Photophysics of Films of Poly(2-vinylnaphthalene) Doped with Pyrene and Tetracyanobenzene†

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ABSTRACT: The fluorescence and delayed-emission spectra of poly(2-vinylnaphthalene) (P2VN) films containing TCNB (1,2,4,5-tetracyanobenzene), pyrene (Py), or TCNB + Py were studied at 77 K and room temperature. It was found that Py is a good trap for the singlet or triplet exciton in P2VN films. In P2VN–TCNB the charge-transfer fluorescence is easily observed, and the phosphorescence is probably multicomponent. In P2VN–TCNB–Py films excitation in the P2VN–TCNB charge-transfer absorption band (~430 nm) yields a strong pyrene phosphorescence, which is interpreted as arising from excitonic sensitization. At room temperature a broad delayed emission is observed, which is assigned to an E-type delayed fluorescence involving Py–TCNB pairs.

I. Introduction

Singlet and triplet energy transport in vinyl polymers with pendent chromophores has been actively studied for the past decade. As well as providing an interesting example of photophysics in disordered media, these studies have potential application to polymer photodegradation, polymer photoconductivity, and the use of polymer arrays as photon-harvesting "antennas" for solar energy collection. In the latter case, energy migration between polymer-bound chromophores is essential for maximum photosensitization efficiency. A significant fraction of the work in polymer photophysics has been on films (usually cast from solution), with special emphasis on poly(*N*-vinylcarbazole)[1] on account of the photoconductivity exhibited by films (often doped) of this material. The following summarizes the main features of the film state:

1. Chromophore crowding is extensive, although the relative extent of intercoil and intracoil contact is not known. As a consequence the emission spectra (either fluorescence, phosphorescence, or delayed fluorescence) are excimeric (structureless and red shifted relative to the emission of the parent chromophore).

2. Energy migration of singlet or triplet excitons is extensive, with easily observed triplet–triplet annihilation. However, only rough estimates of the energy migration length have been available.

3. For any given polymer a number of intrinsic trap types exist that depend on the synthetic method for the polymer preparation,[1] film preparation method and/or history, and possibly the molecular weight of the polymer.[2] These traps have been postulated to be different excimeric chromophore–chromophore configurations. Most film emission is thought to originate from traps, and triplet exciton–trapped triplet heterogeneous annihilation has been suggested as the primary source of delayed fluorescence.[1,2]

There have been only a few studies of polymer films doped with electron acceptors,[3] in contrast to the case of charge-transfer crystals of definite stoichiometry.[4] The present work is motivated by the observation of Iwata et al.[5] that the charge-transfer complex of 1,2,4,5-tetracyanobenzene (TCNB) with naphthalene derivatives exhibits a charge-transfer (CT) singlet absorption to the red of either parent TCNB or naphthalene but that the triplet state is a locally excited naphthalene state. Carried into the context of either polymer films with naphthalene pendent groups or naphthalene–TCNB CT crystals, it suggests that the delocalized naphthalene triplet exciton could be excited by visible radiation in the CT absorption band. This has been observed by Steudle et al.[6] for anthracene–TCNB molecular crystals and, as will be argued below, is suggested by our studies of films of poly(2-vinylnaphthalene) (P2VN) doped with small amounts of TCNB. Thus one has the interesting possibility of sensitizing the triplet exciton in a polymer film by visible radiation, even though the intrinsic absorption of the polymer is in the UV region (~320 nm in the case of P2VN). Shifting the absorption of a polymer "antenna" into the visible region is obviously of significance from the point of view of possible solar energy applications. It turns out that the photophysics of P2VN–TCNB films does not allow easy verification of the presence of triplet excitons. For this reason we have studied ternary mixtures of P2VN, TCNB, and pyrene (Py). The Py probe can trap triplet excitons and phosphoresce. However, one also has the complication of (Py–TCNB) CT pairs, which can play a role in the overall spectroscopic properties of the system, as we will see below. However, the main point we believe we have established in this study is that the naphthalenic triplet exciton (^{3}N*) can be excited via the CT absorption of (N–TCNB) CT pairs, i.e.

$$(\text{N–TCNB}) \xrightarrow[430\text{ nm}]{h\nu} {}^1(\text{N–TCNB})^* \rightsquigarrow {}^3\text{N}^* \overset{\text{Py}}{\rightsquigarrow} {}^3\text{Py}^* \quad (1)$$

in which Py plays the role of a minority "reaction center".

