Journal of Optoelectronics and Advanced Materials Vol. 6, No. 1, March 2004, p. 297 - 305

ELECTRON SPIN RESONANCE AND DC ELECTRICAL INVESTIGATIONS ON CHLORINE DOPED POLYANILINES

M. Chipara[*], Gh. Aldica[a], D. Hui[b], M. Dimonie[c], K. T. Lau[d], L. Georgescu[e], I. Munteanu[e], H. Marascoiu[c]

Indiana University Cyclotron Facility, Bloomington, Indiana, USA
[a]National Institute for Materials Physics, Magurele, Bucharest, Romania
[b]University of New Orleans, Department of Mechanical Engineering, USA
[c]"Politehnica" University, Polymer Chemistry Department, Bucharest Romania
[d]The Hong Kong Polytechnic University, Department of Mechanical Engineering, Hong Kong
[e]University of Bucharest, Faculty of Physics, Magurele, Bucharest, Romania

Electron spin resonance and DC electrical investigations on the effect of chlorine doping on emeraldine base polyaniline are reported. From the experimental data it is concluded that the chlorine doping of polyanilines increases the conductivity and that the charge transport is well described by an one dimensional variable range hopping, up to a doping level of 15% Cl/N. The characteristic temperature rises as the doping level is increased. Electron spin resonance investigations revealed the contribution of polarons to the charge transport. The absence of high spin bipolarons was proved by electron spin resonance data within the experimental errors. At high doping levels, the mesoscopic nature of charge transport in polyanilines is confirmed by the Dysonian shape of the resonance lines.

(Received September 30, 2003; accepted after revision January 30, 2004)

Keywords: Electron spin resonance, Polyaniline, Doping, DC electrical conductivity, Variable range hopping

1. Introduction

Polyaniline (PANI) is a highly conducting polymer with DC conductivity as high as 6,000 S/m [1-3] when it is heavily doped. The conducting form of PANI has outstanding temperature stability; the weight loss of the polymer degraded under an inert atmosphere up to about 800 K is smaller than 20% [4]. The electrical properties and the solubility of polyanilines depend on the oxidation state. Depending on the oxidations state, up to 9 types of polyaniline may be identified (see Fig. 1).

The most frequently reported structures of polyaniline are: The fully reduced polyaniline, named leucoemeraldine (see its structure in Fig. 1.I.). Leucoemeraldine is characterized solely by the presence of benzene rings. Such a polymer is obtained at a high pH and is an insulator. By increasing the degree of protonation a benzene ring is converted into a quinone ring (see Fig. 1.II.). The next chain protonation will increase the number of quinone rings to 2. Such a structure is named emeraldine base (see Fig. 1.III.). It is a half oxidized leucoemeraldine with semiconducting or insulating properties. Typically, this polymer has a high intrinsic gap, of about 3.6 eV [1] and becomes conducting by doping. Further increase of quinone rings increases the conductivity of polyaniline. The polyaniline build of 3 quinone rings and 5 benzene rings is named nigraniline (see Fig. 1.IV) and the polyaniline consisting of 4 quinone and 4 benzene rings is named pernigraniline (see Fig. 1.V.). The violet pernigraniline state is not stable. This fully oxidized polyaniline has an

[*] Corresponding author: mchipara@iucf.indiana.edu; chipara@lycos.com
[*]On leave from National Institute for Materials Physics, Magurele, Bucharest, Romania

energy forbidden band of about 1.4 eV [1]. Theoretically, the polyaniline chain may be further oxidized. Nevertheless, the structures shown in Figs. 1.VI - 1.IX were not observed experimental. This reflects the gradual decrease of the chemical stability of polyaniline as the chain oxidation is increased.

