Intermolecular Excimer Formation for Pyrene-End-Capped Polystyrene: A Model for the Termination Process in Free-Radical Polymerization[1]

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ABSTRACT: The kinetics of intermolecular excimer formation are reported for a polystyrene sample containing one pyrene end group (PS-Py). This reaction serves as a model for the termination process in free-radical polymerization. Fluorescence decay profiles were measured for both monomer and excimer emissions, and from these, the transient contribution to the diffusion-controlled reaction was evaluated. In this way, the mutual diffusion coefficients characteristic of the reaction could be determined. These values ($D_o = 1.4 \times 10^{-6}$ cm² s⁻¹, toluene 20 °C; 1.2×10^{-6} cm² s⁻¹, cyclohexane, 34.5 °C) for the polymer of $M_w = 10\,400$ ($M_w/M_n = 1.05$) are remarkably close to values reported for polystyrene itself ($M_w = 10\,700$) as determined by quasielastic light scattering ($D_o = 1.57 \times 10^{-6}$, toluene 20 °C; 1.23×10^{-6}, cyclohexane, 34.5 °C). This close correspondence between the two sets of values implies that, in this concentration region, excimer formation (and the termination reaction for polymers of this length) is controlled by center-of-mass diffusion of the polymer.

Introduction

In the free-radical polymerization, the termination step involves the reaction between radicals located at the ends of two growing polymer chains. Upon encounter, this pair of radicals either couples to form a new C–C bond or disproportionates via H atom transfer. Since both processes are characterized by very low activation energies, the termination step is diffusion controlled.[3–7] This makes a fundamental description of the termination process both difficult and delicate, since all of the factors that affect polymer diffusion (hydrodynamic screening, excluded volume, entanglements, free volume—especially at high volume fraction of polymer) all affect the termination process. Furthermore, since the polymer molecular weights and volume fraction evolve during the reaction, the dominant factors affecting polymer diffusion change during the polymerization.[7]

The termination step of free-radical polymerization, at low conversion, is thought to be controlled by *segmental diffusion* rather than *center-of-mass* diffusion of the polymeric radicals.[4,5] This idea is developed in terms of the time-independent Smoluchowski equation[8] for diffusion-controlled reactions, where one equates the termination rate constant k_t with the diffusion-controlled rate constant, k_{diff}:

$$k_t = k_{diff} = 4\pi N_A' D_m R_o \qquad (1)$$

where N_A' is Avogadro's number per millimole, D_m is the mutual diffusion coefficient for polymer diffusion, and R_o is the capture radius for the reaction. D_m is equal to the sum of the diffusion coefficients of the two reactants, which, in the limit of low concentration, are each equal respectively to their center-of-mass diffusion coefficients $D_o^{(a)}$ and $D_o^{(b)}$. The argument aginst D_m controlling termination at low conversion presumes that if center-of-mass diffusion is rate limiting, the capture radius must be on the order of the coil dimensions and hence proportional to the sum of the hydrodynamic radii $R_H^{(a)}$ and $R_H^{(b)}$ of the two reacting chains. Since D_o is proportional to (R_H^{-1}),[9] k_{diff} should be independent of chain length, at odds with the known, but poorly understood, chain-length dependence of k.

This issue could be addressed at a deeper level if one could examine model systems in which the transient contribution to the diffusion-controlled process could be examined. Such a model system would involve a polymer chain of narrow molecular weight distribution containing an appropriate fluorescent or phosphorescent group at the one end and a second polymer containing a quencher end group. The idea for using such polymers as models for examining the termination rate coefficient for free-radical polymerization was developed by Horie and Mita,[10] who used phosphorescence quenching measurements to establish definitive evidence for the chain-length dependence of k_t.

We have taken the Horie–Mita[10] idea and extended it to the case of excimer formation. Excimer formation lends itself to investigation of transient effects in diffusion-controlled reactions. From a study of these transient effects, one can determine the D_m and R_o values intrinsic to the reaction itself.

