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Fluorescence dynamics of poly(*N*-vinylcarbazole) in solution as revealed by multicomponent analysis of picosecond time-resolved fluorescence spectra: dependence on tacticity and molecular weight

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The steady-state fluorescence spectra of poly(*N*-vinylcarbazole) (PVCz) with various molecular weights in tetrahydrofuran solution were examined. The spectra of PVCz(r) prepared by radical polymerization were almost independent of the molecular weight, while those of PVCz(c) prepared by cationic polymerization were dependent on it. The difference in the temperature dependence of the spectra between PVCz(r) and PVCz(c) with high molecular weights was found. The time-resolved fluorescence spectra of PVCz(r) and PVCz(c) with high and low molecular weights were analysed by using a principal multicomponent spectral estimation method, whose results indicate clearly that the spectra were composed of only three component fluorescences (monomer, partial overlap excimer and sandwich excimer). The spectra were analysed by means of a least-squares fitting method using the three component spectral shapes, giving rise and decay curves of these component fluorescences. The curves were non-exponential and depended upon tacticity and the molecular weight. On the basis of these results, the excimer dynamics of PVCz in solution was discussed.

(Keywords: sandwich excimer; partial overlap excimer; excimer dynamics)

INTRODUCTION

Poly(*N*-vinylcarbazole) (PVCz) has received much attention as a representative photoconductive aromatic vinyl polymer, and extensive studies on mechanical, physical, chemical and electrical properties have been reported[1]. Steady-state and time-of-flight photocurrent measurements have been carried out in detail[2], and extrinsic carrier photogeneration was pointed out to be a key process for the photoconductivity[3].

On the other hand, the photophysical processes of PVCz have been of great interest because of two spectrally distinct excimer fluorescences and a clear relation between photophysical properties and tacticity, and they are unique, novel and fruitful in understanding photophysics in polymers and related molecular assemblies.

David *et al.* observed two minima corresponding to two different excimers in the curve showing the dependence of the relative intensity of monomer to excimer fluorescence on temperature[4]. Investigating the emission properties of PVCz and poly(*N*-ethyl-2- and -3-vinylcarbazole)s, Johnson reported the following[5]: (1) A second structureless emission band, which appears at higher energy than the normal sandwich excimer, was observed. (2) The polymer conformation appropriate for formation of this state (the second excimer state) exists prior to the initial excitation step. (3) A dimeric structure with considerable deviation from coplanarity of the two carbazolyl chromophores was proposed for the second excimer state. (4) The small binding energy of the state is attributed mainly to charge resonance interactions between interacting carbazolyl chromophores. (5) Finally, a reversible path between the sandwich excimer and the second excimer state exists above 280 K.

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Examining the relation between stereoregularity and the fluorescence spectra of PVCz, one of the present authors (A.I.) revealed the following[6]: One excimer, with a fluorescence maximum at 420 nm, is attributed to a fully overlapped structure of neighbouring carbazolyl chromophores in a totally eclipsed conformation of the isotactic sequence (sandwich excimer). The other excimer, with a maximum at 370 nm, is due to a structure with only one eclipsed aromatic ring from two carbazolyl chromophores in the *tt* conformation of the syndiotactic sequence (second excimer or partial overlap excimer). The assignment of these structures of the excimers was based on the fact that PVCz prepared by radical polymerization (PVCz(r)) has a higher syndiotacticity than that prepared cationically (PVCz(c)), which was revealed by examining n.m.r. spectra and the glass transition temperature of PVCz[7].

De Schryver *et al.* reported that these excimer fluorescences were well modelled by *meso*- and *rac*-2,4-di(*N*-carbazolyl) pentanes, which correspond to isotactic and syndiotactic diads in the PVCz chain, respectively[8]. Evers *et al.* reported, in addition to the fluorescence property of these model compounds, that the partial overlap and sandwich excimers were derived independently from syndiotactic and isotactic diads, respectively[9]. The excimer formation kinetics of these model compounds in solution has been revealed by time-resolved fluorescence spectroscopy[8]. However, no kinetic model of excimer formation of PVCz has been established.

Guillet *et al.*[10] and Phillips *et al.*[11], using time-resolved fluorescence spectroscopy, showed the presence of an interconversion process from the sandwich excimer to the partial overlap one, which supported the report by Johnson[5]. Tagawa *et al.* revealed that most of the partial overlap excimer is formed in a pre-existing site immediately after a 10 ps electron pulse, while most of the sandwich excimer is formed in several nanoseconds[12]. Furthermore, Phillips *et al.* proposed the presence of a third excimer, which emits at 370 nm but does not convert to the sandwich one[13]. Kauffmann *et al.* reported two kinds of excited intermediates in addition to the excited monomer, the partial overlap excimer and the sandwich one[14], and, furthermore, they proposed a time-dependent trapping process of the excitation energy to interpret the rise and decay curve of the sandwich excimer fluorescence[15]. Sienicki and Winnik proposed a theoretical model for excitation trapping in PVCz, which was the extended type of Kauffmann's model[16].

We measured time-resolved fluorescence spectra and fluorescence rise and decay curves of PVCz(r) and PVCz(c) in tetrahydrofuran (THF) solution by using a time-correlated single-photon-counting technique with picosecond time resolution and detected directly for the first time monomeric structured fluorescence in the 10 ps time range[17]. The difference in tacticity was reflected in both the time-resolved fluorescence spectra and the fluorescence rise as well as decay curves monitored at 350, 380 and 475 nm, where the monomer fluorescence band, the partial overlap excimer one and the sandwich excimer one are the main components, respectively. The former two decay curves could be analysed with a five-exponential function with five decay times. The latter one was fitted to a four-exponential function with three rise and one decay times. The rise and decay time constants were almost the same, irrespective of tacticity, and only amplitude factors were different between both PVCz types. The same time constants were also observed for PVCz(r) and PVCz(c) films, although the amplitude factors were different[18].

Following the proposal of the second excimer structure with the partial overlap structure of the neighbouring carbazolyl chromophores of PVCz, partial overlap excimer structures were proposed for pyrene, naphthalene, and so on, and it is generally accepted that various overlapping structures of neighbouring chromophores lead to excimer formation. Ito *et al.* indicated that the excited state of the carbazolyl chromophore in poly(3,6-di-t-butyl-*N*-vinylcarbazole) is stabilized by interaction with the neighbouring chromophores even if there is little overlapping of the carbazolyl planes and, as a consequence, suggested that the relative geometrical structure of carbazolyl chromophores in the excimer of PVCz takes diverse distributions[19].

Concerning the molecular-weight effect on the fluorescence spectra of PVCz(r), effects on fluorescence spectral shape and delayed fluorescence intensity in a rigid glass at 77 K were observed[5,20]. Johnson, however, reported that the results of the temperature dependence of the fluorescence spectra in solution are essentially independent of molecular weight over the temperature range 95–293 K, although an influence of the end carbazolyl chromophores was observed for the low-molecular-weight sample ($M_n = 2400$)[5]. For PVCz(c) with different tacticity from PVCz(r), however, the molecular-weight effect on the fluorescence spectra and rise as well as decay curves has not been investigated.

In measurements under conditions such as the presence of various excimer structures, it has been impossible to detect separately the rise and decay curves of each fluorescent species. In addition, excimer formation in a polymer system is considered to be complicated because of excitation energy migration and conformational change. Hence we have considered it necessary to introduce a new method to analyse the dynamics of excimer fluorescence of PVCz. Thus we have introduced a new method by which we can estimate, without *a priori* spectral information on individual pure components, the spectra of pure components from the spectra of unknown mixtures with various relative concentrations. That is, multicomponent spectral analysis, combined with the least-squares fitting method for quantitative analysis, has been applied to the time-resolved fluorescence spectral data of PVCz(r) and PVCz(c) in solution that we reported previously[17]. We have confirmed numerically that the spectra were composed of only three component fluorescences, and for the first time succeeded in obtaining the rise and decay curves of these three pure components[21]. On the basis of their curves, we discussed the dynamics of two excimers of PVCz.

In the present work, we applied the multicomponent spectral analysis to the picosecond time-resolved fluorescence spectra of PVCz(r) and PVCz(c) with low and high molecular weights in solution. Furthermore, the molecuar-weight dependence of the fluorescence spectra of PVCz(r) and PVCz(c) in solution at room temperature, the temperature dependence of the fluorescence spectra of both PVCz with high-molecular weight, and the temperature dependence of nanosecond time-resolved fluorescence spectra of both PVCz were also investigated. On the basis of these results, we have discussed the excimer dynamics of PVCz in solution from the viewpoint of tacticity.

