

# Direct Detection of the Hole Migration along the Polymer Chain by Means of Picosecond Transient Absorption and Dichroism Measurements: Poly(*N*-vinylbenzocarbazole) Systems in 1,2-Dichloroethane Solution

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Picosecond transient absorption spectroscopy and transient dichroism measurements were applied to the direct elucidation of photoinduced electron-transfer dynamics (charge separation, charge recombination, and hole-transfer reactions) in poly(5-vinylbenzo[*b*]carbazole) (P5VBCz) and poly(7-vinylbenzo[*c*]carbazole) (P7VBCz) as well as the corresponding monomer model systems in 1,2-dichloroethane solution. Electron-transfer dynamics in these polymers was well described by the simple scheme that the cation state of the benzocarbazolyl (BCz<sup>+</sup>) moiety continuously migrates along the pendent BCz moieties in the polymer chain with the charge recombination at the initial position of the charge separation. The rate constants for the hole transfer from the BCz<sup>+</sup> to neighboring ones were found to be (180 ps)<sup>-1</sup> for P5VBCz and (320 ps)<sup>-1</sup> for P7VBCz. These rate constants are several orders of magnitude larger than those estimated by the standard theories of electron transfer assuming a very weak interaction between the reactants. By integrating the present results with those in other aromatic vinyl polymers, the factors regulating the rapid hole-transfer process in aromatic vinyl polymers were discussed.

## Introduction

Transport of electrons initiated by photoexcitation is ubiquitous in nature as well as in artificial systems. In the artificial systems, a great deal of effort has been devoted to the construction of organic photoconductive molecular systems and the elucidation of their dynamics and mechanisms.<sup>1,2</sup> The vinyl polymer with large aromatic groups is one of the most well-known artificial materials where the transport of the electron and/or hole takes place and has been attracting much attention for a long time from various viewpoints.<sup>3–10</sup>

In most of these polymers, the interaction among the pendent aromatic groups are rather small and band structures in the electronic states are not plausible in general. Hence, the photoconduction in these polymers may be regarded as the integrated phenomena of “intermolecular” ET processes such as charge separation, charge recombination, and charge shift reactions from the viewpoint of the photoinduced electron transfer (ET) in condensed phase.<sup>11–14</sup> The direct information on the whole mechanisms of the electron transfer dynamics and, especially, on the charge shift reaction among the aromatic side groups provides important principles not only for the comprehensive understanding of the photoconduction in these polymers but also for the molecular designing of the artificial photoconductors.

Although a number of the investigations have been reported as mentioned above, the direct detection has been scarcely applied to the elucidation of the rate constant of the charge shift reaction between the aromatic side groups and the factors regulating it. One of the obstacles for the direct measurement of the charge shift reaction is related to the fact that the discrimination of the charge shift process in electron transfer dynamics is rather difficult by the usual transient absorption spectroscopy, since the absorption spectrum of the anion or the

cation of the side aromatic groups is not significantly influenced by the charge shift reactions.

Recently, we pointed out that the dichroism measurement of the transient absorption of ionic species directly provides the charge shift reactions in these polymer systems and applied this technique to the detection of the hole migration process in poly(*N*-vinylcarbazole) (PVCz) in solid amorphous systems<sup>15</sup> as well as in solution phase.<sup>16</sup> From these results, it was demonstrated that the rapid hole migration with a time constant of 0.5 to a few ns takes place in solution as well as in solid films. It should be mentioned that the hole escape reaction is endothermic, since the increase in the interionic distance reduces the Coulombic attractive interaction in the ion pair. The activation energy predicted for the reaction  $A^-D_0^+D_1 \rightarrow A^-D_0D_1^+$  by the standard theory of ET reaction<sup>11</sup> is  $\gg 10k_B T$  even in the rather polar solution of 1,2-dichloroethane, and such a large hole migration rate constant on the order of  $10^9 \text{ s}^{-1}$  could not be accounted for within the framework of usual ET theories assuming very weak interaction in the reactants.

