Light-Induced Electron Paramagnetic Resonance Study of Poly(3-alkylthiophene)/Fullerene Composites

Victor I. Krinichnyi,* Eugenia I. Yudanova, and Natalia G. Spitsina

Institute of Problems of Chemical Physics RAS, Semenov Avenue 1, Chernogolovka 142432, Russia

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Radical pairs, polarons, and fullerene anion radicals photoinduced by photons with an energy of 1.98−2.73 eV in bulk heterojunctions formed by poly(3-hexylthiophene) (P3HT) and poly(3-dodecylthiophene) (P3DDT) with [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) and 2-(azahomo[60]fullereno)-5-nitropyrimidine (AFNP) fullerene derivatives were studied by a direct light-induced electron paramagnetic resonance (LEPR) method in a wide temperature range. LEPR spectra of the polymer/fullerene composites consist of contributions of mobile and trapped charge carriers. Concentration and magnetic resonance parameters of these charge carriers were found to depend on the energy of initiated photons. Spin−lattice and spin−spin relaxation times of polarons and fullerene anion radicals were determined by the steady-state saturation method. The interaction of most charge carriers with the lattice is characterized by monotonic temperature dependence, whereas the spin−lattice relaxation time of fullerene anion radicals trapped in the P3DDT matrix demonstrates sharper temperature dependence. Spin−spin interaction is shown to be nearly temperature independent and to be governed by structural properties of polymer/fullerene composites. Longitudinal diffusion of polarons and pseudorotation of fullerene derivatives was shown to follow the activation Elliot hopping model. The replacement of the P3HT matrix by P3DDT accelerates polaron dynamics and increases its anisotropy. The energetic barrier required for polaron interchain hopping mainly prevails upon that of its intrachain diffusion in all composites except P3DDT/AFNP one. Spin dynamics becomes easier when the PCBM fullerene derivative is replaced by the AFNP one.

Introduction

During the last two decades, research has been increasing in the field of synthesis and characterization of molecules with extended π-electron delocalization considering them as promising materials for molecular electronics. Various materials can be used in photovoltaic devices sensing, accumulating, and converting sunlight, for example, phthalocyanine and perylene, azo, and xanthene dyes.[1] Bulk heterojunctions formed by two organic materials with nanoscale phase separation resulting in a three-dimensional interpenetrating network proved[1−3] to be the most effective for organic photovoltaics. Soluble conjugated polymers, for example, poly(3-alkylthiophene) (P3AT), and fullerene derivatives with various structures of their side alkyl substitutes were found[1,3−5] to be the most efficient components for plastic photovoltaics. Polymer macromolecules and fullerene globes in such composites act as electron donors (hole transporter, *p*-type material) and electron acceptors (electron transporter, *n*-type material), respectively. Light irradiation by photons with the energy $h\nu_{ph}$ higher than the $\pi−\pi^*$ energy gap of the conjugated polymer first excites the donor−acceptor (D-A) complex, which is transformed into an ion−radical pair (RP). Such a pair is dissociated into two noninteracting D^+ and A^- species. The D-A system can relax back to the ground state, releasing energy to the "lattice" as either heat or emitted light. This process was revealed by time-resolved spectroscopy[6] to occur in the femtosecond time domain, whereas electron back transfer with charge annihilation is much slower possibly due to dynamics of charge carriers and relatively slow structural relaxation.[7] The mobility of charge carriers in organic polymer semiconductors is some orders of magnitude lower than that of inorganic solids.[8] This limits the design and power conversion efficiency of plastic solar cells, which now attains more than 5%.[1] Within the bulk heterojunction, the donor and acceptor domains are generally disordered in volume. For efficient exciton dissociation and charge generation, fine nanoscale intermixing is required, whereas for the optimal transport of charge carriers, percolation and a certain phase separation are needed to provide undisturbed transport. This can be realized by the optimization of structure of polymer and fullerene derivatives as well as of nanomorphology of a photoactive blend formed by them.

This can be demonstrated considering the arrangement of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of components involved in the formation of the bulk heterojunction. The relative position of the HOMO−LUMO levels and the choice of electrode materials that have to possess suitable work functions are basic requirements to make an optimal solar cell. The HOMO of the donor ($HOMO_D$) should be higher in energy than the HOMO of the acceptor ($HOMO_A$). Additionally, the energy level of the $LUMO_A$ has to be lower than that of the $LUMO_D$. Typically, an organic acceptor possesses a reduction potential and, hence, the LUMO, lower than its HOMO level. If the $LUMO_D − LUMO_A$ difference is relatively high as in the case of the poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), more frequently used in photovoltaics, photoinduced electron transfer occurs within picoseconds, and no back transfer or other disturbing processes can be realized. This is additionally due to extremely high electron affinity of fullerenes and reflects in 100% internal quantum efficiency for the P3HT/PCBM composite. However, the required minimum

* To whom correspondence should be addressed. E-mail: kivirus@gmail.com.

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value for the $LUMO_D - LUMO_A$ difference is still uncertain and will probably depend on the material combination applied.

Different molecular and charge motions can be realized in organic polymer/fullerene systems. The charge can tunnel from the polymer chain to the fullerene globe and hop between the globes uniaxially pseudorotating between polymer chains. Besides, it is quasi-one-dimensionally (Q1D) transferred by a polaron along polymer chains and quasi-three-dimensionally (Q3D) hops between them. Finally, these processes can be modulated by comparatively slow torsion and libration dynamics of polymer chains.[9] One can, therefore, expect the correlation of the main electronic and structural parameters of such solar cells. Understanding the mechanism of electron relaxation and dynamic behavior of fullerene-modified organic polymers is essential for the optimization of devices based on these materials.

Photoinduced charge separation and transfer are accompanied by the formation of pairs of polaron $P^{\bullet+}$ and fullerene radical anion $C_{60}^{\bullet-}$ (or its derivative $C_{61}^{\bullet-}$) each with spin $S = 1/2$. This accounts for the wide use of light-induced electron paramagnetic resonance (LEPR) as a direct method for investigation of such paramagnetic centers (PCs) in polymer/fullerene composites.[4,10–12] LEPR measurements revealed the existence of two radicals with different line shapes, magnetic resonance parameters, and saturation properties. This means that each RP within a short time collapses into two different and independent PCs. It was found that the g factor of the polaron is characterized by rhombic symmetry in regioregular P3HT[13,14] (with[14] $g_{xx} = 2.0028$, $g_{yy} = 2.0019$, and $g_{zz} = 2.0009$) and axial symmetry in, for example, poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV)[14,15] (with[15] $g_{xx} = 2.00341$, $g_{yy} = g_{zz} = 2.00241$ and[14] $g_{xx} = 2.0033$, $g_{yy} = g_{zz} = 2.0022$). PCBM anion radical embedded into the latter matrix is also characterized by rhombic symmetry with $g_{xx} = 2.00031$, $g_{xx} = 2.00011$, and $g_{zz} = 1.99821$.[15]

We justified[16] that among soluble fullerene derivatives with different side alkyl substitutes methanofullerene PCBM indeed appeared to be a more suitable electron acceptor for organic photonics. This is actually up today; nevertheless, one can expect that other fullerene derivatives can be more effective electron acceptors in polymer/fullerene systems.

It was found[17] that the mobility and stability of charge carriers are considerably higher in bulk heterojunctions formed by PCBM globes with the P3HT chains as compared with other polymer/PCBM composites. A much longer charge carrier lifetime achieved in the P3HT/PCBM film is stipulated by a higher concentration of carriers and their reduced recombination rate. It was interpreted to be due to better structural order in the presence of interface dipoles, provoking the creation of a potential barrier for carrier recombination in this composite. The specific nanomorphology of P3AT/PCBM blends could result in screened Coulomb potential between the RPs photoexcited in their bulk heterojunctions and facilitate their splitting into noninteracting charge carriers with a reduced probability of further annihilation. This implies that much longer carrier lifetimes can be achieved at the same concentrations that finally result in higher photocurrent and larger power conversion efficiency of such solar cells. It also should be noted that the regioregularity increases the planarity and decreases the band gap of P3AT.[18] This predestined the use of regioregular P3AT modified by PCBM in our previous LEPR study.[19,20] In particular, it was demonstrated that the main magnetic resonance and electron relaxation properties of charge carriers are governed by the energy of initiated photons $h\nu_{ph}$. For example, the increase in $h\nu_{ph}$ from 1.26 eV up to 1.80 eV redoubles total density of

polarons trapped in the P3HT and poly(3-dodecylthiophene) (P3DDT) matrices and sufficiently changes the bimolecular recombination constant.[21] This makes it possible to use this effect for controlling the texture and other structural properties of photovoltaic devices so then increasing their further efficiency.

