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Some Photophysical Properties of Electronically Excited Phenyldibenzophosphole in Rigid Polymer Matrices

Tapan Ganguly[†] **and Richard D. Burkhart***

Department of Chemistry, University of Nevada, Reno, Reno, Nevada 89557-0020

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Phenyldibenzophosphole (PDP), present as a dopant in polymer matrices, has been subjected to photoexcitation by 308 nm excimer laser pulses. Both polystyrene (PS) and poly(butyl methacrylate) (PBuMA) have been used as hosts. Luminescence spectra and transient absorption spectra and their respective temporal behavior have been recorded for samples varying in PDP content from 2 to 15% by weight. The time regime from several tens of nanoseconds to seconds was investigated. Phosphorescence decays examined at 15 K yield a lifetime component in the microsecond domain as well as a very long-lived component on the order of seconds. In addition to the phosphorescence spectrum, with origin at 427 nm, a shorter wavelength component with origin near 350 nm is found. In polymer hosts a band at 395 nm is also observed. This latter is assigned to delayed excimer fluorescence while the 350 nm component is delayed monomeric fluorescence. Similarly, an emission at 500 nm is found which grows relative to the main phosphorescence peak at 470 nm with increasing solute concentration. This band is assigned to an excited state van der Waals complex. Transient triplet absorption decays were very well represented by a rate equation for concurrent first- and second-order kinetics. Similar first-order rate constants were found both in PS and PBuMA. The second-order component is believed to be due to triplet−triplet annihilation. Phosphorescence decays yield first-order rate constants in excellent agreement with those obtained by transient absorption. All aspects of the photophysics are strongly influenced by the dramatic non-homogeneity of the solute distribution.

Introduction

The photophysical properties of heteroaromatic molecules have provided both photochemists and photophysicists with a rich field of study. It is true that fused ring aromatic hydrocarbons such as naphthalene, anthracene, and their relatives have traditionally played a major role in understanding the processes of photoexcitation and relaxation. It is also true, however, that electronically excited heteroaromatics are often known to take advantage of relaxation channels to dispose of their excess acquired energy which are unusual by comparison and include processes such as photoredox reactions,[1−4] excimer and exciplex[5] formation, and a variety of photochemistries.[6] In these laboratories a particular interest has developed over the years involving the photophysical properties of the carbazole chromophore,[7] initially because of the rich photophysical activity demonstrated by poly(*N*-vinylcarbazole) (PVCA).[8] The lifetime of the excited singlet state of the carbazolyl chromophore depends to some extent on the local environment but is usually found in the low nanosecond time domain.[9] The triplet, on the other hand, has a very long lifetime near 7 s.[10] Other interesting properties of this chromophore include its propensity to form singlet excimers not only when covalently bonded to a carbon chain backbone as in PVCA but also when present along with a neighboring carbazole in bichromophoric molecules such as 1,3-dicarbazolylpropane.[11] Triplet excimers of the carbazole chromophore are also known to form in solution,[12] in doped polymer films,[13] and also in pure polymer films wherein the carbazolyl unit is covalently bonded to the polymer chain.[14] Since the carbazolyl chromophore has been so valuable as a vehicle to enhance our understanding of certain photophysical processes, it was thought that the simple replacement of the nitrogen atom by phosphorus might also provide important new information of photophysical interest.

The phosphorus analogues of carbazoles, the dibenzophospholes, have scarcely been examined by photophysical methods and for good reason. The alkyl-substituted derivatives such as ethyldibenzophosphole are air sensitive and require special techniques to avoid accidental contamination. Thus typical photophysical experiments can become rather complicated. By contrast, phenyldibenzophosphole (PDP) is a rather robust compound, at least in the solid state at ambient temperature, and so was selected for this investigation.

In earlier work on fluid solutions of PDP,[15] time resolution from a few hundred nanoseconds to several milliseconds was used, showing that the photophysics of PDP has the same dependence upon solvent dielectric constant as carbazolyl; that is, ionic processes predominate in high dielectric media and neutral excited states are the major species in low dielectrics. On the other hand, the lifetime of the PDP triplet, even in frozen matrices at 77 K was found to be on the order of 10 μs, but the apparatus used at that time was not suited for measuring longer time events. It will be shown below that a triplet lifetime on the order of 1.7 s is also observed for frozen solutions of PDP. The phosphorescence spectrum of PDP is nearly identical to that of *N*-ethylcarbazole when recorded under similar conditions.

