Singlet Excitation Energy Transfer in the Vinyl Polymers with Pendant Carbazolyl Groups

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The migration of electronic excitation energy in films of poly(*N*-vinylcarbazole) (PVCz) prepared by the radical and cationic polymerizations(PVCz(r) and PVCz(c) respectively), poly[2-(9-carbazolyl)ethyl vinyl ether] (PCzEVE), brominated PVCz(BPVCz), and poly(9-acryloylcarbazole) (PACz) has been studied by means of fluorescence-quenching experiments, using dimethyl terephthalate or perylene as a guest molecule. No clear difference in the concentration of the effective intrinsic trap sites was observed between PVCz(r) and PVCz(c) films. The concentration of the sandwich-like excimer site(c_E) in a PVCz(r) film was nearly equal to that in a PVCz(c) film, while the concentration of the second excimer site (c_S) in a PVCz(r) film was higher than that in a PVCz(c) film by a factor of about 1.6. The value of c_E was much larger than that of c_S for both films. The second excimer site seems to be a shallow trap. The number of carbazolyl chromophores covered by a singlet exciton during the lifetime was in the following order: PCzEVE$>$PVCz(r)$\approx$PVCz(c)$>$PACz$\approx$BPVCz. This order was explained by the concentration of the intrinsic trap sites depending on the distance between neighboring Cz chromophores, the lifetime of the singlet exciton, and the concentration of extrinsic trap sites.

Recently, the emission spectra of aromatic vinyl polymers have been extensively investigated. Studies of singlet energy transfer and migration in vinyl polymer films with large aromatic rings are very important in understanding their electric and optical properties. Klöpffer[1] has reported that the results of fluorescence-quenching experiments in an amorphous PVCz film are consistent with a hopping model of monomer exciton migration, in which excitons can migrate in a polymer film and both excimer-forming sites and guest molecules act competitively as exciton traps. From a lifetime quenching observed in PVCz film doped with perylene, Powell *et al.*[2] has recently proposed a model containing dimer sites besides guest molecules and excimer-forming sites. Concerning an undoped PVCz film, Offen *et al.*[3] suggested the presence of a dimer site as a result of measuring the fluorescence decay time of PVCz films at 77 K. Klöpffer *et al.*[4] showed that the two different types of the spectra were observed in the prompt fluorescence and phosphorescence at 77 K, independent of the polymerization methods.

Recently, we have ourselves revealed, from the NMR spectra and the glass-transition temperatures, that PVCz prepared by the cationic polymerization has a higher isotacticity than the PVCz prepared by the radical polymerization(PVCz(c) and PVCz(r) respectively).[5] It has also been reported that the difference in the tacticity of PVCz is reflected in the fluorescence spectra in fluid and rigid solutions and that the concentration of the second excimer site in a syndiotactic-rich polymer (PVCz(r)) is higher than that in an isotactic-rich polymer(PVCz(c)).[6] Therefore, it is of interest to investigate how the difference in the tacticity of PVCz samples affects the singlet-excitation-energy migration. The studies of singlet-excitation-energy migration in vinyl polymer films with carbazolyl(Cz) chromophores widely spaced on the skeletal chains is of interest in connection with that of PVCz films.

In the present research, we investigated the migration of the electronic-excitation energy in films of PVCz(r), PVCz(c), brominated PVCz(BPVCz), poly[2-(9-carbazolyl)ethyl vinyl ether] (PCzEVE), and poly(9-acryloylcarbazole) (PACz); in the latter two polymers, the Cz chromophores are widely spaced on the skeletal chains by $-O-CH_2-CH_2-$, and $-CO-$ bonds respectively. Dimethyl terephthalate (DMTP) or perylene was used as the guest molecule. In the case of perylene, the long-range resonant energy transfer is somewhat possible.[2,7] However, the long-range resonant energy transfer from a Cz chromophore to a DMTP molecule is quite impossible, because DMTP has no absorption in the wavelength region where the fluorescence of the PVCz film is observed.[7] Therefore, the DMTP is very useful in studying the phenomenon of the single-exciton migration.

