Influence of Ultrasonic, Microwave, and Thermal Effects on Photoinduced Charge Transfer in Poly(3-hexylthiophene)—Methanofullerene Composites: EPR Study[1]

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Abstract—Radical pairs, polarons, and anion radicals of fullerenes that are induced in bulk heterojunctions of two composites, poly(3-hexylthiophene) with 6,6-phenyl-C_{61}-butanoic acid methyl ester and with 6,6-phenyl-C_{62}-butanoic acid bis(methyl ester), by photons with an energy of 1.98–2.73 eV at 77 K are studied via the method of photoinduced electron paramagnetic resonance. It is found that a part of the polarons and anion radicals of fullerenes are entrapped by energy traps of the polymer matrix, the quantity and depth of which are determined by ordering in the composites and the energy of exciting photons. A comparative study of the influence of composite treatment with ultrasonic, microwave, and thermal annealing on the formation and main resonance parameters of spin charge carriers in these bulk heterojunctions demonstrates a sharp gain in the number of charge carriers during illumination of the polymer—methanofullerene system, and the maximum effect is observed for photons with energies of 1.98 and 2.1 eV. This treatment procedure leads to the development of crystalline domains in the polymer matrix and increases the efficiency of light-energy conversion.

INTRODUCTION

In plastic solar cells based on polymer–fullerene composites with bulk heterojunctions [1, 2], whose efficiency of energy conversion is as high as 6–7% [3], light photons generate strongly bound singlet excitons [4]. Such solar cells usually consist of interpenetrating networks of soluble polymer derivatives, for example, poly(3-hexylthiophenes) (PHTs) and fullerene derivatives (1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6.6]C_{61} (PCBM, methanofullerene $mC_{61}^{\cdot-}$) [5]. The planarity and regioregularity of the polymer matrix that are due to the structure of a polymer and methanofullerene side substituents play an important role in the separation of charges in polymer–fullerene composites. Side substituents of a polymer chain affect the torsion and libration dynamics of polarons through a change in the integrals of interaction inside and between polymer chains in the process of charge transfer [6]. Recently, a derivative of fullerene—bis(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6.6]C_{62} (bis(PCBM), methanofullerene $bmC_{62}^{\cdot-}$)—was used as

an electron acceptor [7]. In this derivative, two side functional groups are attached to the fullerene framework and it has a higher (by 0.1 eV) value of the lowest unoccupied molecular orbital ($LUMO_A$) than PCBM has. In fact, as was shown in [8, 9], the quantum efficiency of a plastic solar battery increases after replacement of PCBM with bis(PCBM), but this process is accompanied by deceleration of photoluminescence [10] and charge transfer [11] due to greater localization of electrons on energy traps. The importance of the analysis of the number, depth, and distribution of energy traps in polymer composites defines the need to ascertain the effect of composite morphology on the diffusion and separation of charges.

The most widespread way of changing the conformations and nanomorphologies of polymers consists of their ultrasound, microwave, and thermal modifications. In recent years, microwave chemistry has aroused growing interest as an effective means of synthesis control [12, 13]. The employment of microwave frequencies facilitates more uniform warming of a solvent and local heating of reagents. Under application of an electromagnetic field, the dipole–group polarization of the film composites PHT–PCBM and PHT–bis(PCBM) may be activated; as a result, their

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conformations may change and the processes of their deposition of a ceramic substrate may be accelerated substantially. The effect of ultrasound on the formation of composite films manifest itself as their structuring due to the presence of regions of consequent compression and extension of the polymer matrix. As was shown in [14], the thermal annealing of samples at 120°C (10 min) leads to an additional increase in the sizes of polymer crystallites and fullerene clusters and thus lengthens the lifetime of spin pairs and improves the main electronic properties of plastic solar batteries. There has not been an unambiguous picture of molecular, electron, and relaxation processes occurring in PHT composites with PCBM and bis(PCBM) counterions. Hence, the elucidation of the processes of photoexcitation, dynamics, and recombination of charge carriers hopping in these systems is of interest not only from a fundamental viewpoint but also for use in practice for subsequent controlled manufacture of optimum photovoltaic devices.

Polarons and anion radicals of fullerene photoinduced in an organic solar cell are characterized by the spin $S = 1/2$. This circumstance led to the wide use of light-induced EPR as a direct method for studying electronic properties of such systems [15, 16]. Polarons diffuse along polymer chains, whereas methanofullerenes are located between chains and are characterized by pseudorotational mobility. The separation of these charge carriers in the composite over times on the order of $\sim 10^{-9}$ s makes it possible to assume that the spins of radical pairs do not interact. Charge carriers in these composites are generated in crystalline domains that are arbitrarily disordered in the bulk heterojunction of the polymer and fullerene. The inhomogeneity of the system entails the appearance of energy traps in the polymer matrix that entrap a part of the charges and change their magnetoresonance parameters; as a consequence, the effective light-induced EPR spectrum is complicated. An analysis of spectral data for such bulk heterojunctions and their temperature and frequency dependences makes it possible to gain insight into structural and electronic properties of photovoltaic cells for a further increase in the efficiency of their operation. However, studies in this field have been conducted for the most part at helium temperatures, when the dynamic processes in organic systems are frozen. As was shown recently [17, 18], in fact, the light-induced EPR spectra of PHT−PCBM composites contain contributions from mobile and entrapped charge carriers with different EPR line shapes. In the addition, magnetic, relaxation, and dynamic parameters of these radicals are determined by the energy of initiating photons $h\nu_{ph}$ [16−19].

In this study, the method of light-induced EPR was applied to compare the main properties of charge carriers photoinduced in bulk heterojunctions of PHT−PCBM and PHT−bis(PCBM) composites modified with microwave, ultrasonic, and thermal annealing. The replacement of PHT−PCBM with PHT−bis(PCBM) entails an increase in the planarity of the polymer matrix. In this case, the depth and number of energy traps decrease and the transfer of charges in such bulk heterojunctions accelerates.

EXPERIMENTAL

In this study, the methanofullerenes PCBM and bis(PCBM) (99.5%, Solenne BV) and PHT with an average molecular mass of $M = 50 \times 10^3$ and a regioregularity of 94% (Rieke Metals) were used. Both components (1 : 1) were dissolved in chlorobenzene until a concentration of 1 wt % was attained. The prepared solution was cast as a thin layer on a ceramic plate and dried for a day; then second and third layers were deposited in a similar manner and successively dried. As a result, a film with dimensions of ~4 mm × 10 mm and a thickness of ~0.1 mm was formed. For thermal annealing, the as-dried samples were placed in an oven at 120°C for 10 min.

