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Multifrequency EPR study of charge transfer in poly(3-alkylthiophenes)

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Abstract

The results of an investigation at different (10–140 GHz) wavebands EPR of magnetic, relaxation and dynamics parameters of mobile paramagnetic charge carriers (polarons) in low-dimensional solid-state poly(3-alkylthiophenes) semiconductors are discussed. At high registration frequency all components of the g-tensor of polarons are registered. Relaxation and diffusion rates of such paramagnetic impurities are determined by the method of steady-state saturation of spin packets.

Keywords: EPR; Organic semiconductor; Relaxation; Dynamics

1. Introduction

The magnetic and electronic properties of organic polymer semiconductors with an extended π-conjugated system have been widely studied in the last years [1] owing to their potential use as active materials in molecular electronics. Poly(3-alkylthiophene) (P3AT) seems a suitable model system for understanding the electronic and optical peculiarities of sulphur-based one-dimensional systems with non-degenerate ground states. The transport properties of P3AT are mainly governed by the presence of mobile polarons originating from the synthesis and the adsorption of oxygen from ambient atmosphere. The polaron possesses a spin $S = 1/2$, therefore P3AT is widely studied by the EPR method. At 3-cm waveband EPR the polaron in P3AT is characterized by a single line with peak-to-peak width of 0.6–0.8 mT and g-factor lying near the g-factor of the free electron [2]. However, at comparatively low-frequency ($\nu_e \leqslant 10\,\text{GHz}$) EPR a low spectral resolution and a stronger spin exchange are revealed in the study of organic solids with paramagnetic impurities. Such factor limits significantly the self-descriptiveness and accuracy of the method and can lead to an ambiguous interpretation of the results obtained.

Earlier we have demonstrated [3,4] the advantages of 2-mm waveband EPR spectroscopy in the study of various polymer semiconductors, poly(3-octylthiophene) (P3OT) among them [5].

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This paper reports some results of the investigation at 10–140 GHz EPR of relaxation and dynamic properties of charge carriers in P3AT samples.

2. Magnetic parameters of poly(3-alkylthiophenes)

Nearly symmetric Lorentzian signals are observed in the 3-cm EPR spectrum of the P3AT samples (Fig. 1a). At 2-mm waveband EPR this spectrum becomes more informative (Fig. 1b). Computer simulation of the EPR spectra shown in the figure gives a possibility to determine separately the position and width of all spectral components of polarons in, e.g. P3OT, so then $g_{xx} = 2.00409$, $g_{yy} = 2.00332$, $g_{zz} = 2.00235$, and $\Delta B^{xx}_{\text{pp}} = 0.82\,\text{mT}$, $\Delta B^{yy}_{\text{pp}} = 0.78\,\text{mT}$, and $\Delta B^{zz}_{\text{pp}} = 0.88\,\text{mT}$ have been determined at 2-mm waveband EPR at room temperature. An effective g-factor of a spin localized on sulfur nuclei lies in the region of $2.014 \le g^{\text{S}}_{\text{eff}} \le 2.020$ [3,4,6]. Therefore one can evaluate the upper limit of the time for the duration that a spin spends at the sulfur site in the P3AT samples, $\tau_{\max}$, using the sum shift of the spectral components registered at the above-mentioned positions g^{P3AT}_{ii} relative to the g^{S}_{ii} value typical for sulfur centered radical from the modified Heisenberg equation:

$$\tau^{-1}_{\max} \cong \sum_{i}^{3} (g^{\text{S}}_{ii} - g^{\text{P3AT}}_{ii})\mu_{\text{B}} B_0 h^{-1}, \tag{1}$$

where B_0 is the strength of an external magnetic field and $h = 2\pi\hbar$ is the Planck constant. Using g^{P3OT}_{ii} determined from the EPR spectrum of P3OT we obtain from Eq. (1) $\tau^{-1}_{\max} = 3.4 \times 10^9\,\text{s}^{-1}$ at room temperature.

