Triplet Photophysical Properties of Poly[[4-(*N*,*N*-diphenylamino)phenyl]methyl methacrylate]

Richard D. Burkhart* and Dilip K. Chakraborty

Department of Chemistry, University of Nevada—Reno, Reno, Nevada 89557

Yasuhiko Shirota

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan

Received July 9, 1990; Revised Manuscript Received September 25, 1990

ABSTRACT: The triplet-state properties of the subject polymer, poly[[4-(*N*,*N*-diphenylamino)phenyl]methyl methacrylate] (PDAPM), have been examined in rigid solutions from 77 to 298 K. Solid films of the polymer have been studied in the temperature range from 8 K to ambient. In rigid solutions the triplet emission spectrum consists of a delayed fluorescence band and a phosphorescence band with its origin at 420 nm. In solid films at 8 K, the origin of the phosphorescence band is found at 426 nm and the spectrum is nonexcimeric in character. This nonexcimeric phosphorescence spectrum is gradually replaced by a band at 485 nm with rising temperature from 8 to near 60 K. The 485-nm band is thought to be an excimerlike phosphorescence. Its formation requires an activation energy of 5.1 ± 0.5 kJ/mol. The activation energy found for excimer dissociation implies that the triplet excimer and the nonexcimer triplets in the solid state are nearly isoenergetic. An additional band at 560 nm is found in spectra of solid films and rigid solutions from 8 K to ambient and is also found in concentrated solutions of the monomeric model compound. The species emitting at 560 nm is most likely formed by sensitization, and its supralinear dependence upon excitation intensity suggests it is senitized by mobile triplet excitons. The delayed fluorescence (DF) intensity depends upon the square of the excitation intensity and evidently arises by an annihilative mechanism.

Introduction

Investigations of the triplet-state properties of the triphenylamine chromophore have a long history. Henry and Kasha[1] examined the triplet–triplet absorption spectrum in 1967, Alfimov and co-workers[2] investigated the higher triplet states in 1971, and photochemistry leading to the production of carbazole has been the subject of several studies.[3] A polymer containing the triphenylamine chromophore as the pendant group, poly[[4-(*N*,*N*-diphenylamino)phenyl]methyl methacrylate] (PDAPM), is known to be a photoconductor,[4] and therefore its photophysical properties are a matter of interest.

From molecular models it is clear that a great deal of steric crowding should be expected in PDAPM. Furthermore, as a result of the pyramidal configuration of the amine group, a sandwich type of excimer, typical of other singlet excimers, is not expected to form and, in fact, no excimeric fluorescence is found.[4] The quantum yield for fluorescence in the polymeric system is significantly smaller than that for the monomeric model compound, perhaps as a result of unusually efficient singlet–singlet annihilation as has been found for other vinyl aromatic polymers.[5,6]

Even though the structure of the pendant chromophores may not be suitable for singlet excimer formation, the geometrical requirements for triplet excimer formation are thought to be somewhat different from those for singlets,[7] and so the possibility still exists that triplet excimer formation may occur. Experience with other polymeric systems suggests that the best opportunity for observing triplet excimers is in the examination of solid films. Thus, it was planned to carry out a general photophysical investigation of this polymer and to place an emphasis on the solid-state properties.

Of special interest is the effect of temperature on triplet excimer formation and dissociation. Recently it has been discovered that a small activation energy is associated with the formation of triplet excimers in solid films of poly(*N*-vinylcarbazole).[8] The dissociation of these species also requires significant thermal input.[9] For these reasons it has become evident that any characterization of triplet-state properties of solid polymers requires an examination of their temperature dependence.

An initial investigation of the triplet-state properties of this polymer indicated only a phosphorescence band with an origin at 420 nm and a lifetime, in a dilute rigid solution at 77 K, of 0.55 ± 0.02 s. A solid film of the polymer was also examined and was found to emit a phosphorescence signal, possibly excimeric in origin, having a maximum intensity at 485 nm. These initial experiments utilized delay times between excitation and signal collection on the order of 10 ms. When smaller delay times were used with PDAPM, new emission signals were observed and a much more involved pattern of triplet photophysical events was uncovered. In what follows, a description and interpretation of these events is given with particular emphasis on the possibility of triplet excimer formation and dissociation.

Experimental Section

The corresponding monomer of the PDAPM polymer was prepared starting from triphenylamine according to the literature.[4] The monomer was polymerized in benzene solution with AIBN as an initiator at 60 °C using 1 M monomer and 1×10^{-2} M initiator. The polymer was purified by repeated reprecipitation from THF–*n*-hexane. The number-average molecular weight was determined to be 114 000, and the weight-average molecular weight was 514 000.

The monomeric model compound, [4-(*N*,*N*-diphenylamino)phenyl]methyl isobutyrate, was prepared by the reaction of isobutylyl chloride with 4-(*N*,*N*-diphenylamino)benzyl alcohol. This alcohol was prepared from triphenylamine in THF in the presence of triethylamine and was recrystallized from benzene, mp 78–79 °C. It was identified by IR, mass spectra, and elemental analysis. Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.94; H, 6.73; N, 4.06. Found: C, 80.15; H, 6.72; N, 3.77.

The purification of 2-methyltetrahydrofuran (MTHF) involved passing the solvent through an activated alumina column followed by distillation from lithium aluminum hydride. Benzene was purified by refluxing over concentrated H_2SO_4 followed by washing with dilute base and distilled water. It was then dried over anhydrous Na_2SO_4 and was fractionally distilled.

Polymer film samples were prepared by casting on quartz plates from benzene solution. After air drying for a few hours, the films were placed in a vacuum oven at 100 °C for 72 h. The samples were removed from the oven only after the oven temperature had returned to ambient. Solutions of PDAPM in MTHF were studied by using cylindrical cells having a 1-mm optical path length. The cells were attached to a ground-glass joint, which could be connected to the vacuum system for degassing. The solution was degassed by freezing in liquid nitrogen and pumping out the residual gases. Only two freeze–pump–thaw cycles were used since the cells often cracked if more cycles were used. After evacuation the cell was sealed off by using a hand torch. The 1-mm cells were used for experiments at 77 K. Some luminescence experiments at 77 K were carried out in 4-mm-diameter quartz tubes. These samples were simply immersed in liquid nitrogen using a quartz-walled optical Dewar flask.

For experiments at ambient temperature, cells were used having an optical path length of 10 mm. For these samples, a reservoir and a ground-glass joint were attached to the cell in a T-configuration. The solution was placed in the reservoir, and after attachment of the assembly to the vacuum system degassing was carried out by using multiple freeze–pump–thaw cycles. The cell and reservoir, which are at right angles, were then sealed off using a hand torch. After thawing, the solution was tipped into the cell.

