

would be more favorable in a solvent of high dielectric constant.

A comparison of data on the efficiency of fluorescence quenching of *p*-fluorotoluene in the vapor phase¹⁴ with that in solution shows that the efficiency is greater in the vapor phase. This must be due to the interfering of solvent molecules with the formed energy transfer complex which seems to slow the quenching efficiency.

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Intracoil Triplet-Triplet Annihilation in Poly(2-vinylnaphthalene) in Benzene Solution

James F. Pratte and Stephen E. Webber*

Department of Chemistry and Center for Polymer Research, University of Texas, Austin, Texas 78712 (Received: June 1, 1982; In Final Form: September 7, 1982)

The triplet state of poly(2-vinylnaphthalene) (P2VN) in benzene solution has been sensitized by the benzophenone triplet state and a naphthalenic excimer delayed fluorescence (DF) has been observed. Kinetic models have been tested against the experimental data, including the effect of the molecular weight on the time dependence of the DF. It has been concluded that a homogeneous, intracoil mechanism best fits the trend of the data. This implies that triplet migration along with the P2VN chain is occurring in the solution phase.

Introduction

Since the pioneering work of Eisinger and Shulman¹ and Cozzens and Fox,² the phenomenon of triplet energy migration along a polymer chain in low-temperature, rigid matrices has been known. One of the manifestations of triplet energy migration in polymers is the detection of delayed fluorescence, which arises from intracoil triplet-triplet (T-T) annihilation. Ushiki et al.³ have observed anthracene delayed fluorescence in fluid solution from intracoil and intercoil T-T annihilation between a pair of terminal anthracene groups on a polystyrene chain. To our knowledge, this is the only case in which delayed fluorescence has been detected that originates from intracoil T-T annihilation in fluid solution. Thus far, delayed fluorescence has not been reported for directly excited poly(2-vinylnaphthalene) (P2VN) in room temperature solutions even though it is quite prominent at low temperatures.⁴ However, this is understandable since it has been previously noted that the quantum yield from the optically excited singlet state of P2VN in room temperature solutions is very low.⁵ We have recently observed a long-lived emission peaking at ~410 nm in P2VN solutions containing efficient triplet sensitizers excited by a nitrogen laser (e.g., benzophenone and phenanthrene). Only those results for benzophenone will be discussed herein because the triplet quantum yield of nearly unity eliminates most complications due to singlet-state interactions and prompt fluorescence. The long-lived emission appears to be delayed excimer fluorescence from the polymer-bound naphthalene. A kinetic argument will be presented which analyzes these results in terms of hetero-

ogeneous and homogeneous T-T annihilation in solution.

Experimental Section

Synthesis and characterization of P2VN samples have been described elsewhere.⁶ Benzophenone was purified by several recrystallizations from ethanol. Benzene (MCB spectrograde) was washed with sulfuric acid and then aqueous sodium carbonate. The washed benzene was dried over CaCl₂ and then distilled.

The laser flash photolysis unit was the same as that used in the triplet sensitization experiments,⁶ which were carried out at the Center for Fast Kinetics Research, University of Texas at Austin. This unit incorporates a beamsplitter to divert part of the laser pulse onto a photodiode in order to measure the flash intensity. Data were used only from those laser pulses that had approximately the same intensity readings (within ±3%). The same experimental considerations that applied in the triplet sensitization experiments⁶ obtained in this experiment with the exception that the interrogation light source (150-W xenon) used for the transient absorption study was eliminated in order to record emission. The excitation intensity of the nitrogen laser was attenuated by neutral density filters (OD = 1.0) in order to diminish the T-T annihilation process between excited sensitizer molecules in the sensitizer blank solution. This was done to ensure that the energy transfer mechanism was the dominant process in the decay kinetics of the sensitizer in P2VN solutions. Time-resolved emission spectra were taken by assembling decay curves at every 5 nm. Triplet-triplet absorption was also measured in order to obtain a value for the initial concentrations and decay rates of benzophenone triplets in solution.

