Triplet Excimer Formation of Triphenylamine and Related Chromophores in Polystyrene Films

Richard D. Burkhart* and Nam-In Jhon

Department of Chemistry, University of Nevada, Reno, Nevada 89557 (Received: December 11, 1990; In Final Form: May 9, 1991)

The phosphorescence of triphenylamine (TPA) and of the (*N,N*-diphenylamino)phenylmethyl ester of 2-methylpropanoic acid (DAPM) was investigated in polystyrene films at temperatures from 20 to 230 K. Their phosphorescence spectra at low temperatures are similar to those recorded in rigid glassy solvents at 77 K, but as the temperature is raised, a new phosphorescence band at 470 nm grows in and the low-temperature band gradually disappears. The new emission is due to an excimeric triplet since it is similar to one found earlier from the polymeric analogue of DAPM and is also similar to the totally excimeric phosphorescence of crystalline TPA at 77 K. Rates of excimer formation and dissociation were determined as a function of temperature as were the corresponding activation energies. Triplet exciton migration is not the rate-limiting step in excimer formation. The activation energies for dissociation of the triplet excimers were found to depend upon the concentration of the amine. For DAPM the evidence suggests that excimers formed in dilute samples are in a strained configuration which relaxes slowly compared to the excimer lifetime.

Introduction

When vinyl aromatic polymers are subjected to a pulse of excitation light, the usual photophysical events can occur such as fluorescence, phosphorescence, and various nonradiative relaxation processes.[1] An additional very important process which can occur is the migration of electronic energy from one chromophore to another.[2] In this sense the polymeric system shares features with the photosynthetic apparatus in which antenna chlorophyll provide a migratory route to lead electronic excitation to reaction centers. Indeed, a number of studies have been conducted on synthetic polymers involving explorations of this antenna effect.[3]

In synthetic polymers the rate of energy migration is affected to an important extent by the existence of traps for the migrating excitons. Such traps may be in the form of impurities which can act as energy acceptors. They may also be present, even in highly purified polymers, as sites in the polymer structure that are favorable for the formation of excimers. If excimer formation is occurring, it can usually be detected by the emission of a structureless luminescence spectrum that is red-shifted with respect to the nonexcimeric spectrum. Polystyrene, poly(vinylnaphthalene),[4] and poly(*N*-vinylcarbazole)[5] are examples of polymers that emit an excimeric type of fluorescence.

It is generally believed that the structure of singlet excimers involves a sandwich arrangement of the aromatic rings, one on top of the other.[6] Thus, it is of interest to examine cases in which this favorable bonding geometry is disrupted by the presence of sterically interfering groups. Yamamoto and co-workers have recently carried out such an investigation using 3,6-di-*tert*-butyl groups as the interfering moieties in carbazolyl rings of poly(*N*-vinylcarbazole).[7] Indeed, the expected loss of excimeric emission was observed. Another similar case relevant to the present work is that of poly[4-(*N,N*-diphenylamino)phenylmethyl methacrylate] (PDAPM) in which the chromophore is essentially the same as triphenylamine. This particular polymer is especially interesting because the pendant triphenylamine groups, bonded at every third carbon atom along the backbone of the chain, are rather sterically

demanding in view of the fact that the amine grouping is a trigonal pyramid. It is clearly very difficult to achieve any sort of sandwichlike arrangement of these chromophores, and so it is not surprising that no excimeric fluorescence is observed from this polymer and that the rate of exciton migration is found to be relatively large at 1.8×10^{11} s^{-1}.[8]

A recent study of triplet photophysical properties of PDAPM yielded quite different results.[9] At temperatures below 60 K no evidence for excimeric phosphorescence was found, but above this temperature a red shift and loss of structure signaled the onset of excimeric emission associated with the triplet state. Since no singlet excimer formation had been observed, the observation of excimeric phosphorescence was, at first, surprising. By studying the rates of excimeric and of nonexcimeric decay as a function of temperature, we found activation energies for triplet excimer formation and dissociation yielding values of 5.1 and 4.6 kJ/mol, respectively. These values were very interesting because similar activation energies for triplet excimer formation and dissociation in the carbazolyl system of poly(*N*-vinylcarbazole) (PVCA) were significantly smaller at 2.0 and 2.5 kJ/mol, respectively.[10] It was concluded that the energetics associated with triplet excimer formation in these polymers is determined to a major extent by the nature of the chromophore itself. It is not clear, however, whether a significant energetic contribution is made by internal rotations associated with covalent bonds of the chain backbone or those involved in the pendant structure.

In order to provide an independent assessment of the role played by the polymeric structure itself, it was decided to investigate the triplet photophysical properties of small molecules containing the triphenylamine group present as dopants in polystyrene matrices. The simplest such model compound is, of course, triphenylamine itself. Another compound that is studied here is the monomeric model of PDAPM, the (*N,N*-diphenylamino)phenylmethyl ester of 2-methylpropanoic acid (DAPM).
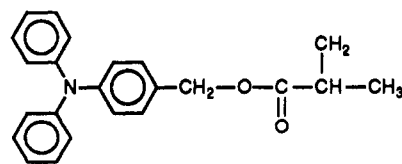
The use of inert polymers as matrices in which to carry out spectroscopic investigations has become very widespread.[11]

(1) For typical examples see: Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: New York, 1985.

(2) For a review of energy migration and trapping in polymeric systems see: Klöpffer, W. *Spectrosc. Lett.* **1978**, *11*, 863.

(3) (a) Itoh, Y.; Webber, S. E.; Rodgers, M. A. *J. Macromolecules* **1989**, *22*, 2766. (b) Nowakowska, M.; White, B.; Guillet, J. E. *Macromolecules* **1989**, *22*, 3903.

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Polymer matrices are particularly convenient for work involving the temperature dependence of various spectroscopic properties since, with judicious selection, they can provide a framework that remains essentially rigid with varying temperature. Work on triplet-state properties of organic molecules is especially well-suited to polymer matrices since the effective lifetimes of the triplet states are generally enhanced at low temperature and, if needed, temperature variations may still be investigated. Furthermore, it is often possible to select a polymer as host that is essentially inert and does not participate in the photophysical events associated with the guest.

