Light-induced EPR spectroscopy of charge carriers photoinduced in polymer/fullerene bulk heterojunctions

V. I. Krinichnyi[a] and E. I. Yudanova
Institute of Problems of Chemical Physics, RAS, Semenov Avenue 1, Chernogolovka 142432, Russia

Composites of conjugated polymers with fullerenes are perspective materials for polymer photovoltaics. Light-induced EPR (LEPR) study of magnetic, relaxation, and dynamic parameters of polaron-fullerene radical pairs photoinduced in fullerene-modified poly(3-alkylthiophenes) is described. Weak interaction between positively charged polaron and negatively charged fullerene ion radical in the pairs allowed to determine separately all their magnetic, relaxation, and dynamics parameters. Paramagnetic susceptibility of charge carriers reflects their activation dynamics and spin exchange in the composite. Decay of long-living polaron and fullerene anion radical depends on a spatial distance between them and the energy of exciting photons. One-dimensional polaron diffusion along the polymer chain and fullerene rotation near its own main molecular axis were shown to follow the activation Elliot hopping model and to be governed by photon energy. The deviation in activation energies for dynamics of charge carriers and the difference in their dependence on the exciting photon energy prove the noninteracting character of charge carriers photoinduced in the polymer/fullerene composite. The dependence of the main magnetic, relaxation, and dynamics parameters of charge carriers on the phonon energy was ascribed to inhomogeneous distribution of polymer and fullerene domains in bulk heterojunctions. This inhomogeneity decreases by the annealing of the composite. © *2009 American Institute of Physics.*
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I. INTRODUCTION

During the past two decades, research has been increasing in the fields of synthesis and characterization of molecules with extended π-electron delocalization considering them as perspective materials for molecular electronics. Among elements of molecular electronics based on conjugated polymers and their composites with fullerenes,[1,2] organic plastic solar cells seem to be the most suitable for polymer photovoltaics that at the present time stipulates their wide investigation.[1,3,4]

Plastic solar cells consist of fullerene molecules embedded into conjugated polymer matrix. They form so-called bulk heterojunction and perform as electron acceptors (electron transporter, *n*-type material) and as electron donors (hole transporter, *p*-type material), respectively. Soluble derivatives of conjugated polymers and fullerene were proved[5,6] to be the most efficient components to be used in plastic solar cells. Beyond photoinduced charge exciting and separation, positive carriers are transported to electrodes by polarons diffusing in the polymer phase and electrons hopping between contacting fullerene domains. A definitive advantage of a bulk heterojunction is that it can be made by simply mixing these materials in an organic solvent and casting with well-known solution deposition techniques, e.g., spin coating.[7]

The irradiation of such bulk heterojunction by visible light with photon energy $h\nu_{\mathrm{ph}}$ higher

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[a] Author to whom correspondence should be addressed. Electronic mail: kivi@cat.icp.ac.ru.
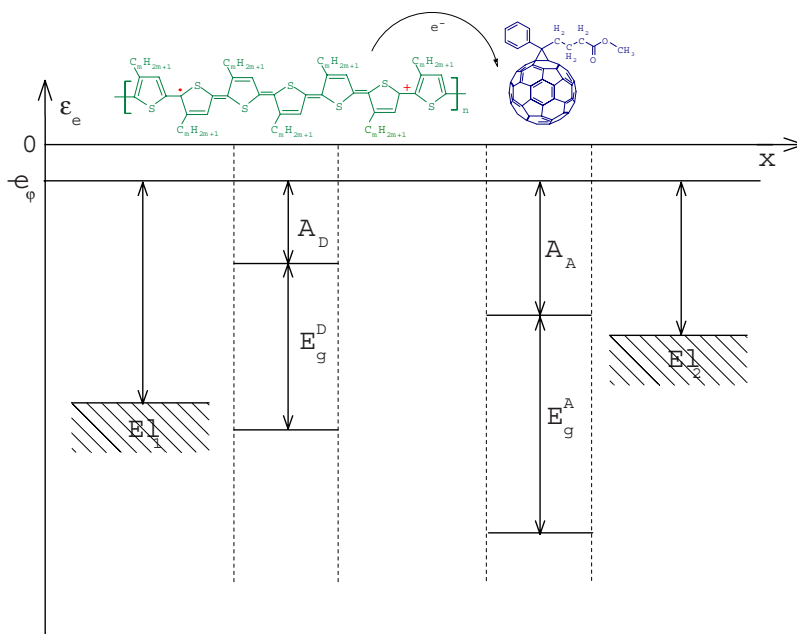
FIG. 1. Schematic band diagram of two semiconductors with different electron affinities before making between them a bulk heterojunction. The electron donor (A_D) and electron acceptor (A_A) affinities are defined vs the electron energy in vacuum at the same electrical potential. E_g^D and E_g^A are the band-gap energies of the electron donor and electron acceptor, respectively. In the top, the P3AT and PCBM are schematically shown as electron donor and electron acceptor, respectively. The appearance of a polaron quasiparticle with a spin and an elemental positive charge in the P3AT chain is shown as well.

than the π-π^* energy gap of the conjugated polymer E_g leads to the formation of ion-radical pairs, polaron $P^{+\bullet}$ on a polymer chain (donor D) and $C_{60}^{-\bullet}$ (acceptor A), and charge separation as follows:[8]

(i)   excitation of polaron on polymer chain: $D+A \rightarrow D^*+A$,
(ii)   excitation delocalization on the complex: $D^*+A \rightarrow (D\text{-}A)^*$,
(iii)   initiation of charge transfer: $(D\text{-}A)^* \rightarrow (D^{\delta+}\text{-}A^{\delta-})$,
(iv)   formation of ion-radical pair: $(D^{\delta+}\text{-}A^{\delta-})^* \rightarrow (D^{+\bullet}\text{-}A^{-\bullet})$, and
(v)   charge separation: $(D^{+\bullet}\text{-}A^{-\bullet}) \rightarrow D^{+\bullet}\text{-}A^{-\bullet}$.

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 either heat or emitted light. This process revealed by time-resolved optical spectroscopy occurs in the femtosecond time domain,[9,10] whereas the electron backtransfer with charge annihilation is much slower possibly due to dynamics and relatively slow structural relaxation in such a system of lower dimensionality. Understanding of photoexcitation, recombination of charge carriers, and other electronic processes realized in conjugated polymers is of fundamental interest for both material characterization and molecular device fabrication.

Bulk heterojunction is characterized by efficient light-excited charge generation at the interface between two organic materials with different electron affinities. Figure 1 illustrates the energy diagram of two intrinsic semiconductors, poly(3-alkylthiophene) (P3AT) and [6,6]-phenyl-C_{61}-butanoic acid methyl ester (PCBM), most frequently used in plastic solar cells, before making contact between them. A heterojunction formed by these materials inserted between a high work-function electrode (El_1) matching the highest occupied molecular orbital (HOMO) level of the donor and a low work-function electrode (El_2) matching the lowest unoccupied molecular orbital (LUMO) level of the electron acceptor should in principle act as a diode with rectifying current-voltage characteristics. Under the forward bias (the low work-function electrode is biased negative with respect to the high work-function electrode) the electron injection into the LUMO of the

acceptor layer from the low work-function electrode as well as the electron extraction out of the HOMO of the donor by the high work-function electrode are energetically possible and a high current may flow through the heterojunction. Under reverse bias (the low work-function electrode is biased positive with respect to the high work-function electrode), the electron removal from the electron donor and electron injection into the electron acceptor are energetically unfavorable.

Efficiency of light conversion of bulk heterojunctions formed by PCBM with poly(3-hexylthiophene) (P3HT) has overcome the 5% barrier and current efficiency is within 5%–6%.[4] This parameter is governed by different factors. The first limitation is originated from the high binding energy of polarons photoinduced in conjugated polymers upon light excitation, so by blending in an electron acceptor, it becomes energetically favorable for the electron to escape a polymer macromolecule and to transfer to an acceptor. This requires the LUMO of a donor to be 0.3–0.5 eV higher than the LUMO of an acceptor.[11,12] However, such energy difference can be much higher for some polymer matrices, which decreases optimal open-circuit voltage, since the latter is ultimately limited by the difference between the HOMO of a donor and the LUMO of an acceptor.[13,14] Raising, e.g., the LUMO of an acceptor it becomes real to increase the efficient factor of plastic solar cells without affecting their light absorption. This approach is theoretically more beneficial for a single-layer solar cell and results in an estimated efficiency of 8.4% when the LUMO offset is reduced to 0.5 eV.[15] The second constraint comes due to the finite number and mobility of charge carriers in organic solar cells which are lower as compared with those of conventional semiconductors. These main parameters depend on the structure and properties of a polymer matrix and the fullerene derivative embedded.[16–18] This is a reason why their power-conversion efficiency appears to be governed also by an ultrafast electron transfer from the photoexcited polymer to the fullerene,[10] a large interfacial area for charge separation due to intimate blending of the materials,[7] and efficient carrier transport across a thin film. Unambiguously, to increase power-conversion efficiency it is necessary to photoinitiate a higher density of charge carriers. However, an increased carrier density causes a reduced lifetime due to bimolecular recombination and the efficiency of solar cells might be reduced.

