Photoinduced Intramolecular Charge Separation in Poly(alkyl methacrylate) Solids Studied by Using a Fluorescent Polarity Probe

Hiroaki Benten, Hideo Ohkita, and Shinzaburo Ito*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan

Masahide Yamamoto

Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

Yasuo Tohda and Keita Tani

Division of Natural Science, Osaka Kyoiku University, Asahigaoka, Kashiwara, Osaka 582-8582, Japan

The rate of photoinduced intramolecular charge separation (CS) k_{CS} in polymer solids was evaluated by the fluorescence lifetime measurement over a temperature range 100−400 K. Nine kinds of carbazole−spacer−acceptor dyads (Cz−S−A) were embedded in a series of poly(alkyl methacrylate) films with various glass transition temperatures (T_g's). The rate k_{CS} of Cz−S−A increased above T_g or melting temperature T_m of each polymer solid. The temperature dependence of k_{CS} in a poly(butyl methacrylate) glassy solid was in agreement with that of the dielectric constant at higher frequencies, indicating that orientational motions faster than the CS rate are effectively coupled to the CS event. The effective dielectric constant (ϵ') for CS was evaluated with a novel fluorescent probe of carbazole−terephthalate cyclophane (Cz−TP). The free energy gap and temperature dependence of k_{CS} were well explained by a single quantum mode electron transfer (ET) formula with ϵ' rather than a static dielectric constant ϵ_S in a poly(butyl methacrylate) glassy solid. In conclusion, CS in poly(alkyl methacrylate)s is promoted above T_g or T_m by enhancement in orientational motions of ester groups with a relaxation time comparable to the CS event.

1. Introduction

Photoinduced inter- and intramolecular electron transfer (ET) in a solution has been investigated by many researchers from both theoretical and experimental viewpoints.[1−8] Marcus revealed that ET can occur only at a nuclear configuration where the total energy of the reactants and surrounding medium is equal to that of the products and surrounding medium because both the Franck−Condon principle and the energy conservation have to be simultaneously satisfied for the ET event. In a classical ET formula, the energy matching is achieved only at a crossing point between the initial and final potential curves. Thus, ET requires thermal fluctuations in nuclear configurations leading to the intersection region. These fluctuations in the nuclear configurations are considered to originate from orientational and vibrational fluctuations of surrounding media and the reactants. In particular, orientational fluctuation of solvents plays a crucial role in the energy matching condition leading to ET in a solution.

In the ET theory of Marcus,[1−4,7] the ET rate is controlled by a free energy gap of reaction $-\Delta G°$ and reorganization energy λ, which depend on the dielectric constant of the solvent. The dielectric constant is a measure of solvation for the reactant and product. In a charge separation, a larger solvation results in a larger $-\Delta G°$ owing to stabilization of the charge separated state and leads to a larger λ owing to a larger difference in the

equilibrium configuration between initial and final states. For the evaluation of the ET rate in fluid solutions, the static dielectric constant ϵ_S is generally used because the orientational relaxation of polar solvent molecules is assumed to be sufficiently faster than the ET rate. However, the orientational relaxation in glassy solids is highly restricted below the glass transition temperature, and most motions are slower than the ET rate. Thus, the static dielectric constant ϵ_S is not always a suitable measure of the solvation of polar groups in solids.[9−12]

In polymer solids, orientational relaxation has a wide distribution in time scale owing to the variety of relaxation modes; for example, there are some transition temperatures such as melting, glass transition, and side-chain relaxation.[13,14] Above the glass transition temperature (T_g), segments in the main chains are freely mobile. Below the T_g, on the other hand, the free rotational and translational motions of main chains become frozen, but local relaxation modes of side chains still remain and have a wide distribution in relaxation time. In other words, the dielectric constant in polymer solids heavily depends on the measuring frequency and temperature.[13,14] In these frozen media, orientational motions slower than the ET rate would not affect the ET event, and an effective $-\Delta G°$ and λ should be introduced on the basis of the effective dielectric constant instead of ϵ_S.[9−12] Ratner et al. explained the full temperature variation of the ET rate within mixed-metal hemoglobin hybrids embedded in polymer solids by using the temperature-dependent reorganization energy.[15] Miller et al. used the empirical time-dependent reorganization energy to represent larger solvent

* To whom correspondence should be addressed. E-mail: sito@photo.polym.kyoto-u.ac.jp. Fax: +81−75−383−2617.

reorganization of ET on a longer time scale in a rigid organic solid.[9] Although a few researchers have discussed ET in glassy solids from a theoretical standpoint,[10,12,16−18] it is difficult to determine explicitly the effective dielectric constant coupled to ET in polymer glassy solids because of the wide distribution of relaxation time and spatial inhomogeneity in polymer solids. Consequently, there are few experimental reports on the ET in polymer glassy solids compared with the extensive studies on the ET in solutions.[15,19,20] In particular, the effective dielectric constant coupled to ET in polymer solids has never been evaluated experimentally although the importance of the change in $-\Delta G°$ and λ in a rigid medium has been recognized.

