Acknowledgment. My thanks to Professor H. J. Harwood for access to Monte-Carlo data and the encouragement he has given me. I also thank Professor E. D. VonMeerwall for informative discussions on the numerical aspects of the problem. Financial support from the Phillips Petroleum Co. in the form of a fellowship and a grant from the General Electric Foundation are gratefully acknowledged.

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Quenching of Triplet Excitons in Poly(2-vinylnaphthalene) and Poly(acenaphthylene) by Biacetyl

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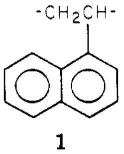
Received March 21, 1979

ABSTRACT: Biacetyl is used as a quencher for triplet excitons in poly(2-vinylnaphthalene) (P2VN) and poly(acenaphthylene) (PAcN) in 2-methyltetrahydrofuran glasses at 77 K. The phosphorescence of a polymer–biacetyl mixture shows a strong component of biacetyl at times very long (1–2 s) compared with the biacetyl triplet lifetime (~2 ms), demonstrating that the triplet exciton continues to sensitize the biacetyl. It is shown that for PAcN the sensitization ceases at earlier times than for P2VN. The biacetyl sensitization is also shown to persist to longer times for a higher molecular weight sample of P2VN than for a lower molecular weight sample. This is consistent with previous results that imply that sensitization is more effective for higher molecular weight polymers of P2VN because of the increased number of quencher–polymer contacts. The results are interpreted as implying the following: (1) triplet excitons in PAcN are confined to relatively short segments of the polymer chain, and (2) triplet excitons in P2VN show essentially no trapping at long times.

One of the earliest characterizations of triplet excitons in polymers was the report by Eisinger and Shulman[1] of the quenching of the phosphorescence of poly(riboadenylate acid) by paramagnetic ions and that by Lashkov and Ermolaev[2] on the phosphorescence quenching of poly(vinylphthalimide). Since that time, the two primary observables that implicate the presence of triplet excitons on a polymer are (1) enhanced efficiency of phosphorescence quenching by extrinsic quenchers and (2) delayed fluorescence arising from triplet exciton annihilation.[3] To date, triplet excitons in four homopolymeric naphthalene derivatives have been studied: poly(1-vinylnaphthalene)[4] (**1**), poly(2-vinylnaphthalene)[5] (**2**), poly(2-naphthyl methacrylate)[6,7] (**3**), and poly(acenaphthylene)[8] (**4**). All members of this set of polymers demonstrate triplet exciton annihilation leading to delayed fluorescence except the last polymer, poly(acenaphthylene). According to David et al.,[8] the sensitivity of the phosphorescence of poly(acenaphthylene) to extrinsic quenchers (piperylene) is the same as that of poly(1-vinylnaphthalene), implying that triplet excitons must be present in both polymers. Thus one has an apparent paradox in that triplet excitons exist in poly(acenaphthylene), but triplet exciton annihilation does not occur. Several possible explanations for this observation may be offered, including: (1) the diffusion length of the triplet exciton may be small in poly(acenaphthylene) (because of slow exciton hopping rates or trapping), (2) triplet exciton annihilation may not lead to excited singlet states because of the unusual orientation of neighboring naphthalene groups (or the strained naphthalene to alkane backbone bonds may be susceptible to a photochemical reaction, even at 77 K), or (3) the quantum yield of fluorescence for poly(acenaphthylene) is low, such that no delayed fluorescence can be observed, even when annihilation occurs. This latter possibility can be definitely discounted because the fluorescence of poly(acenaphthylene) is easily observed at



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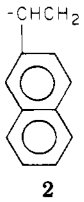

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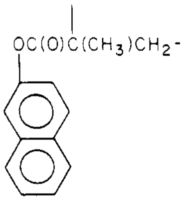

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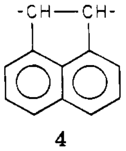

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77 K (or room temperature). Possibility (2) is doubtful because phosphorescence of poly(acenaphthylene) decays as a simple exponential, even at high excitation intensity, implying a negligible contribution of a biexcitonic process to the overall kinetics.

