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Charge Recombination Process in X-Ray Irradiated Pyrene-Doped Polystyrene as Studied by Optically Detected Electron Spin Resonance and Magnetic Field Dependence of the Recombination Fluorescence

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The ODESR spectrum and magnetic field dependence on recombination fluorescence were observed for X-ray irradiated pyrene-doped polystyrene at temperatures of 242—348 K. The ODESR intensity as a function of the pyrene concentration, 0.1—8.9 wt%, showed an unusual minimum at about 1.0%. Two phases were separated in the magnetic field dependence of the fluorescence: one was sharp and saturates at fields of over 50 mT, while the other was broad with a dip at around 60—150 mT. The cause of this dip was naturally attributed to the ST_{-1} level crossing. The sharp magnetic field effect also showed a minimum at around a concentration of 1.0 wt%. These novel findings have been interpreted using a recombination model modified from the previous one for pyrene-doped ethylene–propylene rubber and polyethylene. The essential points of the present model are: (1) although electron hopping within the polystyrene molecule is rapid, electron transfer at the last step of recombination between the polystyrene anion and the pyrene cation proceeds at a moderate rate; (2) the hole-transfer rate in the polymer chain is moderate; (3) electron hopping between the doped pyrene molecules is very much dependent on the concentration; (4) hole hopping between the pyrenes is inhibited.

Charge hopping processed play very important roles in the damaging process of materials by ionizing radiation. For example, it is known that excess electrons can migrate rapidly in a large biological molecule, such as protein.[1] The mode of charge migration in protein is closely related with DNA damage by ionizing radiation. The charge hopping processes may also play important roles in the electronic properties of solid state materials.[2] In a series of recent papers, we tried to clarify the charge-recombination processes in X-ray irradiated pyrene-doped plastics, i.e. ethylene–propylene rubber (EPR)[3] and low-density polyethylene (LDPE),[4] using the optically-detected ESR (ODESR) and magnetic field effect (MFE) on the recombination fluorescence.[5—7] In those studies, we could interpret the results by extending the recombination model postulated in solution studies[8—12] by introducing charge hopping between the doped pyrenes as well as in the matrix molecules, instead of diffusion of the charged molecules. Since the intensities of the MFE as well as the ODESR in polyethylene are more than half of those in squalane, we believe that we observed the main part of the charge recombination process. We concluded that: (1) When the concentration of pyrene is low, e.g. 0.1 wt%, only one component, the electron or the hole, is trapped by the dopant, and the other migrates in the polymer matrix to the dopant ion for recombination. If the electron migrates to the pyrene cation, since recombination occurs within a very short time, phenomena which are dependent on spin correlation, ODESR and MFE, are not observed. On the other hand, if the hole and pyrene anion form a pair, recombination occurs more slowly,[13] and this geminate pair contributes to ODESR and MFE. This slow recombination of the pair might be partly due to the instant formation of olefinic cation after ionization;[11,12] (2) When the concentration is more tnan 1.0%, both charges are trapped by the doped pyrenes, and they hop between those pyrenes to recombine in such a short time that the ODESR or the MFE can be observed. The concentration and temperature dependence of the ODESR linewidth, as well as excess excimer fluorescence with X-ray irradiation, may not be able to be interpreted using the diffusion model.[14]

In the present study, we observed ODESR and MFE for polystyrene doped with pyrene at various concentrations in order to study the electron-transfer process in doped aromatic polymers. The observed phenomena were very much different from those in the pyrene-doped saturated polymers, reflecting the aromaticity of the matrix polymer. We have presented the mechanisms of electron and hole transfer in aromatic polymers doped with pyrene.

We understand charge hopping as being an electron transfer between the same species, and charge migration as being charge transfer within the matrix, which may provide shallow trapping sites for the charges.

