An Investigation of Binding Energies of Triplet Excimers in Carbazolyl-Containing Polymers

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ABSTRACT: The temperature-induced interchange between nonexcimeric and excimeric phosphorescence of poly[*N*-[(vinyloxy)carbonyl]carbazole] (PFCZ) and poly[*N*-[(allyloxy)carbonyl]carbazole] (PACZ) solid films has been investigated from 20 to 240 K. In addition, polystyrene doped with either *N*-ethylcarbazole (NEC) or *N*-(carboethoxy)carbazole has been studied. Activation energies for trapping of triplet excitons at excimer-forming sites in the matrix are all small, between 1.1 and 2.6 kJ/mol, and nearly the same for all of these carbazole species. On the other hand, activation energies for detrapping are much larger for the doped polymer films and for PACZ than for PFCZ or for poly(*N*-vinylcarbazole) which had been investigated earlier. The rate-determining step in triplet excimer formation apparently involves atom and electron rearrangement associated with bond formation as opposed to the translation of the mobile triplet exciton or internal rotations associated with the polymer chain. It is concluded that steric freedom of the reacting chromophore pair leads to excimers in a relaxed configuration whereas more restricted pairs produce excimers having a higher degree of steric strain.

Introduction

Polymeric molecules containing pendant aromatic groups often emit luminescence upon photoexcitation. The particular type of luminescence observed depends very much upon the physical state of the sample, the type of excitation used, and the time resolution of the monitoring system.[1] Prompt fluorescence, for example, can be observed at ambient temperature from such polymers either in solution or in the solid state. To observe luminescence emanating from the lowest triplet state, it is common to use reduced temperatures, which slow down potential quenching reactions and radiationless processes, and to employ rather long delay times (a few microseconds to hundreds of milliseconds) following excitation. Usually a temperature of 77 K is used due to the convenience of liquid nitrogen as a coolant. Under these conditions phosphorescence, and frequently delayed fluorescence, can be observed when a suitable time delay is inserted between the excitation pulse and the monitor pulse. Under low-temperature conditions, the delayed fluorescence observed is usually due to triplet–triplet annihilation[2] or to ion recombination[3] and it decays at a much faster rate than phosphorescence. Thus, by gradually increasing the delay time it is often possible to reduce the delayed fluorescence signal to a negligible level and to isolate the phosphorescence signal.

At 77 K the phosphorescence spectra of many vinyl aromatic polymers display spectral characteristics which depend markedly upon the environment. In rigid solutions of poly(*N*-vinylcarbazole) (PVCA)[4] or poly(1-vinylnaphthalene) (P1VN)[5] at 77 K, for example, a structured phosphorescence spectrum is observed with a distinct zero–zero band. The position of the zero–zero band is usually somewhat red-shifted compared with those of small-molecule analogues of the polymer-bound chromophore. Phosphorescence spectra of solid films of these polymers at 77 K usually have a completely different appearance.[6] In this case the zero–zero band is missing, the remaining structural features disappear, and the entire band envelope is greatly red-shifted. The species thought to be responsible for this structureless phosphorescence are triplet excimers.[7]

In the case of PVCA it has recently been found[8] that further cooling of the solid film sample to temperatures below 77 K causes a gradual reappearance of the structured phosphorescence and a disappearance of the excimeric signal. For this particular polymer the transition from nonexcimeric to excimeric phosphorescence occurs near 40 K and the phenomenon is entirely reversible. Judging from these experimental results, it has been concluded that triplet excimer formation requires a small activation energy. The activation energy for this trapping process was determined, and when combined with earlier activation energies for detrapping,[9] it was possible to provide an estimate for the binding energy of triplet excimers in PVCA.

This sort of behavior is not restricted to PVCA. Another polymer, poly[[4-(*N*,*N*-diphenylamino)phenyl]methyl methacrylate] (PDAPM), has recently been investigated in this laboratory and found to display primarily a nonexcimeric phosphorescence between 8 and 60 K and primarily an excimeric phosphorescence above 60 K.[10] In addition, the monomeric analogue of this polymer, the [(*N*,*N*-diphenylamino)phenyl]methyl ester of 2-methylpropanoic acid (DAPM), as well as triphenylamine (TPA) have been investigated in polystyrene films.[11] In each of these cases a structured monomeric type of phosphorescence was found at sufficiently low temperatures which gradually shifted to a totally excimeric type of phosphorescence at more elevated temperatures. Arrhenius graphs of the rate of decay of both excimeric and nonexcimeric phosphorescence are discontinuous as was found for PVCA, and activation energies for trapping and detrapping have been evaluated for these systems featuring the triphenylamino group.

Behavior similar to that just described for PVCA and the triphenylamino chromophores had also been noted in much earlier work on *N*-ethylcarbazole dissolved in a host matrix consisting of polystyrene.[12] In these studies rates of nonexcimeric phosphorescence decays were measured

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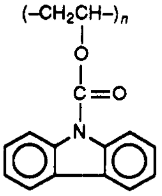
as a function of a temperature. Rates of decay of excimer phosphorescence were not measured, however, and spectra were recorded only at 77 K and ambient temperature.

