

STRUCTURAL AND ELECTRICAL CHARACTERIZATION OF PROTONIC ACID DOPED POLYPYRROLE

V. SHAKTAWAT*, K. SHARMA, N.S. SAXENA

Semi-conductor & Polymer Science Laboratory, 5, Vigyan Bhawan, Deptt. of Physics, University of Rajasthan, Jaipur- 302055, India.

Polypyrrole doped with different protonic acid were chemically synthesized using ammonium persulfate (APS) as an oxidant. These samples were characterized through XRD and FTIR, which confirms the acid doping. I-V characteristics were carried out over the temperature range from 313 K to 483 K, which is found to be linear. The conductivity of PPy[PO₄³⁻] is highest among other doped one. Activation energies have been found to be 119.90, 43.94, 58.63 and 65.46 meV for PPy doped with sulfuric, phosphoric, oxalic and acetic acid, respectively.

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1. Introduction

Electrically Conducting polymers like polyaniline, polypyrrole etc. are of great interest as a new class of materials in the field of technology during last two decades, owing to their unique combination of characteristics: electronic, optical, magnetic properties and processing advantage of polymers [1]. They are implemented in different areas of corrosion protection, electro chromic displays, batteries, electrostatic materials, printed circuit boards, sensors and so on [2,3]. Development of such environmentally, chemically and electrically stable conducting polymers open up the possibility of new application for polymers.

Polypyrrole is readily obtained in its conducting form by electrochemical or chemical oxidation of pyrrole. Chemical synthesis of polypyrrole yields a conducting polymer that incorporates the anion as counterion, which electrically neutralizes the partially charged polymer chain [4]. It has been noticed that the conductivity of polypyrrole film is highly dependent on the nature of the anions in the polymerization solution.

A good deal of work has been done on doped polypyrrole in the film form but very few attempts have been made in the pellet form. In this work, we have focused on the measurement of electrical conductivity of polypyrrole doped with most usable laboratory reagents such as sulfuric, phosphoric, oxalic and acetic acid and an attempt has been made to study the temperature dependence of electrical conductivity of doped polypyrrole in bulk form.

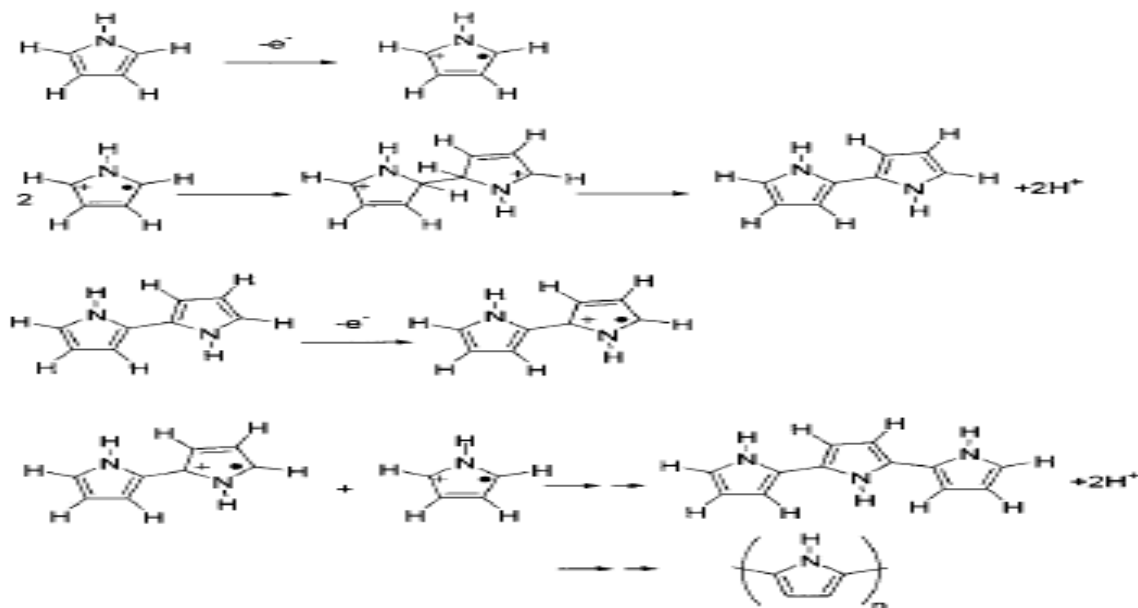
2. Material preparation and experimental techniques:

Polypyrrole was prepared by oxidative polymerisation of double distilled pyrrole using ammonium persulfate, (NH₄)₂S₂O₈ as an oxidant and sulfuric acid as dopant. The polymerisation was performed at 0°C temperature with oxidant/ monomer molar ratio 0.2 and dopant/ monomer molar ratio 0.5. The black precipitate resulting from the reaction is washed with distilled water and

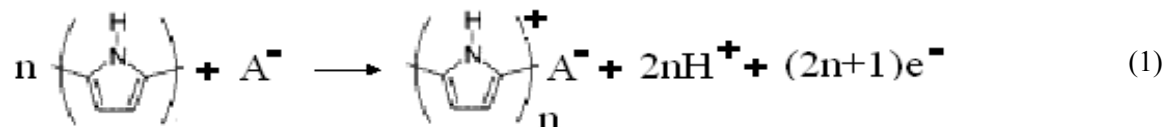
*Corresponding author: s_vinodini@rediffmail.com,

methanol and then dried under vacuum for 6-8 hrs [5]. Similarly, polypyrrole doped with phosphoric acid, oxalic and acetic acid was prepared.

The reaction for the formation of a polymeric unit [6, 7] is as follows:



Reaction with anion [7] as follows :



where, A^- (sulfate, phosphate, oxalate and acetate ion) are the counter anions incorporated along polymer backbone.

For electrical measurements, bulk sample in the form of pellets (diameter 12mm and thickness of approx 2 mm) were prepared and I-V characteristics of all the samples were carried out by Keithley electrometer/high resistance meter –6517 A [7].

3. Characterization

X-ray diffraction patterns of the sample, as shown in Fig.1 were taken at room temperature in order to study the structure of the material. The materials were found to be amorphous in nature. A hump is observed at low angle scattering for pure polypyrrole sample and it splits in to two broad peaks between 10° to 30° when it is doped with acids, as also reported elsewhere [8, 9]. First peak is found to be at $13-14^\circ$ for all doped sample and 2nd peak is shifted to higher value of theta due to larger size of the dopant. A similar investigation has been reported by Min-Kyu Song et al [10]. As the molecular weight of sulfuric and phosphoric acid is almost same, therefore, 2nd peak was found to be at same value of theta i.e. $21-22^\circ$. But as there is increase in the size or molecular weight of other dopant molecules, peak is shifted to higher value of theta for acetic and oxalic acid as dopant.

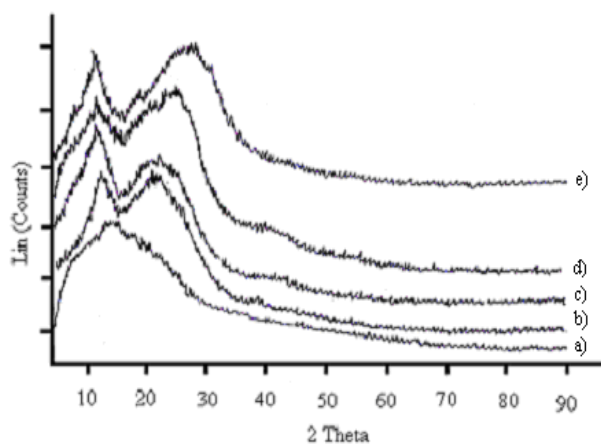


Fig. 1: X-ray diffraction pattern of PPy samples a) Pure b) PPy[SO₄²⁻], c) PPy[PO₄³⁻], d) PPy[C₂O₄²⁻] and e) PPy[CH₃COO]

