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Charge Recombination via Electron Tunneling after Two-Photon Ionization of Dopant Chromophore in Poly(butyl methacrylate) Film at 20 K

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The charge recombination of electron–cation pairs produced in a poly(butyl methacrylate) film through two-photon ionization was examined at 20 K by emission spectroscopy and absorption spectroscopy. Both the isothermal luminescence (ITL) decay and the absorbance decay of the radical cation obeyed the same kinetics at 20 K: the t^{-m} law, $I(t) \propto t^{-m}$ with $m \approx 1$. The temperature dependence of the ITL decay kinetics remained the same from 20 to 200 K far below the glass-transition temperature (293 K). These findings show that the ITL decay at low temperatures can be explained in terms of a long-range electron transfer by electron tunneling. Multi-shot photoirradiation was found to cause a deviation of the ITL decay from the t^{-m} law. Multi-shot photoirradiation probably induces a larger separation of a photoejected electron from the parent cation and/or a deepening of the trap depth.

Luminescence having an extremely long lifetime is observed when a solid matrix is irradiated at low temperature by high-energy radiation, such as γ- and X-rays. The decay of this isothermal luminescence (ITL) intensity has been reported to obey an inverse-power function of time, t^{-1},[1—4] that is, the t^{-m} law with $m \approx 1$, which is also called the Debye–Edwards law by Hamill.[5] This phenomenon has been explained as luminescence resulting from the charge recombination of trapped electrons with the parent cation produced by the irradiation. Historically, Debye and Edwards[2] applied, for the first time, a diffusion mechanism to the ion-recombination reaction under a spatial distribution of ejected electrons. However, in their model, the total amount of produced ionic species is infinite because the distribution function is not normalized. Although Abell and Mozumder[6] resolved this problem using a normalized distribution function, only at an intermediate time scale can the t^{-1} decay be reproduced, even in their model. Namely, the t^{-1} decay kinetics cannot be explained in terms of a simple diffusion mechanism for trapped electrons. In a simple diffusion model, the number of trapped electrons ($N(t)$) is proportional to the square root of the inverse of time ($t^{-1/2}$) in the long-time region, and, thus, since the ITL intensity ($I(t)$) is proportional to $t^{-3/2}$; the t^{-m} law cannot be explained by a simple diffusion model.

Hamill and Funabashi[7] demonstrated that one can explain the t^{-m} decay of the recombination luminescence as a non-Gaussian diffusion process with a hopping time distribution of the asymptotic type proposed by Scher and Montroll. Scher and Montroll[8] adopted the Montroll–Weiss[9] model of a continuous-time random walk (CTRW) to explain the long tail of the transient photocurrent in amorphous solids. They found that the hopping time distribution ($\varphi(t)$) for localized electrons in disordered systems is an asymptotic type ($\varphi(t) \approx t^{-(1+\alpha)}$, $0 < \alpha < 1$), not an exponential type ($\varphi(t) = \lambda \mathrm{e}^{-\lambda t}$, λ = const.) leading to the familiar Gaussian diffusion. The hopping time distribution of the asymptotic type reflects the distribution for space and/or energetic depth of the trap sites. If the activation energy for trapped electrons has a distribution, the rate of thermal-activated electron transfer from one trap to another depends largely upon the temperature changes.

Kieffer, Meyer, and Rigaut[10,11] showed that the decay kinetics of the ITL in an irradiated rigid solution of methylcyclohexane is independent of the temperature between 4 and 77 K. These experimental results indicate that trapped electrons are transferred to the parent cation without thermal activation. Thus, many authors[12—16] have explained the electron transfer independent of temperature using an electron-tunneling model. Hama et al. found that, with the assumption of electron tunneling, the Laplace inverse transformation of an empirical ITL decay function leads to the initial distribution function of the distance between a trapped electron and the parent cation just after the irradiation.[17,18] They used the following equation as an empirical ITL decay function and reported that the value of m should be more than unity to avoid the divergence of the total amount of ionic species:

$$I(t) = \frac{I_0}{(1+\alpha t)^m}. \tag{1}$$

Here, the ITL was observed for a photoirradiated polymer solid doped with a low-molecular-weight aromatic chromophore. An intense near-UV light pulse from an excimer laser (351 nm) was used for the selective photoexcitation of the dopant chromophore. The laser pulse is intense enough to feed another photon to the excited chromophore within the lifetime. Consequently, the dopant chromophore is excited to a higher level, and then ejects an electron to the polymer matrix. The thus-formed parent radical cation and the trapped electron in the polymer have already been reported to be so stable that the color of the parent radical cation can be seen even after a one-year storage from the photoexcitation at room temperature.[19—22)]