In the present work were used P3HT and P3DDT as electron donor matrices as well as PCBM and recently synthesized azahomofullerene 2-(azahomo[60]fullereno)-5-nitropyrimidine (AFNP) as electron acceptors. It was demonstrated that a systematic preliminary investigation of the spectroscopic properties of known and novel donor and acceptor materials represents a helpful tool to evaluate potential materials for plastic photonics applications.

Experimental Section

In the present work, used as electron donors were regioregular P3HT with the HOMO and LUMO equal to[12] −5.20 and −3.53 eV and lattice constants[22] $a = 1.67$ nm, $b = 1.56$ nm, and $c = 0.38$ nm distributed by Rieke Metals (United States) and regioregular P3DDT with the HOMO and LUMO equal to[23] −5.29 and −3.55 eV and lattice constants[24] $a = 2.583$ nm, $b = 0.775$ nm, and $c = 0.777$ nm distributed by Aldrich (United States) without additional rectification. PCBM with the HOMO and LUMO equal to[4] −6.10 and −3.75 eV distributed by the Solenne BV (The Netherlands) and AFNP with the HOMO and LUMO equal to[25] −6.13 and −4.53 eV synthesized using the method described earlier[25] were used as electron acceptors. Their ca. 1 wt % concentration solution in chlorobenzene (C_6H_5Cl) at a 1:1 wt ratio was cast repeatedly into a ceramic plane and dried. Then, the polymer/fullerene composites formed as films with a size of ca. 4×8 mm^2 and a thickness of ca. 0.1 mm.

EPR measurements were made using an X-band (3 cm, 9.7 GHz) PS-100X spectrometer with maximal microwave (MW) power of 150 mW (that is equivalent to the magnetic term B_1 of MW irradiation in the cavity center of 0.51 G) and 100 kHz field ac modulation for phase-lock detection. The LEPR spectra of the polymer/fullerene systems and their components were registered at 90–340 K in dry nitrogen atmosphere using a BRT SKB IOH temperature controller and at 77 K in quartz Dewar filled with liquid nitrogen. The signal-to-noise ratio of the LEPR spectra was improved by averaging several (typically 4–6) acquisitions. The measurements of effective magnetic susceptibility of the "dark" (domestic) paramagnetic centers (PC) and PCs photoinduced in a polymer/fullerene bulk heterojunctions were performed using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) nitroxide radical. Their individual absorption LEPR spectra were doubly integrated far from MW saturation conditions when the magnetic 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. To determine the maximal concentration of polarons that can be stabilized in polymer matrices, both of the initial composites P3HT/PCBM and P3DDT/PCBM were treated for ca. 40 min by dry iodine vapor at $T = 320$ K. Diphenylpicrylhydrazyl (DPPH) single microcrystal standard with $g = 2.0036$ was used for the estimation of the g factor of both charge carriers. The determination accuracies of the line intensity I, g factor, and peak-to-peak line width ΔB_{pp} were 5%, $\pm 2 \times 10^{-4}$, and $\pm 2 \times 10^{-2}$ G, respectively. Processing and simulations of the EPR spectra were done with the Bruker WinEPR SimFonia and OriginLab Origin programs.

Permanent illumination of the sample was realized directly in a microwave cavity of the EPR spectrometer by Luxeon III solid-state LED light sources LXHL-LW3C (5500 K), LXHL-LD3C (625 nm, 1.98 eV), LXHL-LL3C (590 nm, 2.10 eV),
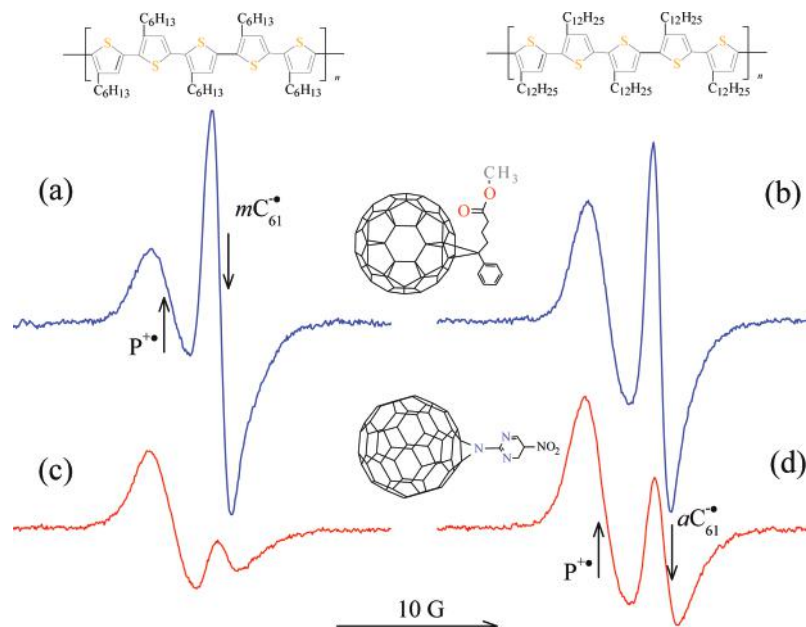
Figure 1. LEPR spectra of spin charge carriers photoinduced in bulk heterojunctions of P3HT/PCBM (a), P3DDT/PCBM (b), P3HT/AFNP (c), and P3DDT/AFNP (d) by light beam with $h\nu_{ph} = 1.98$ eV at $T = 77$ K. The positions of polarons $P^{\bullet+}$, methanofullerene $mC_{61}^{\bullet-}$ and azagomofullerene $aC_{61}^{\bullet-}$ are shown. The structures of P3HT, P3DDT, PCBM, and AFNP are schematically shown at the top left, top right, top center, and bottom center regions, respectively.

LXHL-LM3C (530 nm, 2.34 eV), LXHL-LE3C (505 nm, 2.46 eV), and LXHL-LR3C (455 nm, 2.73 eV) with the half-height width of ca. 0.1 eV (except LXHL-LW3C). Effective integral irradiation of these sources was valued using an IMO-2N output power light irradiation meter 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.

Results and Discussion

All polymer and fullerene components do not demonstrate both "dark" and LEPR signals in the whole temperature range. As a polymer with embedded fullerene derivative is irradiated by visible light directly in the cavity of the EPR spectrometer, two overlapping LEPR lines appear at $T \leq 200$ K. Figure 1 shows the LEPR spectra of the composites irradiated by light beam with $h\nu_{ph} = 1.98$ eV at $T = 77$ K. The lines registered in low and high fields can be attributed to positively charged polarons $P^{\bullet+}$ with isotropic (effective) g_{iso}^P and negatively charged fullerene derivative with g_{iso}^F background photoinduced in bulk heterojunctions of the polymer/fullerene composites, respectively. Detailed analysis of the data obtained at wide variety of experimental conditions showed that LEPR spectra presented in Figure 1 consist of a Lorentzian doublet of mobile RPs (shown in Figure 2 as sum of contributions of mobile polarons P_{mob} and fullerene anion-radicals F_{mob}) and Gaussian contributions of localized polarons (P_{loc}) and fullerene anion radicals (F_{loc}) pinned by a polymer matrix (Figure 2). Moreover, both P3HT/AFNP and P3DDT/AFNP composites show the PCs (F_N in Figure 2) characterized by a broad (5−10 G) line and $g_{iso} \approx$ 2.0039 and 2.0043, respectively. Relatively high g_{iso} and ΔB_{pp} of this PC allowed us to suppose that an unpaired electron delocalized on the AFNP globe interacts with the nearest nitrogen nucleus of the fullerene substitute. Therefore, the main magnetic resonance parameters of such PC become anisotropic,[26] and its apparent line width and susceptibility increase considerably (see below). It can be used as a domestic spin probe for additional analysis of molecular dynamics in a composite. The values $g_{iso}^P = 2.0017$ and $g_{iso}^P = 1.9996$ (P3HT/PCBM) and g_{iso}^P
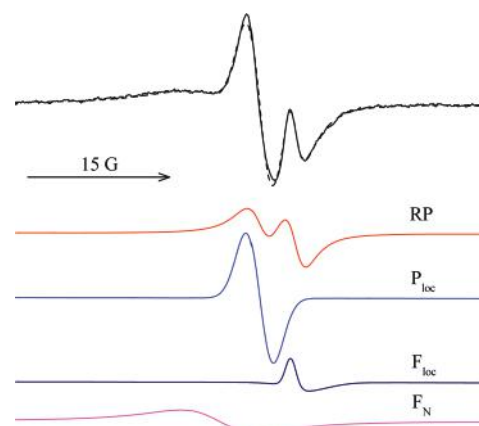

