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PHOTONICS

Influence of Photogeneration Frequency on the Transport of Spin Charge Carriers in the Copolymer–Methanofullerene Composite: EPR Study

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Abstract—The photovoltaic composite formed by narrow-gap copolymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(bithiophene)] and methanofullerene [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) has been studied in a wide energy range of generating photons, 1.32–3.14 eV at $T = 77$ K, by the light-induced electron paramagnetic resonance. It has been shown that some polarons are captured by spin traps formed in the copolymer matrix, and the concentration and depth of such traps are determined by the photon energy. The recombination kinetics of polarons and fullerene radical anions after turning off the light can be described in the framework of a second-order bimolecular process. The formation of spin traps in the copolymer matrix and the exchange interaction between different spin packets cause the extreme sensitivity of magnetic resonance and electronic parameters of charge carriers to the number and energy of generating photons.

Keywords: bulk heterojunction, photoinduced EPR, spin relaxation, charge recombination, charge transfer, polaron, methanofullerene, exciton dissociation

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Organic conjugated polymers have been actively studied recently due to the promise of their use as functional matrices of plastic electronic, spintronic, and photovoltaic molecular devices [1, 2]. Typical organic photovoltaic cells consist of a polymer donor subsystem capable of donating an electron under the action of external radiation, and a fullerene acceptor subsystem that accepts this electron [1]. Photoinitiation and recombination of these charge carriers are oppositely directed processes. The difference in the rate constants of these processes determines the number of free charge carriers reaching the opposite electrodes of the cell and, hence, the efficiency of converting light energy into electrical energy. The structure and morphology of the polymer : fullerene composites play an important role in the course of these processes. In particular, the use in the composite of the narrow-band copolymer poly[*N*-9'-heptadecanyl-2,7-carbazol-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) instead of poly(3-hexylthiophene) (P3HT) traditionally used earlier as the most optimal electron donor of organic solar cells [2], permitted more than twice increase in the cell efficiency [3, 4]. It was shown [5, 6] that the matrix of the copolymer PCDTBT : $PC_{71}BM$ is characterized by a two-layer "stacked" ordering. The higher energetic efficiency of this composite was explained [7] by ultrafast charge separation before localization of excitation and the formation in it of a bound exciton, unlike P3HT-based composites, in which photoinduced charge separation occurs after diffusion of a polymeric exciton to the fullerene subsystem. Such morphology of the copolymer chain prevents its rotation around its main axis, which lowers the energy of the band gap of the composite [8]. This accelerates charge jumps along and between the copolymer layers, which further increases the efficiency of the device.

The process of recombination of charge carriers is determined by various factors depending on the structure and morphology of the polymer : fullerene composite [9]. The simplest first-order mechanism is prompt recombination of the initial quasi-pairs of polarons and free electrons. If the associated charge carriers overcome the force of the Coulomb interaction and separate to a sufficient distance, then they will be able to recombine with oppositely charged carriers of other quasi-pairs, and this process will follow the second order. Elucidation of the processes of separation, transfer, and recombination of charges in such materials at the molecular level is crucial for improving the electronic properties and efficiency of the corresponding elements of molecular electronics.

It was shown [1, 10] that light-induced electron paramagnetic resonance (LEPR) is one of the direct, effective, and accurate methods for studying all spin-dependent processes occurring in polymer : fullerene systems. It permits separate detection and study of the main stages of the formation, separation, and recombination of spin charge carriers. From the analysis of the LEPR spectra recorded in the absence and presence of illumination of the sample, it is possible to determine the effective number of photogenerated spin charge carriers. These carriers are characterized by weakly anisotropic magnetic resonance parameters; therefore, in the 3-cm (9.7 GHz) range, they exhibit a partially overlapped doublet LEPR spectrum. Earlier, we studied spin-dependent processes of generation, recombination, relaxation, and dynamics of spin charge carriers in various polymer : fullerene composites [11], including those based on the narrow-band copolymers PCDTBT and poly[2,7-(9',9'-dioctylfluorene)-alt-4',7'-bis(thiophen-2-yl)benzo-2',1',3'-thiadiazole] (PFO-DBT) [12, 13]. It was shown that, upon illumination of the copolymer : fullerene composites, a portion of the charge carriers is captured by spin traps formed in the copolymer matrix due to its disorder. In the structurally similar nanocomposites PCDTBT : $PC_{61}BM$ and PFO-DBT : $PC_{61}BM$, the first and second order, respectively, of the recombination process of spin charge carriers were identified.

This work presents the results of the LEPR study of the processes of formation, relaxation, and dynamics of spin charge carriers photogenerated at $T = 77$ K in the PFOT : $PC_{61}BM$ polymer nanocomposite in a wide range of photon energy, 1.32–3.14 eV. The dependences of the magnetic, relaxation, and dynamic parameters of charge carriers on their localization were revealed, the sensitivity of these parameters to the photon energy was found, and the order of their recombination in this system was determined.

EXPERIMENTAL

Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(bithiophene)] (PFOT), manufactured by American Dye Source, Inc. (USA), was used as an electron donor. 6,6-Phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$), manufactured by Solenne BV (Netherlands), was used as an electron acceptor. The chemical structures of these components are schematically shown in Fig. 1.