The present experiments were designed to test the hypothesis that the exciton is trapped in poly(acenaphthylene) but is not significantly trapped in poly(2-vinylnaphthalene) (hereafter PAcN and P2VN, respectively). Our method is straightforward. Solutions of the polymer (10^{-3} M in the naphthalene chromophore) in 2-methyltetrahydrofuran are prepared with different concentrations of biacetyl, typically in the range 5×10^{-4} to 5×10^{-2} M. The solutions are frozen at 77 K, forming a clear glass, and excited at 313 nm. This wavelength is absorbed primarily by the naphthalene moiety. In general, the phosphorescence is a mixture of naphthalene and biacetyl emissions, the latter arising primarily by the naphthalene triplet exciton sensitization. The triplet lifetime of naphthalene and biacetyl is ~2 and ~0.002 s, respectively. It is observed that the biacetyl phosphorescence persists for hundreds of its normal lifetimes, implying that the naphthalene triplet exciton remains mobile at longer times and continues to sensitize the biacetyl.[9] In the case of the highest molecular weight sample of P2VN examined, this sensitization persists throughout the time that significant phosphorescence is observed, implying that exciton mobility persists. For PAcN, the sensitization ceases at relatively short times, implying that the triplet exciton becomes "trapped". In addition, the biacetyl sensitization is less efficient for PAcN than for P2VN, implying a slower exciton hopping rate. Taken together, these differences between P2VN and PAcN clarify the reason for the absence of significant delayed fluorescence or triplet–triplet annihilation in PAcN.

Experimental Methods

A. Chemicals. Acenaphthylene was purchased from Aldrich Chemical Co. (99%, mp 80–83 °C, A80-5) and purified by recrystallization from methanol (2×) followed by sublimation under vacuum [at ~50 °C (10^{-5} torr)]. The polymerization of this material was performed as follows: a 1.5 M solution of acenaphthylene and 3.8×10^{-3} M AIBN in spectral grade benzene was placed in an ampule and outgassed several times under vacuum (~10^{-5} torr) before sealing. The ampule was heated to ~63 °C for 3 days and 95 °C for 1 day. The solution was diluted 2× in benzene and precipitated into a tenfold excess of methanol. The polymer was reprecipitated 3× by slowly adding a benzene solution to a 5–10-fold excess of methanol, filtering, and washing with methanol. The final white polymer was dried at room temperature on a vacuum line. A GPC elution curve of the PAcN is presented in Figure 1.

Two P2VN samples were used. The molecular weights of these two samples were 49 200 (P2VN-3) and 505 000 (P2VN-6).[10] The GPC elution curve of these polymers is also presented in Figure 1.

The biacetyl (Fischer Chemical, bp range 88–91 °C) was distilled at room temperature under vacuum (~10^{-5} torr). The biacetyl keeps in a freezer for several months without deterioration after this distillation. Undistilled biacetyl or older samples containing biacetyl always showed a characteristic "impurity" phosphorescence at ~420 nm.

2-Methyltetrahydrofuran (MTHF) was purchased from Aldrich Chemical (bp range 78–80 °C, 15 581-0). The solvent was filtered through freshly activated alumina and refluxed over lithium aluminum hydride under a N_2 atmosphere before use. The MTHF was distilled immediately before use.

B. Sample Preparation. Solutions were made up in quartzware that had been freshly pyrolyzed to remove any organic contamination. The polymer solution was 1.0×10^{-3} M in naphthalene groups, and the biacetyl was added using a micropipet (typically 1–5 μL added). The biacetyl concentration was typically in the range 5×10^{-4} to 5×10^{-2} M. For the higher concentrations, the biacetyl concentration could be verified by the absorption spectrum. The biacetyl concentration determined by the absorption spectrum typically agrees to ~10% with that calculated from the volumetric calculation. Solutions were placed in freshly pyrolyzed 4-mm-o.d. thin-wall, quartz tubes and sealed under high vacuum (~10^{-7} torr). No spectral difference was observed in samples outgassed by several freeze–pump–thaw cycles and those merely sealed under vacuum, so that the latter was the method used for later experiments. All experiments were carried out within a few days of sample preparation, since the biacetyl "impurity" emission referred to above began to be observable after a few weeks, even when samples were kept in a freezer.

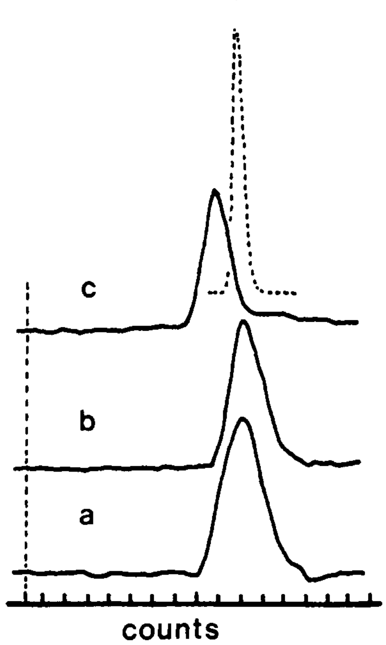

Figure 1. GPC elution curves, taken on a Waters HPLC with the following sequence of μ-styragel columns: 500, 10^3, 10^4, 10^5 Å. The solvent used was methylene chloride. For comparison, a monodisperse polystyrene with mol wt = 37 000 is presented (dashed line). Curves are: (a) PAcN, (b) P2VN-3, (c) P2VN-6. Each count corresponds to 3 mL. The dotted line corresponds to sample injection.