Experimental

The vinyl polymers(PVCz(r), PVCz(c), BPVCz, PCzEVE, and PACz) were prepared by the methods described previously.[8,9] The DMTP and perylene were recrystallized twice from benzene and subsequently sublimed *in vacuo.* Doped films were cast onto quartz or Pyrex glass plates from a dichloroethane solution of the polymer containing a certain amount of the dopant and dried *in vacuo.* The thickness of the film was about 4 μm for PCzEVE and about 7 μm for the other polymers.

The fluorescence spectra were measured with the apparatus described in a previous paper.[8] The spectra at 293 K were measured for the coated plates *in vacuo* (0.1 Torr). The spectra at 77 K were measured for the coated plates immersed in liquid nitrogen. PACz films were excited by 315 nm light, and the others, by 335 nm light.

For the fluorescence-decay time measurements, the samples were excited with a N_2 gas laser. The sample fluorescence was chosen with appropriate glass filters before being detected by a biplanar phototube R 617. Responses from the phototube were led to a Tektronix 475 oscilloscope, and the decay curve was photographed.

Results and Discussion

Fluorescence Spectra of the Vinyl Polymer Films with Pendant Carbazolyl Groups. The fluorescence spectra of PVCz(r) and PVCz(c) films are shown in Figs. 1 and 2.

The difference in the spectra between PVCz(r) and PVCz(c) films observed at 293 and 77 K is similar to that observed in a fluid solution.[6] That is, the fluorescence intensity in the shorter-wavelength region of a PVCz(r) film is larger than that of a PVCz(c) film. Therefore, the emission band in the shorter-wavelength region was assigned to the second excimer fluorescence, and that in the longer wavelength region, to the sandwich-like excimer fluorescence. The fluorescence spectra of both polymer films were resolved into two individual bands. The resolution spectra thus obtained are also shown in Figs. 1 and 2. The intensity of the second excimer fluorescence relative to the sandwich-like excimer one and the fluorescence yields are listed in Table 1.

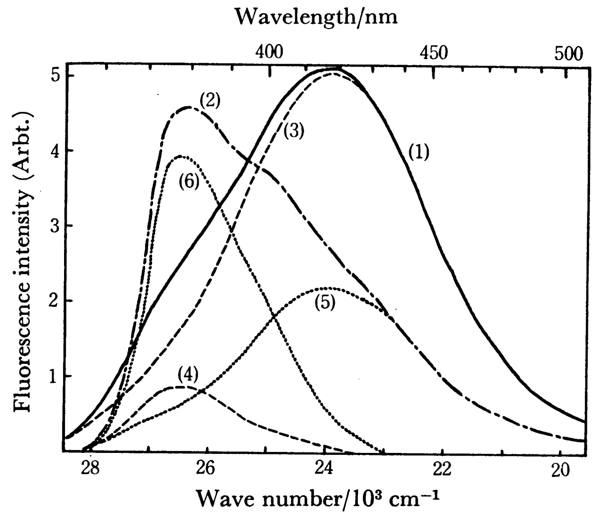

Fig. 1. Fluorescence spectra and the resolution spectra of PVCz(r) films at 293 and 77 K.
(1) 293 K, (2) 77 K, (3) the component of the sandwich-like excimer fluorescence at 293 K, (4) the component of the second excimer fluorescence at 293 K, (5) the component of the sandwich-like excimer fluorescence at 77 K, (6) the component of the second excimer fluorescence at 77 K.

