Triplet Emission from Poly(*N*-vinylcarbazole) Solid Films at Ambient Temperature Studied in the Microsecond Time Regime Using Pulsed Laser Excitation

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ABSTRACT: Delayed luminescence lifetimes and spectra were studied at ambient temperature for three separate samples of poly(*N*-vinylcarbazole) prepared by conventional free radical polymerization. The samples were photoexcited by the use of 6-ns pulses from a nitrogen excimer laser and, under these conditions both delayed fluorescence and phosphorescence emission was easy to detect at times as long as 10 ms following the excitation pulse. The delayed fluorescence lifetime was found to be 1.7 ± 0.1 ms for all three samples and the phosphorescence has a short-time component of 1.5 ± 0.2 ms for the two samples of highest molecular weight. There was also a long-lived phosphorescence component persisting for several hundred milliseconds after the excitation pulse which could be observed for all three samples. The results indicate that in this polymer a significant fraction of the triplet photophysical events at ambient temperature occurs in the submillisecond time regime and that delayed fluorescence arises from the interaction of a mobile exciton and a trapped one. In contrast with low-temperature experiments, in which evidence for several different types of trap sites was found, all of the observations made for this system at ambient temperature can be interpreted in terms of a single type of trap.

Introduction

Poly(*N*-vinylcarbazole) (PVCA) is a polymer possessing a wealth of potential photophysical activity. Even if one restricts the field only to triplet processes, there is to be found monomer-like phosphorescence from rigid solutions,[1] excimer phosphorescence from pure films,[1-3] and delayed excimer fluorescence from pure films and rigid solutions.[3-4] Most of the experiments on pure films or rigid solutions have been conducted at 77 K, where the emission signals are most readily observed and where the triplet lifetimes are longest.

In these laboratories the focus of attention has been primarily on the temperature dependence of the delayed luminescence spectra and the luminescence decay kinetics. It was found, surprisingly, that PVCA emits a phosphorescence signal even at ambient temperatures.[6] In fact, phosphorescence emission has been observed at temperatures up to 90 °C.[7] Furthermore, a small delayed fluorescence signal was obtained in earlier work at ambient temperature but it was difficult to characterize properly because the time resolution of the spectrophotometer was too large.

One of the puzzling aspects of the earlier work centered around the large difference between lifetimes of phosphorescence and delayed fluorescence at room temperature. On the one hand, delayed fluorescence lifetimes on the order of 2–3 ms were observed[5] whereas phosphorescence lifetimes were found as much as 100 times larger.[7] In both cases, of course, it is an excimer-like signal that is emitted and the assumption was that emitting species have a configuration in which neighboring chromophoric groups are strongly interacting. The exact nature of these excimeric configurations is still a matter of speculation and controversy. In fact, the suggestion has been made that at least three different types of triplet excimeric species are responsible for the observed triplet photophysical properties of PVCA.[8]

From the results of our earlier work on the temperature dependence of PVCA delayed luminescence, it was concluded that certain of these excimeric sites can be made ineffective as traps for triplet excitons if only the temperature is raised sufficiently.[5] The rationale behind this conclusion is that the trapping process appears to be reversible, at least for certain chromophore configurations, and that the detrapping process is thermally activated. Webber and Avots-Avotins[9] have postulated the existence of reversible triplet exciton trapping in PVCA on the basis of quenching experiments. Thus, it seemed likely that more progress could be made in understanding the mechanism of triplet photoemission by working at ambient temperature, where fewer types and perhaps only one type, of trap site are present. To be successful, however, such studies require a powerful excitation source coupled with an ability to make observations in the microsecond time regime. Both of these requirements were met in the present work by using pulsed laser excitation in place of a conventional light source and mechanical choppers.

As a result of this work the huge difference between delayed fluorescence and phosphorescence lifetimes observed before at ambient temperature is now understandable. Furthermore, an extreme sensitivity of the triplet emission spectra to the details of polymer synthesis has been found, which could provide a route to more detailed spectroscopic investigations of the polymer microstructure.

Experimental Section

The polymer samples were prepared in the laboratory by free radical polymerization. The *N*-vinylcarbazole was purchased from Polysciences Inc. It was recrystallized five times from methanol and was dried for 2 days in a vacuum oven at room temperature. The free radical initiator, azobis(isobutyronitrile) (AIBN), was purchased from Aldrich Chemical Co. and was recrystallized three times from ethanol before use. The solvent benzene was washed sequentially with concentrated H_2SO_4, dilute base, and distilled water before drying over anhydrous sodium sulfate and distilling twice. Methanol was refluxed over copper sulfate and then distilled. It was then refluxed over calcium and distilled followed by distillation from silver nitrate.