II. Experimental Section

The sample of P2VN was synthesized by free radical polymerization in benzene at 65 °C with AIBN as initiator. The solutions were outgassed by freeze–pump–thaw techniques and sealed before polymerization. The 2-vinylnaphthalene monomer (from Aldrich Chemical Co.) was vacuum sublimed just before use. According to GPC elution (Waters μ-Styragel columns, calibration based on polystyrene samples), the molecular weight of prepared P2VN was approximately 80 000 (polydispersity ~1.5). Previous experience has shown that the viscosity-average molecular weight of P2VN is approximately twice that obtained from GPC elution curves. TCNB (Aldrich Chemical Co.) was purified by vacuum sublimation. Pyrene was refluxed with maleic anhydride in toluene to eliminate anthracene, which is a common impurity of pyrene, recrystallized, and then vacuum sublimed. In this fashion, the yellow color (due to impurity tetracene) was essentially eliminated. As will be seen, the fluorescence and phosphorescence spectra that correspond to pure pyrene are observed.

Polymer films were cast inside a quartz tube for experimental convenience. Benzene solutions of P2VN and various dopants were evaporated in a rotating quartz tube at reduced pressure, outgassed under ~10^{-5}-torr vaccum for ~12 h, and sealed off.

Films of pure P2VN and pyrene-doped P2VN were colorless and TCNB-doped P2VN films were pale yellow. Upon addition

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of excess pyrene to TCNB-doped P2VN, the film color became a deeper orange, presumably indicating the formation of Py–TCNB pairs.[7] Homogeneity of films was inspected visually with a microscope (homogeneity for P2VN–TCNB and P2VN–Py was always satisfactory, unlike P2VN–anthracene, where microcrystals of anthracene were easily observed under the microscope). Delayed-emission spectra were obtained with a home-built phosphorimeter (excitation observation time ~2.4 ms) using a 200-W high-pressure Hg lamp.[8] A Corning 7-54 UV band-pass filter was used to excite P2VN and a blue band-pass interference filter (λ_{pass} 430 nm) was used to excite the P2VN–TCNB charge-transfer complex.

Decay curves were obtained by using a Fabri-Tek signal averager connected to our phosphorimeter. Prompt-emission spectra were obtained with a SPEX Fluorolog with our own low-temperature sample mounting modification. The SPEX Fluorolog was modified by the addition of phase-shifted choppers (1200 rpm, with an observation period of approximately 6.3 ms) in the excitation and emission monochromators. By shifting the relative phase of these two choppers, we could sequentially run the prompt-fluorescence and delayed-emission spectra without removing the sample from its mounted position. The excitation intensity that results from the 150-W Xe lamp and double-excitation monochromator is too weak to produce a significant biphotonic process such as T–T annihilation. All experiments designed to observe delayed fluorescence were carried out on the home-built phosphorimeter mentioned above. It should be noted that the photomultiplier on the phosphorimeter has an S-20 response, which greatly enhances the ^{3}Py* phosphorescence at 595 nm compared to the photomultiplier on the SPEX. We will note these differences in spectra to be presented in the following section.

All spectra were digitized and plotted with an HP-85 microcomputer, which allows convenient scaling and comparison of different spectra.

III. Results

As mentioned in the Introduction, we have used a pyrene dopant as a probe for triplet excitons. Since we will require an analysis of ternary P2VN–TCNB–Py mixtures, it is necessary to consider the binary mixtures P2VN–Py and P2VN–TCNB first. Thus this section will be subdivided into three subsections dealing with the three types of mixtures separately.

A. P2VN–Py. Since pyrene is to be a probe in P2VN films, it is necessary to understand how the P2VN–Py system behaves. Films containing pyrene up to 4 wt % showed no sign of pyrene aggregation either by microscopic inspection or by the characteristic pyrene excimer fluorescence found in the crystalline state (this excimer fluorescence is easily observed at ~10 wt %). The pyrene fluorescence and phosphorescence are structured and easily distinguishable from the corresponding emission features of P2VN films. Excitation of the film at ~290 nm yields fluorescence that arises primarily from Py (but with a discernible P2VN component) for the complete range of pyrene concentrations studied (0.3–2.0 wt %, corresponding to a mole fraction of pyrene from 0.0025 to 0.017). Singlet energy transfer from naphthalene to pyrene is very efficient, which when coupled with the high fluorescence quantum yield of pyrene explains why pyrene dominates the P2VN excimer fluorescence. The shape of the prompt-fluorescence spectrum in Figure 1 is typical of all values of X_{Py} studied for all excitation wavelengths from 350 nm (direct excitation of pyrene) to 280 nm (primary excitation of P2VN) (bandwidth of excitation ≤10 nm). There is no significant change in this spectrum between 77 K and room temperature. By comparing the fluorescence spectra of the ternary mixtures P2VN–TCNB–Py, in which the P2VN singlet is quenched both by the CT singlet and by pyrene, it seems that there is a residual P2VN excimer component in P2VN–Py films *even when*

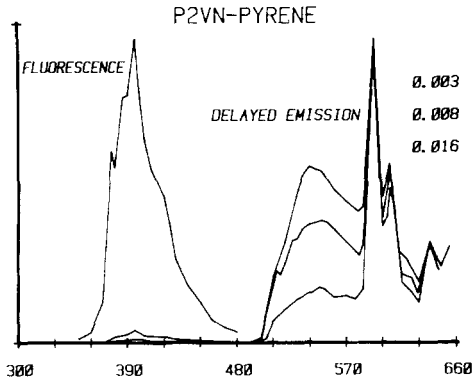


Figure 1. Prompt fluorescence and delayed emission of P2VN–Py films at 77 K. The mole fraction of pyrene for the corresponding delayed-emission spectrum is indicated on the figure. Note that the delayed-emission spectrum was obtained with a more red-sensitive photomultiplier than the prompt emission (see Experimental Section).