One other point that needs to be made is the absorption of naphthalene units at the laser wavelength ($\lambda = 337$).

(1) Eisinger, J.; Shulman, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1969**, *55*, 1387.

(2) Cozzens, R. F.; Fox, R. B. *J. Chem. Phys.* **1969**, *50*, 1532.

(3) Ushiki, H.; Horie, K.; Okamoto, A.; Mita, I., *Polymn. J.* **1981**, *13*, 191.

(4) (a) Pasch, N. F.; Webber, S. E. *Chem. Phys.* **1976**, *16*, 361. (b) Kim, N.; Webber, S. E. *Macromolecules* **1980**, *13*, 1233.

(5) Bensasson, R. V.; Land, E. J.; Ronfard-Haret, M.; Webber, S. E. *Chem. Phys. Lett.* **1979**, *68*, 438.

(6) Pratte, J. F.; Webber, S. E. *Macromolecules* **1982**, *15*, 417. In this earlier work an error was made in the reported degree of polymerization from GPC data such that the quoted degrees of polymerization are in error by a factor of two. This numerical factor does not alter any of the conclusions presented in that paper, however.

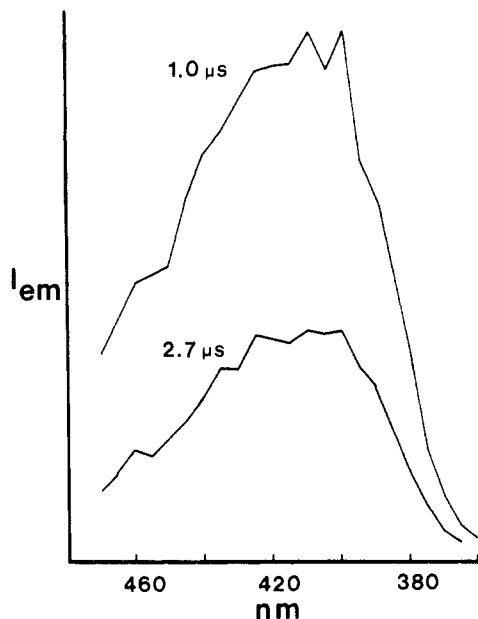


Figure 1. Time-resolved delayed emission spectra of P2VN ($P = 346$) (2×10^{-3} M in naphthalene units) and benzophenone (1×10^{-2}) at indicated time delays following excitation (intensity in arbitrary units).

The amount of absorbance by P2VN at the highest polymer concentration is approximately an OD = 0.1. The optical density of a 10^{-2} M benzophenone in benzene solution is 1.6. Thus, most of the photons ($\geq 97\%$) are absorbed by the benzophenone. The light absorbed by P2VN results in the weak prompt fluorescence in the early part of the decay curve in Figure 2 (e.g., the initial spike). It should be mentioned again that P2VN of these molecular weights have extremely low values for their triplet quantum yield (e.g., ≤ 0.01 , see ref 5). Thus, the combined effect of the high sensitizer absorption and low triplet quantum yield of P2VN would diminish any significant contribution to the initial triplet population of the polymer by direct excitation.

The numerical solutions to the rate equations were performed on the CDC 7600 computer at the University of Texas at Austin. The program consisted of a differential equation solver with the Adam's predictor corrector method from the IMSL library.

Results

Figure 1 shows the time-resolved delayed emission spectrum of 10^{-2} M benzophenone + 2×10^{-3} M P2VN-2 (degree of polymerization (P) = 346) in benzene (the designation P2VN-2 and P2VN-4 follow our earlier work⁶). Steady-state or time-resolved fluorescence spectra of P2VN have a minor component at shorter wavelengths assigned to the "naphthalene monomer". The time-resolved delayed emission spectrum in Figure 1 is composed of the excimer component only. Any monomer component in the fluorescence would be absorbed by the benzophenone in the solution since the absorption of 10^{-2} M benzophenone extends out to $\lambda = 380$ nm. It is also impossible to obtain reliable decay curves in the 320–350-nm region because of interference from the laser line at 337 nm, and at higher P2VN concentrations, prompt fluorescence.

