Macromolecules **1985**, *18*, 1277–1284 **1277**

(22) J. C. Giddings and K. D. Caldwell, in "Treatise on Analytical Chemistry", P. J. Elving, Ed., Wiley, New York, in press.
(23) M. E. Hovingh, G. H. Thompson, and J. C. Giddings, *Anal. Chem.*, **42**, 195 (1970).
(24) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY, 1953, Chapter 14, p 595.
(25) J. J. Gunderson, K. D. Caldwell, and J. C. Giddings, *Sep. Sci. Technol.*, **19**, 667 (1984).
(26) M. Martin, M. N. Myers, and J. C. Giddings, *J. Liquid Chromatogr.*, **2**, 147 (1979).
(27) J. C. Giddings, Y. H. Yoon, K. D. Caldwell, M. N. Myers, and M. E. Hovingh, *Sep. Sci.*, **10**, 447 (1975).
(28) F.-S. Yang, K. D. Caldwell, and J. C. Giddings, *J. Colloid Interface Sci.*, **92**, 81 (1983).
(29) J. C. Giddings, M. N. Myers, K. D. Caldwell, and S. R. Fisher, in *Methods Biochem. Anal.*, **26**, 79 (1980).
(30) J. C. Giddings, G. Karaiskakis, and K. D. Caldwell, *Sep. Sci. Technol.*, **16**, 725 (1981).
(31) C. Strazielle and H. Benoit, *Pure Appl. Chem.*, **26**, 451 (1971).
(32) L. K. Smith, M. N. Myers, and J. C. Giddings, *Anal. Chem.*, **49**, 1750 (1977).
(33) W. Mandema and H. Zeldenrust, *Polymer*, **18**, 835 (1977).

Spectroscopy and Triplet Photophysical Properties of Poly[*N*-((vinyloxy)carbonyl)carbazole] and Its Monomeric Analogue

Richard D. Burkhart* and Oksik Lee

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

Sylvie Boileau[†] and Sylviane Boivin

College de France, 75231 Paris, France. *Received November 12, 1984*

ABSTRACT: The triplet photophysical properties of poly[*N*-((vinyloxy)carbonyl)carbazole] (PFCZ) and of its monomeric model *N*-carbethoxycarbazole (MFCZ) have been investigated and compared with those of the widely studied poly(*N*-vinylcarbazole) (PVCA). Two distinct triplet excimeric emissions are observed in solid films of PFCZ. Phosphorescence spectra of PFCZ and MFCZ in rigid solutions are essentially the same as observed previously for PVCA and *N*-alkylcarbazoles, respectively. The fluorescence spectrum of PFCZ is significantly blue shifted relative to PVCA and, unlike PVCA, yields a structured emission both in solution and in the solid film state. In frozen solutions at 77 K spectral shifts of O_2-saturated vs. N_2-saturated solutions indicate the presence of a weakly bound singlet excimer. Phosphorescence lifetimes of PFCZ and MFCZ in rigid media are 6.2 and 7.0 s, respectively. The delayed fluorescence lifetime in solid films of PFCZ at 77 K is 3.5 s. The intensity of delayed fluorescence from PFCZ both in rigid solutions and in solid films depends upon the square of the excitation intensity and is thus thought to arise from triplet–triplet annihilation.

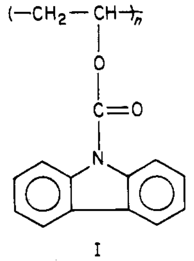
Introduction

Vinyl aromatic polymers demonstrate a strong tendency to form singlet excimers and emit fluorescence signals both in solution and in the solid film state which are characterized by a dominant excimeric component.[1] The phosphorescence spectra, on the other hand, generally are totally monomeric in character in solutions or rigid glasses and totally excimeric in character in solid films.[2] No polymer is more strikingly clear-cut in this regard than poly(*N*-vinylcarbazole) (PVCA).

It is easy to rationalize this strong propensity for excimeric emission in terms of relative conformational arrangements of two carbazolyl groups separated by three sp^3-hybridized carbon atoms. In fact, 1,3-di-carbazolylpropane has served as a useful monomeric model in unraveling the complexities of the photophysical processes of PVCA[3,4] and recent work has shown that *meso*- and *rac-d,l*-2,4-dicarbazolylpentane provide an even better model.[5,6]

In view of the technological importance of PVCA as a photoconductor and since the carbazolyl group is so versatile in its photophysical activity, it is natural to seek generalizations about the characteristics of this activity and several of these have been reported previously. For example, Houben et al.[7] studied fluorescence properties of a variety of carbazolyl-containing polymers, Beck et al.[8] studied singlet exciton trapping in two polymethacrylate esters which contain the carbazolyl group, and several research groups have examined the photophysical properties of PVCA prepared by cationic as well as free-radical polymerization.[9-11]

In the present work it is our purpose to investigate photophysical characteristics of a carbazolyl-containing polymer representing a significant structural departure from those examined to date. Poly[*N*-((vinyloxy)carbonyl)carbazole] (PFCZ) (structure I) possesses two interesting characteristics which make its investigation a matter of keen interest.



I

In the first place, the carbazolyl group is two atoms removed from the backbone carbon atom and thus enjoys greater steric freedom than it does in PVCA. In addition, and perhaps more importantly, the carbazolyl nitrogen is bonded directly to a carboxylate group having significant electron-withdrawing ability. The effects on luminescence properties of substitution at the nitrogen atom will be seen

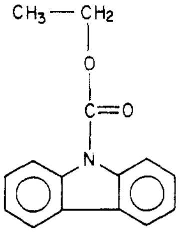
---

[†] Laboratoire de Chimie Macromoléculaire associé au CNRS, LA 24.

0024-9297/85/2218-1277$01.50/0

to be rather significant; in fact, Harvey et al.[12] have already shown that the wavelength corresponding to absorption to the first excited singlet state of several N-substituted carbazoles appears to depend upon mesomeric and inductive effects associated with the substituent.

In the present work an emphasis has been placed upon those photophysical properties associated with the triplet state including phosphorescence, excimer phosphorescence, delayed fluorescence, and delayed excimer fluorescence of the polymer in solution and in pure solid films. Singlet-state properties have been examined in an abbreviated fashion and only as an aid in interpreting the observations made on the longer lived delayed luminescences. In addition, a companion series of experiments was conducted on the monomeric analogue of the polymer *N*-carbethoxycarbazole (structure II).



II

Experimental Section

Chemical Syntheses. The monomeric model compound II is not new but the method of synthesizing it using phase-transfer catalysis is new and simpler than that previously described.[13]

Ethyl chloroformate (purity >99%, Societé Nationale des Poudres et Explosifs), carbazole (Fluka), tetrabutylammonium hydrogen sulfate (TBAH) (Aldrich Chemical Co.), and methylene chloride were used without further purification.

