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Synthesis and Characterization of Polypyrrole Synthesized via Different Routes

Sumaira Nosheen, Muhammad Irfan, Farzana Habib, Syed Zaheer Abbas, Bilal Waseem, Farooq Iftikhar, Badarudin Soomro, Abdul Karim Aziz
PITMAEM, PCSIR Laboratories Complex
Ferozepur Road, Lahore
Pakistan

Sumaira Nosheen
Department of Polymer Engineering & Technology
University of the Punjab, Lahore
Pakistan

***Abstract*— Conducting Polymers move from primarily passive materials such as coatings and containers to active materials with useful optical, electronic, energy storage and mechanical properties. A representative of Conducting polymer (Polypyrrole) was synthesized by facile polymerization of pyrrole monomer using FeCl3 as an oxidant and ammonium per sulfate and sodium dodecyl sulfate as surfactants. Synthesis was carried out by varying oxidants, time, temperature and other parameters to achieve optimum properties in the product. Structural and morphological properties of polymer were studied. FTIR is employed to study the formation of Polypyrrole. Particles of PPy were analyzed using SEM. Conductivity was checked by means of two probe method. Polypyrrole synthesized by using FeCl3 and SDS for 3 hours gave the best product and yield in the process.**

Keywords—Component; formatting; style; styling; insert

I. INTRODUCTION

In current years fundamental conducting polymers comprising conjugated double bonds have been concerned as advanced materials. In History, polymers have been known as insulators and due to their insulating properties, they have wide range of applications. In fact, until now, any electrical conduction in polymers which is generally due to loosely bound ions was mostly regarded as an undesirable fact [1]. Electrically conducting polymers are defined as materials with an extended system of conjugated carbon-carbon double bonds [2].

Conducting polymers, for example Polypyrrole (Ppy), polyaniline (Pani), polythiophene (PTh) along with their derivatives, have been used as the active layers of gas sensors since 1980 [3]. The synthesis of conducting polymers is described in detail in several research articles [4]. Conducting polymers can be synthesized in different ways [5] by means of chemical polymerization, electrochemical polymerization, photochemical polymerization [6] metathesis polymerization [7], concentrated emulsion polymerization [8], inclusion polymerization [9], solid-state polymerization [10], plasma polymerization [11], pyrolysis [12], and soluble precursor polymer preparation. Synthesis of Conducting polymers is considered to be easy through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or other structural derivations [13]. Polypyrrole has strained much attention because of its properties like high conductivity, stability as well as improved mechanical properties. It has been found to have many potential applications in electronic devices, light-weight batteries, various sensors, and chromatographic stationary phases [14]. Polypyrrole can easily be synthesized by an oxidatively chemical or electrochemical polymerization of pyrrole. PPy has rivetted great interest because of its high conductivity and good thermal and environmental stability and ease of synthesis. Moreover, this polymer is electroactive in both aqueous and organic electrolyte solutions [15]. Its properties can be controlled by substituting among its oxidized and reduced states. Its non-toxic nature makes it convenient to be used in various biomedical applications. [16]. That is the reason that various approaches have been reported for synthesizing Polypyrrole according to requirement or application parameters. As a result, in chemical oxidation method, many researchers have reported using different oxidants for synthesizing Polypyrrole considering final product requirements. For instance, iron chloride (FeCl3) has been used as an oxidant for synthesizing polymer films. [17,18] The use of APS (ammonium per sulfate) as an oxidant focuses on conductivity behavior. Some scientists used both to study the behavior of polymer with various fillers [19]. However, it should be noted that oxidants effect the final properties of polymer such as electrical, morphological and thermal. Some researchers also reported the use of SDS (Sodium Dodecyl Sulphate) as a dopant and comparing the performance of these oxidizing agents on conductivity of final polymer. In this project, five approaches were followed to synthesize Ppy along with varying temperature and time of polymerization. The objective was to learn about the optimum conditions which can yield desired properties of final product.

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II. EXPERIMENTAL

Polypyrrole (Ppy) was synthesized following five different routes. In these methods different oxidants were used along with the effect of time of polymerization on the PPy quality and yield were calculated.

