Charge transfer in poly(3-octylthiophene) modified by fullerene derivative

V.I. Krinichnyi*, Y.N. Demianets, S.A. Mironova

Institute of Problems of Chemical Physics, N.N. Semenov Avenue 1, Chernogolovka 142432, Russia

Abstract

Magnetic, relaxation, and electronic dynamic parameters of paramagnetic centers stabilized in an initial and fullerene-modified poly (3-octylthiophene) (P3OT) were studied at the 3-cm (9.7 GHz) waveband EPR in wide (77–320 K) temperature region. Both the systems demonstrate sum spectrum of localized and mobile polarons, whose contribution depends on polymer treatment. Both spin susceptibility and spin–spin relaxation rate were shown to govern by dipole–dipole interaction of the mobile polarons. The spin–lattice and spin–spin relaxation times were determined separately by using the steady-state saturation method. It was shown that the treatment of the P3OT sample with fullerene molecules leads to the decrease in activation energy of spin susceptibility, dipole–dipole interaction, and interchain diffusion. This is accompanied by the acceleration of spin relaxation and increase in the system dimensionality.
© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Conjugated polymers with extended π electron systems in their main chain attract much interest mainly as flexible active matrix of new electronic devices such as light emitting diodes, solar cells, and thin film field effect transistors [1]. The understanding of the basic physics underlying the electrical, thermal, and optical behavior of organic polymeric materials is essential for the optimization of devices fabricated using these materials.

Among side chain substituted polymers the alkyl-substituted polythiophenes [2] are seen as a major milestone in the development of high-performance solution processible electronic polymers. Since the parent polymer, polythiophene, already tends towards backbone planarity, there is a strong cooperative self-assembly of poly (3-alkylthiophenes) (P3AT) into well-ordered lamellar phases [3]. For some applications this behavior has the desirable effect of enhancing interchain p-orbital overlap and thereby improving the electron transport properties. Increasing the interchain overlap also dramatically reduces the photoluminescence yield because non-luminescent interchain processes compete with intrachain singlet exciton formation and recombination. Poly(3-octylthiophene) (P3OT) has emerged as one of the very promising materials and is currently a subject of intense research. For example, P3OT is frequently used as active matrix in elements of molecular electronics [1], solar cells among them [4]. In the latter case fullerene or its derivatives are used as charge acceptor. Electronic processes in such matrix should be governed by the structure of both the polymer and fullerene. Undoubtedly, the charge transfer in an initial polymer matrix and its interaction with lattice phonons should be first studied before its use in solar cells. However, such physics processes determining conductivity of the native polymer and polymer/fullerene compounds are only scarcely understood.

Polarons stabilized in P3AT possess spin $\frac{1}{2}$, and EPR is the powerful direct method for the study of such systems [5,6]. An important information on an amplitude and correlation times of inside fluctuating fields in

---

*Corresponding author. Tel.: +7 496 522 1714; fax: +7 496 515 5420.
E-mail address: kivi@cat.icp.ac.ru (V.I. Krinichnyi).

fullerene-modified P3AT and other new solids can be obtained from electron spin spin–lattice (longitudinal) and spin–spin (transversal) relaxation with the time T_1 and T_2, respectively. The latter value is usually measured from the EPR linewidth; however, inhomogeneous broadening masks frequently the effect of fluctuating fields.

The main aim of this article is to study the magnetic, relaxation, and dynamics properties of the initial P3OT and to clarify how to change these properties at the treatment of this polymer by fullerene derivative.

2. Experimental

Aldrich® regioregular P3OT with the lattice constants $a = 2.030$, $b = 0.480$, and $c = 0.785$ nm [7] and fullerene derivative [6,6]-phenyl-C_{61}-butanoic acid methyl ester (PCBM), synthesized in the laboratory of Prof. J.C. Hummelen, University of Groningen [8], were used without further purification. Both the P3OT and PCBM are shown schematically in Fig. 1. The initial P3OT and also the chlorbenzene solution of P3OT and PCBM taking in 1:1 weight ratio with concentration ca. 1 wt% were placed into ceramic planes and dried, so then the P3OT and its composite with PCBM were formed as films with the size of ca. 4×8 mm^2 and thickness of ca. 0.1 mm.

