

Multifrequency EPR study of metal-like domains in polyaniline

V.I. Krinichnyi^{a*}, S.V. Tokarev^a, H.-K. Roth^b, M. Schrödner^b, B. Wessling^c

^a Institute of Problems of Chemical Physics, Semenov Avenue 1, Chernogolovka 142432, Russia

^b TITK Institute Rudolstadt, Physical Materials Research, Breitscheidstraße 97, Rudolstadt D-07407, Germany

^c Ormecon GmbH, Ferdinand-Harten Str. 7, Ahrensburg D-22926, Germany

Abstract

The magnetic, relaxation and electronic dynamic parameters of paramagnetic centers, polarons in crystalline domains of polyaniline doped by *p*-toluenesulfonic acid (PANI-TSA) being in the metallic state (“organic metal”) were studied at 3-cm (9.7 GHz) and 2-mm (140 GHz) EPR wavebands in a wide temperature range. The polarons in PANI-TSA interact strongly at magnetic fields used and demonstrate the Lorentzian single lines with the Dysonian contribution. Room temperature intrinsic conductivity of metal-like domains in air-containing PANI-TSA determined from the Dysonian spectra was ca. 4000 S/cm. This value decreases sufficiently at the sample evacuation. It was shown that polarons interact strongly and weakly below and above the critical temperature T_c , respectively, due to a phase transition that leads to an extremal temperature dependence of the polymer linewidth. As the registration frequency increases from 9.7 GHz up to 140 GHz, the T_c value is shifted from 160 K down to 130 K. Intrinsic conductivity of PANI does not correlate with its linewidth that indicates polaron localization inside crystalline domains. Charge is transferred according to the Mott variable range hopping mechanism.

Keywords: electron paramagnetic resonance, polyaniline and derivatives, transport measurements

1. Introduction

Electronic and magnetic properties of emeraldine salt of polyaniline (PANI-ES) are intensively studied over the last years [1]. There are some conceptions on the charge transport mechanism in PANI-ES. For instance, Houze and Nechtschein [2] claimed the existence of “single conducting chains” even in highly doped PANI, in which charge is transferred by mobile polarons along and between them. Wang et al. [3] proposed the existence of metal-like crystalline domains characterized as a Fermi glass, in which the electronic states near the Fermi energy ϵ_F are exponentially localized due to disorder, thus, charge is transferred by the phonon-assisted Mott variable range hopping (VRH) [4] between these states. Therefore, fundamental electronic properties of conducting polymers are the matter for discussions so far.

In conducting polymers charge is transferred by polaron with spin $S = 1/2$. For this reason EPR spectroscopy is intensively used in the study of conducting polymers, and, particularly, PANI [5]. Mobile polarons accelerate electron relaxation of spin ensemble on the whole. Therefore, the method allows a direct determination of the dynamics

parameters of such charge carriers. An additional change in electron relaxation appears as a result of an interaction of polarons with oxygen molecules possessing sum spin $S = 1$ [2]. However, at registration frequencies not higher than 10 GHz the method encounters some limitations mainly due to low spectral resolution and a strong interaction between paramagnetic centers (PC). These limitations are reduced with increased registration frequencies up to 140 GHz, so it becomes possible to identify the nature and transfer mechanism of charge in various conducting polymers [6].

We report here the first results on the investigation at wide waveband EPR of magnetic, relaxation and electronic transport properties of crystalline phase in PANI heavily doped by *p*-toluenesulfonic acid (PANI-TSA) in which electronic transport was shown [7] to be governed by quasi-three-dimensional (Q3D) charge hopping between mesoscopic crystalline domains with ca. 8 nm size and Q3D extended electron wave functions. Spin relaxation and charge transfer processes were found to be non-correlated that contradict the “single conducting chain” model and justifies the formation of the Q3D metal-like domains in heavily doped PANI-TSA.

* Corresponding author. Tel: +7-096-522-1714; fax: +1-775-924-5513; E-mail: kivi@cat.icp.ac.ru

2. Experimental

Commercially available powder-like Ormecon[®] polyaniline [8] with $\gamma=0.5$ doping level and 30% crystalline fraction was used [9]. A quartz capillary with 0.6-mm inner diameter was filled with powder-like PANI-TSA with a characteristic size of individual particles of 0.0129 ± 0.0014 mm mixed with diamagnetic MnO powder (1:3) to reduce interparticle interaction. The traces of Mn^{2+} ions in MnO with $g_{\text{eff}} = 2.00102$ and $a = 87.4$ Gauss were used for the g -factor determination. Uncertainty in the determination of the peak-to-peak linewidth ΔB_{pp} and the value of g -factor was consequently $\pm 2 \times 10^{-2}$ Gauss and $\pm 2 \times 10^{-4}$ at 3-cm waveband EPR and $\pm 5 \times 10^{-2}$ Gauss and $\pm 3 \times 10^{-5}$ at 2-mm waveband EPR.