^{1}Py is directly excited.* Thus we speculate that there exist some excimer-forming sites that can be sensitized by ^{1}Py*. However, because of the extensive overlap of the ^{1}Py* and P2VN excimer fluorescence, it is difficult to quantify this excimer sensitization.

The delayed-emission spectrum reveals several interesting features (see Figure 1) (note that these delayed-emission spectra were taken with an S-20-response photomultiplier to enhance the red portion of the ^{3}Py* phosphorescence):

1. At the lower pyrene concentrations no delayed fluorescence at all is observed. Evidently, the trapping of the naphthalene triplet exciton (^{3}N*) by pyrene is so efficient that the usual annihilation process[2] (^3N_T* is a trapped triplet)

$$^3N^* + {}^3N_T^* \rightarrow N + {}^1N_T^* \rightarrow N_T + N + (h\nu)_{fl}^{N_T} \quad (2)$$

is quenched. However, at higher pyrene concentrations a pyrene component of delayed fluorescence is observed. Thus it appears that the following heterogeneous annihilation is occurring:

$$^3N^* + {}^3Py^* \rightarrow N + {}^1Py^* \rightarrow N + Py + (h\nu)_{fl}^{Py} \quad (3)$$

In this case ^{1}Py* fluorescence is more easily observed than ^1N_T* because of the difference in fluorescence quantum yield.

2. The phosphorescence is composed of two obvious components: (1) P2VN phosphorescence from ^3N_T* (which is excimer-like), peaking at approximately 540 nm, and (2) the structured ^{3}Py* phosphorescence, with an origin at ~595 nm. As the pyrene concentration increases, the relative intensity of the pyrene component increases approximately linearly, as one would expect for a simple trapping model.

The presence of ^{3}Py* phosphorescence does not prove that triplet exciton sensitization occurs since the following two routes would excite ^{3}Py* equally well:

$$^1N^* \xrightarrow{Py} {}^1Py^* \rightsquigarrow {}^3Py^* \quad (4a)$$

$$^1N^* \rightsquigarrow {}^3N^* \xrightarrow{Py} {}^3Py^* \quad (4b)$$

$$\downarrow {}^{N_T}$$

$$^3N_T^*$$

However, the observation of heterogeneous annihilation as per reaction 3 does demonstrate that triplet excitons (^{3}N*) are not totally removed by Py and that the ^{3}Py* molecules are accessible to ^{3}N*. In addition to the sensitization processes in eq 4, direct excitation of ^{1}Py* is possible using broad-band 320–350-nm excitation. Thus

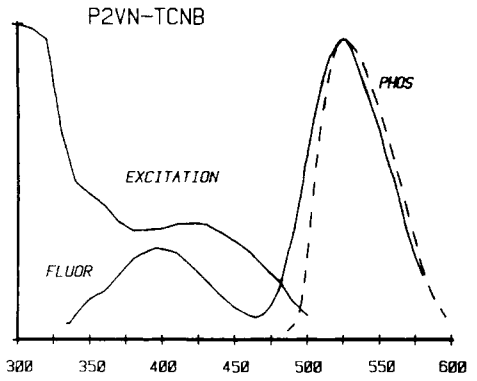


Figure 2. Spectrum of typical P2VN-TCNB at 77 K (X_{TCNB} = 0.008). The excitation spectrum is for the CT fluorescence at ~530 nm. The prompt fluorescence (solid line) and phosphorescence (dashed line) were measured with the same photomultiplier (see text).

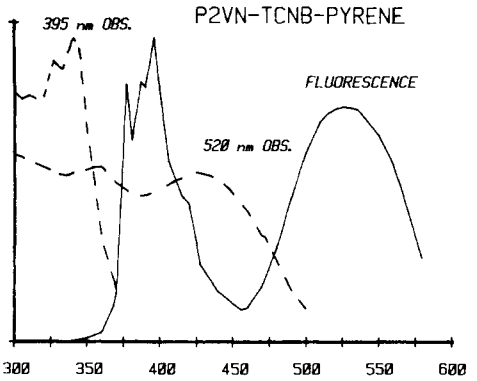


Figure 3. 77 K fluorescence spectrum of P2VN-TCNB-Py (X_{Py} = 0.016) excited at 290 nm (solid line). The excitation spectra (dashed line) at the two observation wavelengths clearly illustrate the pyrene and N-TCNB absorption features, respectively.

the binary P2VN-Py results merely establish that ^{3}Py* can be populated in this system.

