Charge Recombination Luminescence *via* the Photoionization of a Dopant Chromophore in Polymer Solids

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ABSTRACT: The behavior of a photoejected electron with the parent cation formed through two-photon ionization of a dopant chromophore in poly(alkyl methacrylate)s and polystyrene was studied by measurement of the emission spectra of the charge recombination luminescence, *i.e.*, isothermal luminescence (ITL) at 20 K and thermoluminescence (TL) at temperatures from 20 to 300 K. The ITL spectral shape remained the same between 10 min and 10 h after the photoirradiation. On the other hand, the intensity ratio of phosphorescence (I_P) to fluorescence (I_F), I_P/I_F in the TL spectra increased for poly(alkyl methacrylate)s above a temperature where small scale motions of the main chain are released but was almost constant for polystyrene in the temperature range examined. These findings show that, for poly(alkyl methacrylate)s, the photoejected electrons change into more stable anion species with a motional relaxation of the polymer. From the TL spectral change, the depth of the deeper trap at higher temperatures was estimated to be more than 1.8 eV.

1. Introduction

The charge transport in solid systems is of scientific and practical interest, because it is a key process to photoconduction,[1] electroluminescence,[2] and the photorefractive effect.[3] The charge recombination of electron−hole pairs formed in irradiated solids can be observed through the charge recombination luminescence, which is called isothermal luminescence (ITL) at a fixed temperature or thermoluminescence (TL) with increasing temperature.[4]

There have been various investigations on the ITL for irradiated organic glasses or polymer solids at a low temperature. The ITL decay kinetics is reported to obey the t^{-1} law: the ITL intensity is proportional to an inverse power function of time t.[5−8] In most cases, the kinetics is independent of temperature.[7,8] Thus, many authors explained the ITL decay in terms of a long-range electron transfer by electron tunneling.[9−14] In this model, the trap depth is assumed to be unique and constant with time. However, the direct evidence for the assumptions is lacking because of the difficulty of the absorption measurements of the transient ionic species.

On the other hand, the TL method has been historically used to examine the energy level of impurities and defects in an insulator or a semiconductor. It is still a unique method for measuring the trap depth of organic or inorganic insulators. With the pioneer work of Randall and Wilkins,[15] a big step was made in theoretical analysis of the TL. Nikolski and Buben[16] studied TL of polymer solids. They found, for the first time, that the TL glow curve sensitively reflects polymer chain motions. Since then, it has been widely used in the field of polymer chemistry as an effective method for observing the motional relaxation of polymer solids. In particular, Partridge and Charlesby[17,18] investigated the TL for the nonpolar polymer solids such as polyethylene and polypropylene. However, little is known about the mechanism since the nature of the trap for an ejected electron is not understood in detail.

Our measurement system is different from the previously reported high-energy irradiated system in the following two points.

In our system, an aromatic chromophore was doped in polymer solids to clarify the luminescence center; the dopant chromophore clearly acts as a luminescence center because the ITL and TL spectra are identical with the emission spectra of the dopant chromophore. Although several reports have been made on irradiated polymers doped with a chromophore, high-energy irradiation might cause various side reactions because of the direct excitation of the polymer matrix. Thus, we used an excimer laser pulse as an excitation light source instead of the high-energy radiation. The excimer laser pulse is so intense that it can feed two photon simultaneously or another photon within the lifetime of an electronic excited dopant chromophore. The chromophore that absorbed two photons is excited to a higher electronic excited state above the ionization potential and ejects an electron to the matrix polymer. This phenomenon is called two-photon ionization. The dopant aromatic chromophores used here have absorption at 351 nm, which is the wavelength of a XeF excimer laser pulse, but none of the polymer matrices used have absorption at the excitation wavelength. Therefore, two-photon ionization enables us to selectively ionize a dopant chromophore in a polymer solid without direct excitation of the polymer matrix.[19−22]

We observed the emission spectra of the charge recombination luminescence, not the total emission intensity. Most of various attempts[23] for obtaining information on the motional relaxation of polymer solids using the TL glow curve of the irradiated polymer were made by measurement of the total emission intensity of the TL, not the emission spectra. The total emission intensity of TL, *i.e.*, the glow curve, gives us information on the motional relaxation of the polymer solids, but the emission spectra provide information on the change in a trap depth with temperature as well as the motional relaxation of the polymer solids. The intensity ratio of phosphorescence to fluorescence I_P/I_F changes with the trap depth. If the trap depth is constant, the emission spectra hardly change and the intensity ratio I_P/I_F remains the same.