The samples on a ceramic substrate were prepared as follows. A weighed amount of PFOT (1.8 mg) was dissolved in dichlorobenzene (1.1 mL) and sonicated for 10 min in a 50-W DADI DA-968 ultrasonic cleaner. Then the solution was heated at $T = 333$ K for 30 min, after which it was additionally sonicated for 10 min to form a clear yellow solution. Then, to 0.5 mL of the solution thus obtained, 3.7 mg of $PC_{61}BM$ was added, the solution was heated for 2.5 h at $T = 333$ K, and held at room temperature for 20 h. The concentrations of PFOT and $PC_{61}BM$ in the solution were 3×10^{-3} and 2×10^{-3} mol/L, respectively. The solutions obtained were applied on a flat ceramic substrate with drops of volume $V = 5$ μL, gradually drop by drop on each side of the substrate, as it dried. A total of 55 μL of the solution was applied to obtain a sample in the form of double-sided films with a size of about 4×8 mm^2 and a thickness of about 0.1 mm.

The samples were illuminated directly in the resonator of the spectrometer, using a quartz fiber with 5-W Luxeon® achromatic white light sources with a color temperature of $T_c = 15000$, 5500, and 3300 K, as well as almost monochromatic light with photon energy $h\nu_{ph}$/luminosity I_l: of 1.32 eV/750 lx, 1.46 eV/870 lx, 1.61 eV/1160 lx, 1.88 eV/1950 lx, 1.97 eV/1110 lx, 2.10 eV/450 lx, 2.34 eV/960 lx, 2.48 eV/1500 lx, 2.64 eV/2450 lx, 2.95 eV/1520 lx, and 3.14 eV/630 lx. The I_l values of these sources were determined using an IMO-2N broadband bolometric light power meter and an LX-1010BS digital luxmeter and were used for further normalization of the number of spins photogenerated in the sample.

EPR measurements were made on a PS-100X radiospectrometer (3 cm, 9.7 GHz) with a maximum microwave power of 150 mW and a synchronous/phase detection frequency of 100 kHz. The LEPR spectra of the samples were recorded at 77 K by immersing the samples in a quartz cell filled with liquid nitrogen. The signal-to-noise ratio of the LEPR spectra was increased by accumulating signals with multiple scanning. The processing and simulation of the LEPR spectra were performed using the EasySpin and OriginLab programs. The contributions of unpaired electrons of different charge carriers to the effective susceptibility of the sample were determined by decomposing its LEPR spectra into components, as described in [11, 14, 15]. The paramagnetic susceptibility of the sample was determined by double integration of the absorption spectra of the individual spin packets far from the microwave saturation conditions. As a reference, the stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl was used, each molecule of which contains one spin $S = ½$. The Landé g-factor of spin charge carriers was determined using the N,N-diphenyl-N'-picrylhydrazyl (DPPH) standard with $g = 2.0036$. The accuracy of estimating the intensity of the I line, the g-factor, and the linewidth between the positive and negative peaks ΔB_{pp} were 5%, $\pm 2 \times 10^{-4}$, and $\pm 2 \times 10^{-2}$ G, respectively. The times of spin–lattice (T_1) and spin–spin (T_2) relaxation of spin ensembles were determined using the method of continuous microwave saturation [16].

RESULTS AND DISCUSSION

Figure 1 shows some LEPR spectra of the PFOT : $PC_{61}BM$ composite obtained by its illumination with photons of different energies $h\nu_{ph}$ at $T = 77$ K. As in

