Solvent Effect of the Hole Migration along a Poly(*N*-vinylcarbazole) Chain as Revealed by Picosecond Transient Absorption and Dichroism Measurements[†]

Hiroshi Miyasaka,*,[‡] Sazzadur R. Khan,[§] and Akira Itaya[§]

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan, and Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan

Received: July 3, 2001; In Final Form: October 5, 2001

Photoinduced electron-transfer dynamics (charge separation, charge recombination, and hole transfer reactions) in poly(*N*-vinylcarbazole) (PVCz) and solvent effects on the reaction profiles were studied by means of picosecond transient absorption spectroscopy and transient dichroism measurements. Electron-transfer dynamics in PVCz in rather polar solutions was well-described by the simple scheme that the cation state of the carbazolyl (Cz^+) moiety continuously migrates along pendant Cz moieties in the polymer chain with the charge recombination at the initial position of the charge separation. The rate constant of the hole transfer (HT) from the Cz^+ to neighboring ones was $(230\ \mathrm{ps})^{-1}$ in pyridine. With a decrease in the solvent polarity, the HT rate constant drastically decreased, and it was $\leq 10^7\ \mathrm{s}^{-1}$ in chloroform solution. This solvent polarity effect was accounted for not only by the increase in the attractive Coulombic interaction with decreasing solvent polarity but also by the delocalization of the cationic state over Cz units. By integrating the present results with those in other aromatic vinyl polymers, the factors regulating the hole-transfer process in aromatic vinyl polymers were discussed.

Introduction

Photoinduced electron transfer (ET) and its subsequent processes play fundamental and important roles in a number of photochemical reactions in the condensed phase.[1−6] Transport of electrons initiated by photoexcitation is one of the phenomena closely related to the photoinduced ET and ubiquitous in nature as well as in artificial systems. In the natural system, the photosynthetic reaction center in plants is a most representative system in which the electron transport takes place efficiently in three-dimensional arrangements.[5] In the artificial system, a great deal of effort has been devoted to the construction of organic photoconductive molecular systems.[7,8] The vinyl polymer with large aromatic groups is one of the most well-known artificial materials in which the transport of the electron or the hole or both takes place and has been attracting much attention for a long time from various viewpoints.[7−23]

In most of these polymers, the interaction among the pendant aromatic groups is 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 ET in the condensed phase.[1−6] The direct information on the whole mechanism 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 design of artificial photoconductors.

Although a number of investigations have been reported as mentioned above, direct detection has scarcely been 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 because the absorption spectrum of the anion or the cation of the side aromatic groups is hardly influenced by the charge-shift reactions.

Recently, we pointed out that the dichroism measurement of the transient absorption of ionic species directly probes 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) and its related systems in the solid amorphous phase,[17−19] as well as PVCz and other aromatic vinyl polymers in solution phase.[20−23] From these results, it was demonstrated that rapid hole migration with a time constant of 0.2 ns to a few nanoseconds takes place in solution as well as in solid films. It should be mentioned that the hole-escape reaction is endothermic because the increase in the interionic distance reduces the Coulombic attractive interaction in the ion pair. The activation energy predicted for the model reaction of the initial hole-escape reaction, $A^-D_0{}^+D_1 \rightarrow A^-D_0D_1{}^+$, by the standard theory of ET reaction[2] is $\gg 10k_BT$ even in a rather polar solution of 1,2-dichloroethane, and such a large hole-migration rate constant on the order of $10^9\ \mathrm{s}^{-1}$ 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 pendant groups in aromatic vinyl polymers, the solvent effects on the hole-migration process have been investigated in present work. The solvent polarity affects the Coulombic attractive force in the initial ion pair and the energy

---

[†] Part of the special issue "Noboru Mataga Festschrift".

* To whom correspondence should be addressed. Tel: (81:Japan)-(0)6-6850-6241. Fax: (81:Japan)-(0)6-6850-6244. E-mail: miyasaka@chem.es.osaka-u.ac.jp.

[‡] Osaka University.

[§] Kyoto Institute of Technology.

10.1021/jp0125101 CCC: $22.00

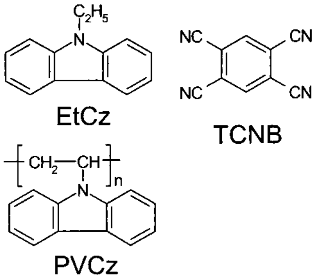


Figure 1. Molecular structures of the compounds used.

gap of the hole-escape reaction. In the following, we will discuss the photoprimary processes in PVCz, 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 polymers and their related systems.

Experimental Section

Poly(*N*-vinylcarbazole) (PVCz) of narrow molecular weight distribution ($M_n = 6.55 \times 10^5$, $M_w/M_n = 1.74$) was prepared by radical polymerization methods [24] and then purified by repeated precipitation from benzene solution with methanol. 1,2,4,5-Tetracyanobenzene (TCNB, Wako GR grade) was recrystallized from ethanol and sublimated before use. All of the solvents (spectral grade) were 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^{3+}:YAG laser was used for measurements. The optical alignments were almost the same as those developed previously.[17,20] The second harmonic pulse at 532 nm with a 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_2O-H_2O (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) to detect the weak transmitted light. Circular polarized probe light was used for the absorption spectroscopy, while a linearly polarized one 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 four measurements. The experimental errors for the transient absorption spectroscopy are less than ±10%, while those for the dichroism are less than ±20%. Chirping of the monitoring white light continuum was corrected. For all of 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 carbazolyl moieties. All of the measurements were performed under O_2-free conditions at 21 ± 2 °C.

Results and Discussion

Photoinduced Electron-Transfer Dynamics in Pyridine Solution. Prior to the discussion on polymer systems, we present photoinduced electron-transfer dynamics of the monomer model systems as references. Figure 2a exhibits time-resolved transient absorption spectra of *N*-ethylcarbazole (EtCz)−1,2,4,5-tetracyanobenzene (TCNB) in pyridine solution excited with a picosecond 532 nm laser pulse. A sharp absorption at 465 nm in each of the spectra is safely assigned to the anion radical of TCNB ($TCNB^-$) on the basis of the coincidence of the absorption maximum and its spectral band shape to those reported previously.[25,26] On the other hand, the absorption bands at 800 and 720 nm are ascribable to the cation radical of EtCz ($EtCz^+$).[14,16] 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.