EXPERIMENTAL

N-Vinylcarbazole (VCz) was purified by the usual method from commercial product. PVCz(r) was prepared by polymerization of a 1.0 M benzene solution of the purified VCz in the presence of azobisisobutyronitrile (AIBN) in an evacuated sealed tube at 65°C for 6 h. The PVCz(r) prepared under two AIBN concentrations of 0.43 and 1.5 mol% were mixed. PVCz(c) was prepared by polymerization of a toluene solution of purified VCz in the presence of 1 mol% BF_3OEt_2 under a nitrogen atmosphere at 20°C for 1.5 h. The PVCz(c) prepared under three VCz concentrations of 0.049, 0.20 and 0.31 M were mixed. The PVCz samples of narrow molecular-weight distribution were prepared by fractional precipitations from their benzene solutions with methanol and purified by reprecipitation three times from benzene with methanol. Gel permeation chromatography analysis of polymers used predominantly for the present investigation showed: $M_n = 4.8 \times 10^5$ (degree of polymerization $DP \simeq 2500$) and $M_w/M_n = 1.51$ for PVCz(r-H); $M_n = 8.1 \times 10^3$ ($DP \simeq 42$) and $M_w/M_n = 1.36$ for PVCz(r-L); $M_n = 4.7 \times 10^5$ ($DP \simeq 2400$) and $M_w/M_n = 1.94$ for PVCz(c-H); and $M_n = 8.5 \times 10^3$ ($DP \simeq 44$) and $M_w/M_n = 1.35$ for PVCz(c-L), respectively. Here H and L in the parentheses mean $DP = 42$ or 44 and $DP = 2500$ or 2400, respectively. ^{1}H n.m.r. spectra were measured in pyridine-d$_5$ at 80°C with a Gemini-200 spectrometer. Poly(methyl methacrylate) (PMMA) was purified by reprecipitation twice from benzene solution with methanol. Polycarbonate (PC) was purified by reprecipitation twice from dichloromethane solution with methanol. PVCz-doped PMMA and PC films were cast on quartz plates from dichloromethane solution containing PVCz(r-H) at room temperature and dried *in vacuo* for several hours.

Time-resolved fluorescence spectra of solution samples of these polymers were measured with a time-correlated single-photon-counting system with picosecond time resolution and corrected for detector sensitivity. Time zero corresponds to the time when the excitation laser pulse takes the maximum intensity. The details were reported previously[17]. The temperature dependence of the fluorescence of the solution samples and time-resolved fluorescence spectra of PVCz(r-H)-doped PMMA and PC films were measured with a nanosecond time-correlated single-photon-counting system with a hydrogen-filled flash lamp; the details were reported previously[22].

The time-resolved fluorescence spectra were analysed by the previously proposed method, which made it possible to separate the multicomponent mixture spectra into individual component ones and to estimate corresponding decay curves of the individual components. In this method[23], the time-resolved fluorescence spectra are supposed to be the linear combination of N component spectra, as follows:

$$x(t) = \sum_{i=1}^{N} c_i(t) s_i \qquad (1)$$

where $x(t)$ and s_i are vector representations of the time-resolved spectrum and the ith component spectrum, respectively, and $c_i(t)$ is the contribution ratio of individual components to the time-resolved spectrum at time t, which corresponds to a decay curve of each component. As the first step, principal component analysis is used for estimating the number of components N, which is given by the number of non-zero eigenvalues of the data matrix composed of $x(t)$. The known component spectra s_i can be expressed as:

$$s_i = \sum_{j=1}^{N} a_{ij} v_j \qquad (2)$$

where v_j are eigenvectors corresponding to the non-zero eigenvalues. The coefficients a_{ij} cannot be determined only from the linear assumption of equation (1), while they can be limited to certain ranges by use of *a priori* knowledge of (1) non-negativity of fluorescence spectra of any components at any wavelengths ($s_i \geq 0$) and (2) non-negative contribution of individual components to any time-resolved spectra ($c_i(t) \geq 0$). These constraints provide a solution set of the component spectrum, which includes the true solution. In order to determine a unique curve as the estimate of each component spectrum, the entropy minimization criterion has been developed, which was defined as:

$$h_i = -\sum_{k=1}^{M} p_{ik} \log p_{ik} \rightarrow \min \qquad (3)$$

where p_{ik} is the second-derivative amplitude of the ith estimated spectrum at wavelength λ_k. This criterion works for removing the algebraic interferences between the estimates of component spectra, so that it selects the optimal curve among the solution set. Substituting the given s_i into equation (1), the contribution ratio $c_i(t)$ can be estimated with the least-squares matrix-inversion technique. By plotting the contribution of a certain component against the delay time, its rise and decay curves are obtained.

RESULTS AND DISCUSSION

Before describing and discussing the results of excimer dynamics of PVCz in solution, we describe briefly the tacticity of PVCz. The tacticity of the polymer has been investigated by many researchers[7,24–30]. Kimura *et al.* proposed, on the basis of X-ray diffraction data, that PVCz consisted of the stereoblock arrangements of isotactic 3/1 and syndiotactic 2/1 helices[24]. Okamoto *et al.* reported that PVCz(c) and PVCz(r) consisted of stereoblock structures with fractions of the isotactic diad sequence (P_{iso}) of 0.50 and 0.25, respectively[7]. After that, Williams and Froix proposed that both PVCz did not have long chains of stereoregular sequences[25]. Griffiths suggested an atactic backbone for PVCz[26]. Several researchers, however, found that PVCz(c) has an isotactic-rich structure compared with PVCz(r). For example, Kawamura *et al.* reported that $P_{iso} = 0.72$ and 0.5 for partially deuterated PVCz(c) and PVCz(r), respectively, and proposed a random atactic structure for the latter polymer[27]. On the other hand, Terrell and Evers reported that $P_{iso} = 0.50$ and 0.31 for PVCz(c) and PVCz(r), respectively, and suggested that chains of both

PVCz consisted of stereoblock structures[28,29]*. Further, they reported the presence of three glass transition temperatures T_g and a single one for PVCz(c) and PVCz(r), respectively. The former triple T_g were interpreted by the correspondence to the whole chain and the syndiotactic and isotactic stereoblocks, while the latter single T_g was interpreted by an absence of long sequences that behave as separate phases due to stereoblocks. That is, the length of each sequence in the stereoblock structure of PVCz(r) was too short to behave as a separate phase for T_g.

In the present paper, we will discuss the results on the presumption that PVCz has the following tacticity: Both PVCz(r) and PVCz(c) consist of stereoblock structures with syndiotactic and isotactic sequences, while the length of each of the sequences is long and short for PVCz(c) and PVCz(r), respectively. PVCz(c) has higher isotactic diad fractions than PVCz(r), and PVCz(r) has syndiotactic-rich configurations compared with PVCz(c).

In addition, we confirmed that the ^{1}H n.m.r. spectra of PVCz in pyridine-d$_5$ solution at 80°C are independent of molecular weight. That is, the spectrum of PVCz(c) with $DP = 6200$ and $M_w/M_n = 1.78$ was quite similar to that of PVCz(c-L), and the spectrum of PVCz(r-H) was also quite similar to that of PVCz(r) with $DP = 140$ and $M_w/M_n = 1.36$.

Molecular-weight and tacticity effects on fluorescence spectra in solution at room temperature

The steady-state fluorescence spectra of PVCz(r) and PVC(c) with various molecular weights in aerated THF solution (5.4×10^{-5} mol l^{-1}) at room temperature are shown in *Figure 1*. The spectra of both PVCz mainly consist of both sandwich excimer fluorescence ($\lambda_{max} = 420$ nm) and partial overlap excimer one ($\lambda_{max} = 370$ nm). We notice that the spectral shape and intensity for PVCz(r) are almost the same irrespective of molecular weight, while those for PVCz(c) depend upon molecular weight. The former result is in agreement with that reported by Johnson[5]. On the other hand, the molecular-weight dependence of the fluorescence spectra for PVCz(c) has not been reported yet. The intensity of the partial overlap excimer fluorescence for PVCz(c) decreases with increasing molecular weight. Since the concentrations of all the PVCz samples are almost the same, the present result indicates that the fluorescence yield of PVCz in THF solution decreases in the order of PVCz(r) > PVCz(c-L) > PVCz(c-H).