All of the photophysical experiments were carried out by using a spectroscopic system constructed in the laboratory and described in earlier publications. The major features of the system include a laser excitation source, a cryotip system for holding samples at various temperatures from 8 K to ambient, a Spex monochromator for detection of emission signals, and a Nicolet 12/70 signal averager to record signals and transmit them on to various computer systems for analysis. Some of the spectral data were obtained by using a Hitachi Model 850 fluorescence spectrometer.

It was learned very early in this investigation that discoloration of the samples occurred after exposure to the 50–100 mJ pulses at 308 nm from the XeCl excimer laser. All subsequent experiments were conducted by using nitrogen laser excitation at 337 nm and having 1–5 mJ/pulse. Although 337 nm is on the rising edge of the PDAPM absorption band, there is still sufficient light absorption at this wavelength to obtain reasonable luminescence signals. No sample discoloration was observed under these conditions. Further tests were conducted to determine whether or not photochemical processes might be competing with observed photophysical events, and these will be described in more detail below.

Experimental Results

Figure 1a provides an illustration of the time dependence of the various triplet emission signals from rigid MTHF solutions of PDAPM at 77 K. Three distinct spectral regions may be observed corresponding to (1) delayed fluorescence (DF) from 350 to 400 nm, (2) phosphorescence that may be associated with an isolated triphenylamine chromophore from 420 to 480 nm, and (3) a long-wavelength phosphorescence band centered at 560 nm. In Figure 1b there is displayed a delayed luminescence spectrum of [4-(*N*,*N*-diphenylamino)phenyl]methyl isobutyrate (DAPB), which is the monomeric analogue of PDAPM. The spectrum was recorded by using MTHF as solvent at a concentration of 1.1×10^{-3} M and at 77 K. The phosphorescence emission at 415 nm is clearly seen here, but the band at 560 nm, which is prominent in the polymer spectrum, is missing. It is worth noting that the peak position of the zero–zero phosphorescence band for the monomeric model is at 415 nm, whereas that for the polymer is at 420 nm within the precision of these measurements. Small red shifts of this sort are commonly observed for polymers and their monomeric analogues. A fluorescence spectrum of the DAPB was also recorded in MTHF at ambient temperature, clearly showing an unstructured band emitting from 345 to 400 nm.

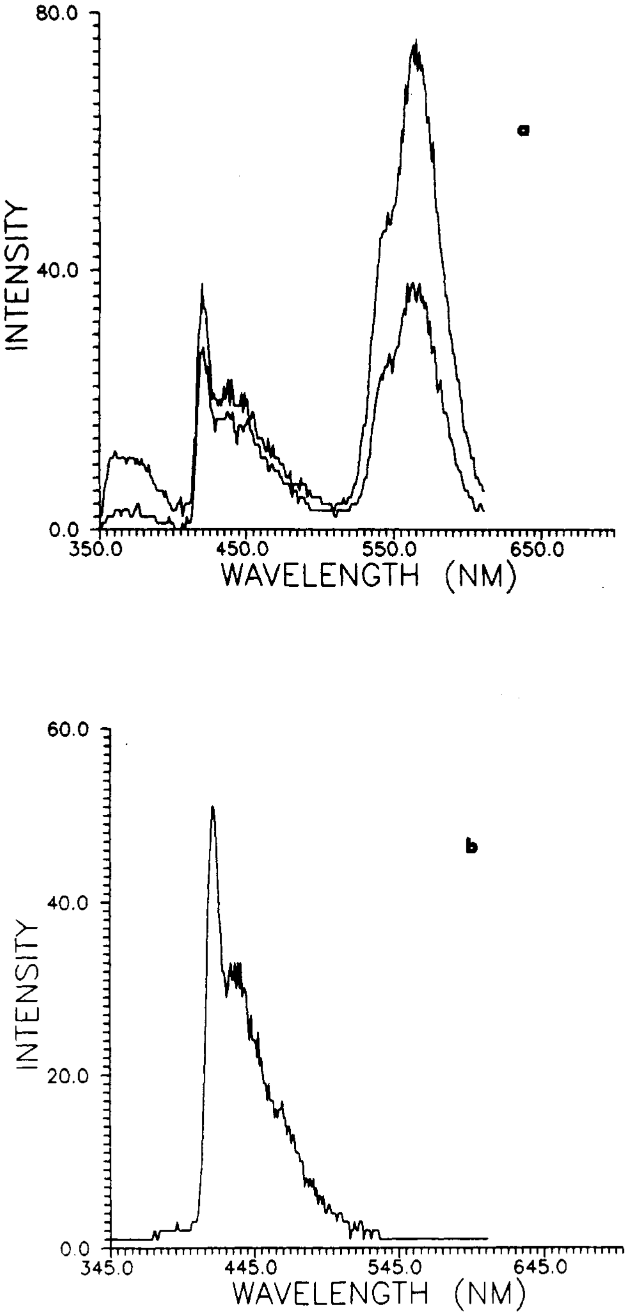

Figure 1. (a) Phosphorescence spectrum of PDAPM in MTHF rigid glass at 77 K: upper curve, at 1-ms delay; lower curve, at 5-ms delay. (b) Phosphorescence spectrum of 1.1×10^{-3} M DAPB in MTHF rigid glass at 77 K.

The DF emission from the polymer is assigned on the basis of its appearance at a wavelength range corresponding to that of prompt fluorescence from the polymer and from the monomeric analogue. The nature of the species responsible for the 560-nm emission is uncertain, and hypotheses regarding its identity will be discussed below. It was of interest, however, to investigate the delayed luminescence properties of the monomeric model at a large chromophore concentration similar to the local chromophore concentration in the polymer coil. Figure 2 gives the results of such an experiment where the concentration was approximately 2 M and the spectrum was recorded at 77 K using MTHF as solvent. Here it was surprising to find that the signal at 560 nm is very strong, indeed indicating that some type of interchromophore interaction may be necessary in order to form the species responsible for this emission. It was also found that the 560-nm signal