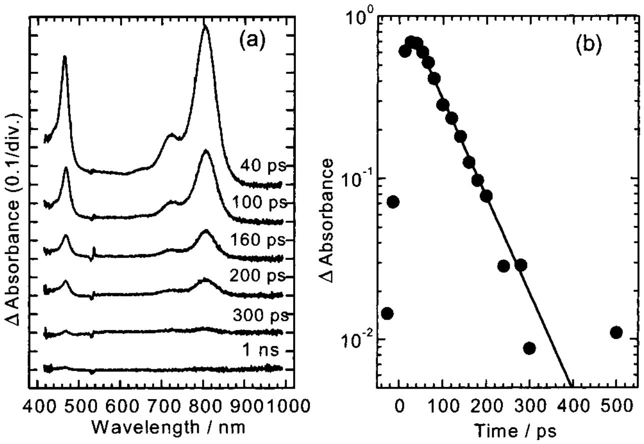


Figure 2. Time-resolved transient absorption spectra of EtCz (0.05 M)−TCNB (0.11 M) in pyridine solution excited with a picosecond 532 nm laser pulse (a) and time profile of the transient absorbance at 465 nm (b).

With an increase in the delay time after the excitation, the absorbance due to the ion pair gradually decreases as shown in Figure 2a. Because the relative ratio between the absorption intensity of the cation and that of the anion keeps a constant value during the decay process and no absorption was observed at and after ca. 1 ns following the excitation, almost all of the deactivation of the ion pair was ascribed to the charge recombination (CR). Figure 2b shows the time dependence of the absorbance due to the ion pair monitored at 465 nm. The decay profile is well described as a first-order kinetics with the time constant of 65 ps. The time constant of the CR in the present system was 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.[27,28]

For the dynamic behaviors of transient ion pair states formed via the photoinduced electron-transfer (ET) process in solutions,[6,27,29] 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 pyridine solution, the ionic dissociation rate constant was estimated to be $\leq 10^8$ s^{-1} by carefully observing the absorption signal that remained after the initial charge recombination decay. This value is much smaller than that in acetonitrile.[16,27,29] This small rate constant of the ionic dissociation is mainly ascribable to the dielectric constant of pyridine ($\epsilon = 12.4$ at 25 °C), which is much smaller than that of acetonitrile.

Figure 3a shows the time-resolved transient absorption spectra of poly(*N*-vinylcarbazole) (PVCz)−TCNB in pyridine solution excited with a picosecond 532 nm laser pulse. Each of the spectra shows two absorption maxima at 465 and ca. 790 nm. The former band at 465 nm is safely ascribed to $TCNB^-$, as

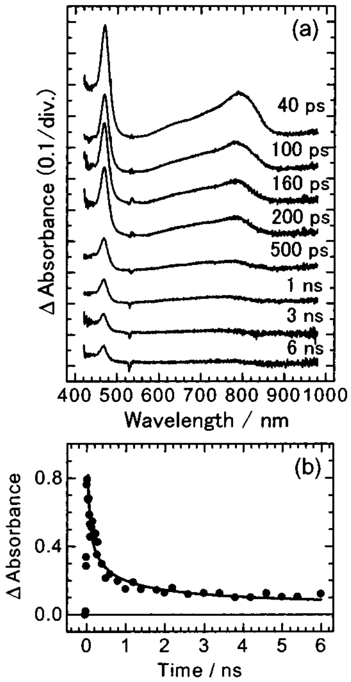


Figure 3. Time-resolved transient absorption spectra of PVCz ([Cz] = 0.36 M)−TCNB (0.25 M) in pyridine solution excited with a picosecond 532 nm laser pulse (a) and time profile of the transient absorbance at 465 nm (b). The solid line is the calculated curve on the basis of Scheme 1 with $k_{HT} = 4.3 \times 10^9$ s^{-1} and $k_{CR} = 1.5 \times 10^{10}$ s^{-1} (see text).

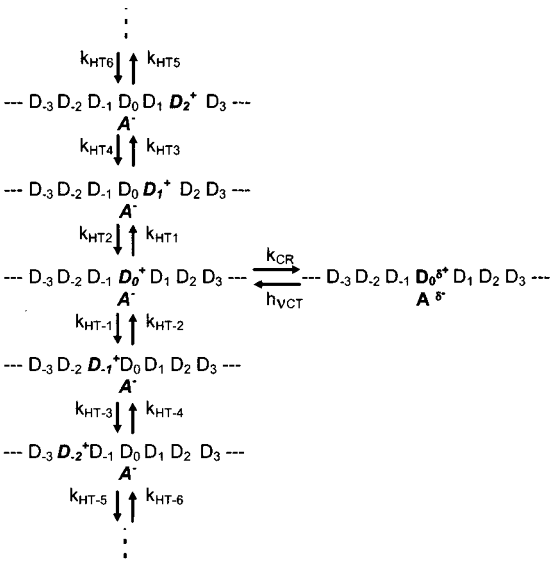
was mentioned in the interpretation of Figure 2a. On the other hand, the latter absorption at ca. 790 nm is attributed to the cation radical of the carbazolyl (Cz) moiety in PVCz on the basis of the coincidence of the spectral band shape and its maximum to reference.[15,20] When this spectrum is compared to the spectrum of EtCz$^+$ in Figure 2a, one can find that the spectral shape of Cz$^+$ in PVCz is broader. According to the detailed investigations on the band shape of the cation in aromatic vinyl polymers and their related compounds,[16a] it was demonstrated that the interaction of the aromatic cation and the neighboring neutral moiety affected the band shape of the cation radical.

Figure 3b shows the time profile of the charge-separated state monitored at 465 nm, indicating that the rather fast decay in the subnanosecond time region is followed by the long-lived ionic species in the several nanosecond region. The single exponential process did not reproduce the fast decay process in the subnanosecond region. In addition, the residual signal did not appreciably decrease in the nanosecond region. It should be noticed here that such residual absorption signal was not detected for the monomer model system as shown in Figure 2.