Microwave-treatment experiments were performed in a microwave oven at a frequency of 2.4 GHz. The solution of a composite on a substrate was placed in its center and illuminated for 5 min at a microwave power of 180 W during drying; then, second and third layers were deposited and likewise consequently dried under the action of microwave radiation.

The ultrasonic treatment of the samples was performed with a UZG-15-0.1/22 ultrasonic disperser. Samples were deposited on the substrate, fastened in front of the ultrasound source, and dried. The procedure was repeated for every new composite layer (every 3−4 layers).

The samples were irradiated with the use of a source based on LXHL-LW3C (5500 K), LXHL-LD3C (625 nm, 1.98 eV), LXHL-LL3C (590 nm, 2.10 eV), LXHL-LM3C (530 nm, 2.34 eV), LXHL-LE3C (505 nm, 2.46 eV), and LXHL-LR3C (455 nm, 2.73 eV) Luxeon III light emitting diodes (LEDs) that mostly had halfwidths of the spectrum transmission band of ~0.1 eV, the exception being the LXHL-LW3C LED. Their relative effective integral light power was estimated with the use of an IMO-2N broadband light bolometer: 1.20 : 1.19 : 0.47 : 0.99 : 1.0 : 1.86. In [14], the absorption spectra of both composites were recorded on a UV−VIS−NIR Shimadzu UV-3101PC scanning spectrophotometer at room temperature. The optical spectra of both composites were practically the same and exhibited extrema typical for regioregular PHT at 2.03 eV (612 nm), 2.20 eV (563 nm), and 2.39 eV (519 nm) [20]. In addition, the spectrum showed two peaks typical for methanofullerenes: at 4.54 eV (273 nm) and 3.8 eV (337 nm). X-ray images of the composite surface (SEM images) were measured by scanning electron microscopy on a Zeiss LEO SUPRA 25 scanning electron autoemission microscope equipped with an INCA energy dispersive X-ray spectroscopy attachment (Oxford

Some characteristics of the studied composites

Composite	Sample	ΔB_{pp}^{P}	ΔB_{pp}^{mF}	$[mF_{mob}^{-\bullet}]/[P_{loc}^{+\bullet}]$	$D_{1D} \times 10^{11}$	$D_{3D} \times 10^{6}$	$\tau_c^{-1} \times 10^{11}$
		G			rad/s		
PHT/PCBM	1	2.36	1.52	5.10	5.35	1.49	0.97
	2	2.63	1.63	2.43	16.8	1.26	0.77
	3	2.26	1.65	27.8	0.15	24.0	2.91
	4	2.32	1.53	4.92	1.26	10.3	1.10
PHT/bis(PCBM)	1	2.52	1.34	2.90	15.9	1.92	1.60
	2	2.90	1.32	1.21	7.31	11.8	1.81
	3	2.88	1.29	2.39	9.27	5.14	1.70
	4	2.63	1.33	2.73	10.4	7.71	1.23

Instruments). The image resolution was from 2 to 4 nm.

The EPR spectra were recorded on a 3-cm PS-100X spectrometer (9.7 GHz) with a maximum microwave power of 150 mW (the magnetic component of the microwave field in the center of the resonator was $B_1 = 0.48$ G); the modulation frequency of the constant magnetic field was 100 kHz. Dark-field and light-induced EPR spectra of polymer–fullerene composites were recorded at 77 K via their immersion in a Dewar quartz flask filled with liquid nitrogen directly in the resonator of the spectrometer. The signal–noise factor of the EPR spectra was increased according to the procedure of signal accumulation under repeated (4–6 times) scanning of the spectrum. Paramagnetic susceptibility was estimated from double integration of the corresponding EPR spectra recorded under conditions far from their saturation, when ultrahigh-frequency field B_1 and modulation amplitude B_m in the center of the resonator did not exceed 0.05 and 1 G, respectively. All relaxation parameters of charge carriers were determined separately with the use of the method of continuous saturation of the EPR spectra [21]. The treatment and simulation of the EPR spectra were performed with the aid of the programs Bruker SimFonia and OriginLab.

RESULTS AND DISCUSSION

EPR Line Shape and g Factor

When PHT–PCBM and PHT–bis(PCBM) composites are illuminated with wideband white light with a color temperature of $T_c = 5500$ K and monochromic light with an energy of photons of $h\nu_{ph} = 1.98–2.73$ eV, two types of paramagnetic sites with overlapping EPR lines appear (Fig. 1). The results of experiments with initial and modified composites illuminated with monochromic light will be discussed below. The table lists the experimental data obtained during photoinitiation of charge carriers with wideband white light with a color temperature of $T_c = 5500$ K in these

