
CHAPTER-II
EXPERIMENTAL

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2.1: INTRODUCTION

Present investigations deal with synthesis and characterization of conducting polymers and its functionalization with phthalocyanine. The conducting polymers chosen were polyaniline, polythiophene, and polypyrrole. The functionalization of these conducting polymers was carried out using macro-cyclic compound like copper phthalocyanine. For the synthesis and functionalization of these conducting polymers two methods were adopted namely (1) Chemical synthesis method and (2) Electrochemical method. The phthalocyanine used in the chemical method is chlorinated derivative of copper phthalocyanine (CuPc green) while in the electrochemical method its non-chlorinated homologue (CuPc blue) has been used. This chapter describes in details the experimental procedure for synthesis of the conducting polymers and their functionalization with phthalocyanine. The characterization of various polymers and their films using FT-IR spectroscopy, UV-VIS spectroscopy, X-ray diffraction studies and ESCA are described in this chapter. It also deals with the detailed procedure for the preparation of various types of samples as well as the property measurement techniques used for studies on chemical vapor sensitivity, cyclic voltammetry, electrical properties etc.

2.2: CHEMICALS USED

The monomers namely, thiophene and pyrrole were obtained from M/S Aldrich Chemical Company, Inc. The aniline monomer was A.R. grade reagent obtained from M/S S.D. Fine Chem. (India). Phthalocyanine green, chlorinated copper phthalocyanine [Hostaperm Green GNX-1] and phthalocyanine blue, copper phthalocyanine [Hostaperm Blue CBR] was obtained from M/S Color Chem / Hoechst (India). The electrolytes lithium perchlorate (LiClO_4), and tetra butyl ammonium

perchlorate $[\text{CH}_3(\text{CH}_2)_3]_4\text{NClO}_4$ (herein after referred to TBAP) were obtained from M/S Aldrich Chemical Company, Inc. Polyethylene oxide (PEO) was obtained from BDH Chemicals Ltd. (England), having approx. molecular weight 3,00,000. Ferric chloride anhydrous (FeCl_3), cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and sodium sulfide flakes ($\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$) were obtained from M/S Loba Chemie (India). The solvents N-methyl pyrrolidone (NMP), nitrobenzene, and benzene were obtained from M/S S.D. Fine Chem. (India) and were used as such without further purification. Iodine crystals obtained from M/S S.D.Fine Chem. (India) and were used for doping the polymers. The chemicals such as ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, Agar-Agar, potassium chloride, potassium iodide were received from M/S Loba Chemie (India) were used as such. The acids namely, hydrochloric and sulfuric acid were concentrated solutions obtained from M/S S.D.Fine Chem. (India). The above mentioned all chemicals were A.R.grade. The solvents methanol and acetone used in the purification of the polymers was of commercial grade and used after distillation. The aqueous medium used in all chemical and electrochemical preparations was doubly distilled water.

2.3: Synthesis Methods

2.3.A. Chemical Synthesis Methods

2.3.A.1: Synthesis of conducting polymers and Its functionalized derivatives

General method of synthesis of these conducting polymers involves the oxidation reaction of monomer aniline, pyrrole or thiophene in solvents such as distilled water, NMP: H_2O (1:1) mixture, nitrobenzene and pure NMP with calculated amount of CuPc green in the range of 1.0 to 20 mole % (with respect to monomer) in the presence of oxidizing agents such as ammonium per sulfate or FeCl_3 in an acidic

medium. The reactions were carried out mainly at room temperature and in some cases at 0°C, with constant magnetic stirring. The reaction time was varied from 2 hours to 24 hours depending on the polymer. The solvent used for synthesis of polyaniline and polypyrrole was mixture of NMP: H₂O (1:1). The nitrobenzene was used in the preparation of polythiophene. In order to compare the polymerization process, the reaction rates, polymer characteristics etc. of polymer synthesized in solvent mixture with standard route, pure NMP as well as distilled water were taken for the preparation of some samples of PANI and PPy. Since different solvents, oxidizing agents and variable reaction parameters are involved in each synthesis; the details of stoichiometry and reaction time for each individual polymer are discussed in each chapter separately in its experimental section.