To analyze this time profile, we have employed Scheme 1, which well reproduced the primary process of electron-transfer dynamics in PVCz−electron acceptor systems and other aromatic vinyl polymers in 1,2-dichloroethane solution.[20−23]

Here, k_{HTi} is the hole-transfer rate constant between the two neighboring Cz moieties. For simplicity, all of the k_{HTi} constants were assumed to be identical (k_{HT}) in the calculation. In addition, the charge recombination was assumed to take place only between TCNB$^-$ and D$_0^+$ (at the initial position of the charge separation). The rate constant of the charge recombination (k_{CR}) was set to be equal to that of the monomer model system (EtCz−TCNB) in pyridine solution. Hence, the parameter in the calculation was only the k_{HT} value. The result of the calculation with $k_{HT} = 4.3 \times 10^9$ s^{-1} was presented as the solid line in Figure 3b, in which the calculated curve reproduces the experimental results on the dynamic behaviors fairly well not only for the nonexponential decay profile in the subnanosecond time region but also for the residual absorption signals in the several nanosecond time region. The above results strongly suggest that the ET dynamic behaviors of PVCz in pyridine solution are well described by Scheme 1, as was confirmed for the dynamics in 1,2-dichloroethane solution.[20−23]

SCHEME 1



To elucidate the hole-migration process more directly, we measured the transient dichroism of the absorption due to Cz$^+$, as well as that of TCNB$^-$. For the usual solute molecules in fluid solutions, the rotational diffusion process diminishes the memory of the polarized excitation. Although such rotational motion is restricted in the polymer system, local motions in the main chain take place and diminish the memory of the polarized excitation. In addition, for the dichroism signal of the cation in PVCz, the hole migration in the polymer chain also seems to decrease the memory of the polarized excitation. Hence, the comparison of the dichroism signals between the cation and the anion seems to provide the direct information on the hole-migration processes in the present system.

For the dichroism measurements in the polymer system, we have adopted a background-free optical system[30,31] because a wider dynamic range in the time profiles was obtained by this method. In this measurement, the polarization angle between the excitation (pump) and the monitoring (probe) light pulses is set at 45°. The analyzer polarizer perpendicular to the polarization of the probe light is placed before the detector. Because the excitation of the ground-state CT complex by the polarized light induces the difference in the transient absorbance of the charge-separated state between the *x* and *y* axes (transient dichroism), the polarization angle of the probe light is modified and a part of the monitoring light can transmit the analyzer.

In the case in which the dephasing process of the memory of the polarized excitation is regarded as an exponential process, the transmitted light intensity, $I_T(t)$, in the homodyned detection is given by[30−32]

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

where $A(t)$ is the time dependence of the population of the ionic species and τ_{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

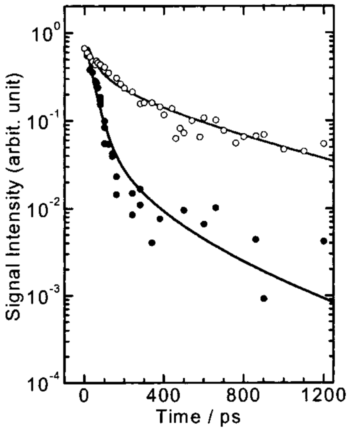


Figure 4. Time profiles of transient dichroism signals of the PVCz−TCNB system in pyridine solution excited with a picosecond 532 nm laser pulse monitored at 790 nm (Cz^+, closed circles) and at 465 nm ($TCNB^-$, open circles). Solid lines are the results calculated on the basis of eq 2 and Scheme 1 (see text).

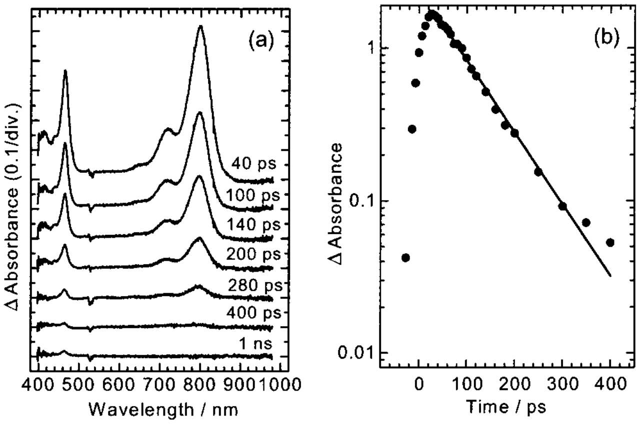


Figure 5. Time-resolved transient absorption spectra of EtCz (0.05 M)−TCNB (0.41 M) in THF solution excited with a picosecond 532 nm laser pulse (a) and time profile of the transient absorbance at 465 nm (b).

as performed in previous works.[17−23] In this optical configuration, the analyzer polarizer was uncrossed slightly (less than 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 ($E_{LO}E_S(t)$) much greater than I_S ($\propto E_S(t)^2$). In this case, the transmitted light intensity is given by the following equation.[32,33]

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

Here, 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.

Figure 4 shows the time profiles of the transient dichroism monitored around 790 nm (Cz^+) and 465 nm ($TCNB^-$). This figure clearly demonstrates that the memory of the polarized excitation in Cz^+ decreases much faster than that of $TCNB^-$, 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.[20−23] 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 3b; the time constants of the charge recombination and the hole transfer were the same as those used in the analysis of Figure 3b. The solid line for the time profile of the anion in Figure 4 is the calculated result on the basis of eq 2 with $\tau_{DP} = 950$ ps. The calculated result shown in Figure 4 reproduces the experimental results fairly well and indicates that the anion attached to the Cz moiety in PVCz rotates with a much longer time constant than that in the monomer model system. On the motions of the aromatic vinyl polymer in fluid solutions, it has been reported that the local motions such as three bond motion and crankshaft motion to result in the conformational change of the pendant aromatic groups were on the order of subnanoseconds to nanoseconds.[34−36] Hence, it is strongly suggested that the present time constant for the dichroism decay of $TCNB^-$ attached to the Cz moiety in PVCz 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 Cz^+ is the result calculated for the time profile of D_0^+ in Scheme 1. Namely, the population decay of the Cz^+, which is directly connected to $TCNB^-$ (Cz which formed the CT complex with TCNB in the ground state before the photoexcitation), is exhibited. Because the hole-shift reaction to neighboring Cz moieties existing in the polymer chain seems to diminish this memory, we examined the time profile of D_0^+. In the calculation, the time constants of both the charge recombination and the hole migration were set to be the same as those used for the analysis of Figure 3b. In addition, the local rotational relaxation time constant of 950 ps was also included. As shown in this figure, the calculated curve reproduces the experimental result for Cz^+ fairly well as for that in $TCNB^-$. By integrating the present result on the dichroism decay with that of the transient absorption time profile in Figure 3b, it can be concluded that the Cz^+ initially produced via the excitation of the ground-state CT complex actually undergoes the hole migration to the neighboring neutral Cz moieties with the time constant of 230 ps ($k_{HT} = 4.3 \times 10^9\ s^{-1}$) as assumed in Scheme 1 and its memory of the polarized excitation decreases mainly via the hole-shift reaction. Compared to the hole-transfer process of PVCz in 1,2-dichloroethene solution (the dielectric constant is 10.36), the k_{HT} value in more polar pyridine solution was 2.2 times larger than that that in 1,2-dichloroethane solution. The solvent effect on the hole transfer process will be discussed in later.