Here we investigated the photoinduced charge separation (CS) of intramolecularly linked donor (D) and acceptor (A) compounds[21] in a series of poly(alkyl methacrylate) glassy solids with different T_g values. The effective dielectric constant coupled to CS in polymer solids was directly evaluated by using a novel fluorescent probe (Cz−TP).[22,23] On the basis of the effective dielectric constant, $-\Delta G_{CS}$ and temperature dependence of the CS rate k_{CS} were well explained.

2. Experimental Section

Materials. *Intramolecular Donor−Spacer−Acceptor Compounds.* A series of nine carbazole (Cz; donor)−cyclohexane (S; spacer)−acceptor (A; acceptor) molecules (Cz−S−A) were synthesized and used as intramolecular donor−spacer−acceptor compounds. *N*-Ethylcarbazole (EtCz) and 1,12-di(9-carbazolyl)-dodecane (Cz−12−Cz) were synthesized and used as reference compounds. Details of the synthesis have been described elsewhere.[21]

Poly(alkyl methacrylate)s. A series of poly(alkyl methacrylate)s having different side-chain lengths and glass transition temperatures (T_g's) were used as matrixes: poly(methyl methacrylate) (PMMA, Scientific Polymer Products, $M_w = 39.5 \times 10^4$, $T_g = 378$ K), poly(ethyl methacrylate) (PEMA, Scientific Polymer Products, $M_w = 28 \times 10^4$, $T_g = 339$ K), poly(butyl methacrylate) (PBMA, Scientific Polymer Products, $M_w = 10 \times 10^4$, $T_g = 293$ K), poly(decyl methacrylate) (PDMA, Scientific Polymer Products, $M_w = 10 \times 10^4$, $T_g = 203$ K), and poly(octadecyl methacrylate) (PODMA, $T_g = 173$ K,[24] $T_m = 318$ K (melting temperature of the crystallized side chains)[25]). These poly(alkyl methacrylate)s were purified by reprecipitation from a benzene solution into methanol for PMMA, PEMA, PBMA, and PODMA and from a dichloromethane solution into methanol for PDMA several times.

Methods. *Preparation of Polymer Film Samples.* Polymer films doped with Cz−S−A were prepared on a quartz plate ($15 \times 15 \times 1$ mm³) by the solution casting method for PMMA, PEMA, PBMA, and PDMA and by the spin coating method for PODMA. Casting solvents were benzene (Wako, Spectroscopic grade) for PMMA, PEMA, and PBMA, dichloromethane (Wako, Spectroscopic grade) for PDMA, and tetrahydrofuran (Wako, Spectroscopic grade) for PODMA without further purification. The molar concentration of Cz−S−A and reference compounds in polymer matrixes was adjusted to be on the order of 10^{-3} mol L⁻¹ to prevent intermolecular processes.

Fluorescence Decay Measurements. Fluorescence decay was measured by the time-correlated single-photon-counting method. The excitation light source was third harmonic pulses (295 nm) generated from a mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami 3950) that was pumped by an Ar⁺ laser (Spectra-Physics, BeamLok 2060). The fluorescence emission was detected with a photomultiplier tube (PMT; Hamamatsu Photonics, R3234) through a monochromator (Ritsu, MC-10N)
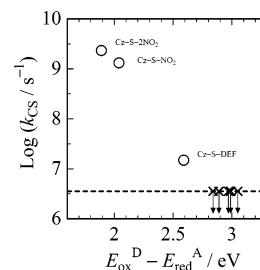

Figure 1. Dependence of k_{CS} of Cz−S−A in a PBMA solid on the potential difference between oxidation potential of Cz (E_{ox}^D) and reduction potential of A (E_{red}^A) at 295 K. Open circles (○) are k_{CS} values of Cz−S−DEF, Cz−S−NO₂, and Cz−S−2NO₂. Crosses (×) are k_{CS} of the other six kinds of Cz−S−A less than $10^{6.6}$ s⁻¹ (- - -), which cannot be any longer ascribed to CS.

with a cutoff filter (UV-34) for the excitation light. The details of this apparatus have been described elsewhere.[26] The total instrument response function has an fwhm of ca. 750 ps at the excitation wavelength. The decay data were fitted with sums of a function that were convoluted with the instrument response function by the nonlinear least-squares method.

