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SPIN RELAXATION AND STRUCTURE OF LIGHT-INDUCED SPIN-CORRELATED PCBM$^-$/P3HT$^+$ RADICAL PAIRS

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The electron spin echo (ESE) technique is applied to determine the spin relaxation times of long-lived light-induced radicals and short-term spin-correlated radical pairs (SCRPs) formed by the laser flash of a composite consisting of [6,6]-phenyl-C_{61}-butyric acid methyl ether (PCBM) and poly-(3-hexylthiophene) (P3HT) at 80 K. The ESE signal dependences recorded to measure the longitudinal relaxation times of P3HT$^+$/PCBM$^-$ SCRPs and the free P3HT$^+$ radical are fitted by the $\exp(-(t/T_1)^{0.6})$ dependence with T_1 values lying in the microsecond time scale. The difference in the transverse spin relaxation times of the P3HT$^+$/PCBM$^-$ radical paira appeared after selective and non-selective echo-detected EPR spectrum excitation is explained by the instantaneous diffusion model. Based on the model, the magnetic interaction energy between the electron spins in P3HT$^+$/PCBM$^-$ SCRPs is estimated; $E/\hbar \sim 10^6$ s^{-1}.

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Keywords: spin-correlated radical pair, fullerenes, conducting polymers, electron paramagnetic resonance, electron spin echo.

INTRODUCTION

Organic photovoltaics is actively being developed. Organic thin-film solar cells with the power conversion efficiency above 10% have been created [1]. The key process of photocurrent generation in a solar cell is the light-induced formation of separated charges in the donor-acceptor system of the solar cell active layer [2]. The power conversion efficiency is substantially affected by both composition and structure [3]. The production of so-called bulk heterojunction solar cells based on composites of donor and acceptor molecules is quite simple.

In this work, a composite of [6,6]-phenyl-C_{61}-butyric acid methyl ether and the conducting polymer regioregular poly-(3-hexylthiophene), named as PCBM and P3HT respectively, were chosen as the objects of the study (Fig. 1).

The PCBM:P3HT composite is actively used as a model active layer in organic solar cells [4]. As a result of light absorption by the PCBM:P3HT composite the photoinduced electron transfer from the P3HT polymer chain to the PCBM molecule occurs in about 100 fs [5]. The quantum yield of the photoinduced charge separation depends on the composite nanostructure and reaches 90% [6,7]. At present, there is a number of works devoted to the investigation of the dynamics of photoinduced radicals in the PCBM:P3HT composite by both time-resolved optical spectroscopy with picosecond time resolution [8-11] and EPR techniques with microsecond time resolution [12-16]. Unlike the optical spectroscopy methods,

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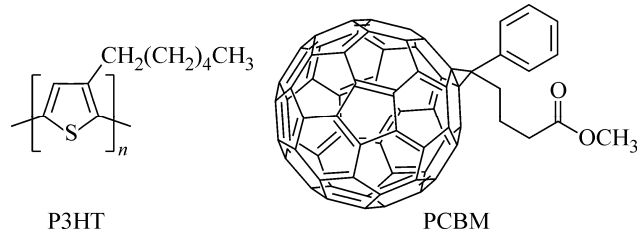

Fig. 1. Structural formulas of poly-(3-hexylthiophene) (P3HT) and phenyl-C_{61}-butyric acid methyl ether (PCBM).

the EPR techniques enable the determination of the parameters of magnetic interaction between the charge carriers. Main values of g-tensors (g_{xx}, g_{yy}, g_{zz}) and the averaged values of g-factors (g_{iso}) of the $P3HT^+$ cation ($g_{xx} = 2.00380$, $g_{yy} = 2.00230$, $g_{zz} = 2.00110$, $g_{iso} = 2.0024$) and the $PCBM^-$ anion ($g_{xx} = 2.00058$, $g_{yy} = 2.00045$, $g_{zz} = 1.99845$, $g_{iso} = 1.9998$) [17] were found. The formation of $PCBM^-/P3HT^+$ spin-correlated radical pairs (SCRPs) after light absorption by the composite was revealed by the EPR techniques [12, 15, 16]. SCRPs have lifetimes of about 10 μs at temperatures of 80-100 K. After the dissociation of SARPs free charge carriers ($PCBM^-$ and $P3HT^+$ radicals) form, which have no significant magnetic interaction between them. These free radicals have the lifetimes of about tens of minutes at a temperature about 100 K [13, 14]. The light-induced EPR signal of the PCBM:P3HT composite is not observed at room temperature, which seems to be due to fast charge recombination at this temperature [18].

