Spatially Restricted Diffusion Process of Photogenerated Hole in Poly(*N*-vinylcarbazole) Film As Revealed by Transient Absorption Spectroscopy

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Charge recombination (CR) kinetics of photogenerated ionic species in poly(*N*-vinylcarbazole) (hereafter abbreviated as PVCz) film doped with an electron acceptor is investigated by transient absorption spectroscopy in the submicrosecond to millisecond time regime. Characteristic initial concentration dependence of the CR kinetics is observed and is qualitatively explained by a spatially restricted hole-diffusion-controlled CR model. From the temperature dependence of CR kinetics combined with a charge transfer (CT) fluorescence decay measurement, it is concluded that a CR with a long-range electron-transfer mechanism occurs under low-temperature conditions. Applicability of a 3-D random walk model in an energy disordered lattice to the CR kinetics is examined by means of a Monte Carlo simulation technique, and it is found that the spatial restriction condition is necessary to reproduce the CR kinetics in a PVCz film.

1. Introduction

Electronic dynamics in disordered systems have been a subject of investigation for more than a few decades. Typical topics in this field include molecular excitation transport in restricted geometries,[1] charge transport in amorphous organic[2] or inorganic[3] solids, and so on. These processes often show nonexponential long time behaviors which cover a wide time regime. Not only experimental but also many theoretical studies have been done, and especially investigations on random walk problems in fractal geometries helped in understanding these phenomena.[1,4] Meanwhile, photoinduced charge separation (CS) and subsequent CR in disordered system are also an important problem, though it has not received much attention. Especially, CR in disordered organic media is considered to be meaningful in relation to the understanding of electronic processes in biological systems. In organic solids, dynamics of charges and charged species are affected by the molecular nature, and thus, knowledge of electronic states of the charges as well as CR kinetics is necessary to understand the CR mechanism. Although most of the previous studies on the photogenerated charges in solids relied on photoconductivity measurements, this method is not capable of revealing the CR dynamics. Time-resolved CR emission measurement gives us some information on CR dynamics. However, from an emission property one cannot get a direct knowledge of the electronic state of charges and the mechanism of CR. On the other hand, transient absorption spectroscopy is well-known as a powerful method to elucidate not only CR kinetics but also their electronic states, and indeed this method has contributed to the increased understanding of photoinduced CS and CR in homogeneous solution. This method is expected to be very useful also for the disordered solid systems.

From these points of view, we have studied CR of photogenerated ions in PVCz films doped with an electron acceptor by transient absorption spectroscopy.[5−7] One reason PVCz is suitable for this investigation is as follows. On the application of transient absorption spectroscopy to disordered solids, it is desirable that photophysical properties and spectroscopic data on the component molecules of the solids are available. As for PVCz, its photophysical properties have been investigated

extensively: steady state[8] and transient[9] luminescence in solution and in film state, transient absorption spectroscopy of a single chain in solution[10−12] and adsorbed on cellulose substrate[13] and on macroreticular resin,[14] and so on. Fluorescence measurements revealed that excimer formation between adjacent carbazole choromophores plays a dominant role in their photophysics and that there exist partial overlap and sandwich excimers which brought about different emission spectra.[8] The overlapping structure dependence of interchromophore interaction in various electronic states such as excited singlet, triplet, cationic, and anionic was studied on dicarbazolyl model compounds with various interchromophore geometries.[15] Especially, geometry-dependent dimer cation formation was identified clearly by absorption spectra.[15]

Another reason for our choice of this material is that PVCz film is a representative photoconductor whose charge generation and charge transporting properties have attracted much attention.[16,17] Steady state and time-of-flight photocurrent measurements have been done in detail, and the mechanism of charge generation and conduction has been discussed. As for the photoinduced charge generation, extrinsic charge separation between the excited state of a carbazole choromophore and a doped electron acceptor compound is important.[17] The PVCz film is a hole photoconductor, and the electronic state of the hole is considered to be close to that of carbazole radical cation, which may be delocarized over some chromophores.[15,18] The hole transporting process is considered to be a sequence of incoherent hole hopping between adjacent carbazole chromophores. Time profiles of the transient currents show very slow decay which are fitted with power law functions and indicate a trap-controlled hopping.[16] To explain this conduction, some physical models are presented such as the multiple trapping model,[19] hopping in exponential distribution of energy,[20] and so on. From the chemical point of view, the molecular nature of the trap sites or barrier for the hole hopping we are interested in and the importance of the dimer cation site as the hole trapping site have been pointed out.[21] Transient absorption study would provide information on the sites, which control the hole hopping, from the viewpoints of molecular science.

