



# Hopping and tunneling transport over a wide temperature range in chemically synthesized doped and undoped polypyrrole

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## ABSTRACT

Polypyrrole was synthesized by the chemical oxidation method in the presence of phosphoric acid by varying oxidant to monomer molar ratio for the optimization of electrical conductivity. The conductivity in doped polypyrrole reached up to a maximum value of 9.18 S/cm. Granular morphology was observed in chemically synthesized polypyrrole. Neutralization of doped polypyrrole was done with aqueous ammonium hydroxide and three orders of reduced conductivity were obtained in neutral polypyrrole. Doped and undoped samples of polypyrrole were then electrically characterized over a wide temperature range of 10–300 K. The measured electrical conductivity rises with the increase in temperature and shows the semiconducting nature of the material. Strong and weak temperature dependence of conductivity was revealed by undoped and doped polypyrrole samples respectively. An effort has been made to explore the electrical transport in doped and undoped polypyrrole by charge transport models. The experimental data obeys Kivelson's hopping model in temperature range of 60–300 K and fluctuation assisted tunneling was the dominant conduction mechanism below 60 K.

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## 1. Introduction

In recent years, intrinsic conducting polymers with an extended  $\pi$ -electron system have been the subject of great attention among researchers worldwide because of their potential applications in modern technology [1–3]. The interest for the development of these materials is growing day by day to use them as standard material in various commercial and industrial applications. One other advantage of these materials is that their electrical conductivity can be tuned during synthesis by controlling the synthesis parameters [2–6]. Among conducting polymers polypyrrole (PPy), which consists of five membered heterocyclic rings, is by far the most investigated material due to its ease of processing, good chemical & environmental stability, higher conductivity compared to many other polymeric materials and no toxicity [2,7].

Polypyrrole can be prepared by oxidation of pyrrole (Py) or substituted pyrrole monomers by chemical or electrochemical methods. The chemical method is more suitable when one desires a large quantity of material and is widely used in an aqueous medium because of its technical simplicity [8–12]. The electrical conductivity of these polymers depends upon conditions of their preparation, primarily on the oxidant & dopant used and temperature of synthesis. By choosing optimum synthesis parameters conductivity can be enhanced to very high

values. In the present communication we have systematically studied the effect of oxidant to monomer molar ratio on the electrical conductivity and polymerization yield of polypyrrole when synthesized in the presence of ortho-phosphoric acid using ammonium persulfate (APS) as oxidant.

Polypyrrole is a non degenerate ground state conducting polymer in which polarons and bipolarons are considered as the source of electrical transport [1–3,10]. Various electrical transport models have been proposed to explain the charge transport in conducting polymers but the transport properties are not yet completely understood due to the great diversity associated with synthesis and processing of these conducting polymers [13–25]. In disordered materials or conducting polymers hopping and tunneling are two fundamental types of charge transport. Mott's variable range hopping (VRH) is the widely used mechanism applicable in PPy and other conducting polymers [16]. In case of electrochemically synthesized PPy a good deal of work has been done to explore the electrical transport [26–29]. However, a very few attempts have been made to explore the wide range temperature dependence of electrical conductivity in chemically synthesized PPy in the bulk form especially in undoped polypyrrole. In this study an attempt has been made to explore the dc-conductivity behaviour of doped and undoped PPy in the wide temperature range of 10–300 K.

## 2. Materials and methods

### 2.1. Materials

Pyrrole (Py) monomer (Spectrochem India), ortho-phosphoric acid and ammonium persulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (APS) provided by

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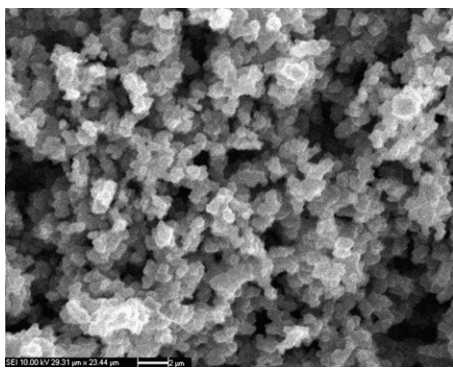


Fig. 1. SEM micrograph of chemically synthesized polypyrrole.

Merck were used as received. De-ionized water from Labpure systems having resistivity 18 MΩ was used in all experiments.