It was not certain, of course, that molecularly doped polystyrene films containing these compounds would emit an excimeric phosphorescence, but there was precedent for such emission in the carbazole system. Thus, in polystyrene films doped with *N*-ethylcarbazole, excimer formation was found to be a temperature-dependent process whereby no excimer formation was observed at 77 K but distinct excimer-like phosphorescence was found at ambient temperature.[12] Similarly, *N*-phenylcarbazole is found to emit an excimeric phosphorescence when present as a dopant in poly(methyl methacrylate) films.[13]

In the present investigation similar behavior was found for DAPM but with one significant difference. The particular distinction of DAPM with respect to excimeric phosphorescence is its clear-cut resolvability from monomeric phosphorescence. As will be seen below, the nonexcimeric phosphorescence band shapes of both DAPM and triphenylamine remain relatively unchanged with increasing temperature. The excimer emission, however, is sufficiently red-shifted from that of the nonexcimer to yield a distinct band. Therefore, in this work an investigation of the temperature dependence of triplet excimer formation and dissociation is undertaken.

Experimental Section

Purification of Chemicals. Commercial polystyrene usually contains acetophenone-like residues which can be difficult to eliminate completely. An effective treatment has been described in earlier work and was followed in the present study.[14] The DAPM used in this study was provided by Prof. Y. Shirota of Osaka University. Triphenylamine from Aldrich Chemical Co. was recrystallized from benzene three times before use. Benzene was washed three times with concentrated H_2SO_4, then with dilute base, and finally with water. After drying over anhydrous Na_2SO_4, it was distilled three times with center fractions being retained in each distillation. The naphthalene was Prinz grade material provided by Prof. A. Prock of Boston University.

Sample Preparation. To prepare molecularly doped films, polystyrene was first dissolved in a small amount of benzene along with the dopant. The solution was purged with oxygen-free nitrogen in a glovebox. The solvent, still under a nitrogen atmosphere, was evaporated by heating with a hot plate/stirrer. When the solvent was evaporated, the molten polystyrene was transferred to a preheated quartz disk and the polymer was allowed to flow out into a film. A second quartz disk was then placed over the film and pressed down, leaving the sample sandwiched between the two plates. Mounting samples in the cryoscopic system was accomplished as follows.

The samples were first mounted in the copper ring sample holder. The copper ring is fixed by means of a threaded connection and indium gasketing to the cryotip assembly. The two quartz plates were sandwiched between two pieces of indium foil having 2-mm × 4-mm slits cut in their centers for entry of the excitation beam and exit of the emission. These foils serve as good thermally conducting gaskets between the copper holder and the quartz plates. The plates, along with their indium gasketing, are mounted

in the sample holder and retained there by a second copper ring fixed into place by several screws placed around the periphery. It is important that all of the connections between quartz, indium, and copper be very tight to facilitate thermal conduction.

Spectroscopic Instrumentation. Spectra were recorded with instrumentation that was assembled from components, and three separate systems have been used in this work. Usually, sample excitation is accomplished by XeCl excimer lasers (either a Tachisto Model 401XR or a Questek Model 2110), although experiments on samples containing TPA/naphthalene mixtures were performed using a nitrogen laser. The emission was focused onto the slits of a SPEX Model 1680B monochromator and was detected by an EMI 9789 photomultiplier. The photomultiplier signal was recorded with a Nicolet Model 12/70 signal averager or a LeCroy system consisting of a Model 1434 CAMAC crate, a Model 8901 GPIB interface, a Model 2323A dual gate generator, and a Model 6810 waveform recorder. The data were stored and processed by means of either an Epson Equity II+ or a Zenith ZCH-1490-Z computer. Each computer contained a National Instruments GPIB-PC interface board and a math coprocessor. These systems were usually used to record kinetic decays of luminescence signals.

For most of the spectroscopic experiments the emission signal was focused on the entrance slits of a SPEX Model 1681C spectrograph fitted with a rotatable grating mount. Gratings of 1200 or 150 grooves/mm could be used. The latter provides an 8-fold increase in wavelength coverage compared to the former. The emission was detected by a Princeton Instruments Model IRY-700-S/B diode array located at the exit focal plane of the spectrograph. Data readout and interaction with the computer were provided by a Princeton Instruments Model ST-120 controller. A Princeton Instruments FG-100 or PG-10 pulser was used for triggering, gating, and delay setting. Time resolution to 11 ns is possible with this system.

Experimental Results

Figure 1 consists of a series of phosphorescence spectra of DAPM present as a dopant in polystyrene. The spectra are recorded under similar conditions except that the temperature has been varied. In these particular samples DAPM is present at a level of 12 wt %. It is interesting to note that between 21 and 120 K there is very little change in the character of the spectra, only a slight broadening of the emission band being observed. Above 120 K the spectrum changes dramatically with a new band growing in having a λ_{max} at 470 nm. As the temperature rises, the nonexcimeric emission declines and the band at 470 nm grows until, at 190 K, only the emission at 470 nm remains. This sort of behavior is very similar to that already observed for polystyrene films doped with *N*-ethylcarbazole.[10] It is assumed in the present case, as was done for *N*-ethylcarbazole, that the new band which appears at 470 nm is a triplet excimer of DAPM.

At first it was thought this new band may be appearing as a result of photochemical reaction. Arguing against this interpretation is the fact that the temperature-induced interconversion between the excimer band and the nonexcimeric one is completely reversible. The new band is also not associated with polystyrene itself since blank samples containing no DAPM produce no phosphorescence emission at the detector sensitivities used here. Evidence that the new band is probably not due to an impurity in DAPM will be provided below in the description of experiments on triphenylamine, which produces similar excimer/nonexcimer phosphorescence spectra.

Further evidence that this red-shifted band is due to excimer emission is provided by the effect on phosphorescence spectra of changing the concentration of the dopant present in the films. Figure 2 provides a summary of spectra at the same temperature but at different levels of dopant concentration from 1 to 12 wt %. It is clear that the excimeric emission is favored at higher concentrations as would be expected for a dimeric species. This is not to say that no excimeric emission is found for these more lightly doped films. In fact, even films containing only 1% of the dopant emit a weak excimeric phosphorescence, but higher tem-

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(12) Abia, A. A.; Burkhart, R. D. *Macromolecules* **1984**, *17*, 2739.