In the present investigation, our plan is to study the photophysical properties of polystyrene (PS) and poly(butyl methacrylate) (PBuMA) solid films with PDP present as a dopant. One of the motivations for this particular approach is that the film provides a matrix which is rigid over a very large temperature range. Thus, in this investigation, temperature dependent phenomena play a central role. The methacrylate polymer was selected for comparison with PS because it is more polar than PS and might promote solid state photoion formation. In these matrices, any second-order rate processes are necessarily brought about by exciton migration as opposed to bulk transla-

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[†] On leave from the Department of Spectroscopy of Indian Association for the Cultivation of Science, Jadavpur, Calcutta, India.

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tion, which is extremely slow in this medium. The most likely such process is triplet−triplet annihilation, leading to delayed fluorescence. Rigid polymer films are also of interest from a technological standpoint, since they serve as the organic counterpart of semiconductor chips.

In this paper we begin with a general description of the triplet state properties of PDP using both emission and transient absorption spectra as the basis for discussion. Time resolved spectra in the low nanosecond realm are presented as an aid in making spectral assignments. Rates of luminescence decay and of transient absorption decay are also provided, and the majority of these data refer to 15 K, which is the practical lower temperature limit of our cryogenic system. We then provide data on the temperature dependence of triplet state processes found in these films and attempt an interpretation based upon a kinetic scheme which fits the available data.

Experimental Techniques

Purification of Chemicals. Polystyrene (PS) was synthesized by anionic polymerization in an O_2-free N_2 atmosphere using *n*-BuLi as initiator. It was purified by multiple reprecipitations using benzene as solvent and methanol as nonsolvent. Poly(butyl methacrylate) from Aldrich Chemical Co. was purified by multiple reprecipitation using toluene as solvent and methanol as nonsolvent. The methods of synthesis and purification of phenyldibenzophosphole (PDP) were reported earlier.[16] In addition to multiple recrystallization of PDP in a nitrogen atmosphere, the samples used in this work were further treated by vacuum sublimation.

Sample Preparation. Molecularly doped films consisting of PDP in PS or PBuMA were made by using the following procedures: Both the polymer and PDP were dissolved in 3 or 4 mL of toluene. The solution was then placed in a glovebox and purged with O_2-free N_2. Still under N_2, about 80% of the solvent was evaporated off by heating with a hot plate/stirrer. The remaining solution was tranferred dropwise to a preheated quartz disk where the residual solvent evaporated and the molten polymer was allowed to flow out into a film. Another preheated quartz disk was placed over the film and pressed down so that the sample would be sandwiched between the two plates. The sample was then mounted in the cryoscopic system. This consisted of placing the sample in the copper ring sample holder. The copper ring was fixed by means of a threaded connection and indium gasketing to the cryotip assembly. The quartz plates were sandwiched between two pieces of indium foil which have 2 mm × 4 mm slits cut in their centers for entry of the excitation beam and exit of the emission (or entry and exit of a probe beam). These indium foils serve as good thermally conducting gaskets between the copper holder and the quartz plates. The quartz plates with their indium gasketing were mounted in the sample holder and fixed there by a second copper retaining ring secured by several screws placed around the periphery. Special care has to be taken to make very tight connections between quartz, indium, and copper to facilitate thermal conduction. A closed cycle liquid helium system was used (APD Cryogenic model CS-202) which could provide temperatures down to 15 ± 0.2 K.

Spectroscopic Instrumentation. The major components of the optical system consist of a xenon probe lamp (Photon Technology Inc. model 1010), the sample holder, and the monochromator or spectrograph. These three components were arranged in a colinear geometry. The beam coming from the XeCl excimer laser (Questek model 2110) was perpendicular to this axis. When using the cryosystem, the laser beam first encounters a mirror placed directly behind the sample and coated specifically to reflect 308 nm light at an angle of 45°. The reflected beam passes through the sample and then encounters a reflecting mirror situated directly in front of the monochromator slit. This prevents entrance of the excitation beam into the detector system. In the case of transient absorption measurements, the collimated beam from the xenon probe lamp passes through the 45° reflector and the sample before entering the slit of the monochromator. This geometry necessarily entails some loss of probe beam intensity, but the loss is entirely negligible. For spectroscopic work a Princeton Instruments diode array system was employed, and for kinetic decays a Hamamatsu R938 photomultiplier working in conjunction with a LeCroy model 9410 digital oscilloscope was used. A mechanical chopper with an optical pick-off was used to initiate timing sequences for events having a lifetime of 1 ms or less. For longer time measurements a Vincent electronic shutter and controller were used along with a Stanford Instruments Delay Generator. A Princeton Instruments PG-10 or FG-100 pulser was used for triggering, gating, and delay setting. Time resolution from 25 ns to over 1 s is possible with this system. Data readout and interaction with the laboratory computer were provided by a Princeton Instruments ST-120 controller.

