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Photogeneration and Recombination Kinetics of Charged Excitations in Conducting Polymer/Fullerene Composites

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The photogeneration and recombination kinetics of charged excitations in composites of regioregular poly(3-alkylthiophene)s and C_{60} have been investigated by a transient response of light-induced electron spin resonance (LESR). The dependence of the prompt decay component on excitation-light intensity I_{ex} shows that quadrimolecular recombination (QR) is dominant at higher I_{ex} while bimolecular recombination is relatively important at lower I_{ex}. The time decay of the LESR intensity is also well explained by the QR model. The temperature dependence of the QR rate constant clearly shows a crossover from hopping to tunneling behavior with decrease of temperature; the activation energy for the hopping of 0.10 eV is obtained.

Key words: light-induced electron spin resonance, regioregular poly(3-alkylthiophene), fullerene, quadrimolecular recombination

1. INTRODUCTION

Photogeneration and recombination kinetics of charged excitations in composites of conducting conjugated polymers and fullerene have been extensively investigated, because the composites show highly-efficient photoinduced electron transfer from polymer onto fullerene with a quantum yield near unity and are applicable to low-cost photovoltaic devices such as plastic solar cells [1,2]. Ultrafast spectroscopic studies tracing the electron-transfer process have clarified the charge-transfer kinetics with a forward transfer time-constant of ~ 45 fs [3]. On the other hand, charge-recombination process can be divided in a few different decay-time regimes, as shown by several experimental methods. For example, transient absorption studies of the composites have showed two decay components: the fast decay component (< 20 ns) attributed to recombination of relatively mobile polarons, and the slower decay phase (300 ns - 1 ms) described with a power-law decay At^{α} (α = 0.4) attributed to recombination of localized polarons [4]. Time-resolved infrared-absorption study has also showed similar power-law decay from the subnanosecond to microsecond time scale [5]. In the above studies [4,5], an another decay phase was observed for time delays longer than 1 ms; this decay cannot be described with At^{α}. Light-induced electron spin resonance (LESR) studies are suitable for investigating the decay kinetics of more long-lived charged excitations and have showed two decay components for the slower decay phase: prompt one with decay times of several tens of millisecond to several tens of second and persistent one with decay times of several hours [6,7]. Decay of the persistent component (> 2 min) at low temperatures has been explained by nongeminate recombination of randomly distributed carriers [6]. However, the decay kinetics in the time regime of 1 ms - 2 min has not been investigated in detail so far. Thus the detailed studies of the prompt decay component provide useful information, because it has been reported that these regimes can be expected to dominate the recombination dynamics in photovoltaic device fabricated from polymer/fullerene cells under solar illumination [4].

In this paper, we report on the photogeneration and recombination kinetics of charge excitations in the composites in the time regime longer than 100 ms by using the LESR method; this method has been applied to detect polarons in conjugated polymers and polymer/fullerene composites [7-9]. We have successfully fabricated the composites using regioregular poly(3-alkylthiophene)s (RR-PATs) and C_{60} [7]; RR-PATs attract much attention because they have a highly ordered lamella structure and exhibit greatly improved field-effect mobilities owing to self-organization [10,11]. We have measured the dependence of the LESR intensity on the excitation-light intensity I_{ex} and time elapse for the RR-PAT/C_{60} composites, in particular for the time regime of 100 ms - 2 min where initial prompt decay of LESR are observed; it has been found that the results cannot be explained by bimolecular recombination of charged excitations often observed in many molecular systems. On the basis of the present results, we propose a novel model considering quadrimolecular recombination of photogenerated charged excitations in the composites, which is probably related to the enhanced structural order resulting from the regioregularity of the system.

