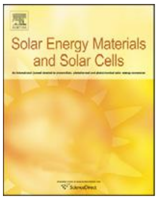
Solar Energy Materials & Solar Cells 95 (2011) 2302–2313

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Structural effect of electron acceptor on charge transfer in poly(3-hexylthiophene)/methanofullerene bulk heterojunctions

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ARTICLE INFO

Article history:
Received 8 February 2011
Received in revised form
26 March 2011
Accepted 30 March 2011
Available online 4 May 2011

Keywords:
LEPR
Polythiophene and derivatives
Fullerene
Polaron
Relaxation
Dynamics

ABSTRACT

Radical pairs, polarons and fullerene anion radicals photoinduced by photons with energy of 1.98–2.73 eV in bulk heterojunctions formed by poly(3-hexylthiophene) (P3HT) with *bis*(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6.6]C$_{62}$ (*bis*-PCBM) methanofullerene have been studied as compared with P3HT/PCBM composite by direct light-induced EPR (LEPR) method in a wide temperature range. A part of spin polarons and methanofullerene anion radicals are pinned in trap sites which number and depth are governed by an ordering of the polymer/fullerene system and energy of initiating photons. It has been shown that dynamics and recombination of mobile polarons and counter methanofullerene anion radicals are governed by their exchange- and multi-trap assisted diffusion. Relaxation and dynamics of both the charge carriers determined by the steady-state saturation method are governed by structure and conformation of their microenvironment as well as by the photon energy. Longitudinal diffusion of polarons was shown to depend on lattice phonons of crystalline domains embedded into an amorphous polymer matrix. The energy barrier required for polaron interchain hopping is higher than its intrachain diffusion. Pseudorotation of fullerene derivatives in a polymer matrix was shown to follow the activation Pike model. The replacement of PCBM by *bis*-PCBM provides higher anisotropy of polaron dynamics and decreases its selectivity to the photon energy. This makes spin dynamics easier and minimizes energy dispersion at charge transfer.

1. Introduction

In bulk heterojunction single-layer solar cells [1,2], in which power conversion efficiency have already attained about 6% [3], light photons generate singlet excitons, which are strongly bound due to weak screening in polymer semiconductor [4]. Such solar cells consist of an interpenetrating adsorbing network of soluble derivatives of polythiophene, poly(3-alkylthiophene) (P3AT), and fullerene embedded, 1-[3-(methoxycarbonyl)propyl]-1-phenyl-[6.6]C$_{61}$ (PCBM methanofullerene, $mC_{61}^{-\bullet}$) [5,6]. A relative position of the HOMO–LUMO levels and the choice of electrode materials which might show suitable work functions are basic requirements to make an optimal solar cell. If the HOMO of the donor (HOMO$_D$) lies higher than that of the acceptor (HOMO$_A$) and additionally LUMO$_D$ > LUMO$_A$, D→A charge transfer becomes energetically favorable for the electron. This provokes the turnover exciton to the (D–A)* complex which collapses into the D$^{+\bullet}$–A$^{-\bullet}$ radical pair due to structural relaxation [7]. To dissociate the exciton must be generated in close vicinity to the donor/acceptor interface, because its diffusion length is typically 5–7 nm [8]. Since a hole possesses high mobility along a polymer backbone, the radicals are scattered in this radical pair, so then two noninteracting spins, D$^{+\bullet}$ and A$^{-\bullet}$, are stabilized in bulk heterojunction. At each step, the D–A system can relax back to the ground state releasing energy to the lattice either as heat or emitted light. To maximize light converting properties, a donor should maintain a low HOMO energy level and a narrow band gap. An optimal energy difference LUMO$_D$–LUMO$_A$ should be 0.3–0.5 eV [9,10]. However, this value of bulk heterojunction formed by PCBM with macromolecules of poly(3-hexylthiophene) (P3HT) is much higher, namely, 1.1 eV. This results in so relatively low efficiency of the P3HT/PCBM solar cells.

There are some ways to reduce the above mentioned energy offset. One of them is to reduce the LUMO$_D$ level, however, it can increase efficiency up to 6.5% only [11]. A higher limit (8.4%) was predicted [11] to be more beneficial for solar cell when the LUMO$_A$ offset is reduced to 0.5 eV. The structure of donor and acceptor as well as the conformation of respective bulk heterojunction can also affect charge transport and recombination [12]. A real polymer/fullerene system consists of domains with different band gaps (i.e. different LUMO$_A$–HOMO$_D$) determining its energetic disordering with Gaussian distributed density of states [13]. Besides, planarity and regioregularity of polymer matrix, governed by structure of the polymer and methanofullerene side substitutes, play an important role in charge separation and transition in the polymer/fullerene composite. The presence of substituents additionally affects torsional and energetic disorder of polymer chains, thereby changing effective mobility of charge carriers. Side chain

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doi:10.1016/j.solmat.2011.03.045

groups accelerate torsional and librational chain dynamics modulating intrachain and interchain charge transfer, respectively. It was shown [14] that the torsional reordering of the backbone rings of conjugated polymers determines their electronic structure and charge transfer mechanism. Sensitivity of the average ring torsion angle between adjacent thiophene rings θ to steric repulsion and electron delocalization is manifested in the effects of derivatization and temperature on optical spectra of these materials. The less is a torsion angle θ, the higher is transfer integral and effective crystallinity. The increase in planarity reduces band gap, increases charge mobility, stability and interactions between parallel polymer planes. Modification of the P3HT/PCBM composite with N- or B-doped carbon nanotubes [15] and self-assembled dipole molecule deposition in plastic light-emitting diodes [16] can, in principle, to enhance their power conversion efficiency. Recently, Lenes et al. [17] have suggested to use another fullerene derivative as electron acceptor, namely, *bis*(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6.6]C_{62} (*bis*-PCBM methanofullerene, $bmC_{62}^{-\bullet}$) in which the fullerene cage is functionalized by two methanobridged PBM side groups, with a higher (by ~0.1 eV) $LUMO_A$ than that of PCBM. Indeed, quantum efficiency of plastic solar cells was appeared [18,19] to be improved as PCBM is replaced by *bis*-PCBM. However, it was shown [20] that photoluminescence dynamics becomes slower at such replacement due to the reorganization of bulk heterojunction. Besides, quantum efficiency can be reduced due to possible formation of triplets from intersystem crossing of the excitons or by intersystem crossing of the charge separated states followed by charge recombination [21]. Hence, the optimization of structure and nanomorphology of bulk heterojunctions as well as the understanding of photo-excitation, dynamics and recombination of charge carriers in such systems is of fundamental interest for controlled fabrication of optimal molecular photovoltaic devices. However, they are not yet understood in detail and there is no generally applicable model describing molecular, electronic and relaxation processes in P3HT with embedded PCBM and *bis*-PCBM counter-ions.

Magnetic, relaxation and dynamics properties of polarons $P^{+\bullet}$ (holes) stabilized in different organic polymer semiconductors were studied by direct conventional [22,23] and high-frequency/high-field [24–26] electron paramagnetic resonance (EPR) spectroscopy. In organic solar cells, fullerene anion radicals also possess spin $S=1/2$ and pseudorotate between polymer chains. As the excitons dissociate into ion radicals, mobile polarons flee from the fullerene anions along a conjugated polymer backbone faster than 10^{-9} s. Effective mobility of polarons in organic solar cells was calculated [27] to be lower than that of free electrons. That is a reason why spins in radical pairs can be considered as noninteracting; they are long-lived and demonstrate separate LEPR spectra. This accounts for a wide use of the light-induced EPR (LEPR) as direct method for investigation of fullerene-modified conjugated polymers [28,29]. LEPR measurements revealed the photoinducing under light irradiation of organic polymer/fullerene composite of polarons and fullerene anion radicals with different line shapes, magnetic resonance parameters and saturation properties. They are stabilized in different phases of a disordered polymer/fullerene bulk heterojunctions. The system inhomogeneity leads to the arising of traps in polymer matrix occupied by some carriers, which changes their magnetic resonance parameters and complicates effective LEPR spectrum. Therefore, by using such direct method it appears to be possible to control the texture and other structural and electronic properties of photovoltaic devices for the further increase in their efficiency. However, to date such LEPR studies are carried out mainly at helium temperatures when dynamic processes in organic photovoltaics appear to be frozen. Recently, we showed [30,31] that a LEPR spectra of charge carriers photoinduced in P3AT/PCBM bulk heterojunctions indeed contains contributions of mobile and pinned charge carriers with different spectrum shapes. Magnetic, relaxation and dynamics parameters of these radicals were demonstrated to be governed by the energy of initiated photons $h\nu_{ph}$ [29–32].

In the present work LEPR spectroscopy was used in a comparative study of main properties of charge carriers photoinduced in the P3HT/PCBM and P3HT/*bis*-PCBM bulk heterojunctions. We demonstrate the increase of dimensionality of this composition under the replacement of PCBM by *bis*-PCBM. Such substitution arranges polymer matrix, which then increases the planarity of a polymer matrix, decreases the number of traps, and, therefore, accelerates charge transfer through bulk heterojunctions.

2. Experimental details

In the study we used 99.5% PCBM and *bis*-PCBM methanofullerenes distributed by Solenne BV and regioregular P3HT with the average molecular weight 50,000 and 94% regioregularity from Rieke Metals. Chemical structures of these components are shown schematically in Fig. 1. Their ca. 1 wt% concentration solution in chlorbenzene at a 1:1 wt ratio was casted serially into a ceramic plane and dried until polymer/fullerene composites were formed as films with the size of ca. 4×8 mm^2 and thickness of ca. 0.1 mm. To determine maximal concentration of polarons which can be stabilized in polymer matrices, initial composites was treated by dry iodine vapor as described earlier [31].

The study was made using Luxeon III LXHL-LW3C (5500 K, 80 lm), LXHL-LD3C (625 nm, 1.98 eV, 100 lm), LXHL-LL3C (590 nm, 2.10 eV, 80 lm), LXHL-LM3C (530 nm, 2.34 eV, 80 lm), LXHL-LE3C (505 nm, 2.46 eV, 80 lm), and LXHL-LR3C (455 nm, 2.73 eV, 450 mW) with a spectral half bandwidth of ca. 0.1 eV (except LXHL-LW3C) LED light sources. Effective integral irradiation of these sources was estimated using an IMO-2N output power light irradiation bolometer to be rationed as 1.20:1.19:0.47:0.99:1.00:1.86, respectively. These rations were used for the further normalization of spin susceptibility. The optical irradiation spectra of the light sources used and absorption spectra of both polymer/fullerene composites shown in Fig. 1 were obtained using a Shimadzu UV–VIS–NIR scanning UV-3101PC spectrophotometer. Both composites demonstrate almost identical optical spectra characterized by the extrema at ca. 2.03 eV (612 nm), 2.20 eV (563 nm), and 2.39 eV (519 nm) lying near those characteristic of regioregular P3HT [33]. Besides, there are two peaks in the spectra (not shown) at 4.54 eV (273 nm) and 3.68 eV (337 nm) attributed to methanofullerenes.