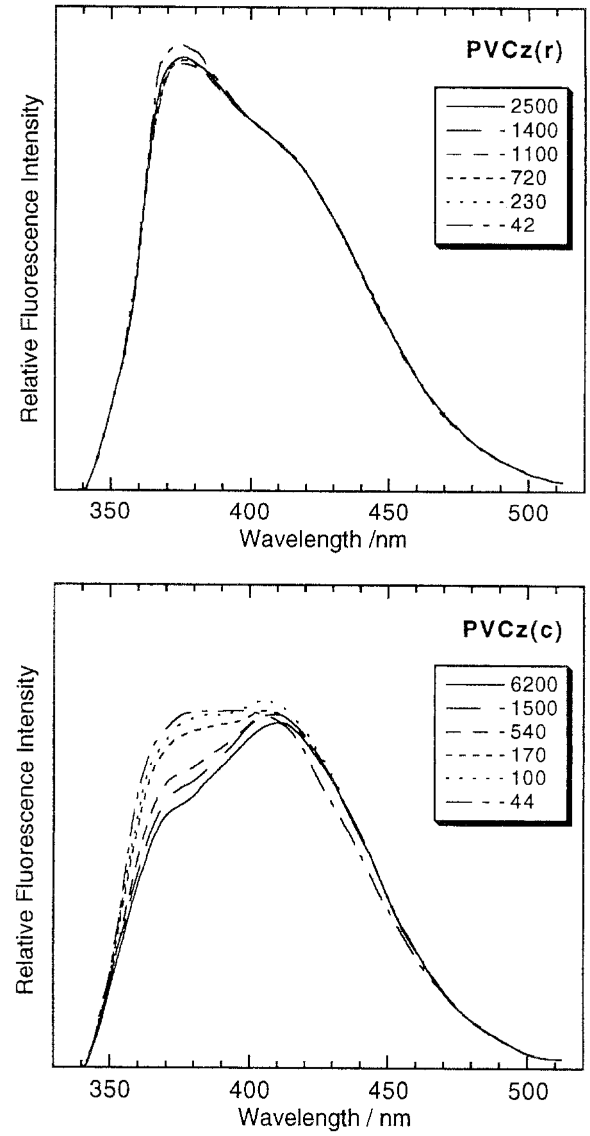

Figure 1 Steady-state fluorescence spectra of PVCz(r) and PVCz(c) with various molecular weights in aerated THF solution at room temperature. Carbazolyl chromophore concentration: 5.4×10^{-5} M. Excitation wavelength: 330 nm. The values in the inset show the degree of polymerization. Values of M_w/M_n were 1.12–1.78 for PVCz(r) except for $DP = 1400$ ($M_w/M_n = 2.25$) and 1.35–1.78 for PVC(c)

The large difference in the spectra between PVCz(r) and PVCz(c) corresponds to the report by Evers *et al.*[9] that 'the ratio of 405 nm intensity (the sandwich excimer) to 367 nm (the partial overlap excimer) one in the fluorescence spectra increases with the ratio (P_{iso}/P_s) of the isotactic to syndiotactic diad mole fractions', and is ascribed to the aforementioned difference in the tacticity of both PVCz: PVCz(c) has higher isotactic diad fractions than PVCz(r). The fact that the fluorescence spectrum of PVCz(r-L) is quite similar to those of PVCz(r) with large *DP*s is consistent with the tacticity of PVCz(r): the content ratio of the syndiotactic diad fraction for PVCz(r) is constant irrespective of molecular weight and each length of the syndiotactic and isotactic sequences for PVCz(r) is short. On the other hand, although the content ratio for PVCz(c) is also independent of molecular weight, a dependence of the fluorescence spectra on molecular weight is observed even for PVCz(c) with rather large *DP*s, suggesting that the migration length of the excitation energy along polymer chains is related to molecular weight for PVCz(c). In the following sections, we will mainly discuss PVCz(r-H), PVCz(c-L) and PVCz(c-H).

Dependence of fluorescence spectra of PVCz(r-H) and PVCz(c-H) on temperature

Figure 2 shows the dependence of the fluorescence spectra of both PVCz(r-H) and PVCz(c-H) on temperature. Although the dependence for PVCz(r) was examined, the highest temperatures measured by Johnson[5], Phillips *et al.*[13] and Evers *et al.*[9] were 283, 295 and 296 K, respectively. The fluorescence behaviour

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*The values obtained under similar polymerization conditions to the present ones were quoted from the table in the literature[28,29]

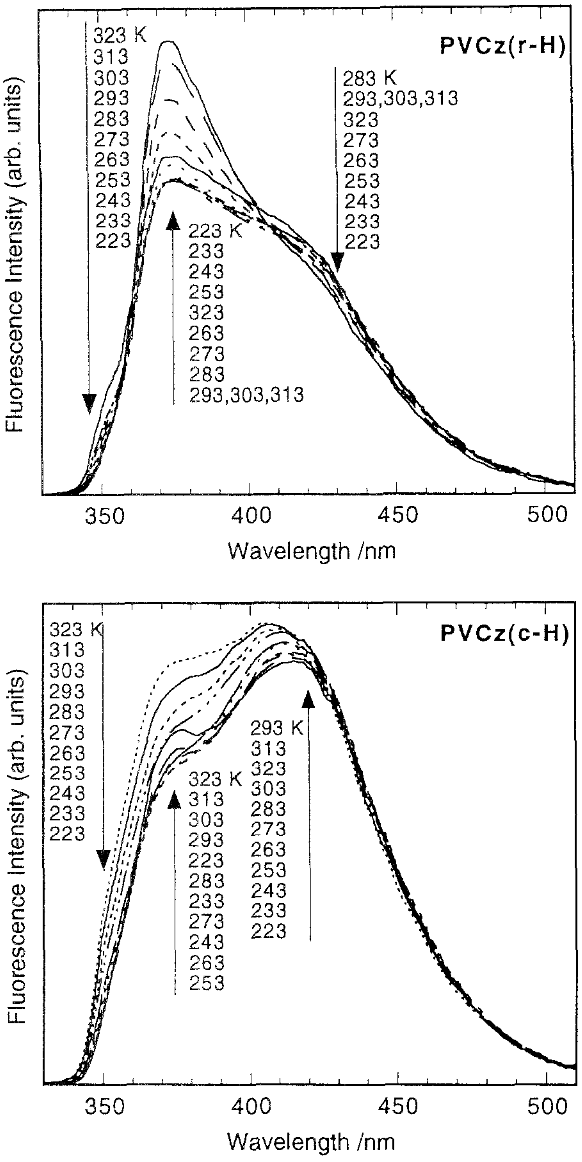


Figure 2 Temperature dependence of the steady-state fluorescence spectra of PVCz(r-H) and PVCz(c-H) in degassed THF solution. Carbazolyl chromophore concentration: 5×10^{-5} M. Excitation wavelength: 295 nm

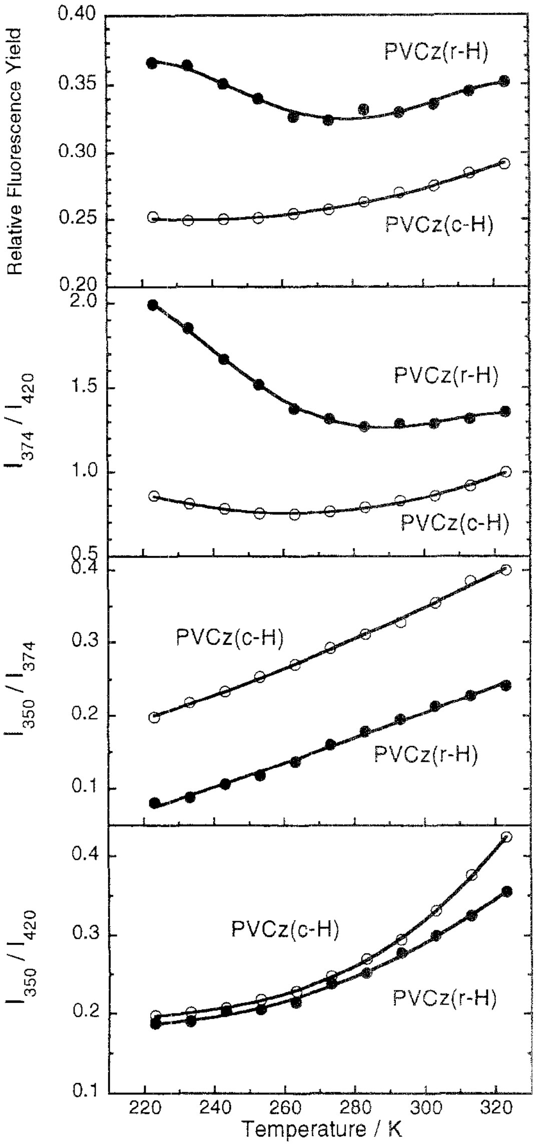


Figure 3 Relative fluorescence yield and relative fluorescence intensity ratios vs. temperature. These figures were obtained from the data of *Figure 2*. The relative fluorescence yields are calculated taking the value of isopropylcarbazole as unity

below 293 K is similar to those reported previously[5,9,13]. Measurement at temperatures above 293 K is very important, and actually it is noticeable that the fluorescence intensity of 350 nm (I_{350}) increases monotonously. The monotonous increment of I_{350} for PVCz(c-H) is clear compared with PVCz(r-H), and the fluorescence intensity of 374 nm (I_{374}) also increases monotonously with temperature from 253 to 323 K. Such intensity behaviour for PVCz(c) has never been reported as far as we know.