Temperature Control. The temperature of the film samples cast on a quartz plate was controlled in a cryostat (Iwatani Plantech Corp., CRT510) with PID temperature control unit (Scientific Instruments, model 9650).

3. Results and Discussion

Redox Potentials of Cz−S−A and k_{CS} in PBMA Glassy Solid at Room Temperature. First, we investigated k_{CS} of nine kinds of Cz−S−A in a PBMA glassy solid at room temperature. These Cz−S−A compounds have different $E_{ox}^D − E_{red}^A$ values ranging from 3.05 to 1.89 eV: this is the energy difference between the oxidation potential E_{ox}^D of Cz donor and the reduction potential E_{red}^A of acceptor.[21] Owing to inhomogeneity of polymer solids, fluorescence decay $I(t)$ of Cz−S−A was well fitted with a sum of three exponential functions as eq 1 by the nonlinear least-squares method. One of them is ascribable to an impurity Cz fluorescence without A moiety, which is a minor component less than 5%.[21] Thus, k_{CS} was calculated by $k_{CS} =$

$$I(t) = I_0 \sum_i A_i \exp(- t/\tau_i) \tag{1}$$

$\langle \tau \rangle^{-1} − \tau_0^{-1}$, where τ_0 is the fluorescence lifetime of the reference compound and $\langle \tau \rangle$ is the averaged lifetime of the major two components in the fluorescence of Cz−S−A. As shown in Figure 1, k_{CS} decreased with an increase in $E_{ox}^D − E_{red}^A$, and no photoinduced CS was observed for Cz−S−A with $E_{ox}^D − E_{red}^A$ larger than 2.80 eV: the difference between $\langle \tau \rangle$ and τ_0 was less than about 5% of τ_0. As reported previously, photoinduced CS is observed for all nine kinds of Cz−S−A in polar solutions and a polar polymer solid.[21] Thus, these results indicate that a strong acceptor with a large E_{red}^A is required for photoinduced CS in a PBMA glassy solid, because the charge separated state is not well stabilized in a nonpolar glassy solid such as PBMA where thermal fluctuations of polar groups are highly restricted.

Temperature Dependence of k_{CS} in a PBMA Glassy Solid. Next, the fluorescence decays of Cz−S−DEF, Cz−S−NO₂, and reference compound EtCz in a PBMA solid were measured over the temperature range 100−400 K. Figure 2 shows the fluorescence decay of Cz−S−DEF (—) and the reference EtCz (- - -) at various temperatures. The fluorescence emission of Cz−S−DEF decayed faster than that of EtCz over the whole
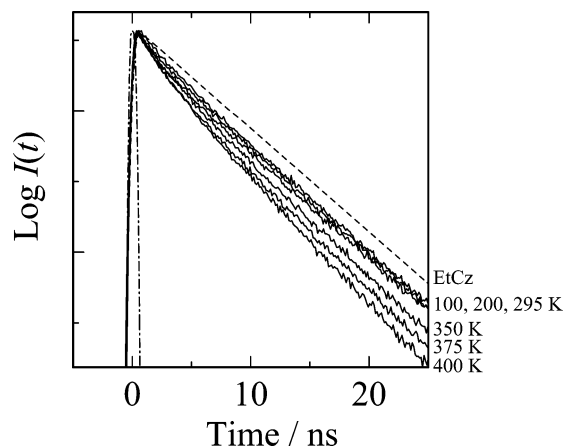
Intramolecular Charge Separation in Polymer Solids

J. Phys. Chem. B, Vol. 108, No. 42, 2004 **16459**

Figure 2. Temperature dependence of fluorescence decay curve $I(t)$ of Cz−S−DEF and the reference EtCz in a PBMA glassy solid. A broken line (- - -) is the fluorescence decay of EtCz. Solid lines (—) are the fluorescence decays of Cz−S−DEF at each temperature, 100, 200, 295, 350, 375, and 400 K, from top to bottom.
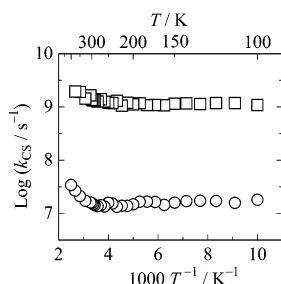

Figure 3. Temperature dependence of k_{CS} of Cz−S−DEF (○) and Cz−S−NO$_2$ (□) compounds in a PBMA glassy solid from 100 to 400 K.

temperature, indicating that the Cz moiety in the excited state is quenched by the DEF acceptor moiety. The decay curve was temperature independent below the T_g, 100, 200, and 295 K, while it decayed rapidly with increasing temperature above the T_g, 350, 375, and 400 K. On the other hand, the decay curve of Cz−S−NO$_2$ was independent of temperature both above and below the T_g. From these decay curves, k_{CS} was evaluated.