Although the ITL from the irradiated polymers has been postulated to be caused by charge recombination of an electron with the parent cation, direct evidence has been scarce to show that the emission intensity of ITL corresponds to the decay of the cationic species. For the case of excitation by high-energy radiation, this is probably due to the difficulty of an adsorption measurement for the produced polymer cation with a very small molar-absorption coefficient. In the present system, we used a chromophore, the radical cation of which has strong absorption in the visible region. We were then able to directly observe the decay of the radical cation by absorption spectroscopy. We thus observed the decay of a radical cation as well as ITL decay.

Herein, we elucidated the mechanism of the ITL resulting from a recombination of electron–cation pairs formed in a polymer solid through two-photon ionization of a dopant chromophore. The effect of multi-shot photoirradiation on the ITL decay kinetics was also examined by the ITL and TL (thermoluminescence) measurement.

Experimental

Chemicals. The polymer sample used in the present work was poly(butyl methacrylate) (PnBMA, $M_w=10^5$, Scientific Polym. Prod., Inc.). The polymer was purified by reprecipitation from a benzene solution into methanol three times. The glass transition temperature (T_g) of PnBMA is 293 K.[23)]

The dopant chromophores used here were perylene (Pe, Aldrich Chem. Co., Inc.) or *N,N,N′,N′*-tetramethylbenzidine (TMB, Wako Pure Chem. Ind., Ltd.). Perylene was purified by silica-gel flash column chromatography eluted with dichloromethane, and TMB was purified by recrystallization several times.

Sample Preparation. Polymer films for measurements were prepared by the solution cast method. A dopant chromophore was dissolved in a benzene (Dojin Spectrosol) solvent with a polymer powder so as to make a dopant concentration of ca. 3×10^{-3} $\mathrm{mol\,dm^{-3}}$ in the final polymer film. The solution was cast on a glass plate in a dry box under a nitrogen atmosphere for two days and then dried by evacuation for one day at room temperature. The film was peeled off from the glass plate, and was finally dried under vacuum above T_g for more than 10 h to remove the remaining trace of the solvent. No change in the absorption or emission spectra of the dopant was observed for the doped polymer films after the above-mentioned heating procedure.

General Procedures. The ITL was measured in a sample chamber of a cryostat in vacuo. The polymer sample film was covered with a quartz plate and set tightly on a copper cold finger of a cryostat (Iwatani Plantech Corp., CRT510). The sample film was cooled down to 20 K and the temperature was kept constant using a PID temperature control unit (Iwatani Plantech Corp., TCU-4). The film temperature was monitored with a calibrated Au+0.07% Fe/chromel thermocouple at the sample film position using an indium gasket.

A dopant chromophore was selectively photoirradiated by a 351-nm light pulse from a XeF excimer laser (Lambda Physik, EMG101MSC, ca. 20 ns fwhm, and ca. 30 $\mathrm{mJ\,cm^{-2}}$). The emission from the sample film (this is ITL or preglow) was measured from 1 min to 25 h after photoexcitation at 20 K. A photon-counting system was used for the emission-intensity measurement, which consisted of a photomultiplier (Hamamatsu, R585) and a photon counter (Hamamatsu, C-1230) connected to a personal computer. The ITL from the sample film became almost negligible 25 h after photoirradiation.

Subsequently, the film temperature was raised from 20 to 300 K at a heating rate of 5 $^\circ\mathrm{C\,min^{-1}}$ in a cryostat using the PID temperature control unit. Emission from the sample film was observed again along with an increase in the sample temperature. This thermal-stimulated emission is called thermoluminescence (TL or glow). The TL intensity was recorded in the same manner as described above. The ITL and TL were not observed at all in control experiments where polymer films without dopant chromophores were excited using the same procedure as mentioned above.

The absorption spectra of photoirradiated sample films were measured in the cryostat with a spectrophotometer (Hitachi, U-3500) using a 2-nm slit width. Ten sheets of the sample films, freshly prepared, were put together so as to gain a high absorbance of the radical cation; the total thickness was ca. 2 mm. The absorption spectra were measured from 5 min to 25 h after photoirradiation at 20 K. The monitor light was shut off between the measurements to prevent the sample film from being photobleached.