Experimental Results

Luminescence Spectra of PDP. Figure 1 contains time resolved delayed luminescence spectra of PDP present at 12% w/w in PBuMA (A) and 1.9% w/w in PS (B). Spectra recorded under similar conditions in PS and PBuMA are essentially identical. Both spectra contain the same features consisting of a shoulder at 370 nm, an emission maximum at 395 nm, a shoulder near 430 nm, a second peak at 470 nm, and an additional structure at 500 nm. Dilute solutions of PDP in frozen methyltetrahydrofuran (MTHF) glasses recorded in earlier work[15] produce a zero−zero phosphorescence band near 430 nm and a λ_{max} at 470 nm. We conclude, therefore, that the extra bands at 370 and 395 nm are related to delayed fluorescence of PDP. These assignments are supported by the fact that the ratios of the 470−370 nm emission peaks increase as the solute concentrations decrease. Furthermore, time resolution of the spectra show that the 370 and 395 nm components decay away much more rapidly than the phosphorescence band.

Exploring these assignments further, luminescence spectra were recorded using delay times on the order of tens of nanoseconds in an attempt to observe prompt luminescence. In Figure 2 are displayed three such spectra: one for a 3×10^{-4} M degassed solution of PDP in MTHF, one for a 12% w/w sample of PDP in PS, and one for a 1.9% w/w sample of PDP in PS. We observe that in MTHF there is a shoulder at 340 nm and a major peak at 365 nm. This spectrum does not possess a third emission feature at 395 nm, which is the major component of the delayed fluorescence band in polymer matrices. This 395 nm emission is, however, observed in the prompt luminescence of the PDP/PS samples, and the 395 nm component is stronger than that at 370 nm with an increase in solute concentration. Since the 395 nm component is observed in both PS and PBuMA; it is not likely due to an impurity in the host material, and since it is not observed in MTHF solution, it is not likely due to an impurity in the PDP. We conclude that it is a genuine manifestation of excited state species in the doped polymer matrices. Since the density of chromophore units is much higher in these matrices than in solution, a reasonable assignment for the 395 nm component is to a singlet excimer.

Removing residual ketonic impurities from polystyrene is known to be extremely difficult,[17] and these residues luminesce

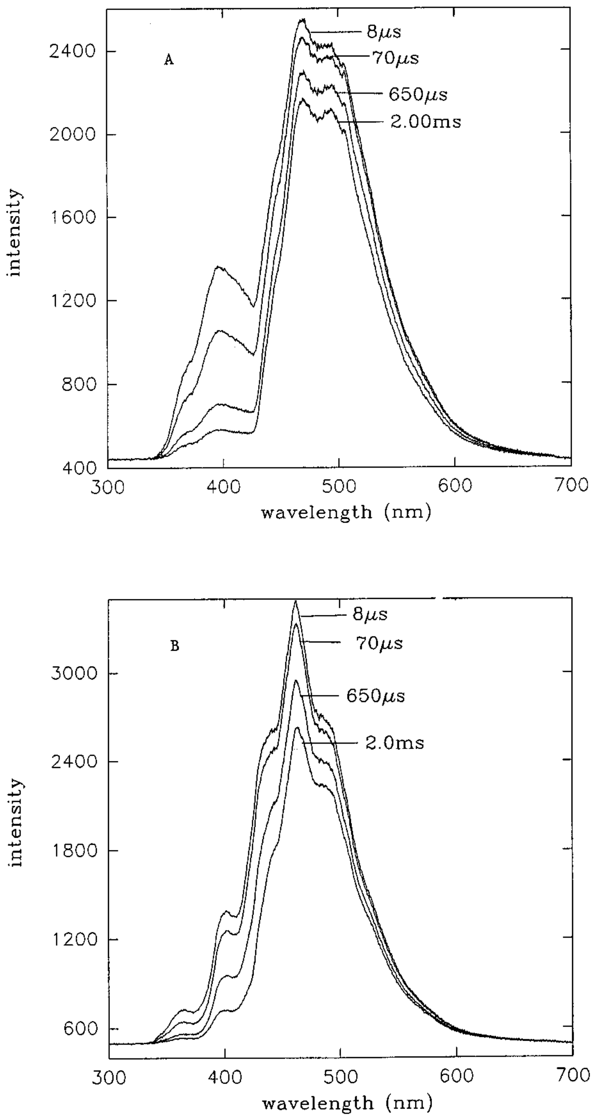

Figure 1. (A) Emission spectra of a film consisting of 12% w/w PDP in PBuMA at 15 K using different delay times and a 1.7 ms gate width. (B) Emission spectra of a 1.9% w/w sample of PDP in PS at 15 K using different delay times at a 1.7 ms gate width.

