Emission Spectra of the Vinyl Polymers with Pendant Carbazolyl Groups

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The emission properties of poly(*N*-vinylcarbazole) (PVCz) prepared by radical and cationic polymerization (PVCz(r) and PVCz(c) respectively), the oligomers of *N*-vinylcarbazole, and poly[2-(*N*-carbazolyl)ethyl vinyl ether] (PCzEVE) were investigated in solutions. The fluorescence spectrum of PVCz(r) was different from that of PVCz(c). This seems to be attributable to the difference in the tacticity between them. On the basis of this result, the structure of the second excimer site is discussed. PCzEVE, in which the carbazolyl chromophores are widely spaced on the skeletal chains by $-O-CH_2-CH_2-$ bonds, showed an interesting, new, structureless emission band with a peak at 27000 cm^{-1}. This was different from both the monomeric structured fluorescence and the sandwich-like excimer one which were observed for the model compounds and the polymers. The emission properties of PCzEVE were unique among the vinyl polymers with aromatic chromophores widely spaced on the skeletal chain.

It is known that 1-ethylpyrene and 1-ethylnaphthalene show the excimer fluorescence in concentrated fluid solutions at room temperature. Poly(1-vinylpyrene)[1,2] and poly(1-vinylnaphthalene),[3,4] in which the pyrenyl and naphthyl groups are connected directly to the skeletal chains, show, almost entirely, only the excimer fluorescence in dilute solutions at room temperature. Poly(1-pyrenylmethyl vinyl ether) (PPyMVE),[1,5] poly(1-naphthylmethyl vinyl ether) (PNMVE),[5] and ploy(1-naphthyl methacrylate) (PNMA),[6] in which the pyrenyl and naphthyl groups are widely spaced on the skeletal chains by $-O-CH_2-$ and $-CO-O-$ bonds, show both the structured monomeric fluorescence and the excimer one in dilute solutions. On the other hand, *N*-ethylcarbazole(ECz) and 9-ethylacridine show no excimer fluorescence in the concentrated solutions.[1,7] Moreover, ECz shows no excimer fluorescence in either the molten state or the solid state.[7] Poly(9-vinylacridine) shows, almost entirely, only the excimer fluorescence in a dilute solution at room temperature.[1] Poly(*N*-vinylcarbazole) (PVCz), both in solution and in film, shows one broad fluorescence, which is not composed of only one component, but of two components. The broad emission at the longer wavelength(λ_{max}; *ca.* 23900 cm^{-1}) is assigned to the sandwich-like excimer fluorescence, which is the same as was mentioned above. On the other hand, the assignment of the broad emission in the shorter-wavelength region (λ_{max}; *ca.* 27000 cm^{-1}) is controversial because of the absence of the structure and of the large Stokes shift. David *et al.* and Yokoyama *et al.* have assigned it to the monomer fluorescence for PVCz in solution.[7,8] On the other hand, recently Johnson has assigned it to the second excimer fluorescence and reported that the polymer conformation appropriate for the formation of this state exists prior to the initial excitation step.[9] Offen *et al.*,[10] Klöpffer *et al.*,[11] and Powell *et al.*[12] have assigned the shorter-wavelength band to another intrinsic trap site, such as a dimer for PVCz films. However, the structure of the species emitting at *ca.* 27000 cm^{-1} has been amibguous thus far.

Recently, we have revealed, as a result of measuring the NMR spectra,[13] that cationic PVCz(c) have a higher isotacticity than radical PVCz(r). Therefore, it was of interest to investigate how the difference in the tacticity is reflected in the fluorescence spectra. In the present investigations, we have found that the difference influences the intensity of the second excimer fluorescence. On the basis of this result, the structure of the second excimer site, emitting at *ca.* 27000 cm^{-1}, was discussed.

Spectroscopic studies of the vinyl polymers with Cz chromophores widely spaced on the skeletal chains are of interest in connection with those of PVCz. In the present project, we investigated the spectroscopic behavior of poly[2-(*N*-carbazolyl)ethyl vinyl ether] (PCzEVE). It has already been found, from the absorption and NMR spectra,[14] that PCzEVE has no appreciable ground-state interaction among the Cz chromophores of PCzEVE.