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In this study, we observed the emission spectra of ITL at 20 K and TL in the wide temperature range from 20 to 300 K for several photoirradiated polymer films doped with an aromatic chromophore. Concerning ITL, we focused on the charge recombination process of a photoejected electron with the parent cation at a temperature as low as 20 K where major motions of polymer chains are frozen, whether the trap depth changes with time or not. We assigned the observed TL glow peaks for each polymer to the motional relaxation of the polymer, elucidated the relationship between the change in depth of trapped electrons[24] and the motional relaxation of the polymer with increasing temperature, and examined the difference in the photoinduced chemical reactivity between poly(alkyl methacrylate)s and polystyrene. Finally, we propose a reaction scheme for the charge recombination of a photoejected electron with the parent cation in polymer solids produced through two-photon ionization and estimate the trap depth from the TL spectral change with temperature.

2. Experimental Part

Sample Preparation. Polymer matrices used in the present work were poly(*n*-butyl methacrylate) (PnBMA, M_w = 10^5, Scientific Polymer Products), poly(ethyl methacrylate) (PEMA, $M_w = 2.8 \times 10^5$, Scientific Polymer Products), and polystyrene (PSt, $M_n = (1.6-1.8) \times 10^5$, Wako Pure Chemical Industries, Ltd.). Poly(alkyl methacrylate)s belong to the category of scission type for radiation.[25,26] Polystyrene is relatively resistant to radiation although it belongs to the category of cross-linking type.[25,26] The glass transition temperatures (T_g) of the polymers are 293 K (PnBMA), 339 K (PEMA), and 373 K (PSt).[27] These polymers were purified by reprecipitation from a benzene solution into methanol three times. *N*,*N*,*N*′,*N*′-Tetramethylbenzidine (TMB, Wako Pure Chemical Industries, Ltd.) was used as a dopant chromophore and was purified by recrystallization several times.

The sample films were prepared by the solution cast method. The films were evacuated above the T_g to remove the remaining trace of the casting solvent (benzene; Dojin, Spectrosol) until no absorption of benzene was observed with a spectrophotometer (Hitachi, U-3500). The concentration of TMB in the final polymer film was *ca.* 3×10^{-3} mol/L. The thickness of the film was *ca.* 200−300 μm.

Measurement. A polymer film doped with TMB was covered with a quartz plate (20 × 30 × 0.5 mm), fixed tightly on a copper cold finger of a cryostat (Iwatani Plantech Corp., CRT510), and then, *in vacuo*, cooled to 20 K. The temperature of the sample film was monitored with a calibrated thermocouple (Au + 0.07% Fe/chromel) and was kept constant using a PID temperature control unit (Iwatani Plantech Corp., TCU-4). The sample film was repeatedly photoirradiated by 351-nm light pulses from an excimer laser (Lambda Physik, EMG101MSC, *ca.* 20 ns fwhm, *ca.* 60 mJ/pulse). The 351-nm laser pulses allow us to selectively ionize the TMB dopant chromophore, because none of these polymers used in the present work have absorption at 351 nm. The emission spectra of the isothermal luminescence (ITL or preglow) were measured with a spectrofluorometer (Hitachi, 850) from 10 min to 10 h after the photoirradiation at 20 K. Subsequently, the temperature of the sample film was raised at a heating rate of 5 °C/min using the PID temperature control unit. The emission spectra of the thermoluminescence (TL or glow) were measured at temperatures from 20 to 300 K. All the emission spectra were measured at a scanning rate of 480 nm/min to escape from the spectral change with time; the time required for the scanning from 400 (λ_F) to 530 nm (λ_P) was *ca.* 16 s.

Temperature Dependence of Steady-State Emission Spectra of TMB Doped in Polymer Solids. From the TMB chromophore doped in a polymer solid, phosphorescence as well as fluorescence was observed even at room temperature. Figure 1 shows the total emission spectra of the TMB doped in a PnBMA film at temperatures from 20 to 300 K. The emission peaks observed around 400 and 530 nm are ascribable to fluorescence and phosphorescence, respectively. As the figure shows, the fluorescence intensity I_F was nearly constant at temperatures from 20 to 300 K while the phosphorescence intensity I_P decreased steeply above 200 K and disappeared near the T_g of the polymer matrix. Similar emission spectra were also obtained for the TMB doped in PEMA and PSt.

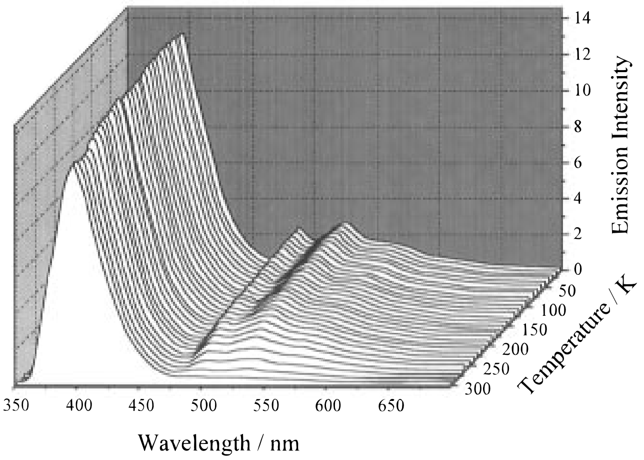

Figure 1. Total emission spectra of the TMB doped in a PnBMA film over the temperature range from 20 to 300 K.