Transient effects[11] in diffusion-controlled reactions arise because closely spaced pairs react at early times, leading to a depletion of such species in the pair distribution. As a consequence, the reaction rate decreases as a function of time until the conjugate effects of molecular diffusion and reaction create a stationary pair distribution function. One normally incorporates the time evolution of the reactant pair distribution into the rate coefficient. In this approach, the reaction rate is equal to the product of the bulk concentration of reactions and a time-dependent rate coefficient [$k_{diff}(t)$]. In the original Smoluchowski formulation,[8] it was assumed that the reaction occured instantaneously once the reactants diffused to within a distance R_o of one another. In the more general Collins and Kimball model,[12,13] one assumes that this pair reacts at a finite rate in competition with diffusion apart. With this assumption, the diffusion-controlled rate coef-

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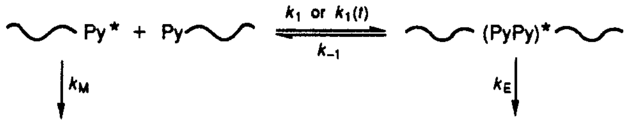
Scheme I



ficient $k_{\text{diff}}(t)$ can be expressed for long enough times as

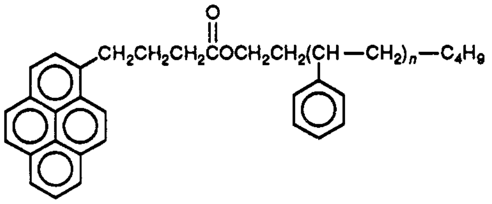
$$k_{\text{diff}}(t) = 4\pi N_A' D_m R_{\text{eff}}[1 + R_{\text{eff}}(\pi D_m t)^{-1/2}] \qquad (2)$$

Here R_{eff} is an effective radius, smaller than R_o, that characterizes the reaction efficiency of encounter pairs, with $R_{\text{eff}} \to R_o$ as $D_m \to 0$. Equation 2 provides a two-parameter description of k_{diff}.

$$k_{\text{diff}} = a(1 + bt^{-1/2}) \qquad (3)$$

If the reaction kinetics can be studied in a way that the parmeters a and b can be determined, the values of D_m and R_{eff} characterizing the diffusion-controlled reaction can be calculated. In this way, by setting $k_t(t) = k_{\text{diff}}(t)$ and modeling the k_t process by intermolecular excimer formation, we can examine, within the context of the above model, the question of which diffusion coefficient and which R_o value characterize the termination process for model polymers.

In this paper we consider a single sample of pyrene-end-labeled polystyrene, (M_n = 10 400; M_w/M_n = 1.05), which has the structure



PS10K-Py
($n \approx 100$)

Experimental Section

The Polymer. Polystyrene was synthesized in Akron by anionic polymerization by standard methods using *sec*-butyllithium as the initiator and ethylene oxide in the termination step to produce polystyrene-CH_2CH_2OH (PS-OH). This species was treated with 4-(1-pyrenyl)butylryl chloride, as previously described,[14] to attach a pyrenylbutyrate group to the chain end. The polymer was characterized by gel permeation chromatography in toluene using Ultrastyragel columns (500, 10^3, 10^4 Å) and tandem UV–vis and differential refractive index detectors. Based upon polystyrene standards, the polymer had M_n = 10 400, M_w/M_n = 1.05.

By UV spectroscopy, the extent of end labeling with pyrene groups was greater than 95%. Solutions of PS-Py in toluene and in cyclohexane were placed in round (7-mm-o.d.) Pyrex tubes, degassed by the freeze–pump–thaw technique, and sealed under a vacuum better than 2×10^{-15} Torr. Concentrations ranged from 1×10^{-6} to 1.35×10^{-2} M.

Fluorescence spectra were run on a Spex Fluorolog 2, without correction for the wavelength sensitivity of the detection system. Fluorescence decays were obtained by the single-proton timing technique as previously described.[14] Samples were excited at 345 nm. Monomer fluorescence was observed at 376 nm and excimer fluorescence at 520 nm.

Results and Discussion

The Model. Pyrene excimer formation is normally described in terms of Scheme I, where k_1 [or $k_1(t)$] is the rate coefficient for excimer formation, and k_{-1} is that for excimer dissociation. The terms k_M and k_E are the reciprocal intrinsic lifetimes of the locally excited pyrene "monomer" decay and excimer decay, respectively. As a consequence, we will identify the behavior of k_1 [and $k_1(t)$] with that of k_t [and $k_t(t)$] for the termination of two polystyrene radicals of comparable length. In terms of the data analysis and eq 3, we will show that

$$k_1 = a = \lim_{t \to \infty} k_1(t) \qquad (4)$$

The coefficient b of the transient term is then obtained by a convolution analysis of the pyrene monomer and excimer fluorescence decay profiles, and from the values of the parameters a and b, D_m and R_{eff} are calculated.

