

Dynamics of photoinduced radical pairs in poly(3-dodecylthiophene)/fullerene composite

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Abstract

Radical pair laser (660 nm) photoinduced in poly(3-dodecylthiophene)/[1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₀] (P3DDT/PCBM) composite were investigated by the X-band light-induced EPR method in a wide temperature region. Two lines with different magnetic parameters were attributed to non-interacting polaron and fullerene ion-radical. The susceptibility of these centres follow activation law and decrease drastically at $T > 180$ K due to their geminate recombination. The spin–lattice and spin–spin relaxation times of these paramagnetic centres were determined separately by the steady-state saturation method. It was shown that two independent spin dynamics processes are mainly realized in illuminated P3DDT/PCBM composite, namely polaron diffusion along the polymer chains with activation energy of 0.071 eV and rotation of fullerene ion-radicals with activation energy of 0.024 eV.

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1. Introduction

Electron and hole transporting materials are of growing interest and importance for photonic and electronic applications. One of the most widely studied photovoltaic devices are thin plastic solar cells [1,2]. If the composite of poly(3-alkylthiophenes) (P3AT) or other conjugated polymers with fullerene or its derivative, [1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₀] (PCBM) is irradiated by light the latter acts as strong electron acceptor attracting an electron from polymer chain. This is accompanied by the simultaneous formation of the donor–acceptor radical pairs of polarons and fullerene ion-radicals C₆₀⁻, both with spin $S = \frac{1}{2}$. The power conversion efficiency of solar cells should depend on dynamics properties of these pairs [3], however, spin motion in such composites has not been studied so far.

Photoinduced radical pairs are paramagnetic, therefore, the light-induced EPR (LEPR) method is widely used for investigation of such composites [4–6].

Here we report the LEPR study of magnetic, relaxation and dynamics parameters of polarons and fullerene ion radical laser photoinduced in the P3DDT/PCBM composite in a wide temperature region. We demonstrate non-interacting feature and therefore different interaction of these independent paramagnetic centres with own microenvironment. This allows to determine separately the relaxation and dynamics parameters in of these paramagnetic centres and to analyse the mechanism of spin dynamics in the P3DDT/PCBM composite. Different activation energies obtained are evidences for independence of the motion of the polaron and fullerene ion-radical charge carriers.

2. Experimental

Regioregular P3DDT (a commercial product of Aldrich[®]) and PCBM synthesized in the laboratory of

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J.C. Hummelen, University of Groningen, [7] were used in the work without any purification. The chlorobenzene solution of P3DDT and PCBM (1:1 wt. ratio) with concentration ca. 1 wt% was placed into ceramic plane and dried, then the composite P3DDT/PCBM was formed as film with the size of ca. $4 \times 8 \text{ mm}^2$ and thickness of ca. 0.1 mm.

EPR experiments were performed using a 3-cm (X-band, 9.7 GHz) PS-100X spectrometer with 100 kHz field AC modulation for phase-lock detection. The LEPR spectra were measured at background illumination of the P3DDT/PCBM composite by the Roithner Lasertechnik RLDH660-40-3 ($\lambda = 660 \text{ nm}$, $P = 40 \text{ mW}$) solid laser module directly in the microwave cavity at 77–340 K in nitrogen atmosphere. The total paramagnetic susceptibility of PC in the samples was determined using double integration of their EPR spectra. Spin–lattice and spin–spin relaxation times of the initial and treated P3DDT samples were measured separately using the steady-state (CW) saturation method [8].

3. Magnetic resonance parameters

As the compound P3DDT/PCBM is irradiated by laser at $T = 77\text{--}200 \text{ K}$, two overlapping LEPR lines with temperature-dependent intensities are observed (Fig. 1). This spectrum was attributed to radical pair of diffusing polarons $\text{P}^{+\bullet}$ with effective $g_{\text{iso}} = 2.0022$ and rotating ion-radicals $\text{C}_{61}^{-\bullet}$ with effective $g_{\text{iso}} = 1.9996$. Earlier it was shown [9,10], that these radicals demonstrate anisotropic magnetic parameters at 3-mm (W-band, 95 GHz) and 2-mm (D-band, 140 GHz) waveband EPR, so we have to fit