Dependence on the Number of Photoirradiation Shots at a Fixed Fluence. After a Pe-doped PnBMA film was photoirradiated, ITL and TL were measured by the procedure mentioned above. The photoirradiation conditions were changed as follows: The energy density for a 1-shot laser pulse was ca. 3 $\mathrm{mJ\,cm^{-2}}$; the laser pulse interval was set at 2 Hz; the number of photoirradiation shots was 1, 10, 50, 100, 500, 1000, 5000, and 10000. The sample film was used repeatedly in this experiment after adequate annealing at 300 K above T_g. This procedure can avoid a difference in the ITL intensity among sample films.

Results and Discussion

ITL Decay and Absorbance Decay of the TMB Radical Cation under the 1-Shot Photoirradiation Condition. In the beginning, we consider, from the viewpoint of decay kinetics, the relationship between the ITL decay and the absorbance decay of the TMB radical cation ($\mathrm{TMB^{\bullet+}}$) produced through two-photon ionization. Figure 1 shows the ITL decay for a PnBMA film doped with a TMB chromophore measured after laser photoexcitation at 20 K. The log–log plots of the observed ITL intensity $I(t)$ vs. time t give a straight line. This linear relationship (the t^{-m} law) was observed over the time range from 1 min to 25 h after photoirradiation: of three or four orders of magnitude for time t.

The ITL decay profile after irradiation ($I(t)$) is empirically expressed by

$$I(t)=\frac{I_0}{(1+\alpha t)^m}, \tag{1}$$

where I_0 is the ITL intensity at $t=0$ just after irradiation, and α and m are parameters.[17,18)] This empirical equation is theoretically explained in terms of the geminate charge recombination of a trapped electron with the parent radical cation on the basis of electron tunneling.[15,17,18)] The ITL decay

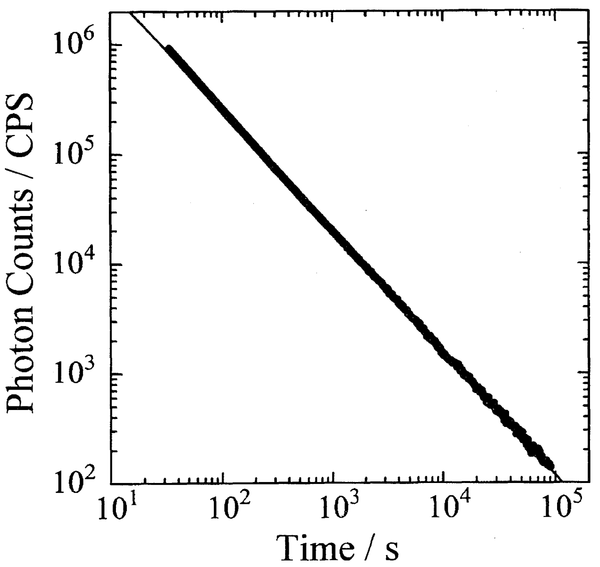

Fig. 1. The ITL decay of a PnBMA film doped with a TMB chromophore measured from 1 min to 25 h after the 351-nm photoirradiation at 20 K. The solid line shows the best fitting using Eq. 1. The fitting parameters are as follows: $I_0 = 1.3\times10^9$ CPS, α=23.0 s^{-1}, and m = 1.11.

shown in Fig. 1 was fitted to Eq. 1 using the least-squares method with I_0, α, and m as fitting parameters. The solid line in the figure shows the best fitting; one of the best-fit values is as follows: $I_0 = 1.3\times10^9$ CPS, $\alpha = 23.0$ s^{-1}, and $m = 1.11$. The values of I_0 and α have some ambiguity because the same quality of fitting is attained using other pair values of I_0 and α. On the contrary, the value of m is unique and close to unity.