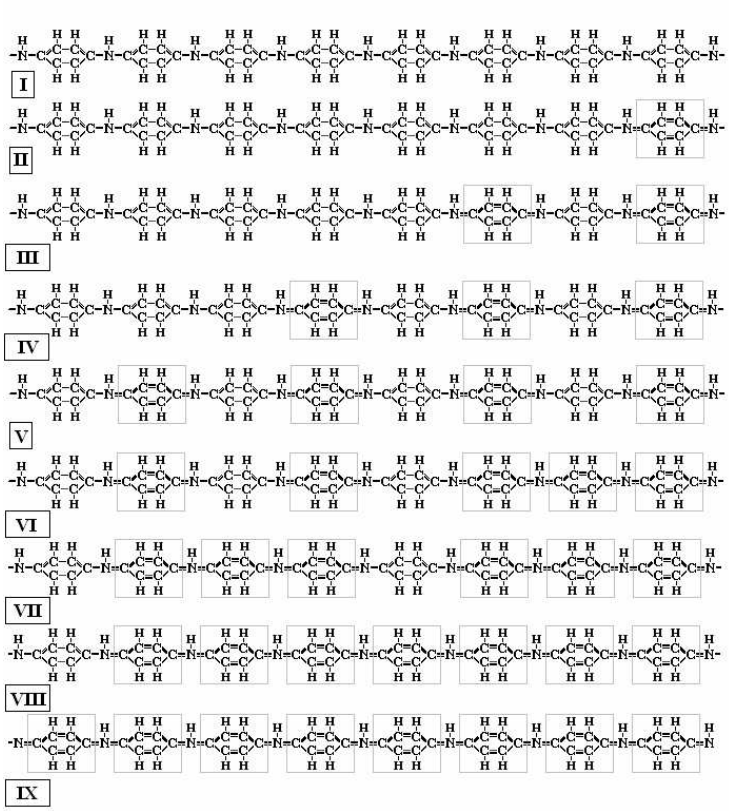

Fig. 1. The structure of polyaniline in different oxidation states. The quinone ring is enclosed in a box.

The applications of highly conductivity polyanilines are limited by poor mechanical features, low solubility, and a reduced processability. To overcome these drawbacks two routes have been considered [3-7]. The first one was to functionalize the polymer in order to achieve the desired degree of processability. The other was to blend the highly conducting polyaniline particles with elastomers [5-8]. Nevertheless, the percolation threshold and the maximum conductivity are controlled by the conducting component of the blend [7, 8].

A detailed study of the effect of halogen doping (various concentrations of HCl) of polyaniline performed by electron spin resonance spectroscopy and DC electric conductivity in a wide range of temperatures is reported. The conductivity of polyaniline depends on the doping level, on the nature of dopants, on the synthesis medium, and on drying details [9, 10]. The importance of such study is related to a debate regarding the crossover from an one dimensional conductivity to a three dimensional conductivity in heavily doped polyaniline [11-15]. The recent developments in spintronics materials revived the debate regarding the presence of bipolarons in conducting polymers. While the presence of bipolarons was proved in the case of highly doped polypyrrole, no agreement was reached in the case of doped polyanilines.

2. Experimental methods

Electron spin resonance, ESR, and DC conductivity studies on pristine and doped emeraldine base polyanilines (EBPANI) are reported. Powders of EBPANI with different degrees of doping expressed by the ratio between Cl and N atoms (0%, 1%, 3%, 5%, 10%, and 15%) were synthesized

as reported elsewhere [9, 10]. The doping has been performed with various amounts of HCl during polymerization. The doping level was measured by FTIR spectroscopy [3, 10]. For DC electric measurements, pellets of polyaniline have been obtained by pressing the powder of polyaniline doped with various amounts of HCl at room temperature. Silver paste has been applied on the faces of the pellets. The DC electrical measurements, in the temperature range 77 K to 300 K were done by using the four-point method. ESR measurements were done by using a JES-ME-3X spectrometer, operating in X band and equipped with a JES-VT-3X variable temperature accessory.

