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# Mechanisms of Formation and Deactivation of Extremely Long-Lived Charge-Separated State following Photoinduced Electron Transfer in Carbazolyl Polymers Coadsorbed with 1,2,4,5-Tetracyanobenzene on Macroreticular Resins

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At room temperature, extremely long-lived (> 8 h) charge-separated (CS) states following photoinduced electron transfer were found for poly(*N*-vinylcarbazole) (PVCz) coadsorbed with 1,2,4,5-tetracyanobenzene as an electron acceptor on a macroreticular resin, Amberlite XAD-8. The formation of the long-lived CS states was ascribed to both a hole-migration process along the polymer chain and a hole-trapping process resulting in the large interionic distance. The temperature dependence on the decay profiles of the long-lived CS states indicated that the charge recombination due to the long-distance electron tunneling was responsible for the disappearance of the CS states in the long time region. The simulation curve taking account of both the long-distance electron transfer and the distribution of the interionic distance reproduced the decay profiles of the CS states fairly well. The effects of both tacticity of PVCz and the modification of the adsorbents on the formation and the deactivation processes of the long-lived CS states were examined. The results revealed that the deep hole-trap sites resulting in the large interionic distance were not simply related to the carbazolyl dimer cation sites but to the carbazolyl moieties adsorbed in the vicinity of the polar ester groups in the adsorbent.

## Introduction

Photoinduced electron transfer (ET) and its related phenomena play fundamental and important roles in a number of chemical reactions in condensed phase.<sup>1–4</sup> One of the purposes of the investigations of the photoinduced ET processes is the fabrication of artificial molecular systems similar to the photosynthetic reaction center in plants. In the biological system, the electron released by the photoinduced charge separation is transported to the target position via charge-shift reactions, and the light energy is utilized efficiently for subsequent chemical reactions. Much effort has been devoted<sup>5,6</sup> to elucidate the efficient charge-transport mechanism and to develop covalently-linked molecular assemblies that provide complicated chromophore compositions similar to such photosynthetic pigments and their three-dimensional arrangements.

For the production of artificial molecular systems where both the long-distance charge transport and the formation of the long-lived charge-separated (CS) state are possible, it is intriguing to utilize photoconductive aromatic vinyl polymers, since the photoconductive properties are attributable to the sequential charge-shift reactions among the pendant chromophores. Along this line, we have investigated the photoinduced ET and its related processes in a typical photoconductive vinyl polymer, poly(*N*-vinylcarbazole) (PVCz), with electron acceptors.<sup>7–11</sup> Recently, we reported that the photoinduced CS state was observed even at 8 h after excitation at room temperature in the heterogeneous system where PVCz was coadsorbed with an electron acceptor on a macroreticular resin, Amberlite XAD-8.<sup>11</sup>

As mentioned above, since an increase in the interionic distance results in a decrease in the electronic tunneling matrix element for the charge recombination (CR), the effective charge

transport is indispensable for the formation of the long-lived CS state. In the PVCz chain, the effective hole migration via the carbazolyl groups along the chain may result in an increase in the interionic distance. It should be remarked, however, that such a long-lived CS state has never been observed for PVCz in solid films, solution, or other adsorbed systems.<sup>7–10</sup> In addition, since each of the polymer chains was adsorbed separately in the pore of the adsorbent, the ET processes were restricted in a finite space. Hence, it was deduced that the long interionic distance attained by the hole migration along the PVCz chain was fixed (the trap of the hole) by some special interaction between Cz moieties and the adsorbent surface.<sup>11</sup>

In the present work, in order to elucidate the origin of the trap site, we have investigated the influence both of the tacticity of PVCz and of the modification of the adsorbent on the formation and the deactivation processes of the long-lived CS states. On the basis of these results and the model calculation taking account of both the long-distance electron transfer and the distribution of the interionic distance, we have discussed the formation and the deactivation mechanisms of the long-lived CS states.

