γ oxidation is initiated indiscriminately, largely at random through the polymer matrix, whereas photooxidation, at least at ambient temperatures, must lead to the production of highly localized zones of high oxidation-product concentration.[14]

References and Notes

(1) F. R. Mayo, *Macromolecules*, 11, 942 (1978).
(2) J. C. W. Chien and D. S. T. Wang, *Macromolecules*, 8, 920 (1975).
(3) V. A. Roginskii and V. B. Miller, *Dokl. Akad. Nauk SSSR*, **215**, 1164 (1974).
(4) V. A. Roginskii, Y. L. Shanina, and V. B. Miller, *Dokl. Akad. Nauk SSSR*, **227**, 1167 (1976).
(5) V. A. Roginskii, Y. L. Shanina, and V. B. Miller, *Vysokomol. Soedin., Ser. A*, **20**, 265 (1978).
(6) J. C. W. Chien and C. R. Boss, *J. Polym. Sci., Part A-1*, **5**, 3091 (1967).
(7) E. Niki, C. Decker, and F. R. Mayo, *J. Polym. Sci., Polym. Chem. Ed.*, 11, 2813 (1973).
(8) A. Garton, D. J. Carlsson, and D. M. Wiles, *Makromol. Chem.*, in press.
(9) D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 597 (1969).
(10) D. J. Carlsson, A. Garton, and D. M. Wiles, *Macromolecules*, **9**, 695 (1976).
(11) P. Yu Butyagin, *Pure Appl. Chem.*, **30**, 57 (1972).
(12) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).
(13) C. Walling and A. R. Lepley, *Int. J. Chem. Kinet.*, **3**, 97 (1971).
(14) A. L. Buchachenko, *J. Polym. Sci., Polym. Symp.*, **No. 57**, 299 (1976).

The Kinetics of Triplet Processes in Poly(N-vinylcarbazole) from 77 to 298 K

R. D. Burkhart* and R. G. Avilés

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

Received June 25, 1979

ABSTRACT: The delayed fluorescence intensity, I_{DF}, from solid films of poly(N-vinylcarbazole) has a temperature dependence which includes two extrema, a minimum at about 145 K and a maximum at about 200 K. Using a trapping–detrapping model originally worked out by Siebrand for an arbitrary number of traps, we can satisfactorily interpret the present data in terms of two traps. A calculated depth for the deep trap agrees to within 20% of the experimentally derived value. The delayed fluorescence decay times are multiexponential over the temperature range studied, but a fast component having a lifetime between 2.0 and 3.6 ms between 77 and 140 K was isolated and was attributed to triplet–triplet annihilation involving directly formed mobile triplets. Similar experiments at room temperature indicate that the mobile triplet lifetime has very little temperature dependence and an average value of about 7 ms. Longer lived delayed fluorescence lifetimes in the low-temperature region arise from interactions between trapped triplets and indirectly formed mobile triplets produced from detrapping.

Poly(N-vinylcarbazole) (PVCA) is a photophysically active substance which emits prompt fluorescence, delayed fluorescence (DF) and phosphorescence. It is also photoconductive.[1] The fluorescence spectrum is of the excimer type with two emitting components at 420 and 375 nm.[2] Both spectral and kinetic data[3,4] have also been obtained indicating two excimer-like components in the phosphorescence of PVCA solid films. The temperature dependence of the fluorescence intensity of PVCA solutions was reported by Johnson,[5] and a study of the temperature dependence of the phosphorescence of PVCA solid films has recently been completed in these laboratories.[4]

In both the singlet and the triplet manifolds, it appears that migrating excitons are trapped at various sites in the polymer structure. Time-resolved fluorescence spectra[6,7] indicate that the shallow traps which lead to 375-nm emission are preformed sites. It is not clear whether or not the deep trap sites are preformed, but it does seem that an interconversion of shallow excimer to deep excimer can occur. It has been suggested that the shallow species corresponds to a partial overlapping of the carbazolyl aromatic rings and that the deep one involves a sandwich-like arrangement of carbazolyl groups.

From studies of the temperature dependence of the phosphorescence lifetimes, triplet trap depths of 0.6 and 3.0 kcal/mol have been determined.[4] Above about 90 K, the emission from shallow traps is very feeble, and from 145 K to room temperature the phosphorescence decays are best characterized by a single exponential. At ambient temperatures, the deep trap phosphorescence has all but disappeared and can only be detected from carefully purified samples.

The role of mobile triplet excitons in these delayed luminescence processes has received relatively little attention. Itaya and co-workers[9] found that phosphorescence lifetimes were unaffected by the incorporation of naphthalene as a triplet quencher but that intensities were markedly reduced. This not only lends further support to the belief that phosphorescence emission originates from immobilized species but also makes possible a Stern–Volmer treatment leading to a quencher rate constant, the value of which is thought to be determined by the rate of mobile exciton hopping. Perhaps it should be emphasized that in this rigid system the term "mobility" carries with it the implication of chromophore-to-chromophore energy transfer, not bulk translational motion.