The ^{3}Py* phosphorescence decay is fit quite adequately by a single exponential $\tau_{^3Py^*} \approx 500$ ms, typical of ^{3}Py*). The P2VN phosphorescence decay is multiexponential, as usual,[2] but there is little effect of Py on the decay rate. This is consistent with earlier work that suggests that the bulk of phosphorescence originates from ^3N_T*.[2,9]

B. P2VN-TCNB. As mentioned in the Introduction, P2VN-TCNB films are light yellow (the CT absorption band extends from approximately 340 to 500 nm; below 320 nm the P2VN absorption prevents an assessment of the CT absorption in this region). Similar to the case of P2VN-Py, excitation in the P2VN absorption region yields a significant CT fluorescence, implying efficient sensitization:

$$^1N^* \rightsquigarrow {}^1(N\text{-}TCNB)^* \rightarrow N\text{-}TCNB + (h\nu)_{fl}^{CT} \quad (5)$$

The CT fluorescence is strongly red shifted away from the polymer fluorescence, yielding a mixed ^{1}N* and ^{1}(N-TCNB)* fluorescence. It appears that the sensitization is not as efficient as for the case of pyrene. Excitation at wavelengths longer than 340 nm yields exclusively CT fluorescence (see Figure 2).

The phosphorescence spectrum is similar to that of neat P2VN, but slightly red shifted and broadened. The phosphorescence spectrum can be excited either in the P2VN absorption band or in the CT absorption band. In the latter case there is a very slight red shift in the phosphorescence. In addition to CT complexes, it is possible that new traps are created by the presence of TCNB (denoted $^3N_{T'}$*) that are slightly different from the normal P2VN traps, ^3N_T*. Undoubtedly, the energy gaps are very small between ^{3}(N-TCNB)*, ^3N_T*, and $^3N_{T'}$*. Consequently, the phosphorescence may originate from a mixture of these species. The phosphorescence decay is multiexponential, with a slightly longer lifetime than for P2VN alone and with a slight dependence on the wavelength of observation, which further implies a multicomponent phosphorescence.

One complication in P2VN-TCNB films is that the CT fluorescence is very close to the phosphorescence emission. This is illustrated in Figure 2, in which the prompt fluorescence (solid line) and phosphorescence (dashed line) are compared. (The broad feature peaking at 400 nm is the usual P2VN excimer fluorescence.) These spectra were both taken on the same instrument (modified SPEX Fluorolog) with in-phase and out-of-phase choppers, respectively (see Experimental Section). In this manner, no correction for photomultiplier response is required and a direct comparison of the spectra is meaningful. The fact that the ^{1}(N-TCNB)* emitting state and the phosphorescent state(s) (possibly $^3N_{T'}$* or ^{3}(N-TCNB)*) are so close in energy makes it difficult to assess the likelihood of ^{3}N* sensitization.

As in the case for P2VN-Py, there is no evidence for TT annihilation, since neither an obvious delayed-fluorescence component nor superlinear or sublinear excitation intensity dependence of any emission feature was observed.[10] However, the absence of these two effects only shows that annihilative processes are unimportant; triplet excitons could still be excited via the CT absorption. It is to this point that the experiments of the next section are addressed.

C. P2VN-TCNB-Py. Results at 77 K. Films containing various mole fractions of TCNB and pyrene were prepared. The results to be discussed explicitly are for films in which X_{TCNB} = 0.008 and X_{Py} ranged from 0.003 to 0.016. The prompt-fluorescence spectrum of these films is composed of a pyrene feature and a CT fluorescence (see Figure 3). As the pyrene content is increased the CT fluorescence is progressively red shifted. This almost certainly reflects an additional component of ^{1}(Py-TCNB)* fluorescence (see below). The formation of Py-TCBN CT complexes despite the relatively small mole fraction of pyrene is not surprising, given the superior electron-donating property of pyrene[11a] and the quenching efficiency of ^{1}Py* by TCNB.[11b]

The excitation spectra for fluorescence at 395 and 520 nm in Figure 3 reflect the presence of pyrene and a CT absorption very similar to that of P2VN-TCNB. At the highest pyrene concentration the 520-nm excitation spectrum does red shift slightly, once again implicating Py-TCNB pairs. The comparison of the prompt fluorescence and the delayed emission using the modified SPEX Fluorolog (Figure 4) demonstrates the proximity of the CT fluorescence and the polymer phosphorescence (cf. Figure 2). The pyrene phosphorescence peaks are barely visible on the long-wavelength side of the polymer phosphorescence. The weakness of these peaks is largely an artifact of the wavelength response of the photomultiplier used in the SPEX. This point is clearly illustrated by the series of phosphorescence spectra in Figure 5a excited at 430 nm (the CT absorption) and observed on the home-built phosphorimeter with an S-20 photomultiplier tube. The decline of the polymer phosphorescence and growth of ^{3}Py* phosphorescence with increasing X_{Py} are evident. Because of the relative strength of the pyrene phosphorescence, the retention of its characteristic structure, and its slightly lengthened phoshorescence lifetime,[12] we propose that the scheme given in eq 1 is