The open circles shown in Fig. 2 denote the absorbance decay of TMB$^{\bullet+}$ measured at 475 nm in a PnBMA film after laser photoexcitation at 20 K. The dopant TMB$^{\bullet+}$ has a strong absorption peak at 475 nm, where the molar-absorption coefficient can be as large as ca. 4×10^4 mol^{-1} dm^3 cm^{-1}.[24,25] Thus, the use of TMB as a dopant chromophore enabled one to observe the radical cation produced in polymer solids through two-photon ionization by absorption spectroscopy. Plots of the absorbance of TMB$^{\bullet+}$ vs. log t gave an approximately linear relationship,[26] and the absorbance of TMB$^{\bullet+}$ decreased from ca. 0.08 to ca. 0.07 over the time range from 3 min to 25 h. In other words, the TMB$^{\bullet+}$ produced through two-photon ionization is so stable at 20 K that most of them survive even 25 h after photoirradiation. The absorbance decay of TMB$^{\bullet+}$ is not due to decomposition, because the absorbance of TMB recovers along with a decrease in the absorbance of TMB$^{\bullet+}$.

If the ITL decay and the absorbance decay of TMB$^{\bullet+}$ result from charge recombination of a photoejected electron with the parent cation, they should obey the same kinetics. Thus, we derive the absorbance decay function from the ITL decay function. Since ITL is caused by charge recombination, the following equation holds:

$$I(t) = -\lambda \frac{\mathrm{d}N(t)}{\mathrm{d}t}, \tag{2}$$

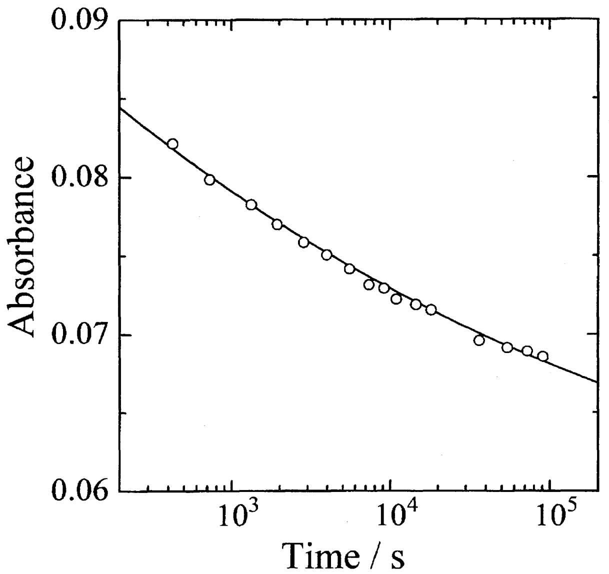

Fig. 2. The fitting result for the absorbance decay of TMB radical cation formed in a PnBMA film through a two-photon ionization at 20 K. The observed wavelength was 475 nm which is the absorption peak wavelength of TMB$^{\bullet+}$. The solid line shows the result of the best fitting for the absorbance of TMB$^{\bullet+}$ denoted by open circles, using Eq. 4 with the same parameters used in the ITL fitting: $I_0=1.3\times10^9$ CPS, α=23.0 s^{-1}, and m =1.11. In other words, the solid line is drawn by the following equation: $Abs(t) = 0.135-0.0836[1-1/(1+23\,t)^{1.11}]$.

where $N(t)$ is the number of electron-hole pairs and λ is a constant that is related to the apparent emission quantum efficiency. Combining and integrating Eqs. 1 and 2, we obtain the following equation:

$$N(t) = N_0 - \frac{I_0}{\lambda\alpha(m-1)}\left[1 - \frac{1}{(1+\alpha t)^{m-1}}\right]. \tag{3}$$

According to the Lambert–Beer law, $N(t)$ is proportional to the absorbance ($Abs(t)$) of TMB$^{\bullet+}$ at 475 nm, and therefore Eq. 3 leads to

$$Abs(t) = Abs_0 - \frac{I_0\varepsilon}{\lambda\alpha S N_{\mathrm{A}}(m-1)}\left[1 - \frac{1}{(1+\alpha t)^{m-1}}\right], \tag{4}$$

where ε is the molar absorption coefficient of TMB$^{\bullet+}$ at 475 nm, S the sample film area, and N_{A} the Avogadro constant. This Eq. 4 connects the ITL decay to the decrease in the absorbance of TMB$^{\bullet+}$ with the assumption that the ITL is caused by the charge recombination of a photoejected electron with the parent TMB$^{\bullet+}$.

As shown in Fig. 2, the experimental data were well fitted using Eq. 4 (solid line) with the same parameters used in the ITL fitting: $I_0 = 1.3\times10^9$ CPS, $\alpha = 23.0$ s^{-1}, and $m = 1.11$. This clearly shows that both the ITL decay and the absorbance decay of TMB$^{\bullet+}$ can be explained on the basis of the same kinetics; the ITL is caused by the charge recombination of a photoejected electron with the parent TMB$^{\bullet+}$.