C. Optical System. The apparatus used was the same as that used in earlier published work.[5,7] Excitation is by means of a high-pressure Hg lamp (200 W), with a Corning 7-54 UV transmission filter and an Oriel 3130 Å (100 Å band pass) interference filter. The delayed emission spectra presented in Figure 2 were taken with a single chopper phosphorimeter with a 2.4 ms excitation/observation period. The decay curves presented in Figure 3 were obtained using a pair of asynchronously driven shutters (Vincent Associates uniblitz shutters, ~1.5 ms to open/close), triggered such that the excitation period was approximately 4.5 s and the observation period was approximately 10 s for all experiments. The decay curves were signal averaged 4–16 times on a FabriTek signal averager (Nicolet Instruments).

Results

The standard phosphorescence spectrum of the naphthalenic polymer plus biacetyl presented in Figure 2 is composed primarily of a biacetyl component, even for a biacetyl concentration of approximately 1×10^{-3} M (for a comparison of the biacetyl and naphthalene phosphorescence spectrum see ref 9). Decay curves, such as those presented in Figure 3, are highly nonexponential, as one would expect in a system composed of quenched and nonquenched polymer triplet excitons. The clearest presentation of our experimental results is the time-resolved emission spectrum, obtained by combining decay curves at different wavelengths. In Figure 4 are presented the spectra obtained in this fashion, for a sample in which

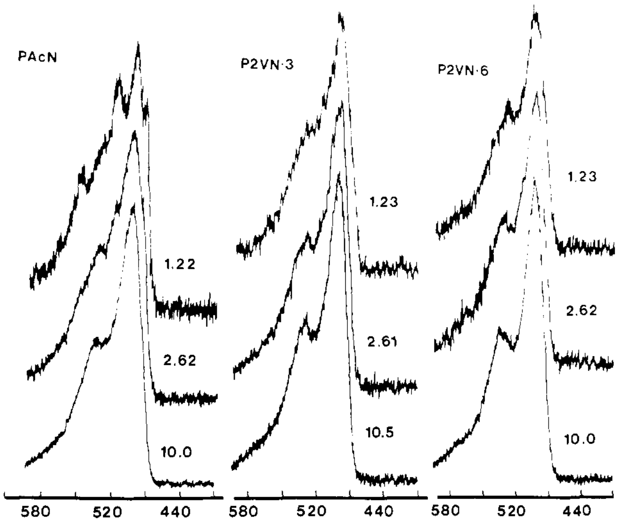

Figure 2. Delayed emission spectra of PAcN, P2VN-3, and P2VN-6 with concentration of biacetyl (in mM) indicated on the spectrum.

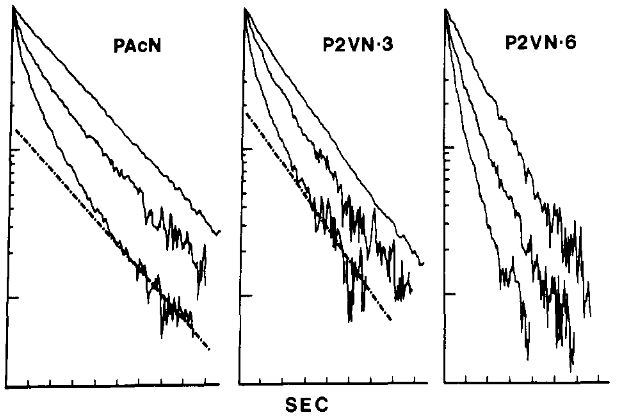

Figure 3. Semilogrithmic presentation of the decay of phosphorescence at 520 nm for PAcN, P2VN-3, and P2VN-6. PAcN, with biacetyl concentrations from top to bottom as follows: 0.0, 2.62×10^{-3}, 1.8×10^{-2} mol/L. P2VN-3, with the following biacetyl concentrations: 0.0, 2.61×10^{-3}, 1.58×10^{-2} mol/L. P2VN-6, with the following biacetyl concentrations: 0.0, 2.70×10^{-3}, 1.01×10^{-2} mol/L. Each division on the time scale is 1 s. For the highest biacetyl concentration for the first two polymers, the long time asymptotic approach to the unquenched decay rate is indicated by the dashed line.

