

Spin Localization in Poly(3-Dodecylthiophen)/PCBM Composite

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Abstract Charge carriers photoinduced in poly(3-dodecylthiophene)/([6,6]-phenyl-C₆₁-butanoic acid methyl ester) (P3DDT/PCBM) by photons with the energy of 1.88–2.75 eV were investigated by X-band light-induced electron paramagnetic resonance (LEPR). LEPR spectra were attributed to non-interacting polarons and methanofullerene anion radicals with different magnetic and relaxation parameters. A part of these charge carriers are trapped in a polymer matrix. Paramagnetic susceptibility and spin–spin relaxation of mobile charge carriers were shown to follow the activation law.

1 Introduction

During the last years, research has been increasing in the field of synthesis and characterization of conjugated polymers with extended π -electron delocalization and their composites with fullerene by perspective utilization in organic plastic solar cells [1–3]. The irradiation of bulk heterojunctions, formed by polymer chains with fullerene globes, by visible light with photon energy $h\nu_{\text{ph}}$ higher than its π – π^* energy gap leads to the formation of ion–radical pairs, polarons $P^{+\bullet}$ (donors, D) on a polymer chain, and fullerene anion radicals $C_{60}^{-\bullet}$ (acceptors, A) pseudorotating near polymer chains. Charge separation results in the following consequent processes [4]:

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- (1) excitation of a polaron on a polymer chain: $D + A \rightarrow D^* + A$,
- (2) excitation delocalization on the complex: $D^* + A \rightarrow (D - A)^*$,
- (3) initiation of the charge transfer: $(D - A)^* \rightarrow (D^{\delta+} - A^{\delta-})$,
- (4) formation of an ion–radical pair: $(D^{\delta+} - A^{\delta-})^* \rightarrow (D^{+\cdot} - A^{-\cdot})$, and
- (5) charge separation: $(D^{+\cdot} - A^{-\cdot}) \rightarrow D^{+\cdot} - A^{-\cdot}$.

The donor and acceptor units are spatially close but are not covalently bonded. At each step, the $(D - A)$ system can relax back to the ground state, releasing energy to the ‘lattice’ in the form of heat or emitted light. The photoinitiation of charge carriers was revealed by time-resolved spectroscopy [5] to occur in the femtosecond time domain, whereas the electron backtransfer with charge annihilation was much slower [6] due to relatively slow structural relaxation [7]. This, therefore, means that one may register an effective number of charge carriers as a result of opposite processes of initiation and recombination. The efficiency of organic photovoltaic systems is lower as compared to silicone prototypes due to the limited number, mobility and lifetime of charge carriers. These parameters are governed by the electronic and structural properties of the polymer matrix and the embedded fullerene derivative [8, 9]. Understanding of all electronic processes related to fullerene-modified conjugated polymers is of fundamental interest for both material characterization and molecular device fabrication.

Soluble conjugated polymers and fullerenes were proved [10, 11] to be the most efficient electron donors and acceptors, respectively, in such plastic solar cells. Photoinduced charge separation and transfer is accompanied by the formation of radical pairs ($P^{+\cdot} - C_{60}^{-\cdot}$) of polarons $P^{+\cdot}$ transferring a positive charge (hole) along the polymer chain toward a negatively charged fullerene globule $C_{60}^{-\cdot}$. These charge carriers possess also spin $S = \frac{1}{2}$ with different density configuration and, therefore, different magnetic, relaxation and dynamics parameters. Such peculiarities account for a wide use of the direct light-induced electron paramagnetic resonance (LEPR) method for investigation of the spin-assisted processes taking part in plastic solar cells [12–14].