EPR measurements were performed using an X-band (3-cm, 9.7 GHz) PS-100X spectrometer with maximal microwave (MW) power of 150 mW and 100 kHz field *ac* modulation for phase-lock detection. The samples placed in the center of MW cavity were permanently irradiated by light sources. “Dark” and photoinduced EPR spectra of the polymer/fullerene system and its ingredients were obtained 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 signal averaging at several (typical 4–6) acquisitions. Diphenylpicrylhydrazyl (DPPH) single microcrystal standard with $g_{iso}=2.0036(0)$ was used for estimation of *g*-factor of both charge carriers. To improve the signal-to-noise ratio of the LEPR spectra the averaging several (typical 4–6) acquisitions was made. The measurements of effective magnetic susceptibility of the “dark” (domestic) paramagnetic centers (PC) and PC photoinduced in polymer/fullerene bulk heterojunctions were performed using a 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) nitroxide radical. Absorption LEPR spectra were doubly integrated far from MW saturation conditions when magnetic

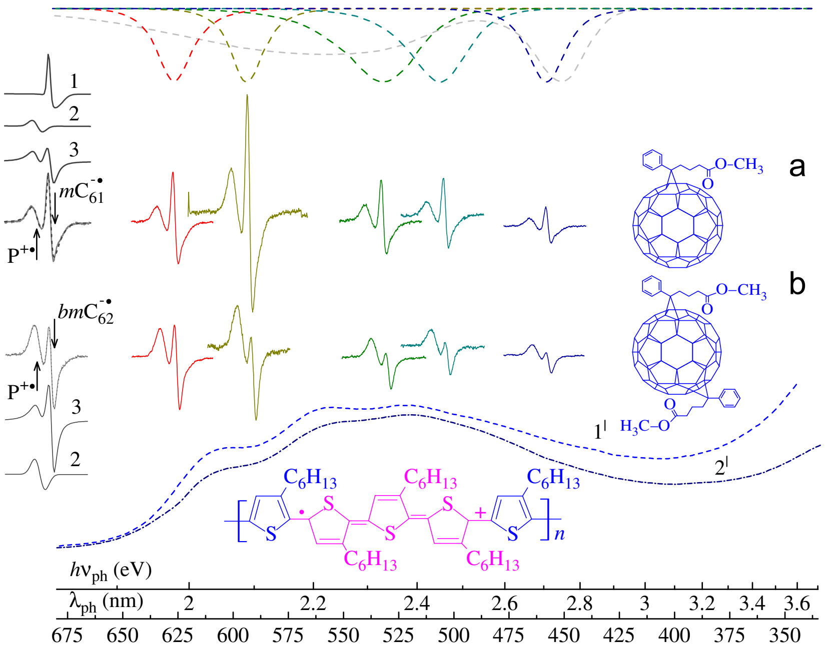

Fig. 1. Normalized LEPR spectra of charge carriers background photoinduced at 77 K in bulk heterojunctions formed by macromolecules of regioregular P3HT with globes of PCBM and *bis*-PCBM as function of the photon energy $h\nu_{ph}$ (linewidth λ_{ph}). From left to right: the spectra obtained at irradiation of the samples by white light and by the light with photon energy of 1.98, 2.10, 2.33, 2.45, 2.72 eV are shown. Dashed lines show irradiation spectra of the light sources (above) and UV–Vis absorption spectra of the P3HT/PCBM (1′) and P3HT/*bis*-PCBM (2′) composites (below). At the left are also shown theoretical sum spectra (dashed lines) and their Gaussian contributions caused by localized methanofullerenes $mF_{loc}^{-\bullet}$ (1), polarons $P_{loc}^{+\bullet}$ (2) and Lorentzian contribution of mobile radical quasi-pairs, $P_{mob}^{+\bullet} \leftrightarrow (b)mF_{mob}^{-\bullet}$ (3) calculated using respective magnetic resonance parameters and a concentration ratios $[P_{loc}^{+\bullet}]$:$[P_{mob}^{+\bullet} \leftrightarrow (b)mF_{mob}^{-\bullet}]$:$[mF_{loc}^{-\bullet}]$ of 6:57:1 for P3HT/PCBM and 15:87 for P3HT/*bis*-PCBM. The charge transfer from P3HT to the methanofullerene accompanied by the formation of polaron on the polymer chain is shown schematically. The positions of LEPR spectra of polarons, $P^{+\bullet}$, and methanofullerene anion radicals, $(b)mC_{62}^{-\bullet}$, are shown as well.

term B_1 of MW field and amplitude B_m of *ac* modulation in the cavity center did not exceed 0.05 and 1 G, respectively. The *g*-factor, amplitude *I* and peak-to-peak linewidth, ΔB_{pp} were determined with $\pm 1\times10^{-4}$, ±1.2% and $\pm 1\times10^{-2}$ G accuracy, respectively. All relaxation parameters of both type charge carriers were determined separately using the steady-state saturation method [34]. The error of determination of activation energies was near 5%. Processing and simulations of the EPR spectra were performed with the Bruker WinEPR SimFonia and OriginLab Origin programs.

3. Results and discussion

3.1. Spectral composition and g-factor

Detached P3HT, PCBM and *bis*-PCBM are characterized by the absence of both “dark” and photoinduced LEPR signals over the entire range of temperatures studied. As these ingredients form a polymer/fullerene composite and it is irradiated by visible light directly in a cavity of the EPR spectrometer, two overlapping LEPR lines appear at $T \leq 200$ K (Fig. 1). Low- and high-field lines photoinduced in the P3HT/*bis*-PCBM composite were attributed to positively charged polarons $P^{+\bullet}$ with isotropic (effective) Lande factor $g_{iso}^{P}=2.0023$ and negatively charged methanofullerene with $g_{iso}^{F}=2.0007$, which differ slightly from $g_{iso}^{P}=2.0017$ and $g_{iso}^{F}=1.9996$ obtained for P3HT/PCBM, however, are close to those obtained for polarons stabilized in other fullerene-modified conjugated polymers [29,35–38] and fullerene anion radicals [39]. Subsequent LEPR measurement cycles of heating up to room temperature, cooling down to $T \leq 200$ K, illumination with light, switching light off and heating up again yield identical data. LEPR spectra of the P3HT/PCBM composite, as in case of PCBM-modified poly(3-dodecylthiophene) (P3DDT) [30], consists of two Lorentzian contributions of mobile polarons, $P_{mob}^{+\bullet}$, and methanofullerene anion radicals, $mF_{mob}^{-\bullet}$ (shown in Fig. 1 as radical quasi-pairs 3, $P_{mob}^{+\bullet} \leftrightarrow mF_{mob}^{-\bullet}$) as well as two Gaussian contributions of localized polarons, $P_{loc}^{+\bullet}$, and methanofullerene anion radicals, $mF_{loc}^{-\bullet}$, pinned in polymer traps. $P_{loc}^{+\bullet}$ and quasi-pairs also contribute into LEPR spectra of the P3HT/*bis*-PCBM composite, however, there is absent contribution of pinned *bis*-methanofullerene radicals, $bmF_{loc}^{+\bullet}$ (Fig. 1). This implies that the number of deep traps able to capture a radical anion in the P3HT/*bis*-PCBM composite is sufficiently lower than that in the P3HT/PCBM one due to the better ordinary of the former. The best fit of the LEPR spectra of the samples was achieved using a convolution of Gaussian and Lorentzian line shapes, which means that electron excitation leads to inhomogeneous and homogeneous line broadening, respectively, due to unresolved hyperfine interaction of unpaired spin with neighboring protons and also to its different mobility.

Methanofullerene anion radicals photoinduced in both systems studied demonstrate nearly temperature independent g_{iso}^{F}. On the other hand, this parameter of polaronic charge carriers, g_{iso}^{P}, was occurred to be a function of temperature and, to a less extent, of photon energy $h\nu_{ph}$ (see Fig. 2). It is seen from Fig. 3 that the temperature increase leads to the decrease in g_{iso}^{P} especially in the P3HT/PCBM composite. It can be noted, that as PCBM counter ions are replaced by *bis*-PCBM ones, the scattering in $g(T)$ dependences decreases possibly due to the ordering of the polymer/fullerene composite. In the other words, this parameter is strongly governed by the structure and conformation of a conjugated π-electron system. Our high-frequency (140 GHz) EPR study of structurally close poly(3-octylthiophene) (P3OT) showed [40,41] that an unpaired electron delocalized on polaron and extended over *L* lattice units weakly interacts with sulfur heteroatoms involved in the polymer backbone. This provokes rhombic symmetry of spin density and, therefore, anisotropic *g*-factor and linewidth. Since the backbone of the polymer can be expected to lie preferably parallel to the film substrate [42], the lowest principal *g*-value is associated with the polymer backbone. The macromolecule can take any orientation relative to the *z*-axis, i.e. the polymer backbone direction as is derives from the presence of both the g_{xx} and g_{yy} components in the spectra for all orientations of the film. Thus, the *g*-factor anisotropy is a result of inhomogeneous distribution of additional fields along the *x* and *y* directions within the plane of the polymer σ-skeleton rather than along its perpendicular *z* direction. The analogous conclusion was made later by Aguirre et al. [43] justified by the 94 GHz EPR study that the spin in polaron induced in the P3HT matrix by light and I_2-doping is also characterized by rhombic symmetry originating anisotropic *g*-factor with $g_{xx}=2.0028$, $g_{yy}=2.0019$, $g_{zz}=2.0009$ and $g_{xx}=2.0029$, $g_{yy}=2.0019$, $g_{zz}=2.0011$, respectively. Similar spin density symmetry and $g_{xx}=2.00031$, $g_{yy}=2.00011$, and $g_{zz}=1.99821$ were obtained at this waveband for the $C_{61}^{-\bullet}$ radical anion embedded into another organic polymer matrix [44]. Our high-frequency/field (140 GHz, 5 kG) EPR study of structurally close poly(3-octylthiophene) (P3OT) showed [40,41] that weak interaction of an unpaired electron delocalized on polaron with sulfur heteroatoms involved in the polymer backbone provokes rhombic symmetry of spin density and, therefore, anisotropic *g*-factor with $g_{xx}=2.00409$, $g_{yy}=2.00332$ and $g_{zz}=2.00235$. Since the backbone of the polymer can be expected to lie preferably parallel to the film substrate [42], the lowest principal *g*-value is associated with the polymer backbone. The molecule can take any orientation relative to the *z*-axis, i.e. the polymer backbone direction as is derives from the presence of both the g_{xx} and g_{yy} components in the spectra for all orientations of the film. Thus, the *g*-factor anisotropy is a result of inhomogeneous distribution of additional fields along the *x* and *y* directions within the plane of the polymer σ-skeleton rather than along its perpendicular *z* direction. Later, Aguirre et al. [43] justified by EPR study at 94 GHz waveband that the spin in polaron induced in the P3HT matrix by light and I_2-doping is also characterized by rhombic symmetry originating anisotropic *g*-factor with $g_{xx}=2.0028$, $g_{yy}=2.0019$, $g_{zz}=2.0009$ and $g_{xx}=2.0029$, $g_{yy}=2.0019$, $g_{zz}=2.0011$, respectively. Similar spin density symmetry and $g_{xx}=2.00031$, $g_{yy}=2.00011$, and $g_{zz}=1.99821$ were obtained at this waveband for the $C_{61}^{-\bullet}$ radical anion embedded into another organic polymer matrix [44].

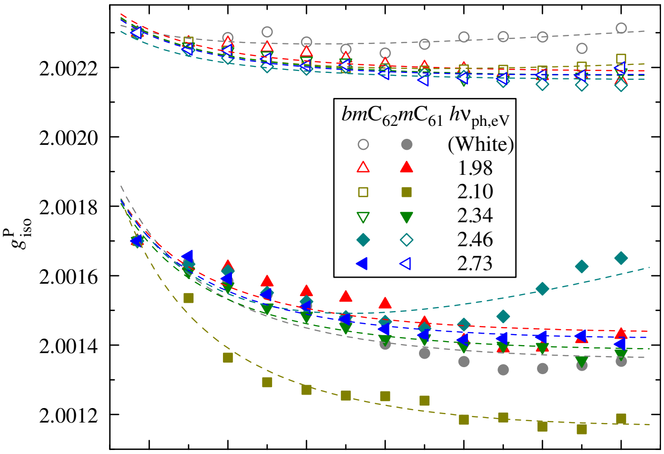

Fig. 2. The value of g_{iso}^{P} for polarons photoinduced in the P3HT/*bis*-PCBM and P3HT/PCBM bulk heterojunctions as a function of photon energy $h\nu_{ph}$ and temperature. The dependences calculated from Eq. (2) with $\hbar\omega_l$ summarized in Table 1 are shown by appropriate dashed lines.