2.3.A.2: Purification of the polymers

After the desired reaction time, the reaction mixture was directly poured into 500 ml. of distilled water, stirred for about half an hour and the precipitated polymer was filtered by conventional methods. The polymer was washed with distilled water several times till the filtrate obtained was colorless and neutral in nature. For the purification of polythiophene polymers, initially 500 ml. methanol was used, till filtrate obtained was colorless and then subsequently it was washed with distilled water. The polymer samples obtained in powder form were dried first at room temperature for few hours and then finally dried in an oven kept at 80°C for 4 hours. The dried polymer powders were then preserved in a dessicator.

2.3.A.3: Doping with Iodine solution

Typically the doping was carried out in a 50 ml. stoppered conical flask in which 1.27-gram iodine crystals were dissolved using, 10-ml. dry benzene. To this

iodine solution, 300 mg. of synthesized polymer were added and the contents were stirred well. The stoppered flask was left standing at room temperature for 20 hours. The doped polymer was then filtered and washed with 5ml-benzene solution to remove excess iodine present in it. The product was then dried at room temperature till it attains a constant weight. This doped polymer was then used for measurement of properties such as conductivity, cyclic voltammetry and chemical vapor sensitivity etc.

2.3.B: Electrochemical Methods

Electrochemical deposition of conducting polymers

Functionalized with phthalocyanine

Initially, gold deposition on clean glass or thick PET (100 μm) transparencies was carried out in a Hind Vac Vacuum coating unit (model 12A4D) using thermal evaporation method. The gold-coated substrates were then cut into 3 cm \times 2 cm size. One edge of this piece was then coated with silver paste to give electrical contact pad for external connections.

The electrochemical deposition was carried out in a single compartment cell with three electrodes system as shown in **Fig. 2.1**. The saturated calomel electrode (SCE) was connected through the salt bridge containing agar-agar / KCl mixture to the electrolytic solution. The counter electrode used was platinum foil and the working electrode was gold substrate on which electrochemically deposited polymer films were to be formed. The electrolyte contained normally 0.2 M solution of the monomer to be polymerized in an appropriate solvent such as NMP: H₂O (1:1) mixture or nitrobenzene. Appropriate oxidizing agent in 0.1-0.4 molar concentrations was dissolved in the electrolyte and it was purged with dry nitrogen gas at least 15 minutes before deposition. The desired amount of phthalocyanine blue ranging from 1 to 5%