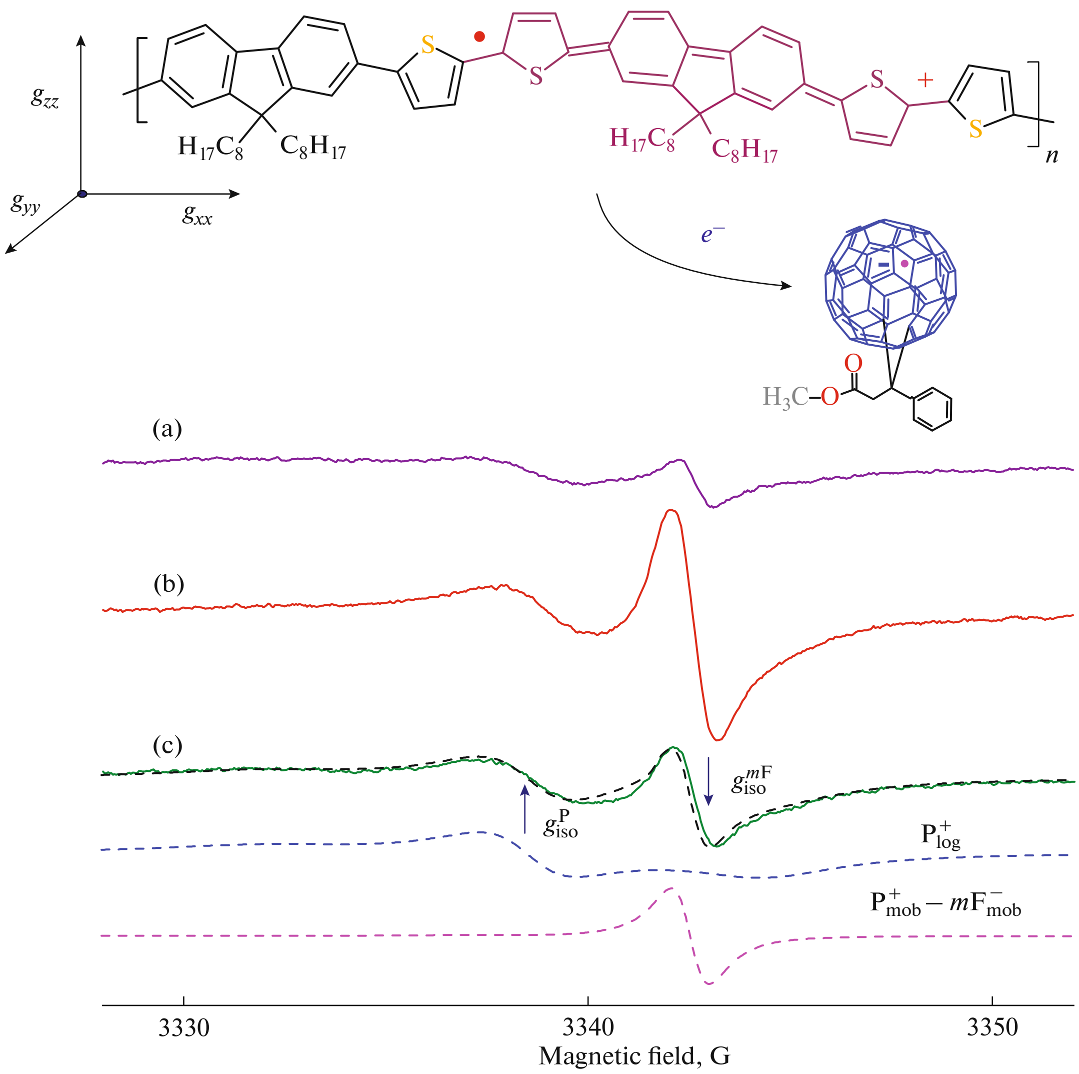

Fig. 1. LEPR spectra of charge carriers in bulk heterojunctions of PFOT : PC$_{61}$BM upon continuous illumination with photons of energy $h\nu_{ph}$ = (a) 1.46, (b) 1.88, and (c) 2.38 eV at 77 K, normalized to the luminosity value I_l of light sources. The dashed lines in (c), top to bottom, show the total spectrum, the LEPR spectra of localized polarons $P_{loc}^{+\bullet}$ and mobile radical pairs $P_{mob}^{+\bullet} \leftrightarrow mF_{mob}^{-\bullet}$ numerically simulated using the values of $\Delta B_{pp}^{P} = 2.91$ G, $\Delta B_{pp}^{mF} = 0.94$ G, and the concentration ratio $[mF_{mob}^{-\bullet}] : [P_{loc}^{+\bullet}] = 1.0 : 9.9$. The scheme above shows charge transfer from the copolymer chain to the methanofullerene molecule, accompanied by the formation of a polaron with an elementary positive charge and a spin $S = ½$.

the case of other polymer : fullerene composites [11], these spectra were assigned to the lines of polarons and radical anions of methanofullerenes (Fig. 1), formed as a result of exciton dissociation. The resulting EPR spectrum was decomposed into individual component lines similarly to previous studies of the polymer : fullerene composites [11, 14, 15]. This made it possible to separately determine the main magnetic resonance parameters of the spin packets photogenerated in the composite by light photons of different energies $h\nu_{ph}$.

Figure 1 also shows the simulated total LEPR spectrum and its contributions related to localized polarons $P_{loc}^{+\bullet}$ captured by spin traps, and mobile pairs of polarons and radical anions of methanofullerenes $P_{mob}^{+\bullet} \leftrightarrow mF_{mob}^{-\bullet}$. The absence in the spectra of the contribution from the localized radical anions of methanofullerene $mF_{loc}^{-\bullet}$ indicates a smaller number of energetically deep traps capable of capturing such paramagnetic centers.

Table 1. Isotropic g-factor of polarons $g_{\rm iso}^{\rm P}$, widths of the LEPR line of polarons $\Delta B_{\rm pp}^{\rm P}$ and methanofullerenes $\Delta B_{\rm pp}^{m\rm F}$, ratio of the concentration of mobile radical anions of methanofullerenes to the concentration of localized polarons $[m{\rm F}_{\rm mob}^{-\bullet}]/[{\rm P}_{\rm loc}^{+\bullet}]$, polaron diffusion coefficients along ($D_{\rm 1D}^{\rm P}$) and between ($D_{\rm 3D}^{\rm P}$) copolymer chains, and libration diffusion coefficient of methanofullerene around its main molecular axis $D_{\rm rot}^{m\rm F}$, determined upon illumination of the PFOT : PC$_{61}$BM composite with achromatic white light of different correlated color temperature $T_{\rm c}$ at $T = 77$ K

$T_{\rm c}$, K Parameter	15000	5500	3300
$g_{\rm iso}^{\rm P}$	2.002$_{22}$	2.002$_{27}$	2.002$_{34}$
$\Delta B_{\rm pp}^{\rm P}$, G	2.89	2.97	3.17
$\Delta B_{\rm pp}^{m\rm F}$, G	1.03	1.07	1.05
$[m{\rm F}_{\rm mob}^{-\bullet}]/[{\rm P}_{\rm loc}^{+\bullet}]$	0.113	0.097	0.077
$D_{\rm 1D}^{\rm P}$, rad/s	6.20×10^{11}	2.93×10^{11}	4.99×10^{11}
$D_{\rm 3D}^{\rm P}$, rad/s	2.68×10^{6}	6.75×10^{6}	2.77×10^{6}
$D_{\rm rot}^{m\rm F}$, rad/s	7.24×10^{10}	1.03×10^{11}	1.23×10^{11}

