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Intracoil Triplet–Triplet Annihilation in Poly(4-vinylbiphenyl) in Benzene Solution

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ABSTRACT: The triplet state of poly(4-vinylbiphenyl) (P4VBP) has been sensitized by benzophenone, and biphenyl excimer delayed fluorescence (DF) has been observed. From numerical solutions of a kinetic model and general physical considerations it has been concluded that an *intracoil* T–T annihilation process yields this DF, which implies the existence of intracoil triplet migration. There is also evidence for intercoil T–T annihilation, which occurs on a much longer time scale than the intracoil process. This latter process is detectable in P4VBP because of the relatively long lifetime of the triplet state in deoxygenated solutions (~40–50 μs).

Introduction

We have recently observed delayed excimer fluorescence in room-temperature benzene solutions of poly(2-vinylnaphthalene) (P2VN) sensitized by benzophenone.[1] A homogeneous, intracoil annihilation mechanism was invoked to fit the trends observed in these data. Such a mechanism implies that triplet energy migration along the P2VN chain occurs in solution. In the present paper we report our observation of a delayed emission from benzene solutions of poly(4-vinylbiphenyl) (P4VBP) sensitized by benzophenone. The time-resolved emission spectrum is identical with the polymer-bound biphenyl excimer.[2-4] Kinetic models similar to that used for P2VN[1] will be used to analyze the results. A mechanism incorporating intra- and intercoil homogeneous annihilation will be shown to provide the best fit to the time dependence of delayed fluorescence. The differences between P2VN and P4VBP data will be discussed in terms of the photophysics of these two chromophores.

Experimental Section

Synthesis and characterization of the P4VBP samples have been described elsewhere.[5] The values for the polydispersity, molecular weight, intrinsic viscosity, and degree of polymerization are listed in Table I. Benzophenone was purified by several recrystallizations from ethanol. Spectrograde benzene was washed with sulfuric acid and then aqueous sodium carbonate. The washed benzene was then dried over $CaCl_2$ and distilled.

All experiments were carried out at the Center for Fast Kinetics Research, The University of Texas at Austin, and the laser flash photolysis unit was the same as that used previously.[1,6] The same experimental conditions were used in this experiment as our previous work[1] with the exception that excitation intensity of the nitrogen laser was attenuated by an OD = 0.5 neutral-density filter (rather than OD = 1.0 as for the P2VN experiment). This was necessary because of the lower overall intensity of delayed fluorescence in the present experiments. The reason for this increase in the laser excitation will be discussed in the Results. Because of the increased laser intensity, the T–T annihilation between benzophenone triplets is more important in solutions with low P4VBP concentration. For example, at the lowest polymer concentration used with a sensitization rate of $0.16 \times 10^6\ s^{-1}$ approximately 25% of the benzophenone triplet decay rate at $t = 0$ is via self-annihilation. The annihilation between benzophenone triplets depletes the number of triplets available to the polymer coil. Thus there is a slight error in our kinetic simulation, in which we ignore this annihilation. At higher P4VBP concentration the triplet benzophenone concentration is decreased by energy transfer such that self-annihilation can be ignored. In all cases the decay of the benzophenone triplet concentration was monitored via T–T absorption at 532 nm. The time-resolved emission spectrum was obtained by assembling decay curves at every 5 nm. A 0.5-cm cuvette was used in order to minimize the reabsorption of the short-wavelength components of the delayed fluorescence by benzophenone. The rate of decay of the delayed fluorescence was monitored at 400 nm, which corresponds to excimer fluorescence. The intensity of individual laser shots was measured, and data collected for laser shots within ±3% of each other were retained.

Table I

	[η], dL/g	P	mol wt	M_w/M_n
P4VBP-1	0.119	149	27 100	1.44
P4VBP-4	0.440	1236	225 000	1.55

The numerical solutions to the rate equations were performed on the CDC 7600 computer at The University of Texas as Austin. The program was the same as that used previously,[1] which consisted of a differential equation solver using the Adam's predictor–corrector method from the IMSL library.

Results

Figure 1 shows the time-resolved (i.e., delayed fluorescence (DF) emission spectrum of 10^{-2} M benzophenone + 6.7×10^{-3} M P4VBP-4 ($P = 1236$) in benzene along with a steady-state fluorescence spectrum of P4VBP-4 in benzene. Both spectra show the familiar broad excimer band that peaks at 380 nm for biphenyl.[2-4] The "structure" in the time-resolved spectrum is an artifact that arises from laser power fluctuations. The quality of this spectrum is diminished relative to our earlier work because of the poor signal-to-noise ratio of the delayed fluorescence. The delayed emission is attenuated at short wavelengths ($\lambda \le 380$ nm) by the absorption of the benzophenone. In addition, it is not possible to obtain reliable data at the short wavelengths (i.e., $\lambda < 360$ nm) because of the interference from the laser wavelength ($\lambda = 337$ nm). Despite these difficulties for shorter wavelengths, the nonzero intensity of the emission at $\lambda = 360$ nm in the time-resolved emission spectrum in Figure 1 indicates that the delayed fluorescence is not composed entirely of excimer emission.