Figure 2 shows two typical response curves of the delayed fluorescence for the P2VN-2 (curve a) and P2VN-4 (curve b) at the same sensitization rate ($k_t[N] = 0.51 \times 10^6$, where k_t is the transfer rate per naphthalene molarity unit). As can be seen, the time at which the emission is a maximum (t_{\max}) is smaller for P2VN-2 ($P = 346$) than P2VN-4 ($P = 2806$). Also, the decay of the long-time

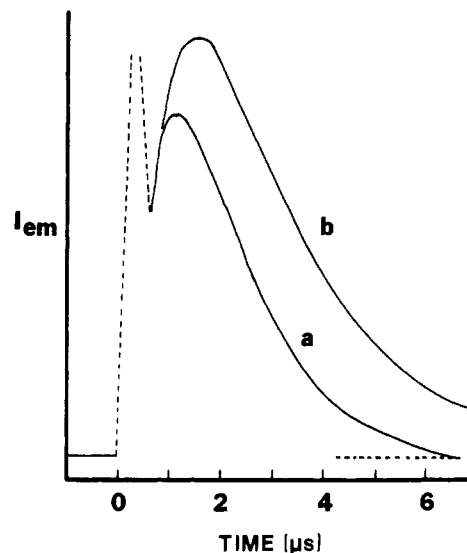


Figure 2. Time response of delayed emission at 430 nm for P2VN ($P = 346$) (curve a) and P2VN ($P = 2806$) (curve b) (intensity in arbitrary units). The initial spike (dashed line) is interference from the excitation pulse and P2VN prompt fluorescence at higher P2VN concentration.

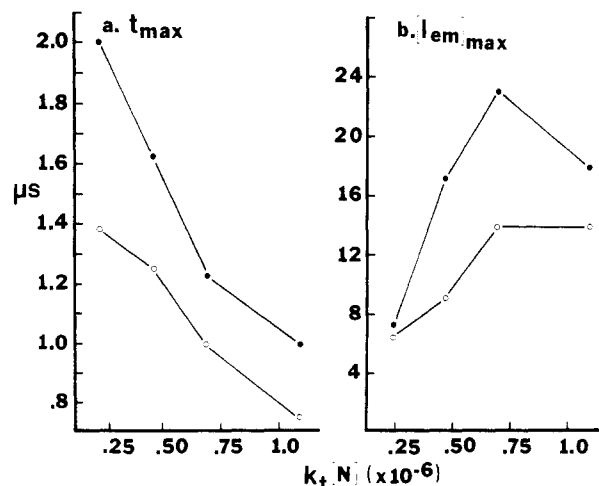


Figure 3. (a) t_{\max} as a function of $k_t[N]$ (see text) for $P = 346$ (O) and 2806 (●); (b) magnitude of maximum delayed emission intensity for $P = 346$ (O) and 2806 (●) as a function of $k_t[N]$.

portion of the curve is slower for the P2VN-4 than for P2VN-2. This behavior was seen in all the sets of the curves at each sensitization rate. The rate of decay for times greater than t_{\max} for the low molecular weight polymer (P2VN-2) was almost the same as the sensitizer decay rate for all the sensitization rates. For the high molecular weight polymer (P2VN-4) this portion of the decay curve did not follow the sensitizer decay as the sensitization rate increased.

