

# Picosecond–Microsecond Dynamics of Photoinduced Electron-Transfer Processes in Amorphous Solid Films of Dimeric Carbazolyl Compounds Doped with 1,2,4,5-Tetracyanobenzene

Akira Itaya,\* Takashi Kitagawa, Takao Moriyama, Tsuyoshi Matsushita, and Hiroshi Miyasaka

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606, Japan

Received: September 10, 1996; In Final Form: November 13, 1996<sup>®</sup>

Picosecond and nanosecond transient absorption spectroscopy and picosecond transient dichroism measurements were applied for elucidating photoinduced charge-separation, charge-recombination (CR), and hole-transfer (HT) processes in amorphous solid films of carbazolyl dimeric compounds (1,3-di(*N*-carbazolyl)propane and 1,2-*trans*-di(*N*-carbazolyl)cyclobutane) doped with 1,2,4,5-tetracyanobenzene (TCNB). Time-resolved fluorescence spectra were also measured for elucidating fluorescent states responsible for recombination emission. These results were compared with those for poly(*N*-vinylcarbazole) (PVCz), where the concentration of carbazolyl (Cz) chromophores is the same as the above dimeric compounds. The ground-state charge-transfer (CT) absorption and the steady-state CT fluorescence spectra were different between the present dimeric and the PVCz films. In both the films, the CR process was in competition with the HT process in the initial charge-separated state produced via the photoexcitation of the ground-state CT complex. The time constants of these processes in the amorphous dimeric compounds films were close to the values obtained for the PVCz ones. The holes (Cz<sup>+</sup>) that escaped from the initial CR process and the immobile TCNB anion disappeared via the CR process with a  $t^{-0.5}$  time dependence. The CR process was interpreted as the hole diffusion-controlled geminate recombination process, as is the same as that of PVCz films. The behavior of time-resolved fluorescence attributable to the geminate CR process was different between the amorphous dimeric compounds and the PVCz films. These differences and similarities between the amorphous dimeric compounds and the PVCz films were discussed.

## Introduction

The transport of electrons initiated by photoexcitation is widespread in nature and in artificial systems. In the former system, the efficient electron transport in photosynthetic reaction centers is one of the typical phenomena related to the processes.<sup>1</sup> A typical example in the latter system is photoconductivity in aromatic vinyl polymer films and molecularly doped polymer films with  $\pi$ -electronic materials.<sup>2,3</sup> Because of the widespread use of these polymer films as xerography, there has been considerable interest in a carrier photogeneration mechanism as well as in a charge-transport mechanism in amorphous materials. In these materials, hole or electron transport is described as a one-electron donor–acceptor process between neutral chromophores and their charged derivatives. Although hole-drift mobilities in vapor-deposited amorphous organic glasses have also been investigated,<sup>4</sup> little attention has been paid to carrier photogeneration processes (initial processes of photoinduced electron transfer) of low-molecular-weight organic materials that form stable amorphous glasses at and above room temperature.

From the viewpoints of the photoinduced electron transfer in condensed phase, the photoconduction in these amorphous materials may be regarded as the integrated phenomena of intermolecular electron-transfer (ET) processes such as charge-separation (CS), charge-recombination (CR), and charge-shift reactions. Hence, the elucidation of each process will make it possible to understand the photoinduced ET processes and the

photoconduction mechanism in amorphous solid materials in detail, to design more photoconductors, and to develop their application.

Along this line, we have focused on poly(*N*-vinylcarbazole) (PVCz), a representative photoconductive aromatic vinyl polymer,<sup>5,6</sup> and have investigated photoinduced CS, CR, and hole-transfer (HT) processes in amorphous PVCz films doped with 1,2,4,5-tetracyanobenzene (TCNB) by picosecond transient absorption spectroscopy and dichroism measurements.<sup>7</sup> The HT process in the initial charge-separated state was in competition with the CR process, and the time constant of the former process was ca. 2 ns. To understand the ET processes in amorphous solid materials in detail, it is also important to compare the processes in amorphous polymer films with those in amorphous low-molecular-weight compounds films under the experimental condition of the same chromophore concentration. In the polymer system, the chromophores connect directly to vinyl backbones, whereas there is no such connection in the low-molecular-weight compound system. It is interesting to examine how the bonds affect the ET processes and their related phenomena.

Photoconductive and photophysical properties of amorphous PVCz films have been investigated extensively.<sup>5–14</sup> Steady-state and time-of-flight photocurrent measurements have been carried out in detail,<sup>8,9</sup> and extrinsic carrier photogeneration was pointed out to be a key process for the photoconductivity. The carrier-photogeneration mechanism was considered in relation to exciplex and excited charge-transfer (CT) complexes;<sup>9</sup> that is, doping of weak electron acceptors such as dimethyl terephthalate into PVCz films results in chemical sensitization of the photoconductivity and gives exciplex fluorescence. Rela-

\* To whom correspondence should be addressed. Telephone: 81-75-724-7832. Fax: 81-75-724-7710. E-mail: itaya@ipc.kit.ac.jp.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, January 1, 1997.

tively strong acceptors such as TCNB form a CT complex with the carbazolyl (Cz) chromophores, and both sensitization of the photocurrent in the corresponding CT absorption region and CT fluorescence are observed. The exciplex and CT fluorescence dynamics have been investigated in relation to the charge-photogeneration mechanism.<sup>11</sup> In addition, dimeric model compounds of PVCz are good molecules for elucidating a relation among the intermolecular interaction, the electronic spectrum, and the geometrical structure;<sup>15–17</sup> that is, a relation between the cationic states and the overlapping structure of carbazolyl chromophores is clearly identified by their absorption spectra. Hence, a comparison of the amorphous PVCz film with amorphous states of low-molecular-weight Cz compounds will provide not only information on the photoinduced ET processes but also information on geometrical structures of fluorescent states and concentration of hole-trap sites related to the photoinduced ET processes.