## 2.2. Chemical synthesis of polypyrrole

Polypyrrole was prepared by the chemical oxidation method using APS as the oxidizing agent in aqueous medium. Ortho-phosphoric acid and pyrrole monomer were completely dissolved in 50 ml of de-ionized water and cooled to 0–5 °C. APS dissolved in 50 ml of water (cooled to 0–5 °C) was added drop wise under continuous magnetic stirring to the cooled solution of Pyrrole and phosphoric acid. The polymerization reaction was carried out for two hours. The precipitate thus obtained were filtered and washed in excess of de-ionized water and methanol. After washing the collected polypyrrole was dried in a vacuum oven at 50 °C for 24 h.

The neutralization or undoping of polypyrrole was done by treating doped polypyrrole with 1 M NH<sub>3</sub>OH in de-ionized water for 10 h. The powder was then washed with de-ionized water and dried in a vacuum oven.

## 2.3. Polypyrrole characterization

For electrical characterization dry PPy powder was compressed into pellets and resistivity measurements were done with a standard four point probe method in order to eliminate the effect of contact resistance. Resistivity was calculated using the relation  $\rho = 4.532t(V/I)$  where,  $t$  is the thickness of the sample,  $I$  is current applied through the outer probes and  $V$  is the voltage measured across inner probes [3]. The four probe setup consists of a current source (Keithley 2400 source meter) and an electrometer (Keithley 6514) for voltage measurement. All measurements were performed in a vacuum sealed cold head by passing current continuously through the samples. Low temperature (10 K) measurements were performed with a closed cycle Helium compressor (Janis Research Inc.) and Lake Shore 331 temperature controller. Morphology of phosphoric acid doped PPy was studied with scanning electron microscopy.

## 3. Results and discussion

### 3.1. Polypyrrole morphology

The morphology of PPy is depicted in Fig. 1. Figure shows agglomerate creation and granular structure. Micrometer and sub micrometer sized granules are observed in the PPy morphology. Such type of morphology is generally reported when polymerization is done in the acidic medium.

### 3.2. Electrical conductivity

Electrical conductivity is the most important property of conducting polymers. In this study we have tried to find the

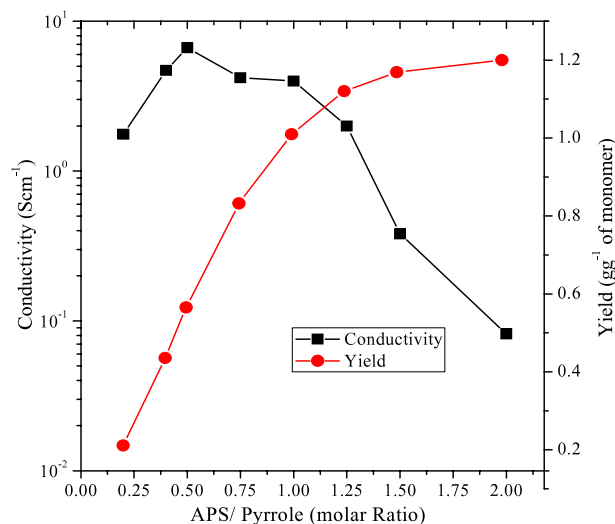


Fig. 2. Variation in electrical conductivity and polymerization yield of doped polypyrrole as a function of oxidant to monomer molar ratio.

