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

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The triplet energy transfer in poly(*N*-vinylcarbazole)(PVCz) prepared by radical and cationic polymerization (PVCz(r) and PVCz(c) respectively), poly[2-(*N*-carbazolyl)ethyl vinyl ether](PCzEVE), and brominated PVCz (BPVCz) has been investigated by measuring the delayed emission spectra in solid films and rigid solutions at 77 K. The prompt and delayed fluorescence spectra both in the solid film and in the rigid solution at 77 K were different for PVCz(r) and PVCz(c). This seems to be due to the difference in tacticity between them. PCzEVE, in which the Cz groups are connected from afar to the skeletal chains by means of $-O-CH_2-CH_2-$ bonds, showed the delayed fluorescence and the phosphorescence both in the rigid solutions and in the solid films at 77 K. The BPVCz film showed only the excimer phosphorescence. In the solid films of PVCz(r), PVCz(c), and PCzEVE, the Cz chromophore-delayed fluorescence increased with an increase in the concentration of triplet quenchers, such as naphthalene and fluorene. This phenomenon suggests the presence of a heterogeneous triplet-triplet annihilation in these aromatic vinyl polymer films. The quenching of the Cz chromophore phosphorescence both by the doping of the naphthalene in the solid films and by the doping of the 1,3-pentadiene in the rigid solutions obeyed the Stern-Volmer equation, and the migration coefficient, λ, and the mean exciton migration length, L, were obtained. The values of λ and L were in the following order; PVCz(r) > PVCz(c) > PCzEVE (> BPVCz) in the solid film and PVCz(r) > PVCz(c) in the rigid solutions. The order was explained by both the concentration of the intrinsic trap sites for triplet excitons and the distance between neighboring Cz chromophores in one polymer chain.

Recently, the emission spectra of aromatic vinyl polymers have been extensively investigated. The triplet energy transfer in a rigid solution at 77 K has been studied in detail on vinyl polymers with large aromatic rings, such as naphthyl and carbozolyl groups.[1–5] The investigations showed that the triplet excitons can migrate along the polymer chain, and that delayed fluorescence is caused by a homogeneous triplet-triplet (T-T) annihilation between two intramolecular migrating triplet excitons. Concerning the triplet energy transfer in the solid films, David *et al.* reported on vinyl polymers with small aromatic rings which emit only phosphorescence and no delayed fluorescence.[6,7] They showed that the triplet exciton migration frequencies in such polymer films were smaller than in the corresponding crystals. Concerning the vinyl polymer films with large aromatic rings, Fox *et al.* and Klöpffer *et al.* have qualitatively studied poly(1-vinylnaphthalene) and poly(*N*-vinylcarbazole) (PVCz) respectively.[5,8] Klöpffer *et al.* showed that the phosphorescence of PVCz films is governed by two kinds of traps, the concentration of which was estimated to be 5×10^{-3} (mol of trap/mol of basic unit) from the saturated concentration of the sensitized dopant phosphorescence, and that PVCz films emitted no delayed fluorescence. However, the triplet energy transfer in solid films has never hitherto been studied quantitatively on such vinyl polymers, to the knowledge of the authors.

Therefore, it seems that it would be interesting to investigate quantitatively the spectroscopic behavior of the triplet excitons in the vinyl polymers with large aromatic rings and to compare the difference between in rigid solutions and in solid films.

A preliminary short report has been published in *Chem. Lett.*[9] In the present work, the authors have investigated the changes in the delayed emission intensity of the vinyl polymers with pendant carbazolyl groups doped with various concentrations of a triplet quencher, such as naphthalene and 1,3-pentadiene, in rigid solutions as well as in solid films at 77 K.

Experimental

The following four vinyl polymers with pendant carbazole (Cz) chromophores were used.

The PVCz(r) was prepared by the polymerization of a 0.5 M benzene solution of purified *N*-vinylcarbazole (VCz) in the presence of 1 mol% azobisisobutyronitrile in an evacuated sealed tube at 70 °C for 7 h. The molecular weight ($\overline{M}_v$), as measured by the viscosimetrical method,[10] was 2×10^5.

The PVCz(c) was prepared by the polymerization of a 0.5 M toluene solution of purified VCz in the presence of 0.5 mol% $BF_3-(OC_2H_5)_2$ under a nitrogen atmosphere at 20 °C for 18.5 h. $\overline{M}_v=1\times10^5$. Both the PVCz(r) and the PVCz(c) were reprecipitated three times from the benzene solution with a methanol-acetone (1 : 1) mixture.

The poly[2-(*N*-carbazolyl)ethyl vinyl ether] (PCzEVE) has the Cz chromophores connected to the skeletal chain at a distance of about 4 Å by $-O-CH_2-CH_2-$ bonds. This was prepared by a method described previously.[11] $\overline{M}_n=7800$.