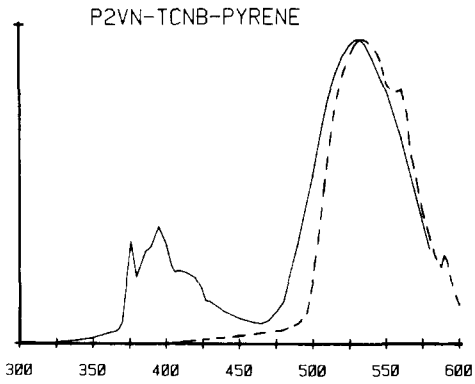


Figure 4. 77 K fluorescence (solid line) and phosphorescence (dashed line) spectrum of P2VN-TCNB-Py (X_{Py} = 0.008) with an excitation wavelength of 290 nm (measured with the same photomultiplier; see text).

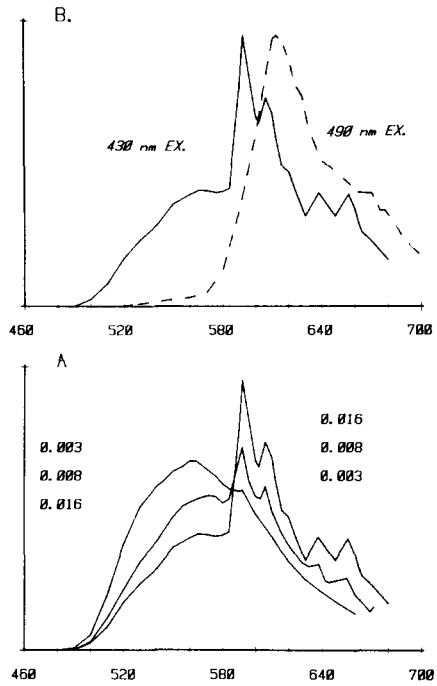
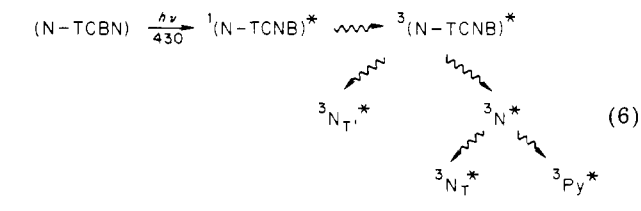


Figure 5. (A) Phosphorescence of P2VN-TCNB-Py excited at 430 nm ordered by X_{Py} as shown (X_{TCNB} = 0.008 for all cases). (B) Comparison of phosphorescence excited at 430 nm and >490 nm for P2VN-TCNB-Py with X_{Py} = 0.016 (all spectra measured with an S-20 photomultiplier tube).

operative, with the modification that a variety of trapped triplet states may also exist, e.g.:



(6)

An alternative explanation for the observed ^{3}Py* phosphorescence is that 430-nm excitation is also effective for Py–TCNB pairs and excitation of these pairs yields a "localized" ^{3}Py* state. The evidence against this is the following:

1. The presence of pyrene only slightly modifies the excitation spectrum for the CT fluorescence in the 360–460-nm region. It would be rather fortuitous if the Py–TCNB absorption spectrum matched that of N–TCNB in this region. Certainly for vapor-deposited CT complexes of Py–TCNB alone (no polymer matrix) the CT absorption

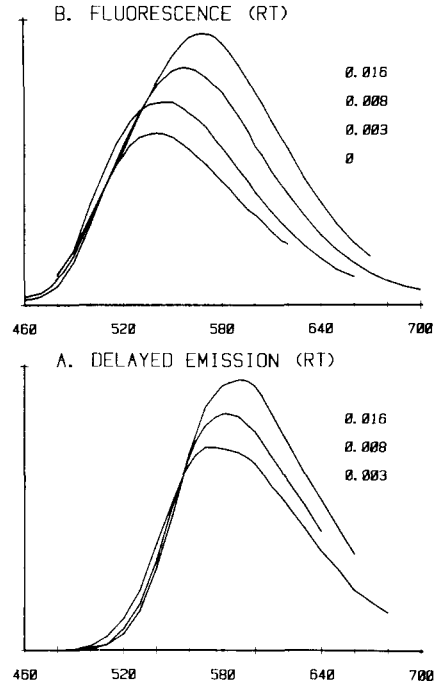


Figure 6. (A) Room-temperature delayed-emission spectra of P2VN-TCNB-Py excited at 430 nm (X_{Py} indicated on figure; X_{TCNB} = 0.008). (B) Room-temperature fluorescence under same conditions as part A (all spectra measured with an S-20 photomultiplier tube).

is significantly to the red of N–TCNB.[13]