Data Analysis. Fluorescence decay curves for pyrene monomer [$I_M(t)$] and excimer [$I_E(t)$] emission were obtained by the single-photon timing technique. When analyzed independently, each fit well to the two-state (Birks) model,[15] which predicts, for δ-pulse excitation

$$I_M(t) = B_1 \exp(-\lambda_1^M t) + B_2 \exp(-\lambda_2^M t) \qquad (5)$$

$$I_E(t) = B_3 \exp(-\lambda_1^E t) - B_4 \exp(-\lambda_2^E t) \qquad (6)$$

In our previous publications on transient effects[14,16,17] in pyrene excimer formation, we have shown that when the data are analyzed according to eqs 5 and 6, the pairs of decay constants λ_1^M, λ_1^E and λ_2^M, λ_2^E are close in value, and within experimental error, but show certain systematic differences that imply the possible breakdown of the two-state model at early times. The essential conclusion to be drawn from this behavior, which is also observed here, is that the magnitude of the transient effect is small and almost imperceptible from this traditional approach to data analysis. As a consequence, these expressions provide reliable data from which the long-time limiting value of k_1, and the values of k_E and k_{-1}, can be determined via the expressions

$$2\lambda_2, \lambda_1 = [(A_x + A_y) \pm [(A_y - A_x) + 4k_1[M]k_{-1}]^{1/2}] \qquad (7)$$

$$A_x = k_1[M] = k_M \qquad A_y = k_E + k_{-1} \qquad (8)$$

$$k_{-1} = (\lambda_2 - A_x)/(A_y - \lambda_1) \qquad (9)$$

where [M] is the molar PS-Py concentration, and k_M is determined as the reciprocal exponential pyrene decay time for PS-Py at low concentration (e.g., 2×10^{-6} M).

If the transient effect were unimportant in this reaction, the data would fit a simultaneous convolution analysis of the $I_M(t)$ and $I_E(t)$ decay curves

$$I_E(t) = \beta I_M(t) k_1 \otimes \exp(-A_y t) \qquad (10)$$

where β is a normalization constant and $\otimes$ indicates a convolution integral. Figure 1 demonstrates that the data give a poor fit to eq 10, especially at early times. The convolution analysis amplifies the sensitivity of the data to transient effects. When the data are reanalyzed in terms of eq 11, with [$k_1(t) = a(1 + bt^{-1/2})$], one gets good fits to

$$I_E(t) = \beta I_M(t) k_1(t) \otimes \exp(-A_y t) \qquad (11)$$

the data (Figure 2), and values for the parameter b can be obtained. In fitting data to eq 11, separate values for a and β cannot be obtained. To calculate D_m and R_{eff}, we obtain values for $a = k_1$ from data analyzed according to eqs 7–9.

Equation 11 is rigorously true for irreversible systems. For reversible reactions, correlated pairs are created owing

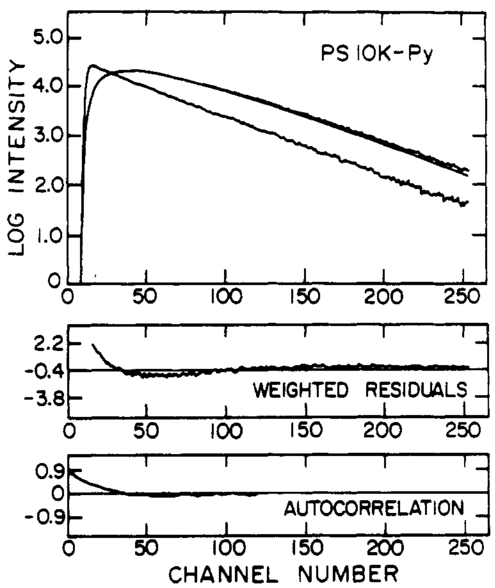


Figure 1. Plot of log I vs t for monomer and excimer emission for a sample of PS10K-Py in cyclohexane at 50 °C. The weighted residuals and the autocorrelation of the residuals refer to fit of the data of eq 10 with k_1 assumed to be time independent.