Figure 2. LEPR spectra of spin charge carriers photoinduced in bulk heterojunctions of the P3DDT/AFNP composite by light beam with $h\nu_{ph} = 1.98$ eV at $T = 90$ K. The contributions coming due to mobile RPs, localized polarons (P_{loc}), and fullerene anion radicals (F_{loc}) as well as spin interacting with nearest nitrogen nuclear (F_N) are shown.

$= 2.0016$ and $g_{iso}^F = 1.9996$ (P3DDT/PCBM) lie near those obtained for RPs photoinduced in other fullerene-modified conjugated polymers.[10,20,27] Subsequent LEPR measurement cycles of heating up to room temperature, cooling down to $T \leq 200$ K, illumination with light, switching off light, and heating up again yield identical results. The value g_{iso}^F of the fullerene anion radicals is almost temperature independent. On the other hand, this parameter of the polaron charge carriers was analyzed to depend on different factors. Figure 3 shows the changes in the isotropic g factor of polarons photoinduced in the P3HT/ PCBM and P3DDT/PCBM composites. It is seen that the temperature increase leads to a decrease in the isotropic g factor of polarons, g_{iso}^P, especially in P3DDT. Such a decrease in g_{iso}^P occurs at the excitation of an electron from the unoccupied shell to the antibonding orbit $\pi \rightarrow \sigma^*$.[28] The energy of antibonding orbits of regioregular P3HT seems to exceed that of P3DDT, and the g factor of the former is less temperature dependent, characteristic of more ordered system.
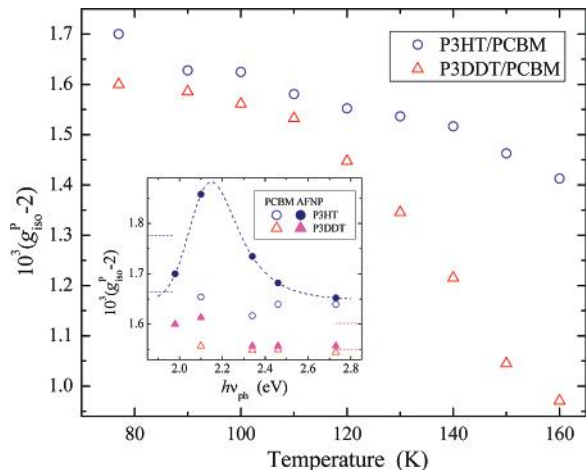
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Figure 3. The g_{iso} of polarons (g_{iso}^p) photoinduced in bulk heterojunctions of the P3HT/PCBM and P3DDT/PCBM composites by light beam with $h\nu_{ph} = 1.98$ eV as a function of temperature. The insert shows g_{iso}^p obtained for different polymer/fullerene systems at $T = 77$ K as a function of photon energy $h\nu_{ph}$. Left and right dashed sectors show respective values determined for this charge carrier initiated by white light in polymers with embedded PCBM and AFNP, respectively.

TABLE 1: Terms and Average Values of the g Tensor $g_{i,ij}^i$ and Peak-to-Peak Linewidth ΔB_{pp}^i (in Gauss) Used for the Simulation of the LEPR Spectra of Polarons P•+ and Methanofullerene PCBM Anion Radicals $mC_{61}^{\bullet-}$ Photoinduced in the P3DDT/PCBM Composite by Light with Photon Energy $h\nu_{ph} = 1.98$ eV at 77 K

radical	g_{xx}	g_{yy}	g_{zz}	g_{iso}	ΔB_{pp}^x	ΔB_{pp}^y	ΔB_{pp}^z	ΔB_{pp}^{iso}
P•+	2.0026	2.0017	2.0006	2.0016	2.5	1.4	1.5	1.8
$mC_{61}^{\bullet-}$	2.0003	2.0001	1.9986	1.9996	0.7	1.6	2.5	1.6

The limiting number of polarons n_p able to be stabilized in a polymer matrix per unit can be evaluated using nonreversible polymer doping, for example, by iodine molecules.[15] Slight I_2 treatment can also be used for comparison of magnetic resonance parameters of polarons reversibly and irreversibly initiated in the same matrix. Note that I_2 doping of the P3HT changed the above-mentioned main terms of the g factor and the line width of polarons to $g_{xx} = 2.0029$, $g_{yy} = 2.0019$, and $g_{zz} = 2.0011$ and $\Delta B_{pp}^x = 9.2$ G, $\Delta B_{pp}^y = 8.9$ G, and $\Delta B_{pp}^z = 6.4$ G.[14] In both cases, however, only an initial polymer was chemically I_2 treated.

To obtain not only the n_p value but also a similar number of fullerene radical anions n_f simultaneously formed in a polymer matrix, we have used I_2 doping of finalized P3HT/PCBM and P3DDT/PCBM composites. The EPR spectra of these systems highly I_2 treated and measured at different temperatures are presented in Figure 4. At high temperature, the P3HT/PCBM and P3DDT/PCBM composites demonstrate single Lorentzian EPR spectra with peak-to-peak line width ΔB_{pp} values of 4.0 and 10.2 G, respectively (Figure 4), much broader than those obtained for polarons stabilized in other conjugated polymers.[33] The broadening of the EPR transitions is most likely due to a dipole–dipole interaction between charged polarons. The contribution to line width due to such an interaction can be estimated as $\Delta B_{dd} = \mu_B R_0^{-3} = 4/3\pi\mu_B n_p$, where μ_B is the Bohr magneton and R_0 is the distance between polarons proportional to their concentration n_p on the polymer chain. Assuming an intrinsic line width of polarons $\Delta B_{pp}^0 = 1.5$ G in regioregular P3HT,[13] from $\Delta B_{dd} = 2.5$ G, one can obtain $R_0 \approx 1.6$ nm for P3HT/PCBM and, analogously, $R_0 \approx 1.1$ nm for P3DDT/PCBM. Limiting paramagnetic susceptibility χ was determined to be 1.2×10^{-5} emu/mol for P3HT/PCBM and 7.7×10^{-6}

The deviation of the g factor of the polaron from the free-electron g factor, $g_e = 2.00232$, is due to its noncompensated orbital momentum, which induces an additional magnetic field due to the of $\sigma \rightarrow \pi \rightarrow \sigma^*$ excitations. The orbital moment due to direct $\pi-\pi^*$ excitation is negligible and shows up on the neighboring C atoms only. Our previous high-field/frequency (D-band, 140 GHz) EPR study of structurally close poly(3-octylthiophene) (P3OT) showed[29,30] that weak interaction of an unpaired electron delocalized on a polaron with sulfur heteroatoms involved in the polymer backbone provokes rhombic symmetry of its g factor (with $g_{xx} = 2.00409$, $g_{yy} = 2.00332$, and $g_{zz} = 2.00235$) and line width. It was confirmed later at W-band (94 GHz) EPR[14] that the polaron photoinduced in the P3HT matrix is also characterized by an anisotropic g factor with the above-mentioned principal values and anisotropic line width with $\Delta B_{pp}^x = 10.7$ G, $\Delta B_{pp}^y = 5.3$ G, and $\Delta B_{pp}^z = 6.4$ G. Because the backbone of the polymer can be expected to lie preferably parallel to the film substrate,[31] the lowest principal g value is associated with the polymer backbone. The molecule can take any orientation with regard to the z-axis, that is, the polymer backbone direction as it derives from the presence of both the g_{xx} and the g_{yy} components in the spectra for all orientations of the film. So, the g factor anisotropy gives rise to the inhomogeneity of distribution of additional fields along the x and y directions within the plane of the polymer σ skeleton and not along its perpendicular z direction.