There have been several reports on photoinduced CS and CR in PVCz films doped with electron acceptor by time-resolved absorption measurements.[5−7,22,23] Here we summarize the

findings so far obtained. On the CS process, a picosecond transient dichroism measurement has been revealed, that after the photoinduced CS between carbazole and an electron acceptor, a hole shift away from the acceptor anion occurs in ca. 2 ns.[22] This hole shift occurs considerably slower than that had been suggested in former model[17] in which the ion pair formation with several sites interionic separation was assumed to occur competing with vibrational relaxation (which occurs on the order of picoseconds). In our previous paper, we have reported on CR and hole scavenging dynamics in PVCz film doped with a hole scavenger molecule by picosecond transient absorption spectroscopy.[23] Anomalous hole scavenging kinetics in the nanosecond time regime were observed, and by analyzing the hole scavenging yield it was concluded that the hole migration region is strongly restricted in several sites from its initial position.[23] Besides, a hole hopping model on an energy disordered 3-D lattice, which is first introduced to interpret a hole conduction in molecularly dispersed conducting polymers,[24] was examined by a Monte Calro simulation, and the observed CR kinetics and the hole scavenging kinetics were explained by the model.[23] From the simulation results, it was also discovered that the presence of the energy disorder in the medium was a necessary condition for a hole migration escaping a Coulomb attraction from anion.[23] In another report, we have also done transient absorption measurement in the micro- to millisecond time regime and found that the CR kinetics appeared to be proportional to $t^{-0.5}$ in this time regime.[7] Combined with a transient CT emission measurement, it was concluded that the CR is hole-diffusion-controlled, and under the condition of the ionic concentration less than 1×10^3 M at 2 μs after excitation, a geminate CR occurs.[7] To extend the understanding of the CR mechanism, a description of the hole diffusion behavior which brings about the $t^{-0.5}$ decay kinetics observed in later than microsecond time regime[7] is necessary. Besides, the applicability of the random walk model in the energy disordered 3-D lattice, which was capable of reproducing the CR in the nanosecond regime,[23] to the CR in later than submicrosecond time regime has not been confirmed.

In this report, we focus our attention on the CR in micro- and millisecond time region of PVCz film doped with 1,2,4,5-tetracyanobenzene (TCNB) as an electron acceptor. We study the initial concentration dependence of the CR kinetics in this time regime. The observed feature indicates a spatially restricted manner of the hole diffusion. We also examine the temperature dependence of the CR kinetics in this time regime and find that a CR by a long-range electron transfer, which can be neglected at room temperature, occurs under low-temperature conditions. We conduct a Monte Carlo simulation of CR kinetics from picosecond to millisecond time regime and examine the applicability of the random walk model in energy disordered 3-D lattice to the kinetics over the wide time regime. As a result, it is found that a spatial restriction condition is additionally essential to reproduce the observed CR kinetics later than the submicrosecond time regime.

2. Experimental Section

Transient absorption spectroscopy at room temperature was performed in the same manner as described in our previous papers.[6,7,23] The excitation light was a XeCl excimer laser pulse (Lambda Physik EMG201SMC, fwhm 25 ns or Lextra 200, fwhm 15 ns, 351 nm) or the second (532 nm) or the third (355 nm) harmonics of a Nd[3+]:YAG laser pulse (JK laser HY750, fwhm 8 ns). On the measurement in the submicro- to microsecond time regime, a 150 W dc Xe lamp (Wacom KXL-150F), which was additionally pulsed for ca. 200 μs in fwhm
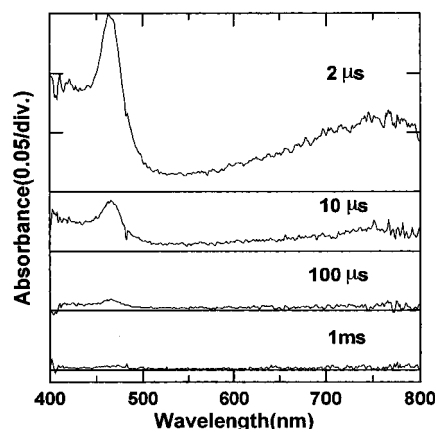
Figure 1. Transient absorption spectra of PVCz films doped with 2 mol % TCNB. The excitation wavelength was 351 nm. The delay times are indicated in the figure.

by a homemade circuit, was used as a probe light source. The probe light was detected by a streak camera (Hamamatsu C2830) equipped with a slow streak unit (Hamamatsu M2548) and a CCD camera (Hamamatsu C3141). On the other hand, in the micro- to millisecond time regime, a pulsed Xe lamp (Hamamatsu L2187, fwhm 1 μs) was used as a probe light source. The delay time between the probe and the pump pulses was stepped by a delay circuit, and the probe light spectra were monitored by a multichannel photodiode array (Otsuka Electronics IMUC-7000). The measurement was done under the multiple reflection condition which was described in our previous paper.[6,7]

For the temperature dependence study of the transient absorption, the second harmonics (532 nm) of the Nd[3+]:YAG laser light was used for the excitation, and the optical setup was a conventional one-path configuration. The temperature was controlled by flowing a vapor of liquid N_2 into a Dewar. The sample film was enclosed in a quartz cell and degassed.