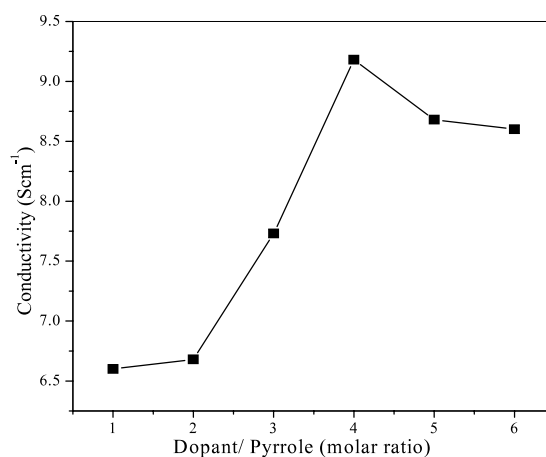
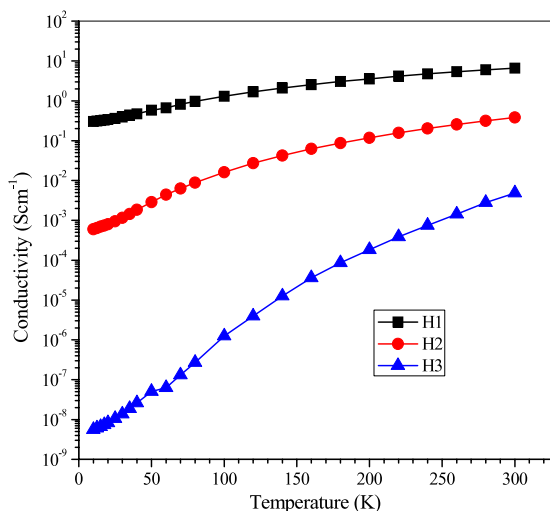


Fig. 3. Variation in electrical conductivity as a function of dopant to monomer molar ratio.

optimum composition for maximum conductivity of polypyrrole in the aqueous medium. The oxidant/monomer ratio was varied in steps from 0.2 to 2 at constant dopant to monomer ratio. The maximum conductivity of 6.65 S/cm was obtained for oxidant to monomer ratio of 0.5 and the conductivity was found to decrease with further increase of oxidant as shown in Fig. 2. A lower conductivity value of  $8.2 \times 10^{-2}$  S/cm was obtained for a molar ratio of 2. It is also observable that conductivity changes within an order of magnitude for oxidant to monomer ratio of 0.2 to 1 and it decreases rapidly after molar ratio of 1.

The yield of conducting PPy obtained in these experiments is also shown in Fig. 2 where it increases almost linearly up to oxidant to monomer ratio of 1 and then gets saturated for higher values. Increase in the amount of APS results in higher yield of PPy and more than 100% yield is obtained for an APS/pyrrole molar ratio of 1 and higher. Yield obtained above 100% may be due to the incorporation of phosphoric acid and due to over oxidation of PPy [30]. Over oxidation lowers the  $\pi$ -conjugation in PPy chains and thus results in reduced conductivity of the polymer. As shown in Fig. 2 the drop off in the value of conductivity obtained for a molar ratio higher than 0.5 may be due to the over oxidation of polypyrrole. Fig. 3 shows the electrical conductivity variation of PPy when various amounts of phosphoric acid was used in polymerization keeping the APS/Pyrrrole molar ratio fixed at 0.5. It was observed that maximum conductivity 9.18 S/cm is obtained



**Fig. 4.** Conductivity versus temperature plot for doped (H1 & H2) and undoped (H3) PPy samples.

for dopant to monomer molar ratio of 4 and also the variation in conductivity is very small with variation in dopant to monomer molar ratio from 1 to 6.

In this study three samples having room temperature conductivity 6.65 S/cm, 0.381 S/cm, and 0.00485 S/cm were selected for further characterization and designated as H1, H2, and H3 respectively. Here sample H3 is obtained after neutralization of PPy ( $\sigma = 9.18$  S/cm) with  $\text{NH}_3\text{OH}$ . Thus three orders of reduced conductivity were obtained after neutralization of doped polypyrrole, which is also in the semiconducting range. This shows that PPy conductivity is environmentally more stable than other conducting polymers where it reduces to insulating levels after similar treatment with ammonium hydroxide [4,31].

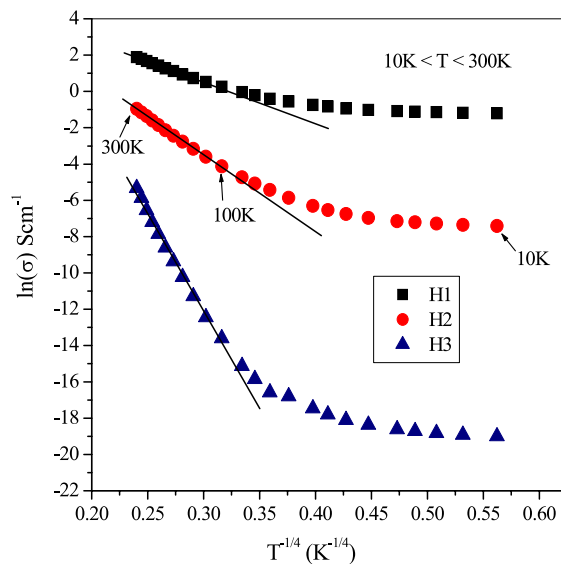
### 3.3. Temperature dependence of dc-conductivity

