency (ca. 10^{10} s^{-1}). T_R describes the conformation equilibrium time for the chain and for $N = 10^3$ takes the value 10^{-4} s. The shorter time, $T_\delta = W^{-1}N_e^{\,2}$, describes the conformational relaxation time for polymer segments between entanglements.

In times less than T_R, $k_2(t)$ is predicted[7] to decrease without limit in a power law relationship: $k_2(t) = (\mathrm{const})t^{-u}$. This form is a consequence of the fact that in three dimensions Rouse chains provide a case of compact exploration for $t < T_R$. The exploration is particularly compact for $T_\delta < t < T_R$ and $k_2(t) \sim t^{-5/8}$. At $t < T_\delta$, the dependence upon time is predicted to be less severe, with $k_2(t) \sim t^{-1/4}$.

Evaluation of $k_2(t)$. From an experimental point of view, there are two different characteristic times. The first, T_m, is the time scale of the measurements. T_m = 1 μs in these experiments and up to 1 ms in those reported by MHT. A second time characterizes noncompact exploration where $k_2(t)$ decays to its steady-state value, k_2. This time scale is defined as

$$T_{ss} = \{k_2[\mathrm{Q}]\}^{-1} \qquad (8)$$

Small molecule diffusion is noncompact. We studied excimer formation in methyl 4-(1-pyrene)butyrate (1), a model for the pyrene group attached to the polystyrene chain end, in toluene–PS mixtures. $I_E(t)$ data were analyzed by the monomer convolution method, eq 6. Here $k_2(t)$ could be fit to the form

$$k_2(t) = a + bt^{-1/2} \qquad (9)$$

where a and b are defined in eq 5. Since the concentration of [1] could be varied independently of the polymer concentration, c, it was possible to obtain R_e (R_e = 8.0 ± 0.6 Å) for excimer formation and D as a function of c.

In the case of our polymer samples, all attempts to fit the data failed when using a power law relationship for $k_2(t)$ in conjunction with eq 6. Good fits could be obtained only for expressions in which there is a steady-state solution for $k_2(t)$. It appears, therefore, that what we are measuring is an example of noncompact exploration.

Equation 9 is not adequate to describe excimer formation in ~PS~Py. It diverges at $t = 0$. The discontinuity derives from the boundary condition of infinite reactivity at the surface of the reaction sphere. A more reasonable expression has been obtained from the theory of partially diffusion-controlled reactions.[5] Here

$$k_2(t) = A[1 + B\exp(C^2t)\,\mathrm{erfc}\,(Ct^{1/2})] \qquad (10)$$

with

$$A = \frac{4\pi DN_AR_e}{1000}\,\frac{\beta R_e}{1 + \beta R_e} \qquad (11)$$

$$B = \beta R_e \qquad (12)$$

$$C = D^{1/2}(1 + \beta R_e)/R_e \ \mathrm{ns}^{-1/2} \qquad (13)$$

where β is a parameter that measures the efficiency of the reaction at the critical distance R_e. Under conditions of high viscosity where $D < 10^{-7}$ cm^2 s^{-1}, the differences between eq 10 and 9 persist into the nanosecond time domain.

The fluorescence decay profiles of all samples of ~PS~Py (cf. Figures 5 and 6) give good fits to eq 6 and 10. Because we normalize the $I_M(t)$ and $I_E(t)$ decay curves in the convolution method, we cannot obtain a value for A. To obtain values of D, we must assume a value of R_e and solve eq 12 and 13. We choose R_e = 8 Å, based on our model studies and also note that for $D < 10^{-7}$ cm^2 s^{-1}, B is so large that the reaction efficiency on encounter is essentially unity. These data are summarized in Table I.

