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Dynamics of charge carriers photoinduced in poly(3-dodecylthiophene)/fullerene bulk heterojunction

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Magnetic and dynamics properties of mobile polarons and fullerene anion-radicals photoinduced by laser beam in the poly(3-dodecylthiophene)/fullerene bulk heterojunction were studied. The number of these charge carriers was found to decrease with the growth in the photon energy. Monotonic temperature dependence for main electron relaxation parameters was obtained. The 1D polaron diffusion along the polymer chain and the fullerene rotation was shown to follow activation Elliot hopping model and to govern by the photon energy. The deviation in activation energies for polaron and anion-radical motion and the difference in their dependence on the laser irradiation photon energy prove a non-interacting character of these charge carriers photoinduced in the polymer/fullerene bulk heterojunction.

1. Introduction

Conjugated polymers and their composites with fullerenes are perspective materials for polymer photovoltaics [1]. One of the most widely studied photovoltaic devices are thin plastic solar cells. There are some important areas of research of such cells, e.g. their stability [2] and large area processing [3].

Generally, solar cells consist of electron donor and acceptor constituents. Soluble fullerene derivative, [6,6]-phenyl-C_{61}-butanoic acid methyl ester (PCBM), being embedded into poly(3-alkylthiophenes) (P3AT) or other conjugated polymer performs as strong electron acceptor whose lowest unoccupied molecular orbital lies below excitonic state. It was found that the irradiation of the “bulk heterojunction” formed by fullerene with a polymer matrix, initiates electron transfer from a polymer chain to a fullerene molecule. This process was revealed by time-resolved spectroscopy to occur in the femtosecond time domain [4,5], whereas the electron back transfer is much slower [6]. Photoinduced electron migration through a heterojunction results in the effective formation of a metastable charge-separated state. Light first excites the donor (D), the excitation is delocalized on the donor–acceptor (D–A) complex before initiation of charge transfer, leading to an ion radical pair and finally charge separation can be stabilized possibly by carrier delocalization on the D^+ (or A^-) species by structural relaxation [7].

The power conversion efficient factor of plastic solar cells reaches 5% for single heterojunctions [8] and 6.5% for tandem cells [9]. This value appears to be due to combined effects of ultrafast electron transfer from photoexcited polymer to fullerene [10], a large interfacial area for charge separation due to intimate blending of the materials [11], and efficient carrier transport across a thin film. Charge recombination is considered to be predominantly non-geminate process governing effectiveness of polymer/fullerene solar cells [5,12]. That is why photoinduction of charge carrier pairs and their recombination are the most interesting points. However, they are not yet sufficiently understood in detail and there is no generally applicable model available.

Charge is transferred in initial conjugated polymers by nonlinear excitations, polarons $P^{\bullet+}$ characterized by spin $S = 1/2$ and high mobility along a conjugated polymer backbone [13]. Their magnetic, relaxation and dynamic properties were studied by conventional [14] and high-frequency [15] electron paramagnetic resonance (EPR) methods. Photoinduced charge transfer is also accompanied by the formation of anion-radicals $C_{61}^{\bullet-}$ with spin $S = 1/2$. This accounts for the widely use of the light-induced EPR (LEPR) method for investigation of fullerene-modified P3AT [16–18] and other conjugated polymers [19]. LEPR measurements revealed the existence of two radicals with different line shapes, magnetic-resonance parameters and saturation properties. Photoinduced radical pairs can annihilate through bimolecular recombination [20] with the activation energy of 0.1 eV [16].

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Except the intermolecular charge transport, a charge transfer by polaron along (Q1D) and between (Q3D) polymer chains and a rotational motion of fullerene molecules are also realized in such polymer/fullerene compounds. These molecular and electronic processes should undoubtedly be correlated in P3AT/PCBM systems. However, such correlation has not been studied so far.

The understanding of the basic physics underlying the electron relaxation and dynamic behavior of fullerene-modified organic polymers is essential for the optimization of devices based on these materials. We report the LEPR study of magnetic, relaxation and dynamic parameters of polarons and fullerene anion-radicals photoinduced in the composite, PCBM embedded in poly(3-dodecylthiophene) (P3DDT) matrix, by laser beam with photon energy of $h\nu_{ph} = 1.88$, 2.22, and 2.75 eV (here $h = 2\pi$ is the Plank constant and ν_{ph} is a photon frequency) in wide temperature region. We demonstrate non-interacting feature of paramagnetic centers (PC) in radical pairs and, therefore, their different interaction with own microenvironment. This allowed to determine separately the relaxation and dynamic parameters of both type of PC and to analyze spin dynamic processes in the P3DDT/PCBM composite.