The isotropic g-factor determined for the radical anions of methanofullerenes was found to be $g_{\rm iso}^{m\rm F} = 1.99989$ and weakly dependent on the photon energy $h\nu_{\rm ph}$. This value is near $g_{\rm iso}^{m\rm F} = 1.99948$ [14] and 1.99987 [15], obtained for PC$_{61}$BM in the 2-mm (130 GHz) range of LEPR measurement. The orientation of the main axes of their g-tensor is shown in Fig. 1. The value of g_{xx} lies in the plane of the polymer π system and is directed perpendicular to the main molecular axis of the copolymer. This value is determined by the energy $\Delta E_{n\pi^*}$ necessary for excitation of the spin $n \to \pi^*$, the coupling constant λ of the spin with the heteroatom, and its density on this heteroatom ρ(0), that is, $g_{xx} \propto \lambda\rho(0)/\Delta E_{n\pi^*}$, which causes its higher sensitivity to interatomic distances and spin–orbit coupling with heteroatoms in the polymer matrix [17]. The term g_{yy} is determined by the difference of the transition energies $\sigma \to \pi^*$, it is proportional to the value of $\lambda\rho(0)/\Delta E_{\sigma\pi^*}$ and is less sensitive to the properties of the polaron microenvironment. Among all the principal values of the g-tensor, g_{zz} is the least sensitive to the properties of the copolymer matrix. The principal values of the g-factors of the polaron in the PFOT : PC$_{61}$BM composite were found to be $g_{xx} = 2.006_{04}$, $g_{yy} = 2.002_{17}$, $g_{zz} = 1.998_{66}$, and $g_{\rm iso}^{\rm P} = 2.002_{29}$. The last value is close to $g_{\rm iso}^{\rm P} = 2.002_{47}$–$2.003_{30}$ determined for polarons photoinduced in some other photovoltaic systems [11, 15] including narrow-gap copolymer composites [12, 13]. The values of $g_{\rm iso}^{\rm P}$ determined upon illumination of the PFOT : PC$_{61}$BM composite with achromatic white light of different correlated color temperatures $T_{\rm c}$ are given in Table 1.

Figure 2 shows the dependence of $g_{\rm iso}^{\rm P}$ for localized and mobile polarons in the PFOT : PC$_{61}$BM composite on the energy of photons $h\nu_{\rm ph}$. It can be seen from the figure that the isotropic g-factor of polarons is characterized by an extreme dependence on the photon energy, which is well described by the Gaussian distribution:

$$g_{\rm iso} = g_0 + \sqrt{\frac{2k_1}{\pi\sigma^2}}\exp\left(-\frac{2(E - E_c)}{\sigma^2}\right), \tag{1}$$

where $E_{\rm c}$ is the characteristic energy, σ is the energy deviation, and g_0 and k_1 are constants. The analysis of the dependences shown in Fig. 2 indicates that the experimental data obtained can be well described by Eq. (1) with $E_{\rm c} = 2.54$ eV and $\sigma = 1.72$ eV. The obtained values of $E_{\rm c}$ and σ exceed the values obtained for the structurally similar composites PFO-DBT : PC$_{61}$BM ($E_{\rm c} = 2.0067$ eV and $\sigma = 1.174$ eV) and PCDTBT : PC$_{61}$BM ($E_{\rm c} = 2.244$ eV and $\sigma = 1.945$ eV) [12, 13], which may be due to the more ordered morphology of the latter. This suggests that the disorder in the polymer composites leads to a uniform distribution of energetic traps in the copolymer chain, which determines the Gaussian dependence of their effective g-factor on the spin photogeneration energy.

Figure 2 shows the dependences of the linewidth of the polarons $\Delta B_{\rm pp}^{\rm P}$ and radical anions of methanofullerenene $\Delta B_{\rm pp}^{m\rm F}$, photogenerated in the PFOT : PC$_{61}$BM composite at $T = 77$ K, on the photon energy $h\nu_{\rm ph}$. These parameters, determined upon irradiation of the sample with white light sources with different color temperatures, are also presented in Table 1. It was previously shown [11] that the main processes occurring