Effective g_{iso}^F of anion radicals $C_{61}^{\bullet-}$ is typical of fullerene anion radicals.[32] The W-band EPR study[15] allowed us to conclude that spin density in the $C_{61}^{\bullet-}$ radical anion embedded in an organic polymer matrix is also characterized by rhombic symmetry and, therefore, an anisotropic g factor with the terms $g_{xx} = 2.00031$, $g_{yy} = 2.00011$, and $g_{zz} = 1.99821$ and line width with appropriate $\Delta B_{pp}^x = 2.3$ G, $\Delta B_{pp}^y = 1.3$ G, and $\Delta B_{pp}^z = 8.8$ G. An asymmetrical distribution of spin density in both polaron and fullerene radical anion leads to a tensorial character of their line width.[15,29,30] This should be taken into account in precise calculations of the effective LEPR spectrum of the P3AT matrix with embedded PCBM. The magnetic resonance parameters used for calculations of these charge carriers are summarized in Table 1.
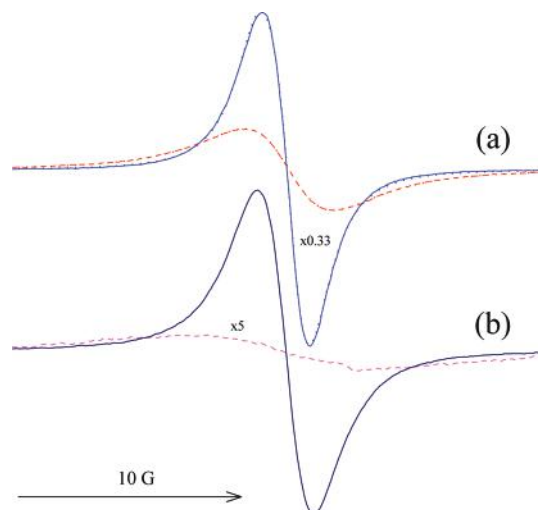

Figure 4. EPR spectra of polarons stabilized in the P3HT/PCBM (a) and P3DDT/PCBM (b) composites after their treatment by iodine vapor for ca. 40 min at $T = 320$ K and registered at 310 (dashed line) and 77 K (solid line).

TABLE 2: Concentration of Polarons n_p and Fullerene Anion Radicals n_f Per One Polymer Unit Initiated in the Polymer/Fullerene Composites by I_2 Doping, $n_{p(max)}$, and Light Irradiation with $h\nu_{ph} = 1.98$ eV at 77 K

	composite			
	P3HT/PCBM	P3HT/AFNP	P3DDT/PCBM	P3DDT/AFNP
$n_{p(max)}$	2.8×10^{-3}		2.2×10^{-3}	
n_p	3.9×10^{-5}	4.2×10^{-5}	1.2×10^{-4}	7.6×10^{-5}
n_f	2.3×10^{-5}	1.1×10^{-5}	6.3×10^{-5}	5.9×10^{-5}

emu/mol for P3DDT/PCBM at $T = 310$ K. As the temperature decreases down to 77 K, these values increase up to 1.2×10^{-4} and 6.9×10^{-5} emu/mol, respectively. Besides, the analysis showed that the cooling of the samples leads to the appearance of an anisotropic Gaussian term in the sum EPR spectra attributed to strongly frozen polarons. The ratio of the number of mobile to frozen polarons is near 8:1 for P3HT/PCBM and 32:1 for P3DDT/PCBM at 77 K. At the transition from P3HT to P3DDT matrix, the ΔB_{pp} value of mobile and localized polarons characterized by Lorentzian and Gaussian distribution of spin packets at 77 K increases from 1.9 and 2.3 G to 2.3 and 2.4 G for P3HT and P3DDT, respectively. The maximum density of polaronic transport states was estimated[21] for regioregular P3HT and P3DDT to be near 10^{21} cm^{-3} assuming that one polaron occupies approximately five monomer units. The intrinsic concentration of doping-initiated polarons counting only upon the polymer fraction in the P3HT/PCBM composite was determined at 77 K to be 1.6×10^{19} cm^{-3}. This value lies near 2×10^{19} cm^{-3} obtained for the concentration of acceptors in ZnO-treated P3HT.[34] An effective concentration calculated counting upon both the polymer and the fullerene components of this composite is 1.8×10^{18} cm^{-3}. The intrinsic and effective concentrations determined for I_2-doped P3DDT/PCBM system are 4.6×10^{18} and 1.0×10^{18} cm^{-3}, respectively. This allows one to evaluate the number of charge carriers per polymer unit initiated in the polymer/fullerene composites by I_2 doping and light irradiation (Table 2). The n_P values obtained are less

considerably than $n_p \approx 0.05$ evaluated for doped polyaniline.[35]

The paramagnetic susceptibility of charge carriers of different mobilities and natures that contributed to the effective LEPR spectrum in the $77-160$ K range derived from their double-integrated spectra is shown in Figure 5. The concentration of main charge carriers decreases dramatically at higher temperatures. Thus, the precision of determination of their spin susceptibility falls significantly.

Both spins of each RP photoinduced in close proximity should interact in the scale of a pair, either by exchange or by dipolar mechanisms. These effects were not registered in the LEPR spectra of the polymer/fullerene composites because polarons diffuse along the conjugated polymer backbone away from the fullerene anion radicals faster than their possible exchange time, that is, $\tau_{ex} \leq 10^{-9}$ s. This particularly leads to an unusually long lifetime of such charge carriers in polymer/fullerene bulk heterojunctions.

Basically, photoinitiation of charge carriers occurs in the femtosecond time domain,[6] whereas electron back transfer with charge annihilation is much slower possibly due to dynamics and relatively slow structural relaxation in such a system of lower dimensionality. This is a reason why effective paramagnetic susceptibility of both charge carriers should inversely depend on the probability of their recombination. This probability is determined by spin multistage diffusion (normally, activation) along a polymer chain and tunneling from a chain to a fullerene anion.[36] Thus, the decay of mobile charge carriers in regioregular P3AT consists of temperature-independent fast and exponentially temperature-dependent slow contributions.[21] The polaron that diffuses between initial i and final j sites spends the energy ΔE_{ij}, so the Miller–Abrahams energy-dependent factor appears in the equation for paramagnetic susceptibility[37]

$$\chi(\Delta E_{ij}) = \chi_0 \exp\left(\frac{\Delta E_{ij}}{k_B T}\right) \tag{1}$$
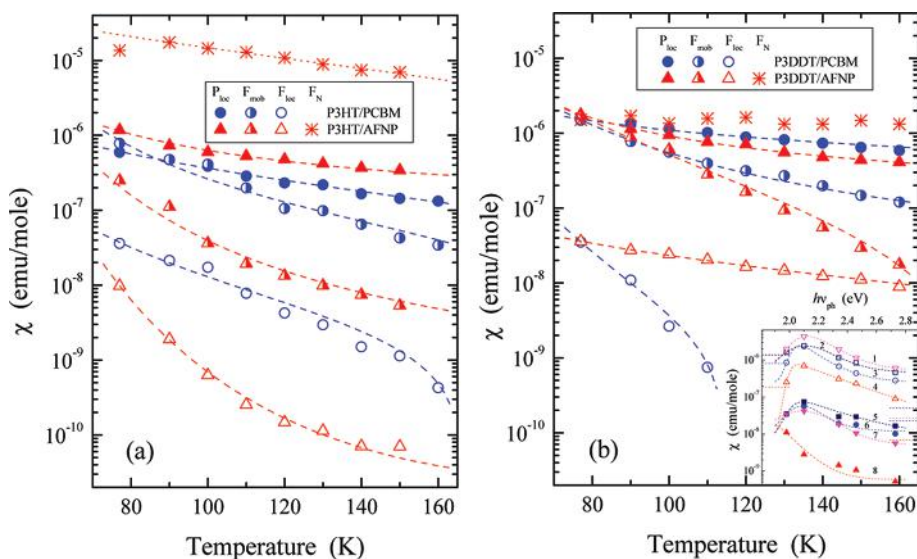