samples. The low-field component of these spectra was attributed to positively charged polarons $P^{+\bullet}$, while the high-field component was ascribed to negatively charged anion radicals of methanofullerene. In the case of the PHT–bis(PCBM) composite, effective g factors were calculated for polarons and bis(methanofullerenes): $g_{iso}^{P} = 2.0023$ and $g_{iso}^{F} = 2.0007$, respectively [14]. These estimates are somewhat different from the corresponding values for the PHT–PCBM composite, $g_{iso}^{P} = 2.0017$ and $g_{iso}^{F} = 1.9996$ but are close to the values obtained for polarons and anion radicals of fullerenes stabilized in other composites of conjugated polymers [16, 22–26]. For the best simulation of the light-induced EPR spectra of the samples, the convolution of Lorentzian and Gaussian EPR lines corresponding to homogeneous and inhomogeneous broadening of components was used. The light-induced EPR spectra of the PHT–PCBM composites, as in the case of poly(3-dodecylthiophene) modified with PCBM [18], are composed of two Lorentzian contributions due to mobile polarons and anion radicals of methanofullerene, $P_{mob}^{+\bullet}$ and $mF_{mob}^{-\bullet}$, as well as two Gaussian contributions from localized polarons and fullerenes entrapped by traps in the polymer, $P_{loc}^{+\bullet}$ and $mF_{loc}^{-\bullet}$. The Gaussian component in the EPR line width corresponds to the inhomogeneous broadening of the spectrum that results from different mobilities of unpaired spins and that is due to the unresolved hyperfine interaction with neighboring protons. In addition, the spectrum of the PHT–bis(PCBM) composite shows contributions from localized polarons and the quasi-pair of mobile radicals, $P_{loc}^{+\bullet}$ and $P_{mob}^{+\bullet} \leftrightarrow bmF_{mob}^{-\bullet}$, respectively. However, our calculations showed that the spectrum lacks the contribution from entrapped radicals of bis(methanofullerenes), $bmF_{loc}^{-\bullet}$. Note that the line shapes of light-induced EPR spectra for both composites subjected to thermal, microwave, and ultrasound modifications are almost the same as those of the spectra of original composites. Figure 1 illus-
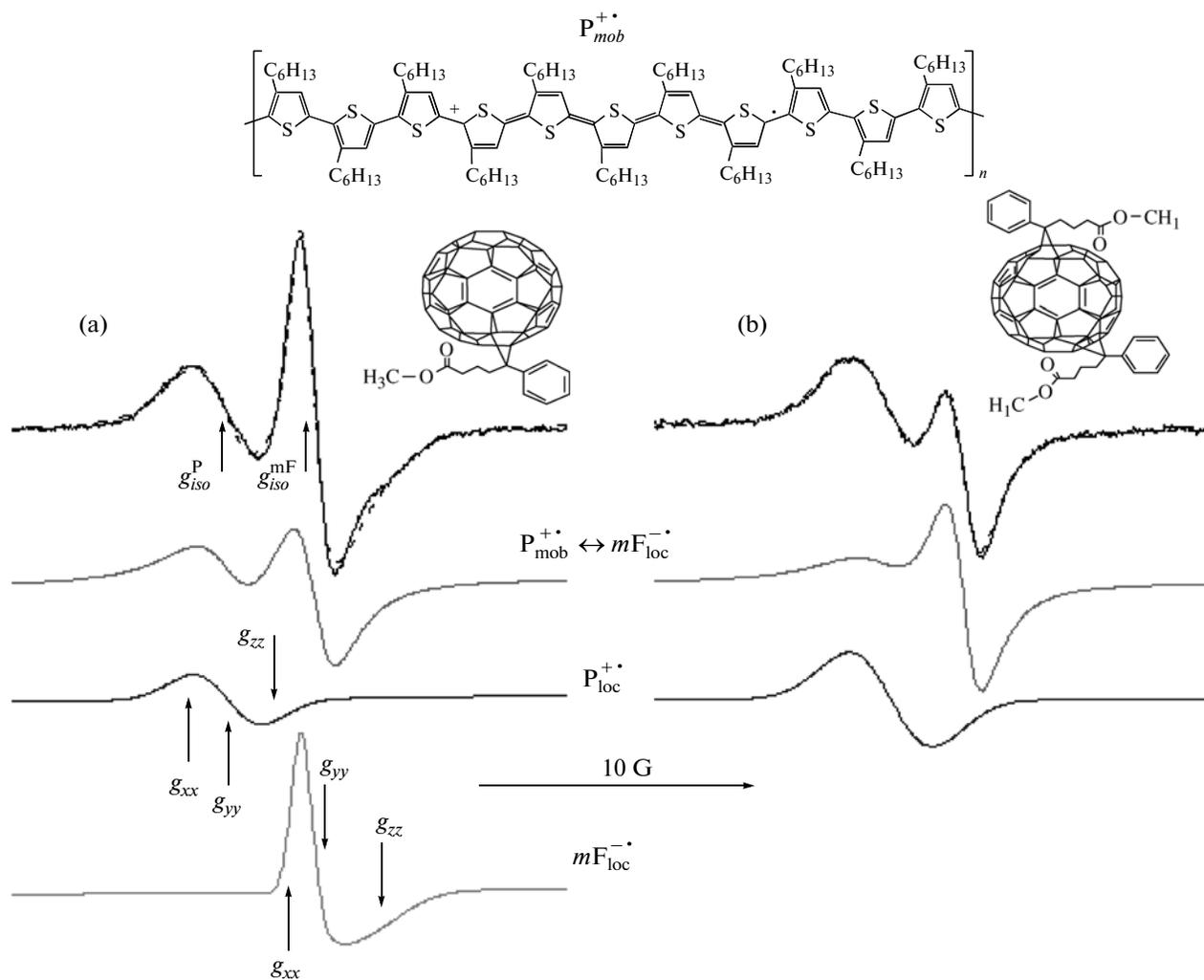
Fig. 1. EPR spectra of (a) PHT−PCBM and (b) PHT−bis(PCBM) composites recorded during their continuous illumination with light with a photon energy of $h\nu_{\mathrm{ph}} = 2.5$ eV at 77 K. Dashed lines refer to theoretical spectra calculated with the use of magnetoresonance parameters obtained in this study. See text for explanations.

trates the simulation of the EPR spectra of the composites that were obtained through summation of the contributions of localized and mobile charge carriers. The calculated line widths of anion radicals of fullerenes and polarons, $F_{\mathrm{loc}}^{-\cdot}$ and $P^{+\cdot}$, for both composites change insignificantly with the energy of exciting photons (Fig. 2). The line width of anion radicals of methanofullerene in the PHT−bis(PCBM) composite, $\Delta B_{\mathrm{pp}}^{m\mathrm{F}}$, is practically independent of the energy of photons and varies in the range 1.3−1.4 G. The anion radicals of methanofullerene in the initial composite PHT−PCBM demonstrate the line with $\Delta B_{\mathrm{pp}}^{m\mathrm{F}} = 1.3$−1.8 H, which becomes narrower during thermal treatment of the sample and broadens during microwave and ultrasound treatments. In the case of the PHT−PCBM composite, the energy of exciting photons affects the line width also (especially at 2.75 eV). The EPR line width of polarons in PHT−

PCBM and PHT−bis(PCBM) composites is $\Delta B_{\mathrm{pp}}^{\mathrm{P}} = 2.3$−3.3 G. This value slightly changes in heat- and ultrasound-modified samples but broadens in the microwave-modified samples. The wavelike dependence of $\Delta B_{\mathrm{pp}}^{\mathrm{P}}$ on the energy of incident photons in both composites after ultrasonic and thermal annealing flattens possibly owing to a decrease in the inhomogeneity of the polymer matrix. The number of energy traps for positive charge carriers should decrease in this case. In contrast, the number of energy traps of polarons increases after microwave modification of the samples; as a result, their EPR lines broaden.