To more clearly elucidate factors regulating rapid hole transfer processes among pendent groups in aromatic vinyl polymers, poly(5-vinylbenzo[*b*]carbazole) (P5VBCz) and poly(7-vinylbenzo[*c*]carbazole) (P7VBCz) have been investigated in the present work. According to the investigation by NMR measurements,<sup>19</sup> it was reported that the interaction between the pendent groups in these polymers was larger than that in PVCz and poly(vinylnaphthalene). In addition, the molecular structures of the benzocarbazolyl moiety attached to the main chain causes the difference in the overlap and the degree of interaction between neighboring aromatic groups in polymer chains. In the following, we will discuss the photoprocesses in the present polymers as well as the corresponding monomer model system, by integrating the present results with those accumulated for the general transient ion pairs in solutions and with the primary electron-transfer processes in other aromatic vinyl polymer and related systems.<sup>15–18</sup>

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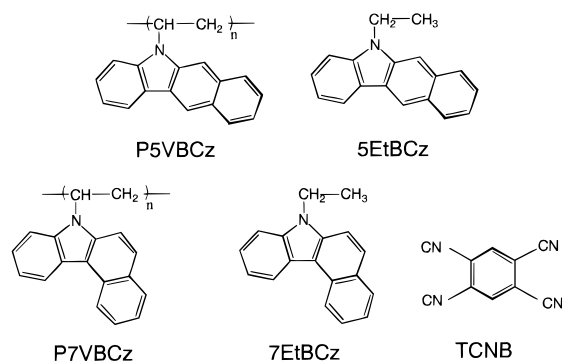


Figure 1. Molecular structures of the compounds used.

## Experimental Section

Poly(5-vinylbenzo[*b*]carbazole) (P5VBCz) ( $M_n = 2.02 \times 10^4$ ) and poly(7-vinylbenzo[*c*]carbazole) (P7VBCz) ( $M_n = 4.72 \times 10^4$ ) were prepared by radical polymerization of the corresponding vinyl monomers<sup>19b</sup> and purified by precipitation three times from 1,2-dichloroethane solution with methanol. 5-Ethylbenzo[*b*]carbazole (5EtBCz) and 7-ethylbenzo[*c*]carbazole (7EtBCz) were synthesized and purified.<sup>19b</sup> 1,2,4,5-Tetracyanobenzene (TCNB; Wako GR Grade) was recrystallized from ethanol and sublimated before use. 1,2-Dichloroethane (Dotite, Spectrosol) was used as received. Molecular structures of the compounds used in the present work are shown in Figure 1.

A microcomputer-controlled picosecond laser photolysis system with a custom-built repetitive mode-locked Nd<sup>3+</sup>:YAG laser was used for measurements. The optical alignments were almost the same as those developed previously.<sup>15</sup> A second harmonic pulse at 532 nm with 15 ps fwhm and ca. 0.5 mJ output power was used for exciting the samples. To avoid the Kerr signal around the time origin, the excitation intensity was attenuated to  $\ll 1/10$  for the dichroism measurements in the background free condition. Monitoring white light was generated by focusing the fundamental light into a 10 cm D<sub>2</sub>O–H<sub>2</sub>O (3:1) cell. Two sets of the multichannel photodetector (Hamamatsu, S4874) combined with a polychromator were used for the detection of the monitoring light in the usual transient absorption spectroscopy. For the measurements of the dichroism signal with the background free condition, we employed the multichannel detector with an image intensifier (Hamamatsu, C4560) in order to detect the weak transmitted light. Circular polarized probe light was used for the absorption spectroscopy, while linearly polarized light was employed for the dichroism measurements. The repetition rate of the excitation light was kept low (<0.5 Hz). Most of the data were accumulated over 10 measurements. The experimental errors for the transient absorption spectroscopy are  $< \pm 10\%$ , while those for the dichroism are  $< \pm 15\%$ . Chirping of the monitoring white light continuum was corrected. For all the systems examined in the present study, the irradiation at 532 nm corresponds to the selective excitation of the ground-state charge-transfer (CT) complexes formed between TCNB and benzocarbazolyl moieties. All the measurements were performed under O<sub>2</sub> free conditions at  $21 \pm 2$  °C.

## Results and Discussion

**Photoinduced Electron-Transfer Dynamics of the Monomer Model Systems in 1,2-Dichloroethane Solution.** Prior to the discussion on polymer systems, we present photoinduced electron-transfer dynamics of the monomer model systems as references. In Figure 2a are exhibited time-resolved transient absorption spectra of 7-ethylbenzo[*c*]carbazole (7EtBCz)–

