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CONSEQUENCE OF OXIDANT TO MONOMER RATIO ON POLYPYRROLE CONDUCTIVITY

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Abstract

In this work, we have synthesized conducting Polypyrrole by Chemical oxidative polymerization of pyrrole monomer using $FeCl_3$ *(ferric chloride) as oxidant for five different oxidant to monomer (O/M) ratios. Characterization of conducting polypyrrole was done using FTIR and conductivity measurement. The FTIR spectra confirmed the expected structure of the polypyrrole. The electrical conductivity was measured using a four-probe method. It was found that the electrical conductivity of the polypyrrole was chiefly dependent on the O/M ratio. It is observed that conductivity increase with O/M ratio and saturates at ratio 2.5*

Keywords: Polypyrrole, FTIR, conducting polymer, O/M ratio.

1. Introduction

Many polymers like polyethylene, polyamide, polyester are non-conducting (Insulators) in nature but conducting polymers are the materials which conducts electricity. Electrically conducting polymers (ECPs) were discovered in 1976 by Heeger, MacDiarmid, and Shirakawa, for this innovative work, they were awarded the 2000 Nobel Prize in Chemistry for the discovery and development of conducting polymers [1-3]. ECPs are known as "synthetic metals" due to their intrinsic electrical conductivity resulting from the full delocalization of π electrons on the long chain aromatic polymer backbone. Polypyrrole is one of the most important conducting polymers due to its properties such as excellent thermal stability, good electrical conductivity, relative ease of synthesis, and environmental stability [4]. Polypyrrole has been actively used in many potential applications such as biosensors [5], gas sensors [6], microactuators [7], solid electrolytic capacitor [8-9], electrochromic windows and displays, and packaging, polymeric batteries, electronic devices and functional membranes, etc. [10–11]. Conducting polymers can be prepared using various methods like, electrochemical polymerization, plasma polymerization, chemical polymerization, etc. but chemical oxidative polymerization is the most advantageous method for producing conducting polymers with the advantage of being a simple technique capable of producing bulk quantities of these polymers (dispersion, powder, and coating), of which the synthesis conditions also play an important role in the chemical, physical, thermal, electrical, morphological, and mechanical properties of the conducting polymers [12-13]. Electrical conductivity is an important parameter for the application of conducting polymer in different areas. In the present work, the conductivity of the polypyrole synthesized under different O/M ratios was investigated.

2. Experimental details

2.1. Materials

$FeCl_3$ (Ferric chloride) was obtained from S. D. Fine-chemical Ltd. and used as received. Pyrrole-C_4H_4NH (S D Fine-chemical Ltd.) was purified by distillation process prior to use. Double distilled water was used as solvent in this experiment.

2.3. Chemical synthesis of polypyrrole

Pyrrole (0.2 M) in 100 ml solution was prepared using distilled water as solvent in a 250 ml conical flask and then the pre-cooled $FeCl_3$ as an oxidant with O/M ratio 0.5 in 50 ml solution, prepared using distilled water was added drop by drop into above prepared pyrrole solution in conical flask with constant stirring. This reaction was carried out at 0 – 4^0C for 4 hrs. [14]. After the completion of reaction, a dark brown solution was obtained which indicates the formation of polypyrrole. Polypyrrole synthesis scheme is given in figure 1. This preparation was kept at room temperature for 24 hours. The polymer was rinsed with distilled water until the filtrate become colourless and precipitate of conducting polypyrrole collected on a Whatman filter paper. This product was dried for 1 day at room temperature. Above procedure was repeated for the preparation of polypyrrole with O/M ratio 1.0, 2.0, 2.3 and 2.5 The final polymer powder sample were identified by the notation $(PPY)_r$ where r is the initial O/M ratio and then these samples were kept in desiccator for characterization.

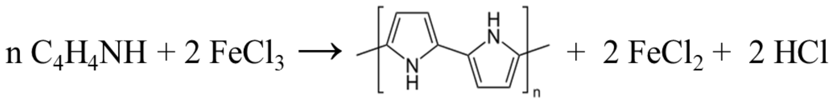

Figure 1. Polypyrrole synthesis scheme

2.4. Preparation of pellets for conductivity

Polypyrrole pellets of 20 mm in diameter and 1mm to 2 mm thick were prepared from polypyrrole powder with O/M ratio 0.5, 1.0, 2.0, 2.3 and 2.5 using a cylindrical die at 5 tonne pressure using a steel die in a hydraulic press.