(13) Ito, S.; Katayama, H.; Yamamoto, M. *Macromolecules* **1988**, *21*, 2456.
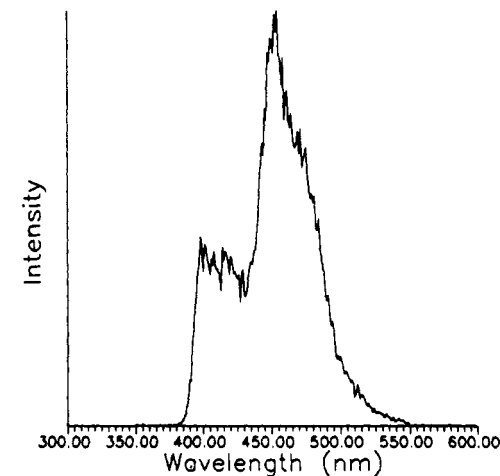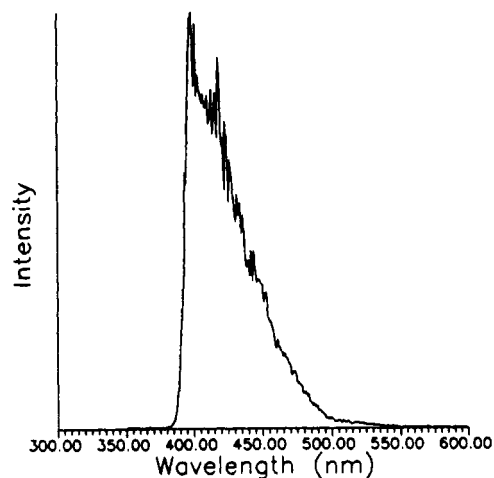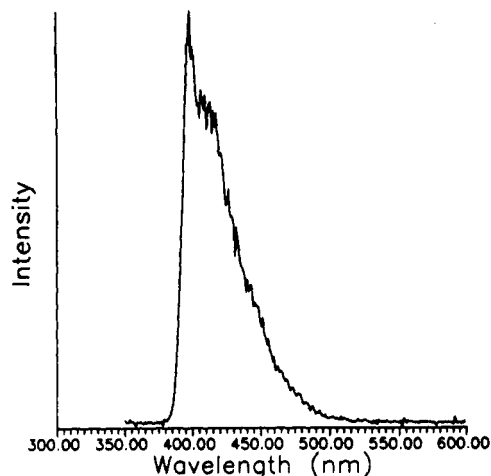
(14) Burkhart, R. D.; Caldwell, N. J.; Haggquist, G. W. *J. Photochem. Photobiol. A* **1988**, *45*, 369.
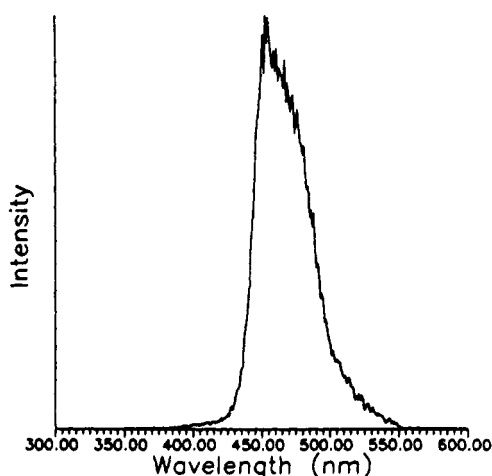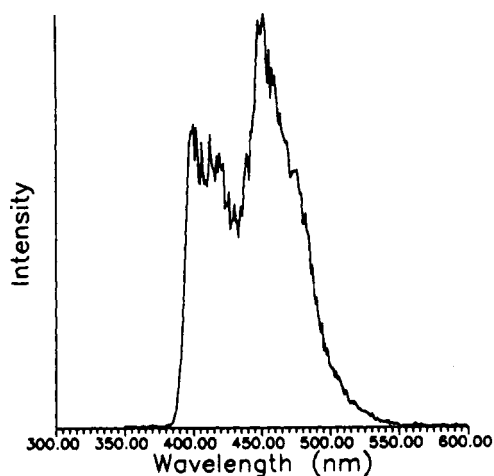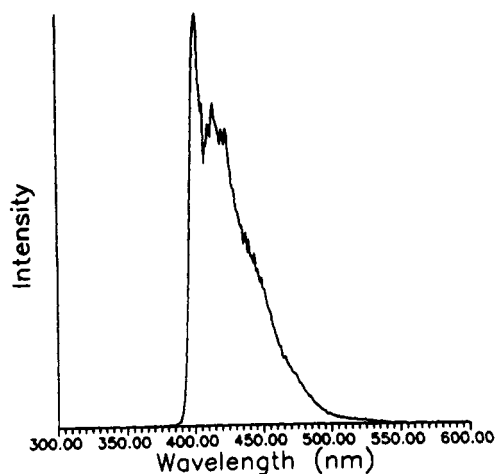
Figure 1. Phosphorescence spectra of a polystyrene film doped with 12% DAPM at three different temperatures: top, 21 K; middle, 160 K; bottom, 255 K.

Figure 2. Phosphorescence spectra recorded at 165 K of three films doped with differing amounts of DAPM: top, 1%; middle, 5%; bottom, 12%.

peratures are required in order to observe it.

Since the medium is rigid at all temperatures used here, there is some question about the mechanism by which an excited triplet-state species can interact with one in the ground state to form an excimer. It is probable that this occurs by a process of energy migration in which the site of excitation migrates randomly among the dopant molecules, but the translational motion of these molecules remains quite limited. In this way an individual triplet exciton may probe a considerable sample volume, and when a configuration suitable to excimer formation is encountered, then trapping at that excimer forming site occurs. If we use the symbol

T_m to indicate this migrating triplet exciton, then at least two reaction channels may be described for this species. They are

$$T_m \rightarrow {}^1M_0 + h\nu/\text{heat} \tag{1}$$

$$T_m + {}^1E_0 \rightleftharpoons {}^3E^* + {}^1M_0 \tag{2}$$
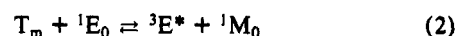
where ${}^1E_0$ represents a site in the polymer structure suitable for excimer formation, ${}^3E^*$ is a triplet excimer, and ${}^1M_0$ is an ordinary ground-state chromophore formed by energy transfer from T_m. These species are also expected to be involved in triplet–triplet annihilation processes leading to delayed fluorescence. In all of
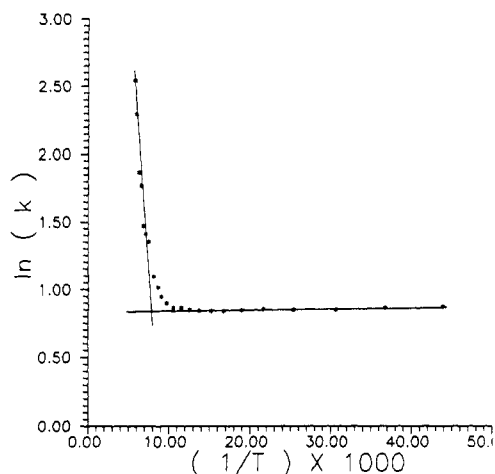
Figure 3. Arrhenius graph for the decay of DAPM phosphorescence monitored at 413 nm (nonexcimer).