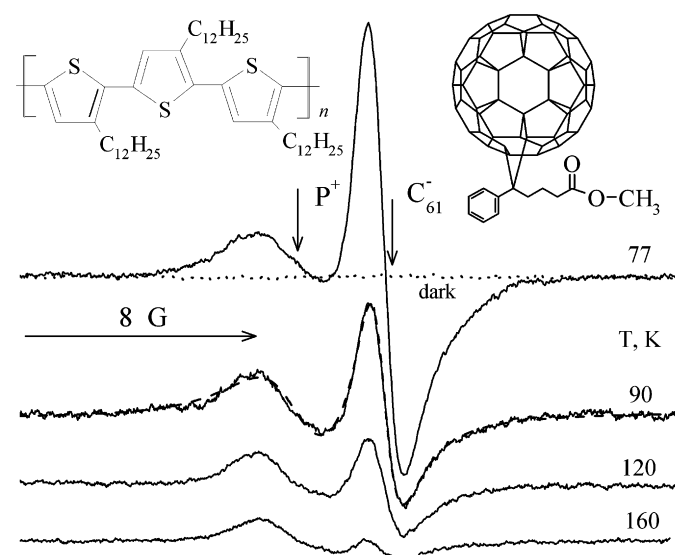


Fig. 1. LEPR spectra of the P3DDT/PCBM composite registered under background laser irradiation ($\lambda = 660 \text{ nm}$, $P = 40 \text{ mW}$) and different temperatures. By the dotted line the spectrum of the composite without irradiation is shown. The dashed line shows the spectrum calculated by using the data of Table 1.

Table 1

The values of g -factors and linewidths ΔB_{pp}^i (in Gauss) used for simulation of the LEPR spectra obtained at 90 K

Parameter	Polaron $\text{P}^{+\bullet}$	PCBM $\text{C}_{61}^{-\bullet}$
g_{xx}	2.00320	2.00061
g_{yy}	2.00225	2.00030
g_{zz}	2.00145	1.99941
g_{iso}	2.00230	2.00011
ΔB_{pp}^X	1.04	0.75
ΔB_{pp}^Y	1.04	0.81
ΔB_{pp}^Z	1.02	2.55
$\Delta B_{\text{pp}}^{\text{iso}}$	1.03	1.37

both the contributions to the LEPR P3DDT/PCBM spectrum using their anisotropic g -factors and linewidths (Table 1). Fig. 1 exhibits also LEPR spectrum calculated with the fitting magnetic parameters presented in Table 1 as well.

Fig. 3 depicts the Arrhenius dependence of spin susceptibility of both paramagnetic centres derived from their double-integrated spectra in non-saturated conditions. The photoexcitation of radical pairs normally occurs in the femtosecond time domain [11,12], therefore this parameter is mainly defined by the probability of their recombination. Assuming that polarons move by tunneling between initial site i to final site j with the energy difference ΔE_{ij} , the recombination rate is [13]

$$v = v_0 \exp\left(-\frac{2R_{ij}}{a_0}\right) \exp\left(-\frac{\Delta E_{ij}}{k_B T}\right), \quad (1)$$

where v_0 is an attempt to recombine frequency, R_{ij} is the distance between charge carriers, a_0 the Bohr radius of charge carrier and k_B the Boltzmann's constant.

It is seen from Fig. 2 that the temperature dependence of spin susceptibility of both contributions of photoinduced radical pairs follows the Arrhenius law at $T \leq 160 \text{ K}$. The activation energies ΔE_{ij} were determined for polaron and fullerene ion-radical diffusion from the slopes of appropriate curves to be 0.006 and 0.021 eV, respectively. If one include Coulomb interactions in this model, these would affect the activation energy for either detrapping or thermally assisted tunneling by an amount $U_C = e^2/4\pi\epsilon\epsilon_0 r$, where e is the elemental charge, ϵ the dielectric constant, and r the charge pair separation. U_C varies from around 0.4 eV for charges separated by one lattice unit, to less than 0.02 eV for charge pairs at the mean separation. Therefore, photoinduced polaron and ion radical should be considered as non-interacting that leads to their long life.