EPR experiments were performed using a 3-cm (X-band, 9.7 GHz) PS-100X spectrometer with 100 kHz field AC modulation for phase-lock detection. The temperature of the sample was stabilized in nitrogen atmosphere by the BRT-IOH controller in the range of 90–320 K with the
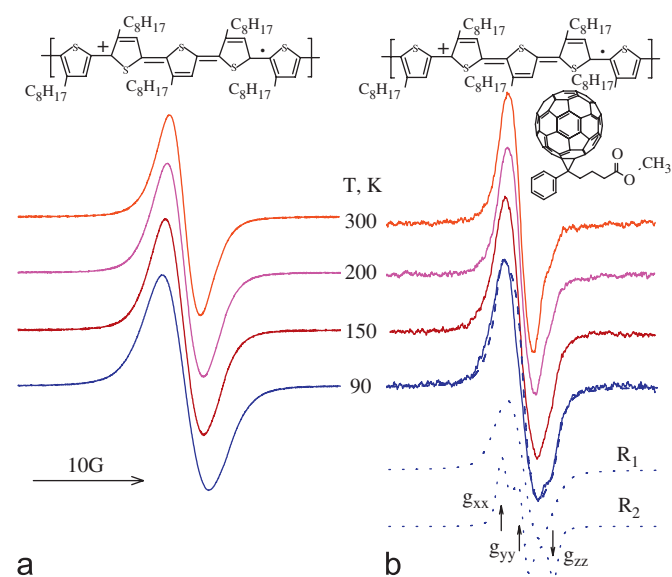

Fig. 1. X-band EPR spectra of polarons in the initial (a) and fullerene-modified (b) P3OT registered at different temperatures. The PCBM and P3OT with polaron possessing a spin and an elemental charge are shown schematically as well. Dashed line shows sum spectrum of mobile polarons R_1 with $\langle g \rangle = 2.0027$, $\Delta B_{pp} = 1.8$ G (dotted line) and localized polarons R_2 with $g_{xx} = 2.0043$, $g_{yy} = 2.0031$, $g_{zz} = 2.0019$, $\langle g \rangle = 2.0031$, $\Delta B_{pp} = 0.5$ G (dotted line) taking with the concentration ratio $[R_1]:[R_2] = 11$.

±0.5° error. Besides, the spectra of the samples were also registered at 77 K in liquid nitrogen. The total paramagnetic susceptibility of paramagnetic centers (PC) in the samples was determined using double integration of their EPR spectra. Effective linewidth of the EPR spectra was determined at low MW power in a cavity when magnetic term B_1 of MW field was equal to 0.015 G. Spin–lattice and spin–spin relaxation times of the initial and treated P3OT samples were measured separately using the steady-state (CW) saturation method [9]. EPR spectra were simulated using the Bruker® WinEPR SimFonia V.1.25 program. The uncertainty in the determination of the peak-to-peak linewidth ΔB_{pp} and the value of g-factor was consequently $\pm 2 \times 10^{-2}$ and $\pm 2 \times 10^{-4}$ G.