3. Results and Discussion

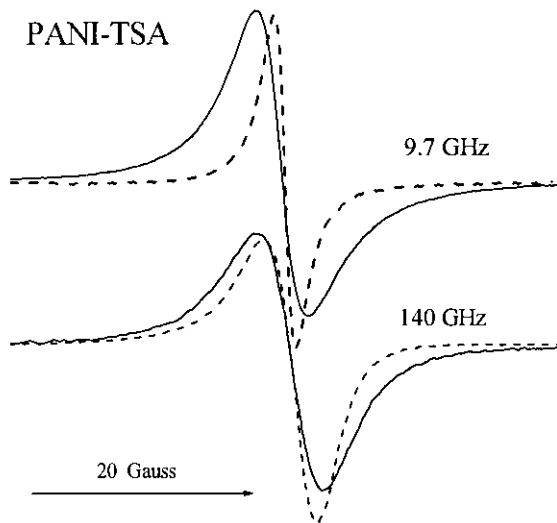


Fig. 1. Room-temperature EPR spectra of the vacuum -processed (dashed lines) and exposed to air (solid lines) PANI-TSA sample registered at different EPR wavebands.

Vacuum-processed samples demonstrate the asymmetric Lorentzian line at 3-cm waveband EPR and room temperature (Fig.1). An exposure of the sample to air leads to the evident line broadening and the increase of line asymmetry. Such line asymmetry can be stimulated by either non-resolved anisotropy of g -factor or the presence of the Dyson contribution in the spectrum [10] due to the interaction of MW irradiation with charge carriers in a skin-layer formed on the surface of conducting particles. To clarify the nature of this effect a higher resolved 2-mm waveband EPR spectrum of PANI sample was registered. It is seen from Fig.1 that at this waveband the polymer also demonstrates the asymmetric Lorentzian single line whose asymmetry increases at sample contacting with air. This fact is evidence of a sufficient interaction of PC even in high magnetic fields and for the appearance of the line asymmetry as a result of the interaction of MW field with mobile charge carriers inside the skin-layer. Generally, the

Dysonian line consists of the absorption A and dispersion D terms. Therefore, the following equation for first derivative of its spin susceptibility is valid:

$$\frac{d\chi}{dB} = A \frac{2x}{(1+x^2)^2} + D \frac{1-x^2}{(1+x^2)^2} \quad (1)$$

where $x=(B-B_0)/\Delta\omega_L$, B_0 is the resonant magnetic field, $\Delta\omega_L = 1/T_2\gamma_e$ is the width of the Lorentzian line, T_2 is the spin-spin relaxation time, γ_e is the gyromagnetic ratio. The coefficients A and D for the skin-layer with thickness of δ on the surface of sphere with radius R and intrinsic conductivity σ_{ac} at registration frequency ω_e can be determined from such Dysonian spectra using the relations [11]

$$\frac{4A}{9} = \frac{8}{p^4} - \frac{8(\sinh p + \sin p)}{p^3(\cosh p - \cos p)} + \frac{8 \sinh p \sin p}{p^2(\cosh p - \cos p)^2} + \frac{(\sinh p - \sin p)}{p(\cosh p - \cos p)} - \frac{(\sinh^2 p - \sin^2 p)}{(\cosh p - \cos p)^2} + 1 \quad (2a)$$

$$\frac{4D}{9} = \frac{8(\sinh p - \sin p)}{p^3(\cosh p - \cos p)} - \frac{4(\sinh^2 p - \sin^2 p)}{p^2(\cosh p - \cos p)^2} + \frac{(\sinh p + \sin p)}{p(\cosh p - \cos p)} - \frac{2 \sinh p \sin p}{(\cosh p - \cos p)^2} \quad (2b)$$

where $p = 2R/\delta$, $\delta = \sqrt{2/\mu_0\omega_e\sigma_{ac}}$, μ_0 is magnetic permeability in vacuum, and ω_e is resonant angle frequency of the electron spin precession. Except the above A and D values and linewidth, this procedure allowed one to determine more correctly an effective g -factor, $g = 2.00280$, paramagnetic susceptibility, $\chi_p = 2.2 \times 10^{-5}$ emu/mole-2 rings, and the density of states at the Fermi level ϵ_F , $n(\epsilon_F) = 0.69$ states/eV-2 rings for vacuum-processed sample. As the sample is exposed to air, these parameters are found to be $g = 2.00274$, $\chi_p = 1.1 \times 10^{-3}$ emu/mole-2 rings, and $n(\epsilon_F) = 34.6$ states/eV-2 rings.