Electrochemical cell

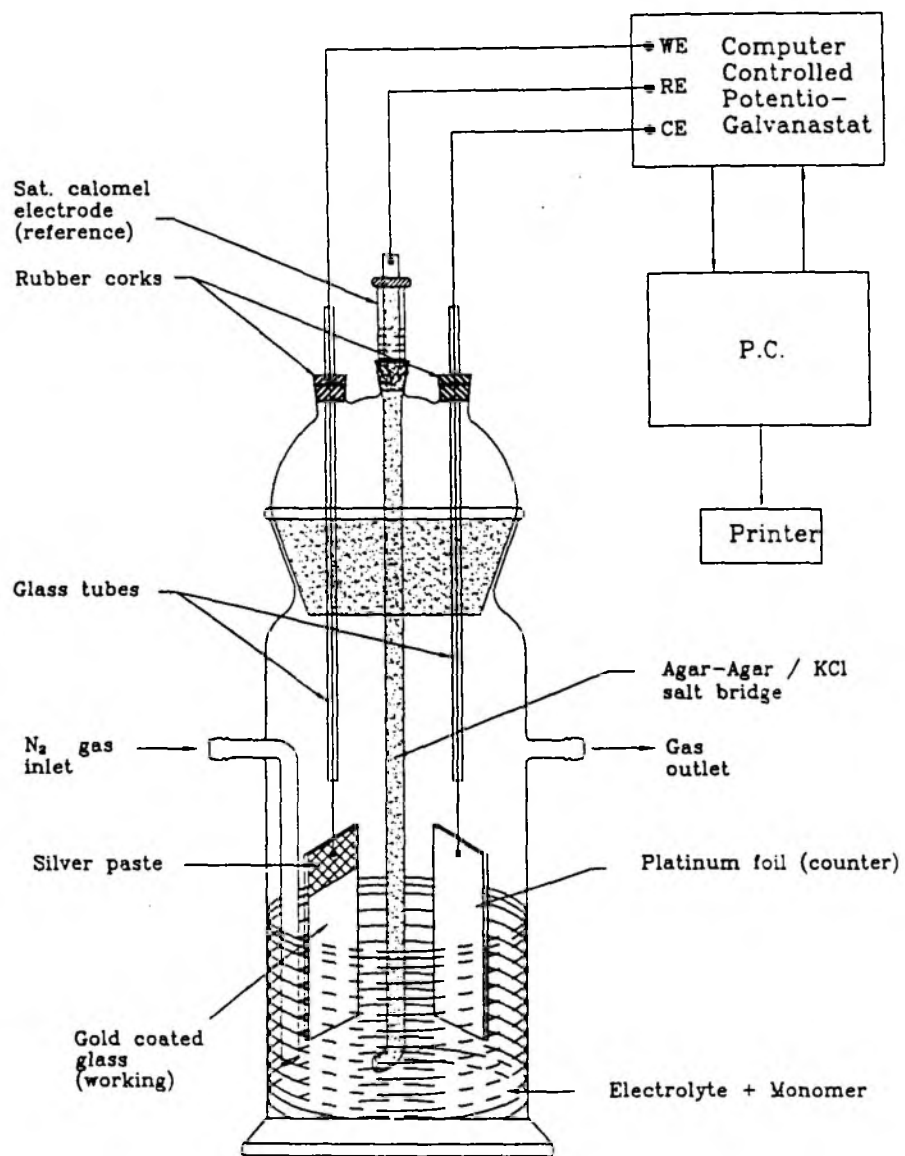


Figure 2.1 : Electrochemical Measurement Apparatus

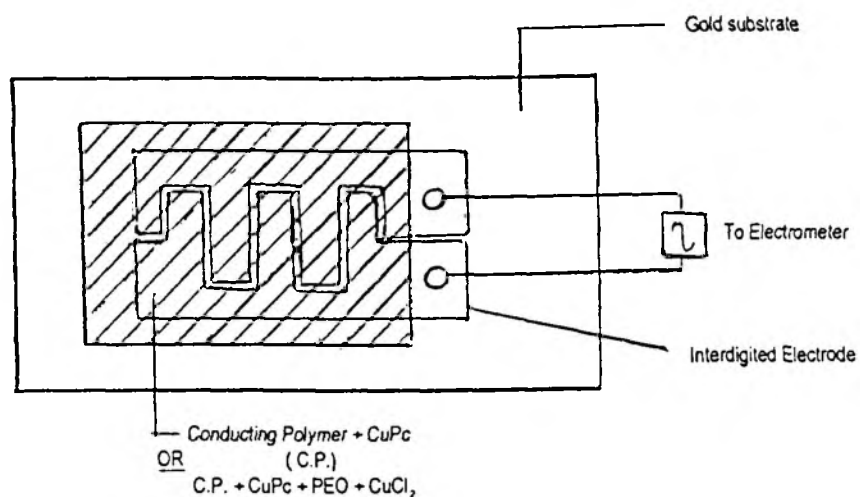
[mole % with respect to monomer] was added to the electrolyte solution and nitrogen gas was bubbled for 10 minutes to form a uniform suspension.

Since, each conducting polymer was synthesized and functionalized under different conditions such as solvent, oxidizing agent, applied voltage and /or deposition time, the details of deposition in each case has been described in corresponding chapter separately.

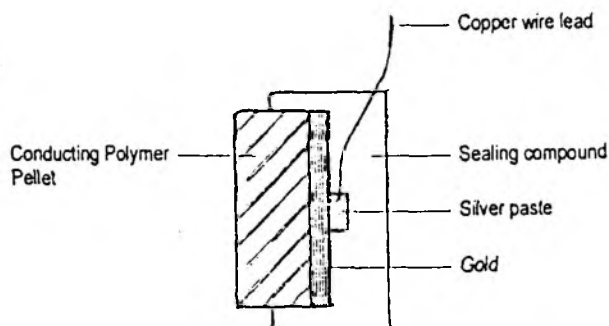
2.4: Samples Preparation for various property Measurements

The various polymers synthesized by methods described in **section 2.3.A.1** and **2.3.A.3** were in powder form. In order to prepare the test samples, 300 mg. of this polymeric powder was pressed in a single ended compaction die held at 5-ton pressure for 60 seconds so as to form thin discs/ pellets (1.1 cm diameter, about 0.1 cm. thick). These pellets were used in conductivity measurements. The pellets used in the C.V. measurements and sensitivity measurements are prepared as described below.

