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The Migration of Electronic Excitation Energy in Copolymers of *N*-Vinylcarbazole with a Small Content of Styrene or Vinyl Acetate[1)]

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Synopsis. The migration of electronic excitation energy in films of copolymers rich in *N*-vinylcarbazole has been studied by fluorescence quenching experiments using dimethyl terephthalate and perylene as guest molecules. The efficiency of the singlet exciton migration is almost the same for the copolymers and for poly-*N*-vinylcarbazole.

The present authors have reported on the significant decrease in the photocurrent in the copolymers of *N*-vinylcarbazole(VCz) with a small content of styrene (St) or vinylacetate(VAc).[1)] For understanding this phenomenon, the efficiency of the migration of the electronic excitation energy in the copolymer films should be compared with the efficiency in a PVCz film.

The migration of the electronic excitation energy in a PVCz film has been studied by Schneider[2)] and by Klöpffer.[3)] Klöpffer has concluded that the energy transfer in a PVCz film occurs by means of the exciton migration mechanism.

Dimethyl terephthalate (DMTP) is a weak electron acceptor and interacts with a carbazole (Cz) chromophor to produce an exciplex which emits a broad fluorescence at 21000 cm^{-1}.[6)] The single-step (dipole-dipole resonance) energy transfer from a Cz chromophor to a DMTP molecule is impossible, because DMTP has no absorption in the wavelength region longer than 300 mμ. DMTP is, therefore, expected to be useful in studying the efficiency of the singlet exciton migration.

Experimental

The polymers were prepared by a method similar to that described perviously.[1)] The molecular weights of the polymers ranged from 7000 to 100000. DMTP and perylene were purified by repeated recrystallizations and then by vacuum sublimation. A spectrophotofluorometer was constructed using a high-intensity grating monochrometor equipped with a 1P 28 photomultiplier. The light from a 500W super-high-pressure mercury lamp was monochromatized by means of interference filters and then used for excitation. The emission spectra were measured with 90° excitation at 20 °C in the air and corrected using quinine sulfate and β-naphthol. A film (1 μ thick) was cast onto a quartz plate from a benzene solution and dried at 50 °C *in vacuo*.

Results and Discussion

Figure 1 shows the fluorescence spectra of the VCz–St copolymers in solution. The copolymers rich in VCz show almost the same fluorescence spectra as that of PVCz. With a decreasing VCz content, the excimer fluorescence (I_E) is reduced and the monomer fluorescence (I_M) is enhanced. The I_E/I_M ratio in the VCz–St copolymer is much smaller than that in the VCz–VAc copolymer with the same VCz content, as is shown in Fig. 2. From the monomer reactivity ratio,[5)] the VCz sequence in the former is considered to be much shorter than that in the latter. Furthermore, the I_E/I_M value in the alternate VCz–fumaronitrile copolymer[6)] is less than 0.1, as is shown by a cross mark in Fig. 2; this is much smaller than the corresponding value (0.4) in the VCz–St copolymer. These results suggest that excimer formation in a dilute solution of PVCz and of the VCz copolymers is mainly between nearest neighboring chromophores in a polymer chain rather than between far-distant neighboring ones.

The host-sensitized energy transfer in films of PVCz and of copolymers rich in VCz doped with DMTP or perylene was investigated. The fluorescence spectra of the films doped with DMTP are shown in Fig. 3.

According to the hopping model of exciton migration, the quenching factor of the host (monomer and excimer) fluorescence (Q_H) can be expressed by Eq. (1), in a way similar to that of the excimer fluorescence (Q_E) in Ref. 3, when that of the monomer fluorescence (Q_M) due to excimer-forming sites is much larger than unity:

$$Q_H = C/C_E \qquad (1)$$

where C and C_E are the concentrations of the guest and the excimer-forming site (mol/mol VCz unit).

The values of Q_H were calculated from Eq. (2):[3)]

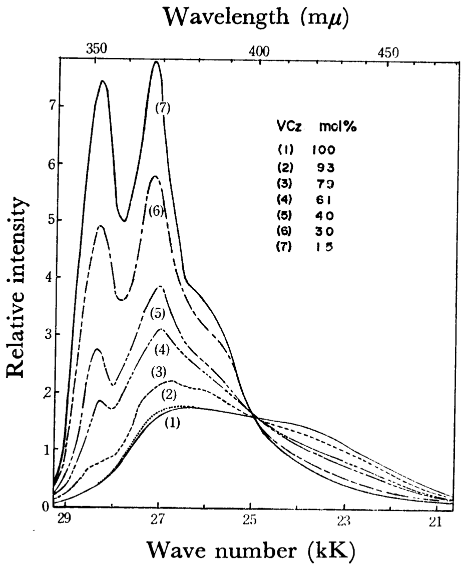

Fig. 1. Fluorescence spectra of VCz–St copolymers in benzene solution (1.5×10^{-4} mol VCz unit/l), 310 mμ excitation.