Generally, *g*-factor is determined by non-compensated orbital momentum of its spin, which induces an additional magnetic field due to the σ→π→σ* excitations [45]:

$$g = g_e - g_e\lambda\rho(0)\left(\frac{1}{\Delta E_{\sigma\pi}} - \frac{1}{\Delta E_{\pi\sigma^*}}\right), \tag{1}$$

where $g_e=2.00232$ is *g*-factor of free electron, λ is constant of spin–orbital coupling of spin with C or S nuclear, $\rho(0)$ is spin density on the nucleus, $\Delta E_{\sigma\pi}$ and $\Delta E_{\pi\sigma^*}$ are energy differences between the σ and π levels, and between the π and σ* levels, respectively. The orbital moment due to direct π–π* excitation is negligible and is pronounced on the neighboring C atoms only. The HOMO energy level depends on the overlap of adjacent thiophene MOs and, therefore, is expected to shift with ring angle [46] similarly to the valence band involved in the π–π* transition. The band gap, LUMO–HOMO, slightly depends on both temperature [47] and torsion angle θ [48], being near 30° in regioregular P3HT [49]. A decrease in g_{iso}^{P} occurs at electron excitation from the unoccupied shell to the antibonding orbit, π→σ* [50]. Comparing the data obtained one may conclude that the energy of antibonding orbits decreases as *bis*-PCBM is embedded into the P3HT

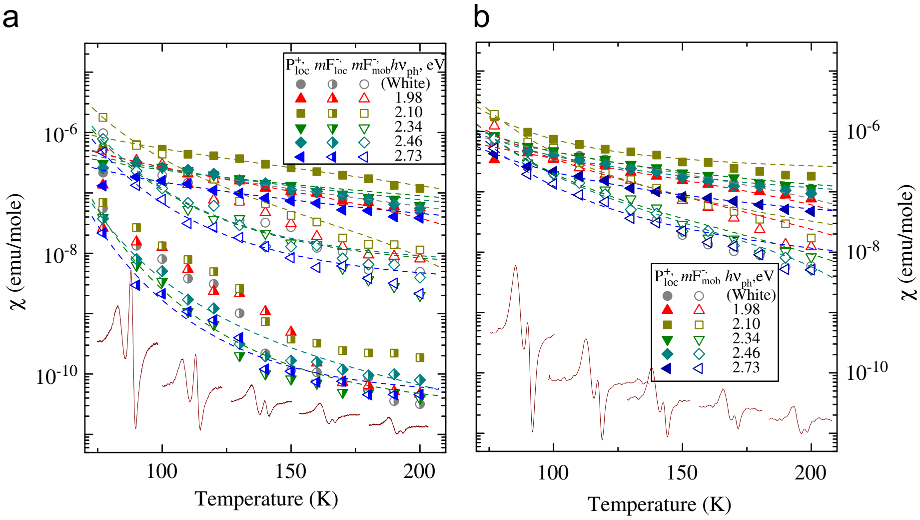

Fig. 3. Temperature dependence of paramagnetic susceptibility of the $P_{loc}^{+\bullet}$, $mF_{loc}^{-\bullet}$ and $mF_{mob}^{-\bullet}$ charge carriers photoinduced in bulk heterojunctions formed by P3HT chains with the PCBM (a) and *bis*-PCBM (b) methanofullerenes by photons with different energy $h\nu_{ph}$. Dashed lines show some dependences calculated from Eq. (5) with ΔE_{ji} summarized in Table 1. LEPR spectra of these heterojunctions registered at respective temperatures are shown at the bottom.

matrix instead of PCBM. This increases $g_{\mathrm{iso}}^{\mathrm{P}}$ of the P3HT/*bis*-PCBM composite and decreases the slope of its temperature dependency characteristic of more ordered system. Indeed, the changes in total energy with the torsion angle θ appear as effective steric potential energy. The angular dependence of this energy is anharmonic, with larger angles becoming more probable with the temperature increase. In this case the decrease of molecular regioregularity or a greater distortion of the thiophene rings out of coplanarity reduces charge mobility along the polymer chains [51]. This is usually attributed to a decrease in the effective conjugation lengths of the chain segments. The intrachain transfer integral $t_{1\mathrm{D}}$ is primarily governed by the degree of overlap between the p_z atomic orbitals of the carbon atoms forming polymer units and, therefore, should evolve a square-cosine function of the torsion angle θ between the planes of the neighboring thiophene rings [52]. This allow one to evaluate the decrease in the θ value by nearly 12° at the replacement of the PCBM by *bis*-PCBM in the P3HT/methanofullerene system. Therefore, this indicates a more planar and ordered polymer matrix in the P3HT/*bis*-PCBM composite than in the P3HT/PCBM one.

The temperature dependences presented in Fig. 3, can be explained *inter alia* by joint harmonic librations of polymer chains together with localized polarons which modulate the charge transfer integrals [53]. This should change effective g-factor as

$$g = g_0 + \frac{A}{\omega_{\mathrm{l}}} \coth\left(\frac{\hbar\omega_{\mathrm{l}}}{2k_{\mathrm{B}}T}\right), \tag{2}$$

where g_0 and A are constants, $h = 2\pi\hbar$ is the Planck constant, $\omega_{\mathrm{l}} = \omega_0 \exp(-E_{\mathrm{l}}/k_{\mathrm{B}}T)$ is librational frequency, E_{l} is the energy required for activation of such a motion, and k_{B} is the Boltzmann constant.

Fig. 2 shows that the $g(T)$ dependences experimentally obtained can be fitted by Eq. (2) with $\hbar\omega_{\mathrm{l}}$ summarized in Table 1. Temperature sensitivity of polaron g-factor decreases at high temperatures. Such effect can be attributed to fluctuations in local symmetry of the hexyl side groups relative to the main polymer axis. These groups begin to move at glass transition of the polymer matrix near 200 K [54], and their local relaxation contributes to the topological disorder in the polymer structure and leads to the increase in energy barriers of charge transport. The temperature dependence of g-factors is argued to be due to a coupling of the holes to local vibrations of the chains or/and side hexyl groups along a backbone of the polymer matrix. Such motion in the P3HT/*bis*-PCBM composite occurs mainly with the lower activation energy than in the P3HT/PCBM one (see Table 1).

Table 1

Energies $\hbar\omega_{\mathrm{l}}$ in Eq. (2), ΔE_{ij} in Eq. (5), E_0 in Eq. (6) determined for activation of polaron librational and intrachain dynamics in the P3HT/PCBM and P3HT/*bis*-PCBM composites irradiated by polychromatic white and monochromatic light with different photon energy $h\nu_{\mathrm{ph}}$ (all in eV).

Parameter	**White**	$h\nu_{\mathrm{ph}}$				
		1.98	**2.10**	**2.34**	**2.46**	**2.73**
P3HT/PCBM						
$\hbar\omega_{\mathrm{l}}$	0.0098	0.0100	0.0097	0.0099	0.0056	0.0095
ΔE_{ij}, [a]	0.0092	0.0054	0.0028	0.0017	0.0048	0.0066
ΔE_{ij}, [b]	0.0607	0.0307	0.0476	0.0663	0.0793	0.0744
ΔE_{ij}, [c]	0.0304	0.0258	0.0438	0.0540	0.0558	0.0569
E_0, [a]	0.0134	0.0519	0.0430	0.0088	0.0082	0.0318
E_0, [b]	0.0103	0.0181	0.0208	0.0113	0.0075	0.0163
E_0, [c]	0.0210	0.0236	0.0296	0.0307	0.0186	0.0169
P3HT/*bis*-PCBM						
$\hbar\omega_{\mathrm{l}}$	0.0053	0.0093	0.0066	0.0097	0.0088	0.0081
ΔE_{ij}, [a]	0.0027	0.0014	0.0288	0.0140	0.0162	0.0177
ΔE_{ij}, [c]	0.0171	0.0239	0.0404	0.0350	0.0375	0.0413
E_0, [a]	0.0309	0.0409	0.0272	0.0184	0.0144	0.0107
E_0, [c]	0.0080	0.0202	0.0136	0.0198	0.0222	0.0227

[a] Determined for $\mathrm{P}_{\mathrm{loc}}^{+\bullet}$.
[b] Determined for $m\mathrm{F}_{\mathrm{loc}}^{-\bullet}$.
[c] Determined for $m\mathrm{F}_{\mathrm{mob}}^{-\bullet}$.

3.2. Paramagnetic susceptibility

To determine the limiting number of polarons able to be stabilized in a polymer matrix and to compare magnetic resonance parameters of polarons reversibly and irreversibly initiated in a polymer matrix, its modification by, e.g., iodine molecules [43,44] can be used. However, this allows one to modify an initial polymer only. As in case of other polymer/fullerene systems [31], to obtain the limiting number of both polarons n_{p} and methanofullerene anion radicals n_{f} simultaneously formed per each polymer unit, we used I_2-doping of both composites under study. Limiting paramagnetic susceptibility χ was determined to be 8.7×10^{-6} emu/mole for P3HT/PCBM and 1.1×10^{-5} emu/mole for P3HT/*bis*-PCBM at $T = 310$ K. As temperature decreases down to 77 K, these values increase to 8.7×10^{-5} and 9.9×10^{-5} emu/mole, respectively. Besides, the analysis showed that the cooling of the samples leads to the appearance of anisotropic Gaussian term in the sum EPR spectra attributed to strongly frozen polarons. The ratio of a number of mobile to frozen polarons at 77 K is near 8:1 for P3HT/PCBM and 7:1 for P3HT/*bis*-PCBM. Mobile polarons initiated in P3HT/PCBM and P3HT/*bis*-PCBM by the I_2-doping at 310 K demonstrate single Lorentzian EPR spectra with peak-to-peak linewidth ΔB_{pp} of 4.0 and 5.6 G, respectively, which are much broader than that obtained for polarons in other conjugated polymers [25]. The broadening of the EPR transitions becomes most likely due to dipole–dipole interaction between charged polarons. The contribution to linewidth due to such interaction can be estimated as $\Delta B_{\mathrm{dd}} = \mu_{\mathrm{B}} R_0^{-3} = 4/3\pi\mu_{\mathrm{B}} n_{\mathrm{p}}$, where μ_{B} is Bohr magneton, R_0 is distance between polarons proportional to their concentration n_{p} on the polymer chain. At the transition from PCBM to *bis*-PCBM counter-anion, the ΔB_{pp} value of mobile and trapped polarons characterized by Lorentzian and Gaussian distribution of spin packets, respectively, changes at 77 K from 1.9 and 2.3 G down to 1.8 and 1.9 G. Assuming intrinsic linewidth of polarons $\Delta B_{\mathrm{pp}}^0 = 1.5$ G in regioregular P3HT [55], one can obtain from the line broadening as a result of dipole–dipole interaction $R_0 \approx 1.6$ nm for P3HT/PCBM and 1.3 nm for P3HT/*bis*-PCBM. Intrinsic concentration of doping-initiated polarons counting only upon polymer fraction in the P3HT/PCBM and P3HT/*bis*-PCBM composites was determined to be 1.6×10^{19} and 2.2×10^{19} cm^{-3}, respectively, at 77 K. This value lies near 2×10^{19} cm^{-3} obtained for concentration of acceptors in ZnO-treated P3HT [56]; however, less sufficiently than 10^{21} cm^{-3} supposed for maximum polaron concentration in regioregular P3HT [57]. Effective concentration calculated for both polymer and fullerene phases in the P3HT/PCBM and P3HT/*bis*-PCBM composites is 1.8×10^{18} and 2.1×10^{18} cm^{-3}, respectively. This allows one to evaluate an effective number of both types of charge carriers per each polymer unit initiated in the polymer/fullerene composites by I_2-doping and light irradiation (Table 2). The n_{P} values obtained are considerably lower than that, $n_{\mathrm{p}} \approx 0.05$, estimated for polarons excited in doped polyaniline [58].

