

## Preparation of Polypyrrole (Ppy) With Oxidant Like Ammonium Per Sulfate (APS) and Dopant Like Lithium Per Chlorate ( $\text{LiClO}_4$ ) and Test Its Electrical Conducting Behavior With Temperature Variations

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### Abstract:

Polypyrrole (Ppy) was synthesized using Ammonium Peroxy Disulfate (APS) as oxidant in a standard ratio of monomer to oxidants by means of chemical oxidative polymerization method is presented. Attempts were made to increase the electrical conductivity by using dopant viz. Lithium per Chlorate ( $\text{LiClO}_4$ ). Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), X-ray diffraction (XRD) techniques were used to study the internal structure, material morphology, chemical nature of conducting polymers. The temperature dependence of the electrical conductivity of the Polypyrrole, prepared with APS and their dopant samples were studied at various temperatures from  $30^\circ\text{C}$  up to  $70^\circ\text{C}$  and was found to be in the range of  $10^{-3}$  S/cm. It was observed that the electrical conductivity decreased gradually with rise in temperature for all the samples. This behavior resembles the metallic conductors. It may be mentioned that pure Pyrrole is more like insulator but behaves like semiconductor in the doped form.

**Keywords:** *Conducting polymers, oxidants, dopants, electrical conductivity,*

### Introduction:

Electroactive conducting polymers have assumed a great importance in several technologies such as Display devices, Solar cells, Gas sensors and Actuators. Their ease of processing together with their chemically tunable properties makes them useful in electro- mechanical devices. Delocalized electronic states combined with the restriction on the extent of delocalization makes most conductive polymers behave like p -type semiconductors. As these polymers are Redox-active their conductivity can be changed by means of doping / de doping. A great deal of sensing applications are designed by exploiting the very nature of conducting polymers. Conducting polymers, such as polypyrrole (Ppy), polyaniline (Pani), polythiophene (PTh) and their

derivatives, have been used as the active layers of gas sensors since early 1980s. Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations .

The electrical transport in polymeric materials has become an area of increasing interest in research because these materials possess a great potential for solid state devices. Conducting polymer composites have attracted considerable interest in recent years because of their numerous applications in variety of electric and electronic devices. It has been found that such composites can exhibit some novel properties. Polypyrrole has been regarded as one of the most studied conducting polymers. The understanding of electrical properties, morphology and crystal structure of polypyrrole may be useful in improving the stability characteristics of these materials which are the key factors in governing the device performance.

Since the first paper of Shirakawa et al. in 1977, conducting polymers have attracted considerable interest because of their excellent physical and chemical properties originating from their unique conjugated system. Polypyrrole (PPy) is one of the most extensively studied materials due to its easy synthesis and good environmental stability. However, pristine Ppy is insoluble and infusible because of the rigidity of its molecular chains of  $\pi$ - conjugated structure. This poor conductivity and processability not only impede further investigation of its structure, but also limit its application in technology. So, efforts to overcome these drawbacks have led to numerous studies on the synthesis of PPy by both electrochemical and chemical routes.

It is well-known that using various dopants has contributed to the development of soluble PPy. Currently, aromatic acid derivatives and organic sulfonates are widely used, such as dodecylbenzene sulfonic acid (DBSA), p-toluenesulfonic acid (TsOH), etc. Lee et al. developed DBSA with surface-active properties as anionic additive to realize pyrrole (Py) solvation. Further studies pointed out that adding other large dopants could reduce the interchain links, resulting in the increase of the conductivity and solubility.

The physical properties of conducting polymers strongly depend on the type of dopant and the doping levels. The doping levels can be easily changed by chemical reactions at room temperatures. In the present paper we report preparation of polypyrrole in pure form and in the doped form by using dopants such as  $\text{LiClO}_4$ .

The oxidative doping of polypyrrole proceeds in the following way. An electron is removed from the p system of the backbone producing free radical and a spin less positive charge. The radical and cation are coupled to each other via local resonance of the charge and the radical. This combination of a charge site and a radical is called a polaron. This could be either a radical cation or radical anion. This creates new localized electronic states in the gap, with the lower energy states being occupied by single unpaired electrons.