Experimental

The vinyl polymers(PVCz(r), PVCz(c), PCzEVE), *N*-vinylcarbazole oligomers(VCz Olig. I and II; degrees of polymerization, 4 and 10 respectively), and the model compounds(*N*-isopropylcarbazole(*i*-PrCz), 1,3-bis(*N*-carbazolyl)-propane(DCzP)) were prepared by the methods described previously.[15,16] The dimethyl terephthalate(DMTP) was recrystallized twice from benzene and subsequently sublimed *in vacuo*. All of the solvents (2-methyltetrahydrofuran(MTHF), tetrahydrofuran(THF), 1,2-dichloroethane) were purified by the usual methods. The solutions were completely degassed by freeze-pump-thaw cycles if necessary.

The emission spectra were measured with a spectrophotofluorometer constructed using a stabilized 500 W xenon lamp, monochromators, and a PM-55 (S-20) photomultiplier. The spectra were calibrated for the detector response by using a standard tungsten lamp. The fluorescence-decay times were measured with a pulsed N_2 gas laser as the exciting light source. Responses from the photomultiplier were led to a sampling oscilloscope(Tektronix 661) and recorded on a X-Y recorder, or led to a Tektronix 475 oscilloscope and the decay curve was photographed.

For the fluorescence polarization, two polarizers were used, and the data were corrected by the method described by Azumi and McGlynn.[17]

Results and Discussion

*Fluorescence in the Shorter-wavelength Region(*ca. *27000 cm^{-1}) of PVCz (r and c).* The fluorescence spectra of the various PVCz samples in aerated THF solutions at room temperature are shown in Fig. 1. The ratio of the second excimer fluorescence intensity to the sandwich-like excimer one in PVCz(r) samples is remarkably larger than that in PVCz(c) samples. Figure 2 shows the fluorescence spectra of PVCz(r) and PVCz(c), which have almost the same concentrations in degassed THF–MTHF solutions at room temperature, and their resolution spectra. The resolutions were carried out on the assumption that the location of the sandwich-like excimer fluorescence band in solution was the same as that in film. The efficiency of the singlet-exciton migration along the polymer chain may be different between PVCz(r) and PVCz(c) because of their different tacticities. However, judging from the fact that no monomeric fluorescence is observed, their efficiencies seem to be very high, so that it seems not to be necessary to consider the difference in their efficiencies in the present case. It may safely be considered that the radiative rate constants of each fluorescence (second and sandwich-like excimer bands) of PVCz(r) are equal to those of PVCz(c). Therefore, Fig. 2 shows that the concentration of the sandwich-like excimer site in PVCz(r) is nearly equal to that in PVCz(c), and that the concentration of the second excimer site in PVCz(r) is higher than that in PVCz(c) by a factor of about 2.4. That is, the difference in the fluorescence spectra between PVCz(r) and PVCz(c) seems not to be attributable to any difference in the concentration of the sandwich-like excimer site, but to the difference in the concentration of the second excimer site.