The polymerization mixture consisted of 5 mL of benzene, 2 g of the monomer, and 0.004 g of AIBN. The reaction vessel consisted of a tube 1 in. in diameter and 5 in. long. At the upper end of this tube was sealed a 10-in. section of 10-mm tubing constricted at two different positions. At the upper end of the tubing was sealed a 19/38 standard taper joint. After the reaction solution was added, another milliliter of benzene was added to be sure all of the solution was washed down into the bottom of the tube. The tube was then attached to a vacuum system and degassed to 5×10^{-4} torr by several freeze–pump–thaw cycles using liquid nitrogen. On the last freeze-down the tube was sealed off with a torch at the upper constriction and was place in an oven previously set to the appropriate polymerization temperature. The mixture was allowed to react overnight, after which the tubing

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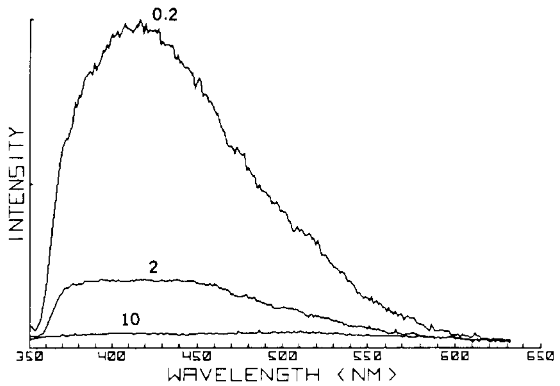

Figure 1. Delayed luminescence spectrum of a PVCA film 0.2, 2.0, and 10 ms after the excitation pulse. Polymer sample A, MW = 5.6 × 10^5.

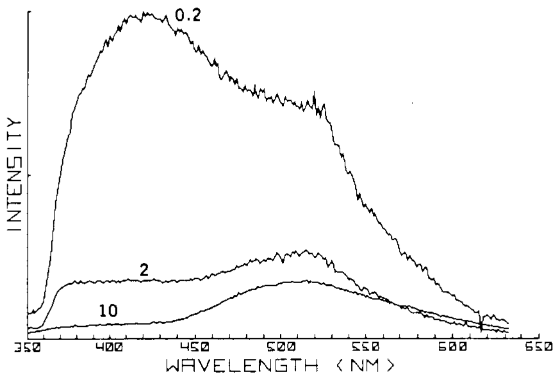

Figure 2. Delayed luminescence spectrum of a PVCA film 0.2, 2.0, and 10 ms after the excitation pulse. Polymer sample B, MW = 3.3 × 10^5.

was cracked open at the lowest constriction and the mixture poured into rapidly stirring methanol. After five reprecipitations in methanol the polymer was subjected to three additional extractions with boiling methanol. It was then dried under vacuum and was stored in an amber bottle under nitrogen. Three separate polymer samples were prepared differing only in the temperature used in their preparation. These are sample A, 65 °C, sample B, 100 °C, and sample C, 125 °C.

Polymer molecular weights were determined by measurements of solution viscosity. The viscosity-molecular weight relationship reported by Uberreiter and Springer[10] for benzene solutions was used. The results were as follows: sample A, 5.6 × 10^5; sample B, 3.3 × 10^5; sample C, 1.8 × 10^5.

The film samples were prepared on optically flat quartz plates by evaporation of a solution consisting of 30 mg of PVCA in 1 mL of benzene. The evaporation was carried out slowly in a closed container in order to form a clear film. The films were then placed in a vacuum oven at 100 °C and were evacuated overnight at 10^{-3} torr.

The spectrometer used in this work has been described in a previous publication.[11] The data handling and analysis have also been previously described.[6]

Results

Figures 1–3 are delayed luminescence spectra at ambient temperature for the three different poly(*N*-vinylcarbazole) samples investigated here. They are presented in a time-resolved fashion in order to emphasize the point that the shorter wavelength component decays faster than the long-wavelength component in all three cases. Using assignments based upon many earlier studies of this polymer, the emission at 420 nm is identified as delayed excimer fluorescence and that at 520 nm as excimer phosphorescence.

