

POLYPYRROLE FILMS PREPARED BY CHEMICAL OXIDATION OF PYRROLE IN AQUEOUS FeCl_3 SOLUTION

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Abstract: Conducting polypyrrole (PPy) films are prepared by mixing a solution of pyrrole with an oxidizing solution of FeCl_3 . UV-VIS and IR spectroscopy are used for determining the reaction mechanisms. The rate of pyrrole polymerization is determined by the rate of the initial electron-transfer reaction. The surface morphology is investigated with SEM.

Keywords: polypyrrole, oxidant, FeCl_3 , polymerization

1. INTRODUCTION

Polypyrrole, a chemical compound formed from a number of connected pyrrole ring structures (Fig. 1.), is an inherently conductive polymer due to interchain hopping of electrons. Polypyrrole is easy to prepare by electrochemical techniques and its surface charge characteristics can easily be modified by changing the dopant anion (X^-) that is incorporated during synthesis. Polypyrrole was the first of conducting polymers that shows relative high conductivity [3].

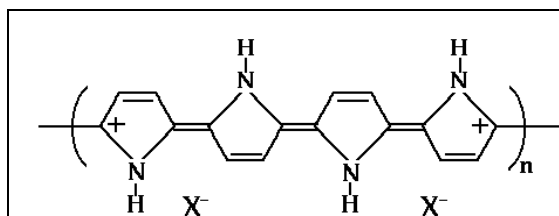


Fig. 1. Polypyrrole structure

Many papers discuss the electropolymerization of pyrrole and the properties of the resulting polypyrrole (PPy) films [1]. Less information exists concerning the chemical polymerization of pyrrole in homogeneous solution. Polymerization occurs readily in the presence of different oxidants, such as FeCl_3 [2,3] and $\text{K}_2\text{S}_2\text{O}_8$ [4]. More studies have been reported about the formation of PPy films on solid surfaces by chemical polymerization of pyrrole [5]. There are reports about the polymerization of pyrrole onto printed circuit boards [6,7] and various textile composites [8,9]. In the present work, the conducting polypyrrole (PPy) films were synthesized by chemical oxidation of pyrrole with FeCl_3 in aqueous methods by mixing a solution of pyrrole with an oxidizing solution of FeCl_3 .

2. POLYPYRROLE SYNTHESIS

Polypyrrole (PPy) was chemically synthesized in water (50 ml) by mixing a solution pyrrole (Py) 0.043 M (2.881 g) with an oxidizing solution of FeCl_3 (0.1 M). The synthesis

was allowed to proceed at 5–7 °C [11,12]. The pyrrole solution was kept in the bath before adding FeCl₃ (16.25 g). Molar ratio of FeCl₃/Py = 2.3.

Since this is an exothermic reaction, the addition was done slowly and at low temperature. The synthesis was performed without agitation and under nitrogen gas atmosphere. The polypyrrole precipitate was collected by filtration, rinsed with distilled water and dried at 25–35 °C.

3. RESULTS AND DISCUSSION

3.1. PYRROLE POLYMERIZATION IN AQUEOUS IRON CHLORIDE SOLUTIONS

The films formed in ferric chloride solution are blue-black in colour if that are fully oxidized. The mechanism reactions of Py polymerization are given in Fig. 2 [12]. The rate of polypyrrole polymerization is determined by the rate of the initial electron-transfer reaction.

