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

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Abstract

Radical pairs, polarons and fullerene anion-radicals, photoinduced by laser with photon energies of 1.88, 2.22 and 2.75 eV in the poly(3-dodecylthiophene)/[6,6]-phenyl-C_{61}-butanoic acid methyl ester (P3DDT/PCBM) bulk heterojunction, were studied over a wide temperature range. The number of these centers was found to decrease with the increase in laser photon energy. Both the spin–lattice and spin–spin relaxation times of fullerene anion-radicals and the spin–spin relaxation time of polarons change monotonically with temperature, whereas the interaction of polarons with the lattice is characterized by extreme temperature dependence. The one-dimensional polaron diffusion along the polymer chain and the rotation of fullerene near it own main axis was shown to follow the activation Elliot hopping model and to be governed by the photon energy. The deviation in activation energies for polaron and anion-radical motion and the difference in their dependence on the laser photon energy prove the non-interacting character of these charge carriers photoinduced in the P3DDT/PCBM bulk heterojunction.

Keywords: LEPR; Polythiophene and derivatives; Fullerene; Polaron; Relaxation

1. Introduction

Conjugated polymers and their composites with fullerenes are interesting materials for various molecular electronic applications, e.g., light-emitting diodes [1] and thin film field effect transistors on flexible substrates [2]. Among the most widely studied photovoltaic devices are thin plastic solar cells [3–5].

The soluble fullerene derivative [6,6]-phenyl-C_{61}-butanoic acid methyl ester (PCBM), when embedded into poly(3-alkylthiophenes) (P3AT) or other conjugated polymer, performs as strong electron acceptor whose lowest unoccupied molecular orbital lies below the excitonic state. It was found that 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 [6–9], whereas the electron back-transfer is much slower [10]. Plastic solar cells with power conversion efficiency up to 5% have been demonstrated [11,12]. 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 [13].

The efficiency of plastic solar cells appears to be due to the combined effects of ultrafast electron transfer from photoexcited polymer to fullerene [14], the large interfacial area for charge separation due to intimate blending of the materials [15] and efficient carrier transport across a thin film. Charge recombination is considered to be a predominantly non-geminate process governing effectiveness of polymer/fullerene solar cells [9,16–20]. That is why photoinduction of charge carrier pairs and their recombination

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are the most interesting points. However, they are not yet sufficiently understood in detail and there is no generally applicable model available.

The charge is transferred in initial conjugated polymers by non-linear excitations, polarons $P^{+\cdot}$ characterized by spin $S = 1/2$ and high mobility along a conjugated polymer backbone [21]. Their magnetic, relaxation and dynamic properties have been studied by conventional [22,23] and high-frequency [24–26] electron paramagnetic resonance (EPR) methods. Photoinduced charge transfer is also accompanied by the formation of anion-radicals $C_{61}^{-\cdot}$ with spin $S = 1/2$. This accounts for the widespread use of light-induced EPR (LEPR) for investigation of fullerene-modified P3AT [27–32] and other conjugated polymers [33,34]. 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 [35] with the activation energy of 0.1 eV [27].

In addition to intermolecular charge transport, charge transfer by polarons along (Q1D) and between (Q3D) polymer chains and the rotational motion of fullerene molecules are also realized in these polymer/fullerene systems. These molecular and electronic processes should undoubtedly be correlated in P3AT/PCBM systems. However, such correlations have not yet been studied.

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 a composite of PCBM embedded in poly(3-dodecylthiophene) (P3DDT) matrix, by a laser beam with photon energies of $h\nu_{ph} = 1.88$, 2.22 and 2.75 eV (here $h = \hbar/2\pi$ is the Planck constant and ν_{ph} is a photon frequency) over a wide temperature range. We demonstrate the non-interaction of paramagnetic centers (PCs) in radical pairs and, therefore, their different interactions with their own microenvironment. This allowed us to determine separately the relaxation and dynamic parameters of both type of PCs and to analyse the spin dynamic processes in the P3DDT/PCBM composite.

2. Experimental

This study used regioregular Aldrich® P3DDT [36] with lattice constants of $a = 2.583$ nm, $b = 0.775$ nm, $c = 0.777$ nm [37] and PCBM synthesized in the laboratory of Prof. J.C. Hummelen, University of Groningen [38]. Both components of the composite are shown schematically in Fig. 1. The chlorbenzene solution of P3DDT and PCBM, in 1:1 w/w ratio with a concentration of ~1 wt.%, was placed on a ceramic plate and dried, so that the P3DDT/PCBM composite was formed as a film ~4 × 8 mm² and ~0.1 mm thick.