In the case of a transient fluorescence measurement at low temperature, the sample temperature was controlled with the same manner as mentioned above. The excitation wavelength was 351 nm, and the emission was detected with the time-gated multichannel photodiode array (Otsuka Electronics IMUC-7000) with a gate width of 5−10 μs.

PVCz (Takasago International Corp.) was reprecipitated three times from a benzene−methanol solution. TCNB (Wako, Special Grade) was recrystalized from ethanol. TCNB was doped as an electron acceptor, and the doping concentration was 2 mol % PVCz chromophore. For the excitation at 351 nm, sample films were prepared with a spin-coating method, which was described previously,[7,23] and the sample thickness were ca. 1 μm. In the case of 532 nm excitation, sample films were cast from 1,2-dichloroethane solution, and its thickness was 10−40 μm.

3. Results and Discussion

A. Transient Absorption Spectra. Figure 1 shows the transient absorption spectra of PVCz film doped with 2 mol % TCNB, with 351 nm excitation, which have been reported previously.[6,7] TCNB forms a CT complex with PVCz in the ground state, and it has been confirmed that the photoinduced CS occurs by the excitation of carbazole chromophore or the CT complex.[6,7] The observed features in Figure 1 are safely ascribed to the absorption of the TCNB anion (465 nm) and hole (PVCz cation) (600−800 nm).[6,7] The hole absorption spectrum is very similar to that of cation state of PVCz single chain in solution.[12,15] Studies on the carbazole oligomers revealed that the absorption spectra of their cation states were
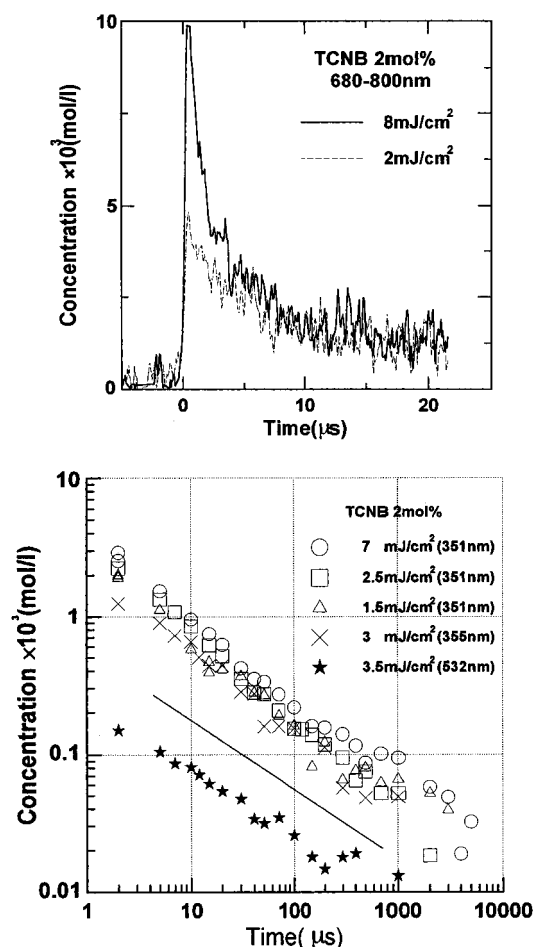
Figure 2. Initial ionic concentration dependence of the CR kinetics in various time regimes. Part a is to 20 μs, and part b is from microsecond to millisecond time regime. In part a, the excitation wavelength was 351 nm. In part b, the excitation wavelength is indicated in the figure. The excitation powers are indicated in the figures. The observation wavelength is (a) 680−800 and (b) 460−470 nm.

independent of the number of chromophores if it was more than 4.[15] The cation spectra of single-chain PVCz and the carbazole oligomers in solution are considered to be a composition of the spectra of various dimer cation or more delocarized (trimer or tetramer) cation states.[15,18] From the similarity of the absorption spectra, the PVCz cation state is considered not to be so delocalized in film state as compared to in solution. The exact degree of delocalization of the cation state in film is still unclear.