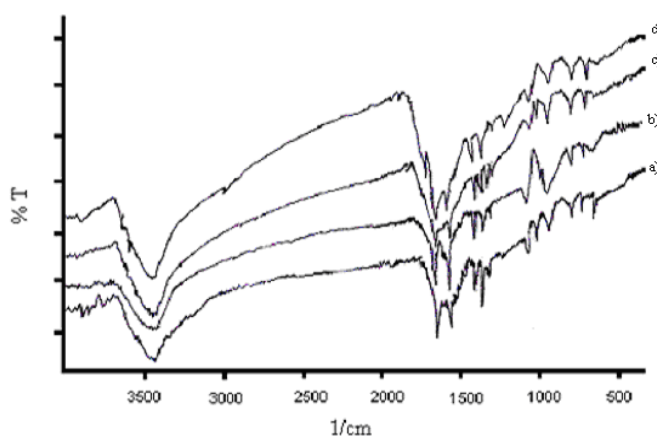


Fig. 2: FTIR spectra of doped polypyrrole a) PPy[SO₄²⁻], b) PPy[PO₄³⁻], c) PPy[C₂O₄²⁻] and d) PPy[CH₃COO]

The FTIR spectra of polymer powder obtained with KBr in pellet form is shown in Fig.2. The peak at 750-780 cm⁻¹ inferred the presence of polypyrrole and peak near 800 cm⁻¹ is due to the N-H out of plane bending absorption. The band observed near 950 cm⁻¹ is due to the C-H out of plane bending. The C=C stretching of aromatic compounds generally occur in the range of 1000-1100 cm⁻¹. The peak near 1300 cm⁻¹ is due to C-N stretching of the polymer and peak at 1380 cm⁻¹ is because of C-N⁺ stretching and C-C vibration [11]. The pyrrole ring stretching is obtained at 1400 cm⁻¹ and the peak at 1560 is due to N-H bending in secondary amines. The C=N stretching is observed at 1640 cm⁻¹. Secondary Amine (-NH) group can be recognized by absorption due to N-H stretching in the region 3300-3500 cm⁻¹[12].

The peak observed at 1035 cm⁻¹ and 690 cm⁻¹ in H₂SO₄ doped PPy are due to the symmetric stretching of sulphate group and the peak at 1008 cm⁻¹ in H₃PO₄ doped PPy is due to stretching of phosphoric group [13]. The peak at 1350 and 1050 cm⁻¹ is due to C-O stretching in polypyrrole doped with oxalic acid. Similarly, Peak at 1680 cm⁻¹ and 1250 cm⁻¹ in CH₃COOH doped PPy is due to C=O and O-H stretching of carboxyl groups present in the dopant [12]. These additional peaks in respective IR spectra confirm the acid doping in the chemically synthesized Polypyrrole samples.

4. Results

I-V characteristics of doped polypyrrole were recorded at different temperatures and are found to be linear as shown in Fig. 3.