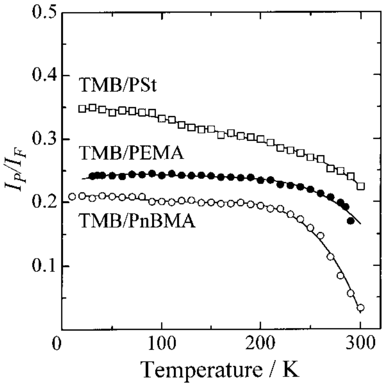

Figure 2. Temperature dependence of the intensity ratio of phosphorescence to fluorescence I_P/I_F for the TMB chromophore doped in polymer matrices: (open circles) TMB/PnBMA; (closed circles) TMB/PEMA; (open squares) TMB/PSt.

Figure 2 shows the dependence of the intensity ratio I_P/I_F on temperature for all the polymer matrices doped with TMB used. As shown in Figure 2, the intensity ratio I_P/I_F for steady-state emission decreased with an increase in temperature; the I_P decreased with increasing temperature because nonradiative deactivation of the dopant chromophore was enhanced at higher temperatures.

3. Results and Discussion

3-1. Spectral Change in Isothermal Luminescence (Preglow) with Time. Most ejected electrons through two-photon ionization are captured by the polymer matrix at a temperature as low as 20 K. However, some of them recombine with their parent−cation chromophores even at a fixed low temperature. As a result of the recombination, the chromophore is electronically excited again and emits fluorescence and/or phosphorescence. This emission is called isothermal luminescence (ITL) or preglow.

Figure 3 shows the spectral change in the ITL for the TMB doped in a PnBMA film that was photoirradiated at 20 K. The phosphorescence intensity I_P of the ITL was larger than the fluorescence intensity I_F of the ITL, contrary to the steady-state emission spectra shown in Figure 2. The intensity ratio I_P/I_F for the ITL was

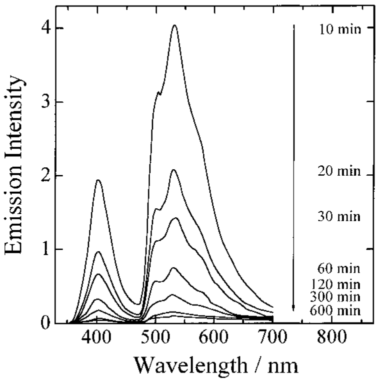

Figure 3. Emission spectral change in the ITL for the TMB chromophore doped in a PnBMA film over the time range from 10 to 600 min after the photoirradiation at 20 K.

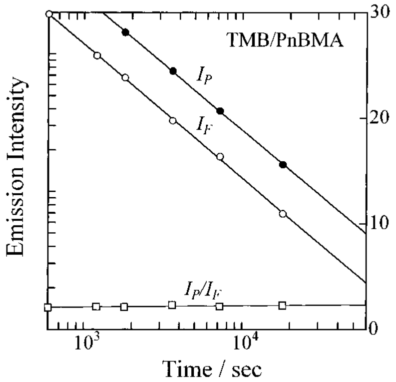

Figure 4. Dependence of the fluorescence intensity I_F (open circles), the phosphorescence intensity I_P (closed circles), and the intensity ratio I_P/I_F (open squares) on time change for the ITL at 20 K of the TMB chromophore doped in a PnBMA film. Solid lines in this figure are fitted using the least squares methods.

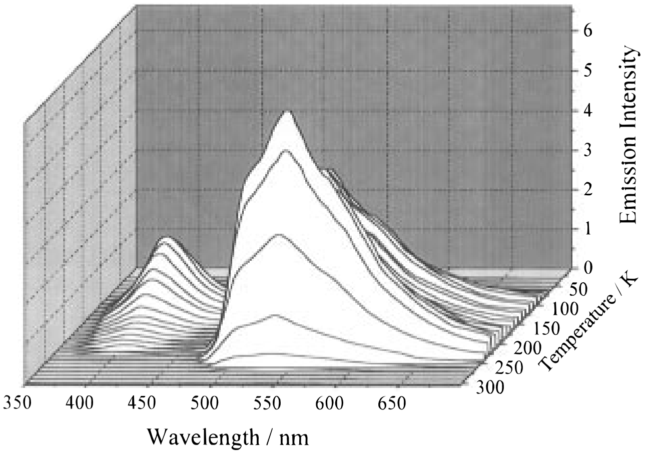

Figure 5. Emission spectral change in the TL of the TMB chromophore doped in a PnBMA film at temperatures from 20 to 300 K. Sample films were photoirradiated at 20 K. The heating rate was 5 °C/min.