In order to explore the current transport mechanism in doped and undoped PPy, the temperature dependence of dc-conductivity was studied in the temperature range of 10–300 K. The dc-conductivity measurements trace the transfer of charge species throughout the specimen controlled by the site and height disorder of potential barriers [23]. Fig. 4 Shows variation of dc-conductivity with temperature for doped (H1 and H2) and undoped (H3) samples. In all cases conductivity increases with rise in temperature in the whole range, this is a characteristic of semiconducting behaviour. The conductivity span within the studied temperature range for doped samples H1 & H2 are small as compared with undoped sample H3. This indicates that the lower conductive sample is more sensitive to temperature changes and can be used as a better temperature sensing material, where larger change in conductivity is detectable for given small change in temperature. Thus for making of precision temperature sensors lower conductive material is better than higher conductive materials.

Generally the temperature dependence of conductivity in case of disordered semiconducting materials is described by Mott's variable range hopping (VRH) model [16]. According to this model conductivity is given by

$$\sigma(T) = \sigma_0 \exp[-T_0/T]^\gamma \quad (1)$$

where  $\sigma_0$  is high temperature limit of conductivity,  $T_0$  is the Mott's characteristic temperature and the exponent  $\gamma = 1/(1+d)$  determines the dimensionality of the charge transport in conducting medium. Value of ( $d = 3, 2, 1$ ) for three, two and one dimensional transport respectively.



**Fig. 5.** Plot of  $\ln(\sigma)$  as a function of  $T^{-1/4}$  in the temperature range of 10–300 K for doped (H1 & H2) and undoped (H3) PPy samples.

The measured dc-conductivity data was fitted in to Mott's 3d VRH model and is shown in Fig. 5. It shows that experimental data follows the VRH only in the temperature range of 300–100 K and below 100 K it shows a deviation from the VRH model.

To investigate the current transport mechanism in PPy another hopping model developed for non-degenerate ground state conjugated polymers is used. This conduction mechanism is known as inter-polaron hopping where hopping takes place between polarons and bipolarons both pinned by counter ions. This model was given by Kivelson and hopping processes are considered as isoenergetic [13–15]. Polymer structure is also considered to be modulated by optical phonons which results in the temperature dependence of conductivity. The temperature dependence of conductivity in such cases are approximated by a power law as [14]

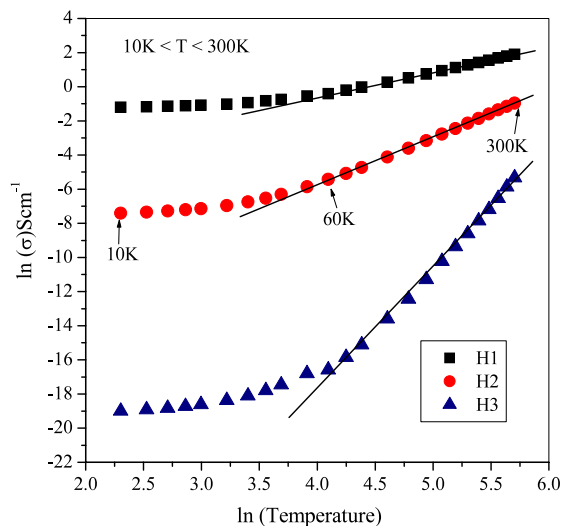
$$\sigma(T) = AT^n \quad (2)$$

where  $A$  is a constant and  $n$  is the power index.