Although the experiments using low temperatures promise to provide additional information about stabilization energies of triplet excimers, there is still very little known about the structure of triplet excimers in polymeric systems. Direct spectroscopic probes of triplet excimers have not, to date, been very successful. However, one indirect way to approach a solution of this problem is to evaluate the effects of chromophore structure on excimer stability. Yamamoto and co-workers have recently used such a method to study the relative stability of the two types of singlet excimers found in PVCA.[13] In their work *tert*-butyl groups were incorporated at the 3 and 6 positions of the carbazolyl ring with the result that the sandwich excimer is eliminated and the half-overlapped excimer is shifted to higher energy. Locke and Lim[14] have also investigated the effects of many structural variations of dinaphthyl compounds to assess the proposal that triplet excimers involving these chromophores are noncoplanar.

In the present work different types of structural modification involving the carbazolyl chromophore are undertaken. In this case poly[*N*-[(vinyloxy)carbonyl]carbazole] (PFCZ) (structure I) and poly[*N*-[(allyloxy)carbonyl]carbazole] (PACZ) (structure II) are the subject molecules. These particular molecules were chosen primarily because of the opportunity they provide to examine the effects of steric variables on the stability of triplet excimers. It has already been demonstrated that the placement of the electron-withdrawing carbonyl group adjacent to the carbazolyl nitrogen reduces the propensity for singlet excimer formation in PFCZ. On the other hand, the triplet-state spectroscopy of the carbazolyl chromophore appears to be essentially unaffected by this structural modification probably because the transition dipole for the triplet is perpendicular to the molecular plane. Thus, the effective electronic environment for the triplet-state transition is essentially the same for PVCA, PFCZ, and PACZ. On the other hand, the three polymers differ considerably in terms of steric freedom of the chromophore. Additionally, in the case of PFCZ, polymers synthesized using two different methods and having different degrees of stereoregularity will be examined. The experiments to be described in this paper will use low-temperature spectra and kinetics to provide activation energies for the formation and dissociation of triplet excimers formed in solid films of these polymers. Similar experiments will be described in which the monomeric analogue of the polymers is present as dopants in polystyrene films.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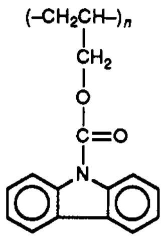
II

On the basis of these results and those obtained earlier on PVCA and PDAPM as well as the monomeric species NEC, DAPM, and TPA, it will be possible to arrive at several conclusions about structural features of chromophores which alter excimer stability and from these results inferences about the structure of the excimers themselves will be forthcoming.

Experimental Section

Polymer Syntheses. The synthesis of PFCZ by the introduction of the carbazolyl group into poly(vinyl chloroformate) has been described in earlier publications.[15] A number-average molecular weight for the polymer was deduced from that of the starting polymer and from the degree of substitution of carbazolyl groups for Cl groups. This polymer is known to be atactic as shown by ^{13}C NMR. A second sample of PFCZ was synthesized by free-radical polymerization of *N*-(carbovinyloxy)carbazole using 1.1 mol % AIBN at 83 °C for 5 h under vacuum conditions. The yield of the polymer recovered by precipitation in acetone was 57%. The number-average molecular weight was 46 000 as determined by GPC in THF using polystyrene of known molecular weight for calibration. Using ^{13}C NMR it was found that this polymer is not purely atactic. Judging from the steric demands of the carbazolyl group, it is assumed that syndiotactic sequences as opposed to isotactic ones are present.

The polymer PACZ has been prepared by free-radical polymerization of the corresponding monomer, *N*-(carboallyloxy)carbazole, which was performed in bulk at 100 °C, under vacuum, by using 3 mol % of *tert*-butyl perbenzoate (TRIGONOX C, Akzo-Chemie). After 64 h of reaction, the polymer was recovered by precipitation in *n*-hexane and then dried under high vacuum (yield $\approx$ 30%). A further purification involving a dissolution of the sample in methylene chloride, followed by a precipitation in acetone, gives a polymer which has a number-average molecular weight of 5000 and a polydispersity index of 1.2 as determined by gel permeation chromatography in tetrahydrofuran using a polystyrene calibration curve. Further details concerning the synthesis of the monomer and the polymer have been published elsewhere.[16]

Sample Preparation. Films of PFCZ were cast from methyltetrahydrofuran onto optically flat quartz plates. They were placed in a Petri dish with a cover and were allowed to air-dry to a clear film. They were then transferred to a vacuum oven and were evacuated overnight at 100 °C. The oven was allowed to cool to room temperature before the samples were removed. Films of PACZ were prepared similarly but benzene was used as the solvent.

The samples were covered by a second quartz plate before being 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.

Samples were also prepared consisting of polystyrene doped with monomeric analogues of the polymers. To prepare these samples, 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 hotplate/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. The sample was finally allowed to cool in the oxygen-free environment. Mounting in the cryoscopic system was accomplished as described above.