Experimental

Pyrene was purchased from Wako Pure Chemicals (Tokyo) and purified by the zone-melting technique. *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) was obtained from Wako Pure Chemicals and purified by sublimation. Polystyrene was from Scientific Polymer Products (Ontario, N.Y.) and used without any further purification. The softened polymer and pyrene were kneaded together for 10 min at 460 K, and the resultant mixture was shaped into rods (o.d. 3 mm×length 40 mm) using a mini molder (Model CS-183MMX, CSI Inc., N.J.), which was modified so as to treat samples under inert gas flow. The ODESR spectrum and the magnetic field effect on recombination fluorescence were observed with an apparatus described elsewhere.[8] Light of $\lambda<300$ nm was filtered off; the fluorescence spectrum for samples containing pyrene showed only peaks from pyrene. The microwave power was monitored with a power meter (573B, Hewlett Packard) attached to the circuit using a directional coupler. The temperature was controlled with cold nitrogen gas using a home-made temperature control unit.

Results

The fluorescence spectrum of the X-ray irradiated polystyrene doped with pyrene at a concentration of less than 3.0 wt% costitutes only the monomer fluorescence of pyrene. At a pyrene concentration of 8.9%, however, the spectra contains a considerable excimer signal as a broad shoulder by the monomer peak. The fluorescence spectra of the UV-excited systems were almost equivalent with those of the X-ray irradiated systems. Therefore, hopping of the hole, which is stabilized at the oligomerized pyrenes to form a dimer (or oligomer) cation, can be neglected in this system, since this dimer cation causes an excess excimer fluorescence for X-ray excited systems.[3,4,9,10] The fluorescence intensity (uncorrected) from polystyrene without an additive (275, 335 nm[15]) was less than 10% of that for a sample with 1.0% pyrene. The ODESR intensity for neat polystyrene was negligibly small (about 0.1% of the total fluorescence). The signal might have been from an impurity.

Figure 1 shows the ODESR spectra of polystyrene doped with pyrene at various concentraions at a temperature of 300 K. Although the spectral width does not change with a change in the pyrene concentration, the intensity changes in a very characteristic way: i.e. it becomes minimum at a pyrene concentration of about 1.0 wt%. This can be easily interpreted by assuming that the radical pair mainly contributing the ODESR signal switches from one to the other along with an increase in the pyrene concentration. By analogy with the model presented in a previous study,[3] a hypothesis that the radical pair contributing ODESR at a low pyrene concentration is of the (Ps^+, Py^-) type and that at a high pyrene concentration is of the (Py^+, Py^-) type is possible. The ODESR linewidth would be scarcely dependent on the pyrene concentration, since at a low pyrene concentration the phenyl group traps the charges in the polymer molecule and the ESR linewidths of those radical ions are predicted to be almost the same as those of the pyrene ions.

Figure 2 shows the ODESR intensity as a function of temperature. This is also contrasted with those for ethylene–propylene rubber and low-density polyethylene.[3,4] In the latter cases, the ODESR intensity changes more steeply as the temperature changes and shows a maximum value at a temperature which is dependent on the "softness" of the polymer matrix. One of the differences between polystyrene and polyethylene or EP-rubber is the fact that although the glass transition temperature of the former is much higher than the experimental temperatures, those of the latter are lower. Therefore, since pyrene molecules in the polystyrene are rigidly embedded in the matrix, thermal activation of charge hopping may not be significant.[16] This is why the slope of the temperature dependence in the ODESR amplitude is gentle for polystyrene, but is steep for polyethylene or EP-rubber, in which thermal activation of reorientaion of pyrenes to achieve a desirable configuration (e.g. face to face) for electron and hole hopping is significant. The gradual decrease in the ODESR intensity with an increase in the temperature may be due to the decrease in T_1 (spin lattice relaxation time of electron spin).