In their analysis of the Stern–Volmer experiments, Itaya et al. assumed that the mobile triplet lifetime was twice the delayed fluorescence lifetime at 77 K; however, it is not clear that the factor-of-two relation holds for these films since it has not been conclusively shown that delayed fluorescence results exclusively from the homofusion of two mobile triplets. Klöpffer and Bauser[2] have suggested that mobile triplet–trapped triplet interactions may be the source of delayed fluorescence, and since a significant population of trapped triplets exists at 77 K, this would appear to be a very reasonable suggestion. Furthermore, DF lifetimes at 77K show a definite multiexponentiality as will be demonstrated below. Earlier work on the temperature dependence of PVCA delayed fluorescence[10] has

0024-9297/79/2212-1073$01.00/0

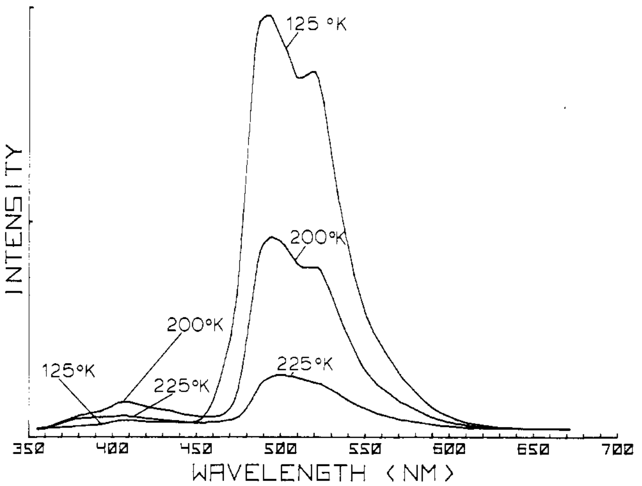

Figure 1. Delayed luminescence spectra at three different temperatures for PVCA solid films.

also provided some evidence that delayed fluorescence arises from heterofusion of mobile and trapped triplets. In the present work an extension of these temperature studies has been carried out both to lower and higher temperatures, and a more detailed analysis of the decay kinetics is undertaken. In the rate studies it has been found that variations in the modulation frequency of the excitation light are especially helpful in isolating the extremes of fast and slow decay components especially when used in conjunction with curve fitting routines for single and double exponentials.

Results

The experimental methods have been thoroughly described in a recent paper,[4] and they need not be repeated here. It is necessary only to say that all spectra and lifetimes are recorded digitally and that all luminescence lifetimes reported are derived by analyzing the data, using either a single exponential fit program or one of three double exponential fit programs. The PVCA used was a purified sample of commercially available Luvican M170.

The delayed luminescence spectra of a PVCA solid film are presented in Figure 1. The main purpose of this figure is to emphasize the point that the temperature dependence of phosphorescence and delayed fluorescence of these PVCA solid films is quite different. The phosphorescence intensity between 460 and 540 nm obviously decreases monotonically, whereas the delayed fluorescence intensity exhibits a maximum at the intermediate temperature. This interesting behavior has been observed before, using different apparatus and film-forming techniques.[10] It has been repeatedly observed in this laboratory, using many different film preparations of PVCA in both ascending and descending temperature variations, and it is therefore believed to be an intrinsic property of the polymer.

The discussion of the results will be divided up into two temperature ranges, but before doing this it is useful to call attention to Figure 2 where a more detailed presentation of the temperature dependence of delayed fluorescence is given over the entire temperature range studied. Here it is seen that two extrema exist, a minimum at about 145 K and a maximum at about 200 K. Intensity variations of this sort have previously been reported for delayed fluorescence of certain molecular crystals,[11] but to our knowledge, this is the first example of such behavior in a polymer. The steep slope of this curve in the neighborhood of 77 K suggests that there may possibly be another maximum at lower temperatures, but our present facilities preclude an examination of this temperature range. Siebrand's analysis[12] of the temperature dependence of delayed fluorescence from molecular crystals, when applied to PVCA, would predict that at least two triplet traps exist here and that the intrinsic lifetimes of the trapped triplets are both greater than that of the mobile triplet exciton. Thus, these results provide an independent verification of the conclusions reached from the phosphorescence lifetime studies that there are two types of triplet species present in photoexcited PVCA in addition to the mobile triplet.