Figure 5. Temperature dependence of paramagnetic susceptibility of charge carriers P_{loc}, F_{loc}, F_N, and F_{mob} (left line of the RP in Figure 2) photoinduced in bulk heterojunctions formed by the P3HT (a) and P3DDT (b) chains with the PCBM and AFNPF fullerene derivatives by photons with $h\nu_{ph} = 1.98$ eV. Dashed lines show the dependences calculated from eq 3 with ΔE_{ji} summarized in Table 4. The insert shows paramagnetic susceptibility of mobile F_{mob} (open points) and pinned F_{loc} (filled points) fullerene anion radicals photoinduced in the P3HT/PCBM (*3,6*), P3HT/AFNP (*4,8*), P3DDT/PCBM (*2,5*), and P3DDT/AFNP (*1,7*) composites at 77 K as a function of photons with $h\nu_{ph}$. The values determined for F_{mob} and F_{loc} initiated by white light are shown by the left and right dashed sectors, respectively. Dashed lines connecting the experimental points are painted arbitrarily.

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TABLE 3: ΔE_{ij}, E_a, and E_b Values Determined from Eqs 3, 5, and 9, Respectively, for Charge Carriers Photoinduced by Light with $h\nu_{ph}$ = 1.98 eV in Bulk Heterojunctions Formed by P3HT and P3DDT Macromolecules with Methanofullerene PCBM and Azagomofullerene AFNP Globes

radical parameter	$P^{\bullet+}_{loc}$	$P^{\bullet+}_{mob}$	$mC^{\bullet-}_{61(mob)}$	$mC^{\bullet-}_{61(loc)}$	$P^{\bullet+}_{loc}$	$P^{\bullet+}_{mob}$	$aC^{\bullet-}_{61(mob)}$	$aC^{\bullet-}_{61(loc)}$	$F^{\bullet-}_N$
			P3HT/PCBM				P3HT/AFNP		
ΔE_{ij} (eV)	0.007		0.034	0.024	0.017		0.048	0.077	0.0015
E_a (eV)	0.012				0.013				
E_b (eV)		0.013[a] 0.102[b]	0.019			0.008[a] 0.051[b]	0.098		
			P3DDT/PCBM				P3DDT/AFNP		
ΔE_{ij} (eV)	0.018		0.024	0.045	0.022		0.017	0.014	
E_a (eV)	0.001				0.023				
E_b (eV)		0.010[a] 0.056[b]	0.068			0.062[a] 0.029[b]	0.012		

[a] Determined for polaron 1D diffusion. [b] Determined for polaron 3D diffusion.

Besides, a positive charge on a polaron is not required to be recombined with the first negative charge but with a charge on the subsequent fullerene. A polaron traveling near the fullerene anion radical, which is localized near a polymer chain, should interact with its unpaired electron. Therefore, the spin flip−flop probability p of a collision of these spins should depend on the exchange interaction and the ω_{hop} value as[35,38]

$$p = \frac{1}{2} \cdot \frac{\alpha^2}{1 + \alpha^2} \qquad (2)$$

where $\alpha = (3/2)2\pi J/\hbar\omega_{hop}$, $\hbar = h/2\pi$ is the Plank constant, and J is the constant of exchange interaction of spins in a RP. Weak and strong exchange limits can be realized for the systems under study. In this case, the increase of ω_{hop} may result in the decrease or the increase in exchange frequency, respectively. If the $J/\hbar$ ratio exceeds the frequency of collision of spins of both types, and the condition of strong interaction is realized in the system leading to a direct relation of spin−spin interaction and polaron diffusion frequencies, then $\lim(p) = 1/2$. In the opposite case, $\lim(p) = 9/2(\pi/\hbar)^2(J/\omega_{hop})^2$. It is evident that the longer both of the above tunneling times or/and the lower the probability p is, the smaller the number of RPs possible to recombine and, therefore, the higher spin susceptibility should be registered. A combination of the above equations takes the general form of this main parameter for polarons in polymer/fullerene composite as

$$\chi(\Delta E_{ij}) = \chi_0 \frac{2(1 + \alpha^2)}{\alpha^2} \exp\left(\frac{\Delta E_{ij}}{k_B T}\right) \qquad (3)$$

Assuming polaron activation multistep hopping with the frequency $\omega_{hop} = \omega^0_{hop} \exp(-\Delta E_{ij}/k_B T)$ and the absence of a dipole−dipole interaction between fullerene anion radicals, one can evaluate ΔE_{ij} and the amplitude of spin−spin exchange interaction from temperature dependences of paramagnetic susceptibility of all PC shown in Figure 5 (see Table 3). As it is seen from the figure, the recombination processes in the composites can be described by eq 3 with ΔE_{ij} presented in Table 3.

It is evident that polaron diffusion in the P3HT matrix in addition to mobile and trapped methanofullerene anion radicals requires lower energy ΔE_{ij} as compared with its diffusion near azagomofullerene one. ΔE_{ij} obtained from $\chi(T)$ for methanofullerene rotating in the P3HT/PCBM and P3DDT/AFNP systems

exceeds the corresponding value of a radical anion trapped in these composites. The opposite situation is realized in the P3HT/AFNP and P3DDT/PCBM matrices (see Table 3). The data obtained indicate that all spin-assisted processes are governed mainly by the structure of ingredients of a composite as well as by the nature and dynamics of charge carriers photoinduced in its bulk heterojunction.

The annihilation of RPs in the polymer/fullerene composites should normally be described as thermally activated bimolecular process.[39] 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 the elemental charge, ε is the dielectric constant, and r is the charge pair separation. U_c varies from ∼0.4 eV for charges separated by one lattice unit to less than 0.02 eV for charge pairs at mean separation. Therefore, both the photoinduced polaron and the radical anion should be considered as noninteracting, which indeed leads to their long life.

The shape and intensity of the resulting LEPR spectrum are governed not only by the number of the photons absorbed but also by their energy $h\nu_{ph}$. Figure 5 shows the changes in spin susceptibility of mobile and localized fullerene anion radicals initiated in polymer/fullerene composites depending on energy of photons, $h\nu_{ph}$ [$P^{\bullet+}$ demonstrate a weaker $\chi(h\nu_{ph})$ dependence, which is not shown here]. It is seen that the χ value of most anion radicals changes extremely with the photon characteristic energy $h\nu_{ph} \approx 2.1$ eV. This value lies near the band gap energy obtained for P3AT.[12] It is seen that χ decreases when the fullerene derivative PCBM is replaced by AFNP one. 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 systems under study. Different spin pairs can be photoinduced as a result of the photon-assisted appearance of traps with different depths in a polymer matrix. However, the revealed difference in the parameters of PC seems to be rather a result of their interaction with their own microenvironment in domains inhomogeneously distributed in polymer/fullerene composites. 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 energy. This can give rise to the change in the interaction of PC with a lattice and other spins. Such photon frequency selectivity is seen to be governed by properties of donor and acceptor involved in bulk heterojunction. Strong selectivity can be used, for example, in plastic sensoric
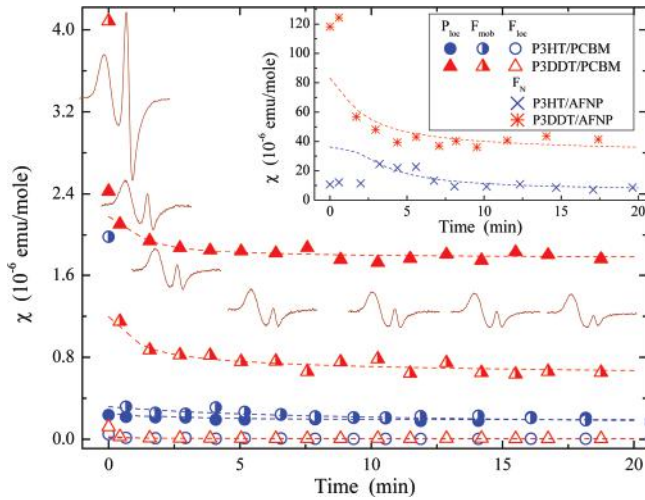
Figure 6. Decay of spin susceptibility of pinned polarons P_{loc} (filled points) as well as methanofullerene $mC_{61}^{\bullet-}$ rotating (F_{mob}, semifilled points) and pinned (F_{loc}, open points) photoinduced in the bulk heterojunction formed by PCBM with the P3HT (circles) and P3DDT (triangles) chains as well as of spins exchange interacting with a nitrogen nucleus of AFNP embedded into P3HT and P3DDT matrix (F_N, × and * symbols, respectively). Typical changes in the LEPR spectrum of a composite polymer/fullerene with appropriate time t are shown.

photovoltaics, whereas the composites with low selectivity seem to be more suitable for efficient conversion of solar irradiation.