Thermal annealing can modify the morphological structure of bulk heterojunction and increase its light conversion efficiency.[19] Such a treatment leads to the formation of crystalline regions in an amorphous polymer matrix. This process can be controlled, e.g., by the UV/visible spectroscopy, grazing-incidence x-ray diffraction, and atomic force microscopy.[20–22] The annealing, e.g., of the P3HT/PCBM composite is accompanied by the shift of its light absorption maximum from around 2.5–2.8 eV to the lower photon energies, 1.9–2.3 eV. The observed shift should evidence also the increase in the conjugation length in the crystallites because the polymer molecules within such crystallites are perfectly oriented and there are no defects such as chain kinks, which limit the conjugation length.

Charge recombination is considered to be a predominantly nongeminate process governing the effectiveness of polymer/fullerene solar cells.[23,24] Normally, the delay of charge carriers consists of prompt and persistent contributions.[25,26] The excitation light intensity dependence of a prompt process is of activation bimolecular type and implies mutual annihilation within the created radical pair.[27] The persistent contribution is independent of the excitation intensity and originates from deep traps due to disorder.[25] Bimolecular and quadrimolecular recombinations were shown[28] to be dominant in the P3AT/fullerene composite, respectively, at lower and higher intensities of excited light. The charge carrier lifetime is usually estimated from photocurrent transients after the excitation by a short light pulse. However, in organic materials this method is inaccurate because the photocurrent transients depend not only on the decay of charge carrier concentration but also on the mobility relaxation within the broad density of states.[29] The estimation of lifetimes from transient absorption techniques is difficult because of the very large dispersion observed, leading to power law decays.[23] So, the photoexcitation of charge carrier pairs and their recombination are the most interesting points. However, they are not yet sufficiently understood in detail and there is no generally applicable model available.

Except for intermolecular charge transport, charge transfer by polaron along (Q1D) and between (Q3D) polymer chains and rotational motion of fullerene molecules are also realized in such

polymer/fullerene system. One can expect that all molecular and electronic processes should correlate. Understanding the basic physics underlying the electron relaxation and dynamic behavior of fullerene-modified organic polymers is essential for the optimization of devices based on these materials. However, processes carried out in plastic solar cells are not yet sufficiently understood in detail and there is no generally applicable model available.

Both the charge carriers of $P^{+\bullet}-C_{60}^{-\bullet}$ radical pairs possess spin $S=\frac{1}{2}$. This accounts for the wide usage of the light-induced EPR (LEPR) spectroscopy as a direct method for the investigation of charge photoexciting, separation, transfer, and recombination in fullerene-modified conjugated polymers.[28,30] LEPR measurements revealed the existence of two radicals with different line shapes, magnetic-resonance parameters, and saturation behaviors. The spins photoinduced should coact with their own charged microenvironment through exchange or dipole-dipole interactions. Such interactions do not register in LEPR spectra of plastic solar cells, which can be interpreted as the recession of mobile polarons on a conjugated polymer backbone and the fullerene anions with the rate faster than 10^{-9} s. That is a reason why both the charge carriers excited in the polymer/fullerene composite are characterized by a considerably long lifetime and can be registered separately.

It was found[31] that the mobility and stability of charge carriers in bulk heterojunction formed by PCBM with macromolecules of P3HT are higher considerably as compared with those of other polymer/fullerene composites. Much longer charge carrier lifetime achieved in the P3HT/PCBM films should, therefore, lead to higher concentration of charge carriers and their reduced recombination rate. Indeed, earlier we have shown[16,17] that among soluble fullerene derivatives with different side alkyl substitutes, PCBM appears to be at the moment the most suitable electron acceptor to be used in plastic solar cells. It was explained by better structural order in the presence of interface dipoles provoking the creation of a potential barrier for carrier recombination in this composite. Specific nanomorphology of P3AT/PCBM composites could result in screened Coulomb potential between the radical pairs photoexcited in their bulk heterojunction and facilitate their splitting into noninteracting charge carriers with a reduced probability of their further annihilation. This implies that much longer carrier lifetimes can be achieved at the same concentrations which finally results in higher photocurrent and larger power-conversion efficiency of such solar cells. This predestined the use in our study of mainly P3HT as electron donor and PCBM as electron acceptor. Their HOMO and LUMO energetic levels were determined cyclic voltammetrically[32] to be equal to -5.20 and -3.53 and -6.1 and -3.75 eV, respectively. For a comparison, respective data of the study of bulk heterojunction of PCBM with poly(3-octylthiophene) (P3OT) and poly(3-dodecylthiophene) (P3DDT) macromolecules are also presented.

II. EXPERIMENTAL

In the study were used PCBM distributed by Solenne BV® (The Netherlands) and regioregular P3AT distributed by Rieke Metals® (USA). Approximately 1 wt % concentration solution of them in chlorobenzene at a 1:1 weight ratio was placed in a ceramic plane and dried repeatedly, so then the polymer/fullerene composites were formed as a film with the size of approximately 4 $\times 8$ mm^2 and thickness of approximately 0.1 mm. At the second stage of the study, P3HT/PCBM was annealed for 1 h at 400 K in inert atmosphere.

EPR experiments were performed using 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 at dry nitrogen atmosphere using the BRT SKB IOH temperature controller and at 77 K in quartz Dewar filled with liquid nitrogen. The LEPR spectra were measured at permanent illumination of the polymer/fullerene composites directly in a microwave cavity of the EPR spectrometer by the Roithner Lasertechnik® RLDH660-40-3 ($\lambda=660$ nm, $h\nu_{ph}=1.88$ eV, $P=41$ mW), MGM2-30 ($\lambda=530$ nm, $h\nu_{ph}=2.22$ eV, $P=38$ mW), and DPSSL-473-40 ($\lambda=450$ nm, $h\nu_{ph}=2.75$ eV, $P=40$ mW) laser modules as well as by the DM-4T white light source with halogen lamp, KGM 12-100-5 (CT 3300 K), accompanied with appropriate glass filter sets. The inaccuracy of the determination of the
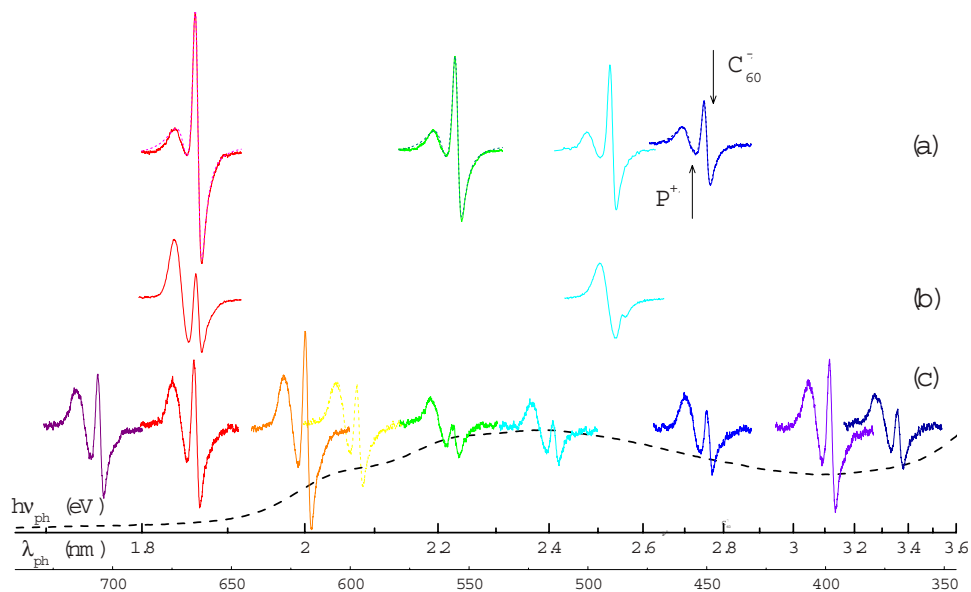
FIG. 2. LEPR spectra of radical pairs background photoinduced at 77 K in bulk heterojunctions of PCBM molecules with macromolecules of regioregular (a) P3DDT, (b) P3OT, and (c) P3HT as a function of the photon energy $h\nu_{\mathrm{ph}}$ (linewidth λ_{ph}). The optical absorption spectrum of the P3HT/PCBM composite is shown by the dashed line. The positions of polaron $P^{+\bullet}$ and fullerene anion radical $C_{60}^{-\bullet}$ are shown as well.