2. Excitation of P2VN-TCNB-Py films at wavelengths longer than 480 nm leads to a much weaker structureless phosphorescence feature that we assign to the ^{3}(Py–TCNB)* state (see Figure 5B, dashed-line portion).[14]

In any case it is certainly the case that visible excitation produces ^{3}Py* very efficiently, which *may* arise from ^{3}N* production.[15] Thus we propose that this system is a model for a sensitized "antenna" for collection of visible light energy by the reaction center (pyrene). It would undoubtedly be of interest to compare the present sensitization scheme with a naphthalene triplet sensitizer in P2VN that does not have the complication of possible complex formation with the triplet exciton probe. Of course, it should be pointed out that sensitizers of this type (e.g., benzophenone and carbazole) do not absorb in the visible region.

Results at Room Temperature. In general, phosphorescence of aromatic molecules tends to be weak at room temperature or above because of the thermally enhanced $T_1 \rightsquigarrow S_0$ radiationless process. This does not mean that triplet processes are quenched at room temperature, as one may cite the well-known room-temperature delayed fluorescence of molecular crystals or, more recently, the temperature-dependence studies of Burkhart et al. on poly(*N*-vinylcarbazole) films.[1b] In the present work we have been able to observe a relatively weak ^{3}Py* phosphorescence in P2VN–Py films at room temperature, which retains the characteristic pyrene spectral progression. However, for the case of P2VN–TCNB–Py excited at 430 nm at room temperature, we observe a very strong delayed emission that is red shifted from the room-temperature prompt emission (cf. Figure 6A,B). While the lifetime of this delayed emission is shorter than that of ^{3}Py* at 77 K ($\tau_{1/e} \sim 30$ ms as compared to 500 ms), it is clearly in the range expected of a triplet state. The delayed-emission spectrum does not correspond to the ^{3}(Py–TCNB)* species as assigned in Figure 5B. While we are not equipped to carry out variable-temperature work,

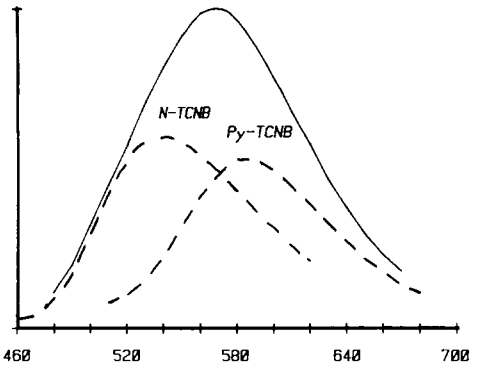


Figure 7. Fit of P2VN–TCNB–Py room-temperature fluorescence spectra as a combination of N–TCNB and Py–TCNB for $X_{Py} = 0.019$ and $X_{TCNB} = 0.016$ (see text).

spectra obtained at a few reduced temperatures (using constant-temperature baths) displayed a decrease of the broad delayed emission shown in Figure 6A and a growth of the typical ^{3}Py* structured emission. Consequently, we assign the room-temperature delayed emission to an E-type delayed fluorescence involving the thermal process ^{3}(Py–TCNB)* ⇝ ^{1}(Py–TCNB)*. We have found that the prompt fluorescence excited at 430 nm can be satisfactorily fit to a linear combination of P2VN–TCNB fluorescence and the fluorescence of P2VN–TCNB–Py films excited at wavelengths longer than 490 nm (see Figure 7). Thus we believe that the red shift of the room-temperature delayed emission results from the enhanced ^{1}(Py–TCNB)* component. The slight bathochromic shift that occurs with increasing X_{Py} is most likely a self-absorption artifact. The ^{1}(N–TCNB)* state is too high in energy to be thermally populated, and in any case its emission peaks near 500 nm, which is too far to the blue to account for the observed shift. Since the room-temperature delayed fluorescence is efficiently excited by the N–TCNB CT absorption, we propose that a scheme like (6) is operative, except that Py–TCNB pairs that are sensitized dominate the delayed-emission spectrum because of the relatively high fluorescence quantum yield of ^{1}(Py–TCNB)*.

IV. Summary and Discussion

In this paper we have explored the photophysics of P2VN films containing a typical electron acceptor (TCNB) that can form charge-transfer complexes with the pendent naphthalene groups. We have attempted to test the hypothesis that excitation in the CT absorption band can produce triplet excitons by using a pyrene dopant as a triplet trap. Consequently, the following three systems were studied separately: P2VN–Py, P2VN–TCNB, and P2VN–TCNB–Py. A schematic representation of the energy levels is presented in Figure 8 which unifies the observations. All states joined to the ground state by a solid line are spectroscopically active in absorption and/or emission. States connected by dashed lines are interconverted by some radiationless process (e.g., intersystem crossing, Förster energy transfer, sensitization, etc.). It must be true that all energy states are better represented as a band of states arising from different local environments. This is explicitly shown only for ^3CT_N* (=^{3}(N–TCNB)*). For most of our observations we do not need to invoke the presence of Py–TCNB pairs shown on the far right side of the energy level diagram. Thus we see that ^{1}N* can sensitize ^{1}Py* or ^{1}(N–TCNB)*, the former particularly efficiently. We (and others) have postulated that the naphthalene phosphorescence originates from trapped naphthalene triplets (^3N_T*). It also seems likely that some phosphorescence originates from trapped ^{3}(N–TCNB)*