Steady-state values of $k_2(t)$ were calculated from

$$k_2 = 4\pi N_AR_eD \qquad (14)$$

One of our samples (c = 0.11 g/mL) can be compared with one reported by MHT (~PS~B, $M_n = 1.3 \times 10^5$, c = 0.15 g/mL).[4] The k_2 values are very close, particularly considering the differences in R_e values and experimental conditions for the two reactions. Table II compares this and other aspects of phosphorescence quenching and excimer formation processes. In Figure 7 we plot the time profiles obtained for $k_2(t)$ in our three samples.

Diffusion Coefficients. For the small molecule 1, we can identify D_3 ($D_3 = D/2 = k_BT/f$) with the self-diffusion coefficient of the molecule. Its variation with c, Figure 8, measures the change in the monomer friction coefficient f.

For ~PS~Py we set $D_e = D/2$. We note with considerable surprise that the values of D_e are close to measured self-diffusion coefficients of PS of similar molecular weights.[19] The D_s values are obtained from experiments in which the diffusion occurs over distances many times larger than R_G. This similarity is found both for our high

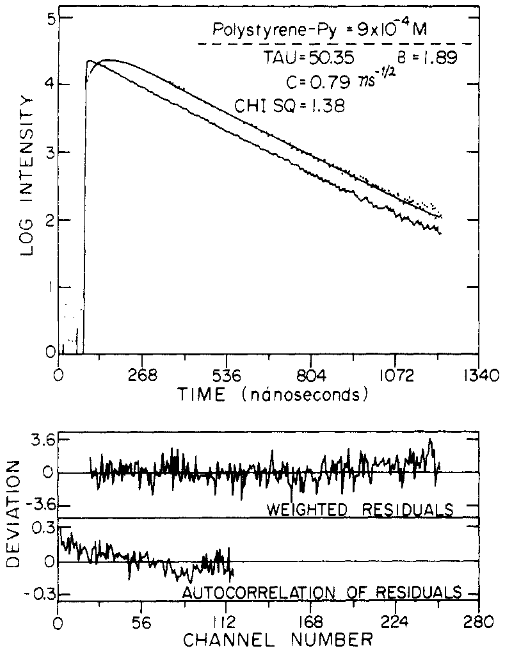

Figure 5. Simultaneous fit of monomer and excimer profiles to the convolution relationship, eq 6b for polystyrene–Py in toluene at $c = 0.11$ g/mL.

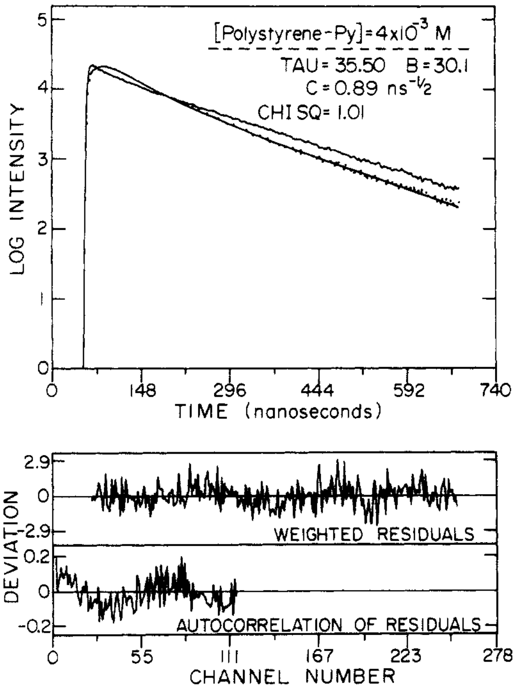

Figure 6. Simultaneous fit of monomer and excimer profiles to the convolution relationship, eq 6b for polystyrene–Py in toluene at $c = 0.51$ g/mL.

and low concentration samples, suggesting that the polymer concentration dependence found here for D_e also follows that reported for D_s. A similar observation was made by MHT[8] who found that k_2 values (and, hence, D_e) obey the relationship $k_2 \sim c^{-\alpha}$ with $\alpha = 1.7$–1.9. This behavior is consistent with the scaling arguments for reptation-type diffusion in the quenching process. The finding that $D_e = D_s$ provides another contrast between our experimental results and the predictions of the theory of de Gennes[7] but is in accord with the assumption of Tulig and Tirrell.[13]