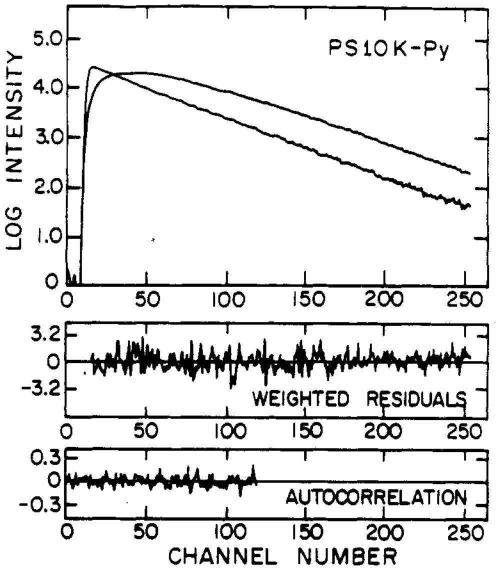


Figure 2. Fit of the same data as Figure 1 to eq 12 with $k_1(t) = a(1 + bt^{-1/2})$.

to excimer dissociation. If the excimer formation rate coefficient has the same time profile for the initially excited molecules and for the ones created by excimer dissociation, an expression formally identical with eq 11 is recovered, but with $k_1(t)$ generally differing from the Smoluchowski expression $[a(1 = bt^{-1/2})]$.[18] Recently, mathematical simulations[18] show that $k_1(t) = a(1 + bt^{-1/2})$ continues to be a reasonable approximation when the extent of excimer dissociation is small, as in the case of pyrene at room temperature. Ware[19] argued that this assumption is reasonable when $(k_{-1} + k_E)^{-1}$ is longer than the time for 90% of the transient effect to decay, a condition that is certainly satisfied here.

It has been our experience that D_m values obtained via eq 11 are in good agreement with diffusion coefficients measured by other means. We will be very much concerned here to see how well the D_m values for polymer-bound pyrene correspond to those obtained by quasielastic light scattering for polymers of similar molecular weight.

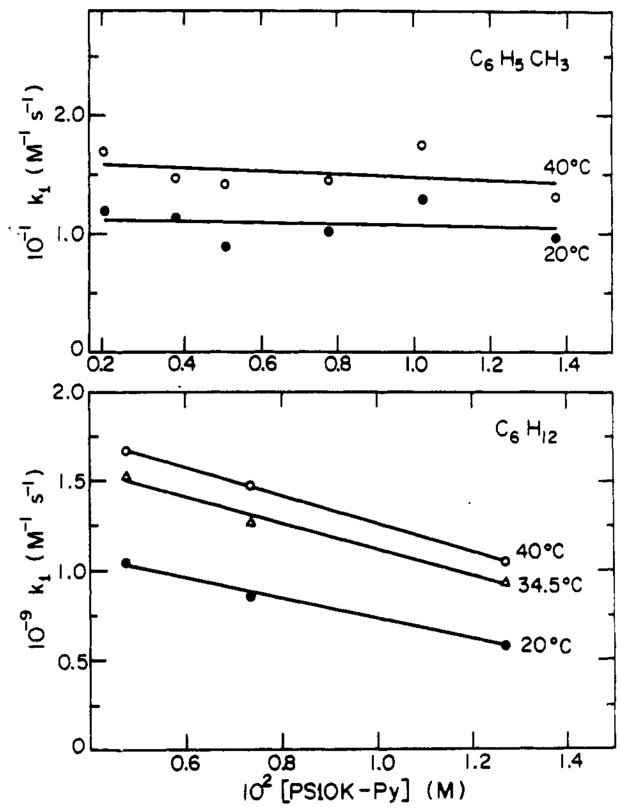


Figure 3. Plot of k_1 vs polymer concentration (M) for PS10K-Py in toluene and cyclohexane.

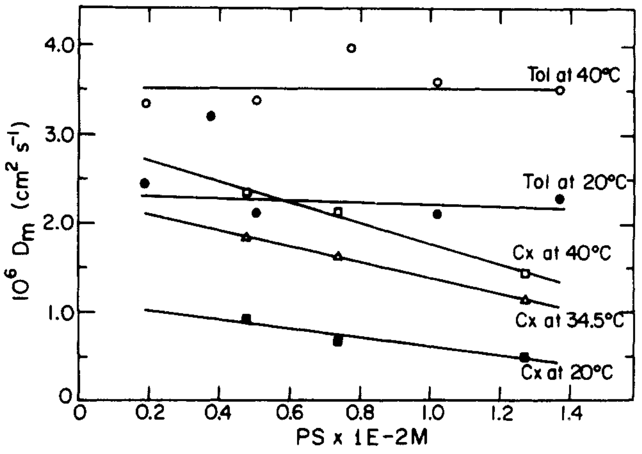


Figure 4. D_m values as a function of molar polymer concentration for PS10K-Py in toluene and in cyclohexane.