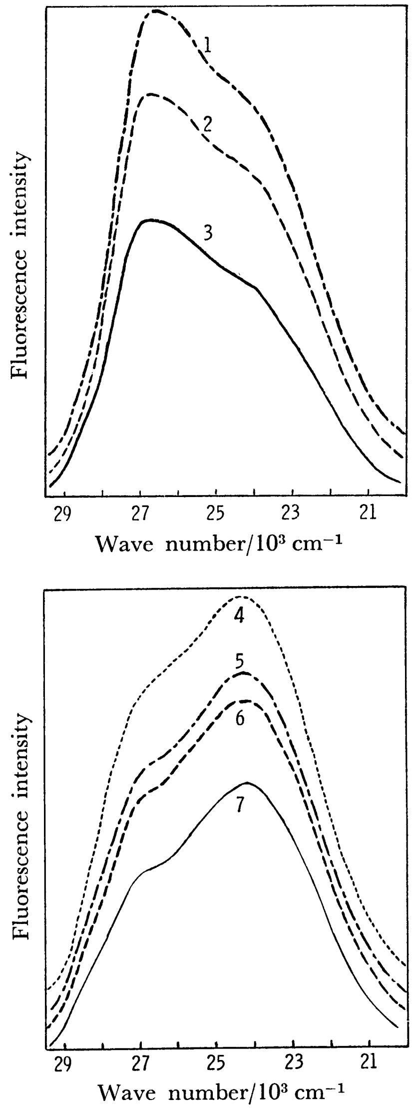

Fig. 1. Fluorescence spectra of PVCz and VCz-vinylnaphthalene(VN) copolymers polymerized by various methods in THF aerated solutions at room temperature. Excitation wavelength; 330 nm.
(1) VCz-VN(0.5 mol% in feed) copolymer polymerized by AIBN (1 mol%) in benzene (1 M) at 70 °C for 2 h, (2) PVCz(r) polymerized by AIBN (1 mol%) in benzene (1.3 M) at 70 °C for 4.5 h, (3) PVCz(r) polymerized by AIBN (1 mol%) in benzene (0.5 M) at 70 °C for 7 h, (4) PVCz(c) polymerized by BF_3OEt_2 (1 mol%) in toluene (0.26 M) at 20 °C for 1 h, (5) VCz-VN (1 mol% in feed) copolymer polymerized by BF_3OEt_2 (1 mol%) in toluene (0.86 M) at 15 °C for 3 h, (6) PVCz(c) polymerized by BF_3OEt_2 (1 mol%) in toluene (0.09 M) at −78 °C for 1 h, (7) PVCz(c) polymerized by BF_3OEt_2 (0.5 mol%) at 20 °C for 18.5 h.

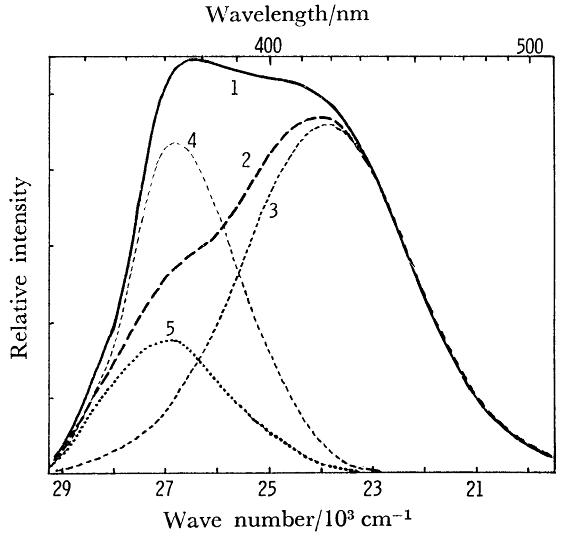

Fig. 2. Fluorescence spectra and the resolution spectra of PVCz(r) and PVCz(c) in MTHF–THF degassed solutions at room temperature. Optical densities at excitation wavelength (310 nm) are 0.132 and 0.131 for PVCz(r) and PVCz(c), respectively.
(1) ——; PVCz(r), (2) — —; PVCz(c), (3) ······; the component of the sandwich-like excimer fluorescence of PVCz(r) and PVCz(c), (4) ----; the component of the second excimer fluorescence of PVCz(r), (5) ······; the component of the second excimer fluorescence of PVCz(c).

In rigid glass at 77 K, a significant difference in the fluorescence spectra between PVCz(r) and PVCz(c) is found, as is shown in Fig. 3. The intensity of the 370 nm band of PVCz(r) is larger than that of PVCz(c). Johnson has pointed out a molecular-weight dependence of the emission spectrum of PVCz(r) in MTHF at 77 K.⁹⁾ The molecular weights of PVCz(r) and PVCz(c) used in this experiment are 1×10^5 and 2×10^5 respectively. Therefore, the difference in the fluorescence spectra between PVCz(r) and PVCz(c) in rigid glasses at 77 K seems not to be attributable to any difference in the molecular weight, but to the

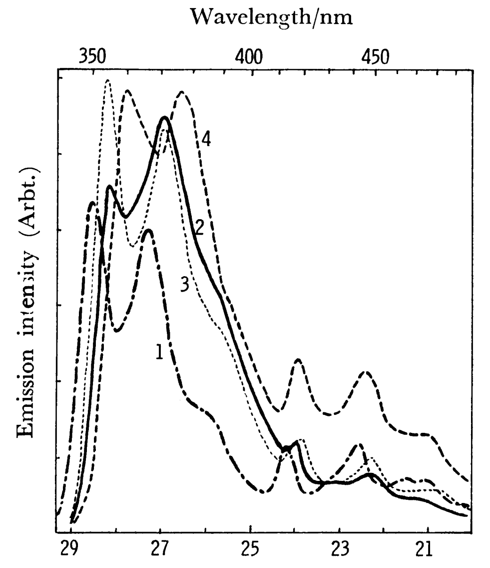

Fig. 3. Emission spectra of (1) ----; VCz Olig, II, (2) ——; PVCz(r), (3) ----; PVCz(c), and (4) ——; PCzEVE in MTHF-THF rigid glasses at 77 K.

difference in their tacticities. The above-described results indicate that the fluorescence spectra both in fluid and in rigid solutions reflect the difference in the tacticity of PVCz and that the concentration of the second excimer site in syndiotactic-rich polymer-(PVCz(r)) is higher than that in isotactic-rich polymer-(PVCz(c)).