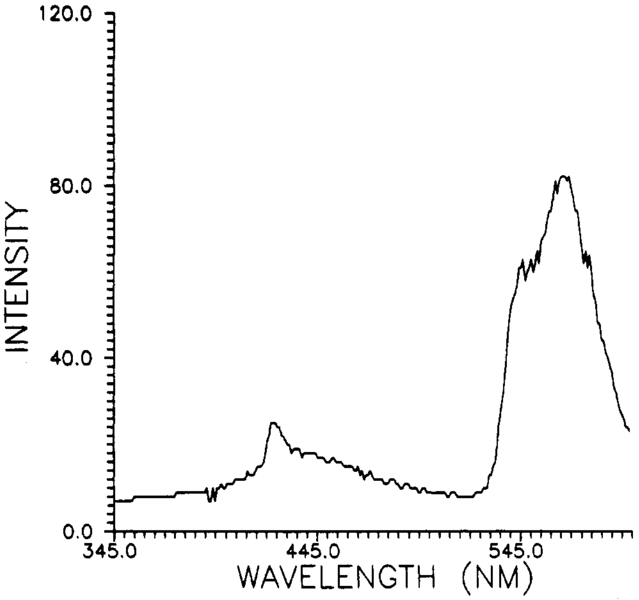

Figure 2. Phosphorescence spectrum of a 2 M solution of DAPB in MTHF rigid glass at 77 K.

could be obtained by preirradiation of a dilute solution of DAPB for 30 min using 300-nm light from the fluorescence spectrometer. The indication is that this band may be associated with some type of photochemical transformation.

When the delayed luminescence of the polymer is viewed in rigid solution at 77 K using delay times longer than about 10 ms, only the monomeric phoshorescence signal remains. The lifetime of this signal was determined from plots of log (intensity) versus time, which were linear over several decades and yielded a lifetime of 0.55 s.

The lifetimes of the DF signal and of the emission at 560 nm were much shorter but still yielded decay curves indicating single-exponential behavior. In fact, the lifetimes were essentially the same for both components and were found to be 12 ms. When screen filters were used to attenuate the excitation beam, the resulting changes in phosphorescence intensity at 420 nm were found to vary linearly with excitation intensity. In three separate experiments the slopes of ln I(420 nm) vs ln (I_{ex}) graphs were 0.97, 0.96, and 0.95, respectively. On the other hand, the DF intensity obeyed essentially a square law relationship. This is illustrated in Figure 3a where a graph of the log of the phosphorescence intensity (at 420 nm) versus the log of the DF intensity is presented. The experimentally determined slope is 2.0. A similar experiment was carried out in which the emission intensity at 560 nm was compared with that at 420 nm using various amounts of attenuation of the excitation beam. In this case the log–log plot, presented in Figure 3b, yielded an average slope of 1.30 with an average deviation of 0.03 in three separate determinations. A similar experiment was carried out by using a solid polymer film and, in this case, the intensity of the 560-nm signal varied linearly with excitation intensity.

Time-resolved delayed emission spectra of a solid film of PDAPM are presented in Figure 4. In these spectra, recorded at 77 K, one notes, at all delay times, an emission signal centered at 485 nm, which is not seen in rigid solutions. Although the resolution obtainable is rather poor, there is also a strong band observable in the range between 350 and 450 nm at the shortest delay times used. It will also be noted that the phosphorescence band at 560 nm is still prominently observed at the smaller delay times. As the delay time between excitation and emission is increased from 0.5 to 2 ms, the 485-nm band emerges as the one having the longest lifetime. At 10 ms after the excitation pulse, only a hint of the 560-nm component is seen and the 485-nm band is essentially all that remains.

In the solid film spectra the delayed fluorescence band between 350 and 450 nm is not well-resolved and strongly overlaps with the 485-nm band. It appears to have a maximum intensity near 440 nm and lacks structure. Its character is, therefore, very excimerlike compared to the delayed fluorescence component from rigid solutions of the polymer at 77 K.

Additional insight involving the delayed luminescence of the solid film is provided by the spectra of Figure 5 recorded at a temperature of 8 K. The remarkable feature of these spectra is that the 485-nm band has been replaced by a phosphorescence signal having the same structural components as those found at 77 K in rigid solutions. The position of the zero–zero band of this structured emission is at 426 nm, that is, slightly to the red of the zero–zero band found in rigid solutions. The spectrum recorded by using the longer delay time suggests that, at 8 K, the DF and 560-nm components are shorter lived than the 426-nm signal, which is also the case for rigid solutions.

The effect of temperature on the character of the phosphorescence band is summarized in Figure 6. These spectra were recorded by using a delay time of 50 ms in order to isolate the phosphorescence band. The decrease in intensity of the zero–zero band with rising temperature is clearly evident along with an overall shift in the center of gravity to the red. The characteristics observed are completely reversible so that the structured spectrum is again recovered upon recooling the sample below the transition temperature. The long time component of the phosphorescence decay measured at 426 nm was force fit to an exponential over this same temperature range, and the resulting Arrhenius graph is given in Figure 7a. The phosphorescence lifetime seems to increase slightly from 20 K to about 54 K at which point there is a sharp decrease that persists to the highest temperature at which measurements could be made. Behavior similar to this has recently been observed for solid films of poly(*N*-vinylcarbazole).[8] In this case, the slope of the steep portion of the curve yields an activation energy of 5.1 ± 0.5 kJ/mol. Similar experiments were conducted monitoring the decay of the 485-nm phosphorescence band between 63 and 112 K. The results are shown in Figure 7b. In this case, there is a discontinuity at 76 K and the slope yields an activation energy of 4.6 ± 0.5 kJ/mol.

The effect of varying the temperature on the total delayed luminescence spectrum in the range between 8 K and ambient temperature is illustrated in Figure 8. In these spectra a delay time of 0.1 ms was used between excitation and emission. The 560-nm band is prominent at all temperatures, but its intensity relative to the delayed fluorescence component decreases with rising temperature. In fact, the delayed fluorescence band, although somewhat red-shifted at the highest temperatures, becomes the most prominent emission at 298 K. In all of the solid film spectra the DF component is red-shifted enough so that its emission strongly overlaps with that of the longer wavelength band at 485 nm. The phosphorescence at 426 nm has essentially disappeared at 77 K and is completely overshadowed by the DF band and the 485-nm band at more elevated temperatures.