The ESE decay time obtained with an increase in the delay after the laser flash is 9 μs for $PCBM^-/P3HT^+$ SCRP at a temperature of 77 K [16]. This time value is consistent with the data obtained by Behrends et al. [12]. According to this work, the time-resolved EPR spectrum of SCRP disappeared completely after a delay of 30 μs at a temperature of 100 K. However, Kobori et al. [15] used very short times of the longitudinal and transverse relaxation of SCRP for the simulation of the of similar time-resolved EPR line shape; these time values were smaller by an order of magnitude than those obtained by the ESE technique [16]. In the work of Krinichnyi et al. [19], from the analysis of the broadening of light-induced continuous wave EPR lines of the PCBM:P3HT composite the transverse relaxation times below 10^{-7} s and the longitudinal relaxation times below 1 μs were obtained. Thus, at present the literature contains a large number of conflicting data on the electron spin relaxation times in these composites.

The main aim of this work was the refinement of these values by direct ESE measurements and the estimation of the magnetic interaction between the radicals in $PCBM^-/P3HT^+$ SCRP. The obtained data on the spin relaxation are necessary for the reliable determination of the structural parameters of SCRP from the simulation of their EPR spectra.

THEORY

Strict expressions for the energy of states of SCRPs are given in [20]. Neglecting the hyperfine interaction with magnetic nuclei, in the case of the weak magnetic interaction the spin Hamiltonian of SCRPs is written as a sum of Hamiltonians of the Zeeman interaction and the magnetic interaction between the A and B spins in the pair

$$H = \hbar(\omega_A S_{Az} + \omega_B S_{Bz} + \Omega(S_{Az} S_{Bz})),$$

where ω_A and ω_B are the Larmor frequencies of A and B spins; $\hbar$ is the Planck constant; S_{Az} and S_{Bz} are the projections of A and B spins on the magnetic field direction; Ω is the magnetic interaction value in the pair

$$\Omega = D(1 - 3\cos^2\theta) + 2J,$$

where D and J are the constants of the magnetic dipole and exchange interactions between A and B spins respectively; θ is the angle between the external magnetic field vector B_0 and the line connecting the electrons with A and B spins. This criterion of the weak magnetic interaction is $|\omega_A - \omega_B| >> |\Omega|$.

In the point dipoles approximation, the dipole interaction constant is determined by the distance r between the spins

in the radical pair. For the identical g-factors of A and B spins, $g = g_A = g_B = 2$ [21]

$$(r / nm)^3 = \frac{\mu_0}{4\pi} \cdot \frac{g^2\beta^2}{D} = \frac{52 \cdot 10^{-3}}{D / \mathrm{rad} \cdot \mathrm{s}^{-1}},$$

where β is the Bohr magneton; μ_0 is the vacuum magnetic permeability.

The instantaneous diffusion effect is the acceleration of the spin relaxation of the A spin due to a change in the B spin projection caused by the microwave pulse in the case of the magnetic interaction Ω between A and B spins [22]. For the spin system in the thermodynamic equilibrium at a high temperature ($\hbar\omega << kT$) an expression describing the transverse relaxation of A spins due to instantaneous diffusion was obtained by Yudanov et al. [24] for nuclear spins and by Emshwiller et al. [23] for electron spins

$$V_A(t) = V_0(t)\cos(\Omega t), \tag{1}$$

where $V_0(t)$ is the amplitude of the ESE signal of the A spin in the absence of the interaction with the B spin.

Expression (1) has clear physical meaning. In the sequence of two microwave pulses $\pi/2$–τ–π–ESE the second microwave pulse changes the B spin projection, and therefore after the second microwave pulse the A spin precesses with a frequency shifted by the Ω value.

Assuming that the probability density of the magnetic interaction Ω is distributed by the Lorentz function with the dispersion Ω_{av}, it is possible to average expression (1) over the ensemble of ESE signals from radical pairs. The averaged expression for the ESE signal value is

$$\langle V_A(t)\rangle = V_0(t)\exp(-\Omega_{av}t). \tag{2}$$

EXPERIMENTAL

The P3HT and PCBM compounds (Sigma-Aldrich) were taken in the amount of 1 mg each and dissolved in 60 μl of chlorobenzene. The solution was transferred into an EPR tube with an outer diameter of 2.8 mm; chlorobenzene was evaporated. The sample obtained on the inner tube walls was annealed at a temperature of 140°C at a pressure of 0.1 Torr for 10 min, after which the tube was sealed. The measurements were performed on an ELEXSYS E-580 EPR spectrometer equipped with Bruker ER 4118 X-MS-3 or Bruker ER 4118 X-MD-5 cavities inside the cryostat with an OXFORD ITC-503 temperature controller. The temperature was kept at 80 K.

