

QUENCHING OF TRIPLET EXCITONS IN POLY(2-VINYLNAPHTHALENE) BY BIACETYL

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For a number of years it has been known that triplet exciton processes occur in a number of polymers of the vinylaryl type (usually studied as isolated molecules in 77 K matrices). The triplet exciton mobility is usually manifested by (1) an enhanced quenching of the triplet state by extrinsic traps (relative to monomeric model compounds), and (2) the observation of triplet-triplet annihilation, leading to delayed fluorescence. In general the processes involving triplet excitons in polymers appear to be more complicated than in crystals or fluids. For example: (1) the decay of delayed fluorescence and phosphorescence is non-exponential and usually does not obey any simple kinetic scheme, and (2) the decay rate of delayed fluorescence is much faster than twice that of the phosphorescence. Typically at times when the phosphorescence intensity is still quite significant the intensity of delayed fluorescence is negligible. There are at least two possible interpretations of this fact: (1) all triplet excitons have been trapped at structural or chemical traps associated with the polymer, such that phosphorescence is possible, but triplet-triplet annihilation is prevented, or (2) mobile triplet excitons still exist, but annihilation has reduced the average triplet exciton occupancy to less than one per chain. To distinguish between these two possibilities the following experiment was performed: a 77 K solution of methyltetrahydrofuran containing poly(2-vinylnaphthalene) (P2VN) at 10^{-3} M and biacetyl (BiA) at 10^{-2} M was excited using 313 nm light, such that essentially all light is absorbed by the naphthalene moiety. The delayed emission shows a delayed fluorescence characteristic of P2VN and a phosphorescence that is very similar to that of BiA. As expected, the triplet state of naphthalene ($\tau_N \approx 1.2$ sec in polymers of this molecular weight) is sensitizing the triplet state of BiA ($\tau_B \approx 2.8$ msec). Since the lifetime of $^3(\text{BiA})^*$ is approximately 10^{-3} of that of $^3(\text{Naph})^*$, the phosphorescence of $^3(\text{BiA})^*$ provides a probe for the continued mobility of naphthalene triplet excitons at long times. The phosphorescence spectra of BiA and P2VN are compared in Fig. 1. In Fig. 2 is presented the phosphorescence of the P2VN:BiA mixture at different times following the cessation of excitation. For time delays in the range 1-100 msec a PAR boxcar integrator (model CW-1) was used. There is essentially no change in the time resolved phosphorescence spectrum over this time range. For longer times the data is obtained by combining decay curves obtained at different wavelengths, with the result that the wavelength resolution is not very good. Nevertheless it is obvious that after more than 2 sec the phosphorescence spectrum still has a significant contribution from BiA.

These spectral changes are consistent with the decay curves presented in Fig. 3. The initial rate of decay of phosphorescence at 500 nm (a prominent $^3(\text{BiA})^*$ peak) is faster than at 520 nm (a prominent $^3(\text{Naph})^*$ peak). In all cases the presence of BiA increases the rate of decay, as expected. It is interesting to note that the decay rate of delayed fluorescence for a quenched polymer sample is essentially the same

as for an unquenched sample over the time range of 0-100 msec. Evidently the bimolecular annihilation process is significantly faster than triplet quenching by BiA so long as a polymer is multiply excited.

We conclude from these observations that the triplet exciton remains mobile in P2VN for times long compared to the delayed fluorescence lifetime. The fact that at longer times the phosphorescence spectrum becomes more naphthalenic could be interpreted in two ways: (1) after a sufficiently long time triplet excitons are trapped (or alternatively, an equilibrium is established between trapped and free excitons) or (2) after a sufficiently long time phosphorescence is observed predominantly from polymer chains that happen to have few contacts with BiA.