Our previous high-field high-frequency (D-band, 140 GHz) EPR study of structurally close poly(3-octylthiophene) showed [15, 16] that weak interaction of an unpaired electron delocalized on a polaron with sulfur heteroatom involved in the polymer backbone provokes rhombic symmetry of its g -factor (with $g_{xx} = 2.00409$, $g_{yy} = 2.00332$ and $g_{zz} = 2.00235$) and line width. The same symmetry of spin density appeared to be characteristic also for a polaron stabilized in poly(3-hexylthiophene) with $g_{xx} = 2.0028$, $g_{yy} = 2.0019$ and $g_{zz} = 2.0009$ [17]. We showed also [18] that among soluble fullerene derivatives with different side alkyl substitutes, [6,6,]-phenyl- C_{61} -butanoic acid methyl ester (methanofullerene $mC_{61}^{-\cdot}$, PCBM) appears to be at the moment one of the most suitable electron acceptors to be used in plastic solar cells. Besides, we pointed out [19] that the main relaxation and dynamics properties of spin pairs photoinduced in a bulk heterojunction formed by PCBM with macromolecules of poly(3-dodecylthiophene) (P3DDT) depend on the energy of excited photons $h\nu_{ph}$. Unpaired electron delocalized on the PCBM anion radical is also characterized by rhombic symmetry with $g_{xx} = 2.00031$, $g_{yy} = 2.00011$ and $g_{zz} = 1.99821$ [20].

Charge recombination is considered to be a predominantly nongeminate process governing the effectiveness of polymer/fullerene solar cells [21]. The annihilation of radical pairs in bulk heterojunction of a composite can be described as a thermally activated bimolecular process [22, 23]. This process can be complicated, e.g., by the formation of additional long-lived massive (with effective mass $m_{\text{eff}} \approx 300m_e$) spin polaron-like excitons [24]. The recombination of the long-lived photoinduced polarons in a polymer matrix follows temperature-independent fast and exponentially temperature-dependent slow decay laws [25]. Besides, some charge carriers may be pinned by traps in a polymer matrix. So, the localization and recombination of charge carriers are the most interesting processes. However, they are not yet sufficiently understood in detail and there is no generally applicable model available. This is because the polymer/fullerene systems were mainly studied at low temperatures when the dynamics of charge carriers seems to be frozen [26].

The aim of the present work was to study the spin composition and recombination of charge carriers photoinduced in bulk heterojunctions of the P3DDT/PCBM system by optical photons with an energy of 1.88–2.75 eV. The results obtained were interpreted in the frames of approaches mainly used in the study of analogous organic polymer/fullerene systems of reduced dimensionality.

2 Experimental

In the study, we used PCBM from Solenne BV[®] (The Netherlands) and regioregular P3DDT from Aldrich[®] (USA) without additional rectification. Into a ceramic plane, ca. 1 wt% concentrated solution in chlorobenzene at a weight ratio of 1:1 was placed and dried repeatedly, so that the P3DDT/PCBM composite was formed as a film with the size of ca. $4 \times 8 \text{ mm}^2$ and thickness of ca. 0.1 mm.

EPR experiments were performed at permanent illumination of the sample by Roithner Lasertechnik RLDH660-40-3 ($\lambda = 660 \text{ nm}$, $h\nu_{\text{ph}} = 1.88 \text{ eV}$, $P = 41 \text{ mW}$), MGM2-30 ($\lambda = 530 \text{ nm}$, $h\nu_{\text{ph}} = 2.22 \text{ eV}$, $P = 38 \text{ mW}$) and DPSSL-473-40 ($\lambda = 450 \text{ nm}$, $h\nu_{\text{ph}} = 2.75 \text{ eV}$, $P = 40 \text{ mW}$) laser modules directly in a microwave cavity of an X-band (3 cm, 9.7 GHz) PS-100X spectrometer with 100 kHz field ac modulation for phase-lock detection. The LEPR spectra of the polymer/fullerene systems and their components were registered at 90–340 K in dry nitrogen atmosphere using a BRT SKB IOH temperature controller and at 77 K in quartz Dewar filled with liquid nitrogen. The signal-to-noise ratio of the LEPR spectra was improved by averaging of several (typical 4–6) acquisitions.

The total paramagnetic susceptibility of photoinduced charge carriers was determined from double integration of LEPR spectra far from their microwave saturation. Diphenylpicrylhydrazyl (DPPH) single microcrystal standard with $g = 2.0036$ was used for estimation of g -factor of both charge carriers. The inaccuracy in determination of the g -factor and peak-to-peak line width ΔB_{pp} was $\pm 2 \times 10^{-4}$ and $\pm 2 \times 10^{-2} \text{ G}$, respectively. Processing and simulations of the EPR spectra were done with the Bruker[®] WinEPR SimFonia and OriginLab[®] Origin programs.

