Synthesis and properties of polypyrrole obtained from a new Fe(III) complex as oxidizing agent

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A new complex is synthesized from FeCl$_3$ and lauryl sulphate and used as oxidizing agent for the synthesis of polypyrrole. This process yields highly conducting polypyrrole (50 S/cm). The polymer is characterized by FT-IR, UV-vis, conductivity measurements and electrochemical and thermal analyses. Cyclic voltammetry of the polymer suggests moderate specific capacitance values.

Keywords: Polymers, Conducting Polymers, Polypyrrole, Conductivity, Oxidizing agents, Iron

Intrinsically conducting polymers (ICP) have attracting the attention of the scientific community ever since polyacetylene was first synthesized by Shirakawa et al. After this breakthrough, many new conducting polymers, such as polyaniline (PANI), polypyrrole (Ppy) and polythiophene (PTh) were discovered. Many applications have been suggested and explored such as corrosion protection, EMI shielding, batteries and in electrocatalysis.

Among the conducting polymers, polypyrrole (Ppy) has been the most studied material. The usefulness of the polymer has been realized as this material exhibits several interesting properties such as reversible redox activity, ability to form thin films, nanowires with room temperature conductivity ranging from 10$^{-7}$ to 10$^{-2}$ S cm$^{-1}$, charge/discharge processes and catalytic activity. Recent studies on the polymer focus on charge storage devices, particularly as supercapacitor material.

Iron(III) chloride is a versatile oxidizing agent for the chemical preparation of polypyrrole since its oxidizing potential suitably matches the oxidation potential of pyrrole (Fe$^{3+}$ + e$^{-}$ → Fe$^{2+}$, $E^0 = 0.77$V). Due to this, the obtained polypyrrole is not overoxidized and gives higher conductivity. Many authors have reported the use of FeCl$_3$ as oxidizing agent for the synthesis of polypyrrole and its composites. The use of surfactants in synthesis of nanostructures of CPs is well known. Surfactants decrease the surface tension of the water and allow the growth of the conducting polymers on it, as a template. In general, templates are classified as soft or hard templates in fabricating nanostructured materials. Hard templates include AAO membranes, MCM-41 and microporous polymeric filtration membranes. Soft templates are long range ordered structures self-assembled from certain surfactants or block co-polymers which provide well defined rooms or channels for conducting polymer chains to grow into micro/nanometer size structures. Use of hard templates give work-up problems like removing the hard templates where as this is easy with soft templates.

The aim of this work is to design a novel oxidizing agent with self-templating and surfactant properties that would influence the properties of the resulting polypyrrole. The present article reports the use of such a new Fe(III)-lauryl sulphate complex as oxidizing agent for the chemical synthesis of polypyrrole. During the synthesis, iron(III) is used as oxidizing agent and lauryl sulphate anions act as soft template in controlling the size of the polypyrrole particles. Lauryl sulphate also acts as dopant to the polymer. There are a few reports available in literature which used dodecylbenzene sulphonate (DBSA) as dopant and ammonium persulphate as oxidizing agent. The obtained polypyrrole is soluble, but is low conducting. In contrast, the polypyrrole obtained in the present synthesis is highly conducting. The polymer is insoluble due to a lower degree of doping by lauryl sulphate (as compared to DBSA), which is also smaller in size and less effective surfactant than DBSA. In another report Omastova et al. used FeCl$_3$ as oxidizing agent in presence of different surface active agents such as sodium dodecylbenzene sulfonate, dodecylbenzene sulfonic acid, sodium dodecyl sulphate. However,
they did not isolate any iron complex in their study and the highest conductivity observed was limited to 5.5-9.9 S/cm. Thus, to the best of our knowledge no report is available where an isolated iron complex is used as oxidizing agent, rendering the present preparative route as a ‘novel technique’.