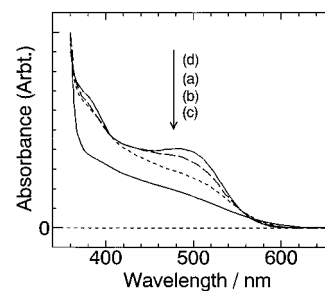
One of the present authors (A.I.) found that 1,3-di(*N*-carbazolyl)propane (DCzP) forms an amorphous state and investigated the absorption and fluorescence spectra, the singlet excitation-energy migration, and the hole-drift mobility of its amorphous film in comparison with those of amorphous PVCz films.<sup>18–20</sup> The absorption spectrum of the amorphous DCzP (DCzP(a)) films was quite similar to that of PVCz films, although a slight blue shift was observed for the former film, while the fluorescence spectrum of DCzP(a) films was quite different from that of PVCz films: the former spectrum consisted of monomer, partial overlap excimer, and sandwich excimer fluorescence, while the latter spectrum shows very weak partial overlap excimer fluorescence and intense sandwich excimer fluorescence.<sup>18</sup> The hole-drift mobility of DCzP(a) films was much larger than that of PVCz films, while the dependence of the drift mobility both on temperature and on the electric field was represented by the same equation as that for PVCz films.<sup>20</sup>

In the present work, we have found that 1,2-*trans*-di(*N*-carbazolyl)cyclobutane (DCzCB) formed also an amorphous state, where the concentration of Cz chromophores is the same as that of solid PVCz films, and investigated the dynamics of the photoinduced charge-separation process and the CT fluorescence in amorphous DCzP and DCzCB solid films doped with TCNB in comparison with those of amorphous PVCz films.

## Experimental Section

**Materials.** DCzP was the same as that used before and was purified again.<sup>20</sup> DCzCB was prepared according to the literature and purified.<sup>21</sup> TCNB was recrystallized from ethanol and subsequently sublimed in vacuo. Methylene dichloride solution containing the dimeric compound and a known amount of dopant was prepared. The solvent was evaporated in vacuo with stirring of the solution. Under N<sub>2</sub> atmosphere, samples were prepared in a cell by rapid quenching of the melt, which is sandwiched between two cleaned quartz plates (20 mm × 20 mm × 1 mm) with a Mylar spacer of 20 μm thickness to obtain a constant sample thickness. Glass transition temperatures of samples doped with TCNB (4 mol %) were ca. 309 and 333 K for DCzP and DCzCB systems, respectively, which were much lower than that of neat PVCz (ca. 500 K).

**Apparatus.** Picosecond transient absorption spectra and dichroism measurements were carried out using the apparatus described in a previous paper.<sup>7</sup> A second harmonic pulse of a custom-built repetitive mode-locked Nd<sup>3+</sup>:YAG laser (532 nm, 16 ps fwhm) was used as an excitation source. The experimental errors for the transient absorption spectroscopy are <10%, while those for the dichroism are <20%. Transient



**Figure 1.** Charge-transfer absorption spectra: (a) DCzP(a)–TCNB (4 mol %) film; (b) DCzCB(a)–TCNB (4 mol %) film; (c) PVCz–TCNB (4 mol %) film; (d) ECz + TCNB/PSt (ECz, 30 wt % for PSt; TCNB, 4 mol % for ECz) film.

absorption spectra in the time region from nanosecond to microsecond were measured using a microcomputer-controlled nanosecond laser photolysis system with an dye laser (390 nm, 15 ns fwhm) pumped by an excimer laser (351 nm, 20 ns fwhm) as an excitation light source.<sup>22</sup> A monitoring lamp was a 150 W dc Xe lamp (Wacom KXL-150F), which was additionally pulsed for ca. 200 μs fwhm by a homemade circuit and synchronized to the laser pulse. The probe light spectra were monitored by an image-intensified multichannel detector with a gated function (Hamamatsu C4560), which was attached to a polychromator. The timing between the laser and the detector was adjusted by a digital delay/pulse generator (Stanford Systems DG535). Transient emission spectra excited by the laser were measured with the same detector.

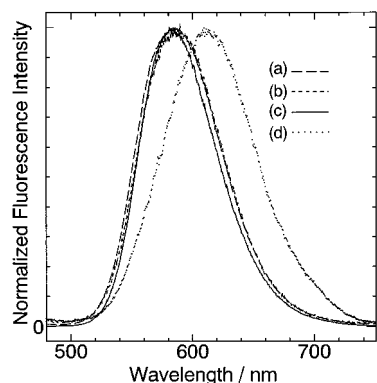
Time-resolved fluorescence spectra and fluorescence rise and decay curves were measured with the apparatus described in the previous paper.<sup>11</sup> A diode laser (Hamamatsu, PLP-01) (417 nm, 26.7 ps fwhm) was used as an excitation light source.

For all the measurements, a CT absorption band was excited. All the measurements were performed under O<sub>2</sub>-free condition at room temperature.