We have mentioned in the Experimental Section that the excitation intensity was increased by ca. 2.5× in order to obtain an adequate signal (i.e., comparable to that of the P2VN sensitization experiment[1]). It has been our experience that the most important factor controlling the signal-to-noise ratio is the value of the average number of excitations per coil (n^*) at the time at which maximum emission occurs (t_{max}). The low and high molecular weight P4VBP samples studied herein have a degree of polymerization (P) slightly less than half that of the corresponding samples in the P2VN experiments.[1] Consequently, for P4VBP and P2VN solutions with the same base-unit molecular concentration the P4VBP will have twice the coil concentration as the P2VN solution. This in turn requires an increase in the concentration of excited benzophenones by approximately a factor of 2 in order to achieve n^* values for P4VBP comparable to those in our P2VN work. We estimate n^* to be ca. 0.2 and 0.8 for

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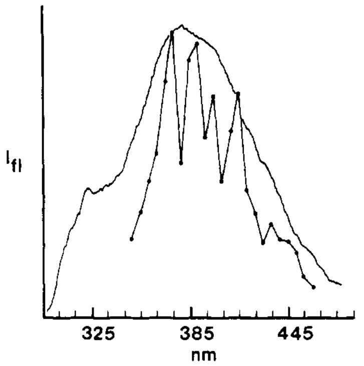


Figure 1. Time-resolved delayed emission (DF) for 1×10^{-2} M benzophenone + 6.7×10^{-3} M P4VBP-4 observed 0.7 μs after laser flash (dash–dot line) and steady-state fluorescence of P4VBP-4 (solid line). The time-resolved spectrum is constructed from decay curves taken at different wavelengths such that pulse-to-pulse variations in laser photon flux lead to the "structure" in the spectrum.

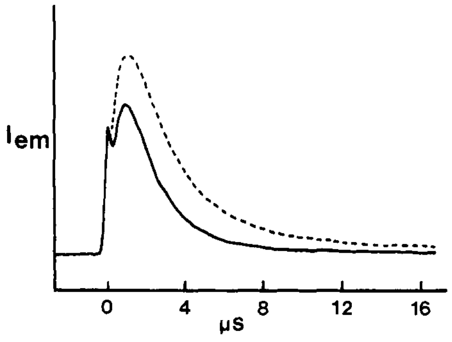


Figure 2. Time dependence of the delayed emission (DF) (observed at 400 nm) of P4VBP-1 (solid line) and P4VBP-4 (dashed line). The intensity units of emission are arbitrary but are at the same sensitivity for both polymers. The initial spike is scattered laser light.

P4VBP-1 and P4VBP-4, respectively. On the basis of a Poisson distribution[1] we calculate doubly excited coils to account for 1.6% and 14% of all coils, respectively.

In Figure 2 decay curves are displayed for P4VBP-1 ($P = 149$) and P4VBP-4 ($P = 1236$) at a concentration of biphenyl base units such that the transfer rate, k_T[BP], is equal for both polymer samples (0.56×10^6 s^{-1}). Note that k_T, the rate of sensitization per base molar concentration, is molecular weight dependent.[5] The k_T values for P4VBP-1 and P4VBP-4 are 2.2×10^8 and 0.78×10^8 M^{-1}, respectively.[5] The maximum intensity after excitation occurs at slightly shorter times for P4VBP-1 than for P4VBP-4. Both polymer samples decay nonexponentially for $t > t_{max}$ with different time dependencies. P4VBP-1 ($P = 149$) has a slowly decaying component that also occurs for both lower and higher sensitization rates (e.g., k_T[BP] = 0.33×10^6 and 0.78×10^6 s^{-1}). We attribute this component to intercoil annihilation (see Discussion). One may remove the effect of this slowly decaying component in the kinetic fit by taking the base line to be the slowly decaying portion of the signal and fitting the remainder of the decay curve for $t > t_{max}$ to a single-exponential function. Following this procedure, we find that for moderate rates of sensitization (e.g., 0.33×10^6 and 0.56×10^6 s^{-2}) the rate constant of the DF decay for P4VBP-1 is essentially the same as the rate constant for the decay of the benzophenone triplet sensitizer as measured by T–T absorption at 532 nm (see Experimental Section). This type of decay behavior is expected when the rate-limiting step of the mechanism is the sensitization process; that is, intracoil annihilation is faster than the quenching of the sensitizer.