g-factor and peak-to-peak linewidth ΔB_{pp} are $\pm 1 \times 10^{-4}$ and $\pm 2 \times 10^{-2}$ G, respectively. For the EPR smoothing its multiple scanning was used. The total paramagnetic susceptibility of the radical pairs photoinduced in the bulk heterojunction was determined from double integration of individual LEPR spectra far from their microwave saturation. Both spin-lattice T_1 and spin-spin T_2 relaxation times were determined using the steady-state microwave saturation method.[33] For this purpose, the magnetic term B_1 of the microwave field in the cavity center was determined from the analysis of the narrowing of the diphenylpicrylhydrazyl single microcrystal EPR single line. Processing and simulations of the EPR spectra were done with the Bruker® WINEPR SIMFONIA program. The optical absorption spectrum of the P3HT/PCBM composite was obtained using the Shimadzu® UV-VIS-NIR scanning UV-3101PC spectrophotometer.

III. RESULTS AND DISCUSSIONS

A. Magnetic-resonance parameters

Detached conjugated polymers and fullerenes are characterized by the absence of both "dark" and photoinduced LEPR signals in the whole temperature range. A dramatic enhancement in the LEPR is observed when mixing both substances together. As the P3AT/PCBM composite is irradiated by visible light directly in a cavity of the EPR spectrometer, two overlapping Lorentzian LEPR lines appear at $T \leq 200$ K. Subsequent LEPR measurement cycles of heating up to room temperature, cooling down to $T \leq 200$ K, illuminating with light, switching light off, and heating up again yield identical results. Figure 2 shows the LEPR spectra of radicals background photoinduced at 77 K in bulk heterojunctions formed by PCBM molecules with various P3AT macromolecules as a function of the photon energy $h\nu_{\mathrm{ph}}$ (linewidth λ_{ph}). The optical absorption spectrum of the P3HT/PCBM composite is presented in the figure as an example.

These spectra can be attributed to radical pairs of positively charged polaron $P^{+\bullet}$ occupying approximately five monomer units and diffusing along polymer chains[26] with isotropic (effective) $g_{\mathrm{iso}}=2.0023$ and negatively charged anion radical $C_{60}^{-\bullet}$ with effective $g_{\mathrm{iso}}=2.0001$ moving near its own main axis. Generally, the deviation Δg of the g-factor of polarons in such conjugated π-electron systems from the free-electron g-factor, $g_e=2.00232$, is due to noncompensated orbital

TABLE I. The terms ΔB_{pp}^i of linewidth LEPR spectra of polarons and fullerene anion radicals used for simulation of the LEPR spectra of the P3DDT/PCBM composite obtained at different laser photon energies $h\nu_{ph}$ and 77 K.

Linewidth	Radical	$h\nu_{ph}$ (eV)		
		1.88	2.22	2.75
ΔB_{pp}^X (G)	$P^{+\bullet}$	1.01	1.07	1.13
	$C_{60}^{-\bullet}$	0.78	0.73	0.81
ΔB_{pp}^Y (G)	$P^{+\bullet}$	1.01	1.07	1.13
	$C_{60}^{-\bullet}$	0.84	0.79	0.87
ΔB_{pp}^Z (G)	$P^{+\bullet}$	1.02	1.09	1.15
	$C_{60}^{-\bullet}$	2.58	2.53	2.61
ΔB_{pp}^{iso} (G)	$P^{+\bullet}$	1.01	1.08	1.14
	$C_{60}^{-\bullet}$	1.4	1.35	1.43

momentum, which induces an additional magnetic field during the consequence of $\sigma \to \pi \to \sigma^*$ excitations.[34] In this case this parameter should depend on the spin-orbit coupling λ and the energy differences between the σ and π levels, $\Delta E_{\sigma\pi}$, and between the π and σ^* levels, $\Delta E_{\pi\sigma^*}$:

$$\Delta g = -\frac{\lambda}{3}(\Delta E_{\sigma\pi}^{-1} - \Delta E_{\pi\sigma^*}^{-1}).\tag{1}$$

The orbital moment due to a direct π-π^* excitation is negligible and shows up on the neighboring C atoms only. On the other hand, the g-factor anisotropy is induced by additional fields along the x and y directions within the plane of the σ skeleton and not along the perpendicular z direction. Indeed, our high-field/frequency EPR study of paramagnetic centers in P3OT showed[35,36] that the interaction of an unpaired electron delocalized on a polaron with sulfur heteroatoms involved in the polymer backbone leads to axial anisotropy of its g-factor, $g_{xx}=2.004\ 09$, $g_{yy}=2.003\ 32$, and $g_{zz}=2.002\ 35$. The effective g_{iso} of the high-field spectrum is typical of fullerene anion radicals.[37] De Ceuster *et al.* showed[38] that the spin density in the $C_{60}^{-\bullet}$ anion radical embedded into an organic polymer matrix is characterized by rhombic symmetry and, therefore, anisotropic g-factor, $g_{xx}=2.000\ 31$, $g_{yy}=2.000\ 11$, and $g_{zz}=1.998\ 21$. As in the case of the initial C_{60} molecule,[39] the deviation of the g-factor of the PCBM anion radical from g_e is due to the fact that the orbital angular moment is not completely quenched. Due to the Jahn–Teller dynamical effect accompanying structural molecular deformation, the isotropic nature of the icosahedral C_{60} molecule is distorted after the formation of the $C_{60}^{-\bullet}$ anion radical, resulting in an axial or even lower symmetry.[40] This is also realized in the case of fullerene derivative radicals,[38] whose high symmetry is lowered by the bond to the phenyl side chain prior to electron trapping. An asymmetrical distribution of spin density in both the polaron and fullerene anion radical leads also to a tensorial character of their linewidth.[35,36,38] As in the case of other polymer/fullerene systems,[38,41] this should be taken into account in the precise calculation of an effective LEPR spectrum of the P3AT matrix with embedded PCBM. For such purposes were used the main values of the **g**-tensors of the $P^{+\bullet}$ and $C_{60}^{-\bullet}$ radicals in, e.g., P3DDT/PCBM composite, $g_{xx}=2.0032$, $g_{yy}=2.0023$, and $g_{zz}=2.0015$ and $g_{xx}=2.0006$, $g_{yy}=2.0003$, and $g_{zz}=1.9994$, respectively, and respective linewidth terms presented in Table I. Some calculated LEPR spectra are shown by dashed lines in Fig. 2 as well.