Photoinduced Electron-Transfer Dynamics in THF Solution. The dynamic behaviors in less polar THF solution ($\epsilon = 7.58$ at 25 °C) are shown in this section. Figure 5a shows the time-resolved transient absorption spectra of the monomer model system (EtCz−TCNB) in THF excited with a picosecond 532 nm laser pulse. As was shown in Figure 2 in pyridine solution, the selective excitation of the ground-state CT complex between EtCz and TCNB produces the ion pair also in THF, followed by the deactivation via the charge recombination with first-order kinetics (Figure 5b). The charge recombination time constant was obtained to be 92 ps.

Transient absorption spectra of PVCz−TCNB in THF solution excited with a picosecond 532 nm laser pulse are shown in Figure 6a. The sharp absorption at 465 nm and broad

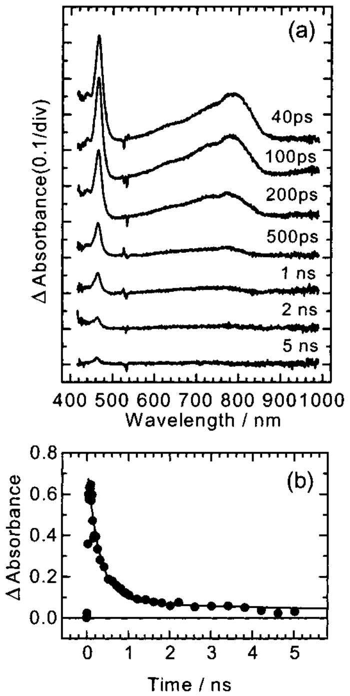


Figure 6. Time-resolved transient absorption spectra of PVCz ([Cz] = 0.13 M)−TCNB (0.38 M) in THF solution excited with a picosecond 532 nm laser pulse (a) and time profile of the transient absorbance at 465 nm (b). The solid line is the calculated curve on the basis of Scheme 1 with k_{HT} = 1.8 × 10^8 s^{-1} and k_{CR} = 3.0 × 10^9 s^{-1} (see text).

absorption at 790 nm are, respectively, assigned to $TCNB^-$ and Cz^+. The time profile of the charge-separated state monitored at 465 nm is exhibited in Figure 6b, indicating that the rather fast decay in the subnanosecond time region is followed by the long-lived ionic species in the several nanosecond region ascribable to the ion pair with longer interionic distance via hole transfer. As for the dynamic behaviors in pyridine solution, the single-exponential decay function did not reproduce the fast decay process in the subnanosecond region.

As performed for pyridine solution, we analyzed the time profile of Figure 6b by applying Scheme 1 with k_{CR} identical to that of the monomer model system. However, the calculated curves with k_{CR} identical to that of the monomer model system did not reproduce the experimental result. The solid line in Figure 6b is the result calculated by changing the CR time constant also as a parameter. To fit the time profile in Figure 6b, the dynamic behaviors of the dichroism signals that will be shown in Figure 7 were taken in into account. The CR and HT rate constants thus obtained in Figure 6b were 3.0 × 10^9 and 1.8 × 10^8 s^{-1}, respectively. The CR time constant was almost one-third of that of the monomer model system. In addition, the HT rate constant in THF was more than 1 order of magnitude smaller than those in pyridine and 1,2-dichloroethane solutions.

The time profiles of dichroism signals of PVCz−TCNB in THF solutions are shown in Figure 7. The same optical setup was employed as in Figure 4. The dynamics of the cation monitored at ca. 780 nm and that of the anion monitored at 465 nm are, respectively, exhibited as closed circles and open circles. Compared to the dichroism behaviors in pyridine solution, the difference in the dynamic behaviors between the cation and the anion was smaller than that in pyridine solution, indicating that the hole transfer process is actually suppressed in THF solution.

The solid line for the time profile of the anion in Figure 7 is the calculated result on the basis of eq 2 with τ_{DP} = 700 ps.

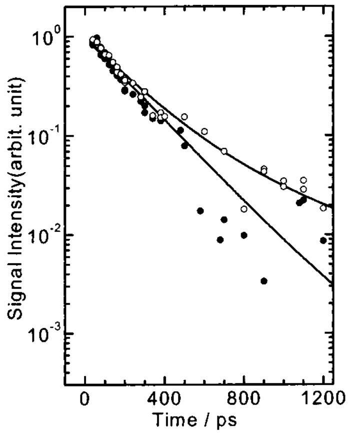


Figure 7. Time profiles of transient dichroism signals of the PVCz−TCNB system in THF solution excited with a picosecond 532 nm laser pulse monitored at 780 nm (Cz^+, closed circles) and at 465 nm ($TCNB^-$, open circles). Solid lines are the results calculated on the basis of eq 2 and Scheme 1 (see text).