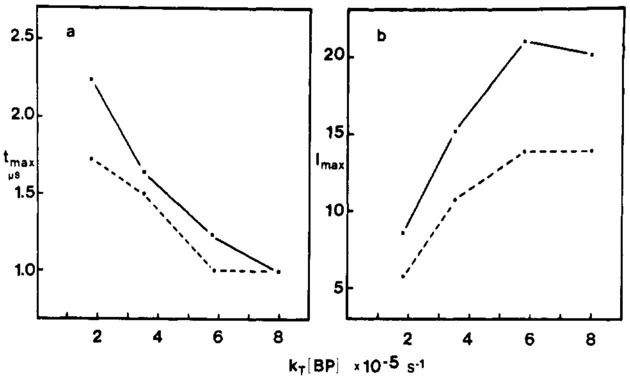


Figure 3. (a) Variation of t_{max} as a function of transfer rate for P4VBP-1 (dashed line) and P4VBP-4 (solid line). (b) Variation of the maximum intensity of delayed emission (i.e., intensity at t_{max}) as a function of transfer rate for P4VBP-1 (dashed line) and P4VBP-4 (solid line).

However, at the highest sensitization rate the DF decay is significantly slower than the decay of the sensitizer. The high molecular weight P4VBP-4 ($P = 1236$) decays nonexponentially for $t > t_{max}$ for all the sensitization rates studied except the lowest rate (k_T[BP] = 0.16×10^6 s^{-1}). The decay of the P4VBP-4 DF is always slower than that of P4VBP-1 at the same sensitization rate. Similar observations were made for P2VN.[1]

Figure 3a shows a plot of t_{max} as a function of transfer rate for both P4VBP-1 and P4VBP-4. The t_{max} values for P4VBP-4 are slightly larger than those of P4VBP-1 for lower concentrations but at the highest sensitization rates they converge to a common value. All the P4VBP-4 values are equal, within experimental error, to those of P4VBP-1. We note that in the P2VN sensitization experiment[1] the t_{max} values for different molecular weight samples did not converge and the t_{max} values for the low and high molecular weight polymers were not within experimental error of each other. The plot of decayed fluorescence intensity at $t = t_{max}$ (i.e., I_{max}) vs. sensitization rate in Figure 3b is similar to that seen in P2VN. Because there are similarities in the P4VBP and P2VN data, it is reasonable to suppose that the same kinetic scheme describing the buildup and decay of the delayed fluorescence applies to both these systems.

Discussion

Since the molecular weight dependence of t_{max} and I_{max} on the transfer rate is superficially similar to that observed for P2VN,[1] it is reasonable to use the same kinetic model for P4VBP. A homogeneous, intracoil annihilation mechanism provided the best fit to the P2VN results. In this mechanism, it is not possible to distinguish between segmental diffusion or "down-chain" triplet energy migration as the cause of delayed fluorescence. In the case of P2VN we were able to ignore intercoil annihilation because the excited-coil concentration was low and the lifetime of the triplet state of P2VN was short. In P4VBP, intercoil annihilation cannot be ignored because of the much longer lived triplet state (4–5 times that of P2VN) and the higher concentration of excited coils. Thus the relevant rate equations (see Appendix for kinetic scheme and derivation of rate equations) that we will use to describe the kinetics of this system are

$$\mathrm{d}[\mathrm{S}^*]/\mathrm{d}t = -(k_0 + k_\mathrm{a}C_0)[\mathrm{S}^*] = -k_\mathrm{S}[\mathrm{S}^*] \tag{1}$$

$$\begin{aligned}\mathrm{d}[\mathrm{C}^*]/\mathrm{d}t = {} & k_\mathrm{a}C_0[\mathrm{S}^*] - 2k_\mathrm{a}[\mathrm{C}^*][\mathrm{S}^*] - k_\mathrm{a}[\mathrm{C}^{**}][\mathrm{S}^*] + \\ & [(k_\mathrm{H2}k_\mathrm{a})/(k_\mathrm{H2} + k_\mathrm{S.P^{**}})][\mathrm{C}^{**}][\mathrm{S}^*] + k_\mathrm{B}[\mathrm{C}^{***}] + \\ & 2k_\mathrm{P}[\mathrm{C}^{**}] - k_\mathrm{P}[\mathrm{C}^*] - k_\mathrm{Q}[\mathrm{C}^*]^2\end{aligned} \tag{2}$$

$$\mathrm{d}[\mathrm{C}^{**}]/\mathrm{d}t = [(k_{\mathrm{S.P}^{**}}k_{\mathrm{a}})/(k_{\mathrm{S.P}^{**}} + k_{\mathrm{H1}})][\mathrm{C}^*][\mathrm{S}^*] - k_{\mathrm{a}}[\mathrm{C}^{**}][\mathrm{S}^*] - 2k_{\mathrm{P}}[\mathrm{C}^{**}] - k_{\mathrm{A}}[\mathrm{C}^{**}] + 3k_{\mathrm{P}}[\mathrm{C}^{***}] \quad (3)$$

$$\mathrm{d}[\mathrm{C}^{***}]/\mathrm{d}t = [(k_{\mathrm{S.P}^{***}}k_{\mathrm{a}})/(k_{\mathrm{S.P}^{***}} + k_{\mathrm{H2}})][\mathrm{C}^{**}][\mathrm{S}^*] - 3k_{\mathrm{P}}[\mathrm{C}^{***}] - k_{\mathrm{B}}[\mathrm{C}^{***}] \quad (4)$$