Spectroscopic Instrumentation. Spectra were recorded using instrumentation which was assembled from components, and three separate systems have been used in this work. In every case, sample excitation is accomplished by XeCl excimer lasers (either a Tachisto Model 401XR or a Questek Model 2110). The emission was focused onto the slits of a SPEX Model 1680B monochromator and was detected using an EMI 9789 photomultiplier. The photomultiplier signal was recorded using a Nicolet Model 12/70 signal averager or a LeCroy system consisting

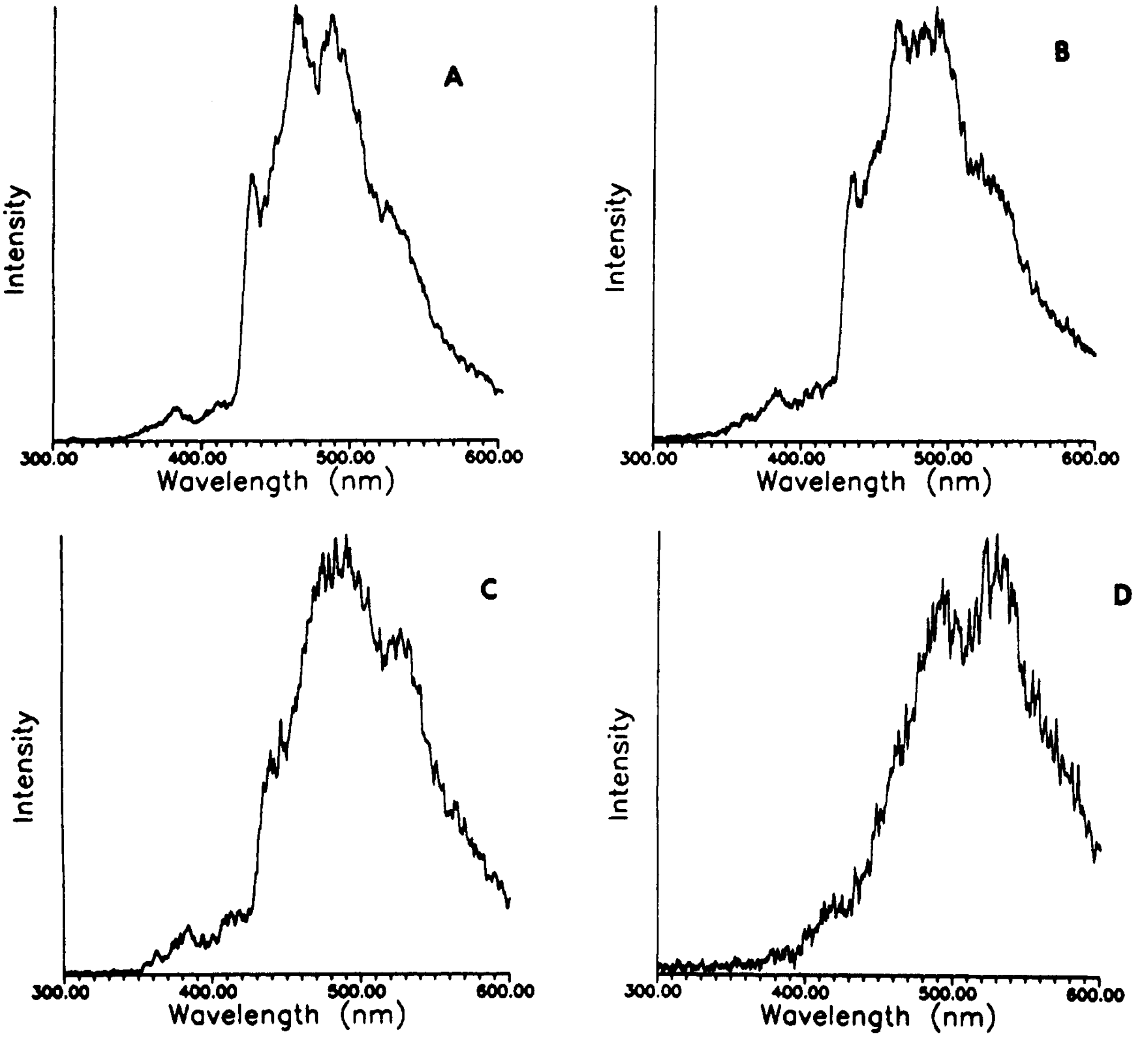

Figure 1. Phosphorescence spectra of PFCZ as a pure solid film at various temperatures. A delay time of 50 ms was used: (A) 15 K, (B) 25 K, (C) 40 K, (D) 94 K.

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 using 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 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

Figures 1 and 2 are phosphorescence spectra recorded at different temperatures for atactic PFCZ and PACZ, respectively. In each case, at the lowest temperatures used, the spectra possess the structured characteristics expected for the carbazolyl chromophore. In particular, the zero–zero band is clearly in evidence and occurs at 415 nm. As the temperature rises, the zero–zero band gradually disappears and there is a shift to the red of the center of gravity of the entire phosphorescence spectrum. For PFCZ, the zero–zero band has been reduced to a shoulder at a temperature of 43 K. Similarly, for PACZ the zero–zero band is essentially absent when the temperature reaches 43 K. Practically identical behavior was recorded earlier for PVCA, and so, apparently, this is a property typical of the carbazolyl chromophore. Temperature-dependent phosphorescence spectra of the partially syndiotactic PFCZ are essentially the same as for the atactic polymer.