The value of t_{\max} is plotted vs. the sensitization rate $k_t[N]$ for P2VN-2 ($P = 346$) and P2VN-4 ($P = 2806$) in Figure 3a. In all cases, for equal sensitization rates t_{\max} for P2VN-4 is greater than for P2VN-2. The value of t_{\max} for both polymer samples decrease as $[N]$ increases with P2VN-4 exhibiting a more nonlinear behavior. Figure 3b is a plot of the intensity of delayed fluorescence at t_{\max} as a function of the concentration of naphthalene base units for P2VN-2 and P2VN-4. As can be seen, the peak intensity increases with naphthalene concentration up to a maximum followed by a leveling off or decrease. Also, the delayed fluorescence intensity is greater for the higher molecular weight P2VN-4 than for P2VN-2 with equal sensitization rate. These results will be interpreted in the next section in terms of heterogeneous and homogeneous

would be approximately $(1/P)$ th (P = degree of polymerization) the probability of sensitization of a second ground-state naphthalene. Diffusion of the excitation along the polymer coil would increase the probability of the sensitizer finding the excitation on the coil, thus increasing the probability of heterogeneous annihilation. There are two mechanisms by which the excitation can diffuse in the polymer coil, triplet energy migration and segmental diffusion. The triplet energy migration mechanism is the same as that for low-temperature glass matrix results,⁴ where the triplet exciton "hops" along the polymer chain. Segmental diffusion is the process of two different segments of the polymer coil interacting with each other. This process has been investigated by Horie et al.^{3,8} and Winnik et al.⁹ for polystyrene, end-capped with probe molecules. The rate of cyclization of the polymer was determined to be inversely dependent on molecular weight. There has also been observed an inverse molecular weight effect on the rate of T-T annihilation in P2VN in low-temperature glass matrices.⁴ Thus, it is not possible in the present experiment to unambiguously distinguish between these two excitation diffusion processes. The values of k_{cyc} ⁹ and k_{intra} ⁸ which represent the rates of cyclization correspond to our rate constant k_A . The values of k_A that fit our data (see below) are at least an order of magnitude larger than those seen by Winnik et al.⁹ and Horie et al.⁸ In fact, our value of k_A for the high molecular weight polymer ($5 \times 10^5 \text{ s}^{-1}$ for $P = 2806$) is almost comparable to that value seen by Winnik et al.⁹ for their lowest molecular weight polystyrene sample ($P = 32$). Thus it seems unlikely that our experimental results can be explained solely by segmental diffusion.

(2) It is necessary to reevaluate our earlier work on the quenching of the triplet state of P2VN in fluid solution, which had the objective to estimate the triplet energy migration.¹⁰ This point was left unresolved, but is now clarified by our more recent work.⁶ The piperylene quencher used in ref 10 is not a diffusion-limited quencher of either 2-ethylnaphthalene or P2VN. In view of our finding that the triplet state of P2VN is approximately 1.5 kcal/mol lower than the triplet state energy of 2-ethylnaphthalene,⁶ our previous estimate of the triplet energy migration constant (Λ_E) is changed. Correcting for this energy difference, we obtain values for Λ_E up to twenty times the diffusion of the small molecules (see Appendix). While it is likely that this crude calculation overestimates the value of Λ_E , it does point to the fact that triplet energy migration does occur in P2VN. This is an important consideration in our kinetic scheme for sensitized delayed fluorescence.

(3) The use of a single rate constant (k_A , k_B) to describe the rate of annihilation in doubly or triply excited coils is clearly a crude assumption that implicitly requires that the rate of energy migration is larger than the rate of the annihilation of neighboring pairs. In fact the decay of doubly or triply excited coils should be intrinsically non-exponential because of the distribution of triplet pair separations that will exist in a randomly excited coil.¹¹ It is to be expected in cases like the present one 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

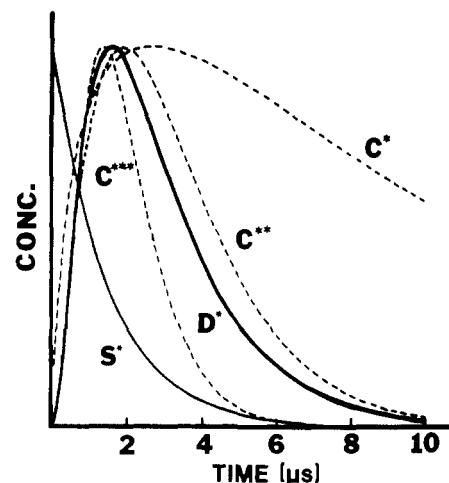


Figure 4. Plot of concentration of relevant species for triply excited coil model with intracoil annihilation (see text) for P2VN ($P = 2806$). All concentrations have been scaled to the same maximum value for ease of comparison.