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 range 90–340 K under a dry nitrogen atmosphere

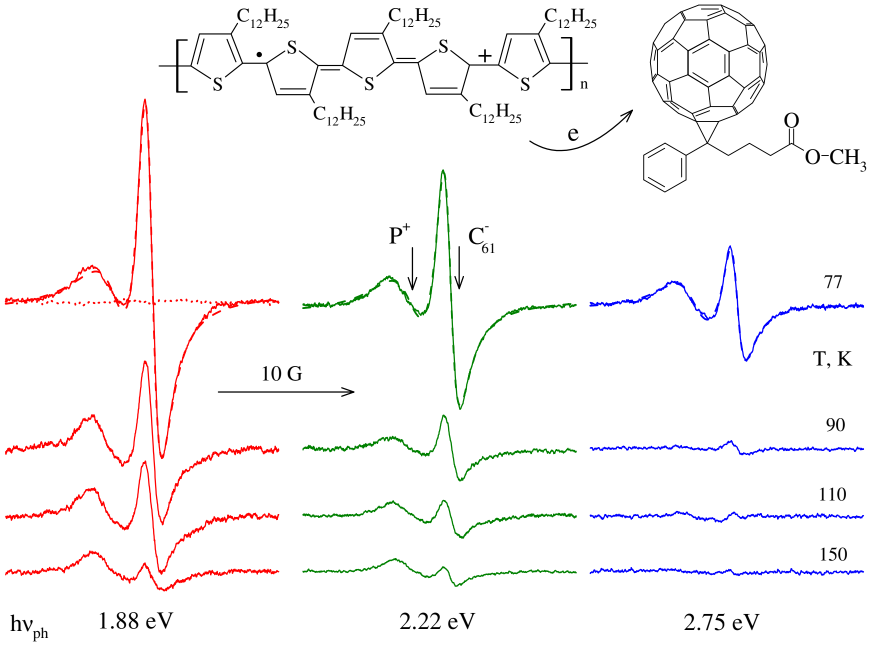

Fig. 1. X-band waveband LEPR spectra of the radical pairs photoinduced in the P3DDT/PCBM system by steady-state laser irradiation with different laser photon energies $h\nu_{ph}$ and registered at different temperatures. The dotted line shows the “dark” spectrum obtained before laser irradiation. Left-right dashed lines show sum LEPR spectra calculated using individual terms of g-tensors (see the text) and linewidth (see Table 1). At the top, both the P3DDT and PCBM components of the composite are also shown schematically.

using a BRT SKB IOH temperature controller and also at 77 K in a quartz Dewar with liquid nitrogen. The LEPR spectra were measured by permanent illumination of the P3DDT/PCBM composite directly in the microwave cavity of the EPR spectrometer by Roithner Lasertechnik RLDH660-40-3 ($\lambda = 660$ nm, $h\nu_{\mathrm{ph}} = 1.88$ eV, $P = 41$ mW), MGM2-30 ($\lambda = 530$ nm, $h\nu_{\mathrm{ph}} = 2.22$ eV, $P = 38$ mW), and DPSSL-473-40 ($\lambda = 450$ nm, $h\nu_{\mathrm{ph}} = 2.75$ eV, $P = 40$ mW) laser modules. The power of laser beam was measured with an error 3.5% by using a LaserMate-Q device situated just before the microwave cavity. 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 program.