For both PACZ and atactic PFCZ kinetic decays of the phosphorescence emission corresponding to the zero–zero band were recorded as a function of temperature. Again, the general behavior is the same for both polymers and is similar to that reported earlier for PVCA. The Arrhenius graph has a very small slope at the lowest temperatures used. As temperature rises, however, there is a temperature interval over which a discontinuity occurs so that a much larger slope is found in the higher temperature range. These results are presented in Figures 3 and 4. A similar type of Arrhenius graph was obtained for the partially syndiotactic PFCZ.

For these polymers it is clear that some additional channel for the disappearance of the triplet state is becoming available as the temperature goes through the transition range. It may be noted that the temperature corresponding to the transition range in the Arrhenius

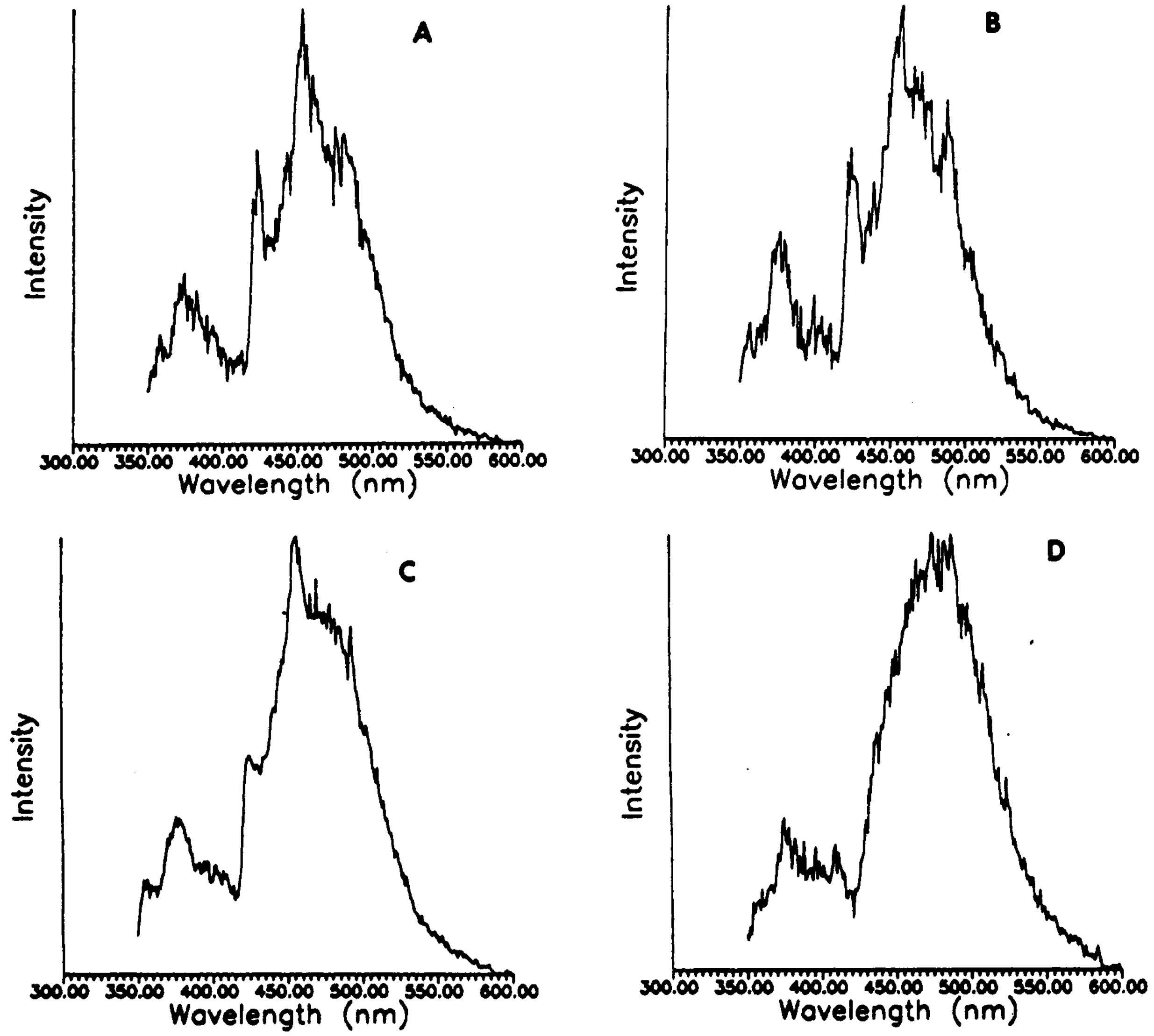

Figure 2. Phosphorescence spectra of PACZ as a pure solid film at various temperatures. A delay time of 50 ms was used: (A) 22 K, (B) 30 K, (C) 57 K, (D) 70 K.

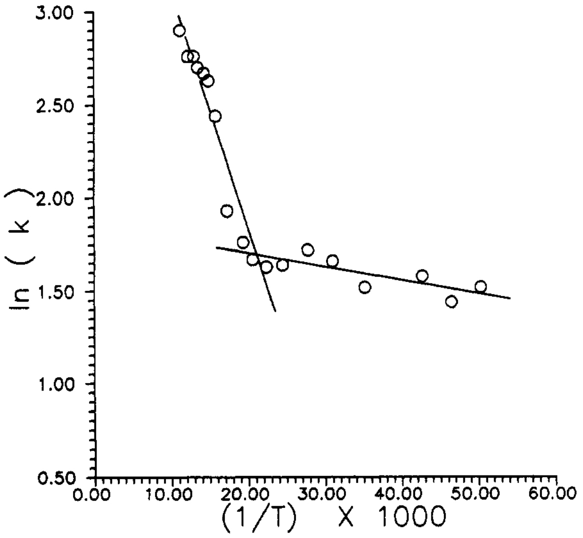

Figure 3. Arrhenius graph of the rate constant for the nonexcimeric phosphorescence decay of a PFCZ solid film.

