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Low Temperature Charge Transport Study in *p*-Toluenesulfonic Acid Doped Polyaniline

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Polyaniline doped with *p*-toluenesulfonic acid was synthesized with chemical oxidation method by varying synthesis parameters. We report the electrical conductivity study of polyaniline doped with p-toluenesulfonic acid in the temperature range of 10 K to 300 K. The conductivity of the samples has been observed to show an increasing trend with increase in temperature. The Arrhenius model, variable range hopping (VRH), and Kivelson model were used to investigate the charge transfer in polyaniline. It has been shown that no one mechanism can completely describe the charge transport in polyaniline over entire temperature range 10 K- 300 K.

Key Words: Polyaniline, Chemical polymerization, Variable range hopping, Kivelson model.

INTRODUCTION

Polymers have been traditionally considered as insulators. However, since the discovery by Shirakawa, Heeger and MacDiarmid that the conductivity of polyacetylene increases significantly upon doping with electron acceptors [1], a large effort has been devoted to make new intrinsically conducting polymers (ICP) and improving the properties of those materials. Conducting polymers could have a variety of applications: corrosion protection coatings and conductive coatings for antistatic and RF shielding purposes [2,3].

A good number of studies on conductivity of Polyaniline (PANI) with the goal of a clear understanding of the electronic transport have been performed during the last decade [4-8]. One of the promises of the conducting polymers is that, unlike inorganic metals and semiconductors, both the synthesis and chemical modification of organic materials offer unlimited possibilities. Properties such as degree of environmental stability, solubility and dopability have made doped polyaniline (PANI) the most suitable material for studies of electron transport phenomenon in conducting polymers [9-13]. Most of the studies are still confined to the transport studies of heavily protonated emeraldine salt materials. In this work, emphasis was given on making an extensive study on the transport properties at low temperature in less protonated polyaniline. In the present work, we report the in-situ chemical polymerization of aniline doped with p-toluenesulfonic acid (PTSA) and its characterization by electrical conductivity measurements.

EXPERIMENTAL

i. Materials

Aniline (monomer, ANI), Ammoniumperoxydisulfate (APS), p-toluene sulfonic acid (PTSA), N,N-Dimethylformamide (DMF), and 1-Methy-2-pyrrolidone (NMP) were purchased from Alfa Aesar and were of analytical grade. All the chemicals were used as received.

ii. Preparations

PANI was synthesized by oxidative polymerization of aniline in acidic medium by using APS. All the solutions were prepared in de-ionized water having resistivity of ~18MΩ. In a typical procedure, the monomer Aniline (0.005mol) was dissolved in DMF (3ml) and cooled down to 0-5^{0}C. It was then slowly added to 50ml aqueous solution of PTSA (0.025mol). The polymerization was initiated by the drop wise addition of the oxidant solution containing 0.005mol of APS. The polymerization was allowed to proceed at room temp for 5hrs with continuous stirring. Dark green colored precipitates of the polymer were isolated by filtration, washed with de-ionized water and finally dried in an oven for 36hrs**.**

iii. Measurements

Electrical conductivity measurements were performed by standard four-probe technique. Dry powdered samples were made into pellets of ~10mm diameter and ~1mm thickness using a steel die in a hydraulic press under pressure of 300MPa. A Keithley source meter (model 2400) and a Keithley electrometer (model 6514) were used as constant d.c. source and volt meter, respectively. Low temperature conductivity measurements were made using Sumitomo cryogenic (model HC 2), as shown in scheme 1. The conductivity (σ) was calculated from the relation [14].

$$\sigma = \frac{\ln 2}{\pi d}\left(\frac{I}{V}\right)$$

(1)

Where I, V and d are applied current, measured voltage and the thickness of the pellet, respectively.

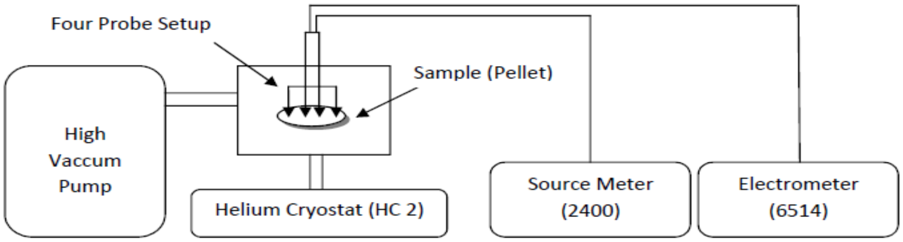

Fig. 1. Schematic setup for conductivity measurement.

RESULTS AND DISCUSSION

Measurements of the d.c. conductivity of PTSA doped polyaniline have been made in the temperature range 10 - 300 K. Fig.2 shows the variation in electrical conductivity with temperature. It is observed from the Fig. 2 that the conductivity increases with rise in the temperature.

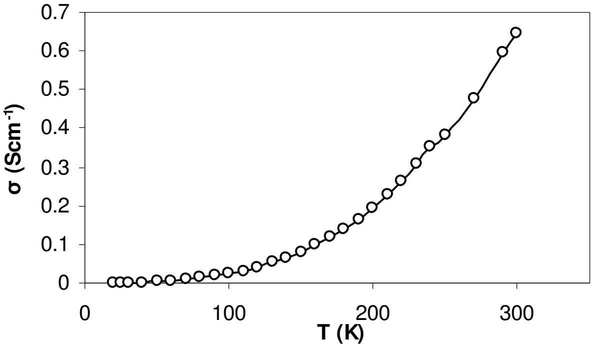

Fig. 2. Dependence of electrical conductivity on temperature.

