BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (1), 79—84 (1978)

Emission Spectra of the Vinyl Polymers with Pendant Benzocarbazolyl Groups

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(Received June 13, 1977)

The emission spectra of poly(*N*-vinyl-5*H*-benzo[*b*]carbazole) (PV5BCz) and poly(*N*-vinyl-7*H*-benzo[*c*]carbazole) (PV7BCz), which are prepared by radical and cationic polymerization, and their monomeric model compounds were investigated in solutions. In the case of PV7BCz, the fluorescence spectra were composed of a second excimer fluorescence at the shorter wavelength and a sandwich-like excimer fluorescence at the longer wavelength. The difference in the spectra between the radical and cationic polymers was quite similar to that of the poly(*N*-vinylcarbazole) (PVCz) system. The intensity of the sandwich-like excimer fluorescence was independent of the polymerization methods, but the intensity of the second excimer fluorescence increased with an increase in the content of the syndiotactic sequence. In the case of PV5BCz, the behavior of the fluorescence spectra of the radical polymers was similar to that of the PVCz and PV7BCz systems. On the other hand, the fluorescence spectra of the cationic polymers differed markedly from those of the above-mentioned polymers. The cationic polymers did not show the second excimer fluorescence, but a monomer-like structured fluorescence, at the shorter wavelength, although it did show the sandwich-like excimer fluorescence at the longer wavelength. This significant difference in the fluorescence spectra between the radical and cationic polymers is attributable to the difference between their tacticities. On the basis of these results, the characteristics of the second excimer site were further clarified.

In recent years there has been a growing interest in the emission spectra of aromatic vinyl polymers. It is known that aromatic vinyl polymers show excimer fluorescence in dilute solutions. Considerable data on the emission properties of poly(*N*-vinylcarbazole) (PVCz) have been accumulated because of an interest in high photoconductive polymers.[1–8] The monomeric model compound, *N*-ethylcarbazole (ECz), shows no excimer fluorescence in either a concentrated solution or a solid state.[5] The PVCz, both in solution and in film, shows one broad fluorescence, which is composed of not only one component, but of two components. The broad emission at the longer wavelength ($\nu_{\max}$; *ca.* 23900 cm^{-1}) is assigned to the sandwich-like excimer fluorescence. On the other hand, the assignment of the broad emission in the shorter-wavelength region ($\nu_{\max}$; *ca.* 27000 cm^{-1}) is controversial because of both the absence of the structure and the large Stokes-shift. David *et al.*[3] and Yokoyama *et al.*[5] have assigned this shorter-wavelength band to the monomer fluorescence for PVCz in solution. P. C. Johnson and Offen,[2] and Powell and Venikouas[6] have assigned it to the emission from a dimer trap site for PVCz films. On the other hand G. E. Johnson[4] has recently assigned it to the second excimer fluorescence for PVCz in solution. Klöpffer and Bauser[8] have also assigned it to the second, more weakly bound excimer fluorescence for PVCz films.

We have reported, on the basis of the NMR spectra and glass transition temperature of PVCz, that the samples prepared by the radical polymerization have higher syndiotacticities than the samples prepared by the cationic one.[9] We have also reported that this difference in tacticity between the radical and cationic polymers is reflected in the fluorescence spectra both in solution and in film, and that the broad emission at the shorter wavelength should be assigned to the second excimer fluorescence,[7] as has been proposed by Johnson and Klöpffer.[4,8] It has also been suggested that the second excimer site, where only one benzene ring in each of the neighboring carbazolyl chromophores overlaps with another, is formed only in the syndiotactic sequence.[7]

Spectroscopic studies of vinyl polymers with aromatic chromophores, which are more bulky than a carbazolyl chromophore, make the above-mentioned suggestion clearer. We have synthesized poly(*N*-vinyl-5*H*-benzo[*b*]carbazole) (PV5BCz), poly(*N*-vinyl-7*H*-benzo[*c*]carbazole) (PV7BCz). From the NMR spectra, the glass transition temperatures, and the solubility of the polymers, it has already been found that the stereoregularity of these polymers depends on the polymerization method, as is the case in PVCz.[9]

Concerning the vinyl polymers with small aromatic chromophores, the relation between the tacticity of the polymer chain and the fluorescence spectrum has been reported on in several investigations. For polystyrene (PS),[10–12] poly(α-methylstyrene),[13] and poly(*p*-methylstyrene),[14] 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.[10] Y.-C. Wang and H. Morawetz have found, from the NMR and fluorescence spectra of polyacenaphthylene, that the polymers prepared by cationic and radical polymerizations have different configurations, and that this is reflected in the ease with which they form excimers.[15] However, to the knowledge of the present authors, such a relation has never hitherto been studied for the vinyl polymers with large and bulky aromatic chromophores such as benzocarbazole.