The temperature dependences of the relative fluorescence yield and of the intensity ratios I_{374}/I_{420}, I_{350}/I_{374} and I_{350}/I_{420} for both PVCz(r-H) and PVCz(c-H) are shown in *Figure 3*, where I_{350}, I_{374} and I_{420} show the main contributions of the monomer, the partial overlap excimer and the sandwich excimer fluorescence, respectively. The differences in the dependence of these values on temperature between PVCz(r-H) and PVCz(c-H) are interpreted by the difference in the tacticity of both polymers. Over the temperatures measured, the relative fluorescence yield of PVCz(r-H) having the high syndiotactic fraction responsible for the partial overlap excimer compared with PVCz(c-H) is larger than that of PVCz-(c-H), and the temperature dependence of the ratio I_{374}/I_{420} for both PVCz is similar to that of the fluorescence yield. That is, the fluorescence yield is affected by the change in the fluorescence intensity of the partial overlap excimer. These behaviours suggest that the binding energy of the partial overlap excimer is small and that the fluorescence yield of the partial overlap excimer is larger than that of the sandwich one. The former corresponds with the report by Johnson[5]. The small change in the intensity ratio I_{374}/I_{420} for PVCz(c-H) compared with PVCz(r-H) is due to the small contribution of the temperature-sensitive partial overlap excimer fluorescence intensity to I_{374} because of the small syndiotactic fraction.

The values of both I_{350}/I_{374} and I_{350}/I_{420} are smaller for PVCz(r-H) than for PVCz(c-H), suggesting that the monomer fluorescence originates mainly from the isotactic sequence. As the temperature increases, the

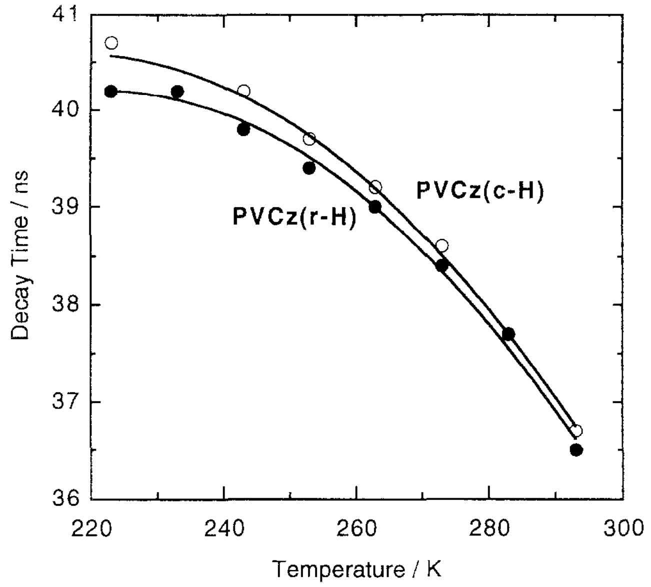


Figure 4 Temperature dependence of the decay time of the sandwich excimer fluorescence (470 nm)

values for both PVCz increase. These results strongly suggest that paths from the sandwich excimer and the partial overlap excimer to the monomer excited state increase with temperature.

The decay time of the sandwich excimer fluorescence monitored at 470 nm decreases with increasing temperature, as shown in *Figure 4*. The decay times and their dependence on temperature are quite similar for both PVCz(r-H) and PVCz(c-H), which is reasonable because the sandwich excimer fluorescence originating from the isotactic sequence is monitored separately. For both polymers, the behaviour of the change in the decay time is opposite to that of I_{350}/I_{420}. These also suggest that the interconversion process from the sandwich excimer to the monomer excited state is accelerated thermally.

Time-resolved fluorescence spectra and fluorescence rise and decay curves

Figure 5 shows the normalized time-resolved fluorescence spectra of both PVCz(r-H) and PVCz(c-H) in degassed THF solution. Although the interpretation of these spectra was already presented in the previous letter[17], here we describe it briefly. In the early-gated spectra the fluorescence maximum was observed at 370 nm, while a shoulder around 350 nm was clearly detected. This shoulder is more distinct for PVCz(c-H) than for PVCz(r-H). Both spectra changed to be broad within 100 ps, while its rate is slower for PVCz(c-H) than for PVCz(r-H). The shoulder around 350 nm is ascribed to the monomer fluorescence and the broad band to the partial overlap excimer fluorescence, because their spectral shapes and positions are identical to those of model compounds. The fact that the shoulder due to the monomer fluorescence is clearer for PVCz(c-H) than for PVCz(r-H) corresponds with the aforementioned description that the monomer fluorescence originates from the isotactic sequence. With time increasing from the picosecond to the nanosecond time region, the sandwich excimer fluorescence (420 nm) appeared clearly and its intensity increased. Its formation rate for PVCz(c-H) is faster than that for PVCz(r-H), which corresponds with the fact that the content of the isotactic sequence responsible for the sandwich excimer is larger for PVCz(c-H) than for PVCz(r-H). Even in the late nanosecond time region, the partial overlap excimer fluorescence was observed, which is in agreement with the findings of Johnson[5], Phillips *et al.*[11,13] and Guillet *et al.*[10], and indicates that the interconversion of the sandwich excimer to the partial overlap one occurs in solution. In this interpretation, the presence of three fluorescent species is assumed.

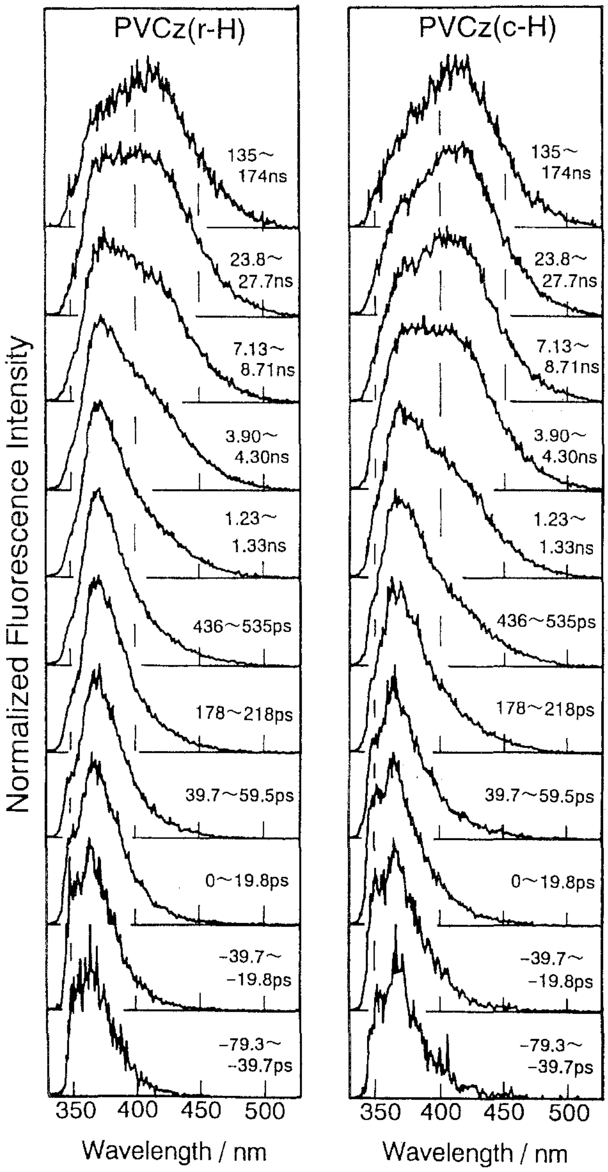


Figure 5 Normalized time-resolved fluorescence spectra of PVCz(r-H) and PVCz(c-H) in degassed THF solution. Excitation wavelength is 295 nm. Time window is given in the figure, where the origin of the axis is set at the time when the excitation laser pulse takes the maximum intensity