2.5. Structural characterization

FTIR spectra of the polypyrrole sample with O/M ratio 2.3 have been observed using Bruker tensor 27 FTIR spectrometer. Pellet of polypyrrole in KBr was prepared to register the IR spectra. Spectrum was collected with a resolution of $4cm^{-1}$ and the scanning range was from 500 to 4000 cm^{-1}. 50 scans were averaged for the sample

2.6. Electrical conductivity of polypyrrole

Electrical conductivity measurements were made at room temperature using a four probe system coupled to a variable dc power supply, a digital voltmeter and digital current meter. Variation in current through sample is recorded by changing the voltage from 0 to 5V across the sample using variable DC power supply. Bulk resistance of all polypyrrole samples were obtained from I-V characteristics. From the values of resistances conductivity has been calculated for all polyptrrole samples using the formula given as below,

$$\sigma = \frac{ln2}{\pi * d * R}$$

Where d is the thickness of polypyrrole pellet and R the resistance of the pellet obtained from I-V characteristics of the sample

3. Result and discussion

3.1. Structural analysis using FTIR

Figure 2 shows the FTIR spectrum of polypyrrole corresponding to O/M ratio 2.3.

We have reported IR spectrum upto 2000 cm^{-1}. The bands with intensity peaks at 1539 cm^{-1} and 1447 cm^{-1} in the spectrum of polypyrrole are assigned to (C=C) and (C-C) stretching vibrations of pyrrole ring respectively. Peak at 1293 cm^{-1} is attributed to C-N stretching vibration in the pyrrole ring. 1151 cm^{-1} peak is assigned to bending vibration of pyrrole. Peak at 1089 cm^{-1} corresponds to in-plane deformation vibration of N-H peak and 893 cm^{-1} is attributed to C-H out-of-plane deformation. Peak at 778 cm^{-1} is assigned to C-H wagging. 656 cm^{-1} peak corresponds to C-C out-of-plane ring deformation or C-H rocking [15]. Almost all bands have been observed which confirms the formation of polypyrrole.

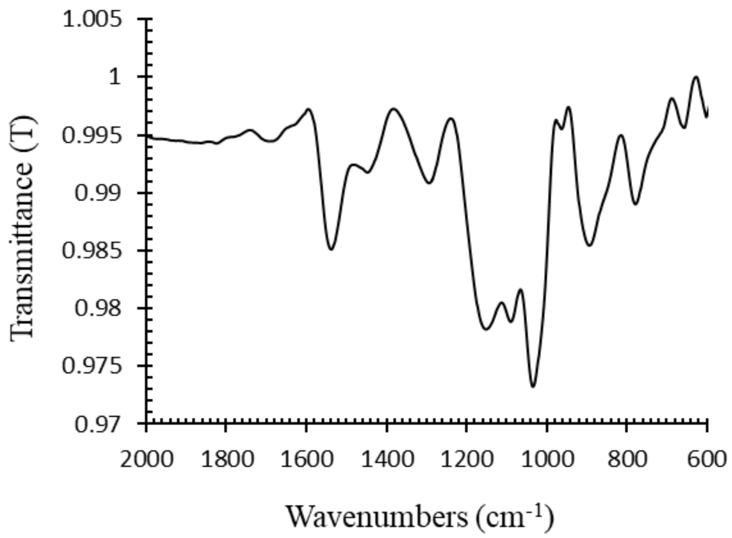

Figure 2. FTIR spectrum of polypyrrole

3.2. Measurement of resistance of polypyrrole for different O/M ratios

I-V characteristics of polypyrrole samples for different O/M ratios are shown in figure 2. Resistance values of samples with different O/M ratios obtained from slope of I-V characteristics are given in table 1. It is observed that the resistance of the polypyrrole samples decreases with the increase in O/M ratio. It may be due to increase in number of cation formation due to more concentration of oxidant, so more number of charge carriers

per unit volume leads to more current through the sample and hence less resistance.