In the present investigation, we have investigated the spectroscopic behavior of PV5BCz, PV7BCz, and their monomeric model compounds (*N*-ethyl-5*H*-benzo[*b*]carbazole(E5BCz) and *N*-ethyl-7*H*-benzo[*c*]carbazole (E7BCz)) and discussed the relation between the tacticity of the polymer chain and the emission spectra.

Experimental

The vinyl polymers (PV5BCz and PV7BCz) were prepared by the methods described previously.[9] The model compounds

(E5BCz and E7BCz) were obtained by the alkylation of benzocarbazole with diethyl sulfate. The E5BCz was recrystallized twice from ethanol and subsequently sublimed *in vacuo* (mp; 149—150 °C). The E7BCz was isolated by column chromatography (silica gel, benzene : hexane = 1 : 2) and was recrystallized twice from methanol (78.5—80.0 °C). All of the solvents used were purified by the usual methods.

The solutions were completely degassed by freeze-pump-thaw cycles if necessary.

The emission spectra and fluorescence-decay times were measured with the apparatus described in a previous paper.[7]

Results and Discussion

The materials used for the present investigation are listed in Table 1. The $I_{H/L}$ value in Table 1 is a measure of the amount of the isotactic sequence relative to the syndiotactic one of the polymer, as is described in Ref. 9. The PV7BCz(c)-III has the largest isotactic sequence, and the free-radical polymer, the smallest.

TABLE 1. CHARACTERIZATION OF MATERIALS USED

Sample	Polymerization[a] temp/°C	Degree of polymerization[b]	$I_{H/L}$[c]
E7BCz	—	—	—
PV7BCz(r)	+75	58	0.32
PV7BCz(c)-I	−78	103	0.51
PV7BCz(c)-II	−40	82	0.68
PV7BCz(c)-III	+10	36	0.92
E5BCz	—	—	—
PV5BCz(r)-I	+100	49	—
PV5BCz(r)-II	+80	13	—
PV5BCz(c)	−78	8	—

a) Initiator; (r): AIBN, (c): BF_3OEt_2. Solvent; none for PV5BCz(r)-I, and toluene for the others. b) The polymer molecular weights were determined by means of a vapor-pressure osmometer. c) The $I_{H/L}$ value is the intensity ratio of the higher-field peak to the lower-field one for the methine proton in the NMR spectra. This value for PV5BCz cannot be obtained because of the highly unresolved NMR spectra.

Absorption Spectra. The absorption spectra in 1,2-dichloroethane solutions are shown in Fig. 1. The absorption bands of the polymers are shifted to frequencies higher by *ca.* 200 cm^{-1} as compared with those of the model compounds. This higher-frequency shift is characteristic for polymers of *N*-vinyl compounds with large π-electronic chromophores. Both the decrease in the intensity (or hypochromism) and the spectral change in the ^1B_b and ^1B_a bands of the polymers, as compared with the spectra of the corresponding monomeric model compounds, are similar to what has been observed for PVCz.[16] The degree of the hypochromism is in the order of PV5BCz(r)-I$\approx$PVCz $>$PV7BCz(r)$>$PV5BCz(c).

Fluorescence Spectra of E7BCz and PV7BCz. The fluorescence spectra of E7BCz and PV7BCz are shown in Fig. 2. The E7BCz shows no excimer fluorescence even in concentrated solutions up to 0.1 M, as is the case of ECz. The polymers show one broad fluorescence which is composed of two components, as in the case of PVCz. That is, the spectra were successfully resolved into two broad spectral bands with peaks of 21950 and 24900 cm^{-1} on the assumption that the location of the longer-wavelength band in solution was the same as that in film. The energy differences be-