A solution of 0.02 mol of ethylchloroformate in 35 mL of CH_2Cl_2 was added under nitrogen to a stirred mixture of 0.01 mol of carbazole, 5×10^{-4} mol of TBAH catalyst, 1 mL of 50% aqueous NaOH, and 35 mL of CH_2Cl_2 at room temperature. The reaction was followed by TLC. After 2 h the volatile products (CH_2Cl_2 and ethyl chloroformate) were removed. The residue was extracted with diethyl ether and the solution was washed with water. The organic layer was dried with Na_2SO_4 and the crude carbamate was obtained after evaporation of the solvent. It was purified by recrystallization from ethanol: mp 76–77 °C. This value is in good agreement with the literature.[13] The yield of pure product is 70%.

The synthesis of the polymer was accomplished by chemical modification of poly(vinyl chloroformate) (PVOCCl). This polymer was prepared by free-radical polymerization of vinyl chloroformate in CH_2Cl_2 at 35 °C using dicyclohexyl peroxydicarbonate as initiator[14] ($\bar{M}_n = 17000$).

Carbazole (0.024 mol), 2 mL of 50% aqueous NaOH, and catalyst (1.25×10^{-3} mol of TBAH) were added to a stirred solution of 0.023 mol (2.5 g) of PVOCCl in 150 mL of CH_2Cl_2. The mixture was stirred at room temperature for 3.5 h. The progress of the reaction was followed by IR. When the carbonyl band of PVOCCl located at 1770 cm^{-1} disappeared, the mixture was filtered, the solution was washed with water, and the polymer was recovered by precipitation of the dried organic layer into petroleum ether. The polymer was then purified by several dissolutions and precipitations followed by drying under high vacuum. The yield of purified polymer was 65% and elemental analysis showed that the degree of substitution was at least 98%.

Since the polymer is not soluble in toluene, it was not possible to determine $\bar{M}_n$ by osmometry. An $\bar{M}_n$ of 38000 for the polymer may be deduced from the known molecular weight of the starting PVOCCl and from the degree of substitution. This polymer has been characterized by ^{13}C NMR and its thermal behavior has been examined.[15]

Sample Preparation. Luminescence data on the two subject compounds were recorded in methyltetrahydrofuran (MTHF) at 77 K. In addition, pure films of the polymer were cast from chloroform solutions and for some experiments the model compound II was dispersed in a polystyrene matrix.

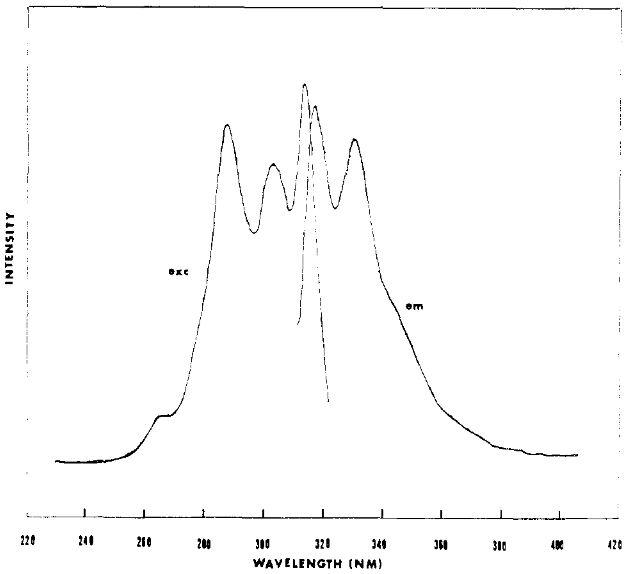


Figure 1. Fluorescence excitation and emission spectra of MFCZ in MTHF at 298 K. Solute concentration is 10^{-5} M.

The solvents used in the sample preparation were purified by distillation. In the case of MTHF the solvent was first passed through an activated alumina column and the distillation was carried out in the presence of $LiAlH_4$. Polystyrene used for matrix preparation either was a commerical material (Scientific Polymer Products) or else was prepared in the laboratory by using conventional free-radical polymerization. In either case the polystyrene was purified by multiple dissolutions and precipitations using toluene as solvent and methanol as nonsolvent. In no instance was there any noticeable effect on the results dependent upon the source of the polymer.

Samples of the pure polymer were cast on optically flat quartz disks from $CHCl_3$ solutions. They were allowed to dry slowly in an atmosphere nearly saturated with solvent and, in this way, very clear films were produced. Some of these films were treated further by heating overnight in a vacuum oven at 100 °C. Some were also treated by heating in a closed glass vessel using an oxygen-free and $CHCl_3$-saturated environment.

The model compound II was dispersed in polystyrene matrices by using techniques identical with those described in recent publications.[16]

Spectroscopic Instrumentation. All fluorescence spectra and some phosphorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrofluorimeter. The majority of the phosphorescence spectra and all luminescence lifetimes were recorded on an instrument built in the laboratory. It has been described in earlier publications;[17] however, it is worth repeating that excitation and emission pulses are produced by out-of-phase mechanical choppers and that signal averaging of luminescence decays and spectra are carried out with a Nicolet Model 1070 instrument. Data analyses were accomplished with locally generated programs using a CDC Cyber C-730 computer.

Experimental Results

Emission Spectra. Fluorescence excitation and emission spectra of the model compound II are presented in Figure 1. The expected mirror relationship is present in some but not all of the vibronic components of the fluorescence band and, as reported earlier,[12] it is interesting to note that the 0–0 energy of MFCZ is significantly higher than that of *N*-alkylcarbazoles. We find this energy to be 31750 cm^{-1} compared to 29000 cm^{-1} for *N*-ethylcarbazole.[20] Evidently the conjugated carbonyl group plays an active role in electronic excitation of this chromophore.

