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Electrical conductivity and optical band gap studies of polypyrrole doped with different acids

V. SHAKTAWAT*, N. JAIN, R. SAXENA, N. S. SAXENA, T. P. SHARMA
Semi-conductor & Polymer Science Laboratory, 5-6, Vigyan Bhawan, Deptt. of Physics, University of Rajasthan, Jaipur-302004, India

Doped polypyrrole samples were synthesized by chemical oxidative polymerization technique with Ammonium peroxydisulphate as an oxidant. Electrical conductivity and optical band gap of chemically synthesized polypyrrole doped with Hydrochloric acid (HCl), Sulfuric acid (H_2SO_4) and Dodecyl benzene sulfonic acid (DBSO) have been studied at room temperature and normal pressure. Electrical conductivity and Energy band gap of these materials are determined by I-V characteristics and absorption spectra in the wavelength range 300 –800 nm by spectrophotometer, respectively. I-V characteristics of all the samples were found to be linear. The conductivity of DBSO doped polypyrrole is higher as compared to polypyrrole doped with HCl and H_2SO_4. From the analysis of absorption spectra, the band gaps of polypyrrole doped with chloride ion (Cl^-), sulfate ion (SO_4^{2-}) and (DBS^-) ions have been found to be 2.38, 2.39 and 2.33 eV, respectively.

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1. Introduction

In the past few years conducting polymers have become one of the most extensively studied materials over the world as they possess several applications such as sensors, anti static films, light emitting diodes, electromagnetic shielding layer, electrochromic devices and so on [1,2]. A large number of gas sensors use conducting polymers because they offer great design flexibility due to their advantageous mechanical properties [3,4]. Conducting polymers such as polyaniline and polypyrrole are becoming increasingly important for their technological importance due to their electrical, optical properties and their high air, chemical and electrical stability at ambient conditions [5,6]. In a number of applications the control of the band gap is essential, be it for light emitting diodes (LED) [7], transparency in the visible region combined with high electrical conductivity [8] etc.

A good deal of work has been done on polypyrrole doped with different anions such as PF_6^-, TSO^-, BF_4^-, [9-10] in the film form. However, a very few attempts have been made to study the properties of polypyrrole in its bulk form. In this work, we focus on the electrical conductivity and energy band gap studies of polypyrrole doped with HCl, H_2SO_4 and DBSO in bulk form. Shujiang Yang et al [11] have studied band gap of various conjugated polymer using linear regression data of oligomer band gaps. They reported that the energy band gap of polypyrrole is 2.38.

2. Material preparation and experimental measurements

Polypyrrole doped with chlorine ions was prepared by oxidative polymerization of double distilled pyrrole using ammonium persulfate (APS), $(NH_4)_2S_2O_8$ as an oxidant described elsewhere [12]. Similarly, polypyrrole doped with sulfate ion SO_4^{2-} and DBS^- ions were prepared.

For electrical measurements, bulk sample in the form of pellets (diameter 12mm and thickness of approx 2 mm) were prepared by compressing the fine powder of polypyrrole and chlorine-doped polypyrrole under a load of 6 tonnes. The pellets were mounted between two copper electrodes in a sample holder for I-V measurements. For that purpose, voltage was applied across the pellet and the resulting current was measured by Keithley electrometer/high resistance meter –6517 A. The temperature range of the study was from room temperature to 100 °C approximately. The circuit diagram used for this study is given elsewhere [13]. This electrometer has an inbuilt capability of output independent voltage source of ± 1000 V. So the same equipment was used to apply voltage across the sample and to measure the current through the sample. To ensure proper connection of the sample, an indigeneously designed sample holder was used with copper electrodes.

Optical absorption spectra of the material sandwiched between two glass plates were measured by normal incidence of light, using a double beam UV-VIS Hitachi Spectrophotometer, in the wavelength range 300-800nm, using a two coupled glass plates as the reference position. The absorption coefficient α of all prepared samples was deduced.

3. Results

Polypyrrole is a non-degenerate ground state polymer with two different type of chain configuration containing repeating units of aromatic as well as quinoid as shown in Fig. 1.

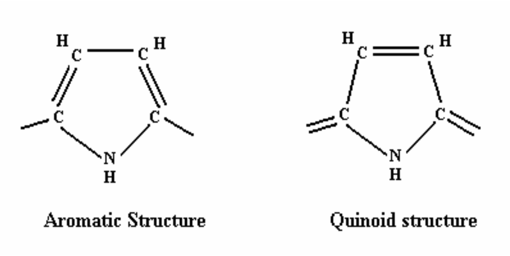

Fig. 1. Structures in polypyrrole.

During oxidative polymerization, pyrrole typically polymerizes by linkage at α position, along with the loss of a proton at each of these positions. The reaction for the formation of a polymeric unit [12,14] is

$$nPy + A^- \rightarrow (PPy)^+ A^- + 2nH^+ + (2n+1)\, e^-$$
(Doped polypyrrole)

where, A^- (Cl^- , SO_4^{2-} and DBS^-) is the counter anions incorporated along polymer backbone.

I-V characteristics of doped polypyrrole were recorded at room temperature and are found to be linear as shown in Fig. 2. From the measured I-V characteristics of these samples, the values of electrical conductivities have been obtained at room temperature.

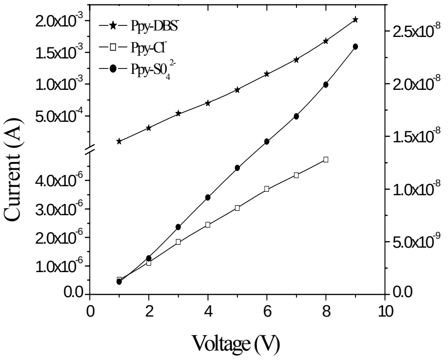

Fig. 2. Current vs. Voltage of polypyrrole doped with Cl^-, SO_4^{2-} and (DBS^-).