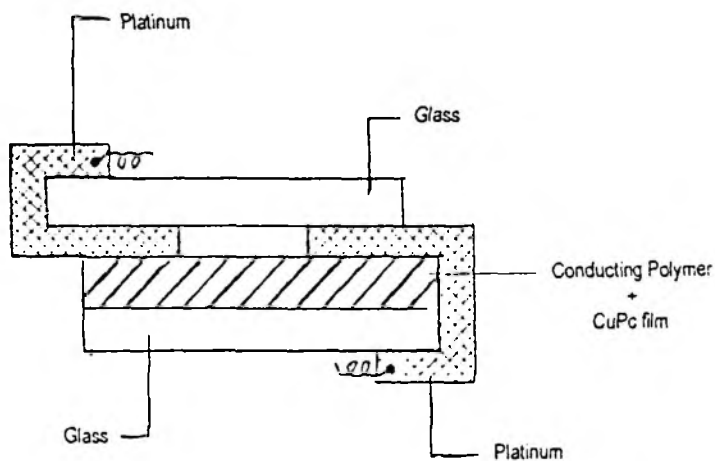
The contacting electrodes on these pellets were then vacuum deposited using pure gold (99.9%). The deposition of gold films was carried out in a vacuum evaporation unit (Hind Hivac Model 12A4D) at 10^{-6} torr by thermal evaporation technique. Thin copper wire leads were connected to these gold film electrodes by means of air -drying silver paste and allowed to dry the same for 4 hours at room temperature. The whole of contact area was then sealed with thermoplastic elastomers (hydrophobic), Kraton 101, by coating with a solution of the same in toluene. The pellet configuration is schematically shown in **Fig. 2.2**. This prevents the backside of the discs from exposure to electrolyte, which may cause enormous peaks in C.V. These samples were then used in cyclic voltammetry (C.V.) measurements as a working electrode and platinum foil as an auxiliary electrode. C.V. measurements in



A : Surface Cell configuration for chemical sensitivity measurements.



B: Pellet configuration for C.V. measurements.



C: Sandwich type cell for films for conductivity measurements.

Figure 2.2 : Schematic diagram of sample configurations

various electrolytes such as LiClO_4 , HCl , Na_2S , KI/I_2 , tetra butyl ammonium tetra fluoro borate (TBATFB), and tetra butyl ammonium perchlorate (TBAP) etc. in 0.1 M concentration of each in water or an organic solvent.

Surface cells are essential for measuring chemical sensitivity of the polymers for sensor application. The pellets of various phthalocyanine modified conducting polymers such as polyaniline, polypyrrole, polythiophene etc. were prepared as described earlier. On one side of the pellets, two gold electrodes with 0.1 mm gap were deposited using vacuum deposition technique. The copper wire leads were attached to these portions with the help of air-drying silver paste. These cells are further used in the measurements sensitivity for various chemical vapours.

The interdigitated gold films were formed on clean glass substrates as described in earlier section [section 2.3.B]. To these films the two leads (copper wires) were attached by means of a silver paste. The polymer composite films were coated on the open area between the two electrodes.

In order to study the chemical sensitivity of modified conducting polymer powders; these were first dispersed in a film-forming matrix and then coated on the electrode. This approach was needed since the conducting polymer powders have no known solvent at room temperature. Polyethylene oxide (PEO) was chosen for dispersing the conducting polymers since it has a variety of solvents, it forms films easily, it has low T_g and T_m , which allows many types of chemical vapors to diffuse through. Earlier studies from this laboratory indicated that PEO is most appropriate for testing chemical sensitivity of conducting polyaniline for applications in sensors.

In order to make the composite films, typically 0.2 gms. of PEO were taken in a petri dish to which 0.02 gms. of $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ and 2.0 ml methanol were added. The

mixture was slightly warmed to form uniform greenish liquid. Desired amount of conducting polymer (ranging from 0.022 gms to 0.11 gms.) was added to the solution and the mixture masticated thoroughly so as to form a paste. The fine smooth paste was then applied on the interdigitated electrodes and dried at room temperature for 24 hrs (**Fig. 2.2**). The electrical conductivity of the sensor was monitored by continuously recording resistivity or currents at constant potential using a stabilized DC power supply a Keithley electrometer and a fast x-y-t recorder [Lienses, Germany].

The chemical sensitivity of these surface cells to various vapors such as methanol, nitrogen dioxide and ammonia was tested using specially designed chamber with facilities for injecting and evacuating vapors, [**Fig.2.3**] which is described in the following section.