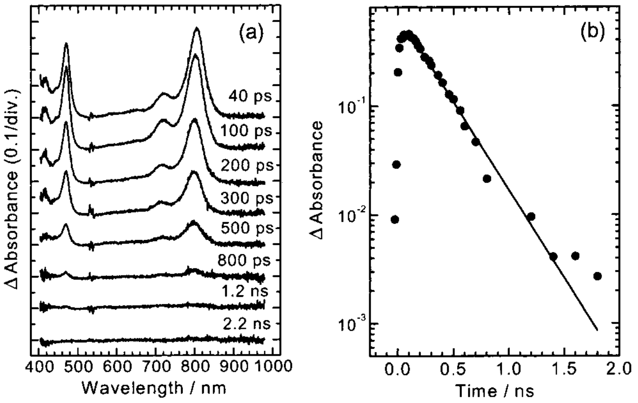


Figure 8. Time-resolved transient absorption spectra of EtCz (0.09 M)−TCNB (0.008 M) in chloroform solution excited with a picosecond 532 nm laser pulse (a) and time profile of the transient absorbance at 465 nm (b).

The CR and HT rate constants were set to be identical with those used in Figure 6b. The time constant, $\tau_{DP,}$ was smaller than that in pyridine solution (950 ps). This may be attributed to smaller viscosity in THF solution. On the other hand, the solid line for the dichroism behavior of Cz^+ was the curve calculated for D_0^+. Also for the calculation of the cation, the time constants of both the charge recombination and the hole migration were set to be the same as those used for the analysis of Figure 6b. In addition, the local rotational relaxation time constant of 700 ps was also included. As shown in this figure, the calculated curve reproduces the experimental result for Cz^+ fairly well as for that in $TCNB^-$. By summarizing the above results and discussion, it is concluded that the ET dynamic behaviors of PVCz−TCNB in THF in the early stage after the excitation is reproduced by Scheme 1 as in pyridine system although the CR time constant in the PVCz−TCNB system is almost three times smaller than that of the monomer model system.

Photoinduced Electron-Transfer Dynamics in Chloroform Solution. Figure 8a shows the time-resolved transient absorption spectra of the monomer model system (EtCz−TCNB) in chloroform solution (ϵ = 4.81 at 20 °C) excited with a picosecond 532 nm laser pulse. As was shown in Figures 2 and 4, the selective excitation of the ground-state CT complex between EtCz and TCNB produces the ion pair also in chloroform, followed by the deactivation via the charge

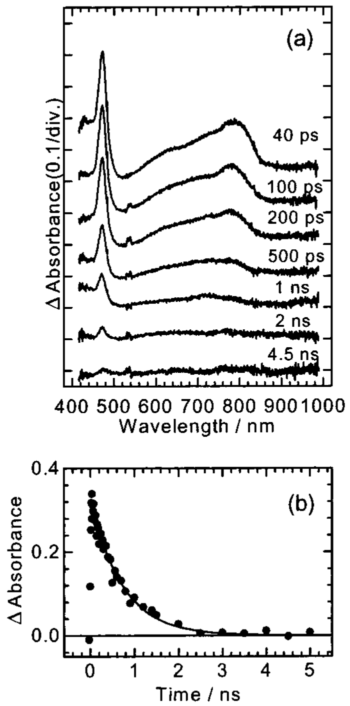


Figure 9. Time-resolved transient absorption spectra of PVCz ([Cz] = 0.24 M)−TCNB (0.01 M) in chloroform solution excited with a picosecond 532 nm laser pulse (a) and time profile of the transient absorbance at 465 nm (b). The solid line is the calculated curve on the basis of monoexponential decay with the time constant of 1.4 × 10^9 s^{-1} (see text).

recombination with first-order kinetics with the CR time constant of 260 ps (Figure 8b).

Transient absorption spectra of PVCz−TCNB in chloroform solution excited with a picosecond 532 nm laser pulse are shown in Figure 9a. The sharp absorption at 465 nm and broad absorption at 790 nm are, respectively, assigned to $TCNB^-$ and Cz^+. The time profile of the charge-separated state monitored at 465 nm is exhibited in Figure 9b. The residual absorption in the several nanosecond time region is very small in chloroform solution, while the dynamic behaviors in pyridine and THF solutions showed the long-living charge-separated species due to the HT process in this time region. In addition, the decay profile was reproduced by a single-exponential function with the time constant of 730 ps as the solid line in Figure 9b. These results suggest that the effective HT process does not take place in chloroform solution in the present time window.

The time profiles of the dichroism signals are shown in Figure 10. The experimental setup was same as that used for pyridine and THF solutions. The decay of the signal due to the Cz cation is identical with that of the anion within the experimental error. This result directly indicates that the effective HT process does not take place in chloroform solution and the cation stays at the initial position of the charge separation. In addition, mutual geometry between the anion and the cation is maintained as in the ion pair prepared by the ground-state CT complex between EtCz and TCNB.[20,23] The solid line is the result calculated with the single-exponential decay process with the CR time constant of 730 ps and the τ_{DP} of 600 ps. As stated in previous sections, the latter process corresponds to the local conformational reorientation time in the polymer main chain leading to the dephasing of the polarized excitation and related to the solvent viscosity. The slow time constant of τ_{DP} may be ascribed to the small viscosity of chloroform. By summarizing the above results and discussion, we can safely conclude that the effective HT process does not take place in chloroform solution and the ion pair produced by the photoexcitation undergoes first-order decay due to the CR process at the initial position of the charge separation. In addition, the CR time constant between $TCNB^-$ and Cz^+ of PVCz in chloroform solution is about 3 times longer than that of the monomer system in the same solvent.

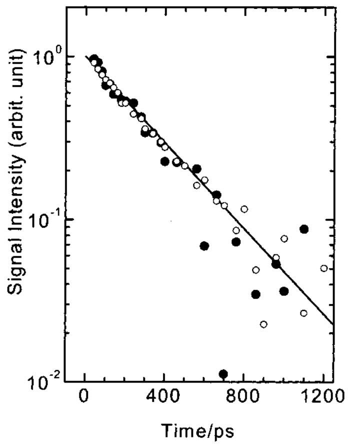


Figure 10. Time profiles of transient dichroism signals of the PVCz−TCNB system in chloroform solution excited with a picosecond 532 nm laser pulse monitored at 780 nm (Cz^+, closed circles) and at 465 nm ($TCNB^-$, open circles). The solid line is the results calculated on the basis of eq 2 (see text).