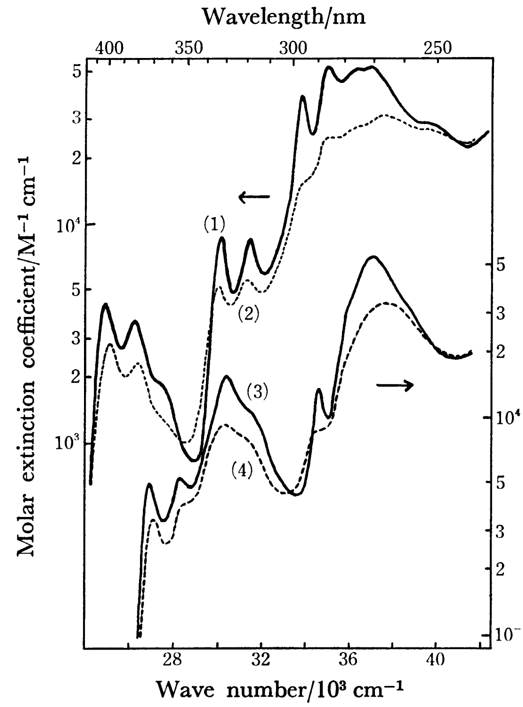

Fig. 1. Absorption spectra of (1) E5BCz, (2) PV5BCz-(r)-I, (3) E7BCz, and (4) PV7BCz(r) in 1,2-dichloroethane solutions at room temperature.

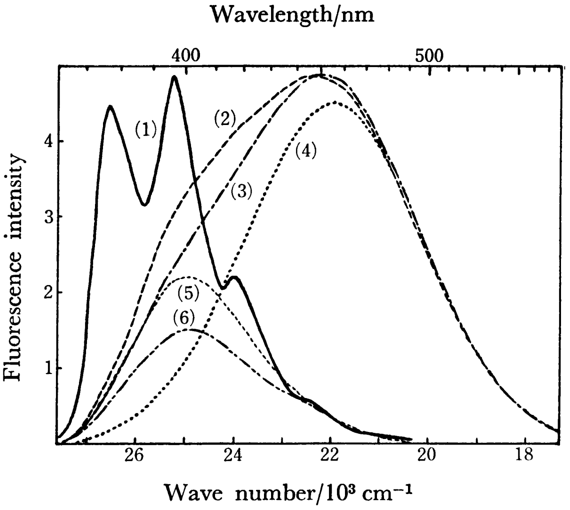

Fig. 2. Fluorescence spectra and their resolution spectra of E7BCz, PV7BCz(r), and PV7BCz(c)-I in MTHF-THF degassed solutions at room temperature. Optical densities of both the polymers at excitation wavelength (350 nm) are 0.249. Fluorescence spectra: (1)——: E7BCz, (2)——, PV7BCz(r), and (3)—— ——: PV7BCz-(c)-I. Resolution spectra: (4)······: the component of the sandwich-like excimer fluorescence of PV7BCz(r) and PV7BCz(c)-I. (5)----, and (6)—-—-—: the component of the second excimer fluorescence of PV7BCz-(r) and PV7BCz(c)-I, respectively.

tween the peaks of these two bands and the 0-0 fluorescence band (26560 cm^{-1}) of the E7BCz are 4610 and 1660 cm^{-1}. These are almost the same as the corresponding energy differences between PVCz and ECz (4630 and 1630 cm^{-1}). The fluorescence excitation spectra of the polymers, obtained by monitoring at several wavelengths (390—500 nm), duplicate the absorption spectra of these solutions exactly. By analogy with the fluorescence spectrum of PVCz, the fluorescence bands at the longer wavelength and at the shorter one can be assigned to the sandwich-like excimer fluorescence and the second excimer one respectively. Figure 2 shows that the concentrations of the sandwich-like excimer site are nearly equal between the radical and cationic polymers, and that the concentration of the second excimer site is larger for the radical polymer than for the cationic polymer by a fac tor of about 1.4. That is, the difference in the fluorescence spectra between these two polymers seems to be attributable to the difference in the concentration of the second excimer site.

The $I_{H/L}$ and $\overline{DP}$ of the cationic polymers vary remarkably with the polymerization temperature (Table 1).[9] This result is different from that for PVCz.[9] Thus, the fluorescence spectra of PV7BCz samples in aerated solutions (5.9×10^{-5} M) at room temperature were compared with one another in Fig. 3. The second excimer fluorescence intensities are in the order of (r) > (c)-I > (c)-II > (c)-III. This order is not correlated to the molecular weight of the polymers, but to the decrease in the $I_{H/L}$ value. That is, the concentration of the second excimer site increases with an increase in the syndiotactic sequence.