Table II
Comparison of Phosphorescence Quenching and Excimer Formation in Benzene and Toluene for Polystyrene of M ≈ 10^5

	phosphorescence quenching[a]	excimer[b] formation
[Q], M	1.5–3×10^{-5}	0.9–4.2×10^{-3}
τ_B	30 μs	200 ns
R_e, Å	14	8
d, Å	400–500	75–120
d/R_G	2–3[c]	0.5–0.7
k_2, M^{-1} s^{-1}	4×10^{8}[c]	3×10^{8}[d]
T_{measd}	1 ms	1 μs
$T_q = k_2[Q]^{-1}$	30–200 μs	4–80 μs

[a] ~PS~B + ~PS~A in benzene. [b] ~PS~Py in toluene, 22 °C, $M_n = 1.2 \times 10^5$. [c] ~PS~B ($M_n = 1.3 \times 10^5$); ~PS~A ($M_n = 3.4 \times 10^5$), $c = 0.15$ g/mL, 20 °C. [d] [Py] = 9×10^{-4} M, $c = 0.11$ g/mL.

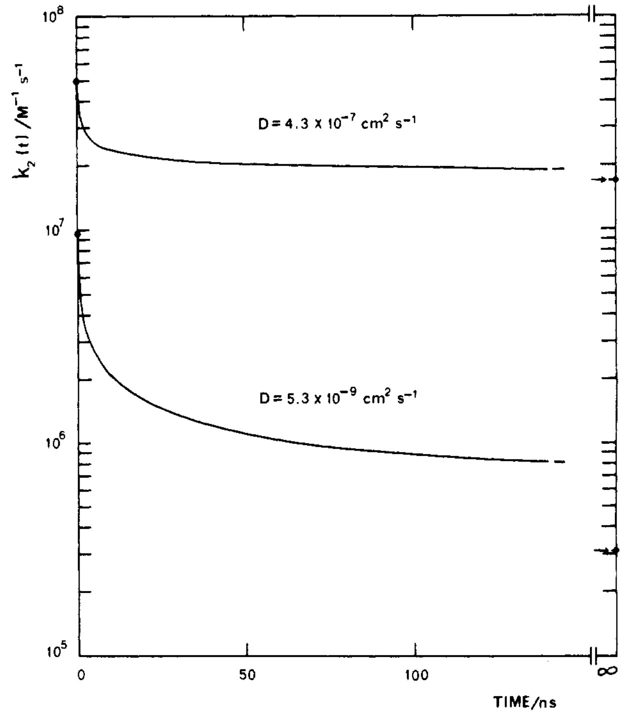

Figure 7. Time profiles of $k_2(t)$ based upon eq 10 using parameters evaluated from fluorescence decay analysis with eq 6b.

In order to focus on the topological constraints to diffusion, D_e values should be corrected for changes in the monomer friction coefficient.[20] In Figure 8 we also present a logarithmic plot of $D_e(f/f_0)$ vs. c, where f values are obtained from D_3 and f_0 refers to $c = 0$. Our data are not sufficiently numerous or precise to place much confidence in the exact value of the slope of this plot. A line of slope -1.75 passes through the data.

We wish to speculate on the origin of the differences between theory and experiment. On one hand, compact diffusion of the chain ends might occur only on a much faster time scale. As a consequence, our reactions, with $d = 0.5R_G$, are essentially dominated by center-of-mass diffusion of the polymer chains, which becomes the rate-limiting step in the termination process.

From another point of view, we note that at the lowest concentration ($c = 0.11$ g/mL), hydrodynamic interactions are not fully screened. A Zimm model may be more pertinent to the analysis of $k_2(t)$ than the Rouse model. In addition, there is another type of problem which has been identified in the diffusion-controlled cyclization reaction of polymers.