If one switches off excited light illumination of the polymer/fullerene system, the concentration of spin pairs excited in its bulk heterojunction starts to decrease as is shown in Figure 6. Calculating LEPR spectra, it is possible to register the decay of mobile and pinned spin charge carriers excited in the polymer/fullerene composites (Figure 6).

The decay curves presented can be interpreted in terms of the approach of recombination of charge carriers with different effective localization radii separated by a time-dependent distance R.[40] The localization radius for a negative charge carrier should be of the order of the radius of the PCBM globule. The distance R should depend, in particular, on the length of a side alkyl chain substitute in a polymer/fullerene composite with a regioregular P3AT matrix.[41] A polaron stabilized in conjugated polymers is normally distributed over five monomer units.[21,42] Assuming that photoexcitation is turned off at some initial time $t_0 = 0$ at charge carrier concentration n_0 and taking into account a time period of geminate recombination $t_1 - t_0$, one can write for the concentration of charge carriers[40]

$$\frac{n(t)}{n_0} = \frac{\dfrac{n_1}{n_0}}{1 + \left(\dfrac{n_1}{n_0}\right)\dfrac{\pi}{6}n_0 a^3\left[\ln^3\left(\dfrac{t}{\tau_0}\right) - \ln^3\left(\dfrac{t_1}{\tau_0}\right)\right]} \quad (4)$$

where t_1 is the time after which solely nongeminate recombination is assumed, n_1 is the charge carrier concentration at time t_1, n_0 is the initial carrier density, a is the effective localization radius of charge carriers, and τ_0 is the typical radiative lifetime of spin pair.

It was shown that eq 4 fits well the experimental data presented in Figure 6. Therefore, the decay of long-living spin pairs photoinduced in the P3AT/PCBM and similar composites can successfully be described in terms 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 large spatial distances that build up among the remaining photoinduced charge carriers, which did not recombine at a shorter time.

The $n_0 a^3$ and τ_0 values determined from eq 4 for charge carriers stabilized in the polymer/fullerene bulk heterojunctions are presented in Table 4. It is seen from the data presented in Table 4 that the product $n_0 a^3$ increases at the transition from the P3DDT matrix to the P3HT one. This fact is in agreement with the higher probability of excitation of mobile polarons in the latter system.[21] Such a transition also prolongs the typical radiative lifetime of spin pair τ_0 that also corresponds to the lower constant of bimolecular recombination in the P3HT as compared with the P3DDT matrix.[21] The latter parameter increases considerably as the methanofullerene acceptor is replaced by the azagomofullerene one.

Effective (isotropic) peak-to-peak linewidths $\Delta B_{pp}^{(0)}$ obtained for the $P^{\bullet+}$ and $C_{61}^{\bullet-}$ radicals are presented in Figure 7 as a function of photon energy and temperature. It is seen from Figure 7a that this parameter determined for both charge carriers in P3HT/PCBM and for fullerene anion radicals in P3HT/AFNP depends extremely on photon energy $h\nu_{ph}$ with a characteristic energy ~2.1 eV. This value lies near the band gap energy of P3AT[12,43] that can be evidence of the interaction of initiated photons with the matrix lattice. As in the case of spin susceptibility, variation in $\Delta B_{pp}^{(0)}(h\nu_{ph})$ registered for other charge carriers can also be attributed to inhomogeneous distribution of domains with different ordering (and, hence, band gap energies) in the polymer/fullerene bulk heterojunction.

The analysis of the data presented in Figure 7b shows that LEPR spectra of most of charge carriers are broadened with composite heating. However, the line width of polarons in the P3DDT/AFNP and fullerene anion radicals in P3HT/AFNP

TABLE 4: $n_0 a^3$ and τ_0 Values Determined from Eq 4 for Spin Charge Carriers Photoinduced at $h\nu_{ph} = 1.98$ eV and 77 K in Bulk Heterojunctions Formed by P3HT and P3DDT Macromolecules with Methanofullerene PCBM and Azagomofullerene AFNP Globes

radical parameter	$P_{loc}^{\bullet+}$	$mC_{61(mob)}^{\bullet-}$	$mC_{61(loc)}^{\bullet-}$	$P_{loc}^{\bullet+}$	$aC_{61(mob)}^{\bullet-}$	$F_N^{\bullet-}$
		P3HT/PCBM			P3HT/AFNP	
$n_0 a^3$	8.4×10^{-4}	9.2×10^{-7}	2.9×10^{-3}	9.7×10^{-10}	4.1×10^{-7}	4.6×10^{-7}
τ_0 (min)	1.31	0.15	1.53	1.1×10^{-6}	21	0.48
		P3DDT/PCBM			P3DDT/AFNP	
$n_0 a^3$	2.1×10^{-5}	1.4×10^{-7}	6.4×10^{-6}	2.2×10^{-7}	8.3×10^{-4}	5.4×10^{-7}
τ_0 (min)	0.27	7.2×10^{-5}	2.2×10^{-5}	1.4×10^{-4}	0.53	0.91

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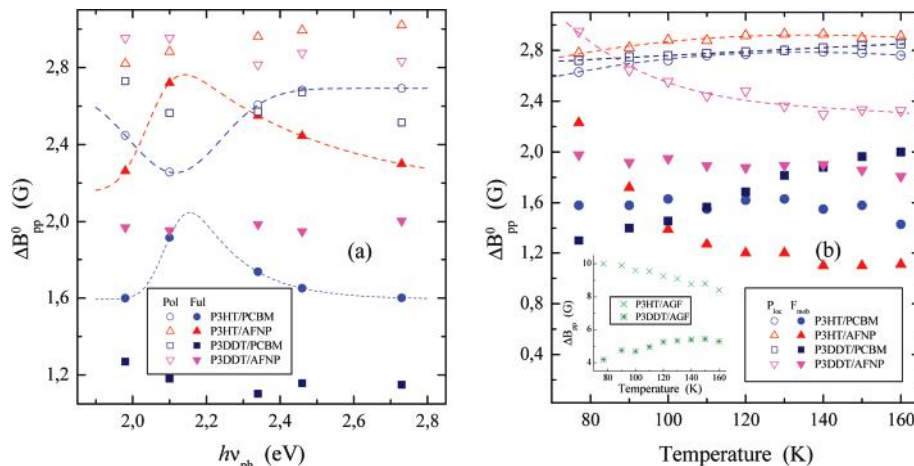*J. Phys. Chem. C, Vol. 114, No. 39, 2010* **16763**

Figure 7. (a) Linewidth of charge carriers photoinduced in the polymer/fullerene composites at 77 K as a function of photon energy $h\nu_{ph}$. Respective values determined for polarons and fullerene anion radicals initiated in the systems by white light are shown by the left and right dashed sectors, respectively. Dashed lines connecting the experimental points are painted arbitrarily. (b) Temperature dependence of line width of charge carriers photoinduced in the polymer/fullerene composites by photons with $h\nu_{ph} = 1.98$ eV. Dashed lines show the dependences calculated from eq 5 with E_a presented in Table 4. The symbol (0) in the $\Delta B_{pp}^{(0)}$ was introduced because of line width measured far of MW saturation, when $B_1 \rightarrow 0$.

decreases with temperature. Moreover, the dependence $\Delta B_{pp}^{(0)}(T)$ of F_N becomes opposite at the transition from the P3HT to the P3DDT matrix (Figure 7b, insert). The line width for polarons photoinduced in the P3HT and the P3DDT matrixes lies near $\Delta B_{pp}^{(0)} = 1.3-1.8$ G obtained for these charge carriers stabilized in different P3AT.[44] However, this value is considerably lower than that determined for undoped polythiophene,[44,45] which is evidence of weaker spin interaction with the P3AT lattice. The LEPR line width should reflect different processes occurring in a polymer/fullerene composite. One of them is the association of mobile polarons with the counter charges. Another process realized in the system is the dipole–dipole interaction between mobile and trapped polarons and fullerenes that broadens the line by $\delta\Delta B_{dd} = \mu_B/R_0^3 = 4/3\pi\mu_B n_P$, where μ_B is the Bohr magneton and R_0 is the distance between dipoles proportional to polaron concentration n_P on the polymer chain. Assuming anisotropic character of the main magnetic resonance parameters of polarons discussed above, one can evaluate $R_0 \approx 2.3-2.5$ nm for a distance between dipoles in the P3AT/PCBM system under study.