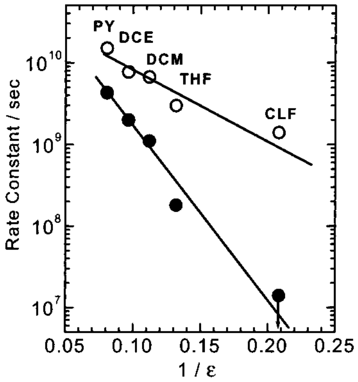


Figure 11. Solvent polarity dependence of the HT (closed circles) and the CR (open circles) rate constants as a function of the reciprocal dielectric constants of solvents. PY is in pyridine, DCE is in 1,2-dichloroethane, DCM is in dichloromethane, THF is in THF, and CLF is in chloroform. The dielectric constants[39] were determined at 25 °C for dichloromethane and chloroform. Those for the other three solvents are at 20 °C. The results in 1,2-dichloroethane solution were taken from ref 20. Solid lines are to guide the eye.

Solvent Dependence of the HT and CR Processes. The dynamic behaviors of PVCz−TCNB in dichloromethane solution ($\epsilon = 8.93$ at 25 °C) were also investigated by means of transient absorption spectroscopy and dichroism measurements. As in pyridine and 1,2-dichloroethane solutions, the electron-transfer dynamics was well reproduced by Scheme 1 with the charge recombination rate constant identical with that of the monomer model system ($k_{CR} = 6.7 \times 10^9$ s^{-1}). The HT rate constant in dichloromethane solution was 1.1×10^9 s^{-1}. The HT and CR rate constants of PVCz−TCNB system in various solutions are plotted in Figure 11 as a function of the reciprocal value of the dielectric constant (ϵ) of the solvent.[39] In this figure, the result in 1,2-dichloroethane solution[20] is also plotted. As shown in this figure, both CR and HT rate constants monotonically decrease with a decrease in solvent polarity.

Prior to the discussion on the solvent polarity dependence of the electron-transfer rate constants, it is worth mentioning that the spatial configuration of the polymer (the extent of the coiling) is generally dependent on the solvent. In good solvents, the radius of gyration increases, and it decreases in poor solvents. The solvent parameters affecting the coiling size of PVCz in 1,2-dichloroethane, tetrahydrofuran, and chloroform were reported to be almost the same as one another.[40] Although the solvent parameters for pyridine and dichloromethane were not reported, the solubility of PVCz in these two solvents strongly suggests that the solvent parameters on the coiling size in these two solvents may be also similar to the other three solvents. In addition, the present time window of the measurements (6 ns) can only cover the hole-transfer dynamics in a small area of the polymer chain (at most less than a few tens of Cz units). Hence, we may conclude that the effect of the coiling size of PVCz depending on the solvent does not seriously affect the electron-transfer (ET) rate constants.

First, we discuss the solvent polarity dependence of the CR process. For the energy-gap (ΔE) dependence of CR rate constants (k_{CR}) of the geminate ion pair produced by the photoexcitation of ground-state charge transfer (CT) complexes in solutions with different polarities, Asahi, Mataga, and coworkers reported the following results:[27] (a) no or very little solvent polarity effect on the k_{CR} vs ΔE (the energy gap for the CR reaction) relations and (b) a $\ln(k_{CR})$ vs ΔE linear relation, $\ln(k_{CR}) = \alpha - \beta|\Delta \mathrm{E}|$, with a gentle slope and α and β independent of the solvents. The present result on the solvent dependence of the CR rate constant in the PVCz−TCNB system may be interpreted in a similar way. Although the donor and acceptor pair is same, the energy gap (ΔE) between the ion pair level ($\mathrm{TCNB}^-{-}\mathrm{Cz}^+$ in PVCz) and the ground state increases with a decrease of the solvent polarity. The energy level of the ion pair scales with $1/\epsilon$ on the assumption that the Born equation can be applied for the energy level estimation in the solvents. The energy gap of the CR process of $\mathrm{TCNB}^-{-}\mathrm{Cz}^+$ in chloroform solution was estimated to be ca. 0.26 eV larger than that in pyridine solution and on the basis of the Born equation with the ion radius of 3.5 Å.

Compared to the solvent polarity dependence of the CR process, the hole-transfer (HT) rate constant is more intensely dependent on the solvent polarity. As briefly mentioned in the introductory section, the model reaction, $\mathrm{A}^-\mathrm{D}_0{}^+\mathrm{D}_1 \rightarrow \mathrm{A}^-\mathrm{D}_0\mathrm{D}_1{}^+$, takes place against the Coulombic attraction and is endothermic. Because the decrease of the solvent polarity increases the attractive Coulombic energy in the initial ion pair, the decrease in the hole-transfer (HT) rate constant with decreasing solvent polarity may be qualitatively reasonable. However, the energy gap for the model reaction is estimated to be endothermic with the energy of +0.2−0.3 eV even in rather polar solvents such as pyridine and 1,2-dichloroethane solutions.[20,23] The activation energy and the rate constant for the initial hole-escape reaction are, respectively, estimated to be $\gg 10k_BT$ and on the order of 10^5-10^6 s^{-1} even in these rather polar solutions by the standard theory of the ET reaction assuming very weak interaction between the reactants.[20] That is, some other factors should be taken into account for the rational interpretation of the large HT rate constants in polar solution.

From the direct investigation on the HT processes of various aromatic vinyl polymers in 1,2-dichloroethane solution,[20−23] it was revealed that the k_{HT} increases with an increase in the overlap between the neighboring two aromatic groups. Namely, the vinyl polymers with large aromatic groups such as benzocarbazolyl and carbazolyl moieties undergo the HT process with large HT constants on the order of 10^9 s^{-1}. On the other hand, the HT rate constant in the polystyrene system was $\leq 10^7$ s^{-1}.[23] 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.

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.[16a] In relation to this, it is noteworthy to mention 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 (monomer model systems of the polymers with large k_{HT} constants) under usual conditions, while rather small aromatics such as 1-ethylnaphthalene, 2-ethylnaphthalene, and benzenes (monomer model systems of the polymers with small k_{HT} constants) form the intermolecular dimer radical cations easily in solutions.[37,38] These results indicate that large aromatic side groups such as carbazolyl and benzocarbazolyl moieties intrinsically have small stabilization energy in the dimer cation formation acting as deep trap sites of the cation. In addition, the hole-transfer process in PVCz in polar solutions was faster than the conformational rearrangement of the local structures in the polymer chain as was indicated by the dichroism decay of the anion. Because 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. By summarizing the above results and discussion, it may be concluded that 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.