Rate Coefficients. One of the more interesting results from a traditional analysis of the excimer formation kinetics is that k_1 values for PS10K-Py decrease linearly with increasing concentration for samples in cyclohexane (Figure 3), but are concentration independent for samples in toluene. This phenomenon has its origin in the concentration dependence of the mutual diffusion coefficients of polymers, which will be examined in more detail below. It is worth emphasizing that one traditional method for obtaining k_1 values for excimer formation, fitting λ values to the expression

$$\lambda_1 + \lambda_2 = k_E + k_M = k_{-1} + k_1[M] \qquad (12)$$

will lead to linear plots but incorrect results whenever k_1 is proportional to [M].

Diffusion Coefficients. Diffusion coefficients calculated from a and b values for experiments carried out in cyclohexane and in toluene at several temperatures are plotted in Figure 4. D_m values are on the order of (1–4) × 10^{-6} cm^2 s^{-1}, and somewhat higher in toluene than in cyclohexane for experiments at similar temperatures. In toluene, D_m values are independent of polymer concentration, whereas in cyclohexane, D_m decreases linearly with increasing concentration.

The concentration dependence of polymer mutual diffusion coefficients is well documented through quasielastic light scattering [QELS] measurements[20] and can be understood as arising from a combination of friction and thermodynamic effects.[9] To relate our D_m values to D values determined by QELS, we recall that D_m is the sum of diffusion coefficients of the reactants, and set $D = D_m/2$. At low polymer concentration, D depends linearly on concentration (c, g/L)

$$D = D_0(1 + k_D c + ...) \qquad (13)$$

The concentration coefficient k_D depends upon polymer properties through the relationship

$$k_D = 2A_2M_w - k_f - \nu_2 \qquad (14)$$

Here k_f describes the concentration dependence of the monomeric friction coefficient f

$$f = f_0(1 + k_f c + ...) \qquad (15)$$

and ν_2 is the partial specific volume of the polymer. A_2 is the second virial coefficient. Its value is positive in good solvents, negative in poor solvents, and zero at the θ temperature of appropriate solvents. Since k_f and ν_2 are both positive quantities, k_D is negative when $(k_f + \nu_2) > 2A_2M$, and positive when A_2M is large.

For polystyrene, cyclohexane is a poor solvent, with a θ temperature of 34.5 °C. In Figure 4 we see that k_D is negative for PS10K-Py at 34.5 °C where A_2 equals zero and is also negative at 20 and 40 °C. This is an indication that, over this small span of temperatures and for this low molecular weight sample, the product A_2M is smaller than $k_f + \nu_2$.

For experiments in toluene, the D_m data are more scattered. Because of the lower viscosity, diffusion is faster, and the transient term makes a smaller contribution to the fluorescence decay profiles. In spite of the scatter, it is clear (Figure 4) that D_m is essentially independent of concentration at both 20 and 40 °C. Toluene is a good solvent for polystyrene, and A_2 should be only very weakly dependent on temperature. Since A_2 is positive and the M_w of our polymer is not very large, the concentration independence of D_m indicates that $2A_2M_w \approx k_f + \nu_2$ for these samples.

These results are in accord with the QELS experiments on low molecular weight polystyrene published recently by the Buchard group.[21] QELS provides a more accurate and unambiguous approach to determining mutual diffusion coefficients for polymers, although the weak signals obtained from low molecular weight polymers make these particular measurements a challenge. The Burchard group reports values of D and k_D for a polystyrene sample of M_w = 10 700 in toluene at 20 °C and in cyclohexane at 34.5 °C. For toluene they find k_D = 1.7 mL g^{-1}, which represents a very small positive concentration dependence of D.

We are in fact surprised by the remarkable agreement between the D_0 values otained from our fluorescence decay measurements and the QELS values (Table I) reported by the Burchard group. This accord not only demonstrates the validity of eq 11 in fitting the $I(t)$ data, it also establishes that excimer formation, and by implication, free-radical termination in this concentration regime, depends upon center-of-mass diffusion of the polymers.