The sample was irradiated by second harmonic pulses of the Surelite-10 Nd:YAG laser with a wavelength of 532 nm, the pulse duration of 10 ns, and a pulse repetition rate of 10 Hz. The energy of the laser flash absorbed by the composite was estimated as 5 mJ.

After the laser flash, the delay T_{DAF} , and a two microwave pulse sequence $\pi/2$–τ–π–ESE the ESE signal was measured (Fig. 2). The $\pi/2$ and π pulses with a duration of 8 ns and 16 ns respectively or 80 ns and 160 ns respectively were used, which were applied with the delay $\tau = 160$ ns. The amplitude of microwave pulses with a duration of 8 ns and 16 ns was set about 10 G, and that of the microwave pulses with a duration of 80 ns and 160 ns was about 1 G. Since in our experiments the ESE signal had a complicated shape with the total duration of about 500 ns, the delay $\tau = 160$ ns was insufficient to detect the whole ESE signal. Taking into account that in our work the ESE signal had a symmetric shape, the ESE signal intensity was measured by numerical integration of the second half of the ESE time dependence over the 240 ns time domain. The dependence of the ESE signal intensity on the external magnetic field B_0 is called the echo-detected (ED) EPR spectrum.

In order to determine the longitudinal relaxation time under continuous irradiation of the sample by the visible light of the incandescent lamp (the light power absorbed by the sample was about 50 mW), the inversion-recovery method was applied. The sequence of three microwave pulses 16 ns–T–8 ns–τ–16 ns–ESE was used with an increase in the delay T. The initial T value was 400 ns, and the τ value was set as 140 ns.

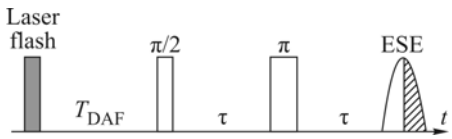

Fig. 2. ESE signal appeared after the laser flash and microwave pulse sequence. The dashed part of the ESE signal was integrated to obtain ESE intensities.

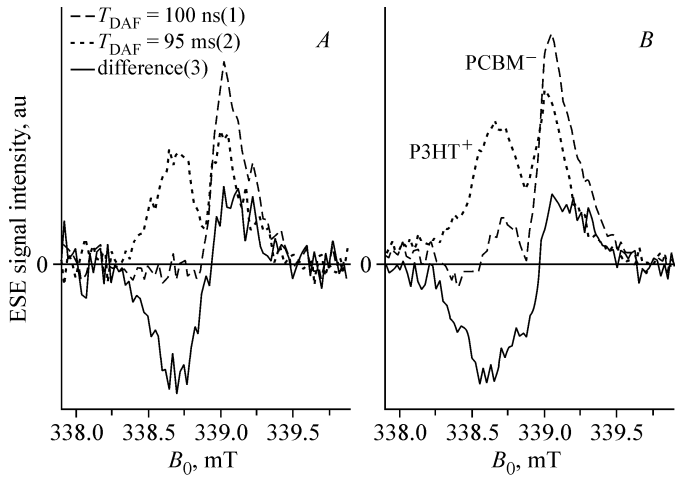

Fig. 3. ED EPR spectra of the PCBM/P3HT composite obtained using the two-pulse sequence π/2 – 160 ns – π – ESE with the π/2 microwave pulse duration of 8 ns (*A*) and 80 ns (*B*). Delays after the photoexcitation pulse are 100 ns (dashed lines) and 95 ns (dotted lines). EDEPR spectra of SCRPs after a delay of 100 ns after photoemission (solid lines).

EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 3 shows the ED EPR spectra of the PCBM/P3HT composite obtained at a temperature of 80 K using the two-pulse mode π/2–160 ns–π–ESE with the π/2 microwave pulse duration of 8 ns (*A*) and 80 ns (*B*). The presented ED EPR spectra were measured at delays after the laser pulse T_{DAF} = 100 ns (dashed lines) and T_{DAF} = 95 ms (dotted lines). The ED EPR spectrum recorded with the delay T_{DAF} = 95 ms has two lines of free $PCBM^-$ and $P3HT^+$ charge carriers with the characteristic values of the *g*-factor [17]. A similar ED EPR spectrum obtained at T_{DAF} = 100 ns has a slightly different line shape because it contains the ESE signal from both free charge carriers and $PCBM^-/P3HT^+$ SCRPs having the lifetimes of about 10 μs [12, 16]. Hence, the difference in the ED EPR spectra measured at delays T_{DAF} of 95 ms and 100 ns is the spectrum of $PCBM^-/P3HT^+$ SCRPs. The spectra shown in Fig. 3*A* and *B* agree well with the data obtained previously [12, 16].