The interaction between aromatic radical cation and neutral moieties is estimated from the charge resonance band of the absorption spectrum in the 1−2 μm near-IR region. For the dimer system such as $(\mathrm{DD})^+$, the charge resonance band shifts toward the blue wavelength region with an increase in the interaction.[38] On the other hand, the charge resonance band shifts toward the red wavelength region under the charge resonance interaction of more than two chromophores.[41,42] Tsuchida et al. reported systematic investigations[42,43] on the charge resonance interaction of more than two chromophores in aromatic vinyl polymers. They measured the charge resonance band of Cz^+ in *N*-vinylcarbazole (VCz) oligomers as well as PVCz in DMF solution by means of nanosecond laser spectroscopy.[43] According to their results, the absorption maximum of the charge resonance band of Cz^+ was dependent on the degree of the polymerization (DP); the charge resonance band red-shifted markedly from DP = 2 to DP = 10 and then was saturated at DP = 20. From these results and discussion on the thermal fluctuation of the main chain conformation, they concluded that the cation state was delocalized over several Cz units. In addition, they suggested the temporal fluctuation of the degree of the charge resonance interaction.[43]

By integrating the present results on the HT processes with those on the relation between the charge resonance band and DP, it is strongly suggested that the delocalization of Cz^+ over several Cz units plays an important role in the effective HT process. The experimental result[44] that the HT process was not detected for the carbazolyl dimer model systems such as 1,2-dicarbazolycyclobutane and 1,3-dicarbazolypropane supports the importance of the hole delocalization over several Cz units. The delocalization of the cation state over several Cz moieties increases the effective interionic distance leading to the decrease in the effective Coulombic attractive force. In addition, the solvent reorganization energy for the HT reaction decreases with an increase in the size of the cation, which is also favorable for the HT reaction to take place quickly.

However, it should be mentioned here that a CR rate constant identical with that of the monomer model system was estimated for the PVCz−TCNB system in polar solutions by the analysis based on Scheme 1. In addition, the dichroism of the cation absorption was observed for all of the solvents examined here. Under the condition that the Cz^+ is delocalized over several Cz units, the dichroism signal may be very small or diminished. These results imply that the localized cation state and the delocalized states may be in rapid equilibrium as suggested by Tsuchida et al.[43]

The decrease of the HT rate constants in less polar solution may also be interpretable from the viewpoint of the charge resonance delocalization. Even if the degree of the charge resonance delocalization is independent of the solvent polarity, the increase of the effective attractive force with decreasing solvent polarity suppresses the HT reaction. In addition, the degree of the charge resonance delocalization itself seems to be dependent on the solvent polarity because the charge resonance delocalization energy relative to the Coulombic attractive energy affects the rapid equilibrium between the localized and delocalized states. From investigation on electron-transfer processes of TCNB−poly(1-vinylpyrene) (PVPy) in which the stable localized dimer cation is effectively produced, the ion pair states in less polar solutions showed biexponential decay.[45] On the basis of the spectral evolution of the cation, the faster and the slower decay components were, respectively, assigned to the CR process of the ion pair between the anion and monomer cation and that between the anion and localized dimer cation. The CR time constant of the ion pair between the anion and localized dimer cation was several times longer than that between the anion and monomer cation. Smaller CR rate constants of the PVCz−TCNB system in less polar solutions than those of the monomer model system suggest that the cation state is localized in a few Cz units in less polar solution. For a quantitative estimation of the degree of the charge resonance delocalization, we are now persuing the investigation with higher time resolution, the results of which will be published shortly.

Acknowledgment. The present work was partly supported by the Grants-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan (Grant 12640497) and CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST).

References and Notes

(1) (a) Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255. (b) Mataga, N. *Pure Appl. Chem.* **1993**, *65*, 1606.

(2) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(3) Rips, I.; Klafter, J.; Jortner, J. In *Photochemical Energy Conversion*; Norris, J. R., Meisel, D., Eds.; Elsevier: New York, 1988; p 1.

(4) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.

(5) Maruyama, K.; Osuka, A.; Mataga, N. *Pure Appl. Chem.* 1994, 66, 867.

(6) (a) Mataga, N.; Miyasaka, H. *Prog. React. Kinet.* **1994**, *19*, 317. (b) Mataga, N.; Miyasaka, H. *Adv. Chem. Phys.* **2000**, *107*, 431.

(7) Mort, J.; Pfister, G. In *Electronic Properties of Polymers*; Mort, J., Pfister, G., Eds.; Wiley-Interscience Publication: New York, 1982; p 215 and references therein.

(8) Van der Auweraer, M.; De Schryver, F. C.; Borsenberger, P. M.; Bässler, H. *Adv. Mater.* **1994**, *3*, 199 and references therein.

(9) (a) Penwell, R. C.; Ganguly, B. N.; Smith, T. W. *J. Polym. Sci., Part D: Macromol. Rev.* **1978**, *13*, 63. (b) Peason, J. M.; Stolka, M. *Poly-(N-vinylcarbazole)*; Gordon and Breach Science Publishers: New York, 1981.

(10) On the photoconductivity in solid phase, e.g.: (a) Pai, D. M. *J. Chem. Phys.* **1970**, *52*, 2285. (b) Gill, W. D. *J. Appl. Phys.* **1972**, *43*, 5033. (c) Okamoto, K.; Kusabayashi, S.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1948. (d) Pfister, G.; Williams, D. J. *J. Chem. Phys.* **1974**, *61*, 2416. (e) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Polym. J.* **1985**, *17*, 557. (f) Bos, F. C.; Guin, T.; Burland, D. M. *Phys. Rev. B* **1989**, *39*, 12633.

(11) On the charge-transfer emission and its relation to the photocurrent, e.g.: (a) Yokoyama, M.; Endo, N.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1538. (b) Okamoto, K.; Oda, N.; Itaya, A.; Kusabayashi, S. *Chem. Phys. Lett.* **1975**, *35*, 483.