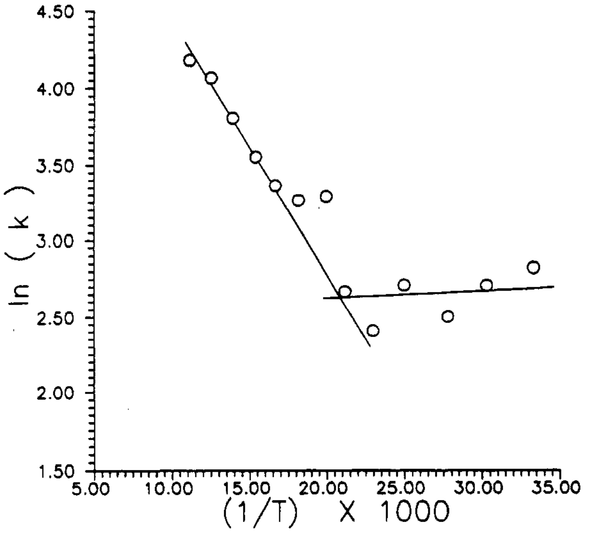

Figure 4. Arrhenius graph of the rate constant for the nonexcimeric phosphorescence decay of a PACZ solid film.

graphs is the same as that found for the switch from nonexcimeric to excimeric phosphorescence. The activation energies from the steep portion of the Arrhenius graph are 1.1 kJ/mol for atactic PFCZ, 1.2 kJ/mol for partially syndiotactic PFCZ, and 2.6 kJ/mol for PACZ. These activation energies are similar to the 2.5 kJ/mol found previously for PVCA. The temperature corresponding to the change in slope is 48 K both for PFCZ and for PACZ; these transition temperatures are only a few degrees higher than those observed previously for PVCA.

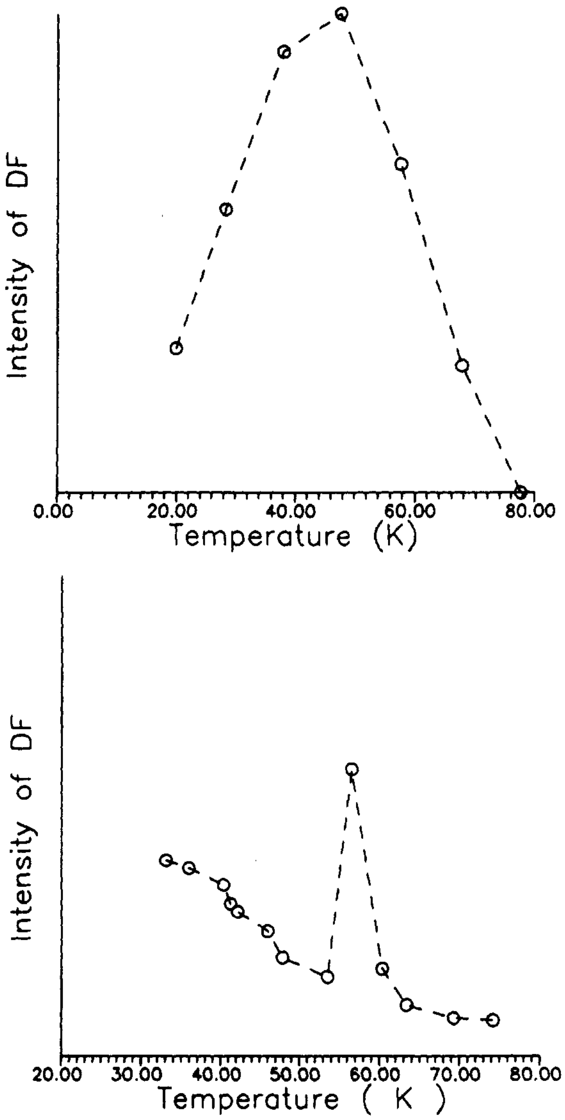

Figure 5. Delayed fluorescence intensity versus temperature for PACZ (upper) and PFCZ (lower) solid film.

Additional information about excimer/nonexcimer transitions can be obtained by investigating the effect of changing temperature on the intensity of the delayed fluorescence. Earlier work on PVCA showed the existence of a maximum near 40 K when the delayed fluorescence intensity is graphed versus the temperature. The graphs of I_{DF} (delayed fluorescence intensity) versus temperature for PACZ and PFCZ are presented in Figure 5. Here again one finds the expected maxima, one at 57 K for PFCZ and one at 48 K for PACZ. The fact that the discontinuity in the Arrhenius graph occurs at nearly the same temperature as the maximum in the plot of delayed fluorescence intensity versus temperature is further indication that a fundamental transitional process is occurring here. The character of the temperature dependence of PFCZ is unusual in that the maximum occurs over a very small temperature range. Furthermore, this maximum is superimposed on a background of declining DF intensity with increasing temperature. The origin of these singular features of PFCZ behavior is unknown at this time.