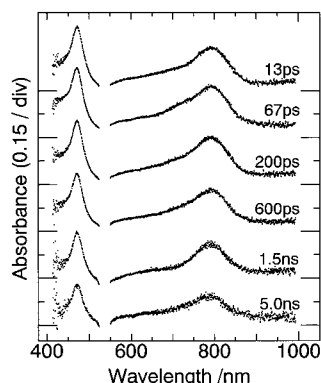
## Results and Discussion

**Ground-State Absorption and Steady-State Fluorescence Spectra.** As shown in Figure 1, ground-state CT absorption spectra of the amorphous dimeric compound films doped with TCNB (DCzP(a)–TCNB and DCzCB(a)–TCNB) as well as TCNB-doped PVCz (TCNB–PVCz) films consist of two bands, which are attributable to transitions HOMO1 → LUMO and HOMO2 → LUMO of a 1:1 CT complex, where HOMO1 and 2 are the two highest occupied molecular orbitals of the donor (Cz chromophore) and LUMO is the lowest unoccupied molecular orbital of the acceptor (TCNB). This is safely assigned on the basis of both the results of the solution system reported for ground-state CT complexes of PVCz and its related compounds with various acceptor molecules<sup>23</sup> and the results of the compositional analysis of PVCz films doped with 2,4,7-trinitrofluorenone.<sup>24</sup> The CT absorption spectra of the present dimeric system resemble that of polystyrene films doped with *N*-ethylcarbazole and TCNB (ECz + TCNB/PSt) rather than that of the PVCz system, while energy positions of the two CT bands are almost identical between the dimeric and PVCz systems. The clear spectral shapes of the dimeric system compared with PVCz films suggest that the relative geometrical structure of Cz to TCNB of the CT complexes in the amorphous low-molecular-weight compound system takes a narrow distribution compared with the amorphous PVCz one.

Steady-state CT fluorescence of both the two-dimeric amorphous films and ECz + TCNB/PSt films are observed in the shorter-wavelength region than that of PVCz–TCNB films (Figure 2). The bandwidths of both the low-molecular-weight



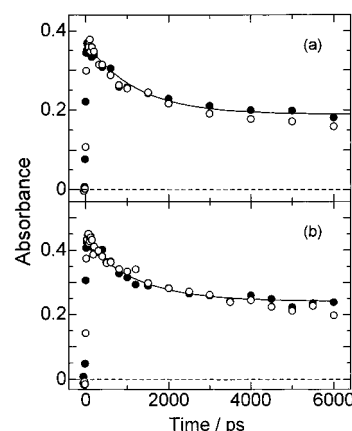
**Figure 2.** Steady-state fluorescence spectra: (a) DCzP(a)-TCNB (4 mol %) film; (b) DCzCB(a)-TCNB (4 mol %) film; (c) ECz + TCNB/PSt (ECz, 30 wt % for PSt; TCNB, 4 mol % for ECz) film; (d) PVCz-TCNB (4 mol %) film. Excitation wavelength is 390 nm.



**Figure 3.** Transient absorption spectra of DCzCB(a)-TCNB (4 mol %) film excited with a picosecond 532 nm laser pulse.

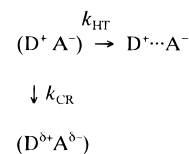
compound films are smaller than that of the PVCz system. In addition, the yields of the CT fluorescence of DCzP(a)-TCNB (4 mol %) and DCzCB(a)-TCNB (4 mol %) films were about 10 and 12 times as large as that of PVCz-TCNB (4 mol %) films, respectively, and were close to the value of ECz + TCNB/PSt films (ECz, 30 wt % for PSt; TCNB, 4 mol % for ECz). The CT fluorescence of PVCz systems was mainly ascribed to a triple complex formed between two Cz chromophores and one TCNB molecule (2:1 complex).<sup>11</sup> It is likely that its broad bandwidth is attributable to various excited triple complexes, where the geometry of a Cz dimer cation ( $\text{CzCz}^+$ ) and the relative geometrical structure of  $\text{CzCz}^+$  and  $\text{A}^-$  in the state take diverse distribution. The CT fluorescence of the ECz + TCNB/PSt film is mainly due to a complex of one Cz chromophore and one TCNB molecule (1:1 complex) because ECz is distributed homogeneously in PSt films and does not form a dimer that leads to excimer upon excitation. The short wavelength CT fluorescence and its small bandwidth observed for both the dimeric compound films compared with PVCz-TCNB films suggest that the CT fluorescence of the dimeric system is mainly attributable to a 1:1 complex and, in addition, that the distribution of the relative geometrical structure of Cz to TCNB in excited CT complexes is smaller for the dimeric system than for the polymer one.

**Photoinduced Charge-Separation Processes As Revealed by Picosecond Transient Measurements.** Each time-resolved absorption spectrum of DCzCB(a)-TCNB (4 mol %) films excited with a picosecond 532 nm laser pulse consists of two absorption bands, as shown in Figure 3. On the basis of the spectral band shapes and the peak positions, the absorption band around 470 nm is safely assigned to the TCNB anion ( $\text{TCNB}^-$ )<sup>25</sup> and that around 800 nm to the Cz cation ( $\text{Cz}^+$ ).<sup>16,17</sup> The time



**Figure 4.** Time profiles of transient absorbance of TCNB anion (●) and carbazolyl cation (○) of (a) DCzP(a)-TCNB (4 mol %) and (b) DCzCB(a)-TCNB (4 mol %) films excited with a picosecond 532 nm laser pulse. The monitoring wavelength of the TCNB anion was 470 nm for (a) and (b) and that of the carbazolyl cation was 800 and 790 nm for (a) and (b), respectively. For (b), the absorbance of the cation was multiplied by a factor of 1.37. The solid lines are the calculated curves based on Scheme 1 with the values of  $k_{\text{HT}}$  and  $k_{\text{CR}}$  listed in Table 1 (see text).

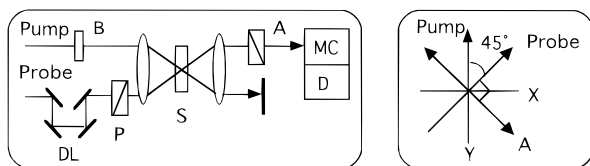
#### SCHEME 1



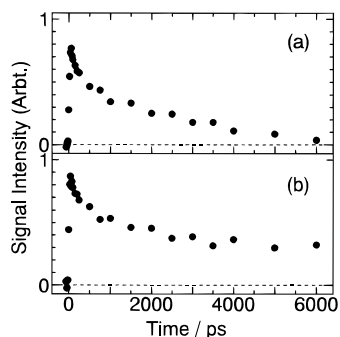
evolution of the absorption spectra indicates that the excitation of the CT absorption band of the weak ground-state CT complex results in a rapid charge separation in the excited state. The absorption spectra decay monotonically without giving any chemical transients in the present time region. The same behaviors were also observed for DCzP(a)-TCNB films.