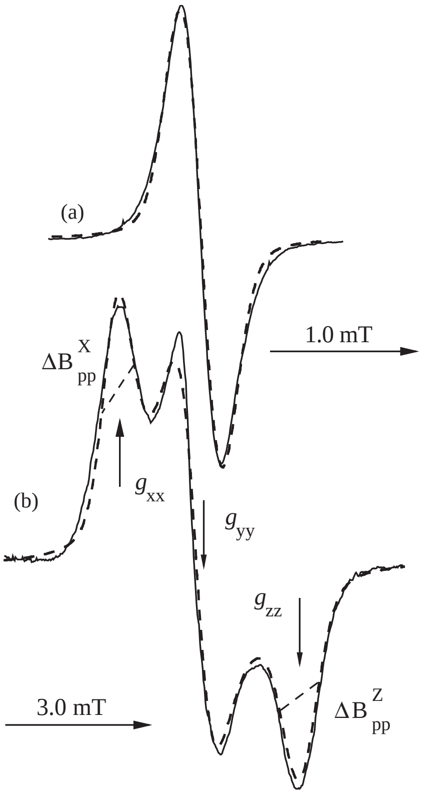

Fig. 1. Absorption EPR spectra of P3OT sample registered at 3-cm (*a*) and 2-mm (*b*) wavebands at 300 K. The spectra calculated with $g_{xx} = 2.004089$, $g_{yy} = 2.003322$, $g_{zz} = 2.002352$, line widths $\Delta B^{X}_{\text{pp}} = \Delta B^{Y}_{\text{pp}} = \Delta B^{Z}_{\text{pp}} = 0.25\,\text{mT}$ (*a*), and $\Delta B^{X}_{\text{pp}} = 0.82\,\text{mT}$, $\Delta B^{Y}_{\text{pp}} = 0.78\,\text{mT}$, $\Delta B^{Z}_{\text{pp}} = 0.88\,\text{mT}$ (*b*) are also shown by dashed lines.

3. Spin relaxation and macromolecular dynamics in poly(3-alkylthiophenes)

As in the case of other organic polymer semiconductors [3,4] in the both in-phase and the $\pi/2$-out-of-phase dispersion components of P3AT the bell-like contribution is detected due to an adiabatically fast passage of the inhomogeneously broadened line (Fig. 2). Both the spin-lattice T_1 and spin–spin T_2 relaxation times can then be calculated from these dispersion components according to the formulas [3,4]

$$T_1 = \frac{3\omega_{\text{m}}(1 + 6\Omega)}{\gamma_{\text{e}}^2 B_{1_0}^2 \Omega(1 + \Omega)}, \tag{2a}$$

$$T_2 = \Omega/\omega_{\text{m}}, \tag{2b}$$

where $\Omega = u^{y}_{3}/u^{y}_{2}$ and B_{1_0} is the polarizing microwave field at which the intensity of the in-phase dispersion component is equal to zero at position g_{yy}.

It is seen from Fig. 2 that the relative intensities of the $\pi/2$-out-of-phase (u_3) term change with temperature. Such an effect is evidence for the saturation transfer (ST-EPR) over the quadrature spectrum [7] due to superslow macromolecular

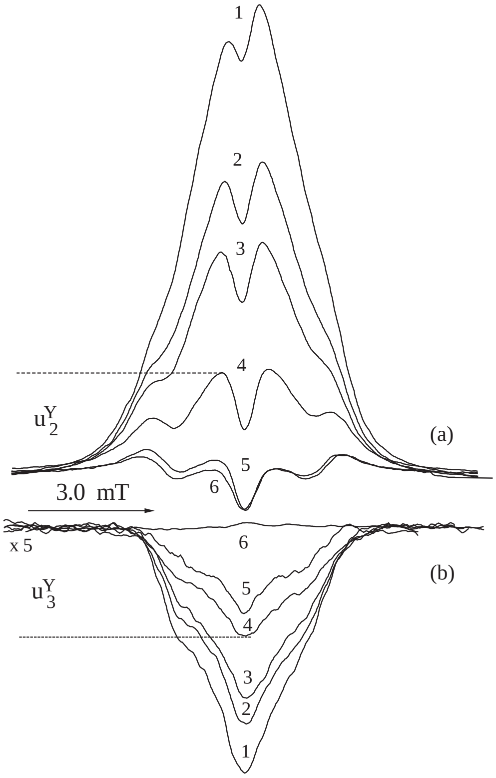

Fig. 2. In-phase (*a*) and $\pi/2$-out-of-phase (*b*) terms of the 2-mm waveband dispersion of the P3OT sample registered at $T = 90\,\mathrm{K}$ (1), 100 K (2), 110 K (3), 145 K (4), 200 K (5) and 250 K (6).