In the conformations for a three-skeletal carbon rotational dyad of syndiotactic and isotactic polymer-chain sequences based on a threefold rotational potential,[18] the conformational states with the lowest energy and those corresponding to the sandwich-like excimer site are shown in Fig. 4 (a) and (b). In the syndiotactic case there are a doubly degenerate ground state (g^+g^+, tt) and a doubly degenerate excimer state (g^-t, tg^-). On the other hand, in the isotactic case there are a doubly degenarate ground state (g^+t, tg^-) and a singlet excimer state(tt). The formation of the sandwich-like excimer conformation from the ground-state conformation requires rotational motion about the carbon–carbon bond. In the ground-state conformations, we note that the tt conformation of the syndiotactic chain (Fig. 4(a)) has a shortest distance between neighboring Cz chromophores. Since the Cz chromophore is bulky, it seems to be easy to approach and mutually overlap the one benzene ring of the neighboring Cz chromophores in the excited state, as is shown in Fig. 5. The ground-state molecules corresponding to this reduced separation have a repulsive interaction.

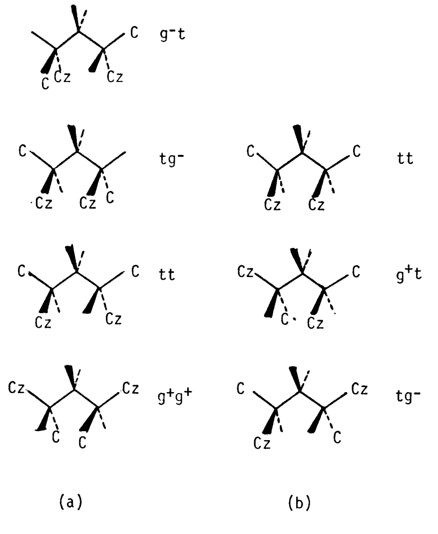

Fig. 4. The lowest energy conformations and excimer forming site ones for a three skeletal carbon rotational dyad of (a) syndiotactic and (b) isotactic polymer chain sequences based on a three fold rotational potential. This figure is quoted from Fig. 10 in Ref. 18.

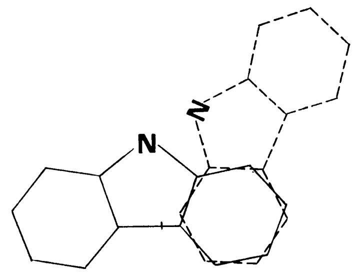

Fig. 5. The model of the second excimer of PVCz.

It has been reported that 1,2-di(1-anthryl)ethane shows a broad excimer fluorescence in solution at room temperature at wavelengths shorter than the fluorescence of a sandwich-like excimer formed by the decomposition of its photodimer in rigid glass at 77 K, and that the structure of the excimer seems to be the overlap of only one benzene ring in the mutual anthracence chromophores.[19] Therefore, it seems reasonable to consider that the structure of the second excimer state may be the overlap of only one benzene ring in the neighboring chromophores. This structure seems to be supported by the fact that the formation of the sandwich-like excimer from the second excimer requires a rotational motion about the carbon-carbon bond.[9]

Concerning poly(α-methylstyrene) (PαMS)[20] andpolystyrene (PS),[20–22] it has been reported that the ratio of the sandwich-like excimer to the monomer fluorescence intensity, I_E/I_M, for the isotactic polymer is larger than that for the atactic polymer, although an opposite experimental result for PS has also been reported.[3] With regard to the relation between the tacticity of the polymer chain and I_E, Longworth[21] has reported that the I_E for isotactic PS is larger than that for atactic PS. In contrast to these results, in the case of PVCz, the concentration of the sandwich-like excimer site in the isotactic-rich polymer is nearly equal to that in the syndiotactic-rich polymer, as has been metioned above. The difference between the former (PαMS, PS) and the latter (PVCz) may be attributable to the existence of a second excimer resulting from the bulky Cz chromophore. No detailed explanation can, however, be offered at present.