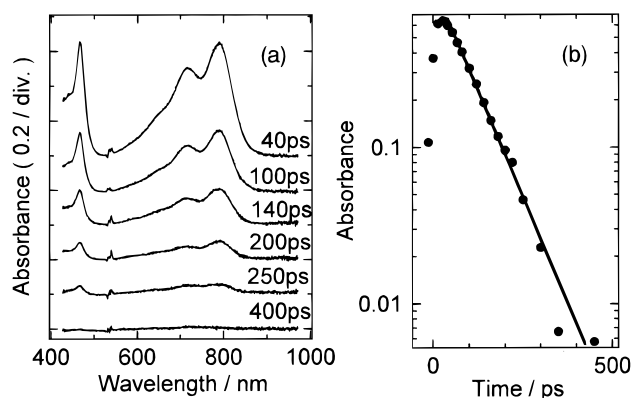
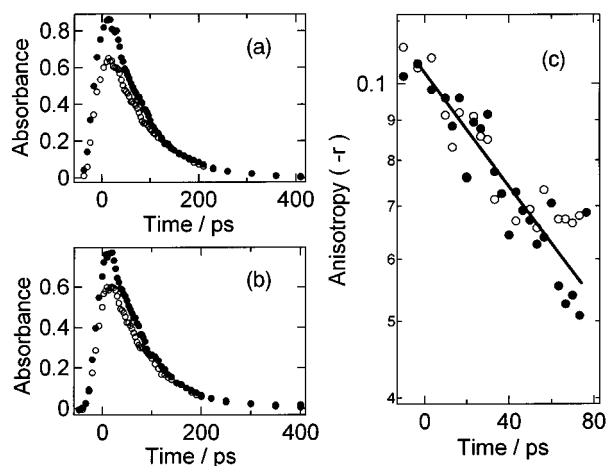


Figure 2. (a) Time-resolved transient absorption spectra of 7EtBCz (0.033 M)–TCNB (0.022 M) in 1,2-dichloroethane solution, excited with a picosecond 532 nm laser pulse. (b) Time profile of transient absorbance at 465 nm.

1,2,4,5-tetracyanobenzene (TCNB) in a 1,2-dichloroethane solution. A sharp absorption at 465 nm in each of the spectra is safely assigned to the anion radical of TCNB (TCNB<sup>•−</sup>) on the basis of the coincidence of the absorption maximum and its spectral band shape to those reported previously.<sup>20,21</sup> On the other hand, the absorption bands at 710 and 790 nm are ascribable to the cation radical of 7EtBCz (7EtBCz<sup>•+</sup>).<sup>22</sup> The time evolution of the spectra in Figure 2a indicates that the excitation of the CT absorption band results in the ion pair formation (charge separation, CS) in the excited state. The time constant for the rise of the ion pair (CS), monitored at 465 nm, was obtained to be 17 ps (not instantaneous).

According to femtosecond and picosecond laser photolysis studies on the photoinduced CS process of weak CT complexes in solutions,<sup>12,21,23</sup> it has been revealed for various donor (D)–acceptor (A) systems that the absorption spectra of the CS state immediately after the excitation of the CT band gradually evolve in time into rather sharp absorption bands with time constants of a few to a few tens of picoseconds. These time constants were dependent on the degree of the charge separation in the excited Franck–Condon state and the polarity of the solvent and were almost independent of the excitation wavelength in the CT band. In addition, the drastic decrease of the CT fluorescence was also observed in the time region. On the basis of these experimental results, these dynamic behaviors of the excited CT complex in the early stage after the excitation were interpreted as due to the conversion of the character of the excited CT complex into the pure ion pair state with the aid of the some small intracomplex geometrical change including the rearrangement of the surrounding solvents.<sup>12,21,23</sup> Also for the present 7EtBCz–TCNB system, it is strongly suggested that such a small intracomplex geometrical change took place. Anyhow, it can be concluded that the charge separation in the excited state occurs in the early stage after the excitation also in the 7EtBCz–TCNB system as reported for various CT complexes.

With an increase in the delay time after the excitation, the absorbance due to the ion pair gradually decreases as shown in Figure 2a. Since the relative ratio between the absorption intensity of the cation and that of the anion is constant during the decay process and no absorption was observed at and after ca. 1 ns following the excitation, almost all the deactivation of the ion pair was ascribed to the charge recombination (CR). Figure 2b exhibits the time dependence of the absorbance due to the ion pair monitored at 465 nm. The decay profile is well described as an exponential process with a time constant of 85 ps. The time constant of the CR in the present system was



**Figure 3.** Dependence of time profiles of transient absorbance of 7EtBCz (0.033 M)–TCNB (0.022 M) in 1,2-dichloroethane solution on the polarization of the monitoring light; monitored at 465 nm (TCNB<sup>−</sup>) (a) and at 790 nm (7EtBCz<sup>+</sup>) (b). The polarization of the monitoring light was parallel (open circles) with or perpendicular (closed circles) to that of the excitation light. (c) Time dependence of the anisotropy signals of TCNB<sup>−</sup> (closed circles) and 7EtBCz (open circles). Excitation wavelength was 532 nm (see text).

