Spin and charge transport in poly(3-octylthiophene)

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Abstract

The magnetic, relaxation and electronic dynamic parameters of polarons in an initial and in modified poly(3-octylthiophene) samples were studied by the steady-state microwave saturation method at 2-mm waveband EPR. It was shown that intrachain spin and charge transfer is mainly determined by the energy of the lattice phonons, whereas activation mechanism prevails in interchain conductivity. These processes can be backfitted by the warming and/or recrystallization of the polymer.

Keywords: electron paramagnetic resonance, polythiophene derivative, spin dynamics, conductivity

1. Introduction

The magnetic and electronic properties of poly(3-alkylthiophene), e.g. poly(3-octylthiophene) (P(3-OT)), semiconductors with nondegenerate ground states system are widely studied in the last years owing to their potential use as active material in polymer electronics and solar cells.

The presence of the absorbed oxygen from ambient atmosphere lead to the existence of positively charged polarons with spin $S = 1/2$. Polarons in P(3-OT) are characterized by a g-factor some higher then the g-factor of free electron and single line with width of 6 - 8 G at 3-cm waveband EPR [1]. This seems a reason that there are only few EPR studies performed on poly(3-alkyltiopenes).

Earlier we have demonstrated [2] the advantages of 2-mm waveband EPR spectroscopy in the study of spin dynamics in organic polymer semiconductors. This report presents first results of the investigation of polaron dynamics in an initial and treated P(3-OT) samples at 2-mm waveband EPR.

2. Experimental

One part of the initial regioregular P(3-OT)-I (Aldrich) was slowly, 2.5 K/min, headed at argon atmosphere from room temperature (RT) up to 450 K. This temperature was keeped for two hours and slowly decreased down to RT, P(3-OT)-T. An other part of the initial samples was solved in chloroform at RT and then recrystallyzed for nearly 150 min. The latter sample was also annealed analogous to the P(3-OT)-T sample, P(3-OT)-ST. EPR experiments were performed using mainly a 2-mm waveband EPR-05 spectrometer [2].

3. Results and Discussion

RT 3-cm and 2-mm experimental and calculated 2-mm EPR spectra of the samples are presented in Fig. 1. It is seen that the high spectral resolution of 2-mm waveband EPR allows to register separately relaxation and dynamics changes in all spectral components.
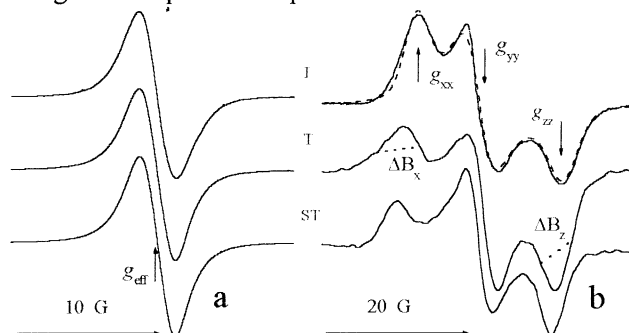

Fig.1. 3-cm (a) and 2-mm (b) RT EPR spectra of P(3-OT)-I, P(3-OT)-T, and P(3-OT)-ST. The spectrum calculated with $g_{xx}=2.00409$, $g_{yy}=2.00332$, $g_{zz}=2.00232$, $\Delta B_x=8.2$ G, $\Delta B_y=7.8$ G, $\Delta B_z=8.8$ G is shown by dashed line.

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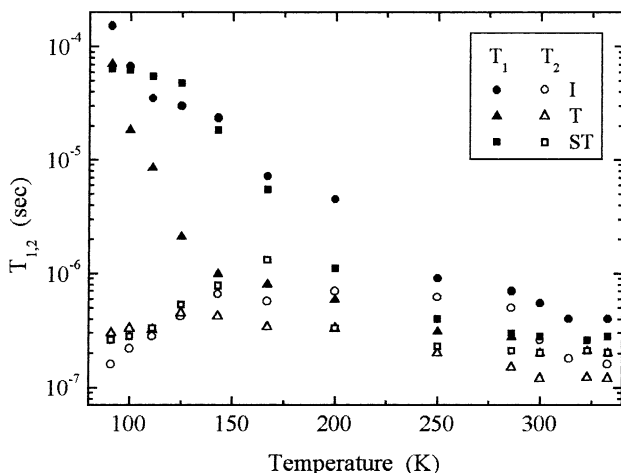E-mail: kivi@cat.icp.ac.ru*

Fig.2. The relaxation times of polarons in P(3-OT)-I, P(3-OT)-T, and P(3-OT)-ST vs. temperature.