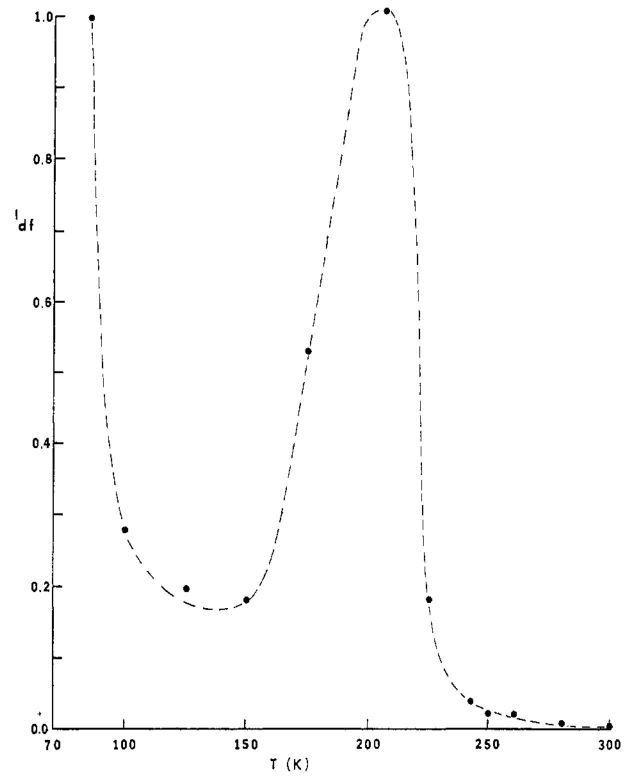

Figure 2. Delayed fluorescence intensity for PVCA solid films between 77 and 298 K.

It is believed that the molecular structure of the polymer includes sites where adjacent chromophoric groups may interact strongly enough in an excited electronic state to act as traps for the migrating exciton. These were called excimer forming sites and trap II sites by Klöpffer and Bauser;[2] however, we shall simply call them the deep and shallow trap symbolized by $^1D^0$ and $^1S^0$ respectively. The triplets trapped at these sites will be symbolized by T_d and T_s, respectively, while the mobile exciton is symbolized by T_m. In addition, we shall use $^1M^0$ to symbolize an ordinary PVCA chromophore and Q to indicate quencher. With these symbols it is then possible to depict the major rate processes as:

$$T_m + {}^1S^0 \rightleftarrows T_s + {}^1M^0 \tag{1}$$

$$T_m + {}^1D^0 \rightleftarrows T_d + {}^1M^0 \tag{2}$$

$$T_m + T_s \rightarrow {}^1M^* + {}^1M^0 \tag{3}$$

$$T_m + T_d \rightarrow {}^1M^* + {}^1M^0 \tag{4}$$

$$T_m + T_m \rightarrow {}^1M^* + {}^1M^0 \tag{5}$$

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

$$T_m + Q \rightarrow {}^1M^0 + Q^* \tag{7}$$

$${}^1M^* + {}^1D^0{}_f \rightarrow {}^1M^0 + {}^1D^* \tag{8}$$

$$^1M^* + {}^1S^0{}_f \rightarrow {}^1M^0 + {}^1S^* \quad (9)$$

$$^1D^* \rightarrow {}^1D^0{}_f + h\nu_{FD} \quad (10)$$

$$^1S^* \rightarrow {}^1S^0{}_f + h\nu_{FS} \quad (11)$$

$$T_d \rightarrow {}^1D^0 + h\nu_{PD} \quad (12)$$

$$T_s \rightarrow {}^1S^0 + h\nu_{PS} \quad (13)$$

$$T_m \rightarrow {}^1M^0 \quad (14)$$

$$T_d \rightarrow {}^1D^0 \quad (15)$$

$$T_s \rightarrow {}^1S^0 \quad (16)$$

Here it is assumed that $^1M^0$ has been directly excited to $^1M^*$ which then undergoes intersystem crossing to produce T_m. It may be noted that direct population of the deep and shallow singlet excimer sites, $^1D^0{}_f$ and $^1S^0{}_f$, is assumed and that these sites are distinguishable from the corresponding triplet sites. These points are not conclusively settled at this time but are not critical in the discussion to be presented below. It will also be noted that no radiative deactivation of T_m has been included in the mechanism since no evidence for emission from this species has been obtained. Furthermore, it is assumed that the heterofusion processes, steps 3 and 4, yield mobile singlet excitons which are subsequently trapped in steps 8 and 9, but it is quite possible that $^1S^*$ and $^1D^*$ may be formed directly in steps 3 and 4, respectively. Again, we are aware of no direct proof favoring one or the other mechanism. The migration of mobile excitons is included in step 6.