The effect of varying the temperature on the rate of decay of excimer phosphorescence is presented in Figures 6 and 7 for the two subject polymers. In these experiments the emission monochromator was set at 500 nm so that little contamination of the luminescence signal from nonexcimeric phosphorescence would occur. Again it is found that the Arrhenius graph for PFCZ exhibits a discontinuity, implying that a new channel for triplet excimer decay has become available near the transition temperature. The activation energy extracted from the steep portions of the curve is 1.4 kJ/mol for atactic PFCZ and 3.6 kJ/mol for partially syndiotactic PFCZ. For PACZ there was a greater degree of uncertainty in the evaluation of phosphorescence decay rates than in other systems we have studied. Because of this, two independent determinations of the activation energy were carried out. As is seen in Figure 7 there was an identifiable temperature range from 70 to 140 K over which the rate constants changed only by about 50%. From 140 to 180 K there was a change in rate constant by over a factor of 3. At temperatures above 180 K there was essentially no change in rate constant up to 250 K at which point measurements were terminated. The activation energy measured over the interval corresponding to the rapid rise in rate was 7.5 kJ/mol. The second determination yielded a similar pattern of behavior, but the measured activation energy was 4.5 kJ/mol. Thus, in Table I the average of these two measurements is recorded with a relative uncertainty of 25%. This value is considerably larger than any of those found so far either for PVCA or PFCZ.

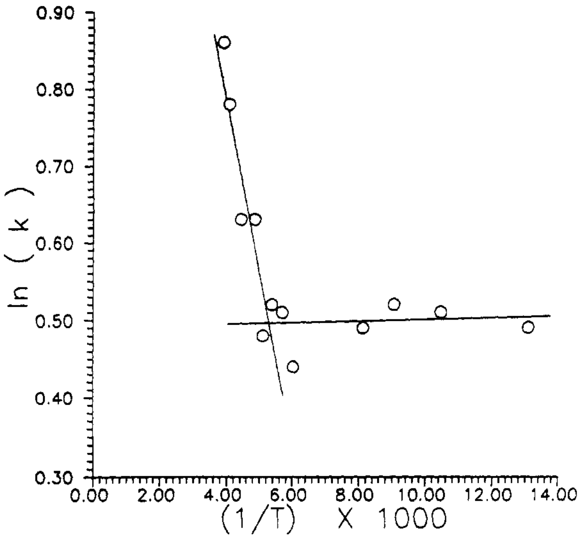

Figure 6. Arrhenius graph of the rate constant for the excimeric phosphorescence decay of a PFCZ solid film.

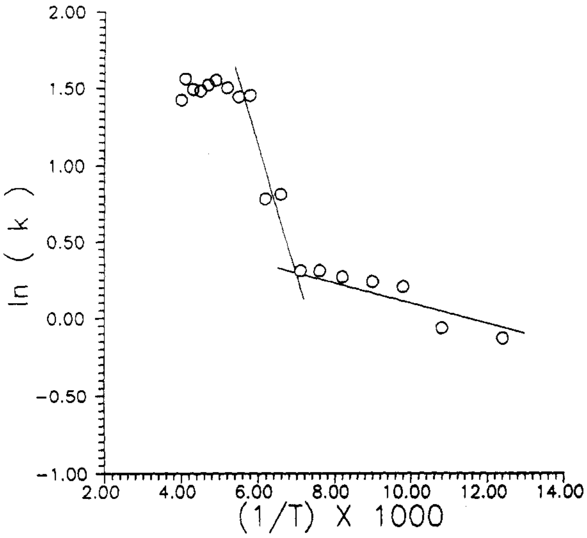

Figure 7. Arrhenius graph of the rate constant for the excimeric phosphorescence decay of a PACZ solid film.

Table I
Activation Energies[a] for Trapping and Detrapping of Triplet Excitons in Pure Polymer Films and Molecularly Doped Polystyrene

sample	E_{act}(trapping)	E_{act}(detrapping)
PVCA	2.0[b]	2.5[b]
PFCZ (atactic)	1.1	1.4
PFCZ (partially syndiotactic)	1.2	3.6
PACZ	2.6	6.0
NEC in PS[c]	1.7[d]	7.4
MFCZ in PS[c]	1.7	7.4

[a] Estimated errors in activation energies are ±10% except for PACZ whose estimated error is ±25%. [b] Taken from ref 8. [c] Polystyrene. [d] Taken from ref 12.

In order to test whether or not these phenomena are peculiar to polymer-bound chromophores, experiments were carried out on polystyrene films containing small-molecule analogues of some of these polymers. A suitable monomeric analogue for PVCA is *N*-ethylcarbazole, and earlier investigations of certain temperature-dependent photophysical properties of this compound in polystyrene films have already been carried out. The results may be briefly summarized by saying that at 77 K the phosphorescence spectrum of N-ethylcarbazole is a structured monomeric type of emission. At ambient temperature, however, the spectrum is a mixture of monomeric emission and excimeric emission. The excimeric phosphorescence is longer lived than the monomeric so that as the delay time after the excitation pulse increases the spectra approach a purely excimeric character. Thus, it seems that the behavior of molecularly doped films is quite similar to that of the pure polymer but the temperature range over which transitions from monomeric to excimeric character occurs is much higher for doped films.