quantitatively in agreement with the global energy gap dependence of the CR rate obtained for the ion pairs produced via the excitation of the ground-state CT complex in various environments.<sup>24,25</sup>

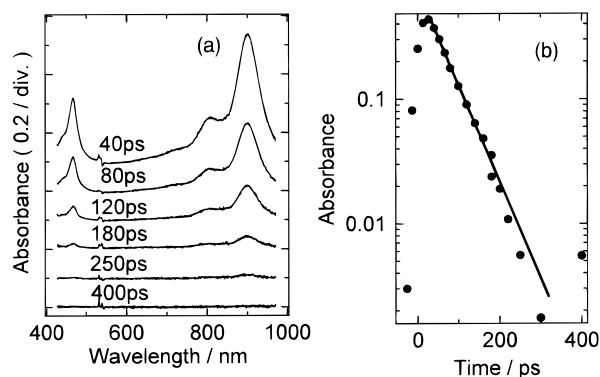
For the dynamic behaviors of transient ion pair states formed via the photoinduced CS process in solutions,<sup>12,23,24</sup> it has been established that the geminate ion pair produced in strongly polar solutions undergoes, in competition with the charge recombination, ionic dissociation with the aid of the thermal diffusive motion. For the present system in a 1,2-dichloroethane solution, the ionic dissociation rate constant was estimated to be  $\leq 10^8$  s<sup>−1</sup> by carefully observing the absorption signal remaining after the initial charge recombination decay. This value is much smaller than that in acetonitrile.<sup>12</sup> This small rate constant of the ionic dissociation is mainly ascribable to the low dielectric constant of the solvent ( $\epsilon = 10.4$  at 25 °C).

To obtain the information on the relaxation process of the configurations between the cation and the anion in the ion pair, the time evolution of the dichroism of the transient absorption was measured for 7EtBCz–TCNB in a 1,2-dichloroethane solution. In these experiments, the time dependence of the dichroism was measured by using the probe light whose polarization was perpendicular or parallel to that of the excitation light. Figure 3, parts a and b, shows the time profiles of the transient absorbance monitored at 465 nm (TCNB<sup>−</sup>) and at 800 nm (7EtBCz<sup>+</sup>), respectively. In both cases, the absorption intensities monitored with the probe pulse perpendicular to the excitation light were higher than those obtained with the parallel probe pulse. The reason for this result may be interpreted as follows. The direction of the CT absorption transition from the ground state is mainly from the donor (D) to the acceptor (A), while the strong absorption transitions of A<sup>−</sup> and D<sup>+</sup> are in parallel with  $\pi$ -planes of ions.

The time dependence of the anisotropy,  $r(t)$ , of the transient absorbance was calculated by the following equation:

$$r(t) = \{A_p(t) - A_s(t)\} / \{A_p(t) + 2A_s(t)\} \quad (1)$$

Here,  $A_p(t)$  and  $A_s(t)$  are the transient absorption intensities obtained by using the monitoring light pulses whose polarization were parallel and perpendicular, respectively. In the present case, the  $r(t)$  value is negative since  $A_s(t)$  values were higher



**Figure 4.** (a) Time-resolved transient absorption spectra of 5EtBCz (0.021 M)–TCNB (0.022 M) in 1,2-dichloroethane solution, excited with a picosecond 532 nm laser pulse. (b) Time profile of transient absorbance at 465 nm.

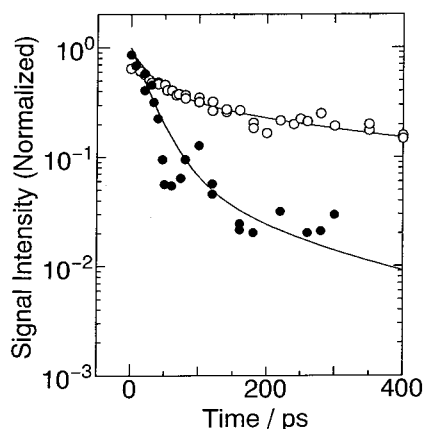
than the  $A_p(t)$  values. Hence,  $-r(t)$  was plotted against the delay time after the excitation in Figure 3c, where the decay profiles of the anisotropy signals for the anion and the cation are exhibited. The  $r(t)$  values for the anion and the cation around the time origin were ca.  $-0.15$ . This result implies that the direction of the CT transition moments is nearly perpendicular to that of the absorption of the ions. In addition, the decay profiles of the anisotropy signals for the anion and the cation are almost the same, indicating that the relative mutual orientation of two ions in the pair is maintained during the rotational relaxation process. From the slope of the decay profiles, the time constant of the rotational relaxation of the ion pair was obtained to be  $110 \pm 20$  ps.