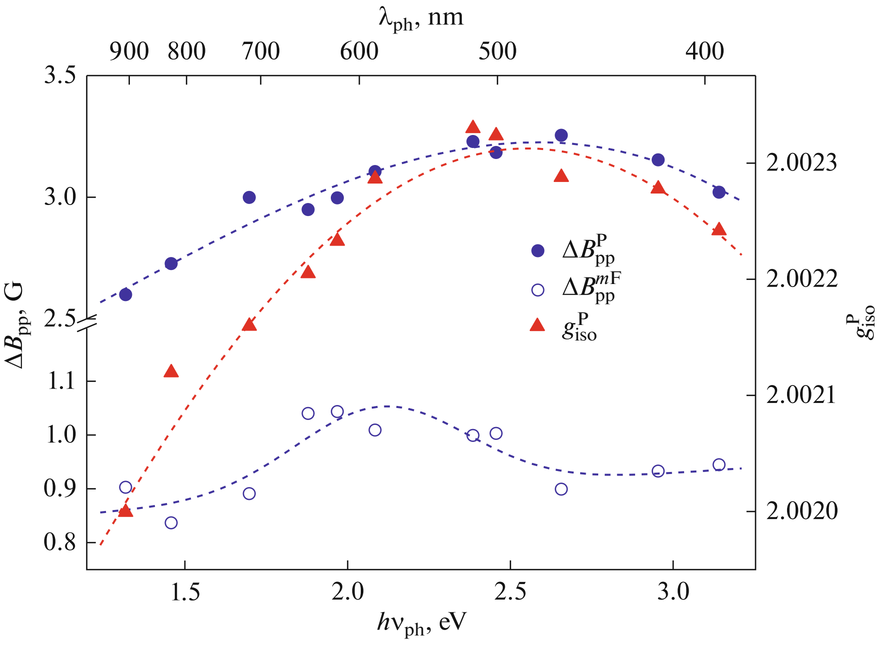

Fig. 2. Dependences of the linewidth of the LEPR spectra of polarons (●) and radical anions of methanofullerenes (○), as well as the g-factor of polarons (▲) photogenerated in PFOT : $PC_{61}BM$ at $T = 77$ K on the photon energy $h\nu_{ph}$. The upper and lower dashed lines are drawn arbitrarily. The middle dashed line shows the dependence calculated from Eq. (1) with $E_c = 2.54$ eV and $\sigma = 1.72$ eV.

in the polymer : fullerene systems are spin-dependent and therefore can be described in the framework of the exchange interaction of polaron spins diffusing along polymer chains with other spin charge carriers, including those trapped by high-energy traps. The analysis of the data shown in Fig. 2 permits a conclusion about the influence of the photon energy on the exchange interaction of spin charge carriers in the sample under study, including those localized in the polymer matrix. In this case, the exchange interaction of the spins should broaden their spectral absorption lines by the following value [18, 19]:

$$\delta(\Delta\omega) = p_{ss}\omega_{hop}n_i, \tag{2}$$

where p_{ss} is the probability of collision of such centers with spin $S = ½$, depending on the exchange integral; n_i is the number of outside spins per each polymer unit; and ω_{hop} is the frequency of hopping Q1D diffusion of the polaron spin. The character of the dependences (Fig. 2) of the widths of the LEPR lines ΔB_{pp}^{P} and ΔB_{pp}^{mF} on the photogeneration energy and the presence of extremes for polarons at $h\nu_{ph} \approx 2.6$ eV and fullerene radical anions at $h\nu_{ph} \approx 2.1$ eV indicate stronger exchange interaction of polaron spins with their microenvironment than that for methanofullerene anion radicals.

Upon illumination, paramagnetic centers are detected in the polymer : methanofullerene composite, which remain after fast irreversible and slow reversible recombinations of spin charge carriers. The probability of the latter process is mainly determined by the multistage diffusion of polarons along the polymer chains through the energy barriers and their subsequent tunneling to methanofullerene anions. Since recombination depends on the number and energetic depth of spin traps formed in the polymer matrix, we may conclude that only a portion of spin charge carriers, equal to the ratio of mobile to localized charge carriers, eventually reaches the electrodes. Figure 3 shows the relative changes in the concentrations of charge carriers in the PFOT : $PC_{61}BM$ composite, calculated from the individual paramagnetic susceptibilities of spin charge carriers, as a function of the energy of generating photons $h\nu_{ph}$. The concentration of localized polarons is characterized by an extremal dependence with characteristic points lying near 1.8 and 2.7 eV. Similar dependences with a right-hand extremum slightly shifted to higher energies were obtained earlier upon photogeneration of charge carriers in structurally similar, but more ambipolar composites PFO-DBT : $PC_{61}BM$ and PCDTBT : $PC_{61}BM$ [12, 13]. From the analysis of the data presented, we may conclude that the concentration of localized polarons $P_{loc}^{+\bullet}$ exceeds the concentration of mobile polarons $P_{mob}^{+\bullet}$ and fullerene radical anions $mF_{mob}^{-\bullet}$, and all these values depend on the photon energy. The specific morphology of the sample under study leads to the predominant formation of localized polarons in its matrix, the number of which was found to be more