In the present investigation NEC-doped polystyrene films have been reexamined. Both Arrhenius data and spectral data have been recorded. The activation energy found for the decay of the nonexcimeric emission is 1.7 kJ/mol, in good agreement with earlier work. For the decay of the excimeric phosphorescence the activation energy found was 7.4 kJ/mol, and this quantity had not been previously determined.

A suitable monomeric analogue for PFCZ is *N*-(carbethoxy)carbazole (MFCZ), and phosphorescence spectra for this compound as a dopant in polystyrene were recorded at different temperatures. Major phosphorescence bands are noted at 415, 440, and 485 nm. As with the pure polymers the entire band envelope shifts to longer wavelengths as the temperature rises and the relative intensity of the zero–zero band decreases monotonically. This band is still just visible at 226 K but does not appear in spectra recorded at higher temperatures.

The rate constants for nonexcimeric phosphorescence decay were recorded at various temperatures, resulting in the now familiar discontinuous Arrhenius graph and yielding an activation energy of 1.7 kJ/mol. The excimeric phosphorescence decays displayed similar behavior and yielded an activation energy of 7.4 kJ/mol.

Discussion

The first question which should be considered has to do with the origin of the activation energies observed. Furthermore, the question has to be discussed at two different levels of specificity. Excimeric emission is thought to arise by the interaction of a mobile triplet exciton, T_m, with a site in the polymer structure which, by virtue of its local configuration, is suitable for the formation of a trapped or excimeric species. The process may be represented as

$$T_m + {}^1E_0 \rightleftarrows {}^1M_0 + T_{tr} \qquad (1)$$

where ${}^1E_0$ is the trap site, T_{tr} is the trapped triplet, and ${}^1M_0$ is an ordinary ground-state chromophore. Of course, mobile triplet species may also disappear by simple first-order relaxation, either radiatively or radiationlessly, to the ground state.

$$T_m \rightarrow {}^1M_0 + h\nu/\text{heat} \qquad (2)$$

With this mechanism in mind then the question is whether or not the rate of step (1) is controlled by the diffusion of the triplet exciton or by some other process associated with the details of bond formation. It has been argued previously[8] that the rate of this reaction is controlled primarily by processes associated with bond formation. The reasoning involved depends to a large extent on the fact that a rather narrowly defined temperature range exists over which the phosphorescence spectra change from being primarily nonexcimeric to primarily excimeric. Furthermore, in every case examined to date, which are eight in number, the discontinuity in slope of the Arrhenius graph coincides with the central part of the temperature range where the spectral transition is occurring. In addition to these facts, the following additional experimental findings point directly to bond formation as the rate-controlling process:

1. Activation energies for excimer formation are similar for all carbazole-containing compounds examined to date independent of their environment (see Table I).
2. Activation energies of excimer formation for compounds containing the triphenylamino group are similar to each other but quite different from those for carbazole-containing compounds.[10,11]
3. The activation energy for triplet excimer formation in *N*-ethylcarbazole is the same when present as a dopant in polystyrene or in poly(methyl methacrylate).[17]
4. Experiments involving competitive reactions of exothermic trapping by a quencher versus triplet excimer formation indicate a considerably smaller activation energy for the quenching process.[11]

If the rate of trap formation were controlled by the rate of exciton migration and if the temperature dependence of this rate has its source in phonon assistance from the host lattice, then one would expect similar temperature dependences for any chromophore doped into a given host polymer such as polystyrene. The experimental results show that this is clearly not the case. For example, carbazole and triphenylamino groups have different activation energies in the same medium. On the other hand, the activation energy for triplet excimer formation should be dependent upon the medium if the rate of exciton migration is rate controlling. Again, this is seen clearly not to be the case. For example, carbazole groups show essentially the same activation energy for excimer formation in the homopolymer, in molecularly doped polystyrene and in molecularly doped poly(methyl methacrylate). Finally, since the rate of exothermic quenching is known to depend upon the rate of exciton migration, one would expect similar activation energies for quenching and for excimer formation if the latter is also dependent upon the rate of exciton migration. Once again, it is found that these expectations are not realized in practice. Thus, on the basis of current knowledge, it seems the preferred conclusion is that the rate of trapping is controlled primarily by the action of bond formation in the excimeric species. Using this hypothesis the interpretation of the discontinuities observed in all of the Arrhenius graphs can be based on the competition between reactions (2) and (1), with the latter representing a channel for relaxation of T_m species which becomes active at sufficiently high temperatures.

If bond formation is, in fact, the source of the activation energy for reaction (1), then more specific questions about the origin of the activation energy may be asked. For example, one potential source of activation energy is the energy input needed to achieve internal rotations about the carbon atoms of the chain backbone or about bonds associated with the pendant group. Another potential source of activation energy is the energy required to relocate atoms and electrons of the chromophore pair in order to achieve the configuration needed for a stable excimer. The activation energies for detrapping presumably would be associated with similar processes.

To aid in the following discussion all of the available data relating to activation energies for trapping and detrapping in carbazole polymer systems have been assembled in Table I.