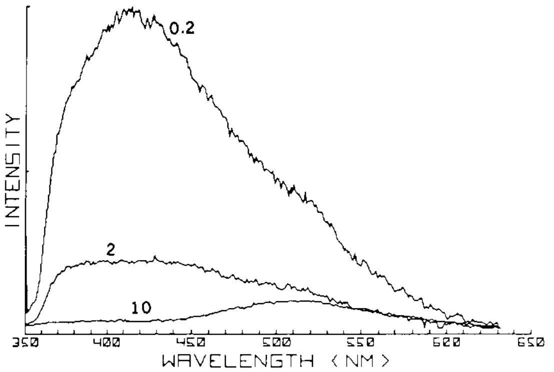

Figure 3. Delayed luminescence spectrum of a PVCA film 0.2, 2.0, and 10 ms after the excitation pulse. Polymer sample C, MW = 1.8 × 10^5.

If one considers, initially, the spectra corresponding to a 0.2-ms delay following the excitation pulse, some interesting differences occur among the three samples. Scarcely any phosphorescence at all is seen in the sample of highest molecular weight at this short delay time. It was surprising to find, however, that the relative phosphorescence intensity does not change monotonically with molecular weight as it does in low-temperature spectra.[12] Here the most prominent phosphorescence signal was found with the sample of intermediate molecular weight. This trend continues at longer times, where it is seen that the relative intensities of phosphorescence and delayed fluorescence are still roughly the same for sample A but that the delayed fluorescence intensity is essentially negligible for sample B. The relative spectral intensities observed here are reproducible for different films of a given polymer and therefore may be considered representative of that particular sample. Of course, one must always retain the reservation that impurities may be responsible for at least part of the emission spectrum observed. In the present case, however, delayed fluorescence emission from solid films of PVCA, essentially the same as that observed here, has also been found in other laboratories.[9,13] The major difference between the delayed fluorescence bands observed here and those found previously is the indication of a sharper cutoff between 350 and 360 nm. Phosphorescence spectra from solid films of PVCA at room temperature and above have also been measured elsewhere with essentially the same results.[7] Furthermore, commercially made PVCA also yields a phosphorescence emission in the film state similar to that found here with locally prepared materials.

The appearance of a sharper delayed fluorescence cutoff at room temperature compared with 77 K is worthy of further comment. All models proposed to account for the properties of triplet emission at 77 K suggest that different types of exciton traps exist. One consequence of such a wide array of emitting sites is a significantly broadened and red-shifted spectrum compared with an isolated chromophore emission. The appearance of a sharper high energy cutoff at 298 K compared with 77 K is indicative of a more narrowly defined set of emission sites at the higher temperature. One may, therefore, be justified in suspecting that fewer different types of traps are effective at room temperature compared with 77 K. The prompt fluorescene spectra for the polymers prepared here were all quite similar and also similar to that for commercial PVCA.

The total surface area of the sample that can be illuminated in the spectrometer is about 1 cm^2. Very little delayed fluorescence could be observed from any of the samples when the excitation beam was made to uniformly illuminate this total surface area. The spectra shown in Figures 1–3 were obtained only after the beam was concentrated down to a 2-mm diameter. Thus, if $I_{DF} = c_1 I_{ex}{}^m$

Table I
Lifetime Measurements of Phosphorescence and Delayed Fluorescence from Films of PVCA at Ambient Temperature[a]

polymer sample	τ_{phos}, ms	τ_{DF}, ms	MW × 10^{-5}
A	1.8	1.5	5.6
B	1.4	1.8	3.3
C	>10	1.8	1.8

[a] Excitation was from a 6-ns pulse from a nitrogen laser. The overall precision in lifetime measurements is about 10%.

and $I_{\text{phos}} = c_2 I_{\text{ex}}^n$, where I_{ex} is the excitation intensity, then evidently $m > n$. In earlier experiments using a conventional light source, the value of m was found to be 1.98;[6] however, in the present experiments a smaller value of 1.35 ± 0.07 was obtained whereas $n = 0.51 \pm 0.05$. These values are expected if, as is likely, the triplet population is greater in the present measurements than in the earlier ones. That is, if the triplet processes include