the biacetyl concentration is $\sim 1.0 \times 10^{-2}$ M. At longer times, the spectrum begins to show naphthalenic character, especially for PAcN. Clearly the amount of naphthalenic character increases in the sequence P2VN-6, P2VN-3, and PAcN. This is reemphasized in Figure 5 in which the spectrum at 1 s after cessation of excitation is compared for the three polymers (all scaled such that the maxima are equal). The PAcN spectrum is essentially identical with that of naphthalene, the P2VN-3 spectrum is a mixture of biacetyl and naphthalene, and P2VN-6 is dominated by biacetyl at all times for which the signal-to-noise ratio allows a meaningful spectrum to be obtained. (Note, however, that a small naphthalenic component at 520 nm has appeared.) Clearly after 1 s or more the triplet excitons in P2VN are still sufficiently mobile to continue sensitization of biacetyl phosphorescence, while the same is not true of PAcN. The difference between P2VN-3 and P2VN-6 is easily ascribed to a molecular weight effect, as will be elaborated in the next section.

There is one feature in our experimental results that will require careful consideration. Suppose that after a certain period of time a triplet exciton is trapped, or equivalently, the triplet excitons that still exist are confined to polymers or segments of polymers that do not happen to have any contact with a luminescent quencher. It would be expected that after this time period (1) the emission spectrum would be that of the exciton only, with little or no quencher contribution, and (2) the decay curve would correspond to that of the exciton without quencher present. The former is what we observe for PAcN and to a lesser extent for P2VN-3. However, at times when the emission spectrum is essentially that of the naphthalene, the phosphorescence decay rate is greater than that of quencher-free polymer (see Figure 3). These data imply that the biacetyl is quenching the naphthalene triplet by two modes: energy transfer, in which case biacetyl phosphorescence results, and a "solvent effect" (similar to the external heavy-atom effect), which shortens the naphthalene lifetime *without* resulting in energy transfer. We are not aware of a similar dual role being played by a quencher of this type in analogous solid-state experiments.[11]

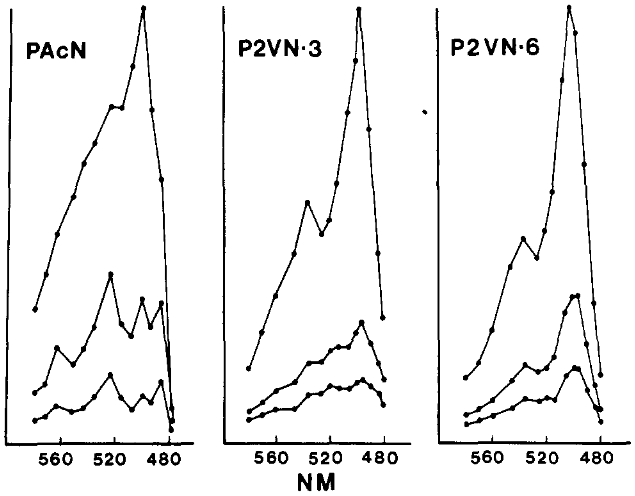

Figure 4. Time-resolved phosphorescence spectrum for naphthalenic polymer (1×10^{-3} M in naphthalene groups and 1×10^{-2} M in biacetyl; all at 77 K, in MTHF, with 313-nm excitation). Each set is in its correct relative intensity for the times cited. PAcN for $t = 0$, 1.0 and 3 s; P2VN-3 for 0, 0.5, and 1.0 s; and P2VN-6 for 0, 0.5, and 1.0 s.

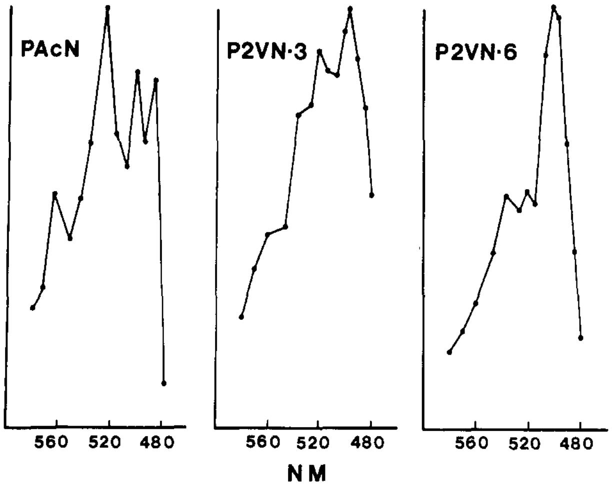

Figure 5. Comparison of the $t = 1.0$ s time-resolved spectrum for PAcN, P2VN-3, and P2VN-6 (all scaled to equal maxima).