Also for the 5-ethylbenzo[*b*]carbazole (5EtBCz)–TCNB system, the same measurements were applied. Figure 4a exhibits time-resolved transient absorption spectra of 5EtBCz–TCNB in a 1,2-dichloroethane solution excited with a picosecond 532 nm laser pulse. A sharp absorption at 465 nm is assigned to TCNB<sup>−</sup>. On the other hand, the absorption bands at 805 and 900 nm are ascribable to the cation radical of 5EtBCz (5EtBCz<sup>+</sup>).<sup>22</sup> The time evolution of the spectra in Figure 4a indicates that the excitation of the CT absorption band results in the ion pair formation (charge separation, CS) in the excited state.

With an increase in the delay time after the excitation, the absorbance due to the ion pair gradually decreases as shown in Figure 4a while keeping a constant ratio between the absorption intensity of the cation and that of the anion. As in the 7EtBCz–TCNB systems, no absorption was observed at and after ca. 1 ns after the excitation, indicating that almost all the deactivation of the ion pair was ascribed to the charge recombination (CR). Figure 4b exhibits the time dependence of the absorbance due to the ion pair monitored at 465 nm. The decay profile is well described as an exponential process with the time constant of 55 ps. Also in this system, the time constant of the CR in the present system was quantitatively in agreement with the global energy gap dependence of the CR rate.<sup>24,25</sup> In addition, the coincidence of the time constant for the rotational relaxation of the cation with that of the anion was also confirmed.

**Photoinduced Electron-Transfer Dynamics of Poly(vinylbenzocarbazole)–TCNB Systems in 1,2-Dichloroethane Solution.** Figure 5 shows the time-resolved transient absorption spectra of poly(5-vinylbenzo[*b*]carbazole) (P5VBCz)–TCNB in a 1,2-dichloroethane solution, excited with a picosecond 532 nm laser pulse. Each of the spectra shows two absorption maxima at 465 and ca. 820–880 nm. The former band at 465 nm is safely ascribed to TCNB<sup>−</sup>, as was mentioned in the interpretation of Figure 2. On the other hand, the latter





**Figure 6.** Time profiles of transient dichroism signals of P5VBCz–TCNB system in 1,2-dichloroethane solution, excited with a picosecond 532 nm laser pulse; monitored at 820 nm (BbCz<sup>+</sup>: closed circles) and at 465 nm (TCNB<sup>−</sup>: open circles). Solid lines are the results calculated on the basis of eq 3 and Scheme 1 (see text).

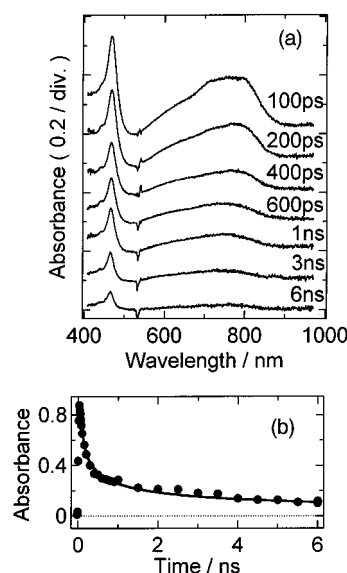
species and  $\tau_{DP}$  is the time constant for the dephasing process of the memory of the polarized excitation. In the actual measurement, we employed the heterodyned detection method as performed in previous works.<sup>15–18</sup> In this optical configuration, the analyzer polarizer was uncrossed slightly (< a few degrees) and the electric field  $E_{LO}$  is present in the absence of the pump pulse.  $I_{LO}$ , which is in proportion with  $E_{LO}^2$ , is adjusted to make the heterodyne term ( $E_{LO} \times E_S(t)$ ) much greater than  $I_S$  ( $\propto E_S(t)^2$ ). In this case, the transmitted light intensity is given by the following equation<sup>28,29</sup>

$$I_T(t) - I_{LO} \propto A(t) \exp(-t/\tau_{DP}) \quad (3)$$

where  $I_{LO}$  is the intensity transmitted in the absence of the pump pulse. The  $I_{LO}$  signal is removed by subtracting the transmitted intensity at delay time  $\ll 0$  ps from the observed signal  $I_T$ . In the heterodyned detection, much larger intensity of the signal can be obtained and the observed time profile arising from the dichroism is proportional to the signal electric field,  $E_S$ , while the signal intensity,  $I_S$ , scales quadratically with  $E_S$  in the homodyned detection.