Let us now turn to the experimental results obtained on films at temperatures above 145 K and focus attention first on the lifetime measurements. Figure 3 shows an Arrhenius plot of the logarithm of the reciprocal delayed fluorescence lifetimes as a function of $1/T$. It should be pointed out that the excitation beam was chopped at a modulation frequency of 4 Hz in these experiments and that the lifetimes quoted are $1/e$ values. The delayed fluorescence decays seem to be multiexponential in this temperature range, but in spite of this fact good linearity for the Arrhenius graph is obtained above 200 K. The activation energy found for this linear region is 3.0 kcal/mol, which is the same as the activation energy for detrapping the T_d species found in earlier studies of the temperature-dependent phosphorescence. It is believed, therefore, that the majority of delayed fluorescence in the temperature range corresponding to the linear portion of Figure 3 arises from $T_m + T_d$ heterofusion. At temperatures below 200 K, the graph is not only nonlinear but also has a positive slope. It is assumed that this effect is due primarily to shifting contributions from the various DF-producing processes rather than to any real increase in DF lifetimes with changing temperature. It turns out that more useful observations of these different lifetime components below 200 K are provided by the use of variable modulation frequencies of the excitation light. Of special interest are the results obtained when the excitation beam was chopped at a frequency of $^1/_2$ Hz. Under these conditions, we are viewing the tail of the DF decay, and the results are summarized in Table I along with the previously measured[4] phosphorescence lifetimes. At both higher and lower temperatures than those quoted in Table I, the uncertainty in the long-lived lifetimes was unacceptably large, but it is clear that in the given temperature range, a DF mechanism is operating which yields lifetimes that are, within experimental error, equal to one-half of the phosphorescence lifetimes at the respective temperatures. The phosphorescence in this temperature range arises primarily from deep traps. Furthermore, an annihilative DF process requires that one of the partners be a mobile triplet. Therefore, the mobile triplets involved in this long-lived DF component must have lifetimes nearly equal to that of the deep trap. The normal decay routes for mobile triplets yield an intrinsic lifetime for these species which is much smaller than the approximately 1 s or so lifetimes indicated by Table I. This fact is indicated not only by the kinetic results at room temperature but also by rate experiments at 77 K to be presented below. It is clear, therefore, that apparent lifetimes of T_m species on the order of 1 s must simply reflect the rate of decay of their source which, in this case, is the deep trap. The failure of the DF decays to adhere to a single exponential form may thus be traced, at least in part, to the multiplicity of sources for T_m, i.e., direct formation by intersystem crossing from $^1M^*$ or by the reverse of steps 1 or 2 in the mechanism. It is also clear that the activation energies for both phosphorescence and delayed fluorescence are the same at 3 kcal/mol in this temperature range, thus providing a complement to the Arrhenius data presented in Figure 3.

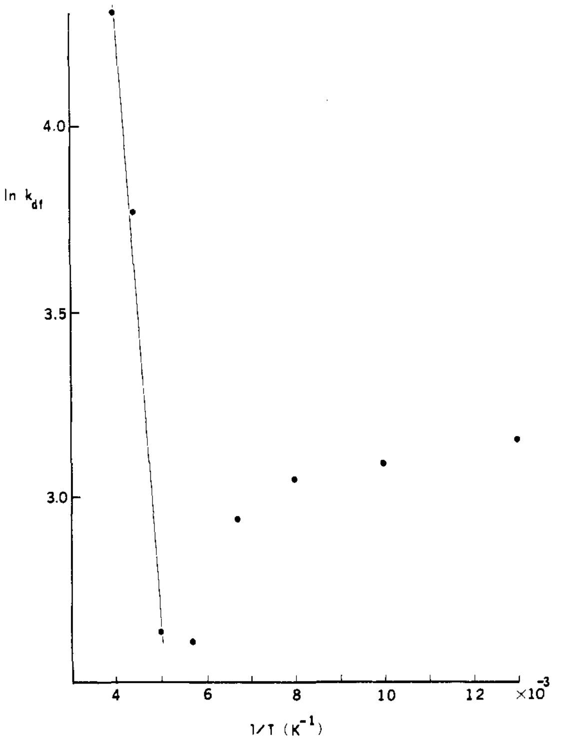

Figure 3. An Arrhenius graph of ln $1/\tau$ vs. $1/T$ where τ is the time required for the delayed fluorescence to drop to $1/e$ of its value at time zero.

Table I
Long-Lived Delayed Fluorescence Lifetimes between 140 and 180 K and Phosphorescence Lifetimes in the Same Temperature Range

temp, K	τ_{DF}, s	τ_p, s
140	1.05 ± 0.24	1.73 ± 0.1
160	0.80 ± 0.09	1.60 ± 0.15
180	0.52 ± 0.10	0.90 ± 0.09

No reports of delayed fluorescence from PVCA films in the neighborhood of room temperature have appeared before. Due to a fortunate combination of film formation procedures and the use of a rather intense excitation source,[4] it has been possible in this work to examine DF spectra and lifetimes at 298 K. Phosphorescence lifetimes and spectra have also been studied at 298 K. The phosphorescence lifetimes show a reasonably good exponential