The sandwich-like excimer fluorescence of each PV7BCz sample has a constant intensity at temperatures from *ca.* −110 to 20 °C, as is shown in Fig. 4. At temperatures above *ca.* 20 °C, the intensity of the sandwich-like excimer fluorescence decreases and the intensity of the second excimer fluorescence increases with an increase in the temperature. This phenomenon is also observed for PVCz.[4] This behavior and the presence of the long-lived component decay at the shorter wavelength (*vide infra*) indicate the presence of sandwich-like excimer dissociation to give back the second excimer.

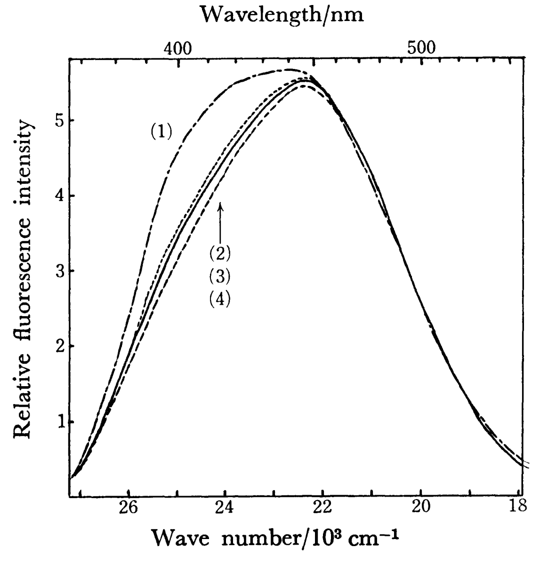

Fig. 3. Fluorescence spectra of (1) PV7BCz(r), (2) PV7-BCz(c)-I, (3) PV7BCz(c)-II, and (4) PV7BCz(c)-III in MTHF-THF aerated solutions at room temperature. Excitation wavelength; 350 nm.

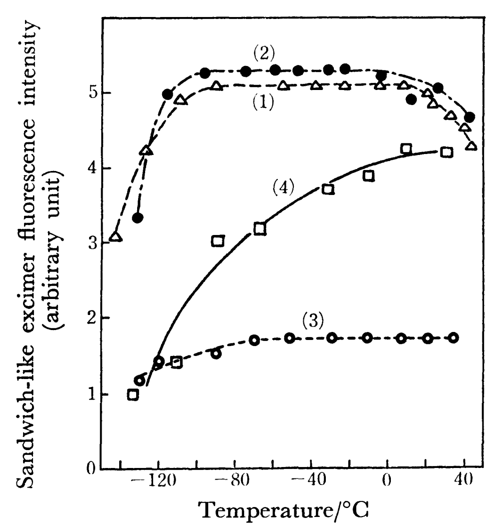

Fig. 4. Temperature dependence of the sandwich-like excimer fluorescence intensity. (1)-△-: PV7BCz(r), (2)-●-: PV7BCz(c)-I, (3)-○--: PV5BCz(r)-II, and (4)-□-: PV5BCz(c).

The above-mentioned results with regard to the concentrations of the sandwich-like excimer site and the second excimer one may be qualitatively explained as follows. If we consider only a part of the syndiotactic sequence in the polymer chain, both the concentration of the second excimer site and that of the sandwich-like excimer site are larger for the radical polymers than for the cationic polymers, because a photodynamic equilibrium between the second excimer and the sandwich-like excimer is established. However, the concentration of the sandwich-like excimer site formed in the isotactic sequence, which cannot form the second excimer site, is larger for the cationic polymers than for the radical polymers. Therefore, a clear difference in the concentrations of the second excimer sites between the radical and cationic polymers is observed, although no clear difference in the concentrations of the sandwich-like excimer sites is observed.

The presence of two kinds of emitting species in the fluorescence was also clarified by measuring the fluorescence-decay times of the polymers. The fluorescence-decay curves of the polymers at room temperature are multi-component in the shorter-wavelength region (36±2 ns and initial fast decay), while they are one-component (36±2 ns) in the longer-wavelength region. The long-lived component corresponds to the sandwich-like excimer fluorescence.