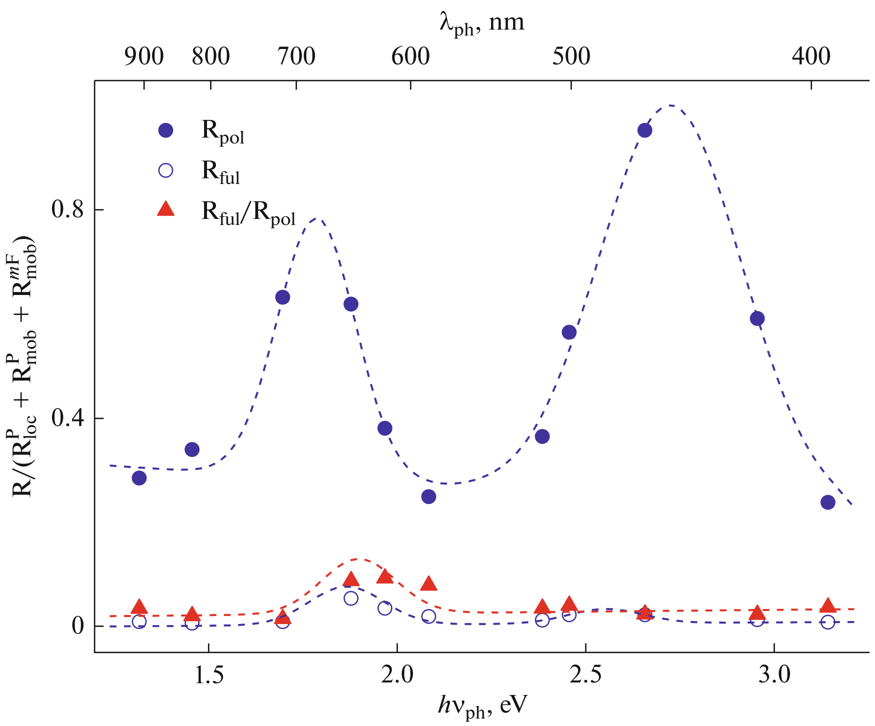

Fig. 3. Relative concentrations $[P_{loc}^{+\bullet}]/[P_{loc}^{+\bullet} + P_{mob}^{+\bullet} + mF_{mob}^{-\bullet}]$ and $[mF_{mob}^{-\bullet}]/[P_{loc}^{+\bullet} + P_{mob}^{+\bullet} + mF_{mob}^{-\bullet}]$ and ratio $[mF_{mob}^{-\bullet}]/[P_{loc}^{+\bullet}]$ of polarons and radical anions of methanofullerenene photogenerated in the PFOT : $PC_{61}BM$ composite at $T = 77$ K as functions of the photon energy $h\nu_{ph}$. The values obtained are normalized to the luminosity of the light sources I_l. The dashed lines are drawn arbitrarily.

sensitive to the photon energy. On the other hand, mobile anion radicals of methanofullerene of the PFOT : $PC_{61}BM$ composite demonstrate weaker dependence of the concentration ratio $[mF_{mob}^{-\bullet}]/[P_{loc}^{+\bullet}]$ with a maximum at about 1.9 eV. The energy conversion efficiency of such composites should increase with increasing the concentration ratios $[mF_{mob}^{-\bullet}]/[P_{loc}^{+\bullet}]$. These parameters, obtained upon irradiating the sample with white light sources with different color temperatures, are listed in Table 1.

Upon switching off illumination, the spin charge carriers begin to recombine, which leads to a decrease in their concentration and the intensity of the LEPR spectrum. Numerical simulation of the total signal allows us to separate the decay processes of the concentrations of all spin charge carriers emerging in the polymer system. Figure 4 shows the time decay of the concentrations of both charge carriers in the PFOT : $PC_{61}BM$ composite since switching off the white light source with a color temperature of $T_c = 5500$ K. The simplest first-order mechanism is characteristic of recombination of pairs of fullerene anion radicals and polarons formed from unseparated corresponding initial excitons. If the positive charge of a polaron leaves such a pair, it can recombine with more distant methanofullerene radical anion located between the layers of the copolymer. Such a recombination process becomes bimolecular and follows the second order. If a fullerene radical anion does not interact with an encountered polaron, then the duration of their collision should be determined by the dynamics of the latter. The order of the recombination process of charge m in a system with spin traps can be estimated from the analysis of the time decay of the concentration of spins $n(t)$ [9]:

$$\frac{n(t)}{n_0} = \left(1 + k_r (m-1) n_0^{m-1} t\right)^{\frac{1}{1-m}}, \qquad (3)$$

where n_0 is the initial number of spin charge carriers at the moment of switching off the light, at $t = 0$, and k_r is the recombination rate constant of an electron. In particular, the value of m determined for the composites PFO-DBT : $PC_{61}BM$ and PCDTBT : $PC_{61}BM$ was found to be 2.25 and 1.23, respectively [12, 13], which permitted a conclusion about different mechanisms of recombination of spin charge carriers in these systems. The parameters k_r and m, determined from Eq. (3) for PFOT : $PC_{61}BM$ by simulation of the experimental curves of the concentration decay $n(t)$, were found to be $k_r = 0.28$ s^{-1}, $m = 2.34$ for $[P_{loc}^{+\bullet}]$ and $k_r = 0.0014$ s^{-1}, $m = 2.23$ for $[mF_{mob}^{-\bullet}]$. This indicates

