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Effect of Molecular Weight on Triplet Exciton Processes. 4. Delayed Emission of Solid Poly(2-vinylnaphthalene)

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ABSTRACT: The delayed emission of solid poly(2-vinylnaphthalene) has been studied at 77 K and has been found to depend on the molecular weight of the polymer. As molecular weight increases the intensity of the delayed fluorescence increases and the phosphorescence develops a new lower energy peak. Both spectra are broad and excimeric in nature. The delayed fluorescence is found to be red-shifted by $\sim 1800\ \text{cm}^{-1}$ relative to the prompt fluorescence, which is taken to show that triplet–triplet annihilation occurs at traps. It is argued that at least part of this molecular-weight dependence arises from the partial localization of the triplet exciton on a single polymer chain.

Introduction

Since the work of Cozzens and Fox[1] in 1969 there have been a number of reports of triplet–triplet annihilation in polymers containing a high fraction of pendent aromatic chromophores. It has been demonstrated by a number of workers that the triplet annihilation occurs by an exciton mechanism involving either exciton–exciton annihilation or exciton-trapped triplet annihilation.[2] It has been found for several polymer systems in low-temperature glasses that the importance of triplet annihilation increases with molecular weight.[3] This dependence has been interpreted as arising from the increased probability of multiple excitations occurring in polymers with a larger number of chromophores. The present series of experiments was carried out to determine what molecular-weight dependence, if any, occurs in films or solid powders of poly(2-vinylnaphthalene) (P2VN). It was thought very likely that there would not be any molecular-weight dependence in solids for the following reason: if interchain contacts are extensive, then interpolymer excitonic migration should be facile and the size of individual polymer chains would be irrelevant. In fact, we have observed a molecular-weight effect that is qualitatively similar to that observed in isolated polymers in low-temperature glasses; i.e., increasing the molecular weight increases the delayed-fluorescence intensity. It will be noted that the delayed-emission spectrum (delayed fluorescence and phosphorescence) of the solid is quite different from that of isolated polymers, with an excimer-like delayed fluorescence and phosphorescence. We will also show that the delayed fluorescence is red-shifted relative to the prompt fluorescence, implying that triplet annihilation preferen-

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tially populates a singlet state at a "trap" or "defect". We speculate that this trap is originally in a triplet state and that the annihilation occurs between a triplet exciton and a trapped triplet. The presence of several different triplet traps in poly(vinylcarbazole) has been demonstrated recently by Burkhart and Avilês.[4]

Experimental Section

All polymer samples were prepared by free radical polymerization in outgassed benzene with AIBN initiator, as previously described.[3b] The molecular weight was controlled by the initiator to monomer ratio. The degree of polymerization and polydispersity were determined from GPC, using Waters μ-Styragel columns with a methylene chloride mobile phase and the calibration curve generated by earlier P2VN samples. The polydispersity was estimated to be ~1.5 for all samples. All monomer was vacuum sublimed immediately before use and the polymer was precipitated 4–6 times before use. Spectroscopic observations were carried out on films of P2VN cast from benzene solution and on the powdered form of the polymer obtained by precipitation of a benzene solution into a large excess of rapidly stirred methanol. The latter proved to be more reproducible and the spectra reported herein are for these powders. If carefully purified benzene is used to prepare cast films and all traces of solvent and oxygen are removed by extended exposure to vacuum (several days), the delayed-emission spectrum is in agreement with that for the powder. Since the delayed-fluorescence intensity tended to be higher in powders than in films, it is assumed that the powders possess fewer triplet quenchers than cast films. It is uncertain whether these quenchers are impurities present in the solvent or merely an additional set of traps that arise from traces of solvent left in the film.[4] In any case, it is certainly true that studies of the present type are very sensitive to the presence of impurities with low-lying triplet states, such that the observed ratio of delayed fluorescence to phosphorescence is always a lower bound of the intrinsic value for a given excitation intensity. In all cases spectroscopic observations were repeated for powder samples that had been stirred in hot methanol to remove any last traces of monomeric species. In most cases the ratio of delayed fluorescence to phosphorescence remained constant, but in one case, in which the precipitations were less extensive, a dramatic increase in this ratio was observed. This demonstrates the efficacy of this method of purifying a powder sample. In another case the powder was melted in vacuo and showed a diminution of the delayed fluorescence, as one would expect if a certain degree of depolymerization or degradation occurred. Thus the possibility exists that the delayed-emission spectrum is a fairly sensitive qualitative indication of the purity of the polymer.