Figure 4 shows time profiles of the absorbance monitored at 470 nm ( $\text{TCNB}^-$ ) and 790 or 800 nm ( $\text{Cz}^+$ ) in the several nanoseconds time region. The same time profiles are observed for the absorption bands of  $\text{TCNB}^-$  and  $\text{Cz}^+$ , indicating that the disappearance of the two transient ionic species is ascribed to the charge-recombination (CR) process. One notices that the absorbance does not disappear in the present time region; that is, it decreases up to ca. 4 ns after excitation and attains a constant value in the longer time region. We have reported that the quite similar time profile was observed for PVCz-TCNB films.<sup>7</sup> For the polymer films, considering the scheme of the primary process of the transient ion pair states formed via the photoinduced charge-separation (CS) process in a polar solvent, in which the scheme has been established,<sup>26</sup> we replaced the ionic dissociation process with the hole transfer (HT) process in the scheme, since the ionic dissociation cannot take place in the solid films; that is, in Scheme 1, the CR process is in competition with the HT process in the initial charge-separated state ( $D^+ A^-$ )\* produced via the photoexcitation of the ground-state CT complex. Thus, we represented the time dependence of the absorbance due to the ionic species (charge-separated state) on the assumption that both the CR and the HT processes obey the first-order kinetics. The scheme was confirmed by the transient dichroism measurement sensitive to the HT processes.<sup>7</sup> Thereby, the rate constants for these processes,  $k_{\text{CR}}$  and  $k_{\text{HT}}$ , were obtained.

Here, measuring the transient dichroism of the absorption of  $\text{Cz}^+$  and  $\text{TCNB}^-$ , we confirmed the applicability of the Scheme 1 to the present amorphous dimeric compound films. For the



**Figure 5.** Schematic diagram of the apparatus for the measurements of the transient dichroism and axis systems for the pump and probe polarizations: B = wave plate, DL = optical delay line, P = polarizer, A = analyzer polarizer, D = photodetector, MC = monochromator, and S = sample.



**Figure 6.** Time profiles of transient dichroism signals of DCzCB(a)-TCNB (4 mol %) film excited with a picosecond 532 nm laser pulse: (a) monitored at 780 nm ( $\text{Cz}^+$ ); (b) monitored at 470 nm ( $\text{TCNB}^-$ ).

dichroism measurements in the present system, we have adopted a background-free optical system, since a wider dynamic range in the time profiles was obtained by this method. Conceptual optical alignment<sup>27,28</sup> is illustrated in Figure 6, where the polarization angle between the excitation (pump) and the monitoring (probe) light pulses is set to be  $45^\circ$ . The analyzer polarizer perpendicular to the polarization of the probe light is placed before the detector. Since the excitation of the ground-state CT complex by the polarized light induces a difference in the transient absorbance of the charge-separated state between the X and Y axes (transient dichroism), the polarization angle of the probe light is modified and a part of the monitoring light can be transmitted to the analyzer.

In the case where the dephasing process of the memory of the polarized excitation is regarded as an exponential process, the transmitted light intensity,  $I_T(t)$ , in the homodyned detection is given by<sup>27-30</sup>

$$I_T(t) \propto \{A(t) \exp(-t/\tau_{\text{DP}})\}^2 \quad (1)$$

where  $A(t)$  is the time dependence of the population of the ionic species and  $\tau_{\text{DP}}$  is the time constant for the dephasing process of the memory of the polarized excitation. In the actual measurement, we employed the heterodyned detection method.<sup>29,30</sup> In this optical configuration, the analyzer polarized was uncrossed slightly ( $<1^\circ$ ) and the electric field  $E_{\text{LO}}$  is present in the absence of the pump pulse.  $I_{\text{LO}}$ , which is in proportion to  $E_{\text{LO}}^2$ , is adjusted to make the heterodyne term ( $E_{\text{LO}}E_S(t)$ ) much greater than  $I_S$  ( $\propto E_S(t)^2$ ). In this case, the transmitted light intensity is given by the following equation:<sup>29,30</sup>

$$(I_T(t) - I_{\text{LO}}) \propto A(t) \exp(-t/\tau_{\text{DP}}) \quad (2)$$

where  $I_{\text{LO}}$  is the intensity transmitted in the absence of the pump pulse. The  $I_{\text{LO}}$  signal is removed by subtracting the transmitted intensity at delay time much less than 0 ps from the observed signal  $I_T$ . In the heterodyned detection, a much larger intensity of the signal can be obtained, and the observed time profile arising from the dichroism is proportional to the signal electric

**TABLE 1: Rate Constants of Charge-Recombination ( $k_{\text{CR}}$ ) and Hole-Transfer ( $k_{\text{HT}}$ ) Processes in Amorphous Solid Films**

	DCzP(a)	DCzCB(a)	PVCz <sup>a</sup>
$k_{\text{CR}}$ ( $\text{s}^{-1}$ )	$4.0 \times 10^8$	$3.6 \times 10^8$	$3.3 \times 10^8$
$k_{\text{HT}}$ ( $\text{s}^{-1}$ )	$4.2 \times 10^8$	$4.7 \times 10^8$	$4.8 \times 10^8$

<sup>a</sup> Reference 7.