The brominated poly(*N*-vinylcarbazole)(BPVCz) was obtained by the bromination of PVCz(Luvican M170) with *N*-bromosuccinimide and was reprecipitated three times from the dichloroethane solution with acetone. The fraction of bromination was determined to be 0.9 from the elementary analysis.

Commercial naphthalene (NAPH) and fluorene of a scintillation grade were purified by zone-refining. Commercial 1,3-pentadiene (1,3-PD), a well-known triplet quencher, was used after repeated distillation. All the solvents used were purified by the usual methods. The solutions (donor concentration; 1×10^{-4} Cz unit M, solvent; 2 : 3 mixture of tetrahydrofuran and 2-methyltetrahydrofuran) for the measurements were deairated by means of freeze-pump-thaw cycles. Doped films were prepared by casting a dichloroethane solution of the polymer with a certain amount of the dopant onto quartz plates. The thicknesses of the films were about 7, 5, and 7 μm for PVCz, PCzEVE, and BPVCz respectively. The coated plates were immersed in liquid nitrogen for the measurement of the emission spectra.

The apparatus and techniques for measuring the delayed emission spectra were described in a previous paper.[9] All the samples were excited by 345 nm light, which was not absorbed by the triplet quenchers. It was confirmed that the application of a phosphoroscope factor[12] was not necessary in the case of solid films. In the case of rigid solutions, the delayed fluorescence spectra were, however, corrected by using a phosphoroscope factor.

Results and Discussion

Delayed Emission Spectra in Rigid Solution and in Solid Film. The delayed emission spectra of PVCz(r), PVCz(c), and PCzEVE in rigid solutions and in solid films at 77 K are in Figs. 1 and 2 respectively. Concerning PVCz (r and c) in rigid solutions, Yokoyama *et al.*[4] and Klöpffer *et al.*[5] have reported as follows: (1) The delayed emission spectrum consists of the delayed fluorescence and the phosphorescence; (2) the intensity and the lifetime of the delayed fluorescence are dependent on the molecular weight, and the delayed fluorescence is not observed for PVCz with a low molecular weight ($\overline{DP}\leqq 50$); (3) the phosphorescence is emitted from the trap site in the polymer chain because the phosphorescence (0-0 band; 420 nm) is located at a lower energy than that of the model compound (*N*-isopropylcarbazole) (0-0 band; 412 nm). However, they have not reported on the relationship of the spectra to the chemical preparation of the samples. In our present results, the delayed fluorescence spectra are a little defferent between PVCz(r) and PVCz(c), as is shown in Fig. 1, although the lifetimes (τ^0_{df}) are almost the same (11 ms for PVCz(r) and 12 ms for PVCz(c)). The phosphorescence spectra are almost the same between PVCz(r) and PVCz(c). The lifetime (τ^0_{ph}) is 1.8±0.2 s for PVCz(r and c).

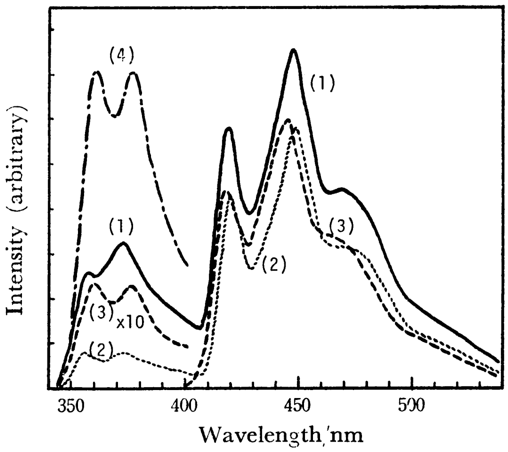

Fig. 1. Delayed emission spectra of (1) PVCz(r), (2) PVCz(c), and (3) PCzEVE in MTHF-THF rigid solutions at 77 K (uncorrected). The prompt fluorescence (4) of PCzEVE in MTHF-THF rigid solution at 77 K was also given for comparison.