In the case of powders the sample was placed in a small quartz tube, outgassed under ~10^{-5}-torr vacuum for ~12 h, and sealed off. In the case of films the film was cast on a quartz plate and then placed in a holder inside a quartz tube that was then evacuated as above and sealed off. All spectra were obtained at 77 K, after the sample had equilibrated in liquid nitrogen. Excitation was effected by a 200-W high-pressure Hg lamp through a Corning 7-54 UV band-pass filter. A home-built phosphorimeter, as previously described,[3b] was used to obtain the delayed-emission spectrum (phosphorimeter excitation/observation time ~2.4 ms) or signal-averaged decay curves (period of excitation ~5 s, observation time variable). Prompt-fluorescence spectra were obtained on the identical samples at 77 K, using a SPEX Fluorolog with our own low-temperature sample mounting modification. The spectra in Figures 1a and 2 have been digitized at ~10-nm intervals and scaled for easy comparison. It is for this reason that the spectra appear artificially free of noise. The *S*/*N* ratios of the original spectra (before digitizing) are equal to or better than that in Figure 1b.

Observations

Our spectroscopic observations are summarized in Figures 1 and 2, which are a compilation of delayed-emission spectra for different molecular weights and a comparison of delayed- and prompt-fluorescence spectra, respectively. The trend toward increased delayed-fluorescence intensity as the molecular weight increases is quite clear in Figure

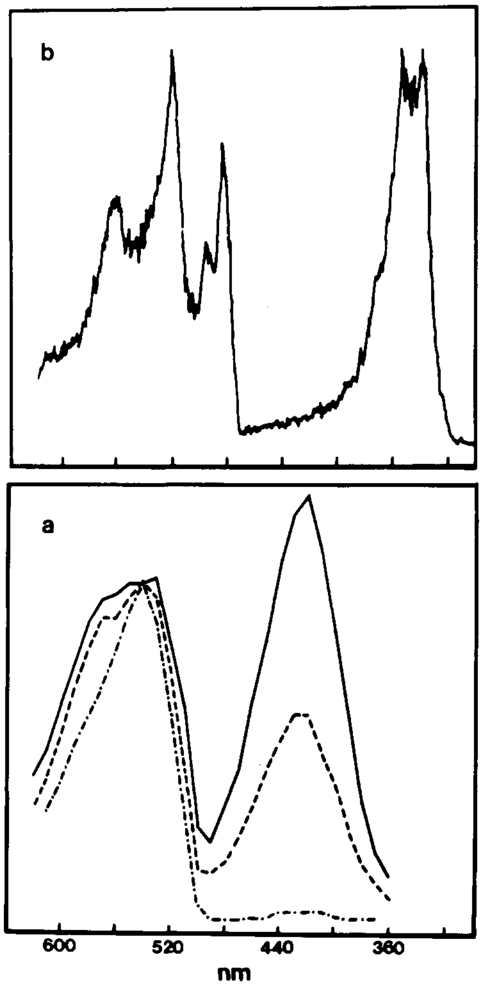

Figure 1. (a) Delayed-emission spectra for P2VN of different molecular weights: (—) 505 000; (- - -) 106 000; (-·-) 49 000. For convenience of comparison the spectra have been digitized and scaled to equal phosphorescence intensity maxima. (b) Delayed-emission spectrum of P2VN in a 77 K MTHF matrix (shown for comparison; see ref 3b).