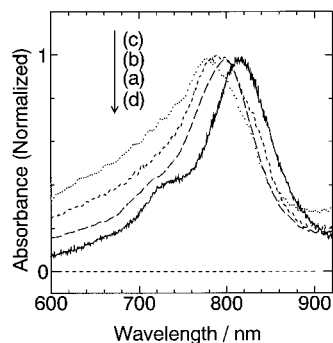
field,  $E_s$ , while the signal intensity,  $I_s$ , scales quadratically with  $E_s$  in the homodyned detection.

Figure 6 shows time profiles of the transient dichroism monitored at 780 ( $\text{Cz}^+$ ) and 470 nm ( $\text{TCNB}^-$ ) of DCzCB(a)-TCNB (4 mol %) films. Some parts of signals around the time origin might be due to the birefringence induced by the excitation light (Kerr effect). As aforementioned, the excitation of the ground-state CT complex by polarized light induces dichroism in the transient absorbance of the CS state. The HT process in amorphous films decreases the memory of the polarized excitation in the cationic state. As shown, the memory of the polarized excitation in  $\text{Cz}^+$  decreases to the background level, while that in  $\text{TCNB}^-$  remains in the nanosecond time region. The latter time profile resembles that of the transient absorbance of  $\text{TCNB}^-$  in Figure 4b. This is reasonable, since the migration of an electron via TCNB chromophores (migration of anion radical) does not take place in this time region because of the low concentration of TCNB. The decrease in the memory of the polarized excitation in  $\text{Cz}^+$  to the zero level indicates that the hole transfer from the initial  $\text{Cz}^+$  in the CS state to neighboring neutral Cz chromophore proceeds in competition with the charge-recombination process in the present time region. The same results were also observed for DCzP(a)-TCNB films. These results indicate that the Scheme 1 proposed for the PVCz system is also applicable to the present dimeric system. Hence, we applied the same analysis method to the present amorphous dimeric compound films. According to the Scheme 1, the time dependence of the absorbance  $\text{Abs}(t)$  due to the CS state is represented by eq 3.

$$\text{Abs}(t) = \text{Abs}(t=0) \{ k_{\text{HT}} / (k_{\text{CR}} + k_{\text{HT}}) + [k_{\text{CR}} / (k_{\text{CR}} + k_{\text{HT}})] \exp[-(k_{\text{CR}} + k_{\text{HT}})t] \} \quad (3)$$

The solid lines in Figure 4 are the calculated curves based on eq 3, where the values of  $k_{\text{CR}}$  and  $k_{\text{HT}}$  in Table 1 are used. As expected, the calculated curves reproduce the experimental results fairly well. The values for PVCz-TCNB films are also listed in Table 1 for comparison. One notices that the  $k_{\text{CR}}$  values for the amorphous dimeric system are close to that obtained for the PVCz one. In addition, these values of both systems are close to that obtained for the photoinduced CS state of the ground-state CT complex between *N*-ethylcarbazole and TCNB in toluene solution,  $3.0 \times 10^8 \text{ s}^{-1}$ . These results are reasonable, since the dielectric constant of the amorphous dimeric compound films is expected to be quite close to that of PVCz films and these values are rather close to that of neat toluene.

As listed in Table 1, the  $k_{\text{HT}}$  values for the dimeric system are also close to that for the PVCz, although the absorption spectra of  $\text{Cz}^+$  are different among these three amorphous films, as shown in Figure 7. It was reported that the interaction between  $\text{Cz}^+$  and the neighboring neutral Cz chromophore affects the absorption spectral shape of  $\text{Cz}^+$ .<sup>16,17</sup> The difference in the absorption spectral shape of  $\text{Cz}^+$  among these films suggests that the interaction between the  $\text{Cz}^+$  and the neighboring neutral Cz chromophore or the neutral Cz chromophores around the  $\text{Cz}^+$  is larger for the PVCz system than for the dimeric ones. In addition, a large hypochromic effect was



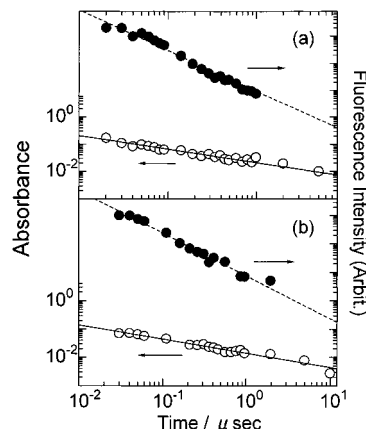
**Figure 7.** Normalized absorption spectra of the carbazole cation at 40 ps after excitation: (a) DCzP(a)-TCNB (4 mol %); (b) DCzCB(a)-TCNB (4 mol %); (c) PVCz-TCNB (3 mol %); (d) ECz + TCNB/PSt (ECz, 30 wt % for PSt; TCNB, 4 mol % for ECz) films.

observed for PVCz in solution but not for DCzP in solution,<sup>31</sup> indicating that the interaction between neighboring Cz chromophores is smaller for DCzP than for PVCz. These large electronic interactions between Cz chromophores of PVCz compared with low-molecular-weight compounds predict that the  $k_{HT}$  value for PVCz is larger than that for the dimeric compound. However, the  $k_{HT}$  values are almost the same for PVCz and the dimeric compounds. This suggests that there are factors that increase the  $k_{HT}$  value in the dimeric films. Since the densities of these three neat materials (1.19 g/cm<sup>3</sup>) are almost the same, the difference in the average distance between neighboring Cz chromophores is unlikely to be one of the factors. On the basis of the dependences of hole-drift mobility in *N*-isopropylcarbazole molecularly doped PSt films and copolymer films of *N*-vinylcarbazole with styrene on the temperature and the electric field, it was suggested that the vinyl backbones of polymers disturb certain chromophore motions that promote the hole transport.<sup>20</sup> Since Cz chromophores in PVCz are directly connected to the rigid skeletal chains, the motions of both hopping-site chromophores and their surrounding chromophores are likely to be easier in the amorphous low-molecular-weight compound films than in the amorphous PVCz ones. Although the mode of the motion is not clear at the present stage, such motion may enhance electronic coupling in electron transfer and, as a result, promote the hole transport.