Diffusion-controlled cyclization has been examined in terms of the Rouse–Zimm model. Wilemski–Fixman[21] theory predicts that the diffusion-controlled rate coefficient (k_{cy}) will, under certain circumstances, become independent of R_e. This point has been examined in detail by Doi[22]

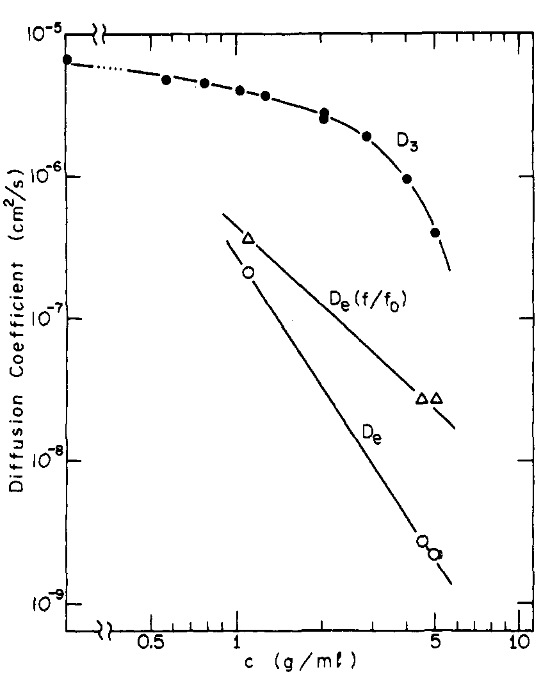

Figure 8. log–log plots of diffusion coefficients as a function of polystyrene concentration, c: (●) D_3 for small molecule 1 in mixtures of PS + toluene; (○) D_e for ~PS~Py in toluene; (△) $D_e(f/f_0)$, corrected for changes in the monomer friction coefficient.

and also by Cuniberti and Perico.[23] In that case, compact exploration requires the inequality $a < R_e \ll R_G$ to be satisfied. The relationship $a < R_e$ makes sense if a refers to the length of a monomer. In terms of the Rouse model, a refers to the length of one spring, a dynamic segment several monomers in length. R_e, however, is smaller than the spring length. In the case of cyclization, finite chains with $a > R_e$ show noncompact exploration and simple Smoluchowski diffusion.[22-24] Our appreciation of de Gennes' theory[7] is not sufficiently deep for us to identify whether a similar problem exists for intermolecular diffusion-controlled polymer–polymer reactions.

Summary

Experiments were carried out to examine the time dependence of diffusion-controlled intermolecular reactions between groups attached to the ends of polymer chains. These experiments allow various forms for the time dependence of the diffusion-controlled rate coefficient $k_2(t)$ to be tested. At short times and elevated polymer concentration, compact diffusion is anticipated,[7] and this in turn predicts a power law form for $k_2(t)$. The data, however, cannot be fit to an expression for $k_2(t)$ without a non-zero steady-state limit. The reaction between the chain ends, therefore, involves noncompact diffusion. Data analysis in terms of a modified Smoluchowski equation gave values of the end-segment diffusion coefficient, D_e. Values of D_e were similar to those of polystyrene self-diffusion coefficients (D_s) in the semidilute concentration domain. Both D_e and D_s showed a similar dependence upon polymer concentration. This result is consistent with an assumption of Tulig and Tirrell[13] in their analysis of the termination rate of free-radical polymerization that the diffusion-controlled interaction between the ends of two polymer chains depends primarily on the sum of the center-of-mass translational diffusion coefficients of the interacting polymer chains.

Our values of D_e are obtained by fitting fluorescence decay data to a model more appropriate for small molecule diffusion than for polymer–polymer interactions. A proper theory of the short-time behavior of polymer noncompact diffusion is not now available. Our most important contribution here is a methodology for testing various models and their predictions of $k_2(t)$. It is in the hopes of stimulating the development of new models that we are publishing our data at this time.

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