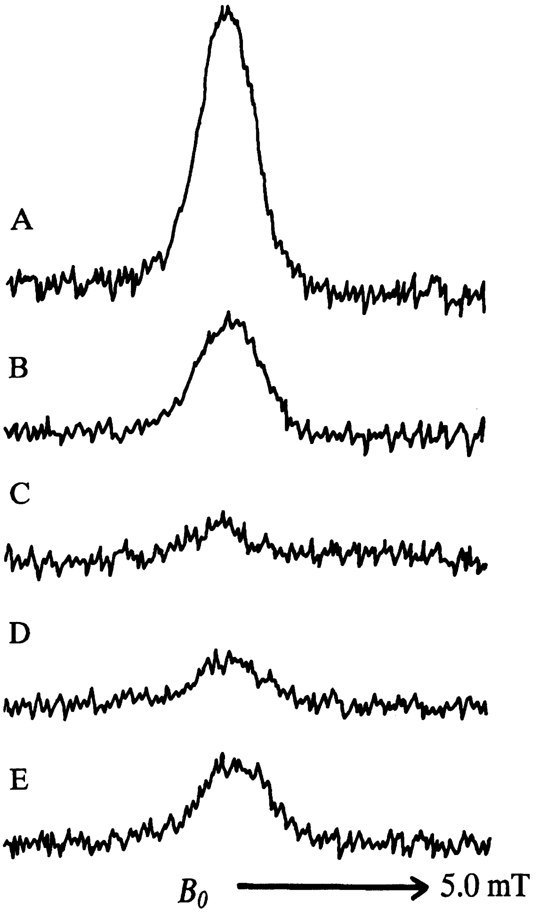

Fig. 1. ODESR spectrum for polystyrene doped with pyrene at 300 K at several concentrations, A: 7.6; B: 2.7; C: 0.9; D: 0.3; E: 0.1 wt%. The microwave power was 1.0 W. The intensity of the ODESR signal relative to the total fluorescence was 1.6% for a concentration of 7.6 wt%. The spectra are drawn with a common vertical scale, thus other signal intensities can be calculated from their heights.

To elucidate more about the mechanism of recombination through electron and hole transfer, ODESR and MFE in recombination fluorescence were observed for polystyrene doped with TMPD. TMPD was selected, since it captures only the hole due to the fact that both the ionic potential and electron affinity are

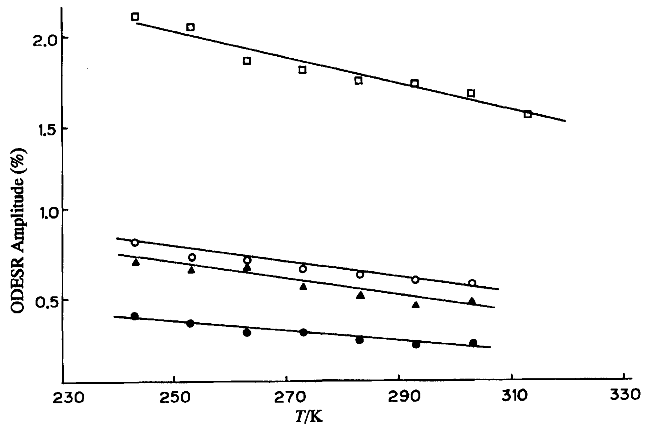

Fig. 2. ODESR amplitude relative to the total fluorescence intensity as functions of the temperature for the system of pyrene doped polystyrene. The concentrations of pyrene are, □ : 8.9 wt%; ○ : 3.0 wt%; ● : 1.0 wt%; ▲ : 0.1 wt%.

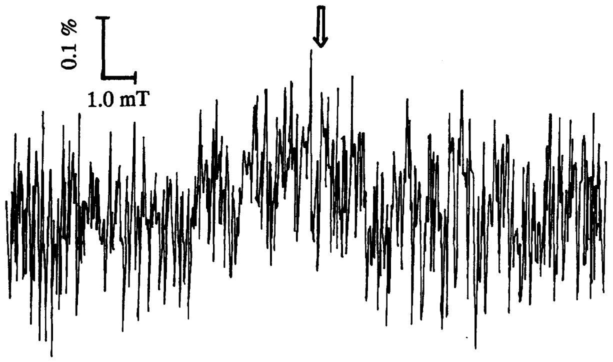

Fig. 3. ODESR spectrum of polystyrene doped with TMPD at the concentration of 1.0 wt% at 303 K. The microwave power is 1.0 W. An arrow indicates the place where the ESR signal should appear.