As shown in Figure 3, there was an explicit difference in the temperature dependence of k_{CS} between Cz−S−DEF and Cz−S−NO$_2$. This difference is probably due to the difference in their $-\Delta G_{CS}$ values. As we previously reported,[21] photoinduced CS of Cz−S−DEF occurs in the normal region and that of Cz−S−NO$_2$ occurs near the top region in the Marcus relation. Thus, the increase in k_{CS} of Cz−S−DEF above the T_g indicates that thermal fluctuations of polar groups induced by the main-chain relaxation enhances the probability of energy matching between the initial and the final state of the charge separation. On the other hand, the temperature independence of k_{CS} of Cz−S−NO$_2$ ensures that the increase in k_{CS} of Cz−S−DEF above the T_g results not from the change in the separation distance between the Cz and A moieties but from activated thermal fluctuations of polar groups.

Temperature Dependence of k_{CS} of Cz−S−DEF in Various Poly(alkyl methacrylate) Solids. To demonstrate that photoinduced charge separation is enhanced by thermal fluctuations of polar groups above the T_g, k_{CS} of Cz−S−DEF in a series of poly(alkyl methacrylate)s was measured over the temperature range 100−400 K. As shown in Figure 4, an increase in k_{CS} was observed for each poly(alkyl methacrylate) except for PMMA. For PEMA and PBMA, k_{CS} increased just above their T_g. For PDMA, it increased above $T = 250$ K. This
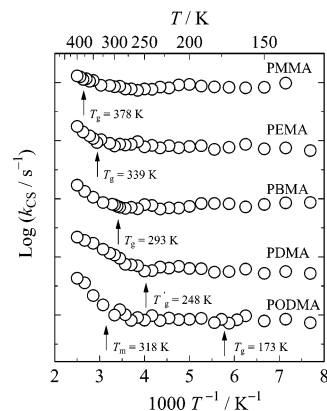

Figure 4. Temperature dependence of k_{CS} of Cz−S−DEF in a series of poly(alkyl methacrylate) solids having various T_g values: PMMA ($T_g = 378$ K); PEMA ($T_g = 339$ K); PBMA ($T_g = 293$ K); PDMA (there are two glass transitions, $T_g = 203$ K and $T'_g = 248$ K);[27,28] PODMA ($T_g = 173$ K[24] and melting temperature of crystallized side chains $T_m = 318$ K[25]).

temperature, 250 K, corresponds to one of the two glass transition temperatures of PDMA, $T_g = 203$ K and $T'_g = 248$ K, which are ascribed to cooperative motions of the long side chains and to main-chain motions, respectively.[27,28] The former T_g cannot induce motions of polar ester groups because they are bound at the root of the main chain. On the other hand, the latter T'_g can enhance motions of polar ester groups enough to be detected by dielectric relaxation measurements. For PMMA, k_{CS} was independent of temperature. This is because PMMA has a higher glass transition temperature below which motions of polar groups are highly restricted due to the frozen main-chain motions. For PODMA, k_{CS} increased at higher temperatures above not $T_g = 173$ K but $T_m = 318$ K. Owing to a long alkyl group in the side chain, PODMA has a melting temperature of the side chain $T_m = 318$ K,[25] which is much higher than the glass transition temperature $T_g = 173$ K.[24] Thus, motions of the side chain are highly restricted below the T_m even above the T_g. Above the T_m, motions of a polar ester group can be drastically released and enhance the charge separation. From these results, we conclude that sufficient thermal fluctuations of polar ester groups enhanced by main-chain motions are required for photoinduced charge separation in a nonpolar polymer glassy solid such as poly(alkyl methacrylate)s.