2. EXPERIMENTAL

Regioregular poly(3-hexylthiophene) (RR-P3HT), regioregular poly(3-octylthiophene) (RR-P3OT), and regioregular poly(3-dodecylthiophene) (RR-P3DDT) (see the inset of Fig. 1) were used to prepare the RR-PAT/C_{60} composites with C_{60} concentrations of 5 and 10 mol%. Cast films of the composites with thickness of ~ 6 μm were directly fabricated inside a

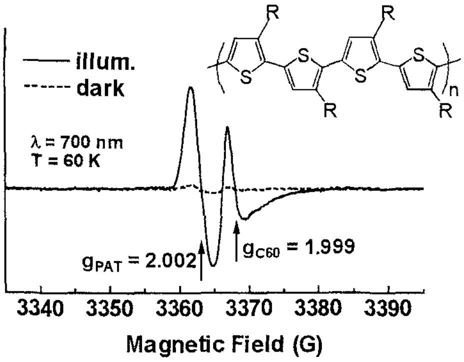

Fig. 1. First derivative ESR spectra of the RR-P3OT/C_{60} composite with 5 mol% C_{60} content under dark condition (dashed line) and 700 nm light illumination (solid line) at 60 K with a microwave power of 0.06 mW. Inset: Polymer structure of regioregular poly(3-alkylthiophene) (RR-PAT).

quartz sample tube [7]. ESR measurements were performed with Bruker E500 and EMX X-band spectrometers equipped with a microwave cavity with optical windows using an Oxford ESR900 gas-flow cryostat. A JASCO SM-5 light source with a 300 mW xenon lamp was used to provide excitation for 300 - 1100 nm at power levels up to 2 mW/cm^2 with an optical fiber delivery [7,9]. For the excitation spectrum, the light intensity was adjusted to give the same photon flux at each wavelength.

3. RESULTS AND DISCUSSION

3.1 Photogeneration of charged excitations

In this subsection, we present the photogeneration of charged excitations in the composites. Figure 1 shows the first derivative ESR spectra of the RR-P3OT/C_{60} composite (5 mol%) under dark condition (dashed line) and 700 nm light illumination (solid line). Two LESR signals due to the photoinduced electron transfer between RR-P3OT and C_{60} are observed. The g value of g_{PAT} = 2.002 and g_{C60} = 1.999 correspond to positive RR-P3OT polarons and C_{60}^{-} radical anions, respectively. Since the results for the composites using RR-P3HT and RR-P3DDT are essentially the same as those for the RR-P3OT/C_{60} composite except for the dark ESR intensity, we will mainly present the results for the RR-P3OT/C_{60} composite in this paper.

The excitation spectrum of the LESR intensity of the RR-P3OT/C_{60} composite is shown in Fig. 2 [7]. The data are plotted using the signal intensity of RR-P3OT (g_{PAT}). For comparison, the absorption spectrum of the RR-P3OT/C_{60} composite (5 mol%) (solid line) and photocurrent spectrum of a composite of regiorandom poly(3-octadecylthiophene) (RRa-P3ODT) and C_{60} (5 mol%) (dashed line) [12] are shown together in Fig. 2. The photoconductivity of the composite is remarkably enhanced upon C_{60} doping due to the photoinduced electron transfer at ~ 1.8 eV where optically forbidden transition of C_{60} monomer ($h_u \rightarrow t_{1u}$) exists. The excitation spectrum of the LESR intensity shows a remarkable enhancement at ~ 1.77 eV (700 nm) and a monotonic increase above 2.5 eV up to 4.1 eV [7,13]. There is almost no excitation-energy dependence of the LESR line shape. The enhancement of the LESR intensity is qualitatively similar to the enhancement of the photocurrent spectrum on the whole, which is consistent with the photogeneration of polarons due to the photoinduced electron transfer. However, the detailed structures of the excitation spectra at around the peaks are quantitatively different with each other. The peak energy of the excitation spectrum of the LESR is slightly lower than that of the photocurrent, and considerable photogenerated signals are observed in the lower photon-energy region even at ~ 1 eV. One possible explanation for the differences of the excitation spectra between LESR and photocurrent is given by considering aggregation effects of the polymer chains. The sample for the photocurrent spectrum is fabricated using regiorandom PAT that has no highly-ordered lamella structure [14]. Therefore, the regioregularity of PATs probably affects the charge-separation processes between PAT and C_{60} in the composites and causes the difference of the excitation spectra between the LESR and photocurrent mentioned above.