Equation 1 describes the rate of decay of the sensitizer (benzophenone), S*. Equation 1 predicts exponential decay of the sensitizer, which agrees with experimental observations at the higher transfer rates (i.e., when T–T annihilation can be neglected). Rate equations (2)–(4) describe the kinetics of singly (C*), doubly (C**), and triply (C***) excited coils. These equations are complex and require numerical integration for solution. On the basis of the overall concentration of excited triplets and careful examination of the numerical solution of the kinetic equations, we have found that one can describe the kinetic behavior displayed by our data by considering a maximum of three excitations per coil.

Using a steady-state approximation for the singlet excimer (^{1}D*) (k_{E} is much larger than most rate constants in eq 1–4), we obtain the following equation:

$$[{}^1\mathrm{D}^*] = [(k_{\mathrm{H1}}k_{\mathrm{a}})/k_{\mathrm{E}}(k_{\mathrm{H1}} + k_{\mathrm{S.P}^{**}})][\mathrm{C}^*][\mathrm{S}^*] + (k_{\mathrm{H2}}k_{\mathrm{a}}[\mathrm{C}^{**}][\mathrm{S}^*])/[k_{\mathrm{E}}(k_{\mathrm{H2}} + k_{\mathrm{S.P}^{***}})] + (k_{\mathrm{A}}/k_{\mathrm{E}})[\mathrm{C}^{**}] + (k_{\mathrm{B}}/k_{\mathrm{E}})[\mathrm{C}^{***}] + k_{\mathrm{Q}}[\mathrm{C}^*]^2 \quad (5)$$

The first two terms in eq 5 are from the heteroannihilation process between an excited coil and a sensitizer molecule. From the numerical simulations we find that if these two terms make a major contribution to delayed fluorescence, then the molecular weight dependence of t_{max} would be exactly opposite to what is observed in P4VBP (see Figure 3a). On the other hand, the decay rate of the delayed fluorescence for P4VBP-1 (P = 149) was the same as that of the sensitizer for all transfer rates except the highest transfer rate. This behavior is predicted from the kinetic model for the case that the diffusion of the sensitizer to the coil is slower than the intracoil triplet energy migration (a similar observation was made for low molecular weight P2VN[1]). If the energy migration constant (Λ_{E}) is sufficiently large, both heterogeneous annihilation and intracoil homogeneous annihilation mechanisms predict that the sensitizer and delayed fluorescence will have the same time dependence. We will return to this point later in the Discussion.

The third and fourth terms in eq 5 describe the contributions from a homogeneous, intracoil mechanism of doubly and triply excited coils, respectively. The pseudo-first-order rate constants, k_{A} and k_{B}, are related to one another by a simple one-dimensional model presented by Swenberg and Webber.[7]

$$k_{\mathrm{B}} = 3^{1.8}k_{\mathrm{A}} \quad (6)$$

where 3 is the number of pairs of excitations for a triply excited coil. It was these two terms that adequately described the results of the P2VN experiment.[1]

The last term in eq 5 takes into account intercoil annihilation. We have ignored the other permutations (k_{Q}[C*][C**], k_{Q}[C**][C**], etc.) in this term because the concentration of multiply excited coils is very low. The rate constant k_{Q} was estimated from the quenching of poly(styrylbenzil) phosphorescence by poly(styrylanthracene) for a polymer of approximately the same coil dimensions as the P4VBP polymers studied, as reported by Horie and Mita.[8] We estimate the value for k_{Q} to be 8×10^8 and 4×10^8 M^{-1} s^{-1} for P4VBP-1 and P4VBP-4, respectively.

Up to now we have emphasized the similarities between the results for P2VN and P4VBP. There are three major differences in the observations for P4VBP and P2VN.

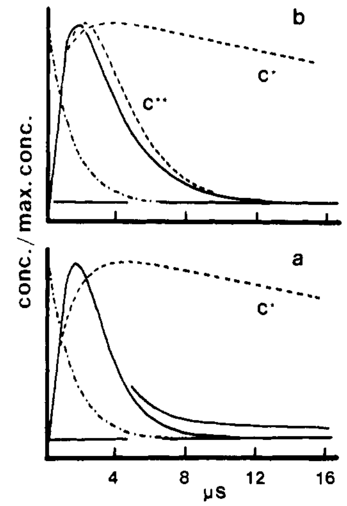


Figure 4. Simulation of the concentration of C*, C** (dashed line), ^{1}D* (solid line), and S* (dash–dot line) for $k_{\mathrm{T}}P$[BP] = 0.56 × 10^6 s^{-1} (see text). (a) P4VBP-1 (C** coincides with ^{1}D*) with intercoil annihilation (upper solid line at longer times) and without intercoil annihilation (lower solid line at longer times). (b) P4VBP-4 (intercoil annihilation can be neglected but C** does not coincide with ^{1}D* because of contribution of C***). S* decay in both cases is identical because the transfer rate to the polymer is identical.