Several trends found in Table I are worth pointing out. As indicated above, one may notice that the activation energies for trapping of all the carbazolyl chromophores are very nearly the same and all quite small. This similarity includes carbazolyl chromophores present as dopants in polystyrene. The implication is that the medium in which the chromophore finds itself is not very important in determining the activation energy for the trapping process. In particular, whether or not the chromophore is bound to a chain backbone appears to be irrelevant. Also, since greater steric freedom is available to the carbazolyl chromophore in PFCZ than in PVCA and even greater freedom is available in PACZ, it can be concluded that rotational motion about bonds of the pendant group must play a minor role in determining activation energies for trapping. In this regard, the similar activation energies of excimer formation for both atactic and partially syndiotactic PFCZ should be noted. Thus, for carbazolyl, the activation energy for excimer formation seems to be associated primarily with rearrangement of atoms and electrons of the chromophore itself and not with internal rotational motion of the polymer.

When one turns to consider the activation energies for detrapping, a different scenario emerges. Here one is struck by the relatively large values of E_{act} found for PACZ and for MFCZ and NEC in polystyrene. These values of E_{act} stand in sharp contrast to those found for PVCA and PFCZ. One characteristic which PACZ, MFCZ, and NEC share is a relatively large steric freedom for the chromophores. It is possible, therefore, that more stable excimeric species are formed under conditions favoring relatively free movement of the two species undergoing reaction. Conversely, one may suppose that the excimers formed in an environment conducive to large steric constraints of the chromophores are highly strained compared to those associated with more sterically relaxed environments. An alternative view that detrapping is an encounter-controlled quenching process is difficult to reconcile with the range of activation energies observed.

Table II
Dissociation Energies for Triplet Excimers on the Ground-State Potential Energy Surface

sample	E_{00}, kJ/mol	E_{max}, kJ/mol	E_B, kJ/mol	E_{diss}, kJ/mol	ref
PVCA (shallow trap)	281.3	250.6	0.5	30.2	8
PVCA (deep trap)	281.3	235.8	10.1	35.4	8
PFCZ (atactic)	275.9	242.9	0.3	32.7	this work
PFCZ (partially syndiotactic)	275.9	242.9	2.4	30.6	
PACZ	281.1	242.9	3.4	34.8	this work
NEC in PS[a]	290.6	249.4	5.7	35.5	this work
MFCZ in PS[a]	286.4	241.4	5.7	39.3	this work

[a] Polystyrene.

A further point which must be discussed has to do with the fact that the transition range for the conversion of phosphorescence spectra from excimeric to nonexcimeric character is quite different for homopolymer films versus molecularly doped polystyrene. In fact the transition temperature is much higher in the case of molecularly doped films. This fact can be understood by appealing to the kinetic mechanism represented by (1) and (2) and recalling that it is the competition between the rates of these two reactions which determines the temperature dependence of the spectra observed. The relative rates of these two processes may be defined by

$$\text{relative rate} = k_1[^1E_0]/k_2 \tag{3}$$

Presumably the population of potential excimer-forming sites is much larger for the homopolymer than for the molecularly doped polymer, but k_2 is expected to be substantially the same for either system. Thus, in order to achieve $\{k_1[^1E_0]\}_{homo} = k_1[^1E_0]\}_{mol\ dope}$, then it is necessary that $k_{1,mol\ dope} > k_{1,homo}$.

A final thermal property associated with excimers which should be considered is their dissociation energy on the ground-state potential energy surface. Here $E_{0,0}$ is the photon energy corresponding to the zero–zero band of the phosphorescence emission spectrum of the nonexcimeric species and E_{max} is the photon energy corresponding to a maximum in the phosphorescence emission spectrum of the excimer. The activation energy for detrapping minus that for trapping is labeled E_B. The dissociation energy of the excimer on the ground-state surface is therefore given by

$$E_{diss} = E_{0,0} - E_B - E_{max} \tag{4}$$

A summary of these derived energies is presented in Table II.

A few trends in these data are worth noting. In particular, it is interesting that values of E_B are generally larger for PACZ and the small-molecule systems than for PVCA (shallow) and PFCZ. This, of course, is a reflection of the larger activation energy for dissociation for these three species.

Conclusions

Homopolymers containing pendant aromatic chromphores generally have nonexcimeric phosphorescence spectra at sufficiently low temperatures in the solid film state. As the temperature rises a transition occurs in which the nonexcimeric emission disappears and the excimeric emission appears. The phenomenon can be consistently interpreted in terms of a competitive disappearance of mobile triplet excitons either by relaxation to the ground state or by trapping at an excimer-forming site in the polymer. Using activation energies for trapping and detrapping of the excimeric species, it is possible to establish binding energies of the triplet excimers involved. These binding energies are generally very small, on the order of a few kilojoules per mole, for the carbazolyl chromophore.

For small-molecule analogues of these chromphores present as dopants in polystyrene the phosphorescence spectra are nonexcimeric at sufficiently low temperatures but then undergo a transition to an excimeric emission with increasing temperature. The transition range for molecularly doped polystyrene films is much higher than for any of the observed homopolymers. Binding energies of triplet excimers in these doped polymer systems have also been determined using activation energies for trapping and detrapping.

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