Fig. 3 illustrates the changes in LEPR spectra of both the composites with their heating and shows temperature dependences of all contributions into sum χ. Since concentration of main charge carriers decreases dramatically at $T > 200$ K, the precision of determination of their spin susceptibility falls significantly. The fitting of their double integrated sum LEPR spectra allowed us to obtain separately all terms of effective paramagnetic susceptibility χ. This value consists of the contributions of mobile and localized polarons χ_{P} and methanofullerene anion

Table 2
Concentration of polaron n_p and methanofullerene n_f charge carriers per each polymer unit induced in the P3HT/PCBM and P3HT/*bis*-PCBM composites by the I_2-doping and irradiation at 77 K by polychromatic white and monochromatic light with different photon energy $h\nu_{ph}$ (in eV).

Parameter	I_2-Doping	White	$h\nu_{ph}$				
			1.98	**2.10**	**2.34**	**2.46**	**2.73**
P3HT/PCBM							
n_p	2.8×10^{-3}	4.9×10^{-5}	3.9×10^{-5}	9.7×10^{-5}	4.2×10^{-5}	4.3×10^{-5}	2.4×10^{-5}
n_f	–	4.2×10^{-5}	2.5×10^{-5}	7.7×10^{-5}	3.1×10^{-5}	3.4×10^{-5}	2.1×10^{-5}
P3HT/*bis*-PCBM							
n_p	3.8×10^{-3}	9.7×10^{-5}	7.6×10^{-5}	1.6×10^{-4}	7.0×10^{-5}	6.5×10^{-5}	4.9×10^{-5}
n_f	–	7.2×10^{-5}	5.2×10^{-5}	7.7×10^{-5}	3.3×10^{-5}	3.2×10^{-5}	2.2×10^{-5}

radicals χ_F. In χ of the P3HT/*bis*-PCBM composite the contribution of localized fullerene anion radicals is absent within the whole temperature range used.

Illuminating a polymer/fullerene bulk heterojunction one can register only the net paramagnetic centers as a difference of forward initiating (fast) and reversed recombination (slow) processes. The probability of the latter is mainly governed by polaron multistage diffusion along a polymer chain through an energetic barrier and electron further tunneling from a fullerene anion to a polymer chain [59]. Motion of polarons is assumed to be described by the a multiple trapping in sites with respective energy E_t [60,61]. Since crystalline subsystems in a composite are characterized by different band gaps, their E_t energies are also different and distributed exponentially. If energy of a trapped polaron exceeds E_t, it is occasionally thermally detrapped to the free state. A positive charge of polaron is not required to be recombined with negative charge on first fullerene. Diffusing along polymer backbone with positive elemental charge it may collide with the nearest fullerene radical anion located between polymer chains and then to recombine with a charge on a subsequent counter-anion. Assuming that polaron motion is not disturbed by the presence of fullerene molecules, we can conclude that the collision duration is governed by polaron diffusion. As it walks randomly along the chain, it passes a given fullerene molecule with frequency $\nu_c \approx \omega_{hop}/L^2$. The polaron that diffuses between initial *i* and final *j* sites spatially separated by distance R_{ij} spends the energy equal to the difference of their depths, ΔE_{ij}. Thus, the Miller-Abrahams energy-dependent factor should appear in the equation for paramagnetic susceptibility [60]

$$\chi = \chi_0 \exp\left(-\frac{2R_{ij}}{r}\right)\exp\left(\frac{\Delta E_{ij}}{k_B T}\right), \tag{3}$$

where *r* is effective localization (Bohr) radius of a charge carrier. A positive charge of polaron is not required to be recombined with negative charge on first methanofullerene, it can to recombine with a charge on a subsequent counter-ion. The fullerene molecules can be considered as fast relaxing impurities, and the spin flip-flop probability *p* during such a collision should depend on the exchange amplitude and the frequency of polaron diffusion ω_{hop} as [58,62]

$$p = \frac{1}{2}\frac{\alpha^2}{1+\alpha^2}, \tag{4}$$

where $\alpha = (3/2)\ 2\pi J/\hbar\omega_{hop}$ and *J* is a constant of exchange interaction of spins in a interim radical pair. It is evident that the longer time of charge tunneling or/and the lower probability *p*, the smaller a number of photoinduced charge carriers able to recombine and, therefore, the higher a spin susceptibility should be registered. Generally, weak and strong exchange limits can be realized in such spin system. In the case of weak or strong exchange, the increase of ω_{hop} may result in the decrease or the increase in exchange frequency, respectively. A combination of Eqs. (3) and (4) affords a general form of this main parameter for polarons in polymer/fullerene composite:

$$\chi = \chi_0 \frac{2(1+\alpha^2)}{\alpha^2}\exp\left(-\frac{2R_{ij}}{r}\right)\exp\left(\frac{\Delta E_{ij}}{k_B T}\right). \tag{5}$$

Assuming the absence of a dipole–dipole interaction between fullerene anion radicals, one can evaluate energy ΔE_{ij} for all charge carriers from temperature dependences of their paramagnetic susceptibility (see Table 1). As it is seen from Fig. 3, the net electronic processes in the composites can be described in terms of spin exchange with ΔE_{ij} presented in Table 1.

It is evident that the energy required for polaron trapping in the polymer matrix is lower than that obtained for other charge carriers. ΔE_{ij} evaluated from $\chi(T)$ for mobile radicals increases considerably indicating higher energy required for their trapping in the system. This value becomes larger for methanofullerene if it is pinned by a polymer matrix of the P3HT/PCBM composite. The data obtained evidence one more that all spin-assisted processes are governed mainly by the structure of radical anion as well as by the nature and dynamics of charge carriers photoinduced in its bulk heterojunction. It is seen that the χ value of both charge carriers becomes distinctly higher at characteristic energy $h\nu_{ph} \approx 2.1$ eV lying near the band gap of P3AT [63]. Such a dependence of spin concentration on photon energy can be explained either by the formation of spin pairs with different properties in homogeneous (higher ordered) composite fragments or by the excitation of identical charge carriers in heterogeneous domains (lower ordered) of the system under study. Different spin pairs can be photoinduced in result of the photon-assisted appearance of traps with different energy depths in a polymer matrix. However, the revealed difference in the parameters of radicals seems to be a result of their interaction with their microenvironment in domains inhomogeneously distributed in polymer/fullerene composite. Different ordering of these domains can be a reason for variation in their band gap energy leading, hence, to their sensitivity to photons with definite but different energies. This can give rise to the change in the interaction of charge carriers with a lattice and other spins. Effective spin susceptibility of the P3HT/*bis*-PCBM composite somewhat exceeds that obtained for P3HT/PCBM one. This effect and the absence of trapped anion radicals in the former allow a conclusion on additionally more ordered bulk heterojunctions in the P3HT/*bis*-PCBM composite which interfere in the formation of traps.

If one includes Coulomb interactions, this should affect the activation energy for either defrosting or thermally assisted tunneling by an amount $U_c = e^2/4\pi\varepsilon\varepsilon_0 r$, where *e* is elemental charge, ε is a dielectric constant, and *r* is charge pair separation. Assuming $\varepsilon = 3.4$ for P3HT [64], minimum separation of charge carriers is equal to the radius of π electrons on the C atoms *a* which two times longer than the Bohr radius, i.e. 0.106 nm, *r* equal to interchain separation, 0.38 nm [65], one obtains the decrease in U_c from ~0.4 eV down to 0.02 eV during dissociation of an initial radical pair. Therefore, both the photoinduced polaron and the anion radical should be considered as noninteracting that prolongs their life.

When initiating background illumination is switched off, photoinitiation of charge carriers in bulk heterojunction stops and the concentration of spin charge carriers excited starts to decrease as shown in the insert of Fig. 4. Live time of charge carriers seems to be much longer than $t \sim 0.1$ μs obtained by optical absorption spectroscopy for relevant recombination times of mobile photoexcitations in organic solar cells [1,2]. Therefore, the data presented are mainly pertinent to carriers trapped in polymer matrix. Charge recombination, generally, is described as a thermally activated bimolecular recombination [66] which consists of temperature-independent fast and exponentially temperature-dependent slow steps [57]. At the latter step, polaronic charge carrier can either be retrapped by vacant trap sites or recombine with electron on fullerene radical anion. Trapping and retrapping of a polaron reduces its energy that results in its localization into deeper trap and in the increase in number of localized polarons with time. So, the decay curves presented can be interpreted in terms of bulk recombination between holes and electrons during their repeated trapping into and detrapping from trap sites with different depths in energetically disordered semiconductor [61]. Analyzing LEPR spectra, it becomes possible to separate the decay of mobile and pinned spin charge carriers excited in the composite. The traps in such a system should be characterized by different energy depths and energy distribution E_0. Polarons fast translative diffuse along a polymer backbone, and fullerene anion radicals can be considered to be immobilized between polymer chains. This approach predicts the following law for decay of charge carriers [61]:

$$\frac{n(t)}{n_0} = \frac{\pi\alpha\delta(1+\alpha)\nu_d}{\sin(\pi\alpha)} t^{-\alpha}, \tag{6}$$

where n_0 is the initial number of polarons at $t=0$, δ is the gamma function, $\alpha = k_B T/E_0$, ν_d is the attempt jump frequency for polaron detrapping.

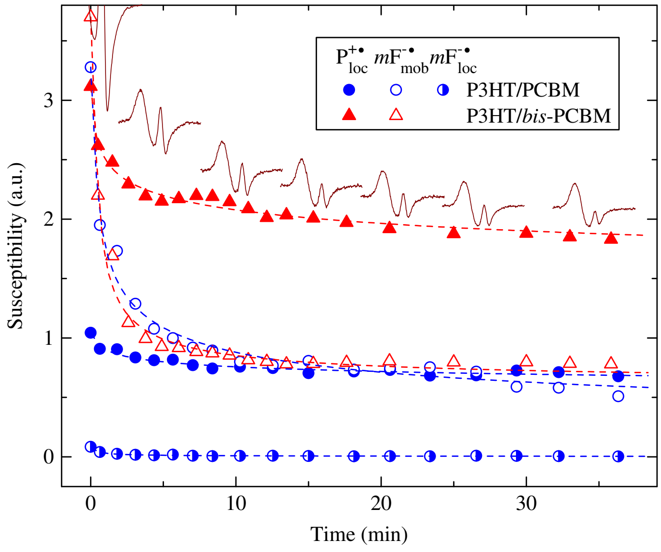

Fig. 4. Decay of spin susceptibility of pinned polarons $P^{+\bullet}_{loc}$ (filled points) as well as pseudorotating ($mF^{-\bullet}_{mob}$, open points) and pinned ($mF^{-\bullet}_{loc}$, semi-filled points) methanofullerenes photoinduced in the bulk heterojunction of P3HT/PCBM (circles) and P3HT/*bis*-PCBM (triangles) systems by photons with $h\nu_{ph}=2.73$ eV at 77 K. Dashed lines show the dependences calculated from Eq. (6) with ΔE_0 summarized in Table 1. Typical changes in the LEPR spectrum of a polymer/fullerene composite at appropriate time *t* is shown as well.