The phosphorescence spectrum of MFCZ is presented in Figure 2, wherein the medium was frozen MTHF at 77 K. This spectrum is identical, even reproducing minor

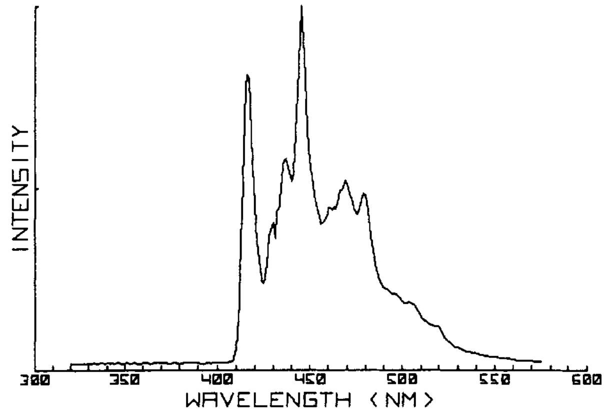


Figure 2. Phosphorescence spectrum of MFCZ in frozen MTHF glass at 77 K.

vibronic components, with that found for *N*-ethylcarbazole. Similar spectra but not as well resolved were found in polystyrene matrices. Thus, it appears that contributions from the carbonyl groups do not become mixed into triplet-state wave functions of MFCZ in sharp contrast to the singlet state. The net result is that a much larger energy gap exists between the first excited singlet state and the lowest triplet state of MFCZ than the analogous energy gap of *N*-alkylcarbzoles.

The fluorescence excitation and emission spectra of PFCZ are presented in Figure 3, a (298 K) and b (77 K). It is noted that a mirror-image relationship is observed between excitation and emission. In addition, a temperature-dependent intensity distribution of the vibronic components of the emission is found. Although the PFCZ fluorescence spectrum is certainly less well resolved at 298 K than either MFCZ or PFCZ at 77 K, the structure is still evident in contrast to PVCA solutions at 298 K. It was suspected that there might be a broad and red-shifted singlet excimer band present in the polymer spectrum but not observable as a separate component because of overlapping with structured emission of individual chromophore groups. If this were the case, it would explain not only the red-shifted fluorescence intensity distribution but also the poor resolution of vibronic components. Using a method employed previously to clarify the excimeric features of the fluorescence spectrum of carbazolyl chromophores,[4] we compared fluorescence spectra of PFCZ in oxygen-saturated and nitrogen-purged solutions both at 298 K and at 77 K. In fluid solutions at 298 K no change in the fluorescence spectrum was observed by this treatment; however, at 77 K there is evidence of oxygen quenching as seen in Figure 3b. One normally expects quenching processes to be much slower in frozen solutions because of decreased translational motion. The present experiments represent a reversal of this expectation; however, there are several reasons that one might expect such behavior in the present circumstances.

The absence of quencher-induced spectral changes at 298 K could arise from an accidental coincidence between excimer and excited monomer lifetimes. It could also arise from the existence of a very mobile equilibrium between excimeric and monomeric states or from the complete absence of an excimer species. On the other hand, a spectral shift induced by oxygen quenching observed at 77 K suggests that at this low temperature excimer species are indeed present. This result also suggests that of the three possibilities cited above to explain the lack of oxygen-induced spectral shifts at 298 K, the most likely is that the excimer formation–dissociation equilibrium is quite mobile. Quantitative determinations of the relevant rate constants must await appropriate lifetime measurements which we are not currently equipped to carry out. In any event, it is quite clear that this chromophore is much more reluctant to form singlet excimers than the carbazolyl group in PVCA.

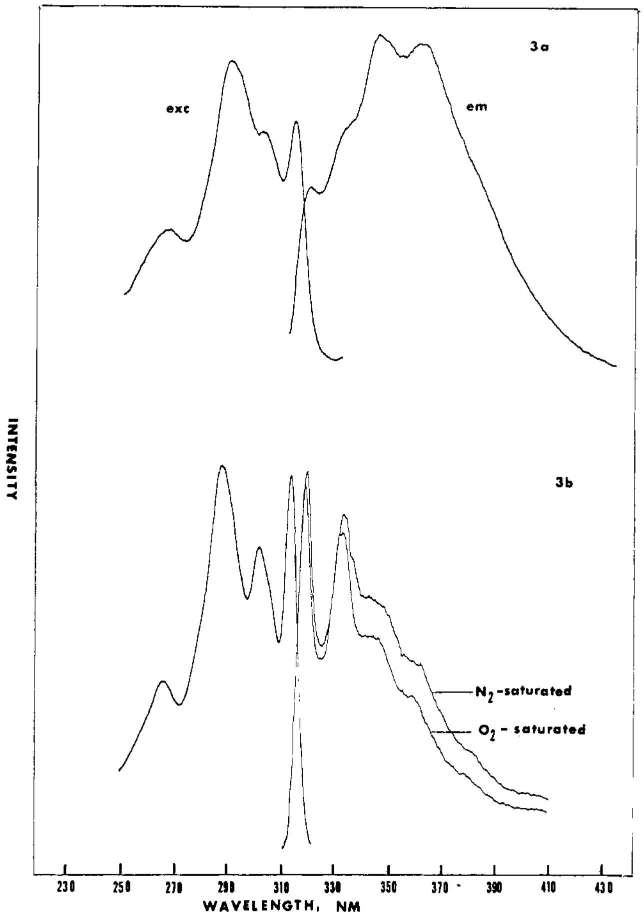


Figure 3. (a) Fluorescence spectrum of PFCZ, 10^{-5} M in monomer units, in MTHF at 298 K. (b) Same as in a but at 77 K comparing O$_2$- and N$_2$-saturated solutions.

The fluorescence excitation and emission spectra of a solid film of PFCZ at 298 K are presented in Figure 4. Once again, a marked contrast is noted between PFCZ and PVCA in that vibronic structure is still present in the PFCZ spectrum whereas solid films of PVCA emit an entirely excimeric fluorescence. Furthermore, in the PFCZ spectrum there is no emergence of the typical carbazole excimer bands at 380 and 420 nm thought to be due to half-eclipsed and sandwhichlike conformations, respectively, of the chromophore. The shoulder at 385 nm in Figure 4 also appears in the solution spectrum at 77 K and is probably a vibronic component. It bears no resemblance to the higher energy excimer band of PVCA.

It should also be recalled that the appearance of the fluorescence spectra of solid films depends to some extent on the orientation of the film with respect to excitation and emission beams. This, of course, is due to reabsorption effects. The spectrum of Figure 4 was recorded by orienting the sample at an angle of 45° to the excitation beam such that the illuminated side of the film faces the emission monochromator (front-side illumination). With back-side illumination the band near 325 nm is completely lost and the 350-nm component is greatly reduced in intensity.