4. Spin relaxation

The spectral linewidth should reflect different processes occurring in the system studied. One of them is the line broadening due to dipole–dipole interaction between mobile

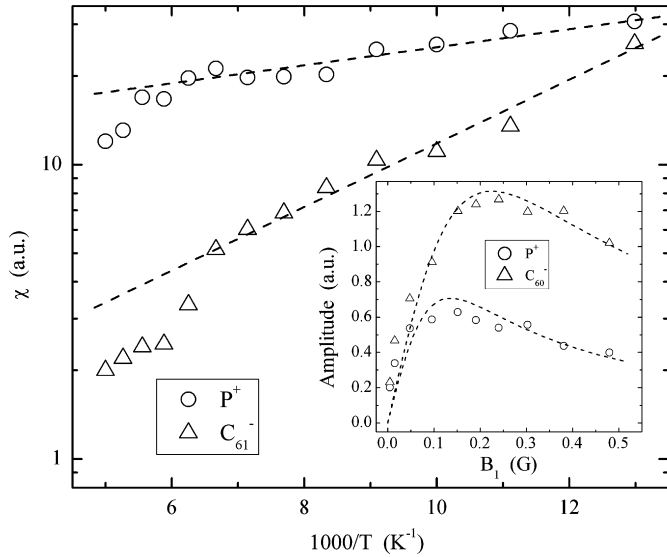


Fig. 2. Arrhenius dependence of susceptibility of both type paramagnetic centres photoinduced in the P3DDT/PCBM system. Above and below dashed lines show the dependences calculated with activation energy 0.006 and 0.021 eV, respectively. Insert—the line intensity of these radicals as function of magnetic term of microwave field B_1 . The lines show the dependences calculated with relaxation times determined at 100 K.

and trapped polarons and rotating fullerenes by $\Delta B_{dd} = \mu_B / R_0^3 = 4/3\pi\mu_B n_{pc}$ [14], where μ_B is the Bohr magneton and R_0 , the distance between dipoles, is proportional to the paramagnetic centre concentration n_{pc} on the polymer chain. Analysis shows that the peak-to-peak linewidth ΔB_{pp} of the P^{\bullet} and C_{61}^{\bullet} radicals changes with the temperature linearity as $\Delta B_{pp}^{iso}(T) = 0.81 + 2.5 \times 10^{-3}T$ Gauss and $\Delta B_{pp}^{iso}(T) = 0.64 + 2.9 \times 10^{-3}T$ Gauss, respectively. Therefore, one obtains $R_0 \approx 2.3$ – 2.5 nm for the dipolar distance in the P3DDT/PCBM system at the lower temperature limit, when $T \rightarrow 0$.

At the increase of magnetic term B_1 of the MW field in the sample the spectra of both the paramagnetic centres are broadened, whereas their linewidth first linearly increases and then starts to decrease as shown in the insert of Fig. 2. Since the signals of these paramagnetic centres were found to be independent of one another, both the spin–lattice T_1 and spin–spin T_2 relaxation times were determined separately by the steady-state saturation method [8] (insert in Fig. 3).

5. Spin dynamics

There are different dynamics of photoinduced spins in the P3DDT/PCBM system, namely the polaron diffusion along and between the polymer chains with respective diffusion coefficients D_{1D} and D_{3D} , and the rotational diffusion of fullerene ion radical around main molecular axis with coefficient D_r . These processes should induce an additional magnetic field in the whereabouts of another

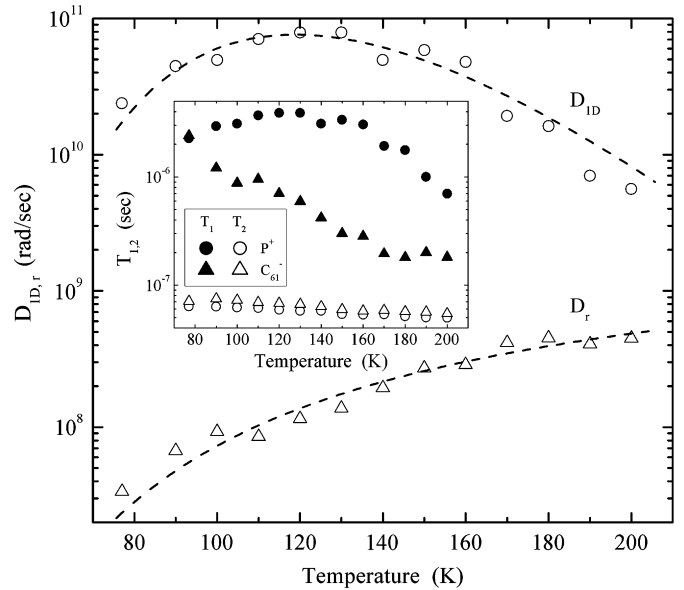


Fig. 3. Temperature dependency of the rate of the polaron P^{\bullet} diffusion along polymer chains D_{1D} and of the C_{61}^{\bullet} rotation D_r in the P3DDT/PCBM sample. The top-to-down lines show dependences calculated from Eq. (3) with $D_{1D}^0 = 623 \text{ rad s}^{-1} \text{ K}^{-2}$, $\alpha = 2.5$, and $E_b = 0.071 \text{ eV}$ and with $D_r^0 = 4.7 \times 10^{-6} \text{ rad s}^{-1} \text{ K}^{-2}$, $\alpha = 0.11$, and $E_b = 0.024 \text{ eV}$. Insert—the temperature dependency of the spin–lattice and spin–spin relaxation times of the polarons P^{\bullet} and ion-radicals C_{61}^{\bullet} photoinduced in the P3DDT/PCBM system.

