CHEMISTRY LETTERS, pp.509-512, 1973. Published by the Chemical Society of Japan

TRIPLET EXCITON MIGRATION IN POLY-N-VINYLCARBAZOLE AND ITS STYRENE COPOLYMERS

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Delayed emission spectra of poly-N-vinylcarbazole and its styrene copolymers in a rigid glass have been measured at 77°K. New observations of delayed fluorescence and phosphorescence of poly-N-vinylcarbazole have been obtained. Delayed fluorescence due to triplet-triplet annihilation resulting from intramolecular migration of triplet excitons exhibits more sensitive dependence on the length of N-vinylcarbazole unit sequence than the kind of end groups. This fact is supported by the experiments on N-vinylcarbazole - styrene copolymers.

It is well-known that vinylpolymers having the pendant π-electron conjugated systems such as polyvinylnaphthalene (PVN)$^{1)}$ and poly-N-vinylcarbazole (PVCz)$^{2)}$ emit not only monomeric fluorescence but also excimer fluorescence due to the interaction between nearby chromophores in solution as well as in solid film. PVCz is remarked also from the viewpoint of its relatively large photoconductivity.$^{3,4)}$ Klöpffer et al.$^{5)}$ have investigated excimer fluorescence of PVCz in detail and have suggested that singlet exciton of PVCz can easily migrate along the polymer chain. As for triplet excited states, however, exciton migration has not yet been reported. Recently Fox et al.$^{6,7,8)}$ have studied on the delayed emission spectra of PVN and copolymers with styrene (PVN/St), and their observations of delayed fluorescence and phosphorescence of the polymer suggest that triplet excitons can also migrate along the polymer chain.

It is very interesting to investigate the spectroscopic behaviors of the excited states of PVCz in order to make clear whether the triplet excitons of PVCz contribute to the process of the photocarrier generation or not. In the present letter, the spectroscopic studies on the emission spectra of PVCz and N-vinylcarbazole - styrene copolymers (PVCz/St), and new observations of delayed fluorescence and phosphorescence of PVCz and PVCz/St will be reported.

In Table 1 are listed polymer samples used in the present study along with the conditions of polymerization. The delayed emission spectra were measured with a Hitachi MPF model 3 spectrofluorophotometer (light source, 150W Xe lamp) with delayed emission attachments. Spectra were uncorrected for either source output or detector response. Phosphorescence decays were traced on an x-y recorder and delayed fluorescence lifetimes were determined from oscilloscope traces. Polymer samples having adequate concentrations with 3:2 methyltetrahydrofuran (MTHF) - tetrahydrofuran (THF) glasses at 77°K in quartz capillary tubes were sealed in vacuum. In Figure 1 are shown the total emission and delayed emission spectra of PVCz at 77°K. The delayed emission spectrum of N-ethylcarbazole (EtCz) corresponding to the monomeric unit of PVCz is also drawn in the figure. The excitation spectra for two maxima of PVCz emission in the shorter (around 370 nm) and longer (around 445 nm) wavelength regions gave a good correspondence with its absorption spectrum, respectively. Both lifetimes (τ_p) of the emissions of PVCz and EtCz in the longer wavelength region were 7.6 sec. The band profiles of these emissions are quite similar to that of carbazole and these values of the lifetime

Table 1. Polymer samples and delayed emission intensity

Sample	Initiator and conditions[a]	VCz contents (%)[b]	Molecular weight[c]	I_{df}/I_p[d]
(a) Homopolymers				
PVCz (commercial)	...	...	10^5	10
PVCz-A	1 mol% AIBN, 60°C, 4hrs	...	$7.9\text{x}10^4$	3.55
PVCz-B	1 mol% AIBN, 80°C, 4hrs	...	$3.5\text{x}10^4$	0.90
PVCz-C	1.5 mol% AIBN, 80°C, 8hrs	...	$3.0\text{x}10^4$	0.70
PVCz-D	2 mol% AIBN, 80°C, 4hrs	...	$2.1\text{x}10^4$	0.55
PVCz-E	hν 310 nm, in DMSO, 5hrs	...	$1.4\text{x}10^4$	0.40
PVCz-F	2,5-DQ, hν, in CH_2Cl_2, 5hrs	...	$0.8\text{x}10^4$	0.0
(b) Copolymers				
PVCz/St-A	3.5 mol% AIBN, 60°C, 15hrs	99	$1.4\text{x}10^4$	0.06
PVCz/St-B	3.5 mol% AIBN, 60°C, 15hrs	98	$0.8\text{x}10^4$	≅ 0.0
PVCz/St-C	3.5 mol% AIBN, 60°C, 15hrs	50	$0.4\text{x}10^4$	0.0
PVCz/IBVE	CA, 80°C, 5hrs, in NB	95	...	0.0
PVCz/VPD	CA, in NB	98	...	0.0