Discussion

There are two important effects that bear on experiments of the present type: (1) fluctuations around the average number (and type) of polymer–quencher contacts, and (2) trapping of triplet excitons, with subsequent loss of quencher efficiency. It is not obvious that these two effects can be differentiated, nor are they mutually exclusive. For example, if there exist polymers without quencher contacts, then at longer times the emission spectrum and the decay rate will be identical with those of a quencher-free sample. The same properties would be present if an exciton becomes trapped (if the trapped triplet is sufficiently like the exciton that the emission spectrum is unchanged). There exists an "intermediate case" in which some excitons happen to be confined to relatively short segments of the polymer that are also devoid of quencher contacts. Even if the triplet exciton does not become trapped per se, the limitation of its motion to a short segment minimizes processes like extrinsic quenching or triplet exciton annihilation. For the present set of polymers, the intensity of delayed fluorescence (from triplet–triplet annihilation), the sensitivity to extrinsic quencher, and the retention in time of a significant quencher component in the emission spectrum consistently have the order of P2VN-6 > P2VN-3 > PAcN. We believe that this ordering represents the diffusion length of the triplet exciton for these three polymers. Whether the difference between PAcN and P2VN triplet exciton diffusion lengths should be ascribed to differences in the exciton hopping rate or to intramolecular barriers to excitonic motion cannot be ascertained from our data.

We can now consider the two effects mentioned above in more detail.

A. Fluctuations in the Number of Polymer–Quencher Contacts. In the following, we assume that biacetyl does not specifically solvate the polymer and that there is a random probability of finding a biacetyl molecule at any separation from a naphthalene. Based on the density of MTHF, the mole fraction of the quencer in MTHF is approximately $X = 0.086\ M_Q$, where X and M_Q are the mole fraction and molarity of the quencer, respectively. If each naphthalene has an average of N_s solvent molecules in contact with it, then the number of naphthalene chromophores required for an average of one quencher contact is given by

$$N_{CH} = (0.086 M_Q N_s)^{-1} \quad (1)$$

For example, if $N_s = 4$ and $M_Q = 10^{-2}$ mol/L, then $N_{CH} = 290$, i.e., there is an average of one quencher contact for every 290 naphthalene chromophores. Thus for P2VN-3 or PAcN, the average number of contacts per polymer is about unity, since the degree of polymerization is on the order of 300.[12] For P2VN-6, the number of quencher contacts would be approximately ten times this number, based on its molecular weight. Thus the differences we have found in the behavior of the time-resolved spectrum and decay curve between P2VN-3 and P2VN-6 can be rationalized purely on the basis of the molecular weight differences. It is possible that the lower sensitization efficiency for PAcN relative to that for P2VN-3 can be ascribed to a difference in N_s that arises from the polymer structure. However, our postulate that the triplet exciton becomes "trapped" in PAcN is consistent with the quenching results presented herein and the absence of detectable delayed fluorescence.

As mentioned in the previous section, the phosphorescence decay of PAcN is perturbed by biacetyl at times when the emission spectrum is essentially purely naphthalenic. We spectulate that biacetyl is capable of quenching a triplet exciton by two modes: energy transfer and a "solvent effect" analogous to the external heavy-atom effect. Since these two mechanisms may operate over significantly different distances, or have different orientational requirements, the appropriate value of N_s used in calculating the number of quencher contacts may be different. If N_s for energy transfer is smaller than N_s for "solvent quenching", then the number of quencher contacts per polymer that can induce this latter relaxation mode is larger than that for energy transfer. Consequently, if an exciton is confined to a relatively short segment of the total polymer chain, it may have a fairly high probability of encountering a "solvent quencher" in this segment but a very low probability of encountering an energy-transfer quencher. Similarly, if the average length of the segment over which an exciton may move is small compared with the length required for a single photon absorption event, then the probability of triplet exciton annihilation is low.[13] Thus we believe that most plausible model for triplet exciton mobility in PAcN is that the exciton is confined to small segments by intrinsic energy transfer barriers (i.e., an unfavorable positioning of neighboring chromophores), with immobilization possibly occurring at later times. For P2VN, the range of exciton mobility is much higher, greater than the 300 chromophores of P2VN-3 but less than or equal to the 3250 chromophores of P2VN-6. No obvious feature present in the structure of these two polymers has suggested itself as a cause of this dramatic difference.