Initially a XeCl excimer laser (308 nm) was used as the excitation source for these experiments. It soon became apparent, however, that some type of photochemical process was taking place upon extended exposure to this pulsed excitation source since the solutions eventually became light yellow in color. It is known that triphenylamine reacts photochemically to produce *N*-phenylcar-

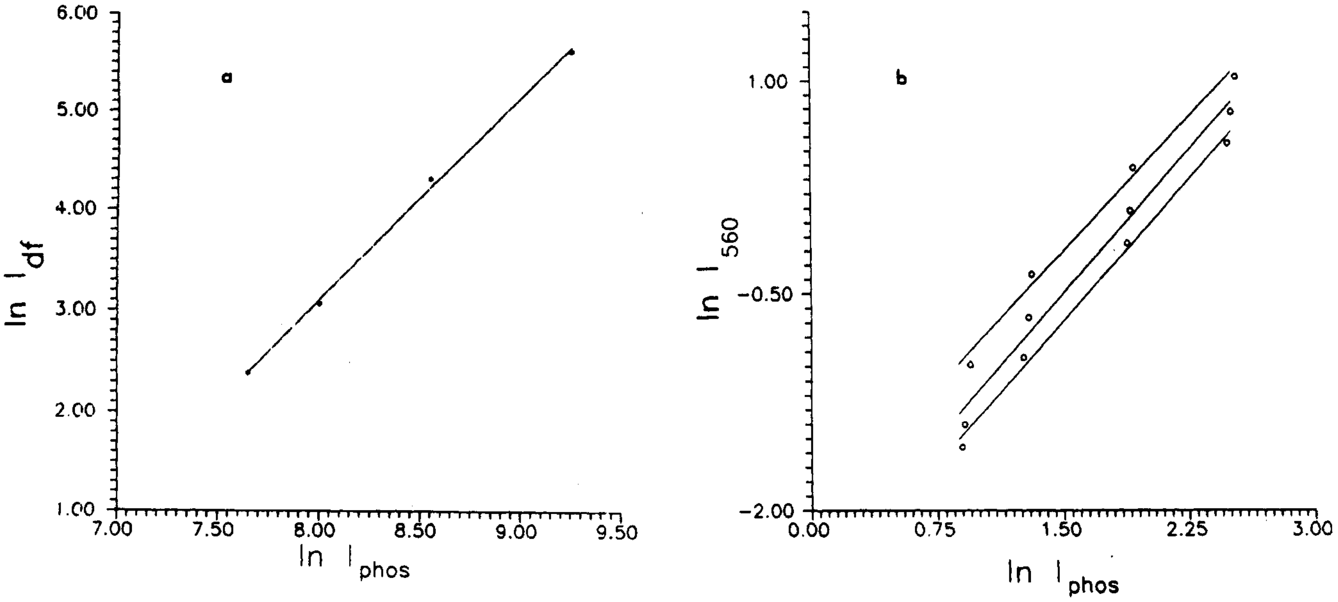

Figure 3. (a) log-log plot of phosphorescence intensity vs delayed fluorescence intensity. Least-squares slope = 2.03. (b) log-log plot of phosphorescence intensities at 420 nm vs 560 nm at various delay times after excitation. Delay times are 1.1 ms (upper), 1.6 ms (middle), 2.1 ms (lower). Least-squares slopes are 1.3.

bazole upon UV exposure in air. It has recently been shown by one of us[10] that PDAPM also reacts photochemically in air, producing *N*-phenylcarbazolyl groups on the chain backbone. All of the experiments described above in this work were carried out under oxygen-free conditions. The solutions were sealed under vacuum, and the solid films were mounted on a cryotip assembly and evacuated in a vacuum-tight shroud during the photophysical measurements. Furthermore, they were all carried out by using excitation from a nitrogen laser at 337 nm where the molar absorptivity of the chromophore is much smaller than at 308 nm. The energy per pulse from the nitrogen laser is about 1% that of the excimer laser. The net result is that using nitrogen laser excitation no color change of the test solutions or films could be detected during these experiments. As a further test, a solution of PDAPM was subjected to pulsed nitrogen laser excitation for 2 h at room temperature before recording the triplet emission spectrum at 77 K. The resulting spectrum was essentially identical with that of a freshly prepared solution. In spite of these precautions, a small amount of photochemical reaction may be occurring. This is evidenced by the consistent appearance of the emission band at 560 nm, which is thought to arise from a photoproduct.

Discussion

A. Photophysical Behavior of Polymer Solutions. Since the results obtained for rigid solutions of this polymer are more easily interpreted, let us begin with these observations. The existence of two phoshporescence bands at 420 and 560 nm implies the presence of two distinct triplet-state species in the system. We will use the symbol T_a to designate the former and T_x to designate the latter. As mentioned above, the similarity between the phosphorescence bands near 420 nm both for the monomeric model compound and for the polymer suggests that the triphenylamine chromophore is essentially responsible for these emissions. There is a small red shift of the zero-zero band for the polymer, 420 nm versus 415 nm, but this is normal in polymeric systems. The emission at 560 nm is found not only in rigid solutions of the polymer but also in rigid dilute solutions of the monomeric compound, DAPB, which had been preirradiated at 300 nm as well as in rigid concentrated solutions of the DAPB. These facts suggest that the species responsible for the T_x emission are formed by a photochemical transformation. In this work it was not our objective to attempt an identification of this photoproduct; however, information about its photophysical characteristics has been gained.

The effect of varying the excitation intensity on the intensity of the emission at 420 nm indicates that it is a strictly monophotonic process, as is expected for ordinary phosphorescence. The delayed fluorescence, on the other hand, appears to be biphotonic in nature since the exponential factor is found to be 2.0. It is proposed, therefore, that the major mechanism for DF production involves triplet-triplet annihilation. For the emission at 560 nm due to T_x the effect of excitation intensity on emission intensity shows a supralinear dependence in solution but a linear dependence in solid films. Any mechanism for its formation, electronic excitation, and luminescence decay will have to account for this fact. One way to understand this result is by postulating that, in any given excitation pulse, one photon results in the formation of the photoproduct and a second photon produces an independent electronically excited species that subsequently sensitizes the formation of T_x. Ideally this would result in a pure biphotonic process on the very first excitation pulse. On subsequent pulses new product is formed along with product formed in earlier excitations. In these subsequent pulses phosphorescence could arise either by direct excitation or by sensitization of chromophores produced in earlier pulses. A linear dependence on excitation intensity would eventually be expected when sufficient photoproduct has been formed. Thus, the effect of excitation intensity upon the emission intensity of this species could vary from linear to biphotonic depending upon the history of the sample. The fact that only a linear dependence is observed in solid films may be due to a very efficient production of photoproduct in the first few pulses. The second photon, which produces the excited-state species, could be associated either with a directly absorbed photon or with an independent electronically excited species that acts as a sensitizer. Arguments will be presented below that suggest that the sensitizer model is preferred.