## Experimental Section

**Materials.** Figure 1 shows the molecular structures of compounds used. Two kinds of PVCz synthesized with different polymerization methods were used. PVCz prepared by the radical polymerization (PVCz(r)) (Takasago Koryo, Tuvicol-60,  $M_w = 10^5$ ) was purified by reprecipitation three times from benzene solution with methanol, followed by the fractional reprecipitation into two fractions with low- and high-molecular weight (low:high = 2:1). In the present experiment, the low-molecular weight PVCz(r) was used. In addition, PVCz prepared by the cationic polymerization (PVCz(c)) ( $M_n = 1.04 \times 10^5$ ,  $M_n/M_w = 1.60$ ) was also used.<sup>12</sup> PVCz has the following tacticity: Both PVCz(r) and PVCz(c) consist of stereoblock structures with syndiotactic and isotactic sequences, while the

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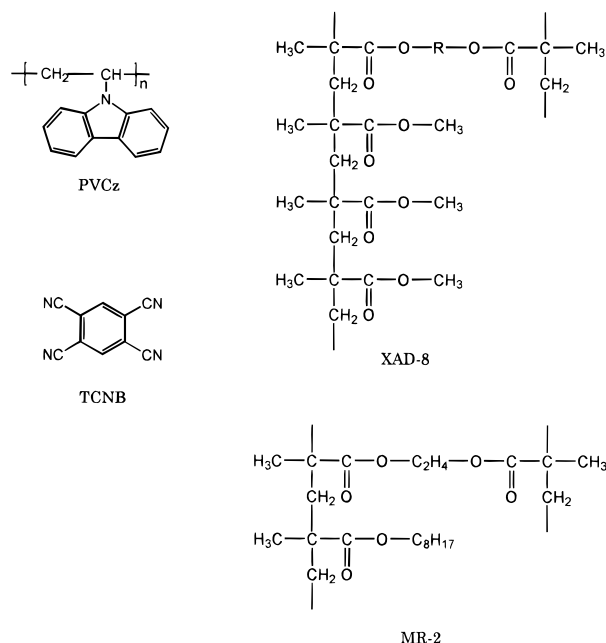


Figure 1. Molecular structures of compounds used in this study.

length of each of the sequences is long and short for PVCz(c) and PVCz(r), respectively. The fractions of the isotactic sequence were reported to be 0.50 for PVCz(c) and 0.25 and 0.31 for PVCz(r).<sup>12–14</sup> The relative contribution of the partial overlap excimer and the sandwich one to fluorescence spectra of PVCz is determined by these fractions; the sandwich excimer is formed only in the isotactic sequence. Actually, it was reported that the formation of the sandwich dimer cation was more rapid for the isotactic-rich PVCz(c) than for PVCz(r).<sup>15</sup> 1,2,4,5-Tetracyanobenzene (TCNB, Wako GR Grade) was recrystallized from ethanol and sublimated before use.

Acrylic macroreticular resin, Amberlite XAD-8 (Rohm & Haus, mean pore diameter = 225 Å, grain size = 250–850 μm), was washed with NaOH(aq) solution, HCl(aq) solution, deionized water, THF and methanol, and dried before use. The structure of XAD-8 is shown in Figure 1, where R is the alkyl chain (–CH<sub>2</sub>– or –CH<sub>2</sub>–CH<sub>2</sub>–). MR-2 (mean pore diameter = 100–200 Å, grain size = 10 μm) was prepared by multistep swelling and copolymerization method of ethylene dimethacrylate and octyl methacrylate,<sup>16,17</sup> and purified in the similar manner to the XAD-8. Although these two adsorbents have similar structures, MR-2 has long octyl groups instead of methyl groups of XAD-8.

Each polymer and TCNB were coadsorbed on the adsorbents in the following manner: A certain amount of adsorbent was put into a 1,2-dichloroethane solution of the polymer ([monomer unit] = 0.02 M) and TCNB (0.013 M), and the solution was kept at 30 °C for more than 24 h. Then, the adsorbents were taken out from the solution by filtration and dried under vacuum. The sample was contained in a quartz cell and degassed under high vacuum for 10 h. Since the pore radii of the adsorbents are almost the same as the radius of the gyration of the polymer (ca. 120 Å) in 1,2-dichloroethane solution, each polymer chain seems to be separately adsorbed on the adsorbent. Even if more than one chain is adsorbed in one pore, it should be remarked that the photoinduced ET reactions take place in a finite space.