(12) On the excimer fluorescence, e.g.: (a) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697. (b) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2082.

(13) On the dynamic behaviors in the excited state, e.g.: (a) Sakai, H.; Itaya, A.; Masuhara, H. *J. Phys. Chem.* **1989**, *93*, 5351. (b) Itaya, A.; Egawa, A.; Umehara, Y.; Sakai, H.; Masuhara, H. *Polymer* **1994**, *35*, 3149. (c) Sakai, H.; Itaya, A.; Masuhara, H.; Sasaki, K.; Kawata, S. *Polymer* **1996**, *37*, 31.

(14) On the model systems of the polymer transient absorption spectra of excited, cationic, and anionic species, e.g.: (a) De Schryver, F. C.; Vandendriessche, J.; Toppet, S.; Demeyer, K.; Boens, N. *Macromolecules* **1982**, *15*, 406. (b) Vandendriessche, J.; Palmans, P.; Toppet, S.; Boens, N.; De Schryver, F. C.; Masuhara, H. *J. Am. Chem. Soc.* **1984**, *106*, 8057.

(15) On the transient absorption spectra of excited, cationic, and anionic species, e.g.: (a) Masuhara, H.; Tamai, N.; Mataga, N.; De Schryver, F. C.; Vandendriessche, J. *J. Am. Chem. Soc.* **1983**, *105*, 7256. (b) Masuhara, H. *Makromol. Chem. Suppl.* **1985**, *13*, 75.

(16) Dynamics in short time regions, e.g.: (a) Masuhara, H.; Itaya, A. In *Macromolecular Complexes: Dynamic Interactions and Electronic Processes*; Tsuchida, E., Ed.; VCH: New York, 1991; pp 61−92. (b) Watanabe, K.; Asahi, T.; Masuhara, H. *Chem. Phys. Lett.* **1994**, 233, 69. (c) Watanabe, K.; Asahi, T.; Masuhara, H. *J. Phys. Chem.* **1996**, *100*, 18436.

(17) Miyasaka, H.; Moriyama, T.; Kotani, S.; Muneyasu, R.; Itaya, A. *Chem. Phys. Lett.* **1994**, *225*, 315.

(18) Miyasaka, H.; Moriyama, T.; Ide, T.; Itaya, A. *Chem. Phys. Lett.* **1998**, *292*, 339.

(19) Itaya, A.; Kitagawa, T.; Moriyama, T.; Matsushita, T.; Miyasaka, H. *J. Phys. Chem. B* **1997**, *101*, 524.

(20) Miyasaka, H.; Moriyama, T.; Itaya, A. *J. Phys. Chem.* **1996**, *100*, 12609.

(21) Moriyama, T.; Monobe, K.; Miyasaka, H.; Itaya, A. *Chem. Phys. Lett.* **1997**, *275*, 291.

(22) Miyasaka, H.; Moriyama, T.; Itaya, A. *J. Phys. Chem. B* **1997**, *101*, 10726.

(23) Miyasaka, H.; Moriyama, T.; Khan, S. R.; Itaya, A. In *Femtochemistry*; De Schryver, F. C., Ed.; Wiley-VCH: Weinheim, Germany, in press.

(24) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Polym. J.* **1985**, *17*, 557.

(25) Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1970**, *6*, 608.

(26) Miyasaka, H.; Ojima, S.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 3380.

(27) (a) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 6575. (b) Asahi, T.; Mataga, N. *J. Phys. Chem.* **1991**, *93*, 1956. (c) Asahi, T.; Ohkohchi, M.; Mataga, N. *J. Phys. Chem.* **1993**, *97*, 13132.

(28) (a) Miyasaka, H.; Kotani, S.; Itaya, A. *J. Phys. Chem.* **1995**, *99*, 5757. (b) Miyasaka, H.; Kotani, S.; Itaya, A.; Schweitzer, G.; De Schryver, F. C.; Mataga, N. *J. Phys. Chem. B* **1997**, *101*, 7978.

(29) (a) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4147. (b) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 5834.

(30) Shank, C. V.; Ippen, E. P. *Appl. Phys. Lett.* **1975**, *26*, 62.

(31) Waldeck, D.; Cross, A. J., Jr.; McDonald, D. B.; Fleming, G. R. *J. Chem. Phys.* **1981**, *74*, 3381.

(32) Fleming, G. R. In *Chemical Applications of Ultrafast Spectroscopy*; Oxford University Press: New York, 1986; p 72.

(33) Easley, G. L.; Levenson, M. D.; Tolles, W. M. *IEEE J. Quantum Electron.* **1978**, *14*, 192.

(34) Gorrin, S.; Monnerie, L. *J. Chim. Phys.* **1970**, *67*, 869.

(35) Matsuo, K.; Kuhlmann, K. F.; Yang, H. W.-H.; Gèny, F.; Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1347.

(36) (a) Uchida, M.; Yamamoto, M. *Bull. Inst. Chem. Res.* **1988**, *66*, 154. (b) Sasaki, T.; Arisawa, H.; Yamamoto, M. *Polym. J.* **1991**, *23*, 103.

(37) Tsujii, Y.; Tsuchida, A.; Ito, S.; Yamamoto, M. *Macromolecules* **1991**, *24*, 4061.

(38) Badger, B.; Brocklehurst, B.; Russel, R. D. *Chem. Phys. Lett.* **1967**, *1*, 122.

(39) Riddick, J. A.; Bunger, W. B. *Organic Solvents*; Wiley-Intersicence: New York, 1970.

(40) León, L. M.; Gonzalez, M. C.; Quintana, J. R.; Zamora, F.; Martine, A.; Guzman, G. M. *Euro. Polym. J.* **1982**, *18*, 229.

(41) Kira, A.; Imamura, M. *J. Phys. Chem.* **1979**, *83*, 2267.

(42) Tsujii, Y.; Tsuchida, A.; Onogi, Y.; Yamamoto, M. *Macromolecules* **1990**, *23*, 4019.

(43) Tsuchida, A.; Nagata, A.; Yamamoto, M.; Fukui, H.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1285.

(44) Miyasaka, H.; Moriyama, T.; Itaya, A., to be submitted for publication.

(45) Khan, S. R.; Miyasaka, H.; Itaya, A., to be submitted for publication.