3. Results and discussions

3.1. Magnetic resonance parameters

3.1.1. Line shape and g-factor

The paramagnetic centers in the initial P3DDT film are characterized by weak "dark" X-band EPR line with effective $g = 2.0025$ in the temperature range 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. When 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). The sum spectrum was attributed to radical pairs of positively charged diffusing polarons $P^{+\cdot}$ with isotropic (effective) $g_{\mathrm{iso}} = 2.0023$ and negatively charged anion-radicals $C_{61}^{-\cdot}$ rotating around the main axis with effective $g_{\mathrm{iso}} = 2.0001$. The latter is typical of fullerene anion-radicals [39]. A high-field/frequency EPR study of poly(3-octylthiophene) has shown [40,41] that the interaction of an unpaired electron of $P^{+\cdot}$ with sulfur heteroatoms involved in 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. have shown [42] that the spin density in $C_{61}^{-\cdot}$ anion-radical embedded into polymer matrix is characterized by rhombic symmetry, and therefore results in an 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 [43–46], the deviation of the $C_{61}^{-\cdot}$ g-factor from that of the free electron, $g_e = 2.00232$, is due to the fact that the orbital angular moment is not completely quenched. Due to a dynamic Jahn–Teller effect accompanying the structural molecular deformation, the isotropic nature of the icosahedral C_{60} molecule is distorted after the formation of the $C_{60}^{-\cdot}$ anion-radical, resulting in an axial or even lower symmetry [47]. This is also realized in case of the $C_{61}^{-\cdot}$ anion-radical [42], 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 the tensor character of their linewidths [40–42]. This should be taken into account to calculate more precisely an effective LEPR spectrum of the P3DDT/PCBM system.

Table 1
The terms $\Delta B_{\mathrm{pp}}^{i}$ of linewidth (in Gauss) LEPR spectra of polarons and fullerene anion-radicals used for simulation of the LEPR spectra obtained at different laser photon energy $h\nu_{\mathrm{ph}}$ (in eV) and 77 K

	PCs		$h\nu_{\mathrm{ph}}$	
Linewidth		**1.88**	**2.22**	**2.75**
$\Delta B_{\mathrm{pp}}^{\mathrm{X}}$	$P^{+\cdot}$	1.01	1.07	1.13
	$C_{61}^{-\cdot}$	0.78	0.73	0.81
$\Delta B_{\mathrm{pp}}^{\mathrm{Y}}$	$P^{+\cdot}$	1.01	1.07	1.13
	$C_{61}^{-\cdot}$	0.84	0.79	0.87
$\Delta B_{\mathrm{pp}}^{\mathrm{Z}}$	$P^{+\cdot}$	1.02	1.09	1.15
	$C_{61}^{-\cdot}$	2.58	2.53	2.61
$\Delta B_{\mathrm{pp}}^{\mathrm{iso}}$	$P^{+\cdot}$	1.01	1.08	1.14
	$C_{61}^{-\cdot}$	1.40	1.35	1.43

The main values and traces of the g-tensors of the $P^{+\cdot}$ and $C_{61}^{-\cdot}$ PCs 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 PCs 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 also shown in Fig. 1.

3.1.2. Paramagnetic susceptibility

Fig. 2 depicts the Arrhenius dependence of spin susceptibility of both PCs over the temperature range 77–200 K

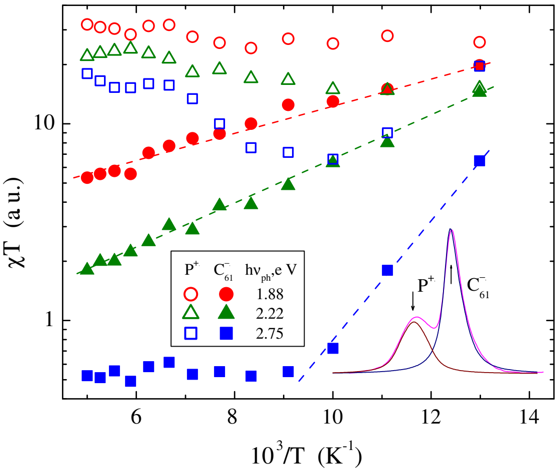

Fig. 2. Arrhenius dependence of paramagnetic susceptibility of the polarons $P^{+\cdot}$ and fullerene anion-radicals $C_{61}^{-\cdot}$ photoinduced in the P3DDT/PCBM system by steady-state laser irradiation with different photon energies. Dashed lines show the dependences calculated using Eq. (2) with ΔE_{ij} presented in Table 2. In the inset, the integrated total low-temperature spectrum as well as the appropriate contributions of these PCs are shown.

derived from their double-integrated spectra in non-saturated conditions, i.e., when the 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 pairs photoinduced in close proximity should interact with each other, either by exchange or by dipolar mechanisms. These effects do not register in the LEPR spectra of the P3DDT/PCBM system, most likely due to diffusion of polarons along the conjugated polymer backbone away from the fullerene anions at a timescale faster than the exchange times, i.e., $\tau_{ex} \leqslant 10^{-9}$ s. This can explain the unusually long lifetime of the charge separation in polymer/fullerene systems [48] and in the P3DDT/PCBM composite studied here.