B. Kinetic Models for the Observed Luminescence Signals. For solutions of small molecules, classical

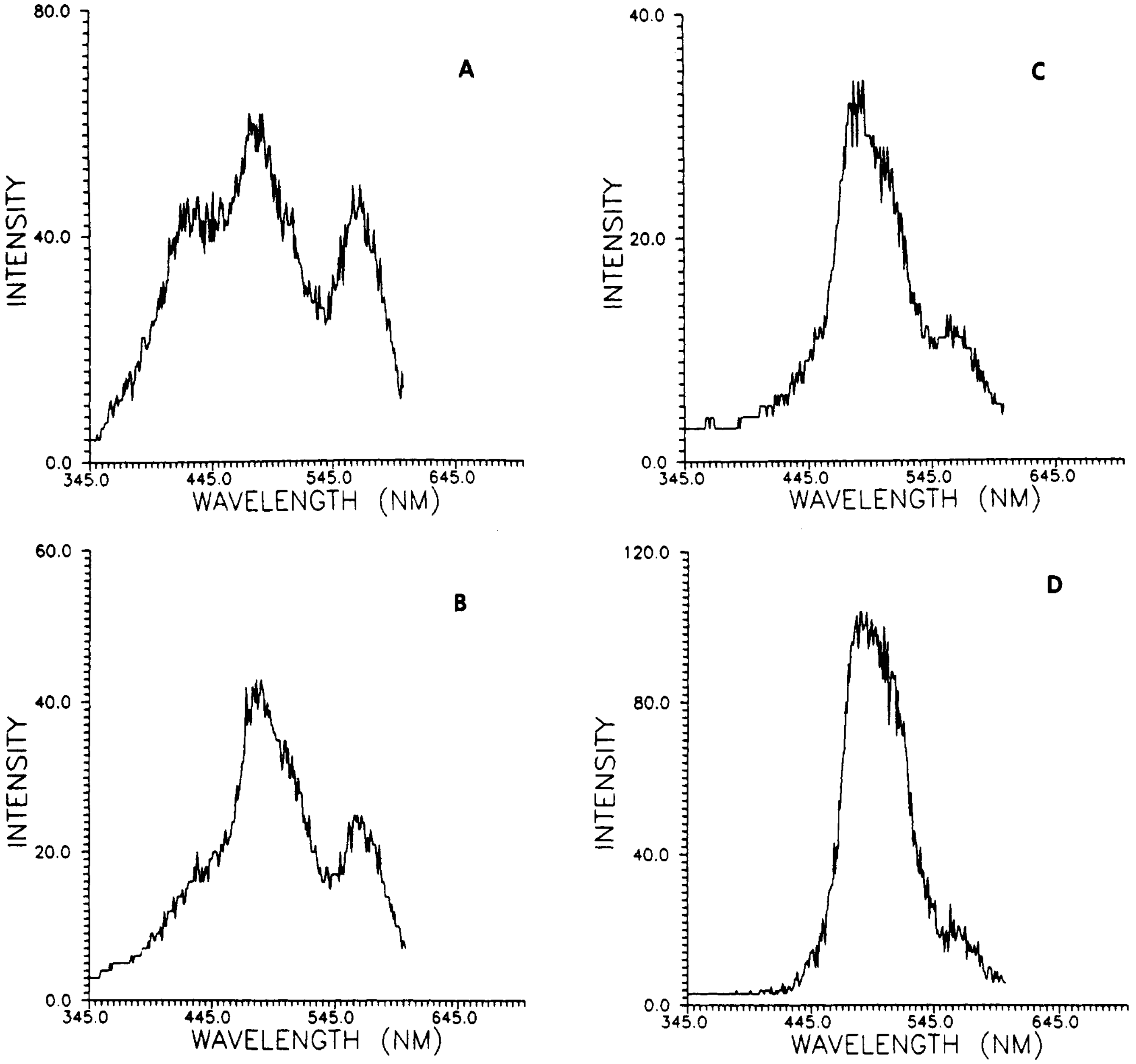

Figure 4. Time-resolved phosphorescence spectra of PDAPM solid films at 77 K. Delay times are (A) 0.5 ms, (B) 1.0 ms, (C) 2.0 ms, (D) 10 ms.

kinetics predict a factor of 2 difference between delayed fluorescence and phosphorescence lifetimes. For many vinyl aromatic polymers, including the present one, it has been observed that the delayed fluorescence signal decays much more than 2 times as fast as the phosphorescence so that some triplet species are still emitting long after the annihilative process has become negligible. It has been proposed, therefore, that in polymers a distinction may be drawn between chromophores capable of participating in energy-tranfer events, the mobile species, and others, which, by virture of their spatial arrangement, are prevented from such participation. In the remainder of this discussion we will use the symbol T_m to represent mobile triplet excitons. It seems likely that the species responsible for the proposed sensitized formation of T_x are, in fact, these mobile triplet excitons. It is also likely that they play a major role in the triplet photophysical processes of solid films as well as rigid solutions of this polymer as we will now demonstrate.

For most solid-state polymer systems studied to date, delayed fluorescence is thought to be produced by a triplet–triplet heteroannihilation involving a mobile triplet exciton and a trapped one. The lifetimes of the trapped excitons may be determined from their corresponding phosphorescence lifetimes. For solid films at 77 K the kinetic data indicate that the 485-nm component has a lifetime on the order of a few tenths of a second. There is no emission signal that is directly attributable to T_m and so its lifetime may be only indirectly inferred from the DF lifetime. Thus, with T_t to represent the trapped exciton, i.e., the excimerlike triplet state, then

$$T_m + T_t \rightarrow {}^1D^* + {}^1S_0 \qquad (1)$$

where ${}^1D^*$ is a singlet excimer. Assuming an essentially first-order decay for both T_m and T_t, we find that $1/\tau_{DF} = 1/\tau_t + 1/\tau_m$. Since τ_{DF} is on the order of 50 times smaller than τ_t, it is clear that $\tau_{DF} = \tau_m$ to a very good approximation. The reason of this large difference between the lifetime of the trapped triplet exciton and the mobile exciton is most likely due to the opportunities that the mobile exciton has for nonradiative decay primarily through trapping interactions. It may be noted that the trapped exciton, which ultimately leads to excimer phosphorescence, is immobilized due to its interaction with a neighboring chromophore unit. In this respect it differs