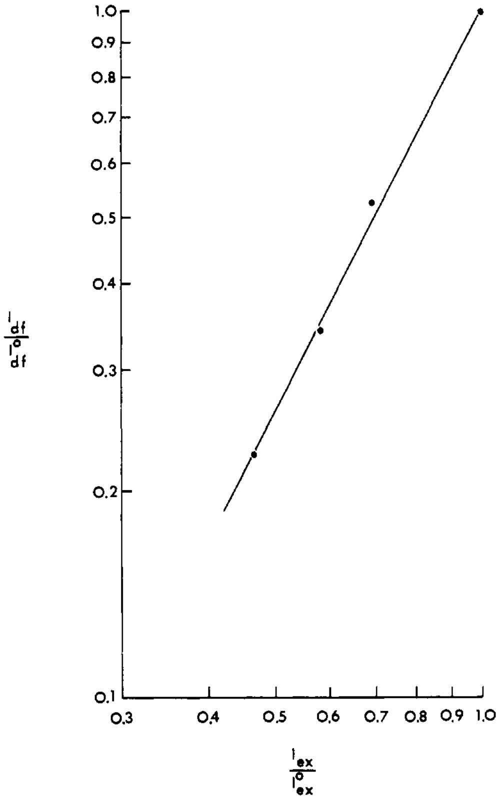

Figure 4. Log–Log plot of the effect of varying excitation intensity on delayed fluorescence intensity. The zero subscript indicates conditions of full light intensity. The least squares slope is 1.98.

decay with a lifetime of 3.4 ms. There is, however, a small shift of these lifetimes to lower values as the excitation intensity increases, which would be consistent with a certain amount of second-order triplet disappearance competing with the first-order process. Referring back to Figure 2, one sees that in the neighborhood of room temperature, the temperature dependence of the delayed fluorescence has declined considerably but is still nonzero. Evidently $T_m + T_d$ heterofusion still occurs at room temperature, but its relative importance is greatly diminished. DF lifetimes at room temperature show a small dependence on the modulation frequency of the excitation light. At 15 Hz, however, a good fit to an exponential decay is obtained yielding a DF lifetime of 2.6 ms. The dependence of the DF intensity on the excitation intensity is strictly second order, as is shown by the data in Figure 4. Steps 4 and 5 are the only two processes which could yield delayed fluorescence at room temperature, and we may discuss the kinetics, using τ_{pd} and τ'_m to represent lifetimes of deep trap phosphorescence and mobile triplet respectively. The delayed fluorescence lifetime will then be given either by $(1/\tau_{pd} + 1/\tau'_m)^{-1}$, $(2/\tau'_m)^{-1}$, or some appropriately weighted combination of the two. Actually, a pure heterofusion may be ruled out since this would yield $\tau'_m = 11$ ms, using $\tau_{df} = 2.6$ ms and $\tau_{pd} = 3.4$ ms. It is a clear physical impossibility for the mobile triplet to have a longer lifetime than the trapped species within the context of a trapping model, and the uncertainties in our τ_{pd} measurement are not large enough to include 11 ms. On the other hand, a pure homofusion would yield $\tau'_m = 5.2$ ms which, although still larger than τ_{pd}, could reasonably be included within the error limits of the τ_{pd} measurement. Thus, one is forced to conclude that the major DF-producing process at room temperature is mobile triplet homofusion with a mobile triplet lifetime on the order of 5 ms.

Let us now turn to the results obtained at temperatures below 140 K. It seems clear that step 3 must now be taken into account so that at least three processes for DF production are occurring, i.e., steps 3, 4, and 5. Since one of our primary reasons for doing this study was to try to understand the temperature dependence of the delayed fluorescence, it is now necessary to interpret the data in terms of these three processes. First it may be noted that all evidence indicates that specific rate constants associated with steps 3, 4, and 5 are temperature independent in the relevant temperature range.[4] It is, therefore, in terms of varying triplet populations that one has to understand the data. In the temperature range from 77 to 145 K, it is proposed that the decline in DF intensity must be due primarily to a decline in the T_s concentration. Detrapping of T_d does not compete effectively with the sum of the rates of steps 12 and 15 in this temperature range, and so T_d populations must remain relatively constant. Transient T_m populations in this temperature range would be expected to increase somewhat because of T_s detrapping. The minimum in DF intensity which occurs at 145 K and the increase from 145 K to about 200 K must result from increasing rates of steps 4 and 5 as a result of an increasing T_m population. Both T_s and T_d species would be expected to decrease at temperatures above about 145 K. The minimum can thus be understood to result from the opposing tendencies produced by a decreasing T_s population on the one hand and an increasing T_m population on the other.