Under steady-state light irradiation, the 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 [49]:

$$v(R_{ij}) = v_0^{|} \exp\left(-\frac{2R_{ij}}{a_0}\right), \tag{1}$$

where $v_0^{|}$ is an attempt to recombine the frequencies. PCs photoinduced in the P3DDT/PCBM system are likely to have different localization radii. The localization radius for the electron is probably of the order of the radius of the solitary PCBM molecule, whereas the polaron occupies approximately five monomer units in regioregular P3AT [50,51]. 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 that this parameter may be considered as constant. A polaron diffuses by tunneling between initial site i to final site j at a cost of energy ΔE_{ij}, so the Miller–Abrahams energy-dependent factor appears in the above equation:

$$\begin{aligned} v(R_{ij}, \Delta E_{ij}) &= v_0^{|} \exp\left(-\frac{2R_{ij}}{a_0}\right) \exp\left(-\frac{\Delta E_{ij}}{k_B T}\right) \\ &= v_0 \exp\left(-\frac{\Delta E_{ij}}{k_B T}\right). \end{aligned} \tag{2}$$

Fig. 2 shows that the polaron charge carriers are characterized by $\chi(T) \propto T^{-1}$ temperature dependence in the P3DDT/PCBM system, whereas the spin susceptibility of fullerene anion-radicals excited by phonons with $h\nu_{ph} = 1.88$ and 2.22 eV at $77\ \mathrm{K} \leqslant T \leqslant 160$ K and with $h\nu_{ph} = 2.75$ eV at $77\ \mathrm{K} \leqslant T \leqslant 110$ K follows Arrhenius' law.

Pristine P3DDT with a band gap 1.93 eV is characterized by an optical absorption spectrum with a maximum at 2.41 eV [28–30]. This spectrum is slightly shifted upon blending the polymer with PCBM. Assuming that the sample absorbs equal numbers of photons with different energies, the values of ΔE_{ij} in Eq. (2) can be determined for fullerene anion-radical from the slopes of appropriate curves (Table 2). It can be seen that ΔE_{ij} increases by factor of 4 as $h\nu_{ph}$ increases from 1.88 up to 2.75 eV. The annihilation of radical pairs in the P3DDT/PCBM compound, as in case of other polymer/fullerene systems [3–5], can be described as a thermally activated bimolecular process. If one includes Coulomb interactions in this model, these should affect the activation energy for either detrapping or thermally assisted tunnelling 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, resulting in their long life.

Table 2
The ΔE_{ij} in Eq. (2) determined for spin susceptibility for fullerene anion-radicals 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 beams with different photon energies $h\nu_{ph}$ (all in eV)

$h\nu_{ph}$	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

The ratio of spin concentrations was found to be near to unity for irradiation of P3DDT/PCBM by light with $h\nu_{ph} = 1.88$ and 2.22 eV; this is in agreement with the fundamental principle of photoinduced charge separation in radical pairs. This value, however, increases at $h\nu_{ph} = 2.75$ eV, probably as the result of the appearance of an additional channel for the electron moving away the fullerene molecule. Electrons hop more easily between fullerenes than from polaron and fullerene, so that effective charge recombination is still limited by the transport of polarons towards fullerene domains. In addition, a direct recombination of polarons in molecular solids depends on their mobility μ or diffusion rate D [52]. Colneri et al. have shown [53] that the formation of diamagnetic bipolarons in poly(3-hexylthiophene) 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, the reason for this effect is not yet evident.

