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Multifrequency EPR study of charge transport in doped polyaniline

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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_{eff}=2.0020 (PANI-AMPSA) and g_{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

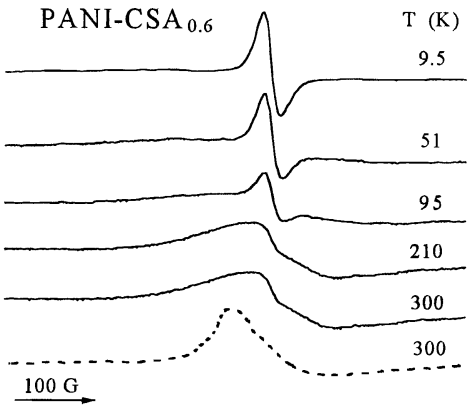

Fig.1. X- and K- (dashed line) waveband EPR spectra of PANI-$CSA_{0.6}$.

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