3. Experimental results

A. ESR data

The ESR resonance spectrum of EBPANI is a narrow single line located close to g = 2.00. Some typical resonance lines of polyaniline, at room temperature, are shown in Figs. 2A and 2B. The resonance line of pristine EBPANI is shown in Fig. 2A. It is observed that the resonance spectrum is symmetric. The absence on any shoulder superimposed on the wings of the resonance line located at g = 2.00 and the lack of any resonance at g = 4.00 indicates (within the experimental errors) the absence of high spin bipolarons, characterized by an effective spin S = 1 [16, 17]. Low spin bipolarons (with an effective spin S = 0) give no ESR spectrum. As polyaniline is doped, the resonance line changes gradually into a Dysonian-like resonance [17]. Such a line, shown in Fig. 2B is asymmetric, in the sense that the amplitude of the positive lobe (I^+) is not equal to the amplitude of the negative lobe, (I^-). This change in the resonance line shape is due to the skin effect. At doping level smaller than 3% Cl, the conducting domains, if present are very small and the microwave field is not damped within these islands. This implies that the size of these islands is smaller than the skin depth at microwaves frequencies of about 10 GHz (the skin depth for fully doped EBPANI is of the order of 10^{-6} m). By increasing the doping level the size of these islands is increased, and becomes comparable to the skin depth at a doping of about 3% Cl/N. This proves the mesoscopic nature of the charge transport in EBPANI indicating that the dependence of the electrical conductivity on the doping level is a percolation like process [18-20].

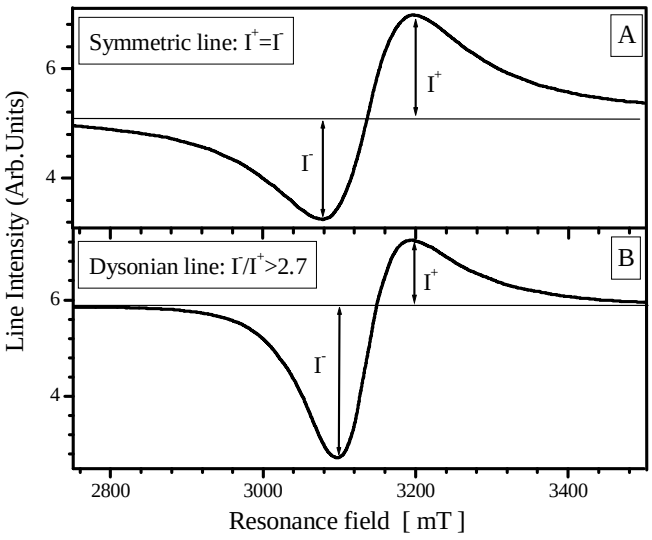

Fig. 2. The Electron Spin Resonance spectra of EBPANI at room temperature. a) The resonance spectra of symmetric pristine EBPANI; b) The Dysonian shape of the resonance line of EBPANI doped by 3% Cl/N.

The temperature dependence of the most important parameters of the resonance line for EBPANI doped with various amounts of HCl, namely the double integral of the resonance line S and the peak to peak linewidth, is shown in Figs. 3A and 3B. The double integral of the resonance spectrum, S, has been estimated by using the relationship [16-17]:

$$S = \frac{KIH_{PP}^2}{A} \tag{1}$$

Where K is the resonance line shape factor, I the resonance line amplitude, H_{PP} the peak to peak amplitude of the resonance line, and A the gain of the spectrometer. At a given temperature, S is proportional to the concentration of uncoupled electronic spins. For isolated spins, the temperature dependence of S obeys an Arrhenius like dependence. As it is inferred from Fig. 3A, S decreases as the temperature of the sample is raised. This suggests that the temperature dependence of S is related to some activation processes or chemical reactions that governs the temperature dependence of the total number of uncoupled electronic spins.

The resonance linewidth, H_{PP}, presents a complex dependence on the sample temperature (see Fig. 3B). The increase in the resonance linewidth above 273 K may be associated to the conversion of ice into water followed by the evaporation of water.