A. PPy synthesis using $FeCl_3$

25ml of de-ionized water was taken in a round bottom flask. Pyrrole monomer (8.5ml) from sigma Aldrich was added into it and mixing was carried out for ten minutes using magnetic stirrer. Further FeCl3 solution (2.5M) was added very slowly as an oxidant to the monomer solution. The appearance of black colour precipitates was observed in the flask immediately after the addition of oxidant. The polymerization was allowed to continue for 24 hours at room temperature. The precipitates were filtered and washed with a mixture of water and ethanol several times to remove any traces of oxidant from product. The filtrate was dried in a vacuum oven and weighed to calculate the yield of final product.

B. PPy synthesis using $FeCl_3$ and Sodium dodecyl sulphate

In this approach, Sodium Dodecyl Sulphate (SDS) was used as a surfactant. SDS (0.86 g) was added to de-ionized water (30ml). The mixture was stirred for thirty minutes to obtain a clear solution. Then pyrrole monomer (3ml) was added drop wise to SDS solution. After addition of monomer, FeCl3 solution of required molarity was added drop wise and allowed to polymerize for three hours at room temperature. The black colored polymer powder formed was filtered and washed several times with the mixture of de-ionized water and ethanol. The polymer powder was dried in vacuum oven for 24 hours.

To study the effect of time on the quality and yield of PPy formed, another reaction was carried out according to same procedure as described above except the time of polymerization was increased to 5 hours.

C. Synthesis using ammonium per sulphate

In this method, pyrrole monomer (0.15M) was taken in a flask and APS [Ammonium persulphate, NH4(SO4)2] (0.014M) was added drop wise into it. The mixture was stirred for 8 hours in an ice bath and afterwards product was filtered and washed with the mixture of ethanol and water. The product was dried in an oven under vacuum for 24 hours.

III. RESULT AND DISCUSSION

The synthesized polymer was confirmed through FTIR spectra. The FTIR spectrum of Polypyrrole particles shows peaks at 1531 cm-1, 1480 cm-1, 1469 cm-1 for pyrrole ring stretching and 1458 cm-1 for conjugated C-N stretching vibrations normally. Fig.1 shows the spectrum of PPy produced by FeCl3 only and polymerized for 24 h in which the absorption peak at 1531 cm−1 is due to intra-ring C=C and inter-ring C–C vibrations of pyrrole ring. The bands at 1305 and 1147 cm−1 may match to =C–H in-plane vibration but the band located at 1026 cm−1 is for the in-plane deformation of C–H bond of Pyrrole ring, while the minor peak below 1000 and 800 cm−1 are attributable to =C–H out-of-plane vibrations. These bands are also termed as bipolaron bands. The intensity of each peak confirmed the formation of polymer but the polymerization is not completed in the reaction as judged from the peak intensities. The Fig.2 shows the spectrum of PPy (PP-02) in which surfactant was incorporated and polymerization time was decreased to 5 hours. The peaks in FTIR spectrum of PPy produced in the presence of surfactant are much sharp as compared to that produced without surfactant which suggests that high degree of polymerization occurred in the presence of surfactant. The vibration peaks at 677cm-1, 1176cm-1, 1740cm-1,1921cm-1confirming the presence of C-H, C-N bonds and Pyrrole ring, respectively.

The FTIR spectrum of PPy produced in the presence of surfactant (SDS) and polymerized for 3 h is given in Fig. 3. Again, all the peaks related to C-H, C-N, Pyrrole ring peaks can be clearly seen in the spectrum. However, all these peaks have lower intensity than the one produced after 5 h polymerization. The lower intensities of peaks might be due to de polymerization of PPy. The polymer synthesized by incorporating APS (ammonium per sulphate) as surfactant showed less polymerization than the earlier methods and some side products are also formed as extra peaks at 3842 cm-1, 3738 cm-1, 3612cm-1can be seen in the spectrum shown in Fig.4