In frozen solutions of vinyl aromatic polymers it is not unusual to find a structured phosphorescence spectrum sometimes accompanied by a delayed fluorescence emission. A relevant example is the spectrum of PVCA in

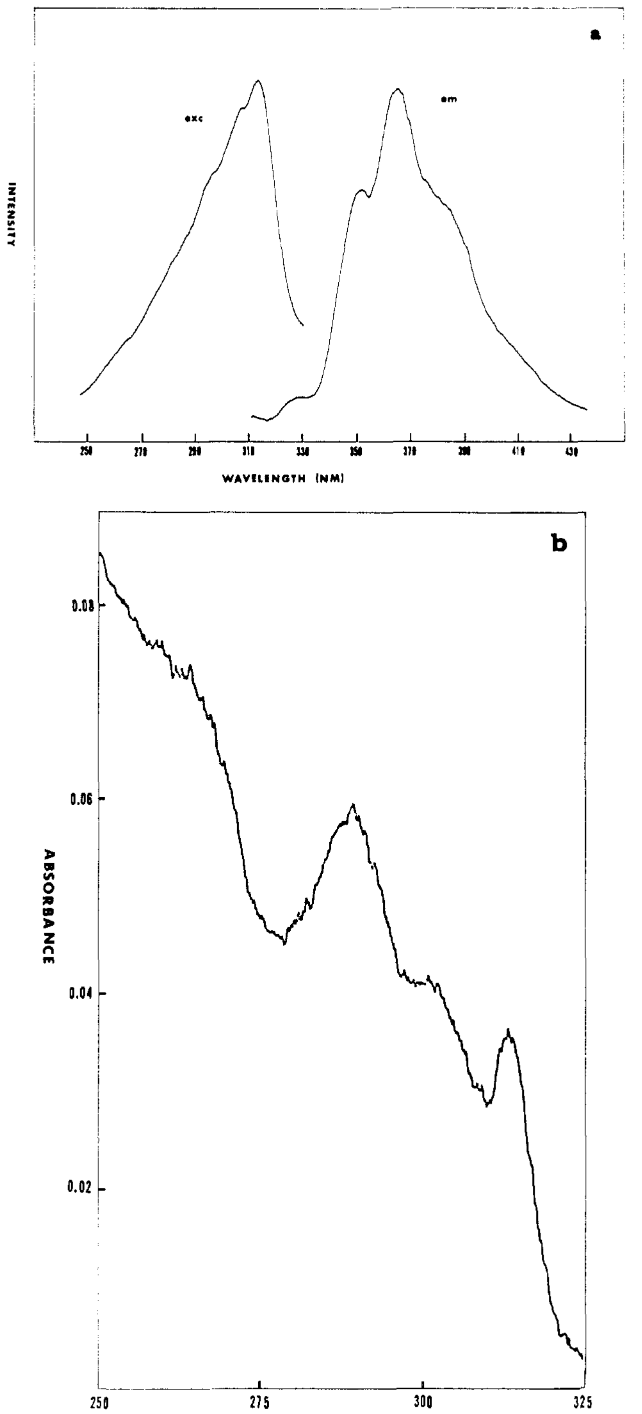


Figure 4. (a) Fluorescence spectrum of a solid PFCZ film on a quartz plate at 298 K. (b) An absorption spectrum of a thin polymer film.

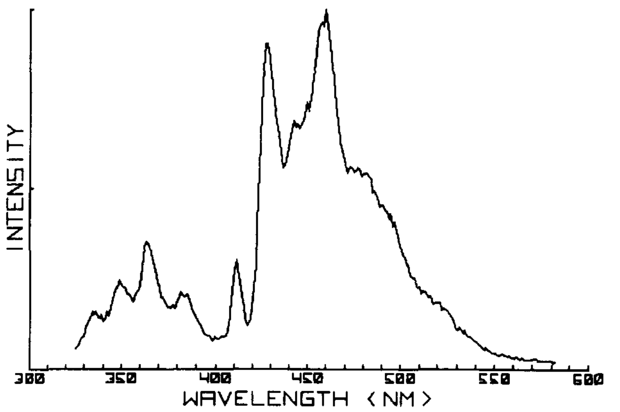


Figure 5. Phosphorescence spectrum of PFCZ, 10^{-3} M in monomer units, in MTHF frozen glass at 77 K.

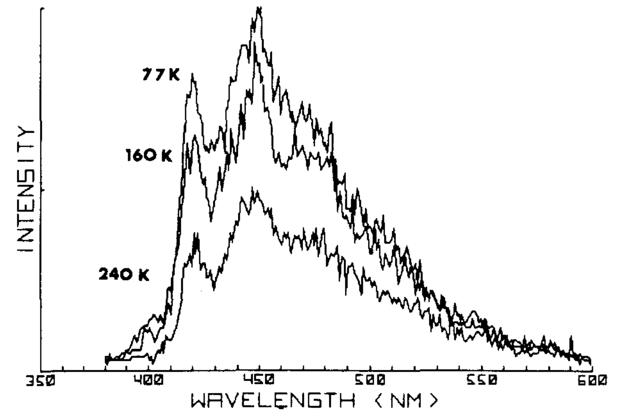


Figure 6. Phosphorescence spectrum of MFCZ dispersed in polysytrene (5 mg per 200 mg of polystyrene) at 77, 160, and 240 K.

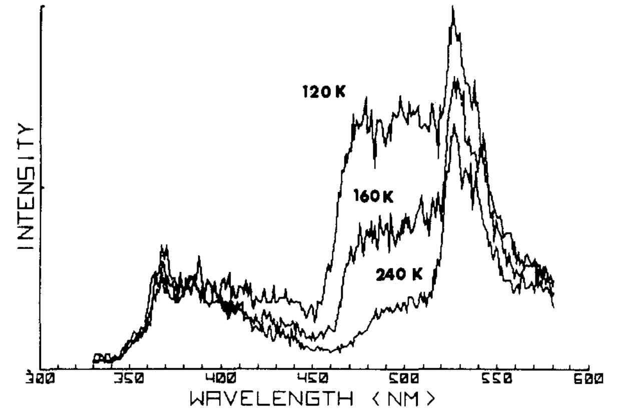


Figure 7. Phosphorescence spectra of a PFCZ solid film on a quartz plate at 120, 160, and 240 K.

frozen MTHF as reported by Klöpffer and Fischer.[2] A spectrum of this sort is also exhibited by PFCZ as is seen in Figure 5. The energy of the triplet-state 0–0 bands are found to be 24 750 ± 100 cm^{-1} for the polymer and 24 570 ± 100 cm^{-1} for MFCZ; that is, they are the same within experimental error. The two most remarkable differences between triplet-state spectra of MFCZ and PFCZ are the existence of the delayed fluorescence band between 340 and 400 nm in the polymer spectrum and the significantly reduced intensity of the 0–0 band emission for the polymer. It is noteworthy that reported spectra for frozen MTHF solutions of PVCA also show a reduced 0–0 band emission relative to the monomeric model compound (*N*-isopropylcarbazole in this case).[2]

In order to complete the picture of triplet-state luminescence of these formate derivatives we need to consider spectra from solid films of PFCZ and from polystyrene matrices containing MFCZ as a dopant species. A spectrum of the latter type is given in Figure 6 at 77, 160, and 240 K. It is seen to be essentially the same as spectra in frozen MTHF but with a nonstructured emission to the high-energy side of the 0–0 band. This structureless emission occurs at a wavelength corresponding to acetophenone phosphorescence and may be due to trace impurities in polystyrene or to acetophenone-like end groups formed by slight oxidative degradation of the polymer.