Normally, the spins photoinduced in close proximity in ion-radical pairs should interact with their own nearest counterions through exchange or dipole-dipole interaction. Since these interactions do not register in the LEPR spectra, one can conclude that the mobile polarons on a conjugated polymer backbone are moving away from fullerene anions faster than 10^{-9} s. That is a reason why both charge carriers excited in polymer/fullerene composite are characterized by a considerably long lifetime and can be registered separately. Such LEPR spectra should reflect different factors affecting bimolecular annihilation of charge carriers in bulk heterojunction. If one
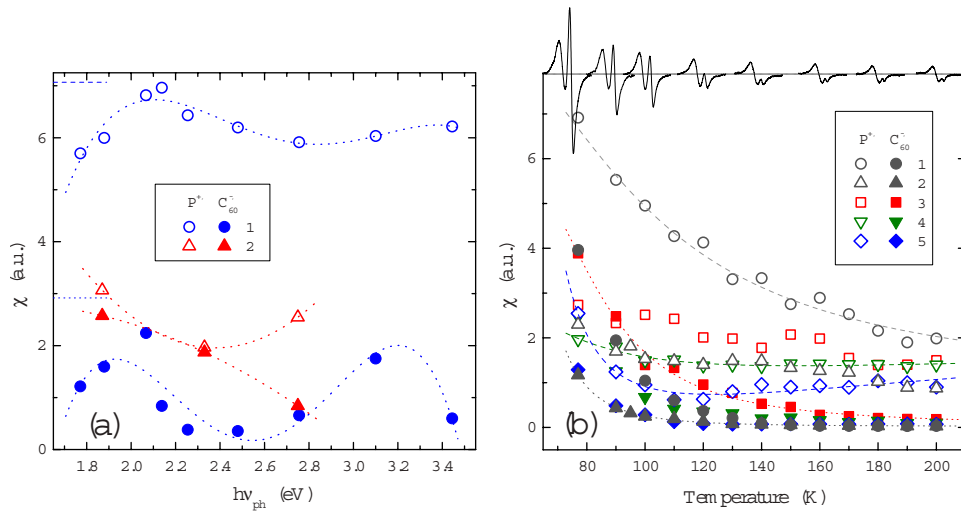
FIG. 3. (a) Paramagnetic susceptibility χ of the polarons $P^{+\bullet}$ (open points) and fullerene anion radicals $C_{60}^{-\bullet}$ (filled points) photoinduced at 77 K in (1) the P3HT/PCBM and (2) P3DDT/PCBM composites as a function of the photon energy $h\nu_{ph}$. Spin susceptibilities determined for these charge carriers initiated by white light in the P3HT/PCBM sample are shown by the dashed and dotted line sections, respectively. Experimental points are connected by sight polynomial dotted lines. (b) Temperature dependence of the χ parameter determined for the $P^{+\bullet}$ (open points) and $C_{60}^{-\bullet}$ (filled points) charge carriers photoinduced by white light in the (1) initial and (2) annealed at 400 K for 1 h P3HT/PCBM composites as well as by the photons with the energies of (3) 1.88 eV, (4) 2.22 eV, and (5) 2.75 eV in the P3DDT/PCBM composite. Some dependences calculated from Eq. (5) with different ΔE_{ij} are shown by dashed lines as an example. In the top are shown the temperature dependence of a typical LEPR spectrum of polymer/fullerene composite.

includes Coulomb interactions in this model, these should affect the activation energy E_a for either detrapping or thermally assisted tunneling by an amount $U_c = e^2/4\pi\varepsilon\varepsilon_0 r$, where e is the elemental charge, ε is the dielectric constant, and r is the charge pair separation. U_c varies from around 0.4 eV for charges separated by one lattice unit down to 0.02 eV or less for a more distinct charge separation. Therefore, both the photoinduced polaron and anion radical should be considered as noninteracting, which is the cause of their long life.

Individual LEPR spectra of both charge carriers are characterized by comparable areas that indicate equal amounts of these spins, which is in accordance to the main principle of charge separation and long-live stabilization. In other words, the shape of the appropriate LEPR spectrum must be independent of the number and energy of photons absorbed by polymer/fullerene compounds with close structure and composition. Besides, the total number of spin charge carriers photoinduced in a polymer/fullerene composite and, therefore, its quantum efficiency should follow its absorption spectrum. However, Fig. 2 evidences that it is rather far from this conception for the P3AT/PCBM systems studied. There are different factors leading to such discrepancy, e.g., a different ordering of the composites used or/and a possible collapse of polaron couples into spinless bipolarons. It was shown[42,43] that a variation of irradiation photon energy $h\nu_{ph}$ can also change P3AT/PCBM LEPR spectra. Indeed, Fig. 3(a) shows that the increase in the $h\nu_{ph}$ value leads to the change in effective concentrations of polarons $P^{+\bullet}$ and fullerene anion radicals $C_{60}^{-\bullet}$ with extremas at $h\nu_{ph} \approx 2.1$ eV and $h\nu_{ph} \approx 2.0$ and 3.1 eV for the P3DDT/PCBM and P3HT/PCBM composites, respectively. This means that the spinless charge carriers formed at irradiation of the P3HT/PCBM composite by photons with $h\nu_{ph} \approx 2.1–2.5$ eV should, probably, prevail over polarons. The finite depth of illumination penetration into the samples bulk should also affect their LEPR line shape. Indeed, Fig. 2 shows that the intensity and shape of the radical pair LEPS spectrum do not correlate with the light penetration into the sample bulk. At the moment, however, there is no unambiguous explanation for such effect. It can probably be interpreted in terms of cooperative light penetration into sample bulk and collapse of polaron pairs photoinduced on its surface into diamagnetic bipolarons.

The nature and dynamics of charge carriers in radical pairs can also contribute to their effective LEPR spectrum. Figure 3(b) shows the temperature dependence of paramagnetic susceptibility χ of charge carriers steady-state photoinduced in some P3AT/PCBM composites. One can notice that the fullerene anion radicals demonstrate stronger $\chi(T)$ dependence than polarons, especially at the low-temperature region. This can be interpreted as follows.

Let a polaron possessing a positive charge diffuse along a polymer chain from one initial site i to another available site j close to a position occupied by a negatively charged fullerene molecule. Charge hops more easily between fullerenes than from a polaron and fullerene, and an effective charge recombination is still limited by the transport of polarons toward fullerene molecules. The recombination is mainly stipulated by sequential processes, namely, charge transfer by polaron hopping along a polymer chain and its transfer from a polymer chain to a site occupied by a fullerene anion. Polaronic dynamics in undoped and slightly doped conjugated polymers is highly anisotropic.[35,36,44] Therefore, the probability of charge transfer along a polymer chain exceeds considerably that of its transfer between polymer macromolecules.

According to the tunneling model,[45] positive charge on a polaron can tunnel from this carrier toward a fullerene and recombine with its negative charge during the time

$$\tau(R_{ij}^{|}) = \tau_{pn}^{0} \exp\left(\frac{2R_{ij}^{|}}{a_0}\right),\tag{2}$$

where τ_{pn}^{0} is the attempt to jump time for positive charge tunneling from polymer chain to fullerene, $R_{ij}^{|}$ is the spatial separation of sites i and j, and a_0 is the effective localization (Bohr) radius. Charge can also be transferred by the polaron thermally assisted multistep tunneling through energy barrier $\Delta E_{ij} = E_j - E_i$ with the time[45]

$$\tau(R_{ij}, E_a) = \tau_{pp}^{0} \exp\left(\frac{2R_{ij}}{a_0}\right)\exp\left(\frac{\Delta E_{ij}}{k_B T}\right),\tag{3}$$

where τ_{pp}^{0} is the attempt for hole tunneling between the polymer chains, k_B is the Boltzmann constant, and T is the temperature. The values in the couples τ_{pn}^{0} and τ_{pp}^{0} and $R_{ij}^{|}$ and R_{ij} may be different due, for instance, to different electronic orbits.

The decay of polaron charge carriers in regioregular P3AT consists of temperature independent fast and exponentially temperature dependent slow contributions.[26] Additionally to the above mentioned tunneling and activation processes, there should be one more contribution of polarons to effective spin susceptibility. The matter is that, undoubtedly, the positive charge on the polaron is not required to be recombined with the first negative charge but with charge on the subsequent fullerene. Thus, the probability of annihilation of charges can differ from the unit. Besides, the polaron is characterized by Q1D mobility. Such fundamental properties of this specific charge carrier require considering also the contribution to its paramagnetic susceptibility due to exchange interaction of both types of paramagnetic centers. Positively charged polaron Q1D hopping from site i to site j with frequency ω_{hop} may collide with the fullerene radical anion located near the polymer matrix. While the polaron is mobile, the fullerene molecule can be considered as a translative fixed one but rotating near its own main molecular axis. In this case the spin flip-flop probability p during a collision should depend on the amplitude of exchange and ω_{hop} value as[46]

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

where $\alpha = (3/2)2\pi J/\hbar\omega_{hop}$, $\hbar = h/2\pi$ is the Planck constant, and J is the constant of exchange interaction of spins in a radical pair. Therefore, weak and strong exchange limits can be realized. In the case of weak or strong exchange, the increase in ω_{hop} may result in the decrease or the increase in exchange frequency, respectively. If the ratio $J/\hbar$ exceeds the frequency of collision of both types of spins, the condition of strong interaction is realized in the system leading to a direct relation of spin-spin interaction and polaron diffusion frequencies, so then $\lim(p)=1/2$. In the

TABLE II. The ΔE_{ij}, E_a, E_{ph}, and E_a values determined from Eqs. (5), (6), (13), and (14), respectively, for radical pairs photoinduced by white light in the initial and annealed P3HT/PCBM composites as well as by laser beam with different photon energies $h\nu_{ph}$ in the P3DDT/PCBM system.