B. Exciton Trapping Model. In what follows we will write down the kinetic equations for a model in which there is a competition for triplet excitons (E) by extrinsic quenchers and intrinsic traps. The extrinsic quenchers may act by energy transfer (quencher Q) or a "solvent effect" (quencher q) that induces the $T_1 \rightsquigarrow S_0$ intersystem crossing within the manifold of states of the triplet exciton. The intrinsic trap immobilizes the exciton forming a trapped triplet. Because of the relatively small number of extrinsic quenchers, we will assume that the trapped triplet decays with the normal decay rate of the triplet state.

The various steps postulated are given here.

$$E + t \xrightarrow[N_t k_t]{} T + G \quad (2a)$$

$$E + Q \xrightarrow[N_Q k_Q]{} Q^* + G \quad (2b)$$

$$E + q \xrightarrow[N_q k_q]{} G \quad (2c)$$

$$E \xrightarrow[K_E{}^0]{} G \quad (2d)$$

$$T \xrightarrow[K_T]{} G \quad (2e)$$

$$Q^* \xrightarrow[K_{Q^*}]{} Q \quad (2f)$$

In the above, G represents a ground state of the chromophore, and the symbols for the rates are also given. N_t represents the number of intrinsic traps, and N_Q or N_q represents the number of quencher contacts with a polymer. In exciting the system, we assume that only excitons are directly excited, because the number of intrinsic traps is small and the excitation wavelength is not absorbed by biacetyl to any appreciable extent. The kinetic equations for n_E, n_{Q^*}, and n_T (the number of E, Q*, and T, respectively) are:

$$(\mathrm{d}n_E/\mathrm{d}t) = -K_E n_E + I_{ex} \quad (3a)$$

$$(\mathrm{d}n_T/\mathrm{d}t) = -K_T n_T + k_t N_t n_E \quad (3b)$$

$$(\mathrm{d}n_{Q^*}/\mathrm{d}t) = -K_{Q^*} n_{Q^*} + k_Q N_Q n_E \quad (3c)$$

where

$$K_E = K_E{}^0 + k_t N_t + k_q N_q + k_Q N_Q \quad (4)$$

Table I
Values of K_E^{-1} for PAcN and P2VN-3

PAcN		P2VN-3	
[BiA], M	$\tau_E{}^a = K_E^{-1}$, s	[BiA], M	$\tau_E = K_E^{-1}$, s
1.22×10^{-3}	0.50	1.23×10^{-3}	0.64
2.48×10^{-3}	0.55	2.61×10^{-3}	0.71
		1.05×10^{-2}	0.35
1.80×10^{-2}	0.45	1.58×10^{-2}	0.38
2.48×10^{-2}	0.41	2.00×10^{-2}	0.27

[a] For PAcN $\langle\tau_E\rangle_{av} = 0.48 \pm 0.6$ s.

The steady state solution to eq 3, which corresponds to our experiment upon cessation of excitation, is:

$$(n_E)_{ss} = I_{ex}/K_E \tag{5a}$$

$$(n_T)_{ss} = ((k_t N_t)/K_T)(n_E)_{ss} \tag{5b}$$

$$(n_{Q*})_{ss} = ((k_Q N_Q)/K_{Q*})(n_E)_{ss} \tag{5c}$$

Since $K_{Q*} \gg K_E > K_T$, we expect that the steady state populations obey the relation $(n_T)_{ss} > (n_E)_{ss} \gg (n_{Q*})_{ss}$. The time-dependent solutions of eq 3 are:

$$n_E(t) = n_E(0)e^{-K_E t} \tag{6a}$$

$$n_T(t) = n_T(0)e^{-K_T t} + [(k_t N_t n_E(0))/(K_E - K_T)](e^{-K_T t} - e^{-K_E t}) \tag{6b}$$

$$n_{Q*}(t) = n_{Q*}(0)e^{-K_{Q*} t} + [(k_Q N_Q n_E(0))/(K_{Q*} - K_E)](e^{-K_E t} - e^{-K_{Q*} t}) \tag{6c}$$

It is interesting to consider the case in which $N_Q = N_q = 0$ and assume that the lifetime of E is equal to that of T except for the intrinsic trapping (i.e., $K_E{}^0 = K_T$ in eq 4). If we further assume that the phosphorescence emission rates of T and E are equal, then under these conditions the phosphorescence is proportional to the sum of excitonic and trapped triplets, i.e.,

$$I_{phos}(t) = K_{rad}(n_E(t) + n_T(t)) = K_{rad}(n_E(0) + n_T(0))e^{-K_T t} \tag{7}$$

Thus the observation of simple exponential decay in the phosphorescence does not necessarily imply the absence of intrinsic trapping.