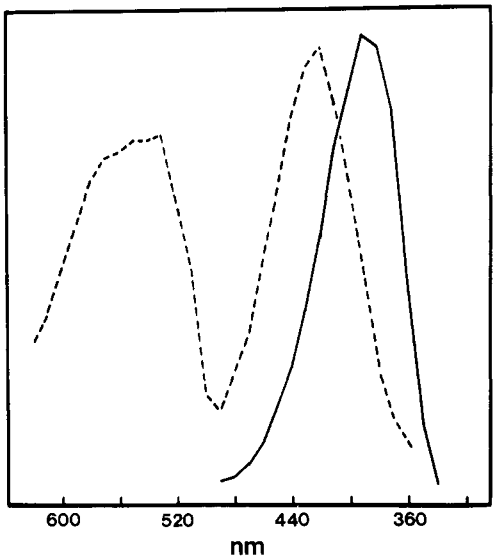

Figure 2. Comparison of prompt fluorescence (—) and delayed emission (- - -) for the sample with a molecular weight 505 000. The spectra are corrected for the different spectral response of the two instruments.

1. The delayed-fluorescence spectral distribution does not depend on molecular weight, but a new longer wavelength feature in the phosphorescence spectrum does appear as

molecular weight increases. These two phosphorescence peaks seem to have essentially the same decay rate, so one must tentatively conclude that they arise from the same or very similar triplet states. This new feature in the phosphorescence does not arise from residual 2-vinylnaphthalene monomer, since the monomer shows a strong and characteristically shaped peak at 550 nm. In Figure 1 we have included a delayed-emission spectrum of P2VN (10^{-3} M in naphthalene groups) in a 77 K methyltetrahydrofuran (MTHF) matrix for comparison. The phosphorescence and delayed fluorescence of the solid are seen to be significantly red-shifted in the solid polymer. This is characteristic of all solid homopolymers studied to date. The red-shift of the delayed-fluorescence feature (which is distinguished by its approximate dependence on the square of the excitation intensity) is usually assumed to imply that it is an excimer-like fluorescence. Presumably this occurs because of the crowding together of naphthalene chromophores in the solid polymer. The phosphorescence is also red-shifted relative to P2VN/MTHF (by approximately[5] 700 cm^{-1}) and has much less structure than a solvated polymer. We note that the film phosphorescence is similar to the room-temperature phosphorescence reported for naphthalene triplet excimers.[6] Our data do not allow one to determine if phosphorescence is occurring only from triplet excimer traps or if the chromophore crowding is so extreme that the triplet exciton in solid P2VN is essentially excimer-like.[7-9] We favor the former possibility because of the spectral shift between delayed fluorescence and prompt fluorescence shown in Figure 2.[10] The shift in the fluorescence maxima is approximately 1800 cm^{-1}. This is a consistent with the mechanism in eq 1, in which triplet annihilation occurs

$$T_{\text{free}} + T_{\text{trap}} \rightarrow S_{\text{trap}}^{**} \rightarrow S_{\text{trap}}^{*} \rightarrow G_{\text{trap}} + (h\nu)_{\text{DF}} \qquad (1)$$

between a trapped and excitonic triplet, producing an excited singlet at the trap site. In eq 1 S_{trap}^{**} denotes the initially formed excited singlet state. The energy of S_{trap}^{**} will lie above the singlet exciton of the polymer solid, but since S_{trap}^{**} is produced near the trapping site, energy migration away from this site is relatively improbable.[11] Our data do not allow an estimate of the relative concentrations of T_{free} and T_{trap}, but if we assume that (1) represents the mechanism for production of red-shifted excimer fluorescence, then it must be true that $[T_{\text{trap}}] \gg [T_{\text{free}}]$. Experiments using phosphorescent quenchers can help resolve this point.[12]

The time dependence of the decay of phosphorescence and delayed fluorescence (DF) does not vary with molecular weight appreciably (unlike isolated polymers in matrices[3b]). As is usual with polymeric systems the decay of phosphorescence is nonexponential and the rate of decay of delayed fluorescence is greater than phosphorescence (see Figure 3). The decay of both delayed-emission features is faster for solid polymer than isolated polymers in matrices ($\tau_{1/e}$ of approximately 35 ms for delayed fluorescence and 150 ms for phosphorescence). The shortening of the triplet-state lifetime is consistent with the lower energy of the phosphorescent state of the solid and the well-known energy gap law relating $E(T_1)$ to τ_{T_1}.[13] On the other hand, the phosphorescence lifetime is not as short as that of typical arylcarbonyls (e.g., benzophenone, $\tau_{T_1} \sim 5$ ms at 77 K), which could be present in the polymer as the result of oxidative degradation or impurities present during the polymerization. Thus our observations are consistent with the assignment of the phosphorescence to a triplet excimer state.