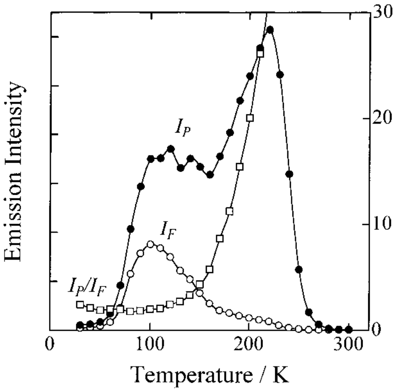

Figure 6. Dependence of the fluorescence intensity I_F (open circles), the phosphorescence intensity I_P (closed circles), and intensity ratio I_P/I_F (open squares) on temperature for the TL of the TMB chromophore doped in a photoirradiated PnBMA film at temperatures from 20 to 300 K. The heating rate was 5 °C/min.

ca. 2, while that for the steady-state emission spectra was *ca.* 0.2. If the energy level of a trapped electron is much higher than the excited singlet state of the parent–cation chromophore, the charge recombination results in both the excited singlet state and triplet state of the dopant chromophore. In the simplest case, the ratio of excited triplet state to excited singlet state produced by charge recombination will be three to one owing to the 3-fold degeneracy of the triplet state, because trapped electrons stay in traps for a much longer time than their spin relaxation time in the case of TL.[28,29]

Figure 4 shows the ITL decay at 20 K for the TMB doped in a PnBMA film; similar results were obtained for the other polymers. The log–log plots of I_F or I_P against time t from the end of the photoirradiation show straight lines; both decays of I_F and I_P for the ITL obeyed the t^{-1} law for all the polymer matrices used.[30] The t^{-1} law has been reported in the field of radiation chemistry.[5–8] This decay kinetics is often theoretically explained using the long-range electron transfer model on the basis of electron tunneling,[9–14] because it is independent of the temperature.[7,8] We observed the ITL at a temperature as low as 20 K where even the side-chain motion of a polymer seems to be almost frozen. Therefore, the ITL is also considered to take place through charge recombination *via* electron tunneling.

The open squares shown in the figure denote the intensity ratio I_P/I_F. The intensity ratio I_P/I_F for all the polymers used is nearly constant over the time range from 10 min to 10 h after the photoirradiation, which indicates that the energy level of trapped electrons is high enough to reproduce both the excited singlet state and triplet state as a result of the charge recombination and the depth of trapped electrons involved in the charge recombination is nearly constant with time at 20 K.[31]

3-2. Spectral Change in Thermoluminescence (Glow) with Temperature. (1) TMB/PnBMA. After the ITL diminished, the emission was observed again when the photoirradiated film was heated. This emission is called thermoluminescence or glow. Figure 5 shows the spectral change in the TL for the TMB doped in a PnBMA film over the temperature range from 20 to 300 K. The emission spectrum of the TL at 20 K was similar to that of the ITL: the I_P was larger than the I_F. The enhancement of the I_P shows that the TL is also based on the charge recombination of a photoejected electron with the parent cation.

First we assigned the glow peaks in the I_F or the I_P to a motional relaxation of the polymer. Figure 6 shows the spectral glow curves for TMB/PnBMA: the I_F reached a peak at around 100 K and then monotonically decreased, while the I_P gave small peaks at around 100 K and rose to the largest peak at around 220 K. The TL method has been widely used to obtain information on the motional relaxation of polymer chains. However, the assignment of an observed result to a motional relaxation is generally difficult because the subtransition depends on the frequency of the stimuli of methods used to detect it. In the TL measurement, it is not measured directly as a function of time of frequency, but as a function of heating rate. Then, the frequency region observed in the TL measurement can be roughly estimated to be on the order of less than 10^{-1} Hz because the heating rate was 5 °C/min at temperatures from 20 to 300 K.[32] Thus, all the assignments of our TL results were based on the comparison with the results hitherto obtained from low-frequency measurements.

According to the dynamic mechanical measurements, the loss peaks appear at around 100−120 K (∼0.5 Hz) for most of the poly(alkyl methacrylate)s with a long side chain except for PEMA.[33] Wada *et al.* reported that the dielectric loss peak is observed at around 120 K (10−100 Hz) for PnBMA.[34] They ascribed the loss peak to the rotation of the *n*-propyl group accompanied by the rotation of the end ethyl group, which is called δ-relaxation. Therefore, the peak at around 100 K is ascribable to the δ-relaxation, that is, the rotation of the ester alkyl group.

On the other hand, the glow peak at around 220 K would be observed at a higher temperature, if it were not for the decrease in the I_P of the TMB doped in a PnBMA film above 200 K, as shown in Figure 2. Actually, the corresponding glow peak was observed at around 250 K for a photoirradiated PnBMA film doped with perylene, the fluorescence intensity of which is independent of temperature between 20 and 300 K.[35] The peak at 220 K here is probably ascribed to the side chain relaxation and/or the local mode relaxation of the main chain,[36−38] that is, the small scale motion of small segments of a main chain at a low temperature where the micro-Brownian motion of the main chain in frozen. This relaxation is generally observed below the T_g, although it can exist above and below the T_g in principle.[36] This assignment will be discussed later in comparison with the result for PEMA.