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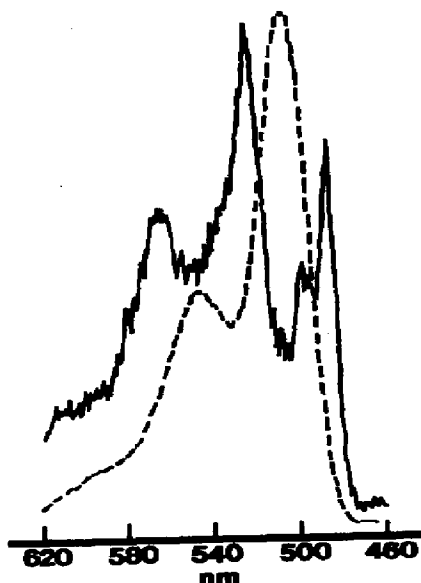


Fig. 1 Phosphorescence of P2VN in absence of BiA quencher (delayed fluorescence occurs at 340 nm) (solid line) and BiA (excited by 430 nm light, dotted line).

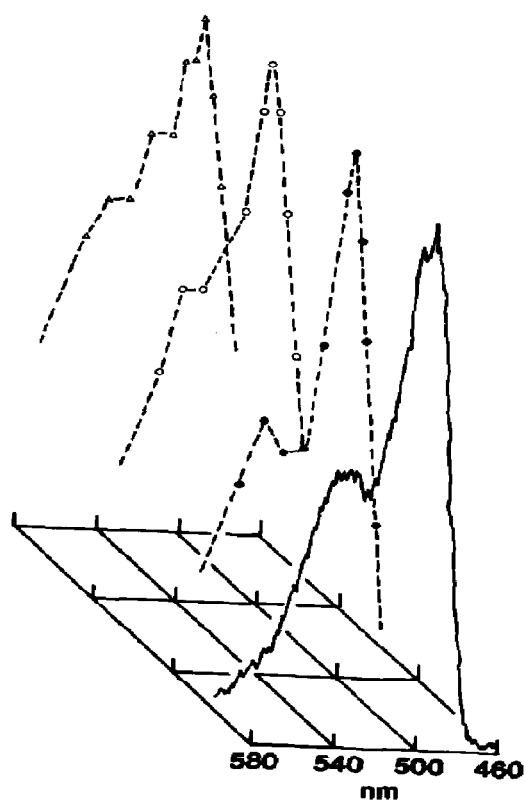


Fig. 2 Time resolved phosphorescence of a solution 10^{-3} M in P2VN, 10^{-2} M in BiA, excited by 313 nm light. The solid line is for a time delay of 100 msec, and the dotted lines are obtained from a series of decay curves at different emission wavelengths. They are: ●, $\Delta T = .04$ sec; ○, $\Delta T = 1.0$ sec; △, $\Delta T = 2.2$ sec where ΔT is the elapsed time from cessation of excitation.

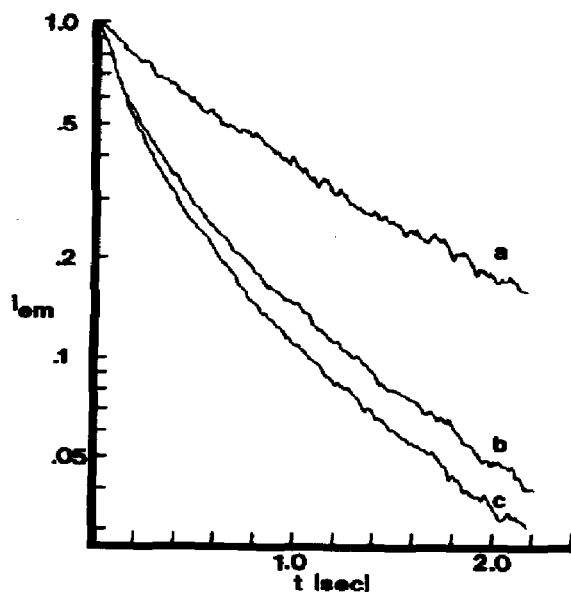


Fig. 3 Semilogarithmic plot of the intensity of emission for P2VN alone and P2VN:BiA mixture: (a) unquenched P2Vn at 520 nm, (b) P2VN:BiA at 520 nm, (c) P2VN:BiA at 500 nm.