

Multifrequency EPR study of charge transport in doped polyaniline

V.I. Krinichnyi ^{a, *}, A.L. Konkin ^b, P. Devasagayam ^c, A.P. Monkman ^c

¹ *Inst. of Problems of Chemical Physics, Chernogolovka, Russia*

² *Department of Physics, Kazan State University, Kazan, Russia*

³ *Department of Physics, University of Durham, Durham, England*

Abstract

Polyaniline highly doped with acrylamido-2-methyl-1-propanesulphonic (PANI-AMPSA) and camphorsulfonic (PANI-CSA) acids have been studied at X- (9.5 GHz) and K- (37.5 GHz) bands EPR. Localized Curie-like and mobile Pauli-like spin charge carriers are stabilized in amorphous and crystalline regions of the samples. AC conductivity contributed from these paramagnetic centers was determined. It was shown that, in contrast with PANI-AMPSA, PANI-CSA with higher both *d.c.* and *a.c.* conductivity is a more ordered metal with more rigid and planar polymer chains.

Keywords: electron paramagnetic resonance, polyaniline and derivatives, conductivity

1. Introduction

EPR studies of emeraldine salt (ES) form of polyaniline (PANI) doped with camphorsulfonic acid (CSA) has shown [1] that the polymer is a disordered metal near the metal-insulator boundary and it contains one type of paramagnetic center (PC). Highly doped PANI-CSA is characterized by Pauli- and Curie-like susceptibility above and below 50 K, respectively. This implies that models that assume transport by spinless bipolarons are not appropriate for PANI-CSA.

Recently we have synthesized a new metal-like PANI doped with 2-acrylamido-2-methyl-1-propanesulphonic acid (AMPSA) [2]. The AMPSA counter ion hydrogen bonds to the PANI in a more complex fashion giving rise to a different crystal structure and lower degree of crystallinity. This allows analyzing the effect of PANI-ES microscopic structure on its charge transport properties.

2. Experimental

PANI-AMPSA and PANI-CSA films of ~50 μm thick were cast from *m*-cresol or dichloroacetic acid solutions onto Si wafers and allowed to dry in air at 313 K [2,3].

EPR spectra of the samples placed into quartz tube filled with inert gas have been registered at X-waveband (9.2 GHz) at 10 – 300 K and at K-waveband (37.5 GHz) at 300 K.

3. Results and Discussion

EPR spectra of *e.g.* PANI-CSA_{0.6} registered at different temperatures are presented in Fig.1. It was shown [4] that the Lorentzian spectra with $g_{\text{eff}}=2.0020$ (PANI-AMPSA) and $g_{\text{eff}}=2.0028$ (PANI-CSA) consist of two Dyson-like lines attributed to Curie (R_1) and Pauli (R_2) PC. Both the line shape and the spin concentration ratio $[R_1]/[R_2]$ depend on doping level and temperature.

The temperature dependences of *a.c.* conductivity due to diffusion of both type PC determined from their Dyson-like

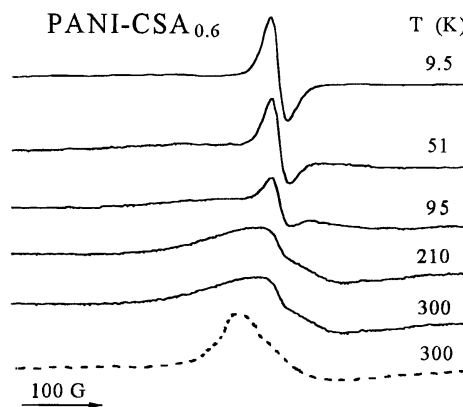


Fig. 1. X- and K- (dashed line) waveband EPR spectra of PANI-CSA_{0.6}.

* Corresponding author. Tel: +7-095-524-5035; fax: +1-775-924-5513; E-mail: kivi@cat.icp.ac.ru