2. Experimental details

In the study was used regioregular Aldrich® P3DDT [21] with the lattice constants of $a = 2.583$ nm, $b = 0.775$ nm, $c = 0.777$ nm [22] and PCBM (see Fig. 1) synthesized in the laboratory of Prof. J.C. Hummelen, University of Groningen [23]. The chlorbenzene solution of P3DDT and PCBM taking in 1:1 (w/w) ratio with concentration ca. 1 wt% was placed into ceramic plane and dried, so then the P3DDT/PCBM composite was formed as film with the size of ca. 4×8 mm^2 and thickness of ca. 0.1 mm.

EPR experiments were performed using a X-band (3 cm, 9.7 GHz) PS-100X spectrometer with 100 kHz field *ac* modulation for phase-lock detection. The "dark" (EPR) and light-induced (LEPR) spectra of the initial polymer and polymer/fullerene system were registered in the temperature region of 90–340 K at dry nitrogen atmosphere using the BRT SKB IOH temperature controller and also at 77 K in quartz Dewar with liquid nitrogen. The light-induced EPR spectra were measured at permanent illumination of the P3DDT/PCBM composite directly in the microwave cavity of the EPR spectrometer by the Roithner Lasertechnik RLDH660-40-3 ($\lambda = 660$ nm, $h\nu_{ph} = 1.88$ eV, $P = 41$ mW), MGM2-30 ($\lambda = 530$ nm, $h\nu_{ph} = 2.22$ eV, $P = 38$ mW), and DPSSL-473-40 ($\lambda = 450$ nm, $h\nu_{ph} = 2.75$ eV, $P = 40$ mW) laser modules. The total paramagnetic susceptibility of the radicals photoinduced in the sample was determined using double integration of their LEPR spectra. Processing and simulations of the EPR spectra were done with the Bruker® WinEPR SimFonia programs.

3. Results and discussion

3.1. Magnetic resonance parameters

3.1.1. Line shape and g-factor

PC in the initial P3DDT film is characterized by weak "dark" X-band EPR line with effective $g = 2.0025$ in the temperature range of 77–340 K. No LEPR signal can be found in the polymer. Neither a "dark" EPR nor LEPR signals have been found in the initial PCBM in the same temperature range. A dramatic enhancement of the LEPR is observed when mixing both substances together. As the compound P3DDT/PCBM is irradiated by laser at $T \leqslant 200$ K, two overlapping LEPR lines with temperature-dependent intensities are observed (Fig. 1). Sum spectrum was attributed to radical pairs of positively charged diffusing polarons $P^{\bullet +}$ with isotropic (effective) $g_{iso} = 2.0023$ and rotating round main axis negatively charged anion-radicals $C_{61}^{\bullet -}$ with effective $g_{iso} = 2.0001$. The latter is typical of fullerene anion-radicals [24]. High-field/frequency EPR study of poly(3-octylthiophene) shown [25] that the interaction of an unpaired electron of $P^{\bullet +}$ with sulfur heteroatoms involving into the polymer backbone leads to anisotropy of its g-factor, $g_{xx} = 2.00409$, $g_{yy} = 2.00332$ and $g_{zz} = 2.00235$. On the other hand, De Ceuster et al. [26] shown that the spin density in

