Chapter 2: Preparation of Polypyrrole films and techniques of investigation

2.1 Introduction

2.2 Various preparation methods

2.3 Preparation of Polypyrrole films

2.4 Fabrication of Sample holder

2.5 Investigation methods
   2.5.1 Fourier Transform Infrared Spectroscopy (FTIR)
   2.5.2 Differential Thermal Analysis and thermogravimetric analysis (DTA and TGA)
   2.5.3 X-ray diffraction analysis (XRD)

References
2.1 INTRODUCTION:

Heterocyclic polymers such as polypyrrole and polythiophene have attracted much attention due to their high conductivity and stability because, the polypyrrole has five membered heterocycles and can easily be synthesized using electropolymerization technique and having dopant counter ions shows high conductive properties. In this chapter various preparation methods are discussed.

2.2 VARIOUS PREPARATION METHODS:

First reported in 1979 polypyrrole stands out to be the most widely studied electronically conducting polymer (Rasika Dias et al 2006). Due to its favorable electronic properties, environmental stability and fast redox switching, polypyrrole finds large applications. Polypyrrole can be synthesized by the methods reported involves an oxidative polymerization route in which the use of oxidants such as Fe$^{3+}$, Ag$^{+}$, I$_2$, Br$_2$, AsF$_5$ or Cu$^{2+}$ has been reported (Bocchi V et al 1986). Out of all these oxidants, Fe$^{3+}$ tends to give very good quality and highly conductive polypyrrole composite. The typical monomer to oxidant ratio required for chemical synthesis is 1:2.33.

In order to improve mechanical properties of polypyrrole, polymerization of pyrrole monomer can be achieved mainly by four methods
1) Chemical polymerization, 2) Electro-polymerization 3) Plasma polymerization and 4) Micro-emulsion polymerization in presence of different counter ions. After polymerization popyrrole is obtained in the form of composite, blend, copolymer and thin film.

Already, research workers have adopted different techniques regarding the formation of composite of polypyrrole. Niva et al (1987) have reported the preparation of polypyrrole with a swollen film of polyvinylchloride (PVC). Chemical polymerization (Whang et al 1989) of pyrrole is carried out with FeCl₃ as initiator. Following reaction mechanism takes place in such a polymerization. Polypyrrole is probably the simplest of the conducting polymers to prepare using techniques based on original (Dall'Olio et al 1968) electrochemical synthesis. Figure (2.1)
shows schematic diagram of electro-polymerization apparatus used by Tsutsumi et al. (1994). Platinum plate (50×50×2 mm³) or glassy carbon (50×50×2 mm³) was used as working electrode and another platinum plate (50×50×2 mm³) was used as counter electrode with a spacing of 3 mm. Reference electrode of Ag/AgCl was connected with glass tube through KCl salt bridge. Constant potential was supplied. Two standard polymerization were employed. The first condition was for obtaining the sample film by varying the concentration of counter ion in polymer bulk. Polymerization was carried out using a platinum electrode in acetonitrile solution with 0.05 ml/L pyrrole monomer. The second condition was for obtaining the sample film by varying the types of counter anions in

\[
\begin{align*}
\text{NH} & \quad \rightarrow \quad \text{NH}^+ + e^- \\
2 \text{NH}^+ & \quad \rightarrow \quad \text{NHNH} + 2H^+ \\
& \quad \rightarrow \quad \text{NHN} \\
\text{N} & \quad \rightarrow \quad \text{NH}^+ + 2H^+ + e^- \\
\end{align*}
\]

Scheme: 2.1

---

Preparation of polypyrrole thin films and techniques of investigation .....48
electrode in propylene carbonate solution with 0.05ml/L pyrrole polymer bulk. Polymerization was carried out using a glassy electrode in propylene carbonate solution with 0.05 ml/L pyrrole monomer. The mechanism of polymerization of pyrrole is believed to produce via the radical cation of the monomer, which then reacts with a second radical cation of monomer to give a dimmer by elimination of two proton (Street et al 1983, Daiz et al 1981).

The plasma polymerization of pyrrole carried out by using a radio frequency source, which is coupled inductively with the reactor tube. Polymerization was initiated by glow discharge in the reactor tube. At the potential needed to oxidized the monomer, dimmer or higher oligomers would also be oxidized and thus could react further with the radical cation of the monomer to build the pyrrole chain as shown in scheme (2.1). Ions like iodine are doped during polymerization. It results in an increase in conductivity.