Fluorescence Spectra of PCzEVE. The fluorescence spectra of the compounds with the Cz chromophores in MTHF–THF dilute solutions (2.0×10^{-4} M) at room temperature are shown in Fig. 6. The emission

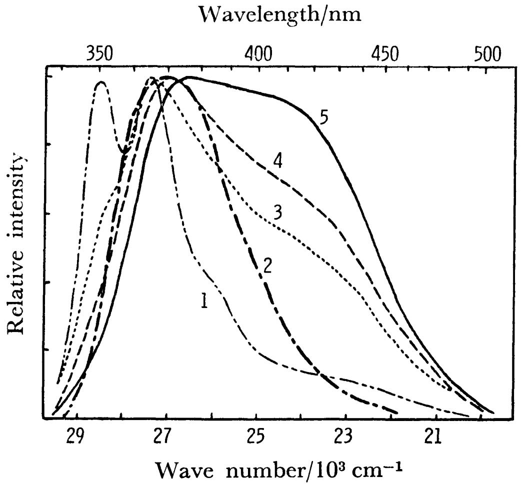

Fig. 6. Normalized fluorescence spectra of the model compound and vinylpolymers in MTHF–THF degassed solution at room temperature. Excitation wavelength; 310 nm.

(1) – – – – –; DCzP, (2) — — —; PCzEVE, (3) - - - -; VCz Olig. I, (4) — — —; VCz Olig. II, (5) ———; PVCz(r).

spectrum of DCzP consists of a monomeric structured fluorescence and a sandwich-like excimer one with a peak at *ca.* 23900 cm^{-1}, as is well-known.[23–25] VCz Olig. I and II show a structureless fluorescence with a peak at 27000—27500 cm^{-1} and a sandwich-like excimer fluorescence, as in the case of PVCz, although VCz Olig. I also shows a monomer fluorescence as a shoulder. On the other hand, PCzEVE shows only a broad, structureless fluorescence with a peak at 27100 cm^{-1}. The Stokes shift (1990 cm^{-1}) is much larger than that of *i*-PrCz and DCzP (380 cm^{-1}). The fluorescence excitation spectra of PCzEVE, obtained by monitoring at several wavelength (350—450 nm) at room temperature, duplicate exactly the absorption spectrum of this solution at room temperature.

The fluorescence decay curve of PCzEVE in the MTHF–THF solution at room temperature is clearly two-component in all wavelength regions (370—430 nm), as is shown in Fig. 7. The decay constant of the long-lived component observed at 370 nm (33±1 ns) is longer than that of *i*-PrCz (17±2 ns) and shorter than that of the sandwich-like excimer fluorescence of PVCz (45±1 ns). The initial fast decay constant is 13±2 ns. This two-component decay of PCzEVE is also observed in rigid glass at 77 K (35±4 and 12±2 ns). The ratio of the short-decay component to the long one in rigid glass at 77 K is larger than that in a fluid solution at room temperature.

Table 1 shows the relative fluorescence quantum yields, taking the value of *i*-PrCz, which forms no excimer, as unity. The fluorescence quantum yield of PCzEVE is higher than that of DCzP, in which the sandwich-like excimer formation is the minimum among the materials used, as is shown in Fig. 6.

The fluorescence spectra of PCzEVE at various temperatures are shown in Fig. 8. At lower temperatures, two peaks appear, and they approach each other with an increase in the temperature. At tem-

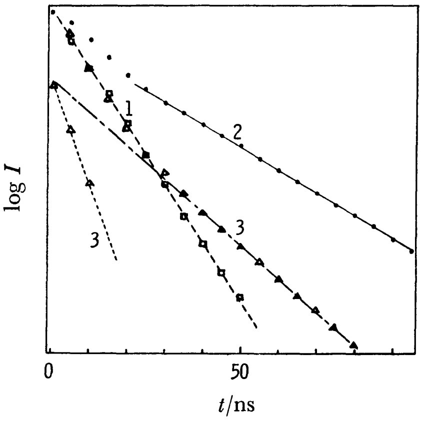

Fig. 7. Fluorescence decay curves of the model compound and vinylpolymers in MTHF–THF degassed solutions at room temperature.

(1) -□--□-; *i*-PrCz (λ_{obsd}=370 nm); τ_f=17 ns.

(2) • • •; PVCz(r) (λ_{obsd}=380 nm), —●—●—; the long-lived component; τ_f=46 ns.

(3) △△△; PCzEVE (λ_{obsd}=370 nm), —△—△—; the long-lived component; τ_f=31 ns, --△--△--; the short-lived compnent; τ_f=11 ns; the difference between the observed decay curve and the long-lived component.