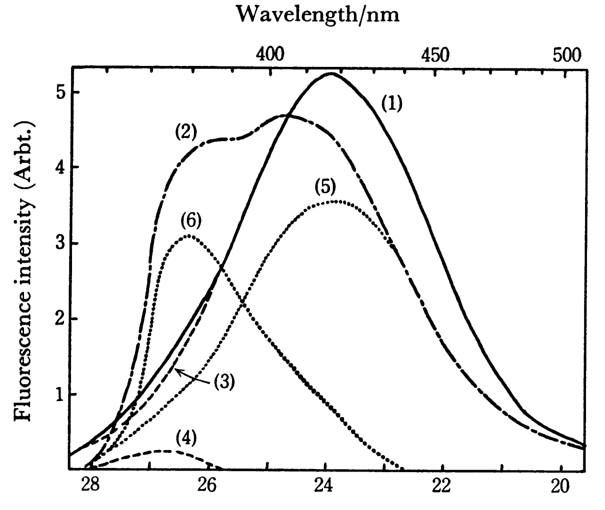

Fig. 2. Fluorescence spectra and the resolution spectra of PVCz(c) films at 293 and 77 K.
(1) 293 K, (2) 77 K, (3) the component of the sandwich-like excimer fluorescence at 293 K, (4) the component of the second excimer fluorescence at 293 K, (5) the component of the sandwich-like excimer fluorescence at 77 K, (6) the component of the second excimer fluorescence at 77 K.

Table 1. The intensity of the second excimer fluorescence relative to the sandwich-like one (I_S/I_E) and the quantum efficiencies of the host fluorescence (η_H)

Host	I_S/I_E	η_H
PVCz(r)	0.083	0.045
PVCz(c)	0.013	0.041
PVCz(r)[a]	0.93	—
PVCz(c)[a]	0.55	—
PCzEVE	—	0.10
PACz	—	0.0002
BPVCz	—	0.001

a) At 77 K.

The presence of two kinds of emitting species in the fluorescence of PVCz(r) and PVCz(c) was also clarified by measuring the fluorescence decay curves of the polymers. The fluorescence decay curves of both polymer films in air at 293 K are clearly two-component (20±3 and 6±1 ns) in the shorter wavelength region, but one-component (22±2 ns) in the longer wavelength region. The intensity of the short-lived component relative to the long-lived one for a PVCz(r) film in the shorter wavelength region is larger than that for a PVCz(c) film. Therefore, the long- and short-lived components correspond to the sandwich-like excimer fluorescence and the second excimer one respectively. Similar results were also obtained at 77 K; the long- and short-lived components are 17±2 and 6±2 ns respectively. These decay constants are roughly in agreement with the values reported by Powell *et al.* (20 and 10 ns).[2] The lifetime of the sandwich-like excimer fluorescence of PVCz films is shorter than that of PVCz in a fluid solution (*ca.* 40—42 ns)[6,10,11] and that of a PVCz film obtained by Offen *et al.* (43 ns).[3]

The fluorescence spectra of a PCzEVE film undoped and doped with DMTP are shown in Fig. 3. A PCzEVE film shows only a broad, structureless fluorescence spectrum with a peak at *ca.* 26050 cm^{-1}. The fluorescence decay curves in air are one-component in both the shorter and longer wavelength regions (4—5 and 10—11 ns respectively). A two-component decay curve is observed in the medium wavelength region. This fact indicates that the two kinds of emitting species are present in a PCzEVE film at 293 K. Although the fluorescence spectrum of a PCzEVE film at 77 K has the structure, it does not seem to be the monomeric fluorescence of a Cz chromophore because of the large Stokes shift (1540 cm^{-1}).

The fluorescence spectra of PACz and BPVCz films undoped and doped with DMTP or perylene are shown in Fig. 4. The fluorescence efficiency of a PACz film is extremely low (Table 1) because of the presence of the intersystem crossing from the lowest $^1\pi, \pi^*$ state to the lowest ^{3}n, π^* state due to a carbonyl group. A PACz film shows a fluorescence spectrum consisting of two components. The spectra of PACz and BPVCz films