Dielectric Relaxation of PBMA Glassy Solid. To evaluate thermal fluctuations of polar groups in a polymer solid, dielectric relaxation spectra were measured for the PBMA glassy solid in the temperature range 200−340 K and frequency range 0.1−100 kHz. The dielectric spectra observed were analyzed with a single Cole−Cole function (eq 2).[14,29] In eq 2, $\epsilon^*(\omega)$ is the complex dielectric permittivity, ϵ_S is the static dielectric constant, ϵ_∞ is the optical dielectric constant, τ_m is the average dipolar relaxation time, β ($0 < \beta \leq 1$) is a parameter describing the distribution of relaxation time, and i is the imaginary unit. Here,

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_S - \epsilon_\infty}{1 + (i\omega\tau_m)^\beta} \qquad (2)$$

the real $\epsilon'(\omega)$ (dielectric constant) and imaginary $\epsilon''(\omega)$ (dielectric loss factor) parts are related to $\epsilon^*(\omega)$ by the following equation: $\epsilon^* = \epsilon'(\omega) - i\epsilon''(\omega)$.

Figure 5 shows the temperature dependence of dielectric constant $\epsilon'(\omega)$ for PBMA at various angular frequencies ω ($\omega = 2\pi f$, f is frequency). Because of the wide distribution in relaxation time, $\epsilon'(\omega)$ showed a different temperature depen-
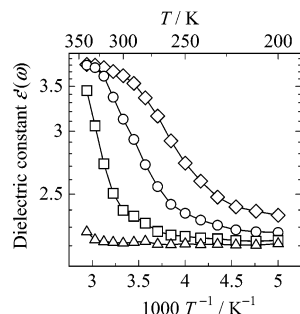
Figure 5. Temperature dependence of dielectric constant $\epsilon'(\omega)$ for PBMA at various angular frequencies ω: 10^{-3} rad s^{-1} ($\Diamond$); 10^0 rad s^{-1} ($\bigcirc$); 10^3 rad s^{-1} ($\square$); 10^6 rad s^{-1} ($\triangle$). These were obtained by fitting analysis with the Cole–Cole equation (eq 2) for dielectric relaxation measurements in the temperature range 200–340 K and frequency range 0.1–100 kHz, respectively.

dence at the measuring frequency ω. In other words, $\epsilon'(\omega)$ heavily depends on the measuring frequency in polymer solids. It is noteworthy that the temperature dependence of $\epsilon'(\omega)$ is in good agreement with that of k_{CS} of Cz–S–DEF at a higher frequency. This finding suggests that fast motions of a polar group observed at higher frequencies effectively promote charge separation in polymer solids. However, we cannot determine specifically the value of $\epsilon'(\omega)$, which is required for a theoretical calculation of k_{CS}.

Evaluation of Local Polarity of Polymer Solids using a Cz–TP Probe. In the ET formula of Marcus theory,[1–4,7] as shown in eqs 3[30,31] and 4, k_{CS} depends on dielectric constant of the matrix through the free energy gap $-\Delta G_{CS}$ and solvent reorganization energy λ_S. For ET in solutions, static dielectric

$$-\Delta G_{CS} = E(S_1) - (E_{ox}^D - E_{red}^A) + \frac{e^2}{4\pi\epsilon_0}\left\{\frac{1}{\epsilon_S r_{DA}} + \frac{1}{2}\left(\frac{1}{r_D} + \frac{1}{r_A}\right)\right.$$
$$\left.\left(\frac{1}{37.5} - \frac{1}{\epsilon_S}\right)\right\} \quad (3)$$

$$\lambda_S = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}}\right)\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_S}\right) \quad (4)$$

constant ϵ_S is used in eqs 3 and 4 because orientational fluctuation of polar solvents is so fast that the dielectric constant $\epsilon'(\omega)$ remains the same as ϵ_S even at high frequencies comparable to the ET rate. As mentioned above, on the other hand, the dielectric constant in polymer solids depends on the measuring frequency. Thus, in general, the dielectric constant at a high frequency comparable to the ET rate should be smaller than ϵ_S. Miller et al. used the empirical time-dependent reorganization energy to explain the peak shift of the ET rate vs $\Delta G°$ curve.[9] Wasielewski et al. reported that the free energy gap of charge separation is shifted as much as 0.8 eV when moved from a polar liquid to a rigid glassy solid.[11] Theoretically, some researchers pointed out that ET in a rigid medium should be modified to take into account any change in the free energy gap and a decrease in the solvent reorganization energy.[9–12,16] They assumed that intramolecular vibrations and part of the solvent dielectric polarization remain dynamic in rigid media while the remaining part of the solvent polarization is frozen. Ratner et al. explained the full temperature variation of the ET rate within mixed-metal hemoglobin hybrids embedded in a polymer glass by using the two-mode ET expression of Hopfield with temperature-dependent reorganization energy.[15] All these treatments demonstrate that the dielectric constant effective for ET in rigid media is different from a static dielectric constant
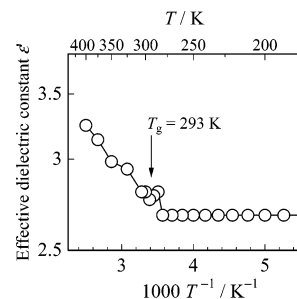

Figure 6. Temperature dependence of the effective dielectric constant ϵ' of a PBMA glassy solid evaluated with a fluorescent Cz–TP probe.