Table 1. Relative fluorescence yields

Substance	η
i-PrCz	1.00
PCzEVE	0.79
DCzP	0.57
VCz Olig. I	0.40
VCz Olig. II	0.37
PVCz(r)	0.33
PVCz(c)	0.27

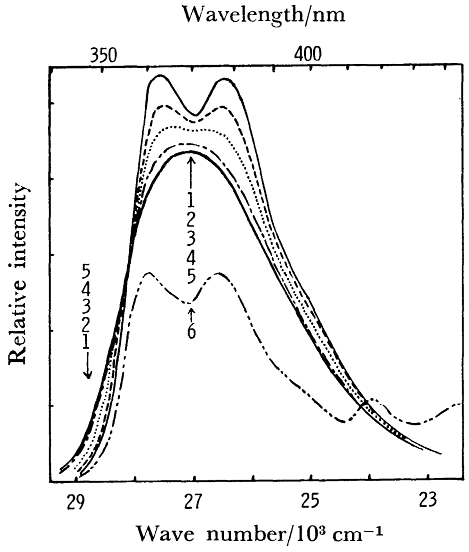

Fig. 8. Temperature dependence of the fluorescence spectra of PCzEVE in MTHF–THF degassed solution. Concentration of PCzEVE; 2.0×10^{-4} M. Excitation wavelength; 310 nm.

(1) 168 K, (2) 208 K, (3) 249 K, (4) 298 K, and (5) 318 K. The fluorescence (6) at 77 K was also given for comparison.

peratures higher than *ca.* 273 K, a structureless fluorescence spectrum with only one peak is observed. The fluorescence intensity decreases with an increase in the temperature. According to the measurement of the temperature dependence of the fluorescence spectra of the such compounds as PVCz(r and c), VCz Olig. I and II, and DCzP, the sandwich-like excimer formation has its maximum at *ca.* 293 K. On the other hand, in the case of PCzEVE, no appreciable change in the fluorescence spectra near 23900 cm^{-1} is observed over a wide temperature range, as is shown in Fig. 8. These facts indicate that PCzEVE does not form the sandwich-like excimer which is formed in PVCz(r and c), VCz Olig. I and II, and DCzP.

The emission spectrum of PCzEVE in rigid glass at 77 K is also shown in Fig. 3. The fluorescence spectrum of VCz Olig. II has, roughly, a so-called "mirror-symmetry" relation between the absorption and the fluorescence spectra (Fig. 3). However, PVCz(r and c) and PCzEVE do not have the mirror-symmetry relation. In particular, the fluorescence spectrum of PCzEVE is at a longer wavelength than that of PVCz(r and c) and has a different shape. The absorption spectra of PVCz(r and c) and PCzEVE in rigid glasses at 77 K are sharper than that in fluid solutions at room temperature, but no appreciable new band is observed. The fluorescence excitation spectra of these polymers in rigid glasses at 77 K are also in agreement with their absorption spectra. The resolution of the phosphorescence spectrum of PCzEVE is lower than those of *i*-PrCz and VCz Olig. I, the spectrum is very similar to that of PVCz(r and c), although its lifetime (6.6±0.1 s) is shorter than that of PVCz(r and c) (8.1±0.2 s).16) Therefore, the excited-state interactions are present among the Cz chromophores in PCzEVE even at low temperatures, at which the solvent becomes rigid (*ca.* 102 K).

It has been reported that the triplet energy migration in PCzEVE occurs in rigid glass at 77 K.16) The degrees of polarization of fluorescence for PVCz(r), PCzEVE, DCzP, and *i*-PrCz in rigid glasses at 77 K are shown in Fig. 9. The degrees are almost the same for PCVz(r) and for PCzEVE. This fact indicates that the singlet energy migration in PCzEVE occurs efficiently along the polymer chain, as is the case in PVCz.7)

The concentrated THF solution of PCzEVE (0.5 M) shows the same spectra as in a dilute solution near 223 K and above.

As has been mentioned above, PPyMVE, PNMVE, and PNMA show both the normal structured monomeric fluorescence and the sandwich-like excimer fluorescence in dilute solutions. On the other hand, poly[2-(9-phenanthryl)ethyl vinyl ether] (PPhEVE), with phenanthryl chromophores widely spaced on the main chain by $-O-CH_2-CH_2-$ bonds, as does PCzEVE, shows, only the monomeric structured fluorescence in a dilute solution at room temperature.26) The fluorescence structure and lifetime in a dilute solution are almost the same as those of 9-ethylphenanthrene. It is well-known that the excimer fluorescence of phenanthrene is not observed at room temperature.27) In the case of PCzEVE, in which aromatic chromophores are widely spaced on the skeletal chain than in PPyMVE, PNMVE, and PNMA, it is surprising that the normal structured monomeric fluorescence is not observed at all. The fact that the sandwich-like excimer fluorescence of PCzEVE is not observed in either dilute or concentrated solutions at room temperature also supports the idea that the sandwich-like excimer formation in PVCz is possible only between two adjacent chromophores.7)