The FTIR spectra of PPy produced in the presence of APS and polymerized for 08h is shown in Fig.5. The FTIR spectra of PPy produced in the presence of APS and polymerized for 16 h is shown in Fig.6. The peaks are not very sharp like in above figure and the PPy produced has improved purity but still many irrelevant peaks can be observed from Fig. 4.6 just like in the above figure. It can be concluded from the above results that although PPy formed in each of these methods, the rate of polymerization slightly varied with varying time period of polymerization, types of surfactant used and temperature. The PPy produced in the presence of surfactant for 3 h polymerization reaction is much better in quality according to FTIR analysis. The electrical conductivity of PPy synthesized by following varying parameters is shown below in the Table 1. The Polypyrrole synthesized by using SDS for 03 hours shows best electrical conductivity i.e. 3.16 S/m which is comparable with the literature. PPy formed by other methods showed conductivity less than this as cleared from graph also. Atomic force microscope was employed to get image of the polymer surface. A sample of PPy was selected and the surface topography was obtained. Fig.7 shows topographic images of the polymer. The average lateral width of particles is 5 μm whereas PPy particles appear to have sizes less than 1 μm. The SEM micrograph for PPy is shown in Fig.8 PPy was produced as particles which can be seen in the image.

IV. CONCLUSION AND FURTHER TRENDS

Conventional polymeric materials are widely used in various engineering fields including electronic, electrical, mechanical and industrial. The properties of these polymers can be further improved by adding different types of fillers to improve existing properties considering mode of applications. The main objective of this research was to prepare Polymer with the aim of improving the properties with percent increase in yield. The main objective of this research was achieved. Moreover, the research has opened a gate for wide range synthesis of hybrids using simple polymerization techniques.

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A. *Figures and Tables*

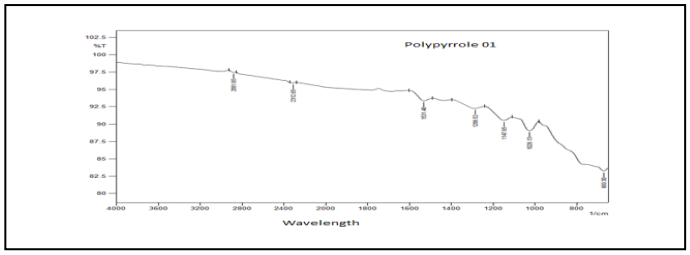

Fig. 1. FTIR Spectra for PP-01 (Polypyrrole), synthesized by using $FeCl_3$ for 24 hours

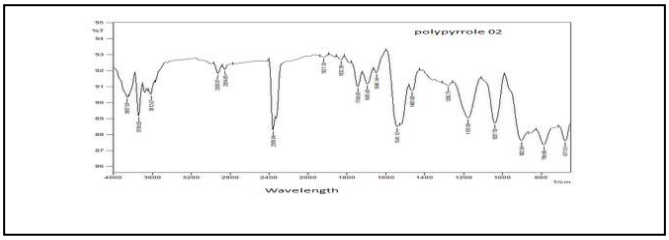

Fig. 2. FTIR Spectra for PPy produced in the presence of surfactant SDS and polymerized for 5 hours

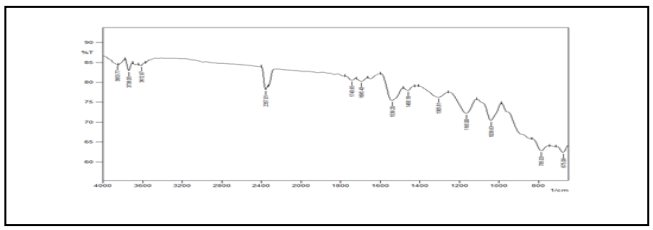

Fig. 3. FTIR Spectra for PPy produced in the presence of surfactant SDS and polymerized for 3 hours

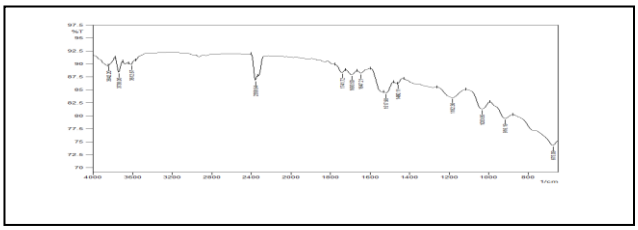

Fig. 4. FTIR Spectra for PPy produced in the presence of surfactant APS and polymerized for 3 hours