dynamics. Earlier, it was shown [3,4] that it is possible from 2-mm waveband ST-EPR spectra to estimate separately the relaxation and molecular dynamics parameters of paramagnetic impurities with anisotropic magnetic parameters due to the presence of heteroatoms (N, O, S), involved into anisotropic superslow motion. The correlation time of the chain segments libration near the main molecular X-axis, τ_c^X, can be determined from the relation

$$\tau_c^X = \tau_{c0}^X \left(u_3^X/u_3^Y\right)^{-\alpha}, \tag{3}$$

where α is a constant determined by g-factor anisotropy.

This value of, e.g. the P3OT sample is shown to decrease as the temperature increases from 90 K up to $T_c \cong 150\,\mathrm{K}$ and to increase above this critical temperature. Note, that Masubuchi et al. [8] have observed the same critical temperature for P3OT ^{1}H NMR T_1 temperature dependency that was attributed to the defreezing of molecular motion of methyl, ethyl or propyl chain end groups. The dependence obtained can be interpreted in the frame of superslow activated 1D libration of the polymer chains near the X-axis with $E_a = 0.069\,\mathrm{eV}$ at $T \leqslant T_c$, whereas its high-temperature part $\tau_c^X \propto T^{1.8}$ can be explained by the defreezing of collective 2D motions at $T \geqslant T_c$. The activation energy obtained lies near those of macromolecular librations in other organic conducting polymers [3,4]. The linear compressibility of normal P3OT with planar chains is strongly anisotropic, being 2.5 times higher for the direction along the a-axis than along the b-axis [9]. This means that different modes should prevail in P3OT above and below T_c. Osterbacka et al. [10] have found that the interchain coupling existing in self-assembled lamellae in P3AT drastically changes the properties of the polaron excitations and that the traditional self-localized polaron in one dimension is delocalized in two dimensions, resulting in a much reduced relaxation energy and multiple absorption bands.

4. Dynamics of polarons and conductivity of poly(3-alkylthiophenes)

The motion of polarons along (1D) and between (3D) polymer chains induces an additional magnetic field in the place of localization of other paramagnetic centers (PC). Their electronic relaxation is therefore modulated by polaron diffusion with the coefficients D_{1D} and D_{3D}, respectively, which can be calculated from relaxation rates as [11]

$$T_1^{-1} = \langle \omega^2 \rangle [2J_1(\omega_e) + 8J_2(2\omega_e)], \tag{4a}$$

$$T_2^{-1} = \langle \omega^2 \rangle [3J(0) + 5J_1(\omega_e) + 2J_2(2\omega_e)], \tag{4b}$$

where $<\omega^2>$ is the second moment of the line, and $J(\omega_e) = (2D_{1D}\omega_e)^{-1/2}$ at $D_{3D} \leq \omega_e \leq D_{1D}$ and $J(\omega_e) = (2D_{1D}D_{3D})^{-1/2}$ at $\omega_e \leq D_{3D}$ is the spectral density function at the spin precession frequency ω_e.

The conductivity due to 1D and 3D motion of the N polarons carrying an elemental charge e can be calculated from the equation [12]:

$$\sigma_{1,3\mathrm{D}} = \frac{Ne^2 D_{1,3D} d_{1,3\mathrm{D}}^2}{k_\mathrm{B} T}, \tag{5}$$

where $d_{i\mathrm{D}}$ are the respective lattice constants.

The temperature dependences of the $D_{i\mathrm{D}}$ and $\sigma_{i\mathrm{D}}$ values calculated from Eqs. (4) and (5) for P3OT with the lattice constants $d_{1\mathrm{D}} = c = 0.785\,\mathrm{nm}$ and $d_{3\mathrm{D}} = b = 0.480\,\mathrm{nm}$ [13] are shown in Fig. 3.