Upon further oxidation the free radical of the polaron is removed, creating a new spinless defect called a bipolaron. At higher doping levels the polarons are replaced with bipolarons. The bipolarons are located symmetrically with a band gap of 0.75 eV for polypyrrole. This eventually, with continued doping, forms into a continuous bipolaron bands. Their band gap also increases as newly formed bipolarons are made at the expense of the band edges. For a very heavily doped polymer it is conceivable that the upper and the lower bipolaron bands will merge with the conduction and the valence bands respectively to produce partially filled bands and metallic like conductivity. This is shown below in Fig. 1.

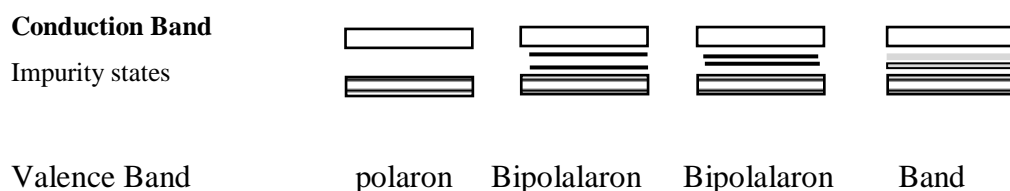


Fig.1 Modification of band gaps in Pyrrole due to polymerization

### Experimental methods and preparations:

Pyrrole was distilled before use and stored in dark place at  $-4^{\circ}\text{C}$ . 1 M Pyrrole solution was prepared by dissolving it in 100 cc of distilled water and stirred for 15 minutes for proper mixing. The Ammonium Peroxy Disulfate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  (APS), obtained from SDL, was of reagent grade and was used as received. The solution APS was used in the ratio of 1: 2.4 (monomer: oxidant) as discussed earlier, mixed in 100 cc of distilled water. The reaction was conducted at a temperature of  $5^{\circ}\text{C}$ .

The Pyrrole solution was mixed with the aqueous APS solution slowly under constant stirring for 30 minutes. Then the polymerization was conducted for 4 hours under constant stirring. This preparation was kept unagitated for 24 hours so that Ppy powder settled down. The Polypyrrole powder was filtered by Whatman's filter paper no.42 in vacuum and washed with

distilled water several times to remove any impurities present. The Polypyrrole was dried for 2 days at room temperature.

The resultant polymer is normally a black precipitate and can be isolated from the reaction medium by filtration. Water is thought to be the best solvent for the reaction taking into account the conductivity values and the percentage yield of Ppy.

In the present work, the preparation of polypyrrole was done in pure form and by using dopants such as LiClO<sub>4</sub>.

As the Polypyrrole obtained is in amorphous in nature, its conductivity can be tested only by preparing pellets of it at high pressures. Pellets of area of cross sectional of 1 sq.cm and thickness of 1mm is prepared under high pressure and vacuum to protect it from getting any impurities to be added. The conductivity was tested by two probe method at room temperature and various temperatures up to 70<sup>0</sup> C in the voltage range from 0 to 12 V.

A Scanning Electron Microscope (SEM) JEOL make JSM – 5400 model was used to examine the orphology of Polypyrrole Chemical structure was examined by FTIR measurements on Perkin – Elmer Ltd. make FTIR spectrometer model system 2000 using KBr pellets.

The Polypyrrole was characterized by XRD using PAnalytical (Philips), Netherland model XpertPro. The XRD pattern was recorded between  $2\theta = 10^0$  to  $40^0$ . The X – ray diffractometer uses CuK $\alpha$  radiation of  $\lambda = 1.5418 \text{ \AA}$  generated at 40Kv/ 20 ma.

The Electrical conductivity was studied using two probe methods which gives an idea about the bulk conducting properties of the sample.