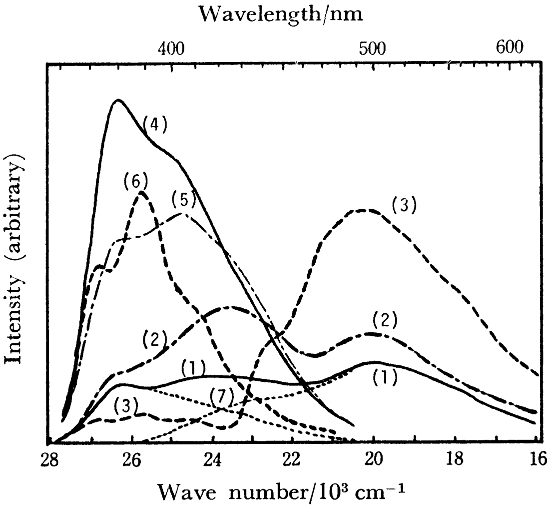

Fig. 2. Delayed emission spectra of (1) PVCz(r), (2) PVCz(c), and (3) PCzEVE films at 77 K. The prompt fluorescence spectra of (4) PVCz(r), (5) PVCz(c), and (6) PCzEVE films at 77 K were also given for comparison. The resolution spectra (7) of delayed emission spectum of PVCz(r) (1) were also given.

In the case of solid films, Klöpffer *et al.*[5] showed that PVCz (r and c) films emitted only a phosphorescence governed by two traps (two component decay; 7.9±1 and 1.4 s), and no delayed fluorescence, and that two different types of spectra were observed in the phosphorescence and in the prompt fluorescence at 77 K, independent of the polymerization methods. In our present results, the delayed emission spectra of PVCz (r and c) consist of two emission bands, as is shown in Fig. 2. The prompt fluorescence spectra of the films and the example of the resolution spectrum (PVCz(r)) are also shown in Fig. 2. The further purification of the polymer (for example; reprecipitation up to ten times and/or extraction with hot methanol) gave no change in the spectra. The broad delayed emission in the longer wavelength region is invariably monophotonic in origin, and this lifetime consists of two components (7.9±0.7 and 1.6±0.5 s). Therefore, this emission is considered to be the phosphorescence emitted both from Trap I (excimer-forming site) and from Trap II, as has been described by Klöpffer *et al.*[5] On the other hand, both the position and profile of the delayed emission band in the shorter wavelength region are the same as those observed for the normal fluorescence at 77 K, as is shown in Fig. 2, and the emission intensity depends quadratically on the excitation light intensity. The lifetime of this emission is about 50 ms for PVCz (r and c). These facts indicate that this emission band can be assigned to the delayed fluorescence resulting from a homogeneous T-T annihilation between two migrating triplet exciton in films, as is the case with rigid solutions. The delayed fluorescence spectra also show two different types. One is rich in the excimer component and is observed for PVCz(c). The other is poor in the excimer component and is observed for PVCz(r). This was different from the results reported by Klöpffer *et al.*, but was confirmed using several samples prepared under different polymerization conditions. The difference between PVCz(r) and PVCz(c) is also observed for the prompt fluorescence in films at 77 K.[13] It has previously been reported that the tacticity of vinyl polymers with large aromatic rings was hardly sensitive at all to method of polymerization.[14] However, recently we have found, by measuring their NMR spectra, that the PVCz, poly(*N*-vinyl-5*H*-benzo[*b*]-carbazole), and poly(*N*-vinyl-7*H*-benzo[*c*]carbazole) prepared by cationic polymerization have a higher isotacticity than those prepared by radical polymerization.[15] Frank *et al.* have found that the concentration of the excimer-forming site depends on the conformation of the polymer chain.[16] Judging from the above-mentioned discussion, the difference in the fluorescence spectra seems to be attributable to the different tacticity between PVCr(z) and PVCz(c).

The delayed emission spectra of PCzEVE in rigid solutions and in solid films at 77 K also consist of two bands, as is shown in Figs. 1 and 2. Both the position ($\bar{\nu}_{\mathrm{max}}$; 360 or 376 nm in rigid solutions and 371, 388, or 409 (shoulder) nm in solid films) and the profile of the emission band in the shorter-wavelength region are nearly the same as is observed for the normal fluorescence ($\bar{\nu}_{\mathrm{max}}$; 361 or 377 nm in rigid solutions and 370, 388.5, or 410 (shoulder) nm in solid films) at 77 K, and the emission intensity depends quadratically on the exciting-light intensity. Therefore, the emission bands of PCzEVE are identified as delayed fluorescence. It is interesting that PCzEVE in a rigid solution emits the delayed fluorescence, in spite of its short skeletal chain length ($\overline{DP}=33$). The τ^0_{df} of PCzEVE in a solid film is 45 ms, while that in a rigid solution could not be determined because of the low intensity. On the other hand, the delayed emission band at a longer wavelength ($\bar{\nu}_{\mathrm{max}}$; 418, 446 nm in a rigid solution and about 495 nm in a solid film) is monophotonic in origin. Therefore, this emission band is identified as the phosphorescence emitted from the trap site, by analogy with PVCz(r and c). The τ^0_{ph} in a rigid solution is 6.6 ± 0.1 s, while that in a solid film consists of two components (3.5 ± 0.2 and 0.7 ± 0.05 s), which is smaller than that of PVCz(r and c) by a factor of about two.

