

## PHOTOPHYSICAL PROPERTIES OF POLY(N-VINYLCARBAZOLE) SOLID FILMS AT ELEVATED TEMPERATURES. EVIDENCE FOR A THIRD PHOSPHORESCENT SPECIES

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The  $\lambda_{\text{max}}$  for phosphorescence emission of poly(N-vinylcarbazole) (PVCz) shifts to lower values as the temperature is raised from 278 to 363 K. A corresponding long-lived phosphorescent emission is found to have a temperature-independent lifetime from 220 to 298 K. Neither of two identified excimer-like phosphorescent components of PVCz have properties consistent with this emission; its properties suggest it is excitonic in origin.

### 1. Introduction

Kinetic studies of the phosphorescent lifetime of poly(N-vinylcarbazole) (PVCz) have led to the conclusion that two distinct types of triplet species exist in solid films at 77 K [1–3]. Arrhenius parameters associated with the lifetimes of these two triplets have been determined and ascribed to detrapping, the activation energies being associated with the trap depth. The lifetime ( $\tau_s$ ) of the shallow trap ( $T_s$ ) was found to be temperature dependent from 77 K to the highest temperatures at which measurements could be made. The deep trap ( $T_d$ ) was reported to have about the same lifetime ( $\tau_d$ ) from 77 to 140 K and then a decreasing lifetime from 140 to 200 K [3]. Although phosphorescence spectra and kinetic data were obtained at ambient temperatures for these polymer films [4], no attempt was made to determine Arrhenius parameters above 200 K and no phosphorescence spectra at elevated temperatures were recorded. In the present work some of these lapses in experimental information have been filled in with the important result that evidence for a third phosphorescing component in PVCz has been found.

### 2. Experimental

Phosphorescence lifetimes were measured using a phosphorimeter in which alternating excitation and emission pulses were provided by synchronously driven choppers. Emission intensities were optimized by using "in-line" excitation and emission, by using excitation light from a 100 W Hg–Xe source which was unfiltered except for a 50 cm water filter, and by using a relatively wide band pass (20 nm) through the emission monochromator. Lifetimes were based on the summation of sixty-four decay events analyzed by a double exponential fit program.

Front surface emission spectra were recorded using a Spex Fluorolog spectrophotometer. The excitation source (320 nm) was an EG&G pulsed xenon flash tube model FX-198U. The frequency of flashes (20 Hz), the signal sampling time (80  $\mu$ s), and the signal delay time after excitation pulse (50  $\mu$ s) were controlled by a Spex digital phosphorimeter attachment. The band passes of excitation and emission were 20 and 2.5 nm, respectively. The emission was detected by an RCA C3103A phototube. The emission signal was integrated over 200 s for a given wavelength, and then recorded with a step-trip chart recorder (Linear Instruments

Corp., model 255/M). The chart paper of the recorder and the wavelength of the emission monochromator were changed synchronously in 0.05 cm and 0.5 nm steps for every 200 s, respectively.

Two samples of PVCz were used in this work. One was prepared in the laboratory from monomer which had been recrystallized five times from methanol. A conventional free-radical polymerization was used and azoisobutyronitrile was employed as the initiator. The molecular weight was determined to be  $6.1 \times 10^5$  from viscosity—molecular weight relations quoted by Uberreiter [5]. The other sample was the commercially available material Luvican M170 (BASF). In both cases the polymers were purified by multiple reprecipitations by methanol from benzene. Films were prepared by slow evaporation of benzene solvent from concentrated solutions deposited on the cell windows. The films were evacuated before use to remove dissolved gases and the last traces of solvent.

### 3. Results

The phosphorescence decay shows multi-exponential behavior but graphs of the logarithm of the phosphorescence intensity ( $\log I$ ) versus time approach a linear behavior after  $\approx 100$  ms following the excitation pulse. This is shown in fig. 1 for an experiment at 260 K.