The electrical conductivity (σ) of the samples has been determined using the relation,

$$\sigma = [(I \times L) / (V \times A)] \qquad (1)$$

where I is the current, V is the voltage, L the thickness, and A the cross-section area of the sample.

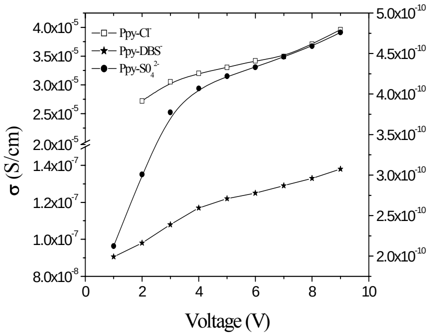

Fig. 3. Conductivity vs. Voltage of polypyrrole doped with Cl^-, SO_4^{2-} and (DBS^-).

Plot of conductivity vs. voltage has been shown in Fig. 3, which suggests that conductivity increases with increase in voltage. A comparative study for all doped polypyrrole samples suggests that the conductivity of DBSO doped polypyrrole is about 10^5 times and HCl doped polypyrrle is 10^2times that of H_2SO_4 doped polypyrrole.

The energy band gap of these materials has been calculated with the help of absorption spectra shown in Fig. 4. To measure the energy band gap from absorption spectra, the tauc relation is used [16,17]

$$\alpha\, h\nu = A\, [\, h\nu - E_g\,]^n \qquad (2)$$

where hν is the photon energy, α is the absorption coefficient, E_g is the energy band gap, A is the constant, n=1/2 for direct band gap.

To measure the energy band gap from the absorption spectra, plot of $(\alpha\ h\nu)^2$ versus hν is plotted. The extrapolation of the straight line to $[(\alpha - \alpha_o)h\nu]^2 = 0$ axis gives the value of the energy band gap.

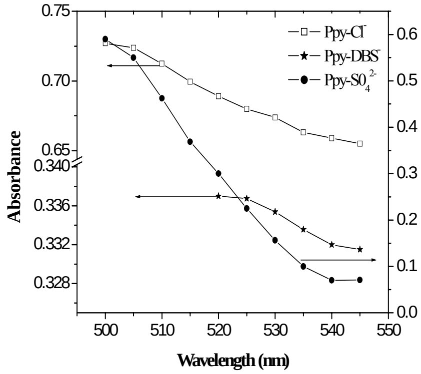

Fig. 4. Plot of absorbance vs. wavelength of polypyrrole doped with Cl^- , SO_4^{2-} and (DBS^-).

Fig. 5 show the plot of $[(\alpha - \alpha_o)h\nu]^2$ versus hν for the polypyrrole doped with Cl^- , SO_4^{2-} and (DBS^-) respectively. From the analysis of these graphs, the value of energy band gap of doped polypyrrole [Cl^- , SO_4^{2-} and (DBS^-)] comes out as 2.38, 2.39 and 2.33 eV respectively.

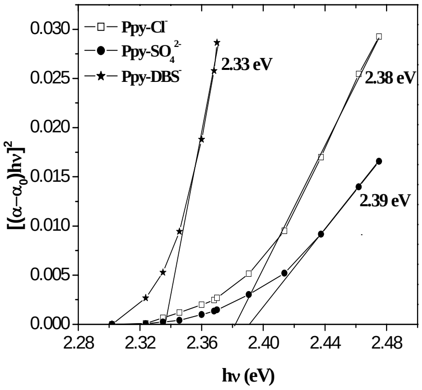

Fig. 5. Plot of $[(\alpha- \alpha_o) h\nu]^2$ *vs. hν for the polypyrrole doped with* Cl^- *&* SO_4^{2-} *and (*DBS^-*).*

4. Discussion

Polarons and bipolarons are dominant charge carriers, which are responsible for the electrical conduction in these samples. As the strength of the applied field increases the number of such polarons and bipolarons increases, resulting in the increment of current [12]. This results into increase in conductivity with voltage as more and more number of polarons and bipolarons are available in the system. Doping causes bond alternation from aromatic configuration to quinoid configuration, which is higher in energy and confines the charge and spin density to a self-localized structural deformation that is mobile along the chain [12]. This polaronic and bipolaronic structures result in a widening of the bonding and antibonding levels into the band gap which is responsible for an increase in the electrical conductivity with doping [15].

The conductivity of Cl^- doped polypyrrole is higher compared to SO_4^{2-} doped polypyrrole but band gap of Cl^- & SO_4^{2-} doped samples is almost same as proton doping is exists in both the samples. Therefore, higher conductivity is due to more acidic strength of Hydrochloric acid (HCl) that is inferred by the slight variation in energy band gap. The higher conductivity and lower energy band gap of DBSO doped polypyrrole is due to doping different form proton one. Here, bulky size of dopant (DBS^-) ion leads to more availability of charge carriers, which contributes to the formation of polaronic, bipolaronic sublevels with in the gap. This decreases the band gap and makes it more conductive. Here, experimentally observed band gap of polypyrrole is in good agreement with the theoretical data observed by Shujiang Yang et al. [11].

5. Conclusion

Alteration of donor groups is a successful methodology for inducing enhancement in conductivity and decrease of band gap in the polypyrrole conjugated polymers.

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[*] Corresponding author: s_vinodini@rediffmail.com