3.1.3. Linewidth

Fig. 3 presents the temperature dependence of effective (isotropic) peak-to-peak linewidth $\Delta B_{pp}^{(0)}$ obtained for the $P^{+\cdot}$ and $C_{61}^{-\cdot}$ radicals in the absence of microwave saturation. It can seen from Fig. 3 that the linewidth of polarons

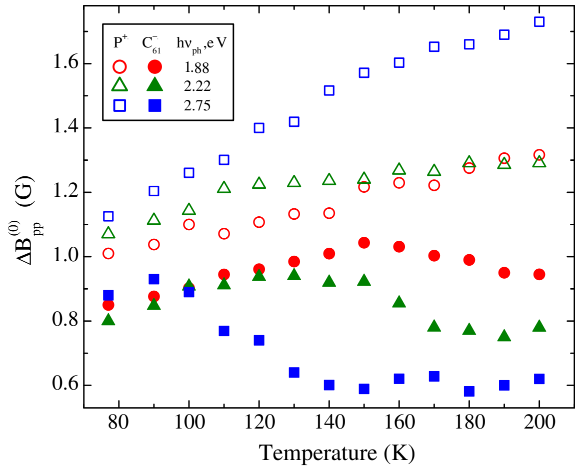

Fig. 3. Lower limit of the peak-to-peak linewidth $\Delta B_{pp}^{(0)}$ of the polarons P^+ and fullerene anion-radicals $C_{61}^{-\cdot}$ photoinduced in the P3DDT/PCBM system by laser irradiation with different photon energies as functions of temperature.

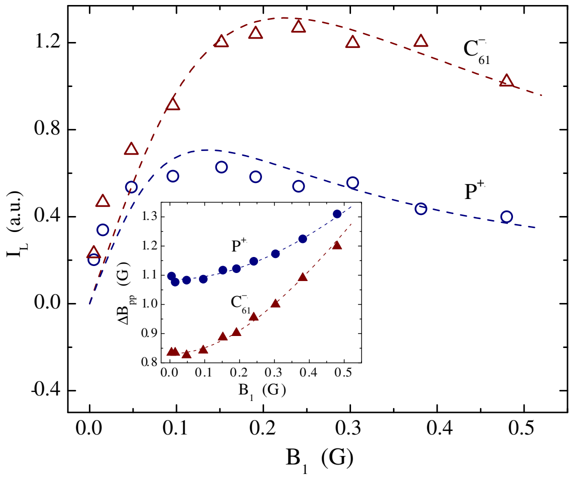

Fig. 4. The intensity I_L and peak-to-peak linewidth (insert) LEPR spectrum of polarons P^+ and anion-radicals $C_{61}^{-\cdot}$ photoinduced by laser with $h\nu_{ph} = 1.88$ eV in the P3DDT-PCBM sample at 100 K as function of polarizing microwave field B_1. The lines show the dependences calculated from Eqs. (3)–(5) with $T_1^{(P^+)} = 2.9 \times 10^{-6}$, $T_2^{(P^+)} = 6.1 \times 10^{-8}$, $T_1^{(C_{61}^-)} = 1.1 \times 10^{-6}$, $T_2^{(C_{61}^-)} = 7.2 \times 10^{-8}$ s.

changes monotonically with temperature, whereas fullerene radicals demonstrate more complex $\Delta B_{pp}^{(0)}$ (T, ν_{ph}) dependence. Extrapolation to room temperature gives 1.4–2.0 G for $P^{+\cdot}$, which lies inside the region $\Delta B_{pp}^{(0)} = 1.3$–$1.8$ G obtained for polarons in different P3AT [13,24]. This value, however, is considerably less then that determined for undoped polythiophene [22,23,54], demonstrating the weaker spin interaction in the system studied here.

The spectral linewidth should reflect different processes occurring in the P3DDT/PCBM composite. One of these is the association of mobile PCs with the counter-charges. Another process 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, which is proportional to the polaron concentration n_P on the polymer chain. Extrapolating temperature dependence to the lower temperature limit, i.e., when the temperature tends to zero, one obtains $\Delta B_{pp}^{(0)} \approx 0.7$–$0.8$ G for polarons and $\Delta B_{pp}^{(0)} \approx 0.5$–$0.6$ G for fullerene anion-radicals, and, therefore, $R_0 \approx 2.3$–2.5 nm for the dipolar distance in the P3DDT/PCBM system.