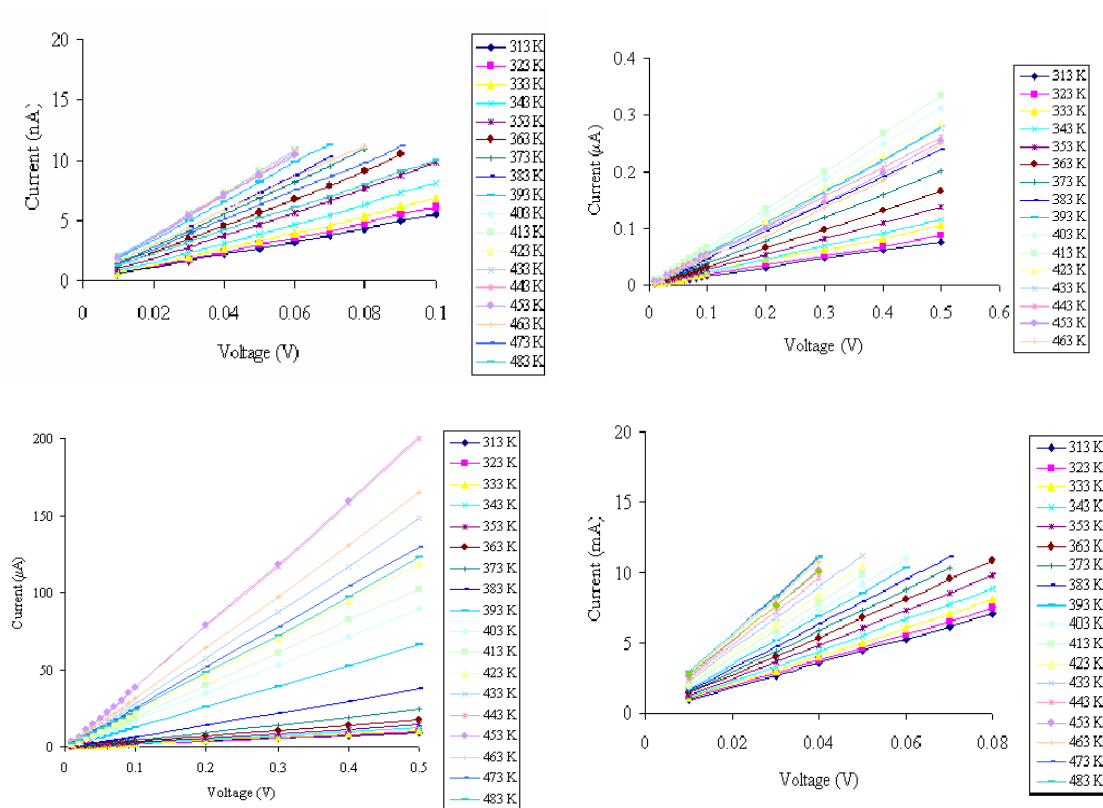


Fig.3: I-V Characteristics of doped polypyrrole (a) acetic acid, (b) oxalic acid, (c) sulfuric acid and (d) phosphoric acid

From the measured I-V characteristics of these samples, the values of electrical conductivities have been obtained at different temperature

$$\sigma = [(I \times L) / (V \times A)] \quad (2)$$

where I is the current, V is the voltage, L the thickness, and A the cross-section area of the sample. A comparative study of all samples suggests that the conductivity (σ) of polypyrrole doped with phosphoric acid (0.0196 S/cm) is higher than other doped sample. The conductivity decreases in the order $\sigma(\text{H}_3\text{PO}_4) > \sigma(\text{H}_2\text{SO}_4) > \sigma(\text{H}_2\text{C}_2\text{O}_4) > \sigma(\text{CH}_3\text{COOH})$. The values of electrical conductivity at 40°C have been tabulated in Table 1.

Table 1: The values of electrical conductivity at 40°C for all the samples

S. No.	Sample	Electrical conductivity (S/cm)
1.	Polypyrrole doped with H_3PO_4	1.96E-02
2.	H_2SO_4	3.26E-06
3.	$\text{H}_2\text{C}_2\text{O}_4$	3.09E-08
4.	CH_3COOH	8.81E-09

It is also observed that the current increases with the increase in temperature. The electrical conductivity of all the samples has been determined in the temperature range from 313 to 483K. Electrical conductivity data for all the polypyrrole samples were found to follow the Arrhenius model [14]:

$$\sigma = \sigma_0 \exp [-E_{ac} / kT] \quad (3)$$

where σ_0 is the conductivity at room temperature, E_{ac} is the carrier activation energy and k is the Boltzmann constant. Plots of $\ln(\sigma)$ vs $1000/T$ have been shown in Fig. 4.