The time-resolved fluorescence spectra of PVCz(r-L) were similar to those of PVCz(r-H), which corresponds with the result on the steady-state fluorescence spectra (*Figure 1*). This suggests that the fluorescence dynamics of PVCz(r) in solution is completed within a chain length of $DP = 42$ and is consistent with the tacticity of PVCz(r): the polymer consists of the stereoblock structure with short sequences. On the other hand, the monomer fluorescence in the early-gated time of the time-resolved spectra of PVCz(c-L) was observed more clearly compared with that of PVCz(c-H). Considering that the shape of the steady-state fluorescence spectrum of PVCz(c-L) is between those of PVCz(r-H) and PVCz(c-H) (*Figure 1*), the present result suggests that the monomer fluorescence in the early-gated time for PVCz(c-L) is partly due to the end carbazolyl chromophore. The clear appearance of the monomer fluorescence of PVCz(c-L) compared with PVCz(r-L) seems to be due to the following reason: when the chain-end carbazolyl chromophore is the end of the syndiotactic sequence, the end carbazolyl chromophore does not show the monomer fluorescence but the partial overlap excimer one, while the chain-end carbazolyl one belonging to the isotactic one shows the monomer fluorescence.

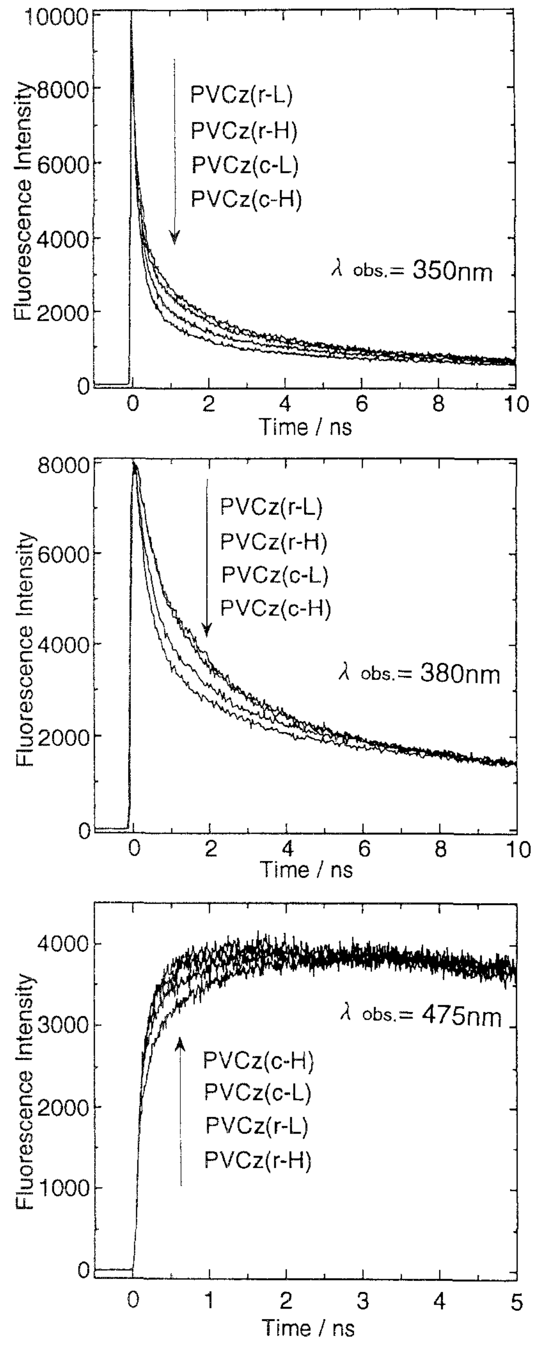


Figure 6 Fluorescence rise and decay curves of PVCz in degassed THF solution. Excitation wavelength is 295 nm. Monitoring wavelength is given in the figure

The fluorescence rise and decay curves of these polymers are shown in *Figure 6*. We should note that the curve monitored at 380 nm, where the partial overlap excimer fluorescence is the main component, raises with the instrumental response function and never shows a slow rise component. The rises of the curves of the sandwich excimer fluorescence monitored at 475 nm become faster in the order of PVCz(r-H) < PVCz(r-L) < PVCz(c-L) < PVCz(c-H). The initial decays of the decay curves monitored at 350 and 380 nm become faster in the order of PVCz(r-L) ≤ PVCz(r-H) < PVCz(c-L) < PVCz(c-H). Thus, as expected from the time-resolved fluorescence spectra, the fluorescence rise and decay curves are different among these polymers. In these curves, the behaviours for PVCz(r-H) and PVCz(r-L) are relatively similar to each other except for that at 475 nm, and PVCz(c-L) shows intermediate behaviour between PVCz(r-H and -L) and PVCz(c-H). These behaviours are quite similar to those observed for the steady-state fluorescence spectra (*Figure 1*). The PVCz with a large syndiotactic mole fraction show strong partial overlap excimer fluorescence in the steady-state fluorescence spectra and show the slow decay in the initial stage of decay curves monitored at 350 and 380 nm and the slow rise at 475 nm. These behaviours show clearly a correlation between the tacticity and the fluorescence rise as well as decay curves.

In the previous letter concerning PVCz(r-H) and PVCz(c-H)[17], we reported the following: the fluorescence rise and decay curves at 350 and 380 nm for both PVCz(r-H) and PVCz(c-H) were not able to be analysed with a triple-exponential function used by Phillips *et al.*[13], but with a five-exponential function with five decay times (ca. 0.02, 0.3, 2, 6 and 35 ns). The curves of the sandwich excimer fluorescence monitored separately at 475 nm could be fitted to a four-exponential function with three rise times (ca. 0.02, 0.3 and 2 ns) and one decay time (35 ns), where the sum of the amplitude factors of the rise components was about 90% of that of the decay component, indicating that most of the sandwich excimer is formed through dynamic processes such as energy migration and not by ultrafast trapping in pre-existing sites. Only amplitude factors were different between both PVCz. Since the decay time of the sandwich excimer fluorescence was nearly equal to the longest decay time of the 380 nm fluorescence, the excimer dynamics was discussed on the basis of the presence of the interconversion from the sandwich excimer to the partial overlap one and the spectral overlap of the two excimer fluorescences at 380 nm. Analysing the rise and decay curves of PVCz(r-L) and PVCz(c-L) with low molecular weights, we obtained the same time constants as those of PVCz(r-H) and PVCz-(c-H), while the amplitude factors were different among these four polymers. In this way, in order to analyse the fluorescence rise and decay curves monitored at a few wavelengths at room temperature, at least four- and five-exponential functions were required. Here one should notice that the fluorescence rise and decay curves of unique species are not analysed because of the spectral overlap of some fluorescent species.

In the above interpretation, the number of fluorescent species of PVCz in solution has been assumed to be five, because of good fitting of the decay curves with a five-exponential function. However, we cannot obtain the fluorescence spectral shape of these five species. As proposed recently, there is the possibility that various overlapping structures of neighbouring chromophores lead to excimer formation, and excimer formation in a polymer system is considered to be complicated because of excitation energy migration and conformational change of polymer chains. Considering the spectral overlap of the fluorescent species in addition to these phenomena, we have adopted a new numerical analysis for analysing the time-resolved fluorescence spectra of PVCz. The new method makes it possible to estimate the spectra of pure components without *a priori* spectral information on individual pure components.

Multicomponent analysis of time-resolved fluorescence spectra

Here, the multicomponent analysis was applied for the time-resolved fluorescence spectra of these four PVCz. Thereby, the number of fluorescent species, the spectral shapes of the fluorescent species (components) and the component fluorescence rise and decay curves were obtained.