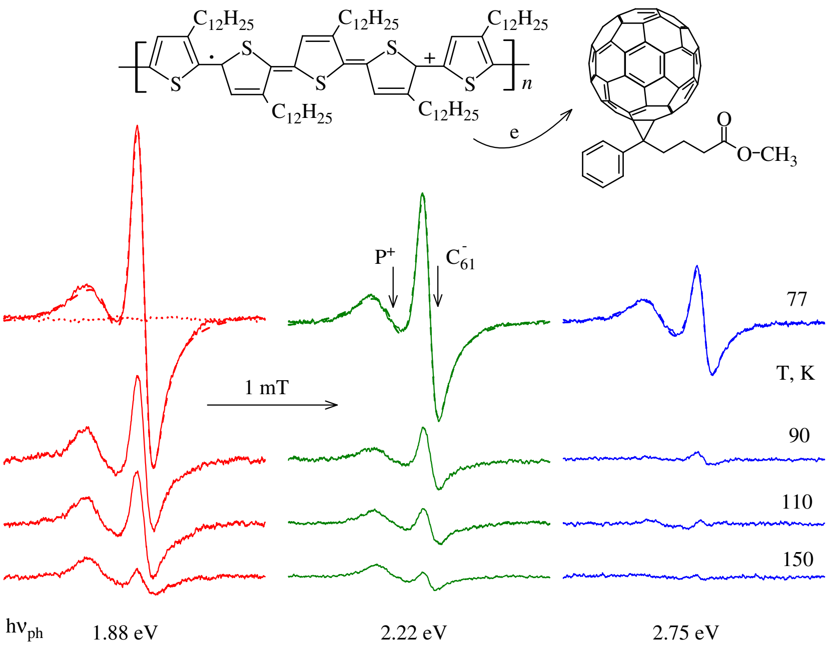

Fig. 1. X-band LESR spectra of the radical pairs photoinduced in the shown above P3DDT/PCBM system by current laser irradiation with different laser photon energy $h\nu_{ph}$ and registered at different temperatures. Dotted line shows the "dark" spectrum obtained before laser irradiation. Left-right dashed lines show sum LEPR spectra calculated using individual terms of **g**-tensor (see the text) and linewidth (see Table 1).

Table 1

The terms ΔB^{i}_{pp} of linewidth (in mT) LEPR spectra of polarons and fullerene anion-radicals used for simulation of the LEPR spectra obtained at different laser photon energy h_{ph} (in eV) and 77 K

	PC	$h\nu_{ph}$		
Linewidth		**1.88**	**2.22**	**2.75**
ΔB^{X}_{pp}	$P^{\bullet +}$	0.101	0.107	0.113
	C_{61}^{-}	0.078	0.073	0.081
ΔB^{Y}_{pp}	$P^{\bullet +}$	0.101	0.107	0.113
	C_{61}^{-}	0.084	0.079	0.087
ΔB^{Z}_{pp}	$P^{\bullet +}$	0.102	0.109	0.115
	C_{61}^{-}	0.258	0.253	0.261
ΔB^{iso}_{pp}	$P^{\bullet +}$	0.101	0.108	0.114
	C_{61}^{-}	0.140	0.135	0.143

C_{61}^{-} anion-radical embedded into polymer matrix is characterized by rhombic symmetry and, therefore, anisotropic g-factor, $g_{xx} = 2.00031$, $g_{yy} = 2.00011$ and $g_{zz} = 1.99821$. As in case of the initial C_{60} molecule [27], the deviation of the C_{61}^{-} g-factor from that of free electron, $g_e = 2.00232$, is due to the fact that the orbital angular moment is not completely quenched. Due to a dynamical Jahn–Teller effect accompanying the structural molecular deformation, the isotropic nature of the icosahedral C_{60} molecule is distorted after formation of the C_{61}^{-} anion-radical, resulting in an axial or even lower symmetry [28]. This is also realized in case of the C_{61}^{-} anion-radical [26], where the high symmetry of the molecule is already decreased by the bond to the phenyl side chain prior to electron trapping. Asymmetrical distribution of spin density in polaron and fullerene anion-radical leads also to tensor character of their linewidth [25,26]. This should be taken into account in order to calculate more precisely an effective LEPR spectrum of the P3DDT/PCBM system.

The main values and traces of the **g**-tensors of the $P^{\bullet +}$ and C_{61}^{-} PC were determined to be, respectively, $g_{xx} = 2.00320$, $g_{yy} = 2.00225$, $g_{zz} = 2.00145$, $\langle g \rangle = 2.00230$ and $g_{xx} = 2.00061$, $g_{yy} = 2.00030$, $g_{zz} = 1.99941$, $\langle g \rangle = 2.0001$. The respective linewidths and the concentration ratios of these PC used for the fitting of sum P3DDT/PCBM LEPR spectra are presented in Table 1. The sum spectra calculated with the fitting magnetic parameters presented in Table 1 are shown in Fig. 1 by dashed lines as well.

3.1.2. *Paramagnetic susceptibility*

Fig. 2 depicts the Arrhenius dependence of spin susceptibility of both PC in 77–200 K region derived from their double-integrated spectra in non-saturated conditions, i.e. when magnetic term B_1 of the polarizing microwave field tends to zero. The concentration of radical pairs decreases dramatically at higher temperatures, so the precision of determination of their spin susceptibility falls significantly.

Normally, the spins of radical pair photoinduced in close proximity should interact with each other, either by exchange or by dipolar mechanisms. These effects do not registered in LEPR spectra of the P3DDT/PCBM system most likely due to diffusion of polarons along the conjugated polymer backbone away from the fullerene anions in a timescale faster than the exchange times, i.e. $\tau_{ex} \leqslant 10^{-9}$ s. This can be a reason for unusual long lifetime of the charge separation in polymer/fullerene systems [29] and in the P3DDT/PCBM composite under study.