Recently a micro-emulsion polymerization technique was used to form a porous non-conducting matrix (Kaplin 1993, Kaplin et al 1994). The micro-emulsion is prepared using a surfactant and two monomers, one hydrophilic and the other hydrophobic. The surfactant affects the pyrrole electro-polymerization and the electrochemical properties of the conductive composites. These composites can be considered for
applications such as biosensor or corrosion protection.

An advance polymerization technique used by Li et al (2007) is lithographic technique called as multiphoton absorption polymerisation (MAP). In this method multiphoton absorption is used to expose a photoresist one volume element (voxel) at a time. Once the prescribed pattern has been scanned, the resist is developed to reveal the desired three dimensional structure.

A schematic setup for performing MAP is shown in figure(2.2). The excitation source is a Ti:sapphire oscillator. Optics may be placed in the laser beam to prevent reflections of returning to the laser and to control the pulse length, intensity and focal volume of the laser in the sample. The laser beam enters a microscope and is reflected through the objective into the sample, where it is focused. Three-dimensional patterns are scanned by moving the laser focus relative to the sample or moving the sample relative to laser. If the substrate upon which the fabrication occurs is transparent, then the fabrication process can be monitored using transmitted light, as exposure of the photoresist generally leads to a visible change to a refractive index. Samples are generally prepared on the substrate to which the photoresist adheres well, and the structure that are fabricated contact the substrate over the large enough area not to be
wash away upon development. The development stage usually involves washing the sample in a solvent or a series of solvents. In the negative-tone photoresist, the solvent washes away the exposed material, whereas for a positive-tone photoresist, it is the exposed area that are washed away. The development step often leads to some degree of shrinkage of the structure as well.

The resolution attainable with MAP is considerably fine. The most meaningful measure of the resolution attainable is the dimension of an isolated voxel. With 800 nm light it has been proven possible to fabricate voxels with transverse dimension smaller than 100 nm.

![Diagram of MAP setup](image)

**Fig. 2.2 Setup for MAP**

---

*Preparation of polypyrrole thin films and techniques of investigation* ....51
2.3 PREPARATION OF POLYPYRROLE FILMS:

Pyrrole monomer (E.Merck, Germany) was taken as received. Reagent grade methanol (Radial) was used as received. Polyvinyl acetate (PVAc) (Radial, medium molecular weight) was used without further purification as a counter polymer to prepare a polypyrrole (PPy) thin films. Reagent grade FeCl₃ (E. Merck, India) was used as oxidizing agent.

Poly (vinyl acetate) was first dissolved in methanol taken in a cleaned borosile test tube. Complete desolution of Poly (vinyl acetate) required 5-6 hours. FeCl₃ was then added to this solution with constant stirring for an hour. Lastly, pyrrole was added to the mixed solution and the system was kept in dark for an hour, so as to avoid the effect of light and to complete the polymerization. The color of solution was observed to be dark-green in initial stage and then it becomes black. After completion of reaction a conducting polypyrrole film, was prepared using solvent evaporation method by casting the mixture on leveled optically plane glass plate at 10-12 places to have the thin films of various thickness. The glass plate was placed as it is for 9-10 hours, so that methanol is completely evaporated. After sufficient drying the films were rinsed with distilled water and then with methanol to remove the excess amount of FeCl₃ from the surface of the film formed due to polymerization of pyrrole.
General formulation of solution was as given below.

For 1-weight percent (wt %) composition of polypyrrole, the concentration of Poly (vinyl acetate) and FeCl$_3$ were 15-wt % and 1 mole respectively. Pyrrole monomer was added $1/2.33$ times the FeCl$_3$ in molar ratio, so as to have maximum oxidation potential and maximum yield (Rasika Dias et al 2006) By using the above procedure, the conducting polypyrrole thin films were prepared for 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12 and 40-wt% by changing the weights of pyrrole monomer in the polyvinyl acetate solution.

For characterization and electrical conduction study, only 1, 5, 8, 10 and 40 wt% of polypyrrole films are taken.