much smaller than those of the pendant phenyl in polystyrene. As can be seen in Fig. 3, the ODESR signal is hardly detected. Therefore, in a system containing pyrene the radical pair (Py^+, Ps^-) does not contribute to the ODESR signal, as postulated a priori in the above explanation for Fig. 1, since recombinations of ($TMPD^+$, Ps^-) and (Py^+, Ps^-) should proceed in an equivalent way. This means that the recombination time of ($TMPD^+$, Ps^-) is either too short or too long to contribute to the ODESR signal. Because MFE in recombination fluorescence is clearly observed, as shown in Fig. 4, the recombination time of the pair must be too short for observing the ODESR signal, but is sufficiently long to contribute to the magnetic field dependence in the fluorescence (see Discussion (2)). The broad magnetic field dependence in the fluorescence is in contrast with the sharp one that is a typical MFE, and has been assigned to mixing between the three levels of the triplet state and the singlet state at low magnetic fields, comparable with or less than the hyperfine interaction.[10)]

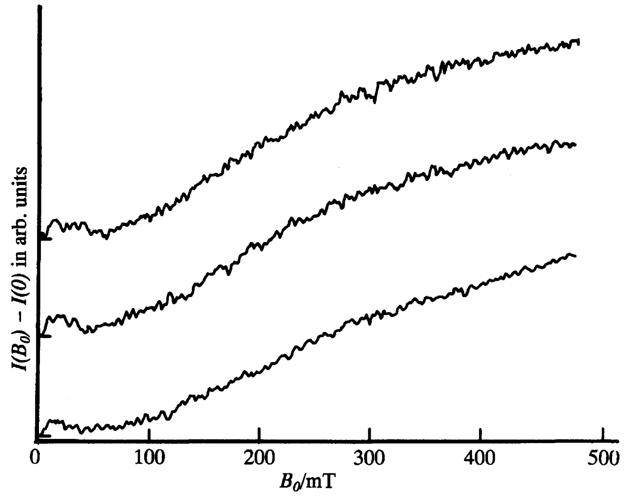

Fig. 4. Magnetic field dependence of the recombination fluorescence, $I(B_0)$–$I(0)$, for TMPD doped polystyrene, at 343 K (top), 303 K (middle), and 253 K (bottom). The intensity were, 1.6, 1.2, and 1.1% for the above temperatures, respectively. Two independent observations are averaged for each MFE curve and the curves were smoothed by averaging five data points (2.5 mT).

Although the relaxation mechanism sometimes explains the gentle slope observed in MFE, this is not the case here, since we could not observe the ODESR signal for the system with TMPD. Thus, it is quite natural to assign this broad MFE to the mixing between T_{-1} and S_0 at a field comparable to the exchange interaction (assumed as positive) between pairing radicals.

Figure 5 shows the magnetic field dependence in the intensity of recombination fluorescence for polystyrene doped with pyrene at 0.1, 1.0, and 8.9 wt%. Two phases are noticed: the sharp MFE saturates at fields over 50 mT, and the other very dull one is accompanied by a broad dip at around 60—150 mT. This dip is most distinct at the lowest pyrene concentration of 0.1 wt%. It is also noticeable that the amplitude of the sharp one is almost parallel with the ODESR intensity and has a minimum at around a pyrene concentration of 1.0 wt%. It is rare that this kind of dip is observed for the geminate ion pair, which is not a biradical.

Figure 6 shows the temperature dependence of the MFE on X-ray induced recombination fluorescence for polystyrene doped with pyrene at 1.0 wt%. It should be noted that at 348 K the sharp component almost disappears, and the position of the broad dip becomes vague. This tendency is also observed for the other concentrations. The disappearance of the sharp component occurs in parallel with the decrease in the ODESR signal at elevated temperatures, and is explained by the shortening of T_1 due to an increase in the temperature.