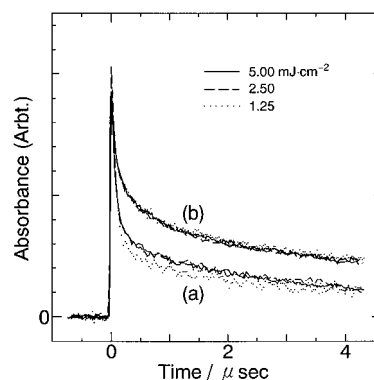
As reported previously, the hole-drift mobility was different between DCzP(a) and PVCz films.<sup>20</sup> In these films, the hole-drift mobility is rate-determined by traps such as dimer cation sites but not by the hole-transfer process presented here (migration process of the  $Cz^+$  initially produced via the excitation of the ground-state CT complex to the neighboring neutral Cz chromophore) (vide infra).

**Behavior of Hole in Nanosecond and Microsecond Time Regions.** We examined the behavior of holes ( $Cz^+$ ) that escaped from the CR process in the CS state initially produced by the excitation of the ground-state CT complex by measuring transient absorption spectra and time-resolved fluorescence spectra in the time region from 20 ns to several microseconds.

The absorption spectra of both  $Cz^+$  and  $TCNB^-$  decayed simultaneously and monotonically without any spectral change also in this time region, indicating that the disappearance of the ionic species is ascribable to the CR process also in this time region. In Figure 8, the absorbance of  $TCNB^-$  and the CT fluorescence intensities integrated over 465–645 nm are plotted against the delay time after a 390 nm nanosecond dye laser excitation on double-logarithmic scale. The decay of the absorbance of  $TCNB^-$  is almost fitted to a straight line with a slope of  $-0.5$ , indicating that the concentration of the ionic

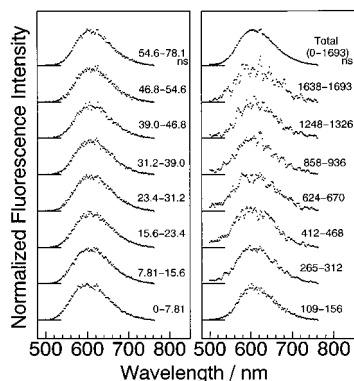


**Figure 8.** Time dependent absorbance of the  $TCNB^-$  (O) and CT fluorescence intensities (●) after a 390 nm dye laser excitation: (a) DCzP(a)-TCNB (4 mol %); (b) DCzCB(a)-TCNB (4 mol %) films. Solid and dashed lines indicate slopes of  $-0.5$  and  $-1.5$  in the log plot, respectively.



**Figure 9.** Decay curves of  $TCNB^-$  anion monitored at 465 nm: (a) DCzP(a)-TCNB (4 mol %); (b) PVCz-TCNB (4 mol %) films. Excitation laser fluence at 390 nm is given in the figure.

species decays with a  $t^{-0.5}$  time dependence.<sup>32</sup> On the other hand, the decay curve of the CT fluorescence intensity approximately obeys a  $t^{-1.5}$  time dependence. This dependence is in agreement with the derivative of the decay curve of the ionic species. If the CR process occurs through a hole-diffusion process followed by the formation of the CT fluorescent state, the number of photons emitted during some time interval should be proportional to the number of ionic species disappearing during the same time interval. In such a case, the time dependence of the CT fluorescence after excitation should be in accordance with the derivative of the time dependence of the ionic species. The present result corresponds with this case, indicating that the CR process in the present time region occurs mainly via a fluorescent CT state, of which the formation is determined by the hole diffusion. That is, the rate-determining step of the CR is a hole-diffusion process. A similar behavior was reported for PVCz-TCNB and PVCz-pyromellitic dianhydride films in the time region from several microseconds to several milliseconds.<sup>14</sup> For these PVCz films, the dependence of the decay dynamics on the initially generated ion concentration was not observed, and consequently, the CR process was interpreted as a hole diffusion-controlled geminate recombination process. In the present amorphous dimeric system, the decay dynamics of the ionic species in the time region from 0.1 to 4.3  $\mu$ s did not change for the excitation laser fluence from 1.25 to 5.0 mJ/cm<sup>2</sup> (Figure 9). Although the range examined is small, the present CR process is also most likely to be due to the hole diffusion-controlled geminate recombination process.



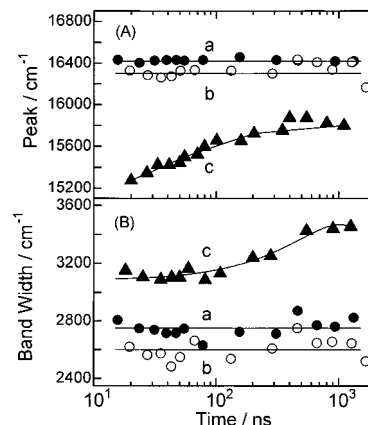
**Figure 10.** Normalized time-resolved CT fluorescence spectra of DCzP(a)-TCNB (4 mol %) films excited at 417 nm. The time window is given in the figure.

As aforementioned, the  $k_{HT}$  value, which is the transfer rate constant of the hole that escapes from the CR process in the initial CS state produced by the excitation of the ground-state CT complex, is almost the same between the amorphous dimeric and polymer systems. As shown in Figure 9, however, the decay of the ionic species in the microsecond time region is more rapid for the DCzP(a) system than for the PVCz one. This is interpreted in the following way. The holes escaping from the initial CR process undergo migration that is rate-controlled by trap sites until the holes encounter the  $TCNB^-$ , which was originally the counterpart in the initial CS state, and in addition, the concentration of the trap sites is much smaller for DCzP(a) films than for PVCz films.