Figure 4. Arrhenius graph for the decay of DAPM phosphorescence monitored at 470 nm (excimer).

these experiments a delay time of 50 ms was inserted between the laser pulse and the commencement of signal collection in order to eliminate the delayed fluorescence emission. The triplet excimer may disappear by dissociation into a mobile triplet exciton and $^1E_0$, that is, by the reverse of eq 2 or by radiative and radiationless relaxation to the ground state

$$^3E^* \rightarrow {}^1E_0 + h\nu/\text{heat} \qquad (3)$$

The rate of decay of nonexcimeric emission was determined for these samples as a function of temperature by setting the emission monochromator at 413 nm and then following the decrease in intensity as a function of time following an excitation pulse. The tail of the decay was fit to an exponential function, and the corresponding rate constant for the process, k, was determined at each temperature. Graphs of ln k versus $1/T$ were prepared, and a typical example is shown in Figure 3 for a sample containing 12% DAPM. There is an obvious discontinuity in this Arrhenius graph near 111 K, and the slope of the steeper part yields an activation energy of 5.0 kJ/mol. It is assumed that in the temperature range corresponding to the change in slope of this graph that a competing channel for disappearance of T_m becomes thermally accessible. Thus, below this temperature the major route for disappearance of triplets is first-order relaxation by a radiative or radiationless process as in eq 1. Above this temperature the trapping process depicted by eq 2 becomes available, and the activation energy of 5.0 kJ/mol corresponds to this formation of triplet excimers. The near coincidence between temperature ranges corresponding to the onset of excimeric phosphorescence and to the change in slope of the Arrhenius graph is probably linked to the competition in rate between these two processes.

At temperatures above that required for excimer formation the emission monochromator may be set to a wavelength corresponding to excimeric phosphorescence (470 nm), and then the temperature dependence of the rate of triplet excimer decay may be examined. A typical example of the resulting Arrhenius graph is shown in Figure 4. Once again a discontinuity is observed, and one finds an activation energy of 3.6 kJ/mol from the steeper portion of the graph which would correspond to the disappearance of these excimeric species. At temperatures below this discontinuity the slope is definitely nonzero, suggesting that a larger activation energy is required for the first-order relaxation of excimer triplets by eq 3 compared to the similar process for nonexcimeric species. It may be recalled that for the polymeric system, PDAPM, the corresponding activation energies for trapping and detrapping were found to be 5.1 and 4.6 kJ/mol,[9] remarkably close to those determined for this monomeric analogue in rather heavily doped films.

In order to be certain that the emission spectra being observed here are truly associated with the triphenylamino group, doped films containing triphenylamine itself were examined. In Figure
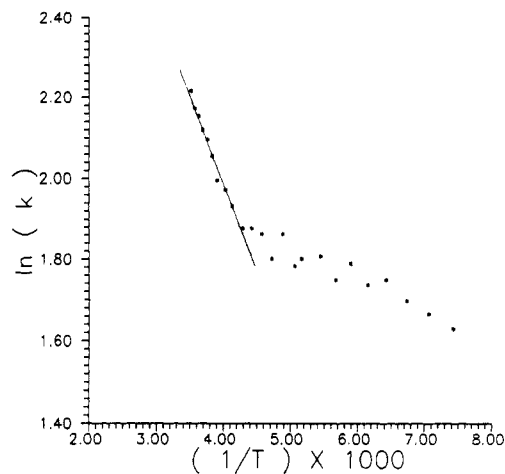
TABLE I: Activation Energies for Formation and Disappearance of Triplet Excimers of DAPM and Triphenylamine in Polystyrene Films

compd	% doping	E_{act}(formation), kJ/mol	E_{act}(disappearance), kJ/mol
DAPM	12	5.0	3.6
DAPM	5	6.4	2.1
DAPM	1	6.9	1.3
TPA	12	4.6	5.8
TPA	5	4.8	7.9
TPA	1	7.6	9.2
PDAPM[a]		5.1	4.6

[a] Taken from ref 9.

5 is a series of spectra recorded for a polystyrene film doped with 12% triphenylamine (TPA). The zero–zero band is found at 408 nm, in agreement with an earlier investigation of this compound.[15] Clearly the behavior found here is similar to that observed with DAPM. The excimeric band occurs at the same wavelength for each of the two compounds, and the nonexcimeric phosphorescence band of TPA does not broaden significantly with rising temperature, thus allowing one to observe easily the development of the excimeric signal. Activation energies for the formation and disappearance of the triplet excimer of TPA were determined as described above for DAPM. A summary of measured activation energies is gathered together in Table I.

Since triplet excimer formation seems to be easily achieved with triphenylamine, a decision was made to examine the phosphorescence emission of a solid crystal of the material at 77 K. The interesting result is presented in Figure 6 which shows that the phosphorescence is entirely excimeric in character. This experiment not only helps to confirm the identity of the phosphorescence band at 470 nm but also gives further evidence that the emission band being assigned to a triplet excimer cannot be originating from impurities in the polystyrene host matrix.