Discussion

1. Recombination Scheme of the Geminate

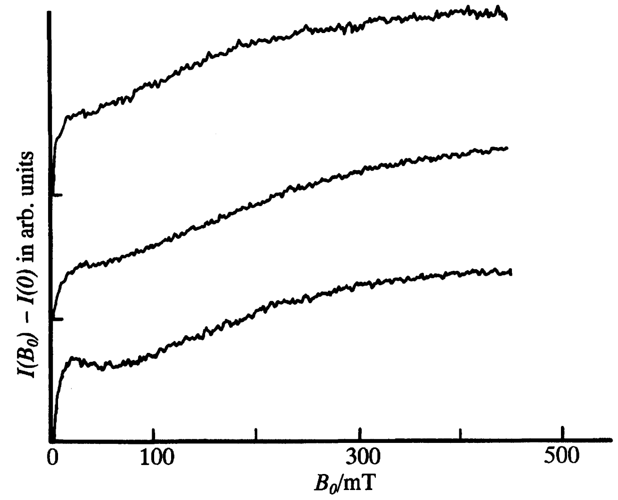

Fig. 5. Magnetic field dependence on the recombination fluorescence, $I(\mathrm{B_0})$–$I(0)$, for polystyrene doped with pyrene at 8.9, 1.0, and 0.1 wt% (from top to bottom) at 293 K. The magnetic field effect, $(I(450\mathrm{mT})-I(0\mathrm{mT}))/I(0)$, are 3.3, 1.7, and 1.7%, respectively, for the above concentrations. Two independent observations are averaged for the lower two MFE curves, which were smoothed further by averaging five data points (2.0 mT).

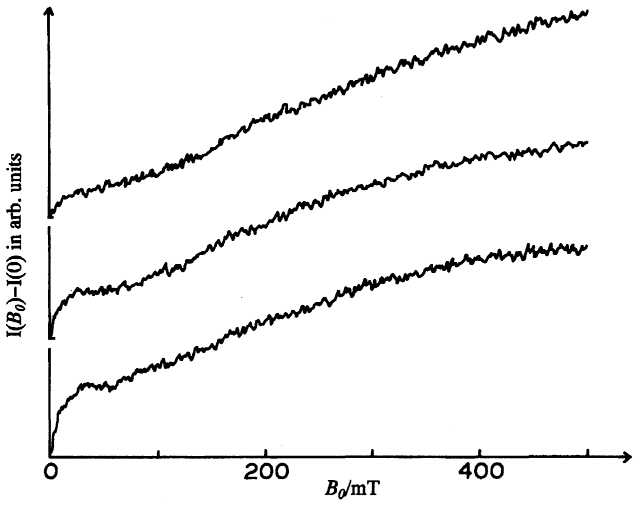

Fig. 6. Magnetic field dependence on recombination fluorescence, $I(\mathrm{B_0})-I(0)$, for polystyrene doped with pyrene at the concentration of 1.0 wt% at 348, 302, and 252 K (from top to bottom). The magnetic field effect, $(I(500\ \mathrm{mT})-I(0\ \mathrm{mT}))/I(0)$, are 2.1, 2.0, and 2.4%, respectively, for the above temperatures.

Pair: The ODESR technique is useful for determining the component radicals of the geminate pair.[6,7] In previous studies, we assigned several types of ion pairs by ODESR in the charge recombination proceses in ethylene–propylen rubber (EP-rubber) and low-density polyethylene (LDPE) doped with pyrene with the help of both MFE and the spectrum of the recombination fluorescence. It was concluded that[3,4] the radical pair which mainly contributes to the fluorescence changes from ($\mathrm{Pol^+}$, $\mathrm{Py^-}$) to ($\mathrm{Py^+}$, $\mathrm{Py^-}$) upon increasing the concentration. Here, "Pol" represents the polymer molecule. In the assignment of the radical pairs, it was assumed that $\mathrm{Pol^+}$, the alkane or olefinic cation of the polymer molecule, gave a very broad signal. Since the ODESR spectra for polystyrene doped with pyrene at various concentrations showed no broad components, neither charge spends time in the main chain of polystyrene but, rather, reside in either pendant phenyls or doped pyrenes. Therefore, by analogy with the conclusions given in previous works,[3,4] the geminate recombination scheme shown in Fig. 7 can be derived. Since the phenyl group can trap an electron, the original geminate pair ($\mathrm{Ps^+}$, $\mathrm{e^-}$) is converted to ($\mathrm{Ps^+}$, $\mathrm{Ps^-}$) {abbreviated as GP0} within a very short time, which then transfers one of the charges to a pyrene molecule. Then, ($\mathrm{Py^+}$, $\mathrm{Ps^-}$) {GP1′} or ($\mathrm{Ps^+}$, $\mathrm{Py^-}$) {GP1} is formed. The latter can be converted further into ($\mathrm{Py^+}$, $\mathrm{Py^-}$) {GP2} upon transferring the positive charge to another pyrene if at least one pyrene molecule exists in the recombination path. Although GP1′ also has some probability to be converted into GP2, the probability may be much smaller than that of GP1, since electron hopping between the phenyls, which are stacked with a separation of 0.66 nm in the isotactic part of polystyrene, is much faster than electron transfer from polystyrene to pyrene, which may be separated more with an unfavorable configuration for electron transfer. Therefore, this path is omitted in Fig. 7 (see Subsect.4). In the previous section we showed that ($\mathrm{Ps^+}$, $\mathrm{Py^-}$) has a rather long lifetime and contributes to the ODESR signal, whereas ($\mathrm{Ps^-}$, $\mathrm{Py^+}$) recombines in a short time and