The ED EPR spectra of $PCBM^-/P3HT^+$ SCRPs consist of two structureless lines having emission polarization for the low-field part and absorption polarization for the high-field one. The analysis of their shape is very difficult because the ED EPR spectra of SCRPs are insufficiently resolved. The use of a more selective sequence of microwave pulses exciting only a part of the spectrum with a width of about 1 G did not result in a substantial increase in the spectral resolution of the ED EPR spectrum of $PCBM^-/P3HT^+$ SCRPs. A similar problem was revealed in [12], in which only an estimate of the magnetic interaction between the radicals in the pair is given, Ω ~ 1 MHz.

In the emission position (B_0 = 3387 G) of the ED EPR spectrum of SCRPs the dependence of the ESE signal on the delay T_{DAF} was measured (Fig. 4*A*, thin line). Here a contribution to the rate of signal disappearance is made by the process of

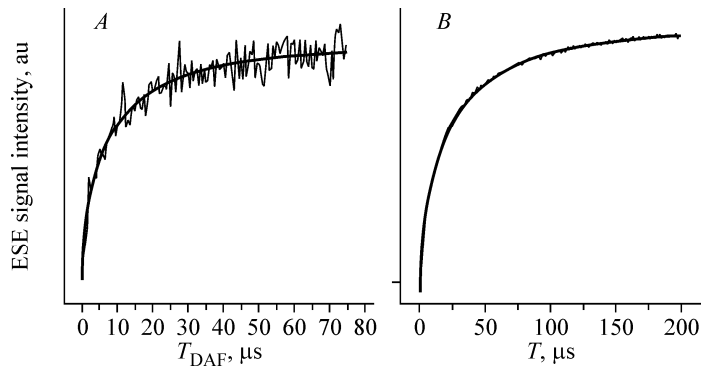

Fig. 4. ESE dependences on the delay T_{DAF} (*A,* thin line) and the ESE inversion-recovery (*B,* thin line), $B_0 = 338.7$ G. Thick lines are the approximation of the experimental curves by expression (3) with the parameters $T_1 = 9 \pm 1$ μs (*A*) and $T_1 = 24 \pm 1$ μs (*B*), $\beta = 0.6$.

SCRP decay and longitudinal spin relaxation [25]. The curve is not described by the exponential dependence; it was approximated by the Kohlrausch–Williams–Watts dependence

$$f(t) = \exp\left(-\left(\frac{t}{T_1}\right)^{\beta}\right) \tag{3}$$

with the parameters T_1 and β. From the approximation of the experimental dependence (Fig. 4*A*, thick line) the parameters $T_1 = 9 \pm 1$ μs, $\beta = 0.6$ were obtained.

In the same position of the ED EPR spectrum at $B_0 = 3387$ G under continuous light irradiation the dependence of the ESE inversion-recovery of free $P3HT^+$ charge carriers was obtained (Fig. 4*B*, thin line). For the approximation of the dependence, function (3) with the parameter $\beta = 0.6$, which was already applied for the approximation of the previous dependence, also suits well (Fig. 4*A*, thick line). The obtained value $T_1 = 24 \pm 1$ μs characterizes the longitudinal relaxation times of unbound charge carriers ($P3HT^+$ radicals) because this T_1 value is too small in comparison with their lifetime having a value of about 10 min at a temperature of 80 K [14].

In order to obtain the transverse relaxation times the dependences of the ESE signal on the delay τ between the microwave pulses were measured at $B_0 = 3387$ G. Different durations of microwave pulses exciting either the whole ED EPR spectrum (Fig. 5*A*) or its part with a width of about 1 G (Fig. 5*B*) were used. As already discussed above, the difference between the dependences obtained at the delay T_{DAF} of 100 ns and 95 ms is caused only by SCRPs (Fig. 5, thin solid lines). The dependences for SCRPs were approximated by exponential dependences (Fig. 5, thick lines), and the transverse relaxation times were determined. For microwave pulse sequences with different durations of the microwave pulses different transverse relaxation times were observed: for the sequence 8 ns–τ–16 ns–ESE the time $T_2^{eff} = 0.5 \pm 0.1$ μs, and for the sequence 80 ns–τ–160 ns–ESE the similar time was $T_2^0 = 1.0 \pm 0.2$ μs. This means that at the microwave pulse excitation of the whole ED EPR spectrum of SCRPs results in a shorter transverse relaxation time than for the excitation of only one component of the ED EPR spectrum.