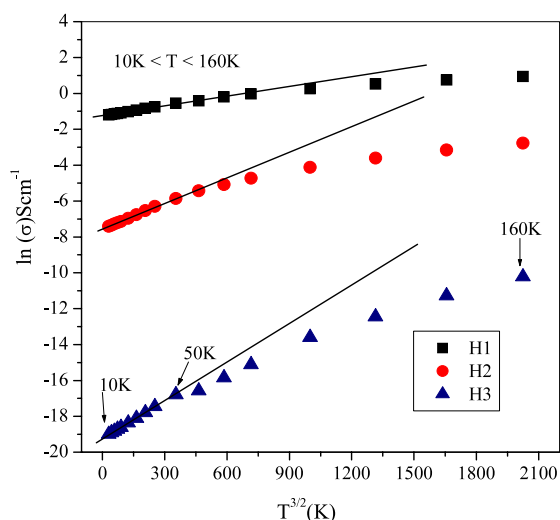
According to the Kivelson's model plot of dc-conductivity versus  $T$  on a log–log scale should give a straight line, if the measured temperature dependent conductivity is dominated by inter-polaron hopping. The measured conductivity data in the present work has been plotted as  $\ln(\sigma)$  versus  $\ln(T)$  for doped and dedoped PPy pellets and shown in Fig. 6. It is evident from Fig. 6 that experimental data follows the power law in the temperature range of 60–300 K and below 60 K it shows a deviation. Thus, the experimental data follows the Kivelson hopping mechanism only in the temperature range of 60–300 K with corresponding power index values 1.43, 2.81 and 7.11 for H1, H2 and H3 respectively. The power index values appear to be inversely related with temperature dependence of conductivity. For weaker temperature dependence (sample H1) the power index value is lower while for stronger temperature dependence (sample H3) it has a higher value.

Below 60 K temperature, PPy exhibits excess conductivity than predicted by the power law. This excess conductivity may arise due to dominance of other mechanisms at very low temperatures. This low temperature conductivity data was analyzed in terms of tunneling mechanism as follows.

According to the Fluctuation assisted tunneling model in case of complex organic molecules a large number of paths or many degrees of freedom are involved in carrier transfer, so it must contain the thermodynamic term entropy in temperature dependent conductivity such that the final form of conductivity can



**Fig. 6.** Plot of  $\ln(\sigma)$  as a function of  $\ln(T)$  in the temperature range of 10–300 K for doped (H1 & H2) and undoped (H3) PPy samples.



**Fig. 7.** Plot of  $\ln(\sigma)$  as a function of  $T^{3/2}$  in the temperature range of 10–160 K for doped (H1 & H2) and undoped (H3) PPy samples.

be written as [25]

$$\sigma(T) = \sigma_0 \exp[(aT)^{3/2}]. \quad (3)$$

Low temperature dc-conductivity data of PPy samples is plotted in Fig. 7 using Eq. (3).

It is evident from the Fig. 7 that experimental data of phosphoric acid doped polypyrrole samples follow this exponential behaviour in the low temperature range. However the upper temperature range for all samples is not the same i.e. sample H1 follows tunneling in the temperature range from 10 to 80 K, H2 follows 10 to 60 K and H3 follows 10 to 50 K. It was observed that higher conductive samples follow the fluctuation assisted tunneling model up to the higher temperature range as compared with lower conductive samples. In this model at lower temperatures in PPy acoustic modes are expected to dominate the electrical transport. So acoustic phonons play an important role at lower temperatures in carrier transport and lead to the  $\sim \exp[(aT)^{3/2}]$  temperature dependent conductivity.

Thus the experimental data shows a crossover for PPy samples in the low temperature near 50 K from exponential temperature

dependence of fluctuation assisted tunneling transport to simple power law behaviour of interpolaron hopping mechanism.

#### 4. Conclusions

We have investigated that electrical conductivity and yield of chemically synthesized polypyrrole is affected by oxidant to monomer molar ratio. The conductivity was found to be maximum for an oxidant to monomer molar ratio of 0.5 and it decreases rapidly for molar ratios greater than 1. However there is a marginal effect of variation in dopant to monomer ratio on electrical conductivity for a fixed oxidant to monomer molar ratio. The electrical conductivity of doped and undoped samples was studied over a wide temperature range. Stronger temperature dependence of electrical conductivity was observed in lower conductive or undoped samples while the temperature dependence is weak in case of doped or higher conductive samples. The temperature dependent electrical transport in doped and undoped PPy reveals the presence of two electrical transport mechanisms which become dominant at a particular temperature range. No single law fits the entire temperature range and PPy samples show dominance of isoenergetic hopping mechanism in the 60–300 K temperature range, and below 60 K fluctuation assisted tunneling mechanism dominates electrical transport.

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