At the steady-state light irradiation, effective paramagnetic susceptibility of polarons and fullerene anion-radicals photoinduced in the femtosecond time domain should inversely depend on the probability of their recombination. Assuming that spatially close charge carriers with effective localization (Bohr) radius a_0 separated by a distance R_{ij} have a much higher recombination rate than distant carriers, their recombination rate can be written as [30]:

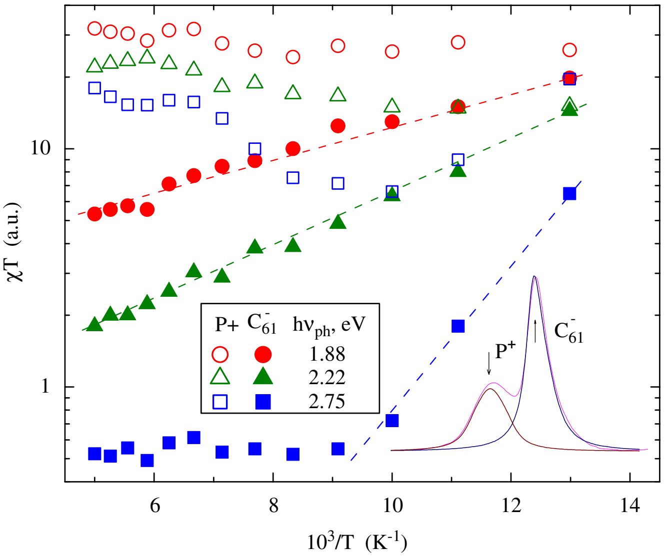

Fig. 2. Arrhenius dependence of paramagnetic susceptibility of the polarons $P^{\bullet +}$ and fullerene anion-radicals C_{61}^{-} photoinduced in the P3DDT/PCBM system by steady-state laser irradiation with different photon energy. Dashed lines show the dependences calculated using Eq. (2) with ΔE_{ij} presented in Table 2. Low-temperature integral contributions of these PC to sum spectrum are shown in the inset as well.

$$\nu(R_{ij}) = \nu_0^{|} \exp\left(-\frac{2R_{ij}}{a_0}\right), \qquad (1)$$

where $\nu_0^{|}$ is an attempt to recombine frequency. PC photoinduced in the P3DDT/PCBM system are likely to have different localization radii. The localization radius for the electron is probably on the order of the radius of the solitary PCBM molecule, whereas polaron occupies approximately five monomer units in regioregular P3AT [31]. Note that although the localization radius is formally expected to depend on the polaron affinity of the initial site, the variation in a_0 over the range of energies considered here is sufficiently small, so that this parameter may be considered as constant. Polaron diffuses by tunneling between initial site i to final site j with the energy spending ΔE_{ij}, so the Miller–Abrahams energy-dependent factor appears in the above equation:

$$\nu(R_{ij}, \Delta E_{ij}) = \nu_0^{|} \exp\left(-\frac{2R_{ij}}{a_0}\right) \exp\left(-\frac{\Delta E_{ij}}{k_B T}\right)$$
$$= \nu_0 \exp\left(-\frac{\Delta E_{ij}}{k_B T}\right). \qquad (2)$$

Fig. 2 shows that the polaron charge carriers are characterized by $\chi(T) \propto T^{-1}$ temperature dependence in the P3DDT/PCBM system, whereas spin susceptibility of fullerene anion-radicals excited by photons with $h\nu_{ph} = 1.88$ and 2.22 eV at $77\,\mathrm{K} \leqslant T \leqslant 160\,\mathrm{K}$ and with $h\nu_{ph} = 2.75$ eV at $77\,\mathrm{K} \leqslant T \leqslant 110\,\mathrm{K}$ follows the Arrhenius law. The values of ΔE_{ij} in Eq. (2) determined for fullerene anion-radical from the slopes of appropriate curves are presented in Table 2. It is seen that ΔE_{ij} increases by factor of forth with the $h\nu_{ph}$ growing from 1.88 to 2.75 eV. The annihilation of radical pairs in the P3DDT/PCBM compound, as in case of other polymer/fullerene systems [32] should be described as thermally activated bimolecular process. If one include Coulomb interactions in this model, these should affect the activation energy for either detrapping or

Table 2

The ΔE_{ij} in Eq. (2) determined for spin susceptibility for fullerene anion-radical and activation energy in Eq. (7) determined for rotational and translation diffusion of the fullerene anion-radicals and polarons, respectively E_a^{C61} and E_a^{P*}, photoinduced by laser beam with different photon energy h_{ph} (all in eV) in P3DDT/PCBM bulk heterojunction

$h\nu_{ph}$	ΔE_{ij}^{C61}	E_a^{C61}	E_a^{P*}
1.88	0.014	0.017	0.048
2.22	0.023	0.010	0.038
2.75	0.058	0.012	0.094

thermally assisted tunneling by an amount $U_c = e^2/4\pi\varepsilon\varepsilon_0 r$, where e is the elemental charge, ε is the dielectric constant, and r is 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, both the photoinduced polaron and anion-radical should be considered as non-interacting that indeed leads to their long life.