The apparatus consists of a thick glass wall chamber fitted with an arrangement of evacuation the system. On one side, there is a stopcock system through which, controlled doses of chemical vapour can be injected into the system. The upper portion of the glass chamber has two-electrodes which are directly connected to a Keithley electrometer. The samples were connected to these two electrodes inside the chamber and their resistance was recorded before and after chemical exposure. The sensitivity factor was calculated using the formula,

$$S = R_v / R_o,$$

Where, R_v and R_o are the resistance after the exposure to chemical vapours and initial resistance respectively.

Sensitivity Measurement Apparatus

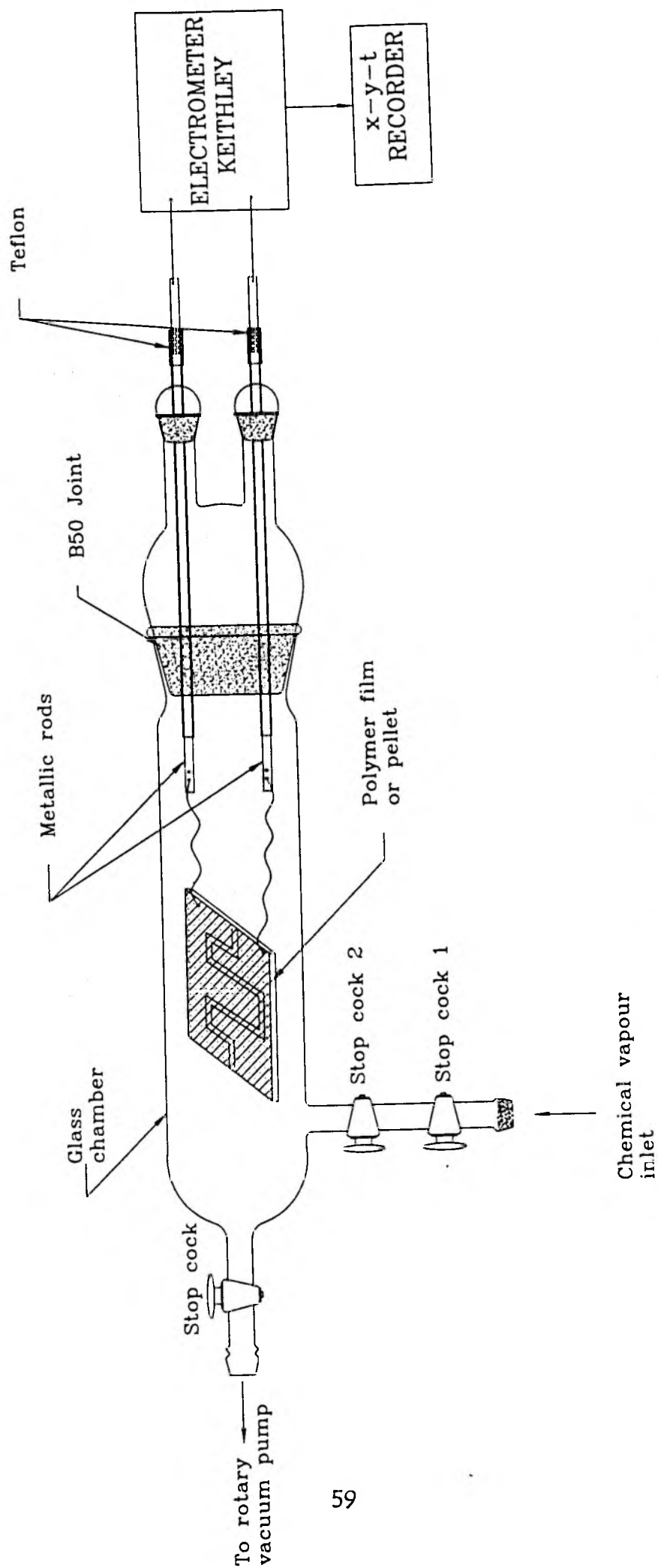


Figure 2.3 : Sensitivity Measurement Apparatus

2.5: CHARACTERIZATION

2.5.1: Infrared (IR) Spectroscopy

Infrared (IR) studies¹⁷⁴ were carried out in order to confirm not only the incorporation of phthalocyanine into various conducting polymer but also the characteristic frequencies of the parent conducting polymers. The polymer powder samples were recorded using a reflection mode on FT-IR spectrometer [Shimadzu model 8201 PC] in few cases. The powdered samples were mulled with dry potassium bromide crystals or nujol and these were mounted in IR cell in the conventional way to record the IR spectra using Perkin Elmer model 1600. The characteristic absorption bands obtained were tabulated and compared with known literature data.