**Apparatus.** Transient diffuse reflectance absorption spectra in picosecond time region were measured by using a microcomputer-controlled picosecond laser photolysis system with the third harmonic (355 nm, 15 ps, ca. 1 mJ/pulse) of a custom-built repetitive mode-locked Nd<sup>3+</sup>:YAG laser as an excitation source. The optical systems are almost the same as reported

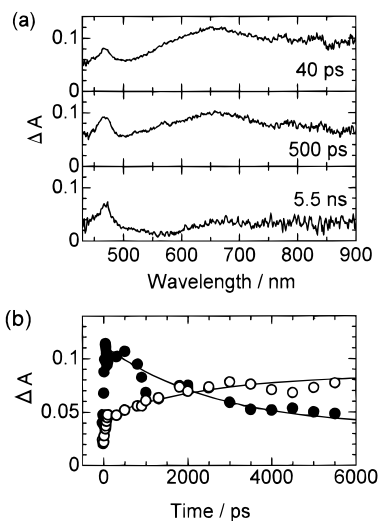


Figure 2. (a) Transient absorption spectra of the PVCz(r)-TCNB on XAD-8 system at 296 K, excited with a picosecond 355 nm laser pulse. (b) Time profiles of TCNB<sup>-</sup> (open circles) and Cz\* (closed circles), monitored at 465 and 660 nm, respectively.

previously.<sup>18</sup> Two sets of multichannel photodiode array combined with a polychromator were used for the detection of the monitoring light. For the measurements in the several tens of nanoseconds to several hours time region, a microcomputer-controlled nanosecond laser photolysis system with an excimer laser (351 nm, 20 ns fwhm, 11 mJ/cm<sup>2</sup>) as an excitation source was used. Monitoring lamps were a 150 W dc Xe lamp which was additionally pulsed for ca. 200 μs fwhm and Xe flash lamp of 1 μs fwhm.<sup>19</sup> The former was used for the measurement of the time profiles of the adsorption intensity in the 100 ns to 200 μs time region. The latter was used for the measurements of transient absorption spectra and their time profiles in time region above 1 μs. The absorption intensity (ΔA) was calculated by the following equation:

$$\Delta A(t) = (I_0 - I_e)/I_0 \quad (1)$$

where  $I_0$  and  $I_e$  are intensities of the diffuse reflected light without and with the excitation laser light, respectively.

All the measurements were performed under vacuum at 296 or 77 K. The spectral data were averaged over several measurements. In order to avoid the influence of the accumulated long-lived species, fresh surface of samples was prepared before each measurement.

## Results and Discussion

PVCz form a weak charge-transfer (CT) complex with TCNB in the ground state. Since the CT absorption was observed in the shorter wavelength region than ca. 540 nm, irradiation at 355 or 351 nm in the present experiment excites both noncomplexed PVCz and the CT complex.

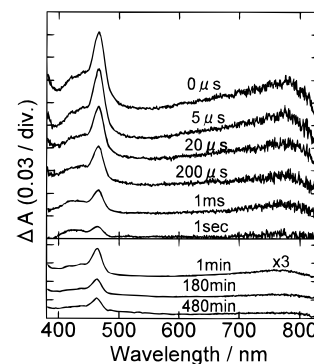
**Photoinduced Charge-Separation Processes As Revealed by a Picosecond Transient Absorption Spectroscopy.** As mentioned in our previous paper,<sup>11</sup> the CS state between PVCz(c) and TCNB adsorbed on XAD-8 was observed even at 8 h after excitation at room temperature. The similar long-lived CS state was observed for the PVCz(r)-TCNB system. Before discussing the formation and the deactivation processes of the long-lived CS state, we describe the photoinduced charge-separation process in the present XAD-8 system.