3.2. Spin relaxation

As the value of B_1 increases, the intensity I_L of both the PCs Lorentzian spectra first increases linearly and, starting from some B_1 value, plateaus and then decreases, as shown in Fig. 4. This is due to the manifestation of a microwave saturation effect causing the change in their LEPR spectra according to the law [55]:

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

where $I_L^{(0)}$ is the intensity of a non-saturated spectrum, γ_e is the gyromagnetic ratio for an electron, and T_1 and T_2 are the spin–lattice and spin–spin relaxation times, respectively. The inflection point for the polaron curve is distinct from that obtained for fullerene anion-radicals. This is evidence of different relaxation parameters of these non-interacting PCs. The second effect of the increase in B_1 value is the broadening of the LEPR spectrum shown in Fig. 4. Since the PCs and their signals were found to be independent of one another, both the relaxation times of these PCs can be determined separately by the steady-state saturation method from the following relations [55]:

$$T_1 = \left[\left(\Delta B_{pp}/\Delta B_{pp}^{(0)}\right)^2 - 1\right] \Big/ \gamma_e^2 B_1^2 T_2 \tag{4}$$

$$T_2 = 2/\sqrt{3}\gamma_e \Delta B_{pp}^{(0)}. \tag{5}$$

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

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

3.3. Spin dynamics

Various PC-aided dynamic processes occur in the P3DDT/PCBM system, e.g., polaron diffusion along the

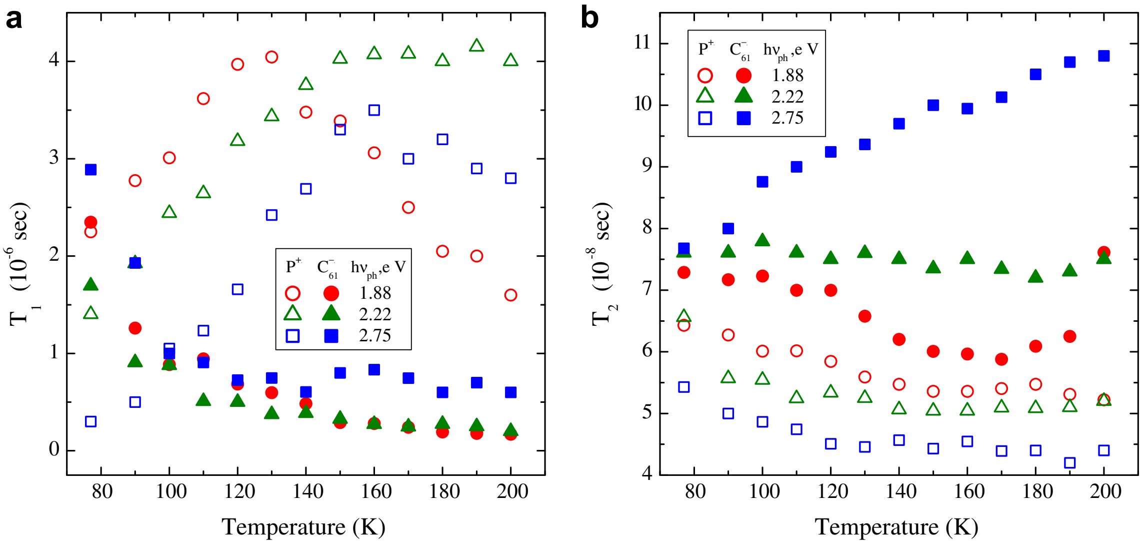

Fig. 5. Temperature dependency of the spin–lattice T_1 (a) and spin–spin T_2 (b) relaxation times of the polarons $P^{+\cdot}$ and fullerene anion-radicals $C_{61}^{-\cdot}$ photoinduced in the P3DDT/PCBM system by laser irradiation with different photon energies.

polymer chains with coefficient D_{1D}, rotational diffusion of fullerene anion-radicals around the main molecular axis with coefficient D_r and charge transfer between polarons and fullerenes at rate D_e. These processes should induce an additional magnetic field in the vicinity 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 the spin–lattice relaxation rate [56]:

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

where $\langle\omega^2\rangle = 1/10\gamma_e^4\hbar^2 S(S+1)n\Sigma_{ij}$ is the constant of a dipole–dipole interaction for powder, n is the number of polarons per monomer, Σ_{ij} is the lattice sum for a powder-like sample, $J(\omega_e) = (2D_{1D}^{|}\omega_e)^{-1/2}$ (at $D_{1D}^{|} \gg \omega_e \gg D_{3D}$) or $J(\omega_e) = \tau_c/(1+\tau_c^2\omega_e^2)$ is a spectral density function, respectively, for Q1D longitudinal or rotational diffusion with correlation time τ_c, $D_{1D}^{|} = 4D_{1D}/L^2$, ω_e is the resonant angular frequency of the electron spin precession, and L is a spin delocalization factor over a polaron equal approximately to five monomer units in P3AT [50,51]. The similar spectral density function was used earlier in a study of spin dynamics in other conjugated polymers [22–26,40,41].