[a] 2,5-DQ: 2,5-dichloroquinone, CA: chloranil, NB: nitrobenzene, DMSO: dimethylsulfoxide, AIBN: 2,2'-azobisisobutyronitrile.

[b] determined by UV absorption. [c] measured by vapor pressure osmometer in benzene at 40°C.

[d] These measurements were made with almost constant excitation light intensity.

are in good agreements with the value of 7.6 sec for the phosphorescence lifetime of carbazole reported by V. L. Ermolaev.[9] The emission band in this region of PVCz, therefore, can be identified with phosphorescence from the PVCz polymer.

On the other hand, the delayed emission band in the shorter wavelength region locates in the same position as the normal fluorescence of PVCz, and moreover the intensity of this band is quenched in high efficiency by piperylene, a well-known triplet quencher, together with phosphorescence. This emission has a lifetime (τ_{df}) of about 10 msec. From the double logarithmic plot of the intensity of this delayed emission band against the excitation light intensity, the attenuation of this band occurs in the second order. These facts indicate that this emission band is considered to be delayed fluorescence taking its rise in the triplet-triplet annihilation of the freely migrating or trapped triplet excitons of PVCz.

In the last column of Table 1 are shown the intensity ratios (I_{df}/I_p) of delayed fluorescence and phosphorescence of PVCz homopolymers, each having different molecular weight. In the case of commercial PVCz, Luvican M170 (BASF Co., Ltd.), which has high molecular weight, delayed fluorescence was observed in much larger intensity than phosphorescence, while in PVCz with low molecular weight of 8 x 10^3 (corresponding to about 50 VCz unit sequence) and, of course, EtCz delayed fluorescence gave no appreciable intensity. These observations lead to a viewpoint that the delayed fluorescence intensity has much dependence upon the molecular weight, that is, the length of the VCz unit sequence. Fox et al.[6] have reported that in the case of PVN delayed fluorescence due to triplet-triplet annihilation is more sensitive to end groups than chain length. Our point of view, however, is supported by the following experiments on PVCz/St copolymers.

As shown in Figure 2, delayed fluorescence could hardly be observed even in the copolymer with 99% VCz contents, and only phosphorescence was observed in the copolymers with VCz contents less than 90%. Since the introduction of St units may disconnect the sequence of VCz units, the intramolecular energy migration of triplet excitons of VCz units may be disturbed, and consequently the intensity of delayed fluorecence decreases. The drastic decrease