In the presence of extrinsic quenchers, eq 6 must be used. If for the conditions of the experiment $n_{Q*}(0) \simeq 0$, and for times such that $K_{Q*}t \gg 1$ (i.e., for 10–20 ms, since $K_{Q*}{}^{-1} \sim 2$ ms), we may write

$$n_{Q*}(t) = ((k_Q N_Q)/K_{Q*})n_E(0)e^{-K_E t} \tag{8a}$$

$$n_E(t) + n_T(t) = n_E(0)(F_E e^{-K_E t} + F_T e^{-K_T t}) \tag{8b}$$

where in (8a) it was assumed that $K_{Q*} \gg K_E$, and

$$F_T = (k_t N_t K_E)/K_T(K_E - K_T) \tag{9a}$$

$$F_E = 1 - (k_t N_t)/(K_E - K_T) = (k_q N_q + k_Q N_Q)/(K_E - K_T) \tag{9b}$$

In (9a) we used the steady state expression for $n_T(0)$ given in (5b). Thus the observed phosphorescence decay is found to be biexponential with a decay rate given by K_E and K_T and weighted at a given wavelength by the spectrum and radiative rate of Q*, E, and T. It is certainly true that the observed phosphorescence decays for P2VN-3 and PAcN can be fit to two exponentials fairly well[14] and the values of K_E so obtained are given in Table I.[15] In all cases, K_T was taken to be equal to the unquenched polymer sample. We see in Table I that K_E changes relatively slowly with biacetyl concentration for the PAcN samples, while for P2VN-3 K_E increases fairly regularly with biacetyl concentration.[16] In the context of this kinetic model the implication is that the PAcN triplet exciton intrinsic trapping rate is dominant even at the highest biacetyl concentrations (but see below). Such is not the case for P2VN-3.

There are several over-simplifications present in this model that make it difficult to assign more than qualitative meaning to the derived rate constants. First, as discussed in the previous section, there can be a significant number of polymers that have no contact with quenchers (especially of the energy transfer type). These polymers will have a triplet exciton decay rate equal to an unquenched polymer. Hence the two-exponential decay law can arise very simply from an inhomogeneous sample of triplet states decaying with different rates. The most appropriate qualitative model for the kinetic behavior of this ensemble would be to average the decay laws of eq 8 over different numbers of quencher contacts. This can easily be done, but no new information is obtained, and these results will not be presented.

Another over-simplification in the above model is that we have ignored the fact that the observed phosphorescence lifetime for unquenched P2VN is dependent on molecular weight (ranging from ~1.45 s for a degree of polymerization of 3250 (P2VN-6)[17] to ~2.1 s for a degree of polymerization of 100). We believe that these differences arise from residual extrinsic quenchers (e.g., O_2) or possibly intrinsic quenching sites that increase in number with molecular weight (e.g., weakly interacting triplet excimer sites). The simplest interpretation of the present data is that the exciton is not trapped in P2VN. Thus we believe that the biexponential nature of the phosphorescence decay of quenched P2VN arises from inhomogeneities in the polymer–quencher contacts.

Conclusions

The set of experimental results presented herein illustrates three phenomena of importance in understanding triplet excitons in polymers contained in a condensed phase: (1) the polymer backbones have a significant effect on the range and/or rate of triplet exciton diffusion (cf. PAcN and P2VN-3), (2) the molecular weight of a polymer will greatly influence the nature of the processes concerning the triplet exciton (cf. P2VN-3 and P2VN-6), and (3) inhomogeneities in the environment of different polymers, in the present case arising from different numbers of polymer–quencher contacts, greatly complicate the interpretation of kinetic or spectroscopic data concerning excitons in polymers.

Our data comparing P2VN-3 and PAcN imply that the diffusion length of the triplet exciton in PAcN is much shorter than P2VN. This difference could arise from either a slower exciton hopping rate or the presence of intramolecular barriers to excitonic motion in PAcN. We note that in an earlier report by David et al.[8] the quenching of phosphorescence in PAcN and poly(1-vinylnaphthalene) yielded identical Stern–Volmer quenching constants. Since the molecular weights of the polymers used were not reported, it is not absolutely clear how to interpret this result. It seems likely to us that the principal difference between PAcN and P1VN or P2VN lies in the presence of exciton barriers in the former, such that the average diffusion length of the exciton is long enough to provide several contacts with extrinsic quenchers but too short to allow multiple exciton occupation[13] under the experimental condition used here or by David et al.[8]

The effect of molecular weight evidenced by the comparison of P2VN-3 and P2VN-6 is consistent with earlier observations.[5,18] Simply stated, if intrinsic exciton barriers and/or traps do not exist in a polymer, then the efficiency of sensitizing an extrinsic quencher should increase with molecular weight because of the increased probability of an exciton encountering a quencher.