The spectral band of the polymers in rigid glass solutions at 77 K is shifted to a lower frequency and broadened as compared with that of E7BCz, as is shown in Fig. 5. This deviation from the monomer-like fluorescence band shape seems to be attributable to a large contribution of the second excimer fluorescence. In the case of the PVCz samples,[7] the cationic

TABLE 2. FLUORESCENCE LIFETIME[a)]

Sample	Monomer[b)]	Monomer-like[c)]	Second excimer[c)]	Sandwich-like excimer[d)]
i-PCz	17±2	—	—	—
PVCz(c)	—	19±2	—	45±1
PVCz(r)	—	17±2	17±2	45±1
E7BCz	13±1	—	—	—
PV7BCz(c)	—	(13)[e)]	25±3	36±2
PV7BCz(r)	—	(13)[e)]	25±1	36±2
E5BCz	24±1	—	—	—
PV5BCz(c)	—	23±2	—	57±3
PV5BCz(r)	—	26[e)]	65—75	57±3

a) Unit; ns. Solvent: MTHF-THF degassed solution. b) At room temperature and 77 K. c) At 77 K. d) At room temperature. e) See text.

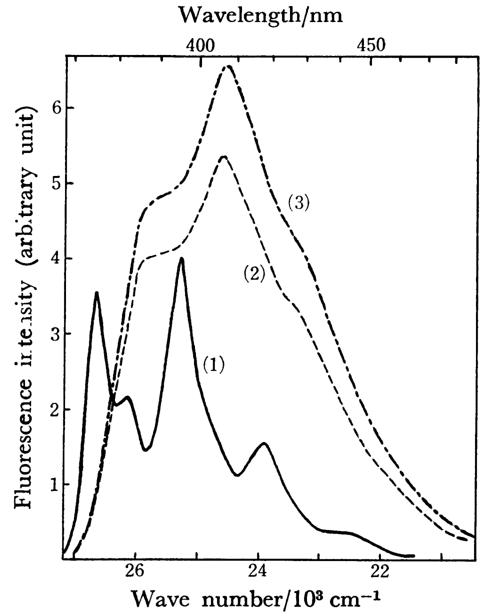

Fig. 5. Fluorescence spectra of (1) E7BCz, (2) PV7BCz-(r), and (3) PV7BCz(c)-I in MTHF-THF rigid glasses at 77 K. Excitation wavelength; 350 nm.

polymer shows a monomer-like structured fluorescence, while the radical polymers shows mainly the second excimer fluorescence. The fluorescence decay times of both the PVCz samples (λ_{obsd}=355—390 nm) are approximately the same as that measured for *N*-isopropylcarbazole (17±2 ns), although a slight departure from a strict first-order decay is observed (Table 2). This fact indicates that the lifetime of the second excimer fluorescence seems to be nearly equal to that of the monomer-like fluorescence. In the case of the PV7BCz samples, the fluorescence decay times of both the polymers at 380 nm are *ca.* 18 ns, while those at the longer wavelength (λ>400 nm) are 25±2 ns. The decay curves are roughly single-exponential. This lifetime (25 ns) is not in agreement with those of the monomeric fluorescence of the model compound (13 ns) and the sandwich-like excimer fluorescence (36 ns). When (at 77 K) the formation of the sandwich-like excimer site from the second excimer site is impossible, this lifetime may correspond to that of the second excimer fluorescence. The decay time (18 ns) at 380 nm seems to be an apparent value due to an overlap of the monomer-like fluorescence and the second excimer one.

Fluorescence Spectra of E5BCz and PV5BCz. The fluorescence spectra of E5BCz and PV5BCz are shown in Fig. 6. The E5BCz shows no excimer fluorescence even in concentrated solutions up to 0.1 M, as is also the case with ECz and E7BCz. The radical polymers show one broad fluorescence, the spectra of which were successfully resolved into two broad bands, with peaks of 20350 and 22550 cm^{-1}, in a manner similar to that in PV7BCz. The energy differences between the peaks of these two bands and the 0-0 fluorescence band (24330 cm^{-1}) of E5BCz are 3980 and 1780 cm^{-1} respectively. The fluorescence excitation spectra of the polymers duplicate exactly the absorption of these solutions. Therefore, the fluorescence bands at the longer and shorter wavelengths can be assigned to the sandwich-like excimer fluorescence and the second excimer one respectively.