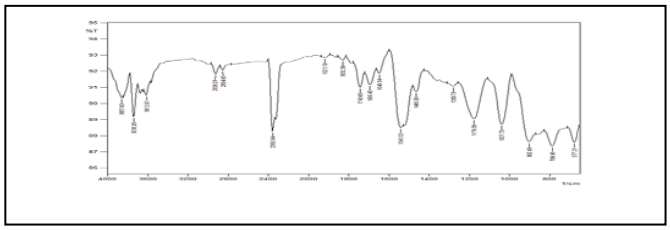

Fig. 5. FTIR Spectra for PPy produced in the presence of APS and polymerized for 8 h

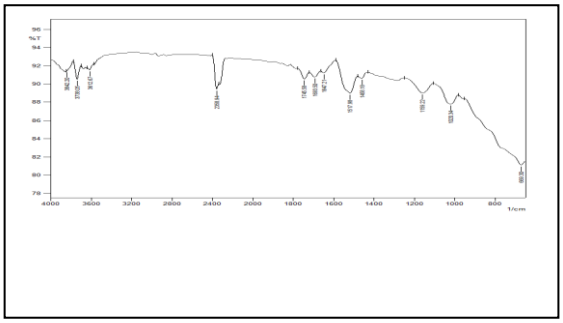

Fig. 6. FTIR Spectra for PPy produced in the presence of APS and polymerized for 16 h

Methods	Percentage yield
PPy synthesized using FeCl3 for 24 hours	64
PPy synthesized using SDS for 5 hours	70
PPy synthesized using SDS for 3 hours	79
PPy synthesized using APS for 3 hours	67
PPy synthesized using APS for 8 hours	60
PPy synthesized using APS for 16 hours	67
PPy synthesized using $FeCl_3$ for 24 hours	64

Table 1: Percentage yield of polymer

Sr.No.	Method	Conductivity (S/m)
1	PPy synthesized using FeCl3 for 24 hours	2.09
2	PPy synthesized using SDS for 5 hours	2.15
3	PPy synthesized using SDS for 3 hours	3.16
4	PPy synthesized using APS for 3 hours	1.25
5	PPy synthesized using APS for 8 hours	1.36
6	PPy synthesized using APS for 16 hours	1.35

Table 2: Conductivity of polymers

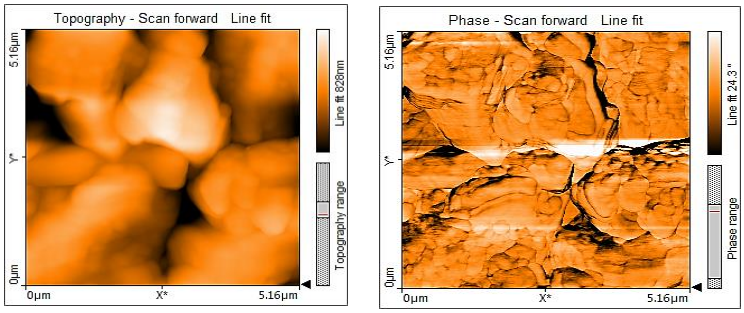

Fig. 7. Topographic image of Polymer

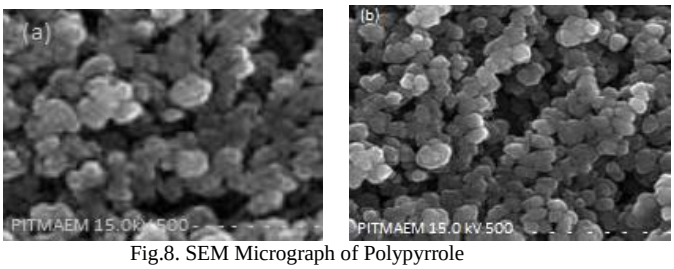

Fig.8. SEM Micrograph of Polypyrrole

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