3. Results and discussions

PC in the initial sample at 3-cm waveband EPR demonstrate Lorentzian exchange-narrowed line with effective $g_{eff} = 2.0032$ (Fig. 1a). As the sample is modified by fullerene, two lateral lines appear in its spectrum (Fig. 1b). This fact evidences for the localization of part of polarons during such modification probably at cross-bonds and/or ends of polymer chains. The intensity of these components decreases at the heating of the sample. To determine more correctly and complete such main magnetic resonance parameters as g-tensor terms, peak-to-peak linewidth ΔB_{pp} and paramagnetic susceptibility χ, one should model EPR spectra of PC in the samples. As in case of other conducting polymers [6], we suppose that first derivative of the sum EPR spectrum are combined from Gaussian inhomogeneously broadened spectrum of polarons localized on the short π-conjugated polymer chains and Lorentzian motional narrowed spectrum of polarons diffusing along the main π-conjugated polymer chains. Earlier, we shown from the study of P3OT at 2-mm waveband EPR [10] that PC in the initial P3OT are characterized by anisotropic g-factor, $g_{xx} = 2.00409$, $g_{yy} = 2.00332$, $g_{zz} = 2.00235$ (the principal X-axis is chosen parallel to the longest molecular c-axis, Y-axis lies in the thiophene rings plane, and Z-axis is perpendicular to X- and Y-axes). Computer simulation shows that indeed two types of PC are stabilized in the P3OT/PCBM composite, namely, mobile R_1 and localized R_2 polarons (Fig. 1b). Simulated sum spectrum is shown in Fig. 1 as well. The effective g-factor of the R_2 PC, $g_{eff} = \frac{1}{3}\Sigma g_{ii}$, lies near to that of the R_1 one. This fact supports the supposition made above concerning the nature of these PC. Spin concentration ratio $[R_1]/[R_2]$ lies near 11 at 90 K and decreases at the temperature growth (Fig. 1b) due to defrosting of polaron diffusion.

Effective spin susceptibility of the samples determined in wide temperature range is shown in Fig. 2. It is seen from the figure that this parameter depends not only on the temperature but also on the polymer treatment. If this parameter is changed nearly linearly with temperature of P3OT, it demonstrates sharper temperature dependence in
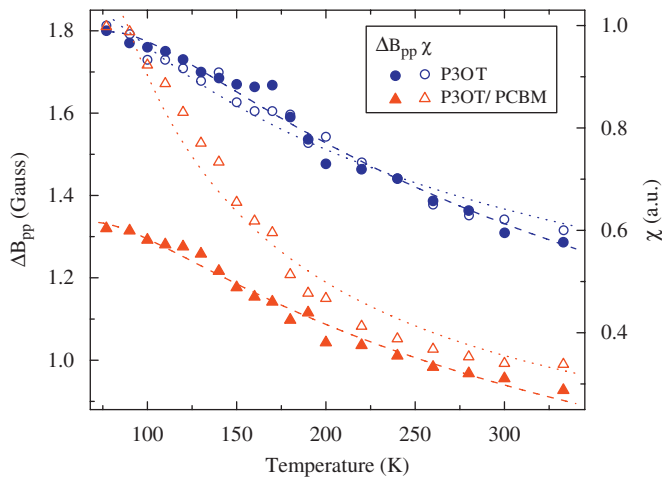
Fig. 2. Linewidth and susceptibility of polarons in the initial and fullerene-modified P3OT as function of temperature. Top to down dotted lines show the dependences calculated from Eq. (1) with $E_a = 2.6$ and 2.2 meV. Top to down dashed lines show the dependences calculated from Eq. (2) with $\Delta B_{pp}^0 \sqrt{T_0} = 4.19$ G K$^{-1/2}$, $E_a = 3.4$ and 3.0 meV $\Delta B_{pp}^0 \sqrt{T_0} = 3.11$ G K$^{-1/2}$.

case of P3OT/PCBM (Fig. 2). The analysis shown that the χ value cannot be described in terms of the model of interacting spins proposed by Kahol et al. [11] for doped organic conductors, regioregular P3AT among them [12].

Generally, temperature dependent static paramagnetic susceptibility of N_1 localized (Curie-like) and N_m Q1D mobile polarons near the Fermi level [13,14] both with $S = \frac{1}{2}$ consists of two appropriate terms χ_l and χ_m:

$$\chi(T) = \chi_l(T) + \chi_m(T) = \frac{N_1 \mu_{eff}^2}{3 k_B T}$$
$$+ k_2 N_m \sqrt{\frac{E_a}{k_B T}} \exp\left(1 - \frac{E_a}{k_B T}\right), \qquad (1)$$

where $\mu_{eff} = \mu_B g \sqrt{S(S+1)}$ is the effective magneton, μ_B is the Bohr magneton, E_a is the activation energy, and k_B is the Boltzmann constant.

