

# Synthesis And Structural Study of Polypyrrole Prepared via Different Routes Using Potassium Permanganate (KMnO<sub>4</sub>) as Oxidants

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**Abstract:** Conducting Polymers move from primarily passive materials to active materials with useful optical, electronic, energy storage, and mechanical properties. A representative of conducting polymer (Polypyrrole) was synthesized by polymerization of Pyrrole monomer using KMnO<sub>4</sub> as an oxidant. Synthesis was carried out by varying various parameters to achieve optimum properties. The internal properties of Polypyrrole were investigated by FTIR, SEM, and X-ray diffraction analysis. Internal electrical conductivity was studied by two probe methods. It was found that Polypyrrole synthesized for 3 hours using KMnO<sub>4</sub> has the best-conducting properties and yield is also maximum in the process.

**Index Terms:** Conducting polymers, Polypyrrole, oxidants, FTIR, SEM

## I. INTRODUCTION

Various conducting polymers, like Polypyrrole (Ppy), Polythiophene (PTh), polyaniline (Pani), along with their derivatives, were used as a gas sensor since 1980 [3]. The synthesis of conducting polymers by various methods is described in detail in several research journals [4]. Conducting polymers can be synthesized in many ways [5] through chemical polymerization, photochemical polymerization [6], inclusion polymerization [9], solid-state polymerization [10], plasma polymerization [11], electrochemical polymerization, and soluble precursor polymer preparation. Chemical or electrochemical Synthesis of conducting polymers is found to be the simplest process with maximum yield, and it also allowed modifying molecular chain structure conveniently by copolymerization or other structural derivations [13]. Polypyrrole has been the master player in conducting polymers because of its high conducting nature, stability towards environmental changes as well as improved mechanical properties. It has been found to have many applications in electronic devices, mobile batteries, various sensors, and chromatographic stationary phases [14]. The easiest way to synthesize Polypyrrole is chemical or

electrochemical polymerization. It has high conductivity and great thermal stability as well as environmental stability. Its properties can be altered by changing its oxidized and reduced states. Its non-toxic nature makes it convenient to be used in various medical applications. [16]. Many researchers have reported polymerization of Polypyrrole using iron chloride (FeCl<sub>3</sub>) [17,18] The use of APS (ammonium per sulfate) as an oxidant is mainly focuses on conductivity behavior. In this research, synthesize Ppy was done using KMnO<sub>4</sub> as an oxidant by varying temperature and time of polymerization. The objective was to try different oxidant which is not so strong and research is focused on to locate optimum conditions which will give maximum yield with desired properties of the final product.

## II. MATERIALS AND METHODS

Pyrrole (Sisco Research laboratory, 99% pure) was distilled before used. 1 M Pyrrole solution was prepared by dissolving it in 100 ccs of distilled water and stirred for 15 minutes for proper mixing. The KMnO<sub>4</sub> obtained from SDL was of reagent grade and was used as received. The solution of KMnO<sub>4</sub> was prepared using 100 ccs of distilled water. The reaction was conducted at a 50C temperature.

As the solubility of KMnO<sub>4</sub> is not very high, only 0.1 M KMnO<sub>4</sub> was prepared in 100 ml distilled water. Thus in this monomer: the oxidant ratio could not be preserved as 1:2.4 as in the case of FeCl<sub>3</sub>. A solution of Pyrrole having 1 molarity was prepared using distilled water. 0.1 M of KMnO<sub>4</sub> solution was prepared. Both these solutions were mixed slowly under constant stirring for 30 minutes. Then the polymerization was conducted for several hours under constant stirring. This preparation was kept unagitated so that Ppy powder settled down. The Ppy powder was filtered out under vacuum and dried completely at room temperature.