### **Conductivity Measurements by two probe method**

The two-probe apparatus used for the conductivity measurements was indigenously build in our own laboratory. It has many facilities like temperature control, vacuum testing by rotary pump. The sample pellet was approximately 1 cm in diameter and is sandwiched between two copper electrodes. The upper electrode is spring loaded so that a pressure contact is made with the sample. The second electrode is at the base and in contact with a heating device. The automatic temperature control device controls the necessary temperature to within  $\pm 1^0$  C. The regulated power supply gives a variable DC voltage up to 15 volts. The voltage was measured with a digital multi meter and current through the sample was measured with the help of a digital ammeter. The voltage was varied from 0 to 12V in steps of 1V and the current was recorded.

The I-V characteristics were determined from room temperature to 70° C in steps of 10° C. The electrical conductivity  $\sigma$  was calculated from the above observations.

### Characterization, Results and Discussions:

#### Polypyrrole without dopant:

#### FTIR spectroscopy:

The FTIR spectrum of Ppy prepared is represented in Fig. 2. It shows strong absorption bands at around 3535  $\text{cm}^{-1}$  corresponding to N-H stretching. Other medium intensity peaks are observed at around 2900  $\text{cm}^{-1}$  - 2894  $\text{cm}^{-1}$  which can be attributed to aromatic C-H stretching vibrations. The presence of 815  $\text{cm}^{-1}$  band confirms that predominantly  $\alpha - \alpha'$  bonding exists.

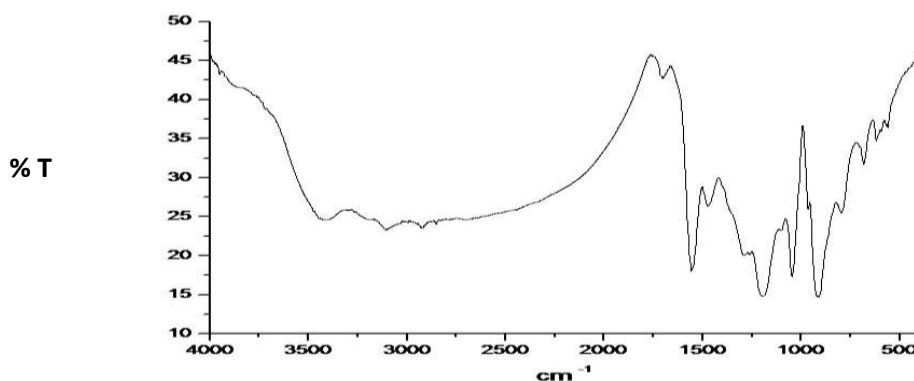


Fig 2: FTIR pattern of pure polypyrrole prepared using APS as oxidant (without dopant)

#### X-ray diffraction analysis:

A typical X ray diffraction pattern for pure polypyrrole is shown in Fig.3. The XRD pattern shows broad peaks in the region  $15^{\circ} < 2\theta < 30^{\circ}$  revealing that the resulting polypyrrole powders is amorphous in nature. This agrees well with the structure reported in literature. Such broad peak confirms that, short range arrangement of chains is formed.

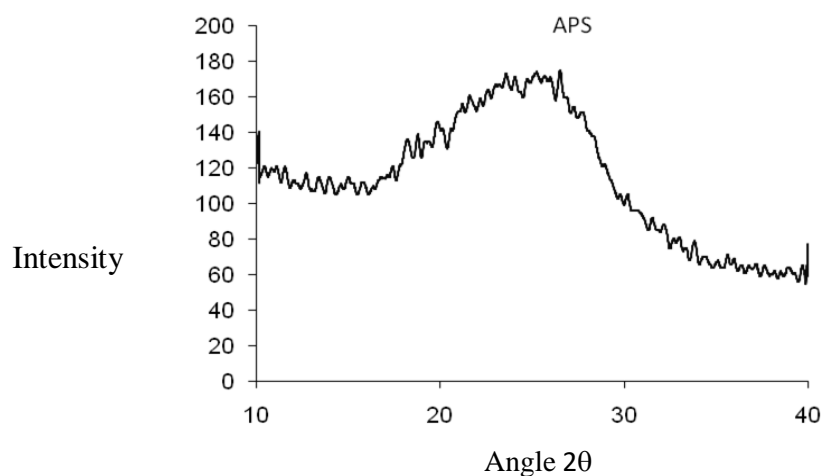


Fig. 3: X ray diffraction pattern for pure polypyrrole

### Morphology:

The morphological features revealed that mostly the growth of a polypyrrole is in the globular form. It can be seen from Figure that when polymerization was done with APS the average size of globules was found to be 0.62  $\mu\text{m}$ . The individual globules observed were nearly spherical and have a close packing. Such morphological features are very useful for gas sensing applications.