Indeed, Fig. 2 shows that the experimental data obtained for P3OT and P3OT/PCBM are fitted well by Eq. (1) with $E_a = 2.6$ and 2.2 meV.

Effective EPR linewidth of PC stabilized in the initial and fullerene-treated P3OT samples is also presented in Fig. 2 as function of temperature. One can see that this value decreases approximately by factor of two at the P3OT treatment. This value is governed by spin–spin relaxation. For localized spin there are several relaxation processes which cause the shortening of T_2 and hence the broadening of an EPR line, e.g. dipole–dipole and hyperfine interactions, respectively, ω_d and ω_h [15]. The dynamics of systems with localized and delocalized spins, polarons diffusing along and between polymer chains in conjugated polymers, may be studied using the Bloch–Hasegawa equations [14]. The linewidth of such system is determined mainly by dipole–dipole interaction between

spins, so then [14,16]

$$\Delta B_{pp}(T) = \Delta B_{pp}^0 \sqrt{\frac{T_0}{T}} \exp\left(-\frac{E_a}{k_B T}\right), \qquad (2)$$

where T_0 is a constant.

The dependences calculated from Eq. (2) with different E_a values are presented in Fig. 2 as well. The figure shows that the temperature dependences of the linewidth determined from the spectra of P3OT and P3OT/PCBM are described well by the above equation with $E_a = 3.4$ and 3.0 meV, respectively. These values lie near those determined above for spin susceptibility. This fact evidences for strong influence of interaction of polarons on their susceptibility and relaxation in both systems under study.

As the value of magnetic term B_1 of MW field increases in MW cavity, both the absorption line intensity and width start to change nonlinearly with B_1. Such effect of steady-state saturation of the spin reservoir allows one to determine separately the effective T_1 and T_2 values using appropriate method described in Ref. [9]. These relaxation parameters of polarons stabilized in the initial and fullerene-treated P3OT are presented in Fig. 3. It is seen from the figure that both the relaxation times change nearly monotonically with temperature. Spin relaxation in P3OT/PCBM becomes faster due possible to appearance of additional channels for spin relaxation at the treatment of the initial P3OT with fullerene molecules.

A part of polarons diffuse along and between the polymer chains with respective diffusion coefficients D_{1D} and D_{3D}. This induces an additional magnetic field in the whereabouts of another spins of spin reservoir and, therefore, leads to the acceleration of electron relaxation of both spin ensembles. As the relaxation times of the spins are defined mainly by their dipole–dipole interaction at
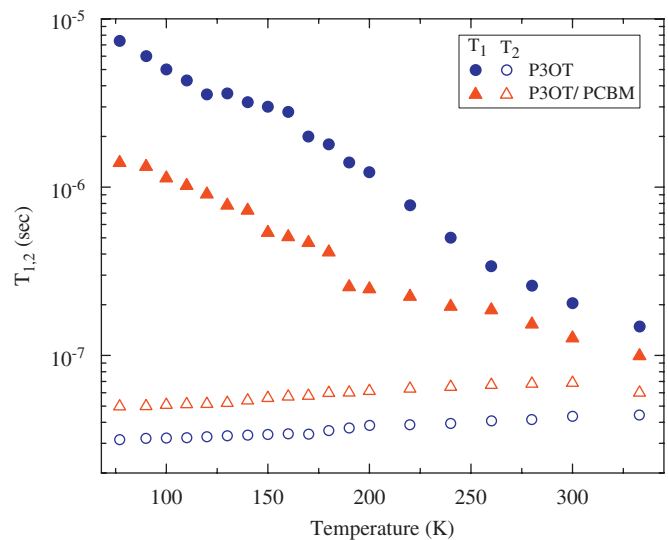