spin, leading to the acceleration of electron relaxation of both spin ensembles. As the relaxation times of the spin reservoir is defined mainly by a dipole–dipole interaction between the spins, the following equations can be written [15]:

$$T_1^{-1}(\omega_e) = \langle \omega^2 \rangle [2J(\omega_e) + 8J(2\omega_e)], \quad (2a)$$

$$T_2^{-1}(\omega_e) = \langle \omega^2 \rangle [3J(0) + 5J(\omega_e) + 2J(2\omega_e)], \quad (2b)$$

where $\langle \omega^2 \rangle = 1/10\gamma_e^4 \hbar^2 S(S+1)n\Sigma_{ij}$ is a constant of the dipole–dipole interaction for powder, n is the number of polarons per each monomer, Σ_{ij} the lattice sum for powder-like sample, $J(\omega_e) = (2D'_{1D}\omega_e)^{-1/2}$ at $D'_{1D} \gg \omega_e \gg D_{3D}$ or $J(0) = (2D'_{1D}D_{3D})^{-1/2}$ at $D_{3D} \gg \omega_e$ is a spectral density function for Q1D motion and $J(\omega_e) = \tau_c / (1 + \tau_c^2 \omega_e^2)$ for rotational motion with correlation time τ_c , $D'_{1D} = 4D_{1D}/L^2$, ω_e is resonant angular frequency of the electron spin precession, and L is a factor of spin delocalization over a polaron equal approximately to five monomer units in P3AT [16]. A similar spectral density function was earlier used in the study of spin dynamics in other conjugated polymers [17,18].

The dynamics parameters calculated from Eq. (2) for both paramagnetic centres in photoinduced radical pairs are presented in Fig. 3 as function of temperature.

To account for the LEPR mobility data obtained, the Elliot hopping model [19] has been used. The model based on a hopping of carriers over barriers E_b predicts a frequency dependence of their mobility, $\mu_{1D} \propto D_{1D} \propto \omega_e^s$ where the exponent $0 < s < 1$ reflects the dimensionality of

the system and depends on the well depth for an isolated wall E_b as $s = 1 - \alpha k_B T / E_b$. The value of E_b was deduced for lightly doped poly(3-methylthiophene) to be 1.1 eV at $\alpha = 6$ [20]. At activation of the charge carriers through the barrier the rotational diffusion of fullerene should follow the temperature as

$$D_{1D,r}(\omega_e T) = D_{1D,r}^0 T^2 \omega_e^s \exp\left(\frac{E_b}{k_B T}\right). \quad (3)$$

The temperature dependences calculated from Eq. (3) with $E_b = 0.071$ and 0.024 eV and shown in Fig. 3 fit the experimental data obtained for radical pairs well. E_b obtained for fullerene lies near that obtained for the triphenylamine/ C_{60} complex [21], however, is considerably lesser than that reported for a pure C_{60} rotation [22]. The E_b values determined are close to the energy of lattice phonons in poly(3-octylthiophene) [9] and other conjugated polymers [18].

6. Conclusion

Under excitation of the P3DDT/PCBM composite, two paramagnetic centres are formed: the positive polaron on the polymer backbone, $P^{+\bullet}$ and the negatively charged fullerene ion-radical $C_{61}^{-\bullet}$. Both radicals are spatially separated due to their low recombination rate, so they can be considered as non-interacting. This leads to difference in their interaction with own microenvironment and, therefore, in relaxation and dynamics parameters, which seems to be an intrinsic feature of the radicals in this composite. For the $P^{+\bullet}$ this gives rise to a more noticeable saturation effect at higher microwave power. Photoinduced charge is transferred by polaron along polymer chain in frames of the activation mechanism and then hops to the fullerene molecule. The activation energy of the charge transfer by polaron differs from that determined for rotation of the fullerene molecule. This allows concluding about independence of these processes in the P3DDT/PCBM composite.

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