The temperature dependence of the fluorescence spectrum of the PV5BCz(r)-II sample is shown in Fig. 7. As may be seen, there is no evidence for the formation of an isoemissive point. The sandwich-like excimer fluorescence has a constant intensity over the temperature range from *ca.* −70 to 40 °C, as is shown in Fig. 4. These phenomena observed for the radical polymers are quite similar to those observed for the PVCz and PV7BCz.

On the other hand, the fluorescence spectrum of the cationic polymer differes markedly from those of the

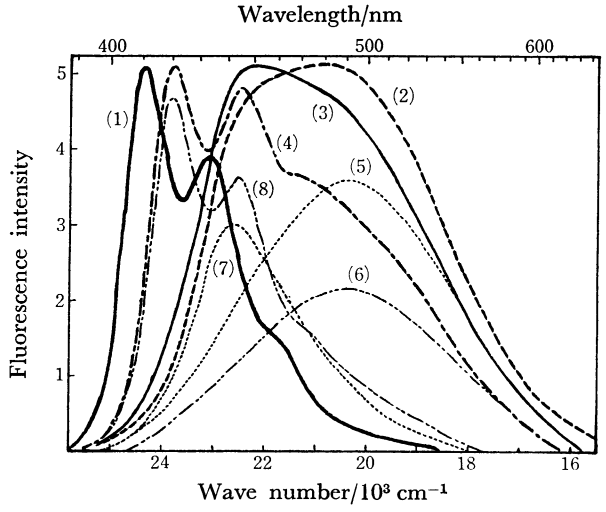

Fig. 6. Normalized fluorescence spectra and their resolution spectra of E5BCz, PV5BCz(r)-I, PV5BCz(r)-II, and PV5BCz(c) in MTHF-THF degassed solutions at room temperature. Excitation wavelength; 350 nm. Fluorescence spectra: (1)——: E5BCz, (2)----; PV5BCz(r)-I, (3)——; PV5BCz(r)-II, and (4)——; PV5BCz(c). Resolution spectra: (5)······, and (6) ———: the component of the sandwich-like excimer fluorescence of PV5BCz(r)-II and PV5BCz(c), respectively. (7)······: the component of the second excimer fluorescence of PV5BCz(r)-II, and (8)———; the component of the monomeric fluorescence of PV5BCz-(c).

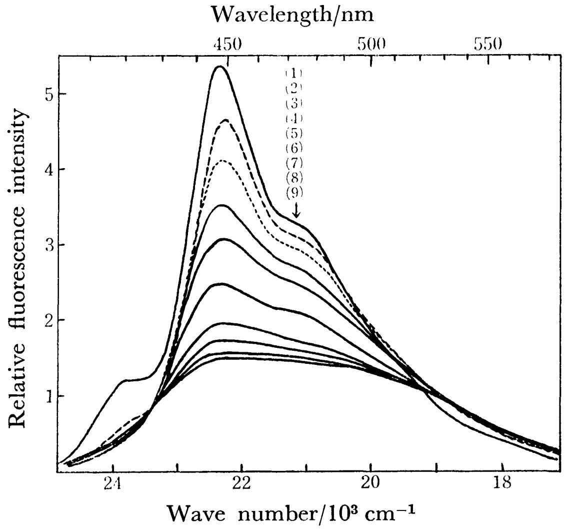

Fig. 7. Temperature dependence of the fluorescence spectra of PV5BCz(r)-II in MTHF-THF degassed solution. Excitation wavelength; 350 nm. (1) 143.5 K, (2) 163 K, (3) 203.5 K, (4) 222 K, (5) 244 K, (6) 263 K, (7) 281 K, (8) 294.5 K, and (9) 308 K.

above-mentioned polymers: (1) The monomer-like structured fluorescence (0-0; 23800 cm^{-1}) in the shorter-wavelength region is observed clearly even at room temperature, while the second excimer fluorescence is not observed, as is shown in Fig. 6. (2) An isoemissive point is clearly observed, as is shown in Fig. 8. (3) The intensity of the sandwich-like excimer fluorescence in the longer-wavelength region increases with an increase in the temperature up to *ca.* 20 °C, as is also shown in Fig. 4.