	Composite									
	P3HT/PCBM						P3DDT/PCBM			
	Initial		Annealed		$h\nu_{ph}$=1.88 eV		$h\nu_{ph}$=2.22 eV		$h\nu_{ph}$=2.75 eV	
Radical parameter	$P^{+\bullet}$	$C_{60}^{-\bullet}$	$P^{+\bullet}$	$C_{60}^{-\bullet}$	$P^{+\bullet}$	$C_{60}^{-\bullet}$	$P^{+\bullet}$	$C_{60}^{-\bullet}$	$P^{+\bullet}$	$C_{60}^{-\bullet}$
ΔE_{ij} (eV)	0.012	0.042	0.008	0.045	0.006	0.028	0.031	0.036	0.084	0.051
E_a (eV)	0.015		0.017		0.041		0.003		0.019	
E_{ph} (eV)	0.034		0.021							
E_b (eV)		0.032		0.007	0.048	0.017	0.038	0.010	0.094	0.012

opposite case $\lim(p) = 9/2(\pi/\hbar)^2(J/\omega_{hop})^2$. It is evident that the longer both the above tunneling times or/and the lesser the probability p, the smaller the number of ion-radical pairs that have the possibility to recombine and, therefore, the higher spin susceptibility should be registered. A combination of the above equations takes, therefore, the general form of this main parameter for polarons in polymer/fullerene composite as

$$\chi_p = \chi_{pn} + \chi_P^0 \frac{\hbar}{J}\left(\alpha + \frac{1}{\alpha}\right). \tag{5}$$

Assuming the above introduced activation character for polaron multistep hopping with the frequency $\omega_{hop} = \omega_{hop}^0 \exp(-\Delta E_{ij}/k_B T)$ and the absence of dipole-dipole interaction between fullerene anion radicals, one can determine ΔE_{ij} (see Table II) and J parameters from individual temperature dependences of paramagnetic susceptibility.

It is seen from Fig. 3(b) that the dependences presented are fitted well by Eq. (5) with the ΔE_{ij} values summarized in Table II. ΔE_{ij} obtained for polarons photoinduced by white light in the P3HT/PCBM composite slightly decreases after its heat treatment, whereas this value determined for fullerene anion radicals changes remarkably smaller (Table II). However, this parameter, obtained for both charge carriers in the P3DDT/PCBM composite, seems to increase monotonically with the growing of the photon energy $h\nu_{ph}$. One can conclude that polaronic dynamics in the P3HT/PCBM composite is activated with comparatively smaller E_a than in the P3DDT/PCBM one. This occurs due, probably, to the more structural inhomogeneity of the latter polymer matrix. The J constant was analyzed to change slightly within 0.2–0.35 eV. This value sufficiently exceeds an appropriate constant of spin collision of nitroxide radicals with paramagnetic ions in liquids, $J \leq 0.01$ eV;[47] however, this lies near the $J \approx 0.36$ eV we obtained for interaction of polarons with the oxygen molecules in polyaniline highly doped by p-toluene sulfonic acid.[48,49] Comparing the above presented data, one can conclude on the higher stability of spin excitons photoinduced in the P3HT/PCBM system especially by the high-energy photons. This can evidence better homogeneity of this composite.

Effective (isotropic) peak-to-peak linewidths $\Delta B_{pp}^{(0)}$ obtained for the $P^{+\bullet}$ and $C_{60}^{-\bullet}$ radicals in the absence of their microwave saturation, when $B_1 \to 0$, are presented in Fig. 4 as a function of photon energy and temperature. It is seen from Fig. 4(a) that this parameter determined for both charge carriers changes nonmonotonically with photon energy $h\nu_{ph}$ with the extremas near 2.0 and 3.1 eV. The first extreme lies near the band-gap energy E_g^{opt}=1.92 eV of the polymer matrix,[50] whereas the second one can probably be attributed to inhomogeneous distribution of domains with different orderings (and, hence, band-gap energies) in the polymer/fullerene bulk heterojunction. Analyzing the temperature data presented in Fig. 4(b) one can notice that the linewidth of polarons in the P3DDT/PCBM composite changes monotonically with the composite heating, whereas fullerene radicals demonstrate more complex $\Delta B_{pp}^{(0)}(T, \nu_{ph})$ dependence. Polarons stabilized in the P3HT/PCBM composite also demonstrate extremal temperature dependence of linewidth. Ex-
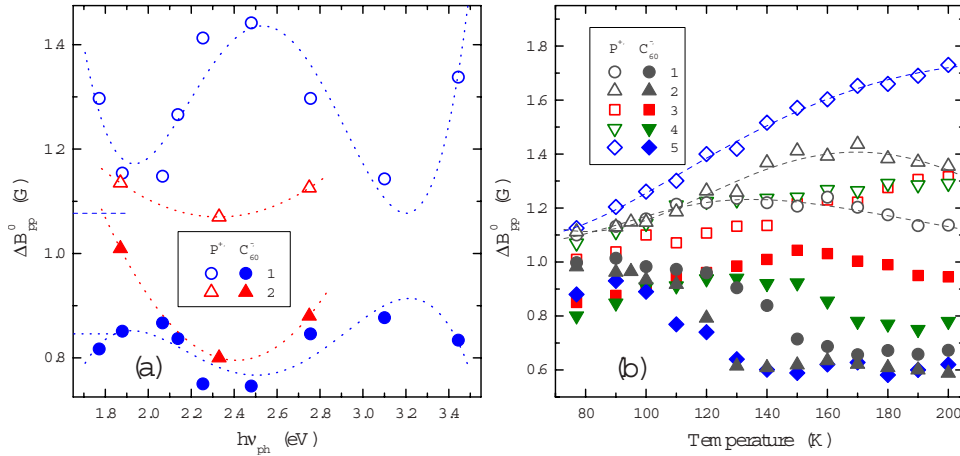
FIG. 4. (a) A lower limit of the peak-to-peak linewidth $\Delta B_{pp}^{(0)}$ of the polarons P$^{+\bullet}$ (open points) and fullerene anion radicals C$_{60}^{-\bullet}$ (filled points) photoinduced at 77 K in the (1) P3HT/PCBM and (2) P3DDT/PCBM composites as a function of the photon energy $h\nu_{ph}$. The $\Delta B_{pp}^{(0)}$ values determined for polarons and fullerene anion radicals initiated by white light in the P3HT/PCBM sample are shown by the dashed and dotted line sections, respectively. Experimental points are connected by sight polynomial dotted lines. (b) Temperature dependence of the linewidth determined for the P$^{+\bullet}$ and C$_{60}^{-\bullet}$ charge carriers photoinduced by white light in the (1) initial and (2) annealed at 400 K for 1 h P3HT/PCBM composites as well as by the photons with the energies of (3) 1.88 eV, (4) 2.22 eV, and (5) 2.75 eV in the P3DDT/PCBM composite. Some dependences calculated from Eq. (6) with different E_a presented in Table II are also shown as an example.

trapolation to room temperature gives 0.9 and 1.5 G for P$^{+\bullet}$ photoinduced, respectively, in P3HT and P3DDT matrices, which lie near $\Delta B_{pp}^{(0)} = 1.3 - 1.8$ G obtained for polarons stabilized in different P3AT.[51] However, this value is considerably less than that determined for undoped polythiophene[51,52] that is evidence of weaker spin interaction with the P3AT lattice. LEPR linewidth should reflect different processes occurring in a P3AT/PCBM composite. One of them is the association of mobile polarons with the countercharges. Another process realized in the system is dipole-dipole interaction between mobile and trapped polarons and fullerenes that broadens the line by $\Delta B_{dd} = \mu_B/R_0^3 = 4/3\pi\mu_B n_P$, where μ_B is the Bohr magneton and R_0 is the distance between dipoles proportional to the polaron concentration n_P on the polymer chain. Extrapolation $B_1 \rightarrow 0$ gives $\Delta B_{pp}^{(0)} \approx 0.7 - 0.9$ G for polarons, $\Delta B_{pp}^{(0)} \approx 0.5 - 0.7$ G for fullerene anion radicals and, therefore, $R_0 \approx 2.3 - 2.5$ nm for a distance between dipoles in the P3AT/PCBM system.