(i) The principal component analysis was applied to estimate the number of fluorescent species. Thirty-eight time-resolved spectra for each of these polymers were examined. The eigenvalues of the second-moment matrix of the spectra are plotted for 10 components in *Figure 7*. Since the magnitude of the fourth eigenvalue for these PVCz is about 10 times as small as the third one, the number of fluorescent components in the time-resolved fluorescent spectra of these PVCz was determined to be three. As described previously, a variety of fluorescent species with various overlapping structures of neighbouring chromophores are considered for this type of polymer system. The present result concerning PVCz, however, indicates that there are three fluorescent species with a large contribution to the fluorescence spectra and that, even if other fluorescent species exist, their contributions to the spectra are quite small. Thus, the aforementioned interpretation is numerically supported, and it is clear that the fluorescence spectra of these PVCz consist of three components: monomer, partial overlap excimer and sandwich excimer.

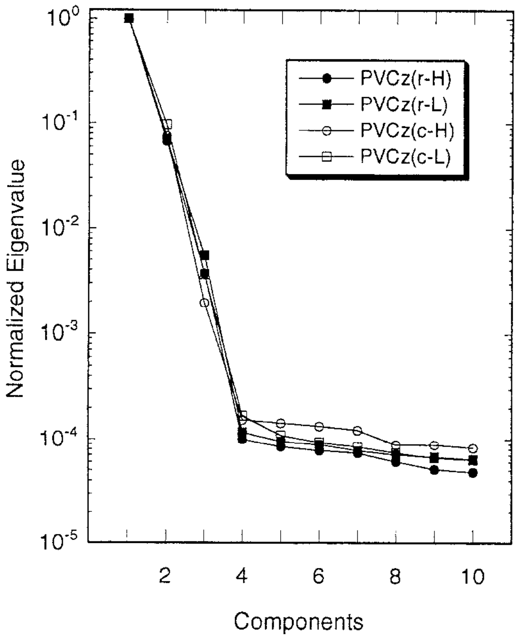


Figure 7 The eigenvalues of the second-moment matrix of the time-resolved fluorescence spectra in order of magnitude. These values were determined for 38 spectra

Applying the principal component analysis to the rise and decay curves for PVCz(c-H) measured in the wavelength region between 340 and 550 nm, we tried to determine the number of fluorescence components consisting of the fluorescence rise and decay curves. For PVCz(c-H), a similar plot to *Figure 7* was obtained and, as a consequence, the number was three. For PVCz(r-H), the difference in magnitude between the third and the fourth eigenvalues was less than one order, but was larger than that between the fourth and the fifth eigenvalues. Consequently, the number of components seems to be three also for PVCz(r-H). The small difference between the third and the fourth eigenvalues for PVCz(r-H) is attributed to the small contribution of the monomer fluorescence to the time-resolved fluorescence spectra compared with PVCz(c-H). In addition, when the present method was applied to the time-resolved spectra of exciplex fluorescence of PVCz films, which show clearly a time-dependent spectral shift[22], a smooth plot of eigenvalues was obtained. Consequently, we could not determine the number of components for the exciplex fluorescence spectra, which is due to a superposition of various exciplex and exterplex species with temporal characteristics. These results support that the result concerning the number of fluorescent species of PVCz in solution is correct and that only three fluorescent species contribute to the time-resolved fluorescence spectra of PVCz.

(ii) We tried to determine spectral shapes of three components from the time-resolved fluorescence spectra by using an entropy minimization method. However, we could not succeed in obtaining the component spectra, because of a poor signal-to-noise ratio of the early-gated spectra and a low contribution of the monomer fluorescence. Hence we proceeded with the analysis on the assumption that the late-gated time-resolved fluorescence spectra are mainly composed of two components (partial overlap and sandwich excimer fluorescence). First, we estimated both excimer fluorescence spectra from the late-gated spectra; the broad spectrum around 420 nm estimated for PVCz(c) is adopted as the sandwich excimer fluorescence, and another spectrum is mainly due to the partial overlap excimer fluorescence. Secondly, considering that the monomer fluorescence also contributes slightly to the spectrum, we decided on a tentative partial overlap excimer fluorescence spectrum by subtracting the time-resolved spectrum of −79.3 to −39.7 ps from the spectrum. Thirdly, we estimated the component spectrum of the monomer fluorescence by subtracting the tentative partial overlap excimer fluorescence spectrum from the early-gated fluorescence spectrum (−79.3 to 0 ps). Fourth, we substituted the time-resolved spectrum used in the second step with the estimated monomer component spectrum and repeated the process as described above until both a 0–1 vibrational band and its descending tail of the estimated monomer fluorescence spectrum agreed with those of the monomer one of *meso*-DCzP in PMMA matrix. The sets of three fluorescence spectra thus estimated for PVCz(r-H) and PVCz(c-H) are shown in *Figure 8*.

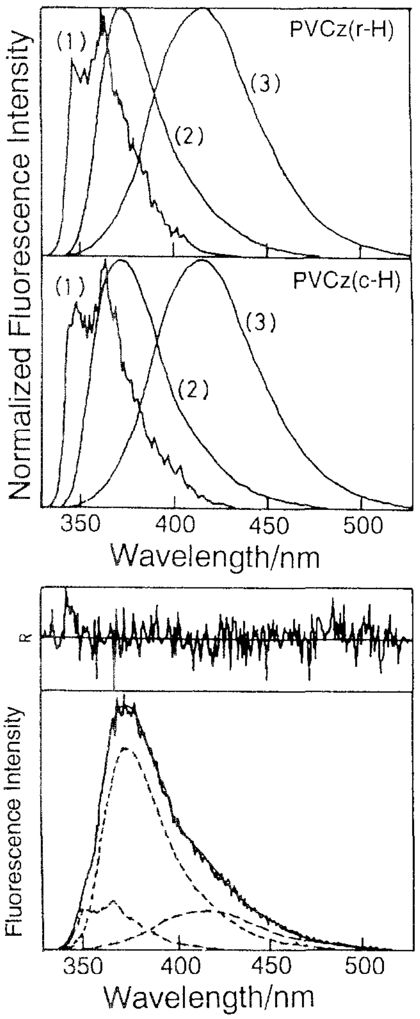


Figure 8 (a) Component fluorescence spectra of (1) the monomer, (2) the partial overlap excimer and (3) the sandwich excimer for PVCz(r-H) and PVCz(c-H). (b) An example of analysis of time-resolved fluorescence spectra (PVCz(r-H), time window 0–0.729 ns of late-time region) by means of the least-squares fitting method using the three component spectra of (a). $\chi^2 = 0.90$

(iii) We analysed the time-resolved fluorescence spectra by means of a least-squares fitting method using the three-component spectra of *Figure 8*, and contributions of these component spectra to the time-resolved fluorescence spectra are plotted against the relevant time in *Figure 9*, giving the fluorescence rise and decay curves of each component. These curves include the convolution effect of the instrumental response function.

As expected from the time-resolved fluorescence spectra and the fluorescence rise and decay curves monitored at 350, 380 and 475 nm, the rise and decay curves of the three components are non-exponential, and differences in the curves among PVCz(r), PVCz(c-L) and PVCz(c-H) are observed. The rise of the sandwich excimer fluorescence becomes faster in the order of PVCz(r) < PVCz(c-L) < PVCz(c-H), which corresponds roughly with that of the rise and decay curves of the sandwich excimer fluorescence monitored separately at 475 nm. Since initial fast decays of the monomer fluorescence are influenced by the instrumental response function, it is difficult to find a clear correlation among these PVCz.

The behaviours of the rise and decay curves of the monomer and the sandwich excimer fluorescence agree roughly with those monitored at 350 and 475 nm, respectively. The rise and decay curves of the partial overlap excimer fluorescence, however, show a slow rise in addition to the fast rise agreeing with the rise of the instrumental response function. The time taken for the peak intensity of the fluorescence is shorter for PVCz(c) (0.17 and 0.16 ns for PVCz(c-H) and PVCz(c-L), respectively) than for PVCz(r) (0.21 and 0.24 ns for PVCz(r-H) and PVCz(r-L), respectively), while the difference in the time between PVCz(c-L) and PVCz(c-H) is not clear. The slow rise component of the partial overlap excimer fluorescence was never observed for the fluorescence rise and decay curves monitored at 370 or 380 nm (*Figure 6*). This is considered to be attributable to the spectral overlap of the monomer and the partial overlap excimer fluorescence at 370 or 380 nm. Although the formation of the partial overlap excimer was considered to be due to ultrafast trapping in pre-existing sites until now, the result of this new analysis indicates that the excimer is formed not only by ultrafast trapping but also through a dynamic process such as energy migration. Considering that partial overlap excimer-forming sites are predominantly due to the *tt* conformation of the syndiotactic sequence and that the ratio of the slow rise component to the fast rise one corresponding with the instrumental response function is larger for PVCz(c) than for PVCz(r), the slow rise component of the partial overlap excimer fluorescence seems to be due to the excitation energy migration from the isotactic sequence to the syndiotactic one.