(1) The homogeneous intercoil annihilation cannot be assumed to be negligible for P4VBP. Parts a and b of Figure 4 show simulations of our kinetic model with and without the intercoil mechanism for P4VBP-1 and P4VBP-4 at a sensitization rate of 0.56×10^6 s^{-1}. The intercoil process contributes a slowly decaying component to [^{1}D*] for $t \geq t_{\mathrm{max}}$. The intercoil mechanism is more important for the low molecular weight polymer (P4VBP-1) than the high molecular weight polymer (P4VBP-4) because of the higher coil concentration in the former case. In comparing the simulations in Figure 4a with the experimental decay curve in Figure 2, we see that inclusion of intercoil annihilation overestimates the magnitude of the slowly decaying part of the curve for the low molecular weight P4VBP-1. On the other hand, the experimentally observed decay of delayed fluorescence for the high molecular weight sample (P4VBP-4) is more nonexponential than that from the simulation (Figure 4b). The simulation for P4VBP-4 implies that this slow, nonexponential decay does not arise from the intracoil annihilation. This nonexponentiality becomes more prominent in P4VBP-4 as the transfer rate increases under conditions in which the rate-limiting step is the intracoil homogeneous annihilation rather than the sensitization of the coil. (Similar observations were made for P2VN[1] except the nonexponentiality is more prominent for the P4VBP-4.) We believe that the nonexponentiality is a result of the distribution of triplet pair separations that will exist in a randomly excited coil.[7] It is expected that the initial rate of decay (corresponding to excited pairs relatively close together) will be faster than at later times (corresponding to distant pairs). This would correspond to the use of time-dependent rate constants k_{A} and k_{B}, which we cannot handle using our classical kinetic treatment. Despite these shortcomings the kinetic model is able to fit qualitatively most of the experimental features seen with P4VBP.

(2) The second major difference between P4VBP and P2VN experiments is in the degree of polymerization and the lifetime of the triplet state of the polymers studied. The degrees of polymerization of the P4VBP polymers are slightly less than half that of their corresponding P2VN

counterparts while the lifetimes of the triplet states are 4–5 times longer than those of P2VN. Because of these two differences between the polymers, comparison of the rate of energy migration between these two polymers is difficult. The longer lifetime of the biphenyl triplet enhances the probability of distant exciton pair annihilation. Thus it is reasonable for the delayed fluorescence decay in P4VBP to be longer lived and more obviously nonexponential than is the case in P2VN since a broader range of distances between excitations on the coil are involved in the annihilation process.[9]

(3) The dependence of $t_{\max}$ on k_T[BP] (Figure 3a) is different from that displayed by P2VN.[1] From Figure 3a one observes that P4VBP-1 and P4VBP-4 depend almost identically on k_T[BP] (within experimental error) and that $t_{\max}$ tends to become independent of k_T[BP] at higher transfer rates. For P2VN there is a clear molecular weight effect on $t_{\max}$ that persists to the highest transfer rate, and $t_{\max}$ is essentially inversely dependent on k_T[N] over the full range studied.

We interpret these differences as implying that Λ_E for P4VBP is significantly smaller than P2VN. The argument is the following:

(1) Since the P4VBP delayed fluorescence persists at times after the triplet sensitizer concentration has been exhausted, the T–T annihilation must be occurring by an intra- and intercoil mechanism exclusively at longer times. On the basis of our simulations the intercoil component is minor (negligible for P4VBP-4) and contributions to the slowly decaying portion of the emission signal. There are two mechanisms for intracoil annihilation (so far as we know, first advanced by Schnabel[10]): (a) down-chain transfer ($\Lambda_E \neq 0$) and (b) cross-chain segmental diffusion. This latter mechanism is diffusive rather than "excitonic" but since both mechanisms transfer energy and can result in T–T annihilation, they cannot be distinguished on the basis of our data. It is reasonable to expect that the segmental diffusion mechanism will be enhanced if the coil density is increased, and this supposition is supported by the intracoil quenching studies of Das and Sciano.[11] In this regard we note that the degree of polymerization for the P4VBP is approximately half that of the P2VN samples[1] and the Mark–Houwink a parameters in 20 °C benzene are 0.619 and 0.72 for P4VBP and P2VN, respectively.[12] Hence the coil density for the P4VBP is substantially larger than that for the P2VN samples studied previously.[1]

