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HETEROGENEOUS TRIPLET-TRIPLET ANNIHILATION IN POLY-N-VINYLCARBAZOLE FILMS DOPED WITH NAPHTHALENE AND FLUORENE

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The triplet energy transfer in poly-N-vinylcarbazole (PVCz) films has been investigated by measuring the delayed emission spectra at 77 K. By doping of a triplet quencher such as naphthalene and fluorene, the PVCz phosphorescence decreased significantly and was replaced by the sensitized dopant phosphorescence. On the contrary, the PVCz delayed fluorescence rather increased with increasing concentration of triplet quenchers. This phenomenon suggests the presence of a heterogeneous triplet-triplet annihilation in PVCz films.

Recently, the emission spectra of aromatic vinylpolymers have been extensively investigated. The triplet energy transfer in rigid solution at 77 K has been studied in detail on the vinylpolymers having large aromatic rings such as naphthyl and carbazolyl groups.[1-4] Concerning the triplet energy transfer in solid films, David et al. have reported on the vinylpolymers having small aromatic rings which emit only phosphorescence and no delayed fluorescence.[5-7] They showed the triplet exciton migration frequencies in such polymer films were smaller than in the corresponding crystals. Concerning the vinylpolymer films having large aromatic rings, Fox et al. and Klopffer et al. have qualitatively studied on poly-1-vinylnaphthalene and poly-N-vinylcarbazole (PVCz), respectively.[8,9] However, the triplet energy transfer in solid films has never been hitherto studied quantitatively on such vinylpolymers to the knowledge of the authors.

The authors have investigated quantitatively the changes in the delayed emission intensity of PVCz films doped with various concentrations of triplet quenchers such as naphthalene and fluorene. As the results, an interesting heterogeneous triplet-triplet (T-T) annihilation has been observed.

N-vinylcarbazole was recrystallized two times from methanol and n-hexane, respectively, and was polymerized by heating with azobisisobutyronitrile in benzene at 70 °C for 7 hr. The polymer was purified three times by reprecipitation from the benzene solution with a methanol-acetone (1:1) mixture. Commercial naphthalene and fluorene of a scintillation grade were purified by zone-refining. Doped films were prepared by casting the dichloroethane solution of PVCz with a certain amount of dopant onto a quartz plate. The coated plates were immersed in liquid nitrogen for the measurement of the emission spectra.

The emission spectra were measured with a spectrophosphorimeter constructed using a stabilized 500 W xenon lamp, monochromators, and a PM 55 (S-20) photomultiplier. The spectra were corrected for the detector response by using a standard tungsten lamp. It was confirmed that application of phosphoroscope factor was not necessary in the present case. Phosphorescence decay curves were recorded by means of an X-t recorder and delayed fluorescence lifetimes were determined from oscilloscope traces. The films were excited by 345 nm light, which was not absorbed by the triplet quenchers.

Delayed emission spectra of PVCz films doped with naphthalene of various concentrations at 77 K are shown in Fig. 1. The spectra of undoped PVCz films consist of two emission bands. The same spectra were obtained for the PVCz films purifed by reprecipitation up to ten times. The broad delayed emission in the longer wavelength region is invariably monophotonic in origin and its lifetime consists of two components (7.5 and 1.7 s). This two component decay was observed also by Klopffer et al.9) This emission is considered to be phosphorescence of PVCz films. On the other hand, the position and profile of the delayed emission band in the shorter wavelength region are the same as the normal fluorescence at 77 K, and the emission intensity depends quadratically on excitation light intensity. This emission has a lifetime of about 50 ms. These facts indicate that this band is assigned to the delayed fluorescence resulting from a homogeneous T-T annihilation, although Klopffer et al. have failed in observing this emission band.9)

By doping of naphthalene, the PVCz phosphorescence decreases significantly and is replaced by a sensitized naphthalene phosphorescence. On the contrary, the PVCz delayed fluorescence increases with increasing the concentration of naphthalene. The changes in the delayed fluorescence (I_{df}) and in the sensitized naphthalene phosphorescence (I_{sph}) as a function of naphthalene mole fraction in polymer films are given in Fig. 2. In the case of the highest concentration of naphthalene (3.52×10^{-2} mol/mol), the PVCz phosphorescence is quenched completely and I_{sph} reaches