Fig.2 shows the temperature dependences of absorption peak-to-peak linewidths ΔB_{pp} of the PANI-TSA sample with and without oxygen molecules determined at both 3-cm and 2-mm wavebands EPR. The data obtained for vacuum-processed sample evidence a weak temperature influence on its linewidth. However, the diffusion of air molecules into the sample leads to reversible broadening in its EPR line and also to the extreme temperature dependence of the ΔB_{pp} value with characteristic temperature $T_c \approx 160$ K (3-cm waveband EPR) and $T_c \approx 130$ K (2-cm waveband EPR) (Fig.2). The interaction of polarons with paramagnetic oxygen molecules should lead to the EPR line broadening [2]

$$\delta(\Delta\omega) = 16/27 \omega_{\text{hop}} C \left[1 + \left(\frac{\hbar\omega_{\text{hop}}}{12J} \right)^2 \right] \quad (3)$$

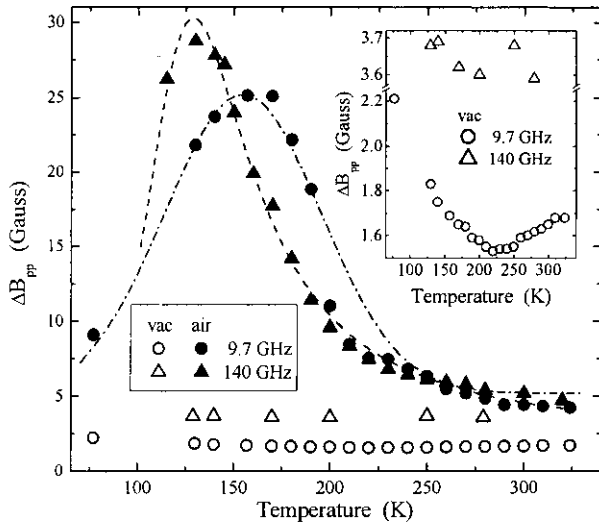


Fig.2. The temperature dependence of peak-to peak linewidth of the vacuum-processed and air-containing PANI-TSA sample registered at 3-cm and 2-mm wavebands EPR. The dependences calculated from Eq.(3) with $\omega_{hop} = 9.6 \times 10^{17} \exp(-0.058 \text{ eV}/k_B T)$, $J = 0.29 \text{ eV}$ (dashed line) and $\omega_{hop} = 3.2 \times 10^{18} \exp(-0.089 \text{ eV}/k_B T)$, $J = 0.21 \text{ eV}$ (dash-dotted line), and $C = 5 \times 10^{-3}$ [2] are shown as well.

where ω_{hop} is the frequency of the polaron intrachain hopping, C is a number of oxygen molecules per each aniline ring, \hbar is the Plank constant, and J is the constant of spin dipole-dipole interaction.

Fig.3 shows the temperature dependences of σ_{ac} calculated by using Eqs.(1) to (2) from Dysonian of both the 3-cm and 2-mm wavebands EPR spectra. Room-temperature intrinsic conductivity of the vacuum-processed PANI-TSA sample lies near 180 S cm^{-1} at spin precession frequency of 140 GHz and near 1500 S cm^{-1} at registration frequency of 9.7 GHz (Fig.3). These values increase respectively up to ca. 1200 and 4000 S cm^{-1} at polymer exposure to air, as it was expected. It should be noted that according to the approach of Q1D polaron diffusion along the “single conducting chain” [2,12] one should expect the temperature correlation between PANI-TSA linewidth and intrinsic conductivity. However, it derives from the data obtained that the linewidth demonstrates an extremal temperature behavior, whereas the σ_{ac} value changes monotonically at all temperatures. Therefore, we can conclude that, as in the case of other PANI samples [6], conductivity of the PANI-TSA sample is mainly determined by mobility of electrons Q3D delocalized inside metal-like domains in which the paramagnetic polarons seem to be localized on strongly interacted parallel polymer chains. Thus, the extremal behavior of temperature dependence of the PANI-TSA linewidth can be explained by the reversible dipole-dipole interaction of localized PC with oxygen molecules diffusing into the metal-like domains with the frequency of $\omega_{hop} = \omega_{diff}^0 \exp(-E_a/k_B T)$ and activation energy E_a . Indeed, it is seen from Fig.3 that the dependence of linewidth vs temperature of PANI-TSA exposed to air is well fitted by Eq.(3). The decrease in the E_a value with the increase of registration frequency should evidence, for example, the effect of an external magnetic field on spin