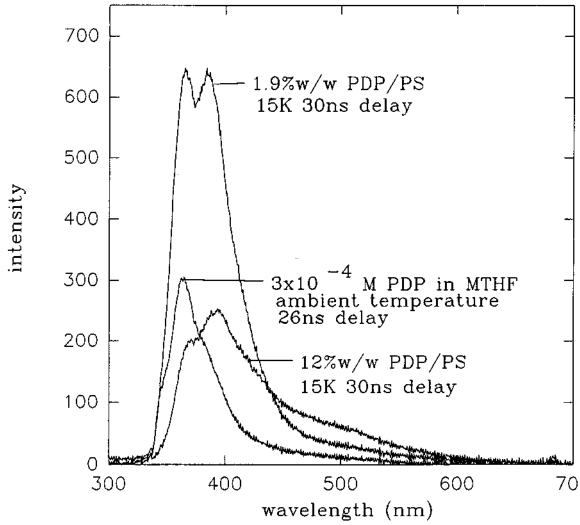

Figure 2. Emission spectra of PDP in different environments time resolved in the nanosecond time domain.

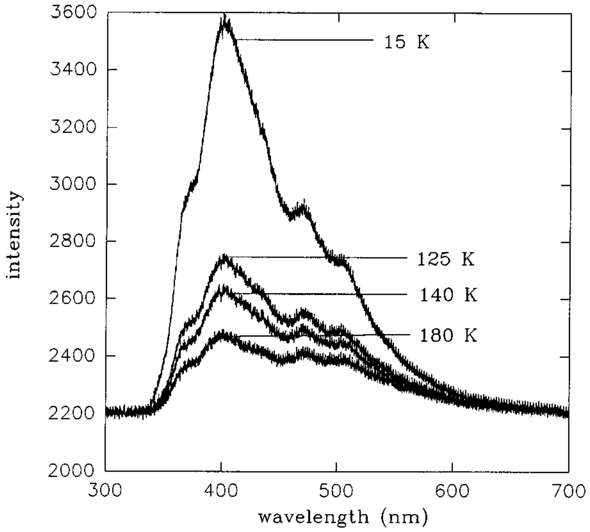

Figure 3. Emission spectra of 12% w/w PDP in PS at various temperatures using a 70 μs gate width and a 1.2 μs delay.

at 15 K with origin near 390 nm and a peak near 420 nm. It must be pointed out that we erroneously characterized such a spectrum as being due to PDP in an earlier publication.[15] Triplet states from these ketonic residues are produced in each excitation pulse, but when PDP is present in as little as 2% w/w, the ketonic triplets are completely quenched. The emission at 395 nm in Figures 1 and 2 was examined carefully because some of its features are similar to this impurity luminescence. We believe the data presented here provide a reasonable basis for assigning this emission in PDP/PS and PDP/PBuMA to a singlet excimer.

Another interesting concentration dependent aspect of Figure 1 involves the ratio I_{500}/I_{470} of the 500 to 470 nm components. This ratio is clearly much larger in the 12% w/w sample. Because of its concentration dependence it is tempting to assign the 500 nm band to an excimer phosphorescence, but additional information associated with its kinetic behavior and thermal characteristics (*vide infra*) suggests an alternative assignment.

At these low temperatures no thermally assisted triplet to singlet excitation (E-type delayed fluorescence) is possible, so it must be inferred that delayed fluorescence occurs by a process of triplet−triplet annihilation (the so-called P-type process). On the other hand, bulk translational motion of PDP is expected to be extremely slow in these rigid matrices, so the annihilative process evidently occurs by triplet exciton migration.[18] A related observation is that the intensity of the phosphorescence band (Figure 1) decreases by almost 20% after a delay time of 2.0 ms. One might conclude from this that the triplet state lifetime is on the order of tens to hundreds of microseconds. It will be shown below, however, that the majority of the triplet population has a lifetime on the order of seconds. Thus, there is a certain fraction of triplets relaxing at a much greater rate than the gross population. Since the delayed fluorescence signal decays away during the same time period as that associated with the fast portion of the triplet decay, it is likely that these short-lived species are lost primarily through T−T annihilation.