It is noteworthy that the intensity ratio I_P/I_F is constant below about 100 K and starts to increase steeply above about 130 K. Since the intensity ratio I_P/I_F decreased with an increase in temperature in the case of steady-state emission, the increase in the intensity ratio I_P/I_F is clearly due to the change in the energy level of electron trap sites with increasing temperature and not to the increase in the rate of nonradiative deactivation. This dependence of the intensity ratio I_P/I_F on temperature can be interpreted as (1) the deepening of trap depth with increasing temperature and (2) the electron transfer from a shallow trap to a deeper trap, which is a possible explanation when there are many pre-existing trap sites with various energetic depths. Both mechanisms result in the increase in the intensity ratio I_P/I_F because ejected electrons firmly captured in deeper trap sites participate in the charge recombination at higher temperatures; the potential energy of electrons in deeper traps is insufficient to reproduce the excited singlet state of a dopant chromophore *via* the charge recombination. Radical species produced by the irradiation have been reported to take part in chemical reactions such as elimination of alkyl group and main-chain scission and consequently change into more stable chemical species with increasing temperature.[39,40] Therefore, the increase in the intensity ratio I_P/I_F can be mainly attributed to the deepening of trap depth caused by chemical reactions with increasing temperature.

(2) TMB/PEMA. Here, the matrix polymer was changed from PnBMA to PEMA to examine the relationship between the energy level of trapped electrons and the motional relaxation of a polymer matrix. As shown in Figure 7a,b, two glow peaks were observed for the TMB doped in a PEMA film, the lower one at 130 K and higher one at 270 K.

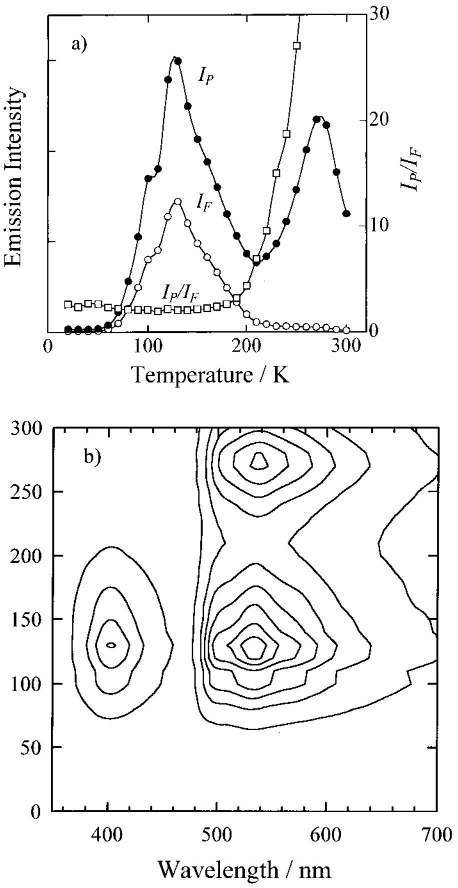

Figure 7. (a) Dependence of the fluorescence intensity I_F (open circles), the phosphorescence intensity I_p (closed circles), and the intensity ratio I_P/I_F (open squares) on temperature for the TL of the TMB chromophore doped in a photoirradiated PEMA film at temperatures from 20 to 300 K. The heating rate was 5 °C/min. (b) TL contour map for the PEMA film doped with a TMB chromophore photoirradiated at 20 K. The heating rate was 5 °C/min.

The relaxation processes observed for a PEMA solid with increasing temperature are the rotation of the ethyl group (δ-relaxation), the rotation of the α-methyl group (γ-relaxation), the motion of the side-chain units including the carbonyl group (β-relaxation), and the micro-Brownian motion of the main chain (α-relaxation). The δ-peak of PEMA has been reported to be observed at 34 K (1.4 Hz),[41] 41 K (9.0 HZ),[42] 55 K (3 kHz),[43] 52 K (9.8 kHz),[44] 60 K (34 kHz),[45] and 75 K (3 MHz).[45] These results show that the peak position is strongly dependent upon the measuring frequency and the peak at low frequencies appears at lower temperatures. In our system, the δ-peak of PEMA is expected to be observed below 30 K because of the low frequency in the TL measurement. However, we failed to detect the glow peak corresponding to the δ-peak. This is probably because a photoirradiation temperature of 20 K was to close to the temperature region of the δ-peak of PEMA; most of the photoejected electrons captured in trap sites with the depth corresponding to the δ-relaxation disappear owing to the charge recombination even at a fixed temperature before the heating procedure. Thus, the glow peak observed at around 130 K cannot be assigned to the δ-relaxation. Furthermore, it is too low in temperature to be ascribed to the β-relaxation, that is, the whole motion of side-chain units including the carbonyl group. Therefore, we ascribe the glow peak at around 130 K to the γ-relaxation, that is, the rotation of the α-methyl group. Furthermore, we carefully reexamined the result for TMB/PnBMA shown in Figure 6 and then noticed that glow peaks appear around 120−140 K. The glow peaks are also ascribable to the γ-relaxation as in TMB/PEMA, although a peak temperature of 130 K observed in our system is much lower than a γ-peak temperature of 220 K in both PMMA and PEMA by ultrasonic measurements at 10 MHz.[46]