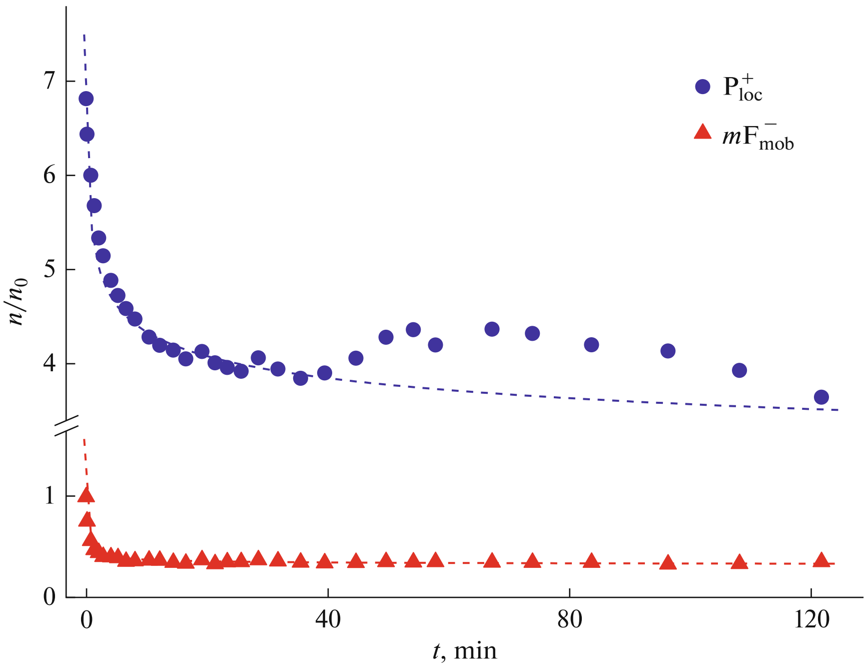

Fig. 4. Kinetics of relaxation of the concentrations of localized polarons $\left[P^{+\bullet}_{loc}\right]$ and radical anions of methanofullerenes $\left[mF^{-\bullet}_{mob}\right]$ photogenerated in PFOT : $PC_{61}BM$ by white light source with a correlation color temperature $T_c = 5500$ K at $T = 77$ K. The upper and lower dashed lines show dependences calculated from Eq. (4) with $E_0 = 0.0486$ and 0.0139 eV, respectively.

the second order of recombination and the similar structural order in the composite under study and PFO-DBT : $PC_{61}BM$.

Spin traps in the polymer matrix play a key role in recombination of spin charge carriers. Indeed, the captured polaron can either be intercepted by a vacant trap, or recombine with the nearest oppositely charged radical anion. Multiple successive captures and releases of a polaron reduce its energy, which ultimately leads to its localization in the deepest spin traps and, hence, to an increase in the concentration of localized carriers with time. The recombination of spin charge carriers in a polymer system with energetically different spin traps should obey the following law [20, 21]:

$$\frac{n(t)}{n_0} = \frac{\pi\kappa\delta(1+\kappa)\nu_d}{\sin(\pi\kappa)} t^{-\kappa}, \qquad (4)$$

where $\kappa = k_BT/E_0$, E_0 is the dispersion of the energies of the traps, δ is the gamma function, and ν_d is the frequency of the hopping diffusion of the polaron when it is released from the trap. The comparison of the experimental data presented in Fig. 4 with theoretically calculated data showed that polarons and radical anions of methanofullerene can recombine within the framework of this theory with the energy dispersion $E_0 = 0.0486$ and 0.0139 eV, respectively, at $t \le t_c \approx 40$ min. At $t \ge t_c$, the dependence $n(t)$ obtained for polarons ceases to be described by Eq. (4). This discrepancy can be explained by the capture of an additional number of mobile polarons in this system by spin traps, beginning at $t \approx t_c$. Hence, the process of recombination of long-lived spin charge carriers formed as a result of dissociation of initial excitons photoinduced in the PFOT : $PC_{61}BM$ composite can indeed be described within the framework of the above model, according to which the recombination rate at low temperatures depends substantially on the number and energy depth of the traps variously distributed in the copolymer.

Polarons captured by spin traps in the copolymer matrix and diffusing along and between its chains with the corresponding diffusion coefficients D^{P}_{1D} and D^{P}_{3D} induce an additional magnetic field at the location of other spins, which accelerates the electron relaxation of all spin ensembles. The librational dynamics of methanofullerene molecules with the coefficient D^{mF}_{rot} also induces a local magnetic field and affects the relaxation of spin charge carriers. The electron relaxation in organic solids is mainly determined by the dipole–dipole interaction of the spins. This permits writing the following equations relating the relaxation of spins with their dynamic parameters [22]:

$$T_1^{-1}(\omega) = \langle\omega^2\rangle\left[2J(\omega_e) + 8J(2\omega_e)\right], \qquad (5)$$

$$T_2^{-1}(\omega) = \langle\omega^2\rangle\left[3J(0) + 5J(\omega_e) + 2J(2\omega_e)\right], \qquad (6)$$