Exhibited in Figure 6 are the time profiles of the transient dichroism monitored around 820 nm (BbCz<sup>+</sup>) and 465 nm (TCNB<sup>−</sup>). This figure clearly demonstrates that the memory of the polarized excitation in BbCz<sup>+</sup> decreases much faster than that of TCNB<sup>−</sup>, although the time constants for the dephasing process of the polarized excitation (rotational relaxation) of the cation and anion in the ion pair were identical with each other in the monomer model system. This result clearly indicates that the dephasing process of the polarized excitation in the cation includes some additional channels in the polymer system.

To quantitatively interpret the time evolution of the dichroism signals in the polymer system, the observed time profiles were analyzed on the basis of Scheme 1. In this calculation, the time profile of the population decay of the anion,  $A(t)$ , was set to be identical with that used for Figure 5; the time constants of the charge recombination and the hole transfer were the same as those used in the analysis of Figure 5. The solid line for the time profile of the anion in Figure 6 is the calculated result on the basis of eq 3 with  $\tau_{DP} = 1.5$  ns. The calculated result shown in Figure 6 reproduces the experimental results fairly well and indicates that the anion attached to the BbCz moiety in P5VBCz rotates with much longer time constant than that in the monomer model system. From the iterative simulation in the curve fitting procedure, the  $\tau_{DP}$  value for the anion was obtained to be  $1.5 \pm 0.2$  ns. On the motions of the aromatic vinyl polymer in

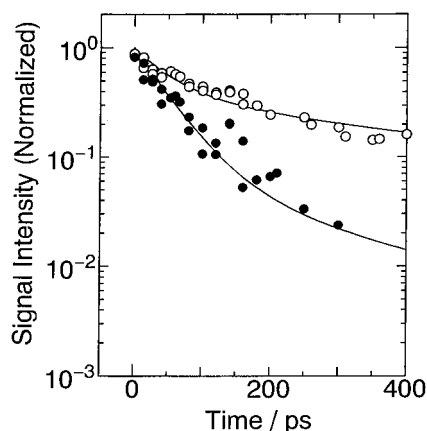


**Figure 7.** Time-resolved transient absorption spectra of P7VBCz ([BbCz] = 0.082 M)–TCNB (0.022 M) in 1,2-dichloroethane solution, excited with a picosecond 532 nm laser pulse. (b) Time profile of transient absorbance at 465 nm. The solid line is the calculated curve on the basis of Scheme 1 with  $k_{HT} = 3.1 \times 10^9$  s<sup>−1</sup> and  $k_{CR} = 1.2 \times 10^{10}$  s<sup>−1</sup> (see text).

fluid solutions, it has been reported that the local motions such as three-bond motion and crankshaft motion result in the conformational change of the pendent aromatic groups on the order of subnanoseconds–nanoseconds.<sup>30–32</sup> Hence, it is strongly suggested that the present time constant for the dichroism decay of TCNB<sup>−</sup> attached to the BbCz moiety in P5VBCz may be attributable to these local motions in the main chain of the polymer.

On the other hand, the solid line for the dichroism decay of the BbCz<sup>+</sup> is the result calculated for the time profile of  $D_0^+$  in Scheme 1. Namely, the population decay of the BbCz<sup>+</sup> which is directly connected to TCNB<sup>−</sup> (BbCz which formed the CT complex with TCNB in the ground state before the photoexcitation) is exhibited. Since the hole shift reaction to neighboring BbCz moieties existing in the polymer chain seems to diminish this memory, we examined the time profile of  $D_0^+$ . In the calculation, both the time constants of the charge recombination and the hole migration were respectively set to be the same with those used for the analysis of Figure 5. In addition, the local rotational relaxation time constant of 1.5 ns was also included. As shown in this figure, the calculated curve reproduces the experimental result for BbCz<sup>+</sup> fairly well, as for that in TCNB<sup>−</sup>. By integrating the present result on the dichroism decay with that of the transient absorption time profile in Figure 5, it can be concluded that the BbCz<sup>+</sup> initially produced via the excitation of the ground-state CT complex actually undergoes the hole migration to the neighboring neutral BbCz moieties with the time constant of 180 ps ( $k_{HT} = 5.6 \times 10^9$  s<sup>−1</sup>) as assumed in Scheme 1 and its memory of the polarized excitation decreases mainly via the hole shift reaction.