Temperature Dependence of ITL Decays at Temperatures from 20 to 300 K. The striking feature of the ITL is that the luminescence has an extremely long lifetime and the decay kinetics is independent of the temperature at low temperatures. Here, we used perylene as a dopant chromophore, because its fluorescence quantum yield is independent of the temperature between 20 and 300 K.[27] Figure 3 shows the ITL decays of Pe/PnBMA at temperatures from 20 to 300 K. The unit of the ordinate is arbitrary; each ITL decay is shifted arbitrarily in the direction of the ordinate. The ITL decays below 200 K obeyed the t^{-m} law; that is, the decay kinetics was the same in the temperature range below 200 K. This strongly suggests that the ITL decay mechanism remains the same below 200 K. Since the thermal energy at 20 K is no more than 1.7×10^{-3} eV, electron detrapping due to thermal activation hardly occurs at 20 K. However, the long-range electron transfer due to the electron-tunneling mechanism can occur even at a temperature as low as 20 K. On the contrary, the ITL decay above 200 K did not obey the t^{-m} law. This deviation observed above 200 K suggests that the scheme for the ITL changes above this temperature.

The concentration of dopant chromophores in the present experiment was so dilute that the charge recombination of a photoejected electron with the parent radical cation can be considered to be a geminate recombination.

Thus, we concluded that ITL decays below 200 K result from geminate charge recombination of a trapped electron with the parent radical cation through a long-range electron transfer by electron tunneling, not through electron detrapping by thermal activation.

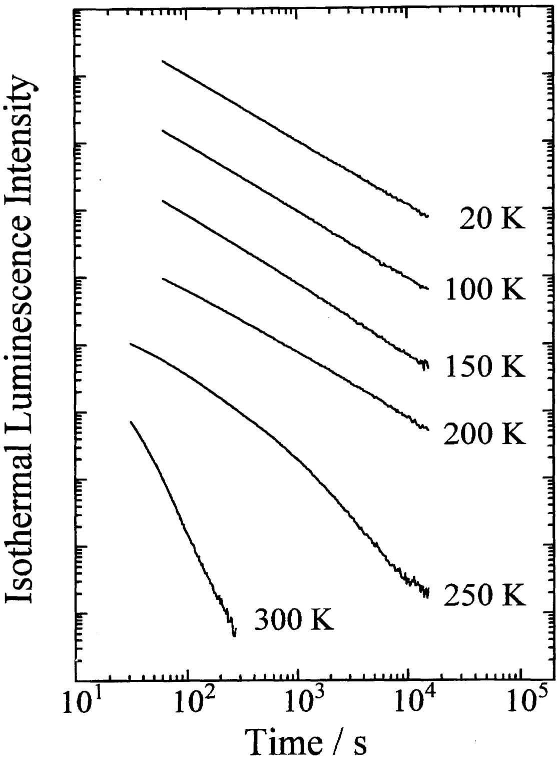

Fig. 3. The ITL decays for Pe/PnBMA system photoirradiated and measured at 20, 100, 150, 200, 250, and 300 K. Each ITL decay is shifted arbitrarily in the direction of the ordinate.

Dependence of Charge Recombinaiton Luminescence on the Number of Photoirradiation Shots at a Fixed Fluence. We examined the dependence of the ITL decay on the number of photoirradiation shots. A PnBMA film doped with a Pe chromophore was photoirradiated at 20 K under multi-shot photoirradiation. To suppress degradation of sample films by multi-shot irradiation, the photon density of the excitation light (ca. 3 mJ cm^{-2}) was made to be about one tenth of that mentioned in the previous section (ca. 30 mJ cm^{-2}). Also, under the photoirradiaiton conditions, two-photon ionization was confirmed; the radical cation of the dopant Pe chromophore was observed by absorption spectroscopy.

Figure 4 shows two tendencies: 1) the ITL intensity increased with the number of photoirradiation shots and 2) the slope of the ITL decay became gentle, that is, the value of *m* decreased along with an increase in the number of photoirradiation shots. It is noticed that the ITL decay kinetics deviates from the t^{-m} law at more than 100-shot irradiation, as the open circles in Fig. 7 shows; the value of *m* is less than unity.