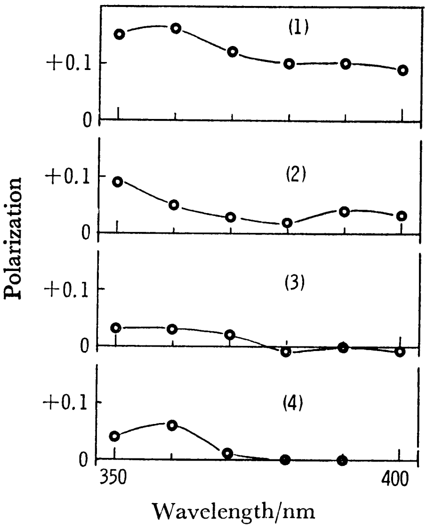

Fig. 9. Fluorescence polarizations of MTHF-THF rigid glasses of (1) *i*-PrCz (6.7×10^{-5} M), (2) DCzP (7.3×10^{-5} M), (3) PCzEVE (9.6×10^{-5} M), and (4) PVC(r) (1.0×10^{-4} M) at 77 K. Excitation wavelength; 334 nm.

The above-described results indicate that the excited-state interaction among the Cz chromophores in PCzEVE is quite different from that is DCzP, VCz Olig. I and II, and PVCz(r and c), and that, in some vinyl polymers with aromatic chromophores widely spaced on the main chain, only PCzEVE is unique. This behavior of PCzEVE may reflect a characteristic of the bulky Cz chromophore.

The position of the PCzEVE fluorescence band in solution at room temperature is almost the same as that of the fluorescence in the shorter wavelength regions of PVCz(r and c) and VCz Olig. I and II, although the appearance of the structure below *ca.* 273 K is different. The initial fast decay constant of the PCzEVE fluorescence (11—14 ns) is nearly equal to the lifetime of the 370 nm fluorescence of PVCz in the polycrystalline THF matrix at 77 K (the order of 15 ns); at 370 nm the emission of PVCz is totally that due to the second excimer.9) Therefore, one of the emitting species of PCzEVE in solution may be the same as a species emitting in the shorter-wavelength region of PVCz in solution (second excimer), although there remains the problems that the fluorescence lifetime of PCzEVE in solution at room temperature is nearly equal to that in rigid glass at 77 K and that the monomeric fluorescence of PCzEVE is not observed, in spite of the small binding energy of second excimer (*vide infra*).

Formation of an Exciplex. The fluorescence spectra

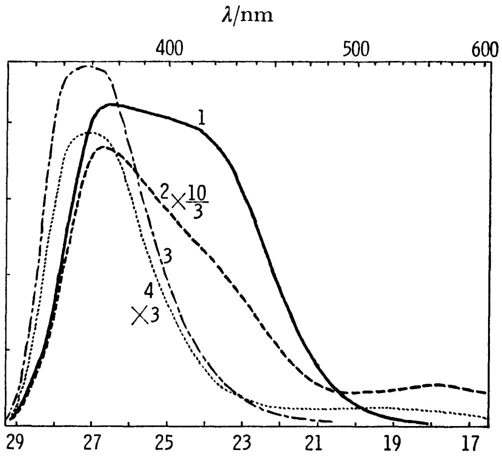

Fig. 10. Fluorescence spectra of PVCz(r) (3.9×10^{-4} M) and PCzEVE (1.9×10^{-4} M) in MTHF-THF degassed solutions in the absence and the presence of DMTP (1.9×10^{-2} M) at room temperature. The intensities of the spectra are not comparative for the different polymers.

(1) ——; PVCz(r) in the absence of DMTP, (2) ----; PVCz(r) in the presence of DMTP, (3) ——; PCzEVE in the absence of DMTP, and (4) ······; PCzEVE in the presence of DMTP.

of PVCz(r) and PCzEVE in degassed THF-MTHF solutions in the absence and in the presence of DMTP (6×10^{-2} M) are shown in Fig. 10. In the cases of PVCz (r and c) and VCz Olig. II, the fluorescence is nonuniformly quenched by DMTP, as in the case of PVCz(r) quenched by acids.[29] That is, the sandwich-like excimer fluorescence is quenched more effectively than the second excimer fluorescence. On the other hand, the fluorescence of PCzEVE is uniformly quenched by DMTP. In all cases, the exciplex fluorescence appears in the longer-wavelength region.