Figure 2a shows transient absorption spectra of the PVCz(r)-TCNB system excited with a picosecond 355 nm laser pulse. The spectrum observed immediately after excitation shows

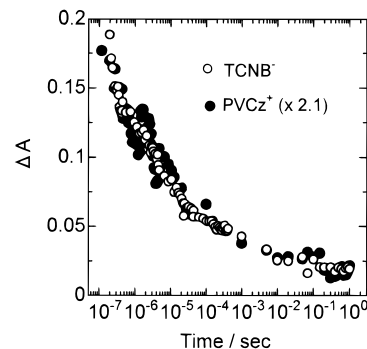
mainly TCNB anion ( $\text{TCNB}^-$ ) at 465 nm<sup>8,20,21</sup> and the excited singlet state of Cz moiety ( $\text{Cz}^*$ ) around 660 nm.<sup>22</sup> The absorption of PVCz cation ( $\text{PVCz}^+$ ) around 700–800 nm is not observed clearly because of overlap with the absorption of  $\text{Cz}^*$ . In the several nanoseconds time region, the absorption spectrum of  $\text{PVCz}^+$  is observed in addition to those of  $\text{TCNB}^-$  and  $\text{Cz}^*$ . Time profiles of the absorbance at 660 nm ( $\text{Cz}^*$ ) and 465 nm ( $\text{TCNB}^-$ ) as shown in Figure 2b. Since at 465 nm the strong absorption of  $\text{Cz}^*$  overlaps with that of  $\text{TCNB}^-$ , the contribution of  $\text{Cz}^*$  at 465 nm was subtracted after resolving each spectrum into two components of  $\text{Cz}^*$  and  $\text{TCNB}^-$ . The absorption of  $\text{TCNB}^-$  appears within the response time of the apparatus immediately after excitation and increases in the several nanoseconds time region. On the other hand, the absorption of  $\text{Cz}^*$  gradually decreases in the several nanoseconds time region. Since the picosecond laser excitation of CT absorption band of the PVCz–TCNB complex in solution,<sup>23</sup> films,<sup>8</sup> and other adsorbed system<sup>24</sup> results in the rapid formation of CS state being identical with the response of the apparatus. The rapid appearance of the ionic species (CS state) may be ascribed to the excitation of the ground-state CT complex. In addition, since each spectral data was averaged over 10 times at the same sample position with repetitive excitation of ca. 0.3 Hz, the accumulated signal of the long-lived CS state might be involved in the absorption of the CS state. The rise profile of  $\text{TCNB}^-$  in the several nanoseconds time region is, within the experimental error, in agreement with the decay one of  $\text{Cz}^*$ , indicating that the dynamic charge separation between  $\text{Cz}^*$  and TCNB, where  $\text{Cz}^*$  migrates among Cz moieties and encounters TCNB, is also responsible for the formation of the CS state. Hence, it is concluded that the charge-separation process in the present system takes place in the singlet manifold within the several nanoseconds time region.

**Role of the Dimer Cation in the Hole-Trapping Process in PVCz–TCNB Adsorbed on the XAD-8 System.** In our previous paper,<sup>11</sup> it was deduced that the long interionic distance attained by the hole migration along the PVCz chain was fixed (the trap of the hole) by some special interaction between Cz moieties and XAD-8. It is widely known that various dimer cations with different degree of the overlap of the Cz moieties are effectively formed in PVCz and that these dimer cation sites act as traps in the hole-transport processes.<sup>15</sup> For elucidating a relation between the dimer cations and the hole-trapping process resulting in the long-lived CS state, we have examined time profiles of the CS states for PVCz with different tacticity. As described in the Experimental Section, the concentration of the sandwich dimer cation sites is expected to be larger for the isotactic-rich PVCz(c) than for the syndiotactic-rich PVCz(r).<sup>15</sup> The difference in the tacticity between PVCz(r) and PVCz(c) is also reflected in the absorption spectra shape of  $\text{PVCz}^+$  (vide infra; Figure 8).