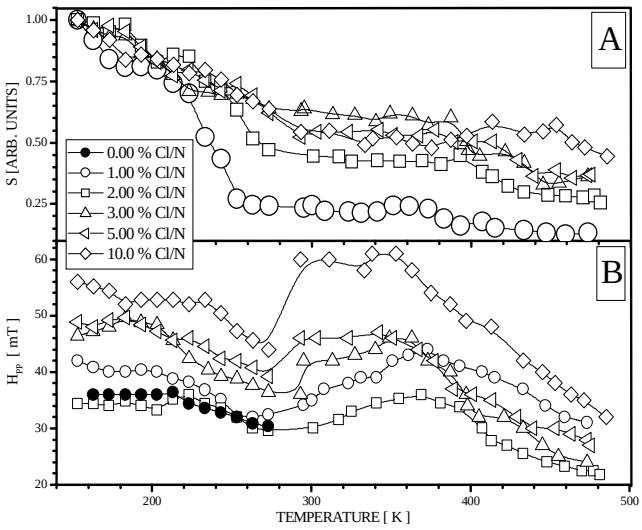

Fig. 3. The temperature dependence of: a). The resonance line double integral, S; b) The resonance line width, H_{PP}, for EBPANI doped with various amounts of Cl/N. The size of the experimental point indicates the experimental errors. The lines are drawn for eye guidance.

The temperature dependence of the resonance line width, in the low temperature range, is accurately fitted by an Arrhenius like dependence (see the bottom panel of Fig. 4):

$$H_{PP} = H_{PP}^{(0)} \exp\frac{E_A}{K_B T} \tag{2}$$

Where $H_{PP}^{(0)}$ is a constant, E_A is the activation energy for the uncoupled electronic spin motions and K_B the Boltzmann constant. As it is shown in the upper panel of Fig. 4, the temperature dependence of the resonance line width, in the high temperature range is also well fitted by an Arrhenius like dependence.

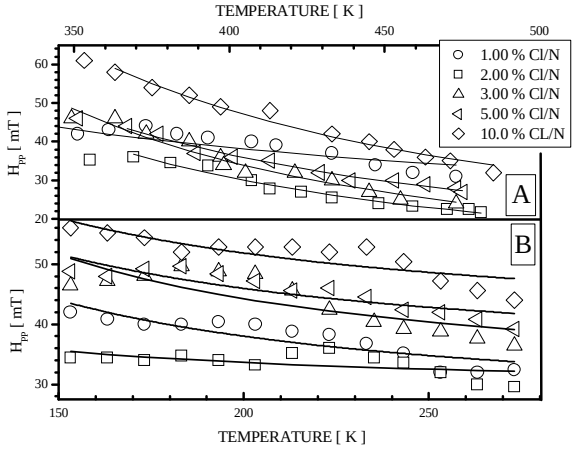

Fig. 4. The temperature dependence of the resonance line width in: a) The high temperature range; b) The low temperature range. The size of the experimental point indicates the experimental errors. The lines represent the best fit of the temperature dependence of the resonance line width, obtained by assuming an Arrhenius like dependence (eq. 2)

The temperature dependence of S, in the low temperature range is shown in Fig. 5. This dependence cannot be accurately fitted by an Arrhenius or Curie like temperature dependence. It was found that in the low temperature range, the temperature dependence of S is rather well fitted by a Variable Range Hopping (VRH) like dependence:

$$S \cong S_0 \exp\left(\frac{T_0^{(S)}}{T}\right)^{\frac{1}{d+1}} \tag{3}$$

The best fit, represented by lines in Fig. 5, has been obtained for an one-dimensional charge transport mechanism. From Fig. 5 it is observed that for low doping levels, the equation (3) is not able to predict accurately the temperature dependence of S. At such low doping levels, the dynamics of electrons is more complicated. It is possible to assume that the electrons are trapped by local defects after a hopping sequence. Accordingly, the temperature dependence of the conductivity is no more described by a simple VRH equation. An improved VRH equation was proposed [19] taking into account that the pre-exponential term is also temperature dependent. Increasing the doping level above 2% Cl/N the deviations of experimental data from a VRH-like dependence (eq. 3) become negligible.