The ratio of spin concentrations was obtained to be near to unit at the irradiation of the P3DDT/PCBM by light with $h\nu_{ph} = 1.88$ and 2.22 eV that is in agreement with fundamental principle of photoinduced charge separation in radical pair. This value, however, increases at $h\nu_{ph} = 2.75$ eV due, probably, to appearing of additional channel for the electron moving away the fullerene molecule. Electron hops more easily between fullerenes than from polaron and fullerene, so that an effective charge recombination is still limited by the transport of polarons towards fullerene domains. Besides, a direct recombination of polarons in molecular solids depends on their mobility μ or diffusion rate D [33]. Colaneri et al. [34] shown the formation of diamagnetic bipolarons in poly(3-hexylthiophene) that results in the decrease of the spin/charge ratio N_s/N_{ch} down to 10^{-3}. This means that the area under the EPR curve should reflect not only the number of spins, but also the lifetime of the photoinduced radical pairs. However, undoubted reason for this effect is not jet evident.

3.1.3. Linewidth

Fig. 3 presents the temperature dependences of effective (isotropic) peak-to-peak linewidth $\Delta B_{pp}^{(0)}$ obtained for the $P^{\bullet+}$ and C_{61}^{-} radicals at the microwave saturation absence. It is seen from the figure that the linewidth of polarons changes monotonically with the temperature, whereas fullerene radicals demonstrate more complex $\Delta B_{pp}^{(0)}(T, \nu_{ph})$ dependence. Extrapolation to room temperature gives 0.14–0.20 mT for $P^{\bullet+}$ that lies inside the region $\Delta B_{pp}^{(0)} = 0.13 - 0.18$ mT obtained for polarons in different P3AT [14,25,35]. This value, however, is less considerably then that determined for undoped polythiophene [14,36] evidencing of weaker spin interaction in the system under study.

The spectral linewidth should reflect different processes occurring in the P3DDT/PCBM composite. One of them is the association of mobile PC with the counter charges. Another reason is the dipole–dipole interaction between mobile and trapped polarons and fullerenes that broadens the line by $\Delta B_{dd} = \mu_B/R_0^3 = 4/3\pi\mu_B n_P$, where μ_B is the Bohr magneton, R_0 is the distance between dipoles proportional to the polaron concentration n_P on the polymer chain. Extrapolating temperature dependences to the lower temperature limit, i.e. when the temperature tends to zero, one obtains $\Delta B_{pp}^{(0)} \approx (7-8)\times 10^{-2}$ mT for polarons and $\Delta B_{pp}^{(0)} \approx (5-6)\times 10^{-2}$ mT for fullerene anion-radicals and, therefore, $R_0 \approx 2.3$–2.5 nm for the dipolar distance in the P3DDT/PCBM system.

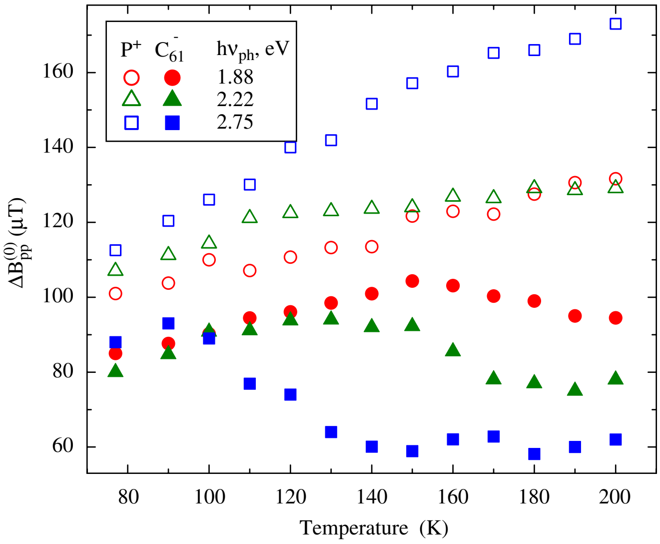

Fig. 3. Lower limit of the peak-to-peak linewidth $\Delta B_{pp}^{(0)}$ of the polarons $P^{\bullet+}$ and fullerene anion-radicals C_{61}^{-} photoinduced in the P3DDT/PCBM system by laser with different photon energy as functions of temperature.