The BPVCz shows only one broad delayed emission band around 20730 cm^{-1}. This emission is invariably monophotonic in origin, and its position and profile are the same as the normal emission at 77 K. It shows a nonexponential decay with an apparent lifetime of 50 ms. The failure to observe a prompt fluorescence of BPVCz seems to be attributable to the high efficiency of the intersystem crossing from the excited singlet state to the triplet state due to the heavy atom effect of bromine. This delayed emission is considered, by analogy with poly(3,6-dibromo-*N*-vinylcarbazole) in a rigid solution at 77 K, to be the excimer phosphorescence.[18]

Triplet Energy Transfer in Solid Films and Rigid Solutions. The delayed emission spectra of PVCz(r), PCzEVE and BPVCz films doped with NAPH of various concentrations at 77 K are shown in Figs. 3—5. In Figs. 3 and 4, the prompt fluorescence spectra of the polymer films are also shown for the sake of comparison. In every polymer film studied, upon the doping of NAPH, the Cz chromophore-phosphorescence(I_{ph}) decreases significantly and is replaced by a sensitized NAPH phosphorescence(I_{sph}). Although the Cz phosphorescence lifetime(τ_{ph}) in PVCz(r and c) films could not be determined because of the overlapping of I_{ph} and I_{sph}, τ_{ph} in a PCzEVE film was found, by observing the decay curve at 444 nm, not to decrease upon the doping of NAPH. Therefore, in these films, the triplet energy seems to transfer from the freely migrating triplet exciton to the dopant, and I_{ph} seems to be emitted from the trapped triplet state.

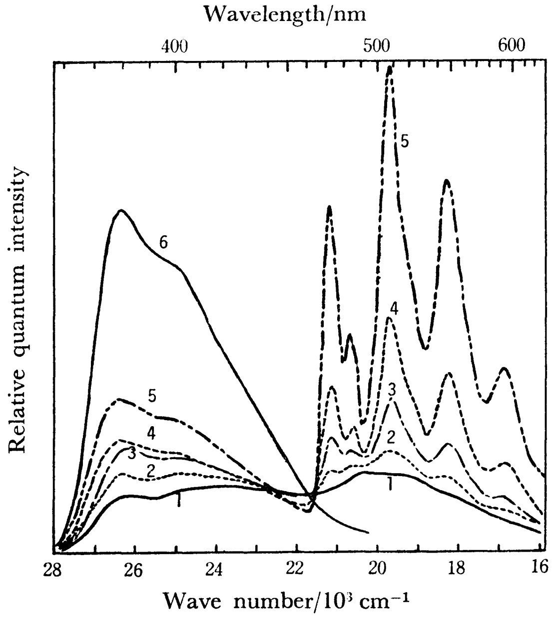

Fig. 3. Delayed emission spectra of PVCz(r) films doped with NAPH at 77 K. NAPH concentration; (1) 0, (2) 1.41×10^{-4}, (3) 7.04×10^{-4}, (4) 1.41×10^{-3}, and (5) 7.04×10^{-3} mol/VCz unit mol. The prompt fluorescence (6) of a PVCz(r) film was also given for comparison.

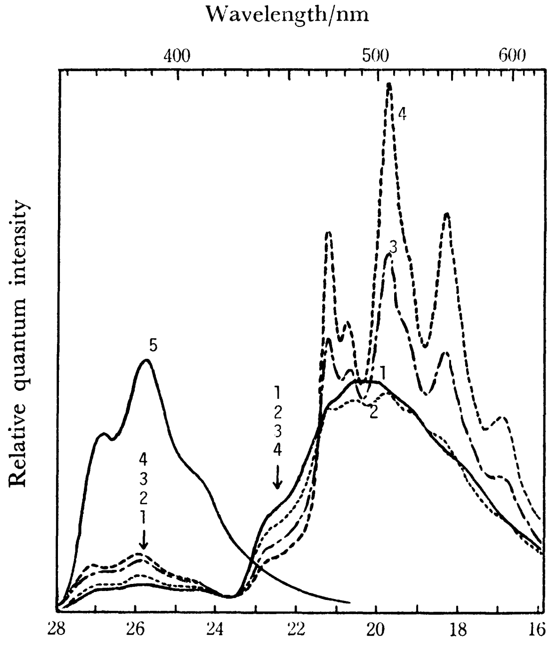

Fig. 4. Delayed emission spectra of PCzEVE films doped with NAPH at 77 K. NAPH concentration; (1) 0, (2) 2.62×10^{-4}, (3) 1.64×10^{-3}, and (4) 8.18×10^{-3} mol/CzEVE unit mol. The prompt fluorescence (5) of a PCzEVE film was also given for comparison.