The glow peak at around 270 K is probably an apparent one owing to the decrease in the I_P at higher temperatures as in TMB/PnBMA. If it were not for the decrease in the I_P, the glow peak at around 270 K would appear above 300 K; in the case of a photoirradiated PEMA film doped with a perylene chromophore, an upswing of the glow curve was observed extending over 300 K.[35] A possible assignment of the apparent glow peak at 270 K is the side-chain relaxation and/or the local mode relaxation of the main chain.

Historically, the β-relaxation for poly(alkyl methacrylate)s has been ascribed to the rotation of the side chain including the carbonyl group. According to the mechanical experiment, the loss modulus peak of β-relaxation at 1 Hz is observed at around 280 K for several poly(*n*-alkyl methacrylate)s: PMMA, PEMA, PnPMA, and PnBMA.[47] On the other hand, the dielectric loss peak at 1 kHz attributed to β-relaxation appears also at almost the same temperature for copolymers of methyl methacrylate with *n*-butyl methacrylate and isobutyl methacrylate.[48] Hence, the rotation of a side chain, β-relaxation, is believed to be governed mainly by the intrachain potential, not by the interchain interaction that affects the micro-Brownian motion of main chains. However, the effect of local mode motions of the main chain on the β-relaxation remains unknown.[36,49] Recently, Spiess and his co-workers investigated β-relaxation in PMMA[50] and PEMA[51] by multidimensional NMR. They elucidated that 180° flips of the side chain are accompanied by main-chain rotational readjustments with an amplitude of *ca*. ±20° around the local chain axis. Futhermore, Johari and Goldstein insisted that the β-relaxation in the glassy state can arise solely from intermolecular processes: such molecular relaxations can be a universal feature of the glassy state.[52−55] Of course, they did not deny the explanations offered hitherto for the β-relaxation in polymers in terms of the rotation of the side chain including the carbonyl group, but they also suggested that other molecular motions, *e.g.*, main-chain motions, take part to some extent in the β-relaxation and that a particular molecular motion, governed by an internal potential when the molecule is isolated, is opposed in the glassy state by a barrier that is primarily intermolecular in origin.

In our previous experiment using perylene as a dopant chromophore,[35] a glow peak at a higher temperature appeared at 250 K for PnBMA while a rise of glow was observed up to 300 K for PEMA: the glow peak temperature increased with the decrease of side-chain length. This indicates that the glow at higher temperatures might be mainly dominated by local interchain interactions. It might be inappropriate to ascribe the glow only to the rotation of the side chain. Local mode relaxation is generally observed for linear polymers without long side chains, and its motion is mainly governed by a local intrachain potential.[38] Thus, it might be also unreasonable to ascribe the glow peaks to the local mode relaxation governed by the local intrachain potential. We should rather conclude that the glow at a higher temperature is ascribed to the small scale motion of the main chain governed by the interchain potential, as Johari and Goldstein pointed out.

Parts a and b of Figure 7 show that in the TL spectra of PEMA above 200 K only phosphorescence was observed while fluorescence diminished. This tendency is consistent with the result for PnBMA; the onset of the increase in the intensity ratio I_P/I_F was observed at around 190 K, while in the case of PnBMA it was observed at around 130 K. This increase in the intensity ratio I_P/I_F also suggests the deepening of trap depth caused by chemical reactions with increasing temperature, just as in PnBMA. More noteworthy is that the temperature at which the intensity ratio I_P/I_F starts to increase is in correspondence with that of the upswing of the largest glow at higher temperatures in both PnBMA and PEMA. This finding indicates that the change in trap depth is closely related to the small scale motion of the main chain. Thus, the increase in the intensity ratio I_P/I_F results from chemical reactions, *e.g.*, elimination of the ester alkyl group and main-chain scission induced by the photoirradiation, and is related to the motional relaxation of polymer matrices.

(3) TMB/PSt. Here, polystyrene was used as a matrix polymer. Although polystyrene is classified as a cross-linking-type,[25,26] it is more resistant to the radiation than poly(alkyl methacrylate)s. Figure 8a shows the spectral glow curves for the TMB doped in a PSt film: a small glow peak appeared at around 120 K along with an upswing of the glow curve up to 300 K. The former peak at 120 K is ascribed to the rotation of the phenyl group, and the latter rise observed up to 300 K, to the local mode relaxation of the main chain. The γ-peak of PSt has been bound by Schmieder and Wolf at 133 K (11.3 Hz)[56] and by Illers and Jenckel at 132 K (1 Hz).[57] On the other hand, the β-peak has been reported to be observed at around 320 K by the dynamic mechanical measurements at 0.3 Hz.[58] Yano and Wada showed the relaxation map of PSt, which consists of the results for mechanical and dielectric loss peaks, NMR narrowing, and the spin−lattice relaxation time.[59] They ascribed the β-peak at 350 K (10 kHz) to the local oscillation mode of main chains and the γ-peak at 180 K (10 kHz) to the rotation of phenyl groups. It can be seen that the glow curve observed for PSt in our system corresponds to their assignments considering the difference in measurement frequency.