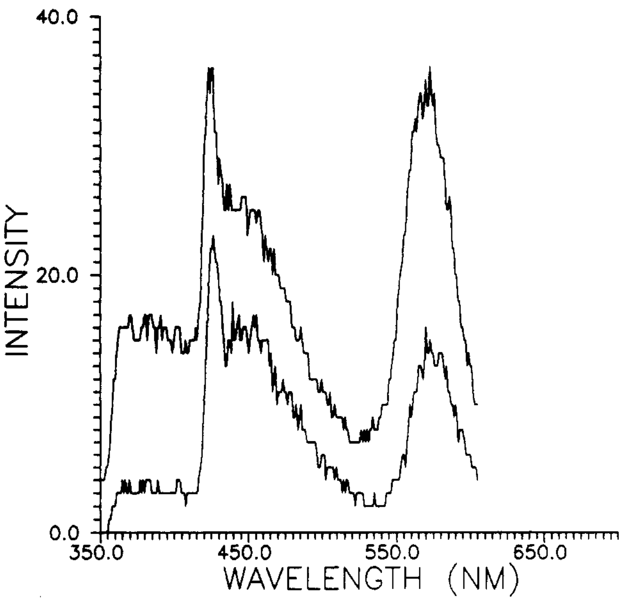

Figure 5. Phosphorescence spectra of PDAPM solid film at 8 K. Delay times were 0.1 ms for the upper spectrum and 0.2 ms for the lower spectrum.

from T_a, which is the source of the 420-nm phosphorescence, and is immobilized by its existence in an environment that favors neither energy migration to a neighbor nor an excimerlike interaction with a neighbor.

An advantage of this hypothesis for the mechanism of DF production in solid films is that it also fits nicely with the suggested mechanism for sensitized phosphorescence of T_x. Thus, if we represent the sensitization process as

$$T_m + {}^1X_0 \rightarrow {}^1S_0 + T_x \qquad (2)$$

then the phosphorescence due to T_x would have the same lifetime as T_m, providing $\tau_m \ll \tau_{X_0}$.

In fact, apart from the requirements of spin conservation, it is not even necessary that T_x be a triplet. The lifetime of ${}^1X_0$, on the other hand, must be significantly larger than T_m. It is probable that ${}^1X_0$ is a stable ground-state species, but on kinetic considerations alone it could also be a very long-lived transient. The supralinear nature of the excitation intensity dependence of T_x may now be seen to result from one photon required to produce T_m and one or less than one photon to produce ${}^1X_0$. The fact that preirradiated dilute solutions of DPAB yield a 560-nm signal while virgin samples do not is further indication that these centers have a rather long lifetime and are probably stable compounds.

In the polymeric system, the detailed mechanism by which sensitization and T–T annihilation occurs probably involves energy migration among chromophores until a reactive partner, ${}^1X_0$ or T_t, is encountered. The high local concentration of chromophores in the polymer would favor such a process. A similar mechanism could account for the presence of 560-nm phosphorescence in 2 M solutions of DPAB since, once again, a dense chromophore population is present. In fact, for these systems having a high density of chromophore groups even very small amounts of ${}^1X_0$ might be detectable due to an unusually efficient sensitization brought about by the assistance of exciton migration. It is probable that the linear dependence of excitation intensity on emission intensity at 560 nm in solid films is due to this efficient energy transfer. For dilute solutions of the monomeric compound, which have not been preirradiated, it may well be that significant concentrations of ${}^1X_0$ are formed in each excitation pulse but that the efficiency of sensitization is markedly reduced due to slow, or possibly absent, exciton migration, thus accounting for the absence of the emission in this case.

C. Energetics of the Excited-State Species. It should be noted that there is a progression to the red of the zero–zero phosphorescence band for dilute rigid solutions of DAPB (415 nm or 288.1 kJ), a rigid solution of PDAPM (420 nm or 284.7 kJ), and, finally, solid films of PDAPM at 8 K (426 nm or 280.7 kJ). This red shift occurs without loss of any structural features in the emission band. It seems clear that interchromophore interaction is effective in producing the red shift in the polymeric system compared with the monomeric analogue. Also, the even greater population density of chromophores in the solid state as opposed to rigid solutions produces an even greater red shift. In the polymeric system it is evidently these low-energy species that are interacting strongly with neighbors that are responsible for the long-lived emission observed. It is important to distinguish these somewhat red-shifted but structured bands from the band observed in solid films at 77 K and centered at 485 nm. The nature of this species will now be considered.

The lifetime of the species is nearly 100-fold larger than that of any of the other components observed at 77 K, and it is proposed that this is a trapped excimerlike triplet state. Its maximum is displaced about 2900 cm^{-1} to lower energy from the zero–zero band of the phosphorescence origin measured at 8 K. Its assignment as an excimeric species is based partially on its temperature dependence. Thus, this band, which is completely absent at 8 K, is only formed at the expense of the monomeric phosphorescence. Similar behavior has recently been observed in poly(2-vinylnaphthalene)[8] and has been exploited to determine trap depths in poly(*N*-vinylcarbazole).[8] Since excimer phosphorescence replaces nonexcimer phosphorescence in the temperature range from 40 to 65 K, it is reasonable to conclude that the decreasing lifetime of the 426-nm phosphorescence with rising temperature, starting at the discontinuity in the Arrhenius graph at 54 K, is due to competition between relaxation to the ground state and trapping at excimer-forming sites. If this is true, then an activation energy for the trapping process can be assigned the value of 5.1 ± 0.5 kJ/mol as derived from the slope of the steep part of this graph. There appears to be a slight increase in phosphorescence lifetime between 20 and 54 K. The effect is very small and a proper interpretation for it is not clear at this time.

An attempt was also made to find an activation energy for detrapping by measuring lifetimes of the excimeric phosphorescence in the temperature range from 63 to 112 K. Above 115 K the signal is too weak to obtain reliable kinetic data. Here also it is found that the lifetimes decrease very gradually from 63 to 76 K, at which point a slope discontinuity occurs, yielding an activation energy of 4.6 ± 0.5 kJ/mol for the steep portion of the curve. In this case the decay of triplet excimers by relaxation to the ground state is no doubt the rate-controlling process below 76 K. Above this temperature a second process begins to compete in rate with the direct relaxation. It is suggested that this second process is detrapping from the excimer state. The fact that the activation energies for the trapping and detrapping processes are the same within experimental error indicates that the excimeric species is essentially isoenergetic with the nonexcimeric species. In spite of this fact, there is a difference of 34 kJ/mol (2900 cm^{-1}) between the emission maximum for the excimeric phosphorescence and the zero–zero band of the nonexcimeric emission. This energy difference may be attributed to the fact that the ground-state potential energy surface associated with the excimer is dissociative. Thus, a dissociation energy of 34 kJ/mol for the excimer on the