Also for the P7VBCz–TCNB system, similar measurements were employed. The time resolved–transient absorption spectra with the selective excitation of the ground-state CT complex at 532 nm are shown in Figure 7a. The absorption peaks at 465 and 700–800 nm are respectively ascribed to TCNB<sup>−</sup> and BbCz<sup>+</sup> from a comparison of the reference data.<sup>22</sup> The time profile of the charge-separated state monitored at 465 nm in Figure 7b indicates that the absorption signal appearing immediately after the excitation is followed by a decrease in the several hundred picosecond time region and a much slower one



**Figure 8.** Time profiles of transient dichroism signals of P7VBCz–TCNB system in 1,2-dichloroethane solution, excited with a picosecond 532 nm laser pulse; monitored at 780 nm ( $\text{BcCz}^+$ : closed circles) and at 465 nm ( $\text{TCNB}^-$ : open circles). Solid lines are the results calculated on the basis of eq 3 and Scheme 1 (see text).

**TABLE 1: Hole-Transfer Rate Constants ( $k_{\text{HT}}$ ) in Aromatic Vinyl Polymer–TCNB Systems in 1,2-dichloroethane Solution**

polymer <sup>a</sup>	$k_{\text{HT}}/\text{s}^{-1}$
P5VBCz	$5.6 \times 10^9$
P7VBCz	$3.1 \times 10^9$
PVCz	$2.0 \times 10^9$
P1VN	$3.0 \times 10^8$
P2VN	$1.3 \times 10^8$
PSt	$\leq 4 \times 10^7$

<sup>a</sup> P5VBCz, poly(5-vinylbenzo[*b*]carbazole); P7VBCz, poly(7-vinylbenzo[*c*]carbazole); PVCz, poly(*N*-vinylcarbazole); P1VN, poly(1-vinylnaphthalene); P2VN, poly(2-vinylnaphthalene); and PSt, polystyrene.

in the nanosecond region. The solid curve in this figure was the calculated result on the basis of Scheme 1. In the calculation, the charge recombination rate constant used for the calculation was set to be the same as that for the monomer model system,  $1.2 \times 10^{10} \text{ s}^{-1}$ . The calculated curve with  $k_{\text{HT}} = 3.1 \times 10^9 \text{ s}^{-1}$  reproduces the experimental results reasonably well.

Time profiles of the dichroism signals monitored at 465 nm ( $\text{TCNB}^-$ ) and at 780 nm ( $\text{BcCz}^+$ ) were exhibited in Figure 8. The solid line for  $\text{TCNB}^-$  is the curve calculated on the basis of Scheme 1 and eq 3 with the value of  $\tau_{\text{DP}}$  (1.5 ns). Also in this calculation, the time profile of the population decay of the anion,  $A(t)$ , was set to be identical with that used for Figure 7b. The calculated curve for the dichroism signal of  $\text{TCNB}^-$  reproduces the experimental result. Moreover, the calculated line for the cation which was obtained by the same procedure as in Figure 6 also reproduces reasonably well the experimental result of the  $\text{BcCz}^+$ .

In Table 1, the hole-transfer rate constants of P5VBCz and P7VBCz in 1,2-dichloroethane solutions are listed together with those of other aromatic vinyl polymers.<sup>16,18</sup> As briefly mentioned in the introductory section, the activation energy and the  $k_{\text{HT}}$  value for the reaction  $\text{A}^-\text{D}_0^+\text{D}_1 \rightarrow \text{A}^-\text{D}_0\text{D}_1^+$  are respectively estimated<sup>16</sup> to be  $\gg 10k_{\text{B}}T$  and on the order of  $10^5$ – $10^6 \text{ s}^{-1}$  even in the rather polar solution of 1,2-dichloroethane by the standard theory of the ET reaction assuming very weak interaction between the reactants.<sup>11</sup> As listed in Table 1,  $k_{\text{HT}}$  for PVCz is, however, on the order of  $10^9 \text{ s}^{-1}$ . Although the  $k_{\text{HT}}$  values in P1VN and P2VN systems are about 1 order smaller than those for the P5VBCz, P7VBCz, and PVCz systems, these are much larger than that predicted by the standard theories of ET. Rather, Table 1 suggests that the  $k_{\text{HT}}$  increases with an increase in the overlap between the neighboring two aromatic