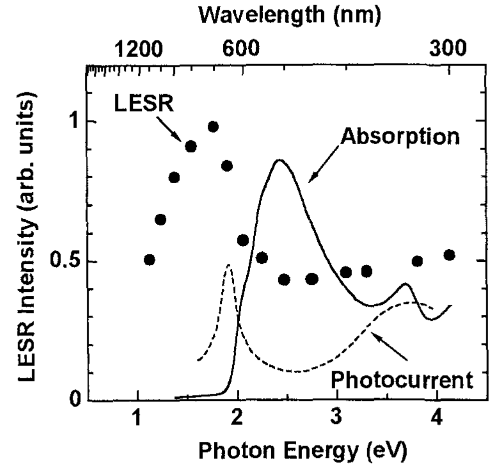

Fig. 2. Excitation spectrum of the LESR signals of the RR-P3OT/C_{60} composite (5 mol%) at 60 K. The solid and dashed lines show the absorption spectrum of RR-P3OT/C_{60} composite (5 mol%) and photocurrent spectrum of RRa-P3ODT18/C_{60} composite (5 mol%) for the comparison, respectively.

3.2 Recombination kinetics of charged excitations

In this subsection, we present the recombination kinetics of charged excitations in the composites. Figure 3 shows a typical transient response of the LESR intensity upon irradiation by repeated light (700 nm) pulses with different time widths. The transient response shows two components: prompt one and persistent one [7], similar to the study for a composite of poly(*p*-phenylene vinylene) (PPV) derivative (MDMO-PPV) and a substituted C_{60} derivative (PCBM) [6]; these LESR components are considered to be caused by shallow and deep traps in the composites, respectively [7,15]. The behavior of the persistent component in the present system is found to be nearly the same as that reported in the MDMO-PPV/PCBM composite, where the behavior of the persistent component at low temperatures has been explained by nongeminate recombination of randomly distributed carriers using tunneling process assuming charge neutrality, in the time regime of 2 - 80 min [6]. Thus, in

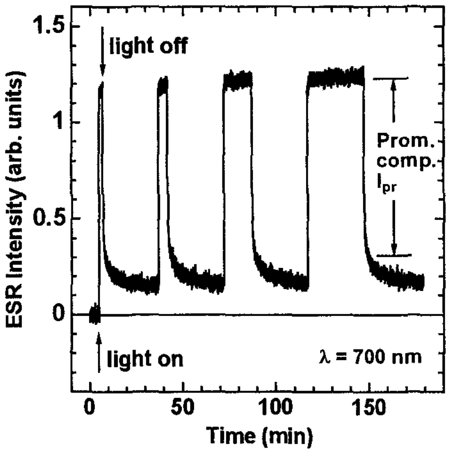

Fig. 3. Transient response of the LESR intensity of the RR-P3OT/C_{60} composite (5 mol%) upon irradiation by repeated light (700 nm) pulses with different time widths. The data were recorded using the lower field peak of the RR-P3OT signal (g_{PAT}) at 100 K. The intensity of the prompt decay component of LESR, I_{pr}, is defined as the subtraction between the LESR intensity under light illumination and at 2 minutes after the termination of irradiation.

the present study, we focus on the geminate recombination kinetics of charged excitations in the time regime of 100 ms - 2 min that is related to the prompt component. The intensity of the prompt decay component of LESR, I_{pr}, is defined as the subtraction between the LESR intensity under light illumination and at 2 minutes after the termination of irradiation.

First, we present the dependence of I_{pr} on I_{ex}. In the LESR studies of the composites [6,7], steady state conditions can be reached under light illumination (see Fig. 3); hence simple dependence of I_{pr} on I_{ex} will give the information about the recombination process of the photogenerated charged excitations. Figure 4 shows the dependence of I_{pr} on I_{ex} for the RR-PAT/C_{60} composites, measured under 700 nm light illumination. In spite of different temperatures measured and C_{60} concentration of the composites, I_{pr} shows an ~ $I_{ex}^{0.25}$ power dependence within the light-power range 0.027-1.26 mW/cm^2, as preliminarily reported [7].