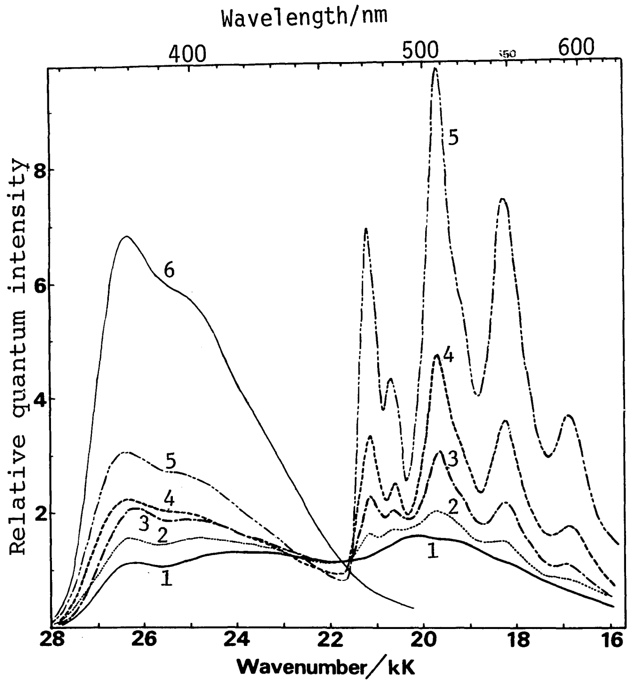

Fig. 1. Delayed emission spectra of PVCz films doped with naphthalene at 77 K. Naphthalene concentration; (1) 0, (2) 1.41 x 10^{-4}, (3) 7.04 x 10^{-4}, (4) 1.41 x 10^{-3}, and (5) 7.04 x 10^{-3} mol/VCz unit mol.
The prompt fluorescence (6) of a PVCz film was also given for comparison.

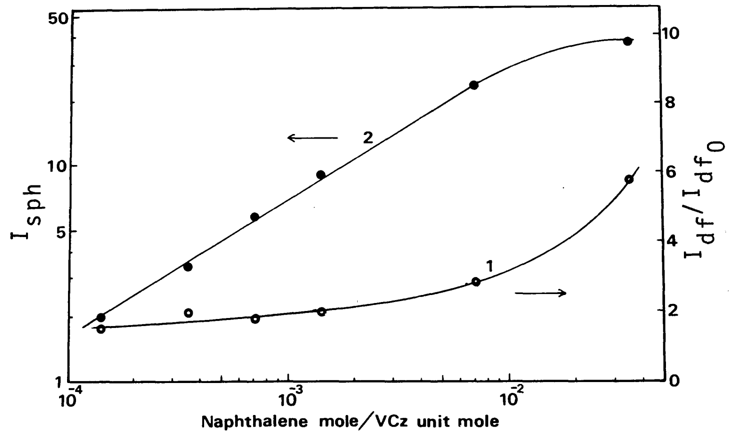

Fig. 2. Intensity dependence of PVCz delayed fluorescence I_{df} and sensitized naphthalene phosphorescence I_{sph} in PVCz films on concentration of naphthalene at 77 K.
(1) I_{df} (2) I_{sph}

saturation, whereas I_{df} increases steeply and is also in second order with respect to the exciting light intensity. The lifetime of the delayed fluorescence is also lengthened gradually with increasing the concentration of naphthalene up to 370 ms at 3.52 x 10^{-2} mol/mol. Similar results were obtained for PVCz films doped with fluorene.

It is clear from the above-mentioned results that both dopants act as effective triplet quenchers for carbazolyl chromophores in PVCz films. The increase in the delayed fluorescence by doping of these triplet quenchers, therefore, strongly suggests that a heterogeneous T-T annihilation process occurs in a fairly good efficiency between freely migrating triplet excitons of PVCz and either the triplet state of the dopant or a shallow trap site introduced by it.

The triplet energy transfer in PVCz was also investigated in rigid solution (2-methyltetrahydrofuran–tetrahydrofuran (3:2) mixture) at 77 K. By doping of naphthalene, the PVCz phosphorescence decreases and is replaced by the sensitized naphthalene phosphorescence, as is the case with the solid films. The PVCz delayed fluorescence shows an anomalous phenomenon, being a little different from that in the sloid films; it increases at low naphthalene concentrations up to 5 x 10^{-3} M and decreases at higher concentrations. On the other hand, in the case of doping of 1,3-pentadiene as a triplet quencher, both the PVCz delayed fluorescence and the PVCz phosphorescence decrease significantly with increasing concentration of 1,3-pentadiene. The degree of quenching is much larger for the former than the latter. This is the behavior observed usually for poly-1-vinylnaphthalene and poly-1-naphthylmethacrylate.[1,3) Judging from these results, in the case of PVCz doped with naphthalene, the heterogeneous T-T annihilation seems to be present even in rigid solution at 77 K.

More detailed report of our studies including another vinylpolymers having carbazolyl groups and the comparison of the behaviors of triplet excitons both in solid films and in rigid solution will be published elsewhere.

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