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(27) Note that eq 24 and 31 are identical. We simply use eq 32 in place of eq 27 when the single-liquid approximation is assumed for *Y*.

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# Triplet Excimer Emission from Carbazolyl Chromophores in Polystyrene Matrices

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*Received March 6, 1984*

ABSTRACT: The delayed emission from polystyrene containing *N*-ethylcarbazole (NEC) and 1,3-bis(*N*-carbazolyl)propane (BNCP) shows no evidence of excimeric emission at 77 K but a distinct excimeric phosphorescence and fluorescence at 298 K. Although excimer fluorescence of BNCP and delayed excimer fluorescence of NEC have been reported earlier, the present work is the first report of triplet excimer emission from these species. A small activation energy of 1.7 kJ/mol was found to be associated with triplet excimer formation, thus explaining why no emission from these species has been observed at 77 K.

## Introduction

*N*-Alkylcarbazoles have frequently served as useful monomeric models in connection with photophysical studies of poly(*N*-vinylcarbazole) (PVCA). For example, fluorescence spectra of *N*-isopropylcarbazole (NIPC), 1,3-bis(*N*-carbazolyl)propane (BNCP), and 1,4-bis(*N*-carbazolyl)butane (BNCB) have been useful in establishing the excimeric nature of the PVCA fluorescence.[1-6] Recent elegant syntheses and spectral analyses of *rac-* and *meso*-2,4-bis(*N*-carbazolyl)pentane[7] have added significant credibility to the earlier proposals that two types of singlet excimers exist and that they correspond to a sandwich-like structure and to a half-eclipsed structure.

In view of the strong propensity for carbazolyl chromophores to engage in intramolecular excimer formation, it is curious that very little evidence has been uncovered in favor of intermolecular excimer formation for any of the *N*-alkylcarbazoles. Since it is now rather commonly accepted that solutions and solid films of PVCA emit fluorescence which is almost exclusively excimeric in character[8] and that the phosphorescence emission from solid films is also exclusively excimeric,[9] it is possible to use these emission spectra as standards against which one may test for the presence of excimeric emission in the *N*-alkylcarbazoles.

In these laboratories, an emphasis has been placed upon the triplet-state properties of various aromatic molecules present as dopants in polystyrene films. It has been noted, for example, that delayed excimer fluorescence is present as a very prominent emission in polystyrene films containing 1,2-benzanthracene.[10] It seemed likely that a dopant such as *N*-ethylcarbazole (NEC) might also display excimeric emission in polystyrene films. The advantage of using polymer films is that reasonably strong triplet emission signals can be obtained over a wide temperature range. In the experimental work which follows, it will be seen that this is, in fact, a critical advantage when one attempts to find and characterize excimeric emission.

## Experimental Section

**Chemicals.** *N*-Ethylcarbazole was obtained from Aldrich Chemical Co. It was purified by two vacuum sublimations followed by zone refining using 100 passes of the molten zone. The middle 75% of the original material was retained. High-purity 1,3-bis(*N*-carbazolyl)propane was supplied to us by Dr. G. E. Johnson of the Webster Research Center, Xerox Corp., Webster, NY. Polystyrene (Scientific Polymer Products) having an average molecular weight of $2.2 \times 10^4$ was purified by multiple reprecipitation using toluene as solvent and methanol as nonsolvent. Reagent grade toluene was purified by shaking with concentrated $H_2SO_4$ until no further discoloration of the acid layer occurred. After washing with water and dilute aqueous NaOH, the toluene was distilled from $P_2iO_5$, discarding the first and last 10% fractions. Methanol (reagent grade) was purified by first refluxing with and then distilling from $CuSO_4$, Ca shavings, and $AgNO_3$, respectively.

**Sample Preparation.** The sample films were prepared by first weighing and dissolving the required amounts of polystyrene and either NEC or BNCP in toluene. The solution was deoxygenated by purging with purified nitrogen gas in a glovebox for about 1 h. Then, still under nitrogen atmosphere, the solvent was slowly evaporated under constant stirring on a hot plate set at 180 °C until a molten solution had formed. The molten material was then deposited on an optically flat quartz disk. A similarly shaped disk was placed over the solution and pressure applied to remove all gas bubbles, thus forming a sandwich film. The disks were preheated to 180 °C prior to making the film and, once the film was made, it was allowed to cool to room temperature before being exposed to the atmosphere. In all cases of film preparation, the resulting films appeared visually to be quite uniform in thickness and were optically clear.

**Instrumentation.** The UV absorption spectra were recorded on a Cary 14 spectrophotometer. Fluorescence and fluorescence excitation spectra were recorded on a Perkin-Elmer (MPF-44A) spectrofluorimeter. Most of the delayed emission spectra and all luminescence lifetimes were obtained on a homemade spectrophosphorimeter described below. All spectra were uncorrected for either source output or detector response.