No significant dependence on the initial concentration of ions and temperature was observed in the absorption spectral shape, under the condition discussed below. It has been reported that the dimer cation spectra depend on the overlapping between adjacent chromophores.[15] PVCz prepared by radical polymerization and cation polymerization shows different cation spectra in solution, owing to the difference in the distribution of sandwich and partial overlapping dimer cations.[12] If such a distribution of the electronic state of the hole in film changes with the ion concentration or temperature, some spectral change would be expected. However, the absence of such an effect indicates that the distribution of the electronic states of cation state is not affected severely by initial hole concentration and temperature under these conditions.

B. Initial Concentration Dependence of the CR Kinetics. Figure 2a shows the excitation power dependence of the decay kinetics of ionic species in the microsecond regime. The peak concentrations of the ions saturate at the excitation power around 8 mJ/cm², and the maximum peak concentration of the ion was

0.03 M. The ion concentration was estimated by the absorbance with the same manner as previously reported.[7] Several microseconds after excitation, the decay kinetics became rather faster at high excitation energy, which means that the bulk recombination, a CR with ions that are not the counterions of the CS, occurs at high ionic concentration. However, later than 20 μs after excitation, the kinetics at different excitation energy are similar to each other, and this is apparent in Figure 2b in which the decay kinetics to several milliseconds under various initial concentrations are plotted. The molar extinction coefficient of the film at 355 and 532 nm are about 1/2 and 1/100 of that at 351 nm, respectively. The initial concentration was varied by changing the excitation power and the excitation wavelength. At later than 20 μs after photoexcitation, the decay curves show the kinetics proportional to $t^{-0.5}$, which corresponds to the kinetics of a geminate CR.[7] As for CR processes in homogeneous solution, once the diffusion length of the mobile charges exceeds the mean interionic (ion-pair) distance, CR kinetics obeys normal second-order reaction and t^{-1} time dependence appears in later time. The initial concentration dependence observed in the PVCz film is a case different from such a normal second-order kinetics.

The observed kinetics change around 20 μs after excitation is qualitatively interpreted by the context of the spatially restricted hole diffusion, which was claimed in our previous paper.[23] By analyzing the hole scavenging yields, the region in which holes can migrate is estimated to be only several sites (carbazole chromophores) away from the initial position.[23] The initial concentration dependent kinetics reported in this study appears under the excitation power of more than 2 mJ/cm² at 351 nm, where the initial concentration is more than 0.01 M and the mean inter-ion-pair distance is less than 60−70 Å. This critical dimension is close to that of the hole migration region, several sites, proposed in our previous paper.[23] Therefore, explanation of the kinetics observed at high initial concentration goes as follows. Since initial ion-pairs distribute at random, there may exist a pair which contains other ion-pairs within its hole migration region at high concentration. In such a region, bulk CR may occurs and the decay kinetics becomes faster. Meanwhile, there also exist pairs which are isolated from other pairs, and these are recombine with the same manner as under the lower concentration condition ($t^{-0.5}$ decay).[7] The actual decay curves will be a combination of these features, and the observed kinetics change at around a few tens of microseconds under the high-concentration condition is qualitatively explained by this model.

C. Temperature Dependence of the CR Process. Figure 3 shows the hole decay kinetics in PVCz film doped with 2 mol % TCNB at various temperature. At low temperature, the ionic decay kinetics becomes slower. It is well-known that PVCz film doped with TCNB brings about broad CT fluorescence around 500−800 nm.[9] Figure 3 also shows decay kinetics of the CT fluorescence intensity at 143 K. In our previous report, the CT fluorescence decay kinetics at room temperature is found out to be proportional to $t^{-1.5}$, which is also proportional to the derivative of the kinetics of the ionic species.[7] The lifetime of the excited state of the CT complex is considered to be on the order of nanoseconds,[22] which is very short as compared to the decay time of ions. If all the CR occurs via a formation of a contact CT complex, the intensity of CT fluorescence radiated during a certain period should be proportional to the number of the ions which disappears during the same period, and the derivative of the decay curve of ions corresponds to the decay of the fluorescence intensity. Thus, at room temperature, ions recombine via the CT complex state
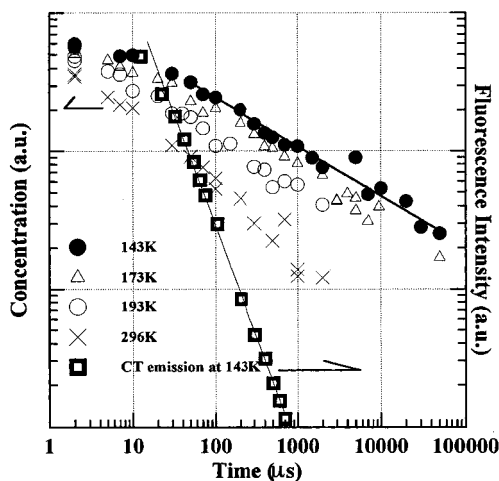
Figure 3. Temperature dependence of the decay kinetics of the absorption of TCNB anion (455−475 nm). The temperatures are indicated in the figure. Decay kinetics of the CT fluorescence at 143 K is also plotted with squares. The observation wavelength is 500−800 nm. The solid and broken lines are guides to eye, and their slopes are −1.66 and −0.33, respectively.

