Excimer Phosphorescene in Poly-3,6-dibromo-*N*-vinylcarbazole

By MASAAKI YOKOYAMA, MASAAKI FUNAKI, and HIROSHI MIKAWA*
(*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka,* 565 *Japan*)

Summary Excimer phosphorescence is observed in the low-temperature phosphorescence spectrum of poly-3,6-dibromo-*N*-vinylcarbazole in rigid solution.

THERE have been many reports on excimer formation in aromatic vinyl polymers having large π-electron systems such as naphthalene,[1] carbazole,[2,3] and pyrene[3,4] rings.

All these investigations are related to the singlet states of excimers, which are stabilized by the intra- or inter-molecular interaction between an electronically excited singlet chromophore and an identical nearby chromophore in its ground state. Until now, the triplet states of excimers in aromatic polymers have not been clearly identified. Excimer phosphorescence from the triplet excimer state has been observed only in a few aromatic hydrocarbons[5] and halogenated derivatives,[6] but there are no reports on excimer phosphorescence in polymer systems. We now report that the low-temperature phosphorescence spectrum of poly-3,6-dibromo-*N*-vinylcarbazole ($PVCzBr_2$) in rigid solution exhibits excimer characteristics analogous to excimer fluorescence in aromatic vinyl polymers.

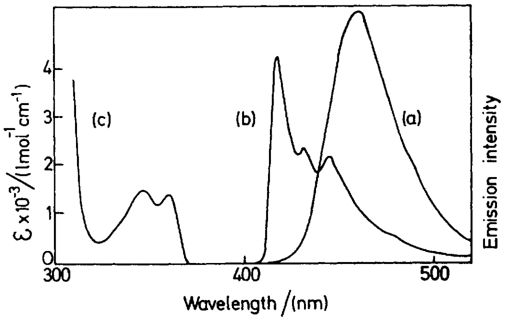

FIGURE. Delayed emission spectra of rigid solutions of (a) $PVCzBr_2$ and (b) $EtCzBr_2$ in 2-methyltetrahydrofuran at 77 K, 10^{-4} mol l^{-1} in the absence of air, excitation at 350 nm. (c) Absorption spectrum of $PVCzBr_2$.

Samples of $PVCzBr_2$ were prepared by cationic polymerization (BF_3,OEt_2) of the corresponding monomer.[7] $PVCzBr_2$ exhibits no emissions in solution at room temperature because of the efficient intersystem-crossing of $S_1 \rightarrow T_1$ enhanced by the heavy atom effect due to bromination. The delayed emission spectra of $PVCzBr_2$ in rigid solution of 2-methyltetrahydrofuran at 77 K, and 3,6-dibromo-*N*-ethylcarbazole ($EtCzBr_2$) as a low molecular model compound are shown in the Figure. The delayed emission spectrum of $EtCzBr_2$ consists of a structured band system built on the 0,0-band of the $T_1 \rightarrow S_0$ transition at 417 nm, and corresponds well to the phosphorescence spectrum of *N*-ethylcarbazole having the 0,0-band at 407 nm.[8] The lifetime of this band is approximately 17 ms. The delayed emission of $EtCzBr_2$ can be identified with phosphorescence from the 3,6-dibrominated carbazole ring. On the other hand, the delayed emission spectrum of $PVCzBr_2$ shows only a broad band around 459 nm having its intensity maximum about 2200 cm^{-1} lower than the 0,0-band of $EtCzBr_2$, and exhibits no normal structured phosphorescence as can be seen in the case of $EtCzBr_2$. This emission band has a lifetime of about 32 ms, slightly longer than the phosphorescence of $EtCzBr_2$. The excitation spectrum of this band agrees well with the absorption spectrum of $PVCzBr_2$, and the intensity depends on a linear function of the excitation light intensity. Special care was paid to impurities in the sample and solvent used, and there was no spectral change due to photochemical decomposition during measurements. The energy of 2200 cm^{-1} corresponds to the energy shift of *ca.* 3000 cm^{-1} between monomer and excimer fluorescence observed for the singlet excimer in poly-*N*-vinylcarbazole (PVCz). Thus the structureless emission band of $PVCzBr_2$ in rigid solution is probably due to excimer phosphorescence emitted from the triplet excimer states.

On the basis of the observation of delayed fluorescence due to triplet–triplet annihilation we have indicated that the triplet excitations of PVCz migrate in high efficiency along the polymer chain.[8] Probably, the triplet excitons of $PVCzBr_2$ enhanced by the heavy atom effect can be considered to migrate along the polymer chain just as in PVCz, and the migrating excitons may be trapped as an energy "sink" at excimer sites, where two neighbouring chromophores are in a convenient orientation for the triplet excimer formation in rigid solution.

(*Received*, 10*th December* 1973; *Com.* 1660.)

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