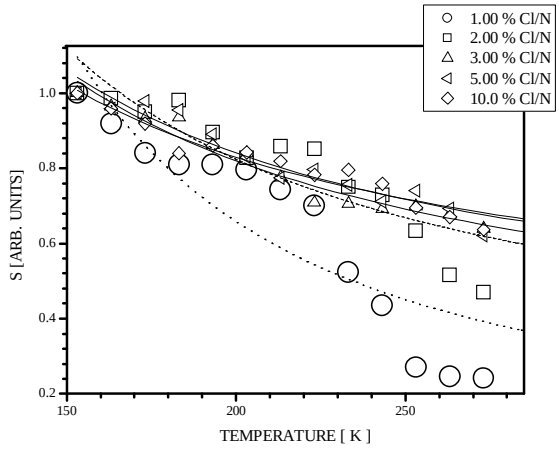

Fig. 5. The temperature dependence of S, in the low temperature range. The size of the experimental point indicates the experimental errors. The lines represents the best fit obtained with the equation (3). For the samples doped with 1 % Cl/N (dotted line) and 2% Cl/N the fit is rather poor.

In Fig. 6A it is shown the dependence of the "ESR characteristic temperature" $T_0^{(S)}$ on the doping level. At $T=T_0^{(S)}$, the concentration of free radicals reaches a constant value S_0, which is not affected by the dimensionality of the hopping process. From Fig. 6A it is concluded that increasing the doping level, the critical concentration of free radicals, S_0, is reached at lower temperatures.

The dependence of the activation energies, E_A^{HIGH} and E_A^{LOW}, in the high and low temperature domains respectively, is shown in Fig. 6B. Both E_A^{HIGH} and E_A^{LOW} exhibit a weak decrease of the activation energy as the doping level is increased (starting from about 3% Cl/N). The experimental data at lower doping levels are affected by larger experimental errors, due to the low concentration of uncoupled electronic spins.

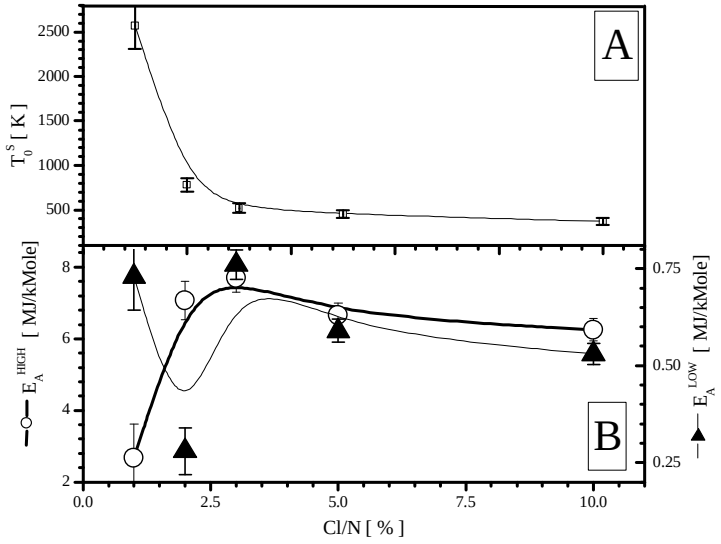

Fig. 6. a) The dependence of the characteristic temperature (as obtained from the best fit of the temperature dependence of S by equation (3)) on the doping level; b) The dependence of the activation energy (as estimated from the temperature dependence of the linewidth) on the doping level. The experimental errors are shown. The lines are drawn for eyes guidance.