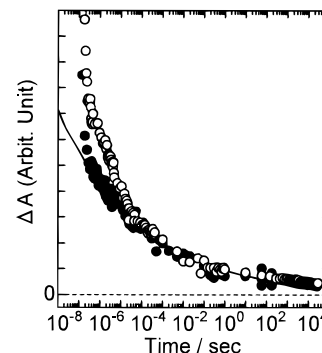
Figure 3 shows transient absorption spectra of the PVCz(r) system at and after 0  $\mu\text{s}$  at room temperature, excited with a 351 nm laser pulse. Each of the spectra indicates two absorption bands at 465 and 780 nm. The former and the latter bands are assigned to  $\text{TCNB}^-$  and  $\text{PVCz}^+$ , respectively, on the basis of their absorption peaks and band shapes.<sup>15</sup> As shown in Figure 4, the simultaneous decrease of the two absorption is observed in the time region from ca.  $10^{-7}$  to 1 s, indicating that the disappearance of ionic species in this time region is ascribed to the charge-recombination (CR) process. In the late time region above 1 min, however, the rate of the disappearance of  $\text{PVCz}^+$  was slightly large compared with that of  $\text{TCNB}^-$ , suggesting that a part of  $\text{PVCz}^+$  is likely to react with the adsorbent before recombining with  $\text{TCNB}^-$  in the late time region.<sup>25</sup> Although



**Figure 3.** Transient absorption spectra of the PVCz(r)–TCNB on XAD-8 system at 296 K, excited with a nanosecond 351 nm laser pulse.



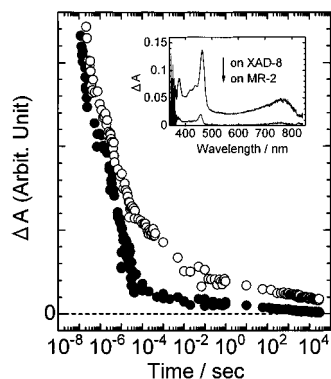
**Figure 4.** Decay profiles of  $\text{PVCz}^+$  (closed circles) and  $\text{TCNB}^-$  (open circles) of the PVCz(r)–TCNB system at 296 K, excited with a nanosecond 351 nm laser pulse.



**Figure 5.** Time profiles of the CS states of PVCz(r)–TCNB (open circles) and PVCz(c)–TCNB (closed circles) adsorbed on XAD-8, excited with a nanosecond 351 nm laser pulse and monitored at 465 nm ( $\text{TCNB}^-$  absorption). The solid line is the calculated value (see text).

a part of  $\text{PVCz}^+$  (less than 15%) disappears without recombination with  $\text{TCNB}^-$ , it is the fact that the absorption due to the CS state (ionic species) is observed even at 8 h after excitation at room temperature. The same results were observed for the PVCz(c) system, where the absorption of  $\text{PVCz}^+$  at 8 h after excitation was observed more clearly compared with the present PVCz(r) system because of its sharp absorption spectral shape.<sup>11</sup> The extremely long-lived CS states were also observed for poly-(5-vinylbenzo[*b*]carbazole) and poly(7-vinylbenzo[*c*]carbazole) coadsorbed with TCNB on XAD-8.<sup>26</sup>

Figure 5 shows a comparison of time profiles of the CS states between both PVCz systems, monitored at 465 nm ( $\text{TCNB}^-$ ). For quantitative comparison, both the ground-state absorption intensity at 351 nm and the intensity of the pump laser pulse were set to be almost the same between these two systems. The decay profiles at and after ca.  $10^{-5}$  s are almost identical with each other, although some difference is observed at the early stage. That is, the time profile of the CS state at and after



**Figure 6.** Time profiles of the CS states of PVCz(r)-TCNB adsorbed on XAD-8 (open circles) and MR-2 (closed circles), monitored at the TCNB<sup>-</sup> absorption band. Inset: the transient absorption spectra at 1 min.

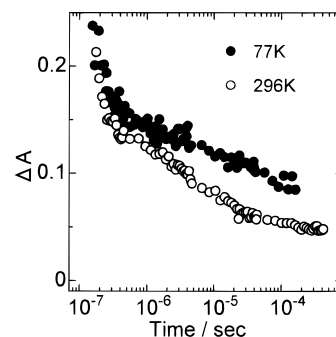
$10^{-5}$  s is independent of the tacticity of PVCz. This result indicates that the hole-trap site responsible for the formation of the extremely long-lived CS state cannot be simply ascribed to the dimer cation-forming sites in the PVCz chains.

