2.1 Introduction

The conversion of closed shell system to a corresponding cation or anion radical and the stability of the product is the most important characteristic feature of monomer molecules for the formation of conducting polymer. The most preferred method of preparation of polymer is either chemical or electrochemical oxidation of monomer in aqueous medium. The synthesis of polymer by either of these methods depends upon the intended application of the polymer. Whenever better ordered polymers are required, the electrochemical method is preferred.

Nowadays, electrochemical synthesis has become a common method to synthesize electrically conducting polymers. The popularity of this method can be attributed to two characteristics namely simplicity and reproducibility.

In the late 1960s, a particularly noteworthy investigation sparked interest in the field of electrochemical synthesis of conducting polymers. In the year 1968, Dall’olio et al. [1] produced ‘pyrrole black’ through the electrochemical oxidation of the pyrrole in aqueous sulfuric acid. Another considerable excitement was generated in 1979 by Diaz et al. [2] in synthesizing coherent free standing film of polypyrrole that had high conductivities. Traditionally, electrochemically initiated polymerization reactions have occurred in bulk solution, and not near the surface of the electrode [3].

2.2 Chemical Synthesis of Polypyrrole

Figure 2.1 (a-c) shows an outline of the polymerization scheme for pyrrole. The mechanism for polymerization can be deduced from several observations. First, a radical cation produced by the initial oxidation of pyrrole dimer, makes an electro-philic attack on a neutral molecule [4]. The coupling of two radical is favored over electro-philic
attack, since the electrochemical polymerization reaction occurs only when the potential applied to oxidize the polymer species present at the electrode surface is essentially zero. Second, the amount of charge consumed during polymer formation has an initial linear time dependent and is independent of pyrrole concentration during constant potential electrolysis [5]. The evidence indicates that the entire electrochemical reaction occurs at the electrode surface.

![Diagram of free cation radical generation](image)

**Figure 2.1(a): Generation of free cation radical**

![Diagram of polymer chain propagation](image)

**Figure 2.1(b): Propagation of polymer chain**

![Diagram of polymer chain formation](image)

**Figure 2.1(c): Formation of polymer chain**

Third, the dimmer bipyrrrole, the trimer and the polymer oxidize more readily than pyrrole monomer, itself and thus are in an oxidized state during polymerization [6].
Therefore coupling is believed to occur between digomer radical cation, and pyrrole radical cation at the electrode surface. Probably, the growth of polypyrrole chains terminates when the ends of the growing chains becomes sterically blocked [7].

Recently, Polypyrrole (PPy) has become one of the most attractive conductive polymers. There are 3 methods generally used to prepare polypyrrole, they are (i) Chemical polymerization in solution [8], (ii) Chemical vapor deposition (CVD) [9] and (iii) Electrochemical polymerization [10]. Most investigators have been interested in the third method. In fact, more than 300 reports concerning electrochemical polymerization of polypyrrole and their electrical morphological and mechanical properties have been published [11]. On the other hand, the chemical polymerization method which can be traced back to 1916 is less popular. Systematic investigation has been not made of chemical polymerization. For example, selection of the polymerization solvent in the process was only by chance. We have recently found that polypyrrole, obtained from chemical polymerization can exhibit very high electrical conductivities. When a suitable solvent is selected and the oxidation potential in the solution is controlled.

Nowadays, the preparation of conductive composite by chemical oxidative polymerization has been developed, since this method is easier and more effective. In the preparation of polypyrrole composite, pyrrole monomer is polymerized by chemical oxidative polymerization using oxidant such as ammonium per sulfate within host polymer solution. In this method, the distribution between polypyrrole and host polymer is good, and thus electrical conductivity and mechanical properties increases. But two phases are basically immiscible, and phase separation still exists between each phase. If
the miscibility of these blends is enhanced between two phases, the electrical properties will be enhanced due to the decrease of interfacial tension between them [12].

In an undoped (pristine) i.e. non-conducting state polypyrrole is generally considered to have the so called benzoid structure, and is usually called the neutral state of polypyrrole. This benzoid structure of polypyrrole in the neutral state, as well as its corresponding schematic band structure is shown in Figure 2.2.