During interpretation of such behavior of the linewidths of polarons and anion radicals of fullerenes, different spin interactions in the composites should be taken into account. In both spin reservoirs, the dipole−dipole interaction of paramagnetic sites
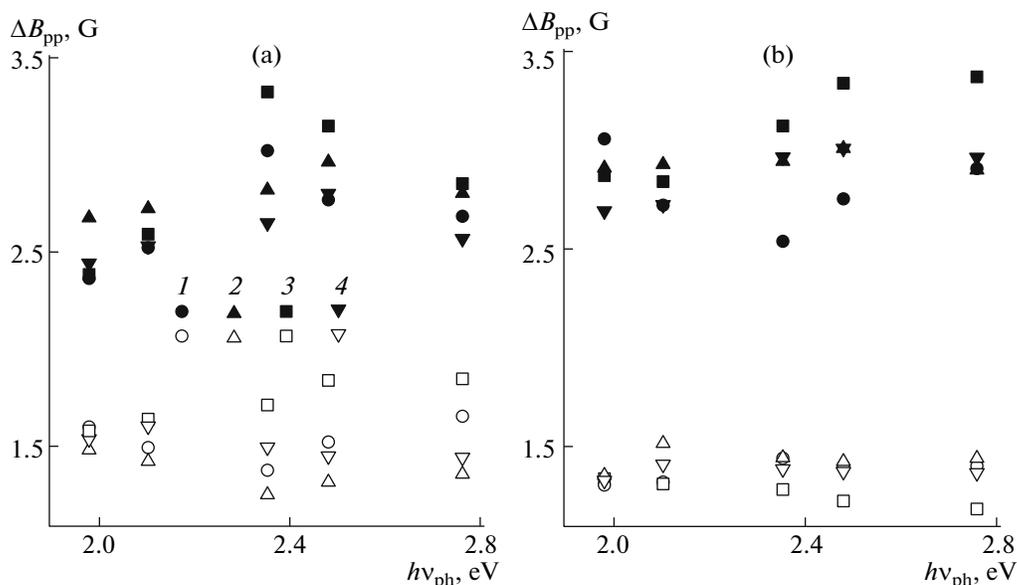
Fig. 2. Linewidths of (closed figures) polarons and (open figures) radical anions of methanofullerenes photoinduced at 77 K in initial and modified composites (a) PHT−PCBM and (b) PHT−bis(PCBM). Here and in Figs. 3–7: (*1*) initial composite and composites modified via (*2–4*) (*2*) thermal, (*3*) microwave, and (*4*) ultrasound treatments plotted against photon energy $h\nu_{ph}$.

occurs. Because atoms of sulfur and hydrogen possess magnetic moments, a hyperfine interaction between corresponding nuclei and unpaired electrons likewise arises in the studied systems. In addition, there are pseudorotation of methanofullerenes and translational diffusion of polarons along and between polymer chains of the matrix. The value of ΔB_{pp} is primarily determined by the time of spin−spin relaxation, T_2. In the polymer−fullerene composite, there are several relaxation processes that decrease time T_2 and hence broaden the EPR line. One of them is spin−lattice relaxation with time T_1. Another possible relaxation mechanism will be denoted as T_2'. Then, effective line width ΔB_{pp} of the Lorentzian shape may be written as follows [27]:

$$\Delta B_{pp} = \frac{2}{\sqrt{3}\gamma_e}\frac{1}{T_2} = \frac{2}{\sqrt{3}\gamma_e}\left(\frac{1}{T_2'} + \frac{1}{2T_1}\right), \quad (1)$$

where γ_e is the gyromagnetic ratio for an electron. During collision of polarons and anion radicals of fullerene, an exchange interaction with probability p should occur between them; hence, their absorption line will additionally broaden by $\delta(\Delta\omega) \sim \Delta B_{pp}/\hbar$ [28]:

$$\delta(\Delta\omega) = p\omega_{hop}n_f = 1/2\omega_{hop}n_f(\alpha^2/(1 + \alpha^2)), \quad (2)$$

where n_f is the amount of methanofullerene radicals per polymer unit, $\alpha = (3/2)2\pi J/\hbar\omega_{hop}$, J is the constant of exchange interaction of spins in the radical pair, and ω_{hop} is the rate of charge hopping between two neighboring equal thiophene rings. The value of ω_{hop} may be estimated with good approximation through the use of the semiclassical Marcus theory for conjugated polymers [29]:

$$\omega_{hop} = \frac{4\pi^2}{\hbar}\frac{t_{1D}^2}{\sqrt{4\pi E_r k_B T}}\exp\left(-\frac{E_r}{4k_B T}\right), \quad (3)$$

where t_{1D} is the energy of the exchange interaction of electrons between the initial and final states (intrachain overlap integral) and E_r is the energy of intra- and outersphere reorganization of charge carriers due to their interaction with lattice phonons. For PHT, E_r was estimated as 1.18 eV [30]; this value somewhat decreased with temperature. It is possible that the ultrasound, microwave, and thermal treatments lead to a change in the distribution of paramagnetic species over the energy of reorganization. A decrease in the energy of reorganization related to temperature oscillations of thiophene rings during composite treatment should broaden the EPR line. This interaction in the studied composites is similar to the modulation of charge transfer in organic crystals by thermal molecular motions [31].