The dynamic parameters calculated from Eq. (6) for both PCs in photoinduced radical pairs using the appropriate spectral density functions are presented in Fig. 6 as a function of temperature. Normally, fullerene anion-radicals are characterized by activation rotational diffusion [57–60]. To account for the LEPR mobility data obtained, the Elliot model [61], based on carrier hopping of over a 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, for example, lightly doped poly(3-methylthiophene) to be 1.1 eV at $\alpha = 6$ [62], whereas a nearly linear dependence of s on E_a was obtained for some other conjugated polymers [63]. Finally, the dynamic parameters obtained should follow the temperature according to

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

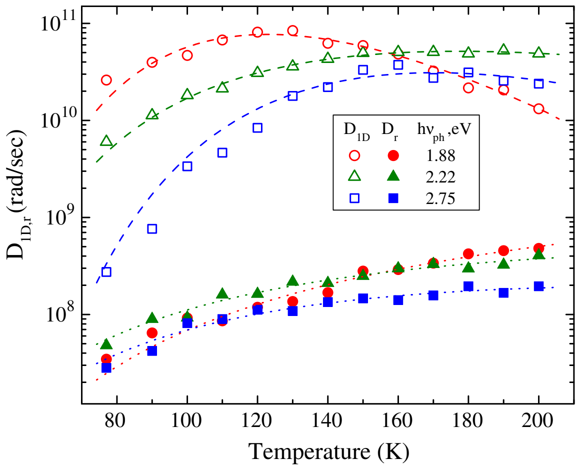

Fig. 6. Temperature dependency of the rates of the polaron $P^{+\cdot}$ diffusion along polymer chains D_{1D} and of the $C_{61}^{-\cdot}$ rotation D_r in the P3DDT/PCBM system irradiated by laser with different photon energies. Up and down lines show the dependences calculated from Eq. (7) with $\alpha = 1.2$ and $E_a = 0.048$ eV, $\alpha = 0.45$ and $E_a = 0.038$ eV, $\alpha = 2.2$ and $E_a = 0.094$ eV (dashed lines) and with $\alpha = 0.04$ and $E_a = 0.010$ eV, $\alpha = 0.03$ and $E_a = 0.017$ eV, $\alpha = 0.06$ and $E_a = 0.012$ eV (dotted lines).

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 can be seen in

Fig. 6 that the temperature dependences calculated from Eq. (7) with the E_a approximate well to the experimental data. The E_a obtained for fullerene is considerably less compared to that determined for fullerene rotating in more crystalline solids [59,64,65], but lies near to that obtained for the fullerene rotation in the triphenylamine complex [57,58]. The E_a values defined for polaron one-dimensional diffusion are close to that of polaron mobility in poly(3-hexylthiophene) [66] and also to the energy of lattice phonons in poly(3-octylthiophene) [40,41] and other conjugated polymers [24–26].

4. Concluding remarks

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 paramagnetic centers with clearly resolved LEPR spectra, namely the positively charged polaron $P^{+\cdot}$ on the polymer backbone and the negatively charged fullerene anion-radical $C_{61}^{-\cdot}$ situated between polymer chains. Both radicals are spatially separated due to the high mobility of a polaron charge carrier. This decreases the probability of recombination of PCs which become non-interacting. Photoinduced charge is transferred by polarons along the polymer chain near to 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 light energy absorbed by the sample. Weak interaction of PCs in the radical pair stipulates a difference in their interaction with own microenvironment and, therefore, in their magnetic and relaxation parameters. The interaction of both types of PCs with the polymer lattice was shown to depend on the energy of optical photons. Spin dynamics induces an additional magnetic field in the vicinity of another spin that accelerates the electron relaxation of both spin ensembles. This allowed us to calculate separately all the dynamic parameters of polarons and fullerene anion-radicals in the system under study. One-dimensional diffusion of polarons and rotation of fullerenes are realized within the framework of the activation mechanism. The activation energies of these charge carrier dynamics are different and are governed by laser photon energy. This allows us to conclude that the dynamics of photoinduced spins taking part in charge transfer in the P3DDT/PCBM composite are independent.

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