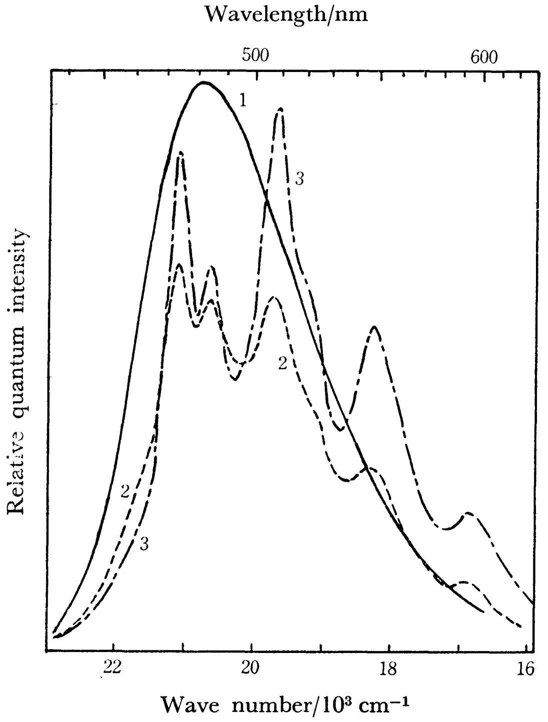

Fig. 5. Delayed emission spectra of BPVCz films doped with NAPH at 77 K. NAPH concentration; (1) 0, (2) 6.16×10^{-3}, and (3) 1.23×10^{-2} mol/BVCz unit mol.

The Cz chromophore-delayed fluorescence(I_{df}) increases with an increase in the concentration of NAPH. The changes in I_{df} and I_{sph} as a function of NAPH mole fraction in solid films are given in Fig. 6. In the case of the highest concentration of NAPH, the I_{ph} is quenched completely and I_{sph} reaches saturation, whereas I_{df} increases steeply and also second-order with respect to the exciting light intensity. The lifetime of the delayed fluorescence(τ_{df}) is gradually lengthened with an increase in the concentration of NAPH, as is shown in Fig. 7. Similar phenomena are observed for PVCz(c and r) and PCzEVE films doped with fluorene.

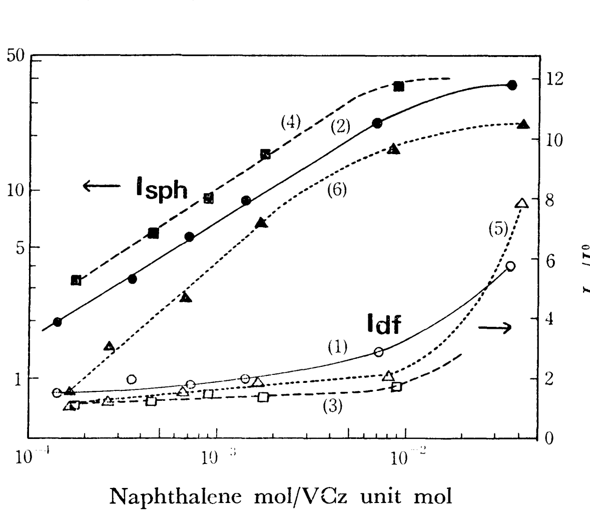

Fig. 6. Dependence of I_{df} and I_{sph} on concentration of NAPH in solid films at 77 K. (1), (2) ——; PVCz(r), (3), (4) ----; PVCz(c), and (5), (6) ······; PCzEVE.

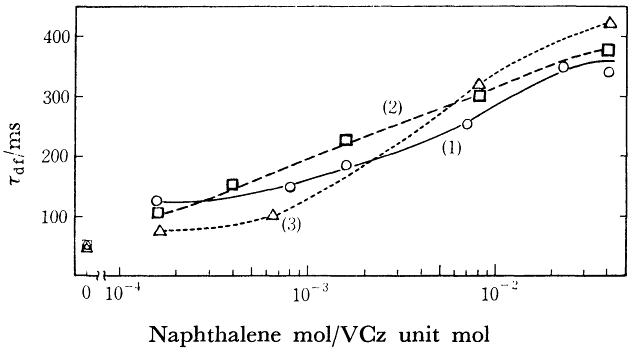

Fig. 7. Dependence of τ_{df} on concentration of NAPH in solid films at 77 K. (1) —○—; PVCz(r), (2) --□--; PVCz(c), and (3) ···△···; PCzEVE.

It is clear from the above-mentioned results that the dopants act as an effective triplet quencher for Cz chromophores in every film. The increase in I_{df} upon the doping of these triplet quenchers, therefore, strongly suggests that a heterogeneous T-T annihilation process occurs with a fairly good efficiency between freely migrating triplet excitons and either the triplet state of the dopant or a shallow trap site introduced by it.