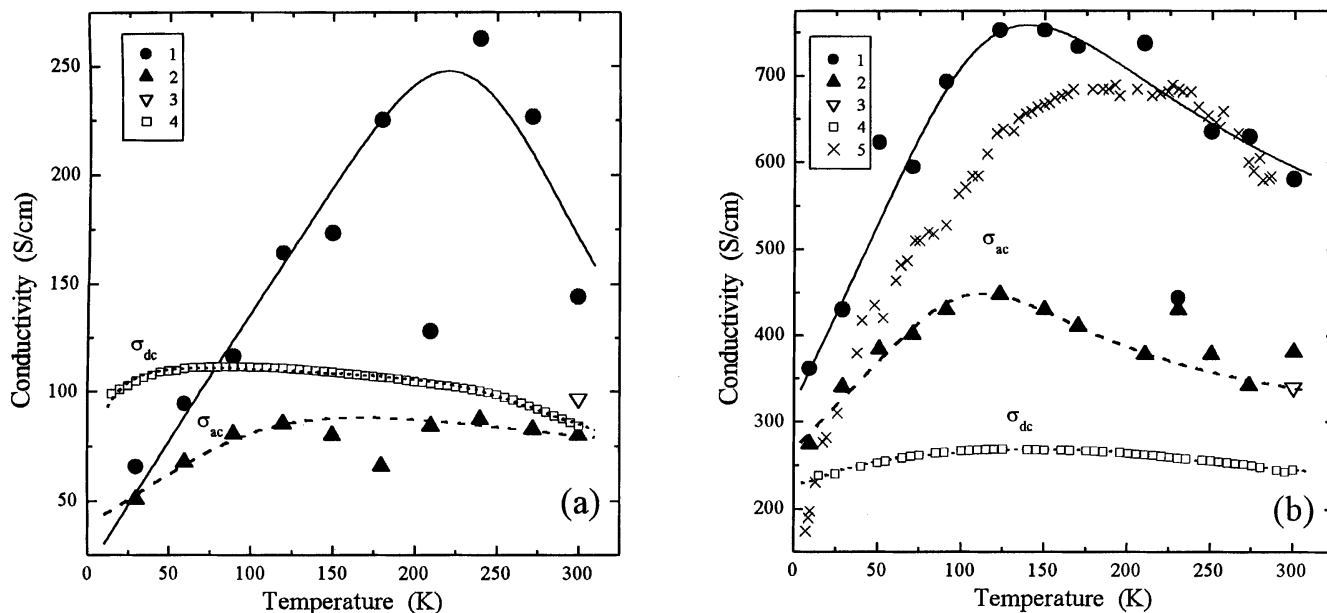


Fig.2. Temperature dependences of the *a.c.* conductivity σ_{ac} due to diffusion of PC R_1 (1) and R_2 (2) calculated from their X- (1,2) and K- (3) waveband EPR spectra and those of the *d.c.* conductivity σ_{dc} (4) for PANI-AMPSA (a) and PANI-CSA (b) samples with $y=0.60$. The functions $\sigma_{dc}(T)$ calculated from Eq.(1) with $T_0=72.4$ K and $E_{ph}=0.23$ eV (a) and $T_0=296$ K and $E_{ph}=0.13$ eV (b) are shown by dotted lines. The functions $\sigma_{ac}(T)$ calculated from Eq.(2) with $E_{ph}=0.031$ eV (a) and $E_{ph}=0.047$ eV (b) and an appropriate coefficients for R_1 and R_2 are shown by solid and dashed lines as well.

spectra according to method described in Ref. [5] and *d.c.* conductivity of the samples [4] are presented in Fig.2. For the comparison, $\sigma_{ac}(T)$ function determined for PANI-CSA_{0.6} by conductometric method at 6.5 GHz [6] is shown (5) in Fig.2b as well.

PANI-ES samples seem to exhibit semiconducting and metal-like behaviors respectively at low and high temperature regions. Therefore, both $\sigma_{dc}(T)$ and $\sigma_{ac}(T)$ dependences can be explained in terms of *e.g.* 1D variable range hopping [7] and the charge carrier scattering on lattice phonons [8]. According to such an approach, both terms of the conductivity can be determined as

$$\sigma_{dc}(T) = k_1 + \left\{ k_2 \sqrt{T} \exp \left[\left(\frac{T_0}{T} \right)^{1/2} \right] + k_3 T^{-1} \left[\sinh^{-1} \left(\frac{E_{ph}}{kT} \right) - 1 \right] \right\}^{-1} \quad (1)$$

$$\sigma_{ac}(T) = k_4 + \left\{ k_5 T^{-1} + k_6 T^{-1} \left[\sinh \left(\frac{E_{ph}}{kT} \right) - 1 \right]^{-1} \right\}^{-1} \quad (2)$$

where $k_1 - k_6$ are coefficients, T_0 is the percolation constant, and E_{ph} is the energy of the lattice phonons.

As it is seen from Fig.2, the functions $\sigma_{dc}(T)$ and $\sigma_{ac}(T)$ calculated are in good agreement with experiment. The conductivity due to diffusion of radicals R_2 weakly depends, at least at high temperatures, on the registration frequency, which is typical of conventional metals. The ratio of the energies of the lattice phonons is near to that of activative spin relaxation [4] indicating strong spin-lattice interaction in the samples.

Both *d.c.* and *a.c.* conductivities determined for PANI-AMPSA are much lower than those of PANI-CSA. This confirms the hypothesis [4] for better charge carriers

dynamics in PANI-CSA compared to PANI-AMPSA because of the greater planarity and closer packing of the chains of the former polymer.

The data obtained allow concluding that R_2 radicals are stabilized in the crystalline domains of the samples and are rather related to charge transport, whereas R_1 centers localized in the amorphous domain of the polymer are involved in this process only indirectly. The crystalline clusters of the polymer are quasi-metallic aggregates with strongly interacting polymer chains and 3D delocalized charge carriers. The charge transport is realized between such clusters through amorphous domains characterized by lower mobility of the spins and charge carriers. From the comparison of the results obtained with those described in Refs. [4,5] one can conclude that the metal-like electronic properties grow in the series PANI-H₂SO₄ → PANI-HCl → PANI-AMPSA → PANI-CSA.

References

- [1] N.S. Sariciftci, A.J. Heeger, Y. Cao, Phys. Rev. 49 (1994) 5988.
- [2] P.N. Adams, P. Devasagayam, S.J. Pomfret, L. Abell, A.P. Monkman, J. Phys. 10 (1998) 8293.
- [3] P.N. Adams, P.J. Laughlin, A.P. Monkman, A.M. Kenwright, Polymer 37 (1996) 3411.
- [4] V.I. Krinichnyi, A.L. Konkin, P. Devasagayam, A.P. Monkman, J. Cond. Matt. Phys. (in press).
- [5] V.I. Krinichnyi, Russ. Chem. Bull. 49 (2000) 207.
- [6] A.J. Epstein, J. Joo, R.S. Kohlman, G. Du, A.G. MacDiarmid, E.J. Oh, Y. Min, J. Tsukamoto, H. Kaneko, J.P. Pouget, Synth. Met. 65 (1994) 149.
- [7] N.F. Mott, E.A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford, 1979.
- [8] S. Kivelson, A.J. Heeger, Synth. Met. 22 (1988) 371.