Fig. 3. Temperature dependences of spin–lattice (filled points) and spin–spin (open points) relaxation times of polarons in the initial and fullerene-modified P3OT.
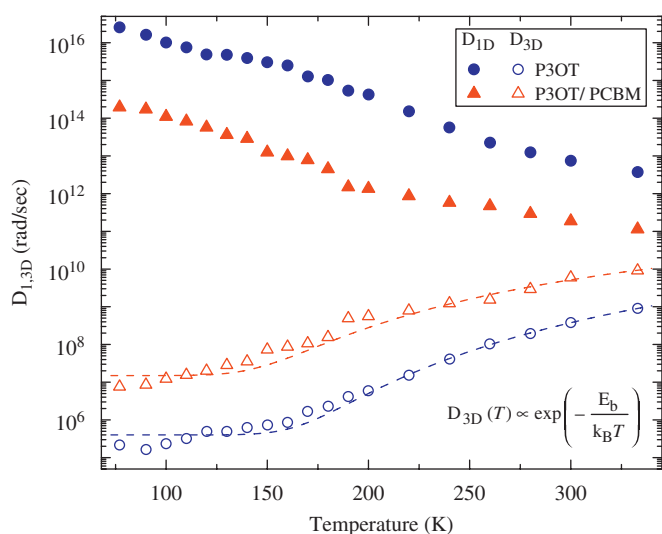
Fig. 4. Temperature dependences of coefficients of the polaron intrachain (filled points) and interchain (open points) diffusion in the initial and fullerene-modified P3OT. Top to down dotted lines show dependences calculated from Eq. (5) with $D_{1D}^0 = 6.2 \times 10^5$ rad/s, $k_1 = 2.5 \times 10^{12}$ rad/s, $E_b = 278$ meV, and $D_{1D}^0 = 1.5 \times 10^7$ rad/s, $k_1 = 2.0 \times 10^{12}$ rad/s, $E_b = 153$ meV, respectively.

resonant frequency ω_e the following equations can be written [17]:

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

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

where $\langle \omega^2 \rangle$ is the constant of a dipole–dipole interaction for powder, $J(\omega_e) = (2D_{1D}\omega_e)^{-1/2}$ 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 a spectral density function for Q1D motion. The similar spectral density function was also used in the study of spin dynamics in other conjugated polymers [5,6].

The coefficients D_{1D} and D_{3D} calculated from Eqs. (3) and (4) for polaron diffusion in the initial and fullerene-modified samples are presented in Fig. 4 as function of temperature. The data show that the D_{1D} value decreases and D_{3D} one increases at the treatment of the initial sample with fullerene (Fig. 4). The decrease of the anisotropy of spin diffusion D_{1D}/D_{3D} can be explained supposing the fullerene molecules introduced into polymer bulk as additional bridges for interchain charge transport. The decrease in anisotropy of spin dynamics reflects also the increase of the system dimensionality.

The temperature dependences can be interpreted supposing that the polarons behave as heavy particles in a band of renormalized width W and weakly scattered by phonons with frequency ω_{ph}. For small enough W, all the states in the band are equally populated, leading to a "metal-like" mobility of charge carriers or $D_{1D}(T) \propto \exp(\hbar\omega_{ph}/k_B T)$ [18]. The exponential law comes from the thermal occupation of the optical phonons, which are assumed to be the main source of scattering. The size of the polaron is comparable with the lattice interchain spacing, its motion is then

dominated by hopping processes: the quasi-particle has to overcome a potential barrier E_b and loses its quantum coherence at each hop, giving rise to an activated law of its mobility and interchain diffusion rate [19–21]:

$$D_{3D}(T) = D_{1D}^0 + k_1 \exp\left(-\frac{E_b}{k_B T}\right). \tag{5}$$

Fig. 4 shows that the temperature dependences calculated from Eq. (5) for polaron interchain diffusion in the P3OT and P3OT/PCBM fit experimental data with $E_b = 278$ and 153 meV, respectively. The former is close to that (340 meV) obtained for mobility of charge carriers in poly(3-methylthiophene) [22].