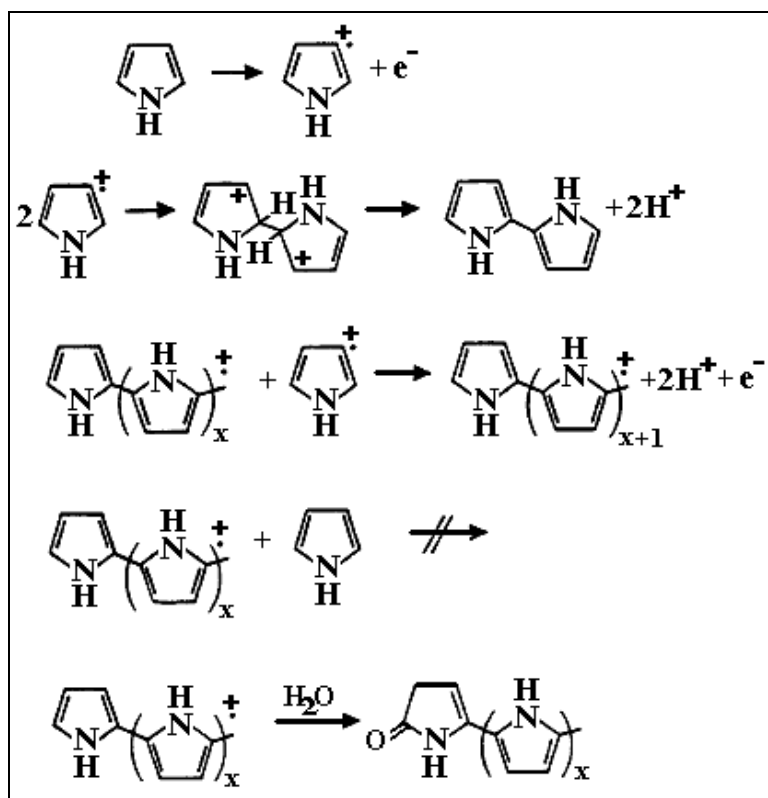
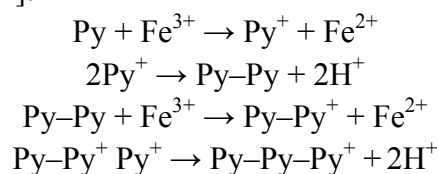


Fig. 2. Chemical preparation of polypyrrole via radical cation formation

Py is the monomer and Py^{•+} is the radical cation which can dimerize with the expulsion of H⁺, such as given below [12]:



The mole ratio of monomer to oxidant affected the quality of the resulting polymer films.

3.2. UV-VIS SPECTROSCOPY

The UV-VIS absorption diffuse-reflectance spectra were recorded on a *SPECORD M400 Carl Zeiss Jena* spectrophotometer with double beam and microprocessor. These spectra (Fig. 3.) are typical spectra for polypyrrole, and a constant and progressive increase of the pyrrole bands is observed due to the radicalic polymerization, associated with the character of the chemical bond between pyrrole rings in polymer chains and the chlorine anions from FeCl_3 .