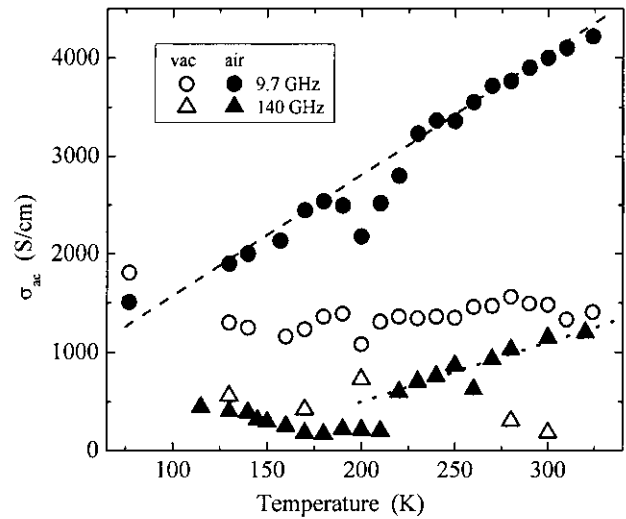


Fig.3. The temperature dependence of ac conductivity, σ_{ac} , of PANI-TSA determined from its 3-cm and 2-mm wavebands EPR spectra at the absence and presence of air in the polymer using Eq.(1). The dependences calculated from Eq.(4) with $\sigma_0 = 13.2 \text{ S cm}^{-1}\text{K}^{-1}$ and $\sigma_0 = 6.1 \text{ S cm}^{-1}\text{K}^{-1}$ are shown by dashed and dotted lines as well.

exchange in the polymer. The shift of the $\Delta B_{pp}(T)$ extreme to lower temperatures with the increase of the external magnetic field (Fig.2) confirms this supposition. The analysis shows that strong and weak spin-spin interaction is realized at $T \leq T_c$ and $T \geq T_c$, respectively.

Intrinsic conductivity of the PANI-TSA sample exposed to air can be explained by the Q3D Mott VRH [4]

$$\sigma_{ac}(T) = \frac{e^2 n^2 (\epsilon_F) \langle L \rangle^3 k_B T \omega_e}{96 s} \ln^4 \frac{\omega_0}{\omega_e} = \sigma_0 T \quad (4)$$

where $\langle L \rangle$ is the average length of the charge carrier wave function, ω_0 is the upper hopping frequency nearly equal to the optical phonon frequency, ω_{ph} , and s is the average cross-sectional area of each chain. Indeed, Fig.2 shows that $\sigma_{ac}(T)$ determined from the analysis of the EPR spectra of vacuum-processed and air-containing samples is fitted well by Eq.(4) with $\sigma_0 = 6.1 \text{ S cm}^{-1}\text{K}^{-1}$ and $13.2 \text{ S cm}^{-1}\text{K}^{-1}$, respectively.

The spin-lattice relaxation time T_1 of PC in PANI-TSA can be determined by using the steady-state saturation method from the relation [13]

$$\left(\Delta B_{pp} / \Delta B_{pp}^{(0)} \right)^2 = 1 + 1/4 \gamma_e^2 B_1^2 T_1 T_2 \quad (5)$$

where $T_2 = 2/3^{1/2} \gamma_e \Delta B_{pp}$ and $\Delta B_{pp}^{(0)}$ is the linewidth of an unsaturated line. Room-temperature relaxation times were calculated for the vacuum-processed and air-containing PANI-TSA to be $T_1 = 1.2 \times 10^{-7} \text{ sec}$ and $T_2 = 3.1 \times 10^{-8} \text{ sec}$, and $T_1 = 1.1 \times 10^{-7} \text{ sec}$ and $T_2 = 1.6 \times 10^{-8} \text{ sec}$, respectively.

Assuming that polarons diffuse along and between solitary polymer chains with the diffusion coefficients D_{1D} and D_{3D} one can calculate these values from the following equations [14]

$$T_1^{-1}(\omega_e) = \langle \omega^2 \rangle [2J(\omega_e) + 8J(2\omega_e)] \quad (6a)$$

$$T_2^{-1}(\omega_e) = \langle \omega^2 \rangle [3J(0) + 5J(\omega_e) + 2J(2\omega_e)] \quad (6b)$$

where $\langle \omega^2 \rangle$ is the constant of 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 the spectral density function for Q1D motion. The similar spectral density function was used to study spin diffusion in various slightly [6] and highly [5,12] doped conducting polymers.