Analogously to the spin 1D diffusion rate, the 1D conductivity of the sample is characterized by strong temperature dependence, at least at $T \leqslant T_\mathrm{c}$ (Fig. 3). Such behavior is usually associated with the scattering of charge carriers on the optical lattice phonons. This model proposed for charge transfer processes in conjugated polymers with metal-like clusters [14] predicts their intrinsic conductivity in the form

$$\sigma_{1\mathrm{D}}(T) = \sigma_0 T\left[\sin h\left(\hbar\omega_\mathrm{ph}/k_\mathrm{B}T\right) - 1\right], \tag{6}$$

where ω_ph is the angular frequency of the optical phonon.

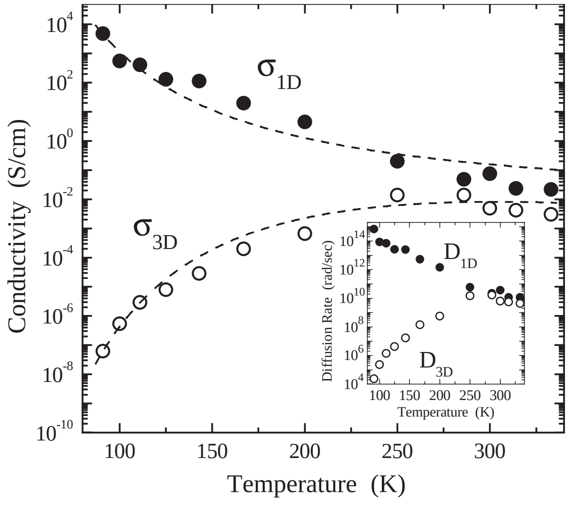

Fig. 3. Temperature dependences of conductivity due to spin/charge diffusion along ($\sigma_{1\mathrm{D}}$, filled points) and between ($\sigma_{3\mathrm{D}}$, open points) polymer chains in the P3OT sample. By the dashed lines are shown the dependences calculated from Eq. (6) with $\sigma_0 = 7.1 \times 10^{-6}\,\mathrm{S\,cm^{-1}\,K^{-1}}$ and $\hbar\omega_\mathrm{ph} = 0.13\,\mathrm{eV}$, and from Eq. (7) with $\sigma_0 = 9.1 \times 10^{-11}\,\mathrm{S\,s^{\gamma}\,cm^{-1}\,K^{-1}}$, $\beta = 2.1$ and $E_\mathrm{a} = 0.18\,\mathrm{eV}$. In the inset are shown the rates of polaron diffusion along (filled points) and between (open points) chains in P3OT as a function of temperature.

The strong temperature dependency for $\sigma_{3\mathrm{D}}$ at low temperatures can be due to a thermal activation of the charge carriers from widely separated localized states in the gap to close localized states in the tails of the valence and conducting bands. In this case interchain conductivity can be written as

$$\sigma_{3\mathrm{D}}(T) = \sigma_0 T\omega_\mathrm{e}^{\gamma} \exp\left(-E_\mathrm{a}/k_\mathrm{B}T\right), \tag{7}$$

where $0 < \gamma < 1$ is a constant reflecting the dimensionality of the system and E_a is the energy for activation of charge carrier to extended states. Parneix et al. [15] showed $\gamma = 1 - \beta k_B T/E_\mathrm{a}$ ($\beta = 6$, $E_\mathrm{a} = 1.1\,\mathrm{eV}$) dependency for poly(3-methylthiophene). So, we can use this approach for the explanation of 3D conductivity in the P3AT samples.

It is seen from Fig. 3 that the $\sigma_{1\mathrm{D}}$ and $\sigma_{3\mathrm{D}}$ values of P3OT sample are fitted well by Eq. (6) with $\hbar\omega_\mathrm{ph} = 0.13\,\mathrm{eV}$ and by Eq. (7) with $\beta = 2.1$ and $E_\mathrm{a} = 0.18\,\mathrm{eV}$. The analogous data can be determined for P3AT with other precursors. The activation energies obtained are near to the energy of lattice phonons of the sample and also to that determined for charge transfer in other conducting polymers [4].