In the case of PVCz(r and c) doped with NAPH in a rigid solution (Fig. 8), I_{ph} decreases and is replaced by I_{sph}, as is the case with solid films. On the other hand, the I_{df} shows an anomalous phenomenon, a little different from that in the solid films; it increases at low NAPH concentrations (up to 5×10^{-3} M) and decreases at higher concentrations. The change in the τ_{df} corresponds approximately to the change in the intensity; for example, the τ_{df} values of PVCz(r) are about 11, 12, 10, and 3 ms for 0, 8.40×10^{-4}, 2.10×10^{-3}, and 1.45×10^{-2} M respectively. In the case of PVCz(r and c) doped with NAPH, the heterogeneous T-T annihilation, therefore, seems to be present even in a rigid solution at 77 K.

In the case of PVCz(r and c) doped with 1,3-PD, a well-known triplet quencher in rigid solutions, both the I_{df} and the I_{ph} decrease significantly with an increase in the concentration of 1,3-PD, as is shown in Fig. 8, where I^0 and I are the Cz chromophore emission intensity in the absence and in the presence of the dopant respectively. The τ_{df} is decreased steeply ($\tau^0_{\mathrm{df}}/\tau_{\mathrm{df}}=4$—5 for 0.25×10^{-2} M). However, the τ_{ph} is hardly decreased by the doping of 1,3-PD ($\tau^0_{\mathrm{ph}}/\tau_{\mathrm{ph}}=1.0$—1.1 for 2.0×10^{-2} M). Therefore, it is considered that the triplet energy transfer mainly from freely migrating triplet excitons to the dopant, as is the case with solid films. The degree of quenching is much larger for the I_{df} than for the I_{ph}. This is the behavior usually observed for poly(1-vinylnaphthalene) (PVN) and poly(1-naphtyl methacrylate) (PNMA).[2,3] When 1,3-PD is used as the triplet quencher, the heterogeneous T-T annihilation is not present. No quenching experiment of PCzEVE has been done, because of its short chain length ($\overline{DP}=33$).

The $I^0_{\mathrm{ph}}/I_{\mathrm{ph}}$ ratios are given in Fig. 9 as a function of the NAPH mole fraction in PVCz(r), PVCz(c), and PCzEVE films. Since the density of the vinyl polymers

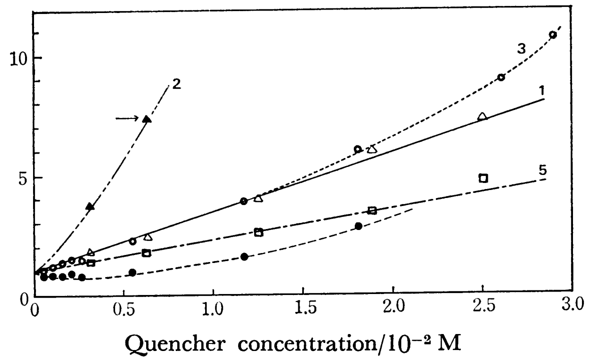

Fig. 8. Stern-Volmer plots ($I^0_{\mathrm{ph}}/I_{\mathrm{ph}}$ and $I^0_{\mathrm{df}}/I_{\mathrm{df}}$) for the quenching of the delayed emission of PVCz(r) and PVCz(c) by NAPH and 1,3-PD in MTHF-THF rigid solution at 77 K.
(1) —△—; Phosphorescence in the PVCz(r)-1,3-PD system. (2) —▲----; Delayed fluorescence in the PVCz(r)-1,3-PD system. (3)···○···; Phosphorescence in the PVCz(r)-NAPH system. (4) --●--; Delayed fluorescence in the PVCz(r)-NAPH system. (5) —□-·-; Phosphoresceence in PVCz(c)-1,3-PD system. The point with arrow was corrected by the phosphoroscope factor which was estimated by assuming the lifetime to be 2 ms.

