

ELECTROLUMINESCENT AND PHOTOVOLTAIC DEVICES

An ESR Study of Photoinduced Charge Transport in the Polymer/Fullerene System

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Conjugated polymers and their composites with fullerenes hold promise for molecular electronics, e.g., as an active matrix of plastic photovoltaic devices [1, 2]. Methyl 6,6-phenyl-C₆₁-butanoate (MPCB), a fullerene derivative, introduced into poly-3-dodecylthiophene (P3DT) forms the so-called bulk heterojunction with the polymer matrix and acts as an electron acceptor. When such a heterojunction is illuminated by visible light, electron detachment from the polymer chain and its transfer to a fullerene molecule take place [3]. This process is accompanied by the formation of a radical pair, the positively charge polaron P⁺ and the negatively charged fullerene radical anion C₆₁^{•-}. The efficiency of photoinduced charge separation must be determined by the basic physicochemical properties of the ingredients of the polymer/fullerene composite. The process of photoinduced generation of radical pairs and their subsequent recombination in this system have not been studied yet.

This work concerns the light-induced electron spin resonance (LESR) study of the magnetic, relaxation, and dynamic parameters of paramagnetic centers photoexcited by a laser beam having a photon energy of 1.88, 2.22, or 2.75 eV in the P3DT–MPCB composite over a wide temperature range.

Regioregular poly-3-dodecylthiophene available from Aldrich® and methyl 6,6-phenyl-C₆₁-butanoate synthesized at the University of Groningen (the Netherlands) were used in the study. Both components in a 1 : 1 mass ratio were dissolved in chlorobenzene to have a concentration of 1%. A specimen was a ceramic plate coated with a 4 × 8 mm² film having a thickness of 0.1 mm prepared by evaporation of this solution. The compound was placed in the cavity of a PC100X X-band 3-cm range ESR spectrometer and illuminated by a laser beam at $T = 77$ –340 K. The paramagnetic susceptibility was determined via the double integration of the ESR spectra.

The laser irradiation of the P3DT/MPCB system at $T \leq 200$ K gives rise to two overlapping LESR lines with a temperature-dependent intensity (Fig. 1). The upfield line with an isotropic g -factor of $g_{\text{iso}} = 2.0023$ and a peak-to-peak width of $\Delta B_{\text{pp}} = 1.3$ –1.7 G was attributed to polaron P⁺, whereas the downfield line with $g_{\text{iso}} = 2.0001$ and $\Delta B_{\text{pp}} = 0.6$ –0.9 G was assigned to the fullerene radical anion C₆₁^{•-} rotating about a particular molecular axis. The dependence of the line intensity of these paramagnetic species on the microwave (MW) power is linear. However, at a certain microwave power, this dependence becomes less steep and even can change its sign. These changes are accompanied by line broadening in the ESR signals of these species. Such a behavior of the LESR parameters is explained in terms of the continuous saturation effects. An analysis showed that the saturation in the spectra of the polaron and the fullerene radical anion is manifested at different MW power levels. Thus, it becomes possible to separately determine the spin–lattice and spin–spin relaxation times T_1 and T_2 , respectively, of both paramagnetic species according to the formulas

$$T_1 = \left[(\Delta B_{\text{pp}} / \Delta B_{\text{pp}}^{(0)})^2 - 1 \right] / \gamma_e^2 B_1^2 T_2, \quad (1)$$

$$T_2 = 2 / \sqrt{3} \gamma_e \Delta B_{\text{pp}}^{(0)}, \quad (2)$$

where $\Delta B_{\text{pp}}^{(0)}$ is the linewidth in the absence of saturation, B_1 is the magnetic component of the microwave field, and γ_e is the gyromagnetic ratio of the electron.

The analysis of these data has shown that the interaction of the C₆₁^{•-} species with the lattice is characterized by a monotonic temperature dependence whereas the spin–lattice relaxation of polarons P⁺ exhibits a nonmonotonic dependence with a characteristic point at $T_c \approx 130$ –160 K depending on the photon energy.