It may be noted that a necessary condition for the validity of this mechanism is that the transient population of T_s must be sufficiently great so that the DF resulting from step 3 is dominant in the range from 77 to 145 K. An estimate of the relative concentrations of T_s and T_d may be gained by an examination of the relative intensities of deep and shallow trap phosphorescence emissions in Figure 1. Let us symbolize these intensities by I_d and I_s, respectively. Because of band overlapping, it is difficult to assign an accurate intensity ratio, but we may use $I_s/I_d \simeq 1.5$ as a rough estimate. If we use τ_s and τ_d to symbolize the lifetimes of these species and ϕ_s and ϕ_d to symbolize their respective phosphorescence efficiences, then

$$[T_s]/[T_d] = I_s\tau_s\phi_d/I_d\tau_d\phi_s \qquad (17)$$

It is known that $\tau_s/\tau_d \simeq 5$. Also, it seems certain that $\phi_d/\phi_s > 1$ below 145 K, because detrapping from the shallow trap is certainly occurring much faster than from the deep trap under these conditions, and intrinsic radiative and radiationless lifetimes should not be appreciably different for the two species. Thus, it is clear that $[T_s]/[T_d]$ is certainly larger than unity and possibly as large as 7.5. It may be noted that rapid interconversion between these two trapped species should favor the deep trap by a factor of 10^6 at 77 K, based on the respective Boltzmann factors. A huge degeneracy difference between the two states would have to be invoked in order to account for the observed inverted population; therefore, it seems likely that any interconversion between these triplet species occurs on a time scale much larger than milliseconds.

The delayed fluorescence lifetimes below 145 K do not obey a single exponential, and attempts to obtain fits to a double exponential decay are not particularly successful. Again some useful information can be gained using various modulation frequencies of the exciting light. At 77 K, for example, a fast DF component was observed having a lifetime between 2.0 and 3.6 ms by using 15 Hz modulation. It is very important to note that this fast decay could be observed with essentially the same lifetime up to 145 K. It is believed that this short-lived decay is most likely due to $T_m + T_m$ homofusion involving directly formed T_m. Other longer lived components with lifetimes in excess of 100 ms are also observed in this temperature range and are probably due to heterofusion processes involving indirectly formed mobile triplets arising from detrapping.

The fast DF component observed between 77 and 140 K would imply the existence of a mobile triplet exciton with a lifetime of between 4.0 and 7.2 ms. This is, of course, not a very precise number, but it is the same order of magnitude as our estimate for the mobile triplet lifetime at 298 K of 5.2 ms. Thus, the interesting conclusion which emerges from these lifetime measurements is that the mobile triplet probably has an intrinsic lifetime on the order of 7 ms and that it has no appreciable temperature dependence. Itaya and co-workers[9] have commented upon their differing values for delayed fluorescence lifetimes of PVCA in solid solutions vs. solid films: 10 ms for the former and 50 ms for the latter. No mention is made in their work of the use of differing excitation modulation frequencies to investigate possible nonexponentiality of the DF decays, and it may be that the longer decay time quoted for the solid film is actually a $1/e$ time. The question is an important one because this mobile triplet lifetime partially determines the value for the triplet quenching rate constant derived from Stern–Volmer experiments. If their DF lifetime is overestimated in the solid film state, then the specific rate constant for triplet quenching will be correspondingly underestimated. Since the present experiments definitely indicate that the shorter lifetime is preferred, then the larger quenching rate constant of 12 000 M^{-1} s^{-1} derived by Itaya and co-workers for solid solution is probably also the more nearly correct value for solid films as well.

As a concluding section in this discussion, it is useful to apply to PVCA solid films a scheme worked out by Siebrand[12] to rationalize the similar temperature-dependent delayed fluorescence of anthracene crystals. In PVCA, the two traps are well separated in energy and so a straightforward application of Siebrand's method is possible. It is assumed that in the temperature range between 145 and 200 K second-order processes for triplet removal are negligible compared with first-order processes and that triplet traps are populated only by the trapping of mobile excitons and not by direct excitation. Applying steady state conditions, employing the convention that rate constant k_n refers to step n in the mechanism, and using T_m, T_s, and T_d to symbolize steady-state concentrations of mobile, shallow, and deep triplets, respectively, one finds for the DF intensity

$$I_{df} = \gamma T_M^2(1 + A_s + A_d) \tag{18}$$

where $k_3 = k_4 = k_5 = \gamma$ and A_s and A_d are defined by

$$A_{s,d} = P_{s,d}/(q_{s,d} + \beta_{s,d}) \tag{19}$$

where

$$\beta_s = k_{13} + k_{16} = 1/\tau_s \tag{20}$$

$$\beta_d = k_{12} + k_{15} = 1/\tau_d \tag{21}$$

$$q_{s,d} = Z[^1M^0] \exp(-E_{s,d}/RT) \tag{22}$$

$$P_s = Z[^1S^0] \tag{23}$$

and

$$P_d = Z[^1D^0] \tag{24}$$

The trap depth for shallow and deep traps respectively is $E_{s,d}$; also $q_s/[^1M^0] = k_{-1}$ and $q_d/[^1M^0] = k_{-2}$. The trapping rate constants k_1 and k_2 are assumed equal and are symbolized by Z. The reciprocal of the mobile triplet lifetime τ_m^{-1} is β $(=k_{14})$, and one further definition is that