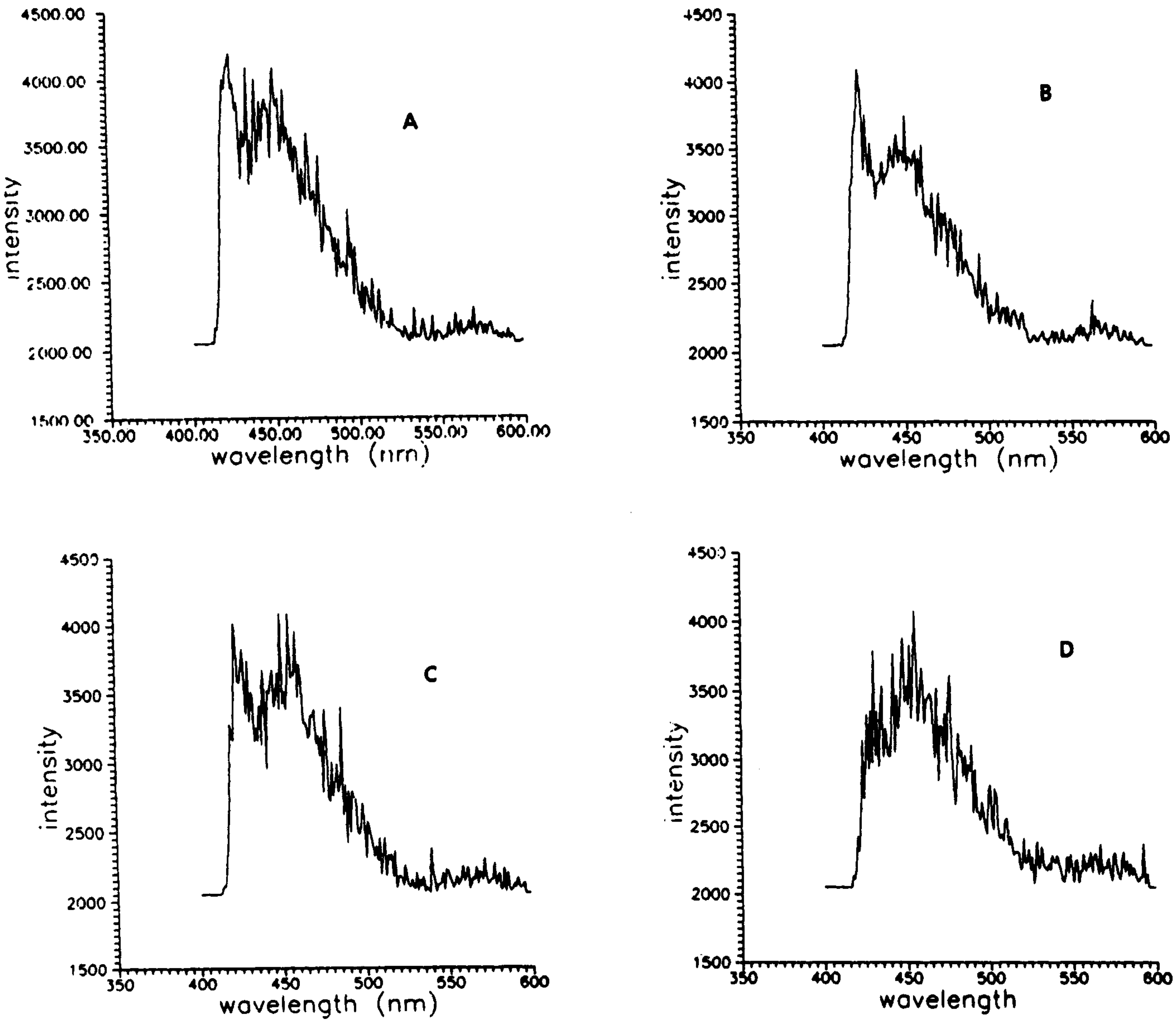

Figure 6. Phosphorescence spectra of PDAPM solid film at various temperatures and a fixed delay time of 50 ms: (A) 22 K, (B) 33.3 K, (C) 42.7 K, (D) 62.2 K.

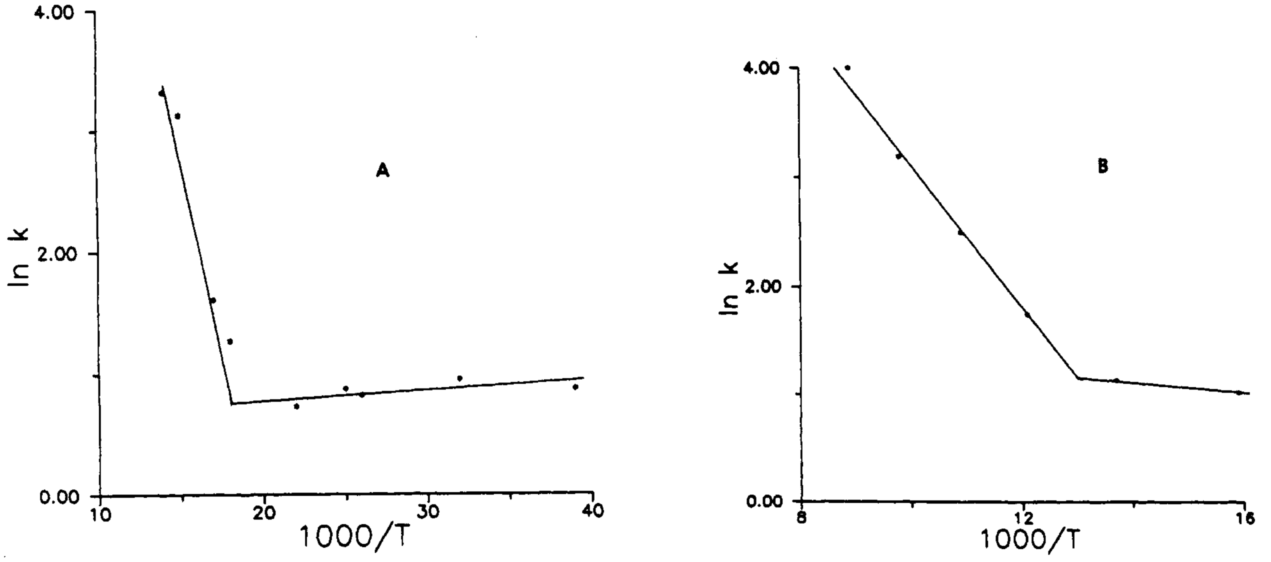

Figure 7. Arrhenius plots for phosphorescence decay: (A) signal monitored at 426 nm, (B) signal monitored at 485 nm.

ground-state surface is implied. For poly(*N*-vinylcarbazole), which has two easily recognizable triplet excimers, their respective dissociation energies were recently found to be 30.2 and 35.4 kJ/mol. Thus, a certain degree of self-consistency seems to be emerging for these ground-state dissociation energies.