Several dynamic processes occur in the P3DT/MPCB system, e.g., the diffusion of polarons

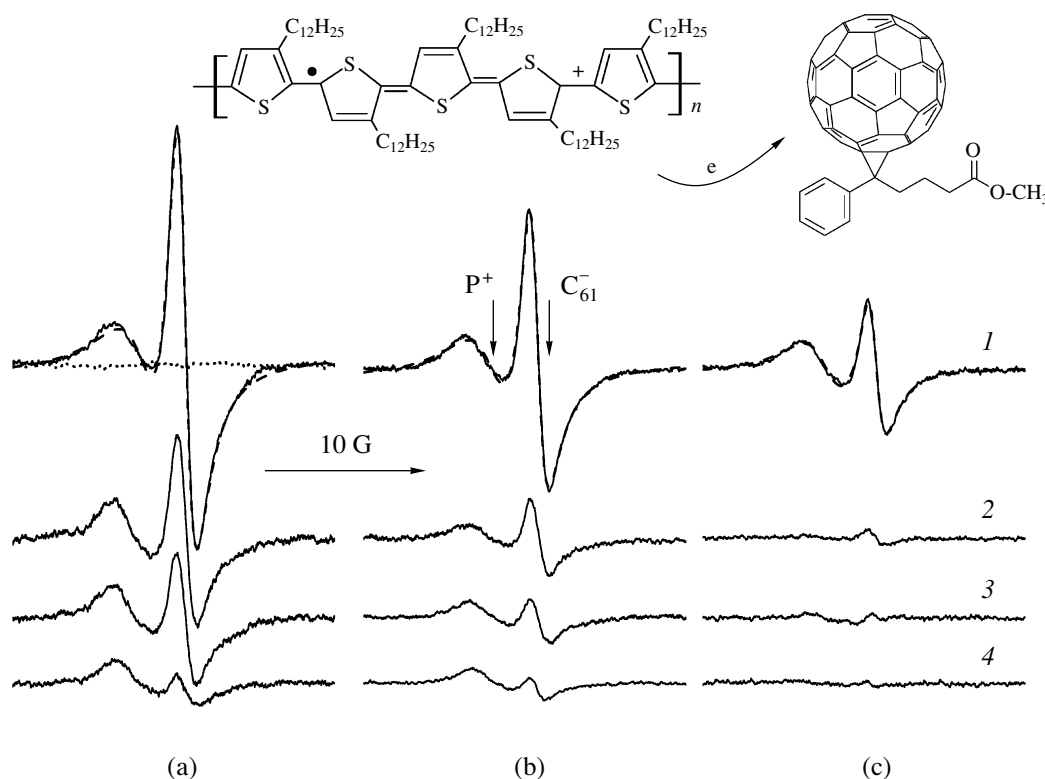


Fig. 1. Light-induced X-band ESR spectra of radical pairs generated in the poly-3-dodecylthiophene/methyl 6,6-phenyl- C_{61} -butanoate system (sketched at the top) by continuous laser radiation at photon energies of (a) 1.88, (b) 2.22, and (c) 2.75 eV as recorded at temperatures (T) of (1) 77, (2) 90, (3) 110, and (4) 150 K. The dotted curve shows the “dark” spectrum recorded before laser irradiation.

along the polymer chains with a coefficient D_{1D} , the rotational diffusion of the fullerene radical ion about the dedicated molecular axis with a coefficient D_r , and charge transfer between the polaron and the fullerene with a coefficient D_e . These processes induce an additional magnetic field at the site of occurrence of paramagnetic species and, consequently, accelerate their electronic relaxation. The relaxation of the spin reservoir as a whole is largely determined by dipole–dipole interaction between mobile and localized spins; therefore, the following equation can be written for the spin–lattice relaxation rate [5]:

$$T_1^{-1}(\omega_e) = \langle \omega^2 \rangle [2J(\omega_e) + 8J(2\omega_e)], \quad (3)$$

where $\langle \omega^2 \rangle$ is the dipole–dipole interaction constant for a powder; $J(\omega_e) = (2D_{1D}\gamma_e)^{-1/2}$ (provided that $D_{1D} \gg \omega_e \gg D_{3D}$) or $J(\omega_e) = \tau_c / (1 + \tau_c^2 \omega_e^2)$ is the spectral density function for the translational Q1D or rotational diffusion with a correlation time τ_c , respectively; and ω_e is the angular resonance frequency of electron precession.

The temperature dependence curves for the dynamic parameters calculated according to Eq. (3) for both types of paramagnetic centers photoinduced in the P3DT/MPCD system are presented in Fig. 2. These

parameters were interpreted in terms of the Elliot hopping model [6] for charge carrier overcoming a barrier E_a . This model predicts the dependence of the carrier mobility in the form

$$D_{1D,r}(\omega_e T) = D_{1D,r}^0 T^2 \omega_e^s \exp\left(\frac{E_a}{k_B T}\right), \quad (4)$$

where $s = 1 - \alpha k_B T / E_a$ and α is a constant.

