tration 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.

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(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

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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

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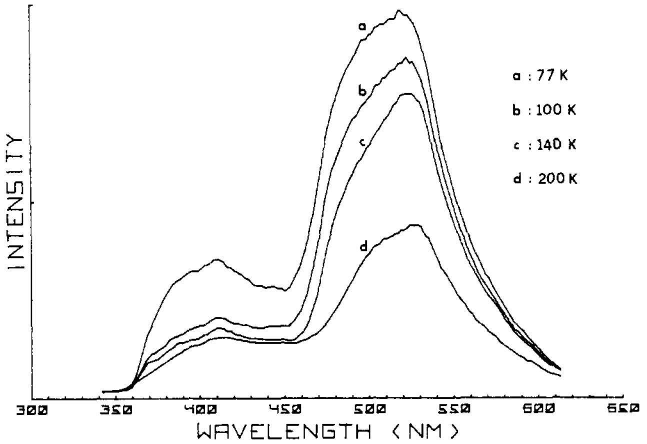

Figure 1. Delayed luminescence spectra of PVCA(c) at four different temperatures.

shift is due to a real change in the relative concentration of trap sites or whether the accessibility of the different types of sites is the cause of these shifts.

In the present work, phosphorescence spectra clearly showing spectral shifts for PVCA(r) vs. PVCA(c) which are quite analogous to those found for fluorescence are presented for the first time. The temperature dependence of DF intensities and of DF and phosphorescence lifetimes is presented and shown to be consistent with mechanisms proposed earlier for delayed luminescence production in PVCA(r). The importance of both primary mobile triplet excitons produced directly by intersystem crossing from the first excited singlet state and secondary ones produced in a delayed fashion by detrapping is also discussed.

Experimental Section

The cationically polymerized PVCA was obtained from Professor A. Ledwith of the University of Liverpool. It was further purified by reprecipitation, using benzene as solvent and methanol as nonsolvent. Both the benzene and methanol had been previously purifed using methods described earlier.[1] Procedures for evaporative film formation, excitation, and monitoring of delayed emission, digital recording of luminescence signals, temperature control, and computational techniques of data analysis have all been previously described.[1]

Results and Discussion

1. Comparison of Delayed Luminescence Spectra of PVCA(r) and PVCA(c) at 77 K. Delayed luminescence spectra of PVCA(c) at different temperatures are shown in Figure 1 and may be compared with the spectrum of a PVCA(r) sample at 77 K in Figure 2. The radically polymerized sample is the commerical polymer, Luvican M 170, which had been used in our previous work. The most obvious difference in the spectra of the two polymers is the shift in the center of gravity of the phosphorescence band to longer wavelengths in PVCA(c). In fact, the peak at 490 nm, seen clearly with PVCA(r), is reduced to a barely discernible shoulder in PVCA(c). A similar shift may be noted in the delayed fluorescence spectrum where the signal at 375 nm is much less intense in the cationically prepared polymer. A similar shift has been found for prompt fluorescence spectra of PVCA(r) and PVCA(c).[6] Thus, a general statement may be made that there is a relative decrease in the emission intensity associated with both triplet and singlet shallow traps compared with that of the deep trap for cationically prepared PVCA vs. the free radically prepared polymer. Houben and co-workers have been careful to point out that this does not necessarily mean that fewer shallow traps are present in PVCA(c).[6] The traps may simply not be as accessible to migrating excitons in this polymer.

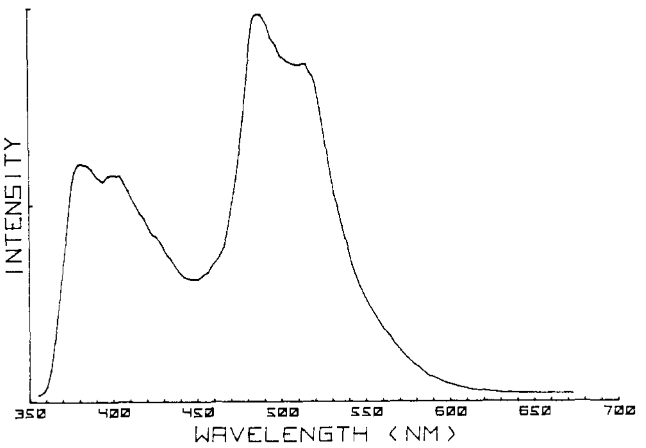

Figure 2. Delayed luminescence spectrum of PVCA(r) at 77 K.