3 Results and Discussions

Both the poly(3-dodecylthiophene) and [6,6]-phenyl-C₆₁-butanoic acid methyl ester (Fig. 1) are characterized by the absence of the dark and LEPR signals in the whole temperature range. As the P3DDT/PCBM composite is prepared and the steady state is irradiated by visible light directly in a cavity of the EPR spectrometer, two partly overlapping LEPR lines appear at $T \leq 200$ K. The composite LEPR spectrum photoinduced by photons with energy $h\nu_{\text{ph}} = 1.88$ eV at 77 K is shown in Fig. 1 [13]. The lines registered in low and high fields can be attributed to positively charged polarons $P^{+\bullet}$ with isotropic (effective) $g_{\text{iso}}^{\text{P}} = 2.0016$ and negatively charged methanofullerene $mC_{61}^{-\bullet}$ with $g_{\text{iso}}^{\text{F}} = 1.9996$ background photoinduced in bulk heterojunctions of the polymer/fullerene composites, respectively. These values lie near those obtained for radical pairs photoinduced in other fullerene-modified conjugated polymers [19, 27–30]. Detailed analysis of the data obtained at a wide variety of experimental conditions allowed to point out that the LEPR

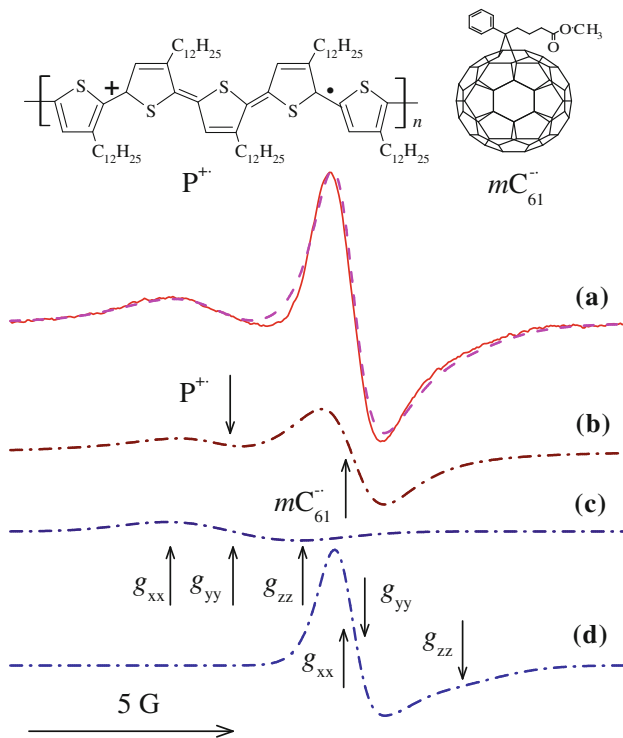


Fig. 1 (a *solid line*) LEPR spectrum of radical pairs ($P^{+\bullet} - mC_{61}^{-\bullet}$) background photoinduced in bulk heterojunctions of the P3DDT/PCBM composite by laser with the photon energy $h\nu_{\text{ph}} = 1.88$ eV at 77 K. (b *dashed line*) Theoretical sum spectrum and its contributions caused by mobile radical pairs ($P^{+\bullet} - mC_{61}^{-\bullet}$) (b *dash-dotted line*) as well as by localized polarons $P^{+\bullet}$ (c *dash-dotted line*) and methanofullerene anion radicals $mC_{61}^{-\bullet}$ (d *dash-dotted line*) calculated using the data of Table 1 are also shown. P3DDT and PCBM are schematically shown at the top. The positions of photoinduced radicals and components of their \mathbf{g} -tensors are shown as well