to time-dependent rate constants k_A , k_B , which we cannot handle using a classical kinetic treatment such as Scheme I. Thus while the results that follow from our kinetic modeling demonstrate some of the salient features of our experimental results, it should be recognized that qualitative agreement is all that one can expect. We will return to this point later.

(4) In trying to understand the kinetics, it is helpful to think of the decay of the benzophenone triplets as that of the decay profile of an excitation pulse. Thus, we are convoluting this excitation pulse with the other various kinetic processes (i.e., deactivation and annihilation of the triplet state) in our kinetic scheme.

(5) Earlier in this discussion we stated P2VN-4 ($P = 2806$) had a significant probability of having three excitations per coil. On the other hand, it is not probable that the P2VN-2 ($P = 346$) sample is triply excited. The computer simulation of the homogeneous mechanism for P2VN-4 ($P = 2806$) presented in Figure 4 bears this out. If only two excitations per coil were considered then the time-dependent concentration of the singlet excimer, $^1D^*$, would exactly follow the doubly excited coil curve, C^{**} . This is the case for P2VN-2 ($P = 346$). However, for the sake of generality, all the computer simulations for both polymers were performed considering up to three excitations per coil even though as we will see later the contribution of C^{***} to the kinetics decreases as the transfer rate increases.

We would now like to compare the two kinetic cases tried by our computer simulations and show how these results qualitatively fit to the experimental observations.

Case I: Intracoil, Homogeneous Annihilation. This case was examined in the limits of small triplet energy migration (Λ_E) ($\Lambda_E/D \sim 1$) and large ($\Lambda_E/D \gg 1$) (see Appendix for the definition of Λ_E/D). In this model, there are two "unimolecular rate constants", k_A and k_B , that can be varied since all other rate constants have been experimentally determined. When a simple one-dimensional model presented by Swenberg and Webber¹¹ is used, a relationship between k_A and k_B of the following form was proposed:

$$k_B = 3^{1.8} k_A \quad (6)$$

where 3 is the number of pairs of excitations for a triply excited coil. Of the two limits tried for this case, the limit of Λ_E smaller than k_{s-p} fits the experimental trends best. In this limit of "small Λ_E ", k_A and likewise k_B are assumed

(8) Horie, K.; Schnabel, W.; Mita, I.; Ushiki, H. *Macromolecules* 1981, 14, 1422.

(9) Winnik, M. A.; Redpath, T.; Richards, D. H. *Macromolecules* 1980, 13, 328.

(10) Pratte, J. F.; Noyes, W. A., Jr.; Webber, S. E. *Polym. Photochem.* 1981, 1, 3.

(11) Webber, S. E.; Swenberg, C. E. *Chem. Phys.* 1980, 49, 231.

to be inversely proportional to molecular weight since two or more excitations in a smaller domain will react faster than in a larger domain. This property has been observed in low-temperature glass matrices for P2VN.⁴ The t_{\max} behavior from the simulations for the two polymer samples (at the same sensitization rate, $k_T[N]$) followed experimental results for judicious (but physically reasonable) choices for k_A . Also, there is another feature that emerges from this model that agrees with experiment. If the concentration of $^1D^*$ is examined as a function of naphthalene base unit concentration we find that at higher concentrations $[^1D^*]_{\max}$ goes through a maximum and then decreases because the average number of excitations per coil decreases at high coil concentrations (i.e., a constant number of triplet excitations is distributed over an increasingly large number of coils). Concentrations for which $[^1D^*]_{\max}$ decreases require $[N] \geq 10^{-1}$ M but the "isolated coil" approximation is no longer valid. This behavior of $[^1D^*]_{\max}$ mimics the I_{DF}^{2806} behavior in Figure 3b. In addition, the ratio of $(I_{DF}^{2806}/I_{DF}^{346})_{\max}$ (i.e., the DF intensity at t_{\max} for each polymer) is similar to that observed experimentally.