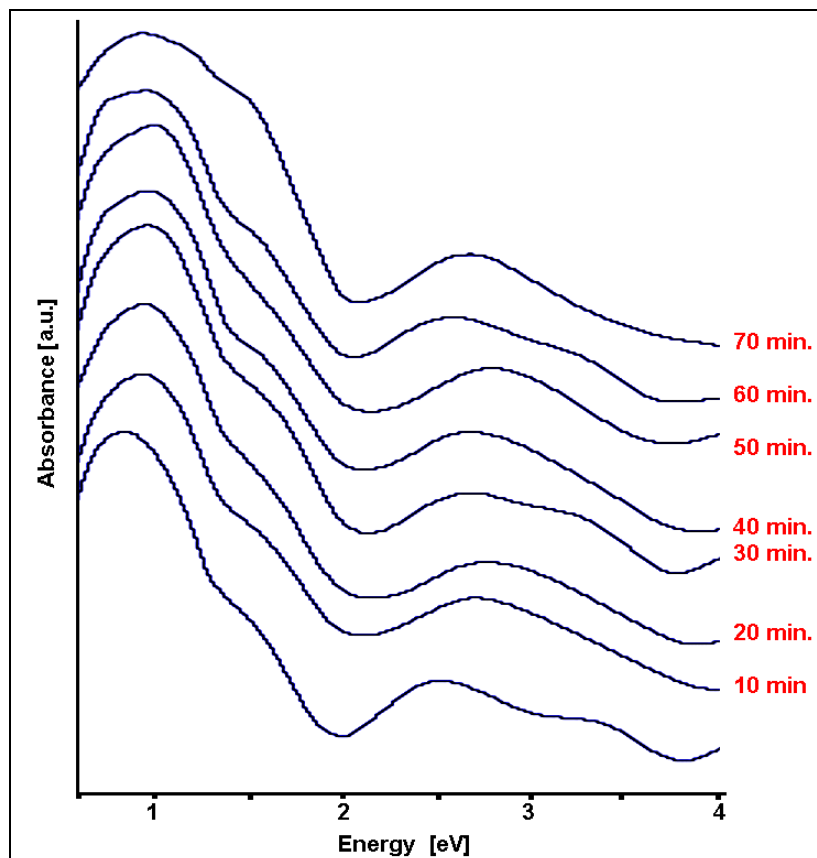


Fig. 3. The UV-Vis spectra of PPy in the presence of FeCl_3 in time ($\Delta t = 10$ minutes)

3.3. IR SPECTROSCOPY

The mechanism and kinetics of the formation of polypyrrole (PPy) films were studied by IR spectroscopy, with a *SPECORD M80 Carl Zeiss Jena* spectrophotometer. IR spectroscopy made it possible to conclude that the anion is linked with the links of a polymer chain with a charge transfer (Fig. 4.).

The IR spectra for pyrrole in water display intensive narrow bands of plane vibrations of deformation $\delta_{\text{pl}}(\text{CH})$ at 1015, 1045, and 1075 cm^{-1} . Immediately, after adding FeCl_3 to the pyrrole solution, new weak bands at 1100, 1125, and 1150 cm^{-1} appear against the background of the pyrrole bands [10, 13]. The intensity of the new bands increases with time, while that of the pyrrole vibrations simultaneously decreases [14]. The full width at half maximum and the mutual arrangement of these bands suggest that they refer to deformation vibrations of the pyrrole ring in a pyrrole complex.

An additional proof for the viability of the assumed mechanism involving a discharge of a complex which includes a protonated molecule of pyrrole with the anion is the fact that a strong quantum chemical interaction exists between anions and chains of pyrrole rings in the film, as will be shown below.

Thus, the discharge of pyrrole complexes with the anion and proton and their partial destruction yields radical-cation and radical species. When interacting with active ends of pyrrole links, these induce the growth and development of polymer chains. The formation of a polypyrrole film may probably be represented by the reactions shown in the Fig. 5.