B. DC electrical data

The temperature dependence of the DC conductivity is shown in Fig. 7. In conducting polymers, several competing processes were considered to explain the temperature dependence of DC conductivity. An Arrhenius like dependence of resistance was suggested [11] if the activation energy $E_A^{(R)}$ is equal with the difference between the Fermi level E_F and the mobility edge E_C;

$$R = R_0 \exp - \frac{E_A^{(R)}}{K_B T} \tag{4}$$

Where R_0 is related to the sample conductivity at the mobility edge [11].

It was noticed that the temperature dependence of the DC conductivity, in the low temperature range obeys, with an acceptable accuracy the predictions Variable Range Hopping model; i.e. the temperature dependence of the resistance is described by the relationship [19-24]:

$$R \cong R_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{d+1}} \tag{5}$$

where d is the dimensionality of the conduction process, T_0 is a characteristic temperature, and R_0 is the DC resistance extrapolated at large temperatures ($T \to \infty$). At 0 K, all phonons are frozen and

accordingly the hopping electric conductivity is zero. The best fit of the temperature dependence of resistance is obtained for d = 1, for all samples. This suggests that the DC electrical conductivity of pristine and doped EBPANI occurs through an one-dimensional hopping of conducting electrons and that the probability of electronic jumps across chains is negligible. The three dimensional variable range hopping in the presence of a Coulomb barrier [1] and the charge energy limited tunneling between conducting islands [15] suggests the same temperature dependence of the conductivity. However, both models are consistent with hopping as the charge transport mechanism.

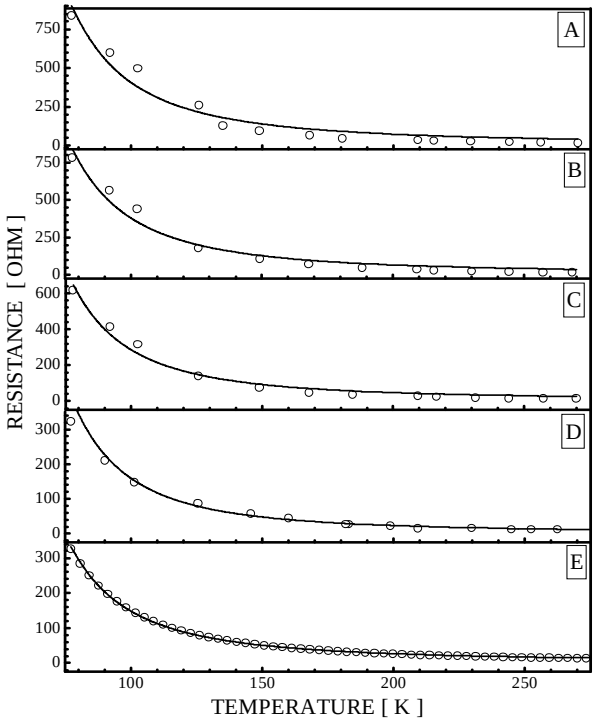

Fig. 7. The temperature dependence of the DC resistance of EBPANI doped with various amounts of Cl. The bold line represents the best fitting assuming a VRH like conduction mechanism. A. 1% Cl/N; B. 2% Cl/N; C. 3% Cl/N; D. 10% Cl/N; E. 15% Cl/N.

As it is observed from Fig. 8A, the characteristics temperature, T_0, increases as the doping level is increased up to 10% Cl/N. This reflects the increase in the number of electrons at the Fermi level as the doping level is increased [20]. It is important to observe that T_0 and $T_0^{(S)}$ have opposite dependencies on the doping level, although in both cases, the temperature dependence of S and R is consistent with an one dimensional conducting mechanism. Nevertheless, the temperature dependence of R is controlled by both mobility and number of charge carriers while the temperature dependence of S reflects solely the temperature dependence of the concentration of uncoupled electronic spins. Further research is required to have a proper understanding of these results. An unexpected drop in the characteristic temperature, T_0, at about 15 % Cl/N is observed. In heavily doped conducting polymers, a transition from an one dimensional conduction mechanism towards a two or even three dimensional VRH was reported [11-15]. However, we failed to notice any change in the dimensionality of the conduction process up to a doping level of 15% Cl/N. Tentatively, this behavior may be associated to electrons interactions (including a weak increase in the dimensionality of the transport mechanism) such as the growth of conducting metallic islands, noticed at room temperature starting from 3% Cl/N. As it is shown in Fig. 8B, the asymptotic value of the sample resistance has an expected dependence on the doping level for all samples (decreases as the doping level in increased).