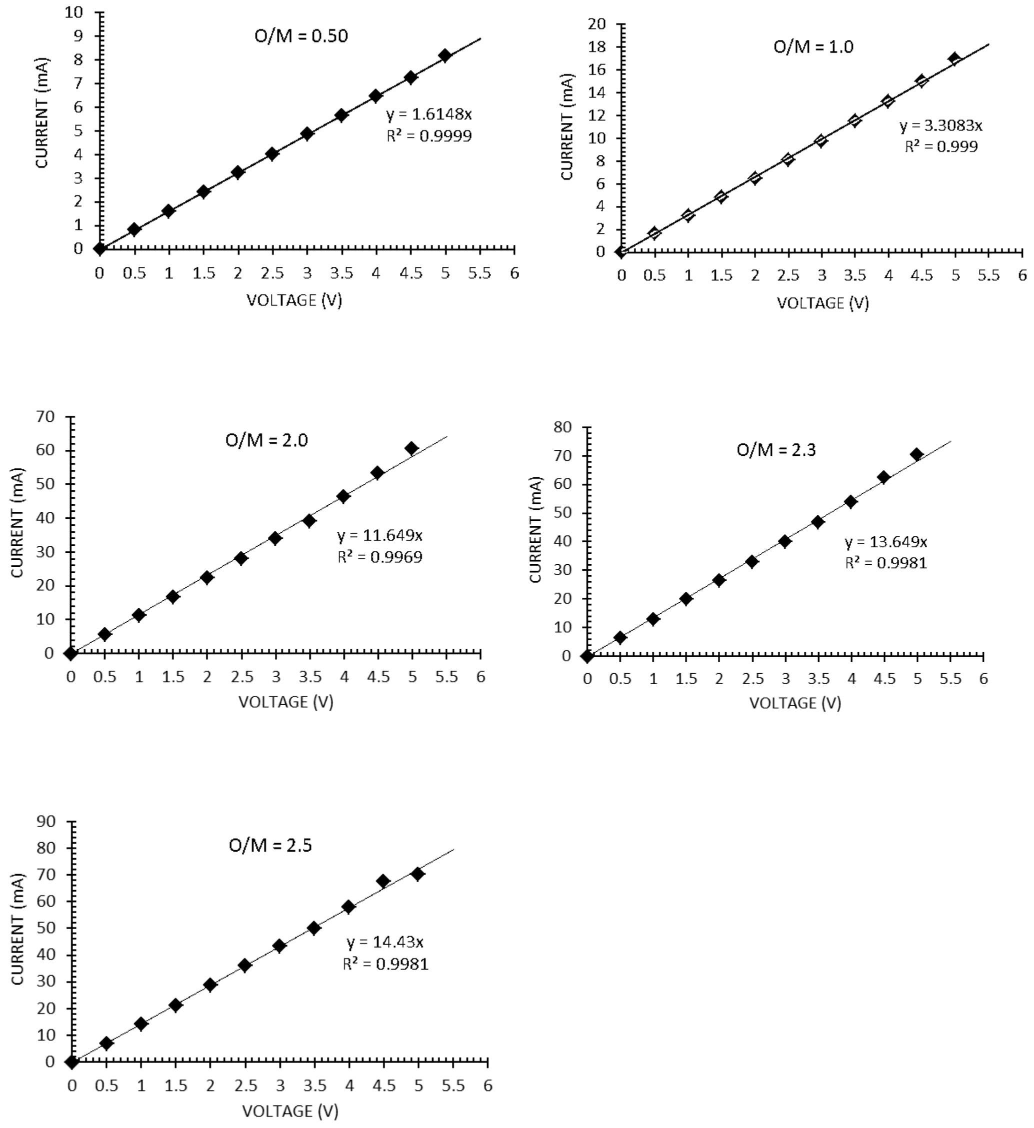

Figure 3. I-V characteristics of polypyrrole samples for different O/M ratios

Table 1. Resistance of polypyrrole pellets with different O/M ratios

Sr. no.	O/M ratio	Slope from I-V characteristics	Resistance (Ω) R = 1/slope
1	0.5	1.615×10^{-3}	619
2	1.0	3.301×10^{-3}	303
3	2.0	11.65×10^{-3}	86
4	2.3	13.65×10^{-3}	73
5	2.5	14.43×10^{-3}	69

3.3. Electrical conductivity of polypyrrole for different O/M ratio

DC electrical conductivities are calculated from the resistance values of polypyrrole samples corresponding to different O/M ratios as shown in the table 2. Increasing the amount of oxidant ($FeCl_3$) leads to the formation of more radical cations (polarons), which increases the rate of the chemical oxidative polymerization of pyrrole and hence conductivity of polypyrrole increases with increase in O/M ratio and then it saturates at O/M ratio 2.5 may be dye to over oxidation [16].

Table 2. DC Conductivity of Polypyrrole for different O/M ratios

Sr. no.	O/M ratio	Thickness of pellet ‘d’ (mm)	Conductivity σ (S/cm)
1	0.5	1.12	3.0×10^{-3}
2	1.0	1.18	6.1×10^{-3}
3	2.0	1.23	20.0×10^{-3}
4	2.3	1.17	25.7×10^{-3}
5	2.5	1.23	25.9×10^{-3}

4. Conclusion

The polypyrrole has been successfully synthesized by chemical oxidation using pyrrole as a monomer and $FeCl_3$ as an oxidant at 0 to 4^0C. A dark brown colour of the solution and powder confirmed the polypyrrole formation. Different bands in FTIR spectra of polypyrrole also confirmed its formation. DC Electrical conductivity of polypyrrole is found to be increased with the O/M ratio increase from 0.5 to 2.5. Hence optimum value of room temperature conductivity of polypyrrole, prepared chemically at 0 to 4^0C is observed at O/M ratio 2.3.

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