The dependences calculated with E_0 presented in Table 1 for charge carriers photoinduced in the bulk heterojunctions studied are also presented in Fig. 4. It is shown that Eq. (6) fits well the experimental data presented in Fig. 4. Therefore, the decay of long-lived charge carriers originated from initial spin pairs photoinduced in the polymer/fullerene composite can successfully be described in terms of the above model in which the low-temperature recombination rate is strongly governed by temperature and the width of energy distribution of trap sites.

The analysis of the experimental data allows one to conclude the crucial role of the photon energy on the formation and energy properties of the traps in a bulk heterojunction of disordered systems. This parameter obtained for the sites occupied by both localized polarons and fullerene anion radicals in P3HT/PCBM changes extremely with $h\nu_{ph}$ attaining the minimum at ~2.4 eV. The width of energy distribution of the traps in the P3HT/*bis*-PCBM system decreases with growing $h\nu_{ph}$. On the other hand, mobile charge carriers are characterized by extremal $E_0(h\nu_{ph})$ dependences with a maximum at ~2.3 eV for P3HT/PCBM and a minimum at ~2.1 eV for P3HT/*bis*-PCBM (Table 1). This indicates that the local structure and ordering govern the depth of spin traps and their distribution in these composites.

3.3. Linewidth

Effective EPR linewidth of both charge carriers photoinduced in the P3HT/fullerene composites is presented in Fig. 5 as a function of temperature and photon energy. It is seen that this value obtained for polarons in the P3HT/PCBM and P3HT/*bis*-PCBM systems is characterized by ∩-like temperature dependence with the extreme lying near 140 and 130 K, respectively, and remain almost unchanged at the exchange of the fullerene derivatives. Linewidth of the methanofullerene anion radicals demonstrates more monotonic temperature dependence and decreases with the system heating (Fig. 5).

This value is mainly determined by transverse (spin–spin) relaxation time T_2. However, there are several relaxation processes in a polymer/fullerene system which cause the shortening of T_2 and hence the broadening of the EPR line. One of them is spin longitudinal (spin-lattice) relaxation on the lattice phonons with time T_1, which shortens the lifetime of a spin state and therefore broadens the line. If we represent all other possible relaxation processes by time $T_2^{|}$, we can write for effective peak-to-peak width ΔB_{pp} of a Lorentzian line [67,68]

$$\Delta B_{pp} = \frac{2}{\sqrt{3}\gamma_e}\frac{1}{T_2} = \frac{2}{\sqrt{3}\gamma_e}\left(\frac{1}{T_2^{|}} + \frac{1}{2T_1}\right). \tag{7}$$

Paramagnetic centers of both spin reservoirs can dipole–dipole interact. Besides, sulphur and hydrogen atoms in a polymer/fullerene composite possess a nuclear magnetic moment initiating the hyperfine interaction between the electrons and the nuclei. Polaron translational and fullerene pseudorotational diffusion in a polymer/fullerene composite should also be taken into account. While polaron possesses high mobility, the fullerene molecule can be considered as a translative fixed one, but pseudorotating near its own main molecular axis. In this case a polaron should interact with its unpaired electron with the collision probability *p* expressed by Eq. (4), so then its absorption line should additionally be broaden by the value [58,62]

$$\delta(\Delta\omega) = p\omega_{hop}n_f = \frac{1}{2}\omega_{hop}n_f\left(\frac{\alpha^2}{1+\alpha^2}\right), \tag{8}$$

where n_f is a number of methanofullerene radicals per polymer unit (see Table 2). The rate of charge hopping between two adjacent identical thiophene rings can be estimated to a good

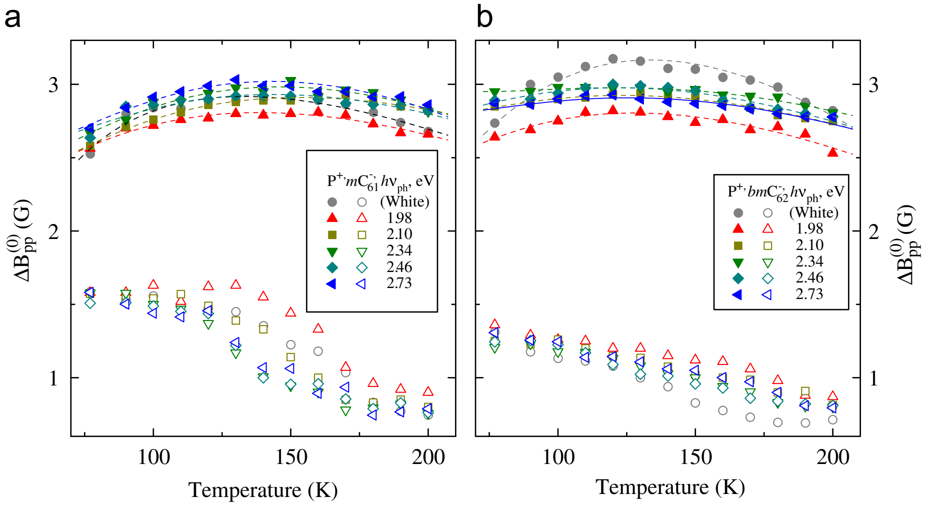

Fig. 5. Linewidth of charge carriers photoinduced in the P3HT/PCBM (a) and P3HT/*bis*-PCBM (b) composites as a function of temperature and photon energy $h\nu_{ph}$. Dashed lines show the dependences calculated from Eq. (10) with E_t presented in Table 3. The symbol (0) in $\Delta B_{pp}^{(0)}$ implies that the LEPR spectra were measured far from MW saturation, when $B_1 \to 0$.

approximation using a semiclassical Marcus theory adopted for conjugated polymers [51,52]

$$\omega_{hop}=\frac{4\pi^2}{\hbar}\frac{t_{1D}^2}{\sqrt{4\pi E_r k_B T}}\exp\left(-\frac{E_r}{4k_BT}\right), \tag{9}$$

where t_{1D} is electronic coupling between initial and final states (intrachain transfer integral) and E_r is both the inner- and outer-sphere reorganization energy of charge carriers due to their interaction with the lattice phonons. The t_{1D} value was obtained for regioregular P3HT to be equal to 1.18 eV and to decrease slightly with temperature, whereas its distribution broadens a line due to thermal motion of the rings [47]. This is similar to charge transfer in organic crystals modulated by disorder caused by thermal molecular motion [69,70]. Note that the n_f parameter is temperature dependent which should be included into finalized equation. Combination of Eqs. (8) and (9) yields

$$\delta(\Delta\omega)=\frac{\pi t_{1D}^2 n_F(T)}{\hbar\sqrt{(E_t k_B T/\pi)}}\,\frac{\exp(-(E_t/4k_BT))}{1+\left[(3J/2t_{1D}^2)\sqrt{(E_t k_B T/\pi)}\exp(E_t/4k_BT)\right]^{-2}}. \tag{10}$$

The dependences calculated from Eq. (10) with E_t summarized in Table 3 are also presented in Fig. 5. The fitting is evidence of the applicability of these approaches for interpretation of electronic processes realized in the composite studied. The energy E_t obtained lies near that evaluated for regioregular P3HT from ac conductometric (0.080 eV) [71] and ^{13}C NMR (0.067–0.085 eV at $T < 250$ K) [54] data. Fig. 5 shows that linewidth of the methanofullerene anion radicals decreases with the system heating. Besides, this value decreases at the replace of the PCBM acceptor by *bis*-PCBM in polymer/fullerene composite. The latter fact additionally indicates more ordered structure of the P3HT/*bis*-PCBM composite as compared with P3HT/PCBM one.

Table 3
Energies E_t in Eqs. (10) and (14), E_{ph} in Eq. (13), σ_0 in Eq. (14), and E_b in Eq. (15) characteristic of mobile charge carriers photoinduced in the P3HT/PCBM and P3HT/*bis*-PCBM composites by polychromatic white and monochromatic light with different photon energy $h\nu_{ph}$ (all in eV).

Parameter	**White**	***hν***				
		1.98	**2.10**	**2.34**	**2.46**	**2.73**
P3HT/PCBM						
E_t, [a]	0.0465	0.0460	0.0452	0.0351	0.0412	0.0473
E_{ph}	0.1132	0.1218	0.0822	0.1042	0.0709	0.0823
σ_0	0.0086	0.0144	0.0212	0.0109	0.0133	0.0183
E_t, [b]	0.1409	0.1441	0.1356	0.1335	0.1267	0.1404
E_b	0.0504	0.1024	0.0739	0.0551	0.0363	0.0454
P3HT/*bis*-PCBM						
E_t, [a]	0.0453	0.0479	0.0495	0.0468	0.0509	0.0503
E_{ph}	0.0615	0.0765	0.0751	0.0909	0.0875	0.0650
σ_0	0.0193	0.0167	0.0219	0.0174	0.0160	0.0206
E_t, [b]	0.1228	0.1283	0.1294	0.1275	0.1189	0.1250
E_b	0.0627	0.0770	0.0423	0.0786	0.0565	0.0588

[a] Obtained from $\Delta B_{pp}(T)$ dependences.
[b] Obtained from $D_{3D}(T)$ dependences.

3.4. Spin relaxation and dynamics

As magnetic term B_1 of microwave irradiation increases, the absorption lines of both photoinduced charge carriers are broadened and their intensity changes nonlinearly. This is due to fast passage of steady-state saturated polarons and methanofullerene anion radicals when spin precession time becomes less than effective relaxation time. Effective spin–lattice T_1 and spin–spin T_2 relaxation times of polarons and fullerene anion radicals determined using steady-state saturation method [34] are presented in Fig. 6 as a function of temperature and photon energy. It is seen from Fig. 6 that the interaction of most charge carriers with the lattice is characterized by monotonic temperature dependence. However, the P3HT/PCBM composite demonstrates sharper $T_1(T)$ functions than the P3HT/*bis*-PCBM one.