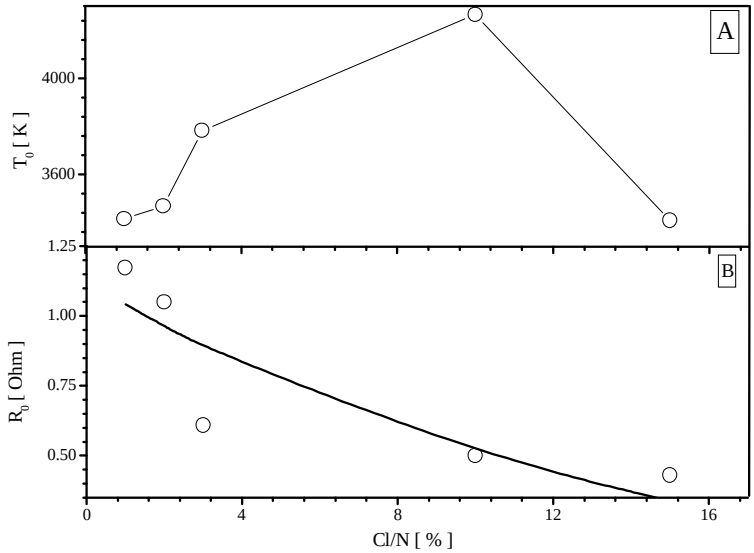

Fig. 8. The dependence of: a) The characteristic temperature, T_0, (as estimated from DC conductivity data) on the doping level. b) Extrapolated resistance at 0 K, R_0, on the doping level. Both T_0 and R_0 were estimated by fitting the temperature dependence of the DC conductivity by a VRH like dependence, assuming an one dimensional electron transport mechanism. The lines are drawn for eyes guidance.

4. Conclusions

ESR data on pristine and doped EBPANI indicate that within the experimental errors the high spin bipolarons are absent and suggest that the main contribution to the conduction process is due to polarons. The mesoscopic nature of conductivity is confirmed by the analysis of the shape of the electron spin resonance spectra. It is suggested that the dependence of the DC conductivity on the doping level has a percolative character. Both DC conductivity and electron spin resonance data are consistent with an one dimensional variable range hopping transport mechanism. The characteristic temperature (as estimated from DC conductivity data) increases as the doping level in increased, reflecting the increase in the number of electrons at the Fermi level. The asymptotic resistance decreases as the doping level is increased. No crossover from an one dimensional variable range hopping towards a three dimensional variable range hopping was noticed, up to 15 % Cl/N.

References

[1] M. Campos, Braz Bello, Mechanism of conduction in doped polyaniline, J. Phys. D: Appl. Phys. **30**, 1531–1535 (1997).
[2] J. Joo, A. J. Epstein, Electromagnetic radiation shielding by intrinsically conducting polymers, Appl. Phys. Lett. **65**(18), 2278-2280 (1994).
[3] R. S. Kohlman, A. Zibold, D. B. Tanner, G. G. Ihas, T. Ishiguro, Y. G. Min, A. G. MacDiarmid, A. J. Epstein, Limits for Metallic Conductivity in Conducting Polymers, Phys. Rev. Lett. **78**, 20, 3915-3918 (1997).
[4] M. G. Han, Y. J. Lee, S. W. Byun, S. S. Im, Physical properties and thermal transitions of polyaniline film. Synth. Met. **124**, 337-343 (2001).
[5] D. Hui, M. Chipara, P. Notingher, M. D. Chipara, A. Lau, D. Panaitescu, On Polyethylene – Polyaniline Composites, Submitted to Composites B-accepted.
[6] M. Chipara, E. Gooverts, M. D. Chipara, I. Munteanu, ESR Investigations on Polyaniline-Polyvinilchloride blends, Mat. Res. Soc. Symp. Vol. **665**, C8.8.1-C8.8.6 (2001).