On the basis of presently available information, it is not possible to assign the origin for the activation energies

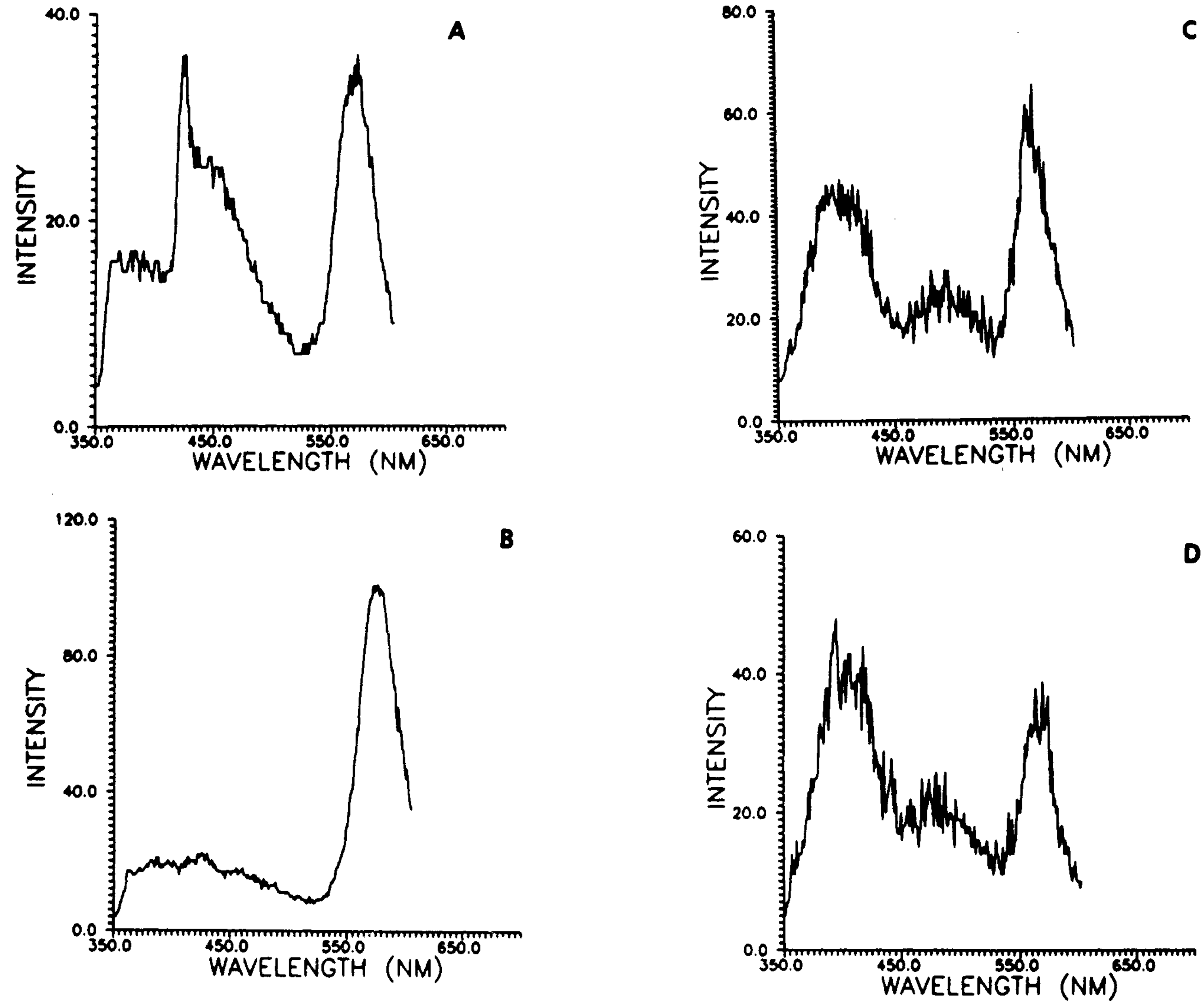

Figure 8. Phosphorescence spectra of PDAPM solid films at various temperatures using 0.1-ms delay in each case: (A) 8 K, (B) 77 K, (C) 180 K, (D) 298 K.

found for trapping and detrapping. It may be noted, however, that the activation energy found here for excimer formation with the triphenylamine chromophore is about 3, 2.5 times as large as that found previously[8] for the carbazole chromophore. Thus, there may be a significant contribution to the activation energy that can be associated with bond formation in the excimer itself. Since the triphenylamine group is pyramidal and the carbazole group planar, it is reasonable to think that excited dimer formation may require greater energy input to the nonplanar system. On the other hand, the activation energies associated with phenyl group oscillations along the backbone of the polystyrene chain have activation energies of 6.7 kJ/mol.[11] Clearly, additional work is needed to provide a definitive assignment for these activation energies.

Acknowledgment. The authors at Nevada are grateful for financial support to the U.S. Department of Energy under Grant No. DE-FG08-84ER45107. We thank Prof. K. Razi Naqvi for helpful discussions.

References and Notes

(1) Henry, B. R.; Kasha, M. *J. Chem. Phys.* **1967**, *47*, 3319.
(2) Alfimov, M. V.; Batekha, I. G.; Sheck, Y. B.; Gerko, V. I. *Spectrochim. Acta* **1971**, *27*, 329.
(3) Forster, E. W.; Grellman, K. H. *J. Am. Chem. Soc.* **1972**, *94*, 634.
(4) Stolka, M.; Pai, D. M.; Renfer, D. S.; Yanus, J. F. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 969.
(5) Masuhara, H.; Tamai, N.; Inoue, K.; Mataga, N. *Chem. Phys. Lett.* **1982**, *91*, 109.
(6) Masuhara, H.; Mataga, N. *J. Lumin.* **1981**, *24/25*, 511.
(7) Lim, E. C. *Acc. Chem. Res.* **1987**, *20*, 8.
(8) (a) Burkhart, R. D.; Chakraborty, D. K. *J. Phys. Chem.* **1990**, *94*, 4143. (b) Chakraborty, D. K.; Burkhart, R. D. *J. Phys. Chem.* **1989**, *93*, 4797.
(9) Burkhart, R. D.; Aviles, R. G. *Macromolecules* **1979**, *12*, 1073.
(10) Shirota, Y., unpublished results.
(11) Yano, O.; Wada, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 669.