groups. The difference in  $k_{\text{HT}}$  values between P1VN and P2VN and that between P7VBCz and P5VBCz also indicate clearly that the degree of the overlap between the neighboring aromatics plays an important role in the hole-transfer process. In addition, according to our preliminary studies on the hole migration process in polystyrene systems, a much smaller  $k_{\text{HT}}$  value than those of the P2VN systems was obtained. These results strongly suggest that the rather large electronic interaction between the cation and the neutral group plays an important role in the hole-transfer process. In fact, it was reported from the NMR investigation<sup>19a,b</sup> that the unusual upfield shift of an aromatic proton was observed in P5VBCz, P7VBCz, and PVCz systems, while such a shift was not detected in poly(vinylnaphthalene) systems.<sup>19c</sup> The upfield shift was interpreted as due to the strong influence of the ring current of the neighboring groups. In addition, the shifts in P5VBCz and P7VBCz systems were slightly larger than that in PVCz, suggesting that the degree of the overlap of the aromatic pendent groups was larger in P5VBCz and P7VBCz.

It should be pointed out here that the stable dimer cation resulting from large interaction, however, is usually regarded as the trapping site of the hole.<sup>10a</sup> In relation to this, it is worth mentioning that the effective dimer cation formation does not take place via the intermolecular interaction in 7-ethylbenzo[*c*]carbazole, 5-ethylbenzo[*b*]carbazole, or *N*-ethylcarbazole under usual conditions, while 1-ethylnaphthalene and 2-ethylnaphthalene form the intermolecular dimer radical cations easily in solutions.<sup>33,34</sup> These results indicate that the carbazolyl and benzocarbazolyl moieties intrinsically have small stabilization energies in the dimer cation formation, leading to an effective hole-transfer reaction. Also for comparison of the two PVN systems, the above discussion seems to be applicable. From the measurements of the charge resonance bands of the dimer cations in PVN and the dimer model systems,<sup>33</sup> it was reported that the stabilization energy of the dimer cation in P1VN is slightly smaller than that in P2VN owing to the increasing repulsive force in P1VN.

In relation to this, it should be also noticed that the hole transfer processes in the present benzocarbazolyl polymers as well as PVCz were faster than the conformational rearrangement of the local structures in the polymer chain as was indicated by the dichroism decay of the anion. Since the stable dimer cation formation requires the conformational rearrangement, it may be deduced that the hole can migrate prior to the stable dimer cation formation in the present case. These results also imply that molecular motion with large activation does not take a part in the rapid hole-transfer processes in P5VBCz, P7VBCz, and PVCz. Actually, according to our preliminary result<sup>36</sup> on the temperature effect on the  $k_{\text{HT}}$  in PVCz in 1,2-dichloroethane solution, it was found that the activation energy of the hole-transfer reaction was very small,  $\leq 2 \text{ kcal/mol}$ . On the other hand, in PVN systems, the hole-transfer rate constants were almost 10 times smaller than the time constant of the local conformational rearrangements ( $\tau = \text{ca. } 950 \text{ ps}$ )<sup>17</sup> in 1,2-dichloroethane. In such a case, the stable dimer cation formation taking place prior to the hole migration actually prohibited the hole migration.

Summarizing above results and discussion, it may be concluded that a rather large interaction between neighboring aromatics under the confined condition in the polymer has an effective role in the hole migration process, while the increase in the interaction leading to the stable dimer cation formation actually reduces the hole migration process. In analogy with the treatment of the interaction between the excited-state molecule and the ground-state one by Förster,<sup>35</sup> the interaction

between the cation and the neutral molecules may be classified into three cases: very strong interaction, weak interaction, and very weak interaction cases. The stable dimer cation formation is regarded as "the case of the strong interaction". On the other hand, the hole shift reaction to which usual theories of the ET is applicable may correspond to "the case of the very weak interaction". The interaction between two extreme cases may be responsible for the effective hole transfer in the present polymer systems, although details of this interaction are not clear at present.

From the viewpoint of the mechanisms underlying rapid hole migration, as we have discussed above, the simple hopping model based on the "intermolecular" electron-transfer reaction is not applicable to the hole-transfer reaction in these polymers with large aromatic groups. On the contribution from the local and transient band structure arising from the electronic interaction among aromatic groups in rapid migration, we are continuing the investigation covering various systems and the temperature effects on them, the results of which will be published soon.

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