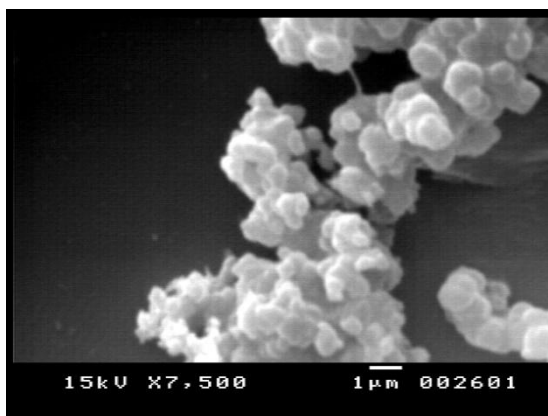


Fig.4: SEM of pure polypyrrole

### I-V characteristics:

Typical plots of I vs. V for polypyrrole prepared using APS as oxidant is given in Fig.5 A peak in rising current is observed at around 8 volts. After this peak there is a decrease in current for further increase in voltage was observed. This observation are well agree with the literature survey and may be due to the opposition of current by the flow of opposite charges in opposite

direction of degradation of sample. The same behavior was repeated for I vs V was studied for higher temperatures. However, voltage for peak current ( $V_p$ ) decreases with temperature. It shows that the charges of opposite kind are generated more in numbers as temperature increases. The conductivities were found in the range of  $1.0$  to  $4.8 \times 10^{-3}$  S/cm.

The justification for the conductivity of polypyrrole can be explained by assuming that, additional energy bands are formed above the valence band and just below the conduction band. This reduces the energy gap and the doping leads to semi conduction. Thus it is expected that increasing temperature will lead to increase of energy for an electron in the valence band which jumps to conduction band and hence the conductivity should increase with the temperature. However the present studies revealed that the materials do not behave like semiconductor but like metals where the conductivity is decreasing with temperature. Such behavior can be caused due to the large number of intermediate energy states in the energy gap region. Voltage for peak current decrease with increase in temperature. This shows that  $V_p$  is inversely proportional to temperature.

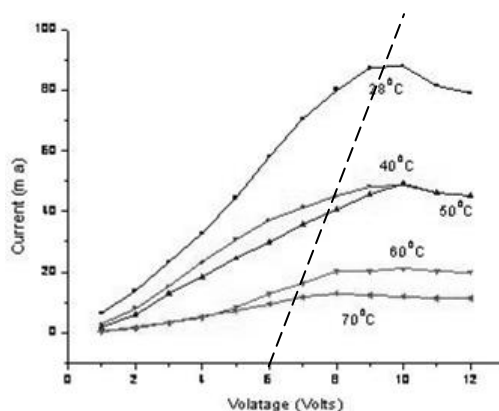


Fig. 5: I vs V graph of Ppy with APS as oxidant at various temperature

#### Effects of dopant $\text{LiClO}_4$ :

The Polypyrrole was prepared by chemical polymerization method using APS as oxidant and dopants such as  $\text{LiClO}_4$ . The structure and morphology of these materials has been investigated using the methods of FTIR, X - Ray diffraction and SEM. The electrical conductivity has been measured by two probe method. All the samples were tested for conductivity for various temperatures from  $30^\circ\text{C}$  to  $70^\circ\text{C}$

### FTIR spectroscopy:

The Polypyrrole powders prepared with dopants were analyzed by FTIR. FTIR spectra showed the main characteristic peaks around  $685\text{ cm}^{-1}$  corresponds to C-C out of plane ring deformation vibrations or C-H rocking,  $982\text{ cm}^{-1}$  to  $925\text{ cm}^{-1}$  corresponds to C-H out of plane deformation vibration band of the ring,  $1047\text{ cm}^{-1}$ . These peaks were observed in the present work for preparations using APS as oxidants and dopant such as  $\text{LiClO}_4$  agrees well with the ones available the literature, confirming the formation of Polypyrrole.