We also notice that the 1/e lifetime of the partial overlap excimer fluorescence decreases in the order of PVCz(r) (2.71 and 3.15 ns for (r-H) and (r-L), respectively) > PVCz(c-L) (2.52 ns) > PVCz(c-H) (1.39 ns). This decreasing order corresponds with the quickening order of the rise of the sandwich excimer fluorescence and with the order of the decrement in the partial overlap excimer fluorescence intensity observed for the steady-state fluorescence spectra (*Figure 1*). As already mentioned, the binding energy of the partial overlap excimer is small, and the excimer may act like shallow traps for the excitation energy. Accordingly the partial overlap excimer is regarded as a species that can migrate along polymer chains. For PVCz with the large isotactic diad fraction, the excitation energy migration from the syndiotactic sequence to the isotactic one increases. Thus, both the initial decay of the partial overlap excimer fluorescence and the rise of the sandwich excimer one are fast for PVCz(c) with a larger isotactic diad fraction than PVCz(r).

For the curves in the late-time region with a time resolution of 792 ps/ch, the decay curves of the three fluorescent components for all PVCz samples have the same decay time constant of 35 ns. This value agrees with the decay time of the sandwich excimer fluorescence monitored at 460 or 475 ns. The presence of the interconversion from the sandwich excimer to the partial overlap one was proposed already on the basis of the observation of the partial overlap excimer fluorescence in the late-time region in the time-resolved fluorescence spectra[10,11,13,17]. The fluorescence intensity ratio of the partial overlap excimer to the sandwich one in the late-time region is in the order of PVCz(c-H)

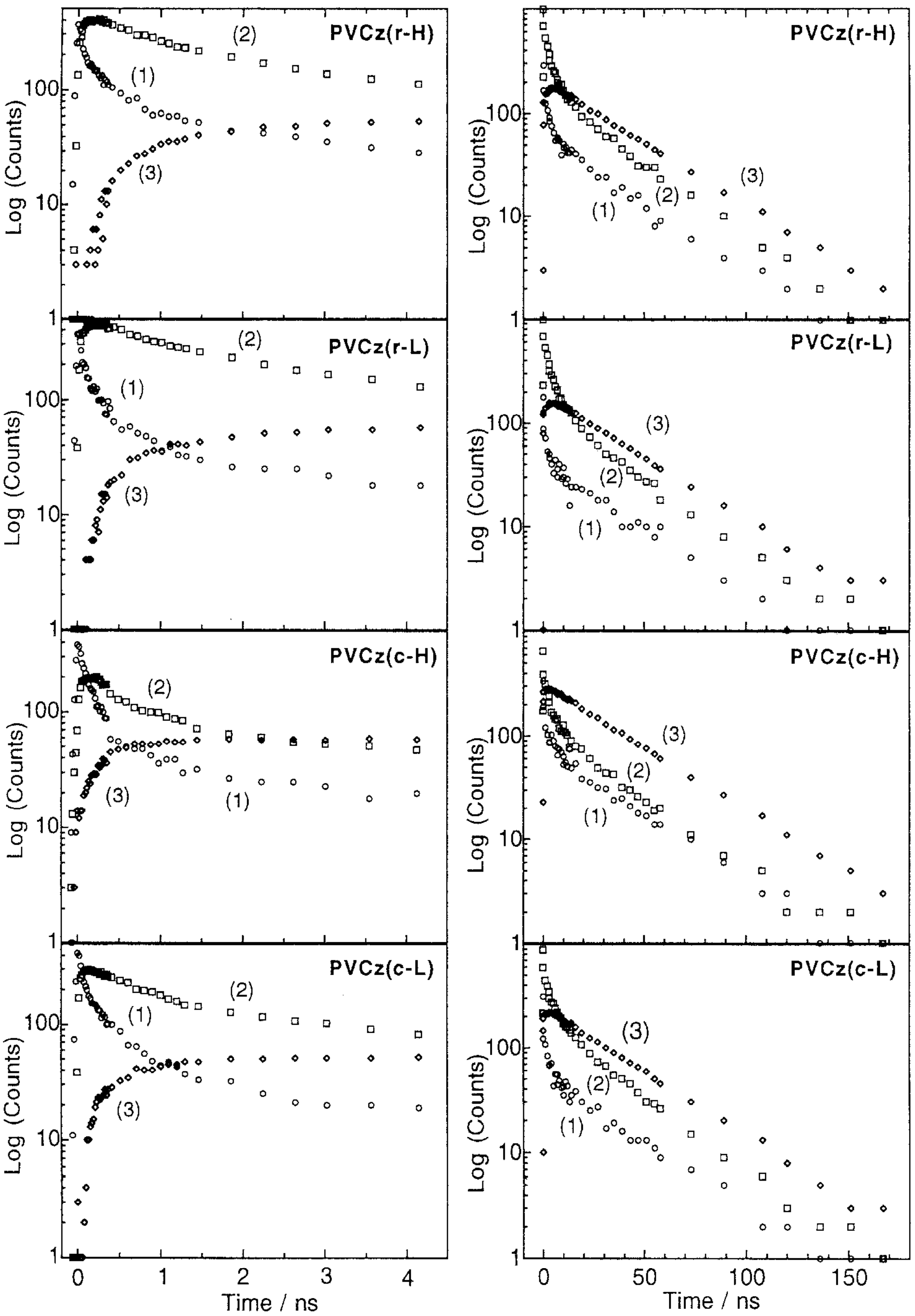


Figure 9 Component fluorescence rise as well as decay curves of (1) the monomer, (2) the partial overlap excimer and (3) the sandwich excimer for PVCz. (a) Early-time region (0–4.5 ns); obtained on the basis of time-resolved fluorescence spectra with a time resolution of 19.8 ps/ch. (b) Late-time region (0–200 ns); obtained on the basis of time-resolved fluorescence spectra with a time resolution of 792 ps/ch

(0.3) < PVCz(c-L) (0.46) < PVCz(r-H and r-L) (0.54), indicating that the partial overlap excimer, formed through the monomer excited state from the sandwich excimer, increases in the order. This is reasonable, judging from the difference in the tacticity and the difference in the steady-state fluorescence spectra (*Figure 1*).

The presence of the decay time constant of 35 ns observed even for the monomer component indicates that not only the partial overlap excimer but also the monomer excited state should be formed from the sandwich excimer in the late-time region. That is, the decay time of the sandwich excimer fluorescence, which is the longest among the three component species, determines the decay of the other two component fluorescences.

Two processes for the formation of the monomer excited state from the sandwich excimer are considered: dissociation associated with the conformational change from the sandwich excimer to the excited monomer state; and formation of the monomer excited state from the sandwich excimer by thermal activation without conformational change. Although the latter process is difficult from the viewpoint of energy level and has been neglected for neat PVCz films, the process was confirmed for PVCz(r-H) in polymer matrices, being probably quite a minor process. That is, as shown in *Figure 10*, in the normalized time-resolved fluorescence spectra with the late-gated time of PVCz(r-H) in PMMA and PC rigid matrices, we notice that the partial overlap