The d.c. conductivity data have been interpreted in light of several models to attribute the most probable mechanism to fit our data. Fig. 3 depicts plots of conductivity as a function of reciprocal of temperature for polyaniline. The data fitted linearly for $T \geq 180$ K and showed a non linear behaviour for temperature less than 180 K. Therefore, this Arrhenius model was found to be applicable for our samples of polyaniline in the higher temperature range [15]. Fig.4. shows the conductivity verses temperature plot in the logarithmic scale for polyaniline to check the power law behaviour. The ln (σ) verses ln (T) plot shows that the power law behaviour or Kivelson model, $\sigma_{d.c.} = AT^n$, fits to the experimental data up to temperature 120 K. It seems worthwhile to mention that Mott's variable range hopping (VRH) model has been extensively applied to various amorphous inorganic semiconductors over the last two decades and has also been applied to organic conducting or semiconducting systems [16,17].

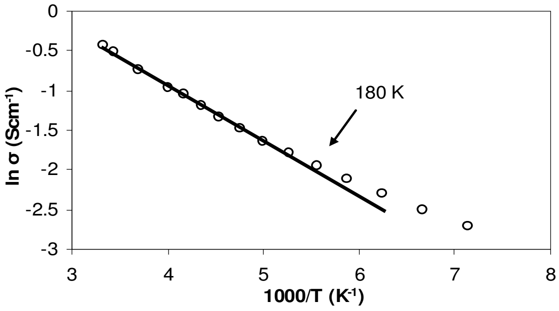

Fig. 3. Variation of conductivity of PANI with T^{-1} showing application of Arrhenius model to the Polyaniline. Conductivity is plotted in logarithmic scale.

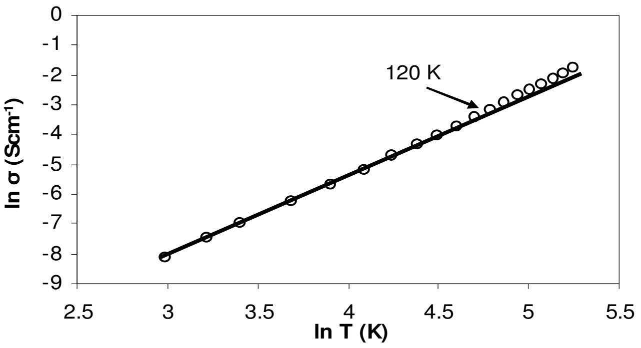

Fig. 4. Application of Kivelson model to the Polyaniline.

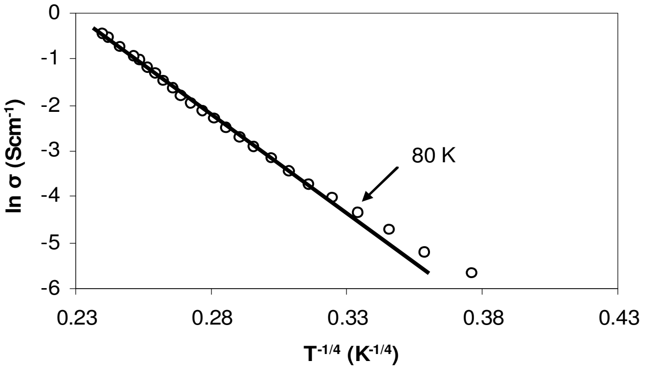

Fig. 5. Variation of conductivity of PANI with T$^{-1/4}$ showing 3D variable range hopping. Conductivity is plotted in logarithmic scale.

According to VRH, the temperature dependence of dc conductivity follows the formula [14]:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{\gamma}$$

(2) where the parameter σ_0 can be considered as the limiting value of conductivity at infinite temperature, T_0 is the Mott characteristic temperature and the exponent γ is related to the dimensionality'd' of the transport process via the equation $\gamma = 1/(1+d)$, where d = 1, 2 and 3 for one dimensional, two dimensional and three dimensional conduction process, respectively. It is evident from the fig. 5, that Mott's three dimensional VRH model gives an excellent fit to the experimental data from 80-300 K. In brief, the comparison of all conduction models reveals that Arrhenius model is applicable at T ≥ 180 K, the Kivelson model shows linear fit up to 120 K and Mott's VRH model has applicability in the temperature range from 80 K to 300 K.

Conclusions

Polyaniline doped with p-toluenesulfonic acid was synthesized by chemical polymerization method using Ammonium peroxydisulfate as an oxidizing agent. An in-depth study has been made on the electron transport properties of PTSA doped polyaniline in the temperature range of 10 - 300 K. The conductivity of samples shows an increasing trend and the variation is noticeably higher at higher temperature. There is more than one mechanism involved in charge transfer in polyaniline depending on the temperature range. Charge transfer in PANI is complex, so that no one mechanism can completely describe it. However, to some extent, conduction in polyaniline can be explained in terms of Mott's three dimensional variable range hopping model.

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