The inhomogeneity present in polymer, excited-state, quenching experiments of the type herein does not seem to have been explicitly recognized in earlier studies. It is difficult to treat this inhomogeneity more quantitatively than the simple estimate provided in the previous section, part A. Fluctuations around some average number of quenchers per polymer chromophore can be treated as a random event if no specific quencher–polymer solvation occurs.[12] Since not only the number of quencher contacts can vary, but also their "type" (i.e., orientation of the quencher–chromophore pair), it is doubtful that more than a qualitative theory of these contacts is possible for solids. For liquids, a number of quencher–chromophore orientations can be established during the excited state lifetime of the latter which may simplify the analysis of the effect of the quencher.

Work on other polymer systems using the technique described herein is continuing, as well as efforts to provide a convenient theoretical framework to describe the kinetics of the exciton population in an essentially inhomogeneous population.

Acknowledgment. This work was supported by the Robert A. Welch Foundation (F-356) and in part by the National Science Foundation (DMR78-02600). We would like to acknowledge early contributions by Dr. San Ardi Lee and Brent Hyman and thank David Foyt of the Center for Fast Kinetics Research for his help in curve fitting.

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(10) The designations 3 and 6 are the same as those used in a previous publication (ref 5) for these polymer samples.

(11) In a recent paper, M. P. Schuh (*J. Phys. Chem.*, 82, 1861 (1978)) includes quenching without energy transfer in the mechanism for *cis*-piperylene quenching of gas phase alkyl benzenes. In addition, this paper provides evidence for steric specificity for effective quencher action.

(12) If the probability of a quencher contacting a naphthalene moiety is random, then we would expect the distribution of quencher–polymer contacts to obey a Poisson distribution of the form $p_n = (L/N_{\mathrm{CH}})^n e^{-L/N_{\mathrm{CH}}}/n!$, where p_n is the probability of n quencher contacts with a polymer containing L chromophores.

(13) Similar to quencher contacts, photon excitation is a random event, such that the probability of n excitons occurring on a segment of length L is given by $p_n = (L/L_0)^n(e^{-L/L_0}/n!)$, where L_0 is the length of polymer required for an average of one excitation (a typical value of L_0 might be 50 to 200, depending on the excitation source). If $L/L_0 < 1$, then p_n for $n > 1$ is small.

(14) The decay rate of P2VN-6 is so enhanced by the presence of biacetyl that extracting a meaningful value of K_{E} for higher biacetyl concentrations is difficult.

(15) Fits of the data to a double exponential (with one decay rate constrained to equal the unquenched phosphorescence) were performed at the Center for Fast Kinetics Research at the University of Texas at Austin.

(16) The trend for P2VN-3 in lifetimes has certain "reversals" in it (i.e., compare the 1.23×10^{-3} and 2.61×10^{-3} data). This probably arises from the inaccuracies in fitting the data to a "constrained" double exponential function.

(17) The phosphorescence decay of P2VN-6 will be nonexponential at higher excitation intensities, where biexcitonic annihilation makes a significant contribution to the phosphorescence decay rate.

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Contribution to the Study of the Mean Square End-to-End Distance $\langle r_n^2 \rangle$ of a Polymer Chain

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ABSTRACT: A recurrence equation is proposed to calculate the mean end-to-end distance $\langle r_n^2 \rangle$ of a polymer chain of length n, when we know the mean end-to-end distance of a chain of length $n - 2$ and the mean end-to-end distance $\langle r_n^2 \rangle_0$ of the class of configurations of the chain n having $x = 0$ primary contacts between nearby segments. We have established for $\langle r_n^2 \rangle_0$ equations of the type $\langle r_n^2 \rangle_0 = n^{E_n^0}$ where the exponent is a function of n.

In a preceding work,[1] we have drawn systematically all the configurations that a polymer chain of n segments can take on a square-planar lattice. These drawings were made up to $n = 11$ (about 6000 configurations, after elimination of the configurations which are identical by symmetry). Then we classified the configurations, taking into account the number x of primary contacts, between nearby segments, presented by each of these configurations.[2] This type of primary contact occurs between neighboring segments of the chain (segments p and $p + 3$), if the distance between them is equal to the side of the lattice cell (Figure 1).

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