As shown in Figure 8a,b, temperature dependence of the I_F was the same as that of the I_P: the intensity ratio I_P/I_F was constant over the whole temperature range measured from 20 to 300 K. Therefore, it can be seen that the energy level of trapped electrons in a PSt matrix does not change with the increase in temperature, in contrast to the poly(alkyl methacrylate)s.

3-3. Reaction Scheme for the Charge Recombination of a Photoejected Electron with the Parent TMB$^{\bullet+}$ in Polymer Solids.

Since the I_P in the ITL was enhanced in comparison with that in the steady-state emission for all the polymers used in the present work and the intensity ratio I_P/I_F was almost constant over the whole time range measured from 10 min to 10 h, we conclude that the observed ITL is due to the charge recombination from a shallow trap.

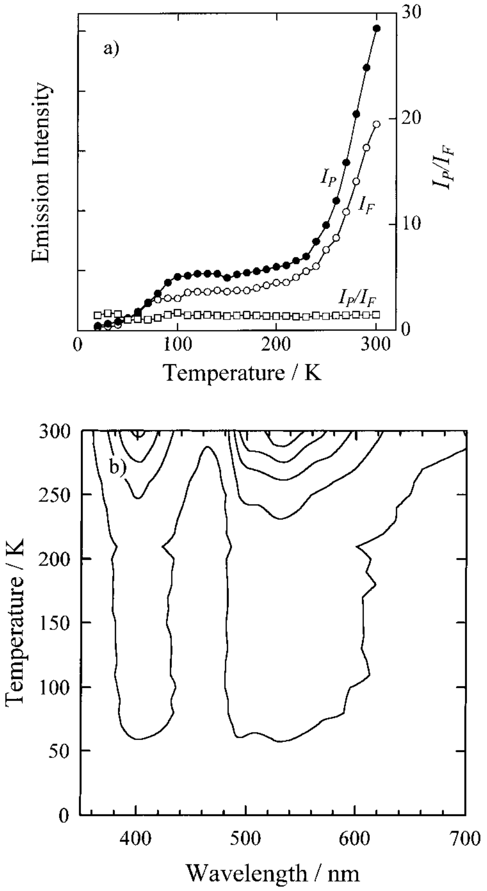

Figure 8. (a) Dependence of the fluorescence intensity I_F (open circles), the phosphorescence intensity I_P (closed circles), and the intensity ratio I_P/I_F (open squares) on temperature for the TL of the TMB chromophore doped in a photoirradiated PSt film at temperatures from 20 to 300 K. The heating rate was 5 °C/min. (b) TL contour map for the PSt film doped with a TMB chromophore photoirradiated at 20 K. The heating rate was 5 °C/min.

The TL showed differences between poly(alkyl methacrylate)s and polystyrene; the intensity ratio I_P/I_F increased with temperature for poly(alkyl methacrylate)s but was constant at temperatures from 20 to 300 K for polystyrene. The increase in the intensity ratio I_P/I_F shows that the energy level of the excited singlet state of a dopant chromophore is higher than that of some trapped electrons participating in the charge recombination; that is, the energy of the trapped electrons is insufficient to reproduce the excited singlet state by the charge recombination, and consequently, the fluorescence intensity I_F decreases.

The energy level of trapped electrons in PnBMA is roughly estimated as follows. The energy of electron−cation pairs formed in a condensed phase, E, is expressed by the following equation:

$$E = IP_g + P_+ + V_0 \tag{1}$$

The gas phase ionization potential IP_g of TMB is reported to be *ca.* 6.5 eV.[60] The polarization energy P_+ can be evaluated using the Born equation:[61]

$$P_+ = -\frac{e^2}{8\pi\epsilon_0 r_+}\left(1 - \frac{1}{\epsilon_s}\right) \tag{2}$$

where e is the elementary charge, ϵ_0 is the vacuum permittivity, r_+ is the radius of the cationic species, and ϵ_S is the relative dielectric constant of the medium. The radius r_+ was roughly estimated[62] to be 3.88 Å from the van der Waals volume[63] of TMB. The dielectric constant ϵ_S of PnBMA has been reported to be 2.8 at 200 K (30 Hz)[64] where the TL glow consisted of only phosphorescence and fluorescence was almost diminished. Thus, the polarization energy was calculated using eq 2: $P_+ = -1.2$ eV. By inserting these values into eq 1, we obtain the energy of electron−cation pairs as a function of the electron trap depth V_0: $E = 5.3 - V_0$ (eV). On the other hand, the energy level of the excited singlet state of the TMB chromophore was estimated to be *ca.* 3.5 eV from the absorption and emission spectrum of TMB. Consequently, the trap depth can be estimated to be more than 1.8 eV in PnBMA above 200 K where the fluorescence component in TL diminished and only phosphorescence was observed.