(2) If Λ_E is large, then at times on the order of $t_{\max}$ it is not possible to distinguish heterogeneous annihilation and intracoil homogeneous annihilation (steps d and j, respectively; see Appendix) since the rate-determining step is the sensitization, which depends on the product [C*]·[S*]. However, since [S*] decays exponentially and the kinetics of [C*] are dominated by first-order processes, we may approximate the product as

$$[\mathrm{S}^*][\mathrm{C}^*] \propto [\mathrm{S}^*]_0{}^2 \exp(-k_s t)[\exp(-k_c t) - \exp(-k_s t)] \quad (7)$$

where k_c is the "apparent" first-order decay constant (simulations show that [C*] behaves very similarly to a sum of exponentials), and k_s is given in eq 1. The time at which this product is a maximum corresponds to $t_{\max}$ and is given by

$$t_{\max} = \ln\,[2k_s/(k_s + k_c)]/(k_s - k_c) \cong \ln 2/k_s = \ln 2/(k_0 + k_T[\mathrm{BP}]) \quad (8)$$

where the second form is appropriate if $k_s \gg k_c$ (which is the case for P4VBP, especially for higher transfer rates). Equation 8 predicts an inverse dependence of $t_{\max}$ on k_T[BP], as was found for P2VN but contrary to our observation for P4VBP.

(3) For P2VN we observed a systematic increase of $t_{\max}$ with increasing molecular weight, which we ascribed to the distribution of triplet pair separations. This is predicted on a down-chain excitonic model of annihilation. For the present case we do not observe this molecular weight dependence, such that it is tempting to conclude that an excitonic model is not appropriate to P4VBP, which by default, leaves the cross-chain segmental diffusion mechanism. Unfortunately, it is not clear if one would expect a significant molecular weight effect in this mechanism. Das and Sciano[11] did demonstrate that changing coil density (by changing solvent) enhances intracoil energy transfer by this mechanism but did not systematically vary molecular weight while holding the mole fraction of energy donor and acceptor constant.

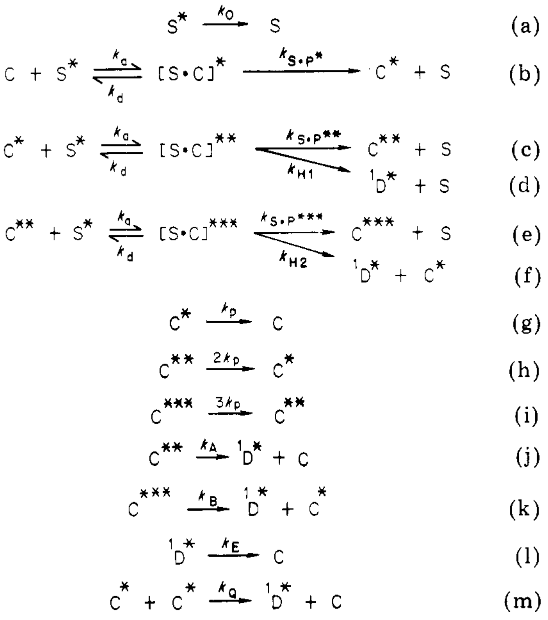
Considering all of our observations for P4VBP, we propose the following "picture" of intracoil T–T annihilation:

(1) Λ_E is small, such that the primary annihilation mechanism is cross-chain segmental diffusion.

(2) This mechanism is analogous to a static quenching model; i.e., only those pairs of triplet excitations on segments that are within some "critical distance" of each other have a significant probability of annihilation. The actual time dependence of annihilation reflects the rate of segmental diffusion, which is not strongly dependent on molecular weight.

(3) The probability of segments lying within this "critical radius" of each other will depend on coil density and hence on molecular weight. This will tend to enhance the rate of annihilation for low molecular weight P4VBP. Offsetting this is the increase in the probability of multiple excitations for a higher molecular weight polymer.

These conclusions seem reasonable based on the present data, but a detailed interpretation is difficult in the absence of a complete theoretical model for intracoil energy transfer. Our overall conclusion that excitonic energy transfer is not facile is also reasonable based on the triplet-state properties of biphenyl. Biphenyl has nonplanar configuration in the ground state (i.e., 23° angle between rings[4] while naphthalene is essentially planar in all electronic states. Wagner[13,14] has studied the triplet state of biphenyl and has concluded that it is in a planar configuration. From his sensitization study using high triplet energy ketones (benzophenone, butyrophenone, etc.) Wagner[1] deduced that triplet energy transfer to biphenyl involves a nonvertical transition in which a geometry change occurs in biphenyl. Wagner[13] also estimated that the difference in energy going from the twisted (23° angle) to the planar ground state required approximately +4 kcal for biphenyl. If we assume that the same considerations apply to triplet energy migration in P4VBP, then the nearest-neighbor chromophores of the excited triplet would be required to undergo an exothermic geometry change preceding energy transfer. Naphthalene does not have this steric barrier to excitation migration. Thus it is reasonable that P4VBP has a slower rate of energy migration per pendant group than P2VN. This steric barrier to energy migration along the chain would be similar to that for cross-chain transfer via segmental diffusion, although the acceptor molecule could be any within the "critical radius" referred to above rather than just nearest neighbors. However, T–T annihilation is not expected to have any steric barrier, such that cross-chain T–T annihilation would be facile once the triplet moieties have diffused within an annihilation radius of each other. Obviously, Scheme I



nearest-neighbor T–T annihilation would also be facile, but the probability of the excitation of nearest neighbors is very low.