TABLE 1: Values of $-\Delta G_{CS}$ for Cz–S–A at 295 K

				A				
	CF$_3$	5F	Cin	2CF$_3$	TP	CN	DEF	NO$_2$	2NO$_2$
$-\Delta G_{CS}(\epsilon_S)^a$ (eV)	−0.03	0.03	0.05	0.13	0.18	0.22	0.43	0.98	1.13
$-\Delta G_{CS}(\epsilon')^b$ (eV)	−0.26	−0.20	−0.18	−0.10	−0.05	−0.01	0.20	0.75	0.90

^{a} $-\Delta G_{CS}$ was calculated with static dielectric constant $\epsilon_S = 3.75$ at 295 K obtained by fitting the dielectric data with eq 2. ^{b} $-\Delta G_{CS}$ was calculated with effective dielectric constant $\epsilon' = 2.76$ evaluated by using a fluorescent Cz–TP probe at 295 K.

used for ET in liquid solutions. However, the effective dielectric constant has been treated as a parameter but never been experimentally evaluated. Here we evaluate the effective dielectric constant for ET in polymer glassy solids by using a novel fluorescent probe (Cz–TP).[22,23]

Photophysical properties of the fluorescent probe have been reported previously.[22] The Cz–TP molecule has two advantages as a local polarity probe for ET. One is that the lifetime of Cz–TP in the excited state has a time scale comparable to that of the ET event in Cz–S–A. Thus, the effective dielectric constant for ET can be evaluated because the Cz–TP probe reflects selectively orientational polarizations within the lifetime of the excited state. The other is that the molecular size of Cz–TP is also comparable to that of Cz–S–A. This size matching ensures that the effective dielectric constant originates from the surrounding medium of Cz–S–A molecules. Figure 6 shows the temperature dependence of the effective dielectric constant ϵ' of PBMA evaluated with the Cz–TP probe.[23] As shown in the figure, the Cz–TP probe detected sensitively even a small change in the dipolar fluctuations at the glass transition temperature. The temperature dependence of ϵ' was in good agreement with that of k_{CS} in Cz–S–DEF: both of them increased just above the T_g. This good agreement clearly shows that thermal fluctuations of polar groups within a time scale of the lifetime of EtCz in the excited state promote photoinduced charge separation effectively. The same tendency was observed for not only PBMA but also the other kinds of poly(alkyl methacrylate)s.[23] As mentioned above, on the other hand, the free energy gap $-\Delta G_{CS}$ also should be modified with the effective dielectric constant. Table 1 summarizes the free energy gap $-\Delta G_{CS}$ of Cz–S–A in PBMA at 295 K: one series $-\Delta G_{CS}(\epsilon_S)$ is estimated from the static dielectric constant $\epsilon_S = 3.75$, the other series $-\Delta G_{CS}(\epsilon')$ is estimated from the effective dielectric constant $\epsilon' = 2.76$ evaluated by the Cz–TP probe. All the $-\Delta G_{CS}(\epsilon_S)$ values are positive except for that of Cz–S–CF$_3$ while only $-\Delta G_{CS}(\epsilon')$ of Cz–S–DEF, Cz–S–NO$_2$, and Cz–S–2NO$_2$ are positive. Because charge separation was observed for Cz–S–DEF, Cz–S–NO$_2$, and Cz–S–2NO$_2$ in PBMA, $-\Delta G_{CS}$ dependence of k_{CS} can be well explained by $-\Delta G_{CS}(\epsilon')$ rather than $-\Delta G_{CS}(\epsilon_S)$. These findings ensure that
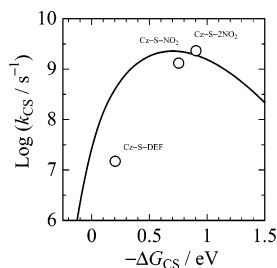
Intramolecular Charge Separation in Polymer Solids