#### Hole-Trap Sites Responsible for the Long-Lived CS State.

The above result suggests that the interaction between Cz moieties and the adsorbent plays an important role in the formation of the hole-trap site. In addition, when porous Vycor glass was used as an adsorbent under the condition that each polymer chain could be adsorbed separately, the CS state produced via the photoinduced ET between PVCz and TCNB completely disappeared within the submilliseconds time region.<sup>24</sup> The difference in the decay behavior of the CS state between the present XAD-8 and the Vycor glass systems suggests that the polar ester groups of XAD-8 play an important role in the hole-trapping process.

In order to elucidate the role of the ester groups in the formation of the deep trap site, we have investigated time profile of the CS state in PVCz(r)-TCNB adsorbed on MR-2. As shown in Figure 1, the MR-2 has long alkyl chains ( $-C_8H_{17}$ ). Since chemical attraction between PVCz and the alkyl chains is expected to be large, the number of Cz moieties adsorbed in the vicinity of ester groups is likely to be larger for XAD-8 than for MR-2. Figure 6 shows transient absorption spectra and time profiles of the CS state. For the comparison, the result of the PVCz(r)-XAD-8 system is also exhibited. Although the absorption bands assigned to PVCz<sup>+</sup> and TCNB<sup>-</sup> were observed also for the MR-2 system even at 1 min after excitation, the ratio of the long-lived CS state to the initial CS state is much smaller for the MR-2 system than for the XAD-8 one, indicating that the number of the deep hole-trap site resulting in the long-lived CS state is much smaller for the MR-2 system. This result combined with the chemical structure of MR-2 strongly suggests that the deep trap sites are the Cz moieties surrounded by the polar ester groups or adsorbed in the vicinity of them.

The presence of the Cz moieties in polar environments was also confirmed by the following experiments: The laser irradiation with high fluence on PVCz(r) adsorbed on XAD-8 and MR-2 produced PVCz<sup>+</sup> via a two-photon ionization process. Although almost the same amount of PVCz(r) was adsorbed on the XAD-8 and the MR-2 and the irradiation-laser fluences were also the same, the absorption intensity of PVCz<sup>+</sup> observed immediately after excitation was much larger for the XAD-8 system than for the MR-2 one. In general, the ionization energy,  $I_e$ , of molecules in condensed phase is represented by  $I_e = I_g + P_+ + V_0$ , where  $P_+$  is the polarization energy of the medium,  $I_g$  is the ionization potential in the gas phase, and  $V_0$  is the



**Figure 7.** Temperature dependence of the time profile of the CS state in the PVCz(r)-TCNB on XAD-8 system, monitored at the TCNB<sup>-</sup> absorption band.

conduction band energy in the condensed phase.<sup>27</sup> Provided that the  $V_0$  value is almost the same between both the adsorbents, the weaker absorption of Cz<sup>+</sup> observed for the MR-2 system suggests that the amount of Cz moieties in polar environments is smaller for the MR-2 system than for the XAD-8 one. That is, it is suggested that the "solvated" Cz moieties in polar environments are effectively formed in the XAD-8 system compared with the MR-2 one. Hence, it is concluded that the Cz moieties surrounded by ester groups of XAD-8 act as deep trap site to fix the large interionic distance.

**Analysis of the Deactivation Process of the Long-Lived CS State.** Here, we have analyzed the deactivation process of the CS state in the PVCz(r) and the PVCz(c)-XAD-8 systems where extremely long-lived CS states were observed clearly. The decay profile of TCNB<sup>-</sup> in the PVCz(r) system at 77 and 296 K is shown in Figure 7, where the absorption intensities at 465 nm are plotted against the logarithmic time. Although a decrease in the temperature increases the lifetime of the CS state to some extent, the temperature effect on the charge-recombination (CR) process in the late time region above  $5 \times 10^{-6}$  s is very small. The temperature dependence of the decay profile of TCNB<sup>-</sup> in the late time region above 10 s was also very small as observed for the PVCz(c) system.<sup>11</sup> That is, the CR process in the late time region has rather small activation energy, suggesting that the CR process in this time region is not regulated by the dynamic hole migration assisted by detrapping processes from the traps, but by the long-distance electron transfer.