Assuming exchange and activation interaction of the fullerene anion radical quasifixed near a polymer chain with polaron hopping along the chain with the rate ω_{hop}, the dependences presented in Fig. 4(b) can probably also be described in terms of the above mentioned Houze–Nechtschein approach.[46] According to this theory, the collision of localized and mobile spins should additionally broaden the absorption line by the value

$$\delta(\Delta\omega) = p\omega_{hop}C = \frac{1}{2}\omega_{hop}C\left(\frac{\alpha^2}{1 + \alpha^2}\right), \tag{6}$$

where p is the probability described by Eq. (4), $\omega_{hop} = \omega_{hop}^0 \exp(-E_a/k_BT)$, E_a is the activation energy, and C is the number of paramagnetic centers per each polymer unit.

The dependences calculated from Eq. (6) with E_a presented in Table II are also shown in Fig. 4(b). The analysis of the data presented allows the conclusion that the energy required for activation of polaron diffusion in the P3HT/PCBM composite changes only slightly at its heat treatment. However, this parameter obtained for the P3DDT/PCBM composite decreases nonmonotonically with the increase in the energy $h\nu_{ph}$ (see Table II). It is seen that the main magnetic-resonance parameters of charge carriers are governed by the energy of exciting photons. This can be realized either at the formation of spin pairs with different properties in homogeneous composite fragments or at the excitation of identical charge carriers in heterogeneous domains of the system under
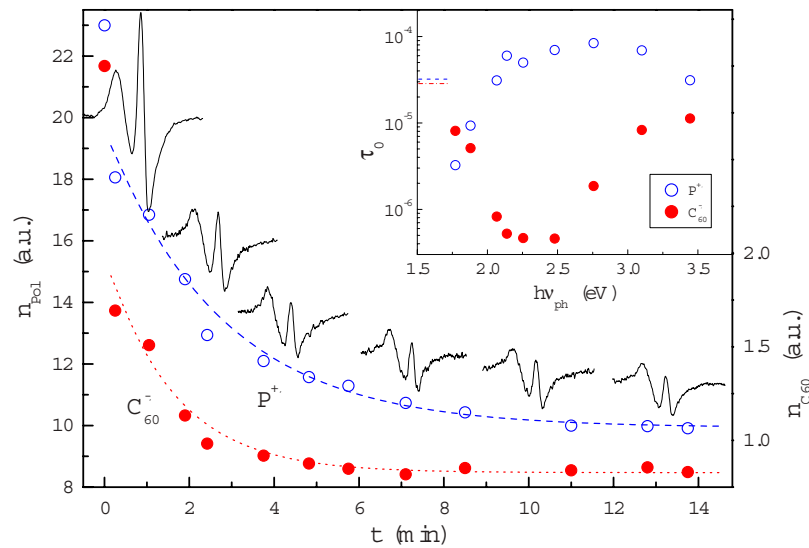
FIG. 5. Typical time dependence of the concentration of polarons $P^{+\bullet}$ (open points) and anion radicals $C_{60}^{-\bullet}$ (filled points) photoinduced in the P3AT/PCBM composite after the light irradiation blackout. The dashed and dotted lines show the dependences calculated from Eq. (10) with $n_0 a^3 = 2.21 \times 10^{-4}$ and $\tau_0 = 7.2 \times 10^{-5}$ min and $n_0 a^3 = 1.4 \times 10^{-3}$ and $\tau_0 = 3.6 \times 10^{-7}$ min, respectively. LEPR spectra of the P3HT/PCBM composite obtained at the respective delays are shown. The right insert demonstrates the change in the lifetime τ_0 of charge carriers photoinduced in the P3HT/PCBM composite on the photon energy $h\nu_{ph}$.

study. Different spin pairs can be photoinduced as a result of photon-initiated appearance of traps with different depths in a polymer matrix. However, the difference in the parameters of paramagnetic centers revealed seems to be rather a result of their interaction with their own microenvironment in domains inhomogeneously distributed in the polymer/fullerene composite. Different orderings of these domains can be a reason for their different band gaps and, hence, their sensitivities to photons with defined but different energies. This can give rise to a variation in an interaction of paramagnetic centers with a lattice and other spins.

B. Recombination of charge carriers

In solar cells, both charges diffusing to the opposite electrodes must reach them prior to recombination. If these chargers after their transfer are still bound by the Coulomb potential, which is typical for the described here compounds with low-mobile charge carriers, they cannot escape from each other's attraction and will finally recombine. When the carrier dissipation distance is longer than the Coulomb radius, the excitons photoinduced can be split into positive and negative charge carriers. To fulfill this condition, the Coulomb field must be shielded or charge carrier hopping distance must exceed the Coulomb radius. In this case charges are transferred to the electrodes either by the diffusion of appropriate carriers or by the drift induced by the electric field. In order to excite a radical pair by each photon, charge carrier transit time t_{tr} should be shorter considerably than the lifetime of a radical pair τ, i.e., $t_{tr} \ll \tau$. The former value is determined by charge carrier mobility μ, sample thickness d, and electric field E inside the film, $t_{tr} = d/\mu E$. If photocurrent is governed by the carrier drift in the applied electric field, the drift distance $l_{dr} = \mu \tau E$. If photocurrent is governed by carrier diffusion, the diffusion distance $l_{diff} = (D\tau)^{1/2} = (\mu \tau k_B T / e)^{1/2}$, where D is the diffusion coefficient, and e is the elemental electron charge. Thus, the $\mu\tau$ product governs the average distance passed by the charge carrier before recombination and, therefore, is an important parameter determining whether the efficiency of solar cells is limited by charge transport and recombination.

If one switches off excited light irradiation of the polymer/fullerene system, the concentration of spin pairs excited in its bulk heterojunctions starts to decrease and the LEPR line shape changes

as it is shown in Fig. 5. There can be different progresses for a radical pair after the irradiation interruption, namely, instantaneous collapse of the radical pairs or their splitting into noninteracting charge carriers due to polaron diffusion away. The rate of charge carrier recombination with effective localization radius a separated by a distance R can be written as[53]

$$\nu(R) = \nu_0 \exp\left(-\frac{2R}{a}\right),\tag{7}$$

where ν_0 is an attempt to recombine frequency. Undoubtedly, both charge carriers have different localization radii. The localization radius of a negative charged carrier should be on the order of the radius of the PCBM globule. The distance R should depend, e.g., on the length of a side alkyl chain substituent in the P3AT/fullerene composite.[54] Polaron stabilized in P3AT is normally distributed over five monomer units.[26,55] The nearest-neighbor distance $R(t)$ of spin pair with the typical radiative lifetime τ_0 changes with time t as

$$R(t) = \frac{a}{2}\ln\left(\frac{t}{\tau_0}\right).\tag{8}$$

Assuming that photoexcitation is turned off at some initial time $t_0 = 0$ at a charge carrier concentration n_0 and taking into account a time period of geminate recombination $t_1 - t_0$, one can write for concentration of charge carriers

$$n(R) = \frac{n}{1 + \dfrac{4\pi}{3}n_1(R^3 - R_1^3)},\tag{9}$$

where R is specified by Eq. (8), $R_1 = R(t_1)$ describes the distance between the nearest-neighbor charge carriers at time t_1 after which solely nongeminate recombination is assumed, and n_1 is the charge carrier concentration at time t_1. It follows from Eq. (9) that the time dependence of residual carrier concentration does not follow a simple exponential decay but shows a more logarithmic time behavior. After very long times, i.e., at large R, one obtains $n(R) = [(4\pi/3)R^3]^{-1}$ which is independent of initial carrier density n_1 and also n_0. As it follows from the above $\nu(R)$ equation, photoexcited charge carriers have comparably long lifetimes which are solely ascribed to the large distances between the remaining trapped charge carriers. The excited carrier concentration n_1 follows directly from LEPR measurements, whereas the a and τ_0 values can be guessed in a physically reasonable range. Finally, the concentration of spin pairs should follow the relation[53]

$$\frac{n(t)}{n_0} = \frac{\dfrac{n_1}{n_0}}{1 + \left(\dfrac{n_1}{n_0}\right)\dfrac{\pi}{6}n_0 a^3\left[\ln^3\left(\dfrac{t}{\tau_0}\right) - \ln^3\left(\dfrac{t_1}{\tau_0}\right)\right]},\tag{10}$$