Mobile polarons diffuse along and between P3HT chains with respective translative diffusion coefficients D_{1D} and D_{3D}. Besides, methanofullerene molecules pseudorotate near own main axis with coefficient D_r in polymer matrix. Such spin dynamics induce additional magnetic fields in the bulk heterojunction accelerating electron relaxation of both spin ensembles. As relaxation times of spins in conjugated polymers are defined mainly by their dipole–dipole interaction [25,72], the following equations connecting their relaxation and dynamics parameters can be written [73,74]:

$$T_1^{-1}(\omega_e)=\langle\omega^2\rangle[2J(\omega_e)+8J(2\omega_e)], \tag{11}$$

$$T_2^{-1}(\omega_e)=\langle\omega^2\rangle[3J(0)+5J(\omega_e)+2J(2\omega_e)], \tag{12}$$

where $\langle\omega^2\rangle=1/10\gamma_e^4\hbar^2S(S+1)n\Sigma ij$ is a constant of a dipole–dipole interaction for powder with n spins per monomer unit and lattice sum Σij, $J(\omega_e)=(2D_{1D}^{|}\omega_e)^{-1/2}$ at $D_{1D}^{|} \gg \omega_e \gg D_{3D}$ or

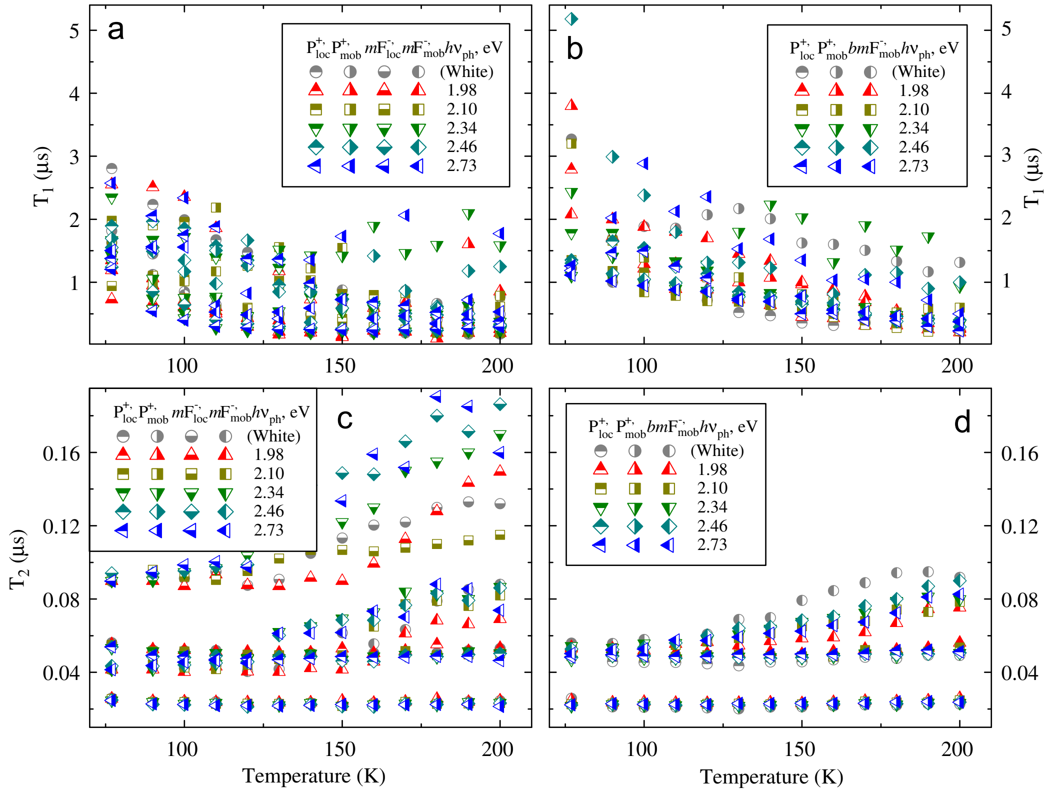

Fig. 6. Temperature dependence of spin–lattice (T_1, a, b) and spin–spin (T_2, c, d) relaxation times of localized ($P^{+\bullet}_{loc}$,$(b)mF^{-\bullet}_{loc}$) and mobile ($P^{+\bullet}_{mob}$,$(b)mF^{-\bullet}_{mob}$) charge carriers photoinduced in the P3HT/PCBM (a, c) and P3HT/*bis*-PCBM (b, d) composites by wide-band white light and by monochromatic light with different photon energy $h\nu_{ph}$.

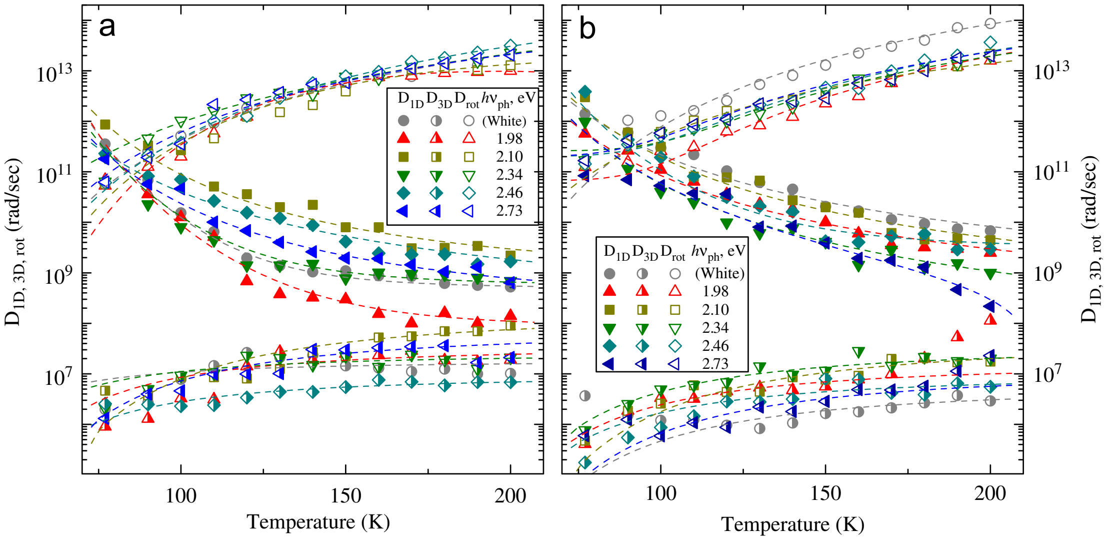

Fig. 7. Temperature dependence of intrachain (D_{1D}, filled points), interchain (D_{3D}, semi-filled points) and rotational diffusion (D_{rot}, open points) coefficients of mobile charge carriers $P^{+\bullet}_{mob}$ and $mF^{-\bullet}_{mob}$ (left and right lines of the quasi-pair in Fig. 1, respectively) photoinduced in the P3HT/PCBM (a) and P3HT/*bis*-PCBM (b) composites by the polychromatic white and monochromatic light with different photon energy $h\nu_{ph}$. Dashed lines show the dependences calculated from Eqs. (13) to (15) with appropriate parameters presented in Table 3.

$J(0)=(2D'_{1D}D_{3D})^{-1/2}$ at $D_{3D} \gg \omega_e$ is a spectral density function for Q1D motion, $D'_{1D}=4D_{1D}/L^2$, ω_e is resonant angular frequency of electron spin precession, and L is the spatial extent of the polaron wavefunction equivalent approximately 4–5 monomer units for organic conjugated polymers, and, particularly, P3AT [57,75]. A similar spectral density function was earlier used in the study of spin dynamics in other conjugated polymers [22,25,76]. A spectral density function for rotational diffusion with correlation time τ_c is $J_{rot}(\omega_e)=2\tau_c/(1+\tau_c^2\omega_e^2)$.

Diffusion coefficients calculated from Eqs. (11) and (12) for both types of charge carriers photoinduced in the polymer/fullerene composite using the relaxation and susceptibility data obtained and the appropriate spectral density functions are presented in Fig. 7 as a function of temperature. Fig. 7 shows that the coefficient of polaron intrachain diffusion D_{1D} is governed sufficiently by the energy of initiated photons $h\nu_{ph}$. The replacement of PCBM by *bis*-PCBM suppresses this effect. Besides, such a replacement increases anisotropy of polaron diffusion D_{1D}/D_{3D} in the P3HT matrix. This fact additionally justifies better planarity of the matrix with *bis*-PCBM molecules embedded. This is due to the fact that these more side–ramified methanofullerenes restrict the number of possible conformations able to be formed by two adjacent thiophene rings rotating about their shared C–C bond. As seen from the data presented, both fullerene anion radicals pseudorotate between the P3HT chains with approximately the same rate in the whole temperature range used (except charge carriers photoinduced in the P3HT/*bis*-PCBM system by white light; see Fig. 7).

To account for the LEPR mobility data obtained, different theoretical models can be used.

Intrachain polaron dynamics in the samples is characterized by strong temperature dependence (Fig. 7). Such a behavior can probably be associated with the scattering of polarons on the lattice phonons of crystalline domains immersed into an amorphous matrix. According to the model proposed for charge dynamics in crystalline domains of doped conjugated polymers, such scattering should affect polaron intrachain diffusion with an appropriate coefficient [77,78]

$$D_{1D}=\frac{\pi^2 M t_0^2 k_B^2 T^2}{h^3\alpha_{eph}^2}\left[\sinh\left(\frac{E_{ph}}{k_BT}\right)-1\right]=D_{1D}^{(0)}T^2\left[\sinh\left(\frac{E_{ph}}{k_BT}\right)-1\right], \quad (13)$$

where M is the mass of a polymer unit, t_0 is the transfer integral equal for π-electron to $\sim$2.5–3 eV, α_{eph} is a constant of electron–phonon interaction, and E_{ph} is phonon energy. This model was also used to interprete intrachain polaron diffusion in other conjugated polymers [25,40,41,79,80].

Fig. 7 evidences that the D_{1D} obtained for polaron from Eq. (11) follows well Eq. (13) with the phonon energy summarized in Table 3. This value lies near the energy of lattice phonons, 0.09–0.32 eV determined for other conjugated polymers [25]. E_{ph} obtained for the P3HT/*bis*-PCBM composite appears to be sensitive to the energy of illuminated photons attaining maximum at $h\nu_{ph}=2.46$ eV.

The interchain spin hopping dynamics can be analyzed, for example, in terms of the Hoesterey–Letson formalism [81] modified for amorphous low–dimensional systems [82]. According to this model, charge hoping between polymer chains should be controlled by the traps with concentration n_t and depth E_t. Taking into account the relation of the trap-controlled interchain mobility μ_{3D} of a charge carrier on its diffusion coefficient D_{3D}, $\mu_{3D}=eD_{3D}d^2/k_BT$ and combining Eqs. (18) and (25) in Ref. [82] in the case of low trap concentration limit, we obtained for the latter

$$D_{3D}=\nu_0\left(\frac{R_{ij}}{d}\right)^2\exp\left(-\frac{2R_{ij}}{r}\right)\exp\left(\frac{E_t}{2k_BT_{cr}}\right)\exp\left[-\frac{E_t}{2k_BT}\left(\frac{\sigma_0}{k_BT}\right)^2\right], \quad (14)$$

where ν_0 is hopping attempt frequency, d is the lattice constant, $T_{cr}=E_t/2k_B\ln(n_t)$ is critical temperature at which the transition from trap-controlled to trap-to-trap hopping transport regimes occurs, and σ_0 is the width of intrinsic energetic distributions of hopping states in the absence of traps.

Fig. 7 shows also the temperature dependences calculated from Eq. (14) with $T_{cr}=111$–126 K (P3HT/PCBM), $T_{cr}=127$–140 K (P3HT/*bis*-PCBM), σ_0 and E_t summarized in Table 3. Fig. 7 evidences that interchain polaron dynamics can be described in the frames of the above mentioned theory. The E_t values obtained for P3HT/PCBM prevail those characteristic of P3HT/*bis*-PCBM (Table 3) that is additional evidence of deeper traps formed in the former polymer matrix. Moreover, the replacement of the PCBM by the *bis*-PCBM somewhat increases T_{cr} of a polymer/fullerene system. This fact, probably, indicates the decrease in trap concentration due the increase in effective crystallinity of the polymer matrix. The data presented show that the photon energy governs simultaneously both the T_{ct} and E_t parameters, which attain the maximal and the minimal values, respectively, at $h\nu_{ph}\approx 2.5$ eV. Assuming all the electron wave functions exponentially decay, the interchain transfer integral, $t_\perp=2e^2r/3\varepsilon a^2\exp(-r/a)$ [83], was roughly estimated for P3HT to be equal to 0.12 eV. It is seen from Table 3 that E_t obtained from Eq. (14) exceeds that obtained above from Eq. (10). Such discrepancy appeared due, probably, to more complex temperature dependence of the interchan spin diffusion coefficient. However, comparing the data presented one can to note rather like extremal $E_t(h\nu_{ph})$ dependences reaching minimum at $h\nu_{ph}\approx 2.4$ eV.