From the above power dependence obtained, we show a novel model considering quadrimolecular recombination (QR) of photogenerated charged excitations as discussed below. Let N_h (N_e) be the number of photogenerated positive RR-PAT polarons (photogenerated C_{60}^- radical anions) per unit volume, γ and β the rate constants of QR and bimolecular recombination (BR), I the photon number of excitation light per unit volume ($I \propto I_{ex}$), and Φ the generation efficiency of photoexcitations, then we may write a phenomenological rate equation as

$$dN_{h,e}/dt = \Phi I - \beta N_h N_e - \gamma N_h^2 N_e^2. \quad (1)$$

Because $N_h = N_e$ [7], we define the number N as $N = N_{h,e}$ that is evaluated from I_{pr} assuming the Curie law ($N \propto I_{pr}$), and use N from now on. Under a steady condition, N is expressed from Eq. (1) as

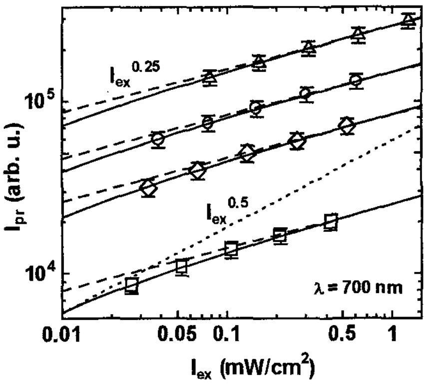

Fig. 4. Dependence of the prompt decay component of LESR I_{pr} on the excitation-light intensity I_{ex} for the RR-PAT/C_{60} composites: the RR-P3OT/C_{60} composite (5 mol%) at 60 K (circles) and 100 K (diamonds), the RR-P3OT/C_{60} composite (10 mol%) at 60 K (triangles), and the RR-P3DDT/C_{60} composite (5 mol%) at 60 K (squares). The solid lines show the Eq. (2). The dashed lines and the dotted line denote $I_{pr} \propto I_{ex}^{0.25}$ and $I_{pr} \propto I_{ex}^{0.5}$, respectively.

$$N = \sqrt{-(\beta/2\gamma)\sqrt{(\beta/2\gamma)^2 + (\Phi I/\gamma)}}. \quad (2)$$

The solid lines in Fig. 4 represent the fitting curves of Eq. (2) to the experimental data; they explain the data very well. The dashed lines in Fig. 4 represent the I_{ex} dependence only of QR described with $N = (\Phi I/\gamma)^{0.25}$, which explain the data at higher I_{ex} (~ 1 mW/cm^2). Therefore, QR is dominant at higher I_{ex} while BR is relatively important at lower I_{ex}. The above result indicates that a pair of a positive polaron and a C_{60}^- radical anion, Coulombically attracted with each other, recombines with another pair of a polaron and an anion *simultaneously*. This probably requires remarkable high mobility of pairs to encounter, which is related to the regioregularity of the present RR-PAT system acting as the matrix for C_{60} moiety. On the other hand, the dotted line in Fig. 4 represents the I_{ex} dependence only of BR described with $N = (\Phi I/\beta)^{0.5}$, which cannot explain the data.

Second, we present the transient decay of I_{pr} to support the above QR model. Figure 5 shows the time dependence of the normalized I_{pr} for the RR-P3OT/C_{60} composite (5 mol%). As temperature increases, the recombination becomes faster. Solid lines in Fig. 5 and its inset represent the decay curves of QR derived from Eq. (1) under $I = 0$ condition as

$$N/N_0 = \left(1 + 3\gamma N_0^3 t\right)^{-1/3}, \quad (3)$$

where N_0 is the number of polarons under a steady condition. The experimental data are described with Eq. (3) very well using the temperature-dependent γ. Therefore, the QR model also well explains the time dependence of I_{pr}. Twice-integrating the first derivative LESR signal, we evaluate N_0 as 1.6 x 10^{17} cm^{-3} at 60 K considering the absorption depth of ~ 16 μm for the 700 nm excitation [7], and then we evaluate γ at 60 K as