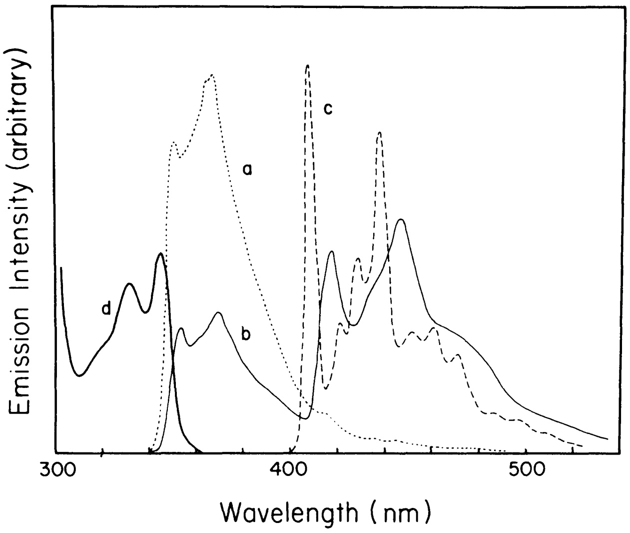

Figure 1. Emission and absorption spectra of PVCz.
(a) Total emission at 77°K, in 8.0 x 10^{-4} mol/l MTHF-THF solution; excitation: 340nm.
(b) Delayed emission of PVCz at 77°K.
(c) Delayed emission of EtCz at 77°K, in 1.0 x 10^{-3} mol/l MTHF-THF solution.
(d) Absorption spectrum of PVCz in 5.6 x 10^{-4} mol/l solution for comparison.

in I_{df} with VCz contents from homopolymer to 99% PVCz/St copolymer is attributed to exhaustion of triplet states through the phosphorescence emission from the trapped triplet excitons arriving at St units before triplet-triplet annihilations occur. In the case of the copolymers with isobutylvinylether and vinylpyrrolidone containing 95% and 98% VCz contents, respectively, delayed fluorescences were not observed with appreciable intensity. Fox et al.8) reported that delayed fluorescence of PVN was still observed in the PVN/St copolymer of only 5% VN contents. As stated above, however, delayed fluorescence of PVCz could not be observed even in the PVCz/St copolymer of 95% VCz contents. Thus, there is a remarkable difference in the behaviors of triplet excitons between the PVN/St and PVCz/St copolymers, although the intensity of delayed fluorescence is partially sensitive to the condition of measurements. Moreover, the delayed fluorescence lifetime of the PVCz polymer is shorter than that of the PVN polymer (about 80 msec).6) These facts suggest the triplet excitons of PVCz migrate in much higher speed along the VCz sequence than those of PVN. The mechanistic viewpoint of these observations will be reported in a forthcoming full paper with some additional results. It will be noticed here only that the phosphorescence band of PVCz/St copolymers shows the slight shift (about 6 nm) to the shorter wavelength comparing with that of homopolymers and becomes sharp with increasing St contents.

Phosphorescence as well as delayed fluorescence due to triplet-triplet annihilation can be observed in the PVCz polymer. The latter emission occurs only when the length of VCz sequence is sufficiently long, and triplet excitons of PVCz migrate in high efficiency along the polymer chain by the interaction between nearby chromophores just as singlet excitons.

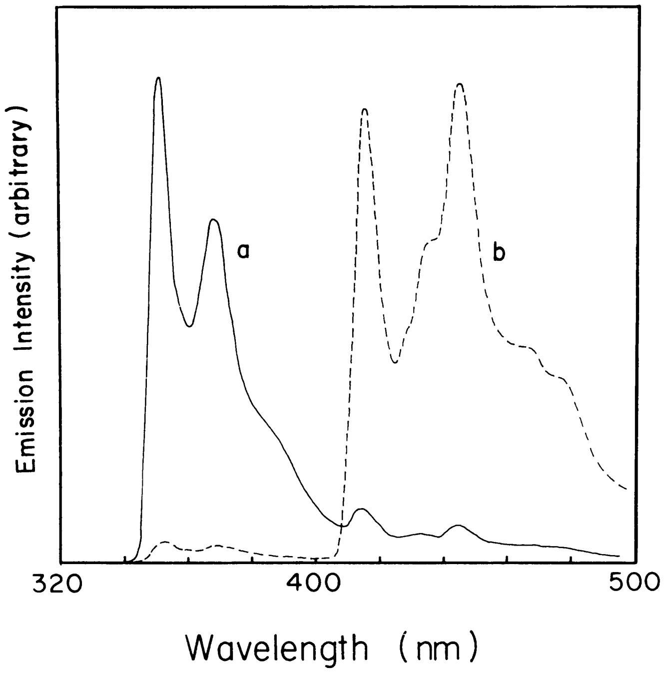

Figure 2. Total emission (a) and delayed emission (b) spectra at 77°K for PVCz/St copolymer of 99% VCz contents in 8.0×10^{-4} mol/l MTHF-THF solution; excitation: 340nm.

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(Received February 28, 1973)