Summary

The long-lived emission from benzophenone-sensitized P4VBP solutions is identified as delayed excimer fluorescence. For experimental reasons it is not possible to accurately measure the relative intensity of the monomer component of the emission. A homogeneous intracoil and intercoil annihilation mechanism provides the best qualitative agreement with our experimental results. The major problem in using a classical kinetic model in the present work is that it does not take into account the essential inhomogeneity in the distribution of separations of excited-state pairs which are created randomly at different "lattice points". It is this feature that leads to the nonexponential decay of the sensitized delayed fluorescence.

It is concluded that in the fluid phase the triplet exciton in P4VBP is much less mobile than in P2VN. Consequently, a mechanism invoking T–T annihilation via segmental diffusion is suggested. The lack of triplet exciton mobility in P4VBP has been attributed to the steric requirement for triplet energy transfer from the excited biphenyl to the ground-state biphenyl along the polymer chain.

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Appendix

The kinetic mechanism[1] is shown in Scheme I, where S, C, $^1D^*$, and the number of asterisks, represent the sensitizer, polymer coil, singlet excimer, and number of triplet excitations per species, respectively. The inclusion of the singlet monomer state into the kinetic scheme would not change the overall kinetics of the annihilation process. Rate constant k_a is equivalent to k_TP since it is the concentration of coils that appear in eq b–m (i.e., $[C] = [BP]/P$). [S.C] represents a sensitizer molecule within the polymer coil. From the volume fraction occupied by polymer coils in these experiments, we may estimate that the concentration of coils containing an excited sensitizer at $t = 0$ is much less than the total coil concentration. The "homogeneous intracoil" T–T annihilation processes produce $^1D^*$ with rates of k_A and k_B for the doubly and triply excited coil, respectively, while the heterogeneous annihilation rate is denoted by k_{H1} and k_{H2}. The rate constant k_Q in eq j was obtained from the work of Horie and Mita[8] for a polymer of similar coil dimensions and degree of polymerization. We have ignored the other permutations for the intercoil mechanism ($k_Q[C^{**}][C^*]$ etc.) because of the much lower concentrations of C** and C***. In our kinetic mechanism we assume $k_{S.P^*} = k_{S.P^{**}} = k_{S.P^{***}}$, $k_{H1} = (1/2)k_{H2}$. Since the reaction between sensitizer (benzophenone) and polymer pendant group (biphenyl) is almost diffusion limited,[15] we assume that $k_{S.P^*}$ is much larger than the rate constants k_d, $k_a[C]$, $k_a[C^*]$, and $k_a[C^{**}]$. Thus we make a steady state approximation for $[S.C]^*$, $[S.C]^{**}$, and $[S.C]^{***}$ along with $[^1D^*]$ (since k_E is very large). The rate equations are then given by

$$d[S^*]/dt = -(k_0 + k_a[C] + k_a[C^*] + k_a[C^{**}])[S^*] \quad \text{(A-1)}$$

$$d[C^*]/dt = k_a[C][S^*] - k_a[C^*][S^*] + [(k_{H2}k_a)/(k_{H2} + k_{S.P^{***}})] \times [C^{**}][S^*] + k_B[C^{***}] + 2k_P[C^{**}] - k_P[C^*] - k_Q[C^*]^2 \quad \text{(A-2)}$$

$$d[C^{**}]/dt = [(k_{S.P^{**}}k_a)/(k_{S.P^{**}} + k_{H1})][C^*][S^*] - k_a[C^{**}][S^*] - 2k_P[C^{**}] - k_A[C^{**}] + 3k_P[C^{***}] \quad \text{(A-3)}$$

$$d[C^{***}]/dt = [(k_{S.P^{***}}k_a)/(k_{S.P^{***}} + k_{H2})][C^{**}][S^*] - 3k_P[C^{***}] - k_B[C^{***}] \quad \text{(A-4)}$$

$$[^1D^*] = [(k_{H1}k_a)/k_E(k_{H1} + k_{S.P^{**}})][C^*][S^*] + [(k_{H2}k_a[C^{**}][S^*])/k_E(k_{H2} + k_{S.P^{***}})] + (k_A/k_E)[C^{**}] + (k_B/k_E)[C^{***}] + (k_Q/k_E)[C^*]^2 \quad \text{(A-5)}$$