Paramagnetic Susceptibility of Charge Carriers in Composites

Effective spin susceptibility χ of paramagnetic sites in the studied composites contains contributions due to mobile and localized polarons, χ_p, and to anion radicals of methanofullerenes, χ_F (Figs. 1, 3). These components were separated via deconvolution of the total light-induced EPR spectrum and subsequent double integration of its components. During illumination in the polymer−methanofullerene bulk, heterojunction paramagnetic sites that remain after rapid irreversible and slow reversible recombinations of spin charge car-
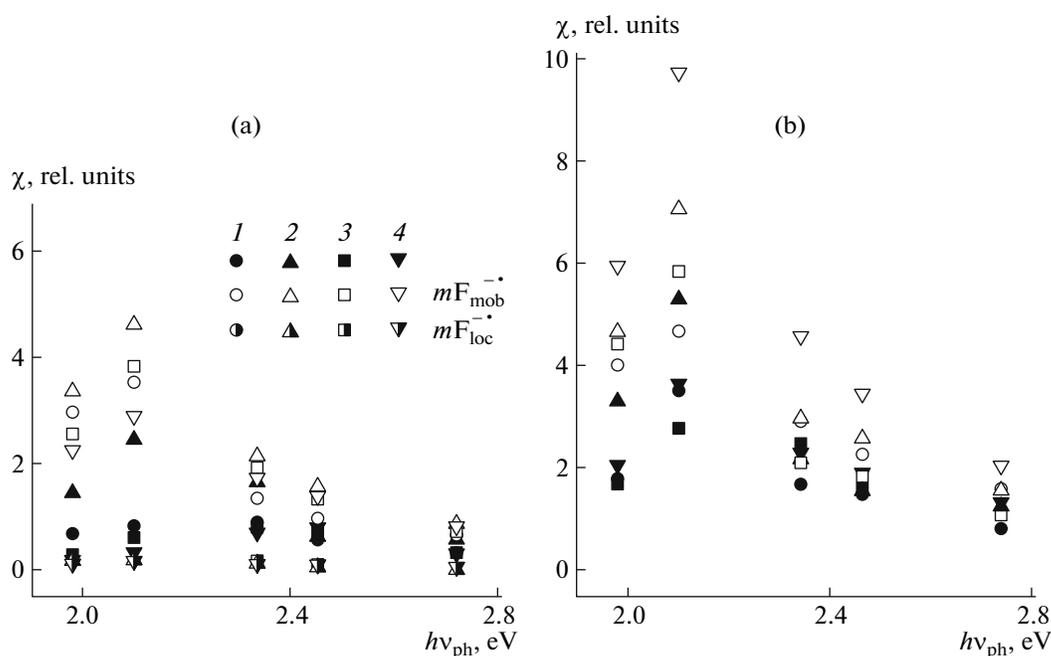
Fig. 3. Effect of the contributions of (closed figures) localized polarons, (half-closed figures) localized radical anions of methanofullerenes, and (open figures) mobile radical anions of methanofullerenes to the effective paramagnetic susceptibility of initial and modified composites (a) PHT−PCBM and (b) PHT−bis(PCBM) on the energy of initiating photons $h\nu_{ph}$. The recording temperature is 77 K.

riers are registered. The probability of the latter process is primarily determined by the multistage diffusion of polarons over polymer chains via energy barriers and their subsequent tunneling to anions of methanofullerene [32]. Because the samples were prepared in a different manner, it was impossible to quantify the resulting concentrations of charge carriers; however, qualitative conclusions about the effect of the mode of composite modification and the energy of incident light on the relative values of χ_p and χ_F can be made. As is clear from Fig. 3, the concentrations of photoinduced polarons and radical anions of fullerene are characterized by a bell-shaped dependence on the energy of incident photons with a maximum at ~2.1 eV. This value is close to the energy gap for PHT: 1.92 eV [33]. Note that the number of entrapped anion radicals of fullerenes in the PHT−PCBM composite, $m\mathrm{F}_{loc}^{-\cdot}$, undergoes practically no change with variation in either the energy of initiating photons or the method of composite preparation. Moreover, it may be inferred that, in the modified composites PHT−PCBM and PHT−bis(PCBM), the number of charge carriers increases; in this case, polarons entrapped by traps are generated with a high probability in the PHT−PCBM composite during illumination with photons with an energy in the range 2.1−2.5 eV, whereas the PHT−bis(PCBM) composite features a narrower extremum (~2.1 eV). It is more important to compare the ratio between the number of mobile radical anions of methanofullerene and the number of

localized polarons in the same sample, $[m\mathrm{F}_{mob}^{-\cdot}]/[\mathrm{P}_{loc}^{+\cdot}]$, because it is independent of the quantity of the sample on the plate (Fig. 4). It is seen that the ratio between the number of mobile paramagnetic sites and localized sites in the PHT−PCBM composite during illumination with photons with an energy of 2.3−2.8 eV is $[m\mathrm{F}_{mob}^{-\cdot}]/[\mathrm{P}_{loc}^{+\cdot}]$ 2 : 1; this value weakly changes during annealing. Parameter $[m\mathrm{F}_{mob}^{-\cdot}]/[\mathrm{P}_{loc}^{+\cdot}]$ obtained for PHT−PCBM initial samples during illumination with photons with an energy of 1.7−2.2 eV attains 4 : 1 and increases to 10 : 1 and 14 : 1 for microwave- and ultrasound-treated samples, respectively. At the same time, the value of $[m\mathrm{F}_{mob}^{-\cdot}]/[\mathrm{P}_{loc}^{+\cdot}]$ decreases upon thermal annealing to 2 : 1 during illumination with an energy of 1.7−2.2 eV. Somewhat different values of $[m\mathrm{F}_{mob}^{-\cdot}]/[\mathrm{P}_{loc}^{+\cdot}]$ are observed for PHT−bis(PCBM) composites. Ratio $[m\mathrm{F}_{mob}^{-\cdot}]/[\mathrm{P}_{loc}^{+\cdot}]$ was ~2 : 1 for the initial PHT−bis(PCBM) in the entire range of energies of initiating photons and weakly changed during thermal, microwave, and ultrasound modifications of this composite. It appears that the annealing of the PHT−PCBM composite leads to a reduction in the number of deep energy traps and hence to an increase in the number of mobile polarons. The structure of the PHT−bis(PCBM) composite is more homogeneous than that of the PHT−PCBM composite; therefore, microwave, ultrasound, and thermal modifications slightly affect the morphology of the energy-trap dis-
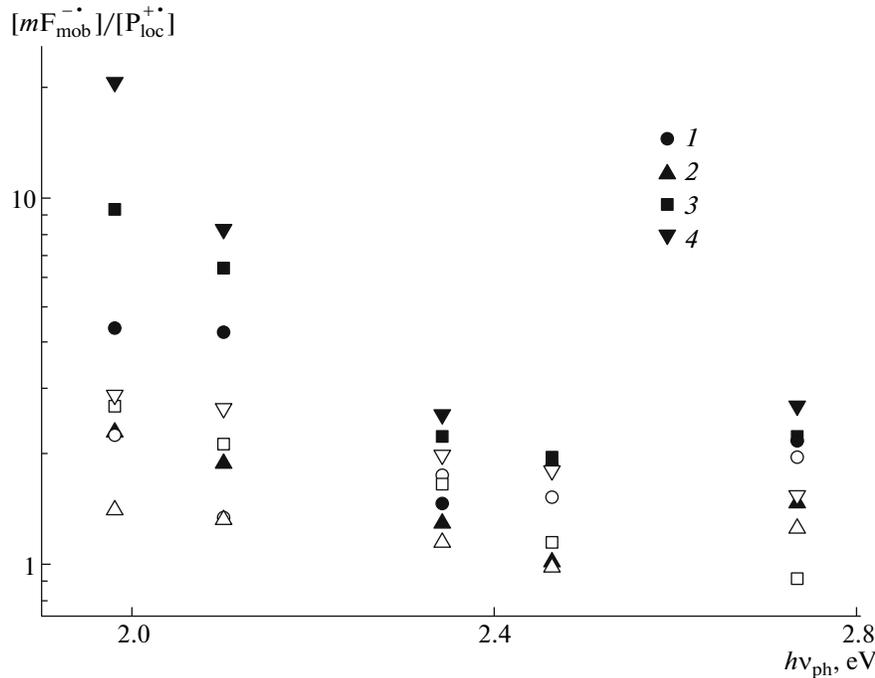
Fig. 4. Ratio of the number of mobile radical anions of methanofullerene to the number of localized polarons, $[mF_{mob}^{-\bullet}]/[P_{loc}^{+\bullet}]$, induced at 77 K in original and modified composites (closed figures) PHT−PCBM and (open figures) PHT−bis(PCBM) plotted against photon energy $h\nu_{ph}$.