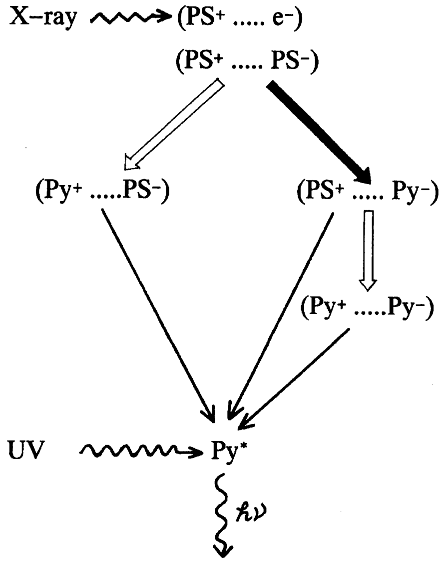

Fig. 7. Charge recombination mechanism in pyrene doped polystyrene. The open arrow and the closed arrow represent hole and electron-transfer process, respectively. The charge recombination step is represented by a thin arrow.

gives no ODESR signal. It is commonly observed that hole hopping is much slower than electron hopping;[1] thus, the former has a longer recombination time than does the latter. In addition, stabilization of the polystyrene cation is expected through an interaction between the two phenyl rings by sharing one hole.

2. Minimum in ODESR Intensity: Since the pair (Py^+, Ps^-) does not contribute appreciably to the ODESR signal, as suggested by the result shown in Fig. 3, the main contributor to the ODESR may switch from (Py^-, Ps^+) to (Py^-, Py^+) upon increasing the pyrene concentration, as predicted from Fig. 7. Thus, the minimum ODESR for polystyrene doped with pyrene at around 1 wt% can be assigned to this switching of radical pairs.

There are two conditions necessary to observe a strong ODESR spectrum: (1) The spin lattice relaxation time (T_1) should be sufficiently long relative to the recombination time (τ_g), since $ST_\pm$ and $T_0T_\pm$ mixing due to the T_1 process diminishes the ODESR intensity; (2) The time required for the microwave field to flip the electron spin (τ_{flip}) should be shorter than τ_g. Since the microwave field of 0.1 mT needs about 360 ns to flip the electron spin by 180 degree, a radical pair with a much shorter life-time than this is difficult to be observed by ODESR, i.e. ODESR monitors only long-lived ion pairs. For an MFE observation, the second condition should be replaced with the next one; (3) The life-time of the geminate pair should be longer than the ST mixing time (τ_{mix}), which is determined by the hyperfine coupling constant (hfc) as being 1/hfc. Since the hfc may be of the order of 0.5 mT for a π-radical (or more for σ radicals), it takes 70 ns or so for the ST-mixing.

Here, we should stress the fact that in case of geminate pairs produced by ionizing radiation, the separation between the component ions is distributed from zero to a very large value. Therefore, the recombination time is also distributed over a wide range; ODESR as well as MFE are thus observed only from geminate pairs whose separation comes in a part of this ditribution.