An analysis shows that the values of E_a determined from Eq. (4) for the 1D polaron diffusion in P3DT/MPCB are 0.048, 0.038, and 0.094 eV for polaron generation with quantum energies of 1.88, 2.22, and 2.75 eV, respectively. The E_a value determined for the rotational diffusion of the fullerene radical ion decreases from 0.17 to 0.10 eV and, then, increases to 0.12 eV in this sequence. The value of E_a obtained for fullerene is well below that found for the rotation of C_{60} in solids with a higher crystallinity [7], although it is close to the energy of fullerene rotation in the triphenylamine complex [8]. The energy E_a determined for the 1D diffusion of the polaron is close to the activation energy of its mobility in poly-3-hexylthiophene [9], as well as to the energy of lattice phonons in poly-3-octylthiophene [10] and other conjugated polymers [11].

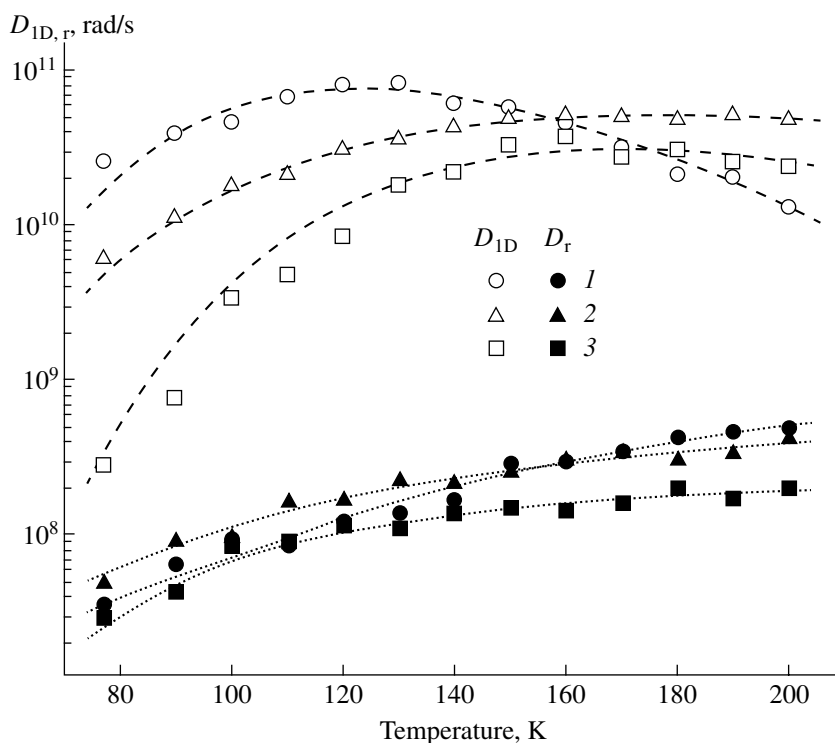


Fig. 2. Temperature dependences for the rates of translational diffusion of polarons $P^{+\bullet}$ along polymer chains, D_{1D} , and rotational diffusion of $C_{61}^{-\bullet}$, D_r , photoinduced in the P3DT/MPCD system by continuous laser radiation at photon energies of (1) 1.88, (2) 2.22, and (3) 2.75 eV as calculated using Eq. (3). The curves show (in descending order) the dependences calculated according to Eq. (4) at (dashed lines) $\alpha = 1.2$, $E_a = 0.048$ eV; $\alpha = 0.45$, $E_a = 0.038$ eV; and $\alpha = 2.2$, $E_a = 0.094$ eV and (dotted lines) $\alpha = 0.04$, $E_a = 0.010$ eV; $\alpha = 0.03$, $E_a = 0.017$ eV; and $\alpha = 0.06$, $E_a = 0.012$ eV.

Thus, the illumination of the bulk heterojunction generates two paramagnetic species with partially overlapping ESR spectra in the P3DT/MPCB composite, namely, the positively charged polaron $P^{+\bullet}$ with axial symmetry on the polymer chain and the fullerene radical anion $C_{61}^{-\bullet}$, which has a rhombic symmetry and is located between polymer chains. Owing to a high polaron mobility, both radicals are spatially separated; as a result, the probability of their recombination is strongly reduced. The photoinduced charge is carried by the polaron along the polymer chain, passing the fullerene molecule with the delocalized opposite charge. The weak interaction between the components of the photoinduced radical pairs leads to a difference in their interaction with their own microenvironment and, hence, in their relaxation and dynamic parameters in the P3DT/MPCB system. This interaction depends on the energy of excitation photons. The spin dynamics induces an additional magnetic field at the site of occurrence of other spins, thereby resulting in acceleration of the electronic relaxation of both spin ensembles. Thus, the dynamic parameters of polarons and fullerene radical ions in the test system can be calculated. The translational 1D diffusion of polarons and the rotational dif-

fusion of fullerene radical anions follow the activation mechanism and depend on the energy of laser photons.

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