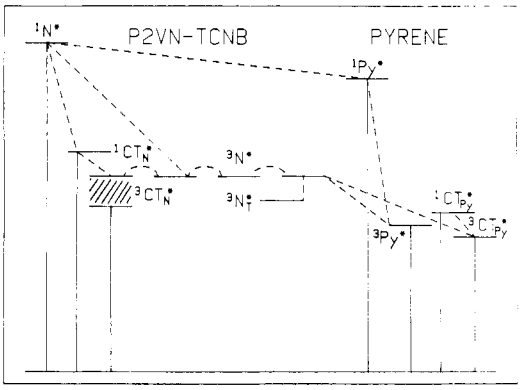


Figure 8. Representation of the energy level diagram and photophysical processes for P2VN films containing pyrene or TCNB. Spectroscopically observed processes are indicated by the solid lines and radiationless processes by the dashed lines.

states (or, equivalently, new traps created by the presence of TCNB). We have also postulated that ^{3}(N–TCNB)* can sensitize triplet excitons (^{3}N*), which in turn can sensitize the ^{3}Py* state. This phenomenon provides a model for producing a polymer film photoresponse in the visible that can efficiently sensitize a "reaction center" (pyrene in this case). However, our results do not prove unambiguously that the ^{3}N* state is produced by ^{1}(N–TCNB)*. For example, it is possible that the latter sensitizes weakly bound Py–TCNB pairs (via the Förster mechanism for example) for which the triplet state is a localized ^{3}Py* rather than ^{3}(Py–TCNB)*. For the reasons presented in IIIC we favor a mechanism like eq 1 for ^{3}Py* sensitization.

An observation that was unexpected was a strong room-temperature delayed emission for P2VN–TCNB–Py films. It is postulated that this is an E-type delayed fluorescence involving the ^{3}(Py–TCNB)* ⇄ ^{1}(Py–TCNB)* thermal equilibrium, where ^{3}(Py–TCNB)* could be sensitized via ^{3}N*. The main significance of this observation is that Py–TCNB pairs are present and that they play a significant role in the P2VN–TCNB–Py photophysics.

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(5) Iwata, S.; Tanaka, J.; Nagakura, S. *J. Am. Chem. Soc.* **1967**, *89*, 2813.
(6) Steudle, W.; von Schütz, J. U.; Möhwald, H. *Chem. Phys. Lett.* **1978**, *54*, 461 and references therein.
(7) While the color change is easily observed visually, the absorption spectrum shows a rather modest red shift.
(8) This phosphorimeter has been described in an earlier publication (Pasch, N. F.; Webber, S. E. *Chem. Phys.* **1976**, *16*, 361).
(9) For similar work on poly(1-vinylnaphthalene) films see: Burkhart, R. D.; Aviles, R. G.; Magorini, K. *Macromolecules* **1981**, *14*, 91.
(10) If any part of the emission spectrum was produced via TT annihilation to form an emitting singlet, then the emission intensity would be proportional to $(I_{ex})^n$ with $n > 1$; if TT annihilation depleted the phosphorescent triplet state, then n

< 1 would be observed. For a beautiful example of this type of behavior in poly(vinylcarbazole) films, see ref 1a.
(11) (a) The ionization potentials are as follows: naphthalene, 8.12 eV; pyrene, 7.58 eV (Matsen, F. A. *J. Chem. Phys.* **1956**, *24*, 602). (b) The quenching constant of Py fluorescence by TCNB is quite large (4600 M^{-1}) as measured by: Grellmann, K. H.; Watkins, A. R.; Weller, A. *J. Phys. Chem.* **1972**, *76*, 3132.
(12) If $^3Py^*$ is populated by triplet excitons with a lifetime on the order of that of isolated $^3Py^*$, the effect will be apparent lengthening of $\tau_{^3Py^*}$.
(13) Kim, N., unpublished results.
(14) According to Möhwald and Sackmann (Möhwald, H.; Sackmann, E. *Z. Naturforsch., A* **1974**, *29A*, 1216) the triplet state of Py–TCNB pairs in a 1:1 naphthalene–TCNB CT crystal is lower by 1400–2200 cm^{-1} than the naphthalene–TCNB triplet exciton. This energy gap is similar to what we observed for the P2VN phosphorescence (λ_{max} ~540 nm) and the structureless emission with λ_{max} ~610 nm.
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Photolysis of Cyclooctyl Nitrite in Solution and in Polymer Medium