As reported, the hole-drift mobility of DCzP(a) films is much larger than that of the PVCz ones.<sup>20</sup> Since the drift mobility is regulated by hole-trap sites such as dimer cation sites, the present results in the microsecond time region are in agreement with the results of the hole-drift mobility.

**CT Fluorescent States Formed by Geminate Recombination Processes.** To examine CT fluorescent states formed by the recombination between hole and the acceptor anion, we measured time-resolved fluorescence spectra of the amorphous dimeric system by a time-correlated single photon counting method. Figure 10 shows normalized time-resolved fluorescence spectra of DCzP(a)-TCNB (4 mol %) films being obtained by the CT band excitation of a 417 nm pulsed diode laser. The spectral shape does not change with time after excitation. This was confirmed by the observation that the fluorescence decay curves were independent of the monitoring wavelengths. The similar fluorescence spectral behavior was also observed for DCzCB(a)-TCNB (4 mol %) films. The peak and bandwidth of the time-resolved fluorescence spectra of the amorphous dimeric system are plotted against time after excitation in Figure 11 with those for PVCz-TCNB (4 mol %) films. For the amorphous dimeric system, both the peak and the bandwidth are almost independent of the time after excitation, whereas for the polymer one, these depend on it. The blue shift of the CT fluorescence peak with time for PVCz-TCNB films has been already reported.<sup>11</sup> In addition, the CT fluorescence of the PVCz systems was assigned to be mainly due to a 2:1 complex formed between two Cz chromophores and one TCNB molecule, as described above.

The fact that the time-resolved fluorescence spectral shape is independent of time after excitation suggests that structures of CT fluorescent states are the same irrespective of time after excitation; that is, the relative geometrical structures of  $TCNB^-$  to  $Cz^+$  in CT fluorescent states formed by the recombination between  $Cz^+$  (hole) and  $TCNB^-$  after the hole-migration process are independent of the time at which the recombination takes



**Figure 11.** (A) Peak wavenumber and (B) bandwidth as a function of time after excitation, obtained from the time-resolved spectra corrected for the detector sensitivity: (a) DCzP(a)-TCNB (4 mol %); (b) DCzCB(a)-TCNB (4 mol %); (c) PVCz-TCNB (2 mol %) films. Solid lines are a guide for the eyes.

place. This suggests that microenvironments around the doped TCNB molecules are quite similar for all the TCNB molecules and that the holes escaping from the initial CR process return to just original Cz chromophores in the initial CS state after migration. On the other hand, the blue shift and the spectral broadening observed for the time evolution of the time-resolved CT fluorescence spectra of PVCz-TCNB films suggest that CT fluorescent sites formed by the late recombination have relatively loose and various overlap structures among two Cz chromophores and the TCNB molecule compared with the CT fluorescent sites that emit at the early stage. In addition, although holes escaping from the initial CR process encounter the  $TCNB^-$  that was originally the counterpart in the initial CS state, not all of the holes return the original Cz chromophores in the initial CS state; it is possible for holes to return to Cz chromophores that form unstable CT fluorescent states compared with the initial CS state. These imply that for amorphous polymer films, microenvironments around the doped TCNB molecules take a diverse distribution, which is quite different from the situation of the amorphous low-molecular-weight compound solid films. These results are consistent with the results of the ground-state CT absorption spectra aforementioned. The difference between the low-molecular-weight compound and polymer systems is likely to be interpreted in the following way. For the dimeric model films, the dopant TCNB molecules can be intercalated to the most suitable position in the amorphous films without steric hindrance, whereas for the polymer films, the Cz chromophores are hindered from approaching the most suitable site in relation to the dopant molecules because of the restricted freedom of pendant Cz chromophores induced by skeletal chains. The restricted motion of Cz chromophores during amorphous film formation may induce a diverse distribution both of the geometry of the Cz dimer cation ( $CzCz^+$ ) and of the relative geometrical structure of  $CzCz^+$  to  $TCNB^-$  in the CT fluorescent state.

## Conclusion

The difference in the ground-state CT absorption and steady-state CT fluorescence spectra between the amorphous dimeric compounds and the PVCz films indicated that the distribution of the relative geometrical structure of Cz chromophores to TCNB molecules of the ground-state and the excited-state CT complexes is smaller for the dimeric compounds system than for the PVCz system. The behavior of the initially photoinduced charge-separation process for both systems was identical with

each other. The values of  $k_{CR}$  and  $k_{HT}$  were also close. The CR process of the hole that escaped the initial CR process was interpreted as the hole diffusion-controlled geminate recombination process. The concentration of hole-trap sites affecting the diffusion process was smaller for the present dimeric compounds system than for the polymer system. The difference in the time-resolved fluorescence between both systems was also observed. These differences were considered to be attributable to the presence and the absence of the direct connection of the Cz chromophores to the backbone chains.

**Acknowledgment.** The present work was partly defrayed by the Grants-in-Aid for Scientific Research on Priority-Area-Research on "Photoreaction Dynamics" from the Ministry of Education, Science, Sports, and Culture of Japan (06239107, 07228235, and 08218233).