A schematic of the phosphorimeter used in this study is given in Figure 1. The instrument was constructed in the laboratory and was modified as necessary to suit the source of excitation, S. When the excitation source was a Hg–Xe arc lamp (Oriel Corp. Model 6140) with a maximum output of 1000 W, two choppers were used in order to create the necessary intermittent irradiation. The first chopper ($C_1$) was positioned in the exciting light beam and the second ($C_2$) in the emission beam. The choppers were driven by synchronous motors of various speeds, motors with speeds of 6, 30, 120, and 900 rpm being used during the course of this study. The choppers could be put in or out of phase by manually retarding one of them. The synchronous choppers enable the observation of the emission after the exciting light has been cut off and at the same time eliminate short-lived emission

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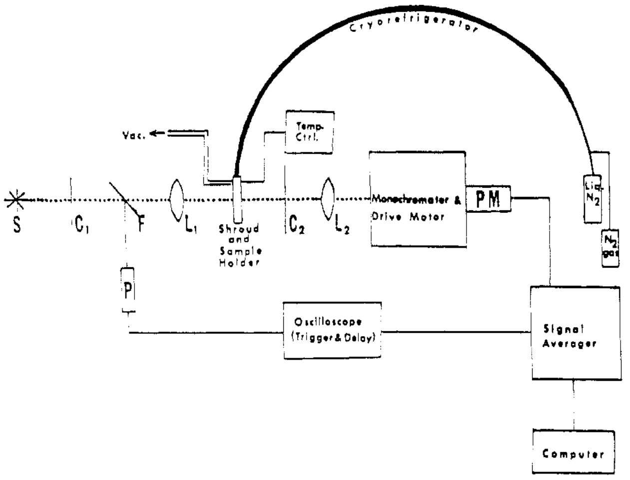

**Figure 1.** Schematic of the spectrophosphorimeter. The source is S, $L_1$ and $L_2$ are lenses, F is a light filter, $C_1$ and $C_2$ are mechanical choppers, P is an auxiliary photomultiplier activated in coincidence with the excitation pulse, and PM is the photomultiplier for luminescence detection.

and scattered light. In the course of a lifetime measurement, however, a slight amount of excitation light was passed along with the emission signal in order to determine the cutoff of the excitation light. The use of a pulsed laser beam for excitation eliminated the need for the emission chopper.

The laser employed during the course of this study was a rare gas halide excimer laser (Lambda Physik Model 101). It was operated with nitrogen gas mixed with a small amount of helium gas and delivered 337-nm light at pulse rates up to 70 pulses/s and 10-W average power. Henceforth, this laser will be called simply a $N_2$ laser. Slower pulse frequencies from the laser were obtained by means of a mechanical chopper driven by synchronous motors and phased to admit a constant fraction of the laser pulses.

A small portion of the excitation beam was directed to an auxiliary photomultiplier which provided a trigger pulse to initiate a luminescence measurement sequence. Generally this pulse was used to start a delay clock which, after a present delay time, sent a secondary trigger to a Nicolet Model 1072 signal averager. The luminescence signal was then recorded. When used in the spectral mode, this luminescence signal would be stored in a given memory channel and then the channel address moved forward one unit while the wavelength drive motor (Spex Model 1673 stepper motor) continued its forward motion. Between each excitation pulse a fixed wavelength interval is traversed and 255 pulses were used for a complete spectrum. In the kinetic mode, the trigger signal initiated a sweep of the 255 channels at some preset dwell time per channel. This yields a graph of intensity vs. time and multiple sweeps were generally employed in order to build an easily readable curve. The emission signal, after traversing a Spex Model 1670 monochromator, was detected by an EMI Model 9789 photomultiplier tube powered by a Brandenburg Model 472R power supply.

Spectral and lifetime measurements were carried out at various temperatures by means of an Air Products and Chemicals liquid transfer cryotip refrigerator Model LT-3-1101. The Cryorefrigerator consists of a liquid nitrogen transfer line and a cryotip to which the copper sample holder is mounted. The sample holder is surrounded by an indium gasket and is encased in a vacuum shroud bounded by quartz windows where necessary. The temperature of the sample was varied by means of a heater element (HK994) attached at the cryotip and also by adjusting the flow of the liquid nitrogen through the cryotip. Ample time was allowed for the stabilization of the sample temperature after each change. The temperature was measured by means of an iron-doped gold–chromel thermocouple on the cryotip and a potentiometer. Temperature regulation is easily better than ±0.5 K.