It was examined whether the ITL for multi-shot irradiation can be reproduced with the summation of the ITL for a 1-shot photoirradiation:

$$I(t)=\sum_{i=0}^{99}\frac{I_0(i)}{(1+\alpha(t+0.5i))^m}, \tag{5}$$

that is to say, whether the 100-shot ITL can be explained as a superposition of the 1-shot ITLs for each photoirradiation. In the equation, the emission intensity ($I_0(i)$) is proportional to the absorbance of TMB, which decreases with an increase in the number of photoirradiation shots (i), and the time (t) in Eq. 1 is replaced by (t+0.5 i) under the condition where the interval of the laser pulses is 0.5 s (2 Hz). As shown in Fig. 5, the superposition of ITL for 1-shot photoirradiation

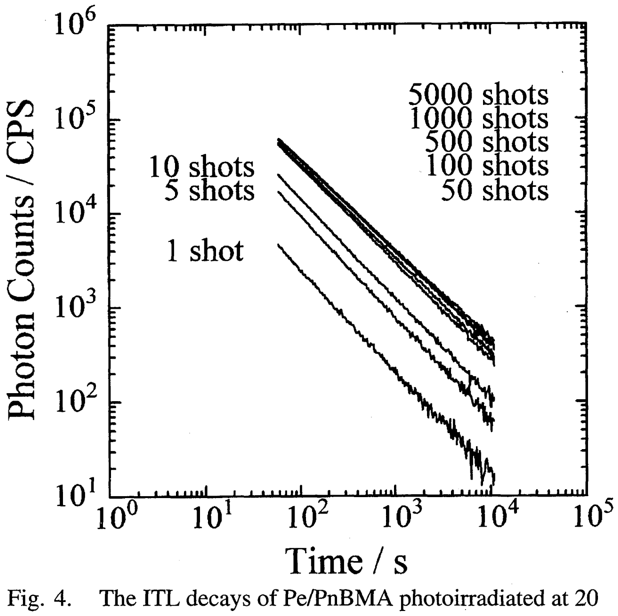

Fig. 4. The ITL decays of Pe/PnBMA photoirradiated at 20 K. The number of photoirradiation shots was 1, 10, 50, 100, 500, 1000, and 5000.

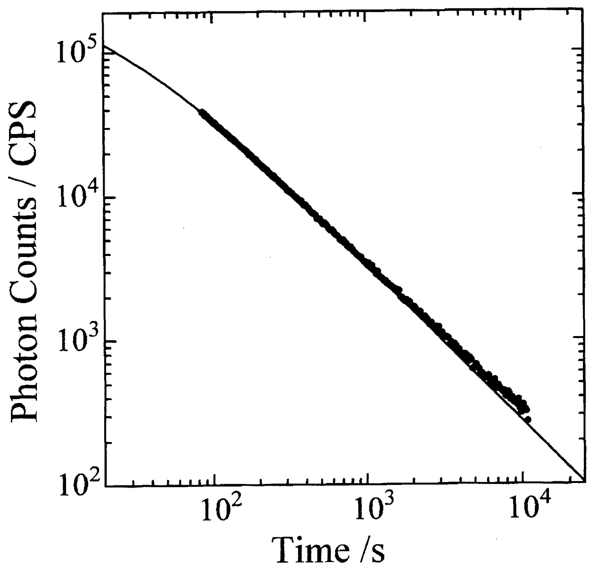

Fig. 5. The closed circles represent the ITL decay of Pe/PnBMA under a 100-shot irradiation ($m \approx 0.99$). The solid line is the best fitting using Eq. 5; the summation of Eq. 1 with the fitting parameters obtained from the ITL decay of Pe/PnBMA under a 1-shot irradiation ($m \approx 1.09$).

($m{\approx}1.09$) reproduced a smaller slope ($m{\approx}0.99$) of ITL for 100-shot photoirradiation in a short time range, but returned to the slope ($m \approx 1.09$) of ITL for 1-shot photoirradiation in a longer time range. This indicates that each ionization process is not independent; the subsequent photoirradiation changes the trapping form of electrons photoejected at the previous photoirradiation.

Next, we examined the glow curves (thermoluminescence, TL) observed in succession after the ITL decay measurement shown in Fig. 4. Figure 6 shows the glow curves measured 3 h after photoirradiation. As shown in the figure, the TL intensity increased along with the number of photoirradiation shots, and the increase in the TL intensity was larger at higher temperatures. This enhancement of the TL intensity shows that the photon energy of irradiation is accumulated as the chemical energy of the charge separated state of ionic species. It is noteworthy that the increase in the glow peak intensity at around 250 K corresponds to the decrease in the value of m with an increase in the number of photoirradiation shots, as shown in Fig. 7.