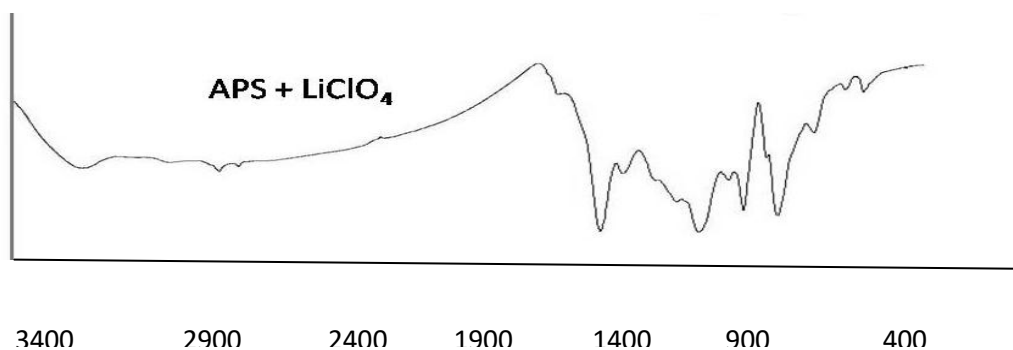


Fig.7. FTIR pattern for polypyrrole prepared using APS as oxidant and  $\text{LiClO}_4$  as dopant

### X-ray diffraction analysis:

The diffraction peak centered at around  $25.4^\circ$  for pure pyrrole shows some displacement when we go to the doped ones. In general the doping leads to shift the peaks toward the lower angle. This indicates that the inter planer spacing increases with the addition of dopants. This would make the chains get apart from each other due to the large sizes of the dopant molecules.

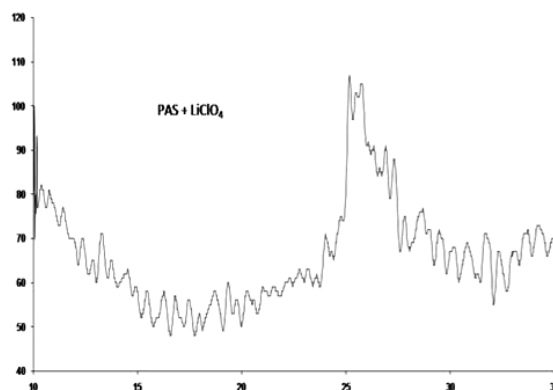


Fig. 8: XRD of Ppy prepared with APS as oxidant and  $\text{LiClO}_4$  as dopant.



### Morphology:

The morphological features of polypyrrole synthesized chemically and electrochemically have revealed that mostly the growth is in the globular form but changes some time due to dopant molecules

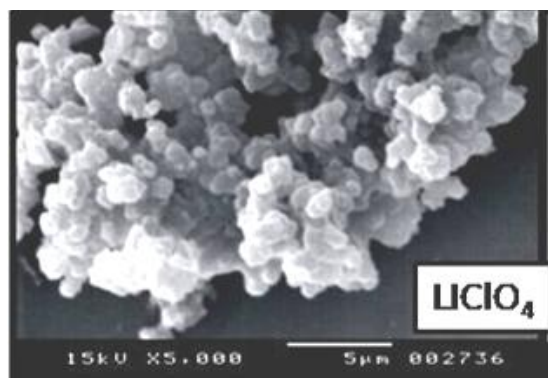


Fig. 9: Improvement in polymerization of Polypyrrole due to dopant LiClO<sub>4</sub> .