**Data Handling and Analysis.** All spectral and lifetime data were transferred to the university's CDC Cyber 730 computer. Locally developed computer programs for multiexponential decays and graphical displays were used. These have been described in earlier publications from the laboratory.[11]

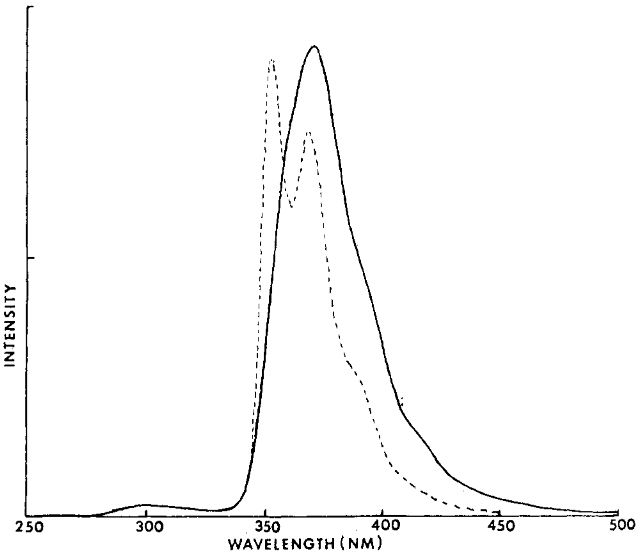

**Figure 2.** Fluorescence spectrum of $6.15 \times 10^{-5}$ M NEC in toluene (dashed line) compared with that of a polystyrene film containing NEC at 0.027 M.

## Experimental Results

Actually, several earlier photophysical studies on NEC in various physical environments had already been carried out before this work began. Yokoyama and co-workers recorded fluorescence spectra of NEC in fluid solutions and in the solid state.[12] For solutions which were 3 M and for the solid, the significantly red-shifted fluorescence maxima were said to be due to reabsorption, and no excimeric emission, even in the molten state, was said to be observed. A similar conclusion was reached by Kato and co-workers in a study of crystalline *N*-ethylcarbazole.[13] By contrast, however, a recent study utilizing laser excitation of fluid solutions of NEC yielded delayed fluorescence spectra which seem to possess a definite excimeric component.[14]

In Figure 2 is displayed a fluorescence spectrum of a $6.15 \times 10^{-5}$ M solution of NEC in toluene. Superimposed on this spectrum is another in which NEC is present at 0.027 M in a polystyrene film. Receall that these polymer film samples are only about 0.003 cm thick and that front-surface illumination has been used to minimize reabsorption. It is clear that the polystyrene sample exhibits the typical structureless and red-shifted emission usually associated with excimeric species. Even in the most dilute samples in polystyrene which we have studied it is the unstructured, red-shifted fluorescence emission which is predominantly found.

The conclusion that this emission is due to an excimer of NEC is supported by a comparison with a solution spectrum of PVCA. In Figure 3, a direct comparison is made between NEC at 0.027 M in polystyrene and PVCA in a toluene solution in which the concentration is $4.12 \times 10^{-5}$ M in chromophore units. Both of these spectra are clearly excimeric in nature but differ in the relative proportions of the low-energy and high-energy excimeric species. The shoulder of the PVCA emission at 400 nm indicates the presence of the sandwich type of excimer mixed with the half-eclipsed species. The NEC emission seems to be due primarily to the half-eclipsed excimeric species.

An excitation spectrum for the red-shifted emission of NEC in polystyrene is presented in Figure 4a. Major peaks are observed at 350 and 300 nm. These same peaks appear prominently in the absorption spectrum of NEC in polystyrene as seen in Figure 4b. It may also be noted

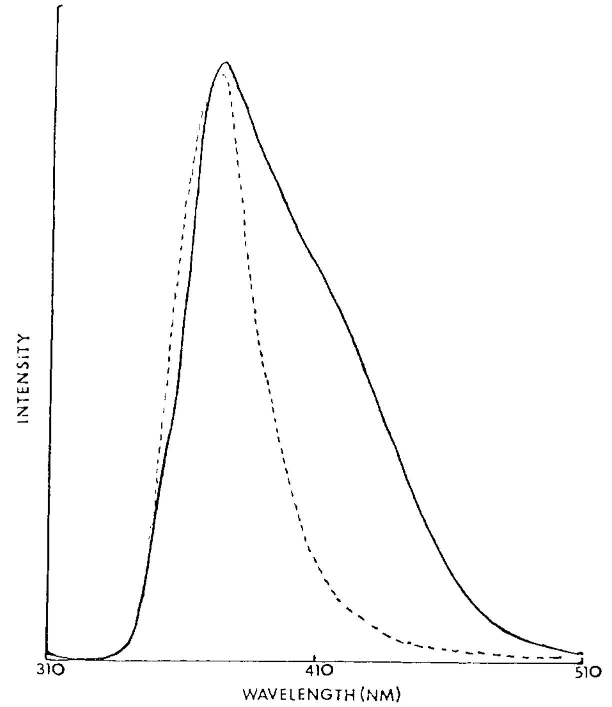

**Figure 3.** Fluorescence spectrum of 0.027 M NEC in polystyrene (dashed line) compared with that of PVCA in toluene solution, $4.12 \times 10^{-5}$ M in chromophore units.