2.5.2: UV-VIS Spectroscopy

Additional mid-gap states formed due to doping and or incorporation of phthalocyanine can be studied by UV-VIS spectroscopy¹⁷⁵. For UV-VIS absorption studies, the various polymeric films deposited on gold plated glass substrates were recorded as such using gold glass film as reference. The powdered samples were dissolved in the conventional solvents such as dilute H₂SO₄ and placing this dilute solution of the polymers in the cuvetts. The spectrum was recorded in the wavelength region of 300-900 nm. These measurements were carried out on Shimadzu Spectrometer with UV-240 model.

2.5.3: Microanalysis

The various polymers synthesized are analyzed for various elements present in it (such as C, H, O, Cl, S, N, Cu etc.) by microanalysis technique¹⁷⁶. These studies

will focus on amounts of various elements present in different proportions. From this one can calculate the possible structural chain arrangement. The elemental analysis was performed on Carlo-Erba Elemental Analyzer (EA 1108 model), while halogen estimations were carried out using Waters Ion Chromatograph Unit. From the halogen estimations and heteroatom in the conducting polymer, one can find out the doping level in the sample.

2.6: CHARACTERATION OF STRUCTURE

2.6.1: X-ray Diffraction Studies

The conducting polymers synthesized by chemical route generally offered a semi crystalline structure whereas the electrochemical deposition route yields an amorphous nature. The phthalocyanine used for this study is reported to have well defined structure. Hence, incorporation of this moiety into the conducting polymers is expected to show some structural changes and crystallinity of modified polymer. These changes are studied using a well-known technique of wide angle X-ray diffraction (WAXD)¹⁷⁷. The crystalline structure of various polymeric compositions was investigated by WAXD, using a powder x-ray diffractometer (Phillips PW 1730 model) using CuK α source and β Ni filter. Also some of the scans were recorded on Rigaku X-ray diffractometer, using Rint 2000 wide-angle goniometer with K-beta filter. All the scans were recorded in the 2θ region of 5-40° at a scan rate of 4°/ min. From the 2θ values for the reflections, 'd' values were calculated using well-known Brag's equation,

$$2 d \sin \theta = n \lambda.$$

These values were compared with those estimated for known/assigned structure.

Energy Dispersive X-ray Analysis [EDAX]¹⁷⁸ was carried out to estimate the doping levels for various polymers. From these studies various atomic ratios such as Cu / S, Cu / Cl etc. can be determined. The copper content in the polymers functionalized with phthalocyanine was carried out using this technique using Kevex model (U.S.A.).

2.6.2: X-ray Photoelectron Spectroscopy (XPS)/ESCA studies

X-ray photoelectron spectroscopy¹⁷⁹ is concerned with a special form of photoemission, namely the ejection of an electron from a core level by x-ray photons of energy $h\nu$. The energy of these emitted photoelectrons is then analyzed by an electron spectrometer and the data are presented as a graph of intensity (counts or counts per second) versus electron energy (eV). The binding energy of photoelectron peaks defines not only the energy level within the atom from which it emerged but also the chemical environment (valence state of atom). Therefore it is also called electron spectroscopy for chemical analysis (ESCA).

The intensity of electrons I , emitted from a depth d is given by the Beer-Lambert's equation,

$$I = I_0 \exp(-d / \lambda \sin \theta)$$

Where I_0 = the intensity from the clean substrate.

λ = Inelastic mean free path (the value is a function of Kinetic energy E_K of emitted electrons).

θ = Angle subtended by the sample surface.

XPS has been employed mainly to determine surface composition. The x-ray photoelectron spectra were recorded using V.G. Scientific ESCA-3 MK II spectrometer. Al-K α (1486.6 eV) and Mg-K α (1253.6 eV) radiation was used for excitation and photoelectron kinetic energy was measured with respect to Fermi level. All the spectra were recorded under identical conditions at 50 eV pass energy, 4mm slit and vacuum better than 10⁻⁸ Torr. The instrumental resolution obtained for the Au 4f_{7/2} levels under this condition is 1.6 eV (Full width at half maximum- FWHM).

2.6.3: Thermo Gravimetric Analysis (T.G.A.)