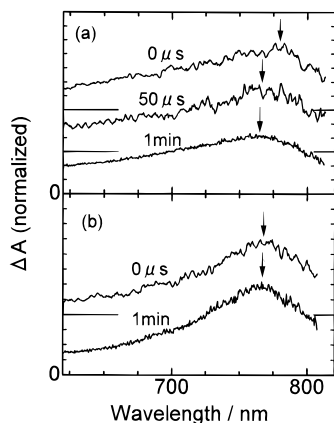
Considering that the disappearance of the CS state is ascribable to the long-distance electron transfer, we have performed simulation to analyze the decay profiles of the CS state. The solid line in Figure 5 is a curve calculated by the following equations:<sup>11</sup>

$$\Delta A(t) \propto \sum_i P(r_i) \exp[-k(r_i)t] \quad (2)$$

$$k(r_i) = k_0 \exp[-(r_i - r_0)/\alpha] \quad (3)$$

$$P(r_i) = P_0 \exp[-r_i/\beta] \quad (4)$$

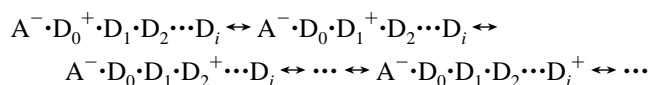
where  $\Delta A(t)$  is the absorption intensity at time  $t$  and  $k(r_i)$  is the distance-dependent CR rate constant. In the calculation,  $\alpha$  and  $k_0$  were set to be  $1 \text{ \AA}$  and  $10^9 \text{ s}^{-1}$ , respectively. Although the attenuating factor,  $\alpha$ , contains important information, it is rather difficult to determine it at the present stage. Hence, we used the average value obtained for the intermolecular electron-transfer processes in frozen media.<sup>1,28</sup> The  $k_0$  value of  $10^9 \text{ s}^{-1}$  is the CR rate constant of the ion pair state between *N*-ethylcarbazole and TCNB in nonpolar solutions.



**Figure 8.** Time dependence of the transient absorption spectra of  $\text{PVCz}^+$  in (a)  $\text{PVCz(r)}-\text{TCNB}$ , and (b)  $\text{PVCz(c)}-\text{TCNB}$ , adsorbed on XAD-8, excited with a nanosecond 351 nm laser pulse.

$P(r_i)$  represents the population of the CS states after the hole was trapped at the site with the interionic distance,  $r_i$ . According to Scheme 1, after the initial charge separation between  $\text{A}^-$  and  $\text{D}_0^+$ , the hole ( $\text{D}^+$ ) migrates along the polymer chain and is trapped at  $\text{D}_i$ . Here, on the assumption that the trapped hole cannot detrapp, the number of the hole trapped at  $\text{D}_i$  is proportional to  $p(1-p)^i$ , where  $p$  is the probability that  $\text{D}_i$  acts as the trap site.

#### SCHEME 1



In addition, on the assumption that the polymer is a one-dimensional chain, the interionic distance ( $r_i$ ) between  $\text{A}^-$  and  $\text{D}_i^+$  is represented by  $i \times r_{\text{av}} + r_0$ , where  $r_{\text{av}}$  and  $r_0$  are the averaged distance between neighboring Cz moieties and the distance between A and  $\text{D}_0$ , respectively. It should be noted that the actual polymer is not a one-dimensional chain but in fractal dimensions. However, the  $i$ th number of the ion pair undergoing the CR within the several seconds hours time region is smaller than ca. 8–10. Hence, we used the above simple one-dimensional approximation. In this approximation,  $\beta$  is represented by the following equation:

$$\beta = -r_{\text{av}} / \ln(1-p) \quad (5)$$

In the actual calculation, we used this  $p$  as a parameter, and other values were fixed. The result calculated with the  $\beta$  value corresponding to  $p = 0.22$  is shown in Figure 5. The calculated curve reproduces fairly well the experimental results for the  $\text{PVCz(c)}$  system in the time region from ca.  $10^{-8}$  to  $10^2$  s and those for the  $\text{PVCz(r)}$  system in the time region from ca.  $10^{-5}$  to  $10^2$  s. The deviation of the experimental points from the calculated curve observed in the time region above  $10^2$  s is likely to be ascribed to the disappearance of  $\text{PVCz}^+$  due to the reaction with XAD-8 aforementioned and/or deviation from the one-dimension approximation.