It is well known [84] that the fullerene globes pseudorotate in solids hopping between the low-temperature and high-temperature phases with respective activation energy. To account for the fullerene pseudorotational mobility data, the Pike's model [85] of single-phonon-assisted hopping of charge carrier between localized states over potential barrier E_b can be used. This model postulates the dependence of the coefficient of rotating diffusion D_{rot} on frequency and temperature

$$D_{rot}=D_{rot}^{(0)}T^2\omega_e^s\exp\left(-\frac{E_b}{k_BT}\right), \quad (15)$$

where the exponent $s=1-\alpha k_BT/E_b$ reflects system dimensionality and α is a constant.

The energies E_b necessary to activate methanofullerene pseudorotational diffusion in the polymer/fullerene composites under study are summarized in Table 3. It is seen from Fig. 7 that the temperature dependences of dynamic parameters calculated from Eq. (15) with E_b determined approximately well fit experimental data. These values depends on photon energy (see Table 3) and lie near those obtained, for example, for molecular dynamics in polycrystalline fullerene [84] and a triphenylamine fullerene complex [86].

4. Summary

In summary, we have studied comparatively charge transfer in bulk heterojunctions formed by P3HT chains with methanofullerenes. The results obtained evidence directly that the main magnetic resonance, relaxation and dynamic parameters of polarons and methanofullerene anion radicals are governed by the structure, conformation and ordering of bulk heterojunctions as well as by the energy of excited photons. This can be partly as a result of structural inhomogeneity of the polymer/fullerene composites, conditioning the photon-initiated appearance of traps with different depth and distribution. The data obtained allowed us to suggest the importance of the ring-torsion and ring-librative motions on the charge initiation, separation and diffusion in disordered organic systems. The substitution of PCBM for *bis*-PCBM increases in planarity and ordering of a polymer matrix. Such replacement decreases the number of traps, facilitates local molecular vibrations and, therefore, accelerates charge transfer through a bulk heterojunction. It was shown that a polaron diffusing along a polymer backbone exchanges with the spin of a counter methanofullerene radical anion in terms of the modified Marcus theory. Charge recombination was interpreted in terms of charge multitrapping in energetically disordered semiconductor whose local structure and ordering govern the number, depth and distribution of charge traps. The interaction of most charge carriers with the lattice is characterized by monotonic temperature dependence. Electron relaxation of charge carriers was shown by the steady-state MW saturation method to be also governed by dynamics, structure and conformation of their microenvironment as well as by photon energy. Polaron scattering on phonons in the P3HT/*bis*-PCBM composite is determined by the energy of illuminated photons. The energetic barrier required for polaron interchain hopping predominantly prevails that of its intrachain diffusion in both composites. Polaron diffusion along and between polymer chains becomes easier as one embeds *bis*-PCBM instead of PCBM in the P3HT matrix. On the other hand, the energy required for pseudorotation of methanofullerene globes in the composites somewhat increases at such acceptor replacement. This can be due to "freezing" of molecular pseudorotation in the P3HT/*bis*-PCBM composite with a higher degree of matrix conjugation. As predicted, the use of *bis*-PCBM methanofullerene with a higher LUMO level instead of PCBM indeed increases the ordering of bulk heterojunctions and minimizes the energy loss in charge transfer in solar cells. The data obtained also show that the specific fullerene structure used governs the energy levels in the polymer/fullerene system and determines the competition between excited states in its bulk heterojunction. The charge-transfer state energy, geminate recombination and the overlap between donor and acceptor in a bulk heterojunction are important factors in triplet formation and should be taken into account when designing new organic photovoltaics.

Acknowledgments

The authors are thankful to Prof. H.-K. Roth for valuable discussions and gift of PCBM sample, Prof. V.A. Smirnov for calibration of light sources, and Dr. L.I. Tkachenko for I_2 doping of the composites. This work was in part supported by the Russian Foundation for Basic Researches (Grant no. 08-03-00133).

References

[1] F. So, J. Kido, P. Burrows, Organic light-emitting devices for solid-state lighting, Mater. Res. Soc. Bull. 33 (2008) 663–669.

[2] G.D. Sharma, Advances in nano-structured organic solar cells, in: Physics of Nanostructured Solar Cells, Nova Science Publishers, New York, 2010, pp. 363 – 462.

[3] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, Solar cell efficiency tables (version 36), Prog. Photovolt. 18 (2010) 346–352.

[4] D. Hertel, H. Bässler, Photoconduction in amorphous organic solids, Chem. Phys. Chem. 9 (2008) 666–688.

[5] S. Sensfuss, M. Al-Ibrahim, A. Konkin, G. Nazmutdinova, U. Zhokhavets, G. Gobsch, D.A.M. Egbe, E. Klemm, H.K. Roth, Characterization of potential donor acceptor pairs for polymer solar cells by ESR, optical, and electrochemical investigations, in: Z.H. Kafafi, P.A. Lane (Eds.), Organic Photovoltaics, vol. IV, SPIE, Bellingham, 2004, pp. 129–140.

[6] B.M. Illescas, N. Martin, [60]Fullerene-based electron acceptors, in: K.D. Sattler (Ed.), Handbook of Nanophysics: Clusters and Fullerenes, CRC Press, 2010, p. 909.

[7] I.W. Hwang, C. Soci, D. Moses, Z.G. Zhu, D. Waller, R. Gaudiana, C.J. Brabec, A.J. Heeger, Ultrafast electron transfer and decay dynamics in a small band gap bulk heterojunction material, Adv. Mater. 19 (2007) 2307–2312.

[8] D.E. Markov, E. Amsterdam, P.W.M. Blom, A.B. Sieval, J.C. Hummelen, Accurate measurement of the exciton diffusion length in a conjugated polymer using a heterostructure with a side-chain cross-linked fullerene layer, J. Phys. Chem. A 109 (2005) 5266–5274.

[9] J.J.M. Halls, J. Cornil, D.A. Dos Santos, R. Silbey, D.H. Hwang, A.B. Holmes, J.L. Bredas, R.H. Friend, Charge- and energy-transfer processes at polymer/polymer interfaces: a joint experimental and theoretical study, Phys. Rev. B 60 (1999) 5721–5727.

[10] C.J. Brabec, C. Winder, N.S. Sariciftci, J.C. Hummelen, A. Dhanabalan, P.A. van Hal, R.A.J. Janssen, A low-bandgap semiconducting polymer for photovoltaic devices and infrared emitting diodes, Adv. Funct. Mater. 12 (2002) 709–712.

[11] L.J.A. Koster, V.D. Mihailetchi, P.W.M. Blom, Ultimate efficiency of polymer/fullerene bulk heterojunction solar cells, Appl. Phys. Lett. 88 (2006) 093511–093513.

[12] P.-T. Wu, G. Ren, S.A. Jenekhe, Crystalline random conjugated copolymers with multiple side chains: tunable intermolecular interactions and enhanced charge transport and photovoltaic properties, Macromolecules 43 (2010) 3306–3313.

[13] H. Bässler, Charge transport in disordered organic photoconductors a Monte Carlo simulation study, Phys. Stat. Sol. B 175 (1993) 15–56.

[14] J.M. Ginder, A.J. Epstein, A.G. MacDiarmid, Ring-torsional polarons in polyaniline and polyparaphenylene sulfide, Synth. Met. 43 (1991) 3431–3436.

[15] J.M. Lee, J.S. Park, S.H. Lee, H. Kim, S. Yoo, S.O. Kim, Selective electron- or hole-transport enhancement in bulk-heterojunction organic solar cells with N- or B-doped carbon nanotubes, Adv. Mater. 23 (2011) 629–633.

[16] J.S. Park, B.R. Lee, J.M. Lee, J.-S. Kim, S.O. Kim, M.H. Song, Efficient hybrid organic-inorganic light emitting diodes with self-assembled dipole molecule deposited metal oxides, Appl. Phys. Lett. 96 (2010) 243306–243308.

[17] M. Lenes, G.J.A.H. Wetzelaer, F.B. Kooistra, S.C. Veenstra, J.C. Hummelen, P.W.M. Blom, Fullerene bisadducts for enhanced open-circuit voltages and efficiencies in polymer solar cells, Adv. Mater. 20 (2008) 2116–2119.

[18] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends, Nat. Mater. 4 (2005) 864–868.

[19] J.H. Huang, K.C. Li, F.C. Chien, Y.S. Hsiao, D. Kekuda, P.L. Chen, H.C. Lin, K.C. Ho, C.W. Chu, Correlation between exciton lifetime distribution and morphology of bulk heterojunction films after solvent annealing, J. Phys. Chem. C 114 (2010) 9062–9069.

[20] D. Jarzab, F. Cordella, M. Lenes, F.B. Kooistra, P.W.M. Blom, J.C. Hummelen, M.A. Loi, Charge transfer dynamics in polymer–fullerene blends for efficient solar cells, J. Phys. Chem. B 113 (2009) 16513–16517.

[21] C. Dyer-Smith, L.X. Reynolds, A. Bruno, D.D.C. Bradley, S.A. Haque, J. Nelson, Triplet formation in fullerene multi-adduct blends for organic solar cells and its influence on device performance, Adv. Funct. Mater. 20 (2010) 2701–2708.

[22] K. Mizoguchi, S. Kuroda, Magnetic properties of conducting polymers, in: H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, John Wiley & Sons, Chichester, New York, 1997, pp. 251–317.

[23] P. Bernier, The magnetic properties of conjugated polymers: ESR studies of undoped and doped systems, in: T.E. Scotheim (Ed.), Handbook of Conducting Polymers, Marcel Dekker, Inc., New York, 1986, pp. 1099–1125.

[24] V.I. Krinichnyi, 2-mm Wave Band EPR Spectroscopy of Condensed Systems, CRC Press, Boca Raton, 1995.

[25] V.I. Krinichnyi, 2-mm Waveband electron paramagnetic resonance spectroscopy of conducting polymers (Review), Synth. Met. 108 (2000) 173–222.

[26] V.I. Krinichnyi, High field ESR spectroscopy of conductive polymers, in: S. Schlick (Ed.), Advanced ESR Methods in Polymer Research, Wiley, Hoboken, NJ, 2006, pp. 307–338 (Chapter 12).

[27] M.M. Mandoc, L.J.A. Koster, P.W.M. Blom, Optimum charge carrier mobility in organic solar cells, Appl. Phys. Lett. 90 (2007) 133504–133506.

[28] C. Brabec, U. Scherf, V. Dyakonov, Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies, Wiley-VCH, Weinheim, 2008.

[29] V.I. Krinichnyi, LEPR spectroscopy of charge carriers photoinduced in polymer/fullerene composites, in: M. Lechkov, S. Prandzheva (Eds.), Encyclopedia of Polymer Composites: Properties, Performance and Applications, Nova Science Publishers, Hauppauge, New York, 2009, pp. 417–446 (Chapter 11).

[30] V.I. Krinichnyi, A.A. Balakai, Light-induced spin localization in poly(3-dodecylthiophen)/PCBM composite, Appl. Magn. Reson. 39 (2010) 319–328.

[31] V.I. Krinichnyi, E.I. Yudanova, N.G. Spitsina, Light-induced EPR study of poly(3-alkylthiophene)/fullerene composites, J. Phys. Chem. C 114 (2010) 16756–16766.