We can classify the contribution of GP1 (and GP2 at high concentration) to the ODESR (and MFE) intensity into the following three types:

(1) At a very high pyrene concentration, e.g. 5—10 wt%, both charges are transferred to pyrenes to form GP2, and may hop between the pyrenes rapidly. Since the local hyperfine fields or the pyrene ions are small, due to spin delocalization over the large molecular plane, T_1 should be rather long. We can therefore expect a large ODESR signal as well as MFE.

(2) At a moderate pyrene concentration, e.g. around 1 wt%, both charges of the geminate pair of GP0 are still transferred to the solute pyrenes,[4] forming GP2. However, the average distance between the pyrenes is so large (3.5 nm in average) that it is rather difficult for the electron to hop from one pyrene to another to recombine in less than T_1. Thus, the intensity of the ODESR spectrum and MFE becomes very small.

(3) At a still lower pyrene concentration, there may be only one pyrene in the path of the geminate recombination. Thus, the positive charge of GP1 may hop in polystyrene molecules toward the pyrene anion where recombination occurs. Since the potential well for the positive charge in the polystyrene molecule is not so deep, due to the high ionization potential of the phenyl group; in addition, since the distance between the phenyls is only 0.6–0.7 nm, the hole can rapidly hop between the phenyl groups. In this case τ_g again becomes shorter than in case (2), resulting in moderate ODESR and MFE signals.

As for GP1′ {(Py^+, Ps^-)}, the other branch for the fate of GP0, since the phenyl group works for the electron as a shallow potential well due to a negative electron affinity, the recombination time should be very short. It therefore contributes only to the dull-shaped MFE with a characteristic dip, as clearly indicated in the experiment using TMPD as the dopant.

Therefore, a pyrene concentration of 1.0 wt%, at which we observed the minimum for both the ODESR intensity and the sharp MFE, must correspond to stage (2). If pyrene is well-dispersed into the plastics, the average separation between pyrenes is about 3.5 nm. Since the average separation of the geminate ion pair in a nonpolar environment is around 7.0 nm or so,[17] it is reasonable that this concentration corresponds to case (2).

3. Broad Magnetic Field Effect with a Dip: Sharp MFE's are commonly observed for solution systems[8,18—20] including MFE's on chemical reactons.[21—25] The fluorescence from X-irradiated ethylene–propylene rubber (EP-rubber)[3] and low-density polyethylene (LDPE)[4] doped with pyrene also show sharp MFE's. The broad dip or broad MFE are rather rare and have been ascribed to level crossing between the singlet and T_{-1} as mentioned above, and was first observed in a recombination fluorescence of the zwit terion biradical produced by a photo-induced intramolecular redox reaction.[26] It was later shown that non ionic biradicals also exhibit the same kind of MFE's.[27,28] Weller et al. studied the MFE on the recombination fluorescence for a redox system comprising an amine and pyrene separated by nine methylene groups, and observed a dip at around 30 mT corresponding to the exchange interaction of this system.[26] Tanimoto tabulated the exchange interactions obtained by the MFE in relation to the carbon number in the methylene chain.[29] According to the table, the exchange interaction of 40—150 mT corresponds to the mutual separation between the two spins of 0.8—1.0 nm or less. Our present observation is rather astonishing in two ways: Firstly, our medium polystyrene is not polar; secondly, although there is no difinite separation between the two spins, it should change incessantly until recombination from the initial separation, which is distributed over a wide range. The effect of level crossing in the MFE has been observed for: (1) ionic biradicals with a short and rather definite separation in a polar media where the ion pair has an sufficiently long linetime due to a reduction in the Coulombic interaction; (2) neutral biradicals where no Coulombic interaction exists. The present observation does not fall within either of these two categories.