that the absorption spectrum of NEC by Kato and workers[13] agrees well with that recorded here. The fact that the intensity ratios ($I_{300}/I_{350}$) are different for the excitation spectrum and absorption spectrum, respectively, is a reflection of the intensity dependence of the xenon excitation source of the MPF 44A. In view of these results, it seems quite clear that light absorption by NEC is the primary step leading to the excimeric emission.

Let us now turn to the triplet-state properties of these doped films. At 77 K, using a film that is 0.27 M in NEC, only the ordinary phosphoresence typical of the carbazolyl chromophore is observed along with a very weak emission between 350 and 400 nm, probably due to delayed fluorescence. Phosphoresence spectra recorded between 77 and 250 K are presented in Figure 5. It is apparent that the center of gravity of the emission band shifts to the red and that structural features become less distinct as the temperature is raised. For comparison, the phosphorescence spectrum at 298 K of 0.014 M BNCP in a polystyrene film is presented in Figure 6. The degree to which spectral features of the monomeric emission may be seen in the BCNP spectrum depends upon delay time following excitation; however, primarily the spectrum is strongly red shifted with an emission maximum at about 500 nm.

The phosphorescence spectra of BNCP and BNCB were investigated by Klöpffer and Fischer in frozen solutions of MTHF.[3] No evidence of an excimeric emission was found and similarly with NIPC, the single chromophore compound, no excimeric emission was observed. It is important to understand why the bichromophoric compounds do not form intramolecular triplet excimers in a frozen glass but do emit an excimer phosphorescence in a polystyrene matrix. The spectra of Figures 5 and 6 suggest that temperature effects are very important and these will be discussed in detail below.

Several phosphorescence spectra of polystyrene films containing NEC at 0.27 M are presented in Figure 7. Spectra in the upper part of the figure were recorded at 298 K and clearly demonstrate the more rapid decay of