Since triplet excitons are trapped at excimer-forming sites with a significant activation energy, it was of interest to examine the competition between trapping of these excitons by a deliberately added quencher versus trapping at excimer forming sites. Naphthalene was chosen as the quencher since its first excited singlet state is significantly higher in energy than that of TPA whereas it lowest triplet state is considerably lower in energy. Several samples were prepared corresponding to weight ratios of 1:1 to 0.02:1 naphthalene:TPA. Phosphorescence spectra at several different temperatures are presented in Figure 7 for a sample containing 5 wt % TPA and 2.6 wt % naphthalene. This is approximately an equimolar mixture. A nitrogen laser was used as the excitation source to be certain that only TPA was being photoexcited. Two important results of this experiment should be noted. First, even at 16 K naphthalene phosphorescence, which
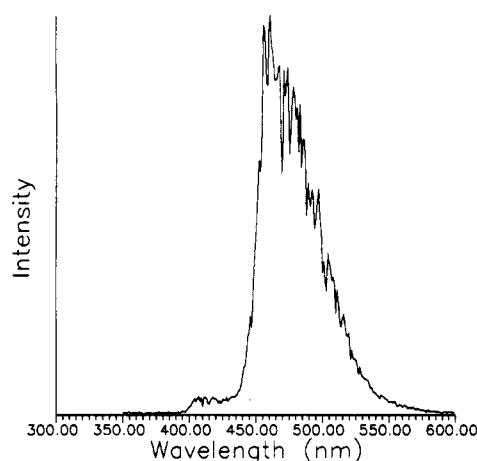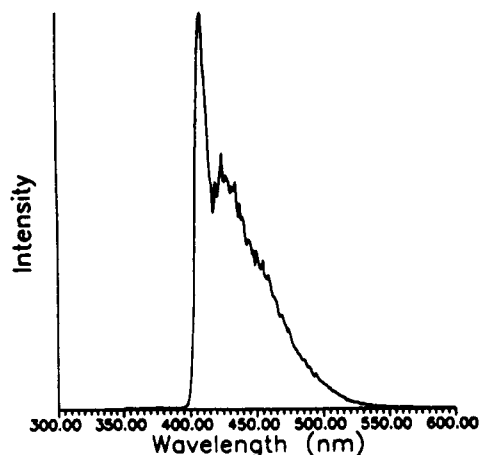
(15) Lewis, G. N.; Kasha, M. *J. Am. Chem. Soc.* **1944**, *66*, 2100.

Figure 6. Phosphorescence spectrum of crystalline TPA recorded at 77 K.

concentrations were used, the naphthalene emission is much more prominent at all temperatures and the phosphorescence due to TPA triplet excimers is completely quenched.

Discussion

Due to the controversy that has surrounded the concept of triplet excimers, it is, perhaps, useful at the outset to summarize the evidence suggesting that the triphenylamino chromophore is indeed involved in the formation of these provocative species. The first example of this red-shifted emission that we attribute to excimeric triplets was found in the phosphorescence spectrum of PDAPM at temperatures near 77 K.[9] At lower temperatures near 10 K the usual nonexcimer phosphorescence was observed. An identical excimeric emission is found from DAPM doped into polystyrene, but only at temperatures above 77 K. As was found for the polymer, experiments at lower temperatures produce a nonexcimeric emission. Thus, for both the polymer and for its monomeric analogue evidence for an excimeric phosphorescence is found but only if the temperature is sufficiently high. These two compounds are, of course, structurally related, but their methods of synthesis are quite different and it is very unlikely that a common impurity might be responsible for both of the red-shifted emissions observed. Finally, the red-shifted excimer-like emission from polystyrene matrices doped with triphenylamine is found to be identical with that found for both DAPM and PDAPM, and the possibility seems even more remote that the same contaminant could exist in all three samples. Furthermore, any contaminant would have to possess a first excited singlet state or a lowest triplet state which lies below these respective levels in TPA or DPAM. We have shown that when a contaminant in the form of naphthalene, having a lowest triplet state that lies below that of TPA and DPAM, is purposely introduced into these samples, the emission is seen even at temperatures as low as 15 K. No excimeric phosphorescence has been found in any samples that we have studied at temperatures this low, not even in homopolymers which are generally found to be efficient excimer formers. Thus, the behavior of a triplet quencher or impurity is quite different than that of an excimeric trap site, and the essence of this difference is that a larger activation energy is required for excimer formation than for trapping by the quencher. When small quantities of naphthalene, on the order of 2% by weight of TPA, are purposely introduced into these films, there is no emission observed from the naphthalene.

A fundamental assumption used in the analysis of these results is that the rate-controlling step in the formation of the triplet excimer is that represented by eq 2 and that this process is not encounter controlled. Thus, the activation energies characterized as those for excimer formation summarized in Table I are thought to be associated with bond formation of the excimeric species. A more detailed justification for this working hypothesis will be presented below. If the rate-controlling process in excimer formation were, in fact, due to exciton migration, then these activation
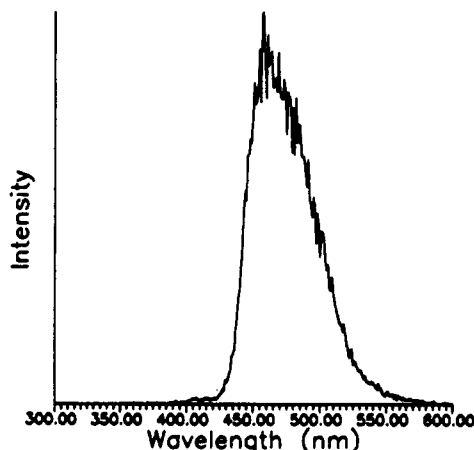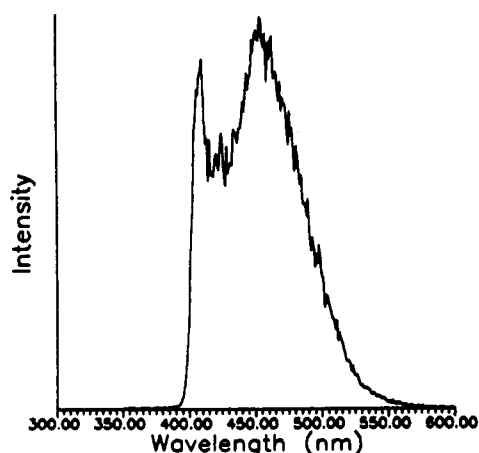