$$\rho_{s,d} = \beta_{s,d}/\beta \tag{25}$$

At 200 K, the kinetics are dominated by deep traps, and shallow traps are no longer operative, thus

$$\rho_d = (2 + A_d(200\ \mathrm{K}))^{-1} \tag{26}$$

As explained above, the fast component of the delayed fluorescence is temperature independent and leads to a mobile triplet lifetime of about 7 ms. Also, at temperatures below 140 K the detrapping of T_d species is much slower than the sum of radiative and radiationless decay and yields a τ_d value of 1.7 s. Thus, $A_d(200\ \mathrm{K}) = 242$. At 145 K, where the minimum in the DF intensity is found, A_d will be even larger than this because q_d will have decreased somewhat.

Also, at 145 K it is likely that A_s will be negligible compared with A_d because of the large value of q_s at this temperature. Furthermore, it is assumed initially that $q_d(145\ \mathrm{K}) \ll \beta_d$.[13] The intensity ratio $I_{df}(200\ \mathrm{K})/I_{df}(145\ \mathrm{K})$ is about 3.0 experimentally and, using the above assumptions,

$$I_{df}(200\ \mathrm{K})/I_{df}(145\ \mathrm{K}) = \{[1 + A_d(200\ \mathrm{K})]/[1 + 5A_d(145\ \mathrm{K})]\}\{[1 + \rho_d A_d(145\ \mathrm{K})]^2/[1 + \rho_d A_d(200\ \mathrm{K})]^2\} \tag{27}$$

Both roots of P_d are positive when eq 27 is solved, but only the larger of the two is physically reasonable and has the value 1.99×10^3 after four iterative cycles.[13] Since P_d is not temperature dependent, it may be inserted in eq 19 along with $A_d(200\ \mathrm{K})$ and β_d to yield $q_d(200\ \mathrm{K}) = 7.6\ \mathrm{s}^{-1}$. Finally, one may now use Itaya's value for Z of 12 000 M^{-1} s^{-1} and $[^1M^0] = 5.8$ M to find E_d from eq 22. The computed value is 3.6 kcal/mol which is in excellent agreement with the experimental value of 3.0 kcal/mol.

To verify that $A_s \ll A_d$ at 145 K, it may be noted that P_s will be somewhat less than 12 000 since presumably $[^1S^0] < 1$. Also from eq 22 with $E_s = 600$ cal/mol one finds $q_s = 8.8 \times 10^3$. Thus A_s is less than 1% of A_d. Perhaps the most questionable assumption in this derivation is that first-order processes for triplet removal overwhelmingly dominate any second-order processes. There is some evidence that this may not be true at room temperature; however, the error introduced at the temperature range of the calculation is probably not large since the corresponding phosphorescence lifetimes fit a single exponential rather well.

Conclusions

The extrema observed in graphs of delayed fluorescence intensity vs. temperature for PVCA films can be interpreted in terms of a trapping and detrapping model for mobile triplet excitons in which two different types of traps are involved. Between 77 and 145 K the monotonic decrease in DF intensity is a result of a decrease in the population of shallow triplets, the rise in DF intensity at temperatures between 145 and 200 K is due to an increasing population of mobile triplets, and the monotonic decrease in DF intensity at temperatures above 200 K is due to a decreasing population of deep trapped triplets. The fast component of the DF intensity is most likely due to triplet–triplet annihilation involving directly formed mobile triplets, and the estimated lifetime of the mobile triplets is about 7 ms independent of temperature. The longer-lived DF components probably result from interactions between trapped triplets and mobile triplets formed indirectly by detrapping. The relative concentration of the shallow and deep trapped triplets is at least 7.5 to 1 in favor of the shallow species at 77 K.

Acknowledgment. This work was supported by the U.S. Department of Energy and by funds from the Research Advisory Board of the University of Nevada.

References and Notes

(1) A great deal of information on PVCA photophysics will be found in the book "Photoconductivity in Polymers"; Patsis, A. V.; Seanor, D. A., Eds.; Technomic Publishing Co.: Westport, Conn., 1976.

(2) Klöpffer, W.; Bauser, H. *Z. Phys. Chem.* (*Frankfurt am Main*) **1976**, *101*, 24.

(3) Klöpffer, S.; Fischer, D. *J. Polym. Sci., Part-C* **1973**, *40*, 43.

(4) Burkhart, R. D.; Avilês, R. G. *J. Phys. Chem.* **1979**, *83*, 1897.

(5) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697.