Table I
Diffusion Coefficients from Excimer Formation and from Quasielastic Light Scattering

	T, °C	M_w	technique	D_0, cm^2/s
cyclohexane	34.5	10 400	excimer[a]	1.2×10^{-6}
		10 700	QELS[b]	1.23×10^{-6}
toluene	22	10 400	excimer[a]	1.4×10^{-6}
	20	10 700	QELS[b]	1.57×10^{-6}

[a] PS10K-Py. [b] Polystyrene, ref 21a.

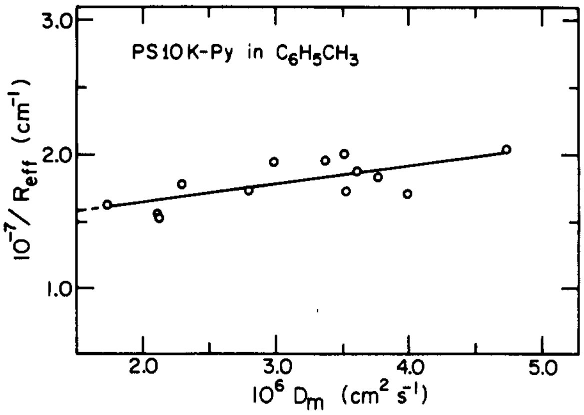


Figure 5. A plot of $(R_{eff})^{-1}$ vs D_m for data obtained from experiments in toluene.

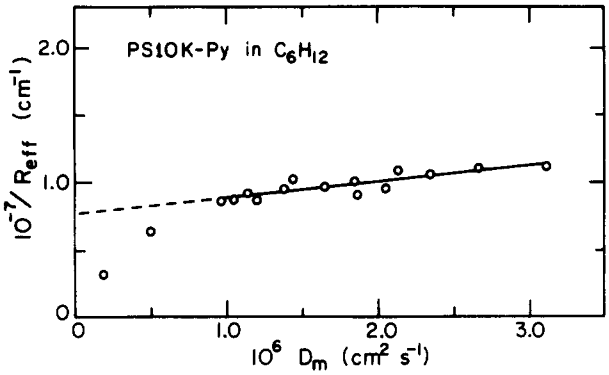


Figure 6. A plot of $(R_{eff})^{-1}$ vs D_m for data obtained from experiments in cyclohexane.

The Capture Radius. The other parameter available from analysis of the transient contribution to the kinetics of excimer formation is the effective capture radius R_{eff}. In the Collins and Kimball model[11-13] R_{eff} is a function not only of the true reaction radius R_0 but also the kinetic competition between reaction and dissociation for proximate pairs. These radii are related by the expression

$$\frac{1}{R_{eff}} = \frac{1}{R_0} + \frac{4\pi D_m}{k_c} \qquad (16)$$

where k_c (in cm^3 s^{-1}) is the intrinsic reaction rate constant. Indeed all of our data for excimer formation in toluene fall on a common line (Figure 5) when plotted according to eq 16, as do all but two of the data points for experiments in cyclohexane (Figure 6). Furthermore, both slopes are identical [(1.3 ± 0.2) × 10^{12} s cm^{-3}], leading to k_c values of 9.7 × 10^{-12} cm^3 s^{-1}. This value of k_c compares very favorably with a value of (1.2 ± 0.5) × 10^{-11} cm^3 s^{-1} determined for excimer formation for methyl pyrenylbutyrate (i.e., the end group itself) in toluene. Taken together, these results indicate that one consequence of attaching the pyrenylbutyrate to the end of the polymer chain is to slow down the rate of molecular diffusion without substantially affecting the intrinsic chromophore reactivity.