At the early stage, the deviation of the experimental points from the calculated curve is observed. The model used for the present simulation is based on the long-distance back electron transfer between  $\text{PVCz}^+$  and  $\text{TCNB}^-$  after the trapping of the hole completed, and other dynamic processes such as the hole migration resulting in the CR are not taken into account. Hence, the deviation at the early stage might be due to the CR between  $\text{TCNB}^-$  and mobile hole ( $\text{Cz}^+$ ) which has not yet been trapped. Figure 8a shows transient absorption spectra of  $\text{PVCz}^+$  for the

$\text{PVCz(r)}$  system, indicating that the spectral shape and position change with time, increasing to the several tens of microseconds time region. This spectral evolution should be attributable to the redistribution of the  $\text{PVCz}^+$  due to the hole migration along the polymer chain, because a large conformational change is not likely to take place in the present adsorbed system. In the time region where no spectral evolution was observed, the time profile of the CS state for the  $\text{PVCz(r)}$  system was in agreement with the calculated curve as shown in Figure 5. In addition, as shown in Figure 7, the rate of the disappearance of the ionic species at the early time region below  $10^{-5}$  s at 296 K is large compared with that at 77 K. These results strongly suggest that the deviation at the early stage is attributable to the CR process due to the dynamic hole migration along the polymer chain. For the  $\text{PVCz(c)}$  system, on the other hand, no time dependence of the absorption spectra of  $\text{PVCz}^+$  was observed in the time region examined, as shown in Figure 8b. In addition, the calculated curve in Figure 5 reproduces the experimental points for this system even at the earlier stage, suggesting that the hole migration in the  $\text{PVCz(c)}$  system completes at the earlier stage than in the  $\text{PVCz(r)}$  one.

Although the model used for the simulation is rather simple and the interpretation should be restricted in the qualitative manner, it is indicated that the difference in the dynamic hole-migration process before the hole trapping between  $\text{PVCz(r)}$  and  $\text{PVCz(c)}$  systems results in the difference in the dynamic CR behavior at the early stage. Although it is rather difficult to elucidate the origin of this difference in the hole-migration process between both  $\text{PVCz}$ , the population of the dimer cations acting as shallow traps may affect the dynamic hole-migration process. Actually, Figure 8 also indicates that there is the difference in the absorption spectral shape of  $\text{PVCz}^+$  between  $\text{PVCz(r)}$  and  $\text{PVCz(c)}$  even in the late time region where the decay profiles of the CS state coincide with each other.

#### Concluding Remarks

At room temperature, extremely long-lived ( $>8$  h) CS states were found for  $\text{PVCz}-\text{TCNB}$  coadsorbed with an electron acceptor on XAD-8. The photoinduced charge separation was due to the direct excitation of the ground-state CT complexes and/or electron transfer from the excited singlet state of Cz to TCNB. The deep trap site of the hole ( $\text{Cz}^+$ ) responsible for the extremely long-lived CS states was not attributable to the dimer cation sites in the polymer chains, but to the Cz moieties surrounded by polar ester groups of XAD-8. The formation of the long-lived CS states was due to the effective hole migration via the Cz moieties along the polymer chain and hole trapping resulting in the ion pairs with large interionic distances. The deactivation of the long-lived CS states was not regulated by the hole migration assisted by detrapping process of the hole, but by the long-distance back electron-transfer process with a small activation energy. The model calculation based on the above CR mechanism reproduced the experimental results fairly well.

Although the proportion of the long-lived CS state was rather small in the hours time regions compared with the initial amount of the CS state, the present result may provide the potential applicability for the control of the electron-transfer rate by heterogeneous microenvironments, in particular, the difference in the polarity in the vicinity of the ions. By the modification and/or the molecular design of adsorbents, the yield of the long-lived CS state may increase. Now, we are going on the investigations along this line, result of which will be published shortly.

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