and the rate-determining step of the CR is the encounter of the hole and the anion, i.e., the CR is hole-diffusion-controlled.[7] At low temperature, the slope of the ionic decay later than 50 μs is ca. −0.36 in log−log scale (broken line in Figure 3). If the CR is a hole-diffusion-controlled one, the slope of the fluorescence decay should be −1.36, though the actual slope of the fluorescence decay curve in Figure 3 later than 50 μs is −1.66 (broken line). The fluorescence decay kinetics becomes faster than the derivative of the ionic decay kinetics, which means that a new CR without CT fluorescence occurs at this temperature. This is ascribed to a long-range electron transfer between a hole and anion which are separated more than adjacent contact position.

D. A Monte Carlo Simulation of CR Process. *Simulation Procedure.* At room temperature, when the ionic concentration is low enough, less than 0.001 M at 2 μs after excitation, the decay kinetics appears to be proportional to $t^{-0.5}$ from microseconds to milliseconds, which is reported previously.[7] As mentioned above, the CR which cause this $t^{-0.5}$ law is considered as a hole-diffusion-controlled one, but the description of the hole diffusion manner is still under debate. It is known that diffusion-controlled CR in 3-D shows $t^{-0.5}$ kinetics and that geminate recombination kinetics by 1-D random walk is also well approximated by $t^{-0.5}$.[7] However, these models in homogeneous media are not applicable to PVCz as has been pointed out by us.[23] On the other hand, Bässler et al. reported on a Monte Carlo simulation study on a diffusion-controlled CR in an energy-disordered 3-D lattice and revealed that the CR kinetics shows a power law decay.[25] They claimed that the distribution of the each site energy mainly originates from the inhomogeneity of the charge-dipole and/or charge-induced dipole interaction between the ionic site and its environments.[26] They assumed a Gaussian function for the distribution of this site energy.[25] In case of 0.1 eV Gaussian width, the time dependence of the CR rate was found to be proportional to $t^{-1.3}$, and this will lead to a decay of ions to be $t^{-0.3}$.[25] It is difficult to compare the simulation results with our experiment, because the decay kinetics depends on many parameters: the Gaussian width, the CR rate at contact position, the preexponential factor of the electron-transfer rate, initial separation of the ion pair, and so on. Thus, we conducted the Monte Carlo simulation of the CR in PVCz film following the procedure used by Bässler

et al.[25] and examined the applicability of the energy disorder model.

The simulation procedure is given below.

(A) Set an energy distribution of each site in a 50 × 50 × 50 space whose lattice constant is 6 Å. The anion is located at the center of the space, (25,25,25), and is fixed during the calculation. The energy distribution is proportional to a Gaussian function.

$$P(E_i) = (2\pi\sigma^2)^{-1/2} \exp(-E_i^2/2\sigma^2) \tag{1}$$

where E_i is the energy of site i and σ is the Gaussian width.

(B) A hole hopping rate from site i to site j, k_j, is calculated by

$$k_j = k_0 \exp(-R/a) \exp(-\Delta G^{\ddagger}/k_B T) \tag{2}$$

where $\Delta G^{\ddagger}$ is the activation energy for the ET, R is the distance between the two sites, and a is a parameter which was assumed to be 1 Å. When we put k' as

$$k' = k_0 \exp(-6 \text{ Å}/a) \tag{3}$$

k' is the rate constant between the nearest-neighbor sites when $\Delta G^{\ddagger}$ equals zero. According to the Marcus theory,[27] $\Delta G^{\ddagger}$ is given by

$$\Delta G^{\ddagger} = (\Delta G_0 + \lambda)^2/4\lambda \tag{4}$$

where ΔG_0 is the difference in Gibbs energy between the reactant and the product, and λ is the reorganization energy. ΔG_0 is given by

$$\Delta G_0 = E_i - E_j - U_i + U_j \tag{5}$$

where i and j are initial and final position of the hole on this hopping, E_i and U_i are the random site energy and the Coulombic potential energy due to the counteranion at site i, respectively.