[7] B. Wessling, D. Srinivasan, G. Rangarajan, T. Mietzner, W. Lennartz, Dispersion-induced insulator-to-metal transition in polyaniline, Eur. Phys. J. E **2**, 207–210 (2000).
[8] P. Mandal, A. Neumann, A. G. M. Jansen, P. Wyder, R. Deltour, Temperature and magnetic-field dependence of the resistivity of carbon-black polymer composites, Phys. Rev. B. **55**(1), 452-456 (1997).
[9] H. Marascoiu, PhD Thesis, "Politehnica" University, Bucharest, Romania (2002).
[10] P. R. Somani, Synthesis and characterization of polyaniline dispersions, Mat. Chem. Phys. **77**, 81–85 (2002).
[11] V. M. Mzenda, S. A. Goodman, F. D. Auret, Conduction models in polyaniline: The effect of temperature on the current–voltage properties of polyaniline over the temperature range 30 < T(K)< 300, Synth. Met. **127**, 285–289 (2002).
[12] D. S. Maddison, T. L. Tansley, Variable range hopping in polypyrrole films of a range of conductivities and preparation methods, J. Appl. Phys. **72**, 10, 4677-4682 (1992).
[13] J. P. Spatz, B. Lorenz, K. Weishaupt, H. D. Hochheimer, V. Menon, R. Parthasarathy, C. R. Martin, Observation of crossover from three- to two dimensional variable range hopping in template synthesized polypyrrole and polyaniline, Phys. Rev. B. **50**, 20, 14888-14892 (1994).
[14] R. S. Kohlman, J. Joo, Y. G. Min, A. G. MacDiarmid, A. J. Epstein, Crossover in Electrical Frequency Response through an Insulator-Metal Transition, Phys. Rev. Lett. **77**, 13, 2766-2769 (1996).
[15] M. Gosh, A. Barman, A. K. Meikap, S. K. De, S. Chatterjee, Hopping transport in HCl doped conducting polyaniline, Phys. Lett. A **260**, 138–148 (1999).
[16] B. Ranby, D. J. Rabek, ESR applications in polymer research, Wiley Science, 1977.
[17] A. Abragam, B. Bleaney, Eelectron paramagnetic resonance of transition metal ions, Clarendon Press, Oxford, 1970, p.490-535.
[18] A. B. Kaiser, Electronic transport properties of conducting polymers and carbon nanotubes, Rep. Prog. Phys. **64**, 1–49 (2001).
[19] N. F. Mott, E. A. Davies, Electronic processes in non-crystalline materials, Clarendon Press, Oxford, 1979.
[20] D. Stauffer, A. Aharony, Introduction to percolation theory, Taylor & Francis, London, 1992.
[21] J. Joo, S. M. Long, J. P. Pouget, E. J. Oh, A. G. Mac Diarmid, A. J. Epstein, Charge transport of the mesoscopic metallic state in partially crystalline polyanilines, Phys. Rev. B **57**, 16, 9567-9580 (1998).
[22] R. Furchioni, P. Vignolo, G. Groso, Transport properties of emeraldine salts: The nature of the metallic state, Phys. Rev. B **60**, 23, 15705-15713 (1999).
[23] A. N. Samukhin, V. N. Prigodin, L. Jastrabik, A. J. Epstein, Hopping conductivity of a nearly 1D fractal: A model for conducting polymers, Phys. Rev. B **58**, 17, 11354-11370 (1998).
[24] S. Capaccioli, M. Lucchesi, P. A. Rolla, G. Ruggeri, Dielectric response analysis of a conducting polymer dominated by the hopping charge transport, J. Phys.: Condens. Matter **10**, 5595–5617 (1998).