### I-V characteristics:

Typical plots of I vs. V for polypyrrole prepared using APS as oxidant and LiClO<sub>4</sub> as dopant is given in Fig.7. It was observed that the electrical conductivity of polypyrrole increased when dopants were used. Nearly linear relationship of the graph of I vs V curve was noted upto 8 volts for samples prepared using APS + LiClO<sub>4</sub>. After these peaks when voltage was increased further, a decrease in current was observed. The reason for such departure from ohm's law is either that the current is mainly contributed by ions or degradation of the sample at higher voltage. However, the latter reason can be ruled out as the temperature variation of the I vs V plot show decreasing current with increase in temperatures.

The temperature dependence of the electrical conductivity of the polypyrrole, prepared with APS and their doped varieties was studied at various temperatures from 30<sup>0</sup>C up to 70<sup>0</sup>C. It was observed that the electrical conductivity decreased gradually for all the samples. This behavior resembles the metallic conductors. It may be mentioned that pure pyrrole is more like insulator but behaves like semiconductor in the doped form. The mechanism of conduction is supposed to be by polarons and bipolarons formation due to the dopants molecules.

In case of polypyrrole the absence of electron in the chain leads to formation of holes i.e. p-type conduction. Thus addition of dopants leads to the modification of energy levels.

Additional energy bands are formed above the valence band and just below the conduction band. This reduces the energy gap and the doping leads to semiconduction. Thus it is expected that increasing temperature will lead to increase of energy for an electron in the valence band which jumps to conduction band and hence the conductivity should increase with the temperature. However, the present studies revealed that the materials do not behave like semiconductor but like metals where the conductivity is decreasing with temperature. Such behavior can be caused due to the large number of intermediate energy states in the energy gap region. In the present studies the doping level

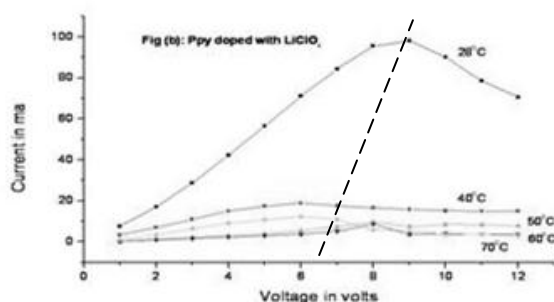


Fig. 10: I vs V graph of Ppy prepared with APS as oxidant at various temperature was 10% which is comparatively high and leads to overlap of a large number of energy states. In addition, the size of the dopants ions  $\text{ClO}_4$  is quite large and overlap of energy states can occur. Thus, the temperature dependence can be understood.

Table 2: X ray peak position, Half width, Globular size and conductivity of Ppy prepared using APS and various dopants.

Sample	X ray Peak position	X ray half width	SEM size of globule	Conductivity at R.T. over a linear portion of curve
Pure Polypyrrole	25.4 <sup>0</sup>	8 <sup>0</sup>	0.59 $\mu\text{m}$	1.70 X 10 <sup>-3</sup>
Polypyrrole with LiClO <sub>4</sub>	25.27 <sup>0</sup>	3.24 <sup>0</sup>	0.89 $\mu\text{m}$	1.02 X 10 <sup>-3</sup>

### **Conclusions:**

It was found that while doing chemical synthesis of polypyrrole in pure or in doped form, the ratio of 1: 2.4 monomers to oxidant is used. Addition of dopants like  $\text{LiClO}_4$  affects positively on the structure and morphology which affects their electrical properties. The electrical conductivity gets enhanced due to addition of dopants. As suggested by structural morphology and XRD the pure Pyrrole is behaving like an insulator but doping convert it in to semiconductor form. This was confirmed by IV characteristics also. This can be explained by considering the formation of additional energy bands between valance and conduction band due to the dopants molecules. This reduces the energy gap and the doping leads to semi conduction. The temperature dependence of the electrical conductivity of the Polypyrrole, prepared with APS and their dopant samples were studied at various temperatures from  $30^{\circ}\text{C}$  up to  $70^{\circ}\text{C}$  and was found to be in the range of  $10^{-3}$  S/cm. It was observed that the electrical conductivity decreased gradually with rise in temperature for all the samples. This behavior resembles the metallic conductors.

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