Probably the most remarkable spectroscopic behavior of the polymer is demonstrated in Figure 7. These are delayed emission spectra of pure solid films of PFCZ. Note that both phosphorescence and delayed fluorescence bands

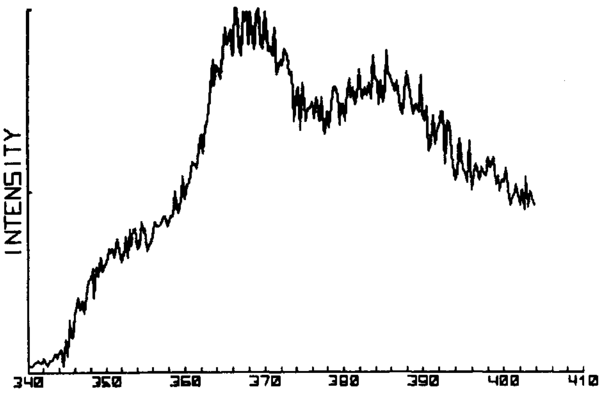


Figure 8. Detailed view of the delayed fluorescence emission from a PFCZ solid film at 77 K.

have been replaced by red-shifted emission signals and that the phosphorescence emission consists of at least two components. Neither the delayed fluorescence band nor the low-energy phosphorescence component demonstrates an appreciable dependence upon temperature and this is in marked contrast to the temperature sensitivity of the higher energy phosphorescence band. This type of spectroscopic behavior for the pure polymer film is completely in accord with that observed for other vinyl aromatic polymers wherein the red-shifted and structureless bands are attributed to excimeric emission. Evidently two distinct triplet excimers exist judging from the obvious two-component phosphorescence spectrum.

The delayed fluorescence band of the solid film is somewhat red shifted relative to the solution spectrum of either prompt or delayed fluorescence. Although it is tempting to ascribe this emission to delayed excimer fluorescence, the absence of prompt excimer fluorescence renders such an interpretation tentative at best. An alternate interpretation is that the apparent red shift of the delayed fluorescence band is due to preferential reabsorption of the emission at the high-energy isde of the emission band. It was not experimentally feasible to carry out phosphorescence spectra by using front-side illumination with available equipment. A high-resolution spectrum of the delayed fluorescence emission is presented in Figure 8. If one compares this spectrum to that of the prompt fluorescence of a solid film (Figure 4), it is clear that both spectra contain the prominent vibronic components at 350, 365, and 385 nm. The existence of this structured emission in the delayed fluorescence region is, to the best of our knowledge, unprecedented for solid polymer films. The clear result of using back-side illumination is that the band at 325 nm is lost and the 350-nm component appears as a weak shoulder. Thus, the role of reabsorption in altering the appearance of fluorescence spectra is significant in these examples and is probably responsible for the absence of high-energy components in the delayed fluorescence emissions.

Kinetic Features of Delayed Luminescence Signals. Phosphorescence lifetimes have been recorded at 450 nm for the model compound II in a polystyrene matrix over a range of temperatures. In every case the luminescence decay exhibited multiexponential behavior. The long-time component of the decay signal was fitted to an exponential form by using computer techniques described in earlier reports.[17] The lifetimes calculated in this way were found to be 7.0, 7.0, 6.6, and 7.0 s at the respective temperatures of 77, 120, 160, and 200 K. Thus, the phosphorescence lifetimes of MFCZ are remarkably resistant to changes in temperature.

Table I
Lifetimes of Luminescence Decays at 540, 480, and 385 nm and Various Temperatures for Solid Films of the Polymer PFCZ

temp, K	τ,[a] s		
	540 nm	480 nm	385 nm
77	2.3	3.4	3.5
160	2.7	4.2	*b*
240	2.0	*b*	*b*
298	1.4	*b*	*b*

[a] Uncertainties in reported values are ±10%. [b] Intensities too weak for reliable measurement.

Table II
Dependence, *n*, of Emission Intensities from Solid Films of PFCZ on Excitation Intensity at Two Different Emission Wavelengths and Various Temperatures

temp, K	n(385 nm)	n(535 nm)
77	2.0	1.1
160	2.1	1.1
240	2.1	1.0
298	2.1	1.1

Luminescence decay experiments for the polymer were carried out both on pure solid films and for frozen MTHF solutions at 77 K. For the latter case of frozen solutions, the phosphorescence decay for a solution of 10^{-3} M in monomer units yielded a good single exponential with a lifetime of 6.2 s. On the other hand, the delayed fluorescence decay approached single-exponential behavior only at long times following the excitation pulse and yielded a lifetime of 2.5 s. For dilute homogeneous solutions of small molecules under conditions of low excitation intensity one expects to find $\tau_{\mathrm{df}} = \tau_{\mathrm{phos}}/2$; however, it has frequently been observed that such is not the case for polymer solutions.[18] This will be discussed in more detail below.

Lifetimes for luminescence decays of the solid polymer film were measured at various temperatures and the data are collected in Table I. Here, the overall impression is that these lifetimes are not strongly affected by changes in temperature although it is noted that lifetimes at 160 K for both 540 and 480 nm are slightly larger than their respective lifetimes at 77 K. It is also interesting that there is no luminescence component of the solid polymer which is as long-lived as the phosphorescence of the model compound II or of the polymer in frozen solution. Thus, if single chromophore units are excited to the lowest triplet level, they are evidently efficiently quenched at excimer-forming sites or by impurities at a much faster rate than by radiative deactivation. If bimolecular processes such as this do, in fact, take place, then triplet-state mobility is clearly implied probably by a mechanism of exciton migration rather than by translational diffusion. Additional information on this point is provided by an examintion of the effect of excitation intensity (I_{ex}) on the intensity of delayed fluorescence emission (I_{df}).

Since delayed fluorescence emission is observed both from frozen solutions and from solid films of PFCZ, it was decided to examine the dependence of I_{df} on I_{ex} in both media. Luminescence spectra were run on frozen solutions of PFCZ in MTHF by using the MPF-44A instrument and employing different settings of the excitation slit. Then a graph of log I_{df} vs. log I_{phos} was drawn and the slope had a value of 1.9. Since it is normally expected that the phosphorescence intensity depends on the first power of the excitation intensity, then these results indicate that the delayed fluorescence from frozen solutions of the polymer depend upon the square of the excitation intensity. The implication, therefore, is that triplet–triplet annihilation is the source of the delayed fluorescence.