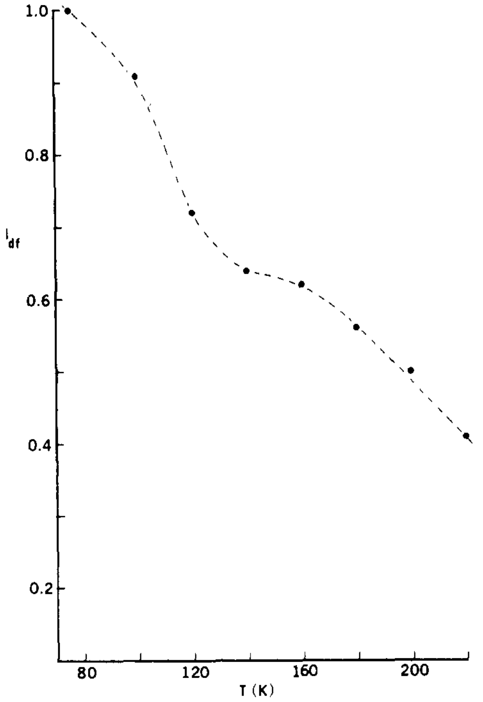

Figure 3. Delayed fluorescence intensity of PVCA(c) as a function of temperature.

2. Temperature Dependence of Phosphorescence and Delayed Fluorescence Intensities. A detailed graph of the delayed fluorescence intensity of PVCA(c) as a function of temperature is presented in Figure 3 where it is seen that a definite change in slope occurs at about 145 K. For PVCA(r) a distinct minimum occurs at 145 K and there is a distinct maximum at 200 K. These observations, as well as the spectral shifts discussed above, are totally consistent with the mechanism proposed previously for delayed luminescence in these polymers.[1] Thus, between 77 and 145 K the majority of the DF signal in PVCA(r) is thought to be due to heterofusion involving mobile triplet excitons (T_m) and shallow trapped species (T_s),

$$T_m + T_s \rightarrow {}^1M^* + {}^1M^0 \qquad (1)$$

where ${}^1M^*$ is a singlet exciton and ${}^1M^0$ is a ground state chromophore. It was suggested that the decline in the delayed fluorescence intensity between 77 and 145 K would then be due to a loss in T_s population due to detrapping, i.e., the reverse of

$$T_m + {}^1S^0 \rightleftarrows T_s + {}^1M^0 \qquad (2)$$

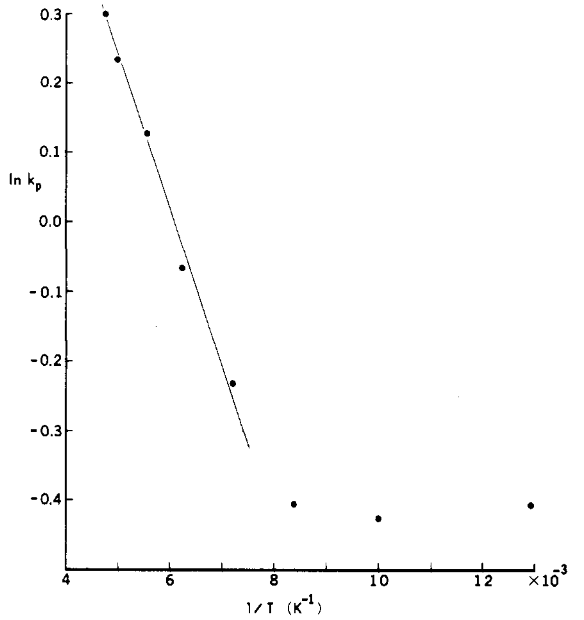

Figure 4. Arrhenius graph of ln k_p vs. $1/T$ for PVCA(c); $k_p = 1/\tau_{phos}$.

where $^1S^0$ is a shallow trap site. In PVCA(c) there is only about a 40% decrease in I_{DF} between 77 and 145 K, whereas a fivefold decrease is observed for PVCA(r) in this same temperature interval. It is evident, therefore, that $T_m + T_s$ heterofusion is making a smaller contribution to the total DF signal in PVCA(c) in this temperature range. This argument may be extended one step further.

The reverse of step 2 produces T_m, i.e., increasing the temperature effectively deactivates the $^1S^0$ as trap sites. Thus, the steady-state concentration of T_m increases as the temperature is raised, thereby increasing the rate of $T_m + T_d$ heterofusion (step 3), T_d being the deep trapped triplet. It also increases the rate of homofusion between T_m species (eq 4)

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

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

Thus, a minimum in the graph of I_{DF} vs. temperature can be understood to result from a decreasing T_s population on the one hand being counterbalanced by an increasing T_m population on the other. In the case of PVCA(c), there are insufficient numbers of T_s species present to actually produce a minimum in the plot of I_{DF} vs. temperature both because the decrease in T_s population and the increase in T_m population are not dramatic enough to produce the effect. The distinct change in slope in the PVCA(c) curve at 145 K, however, indicates that the process is occurring to a modest extent.