### III. CHARACTERIZATION

#### a. FTIR spectroscopy:

FTIR spectrometer model Perkin-Elmer system 2000 was used to study chemical properties using KBr pellets. The FTIR spectrum of the Ppy prepared is represented in Fig.1. It shows strong absorption bands at around  $3408\text{ cm}^{-1}$  corresponding to N-H stretching. Other medium intensity peaks are observed at around  $2923\text{ cm}^{-1}$  -  $2853\text{ cm}^{-1}$  which can be attributed to aromatic C-H stretching vibrations. The absorption band at  $1528\text{ cm}^{-1}$  is related to C=C / C-C stretching vibrations of the Pyrrole ring, which are absent in our spectra. The band at  $1405\text{ cm}^{-1}$  reflects the C-N stretching vibrations of the ring. The region at  $1261\text{ cm}^{-1}$  -  $1164\text{ cm}^{-1}$  corresponds to breathing vibrations of the Pyrrole ring. The peak at  $1262\text{ cm}^{-1}$  attributable to C-N in-plane deformation vibration mode. The bond of C-H in-plane deformation vibration is situated at  $1066\text{ cm}^{-1}$  and of the C-C out of plane ring deformation vibrations or C-H rocking is at  $677\text{ cm}^{-1}$ . The C-H out-of-plane deformation vibration band of the ring has a peak at  $945\text{ cm}^{-1}$ .

To determine the mode of bonding, When  $\alpha - \alpha'$  bonding i.e. 2, 5 coupling exists a strong absorption band occurs at  $788\text{ cm}^{-1}$ . On the other hand, when  $\alpha - \beta'$  bonding i.e. 2,4 coupling occurs, we get absorption bands at  $730\text{ cm}^{-1}$  and  $803\text{ cm}^{-1}$ . It was indeed observed that when  $\text{KMnO}_4$  was used as oxidants in the chemical polymerization method we observed bands at  $730$  and  $803\text{ cm}^{-1}$  with weak intensity. This shows that predominantly  $\alpha - \beta'$  bonding exists.

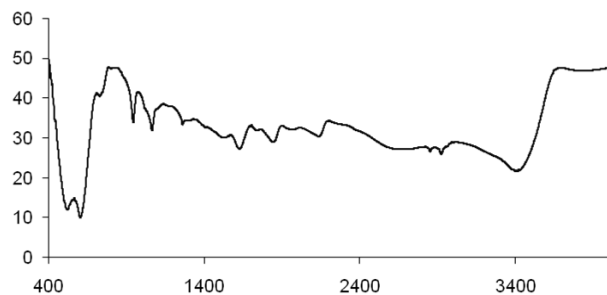


Fig.1. FTIR pattern for polypyrrole prepared using  $\text{KMnO}_4$  as oxidant

Table 1: Bonding structure of FTIR for Polypyrrole prepared using  $\text{KMnO}_4$

#### b X-ray diffraction analysis:

X-ray diffraction pattern for Polypyrrole prepared using  $\text{KMnO}_4$  as oxidant is shown in Fig.2. The XRD patterns for samples using the dopants also show just one peak of low intensity at  $19.47^\circ$ . The remaining part is quite different from the Ppy prepared using  $\text{FeCl}_3$  and APS has given in the preceding sections of this chapter. In addition, two low-intensity peaks at  $33^\circ$  and  $37^\circ$  were also observed.

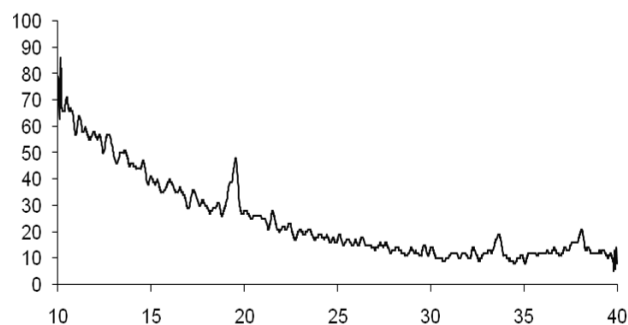


Fig. 2 XRD pattern for polypyrrole prepared using  $\text{KMnO}_4$  as oxidant

#### c Morphology:

The morphological features of polypyrrole synthesized chemically revealed that mostly the growth is in the form of crystalline platelets of somewhat triangular shape. The average size of these plates is about 30 microns on which some globular growths are visible. A typical SEM image is shown in Fig.3 (a & b). The individual granules observed were irregular in shape and sizes. It can be seen from Fig. that when polymerization was done with  $\text{KMnO}_4$  the average size of granules was found to be 0.6  $\mu\text{m}$ . It seems that such granules are growing one over the other and forming a continuous structure.

