2.1 Materials

Materials used in the present study are pyrrole (Py), Ferric Chloride (FeCl$_3$), Hydrochloric Acid (HCl), Dodecyl benzenesulphonic Acid (DBSA), Cholic Acid, Bile salt, bamboo fibres and powdered cellulose extract from cotton linter and bamboo fibre. FeCl$_3$, HCl, DBSA, Cholic Acid and bile salt are high purity analytical grade materials obtained from William’s Lab (London), Fisher Scientific (India) Glaxo India and HIMEDIA Laboratories Pvt. Ltd (Mumbai) respectively, while bamboo fibres were collected as gift sample from Hindustan Paper Corpn.(HPC), Jagiroad, Assam (India). Py with 96% purity is collected from Sigma Aldrich and is double distilled prior to its use. The other chemicals are of analytical grade with high purity and used without further purification. De-ionized water is used as reaction medium all through. The detail method of synthesis has been described in the specific chapters to be followed.

2.2 Method

Polypyrrole is synthesized by chemical oxidative polymerization using Py as monomer and FeCl$_3$ as oxidizing agent [1-5]. The broad scheme for synthesis of PPy has been depicted in Fig.2.1 given below and the detail method of synthesis varies slightly in case of different experiments. These are described in respective chapters to follow.
2.3 Description of the major equipments used

2.3.1 Measurement of electrical properties

I-V characteristics of the synthesized material are studied by Keithley SourceMeter (Model 2400) using silver paste as contact lids. Functional change in direct current (dc) is recorded with changing applied (dc) voltage. It is an important to obtain the current vs voltage relationship to get the resistance of the specimen and is a fundamental way to find out the electrical conductivity of the material. Block diagram of that measurement is shown in Fig.2.2.
Dielectric properties are studied by an LCR meter (HIOKI 3532-50LCR) which is a testing device for determination of inductance, capacitance and resistance of the material, obtained by connecting with an alternating current (ac) voltage source.

### 2.3.2 Fourier transforms infrared (FTIR) spectroscopy

Fourier transform infra red (FTIR) spectroscopy study of the sample is made for assigning the chemical bonds. The basic components of the FTIR spectrometer are shown in Fig 2.3 by means of a ray diagram. It consists mainly of two parts, one the optical system which uses an interferometer and the other a dedicated computer which stores the data and performs computations. In the interferometer, the original IR beam splits into two parts and an interference pattern is created by sending one of the two beams in and out of phase using a sliding mirror. The energy vs mirror displacement data is then converted into energy vs absorbance relationship. Measurement of a single spectrum is faster for the FTIR technique as the information collected at all frequencies is collected simultaneously across a wide
spectrum. In the present study, FTIR set up used is SHIMADZU FTIR Affinity1 spectrophotometer. Spectra are recorded in the range of 300 to 3000 cm\(^{-1}\) at 4 cm\(^{-1}\) resolution.

![Fig 2.3 Schematic of an FTIR apparatus](image)

**2.3.3 UV-Visible absorption spectroscopy**

The UV-Vis absorption spectroscopy is applied [1] to record the electronic state of atom/molecule as well the size of the particles [2-4]. Mercury or Hydrogen lamps are used for UV, Tungsten light is used for visible light and caborundum or silicon carbide for IR signal. The steady state electronic UV-Vis absorption spectra of the sample solution are recorded using a quartz cuvette having a path length of 1 cm. Fig. 2.4 shows the schematic of a UV-Vis spectrophotometer.
2.3.4 Photoluminescence (PL) spectroscopy

PL spectroscopy is an effective tool for evaluation of the defect states present in the material and related optical properties corresponding to various transitions which can determine the photonics of the material. PL measurements can directly explore electronic features. Basically in this set-up light is directed onto the sample where it is absorbed and imparts excess energy to the orbital electrons in a process called photon excitation. The excess energy can be dissipated by the sample through light emission, viz. luminescence which is also known as photoluminescence due to the photonic excitation. The intensity and spectral content of the PL is a direct measure of various properties of the material. Photoluminescence
causes the orbital electrons of the material to move to the permissible excited states which 
afterwards come back to their respective ground state releasing the excess energy, which may 
be manifested as radiative or non-radiative process. The energy of the emitted light is related 
to the electronic state involved with the transition process between the excited states to the 
ground state. The quantity light emission is related to the related contribution of the radiative 
process.

2.3.5 Scanning Electron Microscopy (SEM)

SEM is a kind of electron microscopy in which the image of a microscopic size material 
object is recorded by scanning it with an electron beam to study the microstructure, surface 
morphology, composition and properties of the bulk materials. SEM combines high 
resolution imaging with a large depth of field. Short wavelength of electrons and their ability 
to be focused by electrostatic and electromagnetic lenses enables better resolution. The strong 
interaction of electrons with atoms that make up the sample produces a wide variety of useful 
signals to reveal the material secrets of the scanned object in the microscopic and even 
nanoscopic level. The scanning electron microscope model – ASEM (JEOL LA 6380, 
JAPAN) has been used in our study of surface morphology of the synthesized polymers.