The coefficients D_{1D} and D_{3D} were obtained for spin diffusion in the air-containing PANI-TSA sample from Eqs.(6) to be 8.1×10^{11} rad/s and 2.3×10^8 rad/s, respectively. Anisotropy of spin diffusion obtained is much higher than $D_{1D}/D_{3D} \approx 50$ obtained by Mizoguchi et al. [12] for PANI highly doped by hydrochloric acid.

Due to mobility of N_e polarons possessing positive elemental charge e^+ , the main part of conductivity is expressed as follows

$$\sigma_{1D,3D} = N_e e^2 D_{1D,3D} d_{1D,3D}^2 / k_B T \quad (7)$$

where $d_{1D,3D}$ are the corresponding lattice constants. Room-temperature conductivities due to possible polaron diffusion along and between polymer chains were calculated for highly doped PANI-TSA from Eq.(7) with $N_e = 4.7 \times 10^{20}$ spin/g [15], $d_{1D} = 1.10$ nm and $d_{3D} = 0.44$ nm [9] to be 29 S/cm and 2.4×10^{-3} S/cm, respectively. These values are much smaller than the value σ_{ac} obtained above by a more direct magnetic resonance method that confirms the supposition of polaron localization in PANI-TSA.

4. Conclusions

PANI-TSA consists of Q3D metal-like domains with high crystallinity and conductivity embedded into its amorphous phase. The polarons situated on neighboring conducting chains in crystallites interact strongly that stipulated their localization. In contrast to other conducting polymers, such polaron localization in PANI-TSA does not suppressed by magnetic field up to ca. 5 T. High intrinsic conductivity of the metal-like domains is a reason of appearance of the Dyson contribution in their spectra allowing to determine this parameter directly from such a spectrum. The intrinsic conductivity of the sample is determined by Q3D Mott intradomain charge transfer.

Reversible dipole-dipole interaction of the polarons and oxygen molecules accelerates spin relaxation and increases the intrinsic conductivity. Various character of such interaction at low and high temperature ranges causes extremal temperature dependence of the PC linewidth. The extreme temperature T_c decreases at the registration frequency increase due to the effect of an external magnetic field on the above dipole-dipole interaction.

Acknowledgments

We wish to thank Dr. N.N. Denisov for assistance in the EPR experiments. The work was supported partly by the Russian Foundation for Basic Research, Grant No 03-03-04005.

References

- [1] T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds (Eds), Handbook of Conducting Polymers, 2nd Edition, Marcel Dekker, New York, 1998.
- [2] E. Houze, M. Nechtschein, Phys. Rev. B 53 (1996) 14309.
- [3] Z.H. Wang, E.M. Scherr, A.G. MacDiarmid, A.J. Epstein, Phys. Rev. B, 45 (1992) 4190.
- [4] N.F. Mott, E.A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford, 1979.
- [5] K. Mizoguchi, S. Kuroda, in: H.S. Nalwa (ed.), Handbook of Organic Conductive Molecules and Polymers, Vol. 3, Wiley, 1997, p.251.
- [6] V.I. Krinichnyi, Synth. Met. 108 (2000) 173.
- [7] R. Pelster, G. Nimitz, B. Wessling, Phys. Rev. B, 49 (1994) 12718.
- [8] Ormecon Chemie GmbH & Co., KG, Germany, Zipperling Kessler, 5,567,355, 1987.
- [9] B. Wessling, D. Srinivasan, G. Rangrajan, T. Mietzner, W. Lennartz, Europ. Phys. J. E 2 (2000) 207.
- [10] A.C. Chapman, P. Rhodes, E.F.W. Seymour, Proc. Phys. Soc. B 70 (1957) 345.
- [11] F.J. Dyson, Phys. Rev. B 98 (1955) 349.
- [12] K. Mizoguchi, M. Nechtschein, J.-P. Travers, C. Menardo, Phys. Rev. Lett. 63 (1989) 66.
- [13] Ch.P. Poole, Electron Spin Resonance, A Comprehensive Treatise on Experimental Techniques, Wiley, New York, 1983.
- [14] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford, 1961.
- [15] V.I. Krinichnyi, S.V. Tokarev, Polym. Sci. A 47 (2005) in press.