Multifrequency EPR study of metal-like domains in polyaniline

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Abstract

The magnetic, relaxation and electronic dynamic parameters of paramagnetic centers, polaron 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 wavelengths 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 external 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 $\omega_c$ 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 $S=\frac{1}{2}$. 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 spin $S=\frac{1}{2}$ [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 wavelength (10 MHz-140 GHz) 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 monoclinic 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.

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2. Experimental

Commercially available powder-like Ormecos®
polyaniline [8] with p = 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 Mn²⁺ ions in MnO
with Kf = 2.00102 and μ = 87.4 Gauss were used for the g-
factor determination. Uncertainty in the determination of
the peak-to-peak linewidth ΔBp and the value of g-factor
was consequently ±2×10⁻⁷ Gauss and ±2×10⁻⁷ at 3-cm
waveband EPR and ±5×10⁻⁷ at 2-mm waveband EPR.

3. Results and Discussion

![PANI-TSA](image)

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:

\[
\frac{dx}{dB} = \frac{2x}{(1+x^2)} + D \frac{1-x^2}{(1+x^2)}
\]

(1)

where \(x=(B-B_0)/\Delta B_0\), \(B_0\) is the resonant magnetic field, \(\Delta B_0 = 1/T_2\) is the width of the Lorentzian line, \(T_2\) is the spin-
spin relaxation time, \(\gamma\) is gyromagnetic ratio. The
coefficients \(A\) and \(D\) for the skin-layer with thickness of \(\delta\)

on the surface of sphere with radius \(R\) and intrinsic
conductivity \(\sigma_o\) at registration frequency \(\omega_o\) can be
determined from such Dysonian spectra using the relations

(1a)

\[
A = \frac{8 \pi (\sinh p + \sin p)}{9 p^2 (\cosh p - \cos p) (\cosh p - \cos p)} + \frac{8 \pi \sin p \sin p}{p (\cosh p - \cos p) (\cosh p - \cos p)}
\]

(1b)

\[
D = \frac{8 \pi (\sinh p - \sin p)}{9 p^2 (\cosh p - \cos p) (\cosh p - \cos p)} + \frac{4 \pi \sin^2 p - \sin^2 p}{p (\cosh p - \cos p) (\cosh p - \cos p)}
\]

where \(p = 2 R / \delta\), \(\delta = \frac{2}{\mu_0 \omega_o \sigma_o}\), \(\mu_o\) is magnetic
permeability in vacuum, and \(\omega_o\) 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, \(g = 2.0028\),
paramagnetic susceptibility, \(\chi_p = 2.2 \times 10^{-5}\)
emu/mole-2 rings, and the density of states at the Fermi
level \(n(\varepsilon_F) = 0.69\) states/eV-2 rings for vacuum-
processed sample. As the sample is exposed to air, these
parameters are found to be \(g = 2.00274\), \(\chi_p = 1.1 \times 10^{-5}\)
emu/mole-2 rings, and \(n(\varepsilon_F) = 34.6\) states/eV-2 rings.

Fig.2 shows the temperature dependences of absorption
peak-to-peak linewidths \(\Delta B_0\) 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 \(\Delta B_0\) value with characteristic temperature \(T_c = 160\) K (3-
cm waveband EPR) and \(T_c = 130\) K (2-cm waveband EPR)
(Fig.2). The interaction of polarons with paramagnetic
oxygen molecules should lead to the EPR line broadening

\[
\delta(\Delta B_0) = 16/27 \omega_o \varepsilon_c \left[ 1 + \frac{B_{0,\text{sat}}}{12 J} \right]
\]

(3)
where \( \alpha_{\text{pol}} \) is the frequency of the polaron intrachain hopping, \( C \) is a number of oxygen molecules per each aniline ring, \( R \) is the Plank constant, and \( J \) is the constant of spin dipole-dipole interaction.

Fig. 3 shows the temperature dependences of \( \sigma_{\alpha} \) calculated by using Eqs. (1) to (2) from Dwyman 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. 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 \( \sigma_{\alpha} \) 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 interacting 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 \( \alpha_{\text{pol}} \) and \( \Delta \epsilon \) and activation energy \( E_{\alpha} \). 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 \( \Delta \epsilon \) value with the increase of registration frequency should evidence, for example, the effect of an external magnetic field on spin exchange in the polymer. The shift of the \( \Delta B_{\text{eff}}(T) \) 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 \( T < T_0 \) and \( T \geq T_0 \), respectively.

Intrinsic conductivity of the PANI-TSA sample exposed to air can be explained by the Q1D Mott VRH [4]

\[
\sigma_{\alpha}(T) = \frac{c^{2}T_{\text{eff}}^{2}L_{X}^{1/3}k_{B}T_{\text{D}}}{96} \ln^{1/3} \frac{\alpha_{\text{pol}}}{\alpha_{\text{D}}} = \sigma_{0}T
\]

where \( \langle L \rangle \) is the average length of the charge carrier wave function, \( \alpha_{\text{pol}} \) is the upper hopping frequency nearly equal to the optical phonon frequency, \( \alpha_{\text{D}} \), and \( x \) is the average cross-sectional area of each chain. Indeed, Fig. 2 shows that \( \sigma_{\alpha}(T) \) determined from the analysis of the EPR spectra of vacuum-processed and air-containing samples is fitted well by Eq (4) with \( \sigma_{0} = 6.1 \text{ S cm}^{-1} \) and 13.2 S cm\(^{-1}\), 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]

\[
\frac{\Delta B_{\text{eff}}}{\Delta B_{\text{sat}}} = 1 + 1/4 \frac{\tau_{2}}{T_{1}T_{2}}
\]

where \( T_{1} = 1/2 \sqrt{\tau_{2}} \Delta B_{\text{sat}} \) and \( \Delta B_{\text{sat}} \) is the linewidth of an unsaturated line. Room-temperature relaxation times were calculated for the vacuum-processed and air-containing PANI-TSA to be \( T_{1} = 0.8 \text{ sec} \) and \( T_{2} = 2.3 \times 10^{-5} \text{ sec} \), and \( T_{1} = 1.1 \times 10^{-5} \text{ sec} \) and \( T_{2} = 1.6 \times 10^{-6} \text{ sec} \), respectively.

Assuming that polarons diffuse alone and between solitary polymer chains with the diffusion coefficients \( D_{\alpha} \) and \( D_{\text{D}} \) one can calculate these values from the following equations [14].
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 $T_e$ decreases at the registration frequency increase due to the effect of an external magnetic field on the above dipole-dipole interaction.

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References