Emission spectra recorded between 15 and 180 K are displayed in Figure 3. It is important to note the dramatic alteration of the general appearance of these spectra using different gate widths and delay times. In Figure 3 a 70 μs gate width and 1.2 μs delay are used. This has the effect of emphasizing the delayed fluorescence components compared with the spectra of Figure 1, where a 1.7 ms gate width was used. The primary thermal effect is an overall reduction of intensity with increasing temperature. There is also a decrease in the ratio of delayed fluorescence to phosphorescence intensity from 1.99 at 15 K to 1.50 at 180 K. This may be due to a

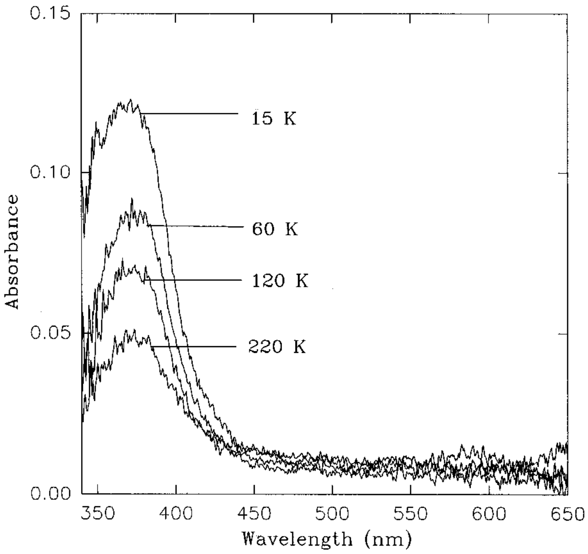

Figure 4. Transient absorption spectra at various temperatures for a sample of 12% w/w PDP in PBuMA using a 0.27 μs delay and a 1.2 μs gate.

faster rate of T−T annihilation at the higher temperature and a consequently smaller triplet population remaining at the delay time used to record the spectra (1.2 μs). It is worth noting that the ratios of the 470 to 500 nm peaks remain essentially constant with a change in temperature.

The delayed luminescence spectrum of pure crystalline PDP was also recorded by placing the powdered material between quartz plates and cooling to 15 K in the usual way. The spectrum consists of a shoulder at 370 nm and an intensity maximum near 390 nm. In fact the emission is similar to the prompt fluorescence observed for PDP in PS host, as seen in Figure 2. On the basis of the assignments given above, we conclude that this emission is a mixture of monomeric and excimeric delayed fluorescence. It is noteworthy that no phosphorescence emission is observed for this crystalline sample.

Transient Absorption Spectra of PDP in Polymer Matrices. Transient absorption spectra of PDP in PS and in PBuMA have been recorded using a variety of conditions. Typical spectra are displayed in Figure 4. Invariably a peak near 370 nm is found which, in earlier work,[15] had been assigned to the PDP triplet. While the temperature is increased from 15 to 220 K, the peak absorbance decreases monotonically. Furthermore, no evidence of absorbances from species other than the PDP triplet are observed either by changing delay time or by increasing temperature. For this reason, decay measurements of the trnasient absorption at 370 nm are thought to yield a direct and unambiguous determination of triplet decay kinetics.

Transient Absorption Decay Kinetics. The best fit to observed transient absorption decays is found for a kinetic equation based upon concurrent first- and second-order processes. The integrated form of this rate equation is

$$A = k_1A_0 \exp(-k_1t)/k_1 + A_0k_2(1 - \exp(-k_1t)) \qquad (1)$$

where A represents absorbance, A_0 is absorbance at zero time, and k_1 and k_2 are the first- and second-order rate constants, respectively. This equation reproduces the experimental data very well not only at the various temperatures used but also in both PS and PBuMA. Attempts to fit these data either to single or to double exponential decays yielded unacceptable results. Experiments were carried out at temperatures ranging from 15 to 200 K, and the results are summarized in Table 1. As expected, the best fits are found at 15 K, and the worst, at 200 K. A typical example for an experiment at 125 K is displayed in Figure 5.

TABLE 1: Rate Constants from Transient Absorption Decays of PDP in PS and PBuMA Recorded at Various Temperatures Using a Rate Equation for Concurrent First- and Second-Order Decay[a]

host matrix	temp (K)	k_1 (s^{-1})	k_2 (A^{-1} s^{-1})[b]
PS	15	0.59	28.2
PS	100	0.74	42.5
PS	140	1.2	78.2
PS	160	2.4	203
PS	180	3.0	301
PBuMA	15	0.61	31.9
PBuMA	125	0.93	33.5
PBuMA	150	1.2	42.3
PBuMA	175	1.7	68.2
PBuMA	200	2.9	153

[a] Uncertainties in these rate constants are no greater than ±10%. [b] A = absorbance units; the molar absorptivity of the PDP triplet is unknown.