tribution in it. This conclusion is confirmed by the SEM study of the surface of composites. Figure 5 displays SEM images of the surfaces of the samples. It can be seen that the surfaces of the original composites PHT−PCBM feature an island structure, which becomes smoother and blurs during heating of the samples. In the microwave- and ultrasound-modified PHT−PCBM samples, the SME image of the composite surface exhibits a continuous very homogeneous texture of the surface that differs appreciably from the surface of the initial samples. In the PHT−bis(PCBM) composite, there is a homogeneous granule-like surface that slightly changes during heat, microwave, or ultrasound treatment.

Electron Relaxation and Dynamics of Charge Carriers

The effective times of spin−lattice relaxation and spin−spin relaxation of polarons and anion radicals of fullerene, T_1 and T_2, respectively, were determined from the saturation curves of their individual light-induced ERP spectra as described in [21]. Mobile polarons that diffuse along polymer chains and between polymer chains of the PHT matrix with corresponding diffusion coefficients D_{1D} and D_{3D} and pseudorotational mobility of methanofullerene molecules about its main axis with correlation time τ_c induce additional magnetic fields accelerating electronic relaxation of both spin ensembles at the centers of location of paramagnetic sites. Because this relax-

ation in conjugated polymers is largely determined by the dipole−dipole interaction of paramagnetic sites [34], the mentioned parameters may be described by the following equations [35]:

$$T_1^{-1}(\omega_e) = \langle\omega^2\rangle[2J(\omega_e) + 8J(2\omega_e)] \qquad (4)$$

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

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 n chaotically distributed spins in a polymer unit; Σij is the lattice sum for a powder sample; $J(\omega_e) = (2D'_{1D}\omega_e)^{-1/2}$ at $D'_{1D} \gg \omega_e \gg D_{3D}$ or $J(0) = (2D'_{1D}D_{3D})^{-1/2}$ at $D_{3D} \gg \omega_e$ is the spectral density function for the quasi-one-dimensional Q1D motion; $D'_{1D} = 4D_{1D}/L^2$, ω_e is the resonance angular frequency of the electron spin procession; and L is the length of delocalization of electron function in a polymer, which is equal to ~4−5 monomer units for conjugated polymers like PHT [36]. The spectral density for rotational diffusion is $J_{rot}(\omega_e) = 2\tau_c/(1 + \tau_c^2\omega_e^2)$. Similar spectral functions were used in the study of spin dynamics in other conjugated polymers [34, 36].

Diffusion coefficients which were calculated for both types of charge carriers induced in the composites through Eqs. (4) and (5) with allowance for the above data, and the corresponding spectral densities are presented in Figs. 6 and 7 in relation to the energy
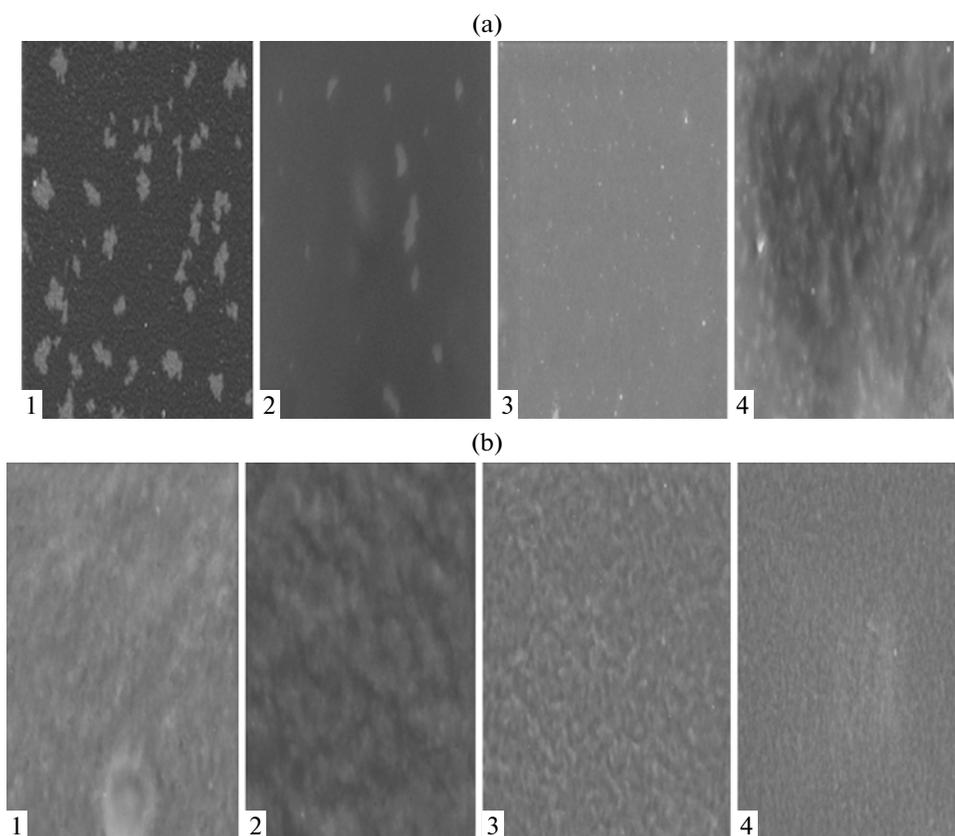
(a)

(b)