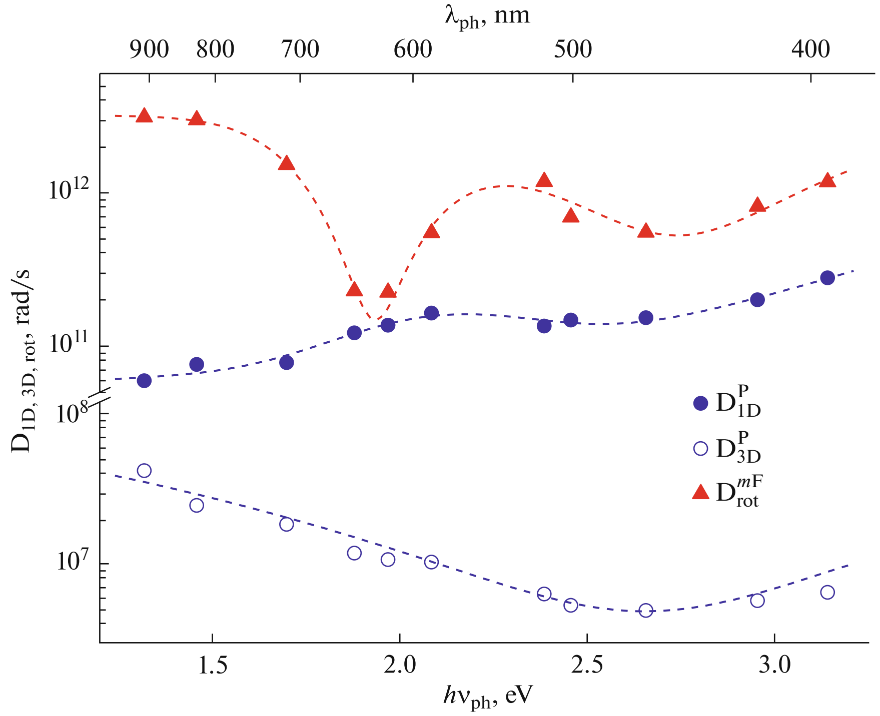

Fig. 5. Translational diffusion coefficients of polarons $P^{+\bullet}$ along polymer chains D_{1D} (●) and between polymer chains D_{3D} (○), as well as libration diffusion coefficients D_{rot} (▲) of methanofullerene radical anions $mF^{-\bullet}_{mob}$, photogenerated in PFOT : $PC_{61}BM$ as functions of the energy of initiating photons $h\nu_{ph}$. The errors do not exceed the sizes of points; the dashed lines are drawn arbitrarily.

where $\langle\omega^2\rangle = 1/10\gamma_e^4\hbar^2 S(S+1)n\Sigma ij$ is the constant of the dipole–dipole interaction of the powdered sample with the total concentration $n = n_1 + n_2/\sqrt{2}$ of localized (n_1) and mobile (n_2) spins per each copolymer monomer, Σ_{ij} is the lattice sum, $J(\omega_e) = (2D^{|}_{1D}\omega_e)^{-1/2}$ (at $D^{|}_{1D} \gg \omega_e \gg D^P_{3D}$), $J(0) = (2D^{|}_{1D}D^P_{3D})^{-1/2}$ (at $D^P_{3D} \gg \omega_e$) are the functions of the spectral density of Q1D mobility of polarons, $D^{|}_{1D} = 4D^P_{1D}/L^2$, ω_e is the resonant angular frequency of the electron spin precession, and L is the degree of spin delocalization within the charge carrier. In calculation of the parameters of spin dynamics in PFOT : $PC_{61}BM$, the value of $L = 3$ was used, which was determined earlier for PCDTBT [15]. The rotational librations of methanofullerene radical anions with the correlation time τ_c were calculated using the corresponding spectral density function $J(\omega_e) = 2\tau_c/(1 + \tau_c^2\omega_e^2)$.

Figure 5 shows the dependences of the coefficients D^P_{1D} and D^P_{3D} of the translational diffusion of polarons and the coefficient D^{mF}_{rot} of the librational diffusion of the methanofullerene radical anions in the PFOT : $PC_{61}BM$ composite, which were calculated from Eqs. (5) and (6), on the photon energy $h\nu_{ph}$. The corresponding parameters of charge carriers photogenerated in the composite upon illumination with white light sources with different correlated color temperature T_c are listed in Table 1. It can be seen from Fig. 5 that the values of D^P_{1D} and D^P_{3D}, obtained for polarons weakly depend on the photon energy; however, the anisotropy of the dynamics of these charge carriers D^P_{1D}/D^P_{3D} increases by one and a half orders of magnitude with increasing the photon energy in the range of 1.32–3.14 eV. Note that the diffusion coefficients D^P_{1D} and D^P_{3D} obtained for PFO-DBT : $PC_{61}BM$ change in the similar way as a function of $h\nu_{ph}$, while in the case of the PCDTBT : $PC_{61}BM$ composite, they increase by about an order of magnitude [12, 13]. On the other hand, the dynamics of methanofullerene globules extremely depends on the photon energy, with characteristic minimums lying near 1.9 and 2.7 eV. Similar dependences were also obtained for the structurally similar composite PFO-DBT : $PC_{61}BM$ [12, 13], which should indicate a significant effect of the morphology of such compounds on the polaron dynamics.

CONCLUSIONS

It has been shown that the processes of formation and relaxation of the spins of polarons and radical anions of methanofullerenes, which appear in the PFOT : $PC_{61}BM$ composite under the action of light, are determined by their interaction with the microenvironment and depend on the frequency of generating photons. Most of the polarons are involved in charge transfer, but some of them are captured by spin traps formed in the bulk of the copolymer due to its disorder. The presence of traps changes the energy levels of spin excitations and causes the Gaussian dependence of the effective *g*-factor of polarons on the photon energy. The concentration of localized polarons exhibits an extremal dependence on the energy of photons with maximums lying near 1.8 and 2.7 eV, whereas the concentration of radical anions of methanofullerene shows a weaker dependence with a maximum near 1.9 eV. The process of recombination of spin charge carriers was interpreted in the framework of multistep capture and release of polarons in the heterogeneous copolymer matrix. The second order of recombination of spins in the composite under study has been established. The anisotropy of the polaron dynamics in PFOT : $PC_{61}BM$ monotonically increases with photon energy, while the rotational mobility of methanofullerene molecules exhibits an extreme dependence with two minimums lying near 2.0 and 2.7 eV, which is similar to the results of the study of the PFO-DBT : $PC_{61}BM$ composite. The dependences obtained indicate a significant effect of the frequency of generating photons on the dynamic processes in the copolymer composites, which should be taken into account upon creation of new elements of molecular electronics controlled by external light and magnetic actions.

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