**Experimental**

All chemicals were AR grade. Pyrrole, FeCl₃, sodium laurylsulphate (SLS) were purchased from CDH Chemicals (India). X-ray diffraction patterns (XRD) were obtained on a PANalytical MPD diffractometer using Cu-Kα radiation. FT-IR spectra of KBr powder-pressed pellets were recorded on a Thermonicolet (model nexus-670) spectrometer. Cyclic voltammetry experiments were performed on AUTOLAB 302 electrochemical system using three-electrode assembly consisting of a platinum foil (2 mm×2.5 mm)/or ss electrode (1 cm²) as working electrode, a GC auxiliary electrode (2 mm dia., 8 cm length) and a SCE as reference electrode. Conductivity of the samples were measured by four-probe method using Keithley nanovoltmeter after pressing the samples into 1.5 mm thick pellets 1 cm of dia. under 3 ton pressure. TGA experiments were performed with TA instruments Inc., on (model SDT Q600) by heating the samples under air at 20 °C per minute. Scanning electron micrographs were taken on a Jeol JSM-35CF instrument. TEM experiments were conducted on a FEI-make Tecnai-20-G² machine with tungsten filament at 200 kV. Microanalysis was conducted on Elementar Vario EL-III instrument (Germany).

The anhydrous ferric chloride (1 g, 6.1 mmol) was dissolved in 80 mL of distilled water and 5.45 g (18.9 mmol) of sodium laurylsulphate (SLS) was added and stirred for 2 h at room temperature. The yellow crystalline precipitate Fe(LS)₃Cl₁, which formed was filtered and dried at room temperature for 24 h.

The above iron(III) complex was dispersed in 100 mL of methanol and pyrrole (1 mL, 14.4 mmol) was added and stirred for 12 h. The black polypyrrole precipitate formed was filtered, washed copiously with water and dried at 50 °C in the oven. FT-IR spectrum and elemental analysis confirmed the formation of polypyrrole with molecular formula [(C₁₆H₁₃N₄Cl₂). (C₁₂H₂₅SO₄)₀.₅]ₙ.

**Results and discussion**

A yellow crystalline complex is readily formed when sodium lauryl sulphate solution is added with stirring to the filtered solution of ferric chloride aqueous solution as described under Experimental. The complex is believed to be an anion complex having six coordination sites around Fe(III) octahedrally, as shown in Scheme 1, three each from chloride and lauryl sulphate ions based on the fact that it exhibited a d-d band at 945 nm in methanol.

When the above complex was stirred with pyrrole monomer in methanol, black coloured polypyrrole (formed slowly over a period of 12 h. The FT-IR spectrum (Fig. 1) of the polypyrrole showed charge carriers, bipolaron bands at 921.6 and 1207.9 cm⁻¹ indicating that the Ppy formed is in the oxidized state. The peaks between 1551 and 1463.8 cm⁻¹ are assigned to fundamental vibrations of pyrrole rings. The peak 3434 cm⁻¹ is assigned to N–H stretching vibration from pyrrole.

To understand the role of dopants involved in the polymer during polymerization, C, H, N and S elemental analysis was conducted on the dried sample and the data is collected in Table 1. These data gave doping evidence for the lauryl sulphate anions. The

![Scheme 1](image)

![Fig. 1 – FT-IR spectrum of polypyrrole.](image)
analysis showed that about 3.5 wt% of lauryl sulphate is incorporated into the polymer matrix. The analysis also suggests that for every four pyrrole rings of the polymer backbone, there are two chloride anions and half lauryl sulphate anions are doped. Thus, the elemental data suggests a molecular formula of \( [C_{22}H_{24.5}Cl_2N_4O_2S_{0.5}]_n \) for the polymer.

The reflectance spectra (Fig. 2) exhibited a rising band at 420 nm, which extends into IR region suggesting high conductivity. The absorption peaks observed around 420 nm are assigned to \( \pi \rightarrow \pi^* \) transition associated with benzenoid ring type moieties\(^4\). The peak around 550 nm is due to cation radicals\(^4\). After this band, there is a continuous increase in the reflectance of the material as a tail which extends into the infra-red region, indicating that the charge carriers are bipolarons or trapped excitons.