To examine the same question with a sample of the pure polymer film, emission intensities at 385 nm and at 535 nm were measured by using neutral-density filters to attenuate the excitation beam by known fractions. In this case the exponent, n, in the equation $I_{\mathrm{em}} = k(I_{\mathrm{ex}})^n$, where em is either df or phosphorescence, was determined by a log–log plot. The values of n found at various temperatures at the two indicated emission wavelengths are summarized in Table II. The conclusion that the delayed fluorescence at 385 nm is biphotonic in character, both in frozen solution and in solid films, seems inescapable. Furthermore, this emission most likely arises from triplet–triplet annihilation. If a competition were involved between an annihilative mechanism and E-type delayed fluorescence, that is, by a thermally activated reverse intersystem crossing from lowest triplet to first excited singlet state, then the n values at 385 nm would be expected to move toward 1.0 as the temperature is raised. Clearly this is not the case.

Discussion

Spectroscopic Features. The first excited singlet state of model compound II at an energy of 31 750 cm^{-1} above the ground state is 1450 cm^{-1} higher in energy than that of carbazole itself. Mataga and co-workers[19] have suggested that this electronic state contains a certain degree of charge-transfer character involving electron transfer from nitrogen to the aromatic rings. Thus, when the N–H hydrogen is substituted by an electron-withdrawing group such as the carboxylate group, the theory would indeed predict a shift to higher energy as is observed. Trends of this sort have already been reported by Harvey and co-workers[12] for a variety of N-substituted carbazoles.

The fact that the lowest triplet state of the model compound displays spectral characteristics nearly identical with those of *N*-alkylcarbazoles implies that charge transfer is not as important here. Furthermore, Johnson[20] has determined that the lowest triplet state of N-substituted carbazoles is predominantly polarized out of the molecular plane with only a small *Z*-axis (the short in-plane axis of the carbazole moiety) polarization. A lack of sensitivity of triplet-state characteristics to N-atom substitution is, therefore, understandable.

The fluorescence spectrum of PFCZ in solution is typical of a system of high-density randomly oriented chromophores in that sharp structural features are lacking. Unlike PVCA, however, there is no clear-cut emergence of a band (or bands) which could be attributed to excimers. Many authors have noted that excimer formation in PVCA is assisted by the special steric constraints imposed by the existence of the large carbazolyl group on every third backbone carbon atom. It is noteworthy, however, that even in a more relaxed steric environment such as in poly(2-*N*-carbazolylethyl vinyl ether)[21] a definite excimeric emission is found. Thus, even though steric effects are quite important, electronic effects probably also play a role in determining the propensity of excimer formation.

In the case of PFCZ, it has already been noted that the orientation of the transition dipole from the ground state to the first excited singlet state is opposed to the electron-withdrawing effects of the carboxylate group. It would therefore be expected that the dipole moment of the first excited singlet state of PFCZ (and also MFCZ) would be less than that of carbazole itself or *N*-alkyl-substituted carbazoles. Most theories of excimer formation have concluded that a mixture of charge resonance and exciton resonance can account for the binding energies observed.[22] It is likely, therefore, that a significant alteration in the dipolar character of the excited singlet state could influence this energy and, in the case of PFCZ, result in a significantly reduced excimer binding energy.

Even though this argument represents an admitted oversimplification of a complex process, it is interesting to pursue it one step further and apply it to the triplet state of PFCZ. Here, in the solid films one does find excimer phosphorescence. As noted earlier there is essentially no difference in energy between the lowest triplet states of PVCA and PFCZ presumably due, at least in part, to the orientation of the transition dipole perpendicular to the molecular plane. Thus, the dipolar characters of the lowest triplet states of PFCZ and PVCA are expected to be similar and, of course, both species form triplet excimers in the solid state in spite of the greater steric freedom of the chromophore in PFCZ.

Triplet Exciton Kinetics and Mechanisms. There are clearly two triplet excimer components in the delayed emission spectra of solid PFCZ films. Let us use the symbols $^1\mathrm{M}^0$, $^1\mathrm{D}^0$, and $^1\mathrm{E}^0$ to represent electronic ground states of individual monomer units and of potential excimer-forming sites, respectively. Furthermore, let us use the symbols $\mathrm{T_m}$, $\mathrm{T_d}$ ($\lambda_{\max}$ = 480 nm), and $\mathrm{T_e}$ ($\lambda_{\max}$ = 540 nm) to represent lowest triplet states associated with individual monomer units and with the two different triplet excimer states observed here having the indicated phosphorescence $\lambda_{\max}$ values.

With the formation of $\mathrm{T_d}$ as an example, three possible mechanisms can be envisioned for its formation. These are (a) trapping of a mobile singlet exciton followed by intersystem crossing of the singlet excimer, (b) trapping of a mobile triplet exciton, and (c) direct excitation of $^1\mathrm{D}^0$ to $\mathrm{T_d}$. These mechanisms would then be represented by the following individual processes:

mechanism a

excitation

$$h\nu + {}^1\mathrm{M}^0 \rightarrow {}^1\mathrm{M}^* \tag{1}$$

energy transfer

$$^1\mathrm{M}^* + {}^1\mathrm{M}^0 \rightarrow {}^1\mathrm{M}^0 + {}^1\mathrm{M}^* \tag{2}$$

trapping (singlet)

$$^1\mathrm{M}^* + {}^1\mathrm{D}^0 \rightarrow {}^1\mathrm{M}^0 + {}^1\mathrm{D}^* \tag{3}$$

intersystem crossing (D)

$$^1\mathrm{D}^* \rightarrow \mathrm{T_d} \tag{4}$$

mechanism b

excitation

step 1

intersystem crossing (M)

$$^1\mathrm{M}^* \rightarrow \mathrm{T_m} \tag{5}$$

trapping (triplet)

$$\mathrm{T_m} + {}^1\mathrm{D}^0 \rightarrow {}^1\mathrm{M}^0 + \mathrm{T_d} \tag{6}$$

mechanism c

direct excitation

$$h\nu + {}^1\mathrm{D}^0 \rightarrow \mathrm{T_d} \tag{7}$$

Mechanism c is, of course, very unlikely because of the spin-forbidden nature of the transition and, of the possibilities a and b, the latter is clearly preferred since it does not require the existence of the, as yet unobserved, $^1\mathrm{D}^*$. Mechanism a could play a role if the $^1\mathrm{D}^*$ to $\mathrm{T_d}$ intersystem crossing were much faster than radiative deactivation of $^1\mathrm{D}^*$ but this point cannot be settled in the absence of $^1\mathrm{D}^*$ emission.