It was noted above that an unpaired electron of polaron activative multihopping along the polymer chain with the rate ω_{hop} can exchange with the spin of the fullerene radical anion quasi-fixed near a polymer chain. Such spin–spin exchange should affect electron relaxation of these charge carriers. The data presented in Figure 7b can probably also be described in terms of the above-mentioned approach of the collision of localized and mobile spins.[35,38] The interaction of a polaron with a fullerene counterion (which concentration is n_f) with the probability p described by eq 2 should additionally broaden the absorption line by the value

$$\delta(\Delta\omega) = p\omega_{hop}n_f = \frac{1}{2}\omega_{hop}n_f\left(\frac{\alpha^2}{1+\alpha^2}\right) \qquad (5)$$

where $\omega_{hop} = \omega_{hop}^0 \exp(-E_a/k_BT)$ and E_a is the activation energy.

Figure 7b also depicts the dependences calculated from eq 5 with E_a fitted from experimental data and summarized in Table 3. The analysis of the data presented allows one to conclude that the energy required for activation of polaron diffusion in the P3HT/PCBM composite exceeds E_a obtained for the P3DDT/

PCBM one. This parameter additionally increases as PCBM is replaced by AFNP (see Table 3).

The data presented are additional evidence that all electronic processes realized in the composites are governed mainly by the structure of polymer matrix and fullerene derivative as well as by the nature and dynamics of charge carriers photoinduced in bulk heterojunction.

With increasing of the magnetic term B_1 of MW irradiation in a sample bulk, intensity I of the spectra of both polarons and fullerene radical anions changes as is shown in the insert in Figure 8. This is due to manifestation of a MW steady-state saturation effect causing the change in their LEPR spectra by the following law[46]

$$I = I_0 B_1\left(1 + \gamma_e^2 B_1^2 T_1 T_2\right)^{-3/2} \qquad (6)$$

where I_0 is intensity of a nonsaturated spectrum, γ_e is a gyromagnetic ratio for electron, and T_1 and T_2 are spin–lattice and spin–spin relaxation times, respectively. The slope of the dependences $I(B_1)$ presented in Figure 8 is evidently governed by the nature, electron relaxation, and mobility of both spin charge carriers. The second effect of the increase in B_1 value is the LEPR spectrum broadening. Because the PCs photoinduced in polymer/fullerene bulk heterojunctions are found to be independent, both relaxation times can be determined separately by the steady-state saturation method.[46] One should only take into account the different distribution of spin packets in the LEPR spectra of mobile and localized charge carriers.

Figure 8 shows the temperature dependences of relaxation times obtained for all charge carriers photoinduced in the P3HT/PCBM and P3DDT/PCBM composites by light with $h\nu_{ph} = 1.98$ eV. Similar data obtained at other $h\nu_{ph}$ also show the dependences of electron relaxation on photon energy and are not discussed here.

The analysis of the data presented shows that the interaction of most charge carriers with the lattice is characterized by monotonic temperature dependences, whereas T_1 of fullerene anion radicals trapped by the P3DDT matrix demonstrates sharper temperature dependence. Spin–spin interaction is seen to be nearly temperature independent. However, it is governed by structural properties of a polymer/fullerene composite (Figure 8).
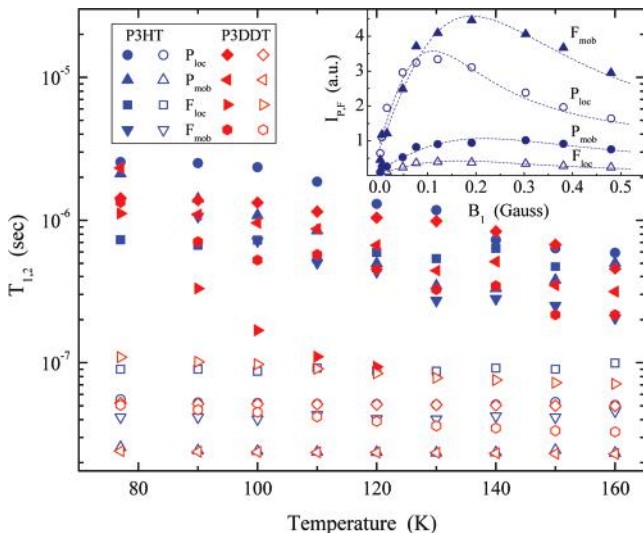
Figure 8. Temperature dependence of spin−lattice (T_1, filled points) and spin−spin (T_2, open points) relaxation times of charge carriers P_{loc} and F_{loc} (Figure 2) as well as P_{mob} and F_{mob} (left and right lines of the RP in Figure 2, respectively) photoinduced in the P3HT/PCBM and P3DDT/PCBM composites by light with $h\nu_{ph}$ = 1.98 eV. The insert shows the changes in intensity of their contributions to the effective LEPR spectrum initiated in the P3HT/PCBM bulk heterojunctions by light with $h\nu_{ph}$ = 1.98 eV at 90 K as a function of the magnetic term B_1 of MW field as well as the dependences shown by dashed lines and calculated from eq 6 with T_1 = 2.5 × 10^{-6} and T_2 = 5.3 × 10^{-8} s, T_1 = 1.4 × 10^{-6} and T_2 = 2.4 × 10^{-8} s, T_1 = 1.1 × 10^{-6} and T_2 = 4.2 × 10^{-8} s, and T_1 = 6.7 × 10^{-7} and T_2 = 9.0 × 10^{-8} s, respectively.

There are different spin dynamic processes in a polymer/fullerene system of lower dimensionality, for example, polaron diffusion along and between the polymer chains with coefficients D_{1D} and D_{3D}, respectively, pseudorotational diffusion of fullerene radical anion near own main molecular axis with coefficient D_{rot}. These processes induce an additional magnetic field in the whereabouts of electron and nuclear spins, which accelerates electron relaxation of all spin ensembles. The relationship between electron relaxation times and parameters of molecular mobility can be generally written as $T_{1,2} = f[J(\omega)]$, where $J(\omega)$ is a function of spectral density, which is of significance in the EPR relaxation theory. Because spin relaxation of the whole spin reservoir in organic conjugated polymers is defined mainly by a dipole−dipole interaction of neighboring electron spins,[33,47] the coefficients D_i can be determined from the following equations[48]

$$T_1^{-1}(\omega_e) = \langle\omega^2\rangle[2J(\omega_e) + 8J(2\omega_e)] \quad (7)$$

$$T_2^{-1}(\omega_e) = \langle\omega^2\rangle[3J(0) + 5J(\omega_e) + 2J(2\omega_e)] \quad (8)$$