These changes in both ITL and TL indicate that the fraction of electron–cation pairs with a slow recombination rate increases with the number of photoirradiation shots. Two interpretations are possible for the slow recombination rate. One is that the distance between a photoejected electron and the parent cation increases with the number of photoirradiation shots. The other is that trap depth is deepened with an increase in the number of photoirradiaiton shots. Multi-shot photoirradiation may cause an increase in the temperature of the film surface even at 20 K and/or the photoexcitation of intermediate anionic species. Electron detrapping by thermal- or photoexcitation leads to a larger separation of a photoejected electron from the parent cation,[28] and/or a deepening of trapped electrons by transfer to more stable trap sites. Even without the presence of electron detrapping, an increase in the temperature may result in a stabilization of

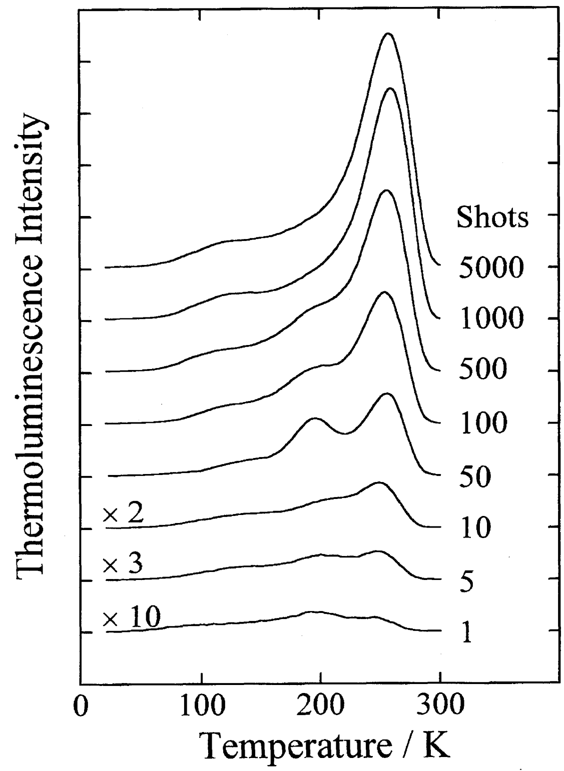

Fig. 6. The TL glow curves of Pe/PnBMA photoirradiated at 20 K under several photoirradiation conditions were observed in succession after the ITL decay measurement. The number of photoirradiation shots was 1, 10, 50, 100, 500, 1000, and 5000.

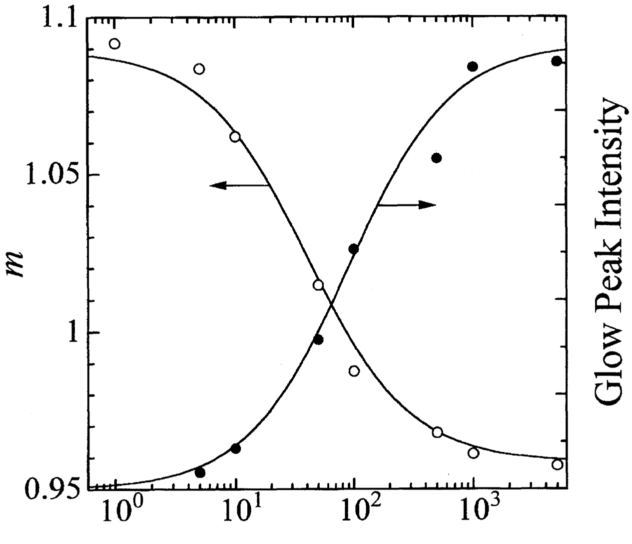

Fig. 7. Plots of the value of m against the number of laser pulses. Open circles denote the slope m of the ITL decay curves obtained from fitting using Eq. 1. Closed circles represent the glow peak intensity around 250 K. The solid curves are drawn arbitrarily.

trapped electrons by small-scale structural relaxation of the matrix polymer. It is difficult to distinguish experimentally which processes are dominant; both processes more or less participate in the effect of multi-shot photoirradiation on ITL and TL.