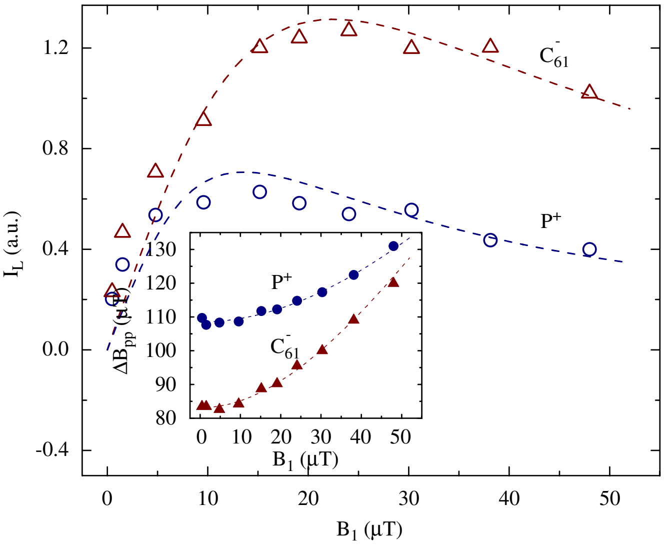

Fig. 4. The intensity I_L and peak-to-peak linewidth (inset) LEPR spectrum of polarons $P^{\bullet+}$ and anion-radicals C_{61}^{-} photoinduced by laser with $h\nu_{ph} = 1.88$ eV in the P3DDT/PCBM sample at 100 K as function of polarizing microwave field B_1. The lines show the dependences calculated from Eqs. (3), (4) and (5) with $T_1^{(P^{\bullet+})} = 2.9\times10^{-6}$, $T_2^{(P^{\bullet+})} = 6.1\times10^{-8}$, $T_1^{(C_{61}^{-})} = 1.1\times10^{-6}$, and $T_2^{(C_{61}^{-})} = 7.2\times10^{-8}$.

3.2. Spin relaxation

At the increase of the B_1 value, the intensity I_L of both the PC Lorentzian spectra first linear increases and, starting from some B_1 value, plateaus and then decrease as it is shown in Fig. 4. This is due to manifestation of a microwave steady-state saturation effect in the LEPR spectrum whom intensity should change as [37]:

$$I_L = I_L^{(0)} B_1 \left(1 + \gamma_e^2 B_1^2 T_1 T_2\right)^{-3/2}, \tag{3}$$

where $I_L^{(0)}$ is intensity of non-saturated spectrum, γ_e is the gyromagnetic ratio for electron, T_1 and T_2 are the spin–lattice and spin–spin relaxation times, respectively. The inflection point characteristic for polarons' curve is distinct from that obtained for fullerene anion-radicals. This is evidence of different relaxation parameters of these non-interacting PC. The second effect of the increase in B_1 value is the LEPR spectrum broadening shown in Fig. 4. Since the PC and their signals were found to be independent of one another, both the relaxation times of these PC can be determined separately by the steady-state saturation method from relations [37]:

$$T_1 = \frac{\left[\left(\Delta B_{\mathrm{pp}}/\Delta B_{\mathrm{pp}}^{(0)}\right)^2 - 1\right]}{\gamma_{\mathrm{e}}^2 B_1^2 T_2}, \tag{4}$$

$$T_2 = \frac{2}{\sqrt{3}\gamma_{\mathrm{e}}\,\Delta B_{\mathrm{pp}}^{(0)}}. \tag{5}$$

The relaxation parameters of PC determined using such a method are presented in Fig. 5 as function of temperature.

The analysis of the figure shows that the interaction of anion-radicals C_{61}^{-} with the lattice is characterized by monotonic temperature dependence, whereas spin–lattice relaxation time of polarons $P^{\bullet+}$ demonstrates extremal temperature dependence with maximum at critical temperature $T_c \approx 130$–160 K. The latter value depends on the photon energy as it is shown in Fig. 5. Spin–spin relaxation of PC was expected from the analysis of Fig. 3 and Eq. (5) to be accelerated monotonically at the temperature increase. This nearly holds for both the polaron and fullerene radicals except T_2 of the C_{61}^{-} photoinduced by laser with $h\nu_{\mathrm{ph}} = 2.75$ eV (Fig. 5). The latter fact is not yet explained.