If mechanism b is taken as the major contributor to T_d (and T_e) formation, one must next consider the origin of delayed fluorescence. Since it is definitely of the annihilative type, then

$$T_m + T_m \rightarrow {}^1M^* + {}^1M^0 \quad (8)$$

$$T_m + T_d \rightarrow {}^1M^* + {}^1D^0 \quad (9)$$

$$T_m + T_e \rightarrow {}^1M^* + {}^1E^0 \quad (10)$$

represent possible mechanisms. In a homogeneous system and in the presence of a single triplet species, elementary kinetic relationships show that the delayed fluorescence lifetime (τ_{df}) will be one-half of the lifetime of the triplet species involved in the annihilation if first-order decay processes occur much faster than second-order ones. In the general case, $\tau_{df}^{-1} = \tau_1^{-1} + \tau_2^{-1}$ for an annihilation between any two triplet species which decay exponentially with lifetimes of τ_1 and τ_2.

Although there are minor differences between triplet luminescence lifetimes at various wavelengths collected in Table I, the most striking characteristic of the data summarized there is their similarity of magnitude especially when comparing delayed fluorescence lifetimes with the phosphorescence components at 480 and 540 nm. In order to decide which of the processes (eq 8, 9, or 10) is primarily responsible for the delayed fluorescence emission one must know the value of τ_M, the lifetime of mobile triplet excitons. Since no emission ascribable to this species is observed from solid film samples, one must resort to the reasonable supposition that the lifetime of the phosphorescence decay of the model compound II (7.0 ± 0.7 s) or of the polymer in frozen MTHF (6.2 ± 0.6 s) would represent an acceptable estimate for τ_M.

If one uses the average of these two measured lifetimes (6.6 s) for τ_M, then the delayed fluorescence lifetime would be predicted to be 3.3 s by eq 8, 1.7 s by eq 9, and 2.2 s by eq 10. Clearly the homoannihilation process gives the best fit to the measured delayed fluorescence. This conclusion contrasts sharply with that reached in earlier studies on solid films of PVCA.[11] In that case delayed fluorescence production seemed to involve a process such as eq 9 or 10, that is, a heteroannihilation.

In comparisons of these two carbazolyl-containing polymers their differing propensities to form singlet-state excimers are a clear-cut distinction. When we now turn to the triplet excimers, another important distinction has emerged. Clearly, process 8 would be favored over process 9 or 10 by an enhanced T_M concentration or a significantly reduced ${}^1D^0$ or ${}^1E^0$ concentration. Since these excimer-forming sites represent traps for T_M, a decrease in their population would yield not only decreased concentrations of T_d and T_e but also enhanced concentrations of T_M. Because of the presence of the carboxylate group in PFCZ it would not be surprising if the quantum yield for triplet formation is higher in PFCZ than in PVCA. Thus, there are many reasons to anticipate a relative enhancement of homoannihilation in PFCZ.

Since the results of the kinetic analysis of delayed fluorescence indicate that a larger steady-state concentration of T_M species may exist in solid PFCZ films than in similar experiments carried out on PVCA, one would expect to see a phosphorescence emission attributable to monomeric carbazolyl units. In most of the film samples the delayed fluorescence band strongly overlaps the wavelength region of monomer phosphorescence; however, in Figure 9b, where the delayed fluorescence is absent, a weak emission in this region is observed.

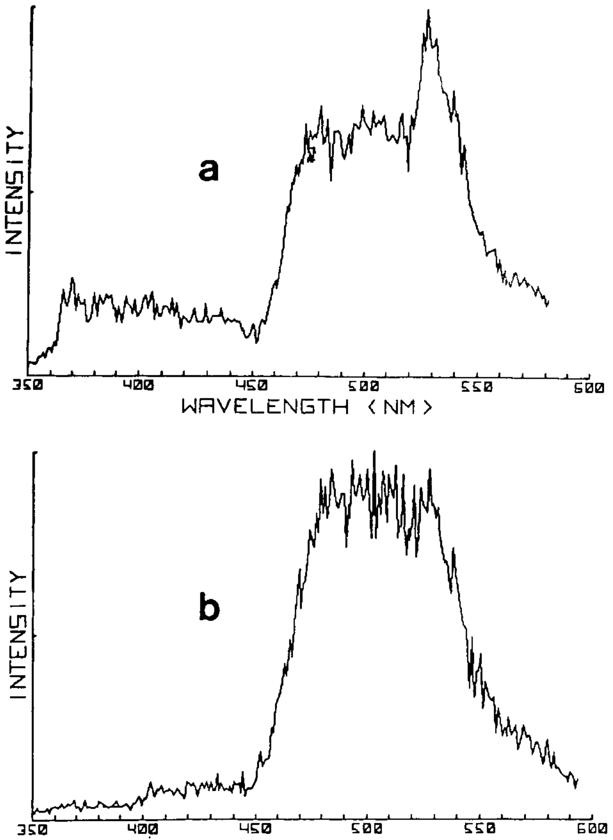


Figure 9. Phosphorescence spectra of PFCZ films after heating for 24 h at 100 °C (a) and before heating (b).

We now turn to the experiments on the effect of temperature on emission intensities and lifetimes. Here we find an interesting contrast between 480- and 540-nm emissions, the intensity of the former being much more sensitive to temperature changes than the latter whereas, in neither case, do the lifetimes show a marked temperature dependence. Thus, one may conclude that the rate constants for radiative and radiationless deactivation, that is, for

$$T_d \rightarrow {}^1D^0 + h\nu_d(480\ \text{nm})/\text{lattice energy}$$

$$T_e \rightarrow {}^1E^0 + h\nu_e(540\ \text{nm})/\text{lattice energy}$$

are not very sensitive to temperature; however, processes leading to the formation of T_d do have significant temperature dependence. A possible explanation for this effect would be that ${}^1D^0$ trap sites can be destroyed by increasing temperature, thus causing a decrease in the rate of process 6.

Another experiment was performed to study the effects on emission spectra of the thermal history of the polymer film samples. It is illustrated in Figure 9. Here the spectrum of a freshly cast polymer film is compared with one which was heated under vacuum at 100 °C for 24 h. A vacuum environment was used for the experiment to avoid oxidative degradation of the polymer. In subsequent experiments the heat treatment was applied to the polymer in an atmosphere purged with nitrogen and saturated with chloroform vapor. Essentially the same spectrum was obtained as for films heated under vacuum.