An interval of about 50 ns or more, which is roughly estimated to be 1/hfc, is needed for ST_{-1} level crossing in the present system. If a radical ion pair can stay for a longer time than 50 ns with a small separation for a large exchange interaction (i.e. J>a) and at the same time the recombination time is shorter than T_1, we should then observe a dip in the MFE due to an ST_{-1} level crossing. We can explain a broad dip at around 50—150 mT as being due to a distribution of J which has a peak at around 100 mT (corresponds to 560 mJ). Although, J changes continuously from zero to several hundred kJ during the recombination, the observed J are distributed over this relatively small range. This indicates that there is a state with a considerably long life-span (longer than the ST-mixing time of ca. 50 ns) with a separation of only ca. 0.8—1.0 nm. This kind of situation may occur in the following way: (1) The electron is separated from the counter ion by about 7.0 nm or so initially upon ionization; (2) Immediately after ionization the electron hops onto the phenyl group of the polymer toward the counter ion of Py^+ in a very short time; (3) The reason why it takes a relatively long time to transfer the electron during the last step of recombination may be due to the large exotherimicity of the reaction. It is well-known that a large exotherimicity of an electron-transfer reaction results in a great reduction in the rate due to a small Franck–Condon corrected density of the final state.[30—32]

The temperature dependence of MFE shown in Fig. 6 can be explained by the general decrease in T_1 with an increase of temperature. The shorter T_1 causes a smaller contribution of the long-lived ion pairs, which contribute mainly to the sharp MFE. However, the mechanism will be fully understood after more detailed analysis involving different kinds of experiments.

4. Hopping vs. One-Step Tunneling for Geminate Recombination: Since the electron transfer (ET) rate is very much (exponentially) dependent on the exotherimicity of the ET reaction, neither of the electron and hole can easily hop between the same chemical species, i.e. doped pyrene molecules when the concentration is low.[30,31] This may be the reason why the ODESR intensity for a system at a pyrene concentration of 1.0 wt% is very low. That is, the recombination time exceeds the spin lattice relaxation time due to a low hopping rate (or recombination rate), since most of the charges are trapped by the pyrene molecules and the average distance between the pyrenes is about 3.5 nm, over which distance electron transfer with a small exotherimicity (due to Coulombic field only) is difficult to occur on the μs time scale.[32] However, when the concentration is increased to 8.9%, the mutual separation decreases to about 1.6 nm, which is sufficiently short for the charges to hop and recombine within the time, while maintaining some spin correlation. This fact corresponds to the large increase (to about 6 times) of the ODESR intensity at this concentration. This fact cannot be explained by the single-step recombination model. It is interesting to note that the ratio between the sharp MFE and the broad one is almost unity for the two widely different concentrations, 0.1% and 8.9%. This fact is nicely explained by the model shown in Fig. 7, i.e. (Py^+, Ps^-) or (Ps^+, Py^-) is formed by nearly the same amount from GP0. The former gives the broad MFE and the latter (or GP2 from the latter at 8.9%) gives the sharp one. This model requires that (Py^+,Ps^-) is not converted into GP2, which is ensured by assuming that the electron travels very fast in the polystyrene chain, by hopping between the phenyl groups.

5. Intensity of MFE and ODESR Relative to the Total Fluorescence: Finally, we discuss the intensities of MFE and ODESR. In the present case those are only as high as 3.0% of the total fluorescence, as given in the figure captions. The main cause of this low intensity of MFE and ODESR is the fact that a large part of the fluorescence is induced by the transfer of excitation from the electronically excited polystyrene to the pyrene. This fluorescence has nothing to do with the radical pair interaction. In fact, the detected photocount was about 5—6 times as high as that for the polyethylene system with the same X-ray output. Nevertheless, since the intensities of MFE and ODESR are still half of those in the polyethylene system, the observed phenomena must be from the main process of the charge recombination.

There are many inherent causes which reduce the intensities of MFE and ODESR. Ion pairs, which recombine in very short times (say less than 10 ns or so) due to very short initial separations or those recombine in very long times (much longer and T_1) including the escaped pair, do not contribute these phenomena. This is why the MFE is small compared with the total fluorescence in an irradiated system. In case of ODESR, in addition to the above reasons for MFE, the fact that only a small part of the radical pairs are on resonance to the microwave at a magnetic field is another factor which reduces the ODESR intensity. Thus, the peak height of a broad (larger than the microwave field) ODESR spectrum is naturally very small compared with the total fluorescence.

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