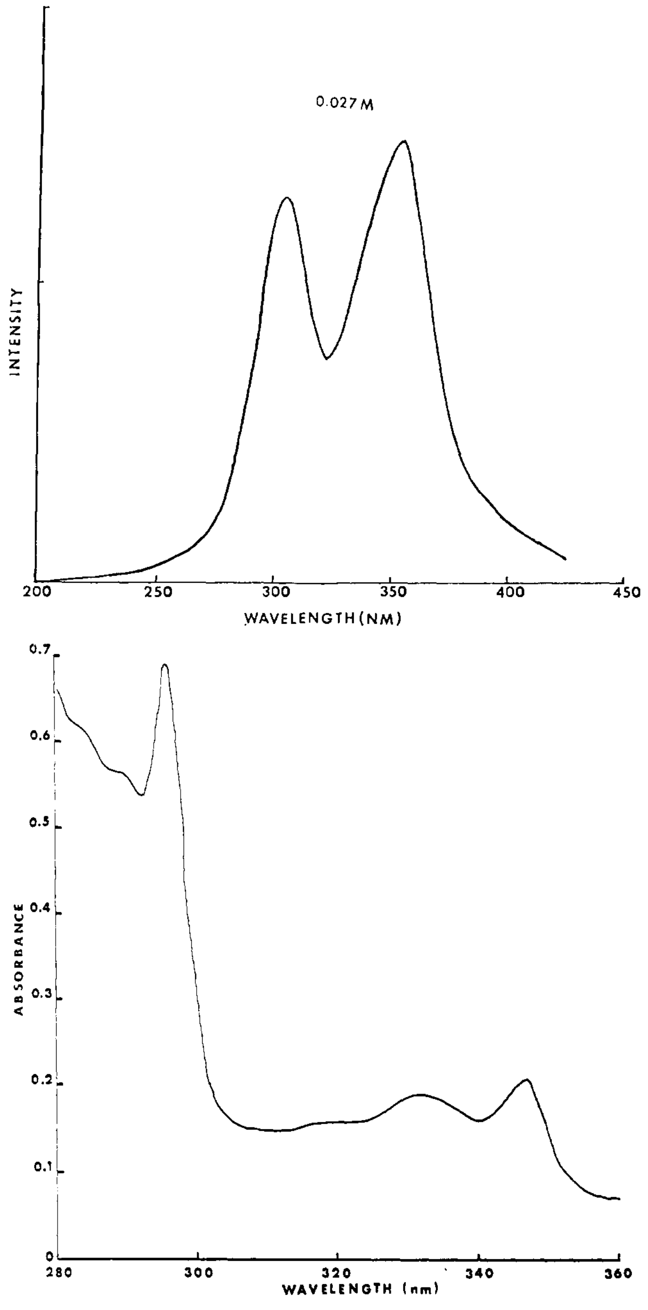

**Figure 4.** (a, Top) Excitation spectrum for the eximer fluorescence of NEC 0.027 M in polystyrene. (b, Bottom) Absorption spectrum for NEC 0.065 M in polystyrene.

monomeric phosphorescence leaving the excimeric species as the primary component at 200 ms after the excitation pulse. It is clear that BNCP and NEC behave similarly in that the emission signal which survives at 200 ms after the excitation is essentially identical for the two solutes.

In the lower portion of the Figure 7 spectra are presented which were recorded at 50 and 200 ms, respectively, after excitation. Except for the disappearance of the delayed fluorescence emission near 370 nm, the spectra are identical and no excimeric component is found. It may be noted that BNCP behaves exactly the same way at 77 K. It may be added that excitation spectra for all of these emissions agree with absorption spectra for NEC.

Let us now inquire further into the details concerning this excimeric emission, specifically with regard to the question of why it occurs in polystyrene films at 298 K but not in frozen glasses such as MTHF. Two mechanistic possibilities come to mind in an attempt to understand this temperature dependence. Let us use the symbol E to

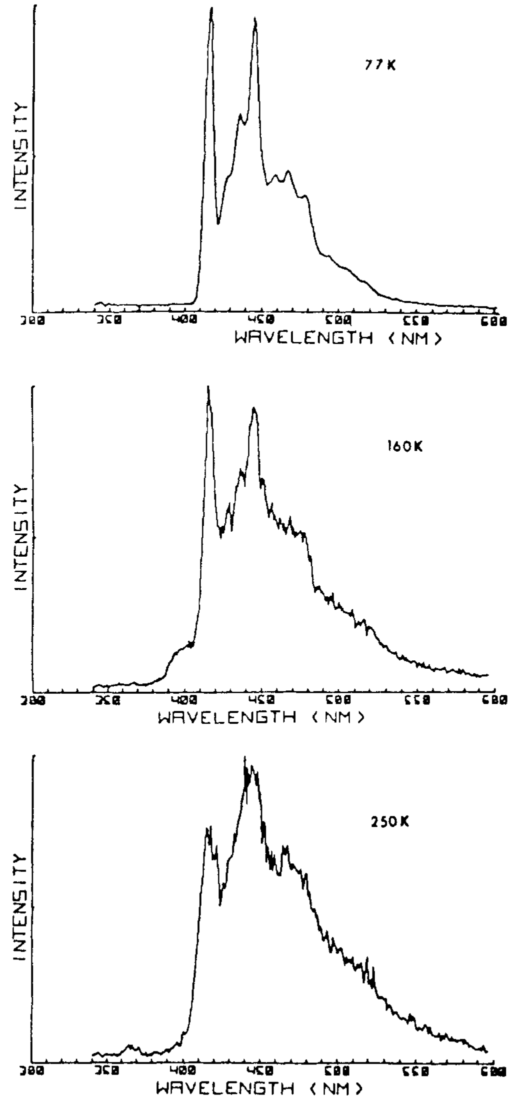

**Figure 5.** Phosphorescence spectra of 0.27 M NEC in polystyrene from 77 to 298 K. A 70-ms delay was used for each spectrum.

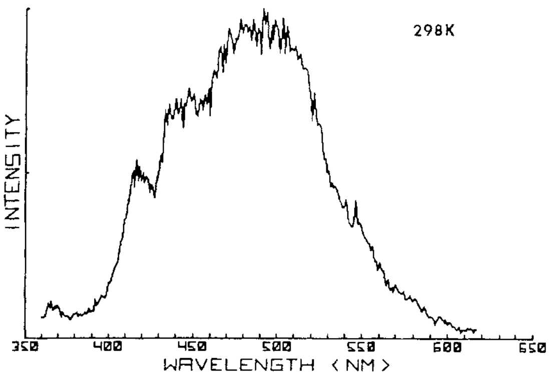

**Figure 6.** Phosphorescence spectrum of BNCP in polystyrene at 298 K.

represent a pair of NEC molecules in a relative geometric configuration such that they will form an excimer if one or the other of them receives the necessary electronic excitation energy. On the other hand, let us use the symbol P to represent a molecular pair in which the component molecules are sufficiently closely spaced but not oriented properly to be an E species. If P and E are separated by a small potential energy barrier then