The conductivity of the PPy tablet is as high as 50 S/cm. The higher conductivity is because of the formation of lower sized and ordered particles due to the presence of lauryl sulphate molecule which acts as an anionic surfactant. It is to be noted that the conductivity of the polypyrrole in the present study is much higher than that reported in other studies based on FeCl\(_3\) used with or without surfactant\(^3\). To the best of our knowledge our report is the first synthetic procedure to obtain high conducting polypyrrole using FeCl\(_3\) modified with surfactant molecules in the form of isolable complex. XRD profile (Fig. 3) of the sample showed a broad peak centred at 2\(\theta\)=18-30, suggesting amorphous nature of the polymer.

The scanning electron micrographs (Fig. 4a) of the material show the globular structure on the surface with high porosity. TEM analysis of the material shows the globular structure on the surface with high porosity.

### Table 1 – Experimental and calculated elemental compositions of polypyrrole for the molecular formula \([C_{16}H_{12}N_4Cl_2](0.5C_{12}H_{25}SO_4)_n\)

<table>
<thead>
<tr>
<th>Element</th>
<th>Expt. (%)</th>
<th>Calc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>57.01</td>
<td>56.95</td>
</tr>
<tr>
<td>H</td>
<td>4.890</td>
<td>5.280</td>
</tr>
<tr>
<td>N</td>
<td>11.65</td>
<td>12.08</td>
</tr>
<tr>
<td>S</td>
<td>3.48</td>
<td>3.45</td>
</tr>
</tbody>
</table>

Fig. 2 – Reflectance spectrum of thin film of polypyrrole on mild steel plate.

Fig. 3 – XRD profile of polypyrrole synthesized in the present study.

Fig. 4 – (a) Scanning electron micrographs and (b, c) TEM images of polypyrrole.
showed that most of the particles (about 80%) exist as round platelets of size 40-75 nm (Fig. 4b), although some longer sized particles do exist in the range 120-220 nm (Fig. 4c).

The electrochemical properties of the conducting polypyrrole were examined by cyclic voltammetry in 1 M KCl solution. The doping-dedoping process exhibited by the polymer is shown Fig. 5a. The CV profiles of the PPy-Pt electrode at different scan rates are shown in Fig. 5a. Upon increasing the scan rate, the current also increased. The shape of the curves is elliptical, which involve in high currents. The specific capacitance of the electrode at a scan rate of 50 mV/s, obtained using the formula \( C_{sc} = (I)/(W).(dv/dt) \) is about 100 F/g which decreased to 45 F/g when scan rate was increased to 200 mV/s.

The polymer was tested for its stability between room temperature to 800 °C by TGA (Supplementary data, Fig. S1). TGA profile of control sample prepared by using pure FeCl₃ and TGA of the present polymer are similar. Due to the presence of decomposable lauryl sulphate anions (compared to Cl⁻ anions), the thermal stability of this polymer is slightly lower than that of the control sample. The TGA profile of present polymer system suggests that there is a considerable amount of moisture/organic solvent (methanol) (about 10%) entrapped in the polymer which is lost in the temperature region of 100 °C. The second step of weight loss (8%) occurs between 100-180 °C due to the loss of dopant (Cl⁻).

The third stage decomposition (70%) of the material starts at 200 °C and continues up to 530 °C which can be attributed to the decomposition of lauryl sulphate molecules as well as the polymer backbone. Thus, the polypyrrole formed by this method is stable up to 100 °C and decomposes after this temperature.

In the present study, highly conducting (50 S/cm) polypyrrole has been synthesized by using a new Fe(III) complex as oxidizing agent where the lauryl sulphate ligand in the complex acts as a surfactant and also as a dopant. The elemental microanalysis showed that lauryl sulphate is present up to 3.5%. The size of the polymer particles ranged from 40-75 nm. The polymer is electroactive and shows moderate specific capacitance.

### Supplementary data

Supplementary data associated with this article i.e., Fig. S1 is available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_52A(06)744-748_SupplData.pdf.

### References