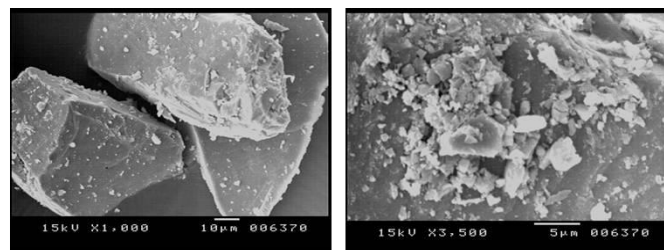


Fig. 3 SEM of Ppy prepared by using  $\text{KMnO}_4$  as an oxidant

#### d. I-V characteristics:

Typical plots of I vs. V for polypyrrole prepared using  $\text{KMnO}_4$  as oxidant is given in Fig. 5. Nearly linear relationship of the graph of the I vs V curve was noted up to 12 volts. The conductivities were found in the range of  $1.0 \times 10^{-3}$  to  $4.6 \times 10^{-3}\text{ S/cm}$ .

The temperature dependence of the electrical conductivity of the polypyrrole, prepared with  $\text{KMnO}_4$  was studied at various temperatures from  $300\text{C}$  up to  $700\text{C}$ . It was observed that the electrical conductivity decreased steadily.

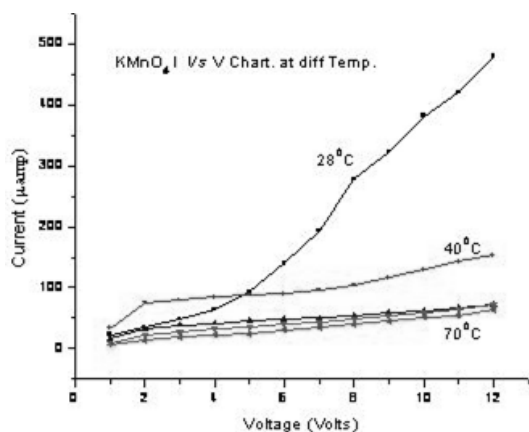


Fig. 5 I vs V graph of Ppy prepared with  $\text{KMnO}_4$  as oxidant at various temperatures

### CONCLUSIONS & RECOMMENDATIONS

The materials prepared by  $\text{KMnO}_4$  as oxidant, when analyzed carefully using several methods, show that the mode of polymerization is different from that observed for materials produced using  $\text{FeCl}_3$ . Based on the experimental results, the following conclusion can be made.

1. The color of the product is brownish-black rather than total black. This shows that the length of the chain may be small in comparison to other polymers.
2. Electrical conductivity is found to be of the order of  $10^{-6}$  S/cm. in contrast to the other products where conductivity is in the range of  $10^{-2}$  S/cm. Further, the electrical conductivity was found to be increasing with temperature for all the doped varieties.
3. The FTIR spectra show that in addition to bonding there also occurs bonding. An absorption band appears at 522 for pure  $\text{KMnO}_4$  with very high intensity. This is rather broadband and shift towards a higher wave number in the case of  $\text{KMnO}_4$  with  $\text{LiClO}_4$  (560),  $\text{KMnO}_4$  with DBSA (551),  $\text{KMnO}_4$  with NSA (517), and  $\text{KMnO}_4$ -p-TS (520) as reported in various journals. The absorption band indicative of a-a' bonding which should appear at 790 is absent in all samples.,
4. SEM photographs reveal that the morphology is more planer flake-like material rather than spherical globules as seen in other varieties. This means that the chain length being small, it does not have sufficient length to coil on itself to produce well-grown spherulites.
5. The X-ray diffraction does not give the broad peak at  $26^\circ$  which is prominently observed when polymerization is carried out using  $\text{FeCl}_3$ . We observe 3 peaks of very low intensities at  $16^\circ$ ,  $33^\circ$ ,  $37^\circ$ . However, when dopants were used, some of these peaks were observed.

Thus the polymerization mechanism seems to be different when  $\text{KMnO}_4$  is used as an oxidant.

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