3.3. Spin dynamics

There are different PC-aided dynamic processes occurring in the P3DDT/PCBM system, e.g. the polaron diffusion along the polymer chains with coefficient $D_{1\mathrm{D}}$, rotational diffusion of fullerene anion-radical around main molecular axis with coefficient D_{r} and charge transfer between polaron and fullerene with the rate D_{e}. These processes should induce an additional magnetic field in the whereabouts of electron and nuclear spins and, therefore, lead especially to the acceleration of electron relaxation of both spin ensembles. As the relaxation of the whole spin reservoir is defined mainly by a dipole–dipole interaction between electron spins, the following equation can be written for spin–lattice relaxation rate [38]:

$$T_1^{-1}(\omega_{\mathrm{e}}) = \langle\omega^2\rangle[2J(\omega_{\mathrm{e}}) + 8J(2\omega_{\mathrm{e}})], \tag{6}$$

where $\langle\omega^2\rangle = 1/10\gamma_{\mathrm{e}}^4\hbar^2 S(S+1)n\Sigma_{ij}$ is the constant of a dipole–dipole interaction for powder, n is a number of polarons per each monomer, Σ_{ij} is the lattice sum for powder-like sample, $J(\omega_{\mathrm{e}}) = (2D_{1\mathrm{D}}^{|}\omega_{\mathrm{e}})^{-1/2}$ (at $D_{1\mathrm{D}}^{|} \gg \omega_{\mathrm{e}} \gg D_{3\mathrm{D}}$) or $J(\omega_{\mathrm{e}}) = \tau_{\mathrm{c}}/(1+\tau_{\mathrm{c}}^2\omega_{\mathrm{e}}^2)$ is a spectral density function respectively for Q1D longitudinal or rotational diffusion with correlation time τ_{c}, $D_{1\mathrm{D}}^{|} = 4D_{1\mathrm{D}}/L^2$, 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 [31]. The similar spectral density function was earlier used in the study of spin dynamics in other conjugated polymers [14,15,25,35].

The dynamic parameters calculated from Eq. (6) for both PC in photoinduced radical pairs using the appropriate spectral density functions are presented in Fig. 6 as function of temperature. Normally, fullerene anion-radicals are characterized by activation

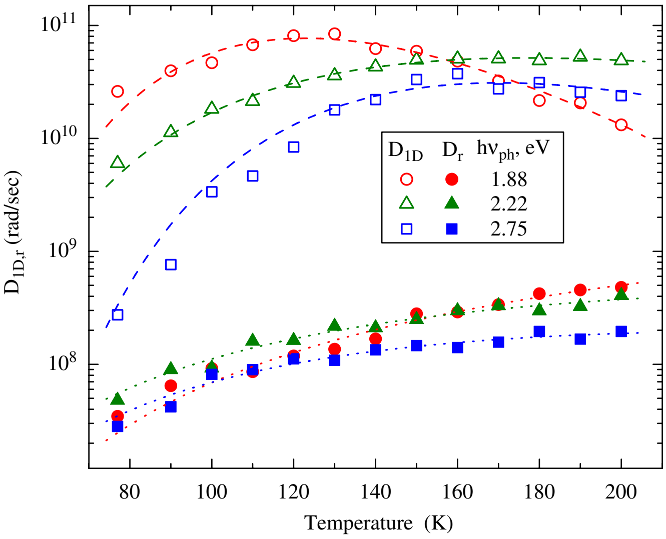

Fig. 6. Temperature dependency of the rates of the polaron diffusion along polymer chains $D_{1\mathrm{D}}$ and of the C_{61}^{-} rotation D_{r} in the P3DDT/PCBM bulk heterojunction irradiated by laser with different photon energy. Top to down lines show the dependences calculated from Eq. (7) with $\alpha = 1.2$ and $E_{\mathrm{a}} = 0.048$ eV, $\alpha = 0.45$ and $E_{\mathrm{a}} = 0.038$ eV, $\alpha = 2.2$ and $E_{\mathrm{a}} = 0.094$ eV (dashed lines) and with $\alpha = 0.04$ and $E_{\mathrm{a}} = 0.010$ eV, $\alpha = 0.03$ and $E_{\mathrm{a}} = 0.017$ eV, $\alpha = 0.06$ and $E_{\mathrm{a}} = 0.012$ eV (dotted lines).