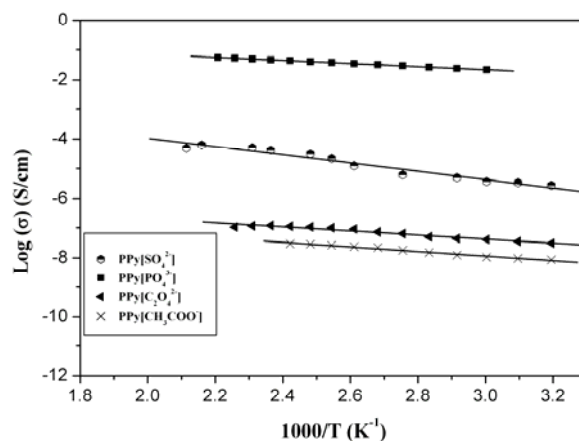


Fig. 4: Plot of $\log(\sigma)$ vs. $1000/T$

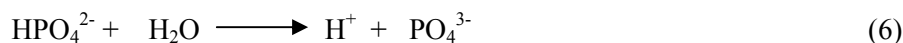
The slope [equal to $E_{ac}/1000k$] of these plots provides information about activation energies E_{ac} . It was found that activation energy is of the order of millielectron volt. Activation energies were found to be 119.90, 43.94, 58.63 and 65.46 meV for polypyrrole doped with sulfuric, phosphoric, oxalic and acetic acid, respectively.

5. Discussion

Under the influence of applied external field the localized (short range) motions of the trapped charges in the sample serves as effective electric dipoles [7], which contribute to the formation of polarons and bipolarons. As the strength of the applied field increases the degree of such lattice distortion increases, resulting in the increment of current. It is also observed that the current increases with the increase in temperature. Elevations in temperature lead to an increase in lattice vibration, which results in chain stretching.

Doping with protonic acid causes bond alternation from aromatic configuration to quinoid configuration, which is higher in energy and confines charge and spin density to a self-localized structural deformation that is mobile along the chain. The conductivity variation relies upon two important factors. The first one is attributed to acidic strength of acids and other to extent of doping in the samples during their preparation. The acidic strength decreases in the order $H_2SO_4 > H_3PO_4 > H_2C_2O_4 > CH_3COOH$. More the acidic strength of acid, more the dissociations of ions is observed during solution polymerization and hence, more and more number of quinoid rings are created along the polymer backbone. This results into more distorted lattice structure, which is responsible for formation of polarons and bipolarons leading to higher electrical conductivity.

Barring H_3PO_4 which in spite of the fact that it bears low acidic strength it still exhibits the higher value of conductivity i.e. three times higher as compared to polypyrrole doped with sulfuric acid. This is due to presence of lone pair and its triprotic nature. Due to its triprotic nature, orthophosphoric acid molecule dissociates up to three times, giving up an H^+ each time [15], as follows



Therefore, extent of doping increases with availability of H^+ ions required for formation of quinoid rings and more and more anions are introduced through out the matrix, which initiates the formation of polarons and bipolarons, which are responsible for conduction. Hence the conductivity increases almost threefold due to high extent of doping.

From Fig. 4, it is an interesting to note that the activation energy of polypyrrole doped with phosphoric is the lowest among other doped ones, but the conductivity is largest. This is due to the fact that larger doping of the anions as explained earlier, so introduced into the sample, produces larger varying fields along the chain. As a result larger number of polarons and bipolarons are created in the sample and the availability of these contributes to the enhancement in the conductivity of the sample. These polaron and bipolaron states are formed with in the gap. Conduction through these localized states is responsible for lower value of activation energy. But, higher value of activation energy of sulfuric acid doped polypyrrole is due to formation of continuous bipolaron bands with the doping. The separation between these bipolaron bands increases at the expense of the band edges.

6. Conclusion

FTIR spectra confirm the acid doping in the polypyrrole samples. Conductivity of polypyrrole doped with phosphoric acid is almost threefold barring its low acidic strength. Activation energies were found to be 119.90, 43.94, 58.63 and 65.46 meV for polypyrrole doped with sulfuric, phosphoric, oxalic and acetic acid, respectively.

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