Lifetimes corresponding to a best fit for the tail of the phosphorescence decay are summarized in table 1. The remarkable insensitivity to temperature of this emission shows that the species involved is probably not an excimer-like trap as has been proposed for  $T_s$  and  $T_d$ . On the other hand, the delayed fluorescence of PVCz films at room temperature is quite feeble, with lifetimes no longer than a few milliseconds [6]. Thus, the species involved in this high-temperature phosphorescence is either not a mobile exciton or else it is physically isolated in some way from other excitons so that annihilation processes are improbable. Additional support for this contention is our observation that phosphorescence lifetimes are not noticeably affected by the intensity of the light used for excitation. For example, phosphorescence lifetimes at 298 K of 189, 163 and 175 ms were obtained for intensities of 100%, 55% and 22%, respectively, of the maximum available intensity. It may be noted parenthetically that these lifetimes were obtained from the laboratory

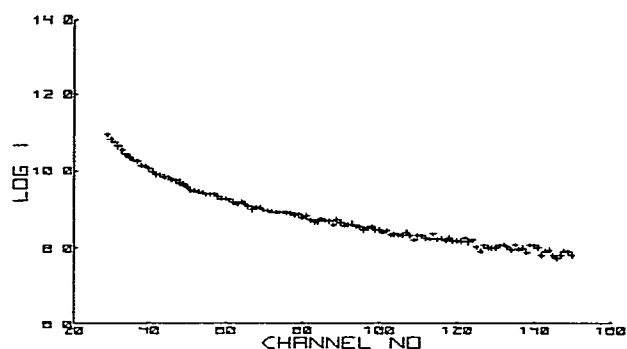


Fig. 1. Logarithm of the phosphorescence intensity versus channel number (4 ms/channel) for a PVCz film at 260 K. The monitor wavelength is 510 nm.

sample of PVCz whereas those of table 1 were obtained from the Luvican polymer. The good agreement found between these results is unlikely if the effect were due to an impurity. Furthermore, lack of a source intensity dependence implies that annihilation events are not a rate-limiting process determining the triplet lifetime.

The phosphorescence spectra shown in fig. 2 provide additional evidence for the excitonic character of this high-temperature emission. The observed band envelopes centered around 500 nm have been found in all samples of PVCz examined in these laboratories and this includes locally made material as well as Luvican M170. It also includes films cast from benzene solution or from methylene chloride. The band shape of the emission at elevated temperatures is quite different from that found at 77 K. A modest amount of structure is seen at 77 K in most spectra of PVCz films and, at the low-wavelength side, some semblance of a band edge appears. The emission at ambient temperatures and above consists of a single gaussian com-

Table 1  
Phosphorescence lifetimes taken from the tail of the luminescence decay of PVCz films between 220 and 298 K

Temperature (K)	Lifetime (ms)
220	178
240	184
260	176
298	198

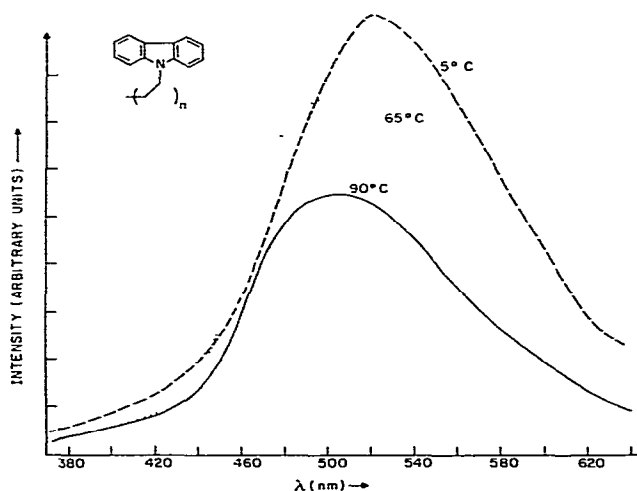


Fig. 2. Phosphorescence spectra of a PVCz film at 5, 65 and 90°C.

ponent for which  $\lambda_{\max}$  moves to lower wavelengths as the temperature is increased. Such an emission is consistent with an electronically excited state which is delocalized over a group of strongly coupled chromophores. The shift of  $\lambda_{\max}$  to higher energy with increasing temperature could correspond to a disruption of this coupling and increased localization of the exciton <sup>‡</sup>.

Another explanation for the decrease in  $\lambda_{\max}$  with an increase in temperature is associated with the possibility that the net signal observed at ambient temperatures is a mixture of phosphorescence from  $T_d$  plus emission from the excitonic state ( $T_e$ ). Although

<sup>‡</sup> A discussion of excitons in glassy substances is given by Dexter and Knox [7].

one expects the trap emission to decrease in intensity along with its decreasing lifetime as the temperature is raised,  $T_d$  would still have a lifetime of a few milliseconds at 298 K based on Arrhenius parameters found for this species at lower temperatures. The  $T_e$  emission, having a higher energy than that of  $T_d$ , would become relatively more important as the temperature is raised, causing a shift to shorter wavelengths. No matter which of these two explanations turns out to be the correct one, it seems clear that the postulation of a third phosphorescing species in PVCz is required.

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