3. Arrhenius Treatment of Phosphorescence Lifetimes. The kinetics of the phosphorescence decay of PVCA(c) have been studied between 77 and 220 K. The lifetime of the short-lived component at 77 K is 1.5 ± 0.1 s, and this has previously been identified as being due to emission from the deep trap. Because of the small population of T_s species, no resolvable long-time component could be obtained with this polymer. Using the definition $k_p = 1/\tau_{phos}$, we made a graph of ln k_p vs. $1/T$ (Figure 4). The Arrhenius parameters obtained are $E_{act} = 0.45 \pm 0.15$ kcal/mol, and the frequency factor is 3.5 s^{-1}. As with PVCA(r), there is essentially no temperature dependence of τ_{phos} below about 145 K. This is interpreted to mean that, with both polymers, the rate of detrapping cannot compete with the sum of the rates of radiative and radiationless deactivation of T_d below this temperature. It will be noted, however, that the frequency factor for PVCA(c) is about 1000 times smaller than PVCA(r) and that the activation energy is about 6.5 times smaller.

Table I
Activation Energies $E_{act,d}(r)$, $E_{act,s}(r)$, and $E_{act,d}(c)$ for Deep and Shallow Traps in PVCA(r) and for the Deep Trap in PVCA(c) Along with the Corresponding Frequency Factors $Z_d(r)$, $Z_s(r)$, and $Z_d(c)$

$E_{act,d}(r)^{a,c}$	2.9 ± 0.1	$Z_d(r)^{b,c}$	3980
$E_{act,s}(r)^c$	0.6 ± 0.2	$Z_s(r)^c$	22
$E_{act,d}(c)$	0.45 ± 0.15	$Z_d(c)$	3.5

[a] Activation energies in kcal/mol. [b] Frequency factors in s^{-1}. [c] Reference 1.

The formation of T_d species by trapping may be represented by

$$T_m + {}^1D^0 \rightleftarrows T_d + {}^1M^0 \tag{5}$$

and we will use k_5 and k_{-5} as the specific rate constants for the forward and reverse reactions. Of the various processes which could influence phosphorescence lifetimes above 145 K, only the reverse of eq 5 would be expected to have a temperature dependence.[1] Thus

$$k_p = k_{-5}[{}^1M^0] = Z_d \exp(-E_{act,d}/RT) \tag{6}$$

It will be observed, however, that the equilibrium constant, K_5, for eq 5 is k_5/k_{-5}, and the activation energy for the reverse process will be approximately equal to the negative of the overall free energy change for the reaction.[9] Thus,

$$k_p = k_5[{}^1M^0] \exp(-E_{act,d}/RT) \tag{7}$$

and so $Z_d = k_5[{}^1M^0]$. A summary of activation energies and frequency factors for PVCA(r) and PVCA(c) is given in Table I.

By inspecting Figures 1 and 2 it seems clear that the peak wavelength corresponding to T_d phosphorescence is nearly the same for PVCA(c) and PVCA(r) at about 520 nm. Thus, the difference $E_{act,d}(r) - E_{act,d}(c)$ must be related to a difference in energy of the mobile triplet level in the immediate neighborhood of the trapped species. The fact that $Z_d(r)$ is over 1000 times larger than $Z_d(c)$ also indicates that structural differences exist between the two polymers in the neighborhood of a deep trap site. It is interesting to note that the data of Table I indicate that there may be some relation between E_{act} and Z; that is, $E_{act,d}(r)$, $E_{act,s}(r)$, and $E_{act,d}(c)$ form a monotonically decreasing series and so do the corresponding frequency factors. More data will be required, however, before any general statements about such a relationship are warranted.