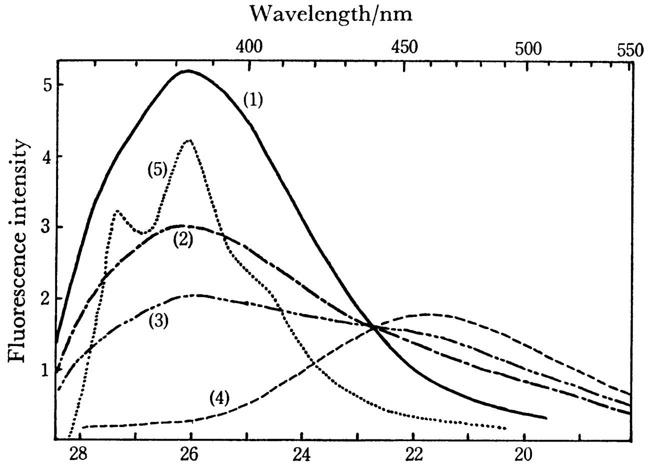

Fig. 3. Fluorescence spectra of PCzEVE films doped with DMTP at 293 K. DMTP concentration; (1) 0, (2) 4.44×10^{-4}, (3) 8.88×10^{-4}, and (4) 1.18×10^{-2} (mol/CzEVE unit mol). Fluorescence spectrum of the undoped film at 77 K is also given by a dotted line (5).

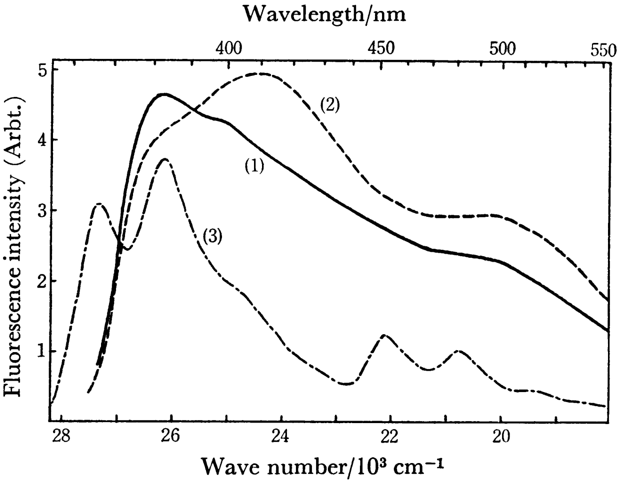

Fig. 5. Fluorescence spectra of PVCz(r), PVCz(c) and PCzEVE films doped with DMTP or perylene at 77 K. (1) PVCz(r) doped with DMTP (3.26×10^{-3} mol/VCz unit mol), (2) PVCz(c) doped with DMTP (3.02×10^{-3} mol/VCz unit mol), and (3) PCzEVE doped with perylene (1.15×10^{-4} mol/CzEVE unit mol).

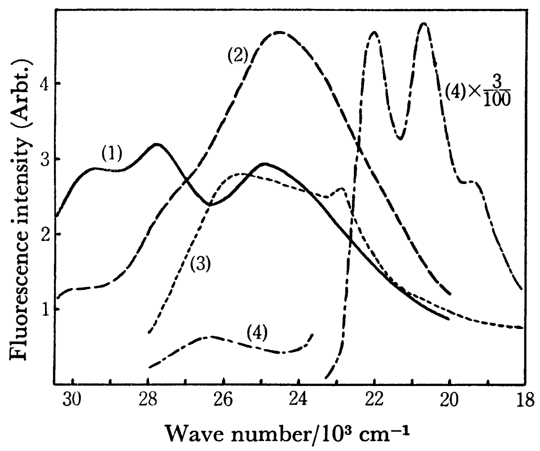

Fig. 4. Fluorescence spectra of PACz and BPVCz films at 293 K. PACz films; (1) undoped, (2) doped with DMTP (2.32×10^{-2} ACz unit mol). BPVCz films; (1) undoped, (2) doped with perylene (5.9×10^{-3} mol/mol basic unit).

change rapidly under irradiation by an exciting light.