This phenomenon can be described by means of the instantaneous diffusion model. Assuming that instantaneous diffusion in SCRPs occurs in the same way as in the systems in the thermodynamic equilibrium, the contribution to the transverse spin relaxation rate due to instantaneous diffusion can be described by expression (2). If we assume that when the selective pulse sequence (80 ns–τ–160 ns–ESE) is used the instantaneous diffusion effect is absent, then the transverse

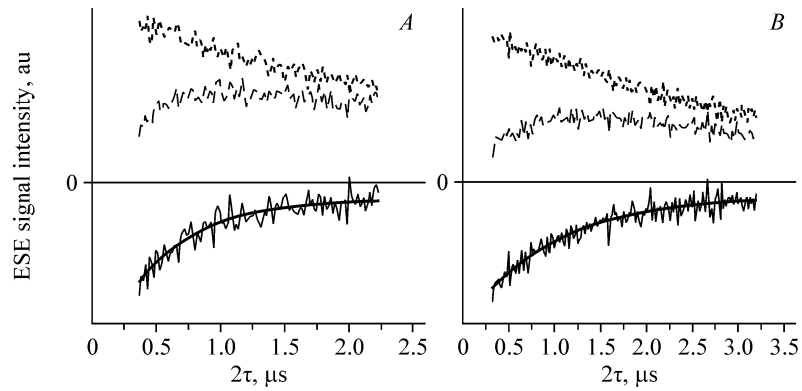

Fig. 5. ESE decays with the τ delay increase at the two-pulse sequence π/2–τ–π–ESE with the π/2 microwave pulse duration of 8 ns (*A*) and 80 ns (*B*), T_{DAF} = 100 ns (dashed lines) and T_{DAF} = 95 ms (dotted lines), B_0 = 338,7 mT. Dependences of the ESE signal of SCRPs (thin solid lines) are fitted by the exponential dependences (thick lines) with times T_2^{eff} = 0.5 ± 0.1 μs (*A*) and T_2^0 = 1.0 ± 0.2 μs (*B*).

relaxation time T_2^0 is governed by other mechanisms, and the ESE signal decreases by the law

$$V_0(\tau) \sim \exp\left(-\frac{2\tau}{T_2^0}\right).$$

In the excitation of the whole spectrum, and hence, of both spins, in SCRPs the transverse relaxation rate increases, according to the model described above. In this case, the time dependence of the ESE signal can be described by the formula

$$V_{eff}(\tau) \sim \exp\left(-\frac{2\tau}{T_2^0}\right)\exp\left(-\Omega_{av}\tau\right).$$

From here it follows that due to the instantaneous diffusion process the transverse relaxation rate increases by the value Ω_{av}

$$\Omega_{av} = 2\left(\frac{1}{T_2^{eff}} - \frac{1}{T_2^0}\right).$$

Therefore the magnetic interaction in $P3HT^+/PCBM^-$ SCRPs can be estimated as $\Omega_{av} \sim 10^6\ s^{-1}$. In this case, it is impossible to distinguish the exchange and dipole interactions in Ω_{av} by the ESE technique. If we assume that the dipole interaction prevails, $D >> J$, then it is possible to estimate the characteristic distance r between the SCRP radicals as $r \sim 4$ nm.

CONCLUSIONS

It is found that the kinetics of the ESE signal recorded at a temperature of 80 K for the determination of the longitudinal relaxation times of both $P3HT^+/PCBM^-$ SCRPs and free $P3HT^+$ radical can be approximated by the equation $\exp(-(t/T_1)^{0.6})$ with the parameters T_1 = 13 μs for $P3HT^+$ in $P3HT^+/PCBM^-$ SCRPs and T_1 = 22 μs for free $P3HT^+$ radicals. Within the instantaneous diffusion model the difference in transverse spin relaxation times of the $P3HT^+/PCBM^-$ complex at complete and incomplete excitation of the ED EPR spectrum by microwave pulses is explained and the magnetic interaction energy between the spins in $P3HT^+/PCBM^-$ SCRPs is estimated: $E/\hbar \sim 10^6\ s^{-1}$. In the assumption that the main contribution to the magnetic interaction of SCRPs is made by the dipole interaction, the characteristic distance r between the SCRP radicals is estimated: $r \sim 4$ nm.

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