Conclusion

We observed the charge recombination of electron–hole pairs formed in a PnBMA film at 20 K by emission (ITL) as well as by an absorption measurement. The ITL decay kinetics corresponds to the absorption decay of the ionic species and obeys the same decay kinetics, the t^{-m} law, at temperatures from 20 to 200 K, far below the T_g of PnBMA. We concluded that the ITL decay at low temperatures results from a geminate charge recombination of a photoejected electron with the parent cation through a long-range electron transfer by electron tunneling. Multi-shot irradiation causes a deviation of the ITL decay from the t^{-m} law. This deviation results from an increase in the distance between a photoejected electron and the parent cation and/or a deepening of trap depth.

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References

1) J. T. Randall and M. H. Wilkins, *Proc. R. Soc. London, Ser. A*, **184**, 390 (1945).

2) P. Debye and J. O. Edwards, *J. Chem. Phys.*, **20**, 236 (1952).

3) Kh. S. Bagdasar'yan, R. I. Milyutinskaya, and Yu. V. Kovalev, *Khim. Vys. Energ.*, **1**, 127 (1967).

4) J. R. Miller, *Chem. Phys. Lett.*, **22**, 180 (1973).

5) W. H. Hamill, *J. Chem. Phys.*, **71**, 140 (1979).

6) G. C. Abell and A. Mozumder, *J. Chem. Phys.*, **56**, 4079 (1972).

7) W. H. Hamill and K. Funabashi, *Phys. Rev. B*, **16**, 5523 (1977).

8) H. Scher and E. W. Montroll, *Phys. Rev. B*, **12**, 2455 (1975).

9) E. W. Montroll and G. H. Weiss, *J. Math. Phys.* (*N. Y.*), **6**, 167 (1965).

10) F. Kieffer, C. Meyer, and J. Rigaut, *Chem. Phys. Lett.*, **11**, 359 (1971).

11) F. Kieffer, C. Meyer, and J. Riaut, *Int. J. Radiat. Phys. Chem.*, **6**, 79 (1974).

12) A. I. Mikhailov, *Dokl. Akad. Nauk SSSR*, **197**, 136 (1970).

13) M. Tachiya and A. Mozumder, *Chem. Phys. Lett.*, **28**, 87 (1974).

14) F. S. Dainton, M. J. Pilling, and S. A. Rice, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1311 (1975).

15) M. Tachiya and A. Mozumder, *Chem. Phys. Lett.*, **34**, 77 (1975).

16) M. J. Pilling and S. A. Rice, *J. Phys. Chem.*, **79**, 3035 (1975).

17) Y. Hama, Y. Kimura, H. Tsumura, and N. Omi, *Chem. Phys.*, **53**, 115 (1980).

18) Y. Hama and K. Gouda, *Radiat. Phys. Chem.*, **21**, 185 (1983).

19) A. Tsuchida, M. Nakano, M. Yoshida, M. Yamamoto, and Y. Wada, *Polym. Bull.*, **20**, 297 (1988).

20) M. Yamamoto, A. Tsuchida, and M. Nakano, *MRS Int. Meeting Adv. Mater.*, **12**, 243 (1989).

21) A. Tsuchida, W. Sakai, M. Nakano, M. Yoshida, and M. Yamamoto, *Chem. Phys. Lett.*, **188**, 254 (1992).

22) A. Tsuchida, W. Sakai, M. Nakano, and M. Yamamoto, *J. Phys. Chem.*, **96**, 8855 (1992).

23) P. Peyser, in "Polymer Handbook," 3rd ed, ed by J. Brandrup and E. H. Immergut, John Wiley & Sons, New York (1989).

24) J. P. Jaget and V. Plichon, *Bull. Soc. Chim. Fr.*, **1964**, 1394.

25) S. A. Alkaitis and M. Grätzel, *J. Am. Chem. Soc.*, **98**, 3549 (1976).

26) When the value of m is close to unity, Eq. 4 can be approximately given by

$$Abs(t) = Abs_0 - \frac{I_0\varepsilon}{\lambda\alpha SN_A}\ln(1+\alpha t). \qquad (6)$$

Thus, the plots of $Abs(t)$ vs. $\log t$ show a linear relationship when the value of m is close to unity.

27) M. Yamamoto, H. Ohkita, W. Sakai, and A. Tsuchida, *Synth. Metals*, **81**, 301 (1996).

28) T. W. Scott and C. L. Braun, *Can. J. Chem.*, **63**, 228 (1985).