The analysis showed that depending on the photon energy $h\nu_{ph}$ the spin concentration initially photoexcited at $t=0$ is governed by some factors. The typical lifetimes τ_0 determined for both charge carriers photoinduced in the P3HT/PCBM bulk heterojunction are also shown in the insert in Fig. 5 as a function of the photon energy $h\nu_{ph}$. As the figure indicates, these values change symbatically with $h\nu_{ph}$. It was shown that Eq. (10) fits well the experimental data presented in Fig. 5. The analogous effects were registered also for other P3AT/PCBM systems. Therefore, a decay of long-living spin pairs photoinduced in P3AT/PCBM and similar composites can successfully be described in the framework of the above model in which the low-temperature recombination rate is particularly strongly dependent on the spatial distance between photoinduced charge carriers. The long lifetimes are solely ascribed to the long spatial distances that build up among the remaining photoinduced charge carriers, which did not recombine at a shorter time.
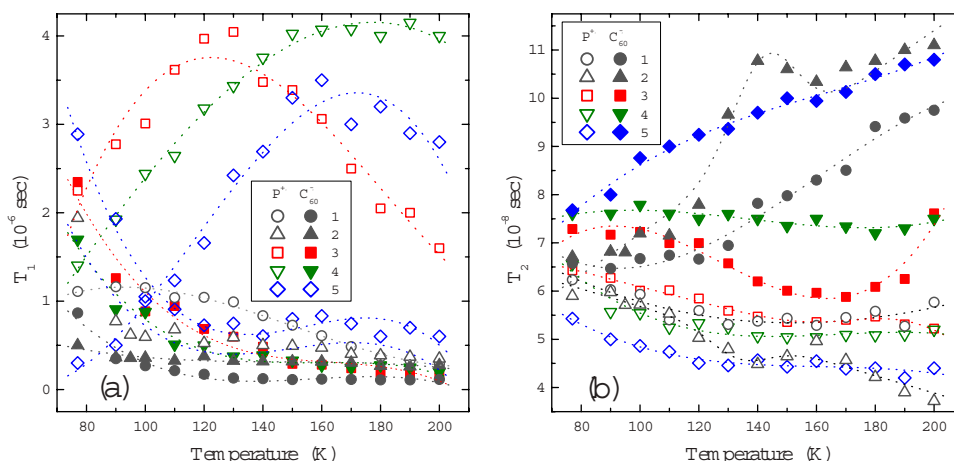
FIG. 6. Temperature dependency of the (a) spin-lattice T_1 and (b) spin-spin T_2 relaxation times of the polarons $P^{+\bullet}$ (open points) and fullerene anion radicals $C_{60}^{-\bullet}$ (filled points) photoinduced by white light in the (1) initial and (2) annealed at 400 K for 1 h P3HT/PCBM composite as well as in the P3DDT/PCBM composite by the photons with the energies of (3) 1.88 eV, (4) 2.22 eV, and (5) 2.75 eV. Experimental points are connected by sight polynomial dotted lines.

C. Electron relaxation and dynamics of charge carriers

The increase in steady-state microwave power leads to the broadening of the LEPR spectrum accompanied by nonlinear increase in its amplitude. As in the case of other conjugated polymers,[44,56] this occurs as a result of microwave steady-state saturation of spin packets excited in bulk heterojunctions. Since polarons and fullerene radical anions were proved to be independent of one another, such effect was used for a separate estimation of their spin-lattice T_1 and spin-spin T_2 relaxation times using a well-known procedure.[33]

The relaxation parameters of polarons and fullerene anion radicals determined using such a method are presented in Fig. 6 as a function of temperature. The analysis of the data obtained shows that the electron relaxation of charge carriers photoinduced in the initial P3HT/PCBM composite changes monotonically with the temperature. The annealing of the composite causes nonlinearity of the $T_2(T)$ functions of both charge carriers near 140 K as well as the decrease in spin-lattice relaxation time of fullerene radical anions (Fig. 7). The interaction of anion radicals $C_{60}^{-\bullet}$ with a polymer matrix in the P3DDT/PCBM composite is also characterized by monotonic temperature dependence, whereas the T_1 value of polarons $P^{+\bullet}$ demonstrates extremal temperature dependence with a critical temperature $T_c \approx 130-160$ K. The latter value depends on the photon energy $h\nu_{ph}$ (Fig. 6). Spin-spin relaxation of these radicals is accelerated monotonically at the temperature increase. This nearly holds for both the charge carriers except T_2 of fullerene anion radicals photoinduced by photons with $h\nu_{ph} = 2.75$ eV [Fig. 6(b)]. Such peculiarities argue that the mechanism and the rate of electron relaxation depend on the structure and conformation of the initial and fullerene-modified polymer matrices. The data obtained show the effect of the photon energy on relaxation parameters of radical pairs photoinduced in polymer/fullerene composites. This can also be explained by the formation of charge carriers in differently ordered domains with their respective band gaps.

Various spin-aided dynamic processes occur in polymer/fullerene composites: polaron diffusion along and between polymer chains with coefficients D_{1D} and D_{3D}, respectively, rotational diffusion of the fullerene radical anion about its own main molecular axis with coefficient D_{rot}, etc. These processes induce an additional magnetic field in the whereabouts of electron and nuclear spins which, in turn, accelerates electron relaxation in both spin ensembles. As relaxation of the whole spin reservoir in an organic conjugated polymer is defined mainly by a dipole-dipole interaction between electron spins,[44,57] these coefficients can be determined from the following equations:[58]
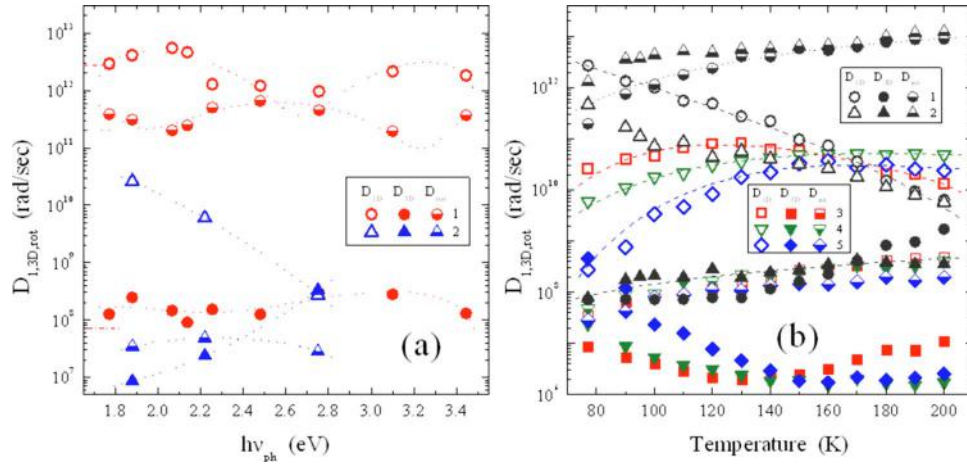
FIG. 7. (a) The coefficients of the polaron $P^{+\bullet}$ hopping along (D_{1D}, open points) and between (D_{3D}, filled points) polymer chains and the coefficient of the fullerene anion radical $C_{60}^{-\bullet}$ rotation near main axis (D_{rot}, semifilled points) in the (1) P3HT/PCBM and (2) P3DDT/PCBM composites at 77 K as a function of the photon energy $h\nu_{ph}$. The respective parameters determined for these charge carriers initiated by white light in the P3HT/PCBM sample are shown by the dashed, dashed-dotted, and dotted line sections, respectively. Experimental points are connected by sight polynomial dotted lines. (b) Temperature dependence of these parameters determined for the charge carriers photoinduced by white light in the (1) initial and (2) annealed at 400 K for 1 h P3HT/PCBM composites as well as by the photons with the energies of (3) 1.88 eV, (4) 2.22 eV, and (5) 2.75 eV in the P3DDT/PCBM composite. Some dependences calculated from Eqs. (13) and (14) with the respective E_{ph} and E_b are also shown as an example.