$$T_m + {}^1D^0 \rightleftarrows {}^1M^0 + T_d \qquad (1)$$

$$T_m + T_d \rightarrow {}^1D^* + {}^1M^0 \qquad (2)$$

$$T_d \rightarrow {}^1D^0 + h\nu_{\text{phos}} \qquad (3)$$

$$T_m \rightarrow {}^1M^0 \qquad (4)$$

then both first-order and second-order pathways exist for the disappearance of triplets. In these equations ${}^1D^0$ represents a ground-state chromophore configuration suitable for excimer formation, T_m is a mobile triplet exciton, ${}^1M^0$ is a ground-state chromophore, and T_d is a triplet species trapped at an excimer site. If $k_2[T_m][T_d] \gg (k_3[T_d] + k_4[T_m])$, then the exponent m would be expected to approach 1.0 whereas the opposite inequality would produce an m close to 2.0. If this mechanism is correct, then the implication is that in the present experiments, the triplet populations are such as to produce relative magnitudes of these rates between the two extremes.

Although the point will be discussed more thoroughly below, it is worth mentioning here that most workers now seem to agree that delayed fluorescence in PVCA films occurs by a heterofusion process as described in eq 2. A homofusion process involving two migrating triplets is, of course, a possible mechanism for delayed fluorescence production but does not seem to occur to a significant extent. Experiments on the decay kinetics of the delayed luminescence will now be described which help to confirm this conclusion.

Rate experiments involving the two types of luminescence decay were carried out by monitoring at 390 and 515 nm respectively for delayed fluorescence and phosphorescence. Various time regimes could be probed by using different delay times following an excitation pulse and different dwell times on the signal averager. In Table I is a collection of lifetimes determined from experiments in which a delay time of 1 ms was used and the dwell time was 20 μs.

It is clear that for two of the three samples, the phosphorescence and delayed fluorescence lifetimes are the same, within experimental error. On the other hand, the lowest molecular weight sample does not follow this pattern. This point is made more clear by referring to Figures 4 and 5, where the natural logarithm of the phosphorescence intensity of two different samples is graphed vs. channel number, each channel corresponding to 20 μs. For the low molecular weight sample, sample C, a period of fast decay is observed, lasting about 0.4 ms, followed by a much slower decay. It is this slow component that has an apparent lifetime greater than 10.0 ms. On the time scale of these measurements no reliable value for the phosphorescence lifetime could be found for this sample.

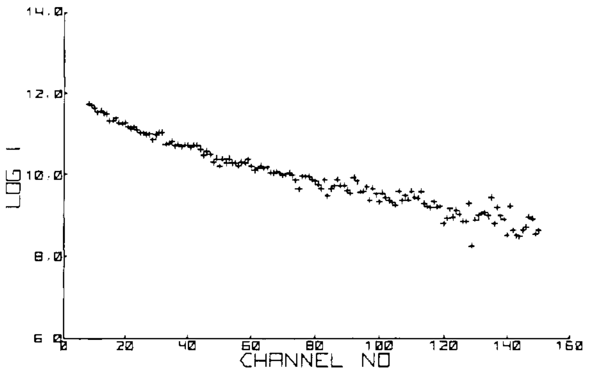

Figure 4. Natural logarithm of the phosphorescence intensity vs. channel number; sample B. Each channel is 20 μs.

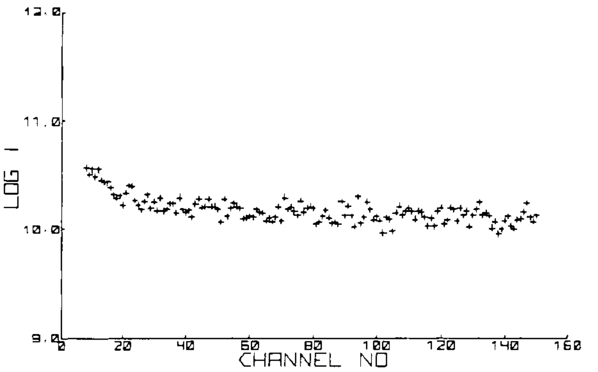

Figure 5. Natural logarithm of the phosphorescence intensity vs. channel number; sample C. Each channel is 20 μs.

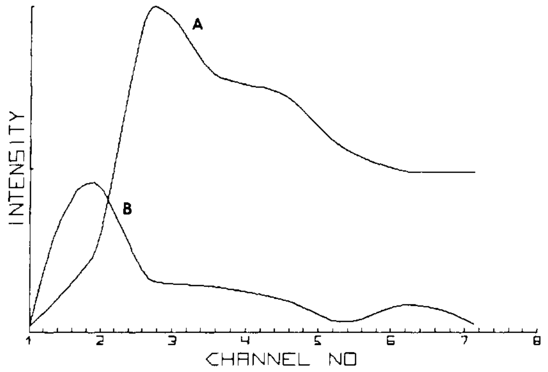

Figure 6. Buildup portion of the delayed luminescence signal for two different samples: curve A, time scale of 40 μs/channel; curve B, time scale of 80 μs/channel.