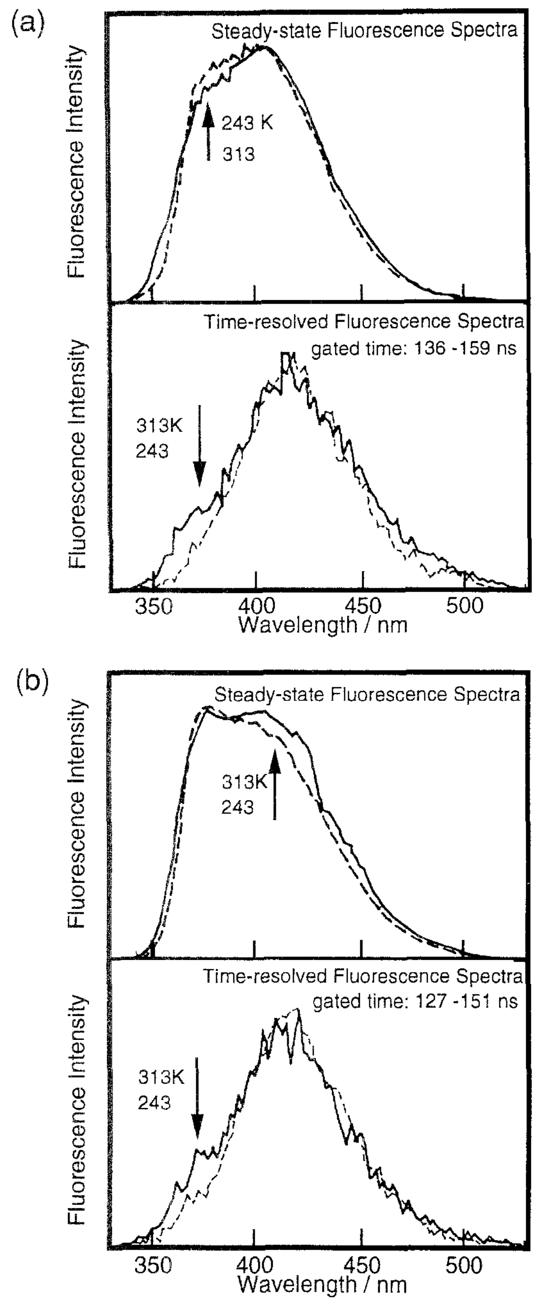


Figure 10 Normalized steady-state fluorescence spectra of PVCz(r-H) in PMMA and PC rigid matrices at 313 and 243 K and their normalized time-resolved fluorescence spectra of PVCz(r-H) with late-gated time: (a) 0.05 wt% doped PMMA rigid and (b) 1.0 wt% doped PC rigid matrices

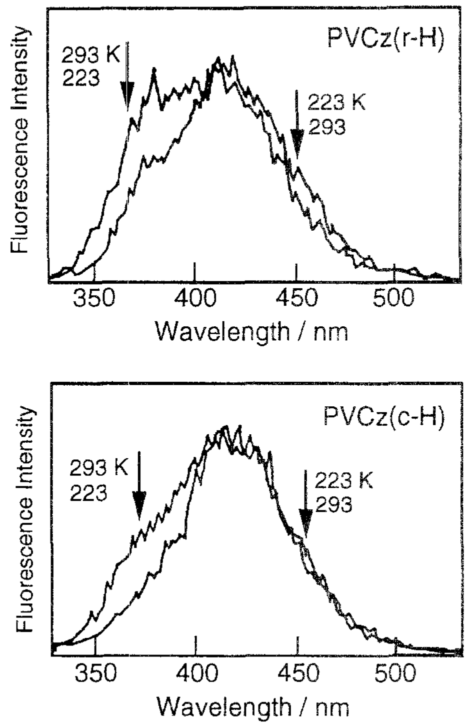


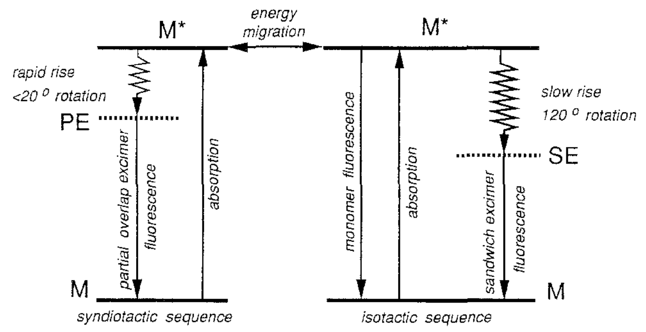
Figure 11 Normalized time-resolved fluorescence spectra with a late-time region of 127–151 ns of PVCz(r-H) and PVCz(c-H) in degassed THF solution at 293 and 223 K

excimer fluorescence is larger at high temperature (313 K) than at a low one (243 K), although the partial overlap excimer fluorescence in normalized steady-state fluorescence spectra of these samples is larger at low temperature than at a high one. Since the conformational change of the PVCz(r-H) polymer chain is impossible in rigid matrices, the intense partial overlap excimer fluorescence observed at high temperature is considered to be ascribed to the migration of the excitation energy (monomer excited state) created from the sandwich excimer in the isotactic sequence by thermal activation to the syndiotactic sequence and subsequent trapping at the partial overlap excimer-forming sites.

Figure 11 shows the normalized time-resolved fluorescence spectra with the late-gated time (127–151 ns) of PVCz(r-H) and PVCz(c-H) in THF solution at 293 and 223 K. The partial overlap excimer fluorescence is larger at 293 than at 223 K for both PVCz, while the fluorescence intensity in the steady-state fluorescence spectra is larger at 223 than at 293 K, as shown in *Figure 2*. These results clearly indicate that the interconversions from the sandwich excimer both to the monomer excited state and to the partial overlap excimer are accelerated thermally, which is in agreement with the result of the temperature dependence of the steady-state fluorescence spectrum.

On the basis of both the tacticity presumed for PVCz and the above experimental and analytical results, we propose a schematic model of the excitation energy relaxation process shown in *Figure 12* for PVCz in solution. In the figure, the initial- and late-time regions after excitation are illustrated separately. The partial overlap excimer and the sandwich one are formed in the syndiotactic and isotactic sequences, respectively. The monomer fluorescence originates predominantly from the isotactic sequence. The content of these sequences is different between PVCz(r) and PVCz(c) and the sequence length is considered to be short and long for PVCz(r) and PVCz(c), respectively, resulting in the difference in the steady-state and time-resolved fluorescence spectra and the rise as well as decay curves of the three components. The *tt* conformation in the syndiotactic sequence is the conformational state with the lowest energy in a threefold rotational potential and, as a consequence, the fraction of the *tt* conformation is large. The partial overlap excimer structure is due to the *tt* conformation. In the isotactic sequence, the formation of the sandwich excimer conformation (*tt* conformation) from the ground-state one (tg^- and g^+t conformations) requires rotational motion of the main-chain carbon–carbon bond. The monomer and the partial overlap excimer fluorescence were observed immediately after

(a) initial time region after excitation



(b) late-time region after excitation

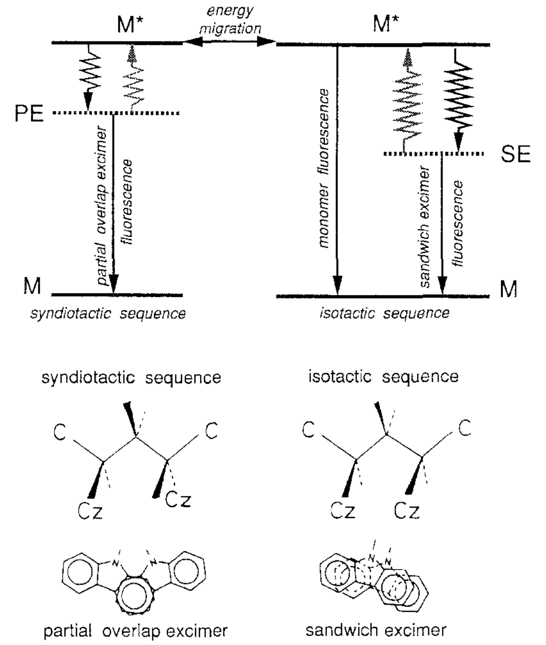


Figure 12 Schematic model of the excitation relaxation process for PVCz solution and structures of two excimer states in syndiotactic and isotactic sequences. This model is proposed on the presumption for the tacticity of PVCz described in the text. (a) Initial-time region after excitation and (b) late-time region. The energy migration process between both isotactic and syndiotactic sequences is illustrated, but that in the sequence is not. The slow rise component of the partial overlap excimer fluorescence seems to be due to the excitation energy migration from the isotactic sequence to the syndiotactic one and the subsequent process

excitation, as seen in the time-resolved fluorescence spectra and the rise as well as decay curves of these components. The rapid rise of the partial overlap excimer fluorescence is attributed to ultrafast trapping in the pre-existing excimer sites formed from the *tt* conformation and/or quite slight conformational change (rotation < 20°) for the formation of the partial overlap of carbazolyl chromophores in the *tt* conformation of the syndiotactic sequence. The slow rise of the partial overlap excimer fluorescence, which was revealed for the first time by the present multicomponent analysis, seems to be due to the excitation energy migration from the isotactic sequence to the syndiotactic one. The sandwich excimer is formed by dynamic processes such as the conformational change of one rotation of the main-chain carbon–carbon bond and/or the energy migration to a very small amount of excimer sites of the *tt* conformation in the isotactic sequence. As shown from the fact that the monomer and the partial overlap excimer components have the same decay time of 35 ns as the sandwich excimer component, which was also revealed for the first time by the present analysis, not only the partial overlap excimer but also the monomer excited state is formed from the sandwich excimer in the late-time region.

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