spectrum, presented in Fig. 1a, consists of a Lorentzian doublet of mobile radical pairs ($P^{+\bullet} - mC_{61}^{-\bullet}$), shown in Fig. 1b, as the sum of isotropic contribution from mobile polarons $P^{+\bullet}$ and fullerene anion radicals $mC_{61}^{-\bullet}$ with equal spin concentrations plus Gaussian anisotropic contributions of these charge carriers pinned in the polymer matrix (shown in Fig. 1c and d, respectively). Since the backbone of the polymer can be expected to lie preferably parallel to the film substrate [31], the lowest principal g -value is associated with the polymer backbone. The molecule can take any orientation with regard to the z -axis, i.e., the polymer backbone direction, as derived from the presence of both the g_{xx} and g_{yy} components in the spectra for all orientations of the film. So, the g -factor anisotropy gives rise to the inhomogeneity of distribution of additional fields along the x and y directions within the plane of the polymer σ skeleton and not along its perpendicular z direction. To determine all main magnetic resonance parameters of all spin ensembles, one should fit each LEPR spectrum analytically as the sum of the above-mentioned contributions with different anisotropy factors. The magnetic resonance parameters used for simulation of effective LEPR spectra of the P3DDT/PCBM composite shown by dashed line in Fig. 1a are summarized in Table 1.

Figure 2 shows the paramagnetic susceptibility χ of mobile and pinned charge carriers photoinduced in the P3DDT/PCBM system as a function of the photon energy $h\nu_{ph}$ and temperature. The data presented evidence that the number of both trapped charge carriers changes weakly with the temperature and photon energy. It is seen from Fig. 2 that mobile radical pairs demonstrate sharper $\chi(T, h\nu_{ph})$ dependence. This fact can be interpreted as follows.

There are two spin-assisted processes taking part in the light-irradiated composite, namely, fast exciting of spin pairs and their further considerably slower recombination. This means that one may register an effective number of spin charge carriers, which depends on the probability that positively charged polaron meets negatively charged fullerene globule. The decay of radical pairs in regioregular P3DDT consists of temperature-independent fast and exponentially temperature-dependent slow contributions [32]. The distances of the phonon-assisted jumps of pinned polarons and their tunneling through the barrier between two adjacent sites and the concentration of the trapped centers in conjugated polymers should follow the activation model [33]. The temperature dependences of χ obtained can be described, e.g., by a simple model of trap-controlled charge carrier transport [34, 35]. The model assumes that states in the valence band-tail with the width ΔE_V are separated by a mobility edge E_V , where transport takes place only in the extended states located below E_V . However, this model was shown [36] to be quite good for

Table 1 Average values of the g -tensor g_{ij} and peak-to-peak line width ΔB_{pp}^i (in Gauss) used for simulation of polarons $P^{+\bullet}$ and methanofullerene PCBM anion radicals $mC_{61}^{-\bullet}$ photoinduced in the P3DDT/PCBM composite by a laser with photon energy $h\nu_{ph} = 1.88$ eV at 77 K

Radical	g_{xx}	g_{yy}	g_{zz}	g_{iso}	ΔB_{pp}^X (G)	ΔB_{pp}^Y (G)	ΔB_{pp}^Z (G)	ΔB_{pp}^{iso} (G)
$P^{+\bullet}$	2.0026	2.0017	2.0006	2.0016	2.5	1.4	1.5	1.8
$mC_{61}^{-\bullet}$	2.0003	2.0001	1.9986	1.9996	0.7	1.6	2.5	1.6