4. Dependence of DF Lifetimes on Temperature and Modulation Frequency. The DF lifetimes for PVCA(c) observed between 77 and 220 K do not generally obey a single exponential decay. In earlier work, part of the reason for this complicated behavior was traced to a multiplicity of sources for T_m; that is, T_m is evidently formed by direct excitation of a chromophore to the first excited singlet level followed by intersystem crossing. However, it also appears to be formed in an indirect manner by detrapping from both T_s and T_d. Since no phosphorescent emission is ever seen from T_m, it may be safely assumed that the lifetime of these species is quite small compared with T_s and T_d, at least in the temperature range from 77 to 220 K. In fact, the T_m lifetime for PVCA(r) was found to be about 7 ms, independent of temperature.[1] Thus, the scenario of events following an excitation pulse is perceived to include a rapid decay of directly formed T_m species due to trapping and homofusion followed by a slow release of T_m from the traps. These

Table II
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	0.75 ± 0.07	1.43 ± 0.17
160	0.63 ± 0.12	1.24 ± 0.17
180	0.54 ± 0.12	0.99 ± 0.11

Table III
Short-Lived Delayed Fluorescence Component of PVCA(c) Solid Films (Modulation Frequency 15 Hz)

temp, K	lifetimes, ms	temp, K	lifetimes, ms
77	3.8	140	3.9
100	3.4	220	4.0
120	3.8		

secondary or indirectly formed mobile triplets will therefore have apparent lifetimes which are the same as the trapped species from which they are formed. It follows from this that a factor of 2 relationship should be observed between phosphorescence and delayed fluorescence lifetimes if only the long-lived tail of the delayed fluorescence decay is observed. We have been successful in obtaining such data only in the limited temperature range from 140 to 180 K. Outside of this range, the uncertainties in the lifetime measurements are too large to be useful. The relevant data are summarized in Table II.

The activation energy for delayed fluorescence is calculated to be 0.41 kcal/mol, which is the same, within experimental error, as that found for phosphorescence decay from the deep trap. Of equal importance is the finding that $\tau_{DF} = {}^1/_2\tau_{phos}$ within the given error limits. On both counts, therefore, it appears that the data are consistent with a model in which the long-lived DF signal arises from T_m, T_d heterofusion and in which the T_m are produced primarily from detrapping of T_d species.

A further implication of this proposed model has to do with the short-lived DF decay. Immediately following an excitation pulse, the T_m produced are lost both by trapping and $T_m + T_m$ homofusion. In the early stages of this period, the majority of the existing T_m were directly formed, and their lifetime will be controlled primarily by trapping and homofusion processes. As the T_m population decreases, it also becomes contaminated by an increasing number of secondary T_m. Thus, to observe T_m lifetimes exhibiting the behavior of the directly formed species a relatively fast chopper speed must be used which will minimize the dead time between the cessation of an excitation pulse and the beginning of an emission period. Using a chopper frequency of 15 Hz, we found that a reasonably good exponential DF decay could be isolated from the beginning of the signal. An average DF lifetime of 3.8 ms was found for five different measurements over a range of temperatures. The data are summarized in Table III. A similar set of values was obtained previously for PVCA(r) with an average lifetime of 3.2 ms. In neither case is there any noticeable temperature dependence of the lifetimes. An average lifetime of about 7 ms is implied for the directly formed mobile triplets in both PVCA(r) and PVCA(c).

Conclusions

The mechanism for phosphorescence and delayed fluorescence production in PVAC(c) solid films can best be described in terms of a model in which two different types of triplet traps are present in addition to a so-called mobile triplet species which can undergo energy transfer reactions with adjacent ground state chromophores. In the first few milliseconds following an excitation pulse, the directly formed T_m are lost by trapping and homofusion processes only to be replaced by secondary T_m which arise from detrapping.

The differing microstructure of PVCA(c) vs. PVCA(r) is manifested photophysically in several different ways. Spectral shifts in both phosphorescence and delayed fluorescence bands indicate a relatively greater importance of the deep trapped species vs. the shallow one in PVCA(c) compared to PVCA(r). The activation energies and frequency factors associated with detrapping of T_d indicate that the energy of the mobile triplet level and its structure in the neighborhood of a deep trap are different for the two polymers. Finally, the temperature dependence of the delayed fluorescence intensity for PVCA(c) indicates that fewer shallow trapped species are present in the material compared to PVCA(r).

Although these experiments are not able to give a definite answer to the question of whether there are relatively fewer shallow trap sites in PVCA(c) or whether they are just not as accessible, some additional considerations are suggested. The data of Table I indicate that structural differences exist in the neighborhood of different types of trap sites which lead to modified rates of exciton migration in the neighborhood of these traps. The available data indicate that as the trap depth decreases the migration rate also decreases. Since the shallow trap depth is presumably less than 0.45 kcal in PVCA(c), then fewer T_s species would be expected in this material for two reasons. First, if the trend suggested by Table I continues, then the rate of trapping will be decreased, and second, the equilibrium constant associated with eq 2 will be closer to unity in PVCA(c) than it is in PVCA(r). Thus, even if the shallow trap site concentrations were the same in the two polymers, fewer T_s species should be present in PVCA(c).

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