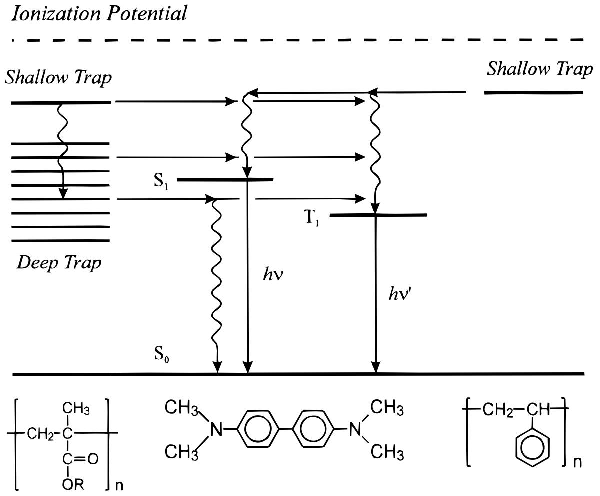

Figure 9. Reaction scheme for the charge recombination of a trapped electron with the parent cation in a polymer solid. As shown to the right, the charge recombination in a polystyrene solid occurs from a shallow trap to the parent cation both in ITL at 20 K and TL at temperatures from 20 to 300 K. On the other hand, the left part of the figure shows the scheme for the charge recombination in poly(alkyl methacrylate)s: in the case of ITL at 20 K and the TL at low temperatures, the charge recombination mainly from a shallow electron trap results in the excited singlet state and triplet state of the parent−cation chromophore, whereas the TL at higher temperatures results from the charge recombination from a deeper trap leading to only the excited triplet state of the parent−cation chromophore.

As described above, the change in the intensity ratio I_P/I_F was observed for poly(alkyl methacrylate)s while no change was observed for polystyrene. This difference shows that the stabilization of trapped electrons results from a photoinduced chemical reaction in polymer solids because poly(alkyl methacrylate)s are classified as the scission type polymer for radiation whereas polystyrene is highly resistant to the radiation.[25,26] Furthermore, the increase in the intensity ratio I_P/I_F was closely related to the small scale motion of the main chain governed by the interchain potential. These findings indicate that the stabilization of trapped electrons requires such certain scale motions as local motions of the main chain. There have been various reports on the mechanism of the main-chain scission investigated in detail by ESR measurement in radiation chemistry.[39,40] Sakai *et al.* reported that two-photon ionization also leads to the main-chain scission of poly(methyl methacrylate) (PMMA), which is initiated through the ester radical anion formation.[65,66] They observed an ester radical anion of PMMA just after the photoirradiation at 77 K, and it changed into a methyl radical even at 77 K; this is an elimination of an ester alkyl group. However, the spectral glow curves in the previous section show that the intensity ratio I_P/I_F is almost constant even at temperatures where the rotation of the ester alkyl group in the side chain of the polymer is released and increases at temperatures where local motions of the main chain governed by interchain potential are released. These findings suggest that the increase in the intensity ratio I_P/I_F results from the stabilization of trapped electrons through the main-chain scission rather than the elimination of an ester alkyl group. We therefore conclude that the photoejected electron is mainly trapped in a shallow trap at 20 K where the motions in the polymer matrix are almost frozen and that trapped electrons in poly(alkyl methacrylate) films change into more stable anion species through chemical reactions, *e.g.*, main-chain scission, at higher temperatures where the small scale motion of the main chain is released.

4. Conclusion

We studied the spectral change in ITL or TL caused by the charge recombination of a trapped electron with the parent cation. The energy level decreased with increasing temperature for poly(alkyl methacrylate)s, which are classified as the scission type for radiation, and the change in the energy level is induced by the small scale motion of the main chain. In poly(alkyl methacrylate) films, photoejected electrons are mainly captured in a shallow trap site at low temperatures where most of the polymer motions are frozen and change into more stable anion species through chemical reactions with increasing temperature. Furthermore, the depth of the deeper trap was estimated to be more than 1.8 eV at 200 K where the phosphorescence component but not the fluorescence component was observed in the TL of a photoirradiated PnBMA film.

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(30) Strictly speaking, the slope of the log−log plots is less than unity. This deviation results from multishot photoirradiation.
(31) The ITL decay can be simulated by the electron tunneling model with the assumption of only one kind of trap depth with no energetic distribution. Then, even if there are deeper trap sites, the trap depth is so deep that the trapped electrons cannot be transferred to the parent cations. In other words, photoejected electrons captured in deeper trap sites cannot recombine with the parent cations at a temperature as low as 20 K.
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