$$\mathrm{P} + \text{heat} \rightleftarrows \mathrm{E} \qquad (1)$$

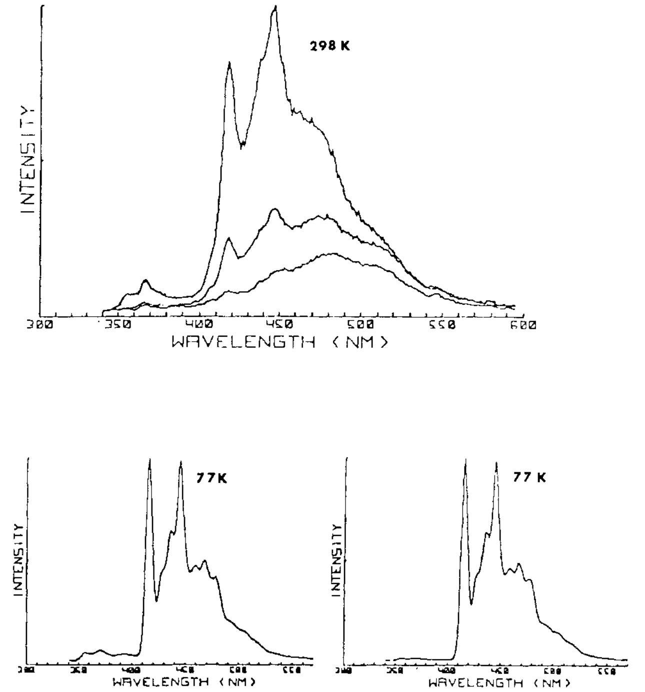

**Figure 7.** Time-resolved phosphorescence spectra of 0.27 M NEC in polystyrene. At 298 K, delay times are 50, 120, and 200 ms, respectively, for upper, middle, and lower spectra. At 77 K, delay times are 50 and 200 ms for left and right, respectively.

may occur producing more incipient excimeric sites as the temperature is raised. This is one possibility.

The other possibility involves recognizing that triplet energies of NEC and polystyrene chromophore groups differ by only about 16 kcal.[3,16] Thus, with increasing temperature, it is possible that the energy-transfer process

$$\text{heat} + \mathrm{T_n} + {}^1\mathrm{PS}^0 \rightarrow {}^1\mathrm{NEC}^0 + \mathrm{T_p} \qquad (2)$$

occurs where $T_n$ is the NEC lowest triplet and $T_p$ is the lowest lying triplet of polystyrene. Similarly ${}^1NEC^0$ and ${}^1PS^0$ represent ground-state NEC molecules and polystyrene chromophore groups, respectively. Following the energy-transfer process (2) a fast migration of triplet excitons along the polymer chain may occur

$$\mathrm{T_p} + {}^1\mathrm{PS}^0 \rightarrow {}^1\mathrm{PS}^0 + \mathrm{T_p} \qquad (3)$$

so that relatively large regions of space may be probed by these excitons. Excimer-forming sites would represent traps for these migrating excitons via the process

$$\mathrm{T_p} + \mathrm{E} \rightarrow {}^1\mathrm{PS}^0 + {}^3\mathrm{E}^* \qquad (4)$$

At the very large dopant concentrations used in this work (0.01–0.27 M) it might be expected that intermolecular triplet migration among solute molecules could play a significant role in the photophysical events. Thus, at 77 K the migratory process

$$\mathrm{T_n} + {}^1\mathrm{NEC}^0 \rightarrow {}^1\mathrm{NEC}^0 + \mathrm{T_n} \qquad (5)$$

could also provide a mechanism for probing large regions of space but it would not be expected to be particularly temperature dependent.

In fact, a simple experiment makes it possible to choose between the mechanistic possibilities of the thermally induced formation of E vs. a thermally assisted energy transfer from $T_n$ to ${}^1PS^0$. The lowest excited singlet state of NEC and polystyrene are so widely separated in energy that essentially no transfer process from ${}^1NEC^*$ to ${}^1PS^0$

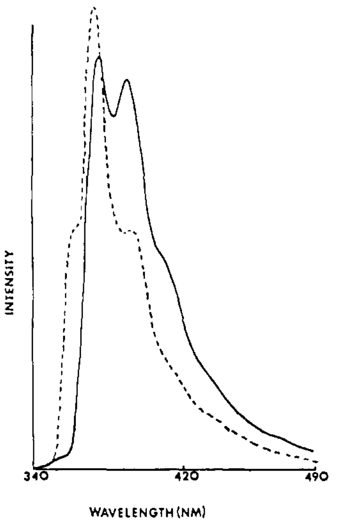

Figure 8. Fluorescence spectra of 0.27 M NEC in a degassed polystyrene film which has been pulverized (solid line, 298 K; dashed line, 77 K).

would be possible at the temperatures used in this study. However, it has already been demonstrated that the fluorescence emission at 298 K from polystyrene films containing NEC emit almost exclusively excimer fluorescence. If this singlet excimer emission also shows a temperature dependence, it cannot arise from a thermally assisted energy transfer and would then necessarily implicate a process of the type shown in eq 1.