(C) The site to which a hopping occurs (the hopping site) is determined with a probability that is proportional to $k_j/\Sigma k_j$. The summation is over 124 sites contained in a 5 × 5 × 5 cube, which are neighboring to the initial hole position on this hopping. The hopping site is chosen among these 124 sites. If the anion site is contained in the 124 sites, k_j to this site is replaced by the CR rate, k_{CR}, and a CR occurs with a probability which is proportional to $k_{CR}/\Sigma k_j$. k_{CR} was set to be 3×10^8 s^{-1} at contact position as used in our previous report,[23] and if the hole is not at the vicinity of the anion, k_{CR} is multiplied by the distance-dependent factor, $\exp(-R/a)/\exp(-6 \text{ Å}/a)$, where R is the distance between the hole and anion. The hopping time t is determined with the probability which is proportional to an exponential function, $\exp(-t/\Sigma k_j)$.

(D) The hopping times are accumulated, and the calculation is continued until the total time exceeds 5 ms or a CR occurs. The temporal evolution of the survival number of the holes and the spatial distribution of the holes were recorded. Results were accumulated for 2000 different ion pairs, and the random energy of each site is reset for every ion pair.

k_0 and λ are assumed to be the same at all sites. k' is considered to be less than 10^{12} s^{-1} in this type of ET reaction. λ is considered to be less than 0.20 eV from the evaluation of the stabilization energy of the cationic state by the measurement of Stokes shift of excimer sites in PVCz film.[26] The Gaussian width σ is considered to be an order of 0.1 eV from the inhomogeneous line width of the ground-state absorption spectra of the PVCz film.[26]

Photogenerated Hole in PVCz Film

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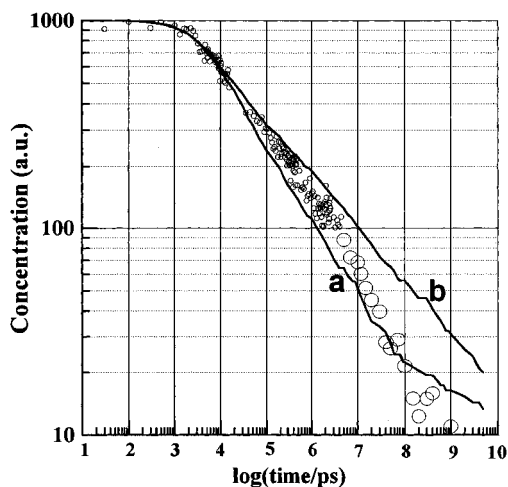
Figure 4. Monte Carlo simulation results of the CR kinetics in a 50 × 50 × 50 lattice. The used parameters are (a) $\sigma = 0.25$ eV, $\lambda = 0.05$ eV, and $k' = 3 \times 10^{11}$ s^{-1}, (b) $\sigma = 0.3$ eV, $\lambda = 0.10$ eV, and $k' = 3 \times 10^{11}$ s^{-1}. Open circles are experimental result of the decay kinetics of ions. The excitation wavelength is 532 nm.
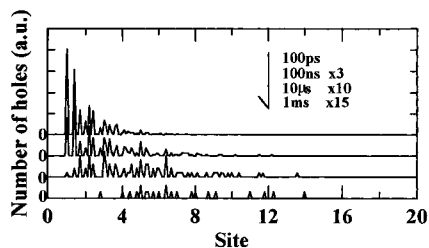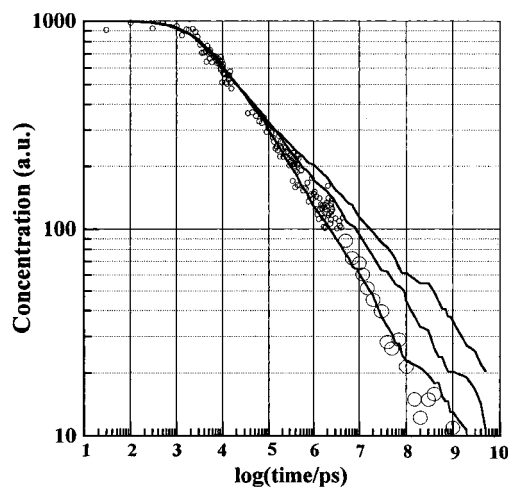

Figure 5. Monte Carlo simulation result of the distribution of the hole–anion distance at various delay times in the case of curve b in Figure 4.

Simulation Without Spatial Restriction. Simulation results are plotted in Figure 4, together with experimental results of the decay kinetics of ions from the subnano- to millisecond time regime. The experimental data in subnano- to nanosecond region is obtained by picosecond transient absorption spectroscopy, which has been reported in ref 23. These experimental results are obtained with 532 nm excitation and the concentration-dependent bulk CR effect discussed in section 3B can be ignored.