Figure 5. Phosphorescence spectra of polystyrene doped with 12% TPA recorded at three different temperatures: top, 55 K; middle, 130 K; bottom, 180 K.
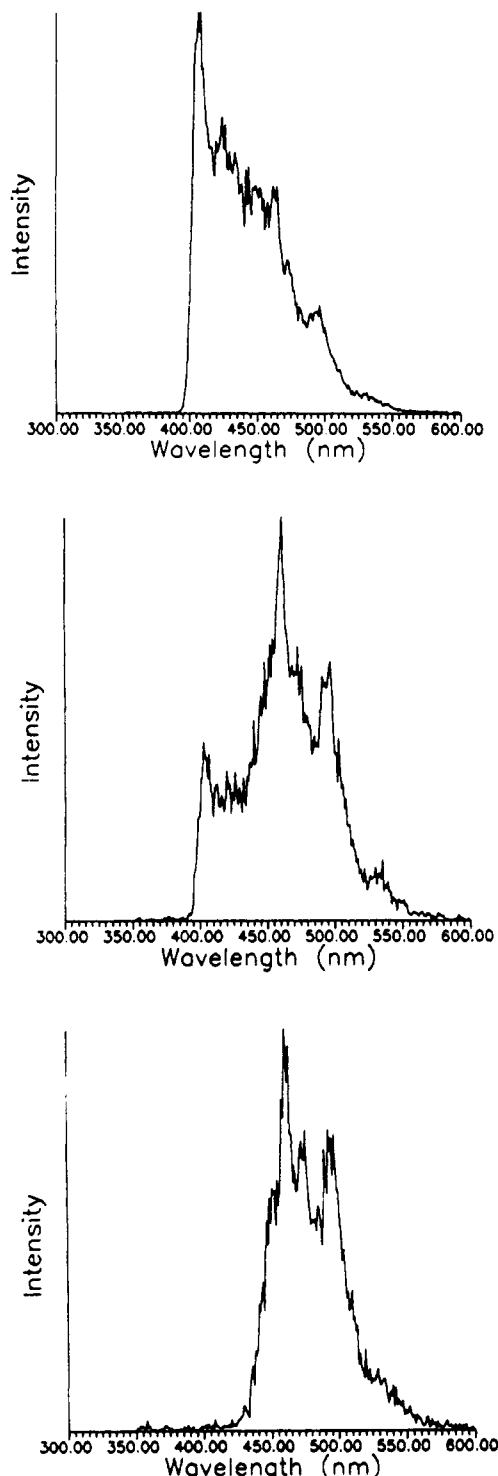
can only arise by energy transfer from TPA, is found to be present. As the temperature rises, the phosphorescence emission from TPA decreases gradually relative to naphthalene. In the temperature interval between 130 and 150 K there is a dramatic decrease in the TPA emission, and the zero–zero band of the naphthalene phosphorescence appears to be convoluted with the TPA triplet excimer band. An Arrhenius graph of the phosphorescence rate constant for TPA phosphorescence was prepared, and it shows the typical discontinuity at 128 K (this occurs also at 128 K for a 5% TPA sample containing no naphthalene) and an activation energy extracted from the steep part of the graph of 5.6 kJ/mol similar to that obtained in the absence of naphthalene. For samples containing smaller amounts of naphthalene relative to TPA, for example, 5 wt % naphthalene and 5 wt % TPA, no emission due to naphthalene is found. When larger naphthalene

Figure 7. Phosphorescence spectra of polystyrene doped with equimolar amounts of naphthalene and TPA recorded at different temperatures: top, 16.5 K; middle, 140 K; bottom, 185 K.

energies would instead be characterized as an average energy of those lattice phonons needed to assist the migration process. The following basic observations are those which the mechanism must be able to explain: (1) The temperature at which the discontinuity in the Arrhenius graph occurs coincides with the onset of excimeric phosphorescence. (2) The activation energy for excimer formation is effectively the same for PDAPM, 12% DAPM in polystyrene, and 12% TPA in polystyrene. (3) The activation energies found for excimer formation in the carbazole system are significantly different from those found for the triphenylamino chromophore. (4) The activation energies both for excimer formation and dissociation depend on dopant concentration in polystyrene matrices. (5) The monotonic decrease in activation energy for excimer formation with increasing DAPM concentration is matched by

a monotonic increase in activation energy for excimer disappearance. (6) The monotonic decrease in activation energy for excimer formation with increasing TPA concentration is matched by a monotonic decrease in activation energy for excimer disappearance. (7) For DAPM the activation energy for disappearance is always less than that for formation. For TPA just the reverse is true.

Observations 4–6 involving the concentration dependence of activation energies for excimer disappearance and formation are among the most interesting and reveal a great deal about the fundamental processes occurring here. On the basis of the competitive processes in eqs 1–3, it is clear that if the concentration of excimer-forming sites, $^1E_0$, decreases and if all other variables are held constant, then the specific rate constant for trapping must assume a larger value if trapping is to compete with first-order relaxation of T_m to the ground state. Therefore, the fact that the transition from nonexcimeric to excimeric phosphorescence occurs at a higher temperature as the dopant level decreases is easy to understand within the context of this mechanism. Less easy to understand is why the activation energy also increases in this same sense; however, this trend may very well be related to the nature of $^1E_0$ itself.

Although $^1E_0$ is symbolized as a distinct chemical species, it is doubtful that these excimer-forming sites all possess an identical structure. It is much more likely that some range of interchromophore distances and relative orientations are acceptable for the ultimate formation of an excimer. Initially, some thought was given to the proposition that the excimeric signal was a result of crystallite formation in the polymer matrix. The phosphorescence spectrum of crystalline TPA, however, suggests that if crystallites were present, then the excimeric signal should be found at 77 K. The data show, however, that this is not the case. Presumably the energy required for reorientation of the chromophore pair to a proper relative configuration for excimer formation constitutes what we call the activation energy. Thus, if there is a range of structures corresponding to $^1E_0$, it would be expected that a range of activation energies would also be found. In fact, it is likely that interchromophore separation distance is an important variable determining these activation energies.

In Table I it will be noted that minimum activation energies are observed for the most heavily doped matrices and for PDAPM. The remaining activation energies are, in general, higher. It is assumed that these cases represent a minimum-energy barrier for the process due to the high density of chromophores which, in turn, produces a large number of potential reactants near the optimum intermolecular separation distance for excimer formation. The remaining entries for DAPM are higher in energy, presumably because smaller fractions of the total dopant population possess this optimum configuration.