Of course, the most striking feature of these comparison spectra is the complete absence of delayed fluorescence in the film which has not received heat treatment. In addition, a significant enhancement of the 540-nm phosphorescence band occurs. Evidently polymer conformations favorable to these emission signals are more readily achieved by prolonged heating of the film. Presumably rotation and translation of chain segments at elevated temperatures provide a mechanism for achieving more thermodynamically stable chain configurations. Similar effects have been observed for singlet excimer emission from polystyrene and other vinyl aromatic polymers.[1]

A concluding comment should be added here concerning the delayed fluorescence lifetime observed for PFCZ in frozen MTHF. It is clearly less than one-half of the phosphorescence lifetime; it is also clear that it originates in triplet–triplet annihilation. Of necessity, therefore, the pool of triplet-state chromophores responsible for delayed fluorescence and that responsible for the long-time component of the phosphorescence are distinct but perhaps overlap to some extent. Cozzens and Fox[18] have discussed this effect concluding that triplet–triplet annihilation must occur by an intramolecular migration of triplet excitons. This, in effect, means that there is a nonhomogeneous distribution of triplet chromophores among chain molecules and that only limited intermolecular triplet migration can occur in these rigid solutions.

Conclusions

The subject polymer PFCZ and its monomeric analogue MFCZ display photophysical properties which are significantly different from poly(*N*-vinylcarbazole). The strong blue shift of the fluorescence of PFCZ relative to PVCA has been related to the nature of the substituent groups bonded to the carbazole nitrogen atom. The very weak excimer fluorescence in PFCZ has likewise been related to the nature of these substituents and to a less constrained steric environment. Phosphorescence and delayed fluorescence spectra and kinetics in solid films of PFCZ suggest that, although excimer-forming sites exist in the polymer film, they are less populous than in PVCA. Furthermore, the relative populations of the two types of sites present are sensitive to the thermal history of the samples. The mechanism of delayed fluorescence production both in solid films and in rigid solutions of PFCZ is triplet–triplet annihilation.

Acknowledgment. The work at Nevada was sponsored by the U.S. Department of Energy under Grant No. DE-AS08-83ER45036. We thank Professor D. A. Lightner for access to the MPF-44A spectrofluorimeter. The gift of the pure vinyl chloroformate and ethyl chloroformate from the Societê National des Poudres et Explosifs is gratefully acknowledged.

Registry No. II, 56995-05-2; ethyl chloroformate, 541-41-3; carbazole, 86-74-8.

References and Notes

(1) For recent reviews see: Semerak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 31. Klöpffer, W. In "Electronic Properties of Polymers"; Mort, J., Pfister, G., Eds.; Wiley-Interscience: New York, 1981; Chapter 5.
(2) Klöpffer, W.; Fischer, D. *J. Polym. Sci., Part C* **1973**, *40*, 43.
(3) Klöpffer, W. *Chem. Phys. Lett.* **1969**, *4*, 193.
(4) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697.
(5) Evers, F.; Kobs, K.; Memming, R.; Terrell, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 5988.
(6) DeSchryver, F. C.; Jandendriessche, J.; Toppet, S.; DeMeyer, K.; Boens, N. *Macromolecules* **1982**, *15*, 406.
(7) Houben, J. L.; Natucci, B.; Solaro, R.; Colella, O.; Chiellini, E.; Ledwith, A *Polymer* **1978**, *19*, 811.
(8) Beck, S.; Hallam, A.; North, A. M. *Polymer* **1979**, *20*, 1177.
(9) Rippen, G.; Klöpffer, W. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 437.
(10) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2037.
(11) Burkhart, R. D.; Avilês, R. G. *Macromolecules* **1979**, *12*, 1078.
(12) Harvey, P. D.; Zelent, B.; Durocher, G. *Spectrosc. Int. J.* **1983**, *2*, 128.
(13) Fletcher, M. A.; Lakin, M. W.; Plant, S. G. P. *J. Chem. Soc.* **1953**, 3898.
(14) Meunier, G.; Hemery, P.; Boileau, S.; Senet, J. P.; Cheradame, H. *Polymer* **1982**, *23*, 849.
(15) Kassir, F.; Boivin, S.; Boileau, S.; Cheradame, H.; Wooden, G. P.; Olofson, R. A. *Polymer*, in press.
(16) Burkhart, R. D. *J. Phys. Chem.* **1983**, *87*, 1566.
(17) Burkhart, R. D.; Avilês, R. G. *J. Phys. Chem.* **1979**, *83*, 1897.
(18) Cozzens, R. F.; Fox, R. B. *J. Chem. Phys.* **1969**, *50*, 1532.
(19) Mataga, N.; Torihashi, Y.; Ezumi, K. *Theor. Chim. Acta* **1964**, *2*, 158.
(20) Johnson, G. E. *J. Phys. Chem.* **1974**, *78*, 1512.
(21) Itaya, A.; Okamoto, K.-I.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 22.
(22) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970; pp 327–31.

Intersystem Crossing and Triplet-State Properties of Dinaphthyl Compounds

James F. Pratte[†] **and Stephen E. Webber***

Department of Chemistry and Center for Polymer Research, University of Texas at Austin, Austin, Texas 78712

F. C. De Schryver*

Department of Chemistry, Universiteit Leuven, Celestijnenlaan 200 F, B-3030 Heverlee, Belgium. *Received December 13, 1983*

ABSTRACT: Triplet–triplet absorption spectra have been measured for diastereoisomers of bis[1-(1- and 2-naphthyl)ethyl] ethers and 1,3-di-β,β'-naphthylpropane. There is no evidence for triplet excimer formation in any of these compounds. In general there is a decrease in the quantum yield of intersystem crossing for those stereoisomers that exhibit a stronger excimer fluorescence (i.e., $\Phi_{\mathrm{isc}}^{\mathrm{meso}} < \Phi_{\mathrm{isc}}^{\mathrm{racemic}}$) but the differences in Φ_{isc} are as large between 1- and 2-naphthyl substitution as between meso and racemic stereoisomers. In the case of *meso*-bis[1-(2-naphthyl)ethyl] ether an anomalously short triplet lifetime was observed.

Introduction

In recent years dichromophoric compounds have been widely used as models for polymeric pairwise sequences and have been very successful in elucidating the photophysical properties of the singlet state of polymers. In particular for diastereoisomers of dichromophoric compounds it has been demonstrated that there is a very strong dependence of the monomer-to-excimer fluorescence ratio and the nature of the excimer state on the stereoisomerism (i.e., in most cases the meso stereoisomer has a much stronger excimer fluorescence than a racemic stereoisomer).[1,2] These differences can be understood in terms of the population distribution of various conformers of these model compounds.

In a number of polymer systems it has been observed that the triplet yield (Φ_{isc}) is greatly diminished relative

---

[†] Present address: Du Pont, Wilmington, DE.

0024-9297/85/2218-1284$01.50/0