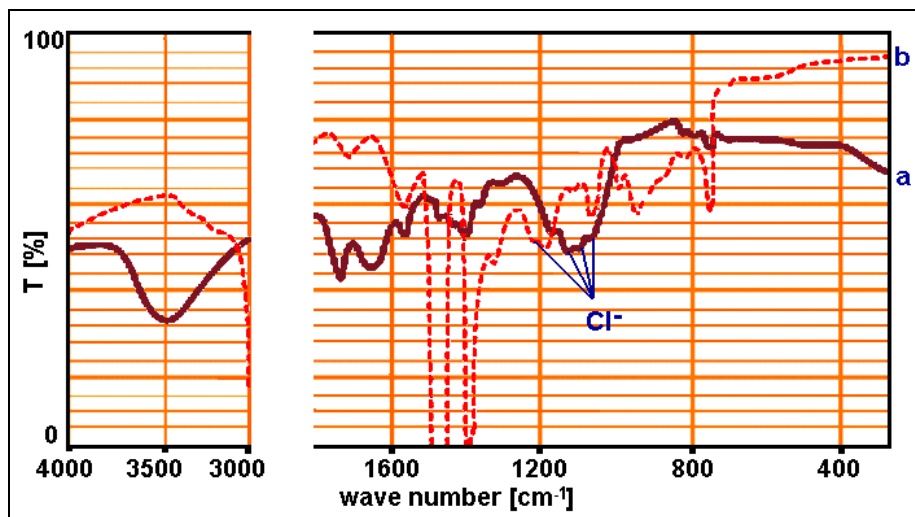


Fig. 4. IR spectra of Py (a) and PPy (b) in the presence of chlorine ions

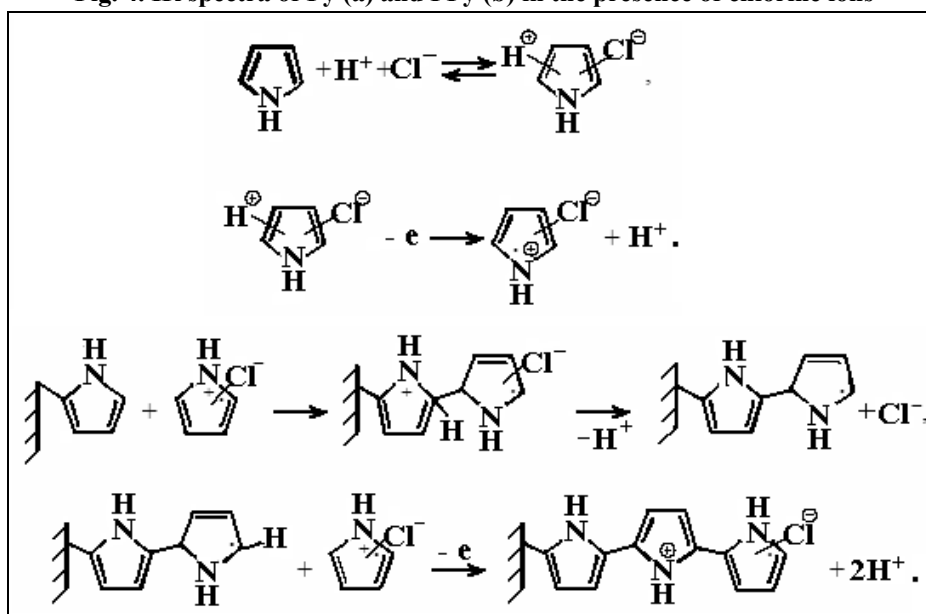


Fig. 5. The development of PPy chains

In this scheme, the formation of a polypyrrole film involves very reactive intermediate species. Their interaction between themselves and the solution components may lead to deviation from ideal stoichiometry $[(\text{C}_4\text{H}_5\text{N})_x\text{Cl}]_n$, which is observed in reality, indeed. The proposed mechanism allows us to explain the dramatic deceleration of the synthesis of a polypyrrole film caused by the solution agitation as resulting from the polymer destruction.

3.4. SEM IMAGE

Fig. 6. represent the SEM image of PPy film in contact with the substrate surface and show the striations on the film surface and many pores and cavities. This result means the chemical synthesized deposition mechanism of the conducting polymer film is realized. The deposition mechanism mainly depends on the substrate material.

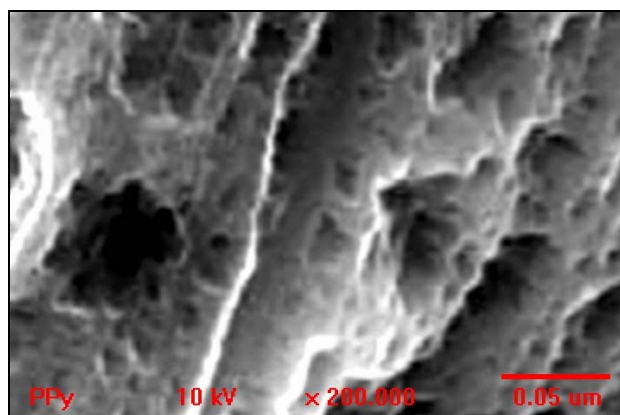


Fig. 6. SEM image of the conducting PPy film surface in contacted with substrate (x200000)

4. CONCLUSIONS

Conducting polypyrrole (PPy) films is prepared by chemical oxidation of pyrrole with FeCl_3 in aqueous methods by mixing a solution of pyrrole with an oxidizing solution of FeCl_3 . The rate of polypyrrole polymerization is determined by the rate of the initial electron-transfer reaction.

The mechanism and kinetics of the formation of polypyrrole (PPy) films were studied by UV-VIS and IR spectroscopy.

IR spectroscopy made it possible to conclude that the anion is linked with the links of a polymer chain with a charge transfer.

The UV-VIS absorption diffuse-reflectance spectra are typical spectra for polypyrrole a constant and progressive increase of the pyrrole bands is observed due to the radicalic polymerization, associated with the character of the chemical bond between pyrrole rings in polymer chains and the chlorine anions from FeCl_3 .

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