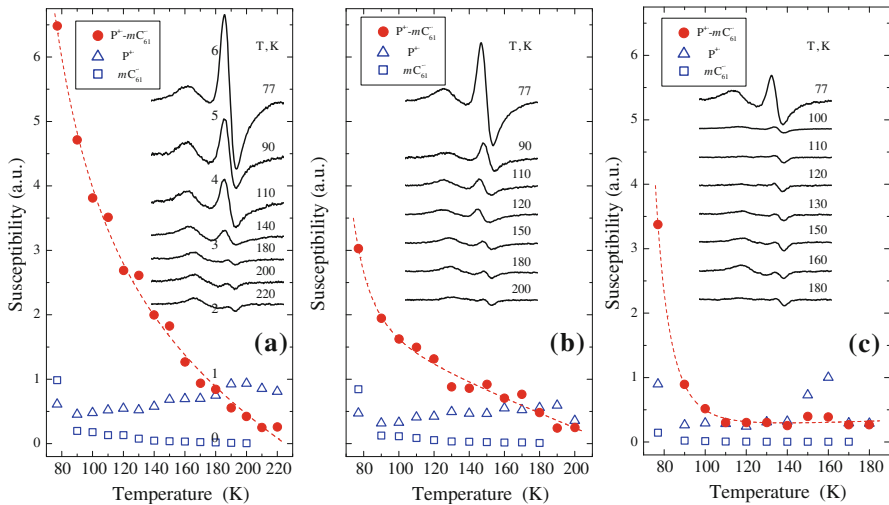


Fig. 2 Temperature dependence of the χ parameter determined for the mobile radical pairs ($P^{+\bullet} - mC_{61}^{-\bullet}$) (filled circles) as well as localized polarons $P^{+\bullet}$ (open triangles) and methanofullerene anion radicals $mC_{61}^{-\bullet}$ (open squares) photoinduced in the P3DDT/PCBM composite by the photons with the energy 1.88 (a), 2.22 (b), and 2.75 eV (c). Insets LEPR spectra registered at different temperatures. The dependences calculated from Eq. (3) with ΔE_{ij} presented in Table 2 are shown by dashed lines

exponential band-tails, exactly for the specific case $k_B T / (\Delta E_V) = 1/2$, which is mainly unreliable in our case (see below). As in the case of charge carriers background photoinitiated in other polymer/fullerene systems (see, e.g., [37, 38]), the data obtained can be interpreted in terms of the Nelson model [39] of the polaron thermally assisted multistep tunneling from one site i to another one j through energy barrier $\Delta E_{ij} = E_j - E_i$ with the rate

$$\omega_{\text{hop}} = \omega_{\text{hop}}^0 \exp\left(-\frac{\Delta E_{ij}}{k_B T}\right), \quad (1)$$

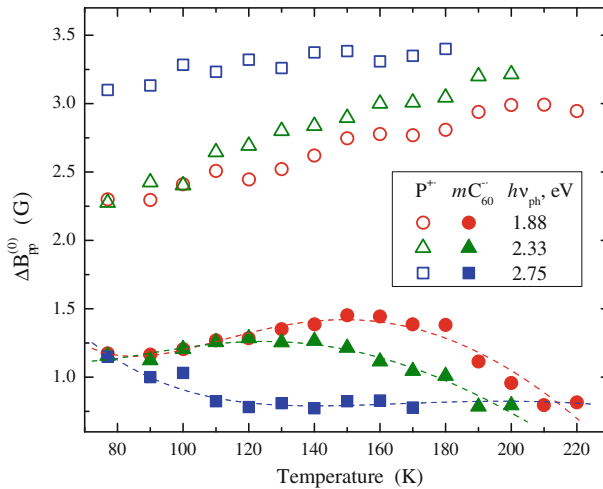
where ω_{hop}^0 is the attempt frequency for a hole tunneling between the polymer chains, k_B is a Boltzmann constant, and T is the temperature. The polaron may recombine not obviously with the first negative charge but with the charge on the subsequent fullerene. So, one should also take into consideration an exchange interaction of both paramagnetic centers and a probability p of spin flip-flop during their collision [40]

$$p = \frac{\alpha^2}{2(1 + \alpha^2)}, \quad (2)$$

where $\alpha = 3\pi J / \hbar \omega_{\text{hop}}$, $\hbar = h/2\pi$ is the Planck constant and J is the constant of exchange interaction of the spins in a radical pair. This means that the slower the polaron hopping along the polymer chain or/and the lesser the probability p , the smaller is the number of ion-radical pairs that have a possibility to recombine and,

Table 2 ΔE_{ij} and E_a values determined from Eqs. (3) and (4), respectively, for radical pairs photoinduced in the P3DDT/PCBM composite by laser beam with different photon energies $h\nu_{ph}$ (all in eV)

	$h\nu_{ph}$		
Parameter	1.88	2.33	2.75
ΔE_{ij}	0.009	0.047	0.071
ΔE_a	0.019	0.016	0.029