The third and last experimental observable that we would like to compare is the decay of the delayed fluorescence at times $> t_{\max}$. As was stated in the Results section, the decay rate of P2VN-2 ($P = 346$) at all the transfer rates was almost the same as the sensitizer decay rate. The reason for this is that the rate-limiting step in the kinetics for P2VN-2 is the diffusion of the sensitizer to and from the polymer coil. This is not the case for P2VN-4 ($P = 2806$) in which the decay of the emission is slower than that of the sensitizer decay rate at all the transfer rates studied except the slowest one. For P2VN-4, the rate-limiting step at high transfer rates is the diffusion of two distant triplet excitations along the polymer coil. When the same values of k_A and k_B that lead to reasonable values for t_{\max} are used, the decay rates of P2VN-2 are correctly predicted. Likewise, there is good qualitative agreement with P2VN-4 in that the model gives "unimolecular" decay rates comparable to the decays of the excimer emission.

While the kinetic model we have been exploring is useful to describe this complex system, it does have the fundamental shortcoming described previously: a single annihilation rate constant, k_A or k_B , is assigned to doubly or triply excited coils. The failure of this assumption is illustrated when one considers the predictions of the kinetic model in the limit of high coil concentration, where the average number of excitations per coil levels off or decreases. As mentioned earlier the model predicts (correctly) that $[^1D^*]$ should saturate. But, it also follows that in this limit $[^1D^*]$ should follow $[C^{**}]$, since $[C^{***}]$ decreases (i.e., the long time decay rate should be a single exponential with rate constant k_A). In addition, the decay rate of $[^1D^*]$ should decrease as the contribution of $[C^{***}]$ is diminished. Neither of these features is found in the data.

We ascribe the nonexponentiality of the decay to the inhomogeneity of triplet pair separations. This is a typical result of a spatially inhomogeneous system (e.g., the inapplicability of the simple Smoluchowski equation at short times¹²). As we will discuss at the end of this section we do not believe that coil-coil annihilation (step m of Scheme I) is significant under our experimental conditions. Consequently, we are led to the conclusion that the distribution of triplet excitation separations must approach a constant functional form in the limit of high coil concentrations,

with a concomitant nonexponential decay. We are not aware of any quantitative theoretical results that are relevant to this point.

The limit of Δ_E large ($\Delta_E/D \gg 1$) fails to model the experimental results at short and long times. The rate-limiting step in this case for both high and low molecular weight polymers is the diffusion of the sensitizer to and from the polymer coil. Once the coil has been doubly excited, annihilation is very fast such that the decay of delayed fluorescence follows the decay of the sensitizer, regardless of molecular weight. Also, the t_{\max} behavior is incorrectly modeled. The buildup of delayed fluorescence in this limit depends solely on the rate of sensitization of the polymer coil (i.e., diffusion of sensitizer to and from the coil). Thus, this would predict the high molecular weight polymer would have the shorter t_{\max} since the concentration of double excited coils builds up more rapidly than for the smaller coil. This is exactly opposite of what is observed experimentally. This limit does predict the correct behavior of the ratio $(I_{DF}^{2806}/I_{DF}^{346})_{\max}$, similar to the small Δ_E case.

Case II: Heterogeneous Annihilation. We now turn our attention to a model in which $^1D^*$ is formed by heterogeneous annihilation. In the limit of Δ_E small we expect $k_{H1} \cong k_{sp}/P$ and $k_{H1} = (1/2)k_{H2}$ (because of the difference in the number of excitations per coil). This model does not mimic any of the experimental results. This is not surprising since for this case the excitation is fixed at a site on the coil and it is more probable for a sensitizer molecule to react with an unexcited pendant naphthyl group than the excited one. The molecular weight effect on t_{\max} for this limit was opposite to the experimental results. Also, at the same sensitization rate, the long time decay behavior of the delayed fluorescence is the same for both high and low molecular weight polymers unlike the experimental observations.