Singlet Excitation Energy Transfer in the Vinyl Polymers with Pendant Carbazolyl Groups. The fluorescence spectra of PVCz(r), PVCz(c), and PCzEVE films doped with DMTP or perylene at 77 K are shown in Fig. 5. In the case of every polymer film studied at 293 and 77 K, by the doping of DMTP or perylene, the host fluorescence decreases and is replaced by the exciplex or guest fluorescence. The exciplex is formed between DMTP and a Cz chromophore. As DMTP has no absorption in the wavelength region where the host fluorescence of these polymers is observed, the dipole-dipole resonance cannot be responsible for the energy transfer to a DMTP molecule.7) In fact, no decrease in the fluorescence lifetimes of PVCz(r) films upon doping of DMTP is observed. That is, the fluorescence lifetimes in the shorter-wavelength region of PVCz(r) films doped with a small amount of DMTP (*ca.* 3×10^{-3} mol/mol basic unit) are 17±3 and 5±2 ns at 293 K and 19±2 and 6±1 ns at 77 K.

In the present case, therefore, the hopping model of monomer-exciton migration is applicable at 293 and 77 K. We should consider the case of the presence of two kinds of traps (for example; the sandwich-like excimer-forming sites, c_E [mol/mol basic unit], and the second excimer sites, c_S [mol/mol basic unit], in the case of a PVCz film) in a way similar to the treatment in Ref. 1. Then, the quenching factor of host fluorescence, Q_H, is expressed by the following equations:

$$Q_H = (\eta_{H,0} - \eta_H)/\eta_H = 0.66nc/[1 + 0.66n(c_E + c_S)],$$
$$n = n_S/(n_e + n_l)$$

where n_S, n_e, and n_l are the relative probabilities (per unit time) of jumping, radiative, and nonradiative decay, where $\eta_{H,0}$ and η_H are the quantum efficiencies of the host fluorescence in the absence and in the presence of the guest molecule in a concentration of c [mol/mol basic unit], and where n is the number of jumps during the lifetime without any trapping sites. The quenching factor of monomer fluorescence, Q_M, may be expressed by:

$$Q_M = 0.66n(c_E+c_S).$$

In the present case, where no monomer fluorescence can be observed, $Q_M \gg 1$. Therefore,

$$Q_H = c/(c_E+c_S). \qquad (1)$$

The ratio of the fluorescence intensities guest/host (I_G/I_H) is:

$$I_G/I_H = c\eta_G/(c_E\eta_E+c_S\eta_S), \qquad (2)$$

where η_G is the quantum efficiency of the guest fluorescence in the host film under direct excitation. The relative intensity of the second excimer fluorescence to the sandwich-like excimer one is expressed by

$$I_S/I_E = c_S\eta_S/c_E\eta_E. \qquad (3)$$

Although the experimental values of Q_H scatter a little, the measurement of Q_H at various concentrations of a

Table 2. Energy transfer by the exciton-diffusion process in polymer films at 293 and 77 K[a)]

Host	Guest	η_G	$(c_E+c_S)\times10^3$ (mol/mol basic unit)	n'	(I_G/I_Hc) $\times10^{-3}$	$c_E\eta_E$ $\times10^5$	$c_S\eta_S$ $\times10^5$	L/Å[d)]
PVCz(r)	DMTP	0.043	2.7	370	0.39	10	0.83	67
PVCz(c)	DMTP	0.039	2.2	450	0.37	(11)[c)]	(0.11)[c)]	74
PVCz(r)[b)]	DMTP	0.17	3.5	290	0.22	40	37	60
PVCz(c)[b)]	DMTP	0.15	3.2	310	0.23	43	23	63
PCzEVE	DMTP	0.034	0.45	2200	1.0	—	—	—
PACz	DMTP	0.004	24[e)] (25)[f)]	42[e)] (40)[f)]	0.08	—	—	—
BPVCz	Perylene	0.27	(19)[g)]	(52)[g)]	14	—	—	—

a) The errors in (c_E+c_S) and n' are ±5% at 293 K and ±10% at 77 K. The error in (I_G/I_Hc) is ±3%. b) At 77 K. c) The values are less reliable because of the large error in the I_S obtained by a resolution of the host fluorescence spectrum. d) $L=an'^{1/2}$, where L is the mean exciton migration length and a is the interchromophore separation (3.5 Å). e) The value were obtained from the value of Q_H, on the assumption that the fluorescence in the shorter and longer wavelength regions is emitted by some intrinsic trap site and an excimer respectively. f) The values were obtained from the ratio of (I_G/I_Hc), on the assumption that the fluorescence in the shorter and longer wavelength regions is emitted by a monomer and an excimer respectively. g) The values were obtained in a way similar to that used in the treatment in Ref. 1, on the assumption that the host fluorescence is emitted by one trap site.