If this rationale for activation energies which vary with composition is accepted, then there must be a reciprocal argument to explain the decreasing activation energies for excimer disappearance with decreasing DAPM concentration. This effect is, in all probability, a manifestation of the rigidity of the medium in which these processes are occurring. The relaxation of internal energy modes of a newly formed excimer to their lowest energy configuration may require a rather large time interval in these matrices compared, for example, to a fluid solution. If dissociation of the species occurs before internal relaxation can take place, then the activation energy for the unrelaxed species will be proportionately smaller. To support this argument, it may be noted that the sum of the activation energies of formation and dissociation in the three different DAPM samples in Table I is essentially constant. This suggests that the increase in activation energy needed to form an unrelaxed excimer is balanced by the decrease in activation energy needed to dissociate it. This argument requires, of course, that the relaxation rate of the excimeric species be significantly larger than its lifetime. In the case of DAPM the lifetimes measured by luminescence decay are on the order of a few tenths of a second. Thus, internal relaxation of these species must be exceedingly slow, suggesting that higher energy configurations are essentially trapped.
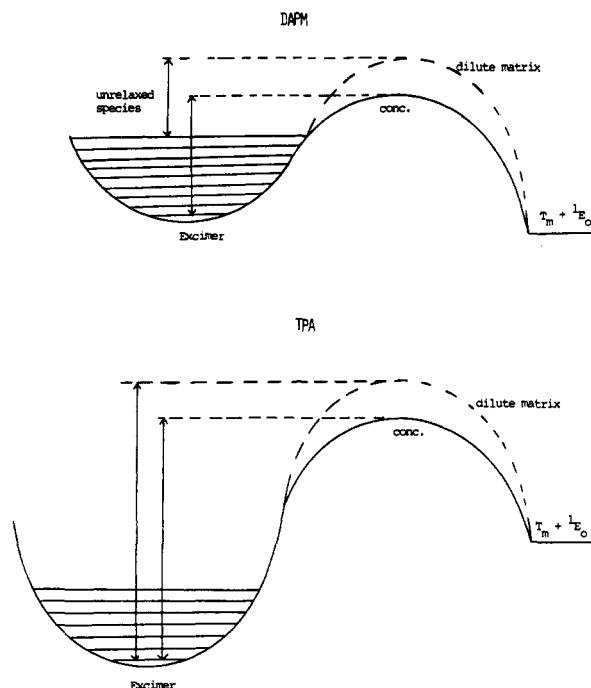
Figure 8. Model energy level diagram for excimer production in dilute and concentrated matrices of DAPM and TPA.

For films doped with TPA the effect of variable dopant concentration upon activation energies for excimer formation and dissociation differs from that found for DAPM. There is an increase in the activation energy for formation with decreasing dopant concentration which matches the observations made for DAPM. On the other hand, the activation energy for dissociation also increases with decreasing dopant concentration, and this effect is not consistent with the model just presented for DAPM which suggests that internal relaxation of the excimeric product is slow. Of course, the only difference between the two chromophores is the existence of the appended carboxylate group on DAPM. This carboxylate appendage is, in fact, a rather bulky group, and the rate of relaxation of excimeric TPA species may be significantly faster than DAPM. If a relaxed excimeric species is produced by the trapping process, then the barrier for detrapping is expected to grow in proportion with that for trapping. Energy level diagrams representing the DAPM and TPA cases are presented in Figure 8.

This simple interpretation for these activation energies for TPA may, in fact, require modification if the species formed upon detrapping is significantly different from the starting reactants. In either case the reactants are $^1E_0 + T_m$, but as mentioned above, the character of $^1E_0$ is averaged over the entire sample and is expected to depend upon the dopant concentration. If the matrix prevents significant internal rotational or large-scale vibrational motions in the excimer, then it is reasonable to suppose that dissociation would produce a $^1E_0$ species that is very similar to the starting one. If, on the other hand, these internal modes are not restricted, then the detrapping process may produce a chromophore pair in which the relative spatial orientation of the two species is significantly different from the initial one. In this latter case it would have to be said that the excimer formation and dissociation is not, in a formal sense, an equilibrium process, and in this event the diagram of Figure 8 has no validity.

This rationale for the observed activation energies has been discussed within the framework of a mechanism assuming that exciton migration is not the rate-limiting process. On the other hand, an attempt to explain the results assuming that the migration process is rate controlling is not very convincing. Such an explanation would require postulating the existence of excimer-forming sites such that the increase in trapping rate with increasing temperature would be due to a larger rate of energy migration toward these traps. An increase in activation energy for excimer formation with decreasing dopant concentration could then be

argued as being due to the increased average intermolecular separation distance. Although this explanation does seem reasonable, it is difficult to go further and explain the apparent connection between activation energies for trapping and detrapping.

Experiments carried out with naphthalene added as a quencher provide further evidence about the nature of the rate-controlling process in triplet excimer formation.[16] When equimolar amounts of naphthalene and TPA are present in a film, phosphorescence from naphthalene and from TPA is found at temperatures from 16 to 150 K. At 130 K and above, the naphthalene emission is considerably broader than would be expected for naphthalene alone, indicating that TPA excimer emission is convoluted with the naphthalene signal. Of course, the naphthalene emission must arise exclusively by energy transfer from TPA triplets. At temperatures from 150 to 241 K, TPA phosphorescence is very weak compared to the much stronger naphthalene and excimer phosphorescence.

The rate of TPA phosphorescence decay in a film containing equimolar amounts of TPA and naphthalene was determined from 16 to 223 K. The resulting Arrhenius graph is similar to that of Figure 3, yielding an activation energy of only 0.03 kJ/mol up to 128 K at which point the usual discontinuity is found. Since naphthalene phosphorescence is found over the entire temperature range, it is assumed that this small activation energy is due to quenching by naphthalene. The slope of the steep portion of the graph yields an activation energy of 5.6 kJ/mol, similar to that found for films containing only TPA. Since evidence for the excimer emission is found at temperatures of 130 K and above but not at lower temperatures, it is assumed that this larger activation energy is due to excimer formation. The excimers cannot be observed spectroscopically when the naphthalene to TPA mole ratio is as high as 3:2. Energy transfer from TPA triplets to naphthalene is undoubtedly an encounter-controlled process and occurs efficiently, even at 16 K. The Arrhenius data indicate that the activation energy for this process can be no larger than 0.03 kJ/mol. In terms of activation energies, therefore, the energy-transfer process is quite different from that involving triplet excimer formation. The distinction, we believe, is that the energy-transfer process is encounter controlled while that for excimer formation is not.