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TABLE 1. ENERGY TRANSFER BY EXCITON DIFFUSION PROCESS IN POLYMER FILMS

No	Host	Guest	η_H	η_G	$C_E \times 1000$ (mol/mol VCz unit)	$1/C_E$
1	PVCz	DMPT	0.03	0.036	2.9	350
2	VCz-St copolymer (VCz 93 mol%)	DMPT	0.03	0.036	3.3	300
3	PVCz	Perylene	0.03	0.3	1.5	670
4	VCz-St copolymer (VCz 79 mol%)	Perylene	0.047	0.4	1.6	630
5	VCz-VAc copolymer (VCz 91 mol%)	Perylene	0.03	0.3	1.1	900
6	VCz-VAc copolymer (VCz 83 mol%)	Perylene	0.035	0.35	1.9	530

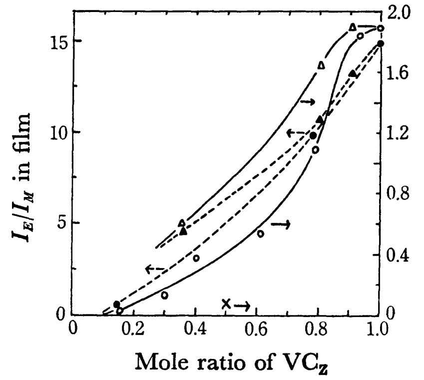

Fig. 2. Dependence of I_E/I_M ratios for benzene solution (1.5×10^{-4} mol VCz unit/l) and for films on VCz content in copolymers. (○) and (●), VCz-St copolymers; (△) and (▲), VCz-VAc copolymers; (X), VCz-fumaronitrile, 310 mμ excitation.

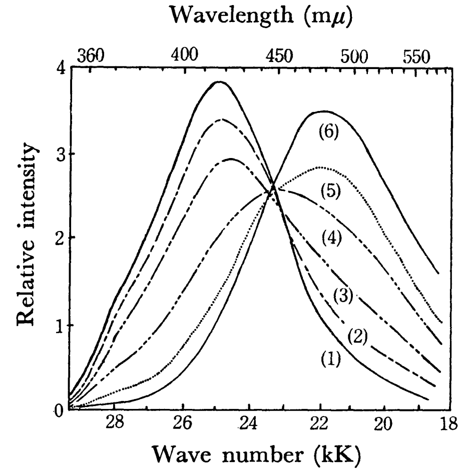

Fig. 3. Fluorescence spectra of PVCz films doped with DMTP, 334 mμ excitation. DMTP concentration; (1) 0, (2) 8×10^{-4}, (3) 2×10^{-3}, (4) 5×10^{-3}, (5) 1×10^{-2} and (6) 3×10^{-2} mol/mol VCz unit.

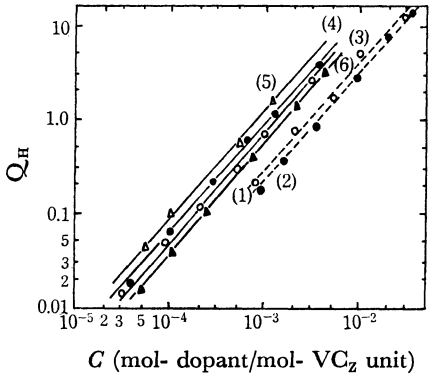

Fig. 4. Q_H *versus C*. See Table 1 as to the number in parentheses.

$$Q_H = (I_G/I_H)(\eta_H/\eta_G) \qquad (2)$$

where I_H and I_G are the fluorescence intensities of the host and the guest and where η_H and η_G are quantum yields. The quantum yields of the exciplex fluorescence (η_G) between a Cz chromophore and DMTP in the films were determined from the exciplex fluorescence intensity in the heavy doping films (C=0.1) where no host fluorescence was observed.

Figure 4 shows the bilogarithumic plots of Q_H thus obtained and C. Straight lines with a slope of 1.0 were obtained for every film as was to be expected from Eq. (1). In the films doped with DMTP, where the single-step energy transfer by the dipole-dipole resonance is impossible, the host fluorescence is quenched significantly by a small amount of DMTP, according to Eq. (1), as in the case of perylene doping. This indicates that the energy transfer both in a PVCz film and in films of copolymers rich in VCz occurs by means of the exciton migration mechanism. The values of C_E were obtained from Fig. 4: they are tabulated in Table 1. The values of C_E obtained from films doped with DMTP are somewhat larger than the values obtained from films doped with perylene. This may imply that in films doped with perylene the single-step energy transfer plays an important role when a singlet exciton comes close to a perylene molecule. In both doping systems, the values of C_E are, however, almost the same for PVCz and for copolymers.

Both in a PVCz film and in films of copolymers rich in VCz, the exciton migration is limited by excimer-forming sites, and the number of Cz rings covered by an exciton during the life-time is represented by $1/C_E$. This number is almost the same for a PVCz film and for copolymers films, it ranges from 400 to 900.

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