Thermo gravimetric analysis¹⁸⁰ was carried out for various polymers to determine the weight loss at different temperatures. These studies were also used to find the onset degradation temperature of the polymers. All the measurements were carried out using TG / DTA 32 (Seiko II SSC 5100 Japan model). The samples in the form of powder were used for analysis under nitrogen atmosphere at a rate of 10° / min. from room temperature to 500°C. The thermal analysis of pure conducting polymer was recorded for comparison as original standard in any given system. The weight loss in functionalized polymer was compared with the original one in order to estimate the fractional component of the polymer at a fixed high temperature so that the thermal stability can be estimated. Also, if the final product after polymerization was a mere physical mixture of the phthalocyanine added to conducting polymer or not can be determined from the TGA curves.

2.7: Property Measurements

2.7.1: Temperature dependence of Conductivity

The temperature dependence of conductivity was determined by placing the pellet or the film in a suitably designed apparatus as shown in Fig 2.4. The pellet used in this measurement is a sandwich type cell wherein the polymer pellet is placed in between two platinum electrodes, which are connected to two terminal of the Keithley electrometer. The polymeric films are connected to the two platinum wires through the aluminum foil, which is known to blocking type electrode. This was very essential because the sample resistance was otherwise quite low and often there was ‘shorting’ of the films observed due to the sudden high current. The apparatus consists of a sample holder, which was enclosed in an electromagnetic shielded cell, which in turn was mounted inside a glass jacket, which could be sealed and connected to a rotary vacuum pump. A small heater was mounted close to the film or pellet and using a suitable control device controlled its temperature (rate of rise). A digital temperature indicator connected to a thermocouple placed near the sample measured the temperature inside the cell. The temperature was varied from room temperature to about 120°C for the doped samples and up to 150°C for undoped samples at a rate of 3°C per minute. The change in the resistivity with temperature were noted using an electrometer (Keithley 614 model) and its conductivity was estimated using the formula:

$$\rho = RA / l \text{ -----(2.1)}$$

$$\sigma = 1 / \rho \text{ -----(2.2)}$$

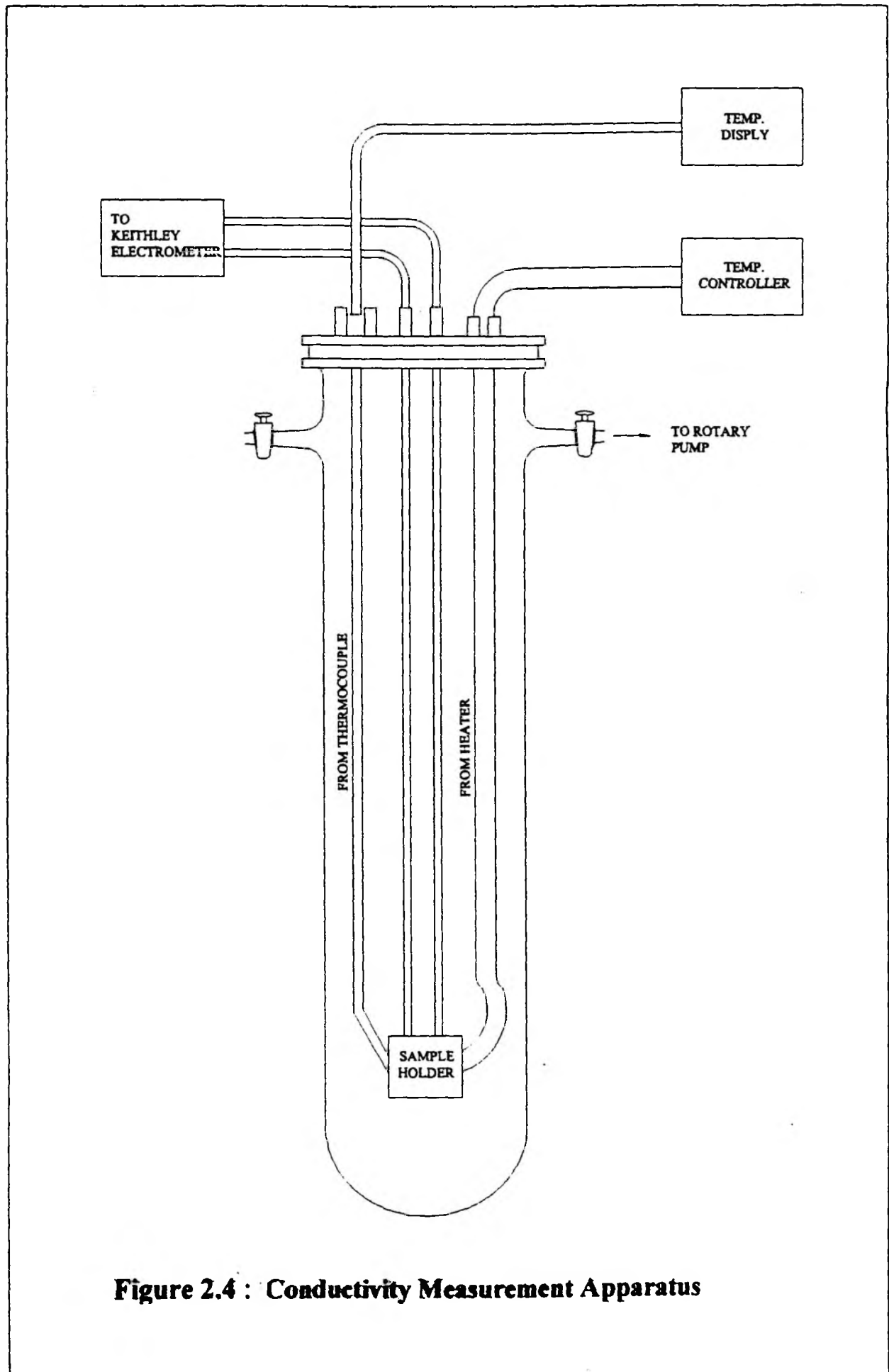


Figure 2.4 : Conductivity Measurement Apparatus

Where ρ is its resistivity, A is the cross sectional area, l is the thickness, R is the sample resistance and σ is conductivity. The conductivity was recorded as a function of temperature. In order to estimate the activation energy (ΔE) for conduction following equation was used:

$$\sigma = \sigma_0 \exp. (\Delta E / kT) \text{ or } \text{-----}(2.3)$$

$$\text{Log } \sigma = \Delta E / kT + \log \sigma_0 \text{ -----}(2.4)$$

Where k is the Boltzman constant. The slope of the plot of σ versus $1/T$ can be calculated as follows:

$$\text{Slope} = \frac{\log \sigma_2 - \log \sigma_1}{1/T_1 - 1/T_2} = \Delta E / k \text{ -----}(2.5)$$

The above equation can be rewritten in a convenient form by substituting the proper values for the constants and converting from natural logarithms to base 10 as:

$$\Delta E = \text{Slope} \times k \text{ -----}(2.6)$$

With $k = 1.96 \times 10^{-4} \text{ eV}$.

2.7.2: Sensitivity Measurements

The conducting polymers like polyaniline, polythiophene etc. are reported to be sensitive towards certain chemical vapours such as alcohol, ammonia and nitrogen dioxide etc. For this study a specially designed glass chamber was used as shown in **Fig. 2.3**. The system was connected to rotary vacuum pump so as to remove the vapors

quickly. The resistance measurements and calculation for sensitivity factor was carried out as described in detail in earlier section.

2.7.3: Cyclic Voltammetry in Dark and Light

Cyclic voltammetry experiments were frequently used to obtain information on the mechanism of polymer growth as well as redox behaviour and mode of electronic conduction. In addition to this, in the present investigations in order to study the effect of the functional group (copper phthalocyanine) on the properties of conducting polymers, cyclic voltammetry (C.V.) with and without illumination i.e. PEC mode, experiments were carried out.

These estimations were carried out in a same electrolytic cell, which was used for electrochemical deposition of the polymers. The source of light was used as a 60 W tungsten filament lamp. The working electrode was the polymeric film/pellet, kept in the cell facing the lamp. The illumination intensity of white light of 0.1 emu/cm^2 . The most of the C.V. measurements were carried out in aqueous solutions having fixed concentration of 0.1 N solutions. Only for coloured electrolytes such as iodine and potassium ferricyanide etc. more dilute solutions of 0.01 N concentrations were used. The cyclic voltammetric measurements were carried out at potentials -1.0 V to $+1.0 \text{ V}$ for three cycles each in the dark and under illumination separately. The various electrolytes used in the present study were LiClO_4 , Na_2S , HCl , KCl , KI/I_2 , $\text{K}_3\text{Fe(CN)}_6$ and tetra butyl ammonium perchlorate etc. The photosensitivity factor could be estimated by taking the ratio of peak current under illumination to that in dark.