This conclusion is reinforced by referring to point 3 in our list of experimental observations. An earlier investigation of polystyrene matrices containing *N*-ethylcarbazole yielded an activation energy for excimer formation of 1.7 kJ/mol or about one-third that found for TPA and DAPM. To interpret these results, we have to describe in some detail how exciton migration could possibly be affected by the temperature of the rigid matrix. The mechanism proposed by Frank and Harrah[17] for thermal activation of exciton migration in polystyrene may be used for this purpose. Here it was assumed that low-frequency acoustic vibrations of the polymer chains modulate interchromophore separation distances. For a dipolar or Förster type of energy migration the rate is inversely proportional to the sixth power of these separation distances. For an electron-exchange mechanism there is an exponential dependence upon interchromophore separation. In any case the rate of energy migration is strongly dependent upon separation distance, and it is reasonable to expect that vibrational motion of the polymer chain will have a modulating influence. To be sure, the model of Frank and Harrah was meant for chromophores covalently bonded to the polymer chain but a mechanism of this sort may also apply to dopant molecules in these rigid matrices, especially for the low temperatures used here and for these rather large molecules which would have small bulk diffusion coefficients. Thus, one would expect the same acoustic vibrations to influence any of the dopant molecules that we have studied resulting in similar activation energies. Since we find significant differences between carbazole species on the one hand and triphenylamino species on the other, we conclude, once again,

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(16) The authors are grateful to a referee for suggesting this experiment.
(17) Frank, C. W.; Harrah, L. A. *J. Chem. Phys.* **1974**, *61*, 1526.

that rates of excimer formation are not controlled by rates of exciton migration.

If one accepts the interpretation provided for DAPM that more dilute samples give rise preferentially to the formation of a greater fraction of unrelaxed excimeric species, it might be thought that this effect should be reflected in spectral shifts for the corresponding phosphorescence. A difference in activation energies for dissociation of 2.3 kJ/mol would produce a spectral shift of 4 nm in this wavelength range. A careful examination of the band centers for phosphorescence indicates that a wavelength shift may be occurring, but the spectral resolution of these broad bands does not permit a firm conclusion. For three typical spectra of 12, 5, and 1% DAPM the band centers were found at 466, 467, and 463 nm. The uncertainties in these wavelengths are 2–3 nm and are larger as the dopant concentration decreases because of decreased signal to noise. Thus, a confirmation of these expected spectral shifts cannot be made with the present data.

A fundamental property of excimers is their dissociation on the ground-state potential energy surface. By combining activation energies for the formation and dissociation of the excimer with the photon energies for emission at the zero–zero band of the monomer, E_{00}, and the λ_{max} of the excimer, E_{ex}, one may evaluate the dissociation energy, D, for the excimeric species. Thus, from the relation $D = E_{00} + E_{act}(\text{formation}) - E_{ex} - E_{act}(\text{diss})$ one finds $D = 34.3$ kJ/mol for DAPM in polystyrene. This may be compared with a dissociation energy of 34.7 kJ/mol for the polymer PDAPM and with dissociation energies of 30.2 and 35.4 kJ/mol for the two triplet excimers of poly(N-vinylcarbazole).

Let us now turn to point 7 in our list of experimental observations having to do with a different pattern of activation energies for TPA and DAPM. For DAPM the fact that the activation energy for dissociation is less than that for formation indicates that the excimer is less thermodynamically stable than the independent triplet state. For TPA, on the other hand, the excimer is more stable than the independent chromophore. It is likely that this difference in relative stability is due to the greater steric requirements associated with the appended carboxylate group of DAPM. It can be inferred, therefore, that the structure of the excimer involves some close approach of the phenyl rings of the two components of the excimer. Additional insight about the excimer structure must be inferred from the fact that only excimeric luminescence is emitted from the crystal.

Unfortunately, due to the difficulty of obtaining single crystals without twinning, the crystal structure of triphenylamine is not known.[18] It is reasonable to assume, however, that the phenyl groups of any given molecule are in close proximity to the nitrogen atom of the neighboring molecule as is the case for triphenylphosphine.[19] The triplet transition of TPA is n,π* in character,[20]

and so for the isolated molecule some charge transfer from nitrogen to the aromatic rings will occur upon formation of the lowest triplet state. If the approach of each nitrogen atom in the crystal to the aromatic rings of the neighboring molecule is sufficiently close, it is likely that triplet excimer formation would occur by a similar n,π* process but, unlike the isolated molecule, this transfer is through space to the aromatic rings of the neighbor. Thus, the suggestion here is that stabilization of the excimer bond would arise by a charge resonance interaction between the nitrogen atom of one molecule and the aromatic rings of a neighbor. Perhaps by the use of additional structural modifications of these chromophores a more detailed influence of excimer structure may be made.

A great deal of controversy has arisen in recent years over the existence of triplet excimers of naphthalene in fluid solutions.[21,22] It has been suggested by Lim[23] that the sandwich type of configuration, suitable for stabilization of singlet excimers, is not necessarily a favorable configuration for triplet excimers. The results of the present investigation suggest that triplet excimers are formed between two chromophores which have a ground-state geometry that is a trigonal pyramid. The actual excimer structure is, of course, not known at this time, but if it is sandwichlike then it must be a very distorted one which may have an umbrella shape. Thus, this work appears to reinforce the view that triplet excimers may form in a variety of configurations determined by the individual circumstances of the parent molecule's structure and the character of its electronic transitions.

Conclusions

The rate-controlling process in the trapping of triplet excitons at excimer-forming sites in polystyrene matrices of TPA or DAPM is the formation of the excimeric bond rather than the rate of exciton migration. The appearance of excimeric phosphorescence in these matrices with rising temperature is a result of competition in rate between radiative relaxation of the independent triplet states on the one hand and the trapping of triplet excitons at a site favorable for excimer formation on the other. Excimeric species in a conformationally relaxed state are preferentially formed in matrices having a relatively high dopant level. A greater fraction of conformationally unrelaxed species is formed as the dopant level decreases, and their relaxation time is greater than their lifetime. A charge resonance interaction is proposed to account for the formation of triplet excimers in these compounds in which a nonbonded electron from a nitrogen atom interacts with the aromatic rings of a neighboring molecule.

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