To investigate this possibility, a film sample was prepared as usual but since it was necessary to use the commercial spectrometer, the sample had to be contained in a quartz tube rather than between quartz plates. Thus, when the solvent had boiled off in the glovebox, the molten polymer was allowed to solidify and it was then crushed to a powder and transferred to a 6-mm quartz tube fitted with a stopcock and ground glass joints for attachment to a vacuum system. It was removed from the glovebox with the stopcock closed and, after evacuation at $10^{-4}$ torr, the sample was sealed off with a hand torch. In Figure 8 are shown spectra of this sample at 298 and 77 K. Clearly there is a significant monomer fluorescence emission component at 77 K which is nearly absent at 298 K. Since both spectra were taken on the same sample, reabsorption effects, if any, would largely cancel out except for small differences which might exist due to line narrowing at 77 K. Thus, it appears that a thermal barrier to excimer formation exists, perhaps involving small relative rotational displacements of the molecular pair. The interpretation given to these experiments carries with it the underlying assumption that achieving the configurational requirement for triplet excimers involves no greater energy expenditure than that required for singlets. This assumption seems reasonable but has not, to our knowledge, been tested at this time.

The lifetime, $\tau_p$, of the phosphorescence signal emitted at 419 nm was determined at various temperatures. From the relation $k_p = \tau_p^{-1}$, a graph of log $k_p$ vs. $1/T$ was prepared and is presented in Figure 9. From 77 to 110 K, there is very little dependence of $\tau_p$ on temperature. Above 110 K, an activation energy of 1.7 kJ/mol is found. Radiative decay constants are temperature dependent only to the extent that the refractive index of the medium depends on temperature. Solid polystyrene would show a monotonic increase in refractive index, if any, over this temperature range and so the commencement of a temperature dependence at some intermediate temperature would be inconsistent with such an explanation of this result. Furthermore, at a temperature so far below its glass transition it would be surprising if the refractive index of polystyrene changes perceptibly in this temperature range.

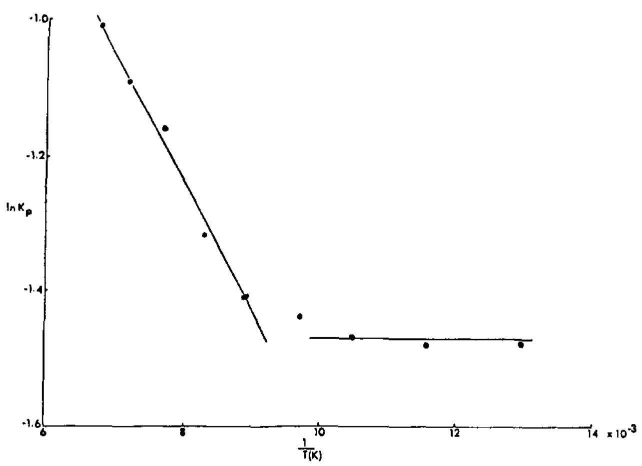

Figure 9. Arrhenius graph of log $k_p$ vs. $1/T$, $k_p$ being the reciprocal of the NEC phosphorescence lifetime.

A more plausible explanation of the Arrhenius plot is that some temperature-dependent process begins to compete with the radiative and radiationless decay at 110 K. We suggest that it is either the process described in eq 1 or else

$$^3P^* \rightleftarrows {}^3E^* \tag{6}$$

The analogous process for singlet excimer formation in BNCP was found by Johnson to be 10 kJ/mol. The sixfold smaller value found here may indicate that the triplet excimer configuration is more relaxed than that of the singlet as suggested by Okajima, Subudhi, and Lim.[17] Another possibility is that the triplet excimer requires only a half-eclipsed structure rather than a sandwich configuration.

## Conclusions

The phosphorescence emission resulting from polystyrene films doped with *N*-ethylcarbazole consists of both monomeric and excimeric components at 298 K. At 77 K, no clear evidence of excimer phosphorescence is seen. The bichromophoric compound BNCP behaves in a similar manner. The present work is consistent with previous observations showing that NEC and BNCP do not yield excimer phosphorescence in frozen glasses. There is a definite indication however that, with increasing temperature, closely spaced molecular pairs can achieve sufficient mobility to attain an excimeric configuration even in a rather rigid solvent such as polystyrene.