A dilute fluid solution of a *N*-vinylcarbazole oligomer ($\overline{DP}=10$) at room temperature does not show any structured fluorescence at the shorter wavelength, but a broad fluorescence which is composed of two excimer fluorescences. Therefore, these three significant differences in the fluorescence spectra between the radical and cationic polymers seem not to be attributable to any difference in the molecular weight, but to the difference in their tacticities. This explanation seems also to be supported by the polymerization results: the cationic polymer is considered to be composed of only an isotactic sequence, judging from the fact that only low-molecular-weight polymers are obtained almost quantitatively in high yields. The radical polymers are composed of stereoblock arrangements of the isotactic and syndiotactic helixes.[9] Therefore, the above-mentioned discussion supports the idea that the second excimer site is not formed within the isotactic sequence, but only within the syndiotactic sequence.

The fluorescence-decay curves of both the radical and cationic polymers at room temperature are multi-component in the shorter-wavelength region (57±3 ns and an initial fast decay), while there is only one component with a long lifetime (57±3 ns) in the longer-wavelength region. The long-lived component corresponds to the sandwich-like excimer fluorescence.

Figure 9 shows the fluorescence spectra of PV5BCz and E5BCz in rigid glass solutions at 77 K. The fluorescence spectra of the cationic polymer is mainly composed of a monomer-like fluorescence, the lifetime of which at 420 nm was 23±2 ns. This is the same value as the decay time of E5BCz. On the other hand, the fluorescence spectra of the radical polymers are markedly broadened as compared with that of the cationic polymer. This fluorescence is mainly emitted from the excited monomer state and the second excimer site, although the fluorescence from the sandwich-like excimer site is slightly involved. The fluorescence lifetime at 410 nm, a wavelength where the fluorescence was mainly emitted from the excited monomer state,

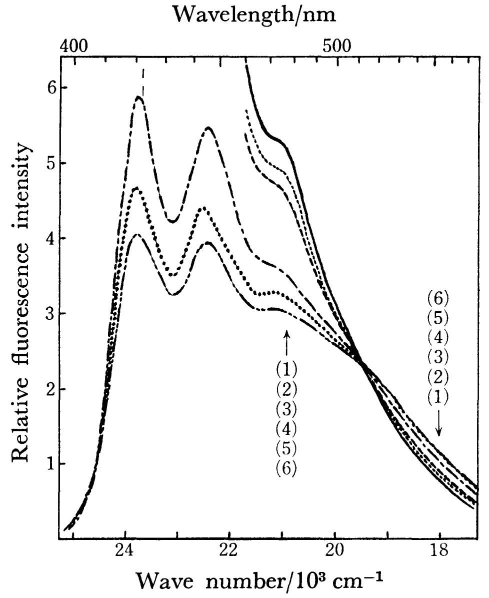

Fig. 8. Temperature dependence of the fluorescence spectra of PV5BCz(c) in MTHF-THF degassed solution. Excitation wavelength; 350 nm. (1) 183.5 K, (2) 202.5 K, (3) 221 K, (4) 262.5 K, (5) 282 K, and (6) 304 K.

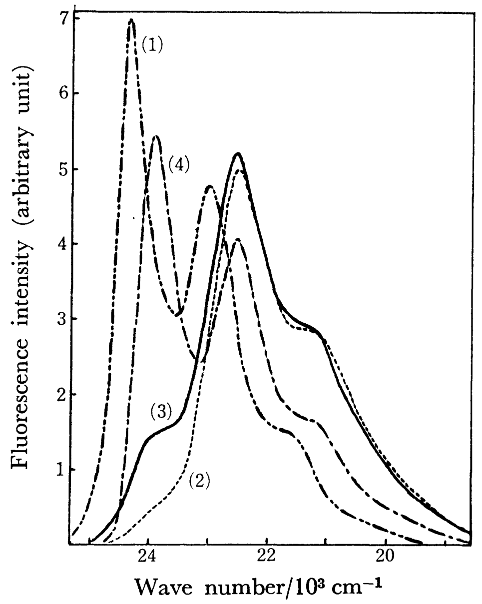

Fig. 9. Fluorescence spectra of (1) E5BCz, (2) PV5BCz-(r)-I, (3) PV5BCz(r)-II, and (4) PV5BCz(c) in MTHF-THF rigid glasses at 77 K. Excitation wavelength; 350 nm.

is *ca.* 26 ns, which is nearly equal to that of E5BCz. The fluorescence decay curves show a departure from the strict exponential decay, with an initial fast component followed by a long tail whose decay constant was 65—75 ns. The ratio of the short-lived component to the long-lived one in the shorter-wavelength region is larger than that in the longer-wavelength region. Therefore, this long-lived component decay may correspond to the lifetime of the second excimer fluorescence of PV5BCz (Table 2).