![Figure 2.2: Types of bonds in Polypyrrole: (a) aromatic and (b) quinoid structure](image)

In the reaction, the monomer is polymerized and charge carriers are generated via doping. As doping of the neutral polymer proceeds, the formation of structure and electronic defects will take place. At low concentrations, the first predominant kind of defect will be polarons, which give rise to the formation of two localized states within the band gap [13].
Figure 2.3: Polypyrrole at different oxidant levels

Further charge transfer from the polymer chain, i.e. higher doping levels, which one hole-polaron, may then proceed either by the formation of another polaron, or by removing the single electron in the lower polaron level. The removal of electrons (oxidation shown in Figure 2.3) can be achieved electrochemically by the application of sufficiently positive potential [14]. This introduction of positive charge carriers makes the material electrically conducting; conjugated polymers (CP) are consequently also known as intrinsically conducting polymers or synthetic metals. Table 2.1 gives the comparison of chemical and electrochemical polymerization [15].
2.3 Materials and Methods

Analytical-reagent-grade Pyrrole, Nickel Oxide (NiO), Niobium Pentoxide (Nb$_2$O$_5$), Cerium Oxide (CeO$_2$) and anhydrous Iron (III) Chloride (AR-grade) were obtained and used in the present study. Pyrrole monomer was purified by distillation under reduced pressure and stored in dark at 4°C.

2.3.1 Synthesis of Polypyrrole

For chemical polymerisation of pyrrole, FeCl$_3$ was used as an oxidant and anhydrous ethanol as solvent.

3.4 ml of pyrrole is added to 25 ml of ethanol and stirred for 10 minutes to obtain ethanol solution of pyrrole. To this solution, 25 ml of FeCl$_3$.6H$_2$O was added drop wise
with continuous stirring. The suspension was left for 24 hours for polymerization. Finally, the suspension was filtered and washed thoroughly with acetone and distilled water in order to remove the unreacted pyrrole and excess ferric chloride. A black precipitate of polypyrrole was obtained which was dried for 1 hr at 60-70°C in vacuum oven.

2.3.2 Synthesis of Polypyrrole-NiO composites

3.4ml of pyrrole was dissolved in 25ml of ethanol and stirred for 10 min. 25ml of FeCl$_3$.6H$_2$O was added drop wise to the ethanol solution of pyrrole. Fine graded powder of Nickel Oxide (NiO) was varied in weight percentages (10, 20, 30, 40 and 50) and added to the polypyrrole solution. This reaction mixture was stirred for 3hr at 0-5°C with magnetic stirrer in order to disperse NiO in the polymer solution. The obtained product was filtered and washed thoroughly with acetone and distilled water in order to remove the unreacted pyrrole and excess ferric chloride. The samples were vacuum dried for 1 hr at 60-70°C.

2.3.3 Synthesis of Polypyrrole-Nb$_2$O$_5$ composites

3.4ml of pyrrole was dissolved in 25ml of ethanol and stirred for 10 min. 25ml of FeCl$_3$.6H$_2$O was added drop wise to the ethanol solution of pyrrole. Fine graded powder of Niobium Pentoxide (Nb$_2$O$_5$) was varied in weight percentages (10, 20, 30, 40 and 50) and added to the polypyrrole solution. This reaction mixture was stirred for 3hr at 0-5°C with magnetic stirrer in order to disperse Nb$_2$O$_5$ in the polymer solution. The obtained product was filtered and washed thoroughly with acetone and distilled water in order to remove the unreacted pyrrole and excess ferric chloride. The samples were vacuum dried for 1 hr at 60-70°C.
2.3.4 Synthesis of Polypyrrole-CeO$_2$ composites

3.4ml of pyrrole was dissolved in 25ml of ethanol and stirred for 10 min. 25ml of FeCl$_3$.6H$_2$O was added drop wise to the ethanol solution of pyrrole. Fine graded powder of Cerium Oxide (CeO$_2$) was varied in weight percentages (10, 20, 30, 40 and 50) and added to the polypyrrole solution. This reaction mixture was stirred for 3hr at 0-5$^\circ$C with magnetic stirrer in order to disperse CeO$_2$ in the polymer solution. The obtained product was filtered and washed thoroughly with acetone and distilled water in order to remove the unreacted pyrrole and excess ferric chloride. The samples were vacuum dried for 1 hr at 60-70$^\circ$C.

2.4 Preparation of Pellets

The powders of Polypyrrole, Polypyrrole-NiO, Polypyrrole-Nb$_2$O$_5$ and Polypyrrole-CeO$_2$ composites so obtained from synthesis techniques discussed in early sections were crushed and finely ground in agate mortar in the presence of acetone medium. The powder is then pressed to form pellets of 10 mm diameter and thickness varying up to 2 mm by applying pressure of 90 MPa in a hydraulic press.

For temperature dependent conductivity and sensor studies, the pellets of polypyrrole and its composites are coated with silver paste on either side of the surfaces to obtain better contacts.
References


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