(6) Hoyle, C. E.; Nemzek, T. L.; Mar, A.; Guillet, J. E. *Macromolecules* **1978**, *11*, 429.

(7) Ghiggino, K. P.; Wright, R. D.; Phillips, D. *Eur. Polym. J.* in press.

(8) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2083.

(9) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2037.

(10) Burkhart, R. D. *Macromolecules* **1976**, *9*, 234.

(11) Singh, S.; Lipsett, F. R. *J. Chem. Phys.* **1964**, *41*, 1163.

(12) Siebrand, W. *J. Chem. Phys.* **1965**, *42*, 3951.

(13) An initial calculation was made neglecting q_d(145 K) compared with β_d. This yields a trial value for E_d from which an initial q_d(145 K) may be determined. After four iterative cycles, subsequent values of E_d differed by less than 0.2%, and q_d(145 K) converged to 0.25 s^{-1}.

Temperature Dependence of Delayed Emission from Poly(*N*-vinylcarbazole). A Comparison of Polymers Prepared by Free Radical and Cationic Initiation

R. D. Burkhart* and R. G. Avilês

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

Received June 25, 1979

ABSTRACT: The photophysical properties of poly(*N*-vinylcarbazole) prepared by cationic polymerization (PVCA(c)) have been studied between 77 and 220 K. Delayed luminescence spectra have been measured at several temperatures, and a detailed study of the temperature dependence of the delayed fluorescence intensity (I_{DF}) has been carried out. Kinetic studies of phosphorescence and delayed fluorescence decay have also been completed. At 77 K the phosphorescence of PVCA(c) shows a red shift compared with free radically polymerized PVCA (PVCA(r)). An analogous red shift had previously been observed for prompt and delayed fluorescence of these polymers. The temperature dependence of I_{DF} combined with these observed spectral shifts for PVCA(c) vs. PVCA(r) are interpreted in terms of differing relative populations of deep and shallow trapped triplets. The data suggest that the energy of the mobile triplet level is different for the two polymers and that structural differences causing modified triplet migration rates exist in the neighborhood of the two types of traps. The data also suggest that mobile triplet excitons of two different origins must be considered to account for observed kinetics. These are termed primary mobile triplets, which arise directly by intersystem crossing from photoexcited singlets, and secondary mobile triplets, produced by thermal detrapping of trapped triplets.

This paper is the third in a series of studies which have been carried out on the temperature dependence of the delayed luminescence of poly(*N*-vinylcarbazole) (PVCA) in the solid film state. Earlier work[1] focused attention on the temperature dependence of phosphorescence and delayed fluorescence (DF) emitted by the commercial polymer, Luvican M 170, which is prepared by free radical polymerization and henceforth will be symbolized by PVCA(r). The purpose of the present work is to compare and contrast the temperature dependence of phosphorescence and DF emitted by PVCA(r) with that of a sample of PVCA prepared by cationic polymerization, PVCA(c).

Several photophysical studies have already appeared involving PVCA(r) and PVCA(c) and the temperature dependence of the luminescence, but most of this work involves prompt fluorescence.[2-5] For example, Johnson[2] has studied the variation of the steady state emission spectra with temperature, and Johnson[2] as well as Venikouas and Powell[3] have studied the kinetics of the prompt fluorescence decay. Ghiggino and co-workers[4] and Hoyle and co-workers[5] have recently reported time-resolved fluorescence spectra of PVCA in the nanosecond time domain. Houben and co-workers[6] studied the prompt fluorescence spectra of a variety of polymers related to PVCA, including PVCA(r) and PVCA(c), and Itaya and co-workers[7] have studied emission from the triplet state of PVCA(r) and PVCA(c) at 77 K in solid films and rigid solutions.

It seems to be generally agreed that the photophysics of PVCA can be interpreted in terms of a model involving two distinct types of traps.[8] The emission wavelengths are at 375 and 420 nm for prompt or delayed fluorescence and 490 and 520 nm for phosphorescence. Different authors have chosen different names for these traps. We shall call them the deep and shallow traps respectively, the former yielding the longer wavelength emission.

Itaya and co-workers used Stern–Volmer quenching studies to estimate triplet exciton migration rates in PVCA solid films and rigid solutions. In each case a more rapid diffusion was observed for free radically prepared samples, and this was interpreted as being due to a smaller concentration of the deep trap in PVCA(r) compared with PVCA(c). In the present study, the thermodynamic properties of a reversible trapping model are used to estimate these migration rates. The question of trap site concentration in PVCA is an important one because it is possibly related to observed features of the fluorescence spectra. In PVCA(c) there is a distinct shift of both prompt[6] and delayed[7] fluorescence to longer wavelengths, i.e., favoring the deep trap, compared to PVCA(r). Houben and co-workers[6] have raised the question of whether this

0024-9297/79/2212-1078$01.00/0