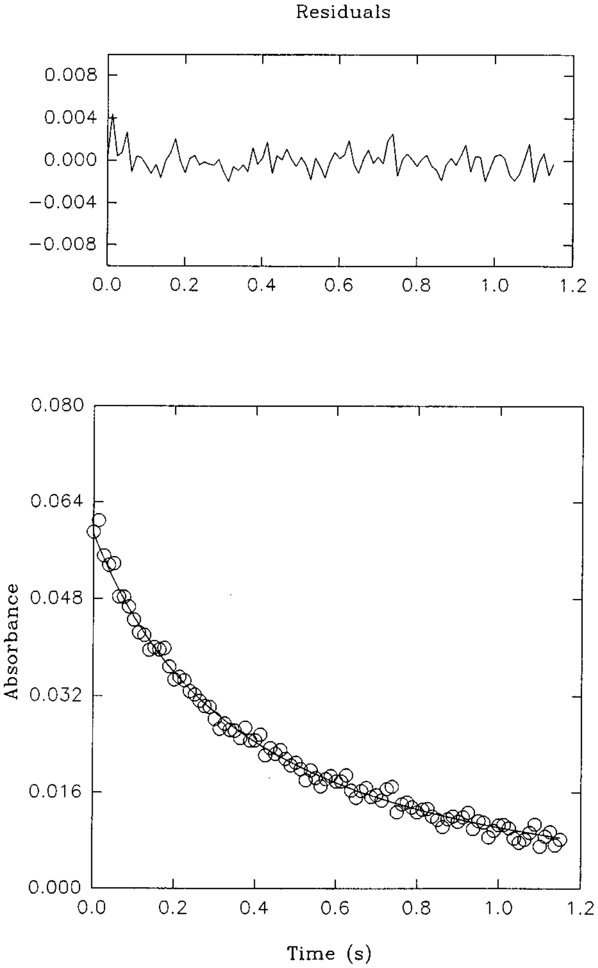

Figure 5. Transient absorption decay for a 12% w/w sample of PDP in PBuMA at 125 K. Only one in fifty data points is shown for clarity; the solid line is the best fit for a concurrent first- and second-order decay.

It is worth noting that, in general, k_1 values are quite comparable in the two different polymer hosts but k_2 values in polystyrene tend to be somewhat larger than those in PBuMA. In particular, it may be observed that k_1 values at 15 K are the same, within experimental error, for the two different hosts. It was expected that activation energies for the first- and second-order processes might be obtained; however, it may be noted from the data that the temperature dependences are nearly

TABLE 2: Rate Constants for Luminescence Decay at 470 and 550 nm of PDP in Polystyrene Hosts[a]

temp (K)	k_1[b] (s^{-1}) 550 nm	k_1[b] (s^{-1}) 470 nm
15	0.63	0.74
125	1.2	0.97
160	1.5	1.5
180	2.5	2.1
200	3.6	3.1

[a] The k_1 vaules are results of fitting data to eq 2. [b] Estimated error is ±10%.

nonexistent between 15 and 125 K. At higher temperatures the Arrhenius graphs exhibit marked curvature, so activation energies could not be obtained. Another interesting point has to do with the relative magnitudes of first- and second-order processes. The fractional contribution of the second-order component is still rather large even at the tail of the decay. For example, when the absorbance has reached 0.005, the second-order process is still making a contribution of 20% to the rate of triplet disappearance.

Luminescence Decay Kinetics. Since the transient absorption decays indicate that first- and second-order processes are occurring concurrently, it is expected that no simple rate equation will be able to account for the luminescence decays. Since a pure phosphorescence signal intensity is directly proportional to the triplet concentration, an equation with a form similar to that used for transient absorption kinetics should provide an acceptable fit for such a decay. The equation used here was

$$I = aA + b \tag{2}$$

where A is the optical absorbance given by eq 1, a converts absorbance into luminescence intensity, b is the photomultiplier signal in the absence of luminescence, and I is the luminescence intensity. In the present case the delayed luminescence consists of at least three different components which overlap to some extent. Decay data were obtained at 470 nm, which should consist primarily of the phosphorescence signal, at 370 nm, which corresponds to the delayed fluorescence component, and at 550 nm, in an attempt to emphasize the excimer-like phosphorescence signal. Even though eq 2 turned out to provide acceptable fits to the 470 and 550 nm data, we could find no reasonable rate equation to fit the delayed fluorescence decay at 370 nm and can only say that the delayed fluorescence emission decays much faster than the phosphorescence.