We can simplify these equations assuming $[C] + [C^*] + [C^{**}] = C_0$, where C_0 is the total coil concentration (we ignore the concentrations $[^1D^*]$ and $[C^{***}]$, which are very small compared to the sum of [C] and [C*]). Substituting this relation into A-1 and A-2, we have

$$d[S^*]/dt = -(k_0 + k_aC_0)[S^*] = -k_S[S^*] \quad \text{(A-6)}$$

$$d[C^*]/dt = k_aC_0[S^*] - 2k_a[C^*][S^*] - k_a[C^{**}][S^*] + [(k_{H2}k_a)/(k_{H2} + k_{S.P^{***}})][C^{**}][S^*] - k_B[C^{***}] + 2k_P[C^{**}] - k_P[C^*] - k_Q[C^*]^2 \quad \text{(A-7)}$$

Equation A-6 predicts a simple exponential decay for the sensitizer, which is experimentally observed. See the main text for a discussion of the numerical solution of these rate equations.

Registry No. P4VBP, 25232-08-0; benzophenone, 119-61-9.

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Interpretation of Electronic Energy Transport Experiments in Polymeric Systems

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ABSTRACT: The theoretical foundation for the interpretation of transient and photostationary fluorescence experiments in the presence of electronic energy transport is reviewed. Transient trapping experiments are described for both uniform and nonuniform disordered media by the decay of $G^D(t)$, the integrated average density of donor excitations. Furthermore, the photostationary-state observables are directly related to the Laplace transform of $G^D(t)$. Expressions are collected for $G^D(t)$ that can be applied to homogeneous systems of donors and traps exhibiting direct or migration-assisted trapping. Similarly, transient fluorescence depolarization experiments can be described by $G^S(t)$, the ensemble-averaged, initial site excitation probability, while photostationary depolarization is interpreted in terms of the Laplace transform of $G^S(t)$. Useful expressions are obtained for the photostationary-state ratio of trap to donor intensities, a nondiffusive "effective migration length", and the steady-state anisotropy. The importance of homogeneity, dimensionality, and proper transition moment averaging is discussed for polymeric and nonpolymeric systems. Finally, the utility of the theory reviewed in this paper is illustrated with several sets of trapping and depolarization data found in the polymer literature.

I. Introduction

The use of fluorescence probes for the characterization of polymer morphology has become widespread in recent years.[1,2] The technique of excimer fluorescence provides direct quantitative information on intra- and intermolecular interactions and has proved useful in the analysis of phase separation and compatibility of solid blends[3-6] and in the study of segmental rotation in solution.[7] Sensitization experiments have been used in polymers and biopolymers to measure intramolecular distances and also to characterize unknown chromophore distributions.[2] Fluorescence depolarization experiments yield useful information on conformational dynamics in solution[8] and furnish a measure of overall coil mobility.[9] Depolarization studies have also been used to characterize fluorescent copolymers, and they provide direct evidence for the presence of electronic energy migration in such systems.[10-17]

The transport and trapping of electronic excitations in polymeric materials is, in general, a very difficult many-body problem. Chromophores attached to polymer chains present an inhomogeneous medium for exciton transport processes. Such systems provide an anisotropic transport pathway with uncertain dimensionality and possibly a nonuniform distribution of transition moments. As a result, care must be taken in the selection of experimental systems and in the subsequent data analysis.

Recent theoretical advances in the treatment of energy migration and trapping in disordered, homogeneous systems have led to the conclusion that these transport processes are *nondiffusive* in nature.[18-25] Very accurate time-dependent solutions to the transport master equation have been obtained and connections made to experimental observables. In this paper we will attempt to review the recent theoretical developments for uniform systems and demonstrate how they can be applied to the analysis of experiments on macromolecules.

II. Trapping Theory

Trapping experiments generally involve the excitation of one type of chromophore, the donor or sensitizer, and the subsequent observation of the fluorescence from a second chromophore type, the trap, activator, or acceptor. The excitation energy can be directly transferred from the excited donor to a trap by a resonant or exchange mechanism[26] or may migrate via a similar mechanism to other donors from which direct trapping can take place. The transient excited donor and trap populations are intimately related to the distribution and concentration of both chromophore types and also to the interaction mechanism. In this paper only excitations that are transferred through a multipolar resonance mechanism will be considered, and the traps will be assumed to be "deep" or nondissociative.

The observables in both transient and photostationary trapping experiments can be directly connected with the donor excitation function, $G^D(t)$, which represents the probability that an excitation resides on a donor chromophore at time t in the absence of other decay processes. Since $G^D(t)$ is in general a nonexponential function, trapping kinetics cannot be described in terms of a trapping rate constant. However, a trapping rate *function* can be defined as[27]

$$k(t) = -\frac{d}{dt}[\ln G^D(t)] \qquad (1)$$

so that the excited donor population obeys the equation

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