**Fig. 3** Temperature dependences of isotropic (effective) peak-to-peak line width $\Delta B_{pp}^{(0)}$ determined far from microwave saturation for the polaron $P^{+\bullet}$ (open points) and methanofullerene anion radicals $mC_{60}^{\bullet-}$ (filled points) photoinduced in the P3DDT/PCBM composite by a laser with different photon energies $h\nu_{ph}$. The dependences calculated from Eq. (4) with E_a presented in Table 2 are shown by dashed lines

therefore, a higher spin susceptibility χ should be registered. Combining Eqs. (1) and (2), we can express χ as

$$\chi_p = \chi_{pn} + \chi_p^0 \frac{\hbar}{J} \left(\alpha + \frac{1}{\alpha} \right). \quad (3)$$

Assuming the absence of dipole–dipole interaction between methanofullerene anion radicals, one can determine ΔE_{ij} (see Table 2) and J parameters from the fitting of temperature dependences of paramagnetic susceptibility presented in Fig. 3.

It is seen from Fig. 2 that Eq. (3) with the ΔE_{ij} values presented in Table 2 and $J = 0.25$ eV fits the experimental data well. Figure 2 shows that localized charge carriers of both types are characterized by weaker $\chi(T)$ dependences as compared to that of mobile radical pairs. ΔE_{ij} obtained for mobile radical pairs increases monotonically with the growing photon energy $h\nu_{ph}$.

A lower limit of the peak-to-peak line width $\Delta B_{pp}^{(0)}$ obtained far from the microwave saturation conditions of the charge carriers depends on the temperature

as seen in Fig. 3. Analyzing the data presented, one can conclude that the effective $\Delta B_{pp}^{(0)}$ value of polarons varies monotonically and weakly depends on the sample heating. At the same time, fullerene radicals demonstrate more complex $\Delta B_{pp}^{(0)}(T, h\nu_{ph})$ dependence characterized by some critical temperature T_c . It is evident from Fig. 3 that both the $\Delta B_{pp}^{(0)}$ and T_c values are governed by the photon energy. Assuming exchange and activation interaction of the methanofullerene anion radical with a polaron diffusing along the polymer chain with the frequency ω_{hop} , the experimental data presented in Fig. 3 can probably also be described in terms of their exchange interaction. According to this approach, the collision of both types of spins should broaden the LEPR line by the value [40]

$$\delta(\Delta\omega) = p\omega_{hop}C = \frac{1}{2}\omega_{hop}C\left(\frac{\alpha^2}{1+\alpha^2}\right), \quad (4)$$

where p is the probability described by Eq. (2), $\omega_{hop} = \omega_{hop}^0 \exp(-E_a/k_B T)$, C is the number of paramagnetic centers per each polymer unit, and E_a is the activation energy.

E_a values determined from experimental data obtained at different photon energies are also summarized in Table 2. The analysis of the data presented allows the conclusion that the energy required for activation of polaron diffusion in the P3DDT/PCBM composite increases nonmonotonically with the energy of the photons initiating charge separation (see Table 2). However, this value seems to correlate with an appropriate change in activation energy of charge carriers dynamics in the P3DDT/PCBM composite [19, 28, 41].

It is seen that the main magnetic resonance parameters of both charge carriers are governed by the energy of excited photons. This can be a result either of formation of spin pairs with different properties in homogeneous composite fragments or of excitation of identical charge carriers in heterogeneous domains of a composite. The latter case when different spin pairs can be photoinduced as a result of photon-initiated appearance of traps with various depths in domains inhomogeneously distributed in the polymer matrix seems to be more realistic. These domains should be characterized by different ordering leading to different band gaps and, hence, by different sensitivity to optical photons.

4 Conclusion

Light excitation of the P3DDT/PCBM composite leads to a charge separation and transfer from a polymer chain to a fullerene globule. This is accompanied by the formation of two noninteracting paramagnetic centers with rhombic symmetry, namely, the positively charged polaron $P^{+\cdot}$ on the polymer backbone and the negatively charged methanofullerene anion radical $C_{60}^{-\cdot}$ situated between the polymer chains. A part of these charge carriers are trapped in a polymer matrix. Photoinduced charge is transferred by a mobile polaron along the polymer chain and can recombine with a fullerene anion radical. The probability of such collapse follows the activation law and depends on the energy of initiating photons. The main magnetic resonance parameters of both charge carriers are also governed by

the energy of light photons. This can be a result of a structural inhomogeneity of the polymer/fullerene composite that leads to the photon-initiated appearance of traps with different depth.

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