In Table 2 is a summary of first-order rate constants obtained at different temperatures using eq 2. Even though this equation provides reliable values for k_1, the values returned for k_2 are not comparable to those found using transient absorption because the intensity units are in millivolts whereas those of Table 1 refer to optical absorbance. Similarly, the values found for A_0, the zero time absorbance, are not in comparable units.

These data show that the 550 and 470 nm components decay at the same rate, within experimental error, over the entire temperature range investigated. Additionally, the k_1 values listed in Table 1 agree with those found for luminescence decay at comparable temperatures.

Discussion

Distinctive Features of PDP. The experimental data provide convincing evidence that the photoexcited species present in these molecularly doped films include triplet states, singlet states, and excimeric singlets. A fourth species, to be discussed below, responsible for the 500 nm luminescence, is also present, and it will be suggested that this species is best characterized as an excited state van der Waals complex. Although it was thought that radical ions might play a role in the photophysics of these films, no evidence for charged species is found. These results bear a distinct similarity to observations made on films containing N-ethylcarbazole and those containing various amino groups.[5] In those instances, however, it was clear that the phosphorescence emission originated not only from monomeric but also from excimeric triplets. In the present case it is doubtful that a truly excimeric triplet is present.

In films of *N*-ethylcarbazole in polystyrene the phosphorescence emission is totally nonexcimeric at 15 K and totally excimeric at 77 K; therefore, it was thought that achieving a relative orientation of chromophore pairs suitable for excimer formation required a certain activation energy. In the case of PDP, excimer-like emission at 500 nm is found even at 15 K, so the physical process associated with this emission evidently occurs with little or no activation barrier. The subsequent discussion will be aided by setting out a reaction sequence which can account for these processes:

excitation $$^1M_0 + h\nu \rightarrow {}^1M^* \tag{3}$$

intersystem crossing $$^1M^* \rightarrow {}^3M^* \tag{4}$$

singlet trapping $$^1M^* + {}^1D_0 \rightleftarrows {}^1M_0 + {}^1D^* \tag{5}$$

triplet trapping $$^3M^* + {}^1E_0 \rightleftarrows {}^1M_0 + {}^3E^* \tag{6}$$

monomer singlet relaxation
$$^1M^* \rightarrow {}^1M_0 + h\nu(\text{fluorescence})/\text{heat} \tag{7}$$

monomer triplet relaxation
$$^3M^* \rightarrow {}^1M_0 + h\nu(\text{phosphorescence})/\text{heat} \tag{8}$$

excimer singlet relaxation
$$^1D^* \rightarrow {}^1D_0 + h\nu(\text{excimer fluorescence})/\text{heat} \tag{9}$$

vdW triplet relaxation
$$^3E^* \rightarrow {}^1E_0 + h\nu(\text{vdW phosphorescence})/\text{heat} \tag{10}$$

Since, in addition to these processes, it is found that triplets disappear by a second-order decay which occurs concurrent with the first-order decay, one additional step must be added:

triplet–triplet annihilation $$2\,{}^3M^* \rightarrow {}^1M^* + {}^1M_0 \tag{11}$$

In these equations, M represents the phenyldibenzophospholyl chromophore, $^1D_0$ is a ground state chromophore pair oriented properly for singlet excimer formation, and $^1E_0$ is a ground state chromophore pair oriented properly for van der Waals complex formation. Excited state species are denoted by an asterisk.

Effects of Variable Temperature. The temperature dependence of rate constants obtained for first- and second-order triplet disappearance as displayed in Table 1 does not yield linear graphs when plotted as log k versus $1/T$. Bässler and coworkers,[19] in an extended series of investigations, concluded that a Gaussian distribution of inhomogeneous states is often encountered in amorphous systems. In these cases, graphs of log k versus $1/T^2$ were found to be linear both for migration of charged species and for triplet exciton migration. Since triplet migration is thought to involve electron exchange, it is expected that charge migration, which involves electron transfer, should have a similar temperature dependence. When such an analysis was applied to the data for PDP/PS or PDP/PBuMA, distinctly nonlinear results were obtained.

An alternative model for charge/triplet migration assumes that excited states reside at isoenergetic sites and that the temperature dependence for the migration originates in local reorganization of the molecules which comprise the environment of the chromophores involved.[20] The predicted temperature dependence for such a model is, however, Arrhenius-like, which we find incompatible with the present data.