The quenching factor, Q, is defined by $Q=(I_0-I)/I$, where I_0 and I are the fluorescence intensity in the absence and in the presence of DMTP respectively. In determining the quenching factor, Q, of PVCz(r), the following equations have been used to separate the contribution of the second and sandwich-like excimer fluorescences at 370 and 420 nm:

$$I_{370} = I_s + 0.174 I_E$$
$$I'_{420} = I_E + 0.064 I_s$$
$$I_{420} = I'_{420} + 0.294 I_{580}$$

where I_{370}, I_{420}, and I_{580} are the heights of the fluorescence intensity measured at 370, 420, and 580 nm respectively, I_E is the height corresponding to the sandwich-like excimer fluorescence intensity emitted at 420 nm, I_s is the height corresponding to the second excimer fluorescence intensity emitted at 370 nm, and I'_{420} is the height obtained by subtracting the contribution of the exciplex fluorescence intensity emitted at 420 nm from I_{420}. The contribution of the exciplex fluorescence intensity emitted at 420 nm has been estimated from the corrected spectrum of the THF solutions of PVCz(r) (9.2×10^{-5} M) and DMTP (0.155 M). The concentrations of the second excimer fluorescence intensity at 420 nm and the sandwich-like excimer fluorescence at 370 nm have been determined from the resolution spectra of PVCz(r) (Fig. 2). The dependence of the quenching factor, Q, of PVCz(r) on the concentration of DMTP is shown in Fig. 11. The second excimer band is linearly quenched, and the sandwich-like excimer band is superlinearly quenched. The quenching of the second and the sandwich-like excimer fluorescence seems to be described by the same reaction scheme as in the case of acid,[28] assuming that the monomer is replaced by the second excimer. Then,

$$K_s = k_a/(k_f+k_r+k_E) = k_a\tau_s = 57\ \mathrm{M}^{-1}$$
$$K_E = k_a'/(k_f'+k_r') = k_a'\tau_E = 13\ \mathrm{M}^{-1}$$

where k_f, k_r, and k_a are the radiative, nonradiative, and quenching rate constants respectively. The letters with prime and nonprime show the second and sandwich-like excimers respectively. The k_E is the rate constant of the conversion of the second excimer to the sandwich-like one. The τ_s and τ_E are the second and sandwich-like excimer fluorescence lifetimes, both in the presence of k_E and in the absence of DMTP respectively. From the measured fluorescence decay curves of PVCz(r) in an aerated THF solution at room temperature,[29] $\tau_s \sim 4\times10^{-9}$ s and $\tau_E \sim 17\times10^{-9}$ s. Then, $k_a \sim 1\times10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $k_a' \sim 8\times10^{8}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Therefore, the quenching reaction is much more efficient for the second excimer than for the sandwich-like one.

If the PVCz–DMTP exciplex was formed between the migrating excited singlet state of the Cz chromophores and DMTP, the second excimer fluorescence would be also superlinearly quenched by DMTP, as is the case of the sandwich-like excimer fluorescence

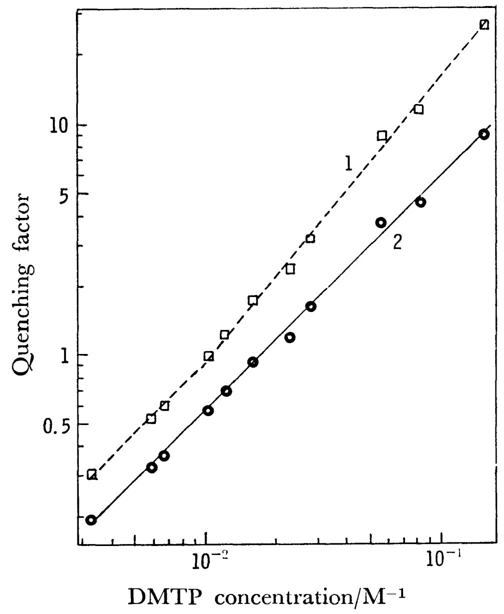

Fig. 11. Quenching of PVCz(r) by DMTP in THF aerated solutions at room temperature. Excitation wavelength; 345 nm.

(1) The sandwich-like excimer band, and (2) the second excimer band.

quenched by DMTP. Therefore, the PVCz–DMTP exciplex seems to be formed between the second excimer site and DMTP. This phenomenon seems to be supported by the fact that the intensity of the PVCz(r)–DMTP exciplex is larger than that of the PVCz(c)–DMTP exciplex when the concentrations of the same donor and acceptor are the same. Therefore, the second excimer has a very binding energy, so it seems to dissociate to form the exciplex by the diffusive approach of DMTP.

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