Fig. 5. SEM images of surfaces of (a) PHT−PCBM and (b) PHT−bis(PCBM) composites.

of irradiating photons. These figures show that diffusion coefficients D_{1D} and D_{3D} of polarons strongly depend on the energy of exciting photons and on modification of the samples. When PCBM was replaced with bis(PCBM), these dependences became less pronounced. Calculations show that, after microwave and ultrasound treatment of the PHT−PCBM samples, ratio D_{1D}/D_{3D} decreases by 1.5−2 order of magnitude. This fact indicates a reduction in the anisotropy of motion of polarons in the polymer matrix of the modified composite. Ratio D_{1D}/D_{3D} obtained for polarons in the PHT−bis(PCBM) composite remains practically the same after its heat and microwave modifications, but, in the case of ultrasound modification, this parameter decreases by approximately an order of magnitude, depending on the energy of photons. The pseudorotational correlation times for anion radicals of fullerene, τ_c, in the initial and annealed PHT−PCBM composites increase almost linearly with an increase in the energy of photons. The reciprocal value of this parameter obtained for ultrasound- and microwave-treated samples exhibits a minimum at 2.35 eV. At the same time, the value of D_{1D} for polarons of the same composites shows a maximum in the range 2.1−2.3 eV. During illumination of ultrasound- and microwave-treated PHT−PCBM composites, the diffusion

coefficients of polarons and the value of τ_c^{-1} change in a different manner (Figs. 6, 7). This circumstance may suggest an increase in the dimensions of crystalline clusters of polymer and fullerene phases after modification of PHT−PCBM (in these composites, the quasi-one-dimensional diffusion of polarons is facilitated, while the pseudorotational mobility of methanofullerene molecules is hindered) and weakening of the polymer−fullerene interaction at the interfacial boundary of these phases. In the case of the PHT−bis(PCBM) composite, there is the opposite dependence of rotational mobility of methanofullerenes on the energy of initiating photons. In initial and annealed PHT−bis(PCBM) samples, the value of τ_c^{-1} for anion radicals of methanofullerene exhibits a dependence peaking at 2.3 eV. The diffusion coefficient of polarons, D_{1D}, in the PHT−bis(PCBM) composite likewise demonstrates a dependence on the photon energy, which features a maximum at 2.1 eV. As opposed to the PHT−PCBM composite, in the case of ultrasound- and microwave-modified PHT−bis(PCBM) composites, diffusion coefficients D_{1D} of polarons and the value of τ_c^{-1} of methanofullerenes with extrema at $h\nu_{ph}$ = 2.10 and 2.35 eV, respectively, change in a symbate manner. This effect is apparently
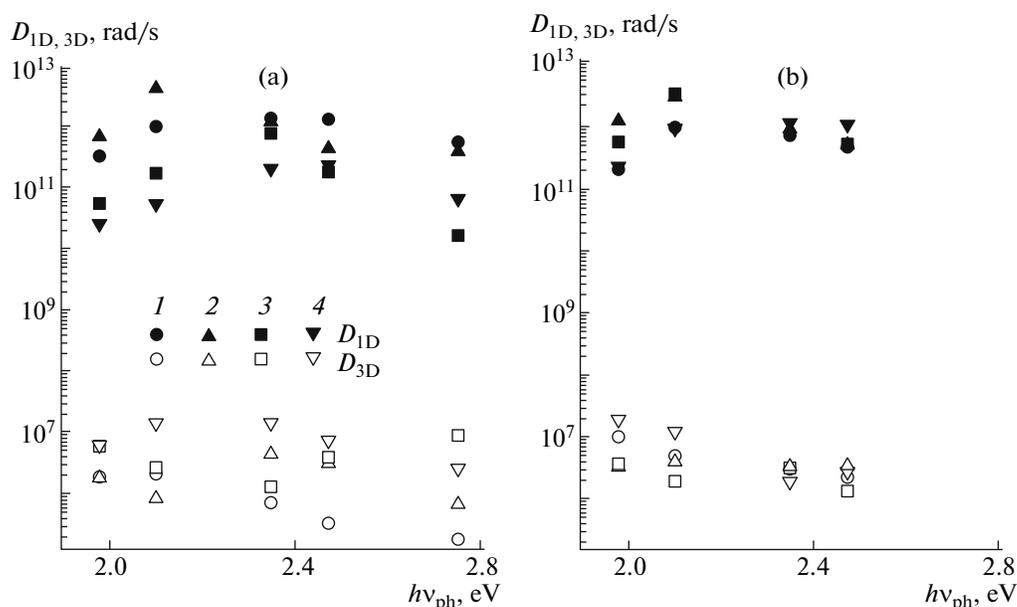
Fig. 6. Diffusion coefficients of mobile polarons, $P_{mob}^{+\bullet}$, (closed figures) along chains and (open figures) between chains for original and modified composites (a) PHT−PCBM and (b) PHT−bis(PCBM) plotted against photon energy $h\nu_{ph}$. The recording temperature is 77 K.
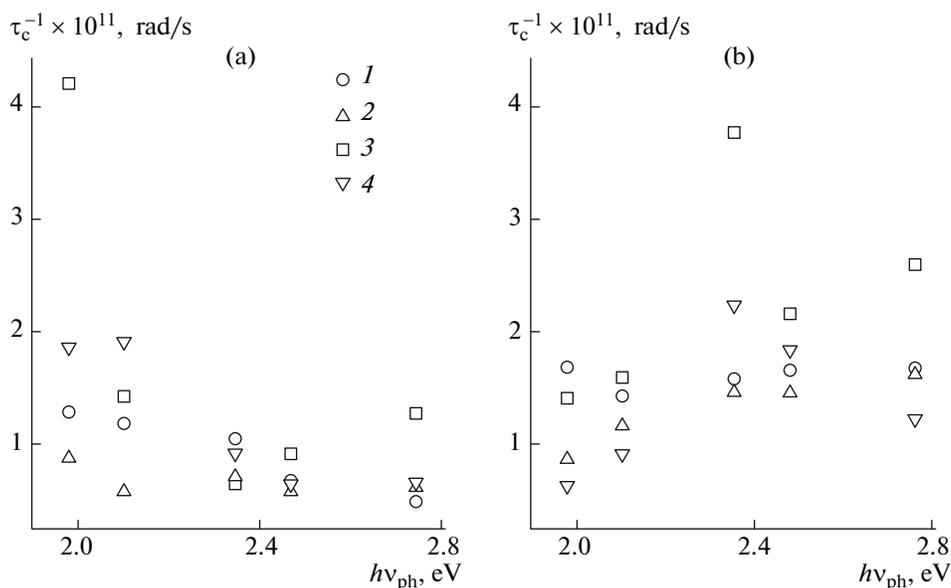

Fig. 7. Reciprocal correlation time $1/\tau_c$ of pseudorotational mobility of anion radicals of methanofullerenes (a) PCBM and (b) bis(PCBM) in the polymer matrix of original and modified composites PHT−PCBM and PHT−bis(PCBM), respectively, plotted against photon energy $h\nu_{ph}$. The recording temperature is 77 K.

related to the presence of two equal functional groups in the PHT−bis(PCBM) composite that are responsible for a more pronounced interaction at boundaries of polymer and fullerene phases in the bulk heterojunction.