Simulation results (curves a and b) shown in Figure 4 is those obtained with parameters that were determined to reproduce the experimental results to 15 ns. We have examined the change of the kinetics in the ranges 0 eV < σ < 0.5 eV, 0.05 eV < λ < 0.15 eV, and 10^{11} s^{-1} < k' < 10^{12} s^{-1} and found that more than one parameter set is suitable. Curves a and b are examples of the simulation results. They reproduce the decay kinetics to 15 ns well, and with the same parameters, the hole scavenging kinetics to 15 ns reported previously[23] are also reproduced. Contrary to the agreement in nanosecond time regime, curves a and b deviate from the experimental result later than 15 ns. Figure 5 shows the distribution function of the distance between a hole and anion at various delay time in the case of (b). Later than microseconds, almost half of the surviving holes have migrated more than five sites away from the anion, and these holes contribute to the slow component in the simulation results.

Simulation with Spatial Restriction. The temporal evolution of the hole distribution in Figure 5 indicates that our 3-D random walk model with a Gaussian energy disorder is inadequate to reproduce the spatial restricted manner of the hole diffusion which is discussed in Section 3B. The critical interionic distance for the kinetics change from a geminate CR to a bulk is 60−70 Å, ca. 10 sites. Therefore, the hole migration may be restricted

Figure 6. Monte Carlo simulation results of the CR kinetics under the spatially restricted condition. Solid curves: the radius of the hole migration region is 25 sites, 6 sites, and 5 sites, from the slower one to faster one, respectively. The parameters are $\sigma = 0.3$ eV, $\lambda = 0.10$ eV, and $k' = 3 \times 10^{11}$ s^{-1}. Open circles are experimental result of the decay kinetics of ions. The excitation wavelength is 532 nm.

within such a dimension. An additional condition seems to be necessary in our simulation, and we further introduced a spatial restriction condition by reducing the size of the space from 50 × 50 × 50 to a spherelike space with several sites radius. The boundary of the space works as a wall to the hole migration, i.e., the hole hopping sites are chosen among the sites whose distance from anion is not longer than the radius. The spatial restriction effect is represented by the solid curves in Figure 6. The parameters are the same as for curve b in Figure 4. The simulation results became faster with restricting the migration region, and in the case of the space with (5) sites radius, the simulation results reproduces the experimental result from subnanoseconds to milliseconds.

There exist other conditions that reproduce the experimental results, such as $\sigma = 0.25$ eV, $\lambda = 0.05$ eV, $k' = 3 \times 10^{11}$ s^{-1}, and $a = 0.8$ Å with four sites radius. It is difficult to determine the parameters uniquely. The important point is that, by introducing the spatial restriction, the random walk model with energy disorder can reproduce the CR in PVCz film with physically appropriate parameters. The spatial restriction is the necessary condition, and without this condition it is impossible to reproduce the experimental result in any case. Once one let some holes migrate away from anion by introducing disorder, the holes have nonnegligible probability of escaping perfectly, as long as one assumes a diffusion-controlled CR.

Low-Temperature Condition. Next, the applicability of the same model discussed above to the low-temperature condition mentioned in section 3C is examined. Figure 7 shows the simulation result under the 143 K temperature condition. The parameters and the spatial restriction condition are those which reproduced the experimental result at room temperature in Figure 6. The ET rate in the nonadiabatic case is expressed in the classical limit as[27]

$$k = (2\pi/h)V_{el}{}^2/(4\lambda k_B T)^{1/2} \exp(-\Delta G^{\ddagger}/k_B T) \qquad (6)$$

where V_{el} is the ET integral and other notations are the same as in eqs 2 and 4. Following this equation, k' is varied to be proportional to $T^{-1/2}$, and other quantities are assumed to be temperature independent.

The simulation result becomes slower than under the room temperature condition (Figure 6) and qualitatively reproduces the temperature dependence of the decay kinetics. However,
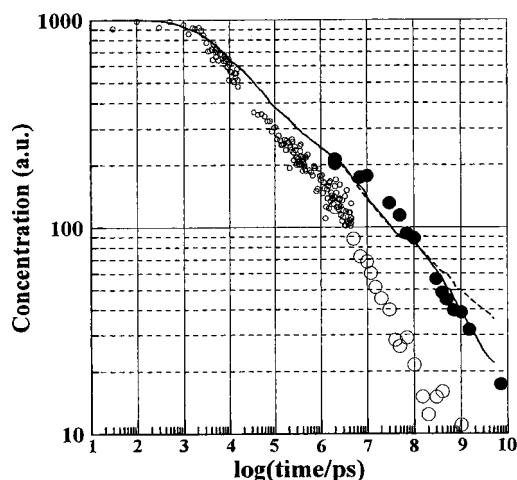
Figure 7. Monte Carlo simulation results of the CR kinetics at 143 K. Broken curve is the result without incorporating the long-range CR. Solid curve is a result when the long-range CR is considered. The parameters are $\sigma = 0.3$ eV, $\lambda = 0.10$ eV, and $k' = 4.3 \times 10^{11}$ s^{-1}. The radius of the hole migration region is five sites. Open circles and closed circles are experimental result of the decay kinetics of ions at room temperature and at 143 K, respectively. The excitation wavelength is 532 nm.