A few experiments were attempted that utilized delay times much closer to the excitation pulse. The early portion of these experiments may be seen in Figure 6, which is a graph of phosphorescence intensity vs. channel number. Rather coarse time resolution was used here of 40 μs/channel in one case and 80 μs/channel in the other. Luminescence maxima were found at channels 3 and 2, respectively, giving a time of 130 μs for the end of the buildup. These experiments are the first examples, to our knowledge, of the buildup period of triplet emission in PVCA. A search of the literature has not yielded an experimental value for the singlet–triplet intersystem crossing rate constant for PVCA; however, for *N*-methylcarbazole the intersystem crossing rate constant is 3.8×10^7 s^{-1}.[14] Thus, it seems safe to conclude that the

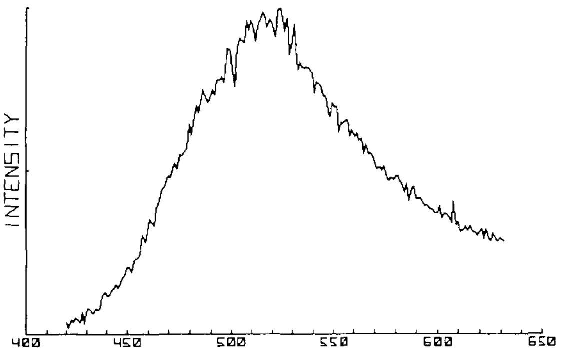

Figure 7. Difference spectrum of PVCA sample B with delayed fluorescence contribution subtracted. Spectrum recorded 2 ms after the excitation pulse.

buildup period here is due to the formation of trapped T_d species rather than to intersystem crossing and that it occurs in a time period on the order of 100 μs.

It was a matter of some concern that much different phosphorescence lifetimes are observed for PVCA at ambient temperatures depending upon the time resolution of the equipment used. For example, recent experiments using a mechanically chopped excitation and emission beam indicated that the phosphorescence lifetime is on the order of several hundred milliseconds.[7] The results depicted in Figure 5 also indicate a long-lived phosphorescence, at least in comparison with the 1.7-ms lifetimes found at early time periods after the laser excitation pulse as indicated in Table I. The spectrum of the long-lived phosphorescence of PVCA between 5 and 90 °C was also reported earlier.[7] It is worthwhile, therefore, to compare the phosphorescence spectra obtained at small delay times after the excitation pulse with the long-time spectra reported earlier in order to find out whether or not a spectral shift is associated with the different lifetimes observed. Unfortunately, the spectra recorded with delay times of only a few milliseconds following the excitation pulse all contain significant amounts of the delayed fluorescence emission. It was noted, however, that the spectrum for sample A in Figure 1, recorded at a delay time of 0.2 ms, contains no discernible phosphorescence. This spectrum was used, therefore, to subtract out the delayed fluorescence component from that of sample B (Figure 2) recorded at a delay time of 2 ms. In order to do this the delayed fluorescence emission from sample A had to be reduced by a scale factor to make it correspond to that of the test spectrum. A wavelength of 370 nm was chosen as the corresponding point. Thus, all points of the sample A spectrum were reduced by a scale factor equal to $I_{370}(\mathrm{A})/I_{370}(\mathrm{B})$, these two quantiites being the emission intensities at 370 nm for samples A and B, respectively. The resulting difference spectrum is presented in Figure 7. In comparison with the long-time spectra reported earlier, the present one is found to have essentially an identical band shape and a $\lambda_{\max}$ at 515 nm compared with maxima between 500 and 520 nm for the comparison spectra. The implication is that either there are two different lifetimes for the same emitting species or else two different species are present that emit at essentially the same wavelength. For reasons summarized in detail below, it appears that the former of these two possibilities is much more likely. Difference spectra were also prepared by subtracting the spectrum of sample A from that of sample C but in this case the emission intensities are sufficiently similar that the resulting spectrum is very noisy, although showing the general shape for the B minus A spectrum of Figure 7.