It is not obvious to us why the phosphorescence spectrum should change its structure as the molecular weight changes. Since the decay of delayed fluorescence or phosphorescence is not faster in high molecular weight polymer solids, this new peak is not easily assigned to a quenching, luminescent "impurity". We may speculate that for larger polymers more interpenetration of polymer coils and/or non-nearest-neighbor chromophore interaction occurs, leading to a geometrically distinct triplet excimer state, with a shifted spectrum but essentially the same τ_{T_1} (similar observations have been made for the naphthalenophanes).[7] Contradicting this interpretation is the fact that the delayed-fluorescence spectrum is not affected by molecular weight. If two different types of T_{trap} are involved in eq 1, then we might well expect a systematic shift in the delayed-fluorescence spectrum, although, once again citing the naphthalenophane example, the effect of chromophore crowding on T_1 and S_1 is not necessarily parallel.[8]

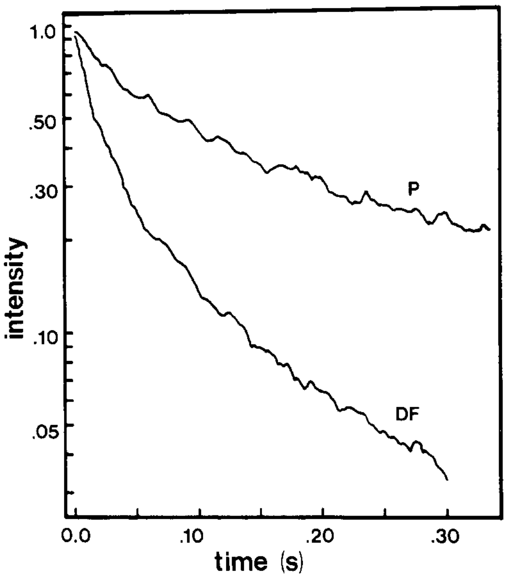

Figure 3. Decay of phosphorescence (P) and delayed fluorescence (DF) for a typical solid polymer sample at 77 K.

Discussion

The properties of the excited states of polymer films are almost certainly dominated by various types of traps whose physical nature is not understood. Since the prompt fluorescence of most polymer films is very similar to the fluid-phase excimer fluorescence, it is assumed that the fluorescent species in films is also excimeric. The phosphorescence of triplet excimers of naphthalene in solution is rather similar to the phosphorescence displayed by the films.[6] The fact that rather different fluorescence and phosphorescence spectra arise from different geometric isomers of the naphthalenophanes[8] shows that changing the degree of overlap of the naphthalene rings strongly perturbs the S_1 and T_1 energy levels. Hence one can speculate that different triplet traps exist that correspond to partially or completely overlapping naphthalene rings[14] (analogous to *anti*- and *syn*-[2.2](1,4)naphthalenophanes). The energy gap separating these two forms from the triplet exciton band may be quite different, such that one may be a deep trap at 77 K and the other a shallow trap, from which thermal detrapping is possible. Following eq 1, the DF is thought to arise primarily from triplet exciton-trapped triplet annihilation.[15] If the fraction of deep-trap sites on the polymer is high then one does not expect to observe significant DF since the process $T_d \rightarrow T_{\text{free}}$ is so improbable (T_d = deep trap). If the fraction of shallow traps exceeds that of the deep traps, then the annihilation process becomes more important. Our observations are that DF increases with molecular weight and simultaneously a new phosphorescence peak at 570 nm appears. Thus our observations can be rationalized as a molecular-weight effect on the fraction of trapping sites of each type. The 570-nm phosphorescence peak would therefore be assigned to the "shallow trap". In contradiction to this proposed mechanism we note that the DF intensity is different for polymers with essentially identical phosphorescence spectra. The above mechanism would suggest that the peak at 570 nm should grow in continuously as molecular weight is increased. Thus another molecular-weight-dependent mechanism may be operating.