For Δ_E large ($k_{H1} = k_{sp}$), the model predicts values for the ratio of $[^1D^*]_{P=2806}/[^1D^*]_{P=346}$ at t_{\max} that agree reasonably well with experiment. However, this model mispredicts the t_{\max} dependence on molecular weight. It is also unable to model the long time decay of $^1D^*$ for the high molecular weight polymer. Since there are no adjustable parameters in these two models of heterogeneous annihilation (i.e., all rate constants except k_{H1} had been experimentally determined), we feel we can eliminate the process of heterogeneous annihilation as a significant contribution to delayed fluorescence.

Throughout this discussion we have assumed that there were no intercoil interactions. This assumption was tested by explicitly including term m in the kinetic scheme. The value of k_Q was taken to be the rate of quenching of the triplet of poly(styrylbenzil) by poly(styrylanthracene) (for polymers of similar coil dimension) as measured by Horie and Mita.¹³ The effect of this additional annihilation channel was negligible in the simulations. This is not surprising since (1) the concentration of excited state coils is very low, similar to the conditions used by Horie et al.⁸ and Winnik et al.⁹ in which intercoil processes were neglected, and (2) the lifetimes of the triplet state of P2VN is much shorter than the polymer-bound triplet-state molecules previously studied.

Summary

A long-lived emission from triplet-sensitized P2VN solutions has been identified by time-resolved emission spectroscopy as delayed fluorescence from the single excimer in P2VN. Various mechanisms which lead to de-

(12) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129.

(13) Horie, K.; Mita, I. *Macromolecules* **1978**, *11*, 1175.

TABLE I: Corrected Quenching Rates, Λ_E/D Values

sample	P	$k_q^{\text{obsd}}, \text{L mol}^{-1} \text{s}^{-1}$	Λ_E/D	$(\Lambda_E/D)_{\text{cor}}^a$
2Et	1	1.3×10^8		
P2VN-3	319	11.7×10^8	0.81	16.7
P2VN-4	683	7.7×10^8	0.2	10.6
P2VN-5	2677	3.4×10^8	<0	4.14

^a Corrected by multiplying k_q^{obsd} for the polymer by a factor of 9.76 (see eq A-4).

layed fluorescence from the singlet excimer have been tested by numerical solutions to a set of rate equations. Models in which $^1D^*$ is produced by an intracoil (homogeneous) mechanism qualitatively fit our data and we have concluded that this is the dominant mechanism of delayed fluorescence in our experiment. An important consideration in our kinetic model is the probability of multiply excited coils that depend on the number of excitations on the coil.

While we feel that our kinetic scheme does illustrate some of the important physical features of the sensitizer-polymer coil-annihilation system, it does not take into account the essential inhomogeneity in the distribution of separations of triplet excited state pairs created randomly at different lattice points. It is this feature that results in nonexponential decay of the sensitized delayed fluorescence even when only doubly excited coils need to be considered (i.e., at high coil concentrations).

One of the most important conclusions of the present work is that the triplet excitation is mobile in P2VN in the fluid phase (i.e., a fluid phase triplet "exciton"). This point was unresolved in earlier experiments.¹⁰ This is an important finding in that it suggests that polymers in solution might be more efficient as triplet-state sensitizers than one would expect from segmental or coil diffusion.