2.4 FABRICATION OF SAMPLE HOLDER:

The sample holder used to measure the various electrical properties was designed and fabricated in the laboratory. It consists of two-brass electrodes, which are fitted on ceramic base with screws. Bolts permanently support one of the electrode with an exact geometrical alignment to a ceramic base. Another electrode is spring loaded with bolts to ce-
ramic base. Both the electrodes are exactly parallel to and in front of each other. This has been ensured by keeping the optically plane glass plate between the two electrodes. This sample holder works up to a temperature limit of 973K. The sample holder is used to measure dc electrical conductivity and for dielectric measurements of thin films. The schematic diagram of sample holder is shown in figure (2.3)
2.5 INVESTIGATION METHODS:

The characterization of materials is the most important factor to ascertain its nature and to determine the conditions of its isolation. In the absence of above information, a justified understanding of the electrical behavior of the conducting polypyrrole is difficult.

The understanding of properties in the solids has relied chiefly upon structural information obtained from the wide range of physical methods. Spectroscopic and resonance techniques have played an important role, of course, but the more definitive structural data has largely been acquired using X-ray diffraction method.

Thermal analysis is made up of various techniques for studying thermal behavior of materials. When the material is heated or cooled, its structure and chemical composition undergo changes; such as decomposition, transition, expansion, melting, fusion etc. To measure transformations different parameters are followed up as a function of temperature.

To characterize the material following techniques have been used.

2.5.1 Fourier Transform Infrared Spectra (FTIR):

The infrared spectra of polypyrrole in its oxidized and neutral forms was first reported by street et al (1982). The FTIR of polypyrrole thin films was studied in the wave number range of 430 to 4000 cm\(^{-1}\) on Bruker
Electrical Conduction In Conducting Polypyrrole Thin Films

IFS 66v FTIR spectrometer. The KBr pellet technique was used. All the spectra are taken at Reginal Sophisticated Instrumentation Centre, Indian Institute of technology, Cennai. The vibrational frequencies and different group positions in polypyrrole thin films were determined. The detailed discussion on FTIR is given in chapter 3.

2.5.2 Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA):

Thermal analysis of polypyrrole incorporates those techniques in which some physical parameters are determined and recorded as a function of temperature. DTA technique was used to determine transition temperature and crystallization temperature. DTA study of sample was done at R.S.I.C. Indian Institute of Technology, Chennai. The experimental conditions for DTA of thin films of polypyrrole with different weight percent are given below.

Range of temperature : Room temperature to 800°C
Rate of heating : 10°/min
Reference : Alumina
Atmosphere : Nitrogen

Thermo-gravimetric analysis gives the useful information like thermal stability of material, weight loss by heating, reaction rate and de-
composition temperature.

2.5.3 X-ray Diffraction Analysis (XRD):

The structure of polypyrrole is investigated by means of X-ray diffraction and macroscopic actuation measurements. X-ray diffraction (XRD) uses the interference of elastically scattered photons of a periodic lattice of atoms to probe the structure of crystalline matter. This technique is very common in chemistry and materials science for evaluating crystal structures (Warren 1969, 1989,) so a complete review will not be provided; however, there are some significant differences when using this technique to look at polymers (Alexander 1969 and Dakudo et al 1972).

The X-ray diffraction spectrum of polypyrrole thin film is shown in figure (3.7). This analysis was done at National Bureau of Soil Survey and Land Use Planning Nagpur by Philips Analytical analyzer.
REFERENCES:


Castillo – Ortega and M M Inoue M (1989) *Synth Metal* **28** C65 – 70


Dall’Olio A, Dascola Y, Varacco V and Bocchi C R (1968) *Academic Sci Ser C* 267


Kaplin D A (1973) *Ph.D. Desertation  Case Western Univerity USA*
Kaplin D A and Qutubuddin S (1994) *Synth Metals* 63 187


Niva O, Kakuchi I and Tananura T (1987) *J Polymer* 19 1291


Visky C, Pinter E, Fulei T and Patakfalva R (2005) *Synth metals* 152 13-16

Vshnuvardhan T, K Kulkarni V R, Basavaraja C and Raghavendra S C 2006 *Bull Mater Sci* 29(1) 77-83

Whang Y E Han I H and Miyata 1989 *Poly Phy* 32 899-906


---

*Preparation of polypyrrole thin films and techniques of investigation*....59
Wynne W and Street G B (1985) *Macromolecules* 18 2361