Temperature dependences of spin-lattice T_1 and spin-spin T_2 relaxation times are shown in Fig.2. From the analysis of the figure one can conclude that the effective relaxation of polarons is accelerated in the treated polymers possibly due to the increase of their interaction with the lattice phonons.

The motion of the spin affects its relaxation rates, so the coefficients of intrachain (D_{1D}) and interchain (D_{3D}) spin diffusion can be determined as [3]

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

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

where $<\omega^2>$ is the constant of the spin dipole interaction and $J(\omega)=(2D_{1D}\omega_e)^{-0.5}$ at $D_{1D} \leq \omega_e \leq D_{3D}$ or $J(\omega)=(2D_{1D}D_{3D})^{-0.5}$ at $\omega_e \leq D_{3D}$ [4], and ω_e is the electron precession frequency.

The conductivity due to such motion of N polarons is

$$\sigma_{1,3D}(T) = Ne^2 D_{1,3D} c_{1,3D}^2 / kT , \qquad (2)$$

were e is the charge of electron and c_{iD} is the lattice constant.

Figure 3 shows the conductivity of the samples vs. temperature calculated from Eqs. (1) and (2). The analysis of the dependences obtained allows to conclude that the intrachain conductivity is mainly determined by interaction of charge carriers with the lattice phonons [5]

$$\sigma_{1D}(T) = \sigma_{01} T |\sinh(h\omega_{ph} / kT) - 1| \qquad (3)$$

(here h is the Plank constant, ω_{ph} is the frequency of the lattice phonons), whereas 3D term of conductivity is mainly determined by interchain activated spin hopping with activation energy E_a

$$\sigma_{3D}(T) = \sigma_{02} T \exp(-E_a / kT) \qquad (4)$$

The Figure shows that the experimental $\sigma_{1,3D}$ values of e.g. the initial P(3-OT) sample are fitted well by Eqs.(3) with $h\omega_{ph} = 0.143$ eV and by Eq.(4) with $E_a = 0.121$ eV at $T \leq 250$ K, respectively. These two energies lie near one to another, so one can conclude there is an interaction of the 1D and 3D charge transport in P(3-OT). The thermal
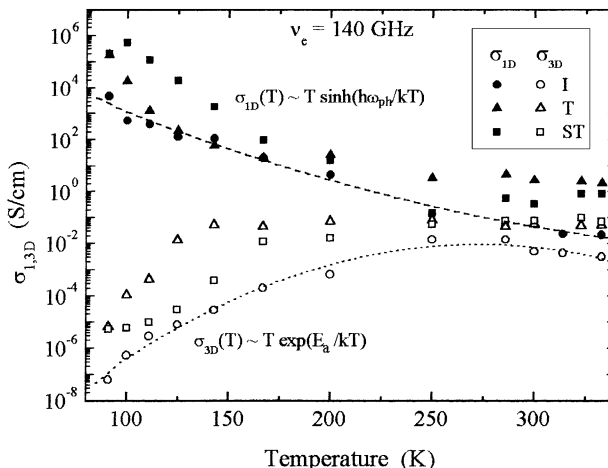

Fig.3. Temperature dependency of ac conductivity of P(3-OT)-I, P(3-OT)-T, and P(3-OT)-ST calculated from Eqs.(1) and (2). By the dashed and dotted lines are shown the conductivity calculated respectively from Eq.(3) with $h\omega_{ph} = .0.143$ eV and from Eq.(4) with $E_a = 0.121$ eV.

treatment of the initial polymer leads to noticeable variation of the polaron's magnetic, relaxation and dynamics parameters probably due to the change of crystallinity and packing of P(3-OT). It can also change the mechanism of charge transfer in the polymer. Indeed, at the sample treatment the anisotropy of its RT conductivity σ_{1D}/σ_{3D} increases from ca. 15 for P(3-OT) first up to 48 for P(3-OT)-T and then decreases down to 5 for P(3-OT)-ST (Fig.3). However, these values determined e.g. at 100 K are respectively ca. $1.1 \cdot 10^9$, $1.7 \cdot 10^8$, and $8.9 \cdot 10^{10}$.

The data obtained on the study of anisotropic dynamics of charge carrier can be used in the understanding and interpretation of electronic processes in molecular poly(3-alkylthiophene)-based solar cells [6] and in polymer transistors [7].

4. Acknowledgments

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