where ω_e is resonant angular frequency of electron spin precession, $\langle\omega^2\rangle = 1/10\gamma_e^4\hbar^2S(S+1)n_p\Sigma_{ij}r_{ij}^{-6}$ is a constant of dipole−dipole interaction for powder, $n_p = n_m + n_l/2^{1/2}$ is the concentration of polarons per polymer unit, n_m and n_l are concentrations of mobile and localized polarons mentioned above, respectively, and $\Sigma_{ij}r_{ij}^{-6}$ is a lattice sum for a powderlike sample. The coefficient $2^{-1/2}$ in n_l is used because two spins diffuse independently in opposite directions. A spectral density function for polaron longitudinal diffusion in Q1D system is $J(\omega_e) = (2D_{1D}^l\omega_e)^{-1/2}$ at $D_{1D}^l \gg \omega_e \gg D_{3D}$ and $J(0) = (2D_{1D}^lD_{3D})^{-1/2}$ at $D_{3D} \gg \omega_e$, $D_{1D}^l = 4D_{1D}L_c^{-2}$, and L_c is the spatial

extent of the polaron wave function equivalent approximately 4−5 monomer units for organic conjugated polymers[42] and, particularly, P3AT.[21] A spectral density function for rotational diffusion with correlation time τ_c is $J_{rot}(\omega_e) = 2\tau_c/(1 + \tau_c^2\omega_e^2)$. If one proposes for simplicity that the spins are located near the points of the cubic lattice with concentration of the monomer units N_c and constant $r_0 = (8/3N_c)^{-1/3}$, then $\Sigma_{ij}r_{ij}^{-6} = 6.8r_0^{-6}$.[49] A similar spectral density function was used in the study of spin dynamics in different conjugated polymers.[33,44,50]

The dynamic parameters calculated from eqs 7 and 8 for both types of charge carriers photoinduced in the polymer/fullerene composites under study using the appropriate spectral density functions are presented in Figure 9 as a function of temperature. Normally, fullerene anion radicals are characterized by activation pseudorotational diffusion.[51,52] To account for the LEPR mobility data obtained, the Elliot model[53] was used. This model based on carrier hopping over the barrier E_b predicts a frequency dependence for its mobility, $\mu_i \propto D_i \propto \omega_e^s$, that is

$$D_{1D,r}(\omega_e T) = D_{1D,r}^0 T^2\omega_e^s \exp\left(\frac{E_b}{k_B T}\right) \quad (9)$$

where the exponent $0 < s < 1$ reflects system dimensionality and depends on the barrier height E_b as $s = 1 - \alpha k_B T/E_b$ (here, α is a constant). The model was used, for example, for interpretation of spin dynamics in slightly doped poly(3-methylthiophene)[54] and some other conjugated polymers.[55]

The energies E_b required for activation of the polaron translational and fullerene rotational diffusion in polymer/fullerene composites are summarized in the Table 3. It is seen in Figure 9 that the temperature dependences calculated from eq 9 with the E_b obtained approximately well experimental data. The E_b determined lies near that obtained for fullerene rotation in the triphenylamine complex,[51] polaron mobility in P3HT[56] and also to the energy of lattice phonons in poly(3-octylthiophene)[29] and other conjugated polymers.[57]

As is seen from the data presented, the rate of the fullerene anion radicals pseudorotation in the P3HT matrix is higher than in the P3DDT one. At the temperature increase, the anisotropy of polaron diffusion D_{1D}/D_{3D} decreases faster in the P3HT matrix than in the P3DDT one. This fact can additionally confirm a better planarity of the P3DDT than P3HT.[58] This is due to the fact that longer side groups restrict the number of possible conformations able to be formed by two adjacent thiophene rings rotating about their shared C−C bond.

Moreover, this parameter of polaron dynamics in the P3DDT/AFNP increases with the temperature (Figure 9). It can, probably, be explained by the conformational realignment of the polymer matrix initiated by the introducing of the AFNP molecules. The energetic barrier E_b required for polaron interchain hopping predominantly prevails upon that of its intrachain diffusion in all composites except P3DDT/AFNP. Generally, polaron dynamics becomes easier as one embeds AFNP instead of PCBM in the P3HT matrix. This is realized also for polaron interchain diffusion in the P3DDT matrix but, however, does not hold for its intrachain dynamics. On the other hand, the E_b value obtained for rotation of fullerene globe in the composite increases at such replacement in the P3HT matrix and decreases if one replaces PCBM by AFNP in more anisotropic P3DDT system. This effect may partly be a result of "freezing" of the molecular rotations, leading to a higher degree of matrix conjugation.[59]
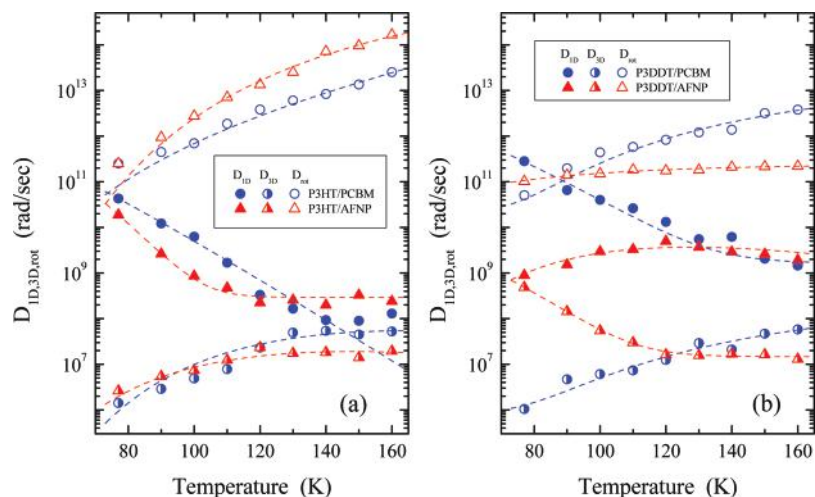
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Figure 9. Temperature dependence of intrachain (D_{1D}, filled points), interchain (D_{3D}, semifilled points), and rotational diffusion (D_{rot}, open points) coefficients of mobile charge carriers P_{mob} and F_{mob} (left and right lines of the RP in Figure 2, respectively) photoinduced in the P3HT/PCBM, P3HT/AFNP (a) and P3DDT/PCBM, P3DDT/AFNP (b) composites by light with $h\nu_{ph} = 1.98$ eV. Dashed lines show the dependences calculated from eqs 7−9 with E_b presented in Table 4.

Conclusions

Excitation of bulk heterojunctions formed by P3HT and P3DDT macromolecules with PCBM and AFNP globes by visible light leads to fast charge separation and further comparatively slow charge recombination. Light illumination is accompanied by the formation of two long-living noninteracting PC with rhombic symmetry, namely, the positively charged polaron $P^{\bullet+}$ (hole) on the polymer backbone and the negatively charged fullerene anion radical $C_{61}^{\bullet-}$ located between polymer chains. A part of these charge carriers can be trapped in a polymer matrix, however, immediately take part in an effective charge transfer. Spatial separation due to charge delocalization over a fullerene globule additionally reduces the recombination rate of these charge carriers. Weak interaction of PC originated from the former RP stipulates a difference in their interaction with their own microenvironment and, hence, in their magnetic resonance parameters. This allows one to determine separately all of these parameters for both charge carriers. It was shown that the probability of the collapse of polarons and fullerene anion radicals follows the activation law and depends on the energy of initiating photons. The main magnetic, relaxation, and dynamic properties of the PC photoinduced in composites were also shown to be governed by the energy of excited photons. This can be a result of structural inhomogeneity of the polymer/fullerene composites, which leads to the photon-initiated appearance of traps with different depth. Such selectivity can be used, for example, in plastic photovoltaic sensors. On the other hand, solar cells should be more homogeneous to be sensitive to all optical photons. It was demonstrated that the unpaired electron stabilized on an AFNP globe interacts with the nitrogen nucleus of its side substitute. Such a state keeps for a long time after switching off light irradiation. Mobile charge carriers photoinduced in the polymer/AFNP composite recombine 2−3 times faster than in the polymer/PCBM system. The energetic barrier E_b required for polaron interchain hopping mainly prevails upon that necessary for intrachain polaron multistep diffusion in all composites except P3DDT/AFNP. Generally, polaron dynamics in the P3HT matrix becomes easier if one replaces AFNP molecules by PCBM ones. The LEPR study described contributes to a better understanding of the correlations of polymer/fullerene composites and their components with their structural, magnetic, and transport properties. Such direct correlations seem to be important for further development and optimization of polymer/fullerene photovoltaic devices.

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