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

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

where $\langle\omega^2\rangle = 1/10\gamma_e^4\hbar^2 S(S+1)n\Sigma_{ij}$ is the constant of dipole-dipole interaction for powder, γ_e is the gyromagnetic ratio for electron, n is the number of polarons per each monomer, Σ_{ij} is the lattice sum for powderlike sample, $J(\omega_e)=(2D_{1D}^{\parallel}\omega_e)^{-1/2}$ (at $D_{1D}^{\parallel}\gg\omega_e\gg D_{3D}$) and $J(0)=(2D_{1D}^{\parallel}D_{3D})^{-1/2}$ (at $D_{3D}\gg\omega_e$) are the spectral density functions for polaron longitudinal diffusion and $J(\omega_e)=\tau_c/(1+\tau_c^2\omega_e^2)$ is the spectral density function for fullerene rotational diffusion with correlation time τ_c, $D_{1D}^{\parallel}=4D_{1D}/L^2$, ω_e is the resonant angular frequency of the electron spin precession, and L is the factor of spin delocalization over a polaron equal approximately to five monomer units in P3AT.[26,55]

The dynamic parameters calculated from Eqs. (11) and (12) for both charge carriers photoinduced in some polymer/fullerene composites are presented in Fig. 7 as a function of photon energy $h\nu_{ph}$ and temperature. These parameters obtained for the P3DDT/PCBM composite demonstrate monotonic dependence on $h\nu_{ph}$. On the other hands, D_{1D} and D_{3D} of polarons photoinduced in the P3HT/PCBM composite nonmonotonically depend on the photon energy. The extremas of these functions lie near those obtained above for other LEPR parameters. This fact proves additionally the existence of domains with different orderings and sensitivity to their respective light photons in the polymer/fullerene composite.

Polarons photoinduced in the P3HT/PCBM bulk heterojunction demonstrate a sharper $D_{1D}(T)$ dependence than those photoinduced in the P3DDT/PCBM composite [Fig. 7(b)]. This can probably be explained, e.g., by a stronger interaction of these charge carriers with lattice phonons in the former matrix and described in terms of the Kivelson–Heeger model[59] of charge carrier scattering in the lattice of an ordered polymer matrix. According to this model, if polarons interact with the lattice optical phonons with energy E_{ph}, the rate of their diffusion should depend on temperature as[59]

$$D_{1D}(T) = D_{1D}^0 T^2 \left[\sinh\left(\frac{E_{ph}}{k_B T} \right) - 1 \right]. \tag{13}$$

Figure 7 shows that the experimental dependences $D_{1D}(T)$ obtained for both the initial and annealed P3HT/PCBM composites are well approximated by Eq. (13) with E_{ph} presented in Table II.

The remainder dynamics data presented in Fig. 7(b) can be explained in the frames of the Elliot model based on carrier hopping over the energetic barrier E_b.[60] This model predicts the frequency and temperature dependent diffusion of a charge carrier with a coefficient

$$D_{1,3D,rot}(\omega_e T) = D_{1,3D,rot}^0 T^2 \omega_e^s \exp\left(\frac{E_b}{k_B T} \right), \tag{14}$$

where the exponent $s = 1 - \alpha k_B T / E_b$ reflects system dimensionality and α is a constant. The values of E_b and α were obtained for, e.g., lightly doped poly(3-methylthiophene) (P3MT) to be, respectively, 1.1 eV and 6.[61]

The energy E_b required to activate polaron longitudinal and fullerene rotational diffusion in the P3AT/PCBM composites is also presented in Table II. It is seen in Fig. 7(b) that the temperature dependences calculated from Eq. (14) with the E_b obtained approximate well the data determined experimentally. The E_b determined for fullerene is considerably lower than that estimated for more crystalline solids.[62,63] However, it is close to that characteristic for the triphenylamine complex.[64] The respective barrier height passed by photoinduced polarons in the P3DDT/PCBM system lie near the energy of lattice phonons in P3OT (Refs. 35 and 36) and other conjugated polymers.[44,56,65] It also close to the activation energy E_a of polaron mobility in P3HT (Ref. 66) but less than E_a determined for polaron diffusion in the P3MT matrix[67] and in the P3OT/PCBM composite.[68]

Comparing the data obtained, one can conclude that the polaron motion in the P3AT/PCBM composite is definitely governed by its matrix. Indeed, the rate of fullerene rotation decreases in P3AT by some orders of magnitude as the length of its alkyl substitute A increases, i.e., at transfer from P3HT to P3DDT matrix. This probably makes it possible to control the main electronic properties of such plastic solar cells by variation of their structure, conformation, and composition. The thermal treatment of the samples also changes their main electronic properties. Such modification reduces the anisotropy of polaron diffusion (see Fig. 7) and both the E_{ph} and E_b values in the P3HT/PCBM composite (see Table II). This is evidence of the increase in crystallinity of the treated system. Besides, at the temperature annealing of the composite with initially low-crystalline polymer matrix the fullerene molecules embedded become more mobile and start to diffuse and form fullerene clusters. Due to such thermally initiated fullerene diffusion, the regions with low fullerene concentration appear in the polymer matrix where the polymer macromolecules can crystallize. As a result, polymer crystallites and fullerene clusters are formed upon annealing of the initial composite. Such treatment indeed improves additionally charge transport properties of the P3AT/PCBM and other polymer/fullerene solar cells.

IV. CONCLUSIONS

Light excitation of the bulk heterojunction in the polymer/fullerene composite leads to charge separation and transfer from a polymer chain to a fullerene molecule. This is accompanied by the excitation of two paramagnetic centers with rhombic symmetry and clearly resolved LEPR spectra, namely, the positively charged polaron $P^{+\bullet}$ on the polymer backbone and the negatively charged fullerene anion radical $C_{60}^{-\bullet}$ located between polymer chains. Both radicals are spatially separated due to the high mobility of a polaron charge carrier, so that they become noninteracting and the probability of their recombination decreases. Weak interaction of paramagnetic centers in this radical pair stipulates a difference in their interaction with their own microenvironment and, therefore, in their magnetic and relaxation parameters. Both radicals are spatially separated due to the high mobility of the polaron charge carrier, so that they become noninteracting and the probability of their recombination decreases. Spatial separation due to delocalization of a charge

over fullerene globule reduces additionally the recombination rate of these long-living charge carriers. Weak interaction of paramagnetic centers in the former radical pair stipulates a difference in their interaction with their own microenvironment and, therefore, in their magnetic-resonance parameters. This allows determining separately all relaxation parameters for both charge carriers.

Photoinduced charge is transferred by polaron diffusion along a polymer chain near the position of a fullerene radical anion where they can recombine. The probability of the collapse of photoinduced radical pairs follows the activation law and is governed by the energy of initiating optical photons. The interaction of charge carriers with their own microenvironment also depends on the photon energy. Spin dynamics induces an additional magnetic field in the whereabouts of other spins that accelerates electron relaxation of both spin ensembles. This allowed all dynamic parameters of polarons and fullerene radical anions in the polymer/fullerene composite to be calculated separately. Q1D longitudinal diffusion of polarons and rotational diffusion of fullerenes follow the activation mechanism and are governed by the photon energy. This can be a result of the formation of identical excitations in heterogeneous domains of the system. The temperature annealing of the composite enhances its dimensionality (crystallinity) due to the formation of polymer crystallites and fullerene clusters that improves the main electronic properties of plastic solar cells.

The LEPR study described contributes to a better understanding of the correlations between the structure, magnetic, and transport properties of polymers and their composites with fullerene. Such direct correlations seem to be useful for a further optimization of the polymer/fullerene solar cells. Thus, the gained knowledge about processes carried out in bulk heterojunction of a polymer/fullerene composite is of great importance from both fundamental and engineering points of view. For enhanced transport and carrier generation in these systems the network morphology of the phase-separated composite material should be optimized; light absorption and the mobility of the charge carriers within the different components of the bulk heterojunction have to be maximized as well. It was demonstrated above that the magnetic, relaxation, and dynamics properties of the paramagnetic centers photoinduced in a composite are governed by the energy of excited photons. This can be due to the formation in the system of charge carriers with different properties in a homogeneous composite or identical spin pairs in heterogeneous domains. In the first case the difference in the photon energy can lead to the formation of traps with different depths in a polymer matrix. The other situation seems to be more realistic when the variety in properties of inhomogeneously distributed domains gives rise to a variation in the main properties of charge carriers. Therefore, the investigation of the properties of paramagnetic centers excited by various photons in the initial and treated polymer/fullerene systems may give a possibility to control their texture and other structural properties of solar cells for the further increase in their efficiency factor.

ACKNOWLEDGMENTS

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