From the intercepts of Figures 5 and 6, we calculate R_0 values of 6.3 ± 0.5 Å for excimer formation in toluene and

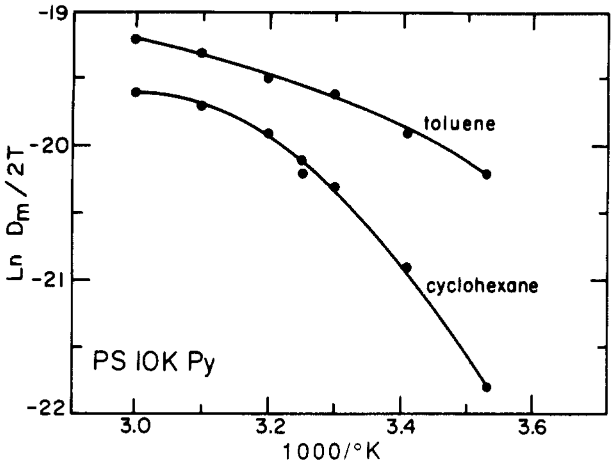


Figure 7. A plot of $\ln D_m/2T$ vs $1/T$ from experiments in toluene (upper curve) and cyclohexane (lower curve).

Table II
Activation Parameters for Excimer Formation and for Solvent Viscosity

M_w	solvent	E_a (k_1/T),[c] kcal/mol	E_a (η_o^{-1}),[d] kcal/mol
7 800[a]	cyclohexane	3.6	2.9
7 800	toluene	2.2	2.1
10 400[b]	cyclohexane	3.9	2.9
10 400	toluene	2.5	2.1

[a] PS7800-Py, data from ref 14. [b] PS10K-Py. [c] From plot of $\ln (k_1/T)$ vs T^{-1}. [d] From plot of $\ln \eta_o^{-1}$ vs T^{-1}.

12.8 ± 0.4 Å for the reaction in cyclohexane. The value in toluene is slightly smaller than the value (8 ± 0.5 Å) determined for methyl pyrenylbutyrate.[16a] Along with the small difference in k_c values this result suggests that the polymer chain may also impose a small steric constraint to the excimer-forming process. We were initially surprised by the larger R_0 values for excimer formation in cyclohexane and considered various ways in which the coil dimensions might affect the reaction radius of the end group. It now appears that these thoughts were misdirected. Recent studies[22] of excimer formation of methyl pyrenylbutyrate in cyclohexane give R_{eff} values larger than 9 Å, suggesting that pyrene excimer formation itself is characterized by a larger R_0 in cyclohexane than in toluene. This point needs further investigation.

Temperature Effects. A common way of analyzing the temperature dependence of diffusion controlled reactions is to compare plots of $\ln (k_{diff}/T)$ and $\ln \eta_o^{-1}$ vs $1/T$, where η_o is the solvent viscosity. Since $k_{diff} \sim D$ and $D \sim \eta_o/T$, an Eyring plot of $\ln (k_{diff}/T)$ and an Arrhenius plot of $\ln \eta_o^{-1}$, will yield identical activation energies if the only effect of temperature on the reaction is to change the viscous drag experienced by the reactants.

When k_1 values are treated in this way, linear plots are obtained. In each case, however, the E_a value formation is larger than those for solvent viscosity. As shown in Table II, these differences are particularly significant for experiments in cyclohexane, where $E_a(k_1/T) = 3.9$ kcal/mol and $E_a(\eta_o) = 2.9$ kcal/mol. The differences are much smaller for toluene, and there is also a suggestion from comparison with earlier work that E_a increases with increasing polymer molecular weight.

On the other hand, Arrhenius plots of the D values themselves show curvature (Figure 7), slight in the case of toluene, and pronounced for cyclohexane. In the case of toluene, the curvature may indicate small temperature effects on the k_{DC} term in eq 13. For cyclohexane, where experiments straddle the θ temperature, the curvature reflects temperature-induced changes in polymer dimensions accompanying changes in solvent viscosity.

Summary

Polymers containing a pyrene end group undergo diffusion-controlled intermolecular excimer formation, and this reaction is a useful model for the termination process in free-radical polymerization. Here we report kinetic studies for a polystyrene-Py sample of $M_w = 10\,400$. By careful examination of the transient contribution to excimer formation, we obtain the mutual diffusion coefficient and the capture distance characteristic of the reaction. We find that this reaction depends upon the *center-of-mass diffusion coefficient* of the polymer, and that R_0 is very similar to that for low molecular weight pyrene derivatives. This is a surprising result because it is widely believed that the rate-limiting step in the diffusive encounter of two polymer chain ends, at low polymer concentration, is the segmental diffusion of one end into the coil of the other polymer. This is clearly not the situation here, but it may turn out that segmental diffusion becomes rate limiting for much longer polymer chains.

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Registry No. S, 100-42-5; PS (homopolymer), 9003-53-6.