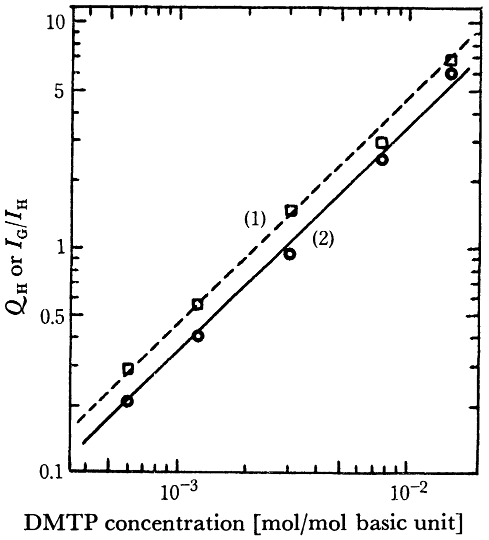

Fig. 6. Ratio of fluorescence intensities guest/host I_G/I_H (1) and quenching factor of host fluorescence Q_H (2) as a function of guest concentration for PVCz(c)–DMTP system at 293 K.

guest gives the values of c_E+c_S according to Eq. 1. The measurement of I_G/I_H at various concentrations of a guest gives the values of $c_E\eta_E$ and $c_S\eta_S$ according to Eqs. 2 and 3, using the values of η_G and I_S/I_E in Tables 1 and 2. Figure 6 shows the bilogarithmic plots of Q_H or I_G/I_H thus obtained and c, as example, in the case of the PVCz(c)–DMTP system. The values thus obtained are listed in Table 2.

In the case of the PVCz(r) and PVCz(c) films, the values of c_E+c_S, $c_E\eta_E$, and $c_S\eta_S$ are obtained by the method mentioned above. The value of c_E+c_S at 293 K is nearly equal to the value of c_E obtained by Okamoto *et al.* in a PVCz(r)–DMTP system, on the assumption that the host fluorescence is emitted only from the sandwich-like excimer.[7)] The value of c_E+c_S is almost the same for a PVCz(r) film and for a PVCz(c) film. The number of Cz chromophores covered by an exciton during the lifetime in the presence of trap sites (abbreviated hereafter to n') is nearly equal to the reciprocal of the concentration of the traps, $[1/(c_E+c_S)]$. This number is almost the same for a PVCz(r) film and for a PVCz(c) film. The value of $c_E\eta_E$ is almost the same for a PVCz(r) film and for a PVCz(c) film, while the value of $c_S\eta_S$ for a PVCz(r) film is higher than that for a PVCz(c) film. It can safely be considered that the fluorescence efficiencies of each fluorescence (η_E and η_S) of PVCz(r) are equal to those of PVCz(c). Therefore, the concentration of the sandwich-like excimer sites (c_E) in a PVCz(r) film is nearly equal to that in a PVCz(c) film. On the other hand, considering that the value of $c_S\eta_S$ for a PVCz(c) film at 293 K is less reliable, the concentration of the second excimer sites (c_S) in a PVCz(r) film is higher than that in a PVCz(c) film by a factor of about 1.6. This difference in the value of c_S does not clearly appear in the value of c_E+c_S. This fact suggests that the value of c_E is larger than that of c_S in both films.