4. Conclusion

Comparative EPR studies of the magnetic, relaxation, and electron dynamics properties of the initial and fullerene-modified P3OT samples was shown that the treatment of the P3OT sample with PCBM molecules leads to the decrease in activation energy of spin susceptibility, dipole–dipole interaction, and interchain diffusion. This is accompanied with the appearance of localized polarons and acceleration of spin relaxation and increase in the system dimensionality. The relaxation and dynamics properties of charge carriers, photoinduced in the P3OT/PCBM and other P3AT/PCBM systems is planned to be studied at the next stage as well.

Acknowledgments

References

[1] T.E. Scotheim, J.R. Reynolds (Eds.), Handbook of Conducting Polymers, CRC Press, Boca Raton, 2007.

[2] M. Jeffries-El, R.D. McCullough, in: T.E. Scotheim, J.R. Reynolds (Eds.), Handbook of Conducting Polymers, vol. 2, CRC Press, Boca Raton, 2007 (Chapter 7).

[3] M.J. Winokur, D. Spiegel, Y. Kim, S. Hotta, A.J. Heeger, Synth. Met. 28 (1989) C419.

[4] S. Sensfuss, M. Al-Ibrahim, A. Konkin, G. Nazmutdinova, U. Zhokhavets, G. Gobsch, D.A.M. Egbe, E. Klemm, H.-K. Roth, in: Z.H. Kafafi, P.A. Lane (Eds.), Organic Photovoltaics IV, Proceedings of SPIE, vol. 5215, 2004, pp. 129–140.

[5] K. Mizoguchi, S. Kuroda, in: H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, vol. 3, Wiley, New York, 1997, pp. 251–317 (Chapter 6).

[6] V.I. Krinichnyi, Synth. Met. 108 (2000) 173.

[7] E.J. Samuelsen, J. Mardalen, in: H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, vol. 3, Wiley, New York, 1997, pp. 87–120 (Chapter 2).

[8] J.C. Hummelen, B.W. Wright, F. Lepec, F. Wudl, J. Org. Chem. 60 (1995) 532.

[9] Ch.P. Poole, Electron Spine Resonance, Int. Sci. Publ., London, 1967.

[10] V.I. Krinichnyi, H.-K. Roth, Appl. Magn. Reson. 26 (2004) 395.

[11] A. Raghunathan, P.K. Kahol, J.C. Ho, Y.Y. Chen, Y.D. Yao, Y.S. Lin, B. Wessling, Phys. Rev. B 58 (1998) R15955.

[12] P.K. Kahol, B.J. McCormick, A.J. Epstein, S.S. Pandey, Synth. Met. 135 (2003) 343.

[13] D.C. Jonston, Phys. Rev. Lett. 52 (1984) 2049.

[14] S.E. Barnes, Adv. Phys. 30 (1981) 801.

[15] S.A. Altshuler, B.M. Kozirev, Electron Paramagnetic Resonance, Academic Press, New York, 1964.

[16] V.A. Atsarkin, V.V. Demidov, J. Exp. Theor. Phys. 86 (1998) 572.

[17] F. Carrington, A.D. McLachlan, Introduction to Magnetic Resonance with Application to Chemistry and Chemical Physics, Harrer & Row Publishers, New York, Evanston, London, 1967.

[18] M.I. Klinger, Problems of Linear Electron (Polaron) Transport Theory in Semiconductors, Pergamon Press, Oxford, 1979.

[19] J. Patzsch, H. Gruber, in: H. Kuzmany, M. Mehring, S. Roth (Eds.), Electronic Properties of Polymers, Springer Series in Solid State Sciences, vol. 107, Springer, Berlin, 1992, pp. 121–124.

[20] S. Fratini, S. Ciuchi, Phys. Rev. Lett. 91 (2003) 256403.

[21] A. Andreatta, Y. Cao, J.C. Chiang, A.J. Heeger, P. Smith, Abstr. Pap. Amer. Chem. Soc. 197 (1989) 21.

[22] S. Tagmouti, A. Outzourhit, A. Oueriagli, M. Khaidar, M. Elyacoubi, R. Evrard, E.L. Ameziane, Sol. Energy Mater. Sol. Cells 71 (2002) 9.