When we compare the fluorescence spectrum of the PV5BCz(r)-II sample in a polycrystalline 1,2-dichloroethane (fp: −36 °C) matrix at 77 K with the spectrum in a MTHF–THF fluid solution at −29 °C, the concentration of the second excimer site in the matrix turns out to be larger than that in the fluid solution, as is shown in Fig. 10. This is attributable to be impossibility of rotational motion from the second excimer site to the sandwich-like excimer site in the polycrystalline matrix. On the other hand, the cationic sample does not form the second excimer site even under such favorable conditions as the polycrystalline 1,2-dichloroethane matrix. Thus, it may be suggested that the second excimer site is not formed within the isotactic sequence, even under favorable conditions.

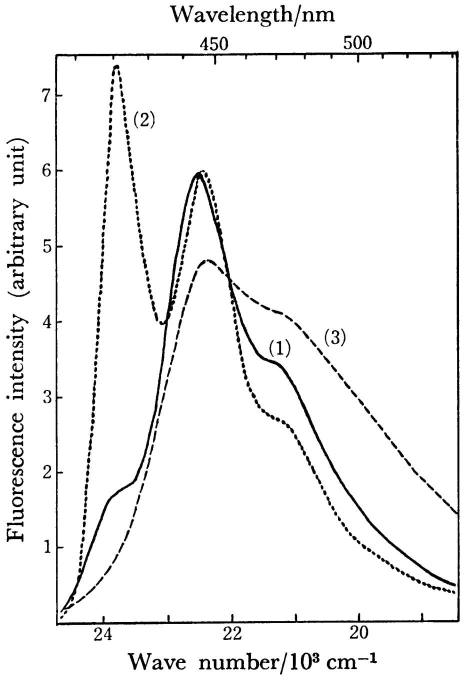

Fig. 10. Fluorescence spectra of (1) PV5BCz(r)-II and (2) PV5BCz(c) in polycrystalline 1,2-dichloroethane matrixes at 77 K. The fluorescence spectra of (3) PV5BCz(r)-II in MTHF–THF fluid solution at −29 °C was also given for comparison.

From the above-mentioned results and discussion, it has further been clarified that the second excimer site is formed only within the syndiotactic sequence. That is, the second excimer site is formed in the conformational state with the lowest energy and the shortest distance between neighboring chromophores in the syndiotactic sequence. Its structure seems to be the overlap of only one benzene ring between the neighboring chromophores, as has been suggested for PVCz.⁷⁾

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

References

1) W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).

2) P. C. Johnson and H. W. Offen, *J. Chem. Phys.*, **55**, 2945 (1971).

3) C. David, M. Piens, and G. Geuskens, *Eur. Polym. J.*, **8**, 1291 (1972).

4) G. E. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).

5) M. Yokoyama, T. Tamamura, M. Atsumi, M. Yoshimura, Y. Shirota, and H. Mikawa, *Macromolecules*, **8**, 101 (1975).

6) G. W. Venikouas and P. C. Powell, *Chem. Phys. Lett.*, **34**, 601 (1975).

7) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **49**, 2082 (1976); *ibid.*, **50**, 22 (1977).

8) W. Klöpffer and H. Bauser, *Z. Phys. Chem. N. F.*, **101**, 25 (1976).

9) K. Okamoto, M. Yamada, A. Itaya, T. Kimura, and S. Kusabayashi, *Macromolecules*, **9**, 645 (1976).

10) M. T. Vala, J. Haebig, and S. R. Rice, *J. Chem. Phys.*, **43**, 886 (1965).

11) J. W. Longworth, *Biopolymers*, **4**, 1131 (1966).

12) T. Ishii, H. Matsushita, and H. Handa, *Kobunshi Ronbunshu*, **32**, 311 (1975).

13) H. Odani, *Bull. Inst. Chem. Res. Kyoto Univ.*, **51**, 351 (1973).

14) T. Ishii, H. Matsushita, and H. Handa, *Makromol. Chem.*, **177**, 283 (1976).

15) Y. -C. Wang and H. Morawetz, *Makromol. Chem. Suppl.*, **1**, 283 (1975).

16) K. Okamoto, A. Itaya, and S. Kusabayashi, *Chem. Lett.*, **1974**, 1167.