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ABSTRACT: The photolysis of cyclooctyl nitrite in solution and in polymeric medium has been followed spectrophotometrically (ultraviolet and infrared). In solution the quantum yield of photolysis, Φ_N, varies between 0.5 and 0.6, depending on the solvent, while in polymer films, it is only about 0.25 on account of enhanced radical cage recombination. On the contrary, the quantum yield of cyclooctanone formation, Φ_K, is much higher in film (0.16 in poly(vinyl chloride)) than in solution (0.08 in dichloromethane); the cyclooctanone results from the disproportionation reaction between the NO radical and the cyclooctyloxy radical within the photolytic cage. Moreover, on the basis of the absence of a nitroso derivative in polymeric medium, it must be concluded that no Barton reaction takes place in film and that cyclooctanone becomes the main reaction product of photolysis.

The Barton reaction is based on the photolysis of alkyl nitrites to alkoxy radicals, followed by intramolecular hydrogen abstraction by the latter and recombination of the resulting carbon radicals with nitrogen oxide to form nitroso derivatives or oximes.[1] The structural requirement of this reaction is that the alkoxy radicals should be formed in potentially close proximity of a hydrogen atom from the δ-carbon atom through a six-membered cyclic transition state.[2-4] In the case of cyclooctyl nitrite, 4-nitroso-1-cyclooctanol dimer is formed by transannular attack of the oxy radical without a noticeable ring-cleavage mechanism.[5] The alkoxy radical produced by photolysis must be axial for intramolecular abstraction of the δ-hydrogen atom. This abstraction includes therefore a conformational change of the cyclooctane ring, while the most stable conformation presents the nitrite in equatorial position.[6] The Barton reaction thus requires in this case a conformational ring mobility, which makes cyclooctyl nitrite well suited for studying the influence of the reaction medium and particularly of a polymeric matrix on the course of this rearrangement. Conversely, it could afford further information about chain segment mobility in polymeric systems.[7,8] It is that aspect that will be considered in the present paper.

Experimental Section

Ultraviolet and infrared spectra were recorded on Perkin-Elmer 124 and 580B spectrophotometers, respectively. NMR spectra were taken on a Varian Associates XL spectrometer. Glass transition temperatures were determined with a Perkin-Elmer Model 2C differential scanning calorimeter (DSC).

Tetrahydrofuran was used in forming the polymer films of PVC and P(VDC-*co*-VC). The other polymers were cast from dichloromethane.

The light intensity values were determined with an IL700 research radiometer fluxmeter (International Light) with a PT1710 no. 1005 detector.

Cyclooctyl nitrite was prepared by reaction of cyclooctanol with nitrosyl chloride.[9] In dichloromethane solution it presents a characteristic nitrite absorption band with λ_{max} 374 nm ($\epsilon_{CH_2Cl_2}$ = 60 L mol^{-1} cm^{-1}). The other, more intense absorption varies with the solvent; e.g., in methylene chloride and in hexane, λ_{max} is equal to 247 nm ($\epsilon_{CH_2Cl_2}$ = 1330 L mol^{-1} cm^{-1}) and 240 nm ($\epsilon_{C_6H_{14}}$ = 1540 L mol^{-1} cm^{-1}), respectively. Most solvents and polymeric matrices interfere, however, with the absorption measurements of this band.

Table I
Quantum Yield of Photolysis of Cyclooctyl Nitrite in Solution[a]

solvent[b]	Φ_N	solvent[c]	Φ_N
dichloromethane	0.56 (0.54)	isopropyl acetate	0.45 (0.44)
diethyl ether	0.67	methanol	0.69 (0.60)
acetonitrile	0.57	ethanol	0.42
cyclohexane	0.50		
n-hexane	0.49		
trichlorotrifluoroethane	0.55		

[a] Values in parentheses correspond to photolysis under an inert atmosphere. [b] Solvents with isosbestic points. [c] Solvents without isosbestic points.

Irradiations were carried out under nitrogen at room temperature using an Osram HB200 high-pressure mercury lamp with an interference filter (λ 367 nm). The photolyses were followed spectrophotometrically in different solvents on the basis of the absorption at 374 nm. The optical densities varied from 0.5 to 1.6 in dichloromethane (30 mg of nitrite in 10 mL of solvent); ketone formation with time was followed by measuring the carbonyl infrared absorption at 1690 cm^{-1}. In trichlorotrifluoroethane the nitroso dimer precipitates during irradiation;[5] it was redissolved in methanol and refluxed for 2 days to form the corresponding 4-oximino-1-cyclooctanol. The oily reaction product was analyzed by IR and NMR. The yield of oxime was determined gravimetrically and by NMR. Polymer films were prepared by casting solutions of 5 wt % polymer and 1 wt % nitrite on a mercury surface. After evaporation of the solvent under an inert atmosphere, the films were dried under vacuum at room temperature. After irradiation the polymer was examined and analyzed by infrared spectrometry (carbonyl absorption) and by UV

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