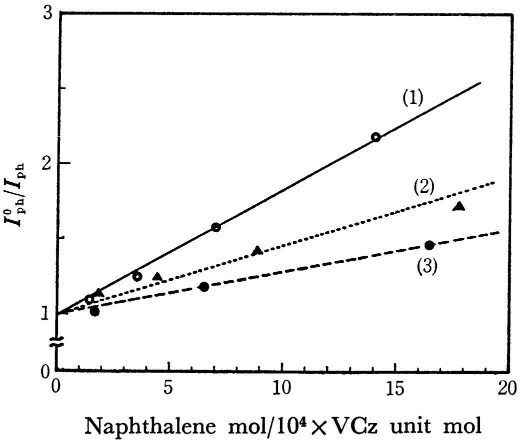

Fig. 9. Stern-Volmer type plots ($I^0_{\mathrm{ph}}/I_{\mathrm{ph}}$) for the quenching of the Cz chromophore phosphorescence of (1) PVCz(r), (2) PVCz(c), and (3) PCzEVE films by NAPH at 77 K.

was measured to be 1.19 g/cm^3, a conversion of the unit on the abscissa in Fig. 8 from mole fraction to molarity results in the Stern-Volmer polt;

$$I^0_{\mathrm{ph}}/I_{\mathrm{ph}} = 1 + k_t\tau[\mathrm{Q}]$$

Here, k_t is the bimolecular quenching rate constant, τ is the excited state lifetime in the absence of a quencher, and [Q] is the quencher concentration of the molarity unit. In the case of PVCz(r and c) doped with 1,3-PD in a rigid solution, Stern-Volmer polts are also obtained, as is shown in Fig. 9. In the case of most aromatic vinyl polymers containing the present polymers, the phosphorescence is emitted not from the freely migrating triplet but from the trapped triplet state, so that the lifetime(τ_{ph}) is considered to be that of the trapped triplet state. Two times the τ_{df} value should, therefore, be used as the value of τ. The value of k_t were thus obtained from the slopes of the Stern-Volmer plots. The theory developed by Voltz *et al.*[19] was applied to the present results,

$$k_t = 4\pi N_0 \lambda R_0 \times 10^{-3}\ \mathrm{M^{-1}\,s^{-1}}$$

where N_0 is Avogadro's number, λ is the migration coefficient, and R_0 is the critical transfer distance between donor and acceptor, for which the transfer probability $p=1$ if $R \leq R_0$ and $p=0$ if $R > R_0$. The value of 15 Å is used as R_0.[20] The mean exciton migration length, L, is defined by;[21]

$L = \sqrt{2\lambda\tau}$ (for a one-dimensional random walk)

$L = \sqrt{6\lambda\tau}$ (for a three-dimensional random walk).

These values are listed in Table 1.

The values of λ and L are in the following order: PVCz(r) > PVCz(c) > PCzEVE in solid films and PVCz(r) > PVCz(c) in rigid solutions. If the distance between neighboring Cz rings is estimated to be 3.5 Å, the number of Cz rings which the triplet exciton can cause to migrate during the lifetime is estimated to be in the order of 400 from the values of λ listed in Table 1 both in solid films and in rigid solutions. Therefore, the difference in λ and L seems not to be attributable to the small difference in the degree of polymerization ($\overline{DP}$) between PVCz(r) ($\overline{DP}$=1000) and PVCz(c) ($\overline{DP}$=500).

It is well-known that the singlet exciton migration is limited by the intrinsic trap site (excimer-forming site).[22] Similarly, the triplet exciton migration seems to be limited by the intrinsic trap site, such as excimer-forming site in the polymers, because the observed phosphorescence was emitted only from the trap sites. Therefore, the difference in λ and L between PVCz(r) and PVCz(c) seems to be attributable to the difference in the concentration of the intrinsic trap site for the triplet exciton.

The value of λ in PCzEVE film is expected to be very small as compared with the case of PVCz(r and c), judging from the large distance between neighboring Cz chromophores. However, it is almost the same as the value for PVCz(c). The concentration of trap sites in PCzEVE film as smallest among the polymer films studied.[13] This is also supported by the facts that prompt fluorescence spectrum of PCzEVE film at 77 K (Fig. 2) is mainly monomeric in origin and that the phosphorescence shows a shoulder at about 440 nm. This is the reason for the relatively large λ value in PCzEVE film. This is also supported by the following consideration.

In using the published data on the triplet energy transfer in rigid solution at 77 K which have already been reported, where τ_{ph} was used as τ in the Stern-Volmer equation, we replace τ_{ph} by $2\tau_{\mathrm{df}}$ as τ. Then, the migration coefficients λ of PVN[1] and PNMA[3] are estimated to be 3.3×10^{-13} and 4.6×10^{-13} cm^2/s respectively, although the molecular weights of these polymers are unknown. Judging from the structure of their polymer and their fluorescence spectra at room temperature, the concentration of intrinsic trap sites in PVN seems to be larger than that in PNMA. The comparable values in λ between PVN and PNMA seems to be explained by the overlap of two opposite

TABLE 1. SLOPES OF STERN-VOLMER PLOTS ($k_t\tau$), CZ PHOSPHORESCENCE AND DELAYED FLUORESCENCE LIFETIME (τ^0_{ph} and τ^0_{df}), BIMOLECULAR QUENCHING RATE CONSTANT (k_t), EXCITON MIGRATION COEFFICIENT (λ), AND MEAN EXCITON MIGRATION LENGTH (L) IN SOLID FILMS AND RIGID SOLUTIONS AT 77 K