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Appendix. Estimation of the Ratio Λ_E/D

In a previous paper the ratio Λ_E/D was estimated by the following equation:

$$\Lambda_E/D = (k_q^{\text{P2VN}} - k_q^{\text{2EtN}})[(1/2)k_q^{\text{2EtN}}]^{-1} \quad (\text{A-1})$$

where Λ_E is the excited-state migration rate, $D = (D_Q + D_{2\text{EtN}})/2$ where D_Q and $D_{2\text{EtN}}$ are the diffusion constants for the quencher and 2-ethylnaphthalene (monomeric

model compound) and k_q^{P2VN} and k_q^{2EtN} are the quenching rate constants for P2VN (per naphthalene group) and 2-ethylnaphthalene, respectively. Equation A-1 is based on the modification of the quenching constant proposed by Voltz et al.¹⁴

$$k_q = 4\pi(D_Q + D_E + \Lambda_E)R_qN_0/10^3 \quad (\text{A-2})$$

where D_E is the physical diffusion of an excited moiety (assumed to be ~ 0 for the polymer) and Λ_E is the excitation migration rate (assumed to be ~ 0 for the monomeric model compound). R_q is the reaction radius for quenching, which was assumed to be identical for P2VN and 2EtN. However, based on the analysis of our more recent study we have found that the energy of $^3\text{P2VN}^*$ is lowered by 1.5 kcal/mol relative to 2EtN, and perylene is not a collisionally limited quencher for $^3\text{2EtN}^*$ (i.e., compare the rate constants of quenching by perylene with the sensitization by benzophenone, which are 1.3×10^9 and $6 \times 10^9 \text{ L mol}^{-1} \text{s}^{-1}$, respectively). If we use the Sandros relation¹⁵

$$k_{\text{obsd}} = k_d/(1 + e^{-\Delta E/RT})^{-1} \quad (\text{A-3})$$

(where k_d is the true diffusion-limited quenching constant) to correct for the energy gap difference between 2-ethylnaphthalene (2EtN) and P2VN, we can make an estimate of k_d^{P2VN} . Based on the comparison of benzophenone and perylene results we estimate ΔE for 2EtN-perylene to be ca. $-0.77 \text{ kcal mol}^{-1} \text{K}^{-1}$. If we correct for the P2VN-2EtN energy difference we obtain (at 300 K)

$$k_d^{\text{P2VN}}/k_d^{\text{2EtN}} = (k_{\text{obsd}}^{\text{P2VN}}/k_{\text{obsd}}^{\text{2EtN}})[(1 + e^{2.27 \times 10^6/600})/(1 + e^{0.77 \times 10^6/600})] = (k_{\text{obsd}}^{\text{P2VN}}/k_{\text{obsd}}^{\text{2EtN}})9.76 \quad (\text{A-4})$$

The result of this energy correction is to increase k_d^{P2VN} relative to k_d^{2EtN} and consequently increase the value of Λ_E/D calculated from eq A-1. These corrected Λ_E/D values are given in Table I. While the corrected Λ_E/D values are undoubtedly an overestimate, the implication is that the triplet energy migration in fluid phase P2VN may be surprisingly facile. For example, if $D \sim 10^{-5} \text{ cm}^2 \text{s}^{-1}$, then for $\Lambda_E \sim 10^{-4} \text{ cm}^2 \text{s}^{-1}$ and a nearest-neighbor separation of $\sim 3 \text{ \AA}$, and $\tau(^3\text{N}^*) \sim 10 \mu\text{s}$, one calculates

$$L_E \sim (2\Lambda_E\tau_E)^{1/2} = 4.5 \times 10^{-5} \text{ cm} \quad (\text{A-5})$$

for the mean exciton diffusion length, which in turn implies ~ 1500 exciton hops during the triplet-state lifetime. Obviously for $P < 1500$ this rough estimate is consistent with extensive intracoil T-T annihilation.

Registry No. P2VN, 28406-56-6; benzophenone, 119-61-9.

(14) Voltz, R.; Laustriat, G.; Coche, A. *J. Chim. Phys.* **1963**, *63*, 1253. Voltz, R.; Klein, J.; Heisel, F.; Lami, H.; Laustriat, G.; Coche, A. *Ibid.* **1963**, *63*, 1259.

(15) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355.