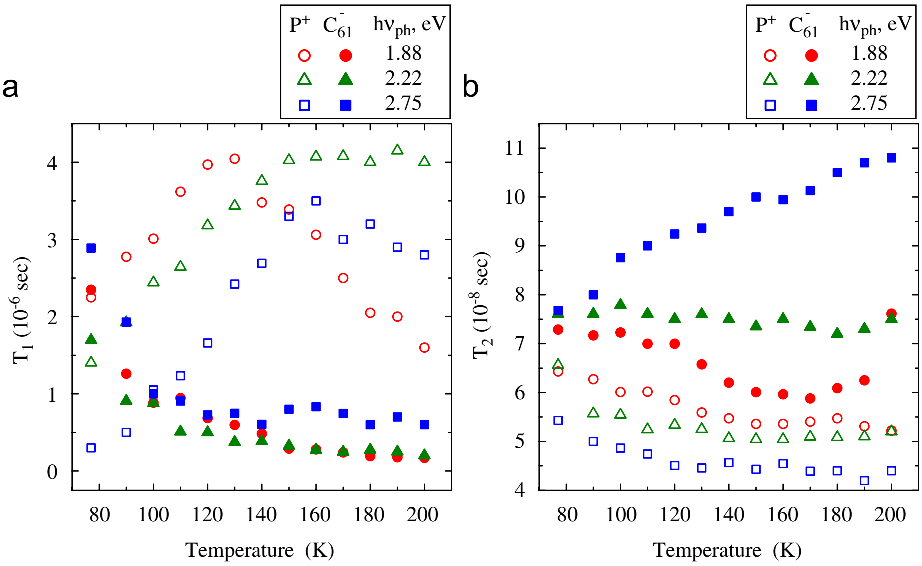

Fig. 5. Temperature dependency of the spin–lattice T_1 (a) and spin–spin T_2 (b) relaxation times of the polarons $P^{\bullet+}$ and fullerene anion-radicals C_{61}^{-} photoinduced in the P3DDT/PCBM system by laser with different photon energy.

rotational diffusion [39–41]. To account for the LEPR mobility data obtained, the Elliot model [42] based on a hopping of carrier over barrier E_a has been used. This model predicts a frequency dependence for carrier 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 barrier height E_a as $s = 1 - \alpha k_B T/E_a$ (here α is a constant). The value of E_a was deduced for, e.g. lightly doped poly(3-methylthiophene) to be 1.1 eV at $\alpha = 6$ [43], whereas a nearly linear dependence of s on E_a is obtained for some other conjugated polymers [44]. Finally, the dynamic parameters obtained should follow the temperature as:

$$D_{1D,r}(\omega_e T) = D^0_{1D,r} T^2 \omega_e^s \exp\left(\frac{E_a}{k_B T}\right). \tag{7}$$

The energies E_a required for activation of the polaron longitudinal and fullerene rotational diffusion in P3DDT/PCBM are also summarized in Table 2. It is seen in Fig. 6 that the temperature dependences calculated from Eq. (7) with the E_a presented approximate well experimental data. The E_a obtained for fullerene is less considerably as compared with that determined for fullerene rotating in more crystalline solids [40,45,46], however, lies near to that obtained for the fullerene rotation in the triphenylamine complex [39]. The E_a^{P*} values obtained for polarons photoinduced in the P3DDT/PCBM bulk heterojunction lie near the energy of lattice phonons in poly(3-octylthiophene) [25] other conjugated polymers [15], are close to that of polaron mobility in poly(3-hexylthiophene) [47] but less then that determined for polaron diffusion in poly(3-methylthiophene) [48] and in poly(3-octylthiophene)/PCBM heterojunction [35].

4. Summary

Light excitation of the "bulk heterojunction" in the P3DDT/PCBM composite leads to a charge transfer from a polymer chain to a fullerene molecule. This is accompanied by the formation of two photoinduced rhombic symmetric PC with clearly resolved LEPR spectra, namely the positively charged polaron $P^{\bullet +}$ on the polymer backbone and the negatively charged fullerene anion-radical $C_{61}^{\bullet -}$ situated between polymer chains. Both radicals are spatially separated due to high mobility of a polaron charge carrier. This decreases a probability of recombination of PC which become non-interacting. Photoinduced charge is transferred by polaron along polymer chain near the position of a fullerene anion-radical where they can recombine. The probability of the collapse of photoinduced radical pairs follows the activation law and depends on the energy of initiating photons. Weak interaction of PC in the radical pair stipulates for a difference in their interaction with own microenvironment and, therefore, in their magnetic and relaxation parameters. The interaction of both types of PC with the polymer lattice was shown to depend on the energy of optical photons. Spin dynamics induces an additional magnetic field in the whereabouts of another spins that accelerates the electron relaxation of both spin ensembles. This allowed to calculate separately all dynamic parameters of polarons and fullerene anion-radicals in the system under study. 1D diffusion of polarons and rotation of fullerenes are realized in frames of the activation mechanism. Activation energies of these charge carriers dynamics are different and are governed by laser photon energy. This allows to conclude the independence of dynamics of photoinduced spins taking part in a charge transfer through the P3DDT/PCBM bulk heterojunction. An analogous investigation of electronic and dynamics properties of heterojunction of fullerene with other P3AT, for instance with poly(3-hexylthiophene), seems to be interesting for in-depth elucidation of fundamental electronic processes in plastic solar cells. Such studies are currently in progress in our laboratory.

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