5. Charge transfer in poly(3-alkylthiophene)/fullerene system

Poly(3-Alkylthiophenes) doped by fullerene molecules in the dark also demonstrate 3-cm waveband EPR spectrum of mobile polarons with effective $g_\mathrm{eff}^\mathrm{P} \approx 2.0033$. Illumination of this system by a laser ($\nu = 488\,\mathrm{nm}$) at 77 K leads to the increase of the polaron signal and also to the appearing of an additional signal with $g = 1.9998$, attributed to the fullerene anion-radical C_{60}^{-} (Fig. 4). As a result of such light-induced charge transfer from the polymer chain to fullerene P^{+}-C_{60}^{-} pairs are formed in P3AT. The number of these PC depends as $I^{0.16}$ on the laser excitation power density I (Fig. 4) and also on the polarizing microwave field B_1.

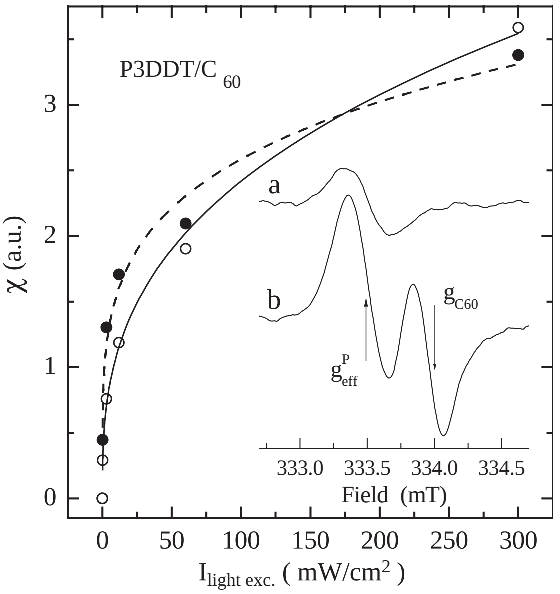

Fig. 4. Spin susceptibility of ion-radicals C_{60}^- (filled points) and additional polarons P^+ (open points) as function of laser excitation power density. Inset—3-cm EPR spectra of P3DDT/C_{60} system without (a) and under (b) laser illumination at 77 K.

The B_1 value is appeared to affect the PC line width at this waveband EPR. This fact is evident of the steady-state saturation of PC in the sample, therefore one can calculate T_1 separately for both PC from, e.g. equation [16]

$$\left(\Delta B_{pp}/\Delta B_{pp}^{(0)}\right)^2 = 1 + \gamma_e^2 B_1^2 T_1 T_2, \tag{8}$$

where $\Delta B_{pp}^{(0)}$ is the non-saturated line width, γ_e is the hyromagnetic ratio for electron, and $2T_2^{-1} = \sqrt{3}\gamma_e \Delta B_{pp}^{(0)}$. The spin-lattice relaxation time was determined for P^+ to be near 8×10^{-5} s, that is considerably longer than that of C_{60}^-.

Generally, different spin motion processes can be realized in the polymer/fullerene system, namely the diffusion of initial and photoinduced polarons along and between polymer chains, charge transfer from the polymer chain to fullerene molecules and the mutual motion of the spin localized on C_{60}. Undoubtedly, these processes should be considered as interacting or intercorrelated and can be studied separately by using both the methods of steady-state saturation and saturation transfer at 2-mm waveband EPR described above.

6. Conclusions

Thus, the interaction of spin charge carriers with heteroatoms in P3AT semiconductors leads to the appearance of *g*-factor anisotropy in their 2-mm waveband EPR spectra. Spin relaxation and dynamics are determined by an interaction of mobile polarons with optical phonons of the polymer lattice. The correlations of the energies of the interchain spin diffusion and the optical lattice phonons indicates the interaction of charge transport and molecular dynamics in such polymer semiconductors.

The relaxation, magnetic and dynamic properties of P3AT are expected to depend also on the alkyl group length and morphology of the sample. We plan to carry out an appropriate investigation also on P3HT and P3DDT to discuss these questions in future publications.

The method provides a registration of fine structural, conformational and electron processes in various systems with their following interpretation in the frames of different theories. In high magnetic fields the interaction between spin-packets in polymers decreases significantly, and they may be considered as non-interacting. This allows using the methods of steady-state saturation of spin-packets and their saturation transfer to obtain more correct and complete information on spin relaxation and molecular dynamics in such organic disordered systems.

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