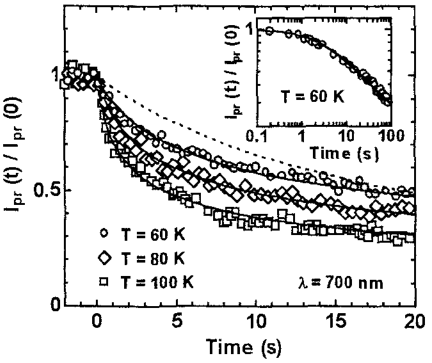

Fig. 5. Decay of the prompt component of LESR I_{pr} for the RR-P3OT/C_{60} composite (5 mol%) after the termination of 700 nm irradiation with I_{ex} ~ 1 mW/cm^2 at 60 K, 80 K, and 100 K. The solid lines show the Eq. (3). The dotted line denotes $N/N_0 = (1+\beta N_0 t)^{-1}$. Inset: Log-log plot of I_{pr} vs time for the RR-P3OT/C_{60} composite (5 mol%) after the termination of 700 nm irradiation at 60 K. The solid line shows the Eq. (3).

3.8 × 10^{-53} cm^{9}s^{-1} by Eq. (3). On the other hand, the decay curve of BR expressed as $N/N_0 = (1+\beta N_0 t)^{-1}$ cannot explain the data (see the dotted line in Fig. 5). Inset of Fig. 5 shows a log-log plot of I_{pr} vs time. This plot clearly represents that the decay cannot be described with $At^{-\alpha}$ observed for the composites in the time regime shorter than 1 ms [4,5].

In order to study the regioregularity effect of PAT on the recombination, we have investigated a composite of regiorandom poly(3-octylthiophene) (RRa-P3OT) and C_{60} (5 mol%). The measurements for the RRa-P3OT/C_{60} composite have showed that the prompt component was almost negligible and only BR of photogenerated charged excitations was observed. Thus we conclude that the QR phenomena require the regioregularity of PAT in the composites and are probably related to the high carrier mobilities resulting from the ordered structure of RR-PATs.

Finally, we present the temperature dependence of γ related to the transport mechanism of photogenerated charged excitations. Figure 6 shows the Arrhenius plot of γ for the RR-P3OT/C_{60} composite. The date below ~ 60 K is almost independent of temperature, as also observed for the slow decay component in the MDMO-PPV/PCBM composite [6], indicating the tunneling process at low temperatures. On the other hand, the data above ~ 90 K follows the activation-type formula [$\exp(-\Delta/kT)$] as plotted by the solid line in Fig. 6, where the activation energy Δ is evaluated as 0.10 eV. Therefore, the above results clearly show a crossover of the transport mechanism from hopping to tunneling with decrease of temperature. It is interesting to note that the above activation energy is close to that of 80 meV measured by the steady-state photoconductivity for a composite of a PPV derivative (MEH-PPV) and C_{60} [16], and is also consistent with the shallow-trap energy of 0.1 eV measured by thermally stimulated currents and photoinduced absorption for a planarized form of poly(para-phenylene) [17]. Therefore, the present Δ is reasonably ascribed to the hopping energy of shallowly trapped polarons causing the prompt component of the LESR.

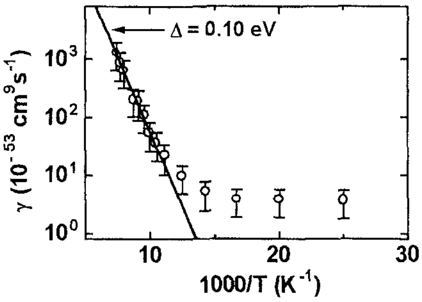

Fig. 6. Arrhenius plot of quadrimolecular-recombination rate constant γ of Eq. (3) for the RR-P3OT/C_{60} composite (5 mol%), measured using 700 nm irradiation.

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