the correspondence in the regime later than 100 μs is not so good. From the disagreement between the CT fluorescence decay and the derivative of the CR kinetics at 143 K (section 3C), it is suggested that, under the low-temperature condition, a CR with a long-range electron-transfer mechanism which does not bring about the CT emission cannot be ignored. Thus, we performed the simulation incorporating this long-range CR. It is done by considering the long-range CR probability in the simulation procedure (C) and multiplying the distance-dependent factor $\exp(-R/a)/\exp(-6 \text{ Å}/a)$ by the CR rate at contact position, where R is the distance between the hole and anion. Figure 7 also shows this simulation result with solid curve. Including the long-range CR probability, the decay kinetics became slightly faster in the regime later than 100 μs and close to the experimental result. It is worth noting that the energy disorder model with a spatial restriction is also applicable to the low-temperature condition.

Interpretation of the Spatial Restriction. Finally, the random walk model in 3-D regular lattice disordered in energy is proved to reproduce the CR kinetics observed in PVCz film covering the wide time regime from subnanoseconds to milliseconds. Introduction of the spatial restriction of the hole diffusion is necessary to reproduce the experimental results. Here, we consider the physical model of this spatial restriction.

In our simulation model, k_0 is assumed to be the same at all the sites. However, according to eq 6, these quantities depend on the ET integral of each hopping reaction. Slowik et al. have calculated the ET integral between two carbazole chromophores with various mutual angles and distances.[28] The quantity varies more than 3 orders of magnitude by changing the mutual angle. On the other hand, the distribution of the mutual distance and angles between adjacent carbazole chromophores in actual PVCz film are determined by that of polymer configuration and conformation. It is straightforward to consider that there are many sites with very small interchromophore ET integrals for interchain and also intrachain pairs of chromophores (such as kinks). These sites will act as walls for the hole hopping, and the hole migration is restricted in a small region bounded by the walls. The meaning of the spatial restriction in our simulation may be to incorporate the effects of the walls on the average. The best fit condition of the spatial restriction was a

sphere with five sites radius, and this may be the average volume of the migration region.

4. Summary

We have studied CR dynamics in PVCz films by transient absorption spectroscopy, and some characteristic CR dynamics have been observed. Concentration-dependent decay kinetics, which indicates bulk CR, is completed within 20 μs, and afterward $t^{-0.5}$ decay appears independently of the initial concentration. This feature is qualitatively explained by the spatially restricted hole diffusion.

The CR kinetics changes dramatically at low temperature. The CT fluorescence decay indicates that at low temperature a CR by a long-range ET occurs. At low temperature, immobilization of the hole would be enhanced and the lifetime of ionic species lengthened, and this makes the long-range CR rate observable.

Following our previous study,[23] applicability of the random walk model in energy disordered 3-D lattice to the CR kinetics later than submicrosecond time regime is examined. It is concluded that an introduction of the spatial restriction into the hole diffusion is the essential condition to reproducing the CR kinetics in the PVCz film. The changes in the CR kinetics and mechanism at low temperature are also reproduced by this model. The physical meaning of the spatial restriction may be to incorporate the effect of sites where the ET integral is so small that work as a wall for a hole hopping. Combining the results obtained so far, a description of the hole diffusion in PVCz films is given as follows. The hole migration is restricted in some region whose boundary is determined by sites where ET integral is very small (such as interchain sites and kinks). Inside the region, holes can migrate by hopping whose manner can be described by the random walk in energy disordered 3-D lattice.

Still, there remains a discrepancy on the hole scavenging yield. In our previous study,[23] we pointed out that our simulation results brought about 4−5 times lower hole scavenging yield than the experiment. This situation is not changed by introducing the spatial restriction which are attempted in this work. This disagreement indicates that the hole migration in PVCz film is more "smooth" than expressed in our simulation, i.e., holes visit more numbers of sites. The hole absorption spectra are composed of various kinds of delocalized (dimer or trimer) cation states. One of the most plausible reasons for the discrepancy may be the neglect of the delocalization effect of the hole over some adjacent carbazole chromophores. To determine the role of this hole delocalization effect will be the remaining work in elucidating the CR mechanism in the PVCz film.

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