It is well-known from studies of isolated polymers in low-temperature glasses that increasing the molecular weight increases the DF intensity.[3] It is thought that this is a manifestation of the excitation statistics of the isolated chains, in which multiple excitation of a long polymer chain is more probable than multiple excitation in a short chain. Possibly the same effect could be operating in solid polymers, which would mean that, at least to some extent, the triplet excitons remain on the original chain that was excited. In other words, interchain energy transfer, especially via triplet excitons, is not as efficient as intrachain energy migration. This implies that the polymer solids studied herein should be regarded as a disordered solid with "domains" within which triplet energy transfer is partially confined and that these "domains" are roughly coincident with individual polymer coils.

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(5) This is calculated by taking the start of the film phosphorescence as 500 nm and the 0,0 P2VN/MTHF peak as 484 nm. The first maximum occurs at 540 nm, which, if assigned to the 0,0 transition, yields a red shift of approximately 2150 cm^{-1}. We note that the P2VN/MTHF system is shifted relative to 2-methylnaphthalene in a 77 K matrix by ~640 cm^{-1}. Also see Aikawa et al. (M. Aikawa, T. Takemura, H. Baba, M. Irie, and K. Hayashi, *Bull. Chem. Soc. Jpn.*, **51**, 3643 (1978)) for a comparison of the energy shift in polymer phosphorescence because of chromophore crowding.

(6) (a) For naphthalene triplet excimers in fluid solution see T. Takemura, M. Aiwawa, H. Baba, and Y. Shindo, *J. Am. Chem. Soc.*, **98**, 2205 (1976), and references therein. (b) For studies of 1,3-di(1-naphthyl)propane see S. Ikajima, P. C. Subudhi, and E. C. Lim, *J. Chem. Phys.*, **67**, 4611 (1977), and references therein.

(7) For example, Froines and Hagerman (J. R. Froines and P. J. Hagerman, *Chem. Phys. Lett.*, **4**, 135 (1969)) found that *syn*- and *anti*-[2.2](1,4)-naphthalenophanes have significantly different 0,0 transitions but very similar τ_{T_1}'s (0.14 (~550 nm) and 0.18 s (~530 nm), respectively).

(8) Chromophore crowding can change the properties of the S_1 and T_1 states significantly (but not necessarily in a parallel fashion). (a) In addition to ref 7, see D. Schweitzer, J. P. Colpa, J. Behnke, K. H. Hausser, M. Haenel, and H. A. Staab, *Chem. Phys.*, **11**, 373 (1975), for triplet-state properties of naphthalenophanes. (b) For TT absorption of some naphthalenophanes see S. Ishikawa, J. Nakumura, S. Iwata, M. Sumitani, S. Nagakura, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **52**, 1346 (1979).

(9) The distinction between these possibilities is the mobility of the triplet state. If there is a high fraction of highly crowded chromophore configurations, then excitonic migration from one preformed excimer site to another would be possible.

(10) Our spectra, including the spectral shift between prompt and delayed fluorescence, seem to agree with those of Fox et al. (R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, *J. Chem. Phys.*, **57**, 2284 (1972)). We do not agree with these authors that the spectral feature beyond 500 nm is an impurity since we have observed this feature in a number of P2VN films and powders with various purification and preparation methods. For example, successive extractions with hot methanol do not reduce the emission intensity in this region nor do further precipitations. Samples of these polymers in 77 K methyltetrahydrofuran glasses show the normal naphthalene phosphorescence, showing that no significant intrinsic impurities (i.e., oxidized pendent groups) are present.

(11) For example, in the heterogeneous triplet–triplet annihilation between phenanthrene excitons and anthracene traps a small component of phenanthrene delayed fluorescence was observed, even though the anthracene singlet state is energetically lower than that of phenanthrene (S. H. Tedder and S. E. Webber, *Chem. Phys. Lett.*, **31**, 611 (1975)).

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(14) A similar interpretation of the two excimer states of poly(vinylcarbazole) has been given by Johnson (G. E. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975)).

(15) If $T_{\mathrm{free}} + T_{\mathrm{free}}$ annihilation dominated, the lifetime for DF should be $^1/_2\tau_{\mathrm{phos}}$, which is not found.