J. Phys. Chem. B, Vol. 108, No. 42, 2004 **16461**

Figure 7. Free energy gap $-\Delta G_{CS}$ dependence of k_{CS} of Cz−S−DEF, Cz−S−NO$_2$, and Cz−S−2NO$_2$ in a PBMA glassy solid at 295 K. The solid line (—) is a theoretical curve calculated by eq 5 with the following parameters: $\lambda_V = 0.56$ eV, $\hbar\omega = 1300$ cm^{-1}, $V = 3.5$ cm^{-1}, $T = 295$ K. Here, $-\Delta G_{CS}$ and λ_S were calculated with the effective dielectric constant $\epsilon' = 2.76$ and the optical dielectric constant $\epsilon_\infty = n^2$ (square of the refractive index n of PBMA, $n = 1.48$) in eqs 3 and 4.

the Cz−TP probe is useful for evaluating the effective dielectric constant, and, furthermore, the change in the free energy gap and reduced solvent reorganization energy, for k_{CS} of Cz−S−A in polymer solids.

Analysis of k_{CS} by Modified $-\Delta G_{CS}$ and λ_S in a PBMA Glassy Solid. Using the effective dielectric constant ϵ' evaluated by the Cz−TP probe, k_{CS} in the PBMA glassy solid was analyzed by a single quantum mode ET formula, which well explains ET in solution and a polar polymer solid above the T_g.[21] Figure 7 shows the $-\Delta G_{CS}$ dependence of k_{CS} of Cz−S−DEF, Cz−S−NO$_2$, and Cz−S−2NO$_2$ at 295 K. The solid curve in the figure represents the theoretical prediction by eq 5.[32] Except for $-\Delta G_{CS}$ and λ_S, the parameters used were the

$$k_{CS} = \frac{2\pi}{\hbar}|V|^2 \frac{1}{\sqrt{4\pi\lambda_S k_B T}} \times$$

$$\sum_m \left\{ \frac{S^m \exp(-S)}{m!} \exp\left[-\frac{(\lambda_S + m\hbar\omega + \Delta G_{CS})^2}{4\lambda_S k_B T} \right] \right\} \quad (5)$$

$$S = \frac{\lambda_V}{\hbar\omega}$$

same as those in our previous report: $\lambda_V = 0.56$ eV, $\hbar\omega = 1300$ cm^{-1}, $V = 3.5$ cm^{-1}.[21] This theoretical result ensures that photoinduced CS of Cz−S−DEF and Cz−S−NO$_2$ in the PBMA glassy solid proceeds in the normal and top region, respectively. For CS in the top region, there is no thermal barrier because the potential energy curve in the final state crosses at the minimum of that in the initial state. Thus, k_{CS} of Cz−S−NO$_2$ is independent of temperature. On the other hand, CS of Cz−S−DEF occurs in the normal region where thermal fluctuations of a medium are required to realize a nuclear configuration meeting the energy matching condition. This energy matching probability is described by the Franck−Condon factor (FC). From eq 5, FC for the ET formula with a single quantum mode can be expressed by eq 6. Figure 8 shows temperature

$$FC = \frac{1}{\sqrt{4\pi\lambda_S k_B T}} \times$$

$$\sum_m \left\{ \frac{S^m \exp(-S)}{m!} \exp\left[-\frac{(\lambda_S + m\hbar\omega + \Delta G_{CS})^2}{4\lambda_S k_B T} \right] \right\} \quad (6)$$

dependence of FC calculated for Cz−S−DEF with the temperature dependent $-\Delta G_{CS}$ and λ_S evaluated by the effective
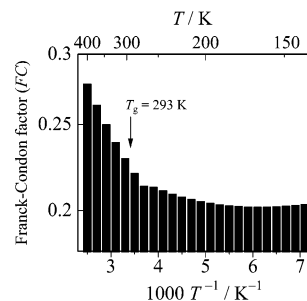

Figure 8. Temperature dependence of FC calculated by eq 6 for Cz−S−DEF with the temperature dependent $-\Delta G_{CS}$ and λ_S evaluated by the effective dielectric constant ϵ' at each temperature in eqs 3 and 4. Other parameters are $\lambda_V = 0.56$ eV and $\hbar\omega = 1300$ cm^{-1}. Optical dielectric constant ϵ_∞ in eq 4 is calculated as the square of the refractive index n^2 of PBMA ($n = 1.48$).