A third mechanism to account for the temperature dependence of these photophysical processes involves thermal activation of acoustic vibrations of the host polymer chains.[21] In this model the interchromophore distance is modulated by the chain vibrational motion. Thus, chromophores which may, at one instant in time, be too distant from a partner to transfer an exciton will, at a later time, experience a sufficiently close encounter for transfer to occur. Temperature dependence of exciton migration is, therefore, associated with an increasing chain vibrational amplitude as the temperature rises. This model would also be expected to give rise to an Arrhenius type of temperature dependence, but superimposed is what appears to be a marked inhomogeneity in solute distribution.

Effects of Inhomogeneous Solute Distribution. The time-resolved spectral data of Figure 1 suggest that regions exist in the host polymer having significantly elevated chromophore populations. The fast (fractional millisecond time scale) portion of the phosphorescence decay is noticeably connected with a similar time scale for delayed fluorescence decay. It was suggested above that about 20% of the chromophore population may be found in high population density regions. For these species, the rate of T−T annihilation is expected to be temperature independent using the acoustic vibration model, since exciton migration need not be assisted by polymer chain vibrational motion. For chromophores which exist in less populated regions, however, temperature dependent exciton migration is expected. Thus, due to the inhomogeneity of chromophore distribution, non-Arrhenius temperature dependence results.

Delayed Fluorescence Kinetics. As mentioned above, delayed fluorescence decays resisted our attempts to model them by any standard kinetic equations. For an annhilative process one expects the delayed fluorescence intensity, I_{df}, to be proportional to the square of the triplet concentration or to the optical absorbance due to triplets. An experiment of this sort was attempted by comparing decay curves for delayed fluorescence with those for a transient absorption decay. Graphs of I_{df} versus A^n could only be fit to a linear relation over short segments of the decay, and at times less than 100 ms only rather large exponents on the order of 4 gave even an approximate fit.

At times greater than 100 ms and at 15 K the df signal is very near the lower limit of detectability with our equipment. This time period is less than one-tenth of the triplet lifetime at this temperature. Evidently the delayed fluorescence emission for PDP is rather inefficient, since it reaches the nondetectability level long before the phosphorescence emission and long before T−T annihilation has become negligible. We note also that at 100 ms and 15 K triplet−triplet annihilation still comprises a major fraction of the total rate of triplet decay. Again, this sort of behavior suggests a dramatic nonhomogeneity in the distribution of dopant molecules in the matrix. In fact, it is convenient to think of the kinetics as consisting of two distinct time regimes, one involving the time delay from zero to 100 ms and consisting of events which occur in high population regions and the second at longer times where conventional kinetics occur and where second-order processes involve triplet exciton migration.

Excited State van der Waals Complex. Although the emission at 500 nm could be due to an impurity, the assignment to an excited state van der Waals complex is more logical. If this signal were due to an impurity, one would expect to see the emission in frozen solutions of PDP in MTHF, but we do not. Furthermore, the ratio of the 500 to 470 nm signal intensities grows as solute concentration increases. This implies a supralinear dependence of the species emitting at 500 nm upon solute concentration. An impurity would be expected to have a linear dependence. This emission has characteristics which distinguish it from triplet excimers observed previously in polymer films doped with nitrogen-containing chromophores such as N-alkylcarbazoles and aromatic amines. We have already mentioned the fact that it is present even at 15 K, but in addition, we find its rate of luminescence decay to be essentially identical to that of the monomeric phosphorescence. This implies that the trapping−detrapping equilibrium (eq 6) occurs on a time scale that is fast compared with that for relaxation to the ground state. This conclusion complements the earlier observation that complex formation occurs with an exceedingly small energy barrier and suggests that the barrier for dissociation is likewise very small. It is expected, of course, that the larger atomic size of phosphorus compared with nitrogen would result in phospholes being more polarizable than carbazoles and thus more susceptible to van der Waals interaction. Probably related to these observations is the fact that metal complexes containing the PDP ligand form in a *cis* isomeric structure even though their steric bulk would suggest that the *trans* isomer would be more stable thermodynamically. X-ray crystallography of these complexes shows that the PDP rings are coplanar with an interplanar spacing of 3.3−3.4 Å. This may be compared with the sum of carbon van der Waals radii, which is also 3.3−3.4 Å.[22]

Lim[23] suggested some time ago that triplet excimers derive a part of their stabilization from van der Waals forces and a part from electrostatic interaction. In the case of PDP the van der Waals component may be especially significant due to the presence of a heavy atom. Whether or not the triplet excited state complex of PDP should be characterized as a triplet excimer or as an excited state van der Waals dimer is, perhaps, debatable, but we prefer the latter description due to its evident exceedingly weak bonding.

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