Discussion

In earlier papers on the photophysical properties of PVCA from these laboratories, it was suggested that a useful distinction might be made between two different types of mobile triplet excitons which would be dependent upon their mode of production.[15] A primary mobile exciton was defined as one that is produced in the initial excitation pulse by direct light absorption plus intersystem crossing. These excitons are thought to have a relatively short lifetime due to their involvement in trapping and annihilation processes. In terms of the mechanism suggested above these are eq 1 and 2. A generalized decay to the ground state for T_m is also included as eq 4. Klöpffer[8] has suggested that there exists a short-lived, nonemitting excimer-like species in PVCA and it is possible that such a channel is available for T_m disappearance even at ambient temperature. In this study we have found no independent evidence for such a species but, in any event, such a decay channel could be included in our simplified kinetic scheme as a contributor to eq 4. Secondary mobile excitons are defined as those produced by the detrapping process, which is the reverse of eq 1.

The essence of the mechanism to be proposed on the basis of the current experiments is that the rate processes occurring in the time domain between 200 μs and 10 ms are largely associated with primary mobile excitons and T_d species. At longer times the involvement of primary mobile excitons appears to be minimal and the results may be understood on the basis of secondary mobile excitons and trapped species.

Let us focus attention initially on sample B, where the phosphorescence emission is quite prominent even at 0.2 ms after the excitation pulse. Judging from our experiments on the buildup period of delayed luminescence, it seems likely that unoccupied $^1D^0$ sites will have reached their lowest concentration at about 0.2 ms and, of course, T_d would be at a maximum. The mobile excitons existing at this point will be mainly the primary excitons left over after the trap sites have been filled. The ratio, R, of delayed fluorescence to phosphorescence intensity for a given sample at this delay time would be given by

$$R = k_2[\mathrm{T_m}]/k_3 \qquad (5)$$

and the relative decline in delayed fluorescence intensity may, therefore, be traced to a decrease in the availability of mobile excitons. A corollary to this statement is that the delayed fluorescence lifetime is controlled primarily by the lifetime of the primary mobile excitons.

If this model is correct, then it also should explain why the short-lived phosphorescence lifetime is the same as the delayed fluorescence lifetime. In order to investigate this possibility let us suppose that the lifetime of primary T_m is controlled by the first-order disappearance. This suggestion is in accord with Klöpffer's model,[8] which was mentioned above. We assume therefore that in this time period between 200 μs and 10 ms, T_d are lost primarily by the annihilation process eq 2. Thus

$$-\mathrm{d}[\mathrm{T_d}]/\mathrm{d}t = k_2[\mathrm{T_d}][\mathrm{T_m}]_0 \exp(-t/\tau_\mathrm{m}) \qquad (6)$$

which may be integrated to yield

$$\ln\,[\mathrm{T_d}]/[\mathrm{T_d}]_0 = -\tau_\mathrm{m}k_2[\mathrm{T_m}]_0(1 - \exp(-t/\tau_\mathrm{m})) \qquad (7)$$

where $[\mathrm{T_d}]_0$ and $[\mathrm{T_m}]_0$ are the concentrations at an arbitrarily chosen time zero and τ_m is the mobile triplet lifetime, which we now equate to the delayed fluorescence lifetime. Since the rapid portion of the phosphorescence decay consumes only a small proportion of the initially

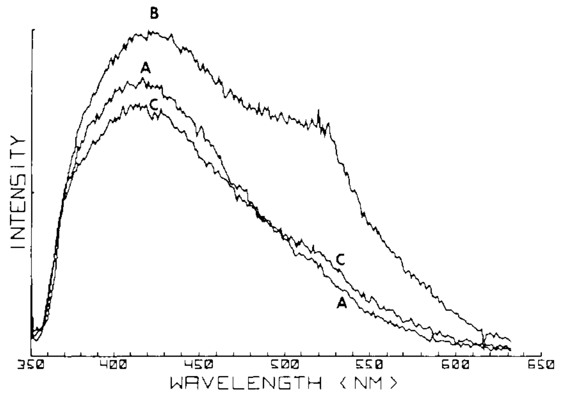

Figure 8. Comparison spectra of samples A, B, and C at 0.2 ms after the excitation pulse.

formed T_d, the left-hand side of eq 7 may be approximated by $([T_d]/[T_d]_0) - 1$ and, in this case one may write

$$[T_d]/[T_d]_0 = A + B\exp(-t/\tau_m) \qquad (8)$$

where $A = (1 - \tau_m k_2[T_m]_0)[T_d]_0$ and $B = [T_d]_0 - A$. Therefore, in this particular time period, the decline in phosphorescence intensity, which is equated to the rate of T_d disappearance, is also equal to τ_m. It must be borne in mind, however, that the intrinsic lifetime of T_d is much larger than τ_m. Thus, as the T_m population approaches zero the apparent lifetime of T_d will increase markedly to its intrinsic value in the absence of this annihilative quenching.