**Acknowledgment.** We thank Dr. D. A. Lightner for access to the MPF-44A spectrofluorimeter, Dr. A. H. Maki of the University of California, Davis, for helpful discussions, Dr. G. E. Johnson of Xerox Corp. for a gift of 1,2-bis(*N*-carbazolyl)propane, the San Francisco Laser Center operated under NSF Grant No. CHE 79-16250 for providing the lasers used in this work, and Ishmael Dawood for the spectra of PVCA. Support of this work by the Department of Energy under Contract No. DE-AS08-83ER45036 is gratefully acknowledged.

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# Sensitivity of X-ray Data to Sequence Distribution for Liquid Crystalline Copolyesters

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ABSTRACT: The sensitivity of X-ray diffraction data to monomer sequence distribution has been investigated for liquid crystalline aromatic copolyesters prepared from 4-hydroxybenzoic acid, 2,6-dihydroxynaphthalene, and terephthalic acid. The meridional intensity maxima in the fiber diagrams are aperiodic, and their positions are reproduced by calculating the theoretical diffraction patterns of copolymer chains, averaged over all possible monomer sequences. The monomer sequence distribution was varied from totally random to highly blocky by variation of the neighbor probabilities in the copolymer chains. For each of three monomer compositions it was found that the best agreement between the observed and calculated meridional data is obtained for completely random sequences and that all but minimal blockiness can be ruled out. Thus it appears that X-ray methods can be used to investigate the monomer sequence distribution of these relatively stiff copolymer chains and hence can provide information not currently available by more usual analytical techniques.

## Introduction

In recent years a number of thermotropic copolyesters with the mesogenic groups in the main chain have been reported in the literature (for a review see ref 1). These materials are of commercial interest in that they can be processed from the melt as self-reinforcing plastics or as high-strength fibers: the latter can have properties that approach those of Kevlar 49.[2,3] Interest is growing in the structure/property relationships of these copolymers, and other laboratories have published the results of investigations on their morphology and thermal properties.[4-7] In this laboratory we are using X-ray methods to determine the structure at the molecular level, and we have shown that, for two sets of wholly aromatic copolyesters, the fiber patterns are consistent with completely random monomer sequences.[8,9] The present paper describes further work on one of these copolymers, that prepared from 4-hydroxybenzoic acid (HBA), 2,6-dihydroxynaphthalene (DHN), and terephthalic acid (TPA), in order to investigate the sensitivity of the X-ray data to deviations from randomness, i.e., blockiness, in the monomer sequence.

The X-ray fiber diagrams of the copolymers of HBA/DHN/TPA (molar ratios: 60/20/20, 50/25/25, and 40/30/30) are shown in Figure 1. Schematics of the same X-ray patterns are shown in Figure 2. These data are characterized by strong diffuse scattering on the equator and some relatively sharp meridional maxima. In addition, within the diffuse intensity there are two sharp equatorial reflections at $d$ = 4.43 and 2.57 Å and one off-equatorial reflection at $d$ = 3.26 Å for all three compositions (see Figure 2). These data indicate a structure comprised of highly oriented chains that are poorly packed in the lateral direction, except that the equatorial and off-equatorial Bragg reflections point to the presence of some three-dimensional order. A very interesting aspect of the X-ray data is that the meridional maxima are aperiodic and vary in their positions with the monomer ratio. In particular, the intense doublet in the $d$ = 3.5–3.0-Å region becomes more separated as the HBA content decreases. This feature is inconsistent with extensive block copolymer character and the data were analyzed in terms of copolymer chains of random sequence. As a consequence of the 1,4-phenylene and 2,6-naphthylene linkages, the chains necessarily have relatively stiff, extended conformations. The meridional intensity is due to the projection of the chain onto the fiber axis, which will be approximately independent of conformation (i.e., of the torsional rotations about the aromatic–ester linkages). Initially the chains were modeled as linear arrays of points separated by the appropriate monomer lengths. It was shown that the positions of the meridional maxima are reproduced very accurately by a model with completely random monomer sequence.[8]

Although the point residue approximations give good agreement for the positions of the intensity maxima, the relative intensities could not be compared because the model did not allow for interferences between the scattering of the atoms of the individual residues. In later work, the calculations were extended to an atomic model for the chain and were shown to predict not only the positions of the maxima but also the relative intensities following refinement of the average orientation of the residues with respect to the fiber axis.[10] Figure 3 shows a comparison of the observed and calculated intensities for the doublet at $d$ = 3.5–3.0 Å. The same methods have been applied to copolymers of HBA and 2-hydroxy-6-

0024-9297/84/2217-2744$01.50/0