## References and Notes

- (1) Kirmaier, C.; Holten, D. *Photosynth. Res.* **1987**, *13*, 225.
- (2) Mort, J.; Pfister, G. In *Electronic Properties of Polymers*; Mort, J., Pfister, G., Eds.; Wiley-Interscience: New York, 1982; Chapter 6, and references therein.
- (3) Van der Auweraer, M.; De Schryver, F. C.; Borsenberger, P. M.; Bassler, H. *Adv. Mater.* **1994**, *3*, 199, and references therein.
- (4) Borsenberger, P. M.; Gruenbaum, W. T.; Magin, E. H. *Jpn. J. Appl. Phys.* **1996**, *35*, 2698, and references therein.
- (5) (a) Stolka, M.; Pai, D. M. *Adv. Polym. Sci.* **1978**, *29*, 1. (b) Penwell, R. C.; Ganguray, B. N.; Smith, T. W. *J. Polym. Sci., Part D: Macromol. Rev.* **1978**, *16*, 63.
- (6) *Poly(N-vinylcarbazole)*; Peason, J. M., Stolka, M., Eds.; Gordon and Breach Science: New York, 1981.
- (7) Miyasaka, H.; Moriyama, T.; Kotani, S.; Muneyasu, R.; Itaya, A. *Chem. Phys. Lett.* **1994**, *225*, 315.
- (8) For examples, see the following. (a) Pai, D. M. *J. Chem. Phys.* **1970**, *52*, 2285. (b) Gill, W. D. *J. Appl. Phys.* **1972**, *43*, 5033. (c) Okamoto, K.; Kusabayashi, S.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1948. (d) Pfister, G.; Williams, D. J. *J. Chem. Phys.* **1974**, *61*, 2416. (e) Muller-Horsche, E.; Haarer, D.; Scher, H. *Phys. Rev. B* **1987**, *35*, 1273. (f) Bos, F. C.; Guin, T.; Burland, D. M. *Phys. Rev. B* **1989**, *39*, 12633.
- (9) For examples, see the following. (a) Okamoto, K.; Kusabayashi, S.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2613. (b) Yokoyama, M.; Endo, N.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1538. (c) Okamoto, K.; Oda, N.; Itaya, A.; Kusabayashi, S. *Chem. Phys. Lett.* **1975**, *35*, 483.
- (10) For examples, see the following. (a) Klopffer, W. *J. Chem. Phys.* **1969**, *50*, 2337. (b) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697. (c) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2082. (d) Sakai, H.; Itaya, A.; Masuhara, H.; Sasaki, K.; Kawata, S. *Polymer* **1996**, *37*, 31.
- (11) (a) Sakai, H.; Itaya, A.; Masuhara, H. *J. Phys. Chem.* **1989**, *93*, 5351. (b) Itaya, A.; Egawa, A.; Umehara, Y.; Sakai, H.; Masuhara, H. *Polymer* **1994**, *35*, 3149.
- (12) (a) Masuhara, H.; Ohwada, S.; Mataga, N.; Itaya, A.; Okamoto, K.; Kusabayashi, S. *J. Phys. Chem.* **1980**, *84*, 2363. (b) Lachish, U.; Anderson, R. W.; Williams, D. J. *Macromolecules* **1980**, *13*, 1143.
- (13) Ueda, T.; Fujisawa, R.; Fukumura, H.; Itaya, A.; Masuhara, H. *J. Phys. Chem.* **1995**, *99*, 3629.
- (14) Watanabe, K.; Asahi, T.; Masuhara, H. *Chem. Phys. Lett.* **1995**, *233*, 69.
- (15) (a) De Schryver, F. C.; Vandendriessche, J.; Toppet, S.; Demeyer, K.; Boens, N. *Macromolecules* **1982**, *15*, 406. (b) Evers, F.; Kobs, K.; Memming, R.; Terrell, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 5988. (c) Vandendriessche, J.; Palmans, P.; Toppet, S.; Boens, N.; De Schryver, F. C.; Masuhara, H. *J. Am. Chem. Soc.* **1984**, *106*, 8057.
- (16) (a) Masuhara, H.; Tamai, N.; Mataga, N.; De Schryver, F. C.; Vandendriessche, J. *J. Am. Chem. Soc.* **1983**, *105*, 7256. (b) Masuhara, H. *J. Mol. Struct.* **1985**, *126*, 145.
- (17) Masuhara, H.; Yamamoto, K.; Tamai, N.; Inoue, K.; Mataga, N. *J. Phys. Chem.* **1984**, *88*, 3971.
- (18) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Chem. Lett.* **1978**, 131.
- (19) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3737.
- (20) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Polymer J.* **1985**, *17*, 557.
- (21) Shiota, Y.; Tada, K.; Shimizu, M.; Kusabayashi, S.; Mikawa, H. *Chem. Commun.* **1970**, 1110.
- (22) Itaya, A.; Inoue, T.; Yamamoto, T.; Nobuto, T.; Miyasaka, H.; Toriumi, M.; Ueno, T. *J. Mater. Chem.* **1994**, *4*, 1539.
- (23) Okamoto, K.; Ozeki, M.; Itaya, A.; Kusabayashi, S.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1362.
- (24) Weiser, Q. *J. Appl. Phys.* **1972**, *43*, 5028.
- (25) (a) Ishitani, A.; Nagakura, S. *Theor. Chim. Acta* **1966**, *4*, 236. (b) Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1970**, *6*, 606.
- (26) (a) Miyasaka, H.; Ojima, S.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 3380. (b) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4147. (c) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 5834. (d) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 7534.
- (27) Shank, C. V.; Ippen, E. P. *Appl. Phys. Lett.* **1975**, *26*, 62.
- (28) Waldeck, D.; Cross, A. J., Jr.; McDonald, D. B.; Fleming, G. R. *J. Chem. Phys.* **1981**, *74*, 3381.
- (29) Fleming, G. R. *Chemical Applications of Ultrafast Spectroscopy*; Oxford University: New York, 1986; p 72.
- (30) Easley, G. L.; Levenson, M. D.; Tolles, W. M. *IEEE J. Quantum Electron* **1978**, *14*, 192.
- (31) Okamoto, K.; Itaya, A.; Kusabayashi, S. *Chem. Lett.* **1974**, 1167.
- (32) Hong, K. M.; Noolandi, J. *J. Chem. Phys.* **1978**, *68*, 5163.