The data collected on the mobility of charge carriers may be interpreted in terms of several classical models. In accordance with [14], the quasi-one-dimensional diffusion of polarons in the samples is strongly temperature-dependent. This effect may be explained by the scattering of polarons on lattice phonons in crystalline domains distributed in the polymer matrix in accordance with the model advanced in [37]. This model was used to interpret

intrachain diffusion of polarons in various conjugated polymers [34, 38–40]. The interaction of charge carriers with photons of the polymer lattice should lead to the following dependence for the coefficient of quasi-one-dimensional diffusion of polarons, D_{1D} [37]:

$$D_{1D} = \frac{\pi^2 M t_0^2 k_B^2 T^2}{h^3 \alpha_{eph}^2}\left[\sinh\left(\frac{E_{ph}}{k_B T}\right)-1\right]$$
$$= D_{1D}^{(0)}T^2\left[\sinh\left(\frac{E_{ph}}{k_B T}\right)-1\right], \qquad (6)$$

where M is the mass of the polymer unit; t_0 is the transfer integral, equal to 2.5–3.0 eV for π electrons; α_{eph} is the constant of electron–photon interaction; and E_{ph} is the energy of photons.

The interchain charge transfer may be interpreted in terms of the formalism of polaron hopping controlled by energy traps with concentration n_t and depth E_t formed on polymer chains of amorphous low-sized systems [41]. On the basis of the fact that the interchain mobility of charge carriers, μ_{3D}, and the diffusion coefficient, D_{3D}, are related through the equation $\mu_{3D} = eD_{3D}d^2/k_B T$ and via combination of Eqs. (18) and (25) [41], in the limiting case of the low concentration of traps, we arrive at the following expression:

$$D_{3D} = \nu_0\left(\frac{R_{ij}}{d}\right)^2\exp\left(-\frac{2R_{ij}}{r}\right)$$
$$\times \exp\left(\frac{E_t}{2k_B T_{cr}}\right)\exp\left[-\frac{E_t}{2k_B T}\left(\frac{\sigma_0}{k_B T}\right)^2\right], \qquad (7)$$

where ν_0 is the initial frequency of hopping; d is the lattice constant; $T_{cr} = E_t/2k_B\ln(n_t)$ is the critical temperature, at which the transition from the trap-controlled transfer of charge carriers to their intermittent transfer from one trap to another occurs; and σ_0 is the width of the initial energy distribution of hopping states in the absence of traps. The interchain dynamics of polarons in the PHT–PCBM and PHT–bis(PCBM) composites is well described within the framework of the advanced theory [14]. It was found that, when counterion PCBM is replaced with bis(PCBM) in such a system, E_t decreases, while parameter T_{cr} somewhat increases. These results indicate that the number and depth of traps decrease owing to an increase in the crystallinity of the polymer matrix.

The above evidence shows that E_t and T_{cr} strongly depend on the energy of initiating photons and achieve their minimum and maximum values at $h\nu_{ph} \sim 2.5$ eV, respectively. The mobility of methanofullerene molecules in the investigated composites may be interpreted in terms of the Pike theory [42] as hopping of these charge carriers under the action of lattice phonons between localized states with an energy barrier of $E_b = 0.04$–0.08 eV [14]. This parameter depends on the energy of photons and is close to the values obtained, for example, via molecular dynamics in polycrystalline fullerenes [43] and their complexes with triphenylamines [44].

CONCLUSIONS

Owing to the structural inhomogeneity of the polymer–fullerene system, energy traps of different depths and distributions that entrap polarons are formed in it under the action of light. A comparative investigation of charge transfer in bulk heterojunctions formed in chains of PHT and methanofullerenes has shown that the main magnetic-resonance, relaxation, and dynamic parameters of charge carriers, polarons, and anion radicals of methanofullerenes are determined by the structure and conformation of the composite and the energy of exciting photons. The replacement of PCBM with bis(PCBM) entails an increase in planarity and causes ordering of such a matrix; as a result, local molecular oscillations in it and, hence, the transfer of charge in the composite are accelerated. The conformation of the PHT–bis(PCBM) composite is more stable above all owing to the presence of additional functional group in methanofullerene. This assumption follows from the weaker effect of IR, microwave, and ultrasound treatments on the ratio of the number of formed mobile and localized charge carriers, $[mF_{mob}^{-\cdot}]/[P_{loc}^{+\cdot}]$, in the PHT–bis(PCBM) composite relative to that in the PHT–PCBM composite. This outcome is additionally confirmed by the results of SEM measurements of sample surfaces. The electronic relaxation of charge carriers that are photo-induced in both composites is determined by the dynamics, structure, and conformation of their microenvironment and appreciably depends on the energy of exciting photons. The energy barrier necessary for the hopping of polarons on the neighboring chain of the polymer matrix for both composites is substantially higher than the barrier of their diffusion along polymer chains. However, after ultrasound and microwave modifications of the PHT–PCBM composites, the anisotropy of polaron diffusion declines significantly. In contrast, when PCBM was replaced with bis(PCBM), the energy of pseudotransformation of the fullerene globule somewhat decreases. This phenomenon is associated with the freezing of the molecular pseudotransformation of fullerene in the more crystalline composite, PHT–bis(PCBM). Therefore, as anticipated, in fact, when bis(PCBM) with a higher $LUMO_A$ value than that of PCBM is used, the structure is more ordered and energy losses during charge transfer in such solar cells are minimized. The energetics of the separation and transfer of charge and the interaction between charge carriers followed by their recombination in the bulk heterojunction are important for generation of triplet states in it. This circumstance should be considered during the design of new organic solar cells.

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