2.3.6 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) provides information about the microstructure and 
the crystal structure of the material. Apart from these, TEM can also provide direct imaging 
of the structure of the particles from which the shape, size and molecular arrangement of the 
molecules can be determined. A high energy electron beam transmitted through a very thin
specimen has been used here to get the image and analyze the microstructure with resolution in the atomic size. In our study it was undertaken in JEM-2100, JEOL, JAPAN. Unlike the limited resolution of the optical microscope in the order of micrometer because of the light used in the visible wavelength range, TEM can produce resolution into hundreds of nanometers as the high energy electron beam is used here to impenetrate the specimen. The electrons accelerated to the range of 100 KeV used to transmit through the specimen have wavelength much smaller than that of light which undergo a series of inelastic and elastic scattering due to interactions with the atoms of the specimen. Most of the electrons are elastically scattered by the atomic nuclei of the specimen, while a small fraction is also scattered in-elastically. The energetic electrons passing through the specimen near the atomic core are accelerated towards the nuclei causing smaller degree of reduction in their wavelength which results in a small phase change. Thus the information obtained about the structure of the specimen gets transferred to the phase of the electrons moving in the outermost orbit. Only the elastically scattered electrons are considered for getting the high resolution images. However, sometimes the inelastic scattering of the electrons can also be useful. Analysis of them can be helpful in obtaining chemical information from a specified region of the spectrum. This information can be obtained from the energy loss in inelastic scattering of the electrons. Electron diffraction from a crystallite can be described as a kinematic process and can also give supplementary information as given by Bragg’s law of X-Ray diffraction.

2.3.7 X-Ray diffractometer

X-ray diffractometer is a convenient, non-destructive and powerful tool to study the structural parameters of a crystalline material. A typical XRD instrument consists of four main
components, viz. X-Ray source, specimen stand, receiving optics and X-Ray detector. When a monochromatic parallel beam of X-ray impinges on the specimen, the constituent atoms which are arranged in a regular manner can diffract the beam to form the interference pattern.

The essential condition for diffraction of X-ray by a crystalline solid is given by the equation [5]

\[ 2d_{hkl} \sin \theta = n \lambda \]  ............... (2.1)

Where \( d \) is the inter planer spacing of the set of planes signified by \((h \ k \ l)\), \( \theta \) is the glancing angle and \( \lambda \) is the wavelength of the X-Ray used. This relation is known as Bragg’s law.

There are a large number of crystal planes with different inter planer spacing. If the direction of the X-ray is fixed then all the crystal planes are not in a position to diffract the X-ray as their orientation i.e. the inter-planer spacing associated with wavelength may not satisfy Bragg’s law. When the crystal is rotated about an axis parallel to the direction of the incident X-ray, the successive planes \((h_1,k_1,l_1)\), \((h_2,k_2,l_2)\), \((h_3,k_3,l_3)\),... etc with inter planer spacing \(d_1\), \(d_2\), \(d_3\)... etc. will make proper glancing angles \(\theta_1\), \(\theta_2\), \(\theta_3\),... satisfying Bragg’s law. Thus, when the specimen is rotated diffracted beam of X-rays will be obtained in different directions since different crystal planes will satisfy Bragg’s law at different positions. This diffracted ray either can be determined by a photographic plate or by an X-ray detecting counter which helps in determining the angle \(\theta\). In X-ray diffractometer, diffracted beam is detected by a counter. In our study, XRD was done by X-Part pro diffraction 1830 X-Ray diffractometer with Cu Kα radiation (wavelength ~ 0.15418 nm) with scanning between 10° to 60°.
2.3.8 Gel permeation chromatography (GPC)

GPC is a kind of liquid chromatography in which molecules are separated by their size when they are allowed to pass through a liquid column. It consists of a pump to push the solvent through the instrument, an injection port to introduce the test sample into the column, a column to hold the stationary phase, one or more detectors to detect the components as they leave the column and a software to control, calculate and display the results. The polymer is first dissolved in a solvent. Once they are dissolved, the molecules get coiled up and take a configuration resembling the beads of a chain with their size directly proportional to their molecular weight. The static liquid present in the pores of the beads is used as the stationary phase and a flowing liquid is used as the mobile phase. The mobile phase can flow between the beads and also in and out of the pores of the beads. The separation mechanism is based on separating the polymer molecules in the solution as per their size. The dissolved polymer molecules entering the column also get partitioned according to their size because of diffusion and the larger sized spheres get the exit first because they cannot diffuse inside the beads and pass through the liquid column freely. The quantity of molecules detected at exit vs molecular weight gives the degree of polymerization as well as distribution pattern of the molecular weight.
The schematic of the separating mechanism of a GPC column is shown in Fig 2.4.

**Fig 2.5** Separation mechanism of molecules in GPC column.
2.4 References