Substance	$k_t\tau/M^{-1}$	τ^0_{ph}/s	τ^0_{df}/ms	$k_t/M^{-1}\,s^{-1}$	$\lambda/cm^2\,s^{-1}$	$L/Å^{b)}$
PVCz(r)	134	7.9±0.7 1.6±0.5	50±3	1300	1.2×10^{-12}	85
PVCz(c)	74	7.9±0.7 1.6±0.5	50±5	740	6.5×10^{-13}	63
PCzEVE	57	3.5±0.2 0.7±0.05	45±5	630	5.6×10^{-13}	55
BPVCz	52	$0.05^{c)}$	—	—	—	—
PVCz(r)$^{a)}$	245	8.1±0.2	10±3	12000	1.1×10^{-11}	66
PVCz(c)$^{a)}$	128	8.1±0.2	11±2	5800	5.1×10^{-12}	47

a) In rigid solution. b) Three-dimensional random walk in solid film. c) Apparent lifetime.

effects—the concentration of the intrinsic trap site and the distance between neighboring naphthalene chromophores.

The $k_t\tau$ in BPVCz film is smallest among the polymers studied. This seems to be caused by the short triplet exciton lifetime resulting from the heavy atom effect of bromine.

In both PVCz(r) and PVCz(c), the lifetime of the triplet exciton in a solid film is larger than that in a rigid solution by a factor of about 5. On the contrary, the diffusion coefficient, λ, in a solid film is smaller than that in a rigid solution by a factor of 10. Although these phenomena are very interesting, a reasonable explanation cannot be offered at the present time. A further investigation of the other vinyl polymers is necessary and is now in progress.

References

1) R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, **50**, 1532 (1965).

2) C. David, M. Lempereur, and G. Geuskens, *Eur. Polym. J.*, **8**, 417 (1972).

3) A. C. Somersall and J. E. Guillet, *Macromolecules*, **6**, 218 (1973).

4) M. Yokoyama, T. Nakano, T. Tamamura, and H. Mikawa, *Chem. Lett.*, **1973**, 509; M. Yokoyama, T. Tamamura, T. Nakano, R. Ogawa, and H. Mikawa, Symposium on Molecular Structure, Nagoya, 8I21, October, 1973.

5) W. Klöpffer and D. Fischer, *J. Polym. Sci., Part-C*, **40**, 43, (1973).

6) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 537 (1970).

7) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 1405 (1970).

8) R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, *J. Chem. Phys.*, **57**, 2284 (1972).

9) A. Itaya, K. Okamoto, and S. Kusabayashi, *Chem. Lett.*, **1975**, 833.

10) N. Kuwahara, S. Higashida, M. Nakata, and M. Kaneko, *J. Polym. Sci., A-2*, **7**, 285 (1969).

11) K. Okamoto, M. Ozeki, A. Itaya, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **48**, 1362 (1975); K. Okamoto, A. Itaya, and S. Kusabayashi, *Polym. J.*, **7**, 662 (1975).

12) C. A. Parker and C. G. Hatchard, *Analyst*, **87**, 664 (1962).

13) A. Itaya, K. Okamoto, and S. Kusabayashi, 23rd Symposium on Macromolecules, Tokyo, G11E09, October, 1974. To be published elsewhere.

14) D. J. Williams, *Macromolecules*, **3**, 602 (1970); A. Kimura, S. Yoshimoto, Y. Akana, H. Hirata, S. Kusabayashi, H. Mikawa, and N. Kasai, *J. Polym. Sci., A-2*, **8**, 643 (1970).

15) K. Okamoto, M. Yamada, A. Itaya, T. Kimura, and S. Kusabayashi, *Macromolecules*, in press.

16) C. W. Frank and L. A. Harrah, *J. Chem. Phys.*, **61**, 1562 (1974).

17) S. Yoshimoto, Y. Akana, A. Kimura, H. Hirata, S. Kusabayashi, and H. Mikawa, *Chem. Commun.*, **1969**, 987.

18) M. Yokoyama, M. Funaki, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, **1974**, 372.

19) R. Voltz, A. Laustriat, and A. Coche, *J. Chim. Phys.*, **63**, 1253 (1966).

20) V. L. Ermolaev, *Soviet Phys. Ospekhi*, **80**, 333 (1963); R_0 value of Cz-1,3-PD system was not reported, so that the value was assumed to be the same as that of Cz-NAPH system.

21) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York (1969), p. 532.

22) W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969); K. Okamoto, A. Yano, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **47**, 749 (1974).