dielectric constant ϵ'. The FC increased steeply above the T_g and well reproduced the temperature dependent k_{CS} of Cz−S−DEF whereas there is no steep increase in the FC calculated with ϵ_S around the T_g. In eq 6, $\lambda_S + \Delta G_{CS}$ is independent of temperature whereas each λ_S and ΔG_{CS} depends on temperature. Therefore, it is safely said that temperature dependent λ_S results in the increase in FC above the T_g. Ratner et al. also used a temperature dependent λ_S based on the Vogel−Fulcher equation to explain a temperature dependence of k_{ET}.[15] On the other hand, our temperature dependent λ_S is experimentally evaluated with the Cz−TP fluorescent probe and can be also expressed as the Vogel−Fulcher equation. The temperature dependent λ_S causes enhancement of the solvent fluctuation in proportion to $\sqrt{2k_B T\lambda_S}$, which promotes the energy matching probability above the T_g. From these findings, we conclude that photoinduced CS is promoted by the increase in the energy matching probability, resulting from the enhanced orientational fluctuations of polar ester groups above the T_g.

Conclusion

In poly(alkyl methacrylate) glassy solids, k_{CS} of Cz−S−DEF increased just above the transition temperature T_g or T_m. The temperature dependence of k_{CS} was well explained with the effective dielectric constant ϵ' evaluated by using a Cz−TP fluorescent probe. The free energy gap dependence of k_{CS} in PBMA was thoroughly investigated. Consequently, it was found that $-\Delta G_{CS}(\epsilon')$ rather than $-\Delta G_{CS}(\epsilon_S)$ gave effective stabilization energy of a charge separated state in a polymer glassy solid. The temperature dependence of k_{CS} above T_g in PBMA was well explained by using the temperature dependent $\lambda_S(\epsilon')$ reflecting the dynamics of main chains. These findings show that photoinduced CS in poly(alkyl methacrylate)s is promoted by orientational motions of ester groups with a relaxation time comparable to the CS event.

References and Notes

(1) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(2) Marcus, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1111.

(3) Marcus, R. A. *J. Electroanal. Chem.* **1997**, *438*, 251.

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

(5) De Vault, D. *Quantum Mechanical Tunneling in Biological Systems*; Cambridge University Press: Cambridge, 1984.

(6) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(7) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.

(8) Kuznetsov, A. M.; Ulstrup, J. *Electron Transfer in Chemistry and Biology*; John Wiley & Sons: New York, 1999.

(9) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057.

(10) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 4963.

(11) Gaines, G. L.; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719.

(12) Chen, P.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 5520.

(13) Karasz, F. E. *Dielectric Properties of Polymers*; Plenum Press: New York, 1972.

(14) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover Publications: New York, 1967.

(15) Dick, L. A.; Malfant, I.; Kuila, D.; Nebolsky, S.; Nocek, J. M.; Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 11401.

(16) Hoffman, B. M.; Ratner, M. A. *Inorg. Chim. Acta* **1996**, *243*, 233.

(17) Onuchic, J. N.; Wolynes, P. G. *J. Chem. Phys.* **1993**, *98*, 2218.

(18) Dakhnovskii, Y.; Lubchenko, V.; Wolynes, P. G. *J. Chem. Phys.* **1996**, *104*, 1875.

(19) Mikkeksen, K. V.; Ratner, M. A. *Chem. Rev.* **1987**, *87*, 113.

(20) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439.

(21) Ohkita, H.; Benten, H.; Anada, A.; Noguchi, H.; Kido, N.; Ito, S.; Yamamoto, M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3977.

(22) Benten, H.; Ohkita, H.; Ito, S.; Yamamoto, M.; Tani, K.; Tohda, Y. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 393.

(23) Benten, H.; Ohkita, H.; Ito, S.; Yamamoto, M.; Tani, K.; Tohda, Y. *Polymer* **2004**, *45*, 2831.

(24) *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975.

(25) Alig, I.; Jarek, M.; Hellmann, G. P. *Macromolecules* **1998**, *31*, 2245.

(26) Ohkita, H.; Ito, S.; Yamamoto, M.; Tani, K.; Tohda, Y. *J. Phys. Chem. A* **2002**, *106*, 2140.

(27) Beiner, M.; Schroter, K.; Hempel, E.; Ressing, S.; Donth, E. *Macromolecules* **1999**, *32*, 6278.

(28) Beiner, M. *Macromol. Rapid Commun.* **2001**, *22*, 869.

(29) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341.

(30) Weller, A. *Z. Phys. Chem. N. F.* **1982**, *133*, 93.

(31) Chibisov, A. *Russ. Chem. Rev.* **1981**, *50*, 1169.

(32) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860.