The values of $c_E\eta_E$ for PVCz(r) and PVCz(c) films obtained at 77 K are larger than those obtained at 293 K by a factor of 4. It may safely be considered that the values of η_E and η_S for a PVCz(r) film change with the temperature in a manner similar as that for a PVCz(c) film. The value of c_E is considered to be determined by the casting temperature(T_{cast}) of the film because of the high glass-transition temperature of PVCz. Therefore, this increase in the value of $c_E\eta_E$ seems to be caused by a change in the value of η_E. On the other hand, the value of $c_S\eta_S$ obtained at 77 K is much larger than that obtained at 293 K. This increase in $c_S\eta_S$ with a decrease in the temperature is too large to be caused only by an increase in η_S. The value of c_S might be considered to vary apparently with the measuring temperature. In the previous paper, we have reported that the second excimer has a small binding energy.[6)] Therefore, this increase in $c_S\eta_S$ might be explained by the assumption that the second excimer site is a shallow trap. That is, the second excimer site acts more effectively as a trap at low temperatures.

It has been reported in a previous paper that the concentration of the trap sites for a triplet exciton in a

PVCz(c) film is somewhat larger than that in a PVCz(r) film.[8] On the other hand, as has been mentioned above, the concentration of the trap sites for a singlet exciton in a PVCz(c) film is nearly equal to that in a PVCz(r) film. This suggests that the conformation of intrinsic trap sites is not necessarily the same for singlet and for triplet excitons. This explanation might be supported by the presence of a conformational difference between the singlet and triplet excimers of 1,3-di(1-naphthyl)propane.[12]

The migration frequency, k'_{mig}, for the triplet exciton was estimated from the following equation:

$$k'_{\mathrm{mig}} = 6\Lambda/a$$

where a is the interchromophore separation and Λ is the migration coefficient; the coefficients have been tabulated in Ref. 8. Assuming that $a=3.5$ Å, then $k'_{\mathrm{mig}}= 6\times10^3$ and $3.3\times10^3\ \mathrm{s}^{-1}$ for PVCz(r) and PVCz(c) films. Therefore, the number of Cz chromophores covered by the triplet exciton during the lifetime ($2\tau_{\mathrm{df}}$) are 600 and 330 for PVCz(r) and PVCz(c) films respectively. Although the conformation of intrinsic trap sites seems to be different for singlet and triplet excitons, the number of the Cz chromophores covered by both excitons in both PVCz films during the lifetimes ranges from 300 to 600 and the mean exciton diffusion length ranges from 60 to 80 Å.

The fluorescence of a PCzEVE film is also emitted from two kinds of traps, as has been mentioned above. The value of $c_{\mathrm{E}}+c_{\mathrm{S}}$ for a PCzEVE film is much smaller than those for the PVCz(r) and PVCz(c) films. This suggests that it is difficult for Cz chromophores to form intrinsic trap sites because of the large distance between neighboring Cz chromophores. The value of n' for a PCzEVE film is expected to be smaller than the values of n' for PVCz(r) and PVCz(c) films, judging from the large distance between neighboring Cz chromophores. However, even in the case of a PCzEVE film, $Q_{\mathrm{M}}\gg1$, that is, the singlet exciton migration is limited by the intrinsic trap sites. Therefore, the value of n' for a PCzEVE film is larger than that for a PVCz film by a factor of *ca.* 5.

In the cases of the PACz and BPVCz films, the emitting species of the host fluorescence are ambiguous. Judging from the profile of the fluorescence spectrum of a PACz film, the broad fluorescence band with a peak at *ca.* 25000 cm^{-1} might be assigned to the excimer fluorescence. The fluorescence band in the shorter wavelength region might be attributable to a monomer or to some intrinsic trap site. The host fluorescence of a BPVCz film is considered to be emitted from some trap site. Irrespective of the treatments used to obtain the value of n' (Table 2), the values of n' for both polymer films are very small. This may be attributable to the short exciton lifetime because of the enhanced intersystem crossing and the presence of extrinsic trap sites(photoproducts and/or impurities introduced during a bromination reaction).

The number of Cz chromophores covered by a singlet exciton during the lifetime was in the following order; PCzEVE>PVCz(r)≈PVCz(c)>PACz≈BPVCz.

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