[32] F. Witt, M. Kruszynska, H. Borchert, J. Parisi, Charge transfer complexes in organic – inorganic hybrid blends for photovoltaic applications investigated by light-induced electron spin resonance spectroscopy, J. Phys. Chem. Lett. 1 (2010) 2999–3003.

[33] R.D. McCullough, The chemistry of conducting polythiophenes, Adv. Mater. 10 (1998) 93–116.

[34] C.P. Poole, Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques, John Wiley & Sons, New York, 1983.

[35] K. Marumoto, Y. Muramatsu, N. Takeuchi, S. Kuroda, Light-induced ESR studies of polarons in regioregular poly(3-alkylthiophene)–fullerene composites, Synth. Met. 135 (2003) 433–434.

[36] R.A.J. Janssen, D. Moses, N.S. Sariciftci, Electron and energy transfer processes of photoexcited oligothiophenes onto tetracyanoethylene and C_{60}, J. Chem. Phys. 101 (1994) 9519–9527.

[37] V.I. Krinichnyi, Dynamics of charge carriers photoinduced in 3 poly (3-dodecylthiophene)/fullerene composite, Acta Mater. 56 (2008) 1427–1434.

[38] V.I. Krinichnyi, Dynamics of charge carriers photoinduced in poly(3-dodecylthiophene)/fullerene bulk heterojunction, Sol. Energy Mater. Sol. Cells 92 (2008) 942–948.

[39] S.S. Eaton, G.R. Eaton, EPR spectra of C_{60} anions, Appl. Magn. Reson. 11 (1996) 155–170.

[40] V.I. Krinichnyi, H.K. Roth, A.L. Konkin, Multifrequency EPR study of charge transfer in poly(3-alkylthiophenes), Phys. B 344 (2004) 430–435.

[41] V.I. Krinichnyi, H.K. Roth, EPR study of spin and charge dynamics in slightly doped poly(3-octylthiophene), Appl. Magn. Reson. 26 (2004) 395–415.

[42] Y. Kim, S. Cook, S.M. Tuladhar, S.A. Choulis, J. Nelson, J.R. Durrant, D.D.C. Bradley, M. Giles, I. McCulloch, C.S. Ha, M. Ree, A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene: fullerene solar cells, Nat. Mater. 5 (2006) 197–203.

[43] A. Aguirre, P. Gast, S. Orlinskii, I. Akimoto, E.J.J. Groenen, H. El Mkami, E. Goovaerts, S. Van Doorslaer, EPR Multifrequency, analysis of the positive polaron in I_2-doped poly(3-hexylthiophene) and in poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene, Phys. Chem. Chem. Phys. 10 (2008) 7129–7138.

[44] J. De Ceuster, E. Goovaerts, A. Bouwen, J.C. Hummelen, V. Dyakonov, High-frequency (95 GHz) electron paramagnetic resonance study of the photoinduced

charge transfer in conjugated polymer- fullerene composites, Phys. Rev. B 64 (2001) 195206/1–195206/6.

[45] H.K. Roth, F. Keller, H. Schneider, Hochfrequenzspectroskopie in der Polymerforschung, Academie Verlag, Berlin, 1984.

[46] E.M. Conwell, C.B. Duke, A. Paton, S. Jeyadev, Molecular conformation of polyaniline oligomers: optical absorption and photoemission of three-phenyl molecules, J. Chem. Phys. 88 (1988) 3331–3337.

[47] D.L. Cheung, D.P. McMahon, A. Troisi, Computational study of the structure and charge-transfer parameters in low-molecular-mass P3HT, J. Phys. Chem. B 113 (2009) 9393–9401.

[48] K. Harigaya, Long-range excitons in conjugated polymers with ring torsions: poly(para-phenylene) and polyaniline, J. Phys. 10 (1998) 7679–7690.

[49] W. Łuźny, M. Trznadel, A. Proń, X-ray diffraction study of reoregular poly(3-alkylthiophenes), Synth. Met. 81 (1996) 71–74.

[50] A.L. Buchachenko, A.M. Vasserman, Stable Radicals (Russia), Khimija, Moscow, 1973.

[51] Y.-K. Lan, C.-I. Huang, A theoretical study of the charge transfer behavior of the highly regioregular poly-3-hexylthiophene in the ordered state, J, Phys. Chem. B 112 (2008) 14857–14862.

[52] A. Van Vooren, J.-S. Kim, J. Cornil, Intrachain versus interchain electron transport in poly(fluorene-alt-benzothiadiazole): a quantum-chemical insight, Chem. Phys. Chem. 9 (2008) 989–993.

[53] V.I. Krinichnyi, 2-mm Waveband saturation transfer electron paramagnetic resonance of conducting polymers, J. Chem. Phys. 129 (2008) 134510–134518.

[54] K. Yazawa, Y. Inoue, T. Shimizu, M. Tansho, N. Asakawa, Molecular dynamics of regioregular poly(3-hexylthiophene) investigated by NMR relaxation and an interpretation of temperature dependent optical absorption, J. Phys. Chem. B 114 (2010) 1241–1248.

[55] D.W. Breiby, S. Sato, E.J. Samuelsen, K. Mizoguchi, Electron spin resonance studies of anisotropy in semiconducting polymeric films, J. Polym. Sci. B 41 (2003) 3011–3025.

[56] S. Marchant, P.J.S. Foot, Poly(3-Hexylthiophene)–zinc oxide rectifying junctions, J. Mater. Sci. 6 (1995) 144–148.

[57] M. Westerling, R. Osterbacka, H. Stubb, Recombination of long-lived photoexcitations in regioregular polyalkylthiophenes, Phys. Rev. B 66 (2002) 165220/1–165220/7.

[58] E. Houze, M. Nechtschein, ESR in conducting polymers: oxygen-induced contribution to the linewidth, Phys. Rev. B 53 (1996) 14309–14318.

[59] B. Yan, N.A. Schultz, A.L. Efros, P.C. Taylor, Universal distribution of residual carriers in tetrahedrally coordinated amorphous semiconductors, Phys. Rev. Lett. 84 (2000) 4180–4183.

[60] J. Nelson, Diffusion-limited recombination in polymer–fullerene blends and its influence on photocurrent collection, Phys. Rev. B 67 (2003) 155209/1–155209/10.

[61] M. Tachiya, K. Seki, Theory of bulk electron–hole recombination in a medium with energetic disorder, Phys. Rev. B 82 (2010) 085201/1–085201/8.

[62] Y.N. Molin, K.M. Salikhov, K.I. Zamaraev, Spin Exchange, Springer, Berlin, 1980.

[63] M. Al Ibrahim, H.K. Roth, M. Schrödner, A. Konkin, U. Zhokhavets, G. Gobsch, P. Scharff, S. Sensfuss, The influence of the optoelectronic properties of poly(3-alkylthiophenes) on the device parameters in flexible polymer solar cells, Org. Electron. 6 (2005) 65–77.

[64] C. Deibel, D. Mack, J. Gorenflot, A. Schöll, S. Krause, F. Reinert, D. Rauh, V. Dyakonov, Energetics of excited states in the conjugated polymer poly(3-hexylthiophene), Phys. Rev. B 81 (2010) 085202/1–085202/5.

[65] T.A. Chen, X.M. Wu, R.D. Rieke, T.A. Chen, X.M. Wu, R.D. Rieke, Regiocontrolled synthesis of poly(3-alkylthiophenes) mediated by Rieke Zinc: their characterization and solid-state properties, J. Am. Chem. Soc. 117 (1995) 233–244.

[66] C. Brabec, V. Dyakonov, J. Parisi, N.S. Sariciftci, Organic Photovoltaic: Concepts and Realization, Springer, Berlin, 2003.

[67] J.E. Wertz, J.R. Bolton, Electron Spin Resonance, McGraw-Hill, New York, 1972.

[68] J.E. Wertz, J.R. Bolton, Electron Spin Resonance: Elementary Theory and Practical Applications, Chapman and Hall, London, 1986.

[69] A. Troisi, G.J. Orlandi, Dynamics of the intermolecular transfer integral in crystalline organic semiconductors, J. Phys. Chem. A 110 (2006) 4065–4070.

[70] J. Kirkpatrick, V. Marcon, J. Nelson, K. Kremer, D. Andrienko, Charge mobility of discotic mesophases: a multiscale quantum and classical study, Phys. Rev. Lett. 98 (2007) 227402/1–227402/4.

[71] J. Obrzut, K.A. Page, Electrical conductivity and relaxation in poly(3-hexylthiophene), Phys. Rev. B 80 (2009) 195211/1–195211/7.

[72] V.I. Krinichnyi, A.E. Pelekh, L.I. Tkachenko, G.I. Kozub, Study of spin dynamics in *trans*-polyacetylene at 2-mm waveband EPR, Synth. Met. 46 (1992) 1–12.

[73] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford, 1961.

[74] F. Carrington, A.D. McLachlan, Introduction to Magnetic Resonance with Application to Chemistry and Chemical Physics, Harrer & Row, Publishers, New York, Evanston, London, 1967.

[75] F. Devreux, F. Genoud, M. Nechtschein, B. Villeret, On polaron and bipolaron formation in conducting polymers, in: H. Kuzmany, M. Mehring, S. Roth (Eds.), Electronic Properties of Conjugated Polymers, Springer-Verlag, Berlin, 1987, pp. 270–276.

[76] M. Nechtschein, Electron spin dynamics, in: T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds (Eds.), Handbook of Conducting Polymers, Marcel Dekker, New York, 1997, pp. 141–163.

[77] L. Pietronero, Ideal conductivity of carbon ã polymers and intercalation compounds, Synth. Met. 8 (1983) 225–231.

[78] S. Kivelson, A.J. Heeger, Intrinsic conductivity of conducting polymers, Synth. Met. 22 (1988) 371–384.

[79] F.L. Pratt, S.J. Blundell, W. Hayes, K. Nagamine, K. Ishida, A.P. Monkman, Anisotropic polaron motion in polyaniline studied by muon spin relaxation, Phys. Rev. Lett. 79 (1997) 2855–2858.

[80] V.I. Krinichnyi, H.K. Roth, M. Schrödner, Spin charge carrier dynamics in poly(*bis*-alkylthioacetylene), Appl. Magn. Reson. 23 (2002) 1–17.

[81] D.C. Hoesterey, G.M. Letson, The trapping of photocarriers in anthracene by anthraquinone, anthrone and naphthacenestar, J. Phys. Chem. Solids 24 (1963) 1609–1615.

[82] I.I. Fishchuk, A.K. Kadashchuk, H. Bässler, D.S. Weiss, Nondispersive charge-carrier transport in disordered organic materials containing traps, Phys. Rev. B 66 (2002) 205208/1–205208/12.

[83] B.I. Shklovskii, A.L. Efros, Electronic Properties of Doped Semiconductors, Springer-Verlag, New York, 1984.

[84] R. Tycko, G. Dabbagh, R.M. Fleming, R.C. Haddon, A.V. Makhija, S.M. Zahurak, Molecular dynamics and the phase transition in solid C_{60}, Phys. Rev. Lett. 67 (1991) 1886–1889.

[85] G.E. Pike, AC conductivity of scandium oxide and a new hopping model for conductivity, Phys. Rev. B 6 (1972) 1572–1580.

[86] N.N. Denisov, V.I. Krinichnyi, V.A. Nadtochenko, Spin properties of paramagnetic centers photogenerated in crystals of complexes between C_{60} and TPA, in: K. Kadish, R. Ruoff (Eds.), Fullerenes. Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials, The Electrochemical Society Inc., Pennington, NJ, 1997, pp. 139–147.