In addition to this mechanism of annihilative quenching, another explanation may be offered for the two distinct phosphorescence lifetimes and for the fact that τ_{df} is the same as the short-lived phosphorescence component.[16] It involves the assumption that phosphorescence emission from mobile triplet excitons is a component of the total phosphorescence envelope. Presumably such an emission would have spectral features very much the same as the monomeric analogue of PVCA, i.e., *N*-isopropylcarbazole. It could not be seen as a separate emission component in the present experiments due to masking by the delayed fluorescence and excimer phosphorescence.

If the effective rate constant for the trapping process, k_{dm}, is set equal to $k_1[^1D^0]$, steps 1, 3, and 4 of the mechanism yield

$$[T_d] = [T_m]_0 f_d[\exp(-k_3 t) - \exp(-k_4 t)] \qquad (9)$$

where $f_d = k_{dm}/(k_4 - k_3)$. If the phosphorescence emission $I_{phos}(t)$ includes contributions both from T_m and T_d, then

$$I_{phos}(t) = [T_m]_0(k_m^{phos} - f_d k_d^{phos})\exp(-k_4 t) + [T_m]_0 f_d k_d \exp(-k_3 t) \qquad (10)$$

and two lifetimes will be observed if $k_m^{phos} - f_d k_d^{phos} > 0$, where k_m^{phos} and k_d^{phos} are the respective rate constants for radiative transitions. Here we identify the long-time component of the phosphorescence lifetime with $1/k_3 = \tau_d$ and the short-time component with $1/k_4 = \tau_m$. Clearly, a delayed fluorescence emission resulting from the heterofusion involving T_m and T_d would have the same lifetime as the shorter-lived species, τ_m. Further experimentation would be required in order to distinguish between these two possibilities.

In Figure 8 a direct comparison is made between the delayed luminescence intensities of the three samples at a delay time of 0.2 ms after the excitation pulse. With the relative phosphorescence intensities as a guide, the mechanism proposed here yields the following inequalities: $[T_d](B) \gg [T_d](C) > [T_d](A)$. In a similar manner, the delayed fluorescence results yield the inequalities $[T_d][T_m](B) > [T_d][T_m](A) > [T_d][T_m](C)$. Thus, one may conclude that $[T_m](A) > [T_m](C)$. This result helps us to understand why the phosphorescence lifetime for sample C is larger than that for sample A. Even at 0.2 ms after the excitation pulse the concentrations of T_m has reached a sufficiently low value that the rate of removal of T_d species by annihilative quenching is not as large as that in sample A. Thus, the lifetime of the T_d species is approaching its intrinsic value even at this short delay time whereas T_m concentrations are large enough in sample A to maintain a higher quenching rate over a longer period of time.

It would be very helpful to be able to relate these observed kinetic and spectroscopic differences for the PVCA samples to the polymerization conditions used. As mentioned in the Experimental Section, it was only the polymerizaton temperature that was varied: 65 °C for sample A, 100 °C for sample B, and 125 °C for sample C. This resulted in the ordering of molecular weights such that A > B > C. If the T_m concentration in sample C is so much lower than that in sample A or B, then what was the fate of the mobile excitons produced? It is suggested here that the short-lived, nonemitting traps that Klöpffer has postulated are present in greater concentration in sample C. Since this is the sample of lowest molecular weight, it is tempting to attribute this effect to the presence of a greater concentration of chain ends but additional data on a wider variety of polymer samples would be needed to confirm such a hypothesis.

Conclusions

The mechanism that has been suggested here to account for the experimental observations consists of only four steps but, if correctly interpreted, succeeds in explaining a rather large number of diverse kinetic and spectroscopic results. The sharply contrasting appearance of the delayed luminescence spectra for three polymer samples which seem, on the surface, to be rather similar in molecular weight and mode of preparation suggests that a great deal of information on the polymer microstructure may be extracted from such studies.

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Registry No. Poly(*N*-vinylcarbazole), 25067-59-8.

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